PRACTICAL
GANIC CHEMISTRY

JULIUS B. COHEN

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PRACTICAL
ORGANIC CHEMISTRY

BY

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PREFACE TO THE FIRST EDITION

THE present volume is an enlarged edition of that published in 1887, and has been completely rewritten. The preparations have all been carefully revised, some of the former ones omitted and many new ones introduced. The chief additions are the introductory chapters on organic analysis and molecular weight determinations, and an extension of the appendix.

The book does not aim at being a complete laboratory guide, but is intended to provide a systematic course of practical instruction, illustrating a great variety of reactions and processes with a very moderate outlay in materials and apparatus.

The objection may be raised that the detailed description of processes makes no demand upon a student's resourcefulness or ingenuity. It must be remembered, however, that the manipulative part of organic chemistry is so unfamiliar to the elementary student that he requires minute directions in order to avoid waste of time and material. Until he has acquired considerable practical skill he cannot accomplish the experimental work requisite for research, and repeated failures will be apt to destroy his confidence in himself.

To satisfy, to a legitimate extent, the prejudices of certain examining bodies, who still adhere to the old system of testing a student's knowledge of practical organic chemistry by means of the qualitative analysis of certain meaningless mixtures, the special tests for some of the more common organic substances have been inserted. At the same time, an attempt has been made at the end of the appendix to systematise the analysis of organic substances on a broader and therefore more rational basis.

The present occasion seems opportune to direct attention to the fact that one of the most familiar, most readily procurable and most cheaply produced of all organic materials is placed beyond the reach of many students by the heavy duty levied upon it. May I, in the name of teachers of organic chemistry, appeal to the Board of Inland Revenue, on behalf of scientific and technical education, to provide institutions for higher education in science with a limited quantity of pure alcohol free of duty, thereby placing schools of chemistry in this country in the same position as those on the Continent?

In conclusion I desire to thank Dr. J. McCrae, who has written the section on Ethyl Tartrate and the use of the Polarimeter, Dr. T. S. Patterson, who has been kind enough to look over the proofs, and Mr. H. D. Dakin, who has given me substantial assistance in the practical work of revision.

J. B. COHEN.

THE YORKSHIRE COLLEGE,
October, 1900.

PREFACE TO THE SECOND EDITION

IN the former edition attention was drawn to certain drawbacks which accompanied the study of practical organic chemistry, among which the heavy duty on alcohol and the unsatisfactory nature of the practical tests demanded by public examining bodies were specially emphasised.

Teachers and students alike must welcome the changes which have since taken place. An excise duty on alcohol used in the laboratory is no longer exacted from students of science, and substantial reforms have been introduced into practical examinations.

One important feature in some of the new examination regulations is the recognition of the candidate's signed record of laboratory work. We are, in fact, beginning to discover an inherent defect in practical chemistry as an examination subject, namely, its resistance to compression into a compact and convenient examination form.

The old and drastic method by which chemistry was made to fit into a syllabus consisted in cutting out the core of the subject, or in other words, in removing all the processes which demanded time, skill, and some intelligence, and in reducing the examination to a set of exercises in a kind of legerdemain. This process has been to a large extent abandoned, but a residuum of it still remains. It is to be hoped that the kind of practical examination in organic chemistry, which consists in allotting a few hours to the identification of a substance selected from a particular list, will in time be superseded or accompanied by a scheme encouraging candidates to show, in addition to their note-books, evidence of skill and originality, as, for example, in submitting specimens of new or rare preparations, or in presenting an account of some small investigation.

The present edition is much enlarged and contains new preparations, reactions and quantitative methods, all of which have been carefully revised. My object has been not to follow any particular syllabus, but to present a variety of processes from which a selection may be made to suit the special needs of different students.

My thanks are due to Mr. Joseph Marshall, B.Sc., and several of my senior students, for their assistance in the work of revision.

J. B. COHEN

THE UNIVERSITY, LEEDS.
July, 1908.

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ORGANIC ANALYSIS

Qualitative Examination.

Carbon and Hydrogen.—Carbon compounds are frequently inflammable, and when heated on platinum foil take fire or char and burn away. A safer test is to heat the substance with some easily reducible metallic oxide, the oxygen of which forms carbon dioxide with the carbon present. Take a piece of soft glass tube about 13 cm. (5 in.) long, and fuse it together at one end. Heat a gram or two of fine copper oxide in a porcelain crucible for a few minutes to drive off the moisture, and let it cool in a desiccator. Mix it with about one-tenth of its bulk of powdered sugar in a mortar. Pour the mixture into the tube, the open end of which is now drawn out into a wide capillary and bent at the same time into the form shown in Fig. 1. This is done by shaking down the mixture to the closed end and revolving the tube in the blow-pipe flame about 2½ cm. (1 in.) beyond the mixture until it is thoroughly softened. The tube is then removed from the flame, drawn out gently and bent. Make a file scratch across the end of the capillary and break it. When the tube is cold tap it horizontally at the edge of the bench, so as to form a free channel above the mixture. Suspend it by a

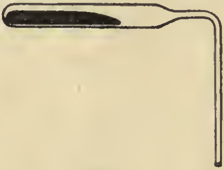

FIG. 1.

copper wire to the ring of a retort stand, and let the open end dip into lime or baryta water. Heat the mixture gently with a small flame. The gas which bubbles through the lime water turns it milky. Moisture will also appear on the sides of the tube, which, provided that the copper oxide has been thoroughly dried beforehand, indicates the presence of hydrogen in the compound. Gases, or volatile substances like ether and alcohol, cannot, of course, be examined in this way; but an apparatus must be arranged so that the gas or vapour is made to pass over a layer of red hot copper oxide and then through the lime water.

Nitrogen.—Many organic nitrogen compounds when strongly heated with soda-lime give off their nitrogen in the form of ammonia. Grind up a fragment of cheese or a few crystals of urea with 5 to 6 times its weight of soda-lime, pour the mixture into a small test-tube (preferably of hard glass) and cover it with an equally thick layer of soda-lime. Heat strongly, beginning at the top layer. Ammonia is evolved and can be detected by the smell, or by holding a piece of moistened red litmus paper at the mouth of the tube. When nitrogen is present in direct combination with oxygen, as in the nitro- and azoxy-compounds, ammonia is not evolved. The following general method is applicable to all compounds and is therefore more reliable. The compound is heated with metallic potassium or sodium when potassium or sodium cyanide is formed. The subsequent test is the same as for cyanides. Pour about 10 c.c. of distilled water into a small beaker. Place a fragment of the substance in a small test-tube along with a piece of metallic potassium or sodium the size of a coffee bean, and heat them at first gently until the reaction subsides, and then strongly until the glass is nearly red-hot. Then place the hot end of the tube in the small beaker of water. The glass crumbles away, and any residual potassium is decomposed with a bright flash, all the cyanide rapidly goes into solution, whilst a quantity of carbon remains suspended in the liquid. Filter through a small filter into a test-tube. Add to the clear solution a few drops of ferrous sulphate solution, and a drop of ferric chloride, boil up for a minute, cool under the tap, and acidify with dilute hydrochloric acid. A precipitate of Prussian blue indicates the presence of nitrogen. If the liquid has a blue colour, let it stand for an hour and examine it again for a precipitate. If no precipitate appears and the solution remains of a clear yellowish-green colour, no nitrogen is present.

If sulphur is present, an excess of alkali metal must be used to prevent the formation of sulphocyanide.

The Halogens.—Many halogen compounds impart a green fringe to the outer zone of the non-luminous flame. A more delicate test is to heat the substance with copper oxide (Beilstein). Heat a fragment of copper oxide, held in the loop of a platinum wire, in the outer mantle of the non-luminous flame until it ceases to colour the flame green. Let it cool down a little and then dust on some halogen compound (bromacetanilide will serve this purpose, see Prep. 55, p. 152). Now heat again. A bright green flame, accompanied by a blue zone immediately round the oxide, indicates the presence of a halogen. The halogen in the majority of organic compounds is not directly precipitated by silver nitrate. Only those compounds which, like the hydracids and their metallic salts, dissociate in solution into free ions give this reaction. If, however, the organic compound is first destroyed, and the halogen converted into a soluble metallic salt, the test may be applied. Heat the substance with a fragment of metallic sodium or potassium as in the test for nitrogen, p. 2. The test-tube whilst hot is placed in cold water, the alkaline solution filtered, acidified with dilute nitric acid and silver nitrate solution added. A curdy, white or yellow precipitate (provided no cyanide is present), indicates a halogen. If a cyanide is present, boil with nitric acid until the hydrogen cyanide is expelled and add silver nitrate.

Sulphur.—The presence of sulphur in organic compounds may be detected by heating the substance with a little metallic sodium or potassium. The alkaline sulphide, when dissolved in water, gives a violet colouration with a solution of sodium nitroprusside. Heat a fragment of gelatine with a small piece of potassium in a test-tube until the bottom of the tube is red hot, and place it in a small beaker of water as described in the test for nitrogen (p. 2). Filter the liquid and add a few drops of sodium nitroprusside solution.

Phosphorus.—The presence of phosphorus is ascertained by heating the substance strongly with magnesium powder and moistening the cold product with water. Magnesium phosphide is formed and is decomposed by the water, giving phosphine which is readily detected by its smell.

Quantitative Estimation.

Carbon and Hydrogen.—The principle of the method is that described under *qualitative examination*, but the substance and the products of combustion, viz., carbon dioxide and water, are weighed. The following apparatus is required.

1. *An Erlenmeyer or other form of Combustion Furnace.*—The usual length is 80–90 cm. (31–35 in.), and it is provided with 30 to 35 burners. Flat flame burners are undesirable.

2. *A Drying Apparatus.*—A form of drying apparatus which is easily fitted together is shown in Fig. 2. It consists of four large U-tubes arranged side by side in pairs. The U-tubes are mounted upon a wooden stand with two uprights, to which the two pairs of tubes are wired. The first of each pair is filled with soda-lime, and the second with pumice soaked in concentrated sulphuric acid. Each soda-lime tube is connected with a sulphuric acid tube by well-fitting rubber corks and a bent glass tube. The two other limbs of the sulphuric acid U-tubes are joined by a three-way-tap forming a T-piece. The free end of the T-piece is attached to a small bulb tube, Fig. 3, containing a drop of concentrated sulphuric acid to mark the rate at which the bubbles are passing through the drying apparatus. The bulb tube is connected with the combustion tube by a short piece of rubber tubing and a short glass tube, which passes through a rubber cork fixed in the end of the combustion tube. The rubber tubing carries a screw-clip. The open ends of

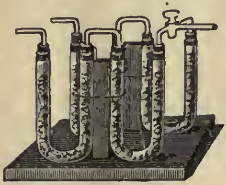

FIG. 2.

FIG. 3.

the soda-lime U-tubes are closed with rubber corks, through which pass bent glass tubes. One of these glass tubes is connected by rubber tubing to an oxygen gas-holder or to a cylinder of compressed oxygen, which must be furnished with an automatic regulating valve, and the other glass tube is attached to a gas-holder containing air. By turning the three-way tap, either oxygen or air may be supplied to the combustion tube.

3. *A Combustion Tube of Hard Glass.*—It should be about 13 mm. inside diameter, and the walls not more than 1·5 mm. thick. Its length should be such that it projects at least 5 cm. (2 in.) beyond the furnace at either end. After cutting the required length, the ends of the tube are carefully heated in the flame until the sharp edges are just rounded. The tube is filled as follows. Push in a loose asbestos plug about 5 cm. (2 in.) from one end. This end, to which the calcium chloride tube and potash apparatus are subsequently attached, may be called the *front end.* Pour in coarse copper oxide at the opposite end and shake it down to the plug until there is a layer about two-thirds the length of the tube. Keep the oxide in position by another plug of asbestos; see that the plugs are not rammed too tight. Make a roll of copper gauze about 13 cm. (5 in.) long to slide easily into the back end of the combustion tube. This is done by rolling the gauze tightly round a stout copper wire until the requisite thickness is obtained. The projecting ends of the wire are then bent over into hooks as shown in Fig. 4. This roll, or spiral, as it is usually called, is subsequently oxidised. It is pushed into the tube or withdrawn as occasion requires by a piece of hooked wire. The combustion tube is placed on a layer of asbestos in the iron trough of the furnace. The arrangement of the tube with boat and spiral is shown in Fig. 5.

FIG. 4.

4. *A Straight Calcium Chloride Tube.*—It is inserted through a rubber cork and fixed in the front end of the combustion tube when the latter is not in use, as copper oxide is very hygroscopic, and it is necessary to protect it from the moisture in the air.

5. *A Potash Apparatus.*—Several forms of potash apparatus are made; that of Geissler (Fig. 6), and Classen (Fig. 7) being perhaps most commonly employed. The latter has the advantage of being very light. The removable side tube is filled with granulated calcium chloride or soda-lime, with a plug of cotton wool at each end. The bulbs of the apparatus are filled with a strong solution of caustic potash containing 25 grams of potash to 50 c.c. of water. This is done as follows. Remove the soda-lime tube and attach in its place a piece of rubber tubing. This serves as a mouthpiece. Pour the potash solution into a basin and dip the other end of the potash apparatus under the liquid. Suck at the rubber tube until the quantity appears sufficient to fill the bulbs. Remove the potash solution and continue to suck until the solution is transferred to the bulbs. The bulbs should be nearly filled. In the case of Classen's apparatus, the liquid should stand half an inch deep in the bottom of the apparatus outside the lowest bulb.

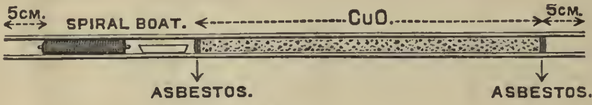

FIG. 5

FIG. 6

FIG. 7.

Wipe the potash solution from the outside and inside of the inlet tube of the apparatus with filter paper. Smear a thin film of vaseline on the ground end of the soda-lime tube before replacing it, and fit to the open ends of the apparatus, stoppers of rubber and glass rod, which are not removed, except when the apparatus is in use. As the potash apparatus has to be refilled after every two combustions, it is advisable to keep a little stock of solution in a bottle fitted with an ordinary cork.

6. *A Calcium Chloride* U*-Tube.*—The form of calcium chloride tube is shown in Fig. 8. It is fitted with sieved calcium chloride to within 2½ cm. (1 in.) of the side pieces, and then with coarser pieces to within ½ cm. (¼ in.). Place a small plug of cotton wool in both limbs above the chloride to keep it in position. Two well-fitting corks, cut off level with the glass and coated with sealing-wax, produce an effective air-tight stopper to the open limbs, but it is preferable to seal them in the blow-pipe flame. The sealing requires a little skill. Carefully wipe off any chloride dust which may have adhered to the open ends of the two limbs. Cork up one limb and stopper one of the side tubes. Attach a short piece of rubber tubing to the other side tube to serve as a mouthpiece. Now soften the end of the open limb in a small blow-pipe flame, and at the same time heat the end of a short piece of glass rod. With the hot end of the rod gather up the edges of the open limb, and whilst rotating the limb backwards and forwards in the flame, draw it out and seal it up. If successful, the appearance of the tube is that shown in Fig. 9. The blob of glass is heated in a small flame, and, by gently blowing and re-heating and blowing again, the blob can be removed, and, finally, by using a rather larger flame, heating and blowing alternately, the end is neatly rounded.

FIG. 8.

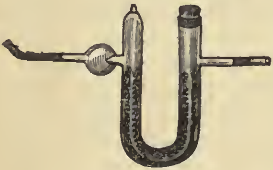

FIG. 9.

7. *A Porcelain or, preferably, a Platinum Boat.*—See that it slips easily into the combustion tube. The boat is kept in a desiccator on a flat cork or support made of glass rod when not in use.

Preparation of the Tube.—Before starting the combustion it is necessary to clean and dry the combustion tube. This is effected by heating the whole length of the tube containing the copper oxide and spiral gradually to a dull red heat, and passing through it a slow stream of dry oxygen from the gas-holder or cylinder. As soon as a glowing chip is ignited at the front end and the moisture, which at first collects there, has disappeared, the gas jets are turned down and finally extinguished. The oxygen is then stopped, and the straight calcium chloride tube inserted into the open end of the tube.

Preliminary Operations.—Grind up a little pure oxalic acid, and carefully weigh out 0·15 to 0·2 gram (not more) in the boat. Weigh also the calcium chloride tube and potash apparatus without stoppers or other accessories. The side tube of the calcium chloride tube, which carries the bulb, is attached directly to the combustion tube with a rubber cork. This cork should be carefully selected, and should exactly fit the combustion tube. The bore hole should be small and smooth, and it is advisable to dust it with graphite or coat it with a film of vaseline to prevent the rubber from clinging to the glass, a matter of frequent occurrence unless this precaution is taken. The cork should be kept exclusively for the combustion. Push the side tube of the calcium chloride tube through the hole until it is flush with the opposite surface, and squeeze the cork tightly into the combustion tube. Attach the potash apparatus to the other limb of the calcium chloride tube by a well-fitting piece of rubber tubing about 3 cm. (1½ in.) long, and bring the ends of the glass as closely as possible together. It should be unnecessary to wind wire round the joint if the rubber is of the right diameter. A little vaseline may be used here with advantage, but only in the thinnest film. The potash apparatus will require to be supported upon a block or stand. Remove the copper spiral from the back of the tube. Introduce the boat and push it into position against the asbestos plug by means of the spiral which is placed behind it. Replace the rubber cork connected with the drying apparatus. The apparatus will present the appearance shown in Fig. 10.

It must now be tested to see that it is air-tight. For this purpose, close the open end of the potash apparatus with a tight stopper and turn on the full pressure from either gas-holder. After the first few bubbles of air have passed through the bulbs of the potash apparatus no further movement of bubbles should appear *in any part* of the apparatus. If it withstands this test, the combustion may proceed. Release the pressure by closing the tap of the gas-holder, screwing up the clip at the back of the combustion tube, and cautiously removing the stopper from the potash apparatus. Then raise the three-way tap from its socket for a moment.

The Combustion.—Turn on the oxygen and adjust the rate of flow through the apparatus by means of the screw-clip so that 2 or 3 bubbles a second pass through the potash bulbs. Throw back the tiles if closed, and light the burners under the front layer of copper oxide to within 10 cm. (4 in.) of the boat and also 2 or 3 burners under the spiral behind the boat, but not within 5 cm. (2 in.) of the boat. Turn up the gas slowly to avoid cracking the tube and in a minute or two, when the tube is thoroughly warmed, close the tiles over the lighted burners and heat to a dull red heat. A vivid red heat during the combustion is not only unnecessary, but undesirable, as the glass is apt to soften and be distorted and even to blow out and become perforated. A combustion tube carefully handled should last indefinitely. When the copper oxide is red hot, turn on the burners very gradually from the spiral towards the boat, but do not close the two pairs of tiles over the boat until the combustion is nearly terminated and the burners are all lighted. The first indication of the substance burning is the appearance of a film of moisture at the front end of the combustion tube and an increase in the speed of the bubbles passing through the potash apparatus. The front end of the tube, which should project 4 to 5 cm. (1½ to 2 in.) from the furnace, must be kept sufficiently hot to prevent moisture permanently condensing there ; but it must never be allowed to become so hot that there is any risk of the cork being burnt, and it should always be possible to place the finger and thumb round the part of the tube where the cork is inserted. A screen made from a square piece of asbestos board, with a slit in it

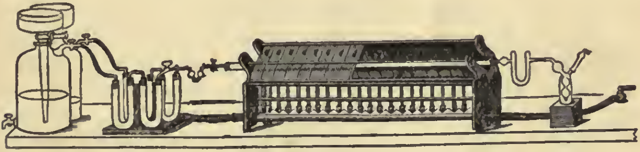
FIG. 10.

slipped over the tube at the end of the furnace, may be used with advantage.

The speed of the bubbles is the best indication of the progress of the combustion. If the rate increases so that the bubbles passing through the last bulb cannot easily be counted, a burner or burners must be lowered or extinguished until the speed slackens. After a time, when the air has been displaced and carbon dioxide largely fills the tube, the gas is nearly all absorbed in the first potash bulb. When this occurs, the current of oxygen may be increased until the bubbles appear synchronously in the bulbs, when the current is again checked. If some copper oxide has been reduced in the first stages of the process, the bubbles in the potash apparatus may entirely cease for a time, but will reappear when the copper has been reoxidised. Here again an increased current of oxygen will hasten the process. The combustion is complete when a glowing chip held at the end of the potash apparatus is rekindled. All the moisture must by now have been driven over into the calcium chloride tube. If this is not the case, warm the end of the tube cautiously with a small flame, or by means of a hot tile held near the tube The time required to complete the combustion is about one-half to three-quarters of an hour from the time the front of the tube is red hot, but more volatile substances, which must be heated more cautiously, will naturally take longer.

The combustion being complete, gradually turn down, and in a few minutes extinguish, the burners. Whilst the furnace cools the oxygen is replaced by a slow current of air. To do this the oxygen supply is stopped and the three-way tap is turned through 180°, so as to connect the tube with the air reservoir, the tap of which is then opened and the stream of air regulated by the screw clip.

Let the air pass through for 20 minutes whilst the furnace is cooling down. Then remove and stopper the potash apparatus and the calcium chloride tube, and after allowing them to stand by the balance case for half-an-hour, weigh.

The results are calculated in percentages of carbon and hydrogen as follows :

w is the weight of substance taken.
a is the increase in weight of the potash apparatus.

b is the increase in weight of the calcium chloride tube.

$$\frac{12 \times a \times 100}{44 \times w} = \text{per cent. of carbon.}$$

$$\frac{2 \times b \times 100}{18 \times w} = \text{per cent. of hydrogen.}$$

Example.—0·1510 gram of oxalic acid gave 0·1055 gram of CO_2 and 0·068 gram of H_2O.

$$\frac{12 \times 0{\cdot}1055 \times 100}{44 \times 0{\cdot}1510} = 19{\cdot}05 \text{ per cent. of carbon.}$$

$$\frac{2 \times 0{\cdot}068 \times 100}{18 \times 0{\cdot}1510} = 5{\cdot}00 \text{ per cent. of hydrogen.}$$

Calculated for $C_2H_6O_6$: C = 19·04 per cent.; H = 4·76 per cent.

As a rule, the carbon is a little too low through loss of moisture from the potash apparatus, whilst the hydrogen is too high, probably through incomplete drying of the air and oxygen from the gas-holders. The discrepancy should not exceed 0·2 per cent. of the theoretical amount. If the substance burns with difficulty it should be mixed with fine copper oxide in the manner described under quantitative estimation of nitrogen.

The Combustion of Volatile and Hygroscopic Substances.—If the substance is a non-volatile liquid it may be weighed in a boat like a solid; if it is hygroscopic the boat must be enclosed and weighed in a stoppered tube. If it is a volatile liquid a glass bulb or tube, drawn out into a neck as shown in Fig. 11, must be used. The bulb is first weighed, and the liquid is introduced by warming the bulb gently to expand the air and then inverting the open neck under the liquid. The operation may require repeating. The tube is then sealed and weighed again. Before introducing the bulb into the tube the neck is nicked with a file and broken off. It is then placed in the boat and pushed into the combustion tube. In the combustion of a substance like naphthalene, which is moderately volatile, the greater part is vaporised by the heat of the copper oxide spiral in contact with the boat. The

FIG. 11.

burners are therefore not lighted under the boat until towards the close of the combustion. In the case of a highly volatile compound like ether, a combustion tube is used, which projects at least 15 cm. (6 in.) beyond the back of the furnace. The bulb containing the substance is then placed just outside the furnace, and then the spiral in contact with it. A small Bunsen flame is placed under the end of the spiral away from the substance, the heat from which is sufficient to completely volatilise the substance at a convenient speed.

The Combustion of Organic Substances containing Nitrogen.—The following modification must be introduced in cases where the organic substances contain nitrogen. As the nitrogen may be liberated in the form of one or other of its oxides, which are liable to be absorbed in the potash apparatus, a source of error is introduced, which may be eliminated in the following way. A spiral of metallic copper is brought into the front end of the combustion tube, which, when red hot, reduces the oxides of nitrogen. The free nitrogen then passes through unabsorbed. About 13 to 15 cm. (5 to 6 in.) of coarse copper oxide is removed from the front end of the tube, and after inserting an asbestos plug, the space left by the oxide is filled with a roll of copper gauze 13 to 15 cm. (5 to 6 in.) long. The copper spiral must have a clean metallic surface, which is easily produced in the following way. Take a large test-tube or boiling tube, an inch or so longer than the spiral, and push down to the bottom a small pad of asbestos. Pour in about 5 c.c. of pure methyl alcohol.

Have a cork at hand which fits loosely into the mouth of the test-tube. Wrap the tube round with a duster. Hold the copper spiral with the crucible tongs in a large blow-pipe flame until it is red hot throughout and slide it quickly into the test-tube. The methyl alcohol reduces the film of oxide on the copper and is at the same time oxidised to formaldehyde, the vapours of which attack the eyes if the tube is brought too near the face. The alcohol takes fire at the mouth of the test-tube. When the flame dies down insert the loose cork and let the tube cool. The spiral, which has now a bright surface, is withdrawn, and the excess of alcohol removed by shaking it. It must now be thoroughly dried. Place the spiral in a hard glass tube a few inches longer than the spiral and fitted at each end with a cork, into which short, narrow glass tubes are inserted. Attach one end of the tube to an apparatus for evolving carbon dioxide, which is thoroughly dried by passing it through concentrated sulphuric acid. When the air is expelled from the tube, heat it gently until the alcohol is removed. Then let the tube cool while the gas is passing through. The spiral is then removed and placed in the front of the combustion tube. The combustion is carried out in the manner already described, but a current of air is substituted for oxygen until all the hydrogen has been expelled, *i.e.*, until water ceases to condense in the front of the tube. The burners under the metallic copper are then gradually extinquished, and the spiral allowed to cool whilst the current of air is replaced by oxygen. By the time the oxygen reaches the spiral, the latter should have so far cooled that it remains unoxidised. The current of oxygen is continued until a glowing chip is kindled at the end of the potash apparatus and the operation is completed by turning on the air as previously described.

A convenient substance to use for analysis is acetanilide, see Preparation 54, p. 151.

Combustion of Organic Compounds containing Halogens and Sulphur.—When the halogens or sulphur are present in an organic compound, they are liable to be absorbed either in the free state or in combination with oxygen in the potash apparatus. In this case, fused lead chromate broken up into small pieces must replace the coarse copper oxide in the combustion tube. The halogens and sulphur are retained by the lead, the former as the halide salt, and the latter as lead sulphate Special care must be taken in using lead chromate, that the temperature of the furnace is not too high, as otherwise the chromate fuses to the glass, and the combustion tube then cracks on cooling.

Nitrogen (Dumas).—According to this method, a weighed quantity of the substance is heated with copper oxide in a tube filled with carbon dioxide. The carbon and hydrogen form respectively carbon dioxide and water, and the nitrogen which is liberated in the form of gas is collected over caustic potash (which absorbs the carbon dioxide) and measured.

The following apparatus is required :—

1. *A combustion furnace* of the ordinary form.

2. *A short furnace* of simple construction, such as used in Turner's method for estimating carbon in steel (Fig. 12). It should carry an iron trough about 30 cm. (12 in.) long, fixed at such a height that it can be heated by an ordinary Bunsen burner.

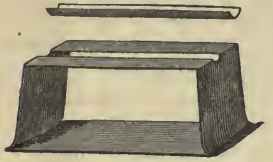

FIG. 12.

3. *A combustion tube*, which may be rather longer than that used in the estimation of carbon and hydrogen.

4. *A short hard glass tube*, 25—28 cm. (10—11 in.) long, and closed at one end.

5. *A bent tube with a bulb*, blown in the centre, as shown at *a*, Fig. 13. This is attached by rubber corks to the ends of the long and short combustion tubes.

6. *A graduated Schiff's Azotometer*, Fig. 13.—A small quantity of mercury is first poured into the bottom of the tube so as to fill it 4—5 mm. above the lower side limb. A solution of potash (1KOH : $3H_2O$) is then poured into the glass reservoir, which is attached to the upper straight side limb by a rubber tube. By raising the reservoir and opening the tap the tube is filled, and remains so on closing the tap and lowering the reservoir. When the tube is filled with potash solution there should be sufficient mercury at the bottom to seal off the potash solution from the bent limb, which connects with the combustion tube.

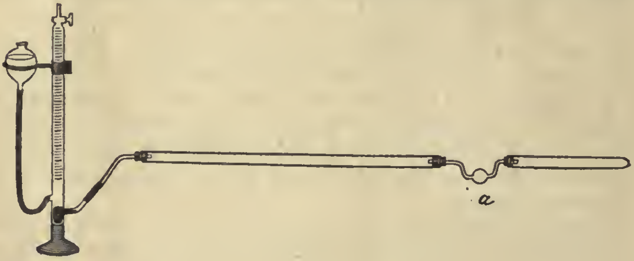

FIG. 13.

7. *Two flasks*, 200 *c.c. and* 300 *c.c.*—The necks are slightly

constricted in the blow-pipe flame, so that the end of the combustion tube slips in as far as the constriction (Fig. 14). The flasks are fitted with good corks.

8. *A spiral of copper gauze* 15 cm. (6 in.) long, which is reduced in methyl alcohol as described on p. 12. The spiral should be reduced just before use when the tube is filled and ready. It is unnecessary to remove all the alcohol from the spiral by heating it in a current of carbon dioxide. It is sufficient to whisk it sharply through the air and shake off the excess of liquid.

FIG. 14.

9. *A sufficient quantity of coarse copper oxide* to fill the combustion tube two-thirds full and a further quantity of fine copper oxide to occupy 10—13 cm. (4—5 in.) of the tube.

10. *Two shallow tin dishes*, 10—13 cm (4—5 in.) in diameter for roasting copper oxide. These dishes can be obtained from the ironmonger in different sizes and are useful in the laboratory for a variety of purposes, such as for oil, metal or sand-baths.

11. *A square of copper gauze* of moderate mesh of the area of the tin dish. It is turned up at the edges and is used for sifting the coarse from the fine copper oxide after each combustion.

12. *Pure sodium bicarbonate*, $NaHCO_3$, in powder free from ammonia.

Filling the Combustion Tube.—A plug of asbestos is first pushed in from one end far enough to leave room for the copper spiral, which should lie well within the furnace. This end of the tube is subsequently attached to the azotometer and may be called the *front* end. The coarse copper oxide is heated over a Bunsen burner in one of the shallow tin dishes and the fine oxide in another. After about a quarter to half an hour the burners are extinguished and the oxides whilst still warm are introduced into their respective flasks with drawn-out necks, The flasks are closed with corks and allowed to cool. The back end of the combustion tube is now pushed horizontally into the neck of the coarse oxide flask and the oxide poured on to the plug by tilting the flask and tube. The tube is filled with oxide about two-thirds of its length. Into the flask containing the fine oxide about 0·2 gram of powdered substance (acetanilide may be conveniently used, see Prep. 54, p. 151) is weighed out by difference from a sample tube, which should contain the approximate quantity. The substance is then well mixed with the oxide by shaking the flask. The contents of the flask are carefully poured into the tube above the coarse oxide in the manner described and the flask is rinsed out with coarse oxide, which is likewise poured into the tube until it is filled to the full length of the furnace. A loose plug of asbestos is pushed in to keep the materials in position and the tube is tapped horizontally on the bench in order to form a channel above the layer of fine copper oxide. The tube is now laid in the furnace, which is tilted a little forwards in order to collect the moisture at the front end of the tube. The short closed tube is well packed with powdered sodium bicarbonate and tapped horizontally so as to form a good channel above the whole length of the substance. It is laid in the small furnace, which is also tilted forwards to drain off the water which is formed. The bicarbonate and the combustion tubes are connected by the bulb tube already described. The copper spiral is now reduced and pushed into the front of the tube up to the plug and finally the azotometer is attached by its bent tube. The arrangement of the tubes and their contents are shown in Figs. 13 and 15.

The Combustion.—The tap of the azotometer is opened and the reservoir lowered so as to empty as far as possible the

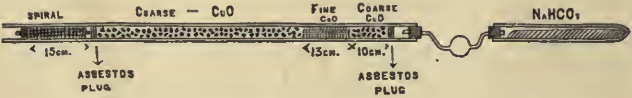

FIG. 15.

graduated tube. The joints of the apparatus being well secured, begin by cautiously heating the bicarbonate near the closed end of the tube with a good burner, and concentrate the heat by tiles placed on each side. A rapid stream of carbon dioxide is at once evolved. When it begins to slacken, push the burner on ½ cm. or so in order to maintain a continuous and rapid stream. The quicker the stream of gas, the sooner is the air expelled, for the gas then pushes the column of air before it like a piston, before the latter has time to diffuse. In about ten minutes, the row of burners beneath the spiral and the coarse oxide to within 10 cm. (4 in.) of the fine oxide may be lighted. In another fifteen minutes, the gas which is passing through the tube may be tested. The current is allowed to slow down a little, and the graduated tube of the azotometer is then filled with potash solution by raising the reservoir and closing the tap. On gradually lowering the reservoir, a few bubbles will pass up the graduated tube.

By the time they reach the top of the tube, the size of the bubbles should have become so minute that when collected at the top they occupy no appreciable volume, but appear as a fine froth. If this is not the case, open the tap, run out the solution and continue as before to drive carbon dioxide through the tube. Repeat the test in another five minutes. Not more than half the bicarbonate should have been utilised in expelling the air. The air being removed, the combustion of the substance is commenced. The azotometer is filled with the potash solution, the tap closed, and the reservoir lowered as far as possible. The current of carbon dioxide is allowed to slacken, but it must not be completely stopped. The front portion of the combustion tube will by this time have reached a dull red heat. A few more burners are now lighted on both sides of the fine oxide. Finally, the layer of fine oxide is gradually heated and the process conducted in much the same manner as that described under the estimation of carbon and hydrogen. The combustion is regulated by the speed of the bubbles passing up the azotometer tube, which should enable them to be readily counted. The burners being all lighted and the tube red hot throughout, the tiles above the substance are closed. The current of gas will shortly slacken. The residual nitrogen is then expelled from the tube by moving on the flame beneath the bicarbonate and causing a fresh stream of carbon dioxide to sweep through the tube. Care must be taken that the stream of gas is not too rapid, as otherwise the potash solution may become saturated and driven completely into the reservoir. The burners may now be extinguished and a reading of the level in the azotometer taken every few minutes until it remains constant and the bubbles are completely absorbed. Remove the azotometer by slipping out the cork from the front of the combustion tube, and hang a thermometer beside it. Do not, however, stop the flow of carbon dioxide until the tube is nearly cold. In this way, the copper spiral remains quite bright and may be used for a second determination without being reduced.

When the azotometer has stood for an hour in a cool place, adjust the level by raising the reservoir so that the liquid in the tube and reservoir stand at the same height. Read off the volume, and at the same time note the temperature and the barometric pressure.

The percentage of nitrogen may be calculated as follows:—

v is the observed volume of nitrogen.
B is the height of the barometer in mm.
t is the temperature.
f is the vapour tension of the potash solution, which may be taken to be equal to that of water without serious error.

The volume corrected to 0° and 760 mm. will be given by the following expression:—

$$\frac{v \times 273 \times (B-f)}{(273+t)\,760}.$$

As the weight of 1 c.c. of nitrogen at 0° and 760 mm is 0·00126 gram, the percentage weight of nitrogen will be given by the expression

$$\frac{v \times 273 \times (B-f)}{(273+t)\,760} \times \frac{0{\cdot}00126 \times 100}{w},$$

where w is the weight of substance taken.

Example.—0·206 gram of acetanilide gave 18·8 c.c. of moist N at 17° and 756 mm. [f at $17° = 14{\cdot}5$ mm.]

$$\frac{18{\cdot}8 \times 273 \times (756 - 14{\cdot}5) \times 0{\cdot}126}{(273+17) \times 760 \times 0{\cdot}206} = 10{\cdot}56 \text{ per cent.}$$

Calculated for C_8H_9ON; $N = 10{\cdot}37$ per cent.

Instead of collecting the gas over dilute potash solution, it is often customary to use a very strong solution consisting of equal weights of potash and water. The vapour tension is practically *nil*. Or, again, the nitrogen may be transferred to a graduated tube standing over water, which gives a result free from any error arising from incorrect vapour tension. The manner of transferring the gas is shown in Fig. 16. The stem of a wide funnel is cut off and attached by rubber to the top of the azotometer. This is then filled with water and the projecting end of the azotometer is also filled with water. A graduated tube is now brought over the end, and by opening the tap and raising the reservoir the gas passes into the tube. The end is now closed with the thumb and transferred to a cylinder of water.

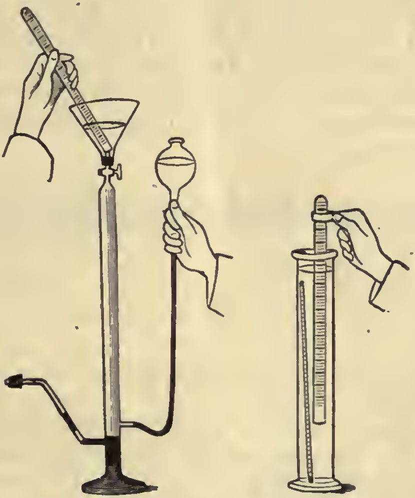

FIG. 16.

The tube is held by a collar of paper, whilst the level is adjusted and the volume and temperature noted.

Before commencing a second determination, the contents of the combustion tube are emptied on to the wire-gauze sieve, placed over one of the tin dishes, and the fine and coarse oxide separated. Both oxides are roasted in order to reoxidise any reduced copper, and transferred as before to their respective flasks. The sodium bicarbonate tube is emptied into a special bottle and then replenished with fresh material. Fresh caustic potash solution is also introduced into the azotometer, unless the stronger solution is used.

Estimation of Nitrogen, Second Method.—Another method which dispenses with the small furnace and bicarbonate tube may also be used. The long combustion tube is closed at one end and magnesite in small lumps is introduced into the tube and shaken down to the closed end until there is a layer of about 13—15 cm. (5—6 in.). This is kept in place by a plug of asbestos and the tube is filled successively with 5 cm. (2 in.) of coarse copper oxide, then fine copper oxide mixed with the substance, a further layer of coarse copper oxide, and finally the copper spiral. The contents of the tube are arranged as shown in Fig. 17.

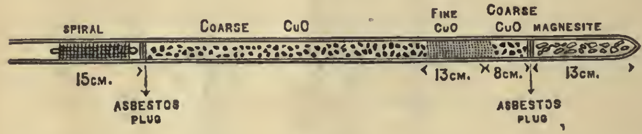

FIG. 17.

The magnesite ($MgCO_3$), which evolves carbon dioxide on heating, takes the place of the sodium bicarbonate in the previous method. The air is displaced at the beginning by heating the magnesite near the closed end of the tube. The magnesite is again heated towards the end of the combustion to sweep out the last traces of nitrogen. The disadvantages of the method are that the magnesite requires to be heated much more strongly than the sodium bicarbonate before it evolves carbon dioxide, and the length of the layer of copper oxide is curtailed.

Kjeldahl's Method.—The organic compound is heated strongly with sulphuric acid, which oxidises the organic matter and converts the nitrogen into ammonium sulphate. The ammonia is then estimated volumetrically by distilling with caustic soda and collecting the gas in standard acid. About 0·5 gram of substance is accurately weighed and introduced into a round Jena flask (500 c.c.), together with 15 c.c. of pure concentrated sulphuric acid and about 10 grams of anhydrous potassium sulphate. The object of the latter is to promote oxidation by raising the boiling-point of the liquid. The flask is clamped over wire-gauze and the contents boiled briskly until the liquid, which first darkens in colour, becomes clear and colourless or faintly yellow. When the decomposition is complete (½—1 hour), the flask is left to cool and the contents then diluted with 2—3 volumes of water. The flask is now attached to the distilling apparatus shown in Fig. 18. It is furnished with a double-bored rubber cork, through one hole of which a bulb adapter is inserted (to retain any alkali which may spirt upwards), the latter being connected with a condenser. The end of the condenser just dips below the surface of 25 c.c. of a half-normal solution of hydrochloric or sulphuric acid, contained in a flask or beaker. A tap-funnel with a bent leg, containing about 30 grams of caustic soda in 60 c.c. of water, is inserted through the second hole in the cork. A few pieces of porous earthenware or granulated zinc are introduced into the flask to prevent bumping. After the apparatus has been fitted together the caustic soda solution is run in slowly and the flask shaken. The liquid is then boiled briskly until no more ammonia is evolved (½—¾ hour). This should be ascertained by testing a drop of the distillate with red litmus paper. If the operation is complete, the liquid is titrated with half-normal sodium carbonate solution, using methyl orange as indicator.

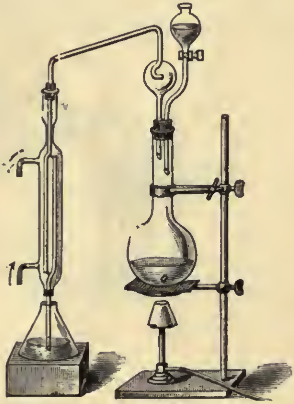

FIG. 18.

Example.—0·5151 gram acetanilide required 17·3 c.c. *N*/2 sodium carbonate :—

$$25 - 17{\cdot}3 = 7{\cdot}7. \quad \frac{7{\cdot}7 \times 0{\cdot}007 \times 100}{0{\cdot}5151} = 10{\cdot}46 \text{ per cent.}$$

The Halogens (*Carius*).—The method of Carius, which is usually employed, consists in oxidising the substance with fuming nitric acid under pressure in presence of silver nitrate. The silver halide which is formed is then separated by filtration and weighed.

The following apparatus is required:—

1. *A piece of thick-walled soft tubing* about 45—48 cm. (18—19 in.) long, and 12—13 mm. inside diameter, the walls being at least 2·5—3 mm. thick. Tubes of hard potash glass are also used, in which case the thickness of the walls may be rather less. The tube is carefully sealed at one end so that there is no thickening of the glass at any point into a blob. If a blob is formed, it may be removed by heating it and blowing gently into the tube and repeating the operation if necessary. Tubes of soft or hard glass may be bought ready sealed at one end. The tube is washed out and dried before use.

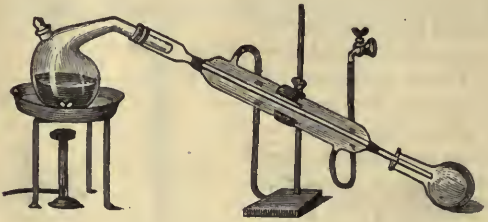

FIG. 19.

2. *A narrow weighing-tube*, 8—10 *cm.* (3—4 in.) long and sealed at one end, which will slip easily into the thick-walled tube.

3. *Pure fuming nitric acid of sp. gr.* 1·5.—This is prepared by distilling equal volumes of concentrated nitric acid (150 c.c.), and concentrated sulphuric acid (150 c.c.) from a litre retort, the neck of which has been bent in the blow-pipe flame as in Fig. 19. The object of this bend is to prevent acid from spirting into the neck and being carried over mechanically into the receiver during distillation. The retort is placed on a sand-bath, and

attached to a condenser. The acids are poured in through a funnel, and a few small bits of broken unglazed pot are dropped in to prevent bumping. The acid is distilled with a moderate flame until about 70 c.c. have collected in the receiver, when the operation is stopped. The distillate is then tested for halogens by diluting largely with distilled water, and adding silver nitrate solution. The liquid should remain perfectly clear. It should also be tested for the presence of sulphuric acid, in case it is required for sulphur estimations, by adding a few drops of barium chloride to a fresh portion of acid diluted as above. If pure, it is kept in a stoppered bottle. If it contains chlorine, it must be redistilled over a few crystals of silver nitrate. Fuming nitric acid has a sp. gr. of about 1·5 at 15°, boils at about 90°, and contains about 90 per cent. of HNO_3. Acid of this strength can be purchased.

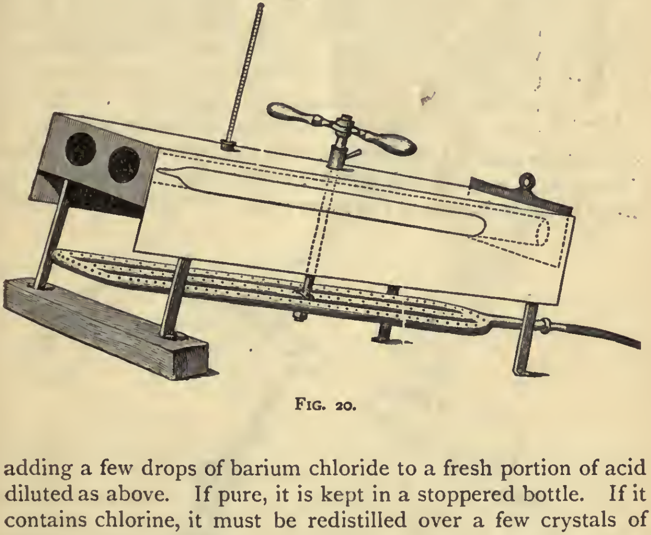

FIG. 20.

4. *A Tube Furnace.*—Various forms of furnace are used. Those which are heated on the principle of the Lothar Meyer hot-air furnace by a number of pin-hole gas jets are easily regulated, and can be raised to a high temperature. The Gattermann furnace, shown in the diagram (Fig. 20), is a very convenient form.

Fig. 21.

Filling and Sealing the Tube.—By means of a thistle funnel with a long stem, about 5 c.c. of fuming nitric acid are first introduced, and the funnel carefully withdrawn so as not to wet the side of the tube. About 0·5 gram silver nitrate in crystals is dropped in, and finally the narrow weighing-tube containing 0·2—0·3 gram of substance is slipped to the bottom of the tube (see Fig. 21). Bromacetanilide (see Prep. 55, p. 152) may be used for this estimation. The open end of the tube is now sealed in the blow-pipe. This operation requires some care and a little skill. About two inches of the tube at the open end is very gradually heated by revolving it for several minutes in the smoky flame of the blow-pipe. The tube is now grasped about the middle with the left hand, and inclined at an angle of about 45°. The blast is turned on slowly, and the end of the tube heated and revolved until the glass begins to soften. The end of a glass rod, about 13 cm. (5 in.) long, held in the right hand, is heated at the same time. The glass rod is then used to press the edges of the glass tube together, as shown in Fig. 23. The subsequent operation depends upon whether soft or hard glass is to be manipulated. If soft glass is used,

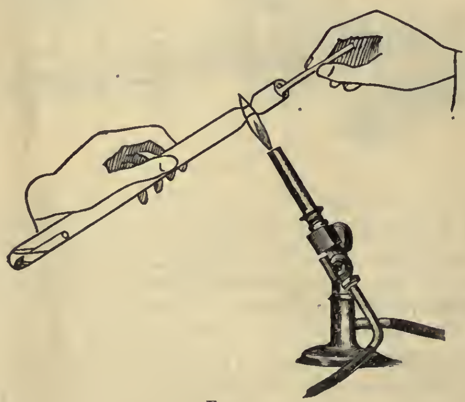

Fig. 22.

the blow-pipe flame is made as hot as possible, but reduced in length to about 8 to 10 cm. (3 to 4 in.). It is directed at a point about 2 to 3 cm. (1 in.) below the open end to which the glass rod is attached, the glass rod now serving as a support whilst the tube is slowly rotated. The glass, if evenly heated and not drawn out, begins to thicken where the flame plays upon it, and the inside diameter of the tube contracts. When the apparent inside diameter of the tube is reduced to about 3 mm. (⅛ in.), the tube is quickly removed from the flame, and a capillary end formed by very slowly drawing out the thickened part of the tube (Fig. 24). When the capillary has so far cooled as to become rigid, it is sealed off. The tube will now have the

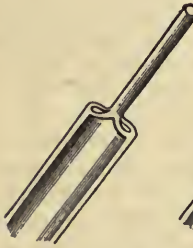
FIG. 23.


FIG. 24.


FIG. 25.

appearance shown in Fig. 25. The tube is kept in a vertical position until cold. If the tube is of hard glass, a somewhat different method of sealing is employed. As soon as the glass is sufficiently soft, it is not thickened, but drawn out at once into a wide capillary, about 1½ cm. long. By directing the flame below this constriction, and continuing to draw out, the capillary is further lengthened. When it has a length of 2 to 3 cm. (1 in.) it is thickened by revolving it in the flame and then sealed off. Hard glass is much more easily manipulated in the oxy-coal gas flame. When cold, the tube is transferred to the metal cylinder of the tube furnace. The furnace, conveniently isolated in case of explosions, should stand on the floor, with the open end raised and facing a wall. The capillary point should project a little beyond the open end of the metal cylinder in which the sealed tube is enclosed. The temperature, indicated by a thermometer fixed in the top of the furnace, is carefully regulated. It is advisable to commence the operation in the morning. The temperature is gradually raised from 150° to 200° during four hours, and then to 230° for a further four hours. The gas is then extinguished, and the tube allowed to cool until the following morning.

Opening the Sealed Tube.—The tube is drawn a little way out of the iron casing, so that the capillary end projects 3 or 4 cm. The tip is then warmed cautiously in the Bunsen flame to expel the liquid which as a rule condenses there. The point is then heated until the glass softens, when the pressure inside perforates the glass and nitrous fumes are evolved. *On no account must the tube be removed from the furnace before this operation is concluded.* The tube is now taken away and opened. A deep file scratch is made in the wide part of the tube, about 3 cm. below the capillary. The end of a glass rod, heated to redness, is then held against the file mark. A crack is produced, which may be prolonged round the tube by touching the tube in front of the crack with the hot end of the glass rod. The top of the tube is now easily removed; but in order to prevent fragments of glass from the broken edge from dropping into the acid, the tube should be held horizontally and the end carefully broken off. Any bits of glass which become detached adhere to the side of the tube, near the open end, and can be easily wiped off. The contents of the tube containing the silver halide are now carefully diluted by adding water a few c.c. at a time, and then washed into a beaker. The mixture is heated to boiling, the silver compound transferred to a filter, and washed with hot water until free from silver nitrate. The filter paper is then dried in a steam oven and the silver salt weighed. A simpler and more accurate method for filtering and weighing the silver halide is to use a perforated or Gooch crucible. A disc of filter paper is cut with a cork cutter of suitable dimensions to fit the bottom of the crucible, which is dried with the crucible in a Victor Meyer air-bath (Fig. 26) heated to 140—150° until constant. The air-bath consists of a jacketed copper vessel fixed upon a tripod. A liquid of constant boiling-point is poured into the outer jacket and the vapours are condensed by an upright condenser or tube which is attached to the outlet tube. The crucible is placed within and covered with a metal lid. There is a small aperture to admit air from below into the inner vessel and a corresponding outlet in the lid. Aniline, b.p. 182°, may be used in the outer jacket in the present case. The Gooch crucible is weighed and fitted to a filter flask and the silver halide filtered and washed at the pump. The crucible is then heated in the air-bath until the weight is constant ($\frac{1}{2}$ hour) and weighed. The result is calculated in percentage of halogen.

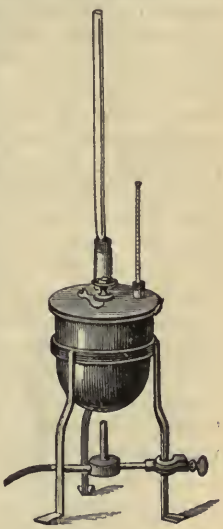

FIG. 26.

Example.—Bromacetanilide gave the following result:—

0·151 gram gave 0·134 gram AgBr.

$$\frac{0{\cdot}134 \times 80 \times 100}{188 \times 0{\cdot}151} = 37{\cdot}51 \text{ per cent.}$$

Calculated for C_8H_8BrNO; Br = 37·38 per cent.

Another Method (Piria and Schiff).—There are some substances which are incompletely decomposed with fuming nitric acid under the conditions described above, and the results are consequently too low. In such cases the following method may be employed. The substance is weighed into a very small platinum crucible, which is then filled up with a mixture of anhydrous sodium carbonate (1 part) and pure powdered quicklime (4 to 5 parts). The crucible is then inverted in a larger crucible, the space between the two being filled with the same mixture of sodium carbonate and lime. The large crucible is now heated, first with a small blow-pipe flame, and then more strongly until the mass is red hot. The contents are then allowed to cool, and dissolved in a large excess of dilute nitric acid. The substance must be added slowly and the acid kept cool. The halogen is then precipitated with silver nitrate and estimated in the usual way.

Sulphur (Carius).—The process is essentially the same as that described under the estimation of halogens (p. 22). The compound is oxidised in a sealed tube with fuming nitric acid, but without the addition of silver nitrate. The resulting sulphuric acid is then precipitated and weighed as barium sulphate. The same quantities of acid and substance (diphenylthiourea may be used ; see Prep. 61, p. 159) are taken, and the process of sealing up and heating, &c., are carried out in precisely the same way as for the halogens. The contents of the tube, after heating, are cautiously diluted with water and then washed out into a beaker, and filtered, if necessary, from fragments of glass. The filter paper is then well washed with hot water and the filtrate diluted to at least 250 c.c. with water. The liquid is heated to boiling, and a few c.c. of barium chloride solution added. On continued heating over a small flame the liquid clears and the precipitate subsides. The addition of another drop of barium chloride will determine if the precipitation is complete. The liquid is then filtered through an ordinary funnel, the precipitate of barium sulphate washed with hot water, dried and weighed in the usual way.

Example.—Diphenylthiourea gave the following result :—

0·2518 gram gave 0·2638 gram $BaSO_4$.

$$\frac{0{\cdot}2638 \times 32 \times 100}{233 \times 0{\cdot}2518} = 14{\cdot}39 \text{ per cent.}$$

Calculated for $C_{13}H_{12}N_2S$; $S = 14{\cdot}05$.

Determination of Molecular Weight

According to Avogadro's law, equal volumes of all gases under similar conditions contain the same number of molecules. Consequently the weights of equal volumes or the densities of gases will represent the ratio of their molecular weights. If the densities are compared with hydrogen as the unit, the ratio

$$\Delta = \frac{W_s}{W_h},$$

in which W_s and W_h are the weights of equal volumes of substance and hydrogen respectively, will give the molecular weight of the substance compared with the molecule or two atoms of hydrogen or half the molecular weight compared with one atom of hydrogen. Consequently the observed density must be multiplied by two in order to obtain the molecular weight compared with one atom of hydrogen.

Vapour Density Method (Victor Meyer).—This method, which is generally employed for substances which volatilise without decomposition, is known as the *air displacement* method of Victor Meyer. It consists in rapidly vaporising a known weight of a substance at a constant temperature at least 40—50° above its boiling-point in a special form of apparatus, which admits of the displaced air being collected and measured. The volume occupied by a given weight of the substance under known conditions is thus ascertained and from these data the density is calculated. The following apparatus is required:—

1. *A Victor Meyer Apparatus* as shown in Fig. 27. It consists of an elongated glass bulb with a narrow stem, and a capillary side-tube. It is provided with a well-fitting rubber cork, which can be pressed easily and tightly into the open end of the stem. The apparatus is clamped within an outer jacket of tin plate or copper, which holds the boiling liquid required to produce a constant temperature. It is represented as transparent in the Fig.

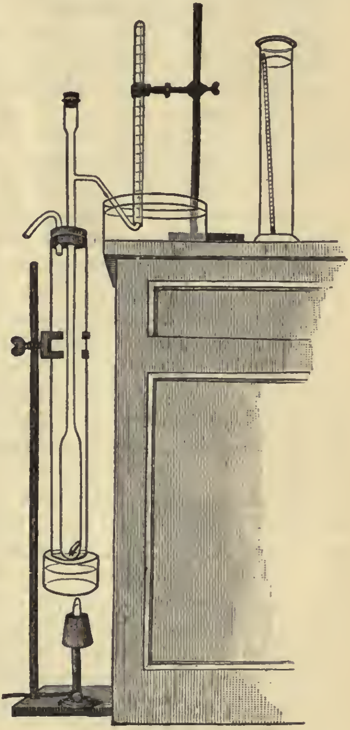

Fig. 27.

2. *Hofmann Bottles.*—The substance, if liquid, is introduced into a small stoppered glass bottle known as a Hofmann bottle (see Fig. 28). The dry bottle with the stopper is carefully weighed and then filled with liquid through a tube drawn out into a wide capillary. The stopper is inserted and the bottle reweighed. It should hold about 0·1 gram of substance.

FIG. 28.

3. *A narrow graduated tube* holding 50 c.c. and divided into tenths of a c.c.

4. *A large crystallising dish* which serves as a gas trough.

5. *A long and wide cylinder* in which the graduated tube can be submerged in water.

6. *A Bunsen burner with chimney.*

The apparatus is set up as shown in Fig. 27. The Victor Meyer apparatus is thoroughly dried by blowing air through by means of a long glass tube, which reaches to the bottom of the bulb. A small quantity of clean dry sand previously heated in a crucible or a pad of asbestos is placed at the bottom of the bulb to break the fall of the Hofmann bottle, when it is dropped in. The bulb of the outer jacket is filled two-thirds full of water and the displacement apparatus is clamped within it, so that it nearly touches the liquid. The apparatus and jacket must be adjusted at such a height that the capillary side limb dips under the water contained in the crystallising dish, placed on the bench. The graduated tube is filled with water and inverted under the water in the crystallising dish and clamped there until required. The burner protected from draughts by the chimney is lighted under the outer jacket and the displacement apparatus left open at the top. To avoid inconvenience arising from the steam, a split cork, into which a bent glass tube is inserted, is pushed loosely into the open end of the jacket.

Whilst the water is boiling steadily and not too violently, the substance is weighed. Chloroform, b.p. 61°, or pure and dry ether, b.p. 34·5° (see Prep. 3, p. 59), may be used for the experiment, as their boiling-points lie well below that of water. Before introducing the bottle and liquid, the apparatus must be tested to ascertain if the temperature is constant. As a rule $\frac{1}{4}$ hour's boiling suffices. Push in the rubber cork and note if within the next minute or two any bubbles escape. If not, slip the graduated tube over the end of the side tube, and carefully remove the rubber cork so that no water enters the stem through the capillary. Remove the stopper of the Hofmann bottle before dropping it in, and at once push in the cork. Very shortly a stream of air bubbles will ascend the graduated tube. When, in the course of a minute or two, the bubbles cease, remove the cork from the apparatus and extinguish the burner. The graduated tube is transferred to the large cylinder of water by closing the open end with the thumb. Leave the tube in the water with a thermometer beside it for $\frac{1}{4}$ hour. Lift the graduated tube, and whilst holding it by a collar of paper adjust the levels inside and out. Read off the volume and note the temperature and barometric pressure.

The density is calculated as follows :—

If v is the volume, t the temperature, B the barometric pressure, and f the vapour tension of water at t°, then the corrected volume is given by the formula

$$\frac{v \times (B-f) \times 273}{760 \times (273+t)}.$$

This multiplied by 0·00009, the weight of 1 c.c. of hydrogen, gives the weight of hydrogen occupying the same volume as the vaporised substance, from which the density $\Delta = \frac{W_s}{W_h}$ is obtained.

Example.—The following result was obtained with ether: 0·1146 gram of ether gave 36·3 c.c. at 11° and 752 mm. $f = 10$ mm. at 11°.

$$\frac{36{\cdot}3 \times (752 - 10) \times 273 \times 0{\cdot}00009}{760 \times 284} = 0{\cdot}00306.$$

$$\frac{0{\cdot}1146}{0{\cdot}00306} \doteq 37{\cdot}4$$

Calculated for $C_4H_{10}O$; $\Delta = 37$.

If substances of higher boiling-point have to be vaporised, the water in the outer jacket is replaced by other liquids of correspondingly higher boiling-point, such as xylene, b.p. 140°, aniline, b.p. 182°, ethyl benzoate, b.p. 211°, amyl benzoate, b.p. 260°, diphenylamine, b.p. 310°, &c. A Lothar Meyer air-bath

(Fig. 29) is, however, much more convenient for obtaining constant temperatures up to 600°. It consists of three concentric metal cylinders, the outer one being coated with non-conducting material. They are so arranged that the heated air from a movable ring burner passes between the two outer cylinders (shown in section in the Fig.), and descends to the bottom of the central cylinder, into which it has access through a ring of circular holes. The hot air is thoroughly mixed by this zigzag flow, and the temperature is equalised. The bulb of the displacement apparatus is clamped in the interior cylinder, and a thermometer is fixed beside it.

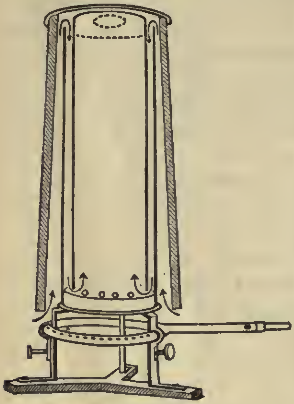

FIG. 29.

The vapour density of freshly distilled aniline, b.p. 182°, may be determined, the temperature of the air-bath being adjusted to about 240°. The adjustment is made by raising or lowering the flame, or by altering the position of the movable ring burner.

Example.—0·1229 of aniline gave 31 c.c. at 7·5° and 750 mm.

$$\Delta = 45{\cdot}87.$$

$$\text{Calculated for } C_6H_7N\ ;\ \Delta = 46{\cdot}5$$

The Cryoscopic or Freezing-point Method (Raoult).—This method depends upon the fact, first demonstrated by Raoult, and afterwards confirmed on theoretical grounds by van't Hoff, that the original freezing-point of a given quantity of liquid is lowered the same number of degrees by dissolving in it different substances whose weights are proportional to their molecular weights. This rule does not, however, apply to salts, acids, &c., which appear to dissociate in certain solvents, nor to substances which form molecular aggregates or *associate* in solution. Supposing the freezing-point of 100 grams of a solvent to be lowered 1° by dissolving 1, 2, 3 and 4 grams respectively, of four different substances, the molecular weights of these substances will be in the ratio of 1 : 2 : 3 : 4. In order to convert these ratios into true molecular weights, the numbers must be multiplied by a coefficient which depends upon the nature of the particular solvent selected, and may be determined empirically by means of substances of known molecular weight or by calculation from thermodynamical data.[1]

If w is the weight of substance and W the weight of solvent, d the depression of the freezing-point, and k the coefficient for the solvent determined for the standard conditions, *i.e.*, for the weight of substance, which produces 1° depression in 100 grams of solvent, the molecular weight M is given by the following expression :—

$$M = \frac{100\,kw.}{dW}$$

The values of k for some of the common solvents with their melting-points are given in the following table :—

	m.p.	k.
Water...	0°	18·5
Nitrobenzene	5·3	70·0
Benzene	5·4	50·0
Acetic acid	17	39·0
Phenol...	40	72·0
p-Toluidine	42·5	51·0

It should be remembered that nitrobenzene, phenol, and acetic acid are hygroscopic.

The following apparatus is required :—

A Beckmann Freezing-point Apparatus.—The form of apparatus is shown in the accompanying Fig. 30. It consists of a glass jar standing on a metal tray and furnished with a stirrer. The cover of the jar has a wide slit to admit the stirrer, and a circular aperture with clips to hold a wide test-tube.

Within the wide test-tube is a narrower one, which is held in position by a cork. The narrow test-tube is sometimes

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[1] *Vide* van't Hoff, *Ztschr. phys. Chem.*, i. p. 481 ; Ostwald, *Outlines of General Chemistry*, chap. vi. p. 139 ; J. Walker, *Introduction to Physical Chemistry*, chap. xviii. p. 176.

furnished with a side tube, for introducing the substance, but it is not necessary. It is provided with a stirrer. A Beckmann thermometer completes the apparatus. This is fixed through a cork so that the bulb nearly touches the bottom of the tube, a wide slit being cut in the side of the cork for moving the stirrer. The Beckmann thermometer is of special construction and requires explanation. As the method involves merely an accurate determination of small differences of temperature, it is not requisite to know the exact position on the thermometer scale. The Beckmann thermometer registers 6 degrees, which are divided into hundredths. The little glass reservoir at the top (*a*, Fig. 30) serves the purpose of adjusting the mercury column to different parts of the thermometer scale by adding or removing mercury from the bulb.

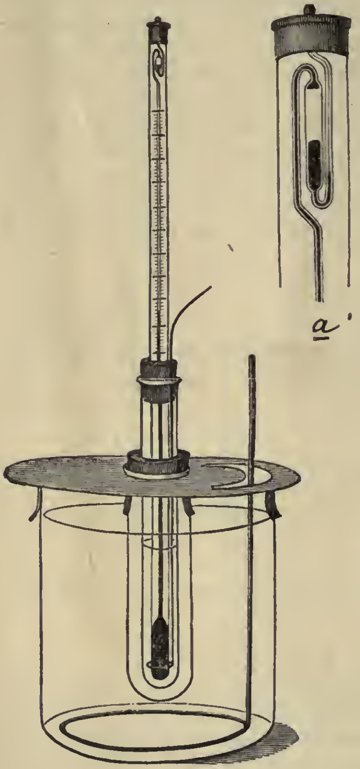

FIG. 30.

Freezing-point Determination.—In the example to be described, pure benzene (see p. 136) is used as the solvent. Carefully dry the inner tube. Fit it with a cork and weigh it together with the cork suspended by a wire to the arm of the balance. Introduce sufficient benzene to cover the bulb of the Beckmann thermometer when it is pushed nearly to the bottom of the tube. About 10 c.c. will be found to be sufficient. Insert the cork and weigh the tube and benzene. Fill up the outer jar with water and small lumps of ice and stir from time to time. Whilst the benzene is cooling in the apparatus the Beckmann thermometer may be adjusted.

Adjustment of the Beckmann Thermometer.—Determine first the value of the mercury thread in degrees between the top of the scale and the orifice of the reservoir. This may be done by warming the bulb in a water-bath along with an ordinary thermometer. As soon as sufficient mercury has collected at the orifice, the burner is removed, the water well stirred, and the little bead of mercury detached by gently tapping the head of the thermometer without removing the bulb from the water. The temperature on the ordinary thermometer is noted and is again read off when the mercury in the Beckmann thermometer has subsided to the top of the scale. Supposing, then, the value of the thread above the scale to have been determined and equivalent to 2°, and the freezing-point of benzene to be about 4°, the thermometer degrees may in this case be made to coincide with the Beckmann degrees, which will bring the thread of mercury well up the scale. The bulb of the thermometer will therefore require to be at a temperature of $6+2=8°$ before removing the excess of mercury. It will, however, be necessary to introduce more mercury into the bulb. This is done by inverting the thermometer and tapping it gently on the palm of the hand, so as to detach a bead of mercury, which slips down to the orifice of the capillary. By warming the bulb the mercury is driven to the top and coalesces with that in the reservoir, so that on cooling the additional mercury runs into the bulb. When sufficient mercury has been added the thermometer is cooled to 8°, and the excess detached as described above The zero should now coincide approximately with that of ice-cold water. If the thermometer is to be adjusted to any other temperature it is placed in water and warmed to that temperature + the number of degrees on the scale above that point + the value of the thread above the scale. The excess of mercury is then detached. The thermometer being adjusted, insert it through the cork so that the bulb is well covered by the benzene, and let the benzene cool well below its freezing-point before stirring. Tap the head of the thermometer occasionally with a pencil. Now stir briskly for a moment. As soon as crystals of the solvent begin to separate the mercury thread will shoot up. Keep stirring occasionally and tapping the thermometer, and read off the maximum point reached by means of a lens. This gives a rough indication of the freezing-point of the benzene. Take out the inner tube and melt the crystals by warming the tube in the hand, and replace it in the apparatus. Repeat the experiment, cooling the solvent not more than 0·2° below its freezing-point before stirring. Make two or three determinations in this way. The results should not differ by more than 0·01°. Fuse some naphthalene in a basin and break it up into small lumps or mould into pellets (p. 39). Weigh a piece of about 0·1 to 0·2 gram on a watch-glass. Raise the cork of the inner tube and drop the naphthalene in. Let it dissolve and then determine the freezing-point of the benzene as before. Repeat the process by dropping one or two fresh pieces of naphthalene into the same solvent. At the end of the operation remove the thermometer and stirrer, and weigh the benzene in the inner tube with the cork. After deducting the weight of naphthalene, the weight of the benzene will be approximately the mean of the first and final weighings.

Example.—Using the same solvent and adding successively three lots of substance (naphthalene), the following results were obtained :—

	w.	*W.*	*a.*	*M.*	*Mean.*
1	0·0985	9·7	0·403	126	125·3
2	0·0729	,,	0·305	123·2	
3	0·1193	,,	0·486	126·8	

Calculated for $C_{10}H_8$; M = 128.

In determining the molecular weight of liquids the apparatus shown in Fig. 82 (p. 210) is convenient for weighing and transferring the liquid to the tube.

The Eykman Depressimeter.—For rapid but less accurate determinations the apparatus of Eykman may be used, which is shown in Fig. 31. It consists of a small vessel, into the neck of which a thermometer is ground. The thermometer is of the Beckmann type but divided into twentieths of degrees. Phenol, m.p. 42·5°, is usually employed as the solvent. The vessel and thermometer are dried and weighed. Phenol melted on the water-bath is poured in to within about 5 c.c. of the neck, the thermometer inserted, and the apparatus weighed again. The melting-point of the phenol must now be ascertained. Warm the metal over a small flame on a sand-bath so as to melt the phenol, leaving, however, a few crystals floating in the liquid, and place the vessel in the cylinder, at the bottom of which is a wire spring or pad of cotton wool. A perforated cork at the top keeps the stem of the thermometer in position. Let the phenol cool down well below its freezing-point, and then shake the cylinder until solidification commences. This will give a first approximation to the freezing-point. The phenol is now warmed gently as before until only a few crystals remain unmelted. The vessel is replaced in the cylinder and the liquid cooled 0·5° to 1° below the point previously ascertained. It is now shaken until crystallisation sets in, and then occasionally until the maximum point is reached. The operation is repeated as often as requisite. The substance is now introduced, a sufficient quantity being taken to produce a depression of at least 0·5°. In order to effect this the phenol is melted and the neck warmed with a small flame until the thermometer is loosened and can be withdrawn. As much phenol as possible is allowed to drain off the neck and off the thermometer, and the weighed quantity of substance introduced. The thermometer is replaced, and any phenol which may have run out is wiped off from the outside of the vessel, which is then re-weighed. The freezing-point is determined as before.


Fig. 31.

The Ebullioscopic or Boiling-point Method (Raoult).—The boiling-point of a liquid is found to be affected by the presence of a dissolved substance in a similar manner to the freezing-point, that is, the boiling-point of a given quantity of a liquid is *raised* the same number of degrees by dissolving in it the same number of molecules of different substances, or, in other words, such weights of these substances as represent the ratio of their molecular weights. These facts were first clearly demonstrated by Raoult.

Statical Method.—The most convenient form of apparatus for determining molecular weight by this method is Beckmann's boiling-point apparatus shown in Fig. 32.

It consists of a boiling-tube, through the bottom of which a stout platinum wire is sealed, which is intended to conduct external heat to the liquid and form bubbles at one point. Above the wire is a layer, about an inch deep, of glass beads. The object of the beads is to break up the bubbles and so prevent superheating and irregular boiling. To the side limb a reflux condenser is attached to condense the vapours given off during the boiling. A Beckmann thermometer is inserted through the mouth of the tube. This thermometer is similar in construction to that used for freezing-point determinations, but it has a smaller bulb. The boiling-tube is placed in the central cavity of a hollow glass or porcelain jacket, which contains the same liquid as the boiling-tube and is also provided with a condenser. This jacket prevents radiation from the boiling-tube. It is provided with two windows of mica. The jacket is clamped on a gauze ring supported on a square tray of asbestos placed upon a

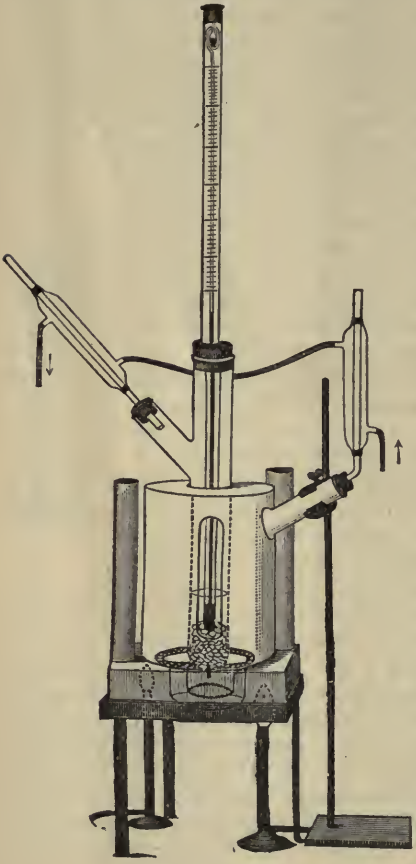

Fig. 32.

tripod. In the figure the lower part of the porcelain jacket and the asbestos tray are made transparent to show the position of the burners and the concentric rings of asbestos below the tray. The asbestos has a circular hole in the centre, which admits the lower end of the boiling-tube. Two asbestos chimneys are fixed upright at the diagonal corners of the tray to carry off heated air and two burners are placed below the other two corners. The boiling-point of the solvent is first ascertained. For this purpose benzene may be used. The Beckmann thermometer must be adjusted so that, when in the boiling liquid, the thread occupies the lower half of the scale. In order to adjust it, the bulb must be placed in water warmed gradually 6°—7° above the boiling-point of benzene, and the bead then detached as already explained in the description of the freezing-point method.

The boiling-tube is carefully dried and weighed with the beads. Sufficient benzene is poured in to cover the bulb of the thermometer, which is pushed down a little way into the beads. The condenser is attached to the side limb. A layer of 1—2 cm. of benzene is poured into the outer jacket, and the condenser fixed in position. The same water supply may be made to traverse both condensers. The two burners under the tray are lighted and the temperature regulated so that the benzene in the outer jacket boils briskly, whilst at the same time sufficient heat finds its way to the boiling-tube, through the gauze ring outside the concentric screens of asbestos below the tray, to keep the benzene in the state of steady ebullition. In about ¼ hour from the time the benzene boils in the inner tube the first reading may be made, and a fresh reading every five minutes until the temperature is constant, *i.e.*, does not vary more than 0·01°. As the atmospheric pressure may produce considerable variations in the reading, it is important to observe the barometer occasionally during the experiment, and to make a correction, which is about 0·043° for every 1 mm. below 760.

The temperature being constant, a pellet (0·1—0·2 gram) of fused naphthalene is carefully weighed and dropped into the boiling-tube through the condenser without interrupting the boiling. These pellets are conveniently made in a small bullet-mould.

The boiling-point will rise and after a few minutes will remain stationary. The temperature is noted. A second and third determination may be made by introducing fresh pellets of naphthalene.

When the observations are complete, the apparatus is allowed to cool and the weight of benzene ascertained by weighing the boiling-tube and benzene.

As in the freezing-point method, the molecular weight is calculated from the weight of substance required to raise the boiling-point of 100 grams of solvent 1°, and the result multiplied by a coefficient which depends upon the nature of the solvent. The following is a list of solvents commonly employed and their coefficients and boiling-points :—

	b.p.	*k.*		b p.	*k.*
Ether	35°	21·1	Ethyl alcohol ...	78°	11·5
Acetone	56°	17·1	Benzene	79°	26·1
Chloroform ...	61°	36·6	Water	100°	5·2
Methyl alcohol ...	66°	8·8	Acetic acid ..	118°	25·3
Ethyl acetate ...	77°	26·8	Aniline	184°	32·2

The molecular weight is determined from the formula

$$M = \frac{100\,kw}{dW}$$

in which w is the weight of substance, W that of the solvent, d the rise of boiling-point, and k the coefficient.

Example.—Using the same solvent and adding successively four pellets of naphthalene, the following results were obtained :—

	w	*W.*	*d.*	*M.*	*Mean.*
1	0 1866	21·313	0·185	126·6	128·3
2	0·1893	,,	0·185	128·3	
3	0·1860	,,	0·185	126·0	
4	0·1901	,,	0·180	132·4	

Calculated for $C_{10}H_8$; M = 128.

A simpler and more convenient form of Beckmann apparatus, requiring much less solvent and giving equally accurate results, is shown in Fig. 33. It consists of a boiling-tube furnished with two side pieces, one of which is stoppered and serves to introduce the substance and the other acts as a condenser. The boiling-tube stands on an asbestos pad and is surrounded by two short concentric glass cylinders surmounted by a mica plate. The other parts of the apparatus are similar to those in the older form and the process is conducted in the same way.

Example—Ten c.c. of benzene were used and two pellets of naphthalene were added.

	w.	*W.*	*d.*	*M.*	*Mean.*
1	0·2072	8·74	0·483	131·1	129·3
2	0·2072	8·74	0·485	127·6	

Dynamical Method.—A third, somewhat different and less accurate, method for determining the boiling-point is one devised by Sakurai and modified by Landsberger and later by Walker and Lumsden. The apparatus of Walker and Lumsden is shown in Fig. 34, and consists of three vessels, a boiling flask, A, a tube, B, graduated, in c.c. and an outer jacket of glass, C. The boiling flask is provided with a safety tube, D, and a bent tube, E, which is connected with another bent tube, F, passing through a cork to the bottom of the graduated tube, B. A thermometer graduated in tenths is inserted through a second hole in the same cork. There is a small hole at G in the graduated tube below the cork through which the vapour of the boiling liquid escapes into the outside jacket, and is condensed by a condenser not shown in the diagram. The outer jacket, C, is attached by a cork surrounding B. A small quantity of solvent (5—10 c.c.) is introduced into the tube B and a larger quantity of the same solvent into the boiling flask, A. The vapour from A passes into B and raises it to the boiling-point, which is read off. The excess of liquid which has condensed is poured out. The weighed

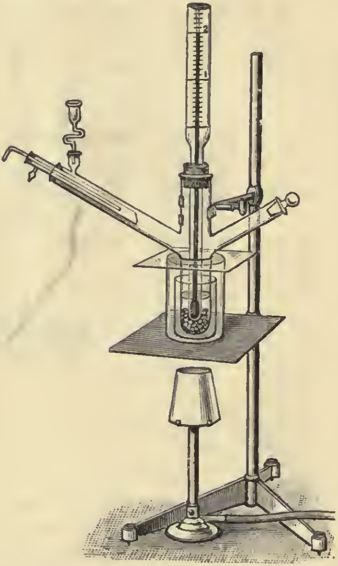

FIG. 33.

substance is introduced and the boiling continued. When a steady temperature is reached, the new boiling-point is determined; the tube is immediately disconnected from the flask, the flame removed, and the volume of the solvent is read off as accurately as possible. By repeating the process, several determinations may be carried out with the same solvent and the same material. The weighing of fresh solvent for each estimation of new portions of substance is also avoided. The main precautions to be taken are (1) to ensure steady boiling in the flask, A, by introducing fragments of porous pot, and (2) to conduct the boiling at such a rate that the drops fall slowly and regularly from the condenser. The inaccuracies of the method arise from constant change of concentration throughout the operation and from impurity in the solvent, the boiling-point of which will have a tendency to rise as the distillation proceeds.

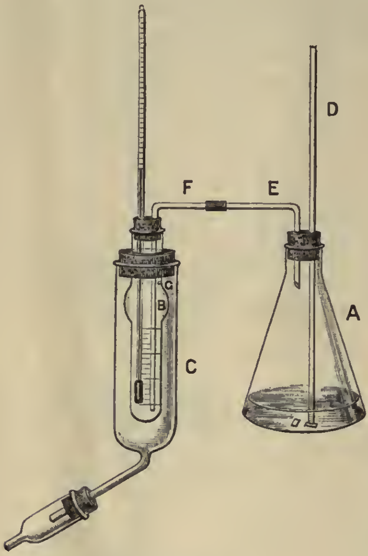

FIG. 34.

Examples.—

	w.	*Volume of solvent.*[1]	*d.*	*M.*	*Mean.*
1	0·8109 grm. (urea)	17·5 c.c. (alcohol)	1·04°	69	67
2	0·8109 ,,	33·1 ,,	0·52	65	

Calculated for CON_2H_4; M = 60.

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[1] The constants for liquids at the boiling-point (= constant divided by the specific gravity of the solvent at the boiling-point) are as follows:—

Alcohol	15·60	Acetone	22·20
Ether	30·30	Chloroform ...	26·00
Water	5·40	Benzene	32·80

Although the boiling-point method is able to dispose of a greater number of convenient solvents than are suitable for freezing-point determinations, it is never so accurate, mainly on account of the difficulty of avoiding fluctuations in the boiling-point, due to radiation, to the dripping of cold liquid from the condenser, to impure solvent, and to barometric fluctuations.

Molecular Weight of Organic Acids

Determination by means of the Silver Salt.—The basicity of an organic acid being known, the molecular weight can be determined by estimating the amount of metal in one of its normal salts. The ratio of metal to salt will be that of the atomic weight of the metal to the molecular weight of the salt. The silver salts are usually selected for these determinations, since they are, as a rule, normal, *i.e.* neither acid nor basic; they are only slightly soluble in water, and are consequently readily obtained by precipitation, and finally they rarely contain water of crystallisation. On the other hand they are very unstable, being quickly discoloured when exposed to light, and often decomposing with slight explosion when heated. Silver benzoate may be prepared by way of illustration. Weigh out roughly 2—3 grams of benzoic acid into a flask, and add about 20 c.c. of water and an excess of dilute ammonia. Boil the solution until the escaping steam has nearly lost the smell of ammonia, and then test the liquid from time to time until it is neutral to litmus. Cool the flask under the tap, and add an excess of silver nitrate solution (3—4 grams $AgNO_3$). Filter with the filter-pump.

Filtration under Reduced Pressure.—A filter-pump is an essential part of a laboratory fitting. It consists of a good water-jet aspirator (see Fig. 35), which is fixed to the water-tap by a stout piece of rubber tubing well wired at both ends. The joint is wrapped round with cloth or leather wired on to the rubber. The side tube of the aspirator is connected by *pump tubing* to an empty filter flask or bottle by means of a glass tap. A second glass tube or side piece is put in connection with the filter flask by means of rubber tubing. The object of inserting a vessel between the pump and the filter flask is to prevent water running back when the aspirator is stopped. Before stopping the pump, close the glass tap. Turn off the water, and then lift the tap out of its socket for a moment to equalise the pressure.

Use a porcelain funnel and filter flask, different sizes of which are shown in Fig. 36. The bottom of the funnel is covered with a disc of filter paper. After filtering, wash three or four times with a little cold water, press the precipitate well down and let it drain. Remove the precipitate and spread it on a piece of porous plate, and place it in a vacuum-desiccator over sulphuric acid. There are several useful forms of vacuum-desiccator, two of which are represented in Fig. 37.

FIG. 35.

The ground rims are greased with vaseline or a mixture of bees-wax and vaseline, and the air is exhausted by attaching the tube of the water-pump to the glass tap of the desiccator.

If the substance is left overnight in the desiccator it will be dry by the next day. The silver salt should be protected as far as possible from the light. When the precipitate is thoroughly dry, weigh about 0·3 gram into a weighed porcelain crucible. Cover with the lid and heat, at first gently, over a small flame. When the first reaction is over, heat the crucible for a few minutes to a dull red heat, and then allow it to cool in a desiccator. The silver salt will be completely decomposed and leave a dull white residue of silver. The crucible is now weighed and the weight of silver determined.

FIG. 36.

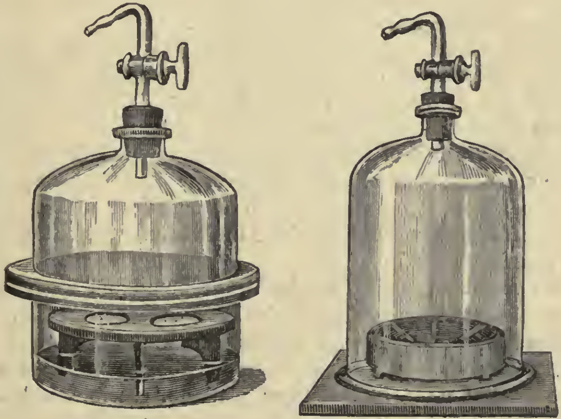

FIG. 37.

If *W* is the weight of salt, *w* the weight of silver, and *n* the basicity of the acid, the molecular weight of the silver salt is determined from the following formula :—

$$\frac{W \times 108\,n}{w}.$$

The molecular weight of the acid is then obtained by deducting *n* atoms of silver and adding *n* atoms of hydrogen.

Example—0·3652 grm. silver benzoate gave 0·1720 grm. silver.

$$\frac{108 \times 0{\cdot}3652}{0{\cdot}1720} - 108 + 1 = 122{\cdot}2.$$

Calculated for $C_7H_6O_2$; M = 122

Molecular Weight of Organic Bases

Determination by means of the Platinum Salt.—The organic bases form, like ammonia, crystalline chloroplatinates with platinic chloride of the general formula $B_2H_2,PtCl_6$. By estimating the amount of platinum present in the salt, it is possible to calculate the molecular weight of the platinum compound, and consequently that of the base.

Dissolve about 1 gram of an organic base (brucine, strychnine, quinine, &c.) in 10 c.c. of a mixture of equal volumes of concentrated hydrochloric acid and water. To the clear hot solution add excess of platinic chloride and let it cool. Yellow microscopic crystals of the chloroplatinate of the base separate. (If the chloroplatinate of the base is very soluble in water, such as aniline, it must be washed with strong hydrochloric acid, pressed on a porous plate and dried in a vacuum-desiccator over solid caustic potash.)

Filter on the porcelain funnel with the pump and wash three or four times with small quantities of cold water. Press the precipitate down and dry on a porous plate in the vacuum-desiccator. When thoroughly dry, weigh out about 0·5 to 1 gram of the compound into a porcelain or platinum crucible, and heat gently with the lid on, and then more strongly until the organic matter is completely burnt away. Cool the crucible in the desiccator and weigh.

The molecular weight of the salt is calculated from the weight w of the platinum, and W of the salt, according to the formula (the atomic weight of platinum being 195):—

$$\frac{W \times 195}{w}.$$

To determine from this the weight of the base, it is necessary to deduct from the molecular weight of the salt that of H_2PtCl_6, and as two molecules of the base are contained in the salt, the result is halved.

Example—0·7010 grm. of aniline chloroplatinate,

$$(C_6H_5NH_2)_2H_2PtCl_6,$$

gave 0·2303 grm. platinum.

$$\frac{0{\cdot}7010 \times 195}{0{\cdot}2303} = 594{\cdot}2. \quad \text{M. W. of the salt.}$$

$$\frac{594{\cdot}2 - 409{\cdot}9}{2} = 92{\cdot}15.$$

Calculated for C_6H_7N ; $M = 93$.

Preparations

General Remarks.—Carefully read through the method. References to the process are given under each heading. Be clear as to the objects of the various steps described and the nature of the materials employed. It cannot be too strongly urged that in all cases where any doubt exists as to the nature of an operation, a preliminary trial should be made in a test-tube with a small quantity of the substance. This is especially necessary in crystallisation where the quantity and character of the solvent are unknown. A vast amount of time and material is thereby saved. A small stock of clean and dry test-tubes ($5 \times \frac{5}{8}$ and smaller sizes) should always be at hand for this purpose; also watch-glasses for microscopic examination of solid substances.

The yield of either the crude or purified product should always be ascertained, and the purity of the product determined either by the boiling-point or melting-point. A small rough balance with celluloid pans, for use on the bench, is indispensable.

Select vessels of a size appropriate to the quantities dealt with. Never use beakers for boiling or evaporating liquids, but flasks and basins. Use ordinary, carefully selected, corks rather than rubber stoppers (which are attacked by many organic liquids), and soften them well before use. The *reactions* described at the end of each preparation are to be done in test-tubes, and should not be neglected.

Above all, work with suitable, compact and clean apparatus on a *clean bench.* The best results are usually obtained when the preparation is carried out with something of the care and accuracy of a quantitative analysis.

Where the *asterisk* occurs, it signifies that the operation must be conducted in the fume cupboard.

Whilst the preparation is in progress, utilise the spare minutes in reading the notes in the *Appendix.*

To facilitate reference to general manipulative processes, which are described as they occur in conjunction with different preparations, the following table is added.

Solids.	Page.
Filtration	53
Filtration under reduced pressure	43
Crystallisation	52
Fractional crystallisation	122
Sublimation	226
Determination of melting-point	72
Liquids.	
Dehydration	56
Determination of boiling-point	58
Distillation under reduced pressure	84
Distillation in steam	107
Fractional distillation	136
Determination of specific gravity	56
Liquids and Solids.	
Heating under pressure	24, 78
Determination of rotatory power	116
Mechanical stirring	90, 147

Purification of Methylated Spirit and Spirits of Wine

Methylated spirit, or spirits of wine 60—70 "over-proof," may generally replace the more costly absolute alcohol as a solvent after undergoing a process of purification. The methylated spirit must be of the old kind, consisting of a mixture of 9 parts spirit of wine and 1 part purified wood-spirit, without the addition of paraffin *i.e.*, it should give a clear solution with water. It is, however, preferable to use rectified spirits 60–70 over-proof which can be bought free of duty by teaching institutions on application to the Inland Revenue Board.

Methylated spirit contains, in addition to ethyl and methyl alcohols, water, fusel-oil, acetaldehyde, and acetone. It may be freed from aldehyde by boiling with 2—3 per cent. solid caustic potash on the water-bath with an upright condenser for one hour, or if larger quantities are employed, a tin bottle is preferable, which is heated directly over a small flame (see Fig. 38). It is then distilled with the apparatus shown in Fig. 39. The bottle is here surmounted with a T-piece holding a thermometer. The distillation is stopped when most of the spirit has distilled and the thermometer indicates 80°. A further purification may be effected by adding a little powdered permanganate of potash and by a second distillation, but this is rarely necessary. The same method of purification may be applied to over-proof spirit, which will henceforth be called *spirit* as distinguished from the purified product or absolute alcohol.

FIG. 38.

Ethyl Alcohol, $C_2H_5.OH$

Commercial absolute alcohol may be used for the preparations which follow. It is obtained by distilling crude spirits of wine over quicklime, and usually contains about 0·5 per cent. of water.

Properties.—Pure ethyl alcohol boils at 78·3°, and has a sp. gr. of 0·793 at 15°. It mixes with water in all proportions

Reaction.—A delicate test for ethyl alcohol is the *iodoform reaction.* Pour a few drops of alcohol into a test-tube and add about 5 c.c. of a solution of iodine in potassium iodide, and then dilute caustic soda solution until the iodine colour vanishes. Shake up and warm very gently to about 60°. If no turbidity or precipitate appears at once, set the test-tube aside for a time. Yellow crystals of iodoform will ultimately deposit, which have a peculiar odour, and a characteristic star shape when viewed under the microscope. The same reaction is given with other substances, such as acetone, aldehyde, &c., but not with methyl alcohol.

FIG. 39.

PREPARATION 1.

Potassium Ethyl Sulphate, $C_2H_5O.SO_2.OK$

Dabit *Ann. Chim. Phys.* 1800, (1) **34**, 300 ; Claesson, *J. prakt. Chem.* 1879 (2) **19**, 246.

70 grms. (87 c.c.) absolute alcohol.[1]
50 „ (27 c.c.) conc. sulphuric acid.

The alcohol is poured into a round flask (½ litre) and the sulphuric acid is slowly added and well mixed by shaking. A

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[1] For the preparation of methyl potassium sulphate the same quantity of methyl alcohol is used ; in other respects the two processes are identical. The yield is 45—50 grams.

considerable amount of heat is developed in the process. The flask is now fitted with a reflux condenser (see Fig. 40) placed upon the water-bath and heated for 2—3 hours. The product now contains in addition to ethyl hydrogen sulphate, free sulphuric acid and unchanged alcohol. The liquid on cooling is poured into ½ litre of cold water in a large basin and well stirred. It is neutralised by adding chalk ground into a thin paste with water. This precipitates the free sulphuric acid as calcium sulphate and converts the ethyl hydrogen sulphate into the soluble calcium salt. The mixture is heated and filtered through a large porcelain funnel (see Fig. 36) at the filter-pump, and the precipitate pressed well down. The clear filtrate is heated on the water-bath and a solution of potassium carbonate (about 50 grams) is added in small quantities until the liquid is slightly alkaline. To ensure complete precipitation a little of the clear liquid should be tested with a solution of potassium carbonate before proceeding.

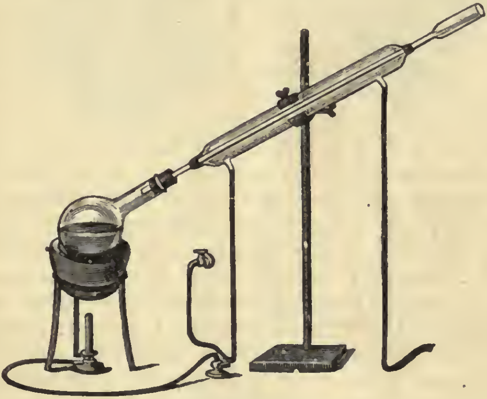

Fig. 40.

The calcium salt is thereby converted into the soluble potassium salt and calcium carbonate is precipitated. The latter is removed by filtration, as before, and the filtrate concentrated on the water-bath to a small volume until a drop of the liquid, removed on the end of a glass rod, crystallises at once on cooling

The potassium ethyl sulphate is filtered and washed with a little spirit or methylated spirit.[1]

Crystallisation.—The substance should now be recrystallised. The success of many operations in practical organic chemistry depends upon skill in crystallisation. The first essential is to select a suitable solvent, that is, one which dissolves much more of the substance at a high than at a low temperature. To discover a suitable solvent a small quantity of the substance (0·1 gram is sufficient) is placed in a test-tube and a few drops of the solvent poured in. The common solvents are water, methyl and ethyl alcohol, ethyl acetate, acetic acid, acetone, benzene (also toluene and xylene) nitrobenzene, petroleum spirit and ligroin, chloroform and carbon tetrachloride. If the substance dissolves on shaking without warming or does not visibly diminish on boiling, it may be discarded as unsuitable. If it dissolves on heating or boiling and crystallises on cooling in considerable quantity, it may be employed. Sometimes solutions can be supercooled. In such cases, rubbing the sides of the test-tube with a glass rod will cause the substance to deposit. A convenient method of crystallisation may be occasionally employed by using two miscible solvents in one of which the substance is soluble and in the other insoluble. The substance is then dissolved in a small quantity of the first solvent and the second added gradually until a turbidity appears. Alcohol and water, and benzene and petroleum spirit are often used in conjunction in this way. If a substance of low melting-point is to be crystallised care should be taken that sufficient solvent is present to prevent the substance separating at a temperature at which it is still liquid. The interval of temperature may be increased after the solution has reached the ordinary temperature, by cooling it in a freezing mixture, when some of the solid will be deposited.

In the present instance spirit or methylated spirit (purified) will be found an efficient solvent for potassium ethyl sulphate. The following is the mode of procedure when a volatile or inflammable solvent is used: the substance is placed in a round flask attached to an upright condenser and heated on the water-bath. The form of apparatus is that already described (see Fig.

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[1] If methylated spirit is used it must be purified according to the method described on p. 48

40.) Small quantities of spirit are added and kept boiling until a solution is obtained. A small quantity of impurity may remain undissolved. The hot solution is at once decanted or filtered through a *fluted filter* (Fig. 41) or hot water funnel (Fig. 42) into a beaker and allowed to cool.

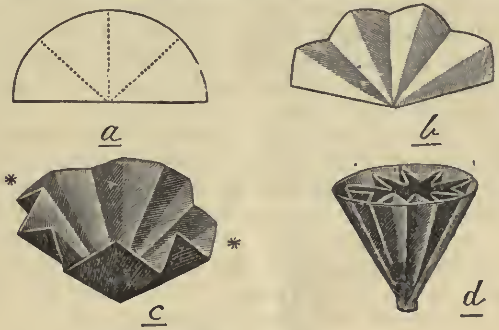

FIG. 41.

A fluted filter is made by first folding a large circular filter paper in the ordinary way. It is then half opened out and the two quadrants folded towards the middle line (see *a*, Fig. 41), This makes three creases with the hollows on the same side. The filter is now turned over and each section folded down the centre so that the hollows of the four new creases alternate with the ridges of the three others as shown at *b*. The paper when opened now appears like *c*. The two rectangular flutings indicated by an asterisk have still to be divided by a crease

FIG. 42.

down the middle. The filter is now pushed well into the funnel, the stem of which is cut off short as shown at *d.*

A hot-water funnel is shown in Fig. 42. It consists of a jacketed metal funnel, with a projecting metal tube. The vessel is partly filled with water which is boiled by placing a small burner under the end of the tube. The glass funnel is placed within the metal-jacket. By keeping the liquid hot, crystallisation in the filter is thus prevented.

Before filtering an inflammable liquid such as alcohol the flame must be removed. The potassium ethyl sulphate is dried on a plate of unglazed earthenware or on a thin pad consisting of three or four sheets of filter paper, with another sheet over the crystals to keep out the dust. On concentrating the mother liquors on the water-bath, a further quantity of crystals may be obtained. Yield 35—40 grams. The following equations express the chemical reactions which occur :

1. $$C_2H_5OH + H_2SO_4 = \underset{\text{Ethyl hydrogen sulphate.}}{C_2H_5SO_4H} + H_2O$$

2. $$2C_2H_5SO_4H + CaCO_3 = \underset{\text{Calcium ethyl sulphate.}}{(C_2H_5SO_4)_2Ca} + H_2O + CO_2$$

3. $$(C_2H_5SO_4)_2Ca + K_2CO_3 = \underset{\text{Potassium ethyl sulphate.}}{2C_2H_5SO_4K} + CaCO_3.$$

Properties. Colourless, foliated crystals ; easily soluble in water and dilute alcohol, less soluble in absolute alcohol.

Reactions. 1. Dissolve a little of the recrystallised salt in water, and add barium chloride solution. There is no precipitate, as the barium salt of ethyl hydrogen sulphate is soluble in water. 2. Boil a little of the solution of the salt with a few drops of dilute hydrochloric acid for a minute and add barium chloride. A precipitate of barium sulphate is formed, as, on boiling ethyl hydrogen sulphate in aqueous solution, it is decomposed into sulphuric acid and alcohol (see *Appendix*, p. 234).

PREPARATION 2.

Ethyl Bromide (Monobromethane), C_2H_5Br.

De Vrij, *Jahresber.*, 1857, 441.

100 grms. potassium bromide.
100 ,, (54 c.c.) conc. sulphuric acid.
60 ,, (75 c.c). absolute alcohol.

Fit up the apparatus as shown in Fig. 43. The distilling flask should have a capacity of not less than 1 litre, and is attached to a long condenser. An adapter is fixed to the end of the condenser, dipping into a conical flask (250 c.c.), which serves as receiver. The alcohol and sulphuric acid are mixed in the distilling flask and cooled to the ordinary temperature under the tap. The potassium bromide, coarsely powdered, is then added. The flask, which is closed with a cork, is fixed to the condenser and heated on the sand-bath. A sufficient quantity of water is poured into the receiver to close the end of the adapter. After a short time the liquid in the flask begins to boil and froth up, and the ethyl bromide, in the form of heavy drops of colourless liquid, distils and collects at the bottom of the receiver. If the liquid threatens to froth over, the flask must be raised from the sand-bath for a moment. The distillation is continued until no further drops of oil appear at the end of the condenser. As the ethyl bromide has a low boiling point (38–39°), it is desirable to surround the receiver with ice during this operation. The distillate is now removed and poured into a separating funnel (Fig. 44), and the *lower layer* of ethyl bromide separated. The water is thrown away and the ethyl bromide poured back together with about an equal bulk of dilute sodium carbonate solution and shaken up. The ethyl bromide is withdrawn, as before, and again shaken up with water. Finally, it is carefully separated from the water and run into a dry distilling flask. The small quantity of water which remains

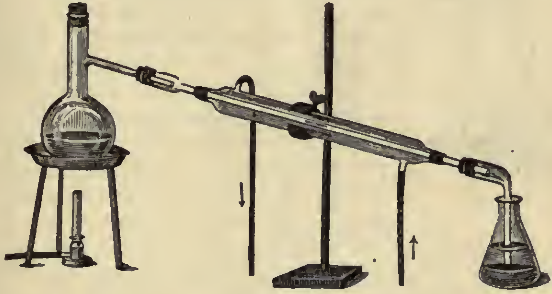

FIG. 43.

and renders the liquid turbid, is removed by adding a dehydrating agent.

Dehydration. Moisture can be readily removed from liquids by adding a solid hygroscopic substance which does not act chemically upon the liquid. The common dehydrating agents are calcium chloride, potassium carbonate, sodium sulphate (anhydrous), quicklime, &c. Alkalis cannot of course be used for dehydrating organic acids, nor can calcium chloride be employed in conjunction with alcohols or organic bases, with which it combines. In the present instance it can be used. A few small pieces of the granulated or fused calcium chloride are added to the liquid. The flask is corked and left to stand for some hours until the liquid becomes clear. It is then distilled. A thermometer is inserted into the neck of the flask with the bulb just below the side tube. The flask is attached to a condenser and heated gently on the water-bath, so that the liquid distils at a moderate speed (2—3 drops a second). The temperature is noted and the portion boiling at 35—43° collected in a separate flask. This consists of ethyl bromide which may contain a little ether. Yield 75—80 grams.

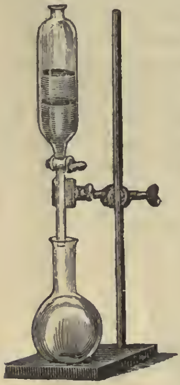

FIG. 44.

$$\underset{\text{Alcohol.}}{C_2H_5OH} + H_2SO_4 = \underset{\text{Ethyl hydrogen sulphate.}}{C_2H_5.H.SO_4} + H_2O.$$

$$C_2H_5.H.SO_4 + KBr = \underset{\text{Ethyl bromide.}}{C_2H_5Br} + KHSO_4.$$

Properties—Colourless liquid ; b. p. 38·8° ; sp. gr. 1·47 at 15° (see *Appendix*, p. 234).

Determination of Specific Gravity.—A simple method for determining the specific gravity of liquids is as follows : A pyknometer, or small glass bottle, is used of about 20 to 30 c.c. capacity, with narrow neck, upon which a mark is etched and which is closed by a ground glass stopper (Fig. 45).

The bottle is thoroughly cleaned and dried by warming and aspirating air through it, after which it is allowed to cool and weighed. It is then filled with the liquid, which is poured in through a funnel, the stem of which is drawn out so as to pass through the narrow neck. The bottle is placed in a mixture of snow or pounded ice and left a quarter to half an hour, until the contents have a temperature of 0°. The meniscus is now adjusted until it coincides with the mark on the neck of the bottle. If more liquid has to be added, this may be done from a small pipette with capillary delivery tube; if some of the liquid has to be removed, a thin roll of filter paper may be inserted which will absorb it. The bottle is then stoppered, dried on the outside, left in the balance case for a quarter of an hour, and weighed. It is then emptied, cleaned, and dried, and filled with distilled water previously boiled. The water is cooled to 0°, the meniscus adjusted and the bottle weighed, the same process being repeated as that just described. The following expression will give the specific gravity of the liquid at 0° compared with water at 0°:—

FIG. 45.

$$\Delta = \frac{w_3 - w_1}{w_2 - w_1}$$

Where w_1 = weight of empty bottle,
w_2 = „ bottle and water at 0°,
w_3 = „ bottle and liquid at 0°;

or, if compared with water at 4°, the above number must be multiplied by the density at 0° = 0·999873.

A very delicate and useful piece of apparatus, which is readily made with the blow-pipe, is Perkins' modification of Sprengel's pyknometer.[1] It is especially adapted for small quantities of liquid and for the more volatile ones. The apparatus (Fig. 46) consists of a U-tube to hold from 2 to 10 c.c., drawn out at each end into a fine capillary. The one capillary limb, *a*, is bent outwards and is furnished with a small bulb; the other, *b*, is bent at a right angle with the first. On the limb *a*, between the bulb and the top of the U-tube a mark is etched. The

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[1] *Trans. Chem. Soc.* 1884, **45**, 421.

tube is dried and weighed, and the liquid drawn in through the limb *b*, until it half fills the small bulb on the limb *a*. The apparatus is cooled in ice and water, and the meniscus adjusted to the mark on *a* by tilting the tube until the limb *b* has a horizontal position. To the end of this limb a piece of filter paper is applied, until the liquid sinks to the desired position in the limb *a*. The U-tube is then brought to the vertical position, loose glass caps placed over the ends of the two limbs, the apparatus carefully dried, and allowed to stand and weighed. The operation is then repeated with distilled water.

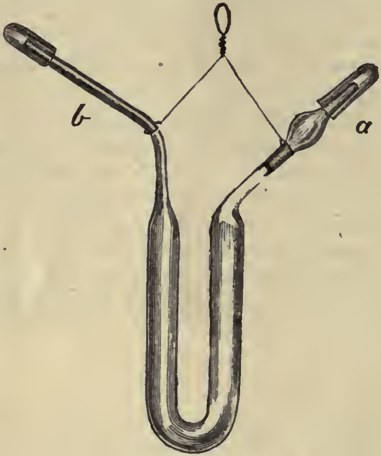

FIG 46.

Example—An experiment with ethyl bromide gave the following result :—

Weight of tube empty	6·242	grams
+ ethyl bromide at 0°	9·472	,,
+ water at 0°	8·417	,,

$$\Delta\frac{0^\circ}{4^\circ} = 0{\cdot}999873 \times \frac{3{\cdot}230}{2{\cdot}175} = 1{\cdot}485.$$

Determination of the Boiling-point.—A correct determination of the boiling-point of a liquid is made with a standard thermometer, *i.e.*, one that has been calibrated, and the 0° and 100° points carefully determined. An ordinary thermometer corrected by a standard thermometer at Kew will serve equally well. Correction must also be made for barometic pressure. This is approximately 0·043° for every 1 mm. below 760 (Landolt). A further correction is required for the thread of mercury, which may project above the vessel. For this correction the following formula may be used :—

$$N(T - t)0{\cdot}000154.$$

Where T = apparent temperature in degrees.
t = temperature of a second thermometer, the bulb of which is placed at half the length N above the vessel.
N = length of the mercury column in degrees from above the vessel to T.
0·000154 = apparent expansion of mercury in glass.

This correction may be avoided by using short (Anschütz) thermometers, in which the mercury thread is entirely immersed in the vapour. A rough correction for points above 100° may be made by determining the boiling points of pure organic substances, such as naphthalene, 216·6°, &c.

PREPARATION 3.

Ether (Diethyl Ether, Diethyl Oxide), $(C_2H_5)_2O$

V. Cordus (1544); *Journ. Pharm.*, 1815, **1**, 97; Williamson, *Phil. Mag.* 1850, (3) **37**, 350.

150 grms. (80 c.c.) conc. sulphuric acid.
85 ,, (110 c.c.) absolute alcohol.

A distilling flask ($\frac{1}{2}$ litre) is fitted with a double-bored cork. Through one hole a thermometer is inserted, the bulb of which must be covered by the liquid in the flask and through the other a tap-funnel passes. The side-tube of the distilling flask is fixed by a cork into the upper end of a long condenser. An adapter is fitted to the lower end and passes through the neck of a flask, which is surrounded by ice. The apparatus is shown in Fig. 47. The sulphuric acid and alcohol are cautiously mixed together in the distilling flask, which is then placed upon a sand-bath and attached to the condenser. The mixture is heated to 140° and alcohol is run in from the tap-funnel at the same speed as the liquid distils (about three drops a second). The temperature must be kept constant at 140—145°. When about twice the quantity of alcohol contained in the original mixture has been added and converted into ether, the distillation is stopped. The receiver now contains, in addition to ether, alcohol, water and sulphurous acid. The liquid is poured into a large separating funnel and a small quantity (30—40 c.c.) of dilute caustic soda added and well shaken. After settling, the caustic soda solution is drawn off below, and about the same quantity of a strong solution of common salt added, and the process of shaking and drawing off repeated. The ether, which is now free from sulphurous acid and from most of the alcohol, still contains water. It is therefore poured into a large dry distilling flask and some pieces of solid calcium chloride added. It is allowed to stand loosely corked overnight. The distilling flask is now attached to a long condenser and heated on the water-bath. The ether, which distils, still contains traces of alcohol and water, which it obstinately retains and from which it can only be freed

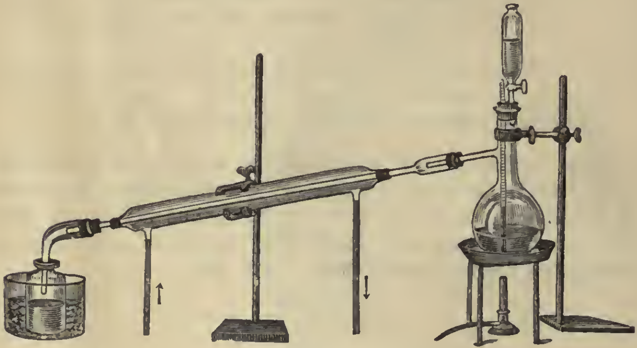

FIG. 47.

by a further treatment with metallic sodium. A few very thin slices of sodium are dropped into the receiver and the vessel closed with a cork, through which an open calcium chloride tube is inserted to allow any hydrogen to escape and to prevent the entrance of moisture.

When the sodium produces no further action, the ether is decanted from the sodium residues into a distilling flask and distilled on the water-bath. A thermometer is placed in the neck of the flask to indicate the boiling-point, which should be constant at 35°.

$$C_2H_5OH + H_2SO_4 = C_2H_5SO_4H + H_2O.$$
$$C_2H_5SO_4H + C_2H_5OH = C_2H_5.O.C_2H_5 + H_2SO_4.$$

Properties.—Colourless, mobile liquid ; b.p. 35° ; sp. gr. 0·720 at 15° ; burns with a luminous flame ; not miscible with water ; 9 parts of water dissolve 1 part of ether, and 35 parts of ether dissolve 1 part of water at the ordinary temperature. See *Appendix*, p. 236.

Commercial Ether is made from methylated spirit and contains alcohol, water, and other impurities, and for many reactions requires to be purified. The following method of purification may be employed. The ether is distilled over a little coarsely powdered caustic potash, then placed in contact with solid calcium chloride for several hours, and finally decanted and treated with metallic sodium. It is convenient to use a sodium knife (Fig. 48) or press (Fig. 49) for preparing the sodium. In the former the metal can be cut into very thin slices, and in the latter it is pressed into fine wire through a circular steel die,

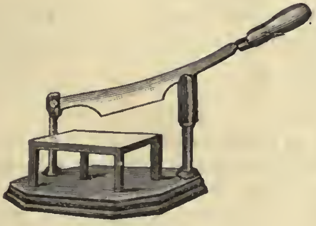

FIG. 48.

FIG. 49.

It must be remembered that ether is highly inflammable, and also exceedingly volatile, and great care should be taken that no flame is in the neighbourhood of the liquid. It must on no account be distilled over the bare flame, but always from the water-bath, and then with a long well-cooled condenser. The distillation of large quantities should be avoided as far as possible. In such cases it is convenient to employ a distilling flask of moderate size (250 c.c.), and to add, as the liquid distils, a fresh supply of ether or ethereal liquid from a tap-funnel inserted through the neck of the flask, which can be done without interrupting the distillation.

PREPARATION 4.

Ethylene Bromide. $CH_2Br.CH_2Br$.

Balard, *Ann. Chim. Phys.* 1826 (2), **32**, 375; Erlenmeyer. Bunte, *Annalen*, 1873, **168**, 64.

25 grms.		(30 c.c.) absolute alcohol.
150	„	(80 c.c.) conc. sulphuric acid.
200	„	(65 c.c.) bromine (which must be measured out in the fume-cupboard).
300	„	of a mixture of 100 grms. (124 c.c.) alcohol and 200 grms. (108 c.c.) conc. sulphuric acid.

Fit up an apparatus as shown in Fig. 50. It consists of a round flask (2 litres), which is furnished with a double-bored cork. A tap-funnel is inserted through one hole and a delivery tube through the other, by which it is connected with two wash-bottles with safety tubes. A useful form of wash-bottle is that shown in Fig. 50 and in section at *a*. Otherwise a three-necked Woulff bottle will serve, with a long tube inserted through the central neck. The wash-bottles are one-third filled with caustic soda solution. The two ordinary wash-bottles standing in the trough of water contain the bromine. The first contains about 50 c.c. of bromine and 1 c.c. of water and the second about 15 c.c. of bromine and 1 c.c. of water. The latter is attached to a wide **U** tube or cylinder containing pieces of soda-lime. If a cylinder is used a layer of glass fragments or marbles should form a layer round the orifice of the inlet tube with the soda-lime above.

The joints being tight, the mixture of 25 grams of alcohol and 150 grams of sulphuric acid is run into the large flask containing a little dry sand and heated with a small flame on the sand-bath until a steady stream of gas is evolved. When this occurs the mixture of alcohol and sulphuric acid is dropped in slowly from the tap-funnel. It is important to moderate the temperature to prevent excessive frothing and the separation of carbon, which, however, cannot altogether be avoided. A considerable quantity of sulphur dioxide which is evolved with the ethylene is removed by the caustic soda in the wash-bottles. If the water surrounding the bromine bottles becomes warm, small lumps of ice should be thrown in. The caustic soda should be occasionally renewed, otherwise sulphur dioxide may pass into the bromine and reduce it to hydrobromic acid. If the pressure in the apparatus causes a back rush of bubbles through the tap-funnel attached to the flask, the difficulty is met by inserting the stopper in the tap-funnel. After a few hours the bromine in both vessels is decolourised or at least changes to a straw colour. The crude ethylene bromide is removed and shaken with dilute caustic soda solution, then with water, separated from the aqueous layer and dehydrated

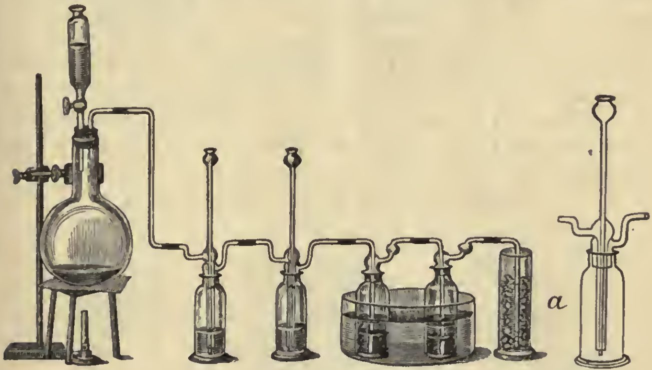

FIG. 50.

over small pieces of calcium chloride. It is decanted or filtered from the calcium chloride and distilled. The distillate is collected at 130—132°. The yield is nearly equal to the weight of bromine taken.

$$C_2H_5(OH) - H_2O = C_2H_4$$
$$C_2H_4 + Br_2 = C_2H_4Br_2.$$

Properties.—Colourless liquid, which solidifies, at 0° to a crystalline mass and melts at 9°; b.p. 131·5°; sp.gr. 2·19 at 15°.

Reaction.—Attach a 100 c.c. flask to a short upright condenser (see Fig. 86) and to the upper end of the condenser attach a vertical delivery tube, dipping into an ammoniacal cuprous chloride[1] solution. Pour 2—3 c.c. of ethylene bromide into the flask with 4 times its volume of strong methyl alcoholic potash, which is prepared by boiling methyl alcohol with excess of caustic potash on the water-bath with upright condenser. On gently heating, a rapid evolution of acetylene occurs and the characteristic brown copper compound ($C_2H_2Cu_2,H_2O$) is precipitated from the cuprous chloride solution.

$$C_2H_4Br_2 + 2KOH = \underset{\text{Acetylene.}}{C_2H_2} + 2KBr + 2H_2O.$$

See *Appendix*, p. 237.

PREPARATION 5.

Acetaldehyde, $CH_3.CO.H$

Liebig, *Annalen*, 1835, **14**, 133; Staedeler, *J. prakt. Chem.*, 1859, (1) **76**, 54.

100 grms. potassium bichromate
420 c.c. water.

A mixture of 100 grms. (125 c.c.) absolute alcohol and 140 grms. (75 c.c.) conc. sulphuric acid.

100 c.c. methylated ether, which has been left to stand over solid caustic potash for a few hours, and then distilled off from the water-bath.

A round flask (1½ litre) is provided with a double-bored cork.

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[1] *Ammoniacal cuprous chloride* is made as follows: Boil up copper oxide and metallic copper with conc. hydrochloric acid for a short time until the liquid is nearly colourless, and pour the liquid into water. The white cuprous chloride is washed once or twice by decantation and dissolved in a strong solution of ammonium chloride. When required a little ammonia is added sufficient to give a clear blue solution.

A bent tube, which passes through one hole, connects the flask with a condenser and receiver. A tap-funnel is inserted through the other hole. The flask is placed upon a sand-bath, and the receiver is cooled in ice. It is important that all the corks should be tight, as a small leak will considerably diminish the yield. The potassium bichromate in small pieces and the 420 c.c. of water are placed in the flask and gently warmed. The flame is then removed, and the mixture of alcohol and sulphuric acid, which may be used warm, is slowly added from the tap-funnel. The flask is occasionally shaken. A considerable rise of temperature occurs and the liquid darkens, whilst aldehyde, with a little water and alcohol, distils. When the mixture has all been added, the flask is heated on the sand-bath until all the aldehyde has distilled (about 150 c.c.), which may be determined by removing the cork from the flask and noticing if the smell of aldehyde is still perceptible. The distillate is now redistilled on the water-bath in the apparatus shown in Fig. 51.

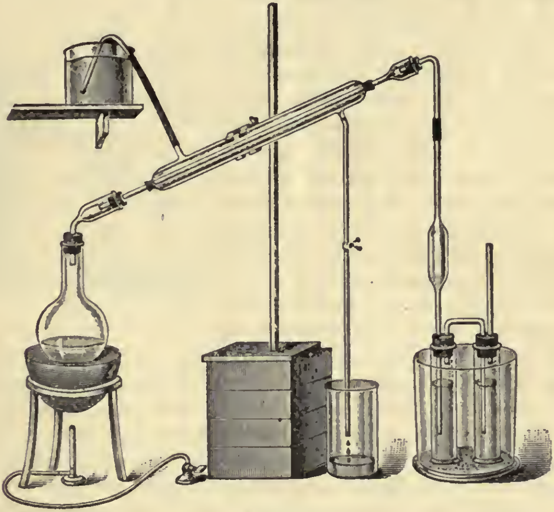


FIG. 51.

The flask is attached to an upright condenser in which the water is kept at a temperature of 30—35°. Alcohol and aqueous vapour condense in the condenser; the aldehyde, on the other hand, passes by a tube attached to a 100 c.c. pipette into two narrow (100 c.c.) cylinders, one-third filled with the dry ether, and cooled in ice-water. The aldehyde readily dissolves in the ether and is rapidly absorbed. If the ethereal solution is now saturated with dry ammonia gas, the whole of the aldehyde separates out in the form of colourless crystals of aldehyde-ammonia, $CH_3.CH.OH.NH_2$. The apparatus for preparing the dry ammonia is shown in Fig. **52.** The flask containing strong ammonia solution is heated by a *small* flame, when the gas is readily evolved and passes up the tower, which is filled with soda-lime or quicklime. The ethereal solution is saturated with the gas, and is then allowed to stand for an hour.

FIG. 52.

The ether is then decanted from the crystals, which are drained at the filter-pump, washed with a little ether, and finally dried in the air on filter-paper. Yield of aldehyde-ammonia, 25—30 grams. It may be used for the reactions described on p. 67.

Pure aldehyde may be prepared from the aldehyde-ammonia as follows: The crystals are dissolved in an equal weight of water and distilled on the water-bath with a mixture of $1\frac{1}{2}$ parts of concentrated sulphuric acid and 2 parts of water, the receiver being well cooled in ice. The temperature of the water-bath is gradually raised until the water begins to boil, and the distillation is then interrupted. The distillate is dehydrated over an equal bulk of calcium chloride, from which it is distilled in the water-bath, heated to 30°. The anhydrous aldehyde is kept in a well-stoppered bottle.

$$3C_2H_5(OH) + K_2Cr_2O_7 + 4H_2SO_4 = 3C_2H_4O + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

$$C_2H_4O + NH_3 = CH_3CH.OH.NH_2$$

$$2CH_3CH.OH.NH_2 + H_2SO_4 = 2CH_3.CO.H + (NH_4)_2SO_4.$$

Properties.—Colourless liquid with a distinctive smell; b.p. 21°; sp. gr. 0·807 at 0°; soluble in water, alcohol and ether.

Reactions.—Acetaldehyde and many of the aliphatic aldehydes are characterised by the following reactions:—

1. Prepare a little ammonio-silver nitrate by adding dilute ammonia drop by drop to silver nitrate solution until the precipitate just dissolves. Add to a third of a test-tube full of the ammonia-silver nitrate solution about 1 c.c. of aldehyde, and place it in a beaker of hot water. A mirror of metallic silver is deposited. $Ag_2O + C_2H_4O = Ag_2 + C_2H_4O_2$ (acetic acid).

2. To 1 c.c. of aldehyde add 2–3 times its volume of a cold *saturated* solution of sodium bisulphite and shake up. The additive compound, $CH_3CH.OH.SO_3Na$, crystallises out on standing. A crystal of the substance introduced into the liquid will hasten its formation. The bisulphite solution is prepared either by dissolving sodium metabisulphite in water, or by passing sulphur dioxide into soda crystals covered with a layer of water. It forms an apple-green solution, smelling strongly of sulphur dioxide. The sulphur dioxide is conveniently obtained from a bottle of the liquid which can be purchased, or by dropping concentrated sulphuric acid on to solid sodium sulphite.

3. A solution of magenta decolourised by sulphur dioxide becomes violet on the addition of a drop of aldehyde (Schiff). Prepare a weak solution of magenta by dissolving a crystal in half a test-tube of water and bubbling in sulphur dioxide until the colour disappears. Now add a few drops of aldehyde.

4. Boil a few drops of aldehyde with 1—2 c.c. of caustic potash solution. The liquid becomes yellow and a brown resinous precipitate is formed.

5. Add a drop or two of concentrated sulphuric acid to 1 c.c. of aldehyde. The mixture becomes hot in consequence of the aldehyde undergoing polymerisation to paraldehyde $(C_2H_4O)_3$, b.p. 124°, which separates as an oil on adding water. See *Appendix*, p. 238.

Methyl Alcohol. $CH_3.OH$

Commercial methyl alcohol is obtained by purifying wood spirit. It often contains a little acetone, which may be detected by the iodoform reaction (see p. 50). It may, if necessary, be purified by boiling it, using an upright condenser, with 3—4 per cent. of solid caustic potash on the water-bath, and then distilling. It is freed from water by standing for twenty-four hours in a flask one-third filled with freshly-burnt quicklime, and re-distilling from the water-bath, using a thermometer.

Properties.—Colourless liquid ; b. p. 66—67° ; sp. gr. 0·796 at 20°.

PREPARATION 6.

Methyl Iodide (Iodomethane), CH_3I

Dumas and Peligot, *Annalen*, 1835, **15**, 20.

18 grms. methyl alcohol.
5 „ red phosphorus
50 „ iodine

Attach a flask (250 c.c.) to an upright condenser, and bring into it the methyl alcohol and red phosphorus. Add the iodine gradually by detaching the flask for a moment from the condenser. A considerable evolution of heat occurs. When the iodine has been added the flask is left attached to the condenser over night, and the contents then distilled from the water-bath using a similar apparatus to that of Fig. 43, p. 55. The distillate is shaken up with dilute caustic soda in a separating funnel, to remove iodine and hydriodic acid. If sufficient caustic soda has been used the lower layer of methyl iodide will be colourless. Separate the methyl iodide, add a few pieces of solid calcium chloride, and after standing until clear, distil from the water-bath with thermometer. Yield 45 grams. Ethyl iodide and the other alkyl iodides are prepared in precisely the same fashion.

$$5CH_3OH + P + 5I = 5CH_3I + H_3PO_4 + H_2O.$$

Properties.—Colourless, highly refractive liquid ; b. p. 45° ; sp. gr. 2·27 at 15°.

Reaction.—Shake a few drops of methyl iodide with an alcoholic solution of silver nitrate. A white precipitate of a compound of silver iodide and silver nitrate is deposited, which is decomposed and gives yellow silver iodide on adding water. See *Appendix*, p. 240.

Amyl Alcohol, $C_5H_{11}.OH$.

Commercial amyl alcohol is contained in fusel oil from fermentation and consists mainly of isobutyl carbinol together with about 13 per cent. of secondary butyl carbinol, which renders the liquid optically active. It turns the plane of polarisation to the left (see p. 116).

Properties.—Colourless, highly refractive liquid with a burning taste and penetrating smell; b. p. 131—132° sp. gr., 0·8113 at 19°; dissolves in 39 parts of water at 16·5°.

PREPARATION 7.

Amyl Nitrite, $C_5H_{11}O.NO$.

Balard; Guthrie, *Quart. J. C. S.*, 1858, **11**, 245; Rennard, *Jahresb.*, 1874, p. 352.

30 grms. (37 c.c.) amyl alcohol.
30 „ sodium nitrite (finely powdered).
18 „ (10 c.c.) conc. sulphuric acid.

The amyl alcohol and sodium nitrite are mixed in a flask (500 c.c.), and whilst the mixture is cooled in ice-water, the conc. sulphuric acid is added drop by drop from a funnel with constant shaking. Towards the end of the process a more vigorous reaction sets in, when care must be taken to add the sulphuric acid more slowly. When the whole of the acid has been added, the top layer of amyl nitrite is decanted into a separating-funnel. A little water is then added to the residue and, after shaking, a further quantity of amyl nitrite separates and is decanted as before. The whole of the amyl nitrite is then separated from water, dehydrated over calcium chloride and distilled. The liquid boiling at 95—100° is collected separately. Yield, 30—35 grams.

$$C_5H_{11}OH + NaNO_2 + H_2SO_4 = C_5H_{11}O.NO + NaHSO_4 + H_2O.$$

Properties.—Yellow-green liquid with a peculiar penetrating and sweet smell, which, on inhaling, causes a rush of blood to the head; b. p. 96°; sp. gr. 0·902. See *Appendix*, p. 240.

Acetone (Dimethyl ketone), $CH_3.CO.CH_3$.

Commercial acetone is obtained from the products of the distillation of wood. To purify it, it is shaken with a saturated solution of sodium bisulphite (see Reaction 2, p. 67). The crystalline mass, $C_3H_6ONaHSO_3$, is filtered and well drained and then distilled with sodium carbonate solution. The distillate is dehydrated over solid calcium chloride and finally distilled.

Properties.—Colourless liquid with a pleasant colour; b. p. 56·3°; sp. gr. 0·792 at 15°; soluble in water.

Reactions.—1. Acetone gives the *iodoform reaction* like ethyl alcohol (p. 50). 2. Dissolve a few crystals of *p*-bromophenylhydrazine or *p*-nitrophenylhydrazine in a few drops of glacial acetic acid, dilute with about 1 c.c. of water and add a drop of acetone. The bromo- or nitro-phenylhydrazone of acetone separate as crystalline precipitates.

PREPARATION 8.

Chloroform (Trichloromethane), $CHCl_3$.

Liebig, *Pogg. Ann.*, 1831, **23**, 444; Dumas, *Ann. Chim. Phys.*, 1834, **56**, 115.

200 grms. bleaching powder (fresh).
800 c.c. water.
40 grms. (50 c.c.) acetone.

A large round flask (4 litres) is fitted with a cork, through which a bent tube passes connecting the flask with a long condenser and receiver. The flask is placed upon a large sand-bath. Grind the bleaching powder into a paste with 400 c.c. of water and rinse it into the flask with the remaining 400 c.c. Add the acetone and attach the flask to the condenser. Heat cautiously until the reaction sets in, which is indicated by the frothing of the liquid. Remove the flame for a time, and when the reaction has moderated, boil the contents until no more chloroform distils. This is easily determined by collecting the distillate in a test-tube and observing if any drops of heavy liquid are present. The distillate is shaken with dilute caustic soda solution in a separating funnel and the lower layer of chloroform run into a distilling flask. A few pieces of solid calcium chloride are added and left until the liquid is clear, when it is distilled from the water-bath with a thermometer inserted into the neck of the flask. Yield about 40 grams.

The bleaching powder acts as though it consisted of a compound of calcium hydrate and chlorine, and the process probably occurs in two stages.

1. $CH_3.CO.CH_3 + 3Cl_2 = CH_3.CO.CCl_3 + 3HCl$.
2. $2CH_3.CO.CCl_3 + Ca(OH)_2 = (CH_3.COO)_2Ca + 2CHCl_3$.

Trichloracetone is first formed, which is then decomposed by the lime into calcium acetate and chloroform.

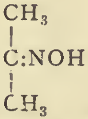
Properties.—Colourless liquid possessing a sweet smell, b. p. 60—62°; sp. gr. 1·498 at 15°; very slightly soluble in water; non-inflammable. As chloroform slowly decomposes in presence of air and sunlight into phosgene, it is usual to add a little alcohol to the commercial product, which arrests the change. Pure chloroform is neutral to litmus, has no action on silver nitrate solution and does not discolour concentrated sulphuric acid when shaken with it for an hour or left for a day.

Reactions.—1. Heat a few drops with double its volume of methyl alcoholic potash. On the addition of water a clear solution is obtained. Potassium formate and chloride are formed. $CHCl_3 + 4KOH = 3KCl + HCO.OK + 2H_2O$.

2. Bring into a test-tube two drops of chloroform, one drop of aniline and 1 c.c. of alcoholic potash and warm *in the fume cupboard.* Note the intolerable smell of phenyl carbamine (carbamine reaction), $CHCl_3 + C_6H_5NH_2 + 3KOH = C_6H_5NC + 3KCl + 3H_2O$. Wash out the contents of the test-tube in the fume cupboard.

PREPARATION 9.

Acetoxime,



$$\begin{matrix} CH_3 \\ | \\ C{:}NOH \\ | \\ CH_3 \end{matrix}$$

V. Meyer, Fanin, *Ber.*, 1882, **15**, 1324.

5 grms. hydroxylamine hydrochloride in 10 c.c. water
3 „ caustic soda in 10 c.c. water
6 „ (7·6 c.c.) pure acetone.

Add the acetone to the mixture of the hydroxylamine hydrochloride and caustic soda in a small flask. The flask is then corked and left for twenty-four hours, during which the crystalline oxime separates. The presence of any free hydroxylamine is then tested in a few drops of the liquid with Fehling's solution, or by merely adding a drop or two of copper sulphate, then a sufficient quantity of caustic soda to produce a clear blue solution and warming. An orange-red precipitate of cuprous oxide indicates uncombined hydroxylamine. If no free hydroxylamine is present, the liquid is shaken up with an equal volume of ether, in which the acetoxime dissolves. The ethereal solution is separated and the process repeated twice with fresh ether. The united ethereal extract is filtered, if necessary, through a dry filter into a distilling flask. The greater part of the ether is distilled off on the water-bath. The remaining liquid is poured into a glass basin and the rest of the ether left to evaporate in the air, the last traces being removed by heating for a few minutes on the water-bath. The acetoxime separates out on cooling in colourless needles. It is dried on a porous plate and recrystallised from a little petroleum spirit m. p. 61—62.° Yield 4—5 grams.

$$\begin{aligned} & CH_3.CO.CH_3 + NH_2OH.HCl + NaOH \\ & \quad = CH_3.C{:}NOH.CH_3 + NaCl + 2H_2O \end{aligned}$$

Properties.—Colourless needles ; m. p. 60°.

Reaction.—Boil a small quantity for a few minutes with dilute hydrochloric acid, and test with Fehling's solution. The oxime is decomposed into acetone and hydroxylamine,

$$CH_3.C(NOH).CH_3 + H_2O = CH_3.CO.CH_3 + NH_2OH.$$

Melting-point Determination.—For this purpose the following apparatus is used (Fig. 53). A small sample of finely powdered substance, which has been carefully dried, is introduced into a capillary tube of about 1 mm. inside diameter sealed at one end. The tube is made from soft thin-walled glass tubing, about 15 mm. diameter, by rotating it in the blow-pipe flame until the glass softens, and then quickly drawing it out. The long capillary is then broken into lengths of about 7 cm. (2½ in.) by scratching across with a writing diamond, and each short tube is sealed at one end. To introduce the substance, it is convenient to scoop up the finely powdered material off a watch glass with the open end. By tapping the closed end on the bench, the powder is shaken down. The quantity introduced should occupy a length of about 2—3 mm. when tightly packed. The tube is attached to a thermometer (preferably with a very small bulb) so that the substance is level with the bulb. The attachment may be made by a narrow rubber ring or by simply moistening the side of the capillary with the thermometer bulb, which has been dipped in the liquid in the bath, and then pressing it against the thermometer stem. The thermometer passes through a cork inserted into a round flask with a long neck, the bulb of which is three-quarters filled with concentrated sulphuric acid, glycerol, or castor oil. The flask is clamped to a retort stand and is heated very gradually by a small flame. Instead of clamping the flask to a retort stand, it can be fixed in a small brass tripod, shown in Fig. 53, which fits on to an ordinary laboratory tripod and from which it can be removed when not required.[1] When a certain temperature is reached the substance, if pure, melts suddenly within one or two degrees. When approaching the melting-point, it is desirable to remove the flame or turn it very low so that the rise of temperature is very gradual. If the liquefaction is protracted, it is an indication that the substance is not pure. The melting-point, obtained in this way, to be quite accurate, must be corrected for the

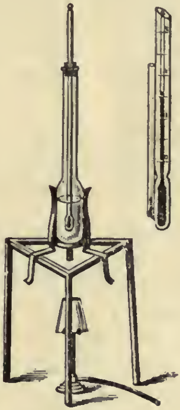


FIG. 53.

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[1] The apparatus (flask and stand) can be purchased from Mr. J. Watkinson, Physics Department, The University, Leeds, price 2*s.* 3*d.*, postage included.

temperature of the thread of mercury outside the liquid, the same formula being used as in the correction for the boiling-point (see p. 58). When the acid becomes discoloured, a crystal of potassium nitrate will remove the colour on warming.

Acetic Acid, $CH_3.CO.OH$.

Commercial acetic acid is manufactured from pyroligneous acid obtained in the destructive distillation of wood. The latter is neutralised with lime, and separated by distillation from wood-spirit and acetone. The crude calcium acetate, which has a dark colour, is then distilled with the requisite quantity of concentrated hydrochloric acid. Anhydrous or glacial acetic acid is obtained by distilling fused sodium acetate with concentrated sulphuric acid.

Properties.—Colourless liquid with pungent smell; b. p. 119°; m. p. 16·7°; sp. gr. 1·055 at 15°. It should not decolorise a solution of permanganate. The vapour of the boiling acid is inflammable.

Reactions.—Add a few drops of alcohol to the same quantity of acetic acid, and an equal volume of concentrated sulphuric acid. Warm gently and notice the fruity smell of ethyl acetate. Neutralise a few drops of acetic acid by adding excess of ammonia and boiling until neutral. Let cool and add a drop of ferric chloride. The red colour of ferric acetate is produced. On boiling, basic ferric acetate is precipitated.

Heat a very small quantity of potassium acetate with an equal bulk of arsenious oxide. The disagreeable and poisonous vapour of cacodyl oxide is evolved.

$$4CH_3.COOK + As_2O_3 = As_2(CH_3)_4O + 2CO_2 + 2K_2CO_3.$$

PREPARATION 10.

Acetyl Chloride, $CH_3.CO.Cl$.

Gerhardt, *Ann. Chim. Phys.*, 1853, (3) **37**, 285; Béchamp *Compt. rend.*, 1855, **40**, 944, and 1856, **42**, 224.

50 grms. glacial acetic acid.
40 „ phosphorus trichloride.

Fit up the apparatus shown in Fig. 54. It consists of a distilling flask (250 c.c.), which is attached to a condenser. A small filter flask serves as receiver, the side tube being attached to a calcium chloride tube. The distilling vessel is provided with a cork, through which a tap-funnel is inserted. The flask is cooled in cold water in the water-bath (outlined in Fig. 54), whilst the phosphorus trichloride is slowly run in from the tap-funnel.* When the phosphorus chloride has been added, the water in the water-bath is warmed to 40—50°, until the evolution of hydrochloric acid gas, which at first is very rapid, begins to abate. The water-bath is then heated to boiling until nothing further distils. The distillate is now redistilled as before, but with a thermometer, and the distillate collected at the boiling-point of acetyl chloride (53—56°). Yield 45 grams.

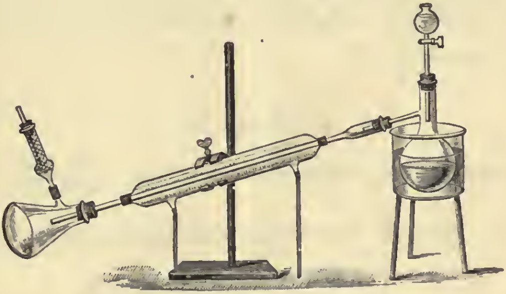


FIG. 54.

$$3CH_3.COOH + 2PCl_3 = 3CH_3.COCl + P_2O_3 + 3\,HCl.$$

Properties.—Colourless liquid with a pungent smell; it fumes in contact with moist air; b. p. 55°; sp. gr. 1·105 at 20°.

Reactions. 1.—Add a few drops of acetyl chloride to about 5 c.c. of water in a test-tube. The acetyl chloride sinks to the bottom of the test-tube, but on shaking rapidly dissolves, and heat is evolved. The acetyl chloride is converted into acetic acid and hydrochloric acid.

$$CH_3.COCl + H_2O = CH_3.CO.OH + HCl.$$

2. To about 1 c.c. of ethyl alcohol in a test-tube, add 1 c.c. of acetyl chloride drop by drop, cooling under the tap. Then

add about 1 c.c. of a solution of common salt. Ethyl acetate, recognised by its fragrant smell, separates out on the surface of the liquid.

$$CH_3.COCl + C_2H_5OH = CH_3.CO.OC_2H_5 + HCl.$$

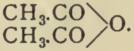
3. Add two drops of acetyl chloride to a drop of aniline. A vigorous action occurs, and a solid separates. This is acetanilide, and may be obtained in larger crystals by dissolving in boiling water and cooling slowly.

$$CH_3.COCl + C_6H_5NH_2 = C_6H_5NH.CO.CH_3 + HCl.$$

See *Appendix*, p. 241.

PREPARATION 11

Acetic Anhydride (Diacetyl Oxide),



$$\left.\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\right>O.$$

Gerhardt, *Ann. Chim. Phys.*, 1853, (3) 37, 311.

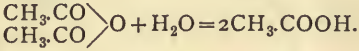
55 grms. sodium acetate (fused).
40 „ acetyl chloride.

A retort (250 c.c.) is attached to a short condenser and receiver, which is furnished, as in the previous preparation, with a calcium chloride tube. The tubulus of the retort is closed by a cork, through which a tap-funnel is fixed. The fused sodium acetate is prepared by fusing crystallised sodium acetate, ($CH_3.COONa + 3H_2O$). The sodium acetate (100 grams) is placed in a shallow tin and heated over a Bunsen burner. It first melts in the water of crystallisation, after which it becomes solid, and finally melts again as the temperature rises. When completely melted it is allowed to cool, powdered, and introduced into the retort. The acetyl chloride is gradually added through the tap-funnel, the retort being cooled in water.* When the acetyl chloride has been added, the contents of the retort are well stirred by means of a thick glass rod pushed through the tubulus. The retort is now closed by an ordinary cork or stopper, and heated over a small flame, which should be moved about to prevent the retort cracking. When nothing further distils, the retort is allowed to cool somewhat, and the distillate poured back and redistilled. Finally it is distilled from a distilling flask with a thermometer, and collected at 130—140°. Yield 40 grams.

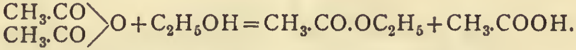
$$CH_3.COCl + CH_3.CO.ONa = (CH_3.CO)_2O + NaCl.$$

Properties—Colourless liquid with an irritating smell ; b. p. 138° ; sp. gr. 1·08 at 15°.

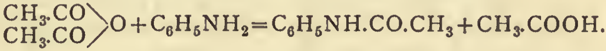
Reactions—Repeat the three experiments described under acetyl chloride. The result is the same in each case ; but as the acetic anhydride reacts less readily than acetyl chloride, the mixture requires to be warmed.

1. 

$$\left.\begin{array}{l}CH_3.CO\\CH_3.CO\end{array}\right\rangle O + H_2O = 2CH_3.COOH.$$

2. 

$$\left.\begin{array}{l}CH_3.CO\\CH_3.CO\end{array}\right\rangle O + C_2H_5OH = CH_3.CO.OC_2H_5 + CH_3.COOH.$$

3. 

$$\left.\begin{array}{l}CH_3.CO\\CH_3.CO\end{array}\right\rangle O + C_6H_5NH_2 = C_6H_5NH.CO.CH_3 + CH_3.COOH.$$

In Reaction 2, combination is not complete, even on boiling, and a little dilute caustic soda must be added to decompose the unchanged acetic anhydride. In Reaction 3, the product remains liquid until water is added, when it becomes solid, and on heating dissolves. See *Appendix*, p. 242.

PREPARATION 12.

Acetamide, $CH_3.CO.NH_2$.

Hofmann, *Ber.*, 1882, **15**, 981 ; Rosanoff, Gulick, and Larkin, *J. Amer. Chem. Soc.*, 1911, **33**, 974.

100 grms. ammonium acetate.

Acetamide may be obtained by boiling 100 grams of ammonium acetate with 120 grams of glacial acetic acid for 5—6 hours with reflux condenser and then distilling the product in the ordinary way. A considerable quantity of water, and acetic acid distils, and when the temperature reaches 180° the apparatus shown in Fig. 55 is used in which the condenser is replaced by a straight wide tube. The distillate solidifies, and consists mainly of acetamide. The yield is about 60 grams. A good result is also obtained by first heating the ammonium acetate in sealed tubes. The ammonium acetate, if not procurable, may be prepared by adding to 70 grms. glacial acetic acid, warmed in a basin on the water-bath, about 80 grms. powdered ammonium carbonate until the acid is neutralised, which is recognised by diluting a sample with a little water, and testing with litmus.

FIG. 55.

Heating under Pressure.—Two tubes are made from the usual thick-walled tubing by sealing one end (see p. 24). These are gently warmed, and the melted acetate poured in until they are about half full. They are then sealed in the manner described on p. 24. The tubes are then placed in a tube furnace (p. 23) and gradually heated to 200°, at which temperature they are maintained for 5—6 hours. Without removing the tubes from the furnace they are allowed to cool, and the capillary end opened by holding a Bunsen burner to the tip until fused, when the pressure within perforates the glass. If a deep file scratch is then made about an inch below the sealed end and the end of a red-hot glass rod held against the scratch, a deep crack is produced and the end easily removed. After heating, the tubes contain a clear, oily-looking liquid, which consists of an aqueous solution of acetamide, together with some unchanged acetate. The contents are poured into a distilling flask and distilled with a straight tube as condenser, and the portion boiling above 180° collected in a small beaker. This distillate, on standing, almost completely solidifies to a colourless crystalline mass. It is freed from mother-liquor by spreading on a porous plate, and purified by a second distillation. The acetamide has then a nearly constant boiling-point. Yield, about 40 grams.

$$CH_3.CO.ONH_4 = CH_3.CONH_2 + H_2O.$$

Properties.—Colourless, rhombohedral crystals, having a peculiar smell of mice. This is due to impurity, which may be removed by recrystallising from benzene ; m.p. 82° ; b.p. 222° ; easily soluble in water and alcohol.

Reaction.—1. Boil a small quantity of acetamide with caustic soda solution. Ammonia is evolved, and sodium acetate is found in solution, $CH_3.CONH_2 + NaOH = CH_3.CO.ONa + NH_3$. See *Appendix*, p. 243.

PREPARATION 13.

Acetonitrile (Methyl cyanide), $CH_3.CN$.

Dumas, Malaguti and Leblanc, *Annalen*, 1848, **64**, 332.

10 grms. acetamide
15 „ phosphorus pentoxide.

The phosphorus pentoxide is introduced into a small distilling flask (200 c.c.) attached to a short condenser. As the pentoxide absorbs moisture rapidly and becomes sticky, it is convenient to push the neck of the distilling flask through a cork which fits the phosphorus pentoxide bottle, and then to shake in the oxide until the required weight is obtained. The powdered acetamide is immediately introduced and shaken up, and the mixture distilled over a small flame, which is constantly moved about. Add to the distillate about half its volume of water, and then solid potassium carbonate, until no more dissolves. The upper layer of liquid, which consists of methyl cyanide, is separated and distilled over a little fresh phosphorus pentoxide with thermometer. Yield, about 5 grams.

$$CH_3.CO.NH_2 - H_2O = CH_3CN.$$

Properties.—Colourless liquid with peculiar smell ; b. p. 82°.

Reaction.—Boil a few grams of the acetonitrile with three times its weight of a mixture of 2 vols. water and 3 vols. concentrated sulphuric acid for an hour with a long upright tube or air-condenser. Distil a few c.c. of liquid, and test the distillate for acetic acid, $2CH_3.CN + H_2SO_4 + 4H_2O = 2CH_3.COOH + (NH_4)_2SO_4$. See *Appendix*, p. 244.

PREPARATION 14.

Methylamine Hydrochloride, $CH_3.NH_2.HCl$.

Wurtz, *Compt. rend.*, 1848, **28**, 223; Hofmann, *Ber.*, 1882, **14**, 2725, and *Ber.*, 1883, **15**, 407 and 762.

20 grms. acetamide
54 " (18 c.c.) bromine
56 " caustic potash.

The dry acetamide and bromine are mixed in a flask (½ litre), and whilst the mixture is cooled in water, a 10 per cent. solution of caustic potash (about 20 grams KOH) is added, until the dark brown liquid changes to a deep yellow colour. The solution, which now contains potassium bromide and acetmonobromamide, is slowly added from a tap-funnel inserted, together with a thermometer, into the neck of a distilling flask (1 litre). The flask contains a concentrated solution of caustic potash (56 grams in 100 c.c. of water), heated to 60—70°. Heat is evolved, and care must be taken that the rise of temperature does not greatly exceed the above limits. The reaction goes on quietly, and the yellow solution is gradually decolourised. The mixture is then digested for a short time at the above temperature until the yellow colour completely disappears. A few bits of broken pot are now introduced into the flask, which is closed with an ordinary cork, and the liquid distilled over wire-gauze. The vapours of methylamine and ammonia, which are cooled, are passed by means of a bent adapter, attached to the end of the condenser, into dilute hydrochloric acid contained in the receiver. Care must be taken that the adapter does not dip too far into the acid, or liquid may be sucked back into the condenser and distilling flask. When the distillate is no longer alkaline, and consequently all the methylamine has been driven over, the hydrochloric acid solution is evaporated to dryness on the water-bath, and the colourless crystalline residue extracted repeatedly with small quantities of absolute alcohol, which dissolves out the methylamine salt from the ammonium chloride. From the hot alcoholic solution foliated crystals separate out on cooling.

$$\underset{\text{Acetamide.}}{CH_3.CONH_2} + Br_2 + KOH = \underset{\text{Acetmonobromamide.}}{CH_3.CONHBr} + KBr + H_2O$$

$$CH_3.CONHBr + KOH = \underset{\text{Methylisocyanate}}{CH_3.N{:}CO} + KBr + H_2O$$

$$CH_3.N{:}C{:}O + 2KOH = \underset{\text{Methylamine.}}{CH_3.NH_2} + K_2CO_3$$

Properties.—Large deliquescent tablets, which melt at 227°, and sublime above that temperature, with slight decomposition. The base is liberated on warming with caustic soda, as an inflammable gas with strong ammoniacal smell. See *Appendix*, p. 245.

PREPARATION 15.

Ethyl Acetate (Acetic Ether), $CH_3.CO.OC_2H_5$.

Scheele, *Chemical Essays*, 1782, p. 307; Frankland, Duppa, *Phil. Trans.*, 1865, **156**, 37; Pabst, *Bull. Soc. Chim.*, 1880, **33**, 350.

50 c.c. conc. sulphuric acid.
50 c.c. absolute alcohol.[1]

Mixture of equal volumes of glacial acetic acid (100 c.c.) and absolute alcohol (100 c.c.).

A distilling flask (½ litre) is attached to a condenser and receiver. The flask is provided with a cork, through which a separating funnel is inserted. The mixture of 50 c.c. of concentrated sulphuric acid and 50 c.c. of absolute alcohol is poured into the flask, which is then heated in a bath of paraffin wax or fusible metal[2] to 140°, and kept at this temperature. The mixture of equal volumes of acetic acid and alcohol is

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[1] *Methyl acetate* may be made in precisely the same way, using methyl alcohol. The product is then fractionated and collected at 57—63°.

[2] A fusible metal bath has the advantage over an oil-bath of neither smelling nor being liable to catch fire. It is made by melting in a small cooking pan one part of lead and two parts of bismuth. This alloy is fluid above 120°.

now added, drop by drop, from the tap-funnel at the speed at which the liquid distils, as in the preparation of ether (p. 59) When all the mixture has been added, the distillate, which contains the ester, and also acetic acid, alcohol, ether, and sulphurous acid, is shaken in a separating funnel with a strong solution of sodium carbonate (50 c.c.) until the upper layer of ethyl acetate ceases to redden blue litmus. The lower layer is removed as completely as possible, and a strong solution of calcium chloride (50 grams in 50 c.c. of water) added, and the shaking repeated. The lower layer of calcium chloride is run off, and the ethyl acetate carefully decanted from the mouth of the funnel into a dry distilling flask. A few pieces of solid calcium chloride are added, and, after standing over night, the ethyl acetate is distilled from the water-bath with a thermometer in the neck of the flask. The portion distilling below 74° contains ether, that boiling at 74—79° is mainly ethyl acetate, and is separately collected. Yield, 80 per cent. of the theory.

$$C_2H_5(OH) + H_2SO_4 = C_2H_5.H.SO_4 + H_2O.$$
$$C_2H_5HSO_4 + CH_3.CO.OH = CH_3.COOC_2H_5 + H_2SO_4.$$

Properties.—Colourless liquid, with an agreeable fruity smell; b. p. 77°; sp. gr. 0·9068 at 15°; soluble in about 11 parts of water; miscible in all proportions with alcohol, ether, and acetic acid.

Reaction.—Weigh out 20 grams of ethyl acetate, and heat in a round flask with three times its volume of aqueous potash ($1KOH : 3H_2O$) with upright condenser over wire-gauze. Add a small piece of porous pot to prevent bumping. After an hour or so the upper layer of ethyl acetate will have disappeared. Distil the product with a thermometer until the temperature reaches 100°. Add solid potassium carbonate to the distillate until no more dissolves. Separate the top layer of alcohol and dehydrate over fresh potassium carbonate or quicklime. Distil with a thermometer and weigh the distillate. Neutralise the alkaline liquid, from which the alcohol was first distilled, with dilute sulphuric acid, and evaporate to dryness on the water-bath. Break up the solid residue, and distil with concentrated sulphuric acid (20 c.c.) until the thermometer marks 130°. Redistil and collect between 115° and 120°. Weigh the distillate. This process furnishes an example of *hydrolysis* or *saponification*,

$$CH_3.COOC_2H_5 + H_2O = CH_3.COOH + C_2H_5OH.$$

See *Appendix*, p. 247.

PREPARATION 16.

Ethyl Acetoacetate (Acetoacetic Ester),

$$CH_3.CO.CH_2.CO.OC_2H_5.$$

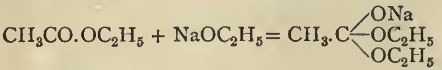
Geuther, *Jahresb.*, 1863, p. 323; Frankland, Duppa, *Phil. Trans.*, 1865, **156**, 37, Wislicenus, *Annalen*, 1877, **186**, 161.

200 grms. ethyl acetate.
20 „ sodium.

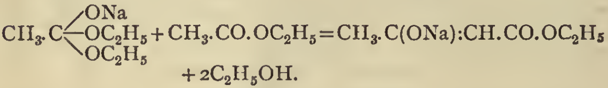
The ethyl acetate, carefully dehydrated as described in the previous preparation, is introduced into a round flask ($\frac{1}{2}$ litre) connected with a long upright condenser. 20 grams well pressed sodium, cut into thin slices, are quickly added, and the flask cooled in water. After a short time a brisk reaction sets in, and ultimately the liquid boils. When the first action is over, and no further evolution of heat occurs, the mixture is heated on the water-bath, without detaching the condenser, until the sodium is completely dissolved. A 50 per cent. acetic acid solution is at once added and well shaken, until the liquid is acid (about 100 c.c.), and then an equal volume of concentrated brine. The liquid divides into two layers; the upper one, consisting of acetoacetic ester and unchanged ethyl acetate, is carefully separated. It is distilled over wire-gauze until the thermometer marks 100°, and all the ethyl acetate has been removed. The distillate is now collected in five fractions (100—130°, 130—135°, 165—175°, 175—185°, 185—200°). The fraction distilling at 175—185° is nearly pure acetoacetic ester. Yield 30—40 grams. A further quantity may be obtained by redistilling the other fractions; but it is undesirable to repeat the process frequently, as acetoacetic ester gradually decomposes at the boiling point. It is for this reason that Gattermann recommends the fractional distillation to be carried out *in vacuo*.

The brown residue remaining in the distilling flask solidifies, on cooling, to a crystalline mass consisting chiefly of dehydracetic acid $C_8H_8O_4$. It is converted into the sodium salt by boiling with soda solution with the addition of animal charcoal. The sodium salt crystallises from the filtrate. On adding dilute sulphuric acid, the free acid is obtained as colourless needles ; m. p. 109°.

1. $2C_2H_5OH + Na_2 = 2NaOC_2H_5 + H_2$

2. 

$$CH_3CO.OC_2H_5 + NaOC_2H_5 = CH_3.C\begin{array}{l}ONa\\ OC_2H_5\\ OC_2H_5\end{array}$$

3. 

$$CH_3.C\begin{array}{l}ONa\\ OC_2H_5\\ OC_2H_5\end{array} + CH_3.CO.OC_2H_5 = CH_3.C(ONa){:}CH.CO.OC_2H_5 + 2C_2H_5OH.$$

4. $CH_3.C(ONa){:}CH.CO.OC_2H_5 + C_2H_4O_2 = CH_3.CO.CH_2.CO.OC_2H_5 + CH_3.CO.ONa$

The formation of ethyl acetoacetate occurs, according to Claisen, in four steps. The presence of a small quantity of alcohol gives rise to sodium ethylate, which forms an additive compound with ethyl acetate. The latter unites with a second molecule of ethyl acetate yielding the sodium salt of ethyl acetoacetate, and splitting off alcohol, which reacts with fresh metallic sodium. The sodium salt on acidifying passes into the tautomeric (ketonic) form of acetoacetic ester.

Properties.—Colourless liquid possessing a fruity smell ; b. p. 181° ; sp. gr. 1·03 at 15°. Boiled with dilute caustic potash, the ester decomposes into alcohol, carbon dioxide, and acetone (ketonic decomposition), with strong or alcoholic caustic potash, sodium acetate and alcohol are formed (acid decomposition).

Reactions.—1. Add a drop of ferric chloride dissolved in alcohol to a few drops of the ester ; a deep violet coloration is produced.

2. Add 1 c.c. of a saturated alcoholic solution of cupric acetate to a few drops of the ester, a bluish-green crystalline precipitate of copper acetoacetic ester, $(C_6H_9O_3)_2Cu$, is formed. See *Appendix*, p. 248.

Distillation in vacuo.—The apparatus is shown in Fig. 56. The distilling flask is provided with a thermometer and attached to a short condenser and receiver. The receiver consists of a second distilling flask, which is tightly attached to the end of the narrow condenser tube, figured at *a* and connected by the side limb by means of pump-tubing to a water-jet aspirator and mercury-gauge. Some small bits of porous pot are placed in the flask, which is heated in a paraffin bath, and the apparatus exhausted to about 35—40 mm. pressure. At this pressure ethyl acetoacetate boils at about 90°. The following table gives the temperatures corresponding to different pressures :—

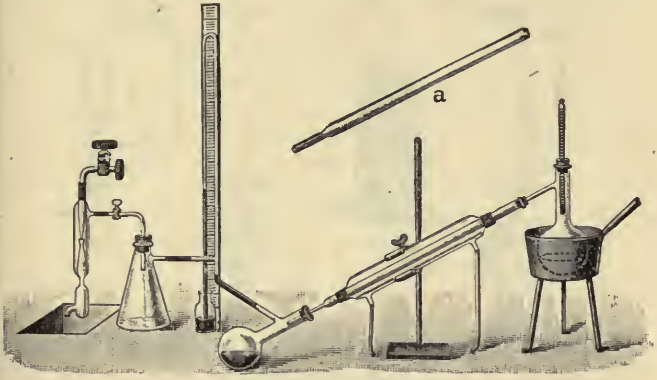


FIG. 56.

t.	*mm.*	*t.*	*mm.*
74°	14	94°	45
79°	18	97°	59
88°	29	100°	80

The chief inconvenience which attends distillation *in vacuo* is the bumping of the liquid in the distilling flask. This may be moderated or removed by various devices, such as the introduction of porous pot, capillary glass tubes, &c., or by driving a rapid stream of fine air-bubbles through the liquid. For this purpose a Claisen flask (Fig. 57), may be used with advantage. A tube is drawn out into a fine capillary and is open at both ends, the wide end being attached to a short piece of rubber tubing and screw-clip. This tube is inserted through a cork in the straight neck of the flask, whilst the thermometer is fixed in the second neck, which is attached to the condenser. The stream of air-bubbles is regulated by the clip. Instead of the long manometer shown in Fig. 56, a more compact, and, for low pressures, a more convenient form is shown in Fig. 58. If the distillate has to be separated into fractions, it is undesirable to interrupt the boiling. Various forms of apparatus for effecting this object are shown in Figs. 59—61. The apparatus (Fig. 59) consists of a double receiver *a* and *b* ; *c* and *e* are ordinary two-way taps, whilst *d* is a three-way tap pierced lengthwise and crosswise as shown in section at *f.* The aspirator is attached to the limb marked with the arrow. During the distillation the taps *c* and *d* connect the apparatus with the aspirator whilst *e* is closed. The distillate collects in *a.* When this fraction is to be removed, *c* is closed and *e* is opened. The

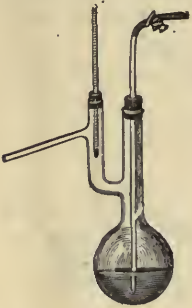


FIG. 57.

FIG. 58.

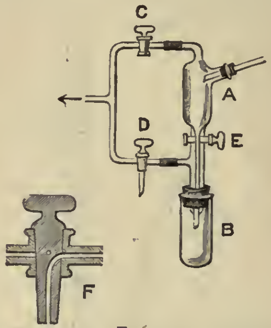


FIG. 59.

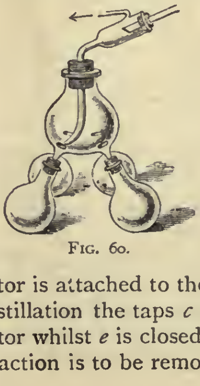


FIG. 60.

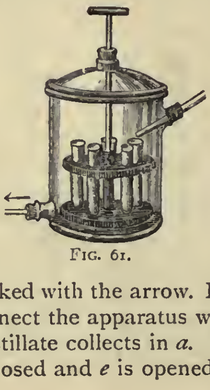


FIG. 61.

liquid is thereby transferred to the second receiver *b*; *e* is now closed, *c* is opened and *d* turned so as to let air into *b*; *b* may now be removed and replaced by a similar vessel and the process repeated. Fig. 60 needs little explanation. There are two or more receivers on one stem. By rotating the stem the distillate falls into one or other receiver. Fig. 61 consists of a vacuum vessel containing a series of test-tubes which can be moved in turn, under the end of the condenser, by means of a vertical axis. It is often preferable to heat the distilling flask in an oil or metal bath instead of using wire-gauze. Distilling flasks above 250 c.c. capacity should not be used for low pressures, as they may collapse. For high boiling liquids, or for substances which may solidify in the condenser, a condenser tube without water-jacket is used. A convenient form of condenser tube is shown at *a*, Fig. 56. It consists of straight tube fused on to a short narrower tail-piece. In certain cases it is found convenient to insert the side-tube of the distilling flask directly into the neck of the receiver (see p. 94).

PREPARATION 17.

Monochloracetic Acid, $CH_2Cl.CO.OH$.

R. Hofmann, *Annalen*, 1857, **102**, 1; Auger, Béhal, *Bull. Soc. Chim.*, 1889, (3) **2**, 145.

100 c.c. glacial acetic acid.
10 grms. red phosphorus.

Fit up the apparatus shown in Fig. 62.* It consists of a stoneware jar one-third full of pyrolusite in lumps, and fitted with exit tube and tap-funnel. It is heated on a sand-bath over a small flame, whilst concentrated hydrochloric acid is allowed to drop in from the tap-funnel. A rapid current of chlorine is thus evolved, which is dried by passing through concentrated sulphuric acid in the Woulff bottle. The Woulff bottle has a safety and exit tube, the latter being connected with a straight tube passing to the bottom of the retort. The retort is tilted upwards and connected with an upright condenser, which is furnished with an open calcium chloride tube. The acetic acid and phosphorus are placed in the retort, and heated on the water-bath. The retort and contents are weighed at the commencement of the operation on a rough balance. A rapid current of chlorine is then passed through for six to twelve hours, and the retort occasionally weighed, until the increase in weight (50 grams) roughly corresponds to the formation of monochloracetic acid. The operation is stopped when a sample solidifies on cooling and on rubbing with a glass rod. The action of the chlorine is greatly facilitated by sunlight. The yellow liquid in the retort is poured into a distilling flask, and distilled over wire-gauze. Some acetyl chloride and unchanged acetic acid first distil, after which the temperature rises and the fraction boiling at 150°—190° is collected separately. It is advisable to run the water out of the condenser when the temperature approaches 170°, as the acid may solidify and block the condenser-tube. The distillate solidifies on cooling. Any liquid is drained off at once, and the solid is redistilled and collected at 180°—190°. It is nearly pure chloracetic acid. Yield 80—100 grams.

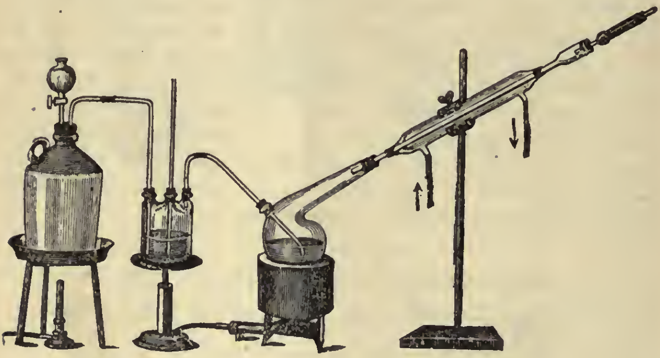


FIG. 62.

$$CH_3.CO.OH + Cl_2 = CH_2Cl.CO.OH + HCl.$$

The phosphorus acts as a "chlorine carrier" by forming probably phosphorus pentachloride, and then reverting to the state of trichloride.

Properties.—Colourless crystals ; m. p. 63° ; b. p. 185°—187° ; readily soluble in water, and deliquescent in moist air. It causes blisters on the skin. See *Appendix*, p. 252.

PREPARATION 18.

Monobromacetic Acid, $CH_2Br.COOH$.

Hell, *Ber.*, 1881, **14**, 891; Volhard, *Annalen*, 1887, **242**, 141; Zelinsky, *Ber.*, 1887, **20**, 2026.

30 grms. (30 c.c.) glacial acetic acid.
105 „ (35 c.c.) bromine.
5 „ red phosphorus.

All the above substances must be dry. The acetic acid is frozen in ice, and any liquid drained off, and the red phosphorus is washed with water to free it from phosphoric acid, dried in the steam oven, and kept over sulphuric acid in a desiccator until required. The bromine is placed in a separating funnel with half its volume of concentrated sulphuric acid overnight, and then separated. The apparatus is shown in Fig. 63. It consists of a round flask (250 c.c.) attached to an upright condenser, which is provided with a cork. A tap-funnel containing the bromine passes through one hole, and a wide bent tube, attached at its lower end to a funnel, passes through the other. As a large quantity of hydrobromic acid is evolved in the reaction, the funnel is made to touch the surface of water contained in a beaker, whereby it is completely absorbed. The phosphorus and acetic acid are placed in the flask, and bromine dropped in from the tap-funnel.[*] A vigorous reaction occurs, and the liquid becomes very warm. After half the bromine has been added the action moderates, and the remainder may be run in more quickly. When the whole has been added, the liquid is boiled gently until the colour of the bromine disappears. It is now allowed to cool, and the liquid decanted into a distilling flask for distillation *in vacuo*. Care must be taken not to touch the substance with the hands, as even a small quantity produces very unpleasant sores. The apparatus for distilling *in vacuo* is shown in Fig. 56 (p. 85).

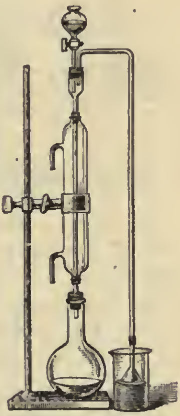


FIG. 63.

The distilling flask is provided with a thermometer, and attached to a short condenser and receiver. The receiver consists of a second distilling flask, which is tightly attached to the end of the condenser and connected by the side limb with pump-tubing to a water-jet aspirator and mercury manometer. Some small bits of of porous pot are placed in the flask, and the apparatus exhausted to about 50—60 mm. pressure. The liquid distils at a nearly constant temperature (about 50°—53°), and consists of nearly pure bromacetylbromide. The calculated quantity of water is added to convert it into bromacetic acid, when the liquid forms a solid crystalline mass.* It may be purified by distillation at atmospheric pressure with condenser-tube only, the portion boiling above 165° being collected separately.

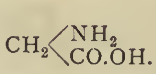
$$3CH_3.COOH + P + 11Br = \underset{\text{Bromacetyl bromide.}}{3CH_2Br.COBr} + HPO_3 + 5HBr.$$

$$CH_2Br.COBr. + H_2O = \underset{\text{Bromacetic acid.}}{CH_2Br.CO.OH} + HBr.$$

Properties.—Colourless crystals; m. p. 50°—51°; b. p. 208°. See *Appendix*, p. 252.

PREPARATION 19.

Glycocoll (Glycine, Aminoacetic Acid).



$$CH_2\begin{cases}NH_2\\CO.OH.\end{cases}$$

Braconnot, *Ann. Chim. Phys.*, 1820, (2) **13**, 114; Perkin, Duppa, *Trans. Chem. Soc.*, 1859, **11**, 22; Kraut, *Annalen*, 1891, **266**, 292.

50 grms. chloracetic acid.
50 c.c. water.
600 c.c. ammonia, 26·5 per cent. (sp. gr. 0·907 at 14°).

Fit up the apparatus shown in Fig. 64. It consists of a large wide-necked bottle, in which the ammonia solution is placed. The solution is stirred by a mechanical stirrer, rotated by means of a water-turbine. The solution of the chloracetic acid in 50 c.c. water, is dropped in from a tap-funnel. After standing 24 hours the liquid is poured into a flask, and the excess of ammonia is removed by passing in a current of steam, and evaporating at the same time on the water-bath until the last traces of ammonia disappear. The solution now contains glycocoll and ammonium chloride. Precipitated carbonate of copper is added to the hot liquid until no further effervescence occurs, and some carbonate remains undissolved. It is filtered and evaporated down on the water-bath until crystallisation sets in. This is determined by removing and cooling a small portion in a test-tube or watch-glass. The blue needles of copper glycocoll, $(C_2H_4NO_2)_2Cu.H_2O$, are filtered and washed, first with dilute and then with stronger spirit. The mother liquor may be further evaporated, and a fresh quantity of crystals obtained. The copper salt is dissolved in water and precipitated hot with hydrogen sulphide, the free glycocoll passing into solution. The precipitate is filtered and well washed, and the filtrate evaporated to a small bulk on the water-bath. Crystals of glycocoll separate out. Yield 15–20 grams. The loss is due to the formation of di- and triglycolaminic acid, $NH(CH_2.COOH)_2$ and $N(CH_2COOH)_3$.

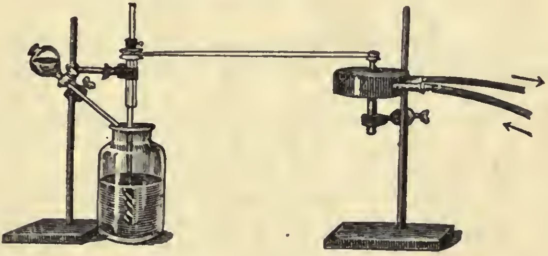


FIG. 64.

$$CH_2Cl.COOH + 2NH_3 = CH_2NH_2.COOH + NH_4Cl.$$

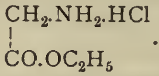
Properties.—Large monoclinic crystals; discoloured at 228°; m.p. 232–236°; scarcely soluble in alcohol and ether, readily soluble in water (1 part glycocoll in 4 parts water).

Reaction.—1. Add a drop of copper sulphate to a solution of glycocoll, and notice the blue colour of the copper salt.

2. Add a drop of ferric chloride to the solution. It gives a deep red colour. See *Appendix*, p. 254.

Preparation 20.

Glycocoll Ester Hydrochloride,



$$\begin{array}{l}CH_2.NH_2.HCl\\ \vert\\ CO.OC_2H_5\end{array}.$$

Klages, *Ber.*, 1903, **36**, 1506, Hantzsch and Silberrad, *Ber.*, 1900, **33**, 70.

250 c.c. formaldehyde solution (40 per cent.).
90 grams ammonium chloride (powdered).
110 „ potassium cyanide (in 200 c.c. water).
63 c.c. glacial acetic acid.

The first part of the process consists in the preparation of methyleneamino-acetonitrile.

$$NH_4CN + 2CH_2O = CH_2:N.CH_2CN + 2H_2O.$$

The formaldehyde and ammonium chloride are mixed in a wide-necked glass jar cooled in a freezing mixture and stirred by means of a stirrer as shown in Fig. 64. When the temperature falls to 5° the potassium cyanide solution is slowly run in from a tap-funnel during three hours, the temperature being maintained below 10°. When half the cyanide solution has been added the ammonium chloride will have completely dissolved. Whilst the second half of the solution is being added, 63 c.c. of glacial acetic acid are dropped in from another tap-funnel at about the same rate, whilst the temperature is kept below 15°. As soon as the acetic acid is added a white crystalline substance begins to separate and gradually fills the liquid. The stirring is continued for another hour after the solutions have been added. The crystalline mass is filtered, washed with water and dried. The yield is 60—70 grams. Methyleneamino-acetonitrile melts at 129°. It may be recrystallised from alcohol, but is usually pure enough for further treatment.

On hydrolysis in presence of alcohol it breaks up into glycocoll ester hydrochloride, ammonium chloride and formaldehyde.

$$CH_2:N.CH_2CN + 2H_2O + C_2H_5OH + HCl = (HCl)NH_2.CH_2.COOC_2H_5 + NH_4Cl + CH_2O.$$

Twenty-five grams methyleneamino-acetonitrile are added to 170 c.c. of absolute alcohol previously saturated in the cold with hydrogen chloride.

Preparation of Hydrogen Chloride.—A filter flask (½ litre) is fitted with a rubber cork, through which a tap-funnel is inserted. The flask is filled one-third full of concentrated hydrochloric acid and is attached to a wash-bottle containing a little concentrated sulphuric acid. A delivery tube is attached to the wash-bottle. The hydrogen chloride is generated by dropping concentrated sulphuric acid from the tap-funnel into the flask containing the hydrochloric acid. As the gas is rapidly absorbed by the alcohol and may in consequence run back into the wash-bottle, it is advisable to run in the acid rather more quickly at the beginning than is necessary later on and to generate the gas for a short time before passing it into the alcohol. The apparatus is shown in Fig. 65.

Fig. 65.

When saturated, the mixture is boiled for an hour with reflux condenser on the water-bath and filtered hot from the ammonium chloride which remains undissolved. On cooling, the greater portion of the ester hydrochloride crystallises. A further quantity may be obtained by concentrating the mother liquors. Yield 30—35 grams.

Properties.—Colourless needles; m. p. 144°, soluble in hot alcohol, very soluble in water.

Glycocoll Ester Hydrochloride from Gelatine.

Mix 100 grams commercial gelatine or size with 300 c.c. concentrated hydrochloric acid and shake until the gelatine is nearly dissolved; then add a few fragments of porous pot and boil over wire gauze with reflux condenser for four hours. The dark coloured product is now evaporated on the water-bath under diminished pressure in the apparatus shown in Fig. 66.

It consists of two distilling flasks (1 litre) fitted together by rubber corks, the one acting as distilling flask and the other as receiver. The receiver which is cooled by a stream of water is attached to a water-jet aspirator. A long capillary, which nearly touches the bottom of the flask, is inserted through the cork of the distilling vessel. It serves to agitate the liquid by introducing a stream of fine air-bubbles which keep it in constant motion. When the water is removed as far as possible, the residue, which forms, on cooling, a thick viscid mass, is mixed with 500 c.c. absolute alcohol. It is heated on the water-bath with reflux condenser for a short time with the addition of a little animal charcoal and filtered. The alcoholic solution is cooled in ice and saturated with dry hydrogen chloride (see p. 93). The liquid is then boiled for half an hour on the water bath, cooled, and, after dropping in a crystal of the substance, left overnight. Glycocoll ester hydrochloride crystallises in colourless needles (m. p. 144°) and is filtered and washed with a little alcohol. Yield 10—15 grams.

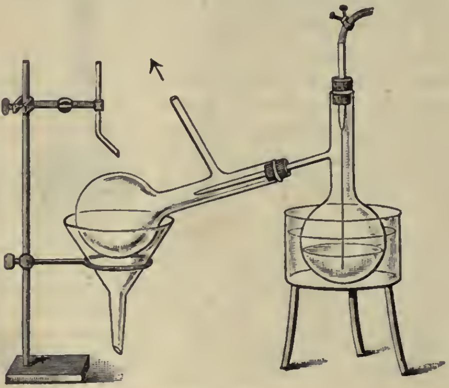
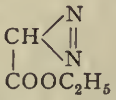


FIG. 66.

PREPARATION 21.

Diazoacetic Ester, 

$$\begin{matrix} & & N \\ CH & \langle & \| \\ | & & N \\ COOC_2H_5 & & \end{matrix}$$

Curtius, *J. prakt. Chem.*, 1888, **38**, 401 ; Silberrad, *Trans. Chem. Soc.*, 1902, **81**, 600.

25 grams glycocoll ester hydrochloride (in 50 c.c. of water).
18 ,, sodium nitrite in fine powder.

The glycocoll ester and sodium nitrite are shaken together in a separating funnel (250 c.c.) until the nitrite is dissolved, a little water being added if necessary. Fifteen c.c. of ether are poured into the funnel, and when the temperature has sunk to about 5°, two or three drops of a ten per cent. sulphuric acid solution are added. The mixture is now well shaken for a minute and the aqueous layer drawn off into a flask standing in ice whilst the yellow ethereal solution, separated as completely as possible from water, is poured from the neck of the funnel into a dry flask. The aqueous portion cooled to 5° is returned to the funnel and the process is repeated five or six times with fresh quantities of ether, a few drops of sulphuric acid being added each time before shaking, and the yellow ethereal layer separated, until the ether is only slightly coloured.

The united ethereal extracts are shaken with very small quantities of sodium carbonate solution until no more carbon dioxide is evolved and the solution remains alkaline. The ether solution is then thoroughly dehydrated over calcium chloride over-night and the ether carefully removed on the water-bath, which should not be heated to boiling. When most of the ether has been distilled off, the flask is taken from the water-bath and the remainder of the ether removed by blowing air over the surface of the liquid. Yield about 15 grams.

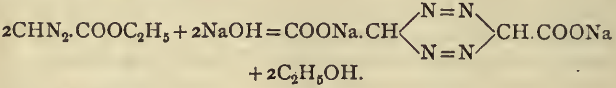
$$HCl.NH_2CH_2.COOC_2H_5 + NaNO_2 = N_2CH.COOC_2H_5 + NaCl + 2H_2O.$$

Properties.—Deep yellow liquid which explodes on boiling; but distils undecomposed under diminished pressure.

Reactions.—Add a drop of the diazoacetic ester to concentrated sulphuric acid. It decomposes explosively. Heat a few c.c. of the ester in turn with water and alcohol. Nitrogen is evolved with the formation of glycollic ester in the first case and ethyl glycollic ester in the second.

$$N_2CH.COOC_2H_5 + H_2O = CH_2OH.COOC_2H_5 + N_2.$$
$$N_2CH.COOC_2H_5 + C_2H_5OH = CH_2OC_2H_5.COO_2H_5 + N_2.$$

Add an ethereal solution of iodine. Nitrogen is evolved and iodacetic ester is formed. Heat a little of the ester with concentrated hydrochloric acid. Nitrogen is evolved and chloracetic ester is formed. Gradually add five grams of the diazoacetic ester to a solution of 8 grams of caustic soda dissolved in 12 c.c. of water heated on the water-bath. A vigorous reaction occurs and yellow crystals of sodium bis-diazoacetate are deposited. Cool, add 10 c.c. of spirit, and filter and wash with spirit.

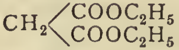


$$2CHN_2.COOC_2H_5 + 2NaOH = COONa.CH\left\langle\begin{matrix} N=N \\ N=N \end{matrix}\right\rangle CH.COONa + 2C_2H_5OH.$$

See *Appendix*, p. 255.

PREPARATION 22.

Diethyl Malonate.



$$CH_2\left\langle\begin{matrix} COOC_2H_5 \\ COOC_2H_5 \end{matrix}\right.$$

Conrad, *Annalen*, 1880, **204**, 126; W. A. Noyes, *Amer. Chem. J.*, 1896, **18**, 1105.

50 grms.	chloracetic acid (in 100 c.c. water)
28 ,,	sodium carbonate (anhydrous)
28 ,,	sodium cyanide (in powder)

The solution of chloracetic acid is poured into a wide basin (20 cm. diam.), and whilst the mixture is heated to 55—60° sodium carbonate (28 grms.) is added until the evolution of carbon dioxide ceases and the liquid is neutral. A solution of sodium chloracetate is thus obtained. Sodium cyanide (28 grms.) is now added, the mixture gently heated and well stirred.* Vigorous effervescence occurs and the flame is removed. When the reaction is over, the contents of the basin are rapidly evaporated on the sand-bath, whilst the mass is continuously stirred with a thermometer until the temperature reaches 135°. The brown semi-fluid mass is allowed to cool and stirred whilst solidifying, and then quickly broken up into coarse powder and introduced into a round flask ($\frac{1}{2}$ litre). The sodium cyanacetate which has been formed is now converted into the ester, and at the same time hydrolysed by boiling with sulphuric acid. Absolute alcohol (20 c.c.) is added, and the flask is then mounted on a water-bath and attached to a reflux condenser. A cold mixture of 80 c.c. absolute alcohol and 90 c.c. concentrated sulphuric acid is added in the course of about ten minutes, and the flask heated for two hours on the water-bath. The mixture is cooled quickly, 100 c.c. of water added, and any insoluble matter filtered off. The filter is washed several times with small quantities of ether, and the filtrate shaken up with the ether and separated. The filtrate is shaken up again with fresh ether when the ester is completely separated, and the united ethereal extracts freed from acid by shaking with water and then with a strong solution of sodium carbonate until the latter remains alkaline. The ether extract is then separated, dehydrated with calcium chloride, and the ether removed on the water-bath. The residual ester is distilled under reduced pressure. Yield 45—50 grams.

$$CH_2Cl.COONa + NaCN = CH_2CN.COONa + NaCl$$

$$CH_2CN.COONa + 2C_2H_5OH + 2H_2SO_4 = CH_2(COOC_2H_5)_2 + NaHSO_4 + NH_4HSO_4.$$

Properties.—Colourless liquid ; b. p. 195° ; sp. gr. 1·068 at 18° See *Appendix*, p. 256.

PREPARATION 23.

Ethyl Malonic Acid, $C_2H_5.CH{<}\begin{smallmatrix}CO_2H\\CO_2H\end{smallmatrix}$

Conrad, *Annalen*, 1880, **204**, 134.

16	grms.	ethyl malonate.
25	,,	(32 c.c.) absolute alcohol
2·3	,,	sodium
20	,,	ethyl iodide.

Sodium ethylate is first prepared by dissolving 2·3 grams sodium in 25 grams alcohol, and the reaction completed, if necessary, on the water-bath as described on p. 83. Whilst the product is still slightly warm, 16 grams malonic ester are added from a tap-funnel. The liquid remains clear at first, but before the ester has all been added a white crystalline body (sodium ethyl malonate) separates out, and soon the whole solidifies. To the solid mass 20 grams ethyl iodide are slowly added. The mass softens and, after continued shaking, completely liquefies with evolution of heat. The product is now heated on the water-bath, when it becomes turbid from the separation of sodium iodide in the form of a fine powder. After one and a half hours the liquid ceases to be alkaline and the reaction is complete. The alcohol is distilled off from a brine-bath (water saturated with common salt) On the addition of water to the residue an almost colourless oil separates out. The oil is removed by extraction with ether, dehydrated over calcium chloride and distilled. When the ether has been driven off, almost the whole of the residue (ethyl diethyl malonate) passes over at 206—208°. Yield about 15 grams.

$$CH_2.(CO.OC_2H_5)_2 + NaOC_2H_5 = \underset{\text{Sodium ethyl malonate.}}{CHNa(CO.OC_2H_5)_2} + C_2H_5OH$$

$$CHNa(CO.OC_2H_5)_2 + C_2H_5I = \underset{\text{Ethyl malonic ester.}}{CH(C_2H_5)(CO.OC_2H_5)_2} + NaI$$

Properties.—Colourless liquid with an agreeable fruity smell; b. p. 207°, sp. gr. 1·008 at 18°.

To obtain the free acid, the ester is hydrolysed with caustic potash. To 15 grams caustic potash in strong aqueous solution, 10 grams of the ester are slowly added from a tap-funnel. At first an emulsion forms, which soon solidifies to a white mass. This is heated on the water-bath with frequent shaking for about three-quarters of an hour, until it becomes completely liquid. The hydrolysis is then complete. The product is diluted with a little water, neutralised with concentrated hydrochloric acid, and the free acid precipitated with a strong solution of calcium chloride as the calcium salt. This is separated from the solution by filtration and concentrated hydrochloric acid added to the calcium salt. From the acid solution the free ethyl malonic acid is extracted by shaking with ether. After evaporating off the ether, the acid remains behind as a syrup, which solidifies when cold. This is redissolved in water, boiled with a little animal charcoal to free it from any adhering colouring matter, filtered, and evaporated to syrupy consistency on the water-bath. The colourless acid crystallises on cooling. Yield about 5 grams.

$$C_2H_5CH(CO.OC_2H_5)_2 + 2KOH = C_2H_5CH(CO_2K)_2 + 2C_2H_5OH$$

$$C_2H_5CH(CO_2K)_2 + 2HCl = \underset{\text{Ethyl malonic acid.}}{C_2H_5CH(CO_2H)_2} + 2KCl.$$

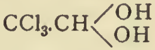
Properties.—Rhombic prisms; m. p. 111·5°, easily soluble in water, alcohol, and ether.

Reaction.—1. Heat a gram or two of the acid in a test-tube over a small flame and have at hand a second test-tube one-third full of lime water. The acid decomposes at 160°

into butyric acid and carbon dioxide. When the effervescence begins to slacken, decant the gas downwards into the test-tube of lime-water, shake up and notice the turbidity. The acid which remains will have a strong smell of butyric acid,

$$C_2H_5CH(CO_2H)_2 = C_3H_7CO.OH + CO_2$$

See *Appendix*, p. 256.



Chloral Hydrate, $CCl_3.CH\begin{matrix}/OH\\ \backslash OH\end{matrix}$

Liebig, *Annalen*, 1832, **1**, 189; Dumas, *Ann. Chim. Phys.* 1834, **56**, 123.

Chloral hydrate is obtained by the action of chlorine upon ethyl alcohol. The solid chloral alcoholate is formed, $CCl_3.CHOH.OC_2H_5$, which, when decomposed with sulphuric acid, yields chloral, $CCl_3.COH$, a liquid which combines with water to form the crystalline hydrate.

Properties.—It crystallises in prisms, which dissolve easily in water, alcohol, and liquid hydrocarbons. It has a peculiar smell; m. p. 57°; b. p. 97·5°. It volatilises on evaporating its aqueous solution.

Reactions.—1. Add a few drops of a solution of chloral hydrate to a little ammonio-silver nitrate solution and warm. Metallic silver will be deposited.

2. Add a little caustic soda to a solution of chloral and warm gently. The heat of the hand is sufficient for the purpose. A smell of chloroform is at once apparent, $CCl_3.CH(OH)_2 + NaOH = CHCl_3 + HCO.ONa + H_2O$. Sodium formate remains in solution.

3. Add a few drops of ammonium sulphide solution and warm gently. A brown colouration or precipitate is formed.

PREPARATION 24.

Trichloracetic Acid, $CCl_3.CO.OH$.

Dumas, *Compt. rend.*, 1838, **8**, 609; Clermont, *Ann. Chim. Phys.*, 1871, (6), **6**, 135.

25 grms. chloral hydrate
20 „ fuming nitric acid; sp. gr. 1·5 (see p. 20).

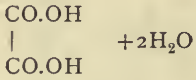
The chloral hydrate is melted in a distilling flask (250 c.c.) and the fuming nitric acid added.* The mixture is heated carefully over a small flame until the reaction sets in. After a few minutes red fumes are evolved, consisting mainly of nitrogen tetroxide. The reaction proceeds without the application of heat, and is complete when, on warming the liquid, nitrous fumes cease to come off. The product is now distilled; below 123° excess of nitric acid distils; between 123° and 194° a mixture of trichloracetic acid and a small quantity of nitric acid pass over, and at 194—196° nearly pure trichloracetic acid collects in the receiver and solidifies on cooling. It is advisable to distil the last fraction with a condenser-tube only. The fraction boiling at 123—190° is treated with a fresh quantity of fuming nitric acid (10 c.c.), and the product purified as before. Yield, 10—15 grams.

$$CCl_3.CO.H + O = CCl_3.CO.OH.$$

Properties.— Colourless, rhombohedral crystals; m. p. 52°; b. p. 195°. See *Appendix*, p. 257.

PREPARATION 25.

Oxalic Acid,



$$\begin{matrix} CO.OH \\ | \\ CO.OH \end{matrix} + 2H_2O$$

Scheele (1776), Naumann, Moeser, Lindenbaum, *J. prakt. Chem.* 1907, **75**, 146.

140 c.c. conc. nitric acid.
20 grms. cane sugar.
0·1 grm. vanadium pentoxide.

The nitric acid is warmed gently on the water-bath in a large flask (1 litre) with the addition of the vanadium pentoxide. It is then placed in the fume cupboard and the cane sugar at once added. As soon as torrents of brown fumes begin to be evolved, the flask is placed in cold water. After the reaction has ceased the liquid is left for twenty-four hours when colourless crystals of the acid separate. A further small quantity may be obtained from the mother liquor on standing. The crystals are drained on a small porcelain funnel without filter paper, and recrystallised from a very small quantity of water. Yield, 15—20 grams.

Properties.—Colourless crystals, which, on heating to 100°, lose their water of crystallisation, melt, and then partly sublime and partly decompose, giving off carbon dioxide and formic acid. M. p. of the hydrated crystals 101·5°. Soluble in water and in alcohol, very slightly soluble in ether.

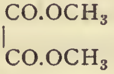
Reactions.—1. Boil a little of the acid with ammonia solution until neutral, and add calcium chloride solution. A white precipitate of the calcium salt is obtained, which is insoluble in acetic acid.

2. Add to a solution of the acid a few drops of dilute sulphuric acid, and warm gently. On adding permanganate solution it is immediately decolourised, $5C_2H_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + 8H_2O + K_2SO_4 + 2MnSO_4$.

3. Heat two or three grams of the crystals with about 5 c.c. concentrated sulphuric acid. Rapid effervescence occurs, and the gas may be ignited at the mouth of the tube, $C_2H_2O_4 - H_2O = CO + CO_2$. See *Appendix*, p. 257.

PREPARATION 26

Methyl Oxalate,



$$\begin{array}{l} CO.OCH_3 \\ | \\ CO.OCH_3 \end{array}$$

Dumas, Peligot, *Ann. Chim. Phys.*, 1836, **58**, 44; Erlenmeyer, *Rep. Pharm.* (2), **23**, 432.

70 grms. crystallised oxalic acid
50 „ (63 c.c.) methyl alcohol.

The oxalic acid is powdered and heated in a basin on a water-bath, which is kept boiling briskly, until no more water is given off (one to two hours). It must be occasionally stirred and powdered up. It is then heated to 110—120° in an air-bath or in a Victor Meyer drying apparatus (see p. 27) until it loses the weight corresponding to two molecules of water. If the Victor Meyer apparatus is used, amyl alcohol, b. p. 132°, should be placed in the outer jacket.

The dehydrated and powdered oxalic acid is mixed with the methyl alcohol, and the mixture heated on the water-bath for two hours with an upright condenser. The liquid is then distilled with a thermometer. When the temperature rises to 100° the receiver is replaced by a beaker, and the water-jacket of the condenser removed. The thermometer rises rapidly to the boiling-point of methyl oxalate, 160—165°, and the distillate solidifies in the receiver. It is drained at the pump and dried. It may be recrystallised from spirit. Yield, 20—25 grams.

$$C_2H_2O_4+2CH_3OH=C_2O_2(OCH_3)_2+2H_2O.$$

Properties.—Colourless plates ; m. p. 54° ; b. p. 163°.

Reactions.—For this purpose the alcoholic mother liquor from the crystals may be used.

1. Add a little caustic potash solution. Crystals of potassium oxalate are deposited. The ester is hydrolysed.

2. Add a few drops of concentrated ammonia. A white crystalline precipitate of oxamide is formed, $C_2O_2(OCH_3)_2+2NH_3=C_2O_2(NH_2)_2+2CH_3OH$.

PREPARATION 27.

Glyoxylic Acid, $CHO.COOH+H_2O$.

Glycollic Acid, $CH_2OH.COOH$.

Tafel and Friedrichs, *Ber.*, 1904, **37**, 3187 ; *Centralblatt* ; 1905 II, 1699.

20 grms. oxalic acid (in fine powder).
100 c.c. sulphuric acid (10 per cent.).

The process is one of electrolytic reduction and the apparatus is similar to that shown in Fig. 77, p. 144. It consists of a small porous cell (8 cm. × 2 cm. diam.) surrounded by a narrow beaker (11 cm. × 6 cm. diam.). The oxalic acid, mixed with 100 c.c. 10 per cent. sulphuric acid (titrated against standard baryta solution) forms the cathode liquid and is placed in the beaker. The porous cell is filled with the same strength of sulphuric acid and forms the anode liquid. The electrodes are made from ordinary clean sheet lead. The anode consists of a thin strip projecting about two inches from the cell and the cathode is made from a rectangular piece 10 × 15 cm. with a long tongue, the square portion being bent into the form of a cylinder surrounding the porous cell, and the projecting tongue serving as attachment to the circuit (see Fig. 77, p. 144). It is advisable to reverse the current before use so as to produce a metallic surface.

The whole apparatus is placed in a good freezing mixture. The electrodes are connected in circuit with an ammeter and resistance as described on p. 144. The reduction requires theoretically 9 ampere-hours and the strength of current may vary between moderately wide limits (2—6 amperes) per 100 sq. cm. of cathode surface. The cathode liquid should be frequently stirred so as to bring the suspended oxalic acid into solution, and, as the yield of glyoxylic acid depends on efficient cooling, it is important that the temperature should not exceed 10°. If the temperature is allowed to rise, glycollic acid is formed. The glyoxylic acid is separated as the calcium salt. The cathode liquid is poured into a basin and the sulphuric and unchanged oxalic acid precipitated with standard baryta solution. The mixture is filtered and the filtrate is concentrated *in vacuo* at 60° (see p. 94), neutralised in the cold with calcium carbonate, boiled up for a short time and filtered. As calcium glyoxylate is only slightly soluble in cold water (1 part in 140 of water at 18°) the greater portion crystallises on cooling. If calcium glycollate, which is much more soluble, is present, it may be separated from the filtrate by concentrating the solution on the water-bath and precipitating with spirit. To obtain free glyoxylic acid, the calcium salt is dried and suspended in water, the calculated quantity of oxalic acid added and the mixture filtered. The filtrate is evaporated in a vacuum desiccator, when the glyoxylic acid remains as a viscid liquid which may crystallise on long standing,

$$\mathrm{COOH.COOH + H_2 = CHO{\cdot}COOH + H_2O.}$$

Properties.—Crystallises in rhombic prisms ; very soluble in water.

Reactions.—1. Add a few drops of the acid solution or solution of the calcium salt to a few c.c. of ammonia-silver nitrate and warm in hot water. A silver mirror is deposited.

2. To the acid, neutralised with potassium carbonate, or to the

solution of the calcium salt, add a solution of phenylhydrazine acetate and a little sodium acetate. The phenylhydrazone separates on standing in minute yellow crystals, which can be recrystallised from alcohol. The neutral salts also combine with sodium bisulphite and hydroxylamine.

Glycollic Acid. If it is required to convert the oxalic acid completely into glycollic acid, the same method is employed as described above, but the temperature is raised to 35° and the number of ampere-hours is doubled. The separation is effected as the calcium salt and precipitated with alcohol as already described.

$$\mathrm{COOH.COOH + 2H_2 = CH_2OH + COOH + H_2O}$$

Properties.—Crystals m. p. 79—80°; very soluble in water. The air-dried calcium salt contains three molecules of water of crystallisation and is soluble in 80 parts of water 15°, and in 19 parts at 100°. See *Appendix*, p. 258.

PREPARATION 28.

Palmitic Acid, $C_{15}H_{31}CO.OH$.

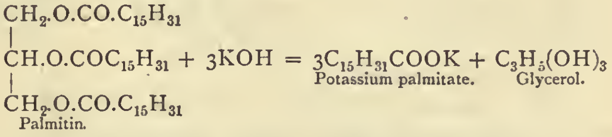
Frémy, *Annalen*, 1840, **36**, 44.

30 grms. palm oil.
24 „ caustic potash.

The caustic potash is dissolved in its own weight of water. The palm oil is melted in a large basin on the water-bath, and the potash solution added with constant stirring. The mixture is heated for half an hour. Half a litre of boiling water is poured in, and, after stirring well, 75 c.c. concentrated hydrochloric acid are gradually added, and the heating continued until the palmitic acid separates out as a transparent brown oil on the surface of the liquid. It is allowed to cool, and the cake of impure acid removed and pressed between filter-paper. The acid is now melted in a small basin on the water-bath and decanted, from any water which may have separated, into a retort (250 c.c.). It must be distilled *in vacuo.* The neck of the retort is fixed into a small filtering tube, which serves as receiver, as shown in Fig. 67. A few small pieces of unglazed pot are dropped into the retort, the tubulus of which is closed with a cork holding a thermometer. Before commencing the distillation the apparatus should be tested to see that it is air-tight. It is then evacuated with the water pump (See Fig. 35, p. 44), and the distillation commenced. During the distillation it is advisable to hold the Bunsen and to heat the retort with the bare flame. Under a pressure of 36 mm. the acid distils at 245°. The pale yellow oil which collects in the receiver is poured out into a basin whilst hot and allowed to cool. The cake of acid is spread on a porous plate and left to drain, when it becomes nearly colourless, and, after one or two crystallisations from small quantities of spirit, is pure, and melts at 62°. Yield about 20 grams.

Fig. 67.

The aqueous portion from which the cake of acid is removed contains free hydrochloric acid, potassium chloride, and glycerol. The latter may be obtained by evaporating to dryness on the water-bath, and extracting the residue with small quantities of alcohol, which dissolves out the glycerol. On evaporating the alcohol impure glycerol is left.



$$\begin{array}{l} CH_2.O.CO.C_{15}H_{31} \\ | \\ CH.O.COC_{15}H_{31} + 3KOH = \underset{\text{Potassium palmitate.}}{3C_{15}H_{31}COOK} + \underset{\text{Glycerol.}}{C_3H_5(OH)_3} \\ | \\ \underset{\text{Palmitin.}}{CH_2.O.CO.C_{15}H_{31}} \end{array}$$

$$C_{15}H_{31}COOK + HCl = C_{15}H_{31}COOH + KCl.$$

Properties.—Crystallises in tufts of colourless needles ; m. p. 62° ; soluble in alcohol and ether ; insoluble in water.

Reactions.—1. Dissolve a small quantity of the acid in caustic soda solution and add salt. Sodium palmitate separates as a curdy white precipitate.

2. Boil another portion of the acid with caustic soda and let it cool. Pour off the liquid from the crust of sodium palmitate, which forms on the surface, wash once or twice with

a little cold water, and dissolve the sodium salt in hot water. On cooling, a thick gelatinous mass of sodium palmitate separates. See *Appendix*, p. 258.

Glycerol (Glycerin), $CH_2(OH).CH(OH).CH_2(OH)$

Scheele, *Opusc.*, 1779, **2**, 175.

Glycerol is obtained by the hydrolysis of fats and oils, and purified by distillation under reduced pressure with superheated steam.

Properties.—A viscid, colourless liquid, with a sweet taste; m. p. 17°, b. p. 290°. It boils, *under ordinary pressure*, with partial decomposition forming acrolein; sp. gr. 1·269 at 12°; miscible with water and alcohol; insoluble in ether and the hydrocarbons.

Reactions.—1. Heat a few drops of glycerol with some powdered potassium hydrogen sulphate. The irritating smell of acrolein is at once perceptible.

2. Make a borax bead and dip it into a solution of glycerol and bring it into the flame. A green colouration due to boric acid is produced.

PREPARATION 29.

Formic Acid, H.CO.OH.

Berthelot, *Ann. Chim. Phys.*, 1856, (3) **46**, 477; Lovin, *Bull. Soc. Chim.*, 1866, (2) **5**, 7; 1870, (2) **14**, 367.

50 grms.	anhydrous glycerol.
200 ,,	oxalic acid (in four portions of 50 grams).

The glycerol is dehydrated by heating it gently in a basin on a sand-bath until a thermometer with the bulb immersed in the liquid indicates 175°. Fifty grams of commercial crystallised oxalic acid and 50 grams of glycerol are heated in a retort (250 c.c.) over wire-gauze, with condenser and receiver. A thermometer is fixed through the tubulus with the bulb in the liquid. The reaction begins at about 80°, and at 90° proceeds briskly, carbon dioxide being evolved. The temperature is maintained at 105–110° until the evolution of gas has slackened. Some aqueous formic acid has meanwhile collected in the receiver. The contents of the retort are now cooled to about 80° and a further 50 grams of oxalic acid added. The reaction recommences on heating with the formation of aqueous formic acid, which becomes more concentrated with each fresh addition of oxalic acid until the distillate eventually contains 56 per cent. of acid. The other portions of oxalic acid are added in the same way. In order to regain the formic acid which remains as monoformin in the retort, the contents are transferred to a round flask, diluted with about 250 c.c. of water and distilled in steam, until the distillate has only a faintly acid reaction (about 250 c.c.).

Distillation in Steam.—The apparatus for distilling in steam is shown in Fig. 68. A large flask, or, preferably, a 1 gallon

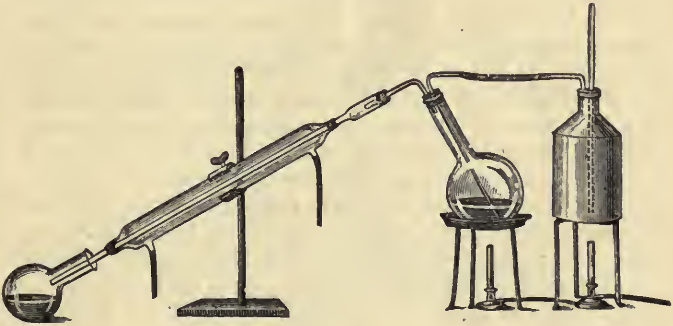
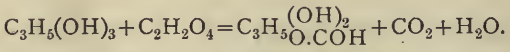


FIG. 68.

tin is closed by a double bored cork. A safety-tube passes through one hole, and a bent tube which terminates below the cork passes through the second hole, and is attached by rubber tubing to the inlet-tube of the distilling flask (1 litre). The flask is sloped to prevent the contents being splashed over into the condenser. It is heated on the sand-bath or asbestos board to boiling, and steam passed in. The united distillates are poured into a basin and neutralised by adding lead carbonate until, on heating, no further effervescence occurs. The liquid is now left for a moment to settle, and the clear solution decanted, whilst hot, through a fluted filter. The residue in the basin is boiled up again with a volume of water equal to that decanted, and again a third and fourth time, and filtered hot each time until no more lead formate is dissolved. The lead formate will have now passed into solution and the liquid is then evaporated down on a sand-bath or ring-burner (see Fig. 69), until crystals appear on the surface, when the liquid is put on one side to cool. Lead formate crystallises out in long white needles. Yield about 150 grams. In order to obtain pure formic acid, hydrogen sulphide is passed over the heated lead salt. It is carried out as follows :—

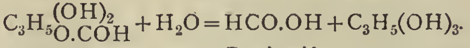
FIG. 69.

The powdered salt, dried on the water-bath, is introduced in a long layer into a sloping wide tube, loosely stopped at the lower end by a plug of glass wool or asbestos.* To the lower end of the tube a receiver, in the form of a distilling-flask, is attached, which is protected from moisture by a drying-tube. The salt is heated gently by moving a flame along the tube whilst hydrogen sulphide, washed through water, and dried by passing through a U-tube containing calcium chloride, is led over the salt in not too rapid a stream. The lead formate blackens, and is slowly converted into lead sulphide and formic acid, which drops into the receiver. The acid, which retains a strong smell of hydrogen sulphide, is freed from the latter by distillation over a little dry lead formate. Yield is nearly theoretical.



$$C_3H_5(OH)_3 + C_2H_2O_4 = C_3H_5{}^{(OH)_2}_{O.COH} + CO_2 + H_2O.$$

Glycerol monoformin.



$$C_3H_5{}^{(OH)_2}_{O.COH} + H_2O = HCO.OH + C_3H_5(OH)_3.$$

Formic acid.

Properties.—Colourless liquid, with a penetrating smell resembling sulphurous acid; b. p. 100°; sp. gr. 1·223 at 0°; solidifies below 0° to colourless crystals ; m. p. 8·6° ; soluble in water and alcohol.

Reactions.—For the following tests use a neutral solution prepared as follows :—Boil a little lead formate with a solution of sodium carbonate, filter, add a slight excess of nitric acid, boil a minute, add dilute ammonia and boil until neutral. 1. Add a drop of ferric chloride. A red colouration is produced, which, on boiling, becomes turbid from the formation of basic ferric formate. (Compare acetic acid, p. 74.)

2. Add to the solution a few drops of a solution of silver nitrate and warm. Metallic silver is deposited as a black powder.

3. Add to the solution a few drops of a solution of mercuric chloride and warm. White mercurous chloride is deposited.

4. Add concentrated sulphuric acid to a little formic acid, solid lead formate, or other salt and heat. Carbon monoxide is evolved, and may be lighted at the mouth of the test-tube. $(HCOO)_2Pb + H_2SO_4 = PbSO_4 + 2H_2O + 2CO$. See *Appendix* p. 259.

PREPARATION 30.

Allyl Alcohol, $CH_2{:}CH.CH_2OH$.

Tollens, Henninger, *Annalen*, 1870, **156**, 129.

50	grms.	oxalic acid.
200	,,	glycerol.
$\frac{1}{4}$	,,	ammonium chloride.

A mixture of the above substances is heated in a retort ($\frac{1}{2}$ litre) over wire-gauze with condenser and receiver.* A rapid evolution of carbon dioxide at first occurs, and the temperature, indicated by a thermometer dipping into the liquid, remains for some time stationary at about 130°. As the temperature slowly rises the evolution of gas slackens, and after a time (at about 180°) entirely ceases. When the temperature has reached 195° the receiver, which contains aqueous formic acid, is changed. At 200—210° carbon dioxide is again given off, and oily streaks are observed to run down the neck of the retort; at the same time a disagreeable penetrating smell is perceptible. By gently heating the contents of the retort, a temperature of 220—230° is maintained for some time, and when it has finally risen to 260° the distillation is stopped. The distillate is a mixture of allyl alcohol and water, and there is also present allyl formate, glycerol, and acrolein. Excess of glycerol remains in the retort and may be used again by repeating the operation with a smaller quantity of oxalic acid (30—40 grams) until the residue is too small or has become dark-coloured and thick. The distillate is submitted to a second distillation, which is continued until no oily layer separates from the latter portions which distil on treating with solid potassium carbonate. This occurs when the temperature reaches about 105°. On adding solid potassium carbonate to the distillate, the allyl alcohol settles out as an oil. This is separated and distilled. Yield about 15 grams boiling at 92—96°.

$$C_2H_2O_4 + C_3H_8O_3 = \underset{\text{Glycerol monoformin.}}{C_3H_5(OH)_2.O.CO.H} + H_2O + CO_2$$

$$C_3H_5(OH)_2.O.CO.H = \underset{\text{Allyl alcohol.}}{C_3H_5OH} + H_2O + CO_2$$

Properties.—Colourless liquid, with a pungent odour; b. p. 96·5°; sp. gr. 0·858 at 15°.

Reaction.—Add bromine water to a little of the allyl alcohol. It is immediately decolourised, $C_3H_5OH + Br_2 = C_3H_5Br_2OH$. See *Appendix*, p. 259.

PREPARATION 31.

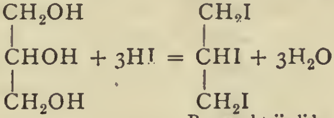
Isopropyl Iodide, $CH_3.CHI.CH_3$

Markownikoff, *Annalen*, 1866, **138**, 364.

60 grms. iodine.
40 ,, glycerol.
32 ,, water.
11 ,, yellow phosphorus.

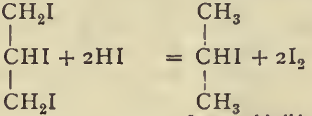
The iodine, glycerol, and water are placed together in a retort (250 c.c.), standing over wire-gauze and attached to a condenser and receiver. The phosphorus is cut up under a layer of water into small pieces, the size of a pea, and, with crucible tongs, dropped gradually into the retort. The introduction of the phosphorus generally produces at the beginning a violent reaction, often accompanied by a vivid flash. If no reaction occurs on adding the first few pieces of phosphorus, the retort must be warmed gently. The last two-thirds of the phosphorus may be added more quickly. The contents of the retort are now distilled as long as any oily liquid passes over. The distillate is poured back into the retort and redistilled. The liquid is then shaken up with dilute caustic soda solution in a separating-funnel, the isopropyl iodide separated, dried over calcium chloride, poured off and fractionated in a distilling flask. It distils entirely at 88—89°. Yield 30—35 grams.

1. $PI_3 + 3H_2O = 3HI + H_3PO_3.$

2. 

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HI = \begin{array}{l} CH_2I \\ | \\ CHI \\ | \\ CH_2I \end{array} + 3H_2O$$

Propenyl triiodide.

3. 

$$\begin{array}{l} CH_2I \\ | \\ CHI \\ | \\ CH_2I \end{array} + 2HI = \begin{array}{l} CH_3 \\ | \\ CHI \\ | \\ CH_3 \end{array} + 2I_2$$

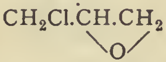
Isopropyl iodide.

Propenyl triiodide is probably formed as an intermediate product, though it does not exist in the free state.

Properties.—Colourless liquid ; b. p. 89·5° ; sp. gr. 1·744 at 0°. See *Appendix*, p. 260.

PREPARATION 32.

Epichlorhydrin,



$$CH_2Cl.\underset{\diagdown O \diagup}{CH.CH_2}$$

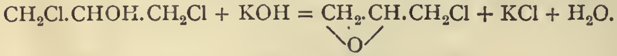
Reboul, *Annalen*, *Spl.*, 1861, **1**, 221.

200 grms. glycerol.
160 c.c. glacial acetic acid.

The glycerol, which must be dehydrated (see p. 106), is mixed with an equal volume of glacial acetic acid. Hydrochloric acid gas (see Fig. 65, p. 93) is passed into the cold liquid for about two hours, when it ceases to be absorbed. The mixture is now heated on the water-bath, and, after standing twenty-four hours, the current of gas is continued for about six hours more. The liquid is distilled with a thermometer.* Hydrochloric acid is first given off, together with acetic acid. As the temperature rises, the dichlorhydrin and acetodichlorhydrin distil. The portion distilling at 160—210°, consisting mainly of dichlorhydrin, is collected separately and used for the preparation of epichlorhydrin. Yield of dichlorhydrin about 120 grams. Epichlorhydrin is obtained by the action of aqueous potash solution upon the dichlorhydrin. A solution of 100 grams of caustic potash in 200 c.c. of water is well cooled and poured slowly, with constant stirring, into the dichlorhydrin. Rise of temperature must be carefully avoided. The epichlorhydrin is separated from the product by adding ether, which dissolves out the epichlorhydrin. The upper layer is separated, shaken up with a little water, and again separated. It is then dehydrated over calcium chloride and decanted into a round flask. The ether is first removed on the water-bath. The residue is then fractionally distilled. This is effected by attaching a fractionating column to the flask (see p. 137). The portion boiling at 115—125° is epichlorhydrin, and is collected separately. The portion boiling above this temperature consists mainly of acetodichlorhydrin. Yield 25—30 grams.

$$CH_2OH.CHOH.CH_2OH + HCl = \underset{\alpha\text{-Monochlorhydrin.}}{CH_2Cl.CHOH.CH_2OH} + H_2O.$$

$$CH_2Cl.CHOH.CH_2OH + HCl = \underset{\alpha\alpha\text{-Dichlorhydrin.}}{CH_2Cl.CHOH.CH_2Cl} + H_2O.$$



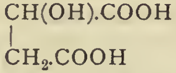
$$CH_2Cl.CHOH.CH_2Cl + KOH = \underset{\diagdown O \diagup}{CH_2.CH}.CH_2Cl + KCl + H_2O.$$

Epichlorhydrin.

Properties.—Mobile liquid, with an ethereal smell; b. p. 117°; sp. gr. 1·203 at 0°.

Reaction.—Warm a little of the epichlorhydrin with caustic potash solution. It dissolves, forming glycerol. See *Appendix*, p. 260.

Malic Acid,



$$\begin{array}{l} CH(OH).COOH \\ | \\ CH_2.COOH \end{array}$$

Malic acid is prepared from the juice of the mountain ash berries by precipitation as the calcium salt.

Properties.—It is soluble in water and alcohol, but not in ether. On heating, it loses water and is converted into fumaric and maleic acids (see p. 125). On oxidation it gives malonic acid and on reduction succinic acid.

Reactions.—1. Make a strong neutral solution, add calcium chloride solution and boil. The calcium salt is precipitated.

2. Mix about 0·5 gram each of powdered malic acid and resorcinol, and add 1 c.c. of concentrated sulphuric acid. Warm the mixture for a moment over the flame until it begins to froth. On cooling and adding water and caustic soda solution, an intense blue fluorescence is produced (von Pechmann).

PREPARATION 33.

Succinic Acid (Ethylenedicarboxylic Acid), $COOH.CH_2.CH_2.COOH$.

Schmitt, *Annalen*, 1860, **114**, 106.

10 grms. malic acid.
30 „ hydriodic acid.
2 „ red phosphorus.

The hydriodic acid is conveniently prepared, according to Gattermann, as follows:—A small round flask (100 c.c.) is provided with a tap-funnel and delivery-tube, the latter being attached to a U-tube as shown in Fig. 70. The U-tube is filled with broken glass or pot, which has been coated with amorphous phosphorus by rubbing it in the phosphorus slightly moistened with water. The flask is first detached from the U-tube and funnel, and 44 grams of iodine introduced.* Four grams of yellow phosphorus, cut in small pieces, are then added. The phosphorus must be cut under water, brought on to filter-paper with crucible tongs, pressed for a moment, and transferred with tongs to the flask. Each piece of phosphorus as it drops in produces a flash. When the phosphorus has been added a dark coloured liquid is obtained, which solidifies on cooling, and consists of PI_3. The flask, when cold, is closed with its cork, and the delivery tube from the U-tube is inserted loosely into the neck of a small flask containing 50 c.c. of water, so that the open end of the delivery-tube is above the surface of the water. It is kept in position by a wedge of cork fixed in the

FIG. 70.

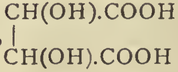
neck. Ten c.c. of water are now added gradually from the tap-funnel. Hydriodic acid is evolved, and, after being freed from iodine in the U-tube, is absorbed by the water. When the water has been added, the liquid is gently heated over a small flame until no more fumes issue from the delivery-tube. The aqueous solution of hydriodic acid is distilled with a thermometer, and the portion boiling at 125° and above is collected separately. It consists of strong hydriodic acid solution, containing about 57 per cent. of HI. The malic acid is dissolved in the hydriodic acid and poured into a stout-walled tube for sealing. The red phosphorus is added, and the tube sealed in the usual way (see p. 24). It is heated in the tube-furnace for six hours at 120°. On removing the tube it is found to be filled with crystals of succinic acid mixed with iodine. The contents are poured into a basin and evaporated to dryness on the water-bath. The residue, when cold, is stirred with a little chloroform to dissolve the free iodine, which is then decanted, and the process repeated if necessary. After warming to drive off the chloroform, the substance is dissolved in hot water and set aside to crystallise. Succinic acid crystallises in long prisms. Yield 5 grams.

$$COOH.CHOH.CH_2.COOH + 2HI = COOH.CH_2.CH_2.COOH + H_2O + I_2.$$

Properties.—Colourless prisms ; m. p. 180°. On distillation, the acid loses water and is converted into the anhydride.

Reaction.—1. Make a neutral solution by boiling with an excess of ammonia, and add to one portion, calcium chloride ; no precipitate is formed ; to another portion add a drop or two of ferric chloride ; a brown precipitate of ferric succinate is thrown down. See *Appendix*, p. 261.

Tartaric Acid (Dihydroxysuccinic Acid),



$$\begin{array}{l} CH(OH).COOH \\ | \\ CH(OH).COOH \end{array}$$

Scheele (1769).

The acid potassium or calcium tartrates are found in many plants ; but the chief source of tartaric acid is the impure acid potassium salt, which separates out as wine-lees, or argol from grape-juice in process of fermentation.

Properties.—The acid crystallises in monoclinic prisms, soluble in alcohol and water, but not in ether. It turns the plane of polarisation to the right; m. p. 167—170°.

Reactions.—1. Heat a crystal of the acid. It gives an odour resembling burnt sugar. Carefully neutralise a solution of tartaric acid with caustic soda, and make the following tests:—

2. Add calcium chloride and stir with a glass rod. A crystalline precipitate of calcium tartrate, $C_4H_4O_6Ca + 4H_2O$, is formed which dissolves in acetic acid and caustic alkalis. Repeat the foregoing test, but add a few drops of acetic acid before the calcium chloride. There is no precipitate. Calcium sulphate also gives no precipitate with tartaric acid or neutral tartrates, (compare reactions for oxalic acid, p. 100).

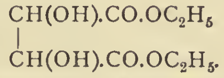
3. Add silver nitrate solution. The white precipitate is the silver salt. Add two or three drops of dilute ammonia until the precipitate is nearly dissolved, and place the test-tube in a beaker of hot water. A silver mirror will be deposited.

4. Add a few drops of acetic acid and a little ammonium or potassium acetate solution to a moderately strong solution of tartaric acid or a neutral tartrate. On stirring with a glass rod, the acid potassium or ammonium tartrate will be precipitated.

5. To a solution of tartaric acid or a tartrate in water add a drop of ferrous sulphate solution and a few drops of hydrogen peroxide and make alkaline with caustic soda. A violet coloration is produced (Fenton's reaction).

PREPARATION 34.

Ethyl Tartrate,



$$\begin{array}{l} CH(OH).CO.OC_2H_5 \\ | \\ CH(OH).CO.OC_2H_5. \end{array}$$

Anschütz, Pictet, *Ber.*, 1880, **13**, 1176.

30 grms. tartaric acid.
160 c.c. absolute alcohol.

The tartaric acid is finely powdered and mixed with half the above quantity (80 c.c.) of absolute alcohol. The mixture is heated on the water-bath with upright condenser until dissolved. The flask is immersed in cold water, and the well-cooled solution saturated with dry hydrochloric acid gas (prepared in the usual way by dropping conc. sulphuric acid into conc. hydrochloric acid, see Fig. 65, p. 93). After standing for an hour or two (or preferably overnight), the hydrochloric acid, excess of alcohol and water are expelled by evacuating the flask and distilling *in vacuo* on the water-bath. The remaining half of the alcohol is added to the residue, and the mixture again saturated in the cold with hydrochloric acid gas. After standing, the acid, alcohol and water are removed as before, and the residue fractionated from an oil or metal bath *in vacuo*. The ethyl tartrate distils as a clear viscid liquid. After a second distillation *in vacuo* the substance is pure.

At 11 mm. it boils at 155°.
" 20 " " " 164°.

The yield is 80 per cent. of the theory. See *Appendix*, p. 262.

Determination of Rotatory Power.—The rotatory power of ethyl tartrate, which is an optically active substance, is determined by means of a polarimeter. One of these instruments known as Laurent's polarimeter is shown in Figs. 71 and 72.

The monochromatic light of a sodium flame is used in these determinations and is obtained by suspending in a Bunsen flame a platinum wire basket containing fused sodium chloride or the more volatile bromide. The latter gives a brighter flame, but the basket requires replenishing more frequently. The light from the flame passes through a cell B, containing a solution of potassium bichromate (or a crystal of this substance), which deprives it of blue or violet rays. It then passes through the polarising nicol prism P. A plate of quartz cut parallel to the optic axis covers half the opening D, and is of such a thickness that it produces a difference of a half-wave length (or an exact odd multiple of a half-wave length) between the two rays, which it gives by double refraction. The light then passes through the substance placed in the tube T and entering at E strikes the analysing nicol N. The telescope OH is focussed on the edge of the quartz plate at D. When N is turned, a pointer moves over the graduated circle C and its position can be read by means of the lens L.

The Theory of the Instrument may be explained as follows:—If, after passing through the nicol P, the plane of vibration is in the direction OB, Fig. 73 *a*, then in the half of the field to the right, uncovered by the quartz plate, it passes on un-

Dorothy Bellow.

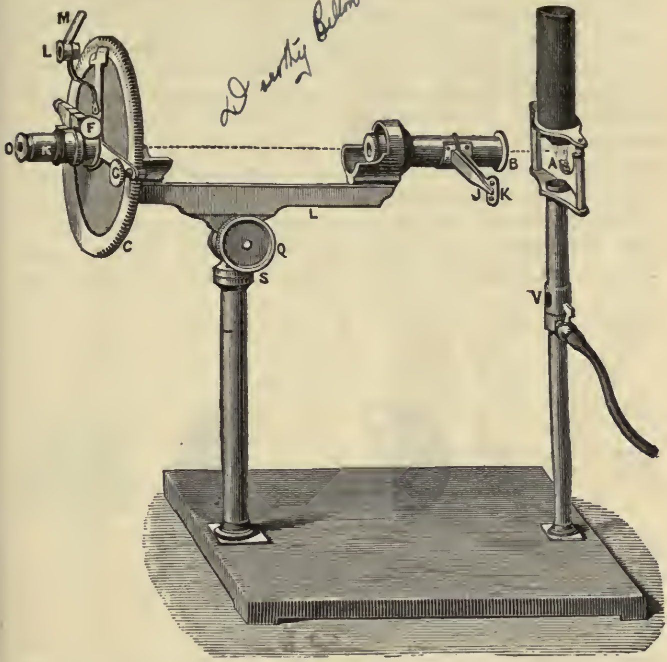


FIG. 71.

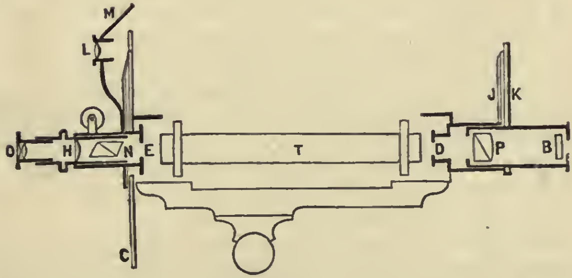


FIG. 72.

changed. When it strikes the quartz the ray is broken up into the two components OY and OX. These traverse the quartz with different velocities, and since one ray is retarded half a wave-length in respect of the other, the vibration of one component will be represented by OY, but the other must be represented by OX′ instead of OX. These two combine on emerging to a plane polarised ray vibrating in the direction OB′ so that the angle AOB′ is equal to the angle AOB.

If now (the tube containing water or other non-rotating liquid) the nicol N be so placed that it is parallel to nicol P, then the light, in the half of the field to the right, will pass through unchanged, but only a portion of the light which has passed through the quartz diaphragm with its plane of vibration in the direction OB′, will pass through N and consequently there will be different intensities of illumination in the two halves of the field, Fig. 73 *b* (if the angle *a* is 45° then the angle BOB will be 90°, and the light in the left half of the field will be completely obscured). Similarly if the plane of the nicol N be made parallel to OB′ there will be a greater intensity of illumination in the left half of the field, Fig. 73 *c*. Between the two positions of the nicol N there must necessarily be one which gives uniform illumination of the whole field, and this is the zero point of the instrument, Fig 73 *d*.

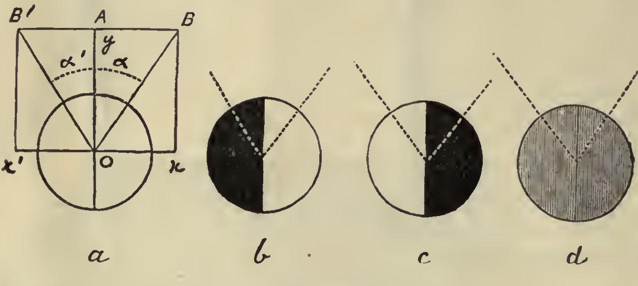


Fig. 73

If the tube T, containing the active substance, be interposed between the two nicols, then both rays OB and OB′ will be rotated through equal angles, and to re-establish uniform illumination in the two halves of the field, the nicol N must be turned through an angle equal to the angle of rotation, which is then measured on the divided circle.

When the angle a is small, *i.e.* when the plane of vibration of the polarised light is almost parallel to the optic axis of the quartz, the greatest degree of sensitiveness is attained, for then a very small change in the position of N causes a great difference in the respective illuminations in the two halves of the field. As a increases, the sensitiveness diminishes, but a greater total intensity of illumination is obtained. By moving J (Fig. 71) the position of the nicol P may be altered. For clear colourless liquids the angle a may be made comparatively small; but in the case of coloured liquids it is necessary to have a larger, and so obtain a greater intensity of light at the cost of sensitiveness.

Calculation of Results; Homogeneous Liquids.—The angle of rotation, represented by a_D (for sodium light), varies with the length of the column of substance through which the light passes. One decimetre has been chosen as unit of length. The angle also varies with the temperature, which must consequently be determined for each observation.

For the comparison of the rotary power of different substances, use is made of the constant *specific rotation*, which may be defined as the angle of rotation, produced by 1 gram of active substance in 1 c.c. by a layer 1 dm. in length. This is obtained by dividing the observed angle of rotation by the product of the length in decimetres, and the density of the substance at the temperature at which the observation was made.

$$[a]_D^t = \frac{a_D^t}{l \times d}$$

Molecular Rotation is the above quantity multiplied by the molecular weight M of the compound, and divided by 100 to avoid unwieldy numbers, and is represented thus—

$$[M]_D^t = \frac{[a]_D^t \times M}{100}.$$

It expresses the angle of rotation of 1 mm. of active substance containing 1 gram-molecule in 1 c.c.

Rotation of Ethyl Tartrate.—Fill a 200 mm. polarimeter-tube with the tartrate prepared. Whilst it is settling determine the zero of the instrument, and if it does not coincide with the zero of the graduated circle, a corresponding correction must be introduced in the subsequent observations. The tube is then placed in the instrument, and the angle of rotation determined by turning the analyser N until equality of illumination is established in the two halves of the field. In making polarimetric observations reliance should not be placed on a single setting of the instrument, but at least five or six readings should be made, which, with a good instrument, should not differ by more than four or five minutes. The temperature at the time of observation must be noted, and the density determined either at that temperature or at two or three other temperatures, and the required density found by extrapolation.

Example :—

Temp.	Length.	α	d	$[\alpha]_D$
20°	199·85 mm.	18° 28′	1·2059	7·66

$$\left.\begin{array}{l}[\alpha]_D^{20} = 7{\cdot}66^\circ \\ [\alpha]_D^{18} = 7{\cdot}47^\circ\end{array}\right\}$$ Anschütz, Pictet, *Ber.*, 1880, **13**, 1177.

$$\left.\begin{array}{l}[\alpha]_D^{16} = 7{\cdot}27^\circ \\ [\alpha]_D^{14} = 7{\cdot}07^\circ \\ [\alpha]_D^{12} = 6{\cdot}86^\circ \\ [\alpha]_D^{10} = 6{\cdot}66^\circ\end{array}\right\}$$ By extrapolation.

Rotation of Tartaric Acid.—The specific rotation of a dissolved substance can be calculated from the rotation of the solution if the concentration is known. The formula to be used for this purpose is :—

$$[\alpha]_D = \frac{100\alpha_D}{l.\ c.}$$

where α is the angle of rotation of solution, l the length of the tube, and c the concentration, *i.e.*, the weight in grams of the dissolved substance contained in 100 c.c. of solution. The formula $[\alpha]_D = \frac{100\alpha_D}{l\,p\,d}$ may also be used (it is, in fact, identical), where p is the percentage (by weight) of substance in solution, and *d* the density of the solution. The specific rotation of dissolved substances varies with the concentration and with the temperature.

Heat some tartaric acid in an air-bath to 110°, until it is quite dry. Weigh accurately about 20 grams of the dry acid and dissolve in water; then make up the solution to exactly 100 c.c. Determine the rotation of the solution in a 200 mm. tube, and note the temperature at which the observation is made.

Take 50 c.c. of the solution and dilute it to 100 c.c. Determine the rotation of this solution *at the same temperature* as that at which the first rotation was observed.

Dilute 50 c.c. of the second solution to 100 c.c., and again determine the rotation at the same temperature.

The same process can be repeated once or twice more. Calculate the specific rotation of the tartaric acid, using the first formula. Plot the results on squared paper, making the ordinates specific rotation and the abscissae concentration.

Example:—

Temp.	Concentration.	Length of tube.	Angle of Rotation.	Spec. Rot. $\frac{100a}{l.c.}$
10°	40	200 mm.	6°	+ 7·5°
10°	20	,,	3° 59′	+ 9·96°
10°	10	,,	2° 11′	+ 10·91°

(Krecke, *Bischoff*, *Stereochemie*, p. 228.)

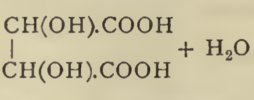
The following table shows the influences of temperature on the specific rotation of an aqueous solution containing 20 grams of tartaric acid in 100 c.c.

Temp.	Length of tube.	Angle of Rotation.	Specific Rotation.
0°	200 mm.	3° 28′	+ 8·66°
10°	,,	3° 50′	+ 9·96°
20°	,,	4° 38′	+ 11·57°
40°	,,	5° 28′	+ 13·66°
60°	,,	6° 28′	+ 16·16°
80°	,,	7° 21′	+ 18·38°
100°	,,	8° 36′	+ 21·50°

(Thomsen, *J. prakt. Ch.* [2] 32, 211.)

PREPARATION 35

Racemic Acid and Mesotartaric Acids.



$$\begin{array}{l} CH(OH).COOH \\ | \\ CH(OH).COOH \end{array} + H_2O$$

Pasteur, *Ann. Chim. Phys.*, 1848, (3) **24**, 442 ; 1850, (3) **28**, 56 ; Dessaignes, *Bull. Soc. Chim.*, 1863, **5**, 356 ; Jungfleisch, *Bull. Soc. Chim.*, 1872, **18**, 201 ; Hollemann, *Rec. trav. chim. Pays-Bas*, 1898, **17**, 66.

100 grms.	tartaric acid.
350 ,,	caustic soda (in 700 c.c. water).

Boil the tartaric acid and caustic soda solution for three hours in a round flask (1 litre), or preferably in a tin bottle furnished with reflux condenser. The use of a tin vessel obviates certain difficulties of filtration which the solution of the silica by the action of the alkali on the glass entails. The liquid, after boiling, is carefully neutralised with conc. hydrochloric acid (it is advisable to remove a little of the solution beforehand in case of overshooting the mark) and an excess of calcium chloride solution is added to the hot liquid. The mixture is left overnight, and the calcium salts filtered off at the pump, washed with water, and well pressed.

The calcium salts are well dried on the water-bath, or a fraction of the whole weight of the moist salts is taken and dried, and the total dry weight estimated. The substance is then suspended in boiling water and the calculated quantity of sulphuric acid added, after which the mixture is boiled for an hour. The calcium sulphate is removed by filtration, well washed with hot water, and the precipitate pressed down. The filtrate is concentrated on the water-bath until crystallisation begins. Racemic acid crystallises first, and after dehydrating on the water-bath melts at 205°. A further quantity is obtained on evaporation. Yield 50—60 grams.

The last mother liquors contain mesotartaric acid, m. p. 143—144°, which is much more soluble in water than racemic acid. To obtain a pure specimen repeated crystallisation is necessary.

The yield varies with the period of boiling, but usually does not exceed 10 grams.

Resolution of Racemic Acid.—The racemic acid is dissolved in water (250 c.c.) and divided into two equal volumes. Half of the solution is carefully neutralised with caustic soda and the other half with ammonia, and the two solutions then mixed.

The liquid is concentrated and poured into a crystallising dish. If, on cooling, the crystals are small and massed together, the solution has been too concentrated, and must be diluted so that small, well-defined crystals deposit. A dozen or so of these are picked out, dried, and put on one side. The remaining crystals are re-dissolved and left to cool in a room of fairly even temperature.

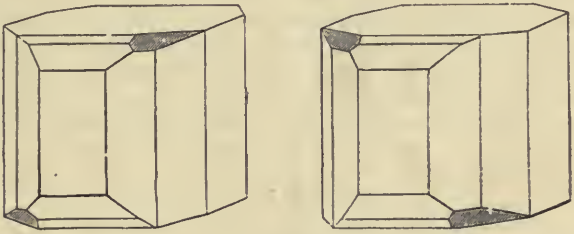


FIG. 74.

When the solution is just cold the crystals, previously removed, are sown evenly over the bottom of the dish at distances of 1—2 cms. apart and left for two days. The crystals will have now grown to a size which will enable the facets to be readily recognised. Each crystal is dried and carefully examined with a pocket lens in order to determine the position of the hemihedral facets, and placed in separate heaps. These facets lie to the right or left hand of the central prism face, as shown in Fig. 74. The crystals should be weighed, dissolved, and the solution diluted and examined in the polarimeter. The specific rotation may then be calculated. See *Appendix*, p. 264.

Preparation 36.

Pyruvic Acid, $CH_3.CO.CO.OH$.

Doebner, *Annalen*, 1887, **242**, 268.

200 grms. potassium hydrogen sulphate.
100 „ tartaric acid.

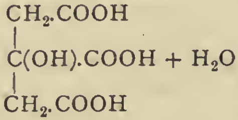
The potassium hydrogen sulphate and tartaric acid must be finely powdered and intimately mixed. The mixture is distilled in a round flask (1 litre), attached to a moderately long condenser tube, from a paraffin bath heated to 220°.* The mass at first froths up, and it is necessary to interrupt the heating when the flask is not more than half full of froth, as otherwise it may boil over. When the temperature of the bath has fallen to about 120°, the heating may be recommenced. The distillation is carried on until no more liquid distils. The distillate, which consists of water and pyruvic acid, and has a yellow colour, is fractionated *in vacuo*. It is collected at 68—70° at a pressure of 20 mm., and is quite colourless. Yield 15—20 grams. It may be fractionated at the ordinary pressure, but is difficult to obtain colourless in this way.

$$CO.OH.CHOH.CHOH.COOH = CH_3.CO.COOH + CO_2 + H_2O$$

Properties.—Colourless liquid; b. p. 165° at atmospheric pressure; m. p. 10—11°; polymerises on keeping.

Reaction.—Dissolve a drop of phenylhydrazine in two drops of glacial acetic acid, dilute with about 1 c.c. of water, and add a drop of pyruvic acid. A yellow crystalline precipitate of the phenylhydrazone, $CH_3.C{:}(N.NH.C_6H_5).CO.OH$, is formed.

Citric Acid,



$$\begin{array}{l} CH_2.COOH \\ | \\ C(OH).COOH + H_2O \\ | \\ CH_2.COOH \end{array}$$

Scheele (1784).

Citric acid occurs in the free state, as well as in the form of the calcium and potassium salts, associated with malic and tartaric acid, in many plants. It is prepared principally from lemon juice, from which it is precipitated as the calcium salt on boiling with chalk and also by the citric fermentation of glucose.

Properties.—The acid, which contains 1 molecule of water, crystallises in prisms ; soluble in water, alcohol, and also moderately soluble in ether ; m. p. 100°. The anhydrous acid melts at 153—154°.

Reactions.—1. Heat a little of the acid and notice the irritating vapours.

Make a neutral solution of sodium citrate by adding caustic soda to a solution of the acid.

2. Add lime water. There is no precipitate of the calcium salt, $(C_6H_5O_7)_2Ca_3+4H_2O$, until the solution is boiled.

3. Add calcium chloride solution and boil, and, to another portion, silver nitrate solution. Note the results and compare the reactions with those of tartaric acid (p. 115).

PREPARATION 37.

Citraconic and Mesaconic Acids.

(Methyl fumaric and Methyl maleic acid).

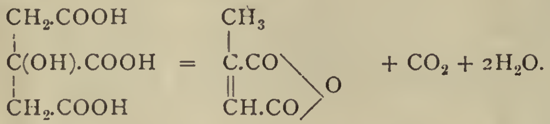
$CH_3.C(COOH):CH(COOH)$.

Kekulé, *Lehrbuch*, **2**, 319 ; Fittig, *Annalen*, 1877, **188**, 73.

250 grms. citric acid (crystallised).

Heat the crystallised citric acid, without powdering, in a porcelain basin to a temperature not exceeding 150°. The water of crystallisation is expelled, and the crystals become pasty and then fluid. When cold, the solid mass is removed from the basin by gently warming, and is coarsely powdered. The anhydrous acid is *rapidly* distilled in portions of 100 grams, from a retort (250 c.c.) with bent neck (see Fig. 19, p. 22), fitted to a condenser, the receiver being a separating funnel. The distillate consists of two layers. The lower layer of impure citraconic anhydride is run off, and the upper layer, consisting of water and citraconic acid, is fractionated, the portion distilling at 190—210° being collected and mixed with the previous lower layer.

The citraconic anhydride is now distilled *in vacuo* and collected at 110—114° under a pressure of 30 mm. Yield 30—35 grams.



Properties.—Colourless liquid; b. p. 213—214° (ordinary pressure). To convert the anhydride into citraconic acid the calculated quantity of water is added (1 mol. acid : 1 mol. water), and the mixture well stirred. The whole solidifies, on standing, to a mass of colourless crystals of citraconic acid, which are dried on a porous plate; m. p. 84—86°.

MESACONIC ACID.—To a saturated solution of citraconic acid in ether (4 parts citraconic acid require about 5 parts of anhydrous ether), about 1 part of chloroform is added, and a few drops of a moderately strong solution of bromine in chloroform. The mixture is placed in strong sunlight, when mesaconic acid, which is insoluble in ether and chloroform, begins at once to deposit on the side of the vessel nearest the light. Drops of bromine are added from time to time until no further precipitation occurs. The pasty mass is then filtered, washed with ether, and dried on a porous plate. Yield 73 per cent. of the citraconic acid; m. p. 202°. See *Appendix*, p. 265.

PREPARATION 38.

Urea (Carbamide), $CO\langle{}^{NH_2}_{NH_2}$

Wöhler, *Pogg. Ann.*, 1828, **12**, 253; Clemm, *Annalen*, 1848, **66**, 382.

50	grms.	potassium cyanide (98—99 per cent.).
140	,,	red oxide of lead.
25	,,	ammonium sulphate.

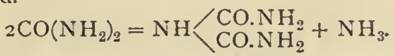
The potassium cyanide is heated in an iron dish over a large burner until it begins to fuse, when 140 grams of red oxide of lead are gradually added in small quantities and stirred in. The heat of the reaction causes the mass to melt and froth up. When it fuses quietly, the dark coloured liquid mass is poured on to an iron plate and allowed to cool. It solidifies and is powdered and separated from the solid cake of metallic lead. 200 c.c. of cold water are poured on to the crude cyanate and, after standing an hour, filtered through a fluted filter and washed with a little cold water. A concentrated solution of 25 grams of ammonium sulphate is immediately added to the filtrate, which is evaporated to dryness on the water-bath, the mass being stirred occasionally to prevent the formation of a surface crust. The cooled residue is powdered and the urea extracted with alcohol by boiling on the water-bath, using a reflux condenser and adding successively small quantities of spirit until the extract leaves only a small residue on evaporation on a watch-glass. The greater part of the alcohol is distilled off on the water-bath, and the residue poured out into a beaker to crystallise. Yield about 15 grams.

1. $4KCN + Pb_3O_4 = 4CONK + 3Pb$
2. $(NH_4)_2SO_4 + 2CONK = 2CON.NH_4 + K_2SO_4$
3. $CON.NH_4 = CO(NH_2)_2$

Properties.—Colourless prisms ; m. p. 132° ; very soluble in water ; soluble in hot alcohol.

Reactions.—1. Add to a strong solution of urea in water a drop of concentrated nitric acid, and to another portion a concentrated solution of oxalic acid ; the crystalline nitrate $CO(NH_2)_2HNO_3$ and oxalate $(.CO(NH_2)_2)_2C_2H_2O_4$ are deposited.

2. Melt a few crystals of urea over a small flame and heat gently for a minute, so that bubbles of gas are slowly evolved. Cool and add a few drops of water, then a drop of copper sulphate solution, and finally a few drops of caustic soda. A violet or pink coloration is produced, depending upon the quantity of *biuret* formed.



$$2CO(NH_2)_2 = NH\langle\begin{matrix}CO.NH_2\\CO.NH_2\end{matrix} + NH_3.$$

Biuret.

3. Add a few drops of sodium hypochlorite, or hypobromite, to a solution of urea in water. Nitrogen is given off, $CO(NH_2)_2 + 3NaOCl = N_2 + 2H_2O + 3NaCl + CO_2$ (which dissolves in the alkaline solution).

4. Add to a solution of urea a few drops of hydrochloric acid and a solution of sodium nitrite. Effervescence occurs and nitrogen and carbon dioxide are evolved.

$$CO(NH_2)_2 + 2HO.NO = 2N_2 + CO_2 + 3H_2O.$$

5. Heat a little urea with soda-lime. Ammonia is evolved. See *Appendix*, p. 267.

PREPARATION 39.

Thiocarbamide (Thiourea),

$$SC\Big\langle{}^{NH_2}_{NH_2}.$$

Reynolds, *Trans. Chem. Soc.*, 1869, **22**, 1 ; Volhard, *J. prakt. Chem.*, 1874, (2), **9**, 10.

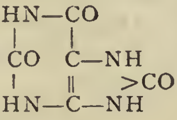
50 grms. ammonium thiocyanate.

The ammonium thiocyanate is melted in a round flask in a paraffin-bath, and kept at a temperature at which the mass remains just liquid (140—145°) for 5—6 hours. The cooled melt is powdered and ground with half its weight of cold water, which dissolves unchanged ammonium thiocyanate, but little of the thiourea. By dissolving the residue in a little hot water, pure thiourea is obtained, on cooling, in colourless, silky needles. Yield 7—8 grams.

$$CNS.NH_4 = CS(NH_2)_2.$$

Properties—Colourless, rhombic prisms (from dilute aqueous solution), long silky needles (from concentrated solutions) ; m. p. 172°. Very slightly soluble in cold water (1 part of thiourea dissolves in about 11 parts of water at the ordinary temperature).

Uric Acid,



Scheele (1776).

Uric acid is a product of the metabolism of the animal organism. It is usually prepared from guano, which is treated first with dilute hydrochloric acid to remove phosphate of calcium. The uric acid is then dissolved out with hot caustic soda and the clear alkaline solution precipitated with acid.

Properties.—Uric acid forms microscopic crystals of a characteristic shape. It is insoluble in water, but dissolves in the presence of many organic substances. On dry distillation it yields ammonia, cyanuric acid, and urea.

Reactions.—Evaporate a little of the acid with a few c.c. of dilute nitric acid to dryness on the water-bath. An orange or red residue remains. On cooling, add ammonia. A fine purple colour is produced (murexide test); see also Reaction for alloxan (p. 130).

PREPARATION 40.

Alloxantin, $C_8H_4N_4O_7 + 3H_2O$

Liebig, Wöhler, *Annalen*, 1838, **26**, 262.

10 grms. uric acid.
20 „ (18 c.c.) conc. hydrochloric acid diluted with an equal weight of water.
2½ potassium chlorate.

The hydrochloric acid is poured over the uric acid. The mixture is heated to 35°, and the potassium chlorate, finely powdered, is added in small quantities at a time with constant shaking. When about two grams of the chlorate have been added, the uric acid will have nearly dissolved, and the liquid has a faint yellow colour. It is diluted with double its volume of water, allowed to stand for about an hour, and filtered. The filtrate is saturated with hydrogen sulphide, and yields, after being left for 12 hours, crystalline crusts, often of a reddish tint, of alloxantin mixed with sulphur. It is filtered and washed with cold water, and the alloxantin dissolved in a small quantity of hot water, and filtered from the residue of sulphur. On cooling the filtrate, colourless crystals separate out. Yield 7—8 grams.

$$\underset{\text{Uric acid.}}{C_5H_4N_4O_3} + O + H_2O = \underset{\text{Alloxan.}}{C_4H_2N_2O_4} + \underset{\text{Urea.}}{CON_2H_4}.$$

$$2C_4H_2N_2O_4 + H_2S = \underset{\text{Alloxantin.}}{C_8H_4N_4O_7} + S + H_2O.$$

Properties.—Hard, colourless crystals, slightly soluble in cold, more readily in hot water.

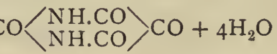
Reactions.—1. Add to the solution of alloxantin a little baryta water ; a violet colouration is produced.

2. Add ammonio-silver nitrate solution and warm ; metallic silver is deposited.

3. Boil the solution with mercuric oxide ; a violet solution of murexide is formed.

PREPARATION 41.

Alloxan (Mesoxalylurea),



$$CO\left\langle\begin{matrix}NH.CO\\NH.CO\end{matrix}\right\rangle CO + 4H_2O$$

Liebig, Wöhler, *Annalen*, 1838, **26**, 256.

5 grms. alloxantin.
5 „ (3·5 c.c.) conc. nitric acid (sp. gr. 1·4).
10 „ (7 c.c.) fuming „ (sp. gr. 1·5).

The finely powdered alloxantin is added to a mixture of the strong and fuming nitric acid, and left to stand. Slight evolution of nitrous fumes occurs, and the alloxantin, which at first remains at the bottom of the vessel, slowly changes into the more bulky crystals of alloxan, which gradually fill the liquid. The reaction lasts about two days, and is complete when a sample dissolves readily and completely in cold water. The crystalline mass is spread upon a porous plate, thoroughly dried in the air, and freed from traces of nitric acid by heating in a basin on the water-bath, until the smell of the acid disappears. Alloxan may be obtained in large crystals by dissolving the dry product in the smallest quantity of hot water, and allowing the solution to evaporate slowly in a desiccator over sulphuric acid. The crystals are liable to effloresce.

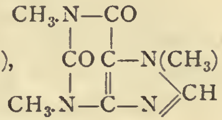
$$\underset{\text{Alloxantin.}}{C_8H_4N_4O_7} + O = \underset{\text{Alloxan.}}{2C_4H_2N_2O_4}.$$

Properties.—Colourless crystals, containing 4 molecules of water of crystallisation.

Reactions.—1. A small quantity of the alloxan solution is evaporated to dryness on the water-bath in a porcelain basin. A reddish residue is left, which turns purple on the addition of ammonia (murexide). See *Appendix*, p. 268.

PREPARATION 42.

Caffeine (Trimethyl xanthine),



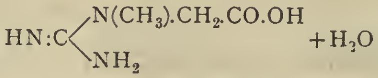
100 grms. tea.

Digest the tea with 500 c.c. boiling water for a quarter of an hour, and filter through cloth into a basin placed over a ring burner (see p. 108), so that the liquid in the filter is kept hot. Moderately fine unsized cotton cloth is used, and is wetted and stretched on a wooden frame as shown in Fig. 75. Wash with a further 250 c.c. of boiling water. Add to the filtrate a solution of basic lead acetate (made by boiling acetate of lead solution with excess of litharge, and then filtering) until no more precipitate is formed. Filter hot through a large fluted filter from precipitated albumin, and wash with water. To the boiling filtrate add dilute sulphuric acid until the lead is precipitated as sulphate. Filter or decant from the sulphate of lead, and concentrate the solution with the addition of animal charcoal to 250—300 c.c. Filter and extract the filtrate three times with small quantities (50 c.c.) of chloroform. Distil off the chloroform on the water-bath, and dissolve the residue in a small quantity of hot water. On allowing the solution to evaporate very slowly, long silky needles of caffeine separate, which may have a slightly yellow tint, in which case they should be drained, re-dissolved in water, and boiled with the addition of animal charcoal. The needles contain one molecule of water, which they lose at 100° and melt at 234·5°. Yield about 1·5 grams. See *Appendix*, p. 269.

FIG. 75.

PREPARATION 43.

Creatine.



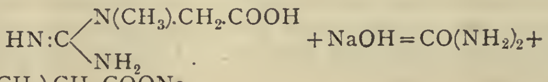
$HN{:}C\begin{cases} N(CH_3).CH_2.CO.OH \\ NH_2 \end{cases} + H_2O$

Neubauer, *Annalen*, 1861, **119**, 27.

500 grms. meat.

The meat, separated as far as possible from fat, is put through a sausage machine, or finely chopped and digested with ½ litre of water at 50—60°, and well stirred from time to time. It is filtered through cloth (see Fig. 75, p. 131), and is then digested with a further 250 c.c. of water in the same way, filtered, and the cloth removed from the frame and squeezed out. The filtrate is heated to boiling to coagulate the albumin, and, on cooling, filtered. Basic acetate of lead is carefully added, just sufficient to precipitate the soluble albumin. The liquid is again filtered through a fluted filter, and the lead removed with hydrogen sulphide, which is passed into the warm liquid. The filtrate from the sulphide of lead is concentrated to a thin syrup on the water-bath and then transferred to a vacuum desiccator, where it is left over sulphuric acid. In a short time, especially on the addition of a crystal of creatine, needle-shaped crystals begin to separate, and when no further crystallisation is observed, the crystals, which have a brown colour, are brought on to a porcelain funnel, and washed with a little spirit. They are recrystallised from a little hot water, with the addition of animal charcoal. Yield about 1 gram. The filtrate from the creatine contains hypoxanthine and sarcolactic acid, but the small quantity of these two constituents render them difficult to extract.

Properties.—Small rhombic prisms; with difficulty soluble in cold water, readily soluble in hot water. On warming with alkalis, it decomposes into urea and sarcosine,

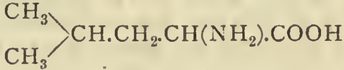


$$HN{:}C\begin{cases} N(CH_3).CH_2.COOH \\ NH_2 \end{cases} + NaOH = CO(NH_2)_2 + NH(CH_3).CH_2.COONa.$$

PREPARATION 44.

Tyrosine, $(OH).C_6H_4.CH_2.CH(NH_2).COOH$

Leucine,



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH.CH_2.CH(NH_2).COOH$$

Beyer, *Zeit.*, 1867, 436; E. Fischer, *Ber.*, 1901, **34**, 433.

100 grms. hoof or horn shavings (washed free from dirt).
250 „ (136 c.c.) conc. sulphuric acid (in 750 c.c. water).

The shavings and acid are heated in a round flask (1½ litres) on the water-bath until the greater part is dissolved, and then boiled with reflux condenser over wire-gauze for about 20 hours, until the solution no longer gives the biuret reaction (p. 127). Add to a little of the liquid two drops of copper sulphate solution and make alkaline with caustic soda; if the colouration is violet or pink instead of blue, continue to boil. After boiling, the dark coloured liquid is poured into a large basin and neutralised whilst hot with slaked lime. The hot liquid is filtered and the residual calcium sulphate replaced in the basin and extracted twice with 300 c.c. of hot water. The united filtrates are concentrated and made up to a litre. The total quantity of oxalic acid (about 20 grams) required to precipitate the dissolved calcium salts is determined by a preliminary estimation with 50 c.c. of the solution. The liquid is boiled before adding the acid and filtered hot from the precipitated calcium oxalate. The precipitate is extracted twice with 250 c.c. of water and concentrated (to about 250 c.c.) until crystals appear on the surface.

Tyrosine.—On cooling, a brown, crystalline crust of impure tyrosine separates. It is filtered, dissolved in the least quantity of boiling water, boiled with a little animal charcoal, and filtered. On cooling, long, white, silky needles of tyrosine are deposited. Yield about 2 grams.

Reactions.—Warm a small quantity of the substance with a drop of strong nitric acid and add ammonia. A yellow solution is produced in the first case, which changes to deep orange with ammonia (xanthoproteic reaction). Warm with a solution of mercury in strong nitric acid (Millon's reagent). The liquid turns red, and a red precipitate is then formed.

Leucine.—The filtrate from the tyrosine is further concentrated on the water-bath to a small bulk, when on cooling a quantity (about 20 grams) of crude leucine in the form of a brown crystalline crust separates, and is collected on a filter and dried on a porous plate. It is converted into the ester hydrochloride as follows: the dry material is dissolved in 120 c.c. absolute alcohol and saturated with hydrogen chloride (p. 93). The alcohol is removed by distilling under reduced pressure at a temperature not exceeding 40° in the apparatus shown in Fig. 66 (p. 94). The same quantity of alcohol is added, saturated with hydrogen chloride, and removed as before. The residue, which consists of the ester hydrochloride of leucine and small quantities of other amino-acids, is converted into the free ester in the following way: it is dissolved in about one-quarter its volume of water, to which an equal volume of purified ether is then added. The liquid is well cooled in a freezing mixture and a cooled 33 per cent. solution of caustic soda is slowly added until the liquid is just alkaline, and then an equal volume of a saturated solution of potassium carbonate. The mass is now well shaken and the ether decanted. In this way the ester, which is rapidly hydrolysed by alkali at the ordinary temperature, is liberated from the hydrochloride without decomposition and dissolves in the ether. The residue is kept in the freezing mixture, a fresh quantity of ether, more caustic soda solution, and sufficient solid potassium carbonate to form a pasty mass are added in succession, shaken up thoroughly and the ether decanted. The residue is extracted two or three times with fresh ether and the united extract, freed as far as possible from water, is shaken up for a minute with solid potassium carbonate and then dehydrated overnight with anhydrous sodium sulphate. The ether is removed on the water-bath and the residue distilled at a pressure not exceeding 15 mm. The colourless liquid, which distils at 80—100°, has an ammoniacal smell and is nearly pure leucine ester. Yield 10—15 grams. The ester is readily hydrolysed by boiling five times its weight of water with reflux condenser until the alkaline reaction disappears (about an hour). The liquid is then concentrated on the water-bath until crystals separate on the surface and cooled. The leucine may be recrystallised from dilute alcohol or dissolved in the smallest quantity of hot water and alcohol added until a turbidity appears. It forms small glistening plates, which melt and sublime at 170°. See *Appendix*, p. 270.

PREPARATION 45.

Grape Sugar. (Glucose, Dextrose.)

Soxhlet, *J. prakt. Ch.*, 1880, (2) **21**, 245.

$CH_2OH.CHOH.CHOH.CHOH.CHOH.CO.H$

250 grms. cane sugar.
750 c.c. spirit.
30 c.c. conc. hydrochloric acid.

The spirit and acid are mixed and warmed to 45—50°, whilst the finely powdered cane-sugar is gradually added and stirred. When the sugar has dissolved the solution is cooled, and a few crystals of anhydrous grape-sugar added. On standing for a day or two the grape-sugar deposits in the form of fine crystals, which continue to increase in quantity. When no further deposition is observed, the crystals are filtered and washed with spirit. The sugar may be purified by dissolving in a little water to a syrup, and adding hot methyl alcohol until a turbidity appears. On cooling, the grape-sugar crystallises out.

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Fructose.}}{C_6H_{12}O_6}.$$

Properties.—Colourless crystals ; m. p. 146° ; soluble in hot and cold water, insoluble in alcohol.

Reactions.—1. Add to a little of the solution of glucose a few drops of caustic soda, and warm. The colour changes from yellow to brown.

2. Add to 2 or 3 c.c. of the solution two or three drops of copper sulphate, and then caustic soda, until a clear blue solution is obtained, and heat to boiling. Red cuprous oxide is precipitated.

3. Add a few drops of glucose solution to half a test-tube of ammonio-silver nitrate solution and place the test-tube in hot water. A mirror of metallic silver is formed.

4. Dissolve about 0·5 gram of glucose in 5 c.c. of water, and add a solution of phenylhydrazine acetate, made by dissolving 1 gram of phenylhydrazine in the same weight of glacial acetic acid, and diluting to 5 c.c. Mix the solutions and warm in the

water-bath. In a few minutes the yellow crystalline phenylglucosazone (m. p. 204—205°) is deposited.

5. Mix a few drops of a glucose solution with a few drops of an alcoholic solution of α-naphthol and pour slowly down the side of the test-tube a few drops of conc. sulphuric acid. A violet colouration is produced. (Molisch's reaction.) See *Appendix*, p. 271.

Benzene.

Pure Commercial Benzene, obtained from coal-tar naphtha, should distil within one degree (80—81°), and solidify completely when cooled to 0°. Other tests are as follows: shaken with concentrated sulphuric acid for a few minutes, the acid should not darken, and a drop of bromine water should not be immediately decolourised. A single distillation over a few small pieces of sodium, which absorb any traces of water, is usually a sufficient purification. If the benzene impart a brown or black colour to the sulphuric acid, it must be repeatedly shaken with about 20 per cent. of the acid until the latter becomes only slightly yellow on standing. This is done in a stoppered separating funnel, and after shaking for a few minutes the mixture is allowed to settle, and the lower layer of acid drawn off. The benzene is then shaken two or three times with water to free it from acid, carefully separated from the aqueous layer, and left in contact with fused calcium chloride until the liquid becomes clear. It is then decanted, frozen in ice, and any liquid (carbon bisulphide, paraffins) carefully drained off, and the benzene finally distilled over sodium.

Properties.—Mobile, colourless liquid ; m. p. 5·4° ; b. p. 80·4° ; sp. gr. 0·874 at 20°. Coal-tar benzene usually contains a little thiophene, C_4H_4S, which may be detected by dissolving a few crystals of isatin (see p. 229) in concentrated sulphuric acid and shaking up with the benzene. If thiophene is present, a blue colour is produced (indophenin reaction).

Fractional Distillation.—It is often possible to separate almost completely by a single distillation, two liquids occurring together in a mixture when their boiling points lie widely apart. The more volatile liquid first passes over, the temperature suddenly rises, and the higher boiling liquid distils.

It is otherwise when a liquid consists of a mixture of substances boiling at temperatures not very far removed from one another, especially in the case of homologous compounds, such as occur in petroleum and coal-tar naphtha. One distillation suffices only to produce very partial separation of the different substances, a portion of the less volatile liquid being carried over in the first distillate, together with the more volatile body,

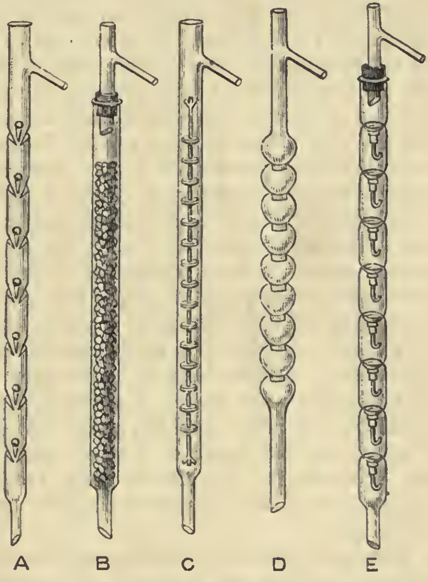


FIG. 76 represents a series of simple and efficient fractionating columns or still-heads. A is that of Vigreux, in which the constrictions are formed by indenting the tube itself; B is Hempel's column and consists of a long wide tube filled with glass beads; C, D, and E are columns devised by Young and Thomas, the last being useful when large quantities of liquid have to be distilled. C contains a series of glass discs fused on to a rod, which can be removed from the tube; D has a series of pear-shaped bulbs blown on the stem, and E is a wide tube with a series of constrictions in each of which a small bent glass dripping tube is suspended in a gauze cup.

the temperature gradually rising throughout the distillation. In order to effect separation of the several substances, recourse is had to the method of fractional distillation.

The liquid is distilled in a round flask over wire-gauze or, better, in a fusible metal bath, a bit of porous pot or a coil of platinum-wire being placed in the flask to prevent bumping. The flask is surmounted with a fractionating column, in which the thermometer is fixed. Various forms of fractionating columns are used (see Fig. 76).

The effect of the column may be explained as follows: the vapour given off from a mixture of liquids contains a larger proportion of the more volatile constituent than the liquid. If this vapour is condensed in its ascent, the vapour above this condensed liquid will be still richer in the more volatile constituent. If, by a series of constrictions or diaphragms, the condensed liquid is obstructed in its return flow, a momentary equilibrium between liquid and vapour is established at each diaphragm, and the longer the column the greater will be the amount of more volatile constituent in the last portion of vapour to undergo condensation. This passes off by the condenser and is collected in the receiver. The apparatus (Fig. 76, *E*) can be made out of a piece of wide tubing. This is constricted in the blow-pipe flame, near one end, and a piece of copper wire-gauze with a circular hole, carrying the little bent tube, is placed on the constriction. A second constriction is made and another gauze diaphragm introduced. The number of diaphragms may vary from 10 to 20, according to the degree of separation required.[1]

Commercial 50 per cent. and 90 per cent. Benzene are mixtures of benzene and larger or smaller quantities of its higher boiling homologues, viz., toluene (b. p. 110°) and the xylenes (b. p. 137—143°). The constituents may be separated by fractional distillation.

Fit up an apparatus with fractionating column and distil 200 c.c. 50 per cent. or 90 per cent. benzene, at a regular speed, so that the drops falling from the end of the condenser may be readily counted. Collect the distillate between every five degrees in separate flasks. Redistil each of these fractions in order, adding the next to the residue of the previous one in the distilling-flask. Collect portions boiling below 85° and above 105°, between every two or three degrees. It will be found that by a repetition of the process the liquid is gradually separated into two large fractions, consisting chiefly of benzene and toluene, and a number of smaller intermediate fractions. The following table gives the volume in c.c., and the boiling points of the

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[1] *Trans. Chem. Soc.*, 1899, **76**, 700.

fractions obtained by this method from 200 c.c., 50 per cent. benzene, each table denoting a complete series of fractionations, using a simple column with two bulbs.

I.

A. 71·5-85°	B. 85-90°	C. 90-95°	D. 95-100°	E. 100-105°	F. 105-110°	G. 110-115°	Residue.
10 c.c.	53 c.c.	26 c.c.	15 c.c.	13 c.c.	17 c.c.	21 c.c.	33 c.c.

II.

	A′ below 79°.	B′. 79-81°	C′. 81-85°	D′. 85-105°	E′. 105-108°	F′. 108-110°	Residue.
A.	5 c.c.	...	...	...	...	...	...
Added B.	...	42 c.c.	(10 c.c.*)	...	...	...	...
Added C.	...	...	(9 c.c.*)	...	...	...	...
Added D. E.	..	...	...	50 c.c.	...	...	...
Added F.	...	...	...	...	(11 c.c.*)	...	...
Added G.	...	...	...	...	...	22 c.c.	42 c.c.
*Refractionated C′.	...	12 c.c.	7 c.c.	...	...	...	...
E′.	...	...	...	...	6 c.c.	5 c.c.	...
	5 c.c.	54 c.c.	7 c.c.	50 c.c.	6 c.c.	27 c.c.	42 c.c.

The fraction 79—81° is further purified in the manner already described.

PREPARATION 46.

Bromobenzene (Phenyl bromide), C_6H_5Br.

Cohen and Dakin, *Trans. Chem. Soc.*, 1899, **76**, 894; Cross and Cohen, *Proc. Chem. Soc.*, 1908.

50	grms.	benzene.
120	,,	(40 c.c.) bromine.
0·5	,,	pyridine.

The apparatus is similar to that shown in Fig. 63, p. 89, but the flask should be placed in a water-bath, in which it can be heated, and the tap-funnel may be dispensed with. The benzene, bromine, and pyridine are placed in the flask and heated to 25—30°, when a vigorous and steady evolution of hydrogen bromide takes place, the gas being absorbed by the water in the beaker. When the action slackens (about 1 hour) the temperature of the water-bath is gradually raised to 65—70°, and the process stopped when most of the bromine has disappeared and the evolution of hydrogen bromide has nearly ceased. The contents of the flask are cooled and poured into dilute caustic soda solution contained in a separating funnel and shaken. Sufficient alkali must be present to give an alkaline reaction after shaking. The lower layer is drawn off and dehydrated over calcium chloride. When perfectly clear the bromobenzene is filtered or decanted into a distilling flask (200 c.c.) provided with a thermometer and distilled over wire-gauze. Unchanged benzene first passes over; the temperature then rises rapidly and the portion boiling at 140—170° is collected separately. It is redistilled and collected at 150—160°. Yield 60 grams.

$$C_6H_6 + Br_2 = C_6H_5Br + HBr.$$

The pyridine acts as "halogen carrier," probably by forming the additive compound $C_5H_5NBr_2$, which gives up its bromine to the benzene.

Properties.—Colourless liquid; b. p. 154—155°; sp. gr. 1·496 at 16°.

Hydrobromic Acid.—The weak solution of hydrobromic acid which collects in the beaker in the course of the above reaction may be concentrated by fractional distillation, as in the case of hydriodic acid (p. 113), and used in the preparation of bromotoluene (p. 167). It boils at 126° at the normal pressure, has a sp. gr. of 1·49, and contains about 47 per cent. of HBr. See *Appendix*, p. 271.

PREPARATION 47.

Ethyl Benzene, $C_6H_5.C_2H_5$

Fittig, *Annalen*, 1864, **131**, 303.

60 grms. bromobenzene.
52 „ ethyl bromide (see p. 54).
26·5 „ sodium.

A quantity of ether, which has been freed from alcohol by distilling over caustic potash, and dried over calcium chloride and sodium (see p. 61), is poured into a round flask (1 litre). The amount of ether should be about twice the volume of the mixed phenyl and ethyl bromides. The sodium, cut into thin slices with the sodium knife, or squeezed into fine wire, is added to the ether, and when all evolution of hydrogen has ceased, the flask is attached to an upright condenser and immersed in a vessel of ice-water. The mixture of bromobenzene and ethyl bromide, both carefully dehydrated, is poured into the flask. The reaction is allowed to commence spontaneously, the fact being indicated by the appearance of the sodium, which becomes darker in colour and sinks to the bottom of the vessel. Although the flask is allowed to remain in the outer vessel, and is cooled by water and ice, the heat evolved often causes the ether to boil. The flask is therefore not removed until the reaction is over. It is convenient to leave it over night. The liquid is then decanted from the sodium bromide, which has a blue colour, into a distilling flask, and rinsed out once or twice with ether. The ether is removed on the water-bath, a bit of porous pot being added, and the residue is fractionated with a fractionating column. The portion boiling at 132—135° is collected separately. Yield 20—25 grams.

$$C_6H_5Br + C_2H_5Br + 2Na = C_6H_5.C_2H_5 + 2NaBr.$$

Properties.—Colourless liquid ; b. p. 134° ; sp. gr. 0·8664 at 22·5°. See *Appendix*, p. 273.

PREPARATION 48.

Nitrobenzene, $C_6H_5NO_2$

Mitscherlich, *Annalen*, 1834, **12**, 305.

50	grms.	benzene.
80	„	(60 c.c.) conc. nitric acid, sp. gr. 1·4.
120	„	(60 c.c.) conc. sulphuric acid.

The two acids are mixed and well cooled, and then slowly added from a tap-funnel to the benzene, which is contained in a flask (½ litre). The contents of the flask are *well shaken* after each fresh addition. Nitrous fumes are evolved, and a considerable amount of heat developed. Care must, however, be taken that the temperature does not exceed 50—60° by immersing the flask, if necessary, in cold water. The nitrobenzene separates out as a brown, oily layer on the surface of the acid liquid. When the acid has all been added, an operation which lasts about half an hour, the mixture is heated for about twenty minutes on the water-bath, and again well shaken. The contents of the flask, on cooling, are poured into a stoppered separating-funnel, the lower layer of acid removed, and the nitrobenzene washed free from acid by shaking once with water (50 c.c.), then with dilute carbonate of soda solution, and again with water, the oil being each time withdrawn from the bottom of the vessel. The nitrobenzene, separated as carefully as possible from water, is allowed to stand over a few pieces of fused calcium chloride, and shaken occasionally until the liquid is clear. The yellow liquid is decanted, or filtered from the calcium chloride, and distilled in a distilling-flask, with condenser tube only. At first a little benzene passes over; the temperature then rises, and the nitrobenzene distils at 204—207°, and is separately collected. The brown residue consists of dinitrobenzene, the quantity depending upon whether the temperature during nitration has been allowed to rise too high. Yield about 60 grams.

$$C_6H_6 + HO.NO_2 = C_6H_5NO_2 + H_2O.$$

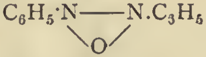
The function of the sulphuric acid is that of a dehydrating agent taking up the water formed in the reaction.

Properties.—Light yellow liquid, with a smell of bitter almonds ; b. p. 206—207°, sp. gr. 1·208 at 15° ; m. p. 3° ; insoluble in water, soluble in alcohol ether, and benzene.

Reaction.—Pour a drop of nitrobenzene into a test-tube with 1 c.c. water and 1 c.c. glacial acetic acid. Add a little zinc-dust on the point of a penknife, and warm for a minute. Dilute with a few c.c. of water, and add caustic soda solution until alkaline, and pour a few drops into a test-tube half filled with sodium hypochlorite solution. A violet colouration, which gradually fades, is produced, due to the presence of aniline (see p. 150). See *Appendix*, p. 274.

PREPARATION 49.

Azoxybenzene,

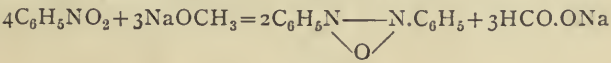


$$C_6H_5{\cdot}\underset{\diagdown O \diagup}{N\text{——}N}.C_3H_5$$

Klinger, *Ber.*, 1882, **15**, 865.

200 grms. methyl alcohol.
20 ,, sodium.
30 ,, nitrobenzene.

Attach an upright condenser to a round flask ($\frac{1}{2}$ litre). Pour in the methyl alcohol and add the sodium in small pieces, 2—3 grams at a time. A good stream of water should pass through the condenser, but otherwise the flask need not be cooled. When the sodium has dissolved, the nitrobenzene is introduced, and the mixture boiled on a water-bath three to four hours. The methyl alcohol is then distilled off in the water-bath. As the liquid is liable to bump, owing to the separation of solid matter, it is advisable to add a few bits of pot. When no more alcohol distils, the residue is poured into a beaker of water and rinsed out. A dark-coloured oil is deposited, which soon solidifies, and is then washed by decantation, and pressed on a porous plate. Yield about 23 grams. It is recrystallised, when dry, from ligroin, in which it is rather soluble.



$$4C_6H_5NO_2+3NaOCH_3=2C_6H_5\underset{\diagdown O \diagup}{N\text{——}N}.C_6H_5+3HCO.ONa$$
$$+3H_2O.$$

Properties.—Yellow needles ; m. p. 36°. See *Appendix*, p. 274.

Azoxybenzene from Nitrobenzene by Electrolysis.—Nitrobenzene can be conveniently converted into azoxybenzene by electrolytic reduction. The apparatus required is shown in Fig. 77.

It consists of a porous cell which forms the cathode chamber and contains 20 grams nitrobenzene and 160 grams 2·5 per cent. caustic soda solution. The two are kept well mixed throughout the operation by a rapidly revolving stirrer. The cathode is a cylinder of nickel gauze (12 cms. × 8·5 cms. = 100 sq. cms.). The anode chamber is the outer glass vessel or beaker, which contains a solution of sodium sulphate acidified with sulphuric acid ; a cylinder of sheet lead serves as the anode. An ordinary ammeter (*A*) and resistance (*R*) are connected in series with the battery and electrodes, and it is also useful, though not essential, to insert a voltameter (*V*) between the two electrodes. A current density of 1 to 5 amperes per 100 sq. cms. is used and 15—20 ampere hours will complete the reduction.[1]

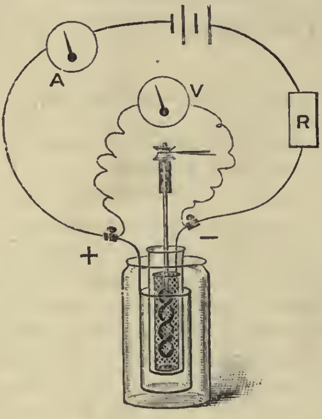


FIG. 77.

The oily liquid which separates in the cathode chamber, and

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[1] The current may be obtained from a number of secondary batteries or from a direct electric light circuit with a suitable resistance.

consists of azoxybenzene mixed with aniline and a little unchanged nitrobenzene, is distilled in steam, which removes the impurities. The residue then solidifies on cooling, and is filtered, dried, and recrystallised. Yield 11 grams (60—70 per cent. of the theory) (Elbs, *Electrolytic Preparations*, trans. by R. S. Hutton, p. 76).

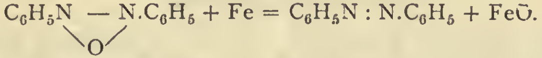
PREPARATION 50.

Azobenzene, $C_6H_5N:N.C_6H_5$

Mitscherlich, *Annalen*, 1834, **12**, 311.

5 grms. azoxybenzene.
15 „ iron filings.

The azoxybenzene and iron filings, both of which must be carefully dried on the water-bath, are powdered together and distilled from a small retort, which is conveniently made by blowing a large bulb on the end of a piece of rather wide tubing $1\frac{1}{2}$ cm. inside diameter, and then allowing the bulb whilst hot to bend over. The mixture is carefully heated, the burner being moved about until the contents are thoroughly hot, and then the mixture is more strongly heated until nothing further distils. The distillate, which forms a solid, dark-red mass, is washed with a little dilute hydrochloric acid and water, and then pressed on a porous plate. It is crystallised from ligroin, in which it is very soluble.



$$C_6H_5\underset{\diagdown O \diagup}{N - N}.C_6H_5 + Fe = C_6H_5N : N.C_6H_5 + FeO.$$

Properties.—Red plates; m. p. 68°; b. p. 295°. See *Appendix*, p. 274.

Azobenzene from Nitrobenzene by Electrolysis.—A good yield of azobenzene can be obtained by the electrolytic reduction of nitrobenzene in alcoholic solution. The apparatus is similar to that shown in Fig. 77, p. 144, but in the present case the cathode chamber is the outer vessel, which should be a deep, narrow glass cylinder or beaker. The cathode liquid is a solution of 20 grams nitrobenzene and 5 grams sodium acetate crystals in 200 c.c. 70 per cent. spirit. The cathode is a cylinder of nickel gauze. A large porous cell forms the anode chamber, and contains a cold saturated solution of sodium carbonate. The anode is a wide strip of sheet lead. A current density of 6 to 9 amperes per 100 sq. cms. is passed for 17·4 ampere hours, and then a lower current density for a further 1—2 ampere hours. During the reduction the cathode liquid becomes very hot and the alcohol which evaporates must be replaced. The cathode liquid at the end of the process contains, in addition to azobenzene, azoxybenzene and hydrazobenzene. It is poured into a flask and the hydrazobenzene is oxidised to azobenzene by aspirating a current of air through the solution for half an hour. The greater part of the azobenzene separates and can be filtered; the remainder, which is less pure, is precipitated from the filtrate by the addition of water. It is recrystallised from ligroin. Yield 90 per cent. of the theory.

(Elbs, *Electrolytic Preparations*, trans. by R. S. Hutton, p. 78.)

PREPARATION 51.

Hydrazobenzene (Diphenylhydrazine) $C_6H_5NH.NHC_6H_5$

Alexejew, *Zeitschr. f. Chem.*, 1867, 33; 1868, 497; E. Fischer, *Anleitung zur Darstellung org. Präparate*, p. 23.

50 grms (42 c.c.) nitrobenzene.
54 ,, caustic soda (in 200 c.c. water).
50 c.c. alcohol.
100—125 grms. zinc dust.

The apparatus is shown in Fig. 78. It consists of a large, round, wide-necked flask (1½ litre) furnished with a cork perforated with three holes. Through one hole a stirrer, moved by a water-turbine or electric motor, passes in the manner shown in Fig. 78. To the stem of the stirrer a short, wide glass tube is attached which revolves in the annular space formed at the end of an adapter by fusing to it an outer concentric piece of wider tubing. When this space is filled with water it serves as a water seal. Through a second hole a wide glass tube is inserted by which the zinc dust is introduced, and is fitted with a cork. The third hole is furnished with an adapter to which a condenser is attached. The nitrobenzene, caustic soda solution, and the alcohol are poured into the flask and the stirrer set in rapid motion so that the contents are kept thoroughly agitated. The thorough mixing of the materials is essential to the success of the process. The zinc dust is added in quantities of 3—4 grams at a time through the wide glass tube, which is closed by a cork after each addition. The mixture soon becomes warm and eventually boils. To prevent the liquid boiling over the frothing is allowed to subside before fresh zinc dust is added. The operation is usually completed in ¾ hour, when the liquid, which has first a deep red colour (azobenzene), becomes pale yellow. To examine the colour a sample should be withdrawn with a pipette and filtered. The stirring is continued for another ¼ hour. A litre of cold water is added which precipitates the hydrazobenzene. The mixture of hydrazobenzene and zinc residues is filtered at the pump and washed free from alkali with water. The precipitate is then pressed down and extracted with 750 c.c. of spirit on the water-bath with reflux condenser and filtered. On cooling in a freezing mixture, the hydrazobenzene crystallises in colourless plates, which are filtered and washed with a little spirit. The mother liquor is used for a second extraction of the zinc residues, and from the filtrate a further quantity of hydrazobenzene is precipitated with water. If the second crop of crystals have a yellow colour crystallisation from alcohol will remove it. Yield 30—35 grams.

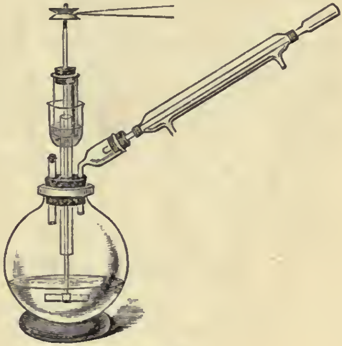


FIG. 78.

$$C_6H_5NO_2 + 3Zn + 6NaOH = C_6H_5NH.NHC_6H_5 + 3Zn(OH)_2$$

Properties.—Colourless plates ; m. p. 125°.

Reactions.—1. Heat a small quantity in a dry test-tube. Notice the colour. On cooling add a little water and pour a few drops into a solution of sodium hypochlorite. A violet colouration indicates aniline. $2C_6H_5NH.NH.C_6H_5 = C_6H_5N:NC_6H_5 = 2C_6H_5NH_2$.

2. Heat a small quantity with Fehling's solution and observe the formation of cuprous oxide. The hydrazobenzene is oxidised to azobenzene.

Benzidine.—Five grams of powdered hydrazobenzene are shaken with 125 c.c. hydrochloric acid (3 per cent.) at 20—30°. In a quarter to half an hour the substance will have completely dissolved. Finally, the mixture is heated to 45—50°, a little water added to redissolve any benzidine hydrochloride, and filtered warm. The benzidine is precipitated from the solution of the hydrochloride by adding to the cold solution an excess of caustic soda solution. It is filtered and washed free from alkali, and recrystallised from boiling water or dilute alcohol. It crystallises in plates with nacreous lustre, m. p. 127°.

$$C_6H_5NH.NHC_6H_5 = NH_2C_6H_4.C_6H_4NH_2.$$

See *Appendix*, p. 275.

PREPARATION 52.

Phenylhydroxylamine, $C_6H_5.NH.OH$

Bamberger, *Ber.*, 1894, **27**, 1548; Wohl, *Ber.*, 1894, **27**, 1432; Friedländer, *Theerfarbenfabrikation*, IV., 48.

6	grms.	ammonium chloride (in 200 c.c. water).
12	,,	nitrobenzene.
18	,,	zinc dust.

Mix the nitrobenzene and ammonium chloride solution in a flask (½ litre). The zinc dust is added in portions of about a gram at a time with constant shaking or stirring by turbine, the temperature being maintained below 15°, by cooling if necessary in ice water. The addition of the zinc dust should take about an hour. The shaking is continued for another quarter of an hour, when the smell of nitrobenzene will have disappeared. The contents of the flask are filtered and washed with 100 c.c. water, so that the water trickles slowly through the filter. The filtrate is saturated with clean salt (80 grams) and cooled to 0°. Colourless crystals of phenylhydroxylamine fill the liquid. They are filtered at the pump, dried on a porous plate, and recrystallised if necessary from benzene. Yield 6—8 grams.

Properties.—Colourless needles ; m. p. 81°.

Reactions.—Add to a solution of phenylhydroxylamine Fehling's solution and warm. Cuprous oxide is precipitated. To another portion add ammoniacal silver nitrate and warm. Silver is deposited. See *Appendix*, p. 276.

Nitrosobenzene.—Dissolve 4 grams of phenylhydroxylamine in the equivalent quantity of ice cold 6 per cent. sulphuric acid (4 c.c. in 66 c.c. water), and add a well-cooled solution of 4 grams potassium bichromate in 200 c.c. water. Yellow crystals of nitrosobenzene are deposited which distil in the vapour of steam with an emerald-green colour ; m. p. 67–68°.

$$C_6H_5.NHOH + O = C_6H_5NO + H_2O.$$

p-Aminophenol.—Add gradually 1 gram of phenylhydroxylamine to 10 c.c. conc. sulphuric acid and 15 grams of ice, dilute with 100 c.c. of water and boil. Test a small sample with bichromate solution in order to see if the smell is that of nitrobenzene or quinone. In the latter case conversion is complete. The acid liquid is neutralised with sodium bicarbonate, saturated with common salt and extracted with ether. On distilling off the ether, *n*-amidophenol crystallises ; m. p. 186°.

$$C_6H_5.NH.OH = OH.C_6H_4.NH_2.$$

PREPARATION 53.

Aniline (Aminobenzene ; Phenylamine), $C_6H_5NH_2$

Zinin, *Annalen*, 1842, **44**, 283.

50 grms. nitrobenzene.
90 ,, granulated tin.
170 c.c. conc. hydrochloric acid (sp. gr. 1·16).

Introduce the tin and nitrobenzene into a round flask (1½ litre), and fit it with a straight upright tube about 2 feet long (air-condenser). Heat the mixture for a few minutes on the water-bath. Then remove the flask and add the concentrated hydrochloric acid in quantities of 5—10 c.c. at a time, and shake repeatedly. The liquid should become hot and boil quietly ; but, if the action becomes too violent it must be moderated by cooling the flask in cold water. In the course of ½—¾ hour all the acid should have been added; the flask is then replaced on the water-bath without the air-condenser, and heated for an hour or more until the reduction is complete. This is ascertained by the absence of any smell of nitrobenzene. The contents of the flask, on cooling, solidify to a crystalline mass (a double salt of stannic chloride and aniline hydrochloride) Whilst still warm, water (100 c.c.) and strong caustic soda solution (140 grams in 200 c.c. water) are added until the stannic oxide, which is first precipitated, nearly redissolves and the liquid has a stongly alkaline reaction. If the mixture begins to boil during the addition of the caustic soda solution it must be cooled. The aniline, which separates out as a dark-coloured oil, is distilled in steam. The apparatus is shown in Fig. 68, p. 107. The flask containing the aniline is gently heated on the sand-bath, and steam is passed in from the tin bottle. It is advisable to heat the aniline mixture on the water-bath before steam is admitted, as otherwise a large quantity of water condenses in the flask. On distillation, aniline and water collect in the receiver, the former as a colourless oil. When the distillate, as it comes over, appears clear instead of milky, the distillation is stopped. The oil is now extracted from the distillate by shaking up the liquid in a separating-funnel three times with small quantities (30 c.c.) of chloroform. The chloroform solution, separated as far as possible from water, is further dehydrated by adding a little solid potassium carbonate. The clear liquid is decanted into a distilling-flask, the flask rinsed with a little chloroform, and the chloroform removed by distillation until the temperature reaches 100°, when the receiver is changed. Aniline distils at 182—183°, and has usually a faint amber colour. Yield, about 30 grams.

$$2C_6H_5NO_2 + 3Sn + 12HCl = 2C_6H_5NH_2 + 3SnCl_4 + 4H_2O$$

Properties.—Colourless, highly refractive liquid, which soon darkens in colour; b. p. 183°; sp. gr. 1·0265 at 15°.

Reactions.—1. Add a drop of the oil to a solution of bleaching powder or sodium hypochlorite. An intense violet colouration is produced, which gradually fades.

2. Heat a drop of the oil with a few drops of chloroform, and

about 1 c.c. of alcoholic potash, *in the fume-cupboard.* Phenyl carbamine is formed, which possesses an intolerable smell. (Hofmann's reaction for primary amines.)

3. Add to a drop of aniline in a basin a few drops of concentrated sulphuric acid, and stir with a glass rod. Then add a few drops of potassium bichromate solution. An intense blue colour is obtained.

4. Dissolve a few drops of aniline in 5 c.c. dilute hydrochloric acid, cool under the tap and add a few drops of a solution of sodium nitrite. Then pour some of the solution into about half a gram of phenol dissolved in a few c.c. of caustic soda solution. An orange solution of sodium hydroxyazobenzene is formed (see Reaction 6, p. 163).

$$C_6H_5NH_2.HCl + HNO_2 = C_6H_5.N_2Cl + 2H_2O$$
$$C_6H_5.N_2Cl + C_6H_5.ONa + NaOH = C_6H_5.N_2C_6H_4ONa + NaCl + H_2O.$$

See *Appendix*, p. 277.

PREPARATION 54.

Acetanilide (Phenylacetamide), $C_6H_5.NH.CO.CH_3$

G. Williams, *Trans. Chem. Soc.*, 1864, **2**, 106.

25 grms. aniline (freshly distilled).
30 c.c. glacial acetic acid.

Boil the mixture gently in a flask (250 c.c.), fitted with an air-condenser, for a day (7—8 hours). As the liquid solidifies on cooling, it is at once poured out, while hot, into a basin of cold water (500 c.c.). It is filtered and washed with cold water. Acetanilide crystallises best from hot water, in which, however, it is not very soluble. Place the moist acetanilide in a large basin, and add gradually about a litre of boiling water. If the substance does not dissolve completely on boiling, a small quantity of spirit will bring it into solution. Filter through a large fluted filter or hot-water funnel (p. 53) and set the solution aside to crystallise. If the product is dark coloured it is redissolved as before, and heated with a little animal charcoal (5—10 grams) for half hour and then filtered. Yield, 30—35 grams.

$$C_6H_5NH_2 + CH_3.COOH = C_6H_5NH.CO.CH_3 + H_2O$$

Properties.—Rhombic plates ; m.p. 112° ; b.p. 295°.

Reaction.—Introduce about 0·5 gram of the substance into a test-tube, and add 3 c.c. concentrated hydrochloric acid. Boil for a minute. On diluting with water, a clear solution is obtained.

$$C_6H_5NHC_2H_3O + H_2O + HCl = C_6H_5NH_2.HCl + CH_3.COOH.$$

See *Appendix*, p. 278.

PREPARATION 55.

p-Bromacetanilide,

$$C_6H_4\left\langle\begin{array}{ll}NHC_2H_3O & 1\\ Br & 4\end{array}\right.$$

Remmers, *Ber.*, 1874, 7, 346.

5 grms. acetanilide.
25 c.c. glacial acetic acid.
6 grms. bromine.

Dissolve the acetanilide in the acetic acid in a flask ($\frac{1}{2}$ litre), and add gradually the bromine, dissolved in about twice its volume of glacial acetic acid, and shake well. When the bromine has been added, let the mixture stand $\frac{1}{4}$ hour and then pour into 200 c.c. water and rinse out with water. Filter the crystalline precipitate at the pump and wash three or four times with water. Press it well down and let it drain. Dissolve the moist substance in spirit (about 60 c.c.) and pour into a beaker to crystallise. Filter the crystals, wash with a little dilute spirit, and dry on filter paper. Yield 6—7 grams.

$$C_6H_5NH.C_2H_3O + Br_2 = C_6H_4Br.NH.C_2H_3O + HBr$$

Properties.—Colourless needles ; m.p. 165—166°. On hydrolysis with concentrated hydrochloric acid, *p*-bromaniline is formed (see above reaction for acetanilide).

PREPARATION 56.

p-Nitraniline.

Bender and Erdmann, *Chemische Präparatenkunde*, vol. ii., p. 438.

25 grms. acetanilide.
25 c.c. acetic acid (glacial).
50 „ conc. sulphuric acid.
10 „ fuming nitric acid (sp. gr. 1·5).

The acetanilide, acetic acid, and sulphuric acid are mixed by means of a mechanical stirrer and cooled in a freezing mixture. The fuming nitric acid is then gradually added from a tap-funnel at such a speed that the temperature does not exceed 20°. After the acid has been added, the mixture is stirred for an hour and poured on to ice. The product is then diluted with water, left to stand for a time, filtered, washed, and dried on a porous plate. It may be recrystallised from dilute alcohol, but is usually pure enough for further treatment. Yield is 80 per cent. of the theory; the remaining 20 per cent. is ortho-compound and remains in solution; m. p. 207°.

$$C_6H_5.NH.COCH_3 + HNO_3 = NO_2.C_6H_4.NH.COCH_3 + H_2O$$

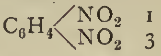
The *p*-nitracetanilide is either boiled with 2½ times its weight of concentrated hydrochloric acid, or heated on the water-bath with twice its weight of equal volumes of sulphuric acid and water until the liquid remains clear on diluting with water. The *p*-nitraniline which is now present in the liquid as the hydrochloride or sulphate, is diluted with water and precipitated by the addition of an excess of caustic soda or ammonia. When cold, the yellow crystalline precipitate is filtered, washed and re-crystallised from boiling water. Yield, 25 grams.

$$NO_2.C_6H_4.NHCOCH_3 + H_2O + HCl = NO_2.C_6H_4.NH_2.HCl + CH_3COOH$$

Properties.—Yellow needles; m. p. 147°; soluble in hot water; very soluble in alcohol.

PREPARATION 57.

m-Dinitrobenzene.



$$C_6H_4\left\langle\begin{matrix}NO_2 & 1\\ NO_2 & 3\end{matrix}\right.$$

Deville, *Ann. Chim. Phys.*, 1841 (3), **3**, 187; Hofmann, Muspratt, *Annalen*, 1846, **57**, 214.

30 grms. nitrobenzene.
35 „ (24 c.c.) fuming nitric acid; sp. gr. 1·5.
35 „ (20 c.c.) conc. sulphuric acid.

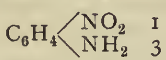
The acids are mixed in a flask (500 c.c.), and the nitrobenzene added in portions of 5—10 c.c. at a time. Heat is evolved, and the mass becomes somewhat deeper in colour. When the nitrobenzene has been added, the flask is heated for a short time on the water-bath. A few drops are then poured into a test-tube of water. The dinitrobenzene should, if the reaction is complete, separate out as a hard pale yellow cake If it is semi-solid, the heating must be continued. The contents of the flask are then poured, whilst warm, into a large quantity of water. The dinitrobenzene, which separates out, is filtered at the pump and well washed with water. It is then dried. The yield is nearly theoretical. A few grams should be recrystallised from spirit. The remainder may be used for the next preparation without further purification.

$$C_6H_5.NO_2 + HNO_3 = C_6H_4(NO_2)_2 + H_2O$$

Properties.—Colourless long needles; m. p. 90°; b. p. 297°. See *Appendix*, p. 279.

PREPARATION 58.

m-Nitraniline.



$$C_6H_4\left\langle\begin{matrix}NO_2 & 1\\ NH_2 & 3\end{matrix}\right.$$

Hofmann, Muspratt, *Annalen*, 1846, **57**, 217.

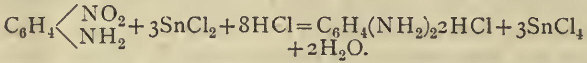
25 grms. *m*-dinitrobenzene.
75 „ (95 c.c.) spirit.
12 „ (13 c.c.) conc. ammonia.

The powdered dinitrobenzene, spirit and ammonia, are mixed together in a flask (½ litre). Hydrogen sulphide, washed through water, is passed into the dark red pasty mass, which is occasionally shaken.* The dinitrobenzene slowly dissolves, whilst, at the same time, flakes of crystallised sulphur are deposited. When the gas has been passing for an hour the flask is removed and heated on the water-bath for a few minutes. After cooling, the liquid is again saturated with hydrogen sulphide and then heated on the water-bath as before. When the gas has been passing in a steady stream for fully two hours the process is complete. Water is now added to the liquid until nothing further is precipitated. The mixture is filtered at the pump and washed with a little water. The solid residue is transferred to a flask and shaken up with successive small quantities of hot dilute hydrochloric acid and the liquid decanted through the original filter. The nitraniline dissolves, leaving the sulphur. When no more nitraniline is extracted (this may be ascertained by adding ammonia in excess to a portion of the acid solution, when no precipitate is formed), the acid solution is somewhat concentrated, cooled, and concentrated ammonia added. The *m*-nitraniline is precipitated, filtered when cold, and purified by recrystallisation from boiling water. The filtrate from the nitraniline may be concentrated on the water-bath and a further small quantity obtained. Yield, about 15 grams.

$$C_6H_4(NO_2)_2 + 3NH_4HS = C_6H_4NO_2.NH_2 + 3NH_3 + 3S + 2H_2O$$

Properties.—Yellow needles; m. p. 114°; b. p. 285°. With tin and hydrochloric acid it is reduced to *m*-phenylenediamine, $C_6H_4(NH_2)_2$.

m-Phenylenediamine. Dissolve 30 grams stannous chloride ($SnCl_2 + 2H_2O$) in 50 c.c. conc. hydrochloric acid in a round flask (½ litre) and gradually add 5 grams *m*-nitraniline. The mixture is heated on the water-bath until no precipitate is formed on adding water (½ hour). The liquid is diluted with 500 c.c. water, heated nearly to boiling and a current of hydrogen sulphide passed in until all the tin is precipitated as sulphide (½—¾ hour). With this object a small quantity should be filtered and tested from time to time by passing in hydrogen sulphide. The precipitate is left overnight to subside, the clear liquid decanted and the residue filtered at the pump through a double-filter. The clear filtrate is concentrated on the water-bath until crystallisation commences and allowed to cool. The crystals of the hydrochloride of phenylenediamine separate and are filtered. A further quantity may be obtained by concentrating the mother-liquors. Yield 6·5 grams.



$$C_6H_4\left\langle\begin{matrix}NO_2\\NH_2\end{matrix}\right. + 3SnCl_2 + 8HCl = C_6H_4(NH_2)_2 2HCl + 3SnCl_4 + 2H_2O.$$

Reaction.—Dissolve a few crystals in water, acidify with dilute hydrochloric acid, and add a drop of sodium nitrite solution. A deep brown solution (Bismarck brown) is obtained. See *Appendix*, p. 279.

PREPARATION 59.

Dimethylaniline, $C_6H_5N(CH_3)_2$

Poirrier, Chappat, *Jahresb.*, 1866, p. 903.

20 grms. aniline hydrochloride.
15 ,, aniline.
22 ,, methyl alcohol.

The aniline hydrochloride is prepared by gradually adding conc. hydrochloric acid to aniline (20 grams in a beaker) until a drop brought on to a piece of filter paper, stained with methyl violet, turns it green. The liquid is quickly cooled and stirred so as to produce small crystals. It is then filtered, well pressed and dried on a porous plate. The dry hydrochloride is brought into a thick-walled tube closed at one end, and the mixture of aniline and methyl alcohol added. The tube is then sealed in the ordinary way and heated in the tube furnace gradually to 150° during two hours, and then to 180—200° for six hours more. The contents of the tube divide into two layers, the lower one consisting of the hydrochloride of the base and water, and the upper one of the free bases. The whole of the contents are poured out into a large separating funnel, and caustic soda added in excess. The addition of a little ether causes the bases to separate out more readily. The top layer is removed, and the lower aqueous portion is shaken up twice with small quantities of ether. The ethereal solution is dehydrated over solid caustic potash, the liquid filtered and the ether removed on the water-bath. The residue is now boiled with 25 grams acetic anhydride, using an upright condenser, for an hour in the same flask, the side limb of which is stoppered. The contents are then distilled. Unchanged acetic anhydride passes over at 130—150°; the thermometer then rises, and the portion boiling at 190—200° is collected separately. When the higher temperature is reached, it is advisable to keep only the lower half of the condenser filled with water. The distillate has a bright amber colour. Yield, 20 grams. The residue in the flask consists of acetanilide and methylacetanilide and solidifies on cooling.

$$C_6H_5NH_2 + C_6H_5NH_2.HCl + 4CH_3OH = C_6H_5N(CH_3)_2HCl \\ + C_6H_5N(CH_3)_2 + 4H_2O$$

Properties.—Colourless liquid; b. p. 192°; sp. gr 0·957 at 20°.

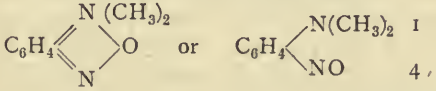
Reaction.—Warm, with an equal volume of methyl iodide; the crystalline quaternary ammonium iodide will be formed,

$$C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_2.CH_3I.$$

See *Appendix*, p. 279.

PREPARATION 60.

p-Nitrosodimethylaniline,



Baeyer, Caro, *Ber.*, 1874, **7**, 810 and 963; Meldola, *Trans. Chem. Soc.*, 1881, **39**, 37.

20	grms.	dimethylaniline.
52	„	(45 c.c.) conc. hydrochloric acid diluted with 100 c.c. of water.
12	„	sodium nitrite (in 20 c.c. of water.)

The dimethylaniline is dissolved in the dilute hydrochloric acid in a beaker and cooled in a freezing mixture. The sodium nitrite, dissolved in a small quantity of water, is then slowly added with frequent stirring. The separation of the hydrochloride of nitrosodimethylaniline in the form of small yellow needles soon begins, and the liquid is gradually filled with a thick crystalline deposit. When, after standing for a short time (half an hour), no further increase in the quantity of crystals is observed, the mass is filtered at the pump and washed with spirit, to which one or two c.c. of concentrated hydrochloric acid has been added. It is then washed once or twice with spirit, drained and pressed on a porous plate. Yield, nearly theoretical. It may be recrystallised by adding small quantities of hot water, until the salt is just dissolved, and then setting aside to cool. If the free base is to be prepared, recrystallisation is unnecessary. Ten grams of the hydrochloride are mixed into a paste with water in a flask, and caustic soda solution added in the cold until alkaline. The yellow colour of the salt changes to green of the free base. Sufficient ether is added to dissolve the green precipitate. The ethereal solution is carefully separated by means of a separating-funnel and most of the ether is then removed by distillation. The remaining liquid is poured out into a beaker and set aside to crystallise. The base remains on evaporation of the ether in the form of brilliant green foliated crystals.

$$C_6H_5N(CH_3)_2HCl + HNO_2 = (NO)C_6H_4N(CH_3)_2.HCl + H_2O$$

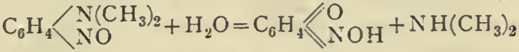
Properties.—Large green foliated crystals; m. p. 85°.

Reactions.—1. Dissolve a few crystals in dilute hydrochloric acid and add a little zinc dust. The solution is decolourised through the formation of dimethyl *p*-phenylenediamine, $(CH_3)_2N.C_6H_4NH_2$.

2. Warm a few of the crystals with yellow ammonium sulphide solution for a few minutes, acidify with hydrochloric acid, and finally add a little ferric chloride. A deep blue colouration is produced, due to the formation of methylene blue.

3. Dissolve 6 grams of caustic soda in 250 c.c. of water and heat to boiling. Add 5 grams of the hydrochloride of nitrosodimethylaniline gradually. The free base, which separates out in oily drops, is allowed to dissolve before each fresh addition. The boiling is continued until the dark green colour of the liquid

changes to reddish-yellow. Dimethylamine is evolved and is easily recognised by its smell. After cooling, acidify the liquid in the flask and extract with ether. On distilling off the ether, nitrosophenol (quinoneoxime) remains in the form of dark-coloured crystals, which are difficult to purify.



$$C_6H_4\left\langle\begin{matrix}N(CH_3)_2\\ NO\end{matrix}\right. + H_2O = C_6H_4\left\langle\!\!\left\langle\begin{matrix}O\\ NOH\end{matrix}\right.\right. + NH(CH_3)_2$$

The presence of a nitroso-compound may be detected as follows: Melt together a minute quantity of nitrosophenol and a few crystals of phenol. Add about 2 c.c. concentrated sulphuric acid and warm very gently. A blue solution is obtained, which changes to red on dilution with water, and back to blue on adding alkali (Liebermann's "nitroso" reaction; see Reaction, p. 180). See *Appendix*, p. 280.

PREPARATION 61.

Thiocarbanilide (Diphenylthiourea), $CS\left\langle\begin{matrix}NHC_6H_5\\ NHC_6H_5\end{matrix}\right.$

Hofmann, *Annalen*, 1849, **70**, 142.

30 grms. aniline.
30 „ carbon bisulphide.
30 „ absolute alcohol.

The aniline, carbon bisulphide,[1] and alcohol are poured into a round flask (½ litre), and heated for a day (8 hours) on the water-bath with upright condenser. As hydrogen sulphide is evolved the operation must either be conducted in the fume cupboard or an exit tube must be attached to the top of the condenser tube dipping into soda-lime. The contents of the flask solidify after a time. When the reaction is complete, the condenser is reversed. and excess of carbon bisulphide and alcohol distilled off on the water-bath. The residue is washed on to a filter with very dilute hydrochloric acid, to remove any unchanged aniline, and then with water. The crystals are dried on a porous plate, and a portion crystallised from spirit. Yield 30--35 grams.

$$2C_6H_5.NH_2 + CS_2 = CS(NHC_6H_5)_2 + H_2S$$

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[1] Carbon bisulphide being very volatile and exceedingly inflammable, great care must be taken when using it in the neighbourhood of a flame.

Properties.—Colourless rhombic plates ; m.p. 151° ; scarcely soluble in water, easily soluble in alcohol or ether.

Phenyl Thiocarbimide (Phenyl Mustard Oil), $C_6H_5N{:}CS$

The thiocarbanilide is boiled with two to three times the weight of concentrated hydrochloric acid in a flask with an upright condenser for half an hour. It is decomposed into triphenylguanidine, which remains as the hydrochloride in solution (it is subsequently separated) and phenyl mustard oil, which separates out as a brown oil. On distilling the product in steam, the phenyl mustard oil is carried over into the receiver. It is separated by shaking out with ether, and removing the ethereal layer with a tap-funnel. It is dehydrated over calcium chloride, and decanted into a small distilling flask. The ether is removed on the water-bath and the mustard oil distilled, with the thermometer, using a short condenser tube. Yield, 9—10 grams.

Properties.—Colourless oil with a peculiar smell ; b. p. 220° ; sp. gr. 1·135 at 15°.

Reactions.—1. Heat gently for a few minutes 0·5 c.c. phenyl mustard oil, 0·5 c.c. alcohol and 1½ c.c. concentrated ammonia. On cooling, thiocarbanilamide, $NH_2.CS.NH.C_6H_5$, crystallises in needles.

2. Heat gently 0·5 c.c. phenyl mustard oil, and 0·5 c.c. aniline ; on cooling and rubbing with a glass rod, thiocarbanilide crystallises.

3. Heat on the water-bath in a small flask with upright condenser 3 grams of phenyl mustard oil and 10 c.c. absolute alcohol for 3 hours, and pour into cold water. Phenylthiourethane, $C_6H_5NH.CS.OC_2H_5$, separates out and may be recrystallised from alcohol. Yield, 2½ grams ; m. p. 67°.

4. Heat a few drops of the mustard oil with yellow mercuric oxide and notice the irritating smell of phenyl carbimide.

$$C_6H_5N{:}CS + HgO = C_6H_5N{:}CO + HgS$$

Triphenylguanidine.—In order to separate the triphenylguanidine remaining in the flask as hydrochloride after distilling off the phenyl mustard oil, the hot solution must be somewhat concentrated. The colourless salt, which crystallises out on cooling, is filtered and washed with a little water. It is then warmed gently for a few minutes with dilute caustic soda solution. The base is liberated, filtered, washed with water and recrystallised from spirit.

$$2CS(NHC_6H_5)_2 + HCl = CSNC_6H_5 + C\begin{matrix}.NHC_6H_5\\ .NHC_6H_5.HCl\\ :NC_6H_5\end{matrix} + H_2S$$

Thiocarbanilide. Phenyl Mustard Oil. Triphenylguanidine Hydrochloride.

Properties.—Colourless needles ; m. p. 143°.

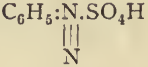
Reaction.—Boil for a short time with moderately strong caustic soda solution. Aniline is formed.

$$C{:}NC_6H_5(NHC_6H_5)_2 + 2NaOH + H_2O = 3C_6H_5NH_2 + Na_2CO_3.$$

See *Appendix*, p. 281.

PREPARATION 52.

Diazobenzene Sulphate, $C_6H_5{:}N.SO_4H$



$$C_6H_5{:}\underset{\underset{\displaystyle N}{|||}}{N}.SO_4H$$

Griess, *Annalen*, 1866, **137**, 76 ; Knoevenagel, *Ber.*, 1895, **28**, 2049.

15 grms. aniline.
140 „ (175 c.c.) absolute alcohol.[1]
30 „ (16 c.c.) conc. sulphuric acid.
20 „ amyl nitrite.

Mix the aniline and alcohol and add the concentrated sulphuric acid in a slow stream with constant shaking. The precipitate of aniline sulphate, which first appears, redissolves. Cool the mixture to 30° and keep at 30—35° (thermometer in the liquid) and out of direct sunlight whilst the amyl nitrite is dropped in from a tap-funnel. Then cool in ice water and leave for half an hour. The diazobenzene sulphate separates as a colourless or pale green mass of needle-shaped crystals. It is filtered at the pump and washed with a little alcohol. Although diazobenzene sulphate is much more stable than the

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[1] Neither methylated spirit nor methyl alcohol can be substituted.

nitrate, it is undesirable to let the precipitate become quite dry. The various reactions described below are carried out with the slightly moist and well pressed precipitate.

$$(C_6H_5NH_2)_2H_2SO_4+2C_5H_{11}ONO+H_2SO_4=2C_6H_5N:N.SO_4H \\ +2C_5H_{11}OH+2H_2O.$$

Properties.—Colourless needles; soluble in water and methyl alcohol; slightly soluble in ethyl alcohol.

Reactions.—The following reactions are performed in test-tubes with about a gram of the substance.

1. Warm the substance with a few c.c. of ethyl alcohol. Vigorous effervescence occurs and the liquid turns red. When effervescence ceases, add water. An oil separates out on the surface consisting of benzene mixed with a little phenetol.

$$C_6H_5N_2SO_4H + C_2H_6O=C_6H_6 + N_2 + C_2H_4O + H_2SO_4$$
$$C_6H_5N_2SO_4H + C_2H_6O=C_6H_5OC_2H_5 + N_2 + H_2SO_4.$$

2. Dissolve about a gram of the substance in a little water, cool in ice and make alkaline with caustic soda. Make an alkaline solution of stannous hydrate by dissolving 3—4 grams of stannous chloride in twice its weight of water and adding strong caustic soda solution until the precipitate redissolves. Cool the diazo solution and add the alkaline stannous hydrate. Effervescence occurs, nitrogen is liberated and benzene separates on the surface of the liquid and can be detected by its smell.

$$C_6H_5N_2.ONa+Sn(ONa)_2+H_2O=C_6H_6+N_2+Na_2SnO_3+NaOH.$$

3. Dissolve the substance in a few c.c. of cold water and add a solution of bromine in potassium bromide until no further turbidity is produced. A black oil collects at the bottom of the test-tube. Pour off the top layer as far as possible, and let the oil stand in cold water. It solidifies. This is the perbromide of diazobenzene.

$$C_6H_5N_2SO_4H + KBr + Br_2=C_6H_5NBrNBr_2 + KHSO_4.$$

Decant any liquid and warm the perbromide with a little alcohol. Nitrogen and bromine are given off and bromobenzene is formed.

$$C_6H_5NBrNBr_2=C_6H_5Br + N_2 + Br_2.$$

4. Dissolve the substance in a little cold water and add

potassium iodide solution. Effervescence occurs and a dark coloured liquid separates out. This is iodobenzene.

$$C_6H_5N_2SO_4H + KI = C_6H_5I + N_2 + KHSO_4.$$

5. Dissolve the substance in water and warm gently. Effervescence occurs and a dark coloured oil separates, which has the smell of phenol. When effervescence ceases, cool and shake up with a little ether. Decant the ether into a dry test-tube. Evaporate the ether and test the residue for phenol, see p. 179.

$$C_6H_5N_2SO_4H + H_2O = C_6H_5OH + H_2SO_4 + N_2.$$

6. Dissolve the substance in cold water and add it to a solution of phenol in caustic soda, drop by drop. An orange crystalline precipitate of hydroxyazobenzene is formed. Repeat, using β-naphthol in place of phenol. A scarlet precipitate is obtained.

$$\begin{aligned} C_6H_5N_2SO_4H + C_6H_5ONa &= C_6H_5N{:}N.C_6H_4ONa + Na_2SO_4 \\ + 2NaOH \quad & \quad + 2H_2O. \end{aligned}$$

7. Dissolve in cold water and add a few drops of aniline, and shake up. Diazoaminobenzene separates out as a yellow crystalline precipitate.

$$C_6H_5N_2SO_4H + C_6H_5NH_2 = C_6H_5N{:}N.NHC_6H_5 + H_2SO_4.$$

8. Heat 0·5 gram of the dry substance on an iron tray. It decomposes with slight explosion.

Any of the diazo-compound which remains over should be dissolved in water and poured away. See *Appendix*, p. 282.

PREPARATION 63.

Toluene from p-Toluidine, $C_6H_5.CH_3$.

Friedländer, *Ber.*, 1889, **22**, 587.

10 grms. *p*-toluidine.
30 c.c. conc. hydrochloric acid (in 60 c.c. water).
7·5 „ sodium nitrite (in powder).
15 „ of caustic soda (in 50 c.c. water).
30 „ stannous chloride (in 75 c.c. water).

The *p*-toluidine, which is placed in a beaker, is dissolved in the hydrochloric acid by warming and is then cooled under the tap, so as to obtain small crystals of the hydrochloride. The beaker is placed in a freezing mixture and the contents cooled below 10°. The sodium nitrite is added in small portions at a time with stirring, the temperature being kept below 10°. The hydrochloride gradually dissolves in the form of the soluble diazonium salt. Towards the end of the operation a drop of the solution is occasionally tested with potassium iodide and starch paper when an excess of nitrite is indicated by a blue stain. The solution is poured very slowly into the solution of caustic soda previously cooled in ice, so that the temperature does not rise above 10°.

$$CH_3.C_6H_4N_2Cl + 2NaOH = CH_3.C_6H_4N_2ONa + NaCl + H_2O.$$

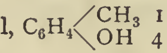
Meantime the stannous chloride solution is converted into sodium stannite by adding a 50 per cent. solution of caustic soda until the precipitate of the hydrate nearly redissolves (about 30 grams of caustic soda). The liquid is placed in a round flask (500 c.c.) attached to a condenser and cooled in ice. The alkaline diazo solution is poured through the top of the condenser in small quantities at a time. After each addition there is a vigorous effervescence and evolution of nitrogen, and a brown oil separates which consists of impure toluene.

$$CH_3C_6H_4N_2ONa + Sn(ONa)_2 + H_2O = CH_3.C_6H_5 + N_2 + Na_2SnO_3 + NaOH.$$

When the solution has all been added the toluene is distilled off in steam, separated from the water, and dehydrated over calcium chloride. It distils at 110°. Yield 5—6 grams. See *Appendix*, p. 284.

PREPARATION 64.

p-Cresol,



$$C_6H_4\left\langle\begin{matrix}CH_3 & 1\\ OH & 4\end{matrix}\right.$$

Griess, *Annalen*, 1866, **137**, 39; Ihle, *J. prakt. Chem.*, 1876, **14**, 451.

25 grms. *p*-toluidine.
25 „ conc. sulphuric acid (in 750 c.c. water).
20 „ sodium nitrite (in 40 c.c. water).

Mix the dilute sulphuric acid and toluidine in a large round flask (1½ litre) and cool to the ordinary temperature. The nitrite solution is gradually added. The clear solution is then gently warmed on the water-bath until the evolution of nitrogen ceases. The solution, which has become very dark coloured, is distilled in steam until the distillate produces only a slight precipitate with bromine water (500 c.c.). A small quantity of tarry residue remains. The distillate is then extracted three times with small quantities (50 c.c.) of ether. The ethereal solution is dehydrated over anhydrous sodium sulphate, filtered, and the ether removed on the water-bath. The *p*-cresol is then distilled over the flame with a condenser tube, and collected at 195—200°. The distillate, which has a yellow colour, solidifies on cooling. Yield 10—15 grams.

$$(CH_3.C_6H_4NH_2)_2\ H_2SO_4 + 2NaNO_2 = 2CH_3.C_6H_4.OH + 2N_2 + Na_2SO_4 + 2H_2O.$$

Properties.—Colourless crystals ; m. p. 36° ; b. p. 202°.

Reactions.—Make a solution of *p*-cresol by shaking up a few drops with 5 c.c. of water. To one portion add a few drops of bromine water. A white precipitate of tetrabromocresol is formed. To another portion add a drop of ferric chloride. A blue colouration is produced. See *Appendix*, p. 284.

PREPARATION 65.

p-Chlorotoluene,

$$C_6H_4\begin{cases}CH_3 & 1\\ Cl & 4\end{cases}$$

Sandmeyer, *Ber.*, 1884, **17**, 2651 ; Wynne, *Trans. Chem. Soc.*, 1892, **61**, 1072.

50 grms. *p*-toluidine.
120 c.c. conc. hydrochloric acid (in 80 c.c. water).
40 grms. sodium nitrite (coarsely powdered).
30 „ copper carbonate to be dissolved in 300 c.c. conc. hydrochloric acid

Dissolve the *p*-toluidine in the hydrochloric acid and then cool quickly in a beaker, and stir so as to obtain small crystals. Place the beaker in ice and salt and, whilst it is cooling, prepare a solution of cuprous chloride. Dissolve the copper carbonate in the hydrochloric acid, and boil with excess of copper turnings until a nearly colourless solution is obtained. The solution is decanted into a large round flask (2 litres) which is loosely corked, and placed in ice. Whilst this solution is cooling to 0° the diazotoluene chloride is prepared by adding the powdered sodium nitrite gradually to the *p*-toluidine hydrochloride and stirring. The temperature should not rise above 10°. When three-quarters of the nitrite has been added, test occasionally with potassium iodide-starch paper until a drop gives an immediate deep blue or dark brown colouration. Add this solution gradually in portions of about 20 c.c. at a time to the cold solution of the cuprous chloride, and shake up well after each addition. A thick crystalline mass of orange coloured needles, consisting probably of the diazo-copper salt separates, and, on standing, decomposes slowly, forming a dark-coloured liquid. After standing a short time, the liquid is distilled in steam. The distillate is shaken up with a little caustic soda to remove cresol, and the chlorotoluene, which sinks to the bottom, is separated. The liquid is further shaken out with a little chloroform, which is then added to the chlorotoluene, and the whole dehydrated with calcium chloride. The liquid is decanted, the chloroform distilled off and the residue collected at 115—165°. Yield, about 45 grams.

$$CH_3C_6H_4NH_2HCl + NaNO_2 + HCl = CH_3C_6H_4N_2Cl + NaCl + 2H_2O.$$

$$CH_3C_6H_4N_2Cl = CH_3C_6H_4Cl + N_2.$$

Properties.—Colourless liquid ; b. p. 162° ; m. p. 7·4

Reactions.—**Chlorobenzoic Acid.**—Boil 10 grams *p*-chlorotoluene with 20 grams permanganate dissolved in 500 c.c. of water in a brine or calcium chloride bath, with upright condenser, for a day. The bath should keep the contents of the flask boiling briskly whilst the permanganate is gradually added. The oily drops of chlorotoluene will gradually cease to drip from the condenser and the permanganate will be nearly decolourised.

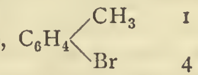
The precipitated manganese dioxide is now dissolved as sulphate by passing in sulphur dioxide gas until the last trace of brown precipitate has disappeared. The colourless chlorobenzoic acid comes down in the acid solution on cooling, and is filtered, washed with water, and recrystallised from spirit ; m. p. 236°. The yield is theoretical.

$$CH_3.C_6H_4Cl + O_3 = COOH.C_6H_4Cl + H_2O.$$

See *Appendix*, p. 284.

PREPARATION 66.

p-Bromotoluene,



$$C_6H_4\begin{matrix}\diagup CH_3 & 1\\ \diagdown Br & 4\end{matrix}$$

Sandmeyer, *Ber.*, 1884, **17**, 2651; Gattermann, *Ber.*, 1890, **23**, 1218.

50 grms. *p*-toluidine.
100 c.c. conc. hydrochloric acid (in 60 c.c. water).
35 grms. sodium nitrite (in powder).
90 ,, crystallised copper sulphate (in 300 c.c. water).
45 ,, potassium bromide (in 100 c.c. water).
150 c.c. hydrobromic acid (sp. gr. 1·49 = 47 per cent. HBr).

The *p*-toluidine is diazotised as described in the previous experiment (Prep. 65) by forming the hydrochloride, cooling and gradually adding the sodium nitrite. The solution of the diazonium chloride is then poured into cuprous bromide dissolved in hydrobromic acid. The cuprous bromide is prepared by adding the potassium bromide solution to the copper sulphate solution and passing in sulphur dioxide until no more precipitate forms. The white cuprous bromide (about 35 grams) is filtered, washed, and well pressed on the funnel and introduced into a round flask (1½ litre). It is dissolved in 150 c.c. hydrobromic acid and well cooled in ice. The diazonium chloride is now added slowly with constant shaking. A thick pasty mass separates and nitrogen is evolved. When the evolution of gas has slackened the flask is heated on the water-bath until effervescence ceases and the bromotoluene is then distilled in steam. The heavy yellow liquid is extracted with chloroform, shaken with caustic soda solution to remove traces of cresol, dehydrated over calcium chloride, and distilled. The distillate is collected at 180—190° On cooling, it solidifies to a pale yellow mass, m. p. 28°; b. p. 185°. Yield, 35 grams.

$$CH_3.C_6H_4N_2Cl + CuBr = CH_3.C_6H_4Br + CuCl + N_2.$$

Gattermann's Method.—According to this method the diazonium bromide is first prepared and then decomposed by finely divided metallic copper. The 50 grams *p*-toluidine is dissolved in 200 c.c. hydrobromic acid previously diluted with 100 c.c. water and diazotised in the usual way. To this solution the copper powder is gradually added. It is prepared by dissolving 100 grams crystallised copper sulphate in 300 c.c. water and dusting in through a fine muslin bag 25 grams zinc dust with constant stirring. It is left until the blue colour of the copper salt has nearly disappeared. The precipitated powder is washed by decantation two or three times with cold water and then with very dilute hydrochloric acid to remove metallic zinc and finally filtered and washed at the pump. The pasty mass is not allowed to dry, but is added at once in small quantities to the diazonium solution with constant stirring. After the evolution of nitrogen has ceased the bromotoluene is distilled in steam and purified as described above. See *Appendix*, p. 284.

PREPARATION 67.

p-Iodotoluene.

Griess, *Annalen*, 1866, **137**, 76.

25 grms.	*p*-toluidine.
50 ,,	(27 c.c.) conc. sulphuric acid (in 250 c.c. water).
20 ,,	sodium nitrite (in 40 c.c. water).
60 ,,	potassium iodide (in 100 c.c. water).

Mix the dilute sulphuric acid and *p*-toluidine in a large beaker (¾ litre) and cool to 0° in a freezing mixture. Stir, whilst cooling, to produce small crystals of the sulphate. Add the solution of sodium nitrite slowly, and if the temperature rises above 10°, add a few lumps of ice. When three-quarters of the nitrite solution has been added, test occasionally with potassium iodide-starch paper until a blue or brown stain is produced. Now add the solution of potassium iodide gradually, and, after well stirring, leave the mixture at the ordinary temperature for an hour, and then warm cautiously on the water-bath until effervescence ceases. The liquid is dark coloured, and a black oil settles to the bottom of the vessel, which when cold solidifies. The oil consists of iodotoluene, and the dark colour of the solution is due to free iodine, which may be removed by the addition of a gram or two of sodium bisulphite. The mixture is now distilled in steam, using a beaker as receiver. Care must be taken to prevent the condenser tube becoming blocked by the iodotoluene, which is solid at the ordinary temperature. This is effected by running the water very slowly through the condenser so that the upper part remains warm. The iodotoluene solidifies in the receiver. It has a yellow tint, which may be removed by recrystallisation from spirit. Yield, 45—50 grams.

$$CH_3.C_6H_4NH_2+NaNO_2+2H_2SO_4=CH_3.C_6H_4N_2.SO_4H+NaHSO_4+H_2O.$$

$$CH_3.C_6H_4N_2.SO_4H+KI=CH_3.C_6H_4I+N_2+KHSO_4.$$

Properties.—Colourless plates ; m. p. 35° ; b. p. 211—212°.

1. **Tolyliodochloride.**—Dissolve 10 grams iodotoluene in five times its weight of chloroform, cool in ice, and pass in dry chlorine until saturated. If a chlorine cylinder is not available, the chlorine is conveniently made by dropping concentrated hydrochloric acid from a tap-funnel on to powdered potassium bichromate or permanganate in a round flask, heated on the water-bath. The chlorine is dried through concentrated sulphuric acid. When chlorine is no longer absorbed, the yellow needle-shaped crystals of the iodochloride are filtered, washed with a little chloroform, and dried on a porous plate.

$$CH_3.C_6H_4I+Cl_2=CH_3.C_6H_4ICl_2.$$

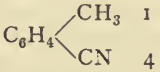
2. **Iodosotoluene.**—Dissolve 2·5 grams caustic soda in 20 c.c. water, and grind with 5 grams of iodochloride in a mortar. Leave overnight and then filter and wash with water. The colourless crystals of the iodoso-compound are dried on a porous plate.

$$CH_3.C_6H_4ICl_2+2NaOH = CH_3.C_6H_4IO+2NaCl+H_2O.$$

See *Appendix*, p. 285.

PREPARATION 68.

p-Tolylcyanide,



$$C_6H_4\begin{cases}CH_3 & 1\\ CN & 4\end{cases}$$

Sandmeyer, *Ber.*, 1884, **17**, 2653.

20 grms. *p*-toluidine.
45 c.c. conc. hydrochloric acid (in 150 c.c. water).
16 grms. sodium nitrite (in 40 c.c. water).
50 ,, copper sulphate (in 200 c.c. water).
55 ,, potassium cyanide (in 100 c.c. water).

The copper sulphate is dissolved in 200 c.c. water on the water-bath in a round flask (2 litres). Pure potassium cyanide is gradually added to the warm solution.* The cuprous cyanide dissolves in excess of the potassium cyanide and cyanogen gas is liberated. $2CuSO_4 + 4KCN = 2CuCN + 2K_2SO_4 + (CN)_2$. The solution is left, whilst the *p*-toluidine is diazotised. The base is dissolved in the dilute hydrochloric acid, cooled in ice, and well stirred. The mixture is kept cold whilst the sodium nitrite solution is gradually added, until it gives an immediate colouration with potassium iodide-starch paper. The diazo-solution is then added in portions of about 10 c.c. at a time to the warm cuprous cyanide solution, with frequent shaking. A rapid effervescence occurs, nitrogen and some hydrocyanic acid being evolved. When, in the course of about fifteen minutes, the diazo-solution has been added, it is left on the water-bath until effervescence ceases ($\frac{1}{4}$ hour). The liquid turns a dark colour, and a black tarry deposit is formed. The product is distilled in steam. This should be carried out in the fume cupboard, as not only is hydrocyanic acid liberated, but a small quantity of isocyanide, which is formed in the reaction, and produces an intolerable smell. The distillation is continued until no more yellow oil passes over. The tolyl cyanide solidifies in the receiver on cooling as a yellow crystalline mass, which is filtered, dried on a porous plate, and may be purified by distillation; but for the preparation of toluic acid this is unnecessary. Yield about 15 grams.

$$CH_3.C_6H_4NH_2.HCl + NaNO_2 + HCl = CH_3.C_6H_4N_2Cl + NaCl + 2H_2O.$$

$$CH_3.CH_4N_2Cl + CuCN = CH_3.C_6H_4.CN + N_2 + CuCl$$

Properties.—Colourless crystals; m. p. 29°; b. p. 218°.

Reaction.—**p-Toluic Acid.**—Boil up 10 grams tolylcyanide with a mixture of 30 c.c. conc. sulphuric acid and 20 c.c. water, in a round flask with upright condenser until colourless crystals of toluic acid appear in the condenser tube (about half an hour). On cooling, the acid crystallises out, and is separated by filtration, washed with water, and recrystallised from hot water; m. p. 179°.

$$CH_3.C_6H_4.CN + 2H_2O + H_2SO_4 = CH_3.C_6H_4.CO.OH + NH_4.H.SO_4.$$

The yield is nearly theoretical.

Terephthalic Acid.—Dissolve 5 grams *p*-toluic acid in dilute caustic soda solution and boil with reflux condenser, adding 12 grams of permanganate in 250 c.c. water gradually from a tap funnel inserted through the top of the condenser. When the red colour of the permanganate persists after continued boiling the solution is treated with sulphur dioxide (see p. 166), which dissolves the manganese dioxide and precipitates the terephthalic acid as a white amorphous powder. The latter is filtered, washed, and dried. It sublimes without melting at 300° and is insoluble in water and alcohol. The yield is nearly theoretical.

$$CH_3.C_6H_4.COONa + NaOH + 2KMnO_4 = NaOOC.C_6H_4.COONa + 2KOH + MnO_2 + 2H_2O.$$

PREPARATION 69.

Diazoaminobenzene, $C_6H_5N{:}N.NH.C_6H_5$.

Griess, *Annalen*, 1866, **137**, 58; Staedel, Bauer, *Ber.*, 1886, **19**, 1952.

20	grms.	aniline.
6	„	conc. sulphuric acid.
600	„	water.
7·4	„	sodium nitrite.

The acid is poured into the water contained in a large beaker (1 litre) and the aniline then added. About half the aniline dissolves as sulphate. The liquid is warmed in the water-bath to 27° and the sodium nitrite, dissolved in a small quantity of water, is slowly added and the whole well stirred. The temperature is maintained at 27—30° for a quarter of an hour. As soon as the sodium nitrite is added the liquid turns yellow and rapidly becomes turbid from the formation of diazoaminobenzene, which separates out in yellowish brown crystalline crusts. The solution is now allowed to stand at the ordinary temperature for half an hour, when nearly the whole of the diazoaminobenzene crystallises out. It is filtered, washed with cold water, pressed well on the filter, and dried on a porous plate or a pad of filter paper. It forms a brown sandy powder and may be purified by recrystallisation from benzene or alcohol. In crystallising, it is necessary to bring the substance into solution as quickly as possible. Boiling spirit (about three times the weight of substance) should be added and the liquid heated for a moment until a clear solution is obtained and then allowed to cool. On prolonged boiling it decomposes. For the preparation of aminoazobenzene the dry powder is sufficiently pure. Yield, nearly theoretical.

$$(C_6H_5NH_2)_2H_2SO_4 + 2NaNO_2 + 2H_2SO_4 = 2C_6H_5N_2.SO_4H + Na_2SO_4 + 4H_2O.$$

$$C_6H_5N_2.SO_4H + C_6H_5NH_2 = C_6H_5N{:}N.NHC_6H_5 + H_2SO_4.$$

N.B.—The sulphuric acid, set free in the second phase of the reaction, acts upon the sodium nitrite, so that one molecule only is required.

Properties.—Golden yellow plates (from alcohol) m. p. 98°; insoluble in water; it explodes when heated above its melting point.

Reaction.—Dissolve a little of the substance in alcohol and add a drop or two of an alcoholic solution of silver nitrate. A red crystalline precipitate of $C_6H_5N{:}N.NAg.C_6H_5$ is deposited. See *Appendix*, p. 285.

PREPARATION 70.

Aminoazobenzene (Aniline yellow), $C_6H_5N{:}NC_6H_4NH_2$.

Mène, *Jahresb.*, 1861, 496; Kekulé, *Zeitsch. f. Ch.*, 1866, **2**, 689; Staedel, Bauer, *Ber.*, 1886, **19**, 1953.

10	grms.	diazoaminobenzene.
25	„	aniline.
5	„	aniline hydrochloride.

The finely powdered diazoaminobenzene, aniline hydrochloride (see p. 156), and aniline are mixed together and heated to 40° for an hour. The mixture forms a clear, deep red solution. After standing for 24 hours at the ordinary temperature, the diazoaminobenzene is converted into aminoazobenzene. A slight excess of moderately strong hydrochloric acid is added, care being taken that no great evolution of heat occurs. On cooling, the aminoazobenzene separates out together with aniline hydrochloride. It is filtered and washed with cold, very dilute hydrochloric acid, when small violet crystals of aminoazobenzene hydrochloride remain on the filter. In order to obtain the free base, the hydrochloride is warmed with dilute ammonia.

The base, which has a brown colour, is filtered and dissolved in hot spirit, with the addition of a few drops of concentrated ammonia. Yield, about 8 grams.

$$C_6H_5N{:}N.NHC_6H_5 + H.C_6H_4NH_2.HCl = C_6H_5N{:}N.C_6H_4.NH_2 + C_6H_5NH_2.HCl.$$

Properties.—Orange prisms ; m. p. 127°.

Reaction.—Make a solution of 4 grams stannous chloride in 10 c.c. conc. hydrochloric acid, add 2 grams aminoazobenzene, and boil for a few minutes. On cooling crystals of the hydrochlorides of aniline and *p*-phenylenediamine separate out. The liquid is filtered and washed with a little conc. hydrochloric acid to remove the tin salts. If the precipitate is dissolved in water and made alkaline with caustic soda, a mixture of liquid aniline and solid *p*-phenylenediamine is precipitated, from which the former may be removed by filtering, washing, and draining on a porous plate.

$$C_6H_5N{:}N.C_6H_4NH_2 + 2SnCl_2 + 4HCl = C_6H_5NH_2 + H_2N.C_6H_4.NH_2 + 2SnCl_4.$$

p-Phenylenediamine, when warmed with dilute sulphuric acid and potassium bichromate or lead peroxide, gives the odour of quinone (p. 192). After warming and cooling, extract with ether. The ethereal solution has a yellow colour. Decant the ether extract on to a watch-glass and leave it to evaporate in the air. A deposit of microscopic yellow crystals remains. See *Appendix*, p. 286.

PREPARATION 71.

Phenylhydrazine, $C_6H_5NH.NH_2$

E. Fischer, *Annalen*, 1878, **190**, 167 ; Meyer, Lecco, *Ber.*, 1883, **16**, 2976 ; Meyer and Jacobson, *Lehrbuch*, **2**, 305.

20	grms.	aniline.
200	,,	(170 c.c.) conc. hydrochloric acid.
20	,,	sodium nitrite (in 100 c.c. water).
120	,,	crystallised stannous chloride (in 100 c.c. conc. hydrochloric acid).

The aniline is dissolved in the concentrated hydrochloric acid and cooled to 0° in a freezing mixture. The solution of sodium nitrite is gradually added, the temperature being kept below 10°, until a drop of the mixture, diluted with water, turns potassium iodide-starch paper blue. To the mixture, still cooled in ice, 120 grams stannous chloride, dissolved in about an equal weight of conc. hydrochloric acid, is added. A thick white crystalline precipitate of phenylhydrazine hydrochloride separates. It is allowed to stand for half an hour and filtered at the pump; it is then separated as far as possible from the mother liquor, and transferred to a flask. The free base is obtained by decomposing the hydrochloride with caustic soda. An excess of caustic soda is added, and the mixture well shaken. The free base, which separates as a reddish coloured oil, is extracted with ether, and the ethereal solution dehydrated over solid potassium carbonate. The ether is then removed on the water-bath, and the residual oil either used without further purification or distilled *in vacuo*. Yield, 15—20 grams.

$$C_6H_5NH_2.HCl + NaNO_2 + HCl = C_6H_5N_2.Cl + NaCl + 2H_2O.$$

$$C_6H_5N_2.Cl + 2SnCl_2 + 4HCl = C_6H_5NH.NH_2.HCl + 2SnCl_4$$

Properties.—Nearly colourless oil when freshly distilled; b. p. 241—242°; m. p. 17·5°; sp. gr. 1·097 at 23°.

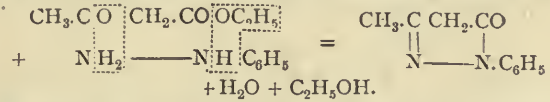
Reactions.—1. Add a few drops of phenylhydrazine to 2 c.c. of water, then a drop or two of copper sulphate solution and excess of caustic soda. Cuprous oxide is precipitated with effervescence and benzene separates, $C_6H_5NH.NH_2 + 2CuO = C_6H_6 + N_2 + Cu_2O + H_2O$. The same reaction takes place if the phenylhydrazine is dissolved in dilute acetic acid and copper sulphate solution added and warmed.

2. Add 2 grams of phenylhydrazine to 4 c.c. water in a boiling tube, warm until dissolved, and then add about 3 c.c. of a warm saturated solution of cupric hydrate dissolved in conc. ammonia. Nitrogen is evolved and cuprous hydroxide dissolves. Add a 10 per cent. caustic potash solution until there is a slight permanent precipitate of cuprous hydroxide and heat the liquid in the water-bath. A copper mirror is deposited on the surface of the glass (Chattaway).

3. Add to a few drops of phenylhydrazine an equal quantity of glacial acetic acid, dilute with a little water, and add a

drop of benzaldehyde. In a short time the phenylhydrazone of benzaldehyde will crystallise out.

4. **Phenylmethylpyrazolone.**—Mix together 10 grams dry phenylhydrazine hydrochloride and 9 grams acetoacetic ester in a flask (200 c.c.), add 3 or 4 drops conc. hydrochloric acid and warm for 10—15 minutes. A clear reddish solution is obtained, which is poured into water and carefully neutralised with caustic soda. The precipitated oil solidifies almost immediately and can be recrystallised from alcohol; m. p. 127°. Yield 8 grams.



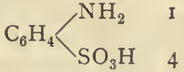
$$\begin{matrix} & CH_3.CO & CH_2.COOC_2H_5 \\ + & NH_2 \text{———} & NH\ C_6H_5 \end{matrix} = \begin{matrix} CH_3.C & CH_2.CO \\ \| & | \\ N \text{———} & N.C_6H_5 \end{matrix}$$

$$+ H_2O + C_2H_5OH.$$

See also the Reactions on pp. 70, and 135, and *Appendix*, p. 287.

PREPARATION 72.

Sulphanilic Acid,



$$C_6H_4\begin{matrix} \diagup NH_2 & 1 \\ \diagdown SO_3H & 4 \end{matrix}$$

Gerhardt, *Annalen*, 1846, **60**, 312; Buckton, Hofmann, *Annalen*, 1856, **100**, 163.

25	grms.	aniline.
80	„	conc. sulphuric acid.

The aniline and sulphuric acid are cautiously mixed in a round flask (250 c.c.) and heated to 180—190° in an oil or metal bath for four to five hours until a sample dissolved in water remains clear on the addition of caustic soda in excess and no aniline separates. The product is poured into cold water, which precipitates the sulphanilic acid as a grey crystalline mass. It is filtered, washed with a little cold water, recrystallised from hot water with the addition of a little animal charcoal, and dried in the air. Yield, 25—30 grams.

$$C_6H_5NH_2 + H_2SO_4 = NH_2.C_6H_4.SO_3H + H_2O.$$

Properties.—Colourless rhombic plates, containing 2 mols. of water of crystallisation, which they lose slowly in the air, and the crystals fall to powder. See *Appendix*, p. 289.

PREPARATION 73.

Methyl Orange (Helianthin), $SO_3Na.C_6H_4N:N.C_6H_4N(CH_3)_2$

10 grms. sulphanilic acid.
2·5 „ anhydrous sodium carbonate (in 100 c.c. water).
3·5 „ sodium nitrite (in 20 c.c. water).
6 „ conc. hydrochloric acid (in 10 c.c. water).
6 „ dimethylaniline (in 6 c.c. conc. HCl and 20 c.c. water).

The sulphanilic acid is dissolved in the sodium carbonate (½ mol.) solution and the sodium nitrite (1 mol.) solution added. The mixture is cooled in ice, and the solution of hydrochloric acid (1 mol.) gradually added. The solution of dimethylaniline (1 mol.) is now poured in, and the liquid made alkaline with caustic soda. The separation of methyl orange at once begins, and is assisted by the addition of a little common salt (20 grams). The precipitate is filtered at the pump, and crystallised from hot water. Yield, nearly theoretical.

$$SO_3Na.C_6H_4NH_2 + NaNO_2 + 2HCl = SO_3Na.C_6H_4N_2.Cl + NaCl + 2H_2O.$$

$$SO_3Na.C_6H_4N_2.Cl + C_6H_5N(CH_3)_2HCl = SO_3H.C_6H_4.N_2.C_6H_4N(CH_3)_2 + NaCl + HCl.$$

$$SO_3H.C_6H_4N:N.C_6H_4N(CH_3)_2 + NaOH = SO_3Na.C_6H_4N:N.C_6H_4N(CH_3)_2 + H_2O.$$

Properties.—Methyl orange is the sodium salt of the sulphonic acid, and dissolves in water with a yellow colour. The free acid is red, and its action as an indicator depends upon this change on the addition of mineral acid.

Reaction.—Methyl orange is decomposed, like the majority of azo-compounds, by stannous chloride in hydrochloric acid into two molecules, produced by the addition of hydrogen to the double-linked nitrogen atoms (see p. 173).

$$HSO_3.C_6H_4N:N.C_6H_4N(CH_3)_2 + 2SnCl_2 + 4HCl = HSO_3.C_6H_4NH_2 + H_2NC_6H_4N(CH_3)_2 + 2SnCl_4.$$

Make a solution of 4 grams stannous chloride in 10 c.c. conc. hydrochloric acid, add 1 gram of methyl orange dissolved in a few drops of hot water, and boil for a few minutes until the red colour disappears. On cooling a crystalline precipitate consisting of sulphanilic acid and dimethyl *p*-phenylenediamine is deposited. In order to separate the base, dilute with water, add caustic soda solution until the precipitate of stannous hydrate redissolves, shake out the cold solution with ether, and dehydrate over potassium carbonate. On distilling off the ether, the dimethyl *p*-phenylenediamine remains as a crystalline solid ; m. p. 41°. On warming with dilute sulphuric acid and lead peroxide the odour of quinone is readily perceived (see p. 192). It also gives the 'methylene blue' reaction, like nitrosodimethylaniline (see p. 158). See *Appendix*, p. 289.

PREPARATION 74.

Potassium Benzenesulphonate, $C_6H_5.SO_3K + \frac{1}{2}H_2O$

Mitscherlich, *Pogg. Ann.*, 1834, **31**, 283 and 364 ; Michael, Adair, *Ber.*, 1877, **10**, 585.

60 c.c. benzene.
60 „ conc. sulphuric acid.

The benzene and sulphuric acid are heated together on a sand-bath in a round flask (½ litre) with upright condenser. The mixture is kept at a gentle boil with frequent shaking (an apparatus like that shown in Fig. 78, p. 147, with mechanical stirrer is preferable) until the top layer of benzene has been nearly absorbed by the sulphuric acid (six to eight hours). On cooling, the dark-coloured liquid is poured into cold water (1 litre) contained in a large basin, boiled up and neutralised with powdered chalk or thick milk of lime. The mass is filtered hot through a porcelain funnel or cloth from the precipitate of calcium sulphate, washed with hot water and somewhat concentrated. The solution, which contains the calcium salt of benzene sulphonic acid, is treated with just sufficient potassium carbonate solution to precipitate the calcium as carbonate and convert the sulphonic acid into the potassium salt. This is ascertained by filtering small samples and testing the filtrate with potassium carbonate. The liquid is again filtered through cloth or through a porcelain funnel and concentrated first over a ring burner, and finally on the water-bath, until a sample crystallises on cooling. The potassium salt is drained at the pump and dried on porous plate. Yield, about 80 grams.

$$C_6H_6 + H_2SO_4 = C_6H_5SO_3H + H_2O.$$

$$2C_6H_5SO_3H + CaCO_3 = (C_6H_5SO_3)_2Ca + CO_2 + H_2O.$$

$$(C_6H_5SO_3)_2Ca + K_2CO_3 = 2C_6H_5SO_3K + CaCO_3.$$

Properties.—Colourless pearly plates, which slowly effloresce in the air and which melt above 300° with slight decomposition; very soluble in water. See *Appendix*, p. 292.

PREPARATION 75.

Benzenesulphonic Chloride, $C_6H_5SO_2Cl$

Gerhardt, Chiozza, *Annalen*, 1853, **87**, 299.

15 grms. potassium benzene sulphonate.
25 „ phosphorous pentachloride.

The potassium benzenesulphonate is carefully dried on the water-bath, powdered, and mixed with the phosphorus pentachloride in a flask.* A vigorous reaction sets in. When it has abated, the flask is heated on the water-bath for one hour,* and the mass occasionally stirred with a glass rod. The product is poured into a flask containing 200 c.c. cold water and allowed to stand an hour. The sulphonic chloride, which separates as an oil, is then extracted with ether, dehydrated over calcium chloride, decanted, and the ether removed on the water-bath. Yield, 10 grams of a light brown oil.

$$C_6H_5SO_3K + PCl_5 = C_6H_5SO_2Cl + POCl_3 + KCl.$$

Properties.—Colourless oil when pure; b. p. 246—247° with decomposition; m. p. 14°; distils undecomposed *in vacuo.*

Reaction.—1. Grind up in a mortar 1 c.c. of sulphonic chloride with 5 grams powdered ammonium carbonate, and leave on the water-bath until the smell of the sulphonic chloride has gone. Add water, filter, and wash, and crystallise the residue of benzene sulphonamide from spirit, $C_6H_5SO_2Cl + 2NH_4HCO_3 = C_6H_5SO_2NH_2 + 2H_2O + 2CO_2 + NH_4Cl$.

2. Add 1 c.c. of the sulphonic chloride to 2 c.c. aniline, stir up well, add water, and acidify with a few drops of concentrated HCl (methyl violet paper). Filter, wash, and crystallise the benzenesulphonanilide from spirit, $C_6H_3SO_2Cl + NH_2C_6H_5 = C_6H_5SO_2NHC_6H_5 + HCl$.

3. Add 2 c.c. absolute alcohol to 1 c.c. sulphonic chloride and excess of caustic soda until alkaline; warm gently for five minutes and add more caustic soda if necessary. Cool, and extract with ether. The residual liquid consists of benzene ethyl sulphonate, $C_6H_5SO_2Cl + HOC_2H_5 = C_6H_5SO_2OC_2H_5 + HCl$.

4. Repeat 3, using phenol in place of alcohol. See *Appendix*, p. 293.

PREPARATION 76.

Phenol (Carbolic acid, Hydroxybenzene), $C_6H_5.OH$

Kekulé, Wurtz, Dusart, *Zeitschr. f. Ch. N. F.*, 1867, 3, 299–301; Degener, *J. prakt. Chim.* 1878, (2), **17**, 394.

20 grms.	potassium benzenesulphonate.
35 ,,	caustic potash.

The caustic potash is dissolved in the smallest quantity of water (5 c.c.) by heating in a silver or nickel basin or crucible, and the powdered potassium benzenesulphonate added. The temperature of the melt, which during the process is kept constantly stirred, must not exceed 250°. It is convenient to use the thermometer as stirrer, the bulb and part of the stem being encased in a glass tube closed at one end. When the requisite temperature has been reached, a small flame is sufficient to maintain it. The mass is first thick and pasty, but soon becomes semi-fluid and remains in this condition, gradually changing in colour from yellow to brown. Towards the end of the operation (one hour) it regains somewhat its original consistency. On cooling, the melt is dissolved in a little water and the alkaline reddish-brown liquid (potassium phenate and excess of alkali) acidified with concentrated hydrochloric acid in the cold. Phenol separates out as a light yellow oil, which is extracted three times with ether. The ethereal solution dehydrated over anhydrous sodium sulphate is distilled, first on the water-bath until the ether is removed, and then over the flame. The portion boiling at 175—185° is nearly pure phenol. It distils as a colourless liquid and solidifies at once on cooling. Yield, 6—7 grams.

$$C_6H_5SO_3K + KOH = C_6H_5OK + KHSO_3.$$
$$C_6H_5OK + HCl = C_6H_5OH + KCl.$$

Properties.—Colourless needles, with a characteristic smell; m. p. 42—43°; b. p. 182°; easily soluble in alcohol and ether; and in about 15 parts of water at the ordinary temperature; produces blisters on the skin.

Reactions.—1. Make a solution of phenol in water, and to one portion add a drop of ferric chloride. A violet colouration is produced.

2. Add to another portion a drop of bromine water. A white crystalline precipitate of tribromophenol is formed.

3. To a third portion add an equal volume of dilute ammonia and a few drops of sodium hypochlorite and warm gently. A copper-sulphate-blue colour is produced.

4. Add a small fragment of solid sodium nitrite to 5 c.c. concentrated sulphuric acid and warm very gently until dissolved. On adding about 0·5 gram of phenol, a brown solution is obtained, which rapidly changes to deep blue. If the blue solution is poured into water, a cherry red colouration is produced, which changes to blue on the addition of an alkali (Liebermann's 'nitroso' reaction, see p. 159).

5. Mix 1 gram of phenol with 1 c.c. of dimethyl sulphate[1] and add 4 c.c. of a 10 per cent. solution of caustic soda. Warm and shake. The odour of phenol is replaced by that of anisole, which can be extracted from the liquid by ether (Ullmann's reaction). See *Appendix*, p. 294.

$$C_6H_5ONa + (CH_3)_2SO_4 = C_6H_5OCH_3 + CH_3NaSO_4.$$

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[1] The vapour of dimethyl sulphate is very poisonous, and care should be taken not to breathe it.

PREPARATION 77.

Anisole (Methyl phenate, Phenyl methyl ether), $C_6H_5.O.CH_3$

Cahours, *Annalen*, 1851, **78**, 226.

5 grms.	sodium.
100 c.c.	methyl alcohol.
20 grms.	phenol.
40 „	methyl iodide.

The methyl alcohol is poured into a round flask (250 c.c.) connected with an upright condenser. The sodium, cut into small pieces, is then added, the flask being detached from the condenser for a moment and replaced. When the sodium has dissolved, the phenol and methyl iodide are added. The mixture is heated on the water-bath until the solution has no longer an alkaline reaction (two to three hours). As much as possible of the methyl alcohol is distilled off on the water-bath and water added to the amber-coloured residue. A colourless oil separates out, which is extracted with ether. The ethereal solution is dehydrated over calcium chloride and distilled, first on the water-bath until the ether has been driven off, and then over the flame. Almost the whole of the residue distils at 150—155°. Yield, nearly theoretical.

$$C_6H_5OH + CH_3ONa = C_6H_5ONa + CH_3OH.$$
$$C_6H_5ONa + CH_3I = C_6H_5OCH_3 + NaI.$$

Properties.—Colourless liquid, possessing an agreeable smell, b. p. 154°; sp. gr. 0·991 at 15°. See *Appendix*, p. 294.

PREPARATION 78.

Hexahydrophenol (Cyclohexanol), $C_6H_{11}.OH$

Sabatier and Senderens, *Compt. rend.*, 1901, **132**, 210.

50 grms. phenol.

The phenol is reduced with hydrogen in presence of finely divided metallic nickel; which acts as a catalyst. The apparatus is shown in Fig. 79.

It consists of an oblong Lothar-Meyer air-bath about 60 cms. (24 ins.) long and 15 cms. (6 ins.) wide. It is heated on each side by a series of small gas jets made by perforating an iron pipe which runs below the air-bath. The hot air passes up the space between the outside metal casing and an inner rectangular metal box, and then down and into the interior of the air-bath through a number of round holes at the bottom of a central rectangular chamber, and finally escapes through a series of holes in top of the outer cover. The air-bath is perforated at both ends so as to admit a piece of wide glass tubing. This tubing (1·5—2 cms. diam.) is of such a length that it projects about 2—3 cms. at one end and 5–6 cms. at the other, the latter being bent and connected to a receiver. The shorter end is attached by a cork to a small distilling flask through which a current of dry hydrogen is passed from a Kipp by a delivery tube, which reaches to the bottom of the flask.

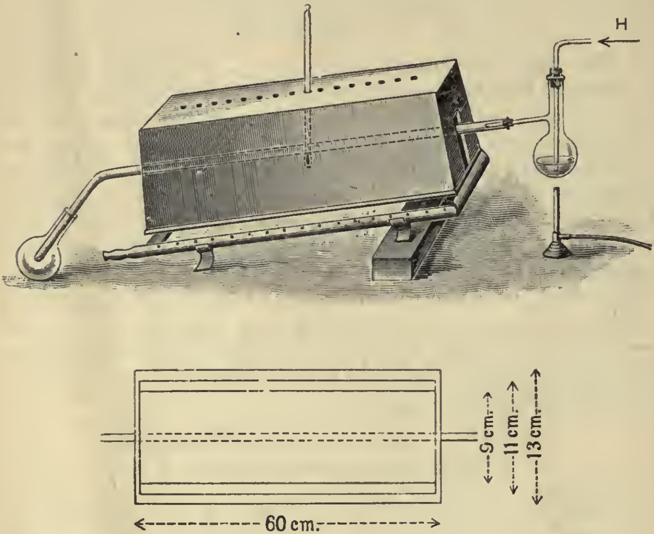


Fig. 79.

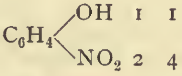
Small pieces of pumice impregnated with a paste of nickel oxide (NiO) and water is dried on the water-bath and packed into the wide tube, which is then loosely plugged at each end with asbestos. The phenol is melted and poured into the distilling flask. The air-bath is slightly tilted so that any liquid which may collect in the tube can run down into the receiver. The process is conducted as follows: the delivery tube from the Kipp is first raised above the surface of the phenol and a slow current of pure dry hydrogen passed through the apparatus, the temperature of which is maintained at 300° for 20 minutes. The nickel oxide is thereby reduced and changes from black to pale yellow. After reduction, the temperature is lowered to 160–170° and kept at this point. The phenol in the flask is now melted and heated just below its boiling-point, whilst a fairly rapid current of hydrogen is passed through the delivery tube, which is thrust well into the liquid. The hexahydrophenol slowly distils and condenses in the receiver. Care must be taken that the phenol does not condense in the tube, but that only the vapour passes over. When sufficient liquid has collected, it is shaken with caustic soda solution, extracted with ether, dehydrated over potassium carbonate and distilled.

$$C_6H_5OH + 6H = C_6H_{11}OH.$$

Properties.—Colourless liquid ; b. p. 170° ; pleasant aromatic smell distinct from phenol ; insoluble in water and solutions of caustic alkalis. See *Appendix*, p. 295.

PREPARATION 79.

o- and **p-Nitrophenol,**



$$C_6H_4\begin{array}{lll} OH & 1 & 1 \\ NO_2 & 2 & 4 \end{array}$$

Hofmann, *Annalen*, 1857, **103**, 347 ; Fritsche, *Annalen*, 1859, **110**, 150 ; Kekulé, *Lehrbuch d. org. chem.*, 3, 40.

40 grms. phenol.
70 „ (50 c.c.) conc. nitric acid (in 170 c.c. water).

The phenol, melted in a basin on the water-bath, is slowly added in small quantities to the nitric acid and water contained in a large round flask (1 litre), and the contents of the flask well shaken or stirred mechanically. The temperature should be maintained below 30° by cooling with water. On the addition of the phenol, the liquid immediately changes to a deep brown or black colour, and a heavy dark-brown oil separates out. When the phenol has been added, the mixture is allowed to stand for 12 hours. The oil has by that time collected at the bottom of the vessel, and may be freed from acid by repeatedly decanting and pouring in fresh water (three or four times). The contents of the flask consist of nearly equal quantities of para- and ortho-nitrophenol mixed with resinous products. In order to separate the two isomers, the product is distilled in a current of steam (see Fig. 68, p. 107) until the distillate is almost colourless. The ortho-compound distils in the form of a yellow oil, which may solidify in the condenser, in which event the water is temporarily run out of the condenser. The solid in the receiver is separated by filtration and dissolved in spirit at 40°, to which water is then added, drop by drop, until a turbidity is produced. Yield, 15 grams. The solid residue contains the para-compound mixed with black, resinous substances, from which it is separated by repeatedly extracting with boiling water. The united portions of the aqueous extract are boiled with animal charcoal for half an hour in a large basin, and filtered through a fluted filter moistened with water. The filtrate is made alkaline with caustic soda solution, and concentrated to a small bulk (100 c.c.). If tarry matter separates, it must be filtered through a wet filter. To obtain the free para-compound, the concentrated aqueous solution of the sodium salt is cooled, and the separated sodium salt filtered. The crystals are dissolved and acidified with concentrated hydrochloric acid, and the nitrophenol, which separates, is filtered and recrystallised from hot water. Yield, 10 grams.

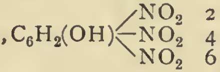
$$C_6H_5OH + HONO_2 = OHC_6H_4NO_2 + H_2O.$$

Properties.—o-*Nitrophenol*, sulphur-yellow needles, possessing a peculiar smell ; m. p. 45° ; b. p. 214° ; distillable with steam ; soluble in alcohol, ether, and hot water ; less soluble in cold water.

p-*Nitrophenol*, colourless needles ; m. p. 114° ; easily soluble in alcohol and hot water; slightly soluble in cold water. See *Appendix*, p. 295.

PREPARATION 80.

Picric Acid (Trinitrophenol),



$$C_6H_2(OH)\left\langle\begin{matrix}NO_2 & 2\\ NO_2 & 4\\ NO_2 & 6\end{matrix}\right.$$

Woulfe, 1771; Schmidt, Glutz, *Ber.*, 1869, **2**, 52.

25 grms. phenol.
125 „ (68 c.c.) conc. sulphuric acid.
100 „ (70 c.c.) conc. nitric acid, sp. gr. 1·4.

The phenol and concentrated sulphuric acid are heated together in a porcelain basin for half an hour on the water-bath, until a clear solution of phenol sulphonic acid is obtained. It is diluted with 100 c.c. of water, well cooled, poured into a flask (1 litre), and then 50 c.c. nitric acid slowly added, in small quantities at a time, from a tap-funnel, and well shaken.* The liquid assumes a deep red colour, a considerable rise of temperature occurs, and red fumes are evolved. When the nitric acid has been added, the flask is placed on the water-bath and heated, with the addition of the remaining 20 c.c. of nitric acid, for 1—2 hours.* On cooling, picric acid separates out as a yellow, crystalline mass. It is diluted with water, filtered at the pump, and washed free from the mother liquor with cold water. It is then purified by recrystallisation from a large quantity of hot water acidified with a few drops of sulphuric acid. Yield, about 30 grams.

$$C_6H_5(OH)+H_2SO_4=C_6H_4(OH).SO_3H+H_2O.$$

$$C_6H_4(OH)SO_3H+3HONO_2=C_6H_2(OH)(NO_2)_3+3H_2O+H_2SO_4.$$

Properties.—Yellow, prismatic crystals; m. p. 121·5°; sublimes on gently heating; explodes on detonation; easily soluble in alcohol and ether; with difficulty in cold, more readily in hot water; the solution has a bitter taste.

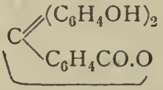
Reactions.—1. To an aqueous solution of picric acid add a little potassium cyanide solution, and warm. A brown crystalline precipitate of isopurpuric acid separates.

2. Add picric acid and a few drops of caustic soda to a dilute solution of grape sugar and warm. The liquid turns deep brown

3. Dissolve naphthalene in a little spirit, and add an equal quantity of a solution of picric acid in spirit. On cooling, yellow needles of naphthalene picrate separate, $C_{10}H_8.C_6H_2OH(NO_2)_3$. Benzene forms colourless crystals, anthracene, scarlet needles, having a similar composition. See *Appendix*, p. 295.

PREPARATION 81.

Phenolphthalein,

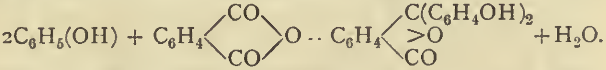


$$C\left\langle\begin{array}{l}(C_6H_4OH)_2\\ C_6H_4CO.O\end{array}\right.$$

Baeyer, *Ber.*, 1876, **9**, 1230, and *Annalen*, 1880, **202**, 68.

10 grms.	phthalic anhydride.
20 ,,	phenol.
8 ,,	conc. sulphuric acid.

The phthalic anhydride, phenol, and concentrated sulphuric acid are heated together to 115—120° in the oil-bath 8—9 hours. The mass becomes semi-fluid and of a dark red colour. It is poured, whilst hot, into a basin of water (500 c.c.) and boiled until the smell of phenol has disappeared, the water being renewed as it evaporates. The undissolved yellow granular precipitate, on cooling, is separated from the liquid by filtration, and washed with water. It is then dissolved in dilute caustic soda solution, filtered from the undissolved residue, and the filtrate acidified with acetic acid and a few drops of hydrochloric acid. The phthalein separates out, after standing for some hours, as a light yellow, sandy powder, which is filtered and dried. It is purified by dissolving in absolute alcohol with the addition of animal charcoal (1 part phenolphthalein, 6 parts alcohol, and ½ part charcoal) and boiling the solution on the water-bath for an hour. The mass is filtered hot, washed with 2 parts boiling alcohol, and the filtrate evaporated down to two-thirds its bulk on the water-bath. On adding 8 times the quantity of cold water to the cooled solution, the latter becomes turbid. The liquid is well stirred, and, after standing a few seconds, filtered through cloth from the resinous oil which separates. On heating the filtrate on the water-bath to expel excess of alcohol, phenolphthalein crystallises out in the form of a white powder. Yield, 5 grams.

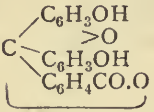


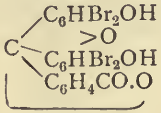
$$2C_6H_5(OH) + C_6H_4\left\langle\begin{matrix}CO\\ \\ CO\end{matrix}\right\rangle O \;..\; C_6H_4\left\langle\begin{matrix}C(C_6H_4OH)_2\\ >O\\ CO\end{matrix}\right. + H_2O.$$

Properties.—White, granular, crystalline powder; m. p. 250—253°; very slightly soluble in water, readily soluble in hot alcohol; soluble in alkalis with a crimson colour. See *Appendix*, p. 296.

PREPARATION 82.

Fluorescein and Eosin,





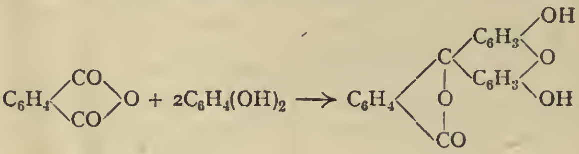
Baeyer, *Annalen*, 1876, **183**, 3.

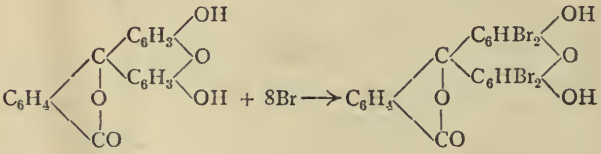
10 grms. phthalic anhydride.
15 „ resorcinol.
7 „ zinc chloride (fused and powdered).

The phthalic anhydride and resorcinol are ground together and heated in a deep tin dish or cylinder to 180°. To the fused mass the zinc chloride is added with continual stirring in the course of ten minutes. The temperature is now raised to 210° and the heating continued until the mass is quite hard (about 2 hours). On cooling, the melt is chipped out, pulverised, and boiled for ten minutes with 150 c.c. water and 10 c.c. conc. hydrochloric acid. The fluorescein is filtered off, washed, and boiled with a small quantity of absolute alcohol to dissolve impurities. The residue is then dried on the water-bath. Yield 20 grams.

Eosin.—Fifteen grams of the fluorescein are mixed in a flask with 80 c.c. spirit and 11 c.c. bromine are dropped in from a burette in the course of quarter of an hour. Heat is developed and the fluorescein gradually dissolves until, when half the bromine has been added, a clear solution is obtained. Further addition of bromine precipitates the tetrabromo-compound (eosin). After standing two hours the precipitate is filtered, washed with spirit, and dried at 110° to expel alcohol of crystallisation. Yield 30 grams.

In order to obtain the sodium compound, 6 grams of the product are ground in a mortar with 1 gram of sodium carbonate, placed in a beaker, and moistened with alcohol. Five c.c. of water are added and the mixture boiled until the evolution of carbon dioxide ceases. To the sodium salt 25 c.c. spirit are added and the mixture boiled and filtered. On standing for a day or two, the sodium salt crystallises in brown needles.



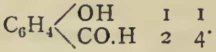


See *Appendix*, p. 296.

PREPARATION 83.

Salicylaldehyde (*o*-Hydroxybenzaldehyde) p-Hydroxybenzaldehyde,

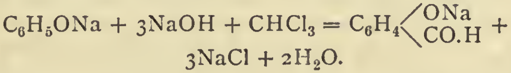
Reimer, Tiemann, *Ber.*, 1876, 9, 824.



$$C_6H_4\begin{cases}OH & 1 \quad 1\\ CO.H & 2 \quad 4.\end{cases}$$

50	grms.	phenol.
100	,,	caustic soda.
160	,,	water.
75	,,	chloroform.

The phenol, caustic soda and water are mixed together in a round flask (1 litre) attached to an upright condenser and heated to 50—60°. The chloroform is then added gradually through the top of the condenser and, after each addition, the flask is well shaken. A gentle reaction sets in, and the temperature rises. At the same time the surface of the brownish yellow solution takes a violet tint, which rapidly fades, the liquid finally assuming a deep red colour. When all the chloroform has been added, the contents of the flask are boiled for half an hour. A yellow semi-solid mass separates out of the solution. The unattacked chloroform is now distilled off on the water-bath, the liquid diluted with water and strongly acidified with dilute hydrochloric or sulphuric acid. A thick red oil separates out on the surface and is subjected to distillation in steam. An oil, having a faintly yellow colour, distils over with the water, and settles to the bottom of the receiver. When drops of oil cease to condense, the distillation is stopped. The distillate, which contains salicylaldehyde and phenol, is extracted with ether, and the ethereal solution well shaken with a saturated solution of sodium bisulphite (see Reaction 2, p. 67). The bisulphite compound of salicylaldehyde separates out in colourless needles, which are filtered, washed free from traces of phenol with alcohol and then decomposed by heating with dilute sulphuric acid. The aldehyde which separates is taken up with ether, dehydrated over calcium chloride, the ether driven off and the aldehyde distilled. Yield, 10 grams. In the distilling flask from which the salicylaldehyde has in the first instance been removed with steam, there remains a brownish liquid and a dark red substance, which sinks to the bottom of the vessel, and forms a brittle resin on cooling. The aqueous portion is filtered hot through a moistened filter, which retains the resin, and the filtrate, containing *p*-hydroxybenzaldehyde, is extracted when cold with ether. On distilling off the solvent, the aldehyde remains in the form of a yellow mass of stellar-shaped needles, which may be purified by crystallisation from hot water. Yield, about 2 grams.



$$C_6H_5ONa + 3NaOH + CHCl_3 = C_6H_4\begin{cases}ONa \\ CO.H\end{cases} + 3NaCl + 2H_2O.$$

Properties.—Salicylaldehyde. Colourless fragrant oil, b. p. 196·5°; sp. gr. 1·173 at 13·5°; solidifies at 20°, forming large crystals. Volatile in steam; soluble in water; miscible in all proportions with alcohol and ether.

Reaction.—Add a drop of ferric chloride to the aqueous solution of the aldehyde. A deep violet colouration is produced

p-Hydroxybenzaldehyde.—Colourless needles, m. p. 115—116°; scarcely soluble in cold water, readily in hot water, alcohol and ether. Non-volatile in steam. The bisulphite of sodium compound dissolves readily in water.

Reaction.—The same as above; but the colouration is less intense. See *Appendix*, p. 297.

PREPARATION 84.

Salicylic Acid (*o*-Hydroxybenzoic Acid),

$$C_6H_4\left\langle\begin{matrix}OH\\CO.OH\end{matrix}\right.$$

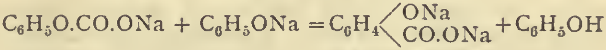
Kolbe, *J. prakt. Chem.*, 1874, (2), **10**, 95.

10 grms. caustic soda.
23 „ phenol.

This preparation should be commenced first thing in the morning. Dissolve the caustic soda in about 10 c.c. of water in a small porcelain basin and add the phenol. Heat the basin on wire-gauze over a very small flame, and, whilst holding it firmly with a small clamp (tongs are too insecure), keep constantly stirring with a glass rod. After a short time the mass becomes stiff and balls together. The basin should now be removed from the gauze, and the mass stirred and broken up as it cools. When still warm, it is sufficiently hard to powder in a mortar. It is quickly powdered and transferred to a small retort (200 c.c.) heated in an oil or paraffin bath to 130—140°, and dried by passing over it a fairly rapid current of dry hydrogen from a Kipp. In about an hour all the moisture is removed, and the body of the retort appears dry. The light coloured mass in the retort is allowed to cool whilst the hydrogen is passing through, then broken up and shaken into a mortar, when it is quickly powdered and replaced. The object of the above operation is to obtain perfectly dry, uncharred and well-powdered sodium phenate, upon which the success of the preparation entirely depends. A moderate stream of carbon dioxide, dried through concentrated sulphuric acid, is now passed over the surface of the sodium phenate by means of a bent tube fixed through the tubulus of the retort, and terminating just above the substance. The temperature of the oil-bath is gradually raised from 140° to 180—190°, whilst fresh surfaces are exposed by occasionally stirring with a glass rod inserted for a moment through the tubulus. At the end of four hours the temperature is raised to 190—200° for another hour, and the process stopped. During the heating a considerable quantity of phenol distils, and solidifies in the neck of the retort, whilst the contents become dark coloured. The mass is shaken out into a basin without disturbing the phenol in the neck, and the residue dissolved by filling the retort two-thirds full of water. This is poured into the basin containing the other portion, which soon dissolves. The solution is acidified with concentrated hydrochloric acid, which throws down impure salicylic acid in the form of a dark brown precipitate. When cold, the precipitate is filtered at the pump, and washed with a little cold water. A further quantity may be obtained by evaporating the filtrate to a small bulk. It is purified by dissolving in water, boiling with a little animal charcoal and filtering. The filtrate deposits the acid, on cooling, in colourless needles. Yield about 6 grams.

1. $C_6H_5ONa + CO_2 = C_6H_5O.CO.ONa$

Sodium phenyl carbonate.

2. 

$$C_6H_5O.CO.ONa + C_6H_5ONa = C_6H_4\left\langle\begin{matrix}ONa\\CO.ONa\end{matrix}\right. + C_6H_5OH$$

Disodium salicylate.

Properties.—Colourless needles; m. p. 155—156°; soluble in alcohol and hot water. 100 parts water dissolve 0·225 part at 15° and 7·925 parts at 100°.

Reactions.—1. Dissolve a little of the acid in water and add a drop of ferric chloride. A violet colouration is obtained.

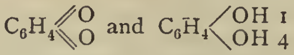
2. Grind up some of the acid with soda-lime and cover with a shallow layer of the same substance. On heating strongly the smell of phenol is perceived.

$$C_6H_4(OH)CO.OH + CaO = C_6H_5OH + CaCO_3.$$

See *Appendix*, p. 297.

PREPARATION 85.

Quinone and Quinol (Hydroquinone),



$C_6H_4\left\langle\begin{matrix}O\\O\end{matrix}\right.$ and $C_6H_4\left\langle\begin{matrix}OH & 1\\OH & 4\end{matrix}\right.$

Woskresensky, *Annalen*, 1838, **27**, 268; Nietzki, *Ber.*, 1886, **19**, 1467; Meyer and Jacobson, *Lehrbuch*, vol. ii., 421.

25 grms. aniline.
200 „ (110 c.c.) conc. sulphuric acid.
750 c.c. water.
80 grms. potassium bichromate.[1]

The water and aniline are mixed together in a large glass jar ($1\frac{1}{2}$ litres) and the sulphuric acid added. The mixture is cooled in ice and stirred with a turbine (see Fig. 64, p. 91). The finely-powdered bichromate is added every few minutes in small quantities on the end of a small spatula, until about one-third has been added, care being taken that the temperature does not exceed 10°. The mixture is then left to stand over night, and the remaining two-thirds of the bichromate introduced as before. Aniline black separates out in the first part of the operation, and in the second part of the process gradually dissolves, giving a deep brown solution. The liquid, after standing for four to five hours more, is divided into two about equal portions. One half is shaken up, not too vigorously, with a large quantity (200 c.c.) of ether three times. The same ether may be distilled and used again. Vigorous shaking produces an emulsion, which very slowly separates. On distilling off the ether, the quinone remains in the form of yellow needle-shaped crystals, which may be purified by sublimation. The substance is placed in a flask attached to a condenser, and a rapid current of steam blown through. The quinone sublimes and collects in the receiver, and is separated from the water by filtration, and dried. Yield about 10 grams.

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[1] Or an equivalent quantity of sodium bichromate (75 grams), which may be dissolved in 3—4 times its weight of water and delivered from a tap-funnel.

The reaction consists in the oxidation and elimination of the amino-group and simultaneous replacement of two hydrogen atoms in the benzene nucleus by oxygen, and cannot well be expressed in the form of equation.

Properties. — Golden-yellow, needle-shaped crystals; m. p. 116°; with difficulty soluble in water, readily soluble in alcohol and ether; sublimes on heating; its vapour has a penetrating smell and attacks the eyes.

Reaction.—Dissolve a few crystals in water and add a solution of sulphur dioxide. The solution first darkens from the formation of quinhydrone, $C_6H_4.O_2.C_6H_4(OH)_2$, and then becomes colourless and contains quinol.

Quinol.—The other half of the product is treated with a current of sulphur dioxide until, after standing for a time, it retains the smell of the gas.* The sulphur dioxide is most conveniently obtained from a bottle of liquid, or it may be prepared by dropping concentrated sulphuric acid from a tap-funnel on to sodium sulphite. The liquid, after standing one to two hours, is extracted with ether until no more quinol is removed. The ether is distilled off, and the dark coloured residue recrystallised from water with the addition of sulphur dioxide and a little animal charcoal. Yield about 10 grams.

$$C_6H_4O_2 + SO_2 + 2H_2O = C_6H_4(OH)_2 + H_2SO_4.$$

Properties.—Colourless prisms; m.p. 169°; sublimes at a gentle heat; easily soluble in alcohol, ether, and hot water.

Reactions.—1. To a solution of quinol in water, add a few drops of ferric chloride. The solution turns brown and ether now extracts quinone.

$$C_6H_4(OH)_2 + 2FeCl_3 = C_6H_4O_2 + 2FeCl_2 + 2HCl.$$

2. Add to the solution of quinol in water, a drop of copper sulphate, and caustic soda, and warm. Cuprous oxide is precipitated.

$$C_6H_4(OH)_2 + 2CuO = C_6H_4O_2 + Cu_2O + H_2O.$$

See *Appendix*, p. 297.

PREPARATION 86.

Benzyl Chloride, $C_6H_5CH_2Cl$

Cannizzaro, *Annalen*, 1853, 88, 129.

100 grms. toluene.
1 ,, phosphorous trichloride.

The apparatus consists of vessels for evolving and drying chlorine (see Fig. 62, p. 88) and a weighed retort (300 c.c.) standing on wire-gauze, into which the toluene is brought. (Fig. 80.) The chlorine enters through an inlet tube, fixed through the tubulus of the retort, the neck being fixed to a reflux condenser. The dry chlorine is conducted into the toluene, which is kept boiling gently until it has gained about 37 grams in weight.* The liquid turns yellow, and hydrochloric acid fumes are evolved at the upper end of the condenser. When the reaction is complete the contents of the retort are distilled.* At first unchanged toluene distils; the fraction boiling at 165—185° contains nearly the whole of the benzyl chloride, and forms the greater part of the product. The liquid, which passes over above 185°, is a mixture of higher chlorinated compounds, and consists chiefly of benzal chloride, $C_6H_5CHCl_2$, and benzotrichloride, $C_6H_5CCl_3$.

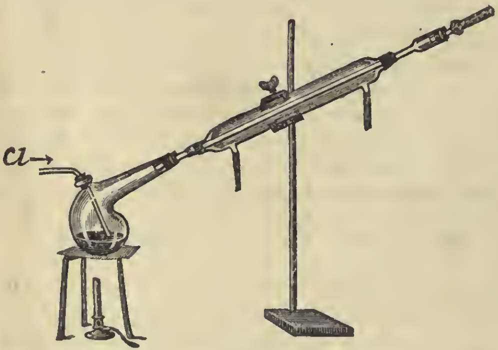

FIG. 80.

The portion containing the benzyl chloride is repeatedly fractionated until a liquid is obtained, boiling at 176—180°, which is nearly pure benzyl chloride. Yield 80—90 grams.

$$C_6H_5CH_3 + Cl_2 = C_6H_5CH_2Cl + HCl.$$

Properties.—Colourless liquid with an irritating smell; b. p. 176°; sp. gr. 1·107 at 14°. See *Appendix*, p. 299.

PREPARATION 87.

Benzyl Alcohol, $C_6H_5CH_2OH$

Söderbaum, Widman, *Ber.*, 1892, **25**, 3290.

20 grms. benzyl chloride.
16 „ potassium carbonate (in 200 c.c. water).

In a round flask (½ litre) attached to a reflux condenser, boil the mixture of benzyl chloride and potassium carbonate solution over wire-gauze with the addition of a few bits of porous pot. The boiling must be continued until the smell of benzyl chloride has disappeared (6—8 hours). Extract the liquid with ether, dehydrate over potassium carbonate, decant through a filter and distil off the ether on the water-bath. Continue the distillation over wire-gauze, run the water out of the condenser and collect at 200—210°. Yield 12—15 grams.

$$2C_6H_5CH_2Cl + H_2O + K_2CO_3 = 2C_6H_5CH_2OH + 2KCl + CO_2.$$

Properties.—Colourless liquid with a faint aromatic smell; b. p. 206·5°; sp. gr. 1·05 at 15·4°; moderately soluble in water.

Reactions.—1. Boil 2 or 3 drops with 2—3 c.c. dilute nitric acid ($1HNO_3,4H_2O$); benzaldehyde is first formed and is detected by the smell. On continued boiling, benzoic acid is formed and separates on cooling in crystals.

2. Warm 1 c.c. of the alcohol with 1 c.c. concentrated hydrochloric acid. The clear solution becomes turbid and benzyl chloride separates out.

$$C_6H_5CH_2OH + HCl = C_6H_5CH_2Cl + H_2O.$$

See *Appendix*, p. 300.

PREPARATION 88.

Benzaldehyde (Bitter Almond Oil), $C_6H_5.CO.H$

Liebig, Wöhler, *Annalen*, 1837, **22**, 1; Lauth, Grimaux, *Annalen*, 1867, **143**, 186.

50	grms.	benzyl chloride.
40	„	copper nitrate.
500	c.c.	water.

The mixture of benzyl chloride, copper nitrate and water is heated to boiling in a round flask ($1\frac{1}{2}$ litre) with upright condenser on the sand-bath for a day (8—9 hours). A slow current of carbon dioxide is at the same time passed through the liquid to prevent oxidation of the benzaldehyde by absorption of oxygen from the air. During the process nitrous fumes are slowly evolved. When the reaction is complete, the contents of the flask are extracted with ether, and the yellow oil remaining, after distilling off the ether, is well shaken with a saturated solution of sodium bisulphite[1] and allowed to stand for a time. The colourless crystalline mass which separates out is filtered, washed with a little alcohol and ether, and then drained on a porcelain filter. The aldehyde is regained by adding dilute sulphuric acid in excess and distilling in steam. The distillate is extracted with ether, dehydrated over calcium chloride, decanted, and the ether distilled off. Yield, about 15 grams.

$$2C_6H_5CH_2Cl + Cu(NO_3)_2 = 2C_6H_5COH + CuCl_2 + 2HNO_2.$$

Properties.—Colourless liquid, with a pleasant smell; b. p. 179°; sp. gr. 1·0504 at 15°; it quickly oxidises in the air, forming benzoic acid.

Reactions.—1. Leave a drop of benzaldehyde on a watch-glass. It solidifies by becoming oxidised to benzoic acid.

2. Add 5 c.c. concentrated ammonia to 1 c.c. benzaldehyde, cork up and leave two days. Crystals of hydrobenzamide,

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[1] The solution is prepared either by dissolving solid sodium bisulphide in water or by passing sulphur dioxide into powdered sodium carbonate covered with a shallow layer of water. The carbonate dissolves with effervescence, forming a heavy apple-green liquid smelling strongly of sulphur dioxide

$(C_6H_5CH)_3N_2$, separate out, which may be recrystallised from spirit.

$$3C_6H_5COH + 2NH_3 = (C_6H_5CH)_3N_2 + 3H_2O.$$

3. Heat on the water-bath 2 c.c. benzaldehyde and 2 c.c. aniline for an hour. Crystals of benzalaniline are formed on cooling, $C_6H_5COH + C_6H_5NH_2 = C_6H_5CH{:}N.C_6H_5 + H_2O$, which may be filtered and crystallised from spirit; m. p. 42°.

4. Shake up together 10 grams of benzaldehyde with 9 grams caustic potash in 6 c.c. of water until a permanent emulsion is formed and let stand 3—4 hours. Dissolve the solid product in a little water and shake out with ether twice. On acidifying the aqueous portion with hydrochloric acid, benzoic acid is precipitated. Filter and wash with a little cold water and dry. Distil the ether from the ethereal solution. The residue is benzyl alcohol (Cannizzaro).

$$2C_6H_5COH + KOH = C_6H_5COOK + C_6H_5CH_2OH.$$

See also Reactions on p. 135 and p. 174, and *Appendix*, p. 300.

PREPARATION 89.

α- and β-**Benzaldoximes**, $C_6H_5CH{:}NOH$

Beckmann, *Ber.*, 1890, **23**, 1684.

21 grms. benzaldehyde.
15 „ hydroxylamine hydrochloride.
14 „ caustic soda (in 40 c.c. water).

The solution of caustic soda and benzaldehyde are mixed and the hydroxylamine hydrochloride gradually added with constant shaking. The liquid becomes slightly warm and the oil eventually dissolves, forming a yellow solution which has lost the smell of benzaldehyde. On cooling, a crystalline mass of the hydrochloride of benzaldoxime separates. Sufficient water is added to form a clear solution, through which a current of carbon dioxide is passed. A colourless emulsion of the α- or *anti*-aldoxime separates on the surface and is extracted with ether, dehydrated over anhydrous sodium sulphate and the ether removed on the water-bath. Impure benz*anti*aldoxime remains and is purified as follows. It is poured into a saturated solution of sodium ethoxide in alcohol (prepared by dissolving 5 grams sodium in 60 c.c. alcohol), when the aldoxime separates as the sodium compound in the form of a semi-solid mass. It is filtered and washed with a saturated solution of sodium ethoxide in alcohol to dissolve out the β-oxime. The product is dissolved in water, saturated with carbon dioxide and extracted with ether as before. Dry air is then drawn through the liquid to remove the last traces of ether when, if pure, the oxime, on cooling to 0°, solidifies. If not, it should be distilled *in vacuo*. At 12 mm. it boils at 122—124° : at 10 mm. at 118—119°.

Yield, 10 grams.

$$+ 3HO_2.$$

$$C_6H_5.CHO + NH_2OH.HCl + 2NaOH = C_6H_5CH{:}NONa + NaCl$$

$$C_6H_5CH{:}NONa + CO_2 + H_2O = C_6H_5CH{:}NOH + NaHCO_3.$$

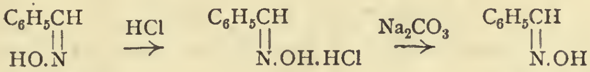
Properties of α-Benzaldoxime.—Colourless needles, m. p. 34—35°.

Reaction.—Dissolve a small quantity of the α-oxime in a few drops of acetic anhydride, warm if necessary, and cool quickly by adding a little ice. Add to the clear solution solid sodium carbonate and a little caustic soda solution. The solution becomes clear on shaking or warming.

β-Benzaldoxime.—The various steps in the preparation of the β-oxime must be carried out continuously, and it is therefore necessary to be provided beforehand with about 300 c.c. of pure anhydrous ether.

The α-compound is dissolved in 50 c.c. pure dry ether, and dry hydrogen chloride is passed in with constant shaking to prevent the delivery tube from becoming blocked. Colourless crystals of the hydrochloride of the β-oxime separate and are filtered and washed with dry ether and then placed in a separating funnel and covered with a layer of ether. A concentrated solution of sodium carbonate is gradually added with constant shaking until no further effervescence is observed. Sodium chloride is precipitated and the β-oxime dissolves in the ether. The ether extract is separated, dehydrated over sodium sulphate, and the ether removed as rapidly as possible at the ordinary temperature by evaporation *in vacuo*. The residue crystallises, and when pressed on a porous plate leaves a mass of small silky needles, m. p. 126—130°. It may be recrystallised by dissolving it in the smallest quantity of ether and then adding petroleum ether.

The yield is theoretical.



$$\begin{matrix} C_6H_5CH \\ \| \\ HO.N \end{matrix} \xrightarrow{HCl} \begin{matrix} C_6H_5CH \\ \| \\ N.OH.HCl \end{matrix} \xrightarrow{Na_2CO_3} \begin{matrix} C_6H_5CH \\ \| \\ N.OH \end{matrix}$$

α- or *anti*-oxime. β- or *syn*-oxime.

Properties of the β-Benzaldoxime.—Colourless needles, m. p. 130°.

Reaction.—Repeat the reaction for α-benzaldoxime. In this case benzonitrile is formed, which separates in oily drops having a characteristic smell. See *Appendix*, p. 301.

PREPARATION 90.

Benzoic Acid, $C_6H_5CO.OH$

5 grms. benzyl chloride.
4 „ anhydrous sodium carbonate (in 50 c.c. water).
8·5 „ potassium permanganate (in 150 c.c. water).

The benzyl chloride and sodium carbonate solution are mixed in a round flask (½ litre) attached to a reflux condenser, and boiled gently over wire-gauze, whilst the permanganate solution is gradually dropped in from a tap-funnel pushed through the top of the condenser. In the course of 2—3 hours the pink colour of the permanganate will have vanished and been replaced by a mass of dark brown precipitate of manganese dioxide. When the liquid is cold, a stream of sulphur dioxide is passed in until the manganese dioxide is dissolved (see p. 166). The liquid is allowed to cool and the benzoic acid, which separates, is filtered at the pump, washed with a little cold water and recrystallised from hot water; m. p. 121°. The yield is theoretical. The reaction probably occurs in two steps.

$$1.\ 2C_6H_5CH_2Cl + Na_2CO_3 + H_2O = 2C_6H_5CH_2OH + 2NaCl + CO_2.$$

$$2.\ 3C_6H_5CH_2OH + 4KMnO_4 = 3C_6H_5COOK + 4MnO_2 + KOH + 4H_2O.$$

Properties.—Crystallises in needles; m. p. 121°; on heating it melts and sublimes; soluble in hot water, alcohol and ether. It distils in steam.

Reactions.—1. Make a neutral solution of ammonium benzoate by adding excess of ammonia to benzoic acid and boiling until neutral. To different portions add solutions of calcium chloride, ferric chloride, silver nitrate and lead acetate and note the results.

2. Grind up 0·5 gram of the acid with four times the weight of soda-lime and heat gently at first and then more strongly. Vapours of benzene will be given off, which may be detected by the smell. $C_6H_5CO.OH + CaO = C_6H_6 + CaCO_3$.

See *Appendix*, p. 302.

PREPARATION 91.

m-Nitro-, m-Amino- and m-Hydroxybenzoic Acids,

$$C_6H_4{<}\begin{matrix}NO_2\\COOH\end{matrix},\quad C_6H_4{<}\begin{matrix}NH_2\\COOH\end{matrix},\quad C_6H_4{<}\begin{matrix}OH\\COOH\end{matrix}\quad\begin{matrix}1\\3\end{matrix}$$

40 grms. benzoic acid.
80 „ potassium nitrate.
100 c.c. conc. sulphuric acid.

The benzoic acid and potassium nitrate are mixed and carefully powdered. The sulphuric acid is warmed to 70° and stirred mechanically, whilst the mixture of benzoic acid and nitrate is added slowly, so that the temperature does not exceed 80°. When all is added the temperature is raised to 90°, and kept at this temperature until the nitrated acid separates as an oily layer on the surface. On cooling, the layer solidifies and can be separated. It is then distilled in steam to remove benzoic acid. The residue containing the nitrobenzoic acid is heated to boiling and made slightly alkaline with baryta. Two litres of water are added and the liquid raised to the boiling point by passing in steam and then filtered. On cooling, the barium salt crystallises and is filtered off and decomposed with hot dilute hydrochloric acid. The precipitated acid is recrystallised from water; m. p. 141°. Yield, 28 grams.

m-Aminobenzoic Acid

20 grms. nitrobenzoic acid.
40 „ granulated tin.
120 c.c. conc. hydrochloric acid.

The nitrobenzoic acid, tin, and hydrochloric acid are mixed in a litre flask and warmed until the reaction begins. When the first vigorous action is over, the mixture is heated on the water-bath until the tin is dissolved. The liquid is poured into a basin and evaporated on the water-bath to expel the excess of hydrochloric acid. The tin is then precipitated by passing into the hot, dilute solution a current of hydrogen sulphide. The sulphide is filtered and washed with hot water, and the filtrate evaporated to dryness. To obtain the free acid, a small portion of the residue is dissolved in very little water made alkaline with ammonia, and acidified with acetic acid. It is recrystallised from water, and melts at 174°.

m-Hydroxybenzoic Acid,

15 grms. *m*-aminobenzoic acid hydrochloride (in 200 c.c. water).
6·5 „ sodium nitrite (in 15 c.c. water).

The nitrite solution is slowly added to the solution of the hydrochloride dissolved in water. The liquid is heated on the water-bath until the evolution of nitrogen ceases, and then filtered and concentrated. The hydroxybenzoic acid separates on cooling as a brown mass, which may be purified by dissolving in water and boiling with animal charcoal. It separates in colourless crystals, m. p. 200°. Yield, 7 grams. See *Appendix*, p. 303.

PREPARATION 92.

m-Bromobenzoic Acid,

$$C_6H_4{<}\begin{matrix}\text{Br} & 1\\ \text{CO.OH} & 3\end{matrix}$$

Hübner, Petermann, *Annalen*, 1869, **149**, 131.

5 grms. benzoic acid.
7 „ bromine.
30 c.c. water.

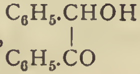
The mixture is brought into a thick-walled tube, closed at one end and sealed in the usual way. The tube is heated in the tube furnace to 140—150° for eight to nine hours. After cooling, the capillary is opened and the tube removed from the furnace. The bromine will have completely disappeared, and colourless crystals of bromobenzoic acid now fill the tube. The contents are removed, filtered, and boiled with water (100 c.c.) in a basin to drive off unchanged benzoic acid. The liquid is cooled, filtered, and the bromobenzoic acid crystallised from hot water. Yield, 5 grams.

$$C_6H_5CO.OH + Br_2 = C_6H_4Br.CO.OH + HBr.$$

Properties.—Colourless needles ; m. p. 155°.

PREPARATION 93.

Benzoin,



$$\begin{array}{l} C_6H_5.CHOH \\ \quad\;\; | \\ C_6H_5.CO \end{array}$$

Liebig, Wöhler, *Annalen*, 1832, **3**, 276 ; Zinin, *Annalen*, 1840, **34**, 186.

25 grms. benzaldehyde.
5 „ potassium cyanide (in 20 c.c. water).
50 c.c. absolute alcohol.

The mixture of benzaldehyde, potassium cyanide and alcohol is heated on the water-bath with an upright condenser for about half an hour. On cooling the liquid, the benzoin separates out as a mass of small colourless crystals, which are filtered and washed with a little alcohol. Yield, about 20 grams. A portion of the substance may be purified by recrystallisation from spirit.

$$2C_6H_5COH = C_6H_5CO.CH(OH).C_6H_5.$$

Properties.—Colourless prisms ; m. p. 137° ; slightly soluble in water ; soluble in alcohol and ether.

Reaction.—Add Fehling's solution to benzoin dissolved in alcohol. Benzil is formed and cuprous oxide precipitated. Benzil is also formed on oxidation with nitric acid.

Benzil, $C_6H_5CO.CO.C_6H_5$

15 grms. benzoin.
35 „ conc. nitric acid, sp. gr. 1·4.

The benzoin and nitric acid are heated on the water-bath with an air condenser, the flask being occasionally shaken. Nitrous fumes are evolved, and the crystals of benzoin are converted into a yellow oil, which, after two hours' heating, is free from unchanged benzoin. The contents of the flask are now poured into water, and the yellow crystalline deposit separated by filtration, washed with water, and recrystallised from alcohol. Yield, 10—12 grams.

Properties.—Yellow prisms; m. p. 95°; insoluble in water; soluble in hot alcohol.

Reaction.—1. Dissolve a small quantity of benzil in a little alcohol, add a fragment of caustic potash and boil. A violet solution is obtained.

Benzilic Acid, $(C_6H_5)_2C(OH).CO_2H$

10 grms. benzil.
50 „ caustic potash.

The caustic potash is melted with a small quantity of water in a silver or nickel crucible. The temperature of the mass is brought to 150°, and the finely powdered benzil added. The benzil melts, and the mixture shortly changes to a solid mass of potassium benzilate. The cooled melt is dissolved in water, and the alkaline solution acidified with hydrochloric acid, which precipitates the benzilic acid. The crystalline mass, which contains small quantities of benzoic acid, is separated from the mother-liquor and washed with cold water. It is then transferred to a porcelain basin, dissolved in hot water, and the solution boiled until the smell of benzoic acid has gone. On cooling, benzilic acid crystallises out, and is purified by a second crystallisation from hot water.

$$C_6H_5.CO.CO.C_6H_5 + KOH = (C_6H_5)_2C.(OH).COOK.$$

Properties.—Colourless needles; m. p. 150°; scarcely soluble in cold, readily in hot water and alcohol.

Reaction.—Add a little concentrated sulphuric acid to benzilic acid. It dissolves with an intense red colour. See *Appendix*, p. 303.

PREPARATION 94.

Cinnamic Acid (Phenylacrylic Acid),

$C_6H_5.CH:CH.CO_2H$

Bertagnini, *Annalen*, 1856, **100**, 126; Perkin, *Trans. Chem. Soc.*, 1868, **21**, 53; Fittig, *Ber.*, 1881, **14**, 1826.

20	grms.	benzaldehyde.
10	„	sodium acetate (fused).
30	„	acetic anhydride.

The mixture of benzaldehyde, sodium acetate, and acetic anhydride is heated to 180° in a small round flask with upright condenser in an oil-bath for about eight hours. The mass is poured out whilst hot into a large round flask (1 litre), sodium carbonate added until alkaline, and any unchanged benzaldehyde distilled off with steam. After filtering from undissolved resinous by-products, hydrochloric acid is added, which precipitates the free cinnamic acid in white crystalline flakes. It may be purified by recrystallisation from hot water. Yield, 15—20 grams.

1. $C_6H_5CO.H + CH_3.CO.ONa = C_6H_5CH:CH.CO.ONa + H_2O.$

2. $$C_6H_5.CH:CH.CO.ONa + H_2O + (CH_3.CO)_2O = C_6H_5.CH:CH.COOH + CH_3CO.ONa + CH_3.COOH.$$

Properties.—Colourless prisms; m. p. 133°; b. p. 300—304°. See *Appendix*, p. 304.

PREPARATION 95.

Hydrocinnamic Acid (Phenylpropionic Acid),

$C_6H_5CH_2.CH_2.CO_2H$

Erlenmeyer, Alexejeff, *Annalen*, 1862, **121**, 375, and 1866, **137**, 237.

10	grms.	cinnamic acid.
100	„	water.
170	„	sodium amalgam ($2\frac{1}{2}$ per cent.).

The sodium amalgam is prepared by warming 200 grams of mercury in a porcelain basin for a few minutes. The mercury is poured out into a mortar which is placed in the fume cupboard, the window of which is drawn down so as to protect the face. Five grams of sodium are introduced in small pieces, the size of a pea, and pressed with a pestle under the surface of the mercury. Each piece dissolves with a bright flash. The amalgam is poured out whilst semi-fluid on to an iron tray, broken up, and kept in a wide-necked stoppered bottle.[1]

The cinnamic acid and water are introduced into a strong beaker or bottle (300 c.c.), and the liquid made slightly alkaline with caustic soda, which dissolves the acid forming the sodium salt. The sodium amalgam is added in small pieces from time to time and the liquid thoroughly agitated. The solution, which remains clear, becomes slightly warm, and the amalgam soon liquefies, but no hydrogen is evolved until towards the end of the operation. When the whole of the amalgam has been added, and bubbles of gas cease to be given off, the solution is decanted from the mercury, which is rinsed with water. On acidifying the solution with hydrochloric acid, hydrocinnamic acid is precipitated as a colourless oil, which solidifies on standing. It may be recrystallised from a large quantity of warm water. Yield, 8—9 grams.

$$C_6H_5.CH{:}CH.CO_2H + H_2 = C_6H_5.CH_2.CH_2.CO_2H.$$

Properties.—Long colourless needles; m. p. 47°; b. p. 280°; soluble in water and alcohol; volatile in steam. See *Appendix*, p. 306.

PREPARATION 96.

Mandelic Acid, $C_6H_5.CH(OH).COOH$

Friedländer, *Theerfarbenfabrikation* IV, 160.

15 grms. benzaldehyde.
50 c.c. conc. sodium bisulphite solution.
12 grms. potassium cyanide (in 20 c.c. water).

The benzaldehyde and sodium bisulphite are mixed together and stirred. The mixture forms a semi-solid mass of the

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[1] If larger quantities of amalgam are required, the mercury is heated in a small enamelled pan, or crucible, the sodium added in one lot, and the vessel immediately closed with a lid, which is held down with long crucible tongs until the reaction is over, and then poured out whilst fluid.

bisulphite compound, which after standing for half an hour is filtered and pressed at the pump and washed with a little water and spirit. The mass is then ground to a thick paste with water and the solution of potassium cyanide added. After a short time mandelic nitrile separates as a reddish oil and is removed by means of a tap-funnel with the addition of a little ether.

$$C_6H_5CH(OH)SO_3Na + KCN = C_6H_5CH(OH).CN + (K)(Na)SO_3$$

The ether is allowed to evaporate on the water-bath and the nitrile is then hydrolysed by continuing to heat it on the water-bath with the addition of 4—5 times its volume of conc. hydrochloric acid until crystals appear on the surface. Water is added and the hot liquid decanted and filtered from any oil. On cooling, the crystals are filtered, washed with a little cold water and dried. A further quantity can be extracted from the filtrate with ether. It may be recrystallised from benzene. Yield, 10—15 grms.

$$C_6H_5CH(OH)CN + HCl + 2H_2O$$
$$= C_6H_5CH(OH).COOH + NH_4Cl.$$

Properties.—Colourless needles, m. p. 118–119°; dissolves readily in hot water and in 6 parts of water at 20°. The acid is racemic; the active components exhibit a rotation of $[\alpha]_D^{20^\circ} = \pm 157^\circ$ in aqueous solution. See *Appendix*, p. 306.

PREPARATION 97.

Phenyl Methyl Carbinol, $C_6H_5\,CH(OH).CH_3$

Grignard, *Compt. rend.* 1900, **130**, 1322; Klages and Ullendorf, *Ber.*, 1898, **31**, 1003.

36 grms. methyl iodide.
150 c.c. ether (purified and carefully dried over sodium).
6 grms. magnesium ribbon or powder.
26 ,, benzaldehyde.

The magnesium methyl iodide is first prepared and is formed by the action of methyl iodide on the metal. The magnesium ribbon or powder is placed in a dry, round flask

(1 litre), connected with a long condenser and dropping funnel as shown in Fig. 81.

The methyl iodide and 50 c.c. of dry ether are mixed in a separate vessel and 20 c.c. of this mixture poured on to the magnesium. In a few seconds a vigorous action usually sets in or if it is delayed may be started by adding a crystal of iodine. When the first reaction has subsided, 70 c.c. of dry ether are added, and the remainder of the alkyl iodide and ether mixture run in drop by drop from the tap-funnel. The contents of the flask are then boiled on the water-bath for half an hour when (if there has been no loss of alkyl iodide) the magnesium completely dissolves.

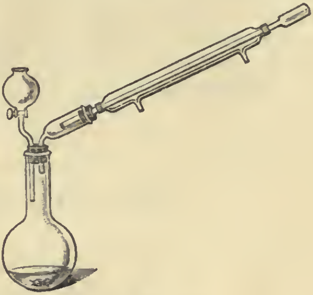


FIG. 81.

$$CH_3I + Mg = Mg\left\langle{CH_3 \atop I}\right. .$$

The flask is now disconnected and whilst it is kept cool in ice-water the benzaldehyde mixed with an equal volume of dry ether is dropped in from a tap-funnel with constant shaking. The white solid magnesium compound separates and is left overnight.

$$Mg\left\langle{CH_3 \atop I}\right. + C_6H_5CHO = C_6H_5CH\left\langle{OMgI \atop CH_3}\right. .$$

The contents of the flask are cooled under the tap whilst water and just sufficient hydrochloric acid to dissolve the magnesia are added, the acid being cautiously dropped in from a tap-funnel. The aqueous layer is removed in a separating funnel and the ether washed first with sodium bicarbonate solution, then with sodium bisulphite (to remove free iodine) and again with sodium bicarbonate.

$$C_6H_5CH\left\langle{OMgI \atop CH_3}\right. + HCl = C_6H_5CH(OH).CH_3 + Mg(Cl)(I).$$

The ether extract is then dried over potassium carbonate and the ether removed by distillation on the water-bath. The phenyl methyl carbinol which remains is distilled under reduced pressure; b. p. 100° at 15 mm.; 110–111° at 28 mm.; 118° at 40 mm. Yield, 20 grams.

The same method may be used without modification for preparing phenyl ethyl carbinol using a corresponding quantity of ethyl iodide. See *Appendix*, p. 307.

PREPARATION 98.

Benzoyl Chloride, $C_6H_5CO.Cl$

Wöhler, *Annalen*, 1832, **3**, 262; Cahours, *Annalen*, 1846, **60**, 255.

28 grms.	benzoic acid.
50 ,,	phosphorous pentachloride.

A round flask (250 c.c.) is fitted with an air-condenser. The phosphorous pentachloride is introduced from the bottle and weighed by difference. The operation must be conducted in the fume-cupboard. The benzoic acid is then added, and the air-condenser attached to the flask.* The action begins almost immediately, and clouds of hydrochloric fumes are evolved. The whole contents become liquid and consist of benzoyl chloride (b. p. 200°), phosphorous oxychloride (b. p. 107°), and unchanged pentachloride. Most of the oxychloride may be removed by distilling *in vacuo* on the water-bath. The remainder is fractionated at the ordinary pressure and collected at 190–200°. Yield, 20–25 grams.

$$C_6H_5COOH + PCl_5 = C_6H_5CO.Cl + POCl_3 + HCl.$$

Properties.—Colourless liquid, which fumes in the air and possesses a pungent smell; b. p. 198·5°; sp. gr. 1·214 at 19°.

Reactions.—1. Add a few drops of benzoyl chloride to 1 c.c. of water; the benzoyl chloride does not decompose at once, and requires warming for some time before it is completely dissolved (compare acetyl chloride, p. 74).

2. Add 2 c.c. ethyl alcohol to 1 c.c. benzoyl chloride and caustic soda solution until alkaline, and warm gently. After a time the smell of benzoyl chloride disappears, and ethyl benzoate

remains as an oily liquid with a fragrant smell. $C_6H_5COCl + C_2H_5OH + NaOH = C_6H_5COOC_2H_5 + NaCl + H_2O$. Repeat the same reaction with phenol and separate the solid phenyl benzoate. (Schotten-Baumann reaction.)

3. Add 5 grams benzoyl chloride to 10 grams ammonium carbonate in a mortar* and grind up well. The reaction proceeds quietly. If after ten minutes the smell of benzoyl chloride still remains, add a few drops of concentrated ammonia. Add cold water and filter. Benzamide remains on the filter in the form of a white crystalline powder, and may be recrystallised from hot water; m. p. 128°. $C_6H_5COCl + 2NH_4HCO_3 = C_6H_5CONH_2 + NH_4Cl + 2CO_2 + 2H_2O$. See *Appendix*, p. 308.

PREPARATION 99.

Ethyl Benzoate (Ethyl Benzoic Ester), $C_6H_5CO.OC_2H_5$

E. Fischer and Speier, *Ber.*, 1895, **28**, 1150.

25 grms. benzoic acid.
75 ,, (90 c.c.) absolute alcohol.

Pass dry hydrochloric acid gas (see p. 93) through the alcohol, cooled in water until it has increased about 3 grams in weight. Add the benzoic acid and boil the mixture with upright condenser over wire-gauze for two hours. On pouring a small quantity of the product into water, only the ester, which is a heavy oil, should separate, but no solid benzoic acid. The excess of alcohol is now distilled off on the water-bath and the residue poured into water. Any free hydrochloric or benzoic acid is removed by shaking with a dilute solution of sodium carbonate. On adding ether and shaking, the ester dissolves in the top layer of ether, which is separated and dehydrated over calcium chloride. The ether is removed on the water-bath, and the ethyl benzoate is then distilled over wire-gauze, a few bits of porcelain being added to prevent bumping. The distillate is collected between 205° and 212°. Yield, about 22 grams.

$$C_6H_5COOH + HOC_2H_5 = C_6H_5COOC_2H_5 + H_2O.$$

Properties.—Colourless, sweet-smelling oil; b. p. 211°; sp. gr. 1·05 at 15°.

Quantitative Hydrolysis of Ethyl Benzoate.—The quantitative estimation of an ester by hydrolysis is conducted as follows: a standard half-normal solution of alcoholic potash is prepared by dissolving 7 grams of caustic potash in about an equal weight of water and diluting to 250 c.c. with absolute alcohol. The liquid is allowed to stand overnight in a stoppered flask and filtered through asbestos into a clean dry bottle closed with a cork through which a 25 c.c. pipette is inserted. The solution is first standardised by titration against half-normal sulphuric acid, using phenolphthalein as indicator. About 1 gram of ethyl benzoate is carefully weighed by difference by means of the apparatus shown in Fig. 82.

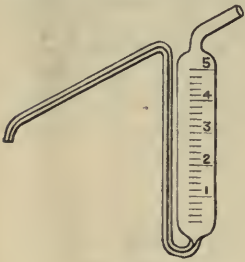


Fig. 82.

A volume corresponding to about 1 gram is delivered into a round flask (200 c.c.) by attaching a piece of rubber tubing to the wide end of the apparatus and blowing until the liquid descends to the required graduation on the wide limb. Twenty-five c.c. of the standard alcoholic potash solution is added, and the mixture boiled on the water-bath with reflux condenser for twenty minutes.

$$C_6H_5COOC_2H_5 + KOH = C_6H_5COOK + C_2H_5OH.$$

The amount of free alkali is estimated by titration with standard sulphuric acid and the quantity of ester calculated.

Example.—1·355 grams required 15·1 c. c. $N/2H_2SO_4$

$$\frac{15{\cdot}1 \times 0{\cdot}150 \times 100}{2 \times 1{\cdot}1355} = 99{\cdot}7 \text{ per cent.}$$

See *Appendix*, p. 308.

PREPARATION 100.

Acetophenone (Phenylmethylketone, Hypnone), $C_6H_5.CO.CH_3$

Friedel, Crafts, *Ann. Chim. Phys.*, 1884, **1**, 507; **14**, 455.

30 grms.	benzene.
50 ,,	aluminium chloride (anhydrous).
35 ,,	acetyl chloride.

The various reactions, known as the Friedel-Crafts reactions, are effected by means of anhydrous aluminium chloride. The aluminium chloride, being very hygroscopic, cannot be kept long, even in a stoppered bottle, without undergoing gradual decomposition. As the success of the reaction depends entirely on the quality of the chloride, it should be either freshly procured from a reliable firm or resublimed from a retort. It may also be prepared on a small scale by passing dry hydrochloric acid over heated aluminium foil or filings, but the operation is troublesome and scarcely repays the time spent. Attach a round flask (500 c.c.) to an upright condenser, and bring into it the aluminium chloride, which should be well powdered, and immediately cover it with the benzene. Place the flask in ice-water, and add the acetyl chloride drop by drop from a tap-funnel, which is pushed into the top of the condenser.* A vigorous effervescence occurs, and hydrochloric acid is evolved. The contents of the flask are converted into a brown, viscid mass, which, after standing an hour, is stirred up and shaken into a beaker containing ice and water (250 c.c.). The mass decomposes with evolution of heat, and a dark oil separates on the surface. The liquid is poured into a separating-funnel and a little benzene added. The aqueous portion is drawn off, and the benzene layer shaken up with dilute caustic soda and then with water. The benzene solution is finally separated, dehydrated over calcium chloride, filtered, and distilled. The benzene first passes over. The thermometer then rises quickly to 195°. The receiver is now changed, the water run out of the condenser, and the distillate, which boils at 195—200°, collected separately. It forms a pale yellow oil with a characteristic sweet smell, and solidifies completely on standing. Yield, 20—25 grams.

$$C_6H_6 + CH_3COCl = C_6H_5.CO.CH_3 + HCl.$$

Properties.—Colourless plates; m. p. 20°; b. p. 202°; insoluble in water.

Reactions.—1. **Acetophenoneoxime.**—Mix together 5 grams of hydroxylamine hydrochloride dissolved in 10 c.c. of water, 8 grams of acetophenone, and 3 grams of caustic soda dissolved in a very little water. Add spirit until, on warming, the solution becomes clear, and boil it on the water-bath 2—3 hours.

Pour into 100 c.c. water, and extract with ether. Distil off the ether and crystallise the solid residue from petroleum spirit. Yield, 8 grams; m. p. 58—60°. $C_6H_5.CO.CH_3 + NH_2OH.HCl + NaOH = C_6H_5C(NOH).CH_3 + NaCl + 2H_2O$.

2. **Acetophenonesemicarbazone.**—Mix 1 gram of semicarbazide hydrochloride with 1·5 grams of crystallised sodium acetate, and dissolve in the smallest quantity of warm water. Add 1 gram of acetophenone and sufficient spirit to produce a clear solution when hot. Continue to heat for a few minutes. On cooling, the semicarbazone deposits as a yellow, crystalline mass. $C_6H_5.CO.CH_3 + NH_2.NH.CO.NH_2.HCl + NaC_2H_3O_2 = C_6H_5C(N.NH.CONH_2)CH_3 + NaCl + C_2H_4O_2$. Theoretical yield; m. p. 185—188°.

3. **Beckmann's Reaction.**—Dissolve 1 gram of acetophenoneoxime in 30 c.c. anhydrous ether, and add gradually 1·5 grams of powdered phosphorus pentachloride. Distil off the ether, and add a little water to the residue. On cooling, crystals of acetanilide separate. Recrystallise from water, and determine the melting point.

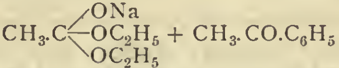
$$1.\ C_6H_5.C(NOH).CH_3 + PCl_5 = C_6H_5.C(NCl).CH_3 + POCl_3 + HCl.$$

$$2.\ C_6H_5C(NCl)CH_3 + H_2O = C_6H_5NH.CO.CH_3 + HCl.$$

4. **Benzoylacetone** (*Claisen's Reaction*).—Six grams of dry, powdered sodium ethoxide are added to 20 grams of dry ethyl acetate, and cooled in water. The sodium ethoxide is prepared by dissolving 4 grams of sodium in 40 c.c. absolute alcohol, and distilling off the excess of alcohol, first from the water-bath, and then from the metal-bath, in a current of dry hydrogen, the temperature of the bath being raised gradually to 200°, until nothing more passes over. The white cake is detached rapidly powdered, and the requisite quantity quickly weighed out and added to the ethyl acetate. After standing a quarter of an hour, 10 grams of acetophenone are added, when sodium benzoyl acetone begins to separate. A little ether is added, and, after standing for a few hours, the sodium compound is filtered and washed with ether. The sodium compound is then dried in the air, dissolved in cold water, and acidified with acetic acid. Benzoylacetone separates out. Yield, 9—10 grams; m.p. 60—61°.

It behaves towards ferric chloride and copper acetate like ethyl acetoacetate (see Reactions, p. 84).

1.



$$CH_3.C\left\langle\begin{matrix}ONa\\ OC_2H_5\\ OC_2H_5\end{matrix}\right. + CH_3.CO.C_6H_5$$

$$= CH_3.C(ONa):CH.CO.C_6H_5 + 2C_2H_5OH$$

2.

$$CH_3.C(ONa):CH.COC_6H_5 + C_2H_4O_2$$
$$= CH_3.CO.CH_2.CO.C_6H_5 + NaC_2H_3O_2.$$

See *Appendix*, p. 309.

PREPARATION 101.

Diphenylmethane, $C_6H_5.CH_2.C_6H_5$

Cohen, Hirst, *Trans. Chem. Soc.*, 1895, **67**, 826.

60 grms. benzene.
30 ,, benzyl chloride.
1 ,, aluminium-mercury couple.

The benzene is placed in a flask attached to an upright condenser.* The aluminium-mercury couple is then added. It is prepared by pouring a saturated solution of mercuric chloride on to aluminium foil, which is cut into strips or formed into rolls. After about a minute, the surface of the aluminium is coated with a film of metallic mercury. The solution is poured off, the foil well washed with water, then with alcohol, and finally with a little benzene. This must be done quickly and the pieces of couple dropped into the benzene. The benzyl chloride is added slowly from a tap-funnel inserted through the top of the condenser. A brisk effervescence occurs, accompanied by a considerable rise of temperature, and fumes of hydrochloric acid are evolved. When, in the course of an hour, the benzyl chloride has been added, the flask is heated on the water-bath for ten to fifteen minutes. The contents of the flask are now shaken up with water containing a little caustic soda, and the benzene solution separated in a tap-funnel. The aqueous portion is again extracted with benzene, and the whole of the benzene solution is dehydrated over calcium chloride. The benzene is then distilled off, and when the thermometer reaches 100° the distillation is continued *in vacuo*. At 80 mm. diphenylmethane boils at 174—176°. This fraction solidifies completely on cooling, and is pure diphenylmethane; m. p. 25—26°. Yield, 14 grams.

$$C_6H_5CH_2Cl + C_6H_6 = C_6H_5CH_2C_6H_5 + HCl.$$

Properties.—Colourless needles; m. p. 26—27°; b. p. 262°. On boiling with potassium dichromate and sulphuric acid it is oxidised to benzophenone, $C_6H_5CH_2C_6H_5 + O_2 = C_6H_5.CO.C_6H_5 + H_2O$. See *Appendix*, p. 312.

PREPARATION 102.

Triphenylmethane, $CH(C_6H_5)_3$

Friedel, Crafts, *Compt. rend.*, 1877, 1450; E. and O. Fischer, *Annalen*, 1878, **197**, 252; Biltz, *Ber.*, 1893, **26**, 1961.

200 grms. (230 c.c.) benzene.
40 „ (26 c.c.) chloroform.
30 „ aluminium chloride.

The benzene and chloroform are mixed together and dehydrated over calcium chloride overnight before use. The liquid is then decanted into a retort connected with an upright condenser,* and the powdered aluminium chloride added in portions of about 5 grams at a time at intervals of five minutes and well shaken. On the addition of the chloride the reaction sets in spontaneously, and the liquid begins to boil with evolution of hydrochloric acid. The aluminium chloride gradually dissolves, forming a dark-brown liquid. The reaction is completed by boiling for half an hour on the sand-bath. When cold, the contents of the retort are poured into an equal volume of cold water, which decomposes the aluminium compound with evolution of heat, and the free hydrocarbon dissolves in the excess of benzene with a reddish-brown colour. The upper layer of benzene is separated from the aqueous portion, and the former dehydrated over calcium chloride. The excess of benzene is distilled off on the water-bath, and the dark-coloured residue fractionated up to 200°. It is then distilled *in vacuo* from a retort without condenser. At first an oil distils, which consists of impure diphenylmethane. When most of the diphenyl compound has passed over, the distillation suddenly slackens. The receiver is now changed, and the retort more strongly heated. An orange-coloured oil passes over, which crystallises in the receiver. The distillation is continued until the distillate no longer solidifies on cooling. A black, resinous mass remains in the retort. The crude triphenylmethane in the receiver is recrystallised from hot benzene, with which it forms a crystalline compound of the formula $C_{19}H_{16}.C_6H_6$. This is again crystallised. By heating the substance on the water-bath it loses benzene, and the hydrocarbon is finally crystallised from hot alcohol. Yield, 25—30 grams.

$$CHCl_3 + 3C_6H_6 = CH(C_6H_5)_3 + 3HCl.$$

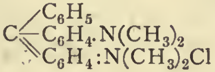
Properties.—Colourless plates ; m. p. 92° ; b. p. 360°.

Reactions.—**Synthesis of Pararosaniline.**—Dissolve a gram of the hydrocarbon in about 5 c.c. cold fuming nitric acid, pour into water, filter, wash, dry on porous plate, and dissolve in 5 c.c. glacial acetic acid. Add a gram of zinc dust on the point of a knife gradually, and shake up. The colour changes to brown, and the leuco-base of pararosaniline is formed. It is diluted with water and precipitated by ammonia. It is then filtered and dried. On gently warming the dry precipitate with a few drops of concentrated hydrochloric acid in a porcelain basin and then diluting with water, a magenta colouration is produced from the formation of pararosaniline hydrochloride (E. and O. Fischer). See *Appendix*, p. 312.

PREPARATION 103.

Benzaldehyde Green (Malachite Green)

(Tetramethyldiaminotriphenylmethane),



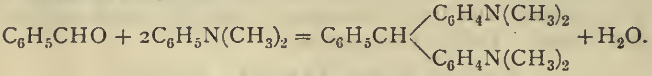
$$C\begin{array}{l}\diagup C_6H_5\\ - C_6H_4.N(CH_3)_2\\ \diagdown C_6H_4:N(CH_3)_2Cl\end{array}$$

O. Fischer, *Annalen*, 1883, **217**, 250, 262.

50 grms. dimethylaniline.
20 „ benzaldehyde.
40 „ zinc chloride (fused and powdered).

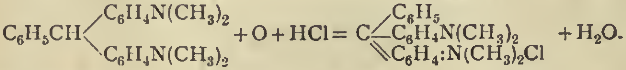
A mixture of the above is heated on the water-bath in a porcelain basin until the smell of benzaldehyde has disappeared

(4 hours). The viscous mass is melted in boiling water, transferred to a round flask ($1\frac{1}{2}$ litre) and distilled in steam until no more dimethylaniline passes over. On cooling, the base adheres to the flask and is washed by decantation. It is recrystallised from absolute alcohol and is colourless. The yield is nearly theoretical. This is the leuco-base, and is formed according to the following equation :



$$C_6H_5CHO + 2C_6H_5N(CH_3)_2 = C_6H_5CH\left\langle\begin{array}{l}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{array}\right. + H_2O.$$

It is converted into the colouring matter by oxidation. Ten grams of the base are dissolved by slightly warming with dilute hydrochloric acid containing exactly 2·7 grams of hydrogen chloride (made by diluting conc. hydrochloric acid with twice its volume of water and then determining the specific gravity or titrating with standard caustic soda). The liquid is diluted with 800 c.c. water, and 10 grams of a 40 per cent. acetic acid solution added. The mixture is cooled with a few lumps of ice, and a thin paste of freshly precipitated lead peroxide containing exactly 7·5 grams PbO_2 (estimated by drying a small weighed sample on the water-bath) is added in the course of five minutes with frequent shaking. The product is left 5 minutes, and then a solution of 10 grams sodium sulphate in 50 c.c. water is run in and the solution filtered from lead sulphate. To the filtrate a solution of 8 grams zinc chloride in a little water is added, and then a saturated solution of common salt until no more of the dye is thrown down. It is filtered, and recrystallised by dissolving in water and adding salt solution. Yield, 80 per cent. of the theory of zinc salt.



$$C_6H_5CH\left\langle\begin{array}{l}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{array}\right. + O + HCl = C\left\langle\begin{array}{l}C_6H_5\\C_6H_4N(CH_3)_2\\C_6H_4{:}N(CH_3)_2Cl\end{array}\right. + H_2O.$$

See *Appendix*, p. 313.

Naphthalene, $C_{10}H_8$

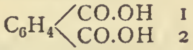
Naphthalene is obtained from the "middle oil" in the distillation of coal-tar. It crystallises in colourless, glistening plates, which have a characteristic smell.

Properties.—M. p. 80°; b. p. 218°; sp. gr. 1·145 at 4°. It sublimes readily, and can be distilled in steam. It is soluble in most of the common organic solvents.

Reaction.—Make strong solutions of about equivalent quantities of naphthalene and picric acid in acetic acid, or alcohol, and pour them together. On cooling, yellow, needle-shaped crystals of naphthalene picrate separate: $C_{10}H_8 + C_6H_2(NO_2)_3OH$; m. p. 149°.

PREPARATION 104.

Phthalic Acid,



$$C_6H_4\left\langle\begin{matrix}CO.OH & 1\\ CO.OH & 2\end{matrix}\right.$$

Friedländer. *Theerfarbenfabrikation*, iv, 164.

15 grms. naphthalene.
120 c.c. conc. sulphuric acid.
7·5 grms. mercuric sulphate.

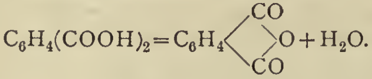
The mixture of naphthalene, sulphuric acid, and mercuric sulphate is placed in a retort (300 c.c.). The retort is clamped with the neck sloping upwards, and heated gently over wire-gauze with occasional shaking until the liquid surface layer of naphthalene dissolves.* The retort is now placed in the ordinary position, with the neck sloping down, to which a condenser tube is attached by means of a roll of asbestos paper, or a lute of plaster of Paris. The end of the condenser tube is provided with a receiver containing water (100 c.c.), and cooled in cold water.

The retort is now heated (at first cautiously and then strongly) over the bare flame, and the contents distilled. The liquid rapidly darkens in colour. At about 250° oxidation begins, with evolution of sulphur dioxide, which becomes very vigorous as the temperature of the liquid rises to the boiling-point. A little naphthalene first distils, and after a time crystals of phthalic anhydride appear in the condenser tube, whilst phthalic acid collects in the receiver. The distillation is continued until the residue becomes viscid or even dry. The contents of the receiver, when cold, are filtered and washed, and then dissolved in caustic soda. Any undissolved naphthalene is removed by filtration, and the acid reprecipitated by hydrochloric acid. The acid may be recrystallised from water or dilute alcohol. Yield, about 7 grams.

$$C_{10}H_8 + 9H_2SO_4 = C_6H_4(COOH)_2 + 2CO_2 + 9SO_2 + 10H_2O.$$

Properties.—Crystallises in plates with no definite melting-point, as the acid passes into the anhydride on heating. Soluble in alcohol and in hot water, slightly soluble in cold water.

Reactions.—Sublime a little of the acid in a test-tube or in a clock glass covered with a filter paper and funnel. Phthalic anhydride sublimes in long needles, m. p. 128°.



$$C_6H_4(COOH)_2 = C_6H_4\left\langle\begin{matrix}CO\\ \\CO\end{matrix}\right\rangle O + H_2O.$$

Heat about 0·25 gram of the anhydride with 0·5 gram of resorcinol in a test-tube over a small flame for a few minutes, so that the temperature remains at about 200°. Cool, dissolve in dilute caustic soda solution, and pour into water. A green fluorescence is produced, due to the formation of fluorescein (p. 187). See *Appendix*, 314.

PREPARATION 105.

β-Naphthalenesulphonate of Sodium, $C_{10}H_7SO_3Na$

Merz, Weith, *Ber.*, 1870, **3**, 196.

50 grms. naphthalene.
60 „ conc. sulphuric acid.

The mixture is heated in a round flask (250 c.c.) in the metal-bath to 160—170° for four or five hours. . The liquid is then poured into a basin of water (1 litre), which is heated up and neutralised with chalk or slaked lime in the form of a thick cream. The hot liquid is filtered through cloth, squeezed out, and washed with hot water. The filtrate is evaporated on a ring-burner until a sample crystallises on cooling. The crystalline mass of the calcium salt of naphthalene sulphonic acid is filtered and well pressed. It is redissolved in hot water, and a solution of sodium carbonate added, until the calcium is just precipitated. The liquid is again filtered through cloth, or at the pump, washed and well pressed. The filtrate is evaporated to crystallisation as before. The sodium naphthalene sulphonate is separated by filtration, and dried in a basin on the water-bath. The mother-liquor, on evaporation, yields a further quantity of the salt. Yield, about 60 grams.

1. $C_{10}H_8 + H_2SO_4 = C_{10}H_7SO_3H + H_2O$.
2. $2C_{10}H_7SO_3H + CaO = (C_{10}H_7SO_3)_2Ca + H_2O$.
3. $(C_{10}H_7SO_3)_2Ca + Na_2CO_3 = 2C_{10}H_7SO_3Na + CaCO_3$.

Properties.—Foliated crystals; soluble in water. See *Appendix*, p. 315.

PREPARATION 106.

β-Naphthol, $C_{10}H_7.OH$

Eller, *Annalen*, 1869, **152**, 275; E. Fischer, *Anleitung z. d. org. Präparate.*

30 grms. β-naphthalene sulphonate of sodium.
90 „ caustic soda.
3 c.c. water.

The caustic soda and water are heated in a nickel or silver crucible, and stirred with a thermometer, protected as described under the preparation of phenol (p. 179). When the temperature reaches 280°, the powdered naphthalene sulphonate is added a little at a time. When all has been added, the temperature is raised. At about 300° the mass froths up and becomes light yellow in colour, which indicates the commencement of the reaction. The temperature is maintained at 310°—320° for a few minutes, and the end of the process is indicated by the yellow mass becoming thinner and also darker in colour, and separating into two layers. The stirring is now stopped and the flame withdrawn. The product, when cold, is dissolved in a little water, and acidified with a mixture of equal volumes of concentrated hydrochloric acid and water.*

The naphthol is filtered off when cold, and is recrystallised from water. Yield, 15 grams.

$$C_{10}H_7SO_3Na + NaOH = C_{10}H_7ONa + NaHSO_3.$$

Properties.—Colourless leaflets; m. p. 122°; b. p. 286°.

Reactions.—Add to a solution of the naphthol in water a few drops of ferric chloride. A green colouration is produced, and after a time a flocculent precipitate of dinaphthol, $C_{20}H_{14}O_2$.

See also Reaction 6, p. 163.

β-Naphthyl methyl ether.—Dissolve 3·6 grams β-naphthol in 12·5 c.c. 10 per cent. caustic soda solution, add 3 c.c. methyl sulphate, warm the liquid gently and shake vigorously. In a short time the naphthyl methyl ether separates as a solid mass. The product is heated for ten minutes on the water-bath, a little water is added, and the naphthyl ether filtered and washed with water. It is crystallised from alcohol and deposits in lustrous plates; m. p. 70—72°. The yield is theoretical. It may be used for analysis by Zeisel's method.

Zeisel's Method.—The method consists in estimating methoxyl or ethoxyl groups by decomposing the substance with strong hydriodic acid and eliminating the alkyl group as alkyl iodide. The alkyl iodide is passed through an alcoholic solution of silver nitrate, which decomposes the alkyl iodide and the silver iodide is weighed.

$$R.OCH_3 + HI = R.OH + CH_3I.$$

The apparatus devised by W. H. Perkin, senior, is shown in Fig. 83 (*Proc. Chem. Soc.*, 1903, **19**, 1370).

It consists of a distilling flask (100 c.c.) with a long neck; the distance between the bulb and side tube is about 20 cms. (8 ins.). It is provided with an inlet tube which terminates above the surface of the liquid and is attached at the other end with a carbon dioxide Kipp and wash-bottle containing silver nitrate solution to remove traces of hydrochloric acid or hydrogen sulphide. The side tube of the distilling flask is attached to two small 100 c.c. Erlenmeyer flasks, provided with double-bored rubber corks. The first bent tube which is attached to the side tube of the distilling flask is cut off below the cork, the second terminates just above the surface of the liquid in the first flask and dips below the liquid in the second. The third or outlet tube is bent at right angles and is cut off below the cork.

The distilling flask is heated in a basin containing glycerol. The first Erlenmeyer flask is charged with 20 c.c. alcoholic silver nitrate, and the second with 15 c.c. of the same solution which is prepared by dissolving 2 grams of fused silver nitrate in 5 c.c. water and adding 45 c.c. absolute alcohol. An accurately weighed quantity (0·3—0·6 gram) of substance is introduced in a small weighing tube into the distilling flask and 15 c.c. of strong hydriodic acid (acid of sp. gr. 1·7 for Zeisel's estimations can be purchased). When the apparatus has been carefully fixed together the glycerol bath is heated to 130—140° and a slow current of carbon dioxide (two bubbles a second) is passed through the apparatus. The temperature of the glycerol bath is slowly raised until the hydriodic acid begins to boil gently. A white deposit (a compound of silver iodide and nitrate) begins to form on the surface of the first flask and gradually settles to the bottom, but usually only a trace appears in the second vessel. The operation is generally completed in one hour; but before stopping the process it is advisable to test the vapour passing through by removing the flasks and attaching the small bent **U**-tube (shown in the Fig. and containing a little alcoholic silver nitrate solution) to the end of the side tube. If in the course of ten minutes no turbidity appears, the operation may be considered at an end, otherwise it is necessary to connect up the flask and continue the heating for another twenty minutes.

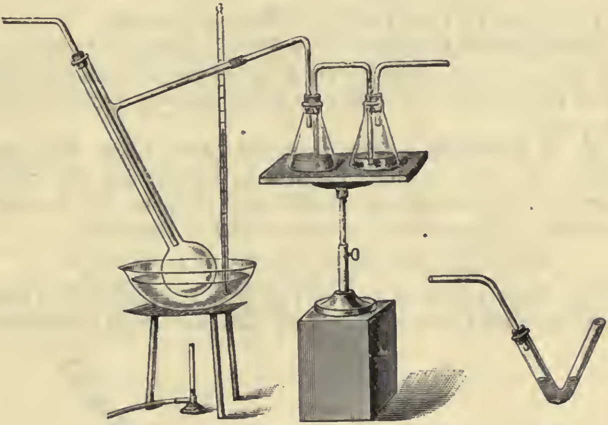


FIG. 83.

About 50 c.c. of water are heated to boiling in a beaker (250 c.c.) and the contents of both flasks gradually added and well washed out with hot water. The white precipitate changes to the yellow iodide and the alcohol is driven off.

When the top liquid is no longer opalescent but clear, the precipitate is collected in a Gooch crucible and dried and weighed as described on p. 26.

For volatile substances like anisole this method cannot be employed.

Example.—0·3150 gram naphthyl ether gave 0·468 gram AgI:

$$\frac{31 \times 0{\cdot}468 \times 100}{235 \times 0{\cdot}3150} = 19{\cdot}6 \text{ per cent.}$$

Calculated for $C_{10}H_7OCH_3$:CH_3O = 19.6 per cent.

β-Naphthyl Acetate.—Boil gently 5 grams β-naphthol and 10 grams acetic anhydride for ½ hour with air condenser and pour the product into water. Crystallise from dilute alcohol; m. p. 70°.

A. G. Perkin's Acetyl method. (*Proc. Chem. Soc.*, 1904, **20**, 171). The method consists in hydrolysing the acetyl derivative in presence of alcohol and distilling off the ethyl acetate and then estimating the quantity by hydrolysis.

$$R.O.COCH_3 + C_2H_5OH = R.OH + CH_3.COOC_2H_5.$$

The apparatus is shown in Fig. 84. It consists of a small distilling flask (200 c.c.) with bent side-tube which is fitted to a long condenser A tap-funnel is inserted into the neck and the flask is heated over wire-gauze. About 0·5 gram of naphthyl acetate is accurately weighed out of a small sample tube by

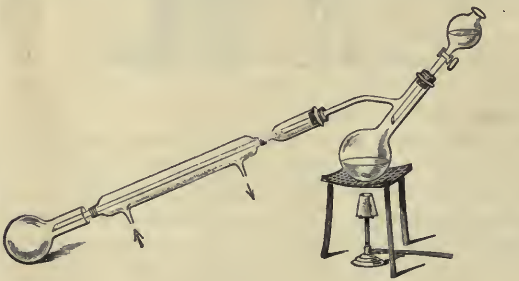


FIG. 84.

difference and any dust adhering to the neck of the flask washed down with 5 c.c. pure conc. sulphuric acid and 30 c.c. pure alcohol, which are slowly run in with shaking. A small fragment of porous pot is also added. Twenty c.c. half-normal alcoholic potash (see p. 210) are introduced into the round flask (200 c.c.) which serves as receiver and 20 c.c. pure alcohol are poured into the tap-funnel. The liquid in the flask is slowly distilled whilst the alcohol is delivered drop by drop from the tap-funnel at about the same rate as the liquid distils. The distillation is continued until about half the bulk of liquid originally present in the flask remains. This residue should be quite colourless. The receiver is now attached to a reflux condenser and boiled on the water-bath for ½ hour and finally titrated with half-normal sulphuric acid, using phenolphthalein as indicator.

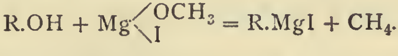
The method does not give good results with acetamido-compounds like acetanilide, &c.

Example.—0·663 gram naphthyl acetate required 7·5 c.c. N/2 KOH.

$$\frac{7{\cdot}5 \times 0{\cdot}043 \times 100}{2 \times 0{\cdot}633} = 23{\cdot}6 \text{ per cent.}$$

Calculated for $C_{10}H_7.O.COCH_3$; $C_2H_3O = 23{\cdot}1$ per cent.

Tschugaeff's Hydroxyl Method.—This method rests upon the action of hydroxyl compounds on magnesium methyl iodide by which methane is evolved.



$$R.OH + Mg\begin{cases}OCH_3\\I\end{cases} = R.MgI + CH_4.$$

The apparatus is an ordinary Lunge nitrometer filled with mercury, which together with the attached Erlenmeyer flask is kept at constant temperature by a flow of water through an outer jacket. The three-way cock is connected with the Erlenmeyer flask (150 c.c.) by stout rubber tubing. A stock solution of magnesium methyl iodide is first prepared by mixing together in a flask connected with a reflux condenser 100 grams amyl ether distilled over sodium, 9·6 grams clean magnesium ribbon and 35·5 grams dry methyl iodide and a few iodine crystals. After the first reaction is over the mixture is heated for 1—2 hours on the water-bath with condenser to expel unchanged methyl iodide, and preserved in a vaselined stoppered vessel. About 0·1—0·15 gram β-naphthol is accurately weighed in a tube which is of such a length that it rests against the side of the nitrometer flask. About 10 c.c. of the reagent are poured into the flask ; the tube containing the substance, which is dissolved in a little amyl ether, is slipped in ; the flask is attached to the side tube of the nitrometer and is then cut off from the nitrometer tube by turning the tap. A little moisture and oxygen in the flask are absorbed by the reagent and the pressure falls. After standing for ¼ hour the nitrometer tube is nearly filled up with mercury, the tap is withdrawn for a moment to readjust pressure and the tube then completely filled with mercury. The tap is now turned so as to establish communication between the flask and nitrometer tube and the mercury reservoir lowered. The tube containing the solution of the naphthol is inverted and shaken. Evolution of methane rapidly occurs and in a short time the volume remains constant. The volume, temperature and pressure are read off and the percentage of hydroxyl calculated.

Example.—0·120 gram β-naphthol gave 20 c.c. methane at N.T.P.

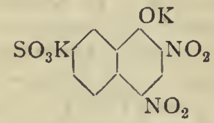
$$\frac{20 \times 17 \times 100}{22400 \times 0{\cdot}120} = 12{\cdot}6.$$

Calculated for $C_{10}H_7OH$; OH = 11·8 per cent.

(Tschugaeff, *Ber.*, 1902, **35**, 3912 ; Hibbert and Sudborough, *Proc. Chem. Soc.*, 1903, **19**, 285 ; Zerewitinoff, *Ber.*, 1907, **40**, 2023.) See *Appendix*, p. 315.

PREPARATION 107.

Naphthol Yellow,



Friedländer, *Theerfarbenfabrikation*, I, 322, II., 215 ; Cain and Thorpe, *The Synthetic Dyestuffs*, p. 226.

20 grms. α-naphthol.
80 „ (45 c.c.) conc. sulphuric acid.
40 „ (30 c.c.) conc. nitric acid (sp. gr. 1·4).

The mixture of α-naphthol and sulphuric acid is heated for 2 hours to 120° and then dissolved in 120 c.c. water. The solution is cooled to 20° and stirred mechanically whilst the nitric acid is run in drop by drop. As the temperature should not rise above 40° it will be found necessary at the beginning to cool the vessel in a freezing mixture. After the nitric acid has been added the stirring is continued for another ½ hour and the product is then left overnight. The naphthol yellow crystallises out and is filtered and washed with small quantities of a cold, saturated solution of salt. The precipitate is then dissolved in a large basin of hot water and potassium carbonate solution added until the liquid gives an alkaline reaction. On cooling, the potassium salt separates in small orange needles, and is filtered and dried on a porous plate. Yield, 20—25 grams.

$$C_{10}H_7OH + 3H_2SO_4 = C_{10}H_4(OH)(SO_3H)_3.$$

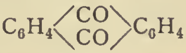
$$C_{10}H_4(OH)(SO_3H)_3 + 2HNO_3 = C_{10}H_4(OH)(NO_2)_2SO_3H + 2H_2SO_4.$$

$$2C_{10}H_4(OH)(NO_2)_2SO_3H + K_2CO_3 = 2C_{10}H_4(OH)(NO_2)_2SO_3K + CO_2 + H_2O.$$

See *Appendix*, p. 315.

PREPARATION 108.

Anthraquinone,



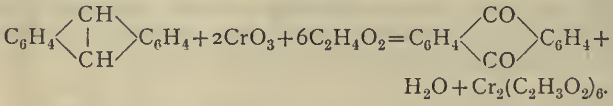
$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4$$

Graebe, Liebermann, *Annalen*, *Spl.*, 1869, **7**, 28

10 grms. anthracene (pure).
120 c.c. glacial acetic acid.
20 grms. chromium trioxide dissolved in 15 c.c. water, and then 75 c.c. glacial acetic acid added.

The anthracene is dissolved in the acetic acid by boiling them together in a round flask (½ litre) with upright condenser over wire-gauze. The solution of chromium trioxide is then dropped in from a tap-funnel pushed into the top end of the condenser whilst the liquid is kept boiling. The operation should last about an hour. The solution becomes a deep green. It is allowed to cool and poured into water (500 c.c.), which precipitates the anthraquinone in the form of a brown powder. After standing an hour, it is filtered through a large fluted filter, washed with a little hot water, then with warm dilute caustic soda and water again. Yield, 10—12 grams.

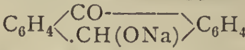
Sublimation.—A portion of the dry substance may be purified by sublimation. It is placed (2—3 grams) on a large watch-glass, which is heated on the sand-bath over a very small flame. The watch-glass is covered with a sheet of filter paper, which is kept flat by a funnel placed above. After five minutes or so pale yellow, needle-shaped crystals of anthraquinone will have sublimed on to the filter paper.



$$C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4+2CrO_3+6C_2H_4O_2=C_6H_4\left\langle\begin{matrix}CO\\ \\CO\end{matrix}\right\rangle C_6H_4+H_2O+Cr_2(C_2H_3O_2)_6.$$

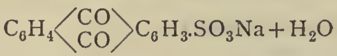
Properties.—Yellow needles: m. p. 277°; sublimes at 250°; b. p. 382°; insoluble in water, soluble in acetic acid, less soluble in benzene and other organic solvents.

Reaction.—Add a little dilute caustic soda to a small quantity of anthraquinone, and then a little zinc dust. On heating to boiling, an intense red colouration is produced, which disappears on shaking. Sodium oxanthranolate, $C_6H_4\left\langle\begin{matrix}CO\text{-----}\\.CH(ONa)\end{matrix}\right\rangle C_6H_4$, formed, which oxidises in the air to anthraquinone. See *Appendix*, p. 316.



PREPARATION 109.

Anthraquinone β-monosulphonate of Sodium,



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_3.SO_3Na+H_2O$$

Graebe, Liebermann, *Annalen*, 1871, **160**, 131; A. G. Perkin. Private communication.

30 grms. anthraquinone.
30 „ fuming sulphuric acid (40 per cent. SO_3).[1]

The 40 per cent. fuming sulphuric acid is removed from the bottle by cautiously melting it in a sand-bath, and it is then weighed out in a flask (½ litre). The anthraquinone is added, and the flask attached by a cork to an air-condenser. The

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[1] As fuming sulphuric acid is difficult to keep in an ordinary stoppered bottle without absorbing moisture, it is advisable to coat the stopper with a layer of paraffin wax, and a substantial covering of plaster of Paris above this.

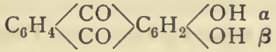
mixture is heated in a paraffin or metal-bath to 150—160° for 8 hours. The dark coloured mass is poured *whilst hot* into a large basin containing about a litre of cold water, and boiled for an hour. The unattacked anthraquinone, which does not dissolve, is removed by filtration at the pump. The precipitate is then replaced in the basin and boiled up again with about ½ litre of water, filtered and finally washed once or twice with boiling water. The combined filtrate and washings, which have a deep brown colour, are evaporated with the addition of 0·2 gram of potassium chlorate until about ½ litre of liquid remains. It is now nearly neutralised with sodium carbonate solution (about 120 grams soda crystals) but not completely, as the sodium salt of the monosulphonic acid is less soluble in presence of acid. It is therefore convenient to pour out half a test-tube of the acid liquid, and proceed to neutralise the remainder. The small quantity of acid liquid is then replaced. The liquid is evaporated on the water-bath until a scum covers the surface, and it is then left to cool. The sodium salt of the sulphonic acid crystallises in pale yellow, silky crystals, and is separated at the pump. After being washed three or four times with a very little slightly acid water, it is dried on a porous plate. Yield, 20—25 grams. A further quantity of the salt may be obtained by evaporating the mother-liquor, but it is liable to contain sodium sulphate.

$$C_{14}H_8O_2 + H_2SO_4 = C_{14}H_7O_2.SO_3H + H_2O.$$

Properties.—The sodium salt of the sulphonic acid crystallises, when pure, in colourless leaflets, slightly soluble in cold water, insoluble in alcohol.

PREPARATION 110.

Alizarin,

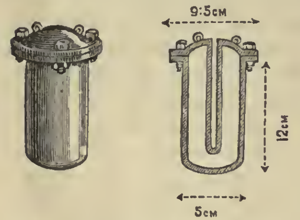


$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_2\left\langle\begin{matrix}OH\ \alpha\\OH\ \beta\end{matrix}\right.$$

Graebe, Liebermann, *Annalen*, *Spl.*, 1869, 300; Perkin, *Engl. Patent*, 1869, No. 1948; A. G. Perkin. Private communication.

20 grms. anthraquinone monosulphonate of sodium.
90 „ caustic soda.
5 „ potassium chlorate.

The caustic soda is dissolved in about half its weight of water, and is added hot to the anthraquinone sulphonate of sodium, previously mixed into a paste with the potassium chlorate dissolved in about 50 c.c. of water. The mixture, which forms a stiff paste, is transferred at once to a small metal pressure tube of steel or phosphor-bronze of the shape and dimensions shown in Fig. 85.[1] The mixture fills it about two-thirds full. A sheet of asbestos cardboard is inserted between the body and the top of the vessel, and the metal top is then screwed firmly on. The pressure tube is heated for three hours in a paraffin or oil-bath, so that the thermometer inserted into the inner tube, which contains a little paraffin, registers 190—200°. The dark violet coloured mass, after cooling, is scraped out and digested with boiling water for an hour. Milk of lime is added until the violet calcium alizarate is all precipitated. This can be ascertained in a small filtered sample by adding a little milk of lime, when no violet precipitate should be formed. The precipitate is filtered at the pump and washed with boiling water until the filtrate is no longer red. The red filtrate contains a little monohydroxyanthraquinone, which may be precipitated by hydrochloric acid. The calcium alizarate on the filter is suspended in a large quantity of hot water, and decomposed by adding hydrochloric acid. The alizarin, which separates as an orange, flocculent precipitate, is filtered cold, washed about eight times with cold water, and finally dried and crystallised from alcohol or preferably cumene. Yield, 10—15 grams.



The thickness of the metal is 1 cm.

FIG. 85.

$$3C_{14}H_7O_2SO_3Na + 9NaOH + 2KClO_3 = 3C_{14}H_6O_2(ONa)_2 + 3Na_2SO_4 + 2KCl + 6H_2O.$$

Properties. Orange needles; m. p. 289—290°; sublimes completely at 140° without decomposition; soluble in alkalis with a deep purple colour (sodium alizarate). It is reduced to anthracene on heating with dry zinc dust.

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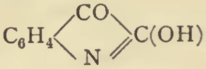
[1] The apparatus was made for us by West's Gas Improvement Co., Miles Platting, Manchester.

Reaction.—Make a small quantity of solution of alizarin in caustic soda, and pour into a beaker containing a strong solution of alum. The insoluble aluminium alizarate is precipitated as a red lake. See *Appendix*, p. 316.

PREPARATION III.

Isatin from Indigo,



$$C_6H_4\left\langle \begin{matrix} CO \\ N \end{matrix} \right\rangle C(OH)$$

Erdmann *J. prakt. Chem.*, 1841, **24**, 11; Knop, *Jahresb.* 1865, 580.

100 grms. indigo (in fine powder).
50 c.c. conc. nitric acid diluted with 10 c.c. water.

Mix up the indigo into a paste with 300 c.c. of boiling water in a large basin. Heat to boiling and remove the flame. Then add the nitric acid to the hot liquid from a tap-funnel at the rate of a drop or two a second, so that it is all added in the course of twenty minutes, and stir well all the time. The mass, which is at first pasty, froths up, and towards the end becomes thinner. Boil up for about two minutes, as soon as the acid has all been added, and then pour out about half the liquid into a second large basin and add a litre of boiling water to each. Boil up for five minutes, and decant from the floating lumps of tarry matter through a large fluted filter paper previously moistened with water. Add another litre of hot water to each basin, boil up, and filter. Evaporate the combined red coloured filtrates to about 1½ litre, and filter again, if necessary, from a further deposit of tar. On cooling, a quantity of red crystals discoloured with tar will separate. Filter and concentrate the filtrate. Redissolve the crystals in the smallest quantity of boiling water, and let the liquid cool somewhat, so that some of the tarry matter may separate; filter and evaporate the filtrate, until crystals of isatin nearly cover the surface; then cool and filter off the red crystalline deposit. A further quantity of crystals may be obtained by evaporating the mother-liquors, which must be frequently filtered from tarry deposit. The crystals obtained in this way may be purified by dissolving them in caustic potash solution, and adding concentrated hydrochloric acid to the clear liquid so long as a black precipitate is formed. The liquid is then filtered, and the purified isatin completely thrown down in the filtrate with more acid. The substance is then filtered and recrystallised from water. Yield, about 10 grams.

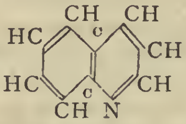
$$C_{16}H_{10}N_2O_2 + O_2 = 2C_8H_5NO_2.$$

Properties.—Red monoclinic prisms; m. p. 201°; soluble in hot water and alcohol.

Reaction.—Dissolve a few crystals in concentrated sulphuric acid in the cold and shake up with a little coal-tar benzene. A blue colour due to thiophene is produced. See *Appendix*, p. 318.

PREPARATION 112.

Quinoline,



Skraup, *Monatsh.*, 1880, **1**, 316; 1881, 2. 141; Königs, *Ber.*, 1880, **13**, 911.

24	grms.	nitrobenzene.
38	,,	aniline.
120	,,	glycerol.
100	,,	conc. sulphuric acid.

A large round flask ($1\frac{1}{2}$—2 litres) is attached to an upright condenser. The mixture of nitrobenzene, aniline, glycerol, and sulphuric acid is poured in and heated on the sand-bath until the reaction sets in (ten to fifteen minutes), *i.e.* until white vapours rise from the liquid. The flask is now raised from the sand-bath or the burner extinguished, and when the first reaction is over the contents are gently boiled for two to three hours. The dark coloured product is diluted with water, and unchanged nitrobenzene driven over with steam. The residue is made strongly alkaline with caustic soda, and the oily layer (quinoline and aniline) distilled off with steam. In order to remove the aniline present, the distillate is acidified with sulphuric acid, and sodium nitrite added, until a sample of the liquid ceases to give the aniline reaction with sodium hypochlorite. It is then boiled, whereby the aniline is converted into phenol. The liquid is again made alkaline with caustic soda, and submitted to a third distillation with steam. The distillate is extracted with ether, dehydrated over solid caustic potash, and, after decanting and driving off the ether, the residue is distilled. Yield, 40 grams of a pale yellow oil.

$$C_6H_5NH_2+C_3H_5(OH)_3+O=C_9H_7N+4H_2O.$$

Properties.—Colourless liquid; b. p. 237°; sp. gr. 1·108 at 0°; insoluble in water; soluble in alcohol and ether.

Reactions.—1. Dissolve a few drops of quinoline in a little hydrochloric acid and add platinic chloride. Orange crystals of the chloroplatinate are deposited $(C_9H_7N)_2H_2PtCl_6+H_2O$.

2. Add to a solution of quinoline in acid, potassium chromate solution; the dichromate, $(C_9H_7N)_2H_2Cr_2O_7$, is precipitated.

3. Add to 1 c.c. of quinoline 1 c.c. of methyl iodide and warm. A reaction sets in, and on cooling, the quaternary ammonium iodide, $C_9H_7N.CH_3I$, crystallises in yellow crystals.

4. To a few drops of quinoline add a solution of bromine in chloroform. A crystalline compound, $C_9H_7N.Br_2$, is formed. See *Appendix*, p. 318.

PREPARATION 113.

Quinine Sulphate from Cinchona Bark,

$$C_{20}H_{24}N_2O_2.SO_4H_2+8H_2O$$

Pelletier, Caventou, *Ann. Chim. Phys.*, 1820, (2), **15**, 291.

100 grms. cinchona bark (ground in a coffee mill).
20 „ quicklime.

Slake the quicklime, and mix it into a thin cream with 200 c.c. water. Pour the liquid into a basin containing the powdered bark and stir up the mass well. Dry the mixture thoroughly on the water-bath, taking care to powder up the lumps that ball together. When cold place the powder in a flask, pour over it 200 c.c. chloroform, and let the mixture stand overnight. Filter through a porcelain funnel and wash with a further 200 c.c. chloroform. The chloroform solution, which has now a faint yellow colour, is shaken up well with 50 c.c. and again with 25 c.c. dilute sulphuric acid, and then with water until the aqueous solution has no longer a blue fluorescence. The combined acid and aqueous extracts are carefully neutralised with ammonia and the liquid concentrated on the water-bath until crystals of quinine sulphate begin to form on the surface. The liquid is allowed to cool and filtered. A further quantity of crystals may be obtained from the mother-liquor by evaporation, but the product is not so pure. The crystals are purified by recrystallisation from water. Yield, 1 to 2 grams, or more, according to the quality of the bark.

Properties.—The free base, which is precipitated with sodium carbonate from a solution of its salts, crystallises with $3H_2O$. The anhydrous base melts at 277° ; soluble in alcohol and ether.

Reactions.—Use a solution of the hydrochloride prepared by adding a few drops of hydrochloric acid to the sulphate mixed with water.

1. Add to a little of the solution a few drops of iodine solution ; a brown amorphous precipitate is formed. This reaction is given by many of the alkaloids.

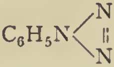
2. Add chlorine water and then ammonia in excess. An emerald green colouration is produced.

3. Add sodium carbonate solution and then shake with ether. The free base is precipitated and dissolves in the ether. Decant the ether on to a watch-glass and let it evaporate. Crystals of the base remain.

4. Dissolve in a few drops of acetic acid and add a large volume of water. A blue fluorescent liquid is obtained. See *Appendix*, p. 319.

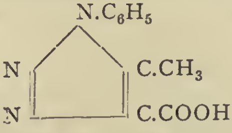
PREPARATION 114.

Diazobenzolimide,



$$C_6H_5N\left\langle\begin{matrix}N\\ \| \\ N\end{matrix}\right.$$

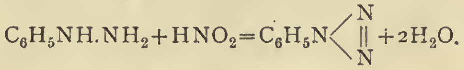
Phenylmethyltriazole carboxylic Acid,



Dimroth, *Ber.*, 1902, **35**, 1,029.

30 grms. phenylhydrazine.
45 c.c. conc. hydrochloric acid (in 400 c.c. water).
24 grms. sodium nitrite (in 50 c.c. water).

The phenylhydrazine and hydrochloric acid are mixed together, stirred mechanically and cooled with a few lumps of ice whilst the nitrite solution is added, until the test with starch-iodide paper shows that an excess is present. The hydrochloride dissolves, and diazobenzolimide separates out as an oil.

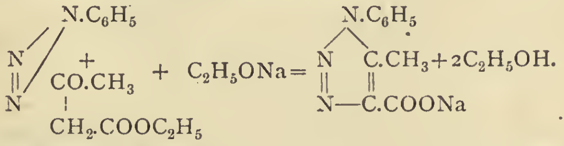


$$C_6H_5NH.NH_2+HNO_2=C_6H_5N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right.+2H_2O.$$

Part of the water is removed by a syphon and the oil is extracted with ether; after removing the ether, the diazobenzolimide is purified by distillation in steam. It is again extracted and separated with ether as before. Yield, about 25 grams.

4 grms. sodium.
68 c.c. absolute alcohol.
22 grms. acetoacetic ester.
20 „ diazobenzolimide.

The sodium is dissolved in the alcohol, and to the cold solution a mixture of the acetoacetic ester and diazobenzolimide is added, and then warmed to boiling with reflux condenser. As soon as this occurs, the flask is removed and cooled, if the action becomes too violent. After the reaction is over, the mixture is heated for an hour on the water-bath with reflux condenser, when the contents of the flask become almost solid. The mass is dissolved in the smallest quantity of hot water, and the liquid, if neutral, made strongly alkaline and boiled again for an hour. About 350 c.c. hot water are added, and sufficient hydrochloric acid to precipitate the triazole carboxylic acid. It is filtered and washed with a little water, and is then nearly pure; m. p. 155°. Yield, about 27 grams.



See *Appendix*, p. 320.

APPENDIX

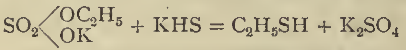
NOTES ON THE PREPARATIONS

PREPARATION 1.

Ethyl Potassium Sulphate.—The combination between alcohol and sulphuric acid is not complete, a condition of equilibrium being reached before either constituent is completely converted. The reaction is known as a *reversible* one and may be represented thus :

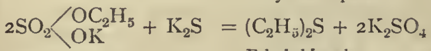
$$C_2H_5OH + H_2SO_4 \rightleftarrows C_2H_5HSO_4 + H_2O,$$

which implies that the alkyl sulphate reacts with water, regenerating alcohol and sulphuric acid. The free alkyl acid sulphates are, as a rule, viscid liquids, which cannot be distilled without yielding the olefine. On boiling with water, the alcohol is regenerated. The salts are used for preparing various alkyl derivatives, such as mercaptans, thio-ethers and cyanides.



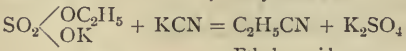
$$SO_2\Big\langle\begin{matrix}OC_2H_5\\ OK\end{matrix} + KHS = C_2H_5SH + K_2SO_4$$

Ethyl mercaptan.



$$2SO_2\Big\langle\begin{matrix}OC_2H_5\\ OK\end{matrix} + K_2S = (C_2H_5)_2S + 2K_2SO_4$$

Ethyl thio-ether.



$$SO_2\Big\langle\begin{matrix}OC_2H_5\\ OK\end{matrix} + KCN = C_2H_5CN + K_2SO_4$$

Ethyl cyanide.

Compare the action of sulphuric acid on phenol (see Prep. 74, p. 177).

PREPARATION 2.

Ethyl Bromide.—The replacement of the hydrogen by halogen (Cl, Br) may be effected by the direct action of the halogen on the paraffin.

$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl.$$

A simpler method is to replace the alcohol *hydroxyl* by halogen by the action of hydracid (HCl, HBr, HI),

$$C_2H_5OH + HCl = C_2H_5Cl + H_2O.$$

Or by that of the phosphorus compound (PCl_3, PBr_3, PI_3),

$$3C_2H_5OH + PCl_3 = 3C_2H_5Cl + P(OH)_3.$$

The preparation of ethyl bromide may be taken as an example of the first method, in which the hydracid is liberated by the reaction,

$$KBr + H_2SO_4 = HBr + KHSO_4.$$

A further example is that of isopropyl iodide: see Prep. 31, p. 110, in which the hydriodic acid is obtained by the action of water on phosphorus iodide,

$$PI_3 + 3H_2O = 3HI + P(OH)_3.$$

The action of HCl is much more sluggish than that of HBr or HI, and in the preparation of ethyl chloride a dehydrating agent ($ZnCl_2$) is usually added to the alcohol, which is kept boiling whilst the HCl gas is passed in. In the case of polyhydric alcohols, all the hydroxyl groups cannot be replaced by Cl by the action of HCl. Glycol gives ethylene chlorhydrin and glycerol yields the dichlorhydrin (see Prep. 32, p. 111). The use of PBr_3, PI_3 does not necessitate the previous preparation of these substances. Amorphous phosphorus is mixed with the alcohol, and bromine or iodine added as in the preparation of methyl iodide (see Prep. 6, p. 68). PCl_5 or PCl_3 will always replace OH by chlorine in all hydroxy-compounds, including phenols, on which HCl does not act.

The alkyl halides are utilised in a variety of reactions, examples of which are given, ethyl iodide being taken as the type.

1. *Aqueous* potash or water with metallic oxide (Ag_2O, PbO) yields the alcohol (see Prep. 87, p. 195),

$$C_2H_5I + KOH = C_2H_5OH + KI.$$

2. *Alcoholic* potash gives an olefine,

$$C_2H_5I + KOH = C_2H_4 + KI + H_2O.$$

3. Sodium alcoholate gives an ether,

$$C_2H_5I + NaOC_2H_5 = C_2H_5OC_2H_5 + NaI.$$

4. Alcoholic ammonia forms a mixture of primary, secondary and tertiary amines,

$$C_2H_5I + NH_3 = C_2H_5NH_2 + HI$$
$$2C_2H_5I + NH_3 = (C_2H_5)_2NH + 2HI$$
$$3C_2H_5I + NH_3 = C_2H_5)_3 N + 3HI.$$

The tertiary amines unite with the alkyl iodide to form the quaternary ammonium iodide, which is produced at the same time as the other products.

$$(C_2H_5)_3N + C_2H_5I = (C_2H_5)_4NI.$$

5. Potassium cyanide forms alkyl cyanide,

$$C_2H_5I + KCN = C_2H_5CN + KI.$$

6. Potassium hydrosulphide gives the mercaptan,

$$C_2H_5I + KSH = C_2H_5SH + KI.$$

7. Potassium sulphide forms the thio-ether,

$$2C_2H_5I + K_2S = (C_2H_5)_2S + 2KI$$

8. Silver nitrite gives the nitro-paraffin,

$$C_2H_5I + AgNO_2 = C_2H_5NO_2 + AgI.$$

9. Silver salts of organic or inorganic acids yield the alkyl esters,

$$2C_2H_5I + Ag_2SO_4 = (C_2H_5)_2SO_4 + 2AgI.$$
$$C_2H_5I + CH_3.COOAg = CH_3.COOC_2H_5. + AgI.$$

PREPARATION 3.

Ethyl Ether.—This reaction is of a general character. By using a different alcohol in the reservoir from that in the flask, a *mixed* ether may be obtained. Thus, ethyl alcohol and amyl alcohol may be combined to form ethyl amyl ether,

$$C_2H_5OH + H_2SO_4 = C_2H_5SO_4H + H_2O.$$
$$C_2H_5HSO_4 + C_5H_{11}OH = C_2H_5OC_5H_{11} + H_2SO_4.$$

That the sulphuric acid acts in the above manner and not merely as a dehydrating agent appears not only from the formation of mixed ethers, but also from the fact that the sulphuric acid may be replaced by phosphoric, arsenic and benzene sulphonic acids.

The ethers are also formed by the action of sodium alcoholate on the alkyl iodide (Williamson),

$$C_2H_5ONa + C_2H_5I = C_2H_5.O.C_2H_5 + NaI,$$

and by this method mixed ethers may also be prepared.

The inertness of the ethers arises probably from the fact that the whole of the hydrogen present is united to carbon. Note the action of sodium and PCl_5 on alcohol and on ether. The ethers are not decomposed with PCl_5 except on heating, when they give the alkyl chlorides,

$$(C_2H_5)_2O + PCl_5 = 2C_2H_5Cl + POCl_3.$$

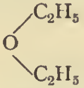
Hydracids, especially HI, have a similar action—

$$(C_2H_5)_2O + 2HI = 2C_2H_5I + H_2O.$$

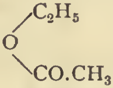
Hot, strong sulphuric acid breaks up ether into ethyl sulphuric acid and water,

$$(C_2H_5)_2O + 2H_2SO_4 = 2C_2H_5.SO_4H + H_2O.$$

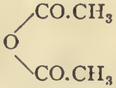
Compare the action of caustic alkalis on ethers, esters and anhydrides.



Diethyl ether.



Ethyl acetate.



Acetic anhydride.

PREPARATION 4.

Ethylene Bromide.—The formation of olefines by the action of conc. H_2SO_4 and other dehydrating agents on the alcohols is a very general reaction. Among the higher alcohols the action of heat alone suffices; cetyl alcohol, $C_{16}H_{34}O$, gives cetylene, $C_{16}H_{32}$, on heating. The olefines are also obtained by the action of alcoholic potash on the alkyl bromides and iodides,

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O,$$

and by the electrolysis of the dibasic salts; potassium succinate gives ethylene,

$$C_2H_4(COOK)_2 = C_2H_4 + 2CO_2 + K_2(H_2).$$

The olefines combine with:

(1) Hydrogen in presence of platinum black, or finely divided nickel (see Prep. 78, p. 181).

$$\underset{\text{Ethylene.}}{CH_2:CH_2} + H_2 = \underset{\text{Ethane.}}{CH_3.CH_3}.$$

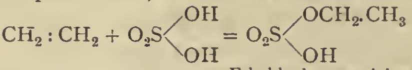
(2) The hydracids (HCl, HBr, HI), in which case the halogen attaches itself to the carbon with the least number of hydrogen atoms,

$$\underset{\text{Propylene.}}{CH_3.CH{:}CH_2} + HI = \underset{\text{Isopopyl iodide.}}{CH_3.CHI.CH_3}.$$

(3) The halogens (Cl, Br, I),

$$\underset{\text{Ethylene.}}{CH_2{:}CH_2} + Cl_2 = \underset{\text{Ethylene chloride.}}{CH_2Cl.CH_2Cl}.$$

(4) Conc. sulphuric acid,



$$CH_2 : CH_2 + O_2S\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} = O_2S\begin{matrix}\diagup OCH_2.CH_3\\ \diagdown OH\end{matrix}$$

Ethyl hydrogen sulphate.

(5) Hypochlorous acid,

$$CH_2{:}CH_2 + HOCl = \underset{\text{Ethylene chlorhydrin.}}{CH_2OH.CH_2Cl}.$$

Potassium permanganate oxides the olefine, forming in the first stage the corresponding glycol. By further oxidation the molecule is decomposed by the parting of the carbon atoms at the original double link,

$$\underset{\text{Propylene.}}{CH_3.CH : CH_2} + H_2O + O = \underset{\text{Propylene glycol.}}{CH_3.CHOH.CH_2OH}.$$

$$CH_3.CHOH.CH_2OH + 2O_2 = \underset{\text{Acetic acid.}}{CH_3.COOH} + CO_2 + 2H_2O.$$

Alkylene chlorides and bromides with both halogen atoms attached to the same carbon are obtained by the action of PCl_5 and PBr_5 on aldehydes and ketones.

$$CH_3.CO.CH_3 + PCl_5 = \underset{\beta\beta\text{-Dichloropropane.}}{CH_3.CCl_2.CH_3} + POCl_3.$$

PREPARATION 5.

Acetaldehyde.—The formation of aldehyde from alcohol probably occurs by the addition of oxygen and subsequent elimination of water,

$$CH_3CH_2OH + O = CH_3.CH(OH)_2 = CH_3.CO.H + H_2O.$$

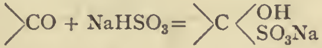
The aldehydes may also be obtained by the reduction of acid chlorides and of anhydrides in some cases, but the method is rarely adopted. Aldehydes can only be obtained directly from the fatty acids by distilling the calcium salt with calcium formate; but in no case by direct reduction, unless in the form of lactones,

$$(CH_3.COO)_2Ca + (HCOO)_2Ca = 2CH_3.CO.H + 2CaCO_3.$$

The aldehydes are readily reduced to the alcohols. Characteristic properties of the aldehydes are the formation of aldehyde ammonias, Schiff's reaction, the reduction of metallic salts and the production of *acetals* by the action of alcohol in presence of hydrochloric acid gas (E. Fischer).

$$CH_3.CO.H + 2C_2H_5OH = \underset{\text{Acetal.}}{CH_3.CH(OC_2H_5)_2} + H_2O.$$

They also polymerise readily. These reactions should be compared with those of benzaldehyde (Prep. 88, p. 196). There are many reactions which are common to both aldehydes and ketones, *i.e.*, to all substances which contain a ketone CO group Such, for example, are: (1) The formation of an additive compound with sodium bisulphite.

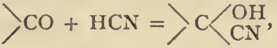


$$>CO + NaHSO_3 = >C\langle{}^{OH}_{SO_3Na}$$

(2) The action of PCl_5, which replaces oxygen by chlorine,

$$>CO + PCl_5 = >CCl_2 + POCl_3.$$

(3) The formation of a cyanhydrin with hydrocyanic acid,



$$>CO + HCN = >C\langle{}^{OH}_{CN},$$

which on hydrolysis yields a hydroxy-acid.

(4) The formation of an oxime with hydroxylamine (see Preps. 9, p. 71, and 89, p. 197).

$$>CO + H_2NOH = >C:NOH + H_2O.$$

(5) The formation of a phenylhydrazone with phenylhydrazine.

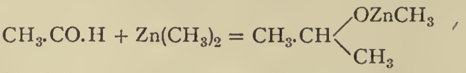
$$>CO + H_2N.NH.C_6H_5 = >C:N.NHC_6H_5 + H_2O.$$

(6) The formation of a semicarbazone with semicarbazide (see Prep. 100, p, 212).

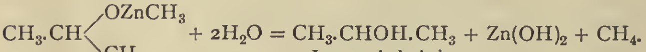
$$>CO + H_2N.NH.CO.NH_2 = >C{:}N.NH.CONH_2 + H_2O.$$

Both aldehydes and ketones readily undergo *condensation*, and a great variety of syntheses have been effected in this way (see Preps. 94, p. 204, and 103, p. 215).

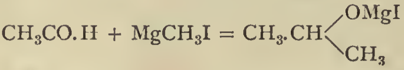
The aldehydes unite with zinc alkyl (Wagner) and magnesium alkyl halide (Grignard, see p. 206) to form additive compounds, which decompose with water, yielding secondary alcohols.



$$CH_3.CO.H + Zn(CH_3)_2 = CH_3.CH\left\langle\begin{array}{l}OZnCH_3\\CH_3\end{array}\right.$$



$$CH_3.CH\left\langle\begin{array}{l}OZnCH_3\\CH_3\end{array}\right. + 2H_2O = \underset{\text{Isopropyl alcohol.}}{CH_3.CHOH.CH_3} + Zn(OH)_2 + CH_4.$$



$$CH_3CO.H + MgCH_3I = CH_3.CH\left\langle\begin{array}{l}OMgI\\CH_3\end{array}\right.$$

$$CH_3.CH\left\langle\begin{array}{l}OMgI\\CH_3\end{array}\right. + H_2O = CH_3.CHOH.CH_3 + Zn(OH)_2 + CH_4.$$

Acetaldehyde, in presence of HCl, polymerises, forming aldol. With zinc chloride the reaction goes a step further and crotonaldehyde is formed,

$$CH_3.COH + CH_3.COH = \underset{\text{Aldol.}}{CH_2.CH(OH).CH_2.COH.}$$

$$CH_3.CHOH.CH_2.COH = \underset{\text{Crotonaldehyde.}}{CH_3.CH{:}CH.COH + H_2O.}$$

PREPARATION 6.

Methyl Iodide.—Read notes on Prep. 2, p. 234.

PREPARATION 7.

Amyl Nitrite.—The nitrites of the general formula $R'.O.NO$ are isomeric with the nitro-paraffins $R'NO_2$. Whereas the nitrites are hydrolysed with KOH like other esters into the alcohol and the acid,

$$C_2H_5ONO + KOH = C_2H_5OH + KNO_2,$$

and are decomposed by reducing agents into the alcohol and ammonia (and in some cases hydroxylamine), the primary nitroparaffins are not hydrolysed by potash, but dissolve, forming the soluble potassium salt, and on reduction give the primary amine,

$$C_2H_5NO_2 + 3H_2 = C_2H_5NH_2 + 2H_2O.$$

Amyl nitrite is used in the preparation of diazo-salts (see Prep. 62, p. 161).

PREPARATION 10.

Acetyl Chloride.—Either PCl_3 or PCl_5 are almost invariably used in the preparation of acid chlorides. In the case of PCl_5 only a portion of the chlorine of the reagent is utilised (see Prep. 98, p. 208), $POCl_3$ being produced in the reaction. The use of one or other reagent is determined by the nature of the product. If the latter has a low boiling-point the trichloride is preferred, if a high boiling-point, the pentachloride may be used and the oxychloride expelled by distilling *in vacuo* from a water-bath (see Prep. 16, p. 85). The pentachloride is more frequently used in the preparation of aromatic acid chlorides, but there are occasions, which experience can only determine, when the trichloride is preferable.

Phosphorus oxychloride and the sodium salt of the acid can also be used.

$$2CH_3.COONa + POCl_3 = 2CH_3.COCl + NaPO_3 + NaCl.$$

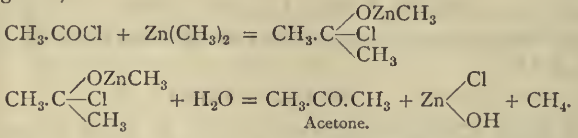
Also thionyl chloride, $SOCl_2$, may often be used with advantage in place of the chlorides of phosphorus,

$$CH_3.COOH + SOCl_2 = CH_3.COCl + HCl + SO_2.$$

Acid chlorides react with alcohols and phenols, and in general with substances containing a "hydroxyl" (OH) group. Acid anhydrides have a similar behaviour, and both substances may be used in determining the number of such groups in a compound. Thus glycerol forms a triacetyl derivative, whilst glucose yields a pentacetyl compound. By hydrolysing the acetyl derivative with alkali, and then estimating the amount of alkali neutralised by titration, the number of acetyl groups can be estimated (see p. 222).

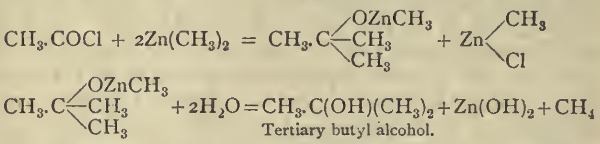
The presence of the "amino" (NH_2) group is determined by a similar reaction.

The synthesis of aromatic ketones may be effected with the acid chlorides, using the Friedel-Crafts' reaction (see Prep. 100, p. 210), also of aliphatic ketones and tertiary alcohols with zinc methyl and ethyl, &c. (Butlerow) or magnesium alkyl halide (Grignard).

(1)


$$CH_3.COCl + Zn(CH_3)_2 = CH_3.C\begin{matrix}\diagup OZnCH_3\\ -Cl\\ \diagdown CH_3\end{matrix}$$

$$CH_3.C\begin{matrix}\diagup OZnCH_3\\ -Cl\\ \diagdown CH_3\end{matrix} + H_2O = \underset{\text{Acetone.}}{CH_3.CO.CH_3} + Zn\begin{matrix}\diagup Cl\\ \diagdown OH\end{matrix} + CH_4.$$

(2)


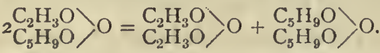
$$CH_3.COCl + 2Zn(CH_3)_2 = CH_3.C\begin{matrix}\diagup OZnCH_3\\ -CH_3\\ \diagdown CH_3\end{matrix} + Zn\begin{matrix}\diagup CH_3\\ \diagdown Cl\end{matrix}$$

$$CH_3.C\begin{matrix}\diagup OZnCH_3\\ -CH_3\\ \diagdown CH_3\end{matrix} + 2H_2O = \underset{\text{Tertiary butyl alcohol.}}{CH_3.C(OH)(CH_3)_2} + Zn(OH)_2 + CH_4$$

An additive compound with zinc methyl is formed, in the first reaction with one molecule, in the second with two molecules, and the product in each case is then decomposed with water. The reaction with magnesium methyl iodide is similar.

PREPARATION 11.

Acetic Anhydride.—The anhydrides may be regarded as oxides of the acid radicals, just as ethers are the oxides of the alcohol radicals, and, like the ethers, both simple and mixed anhydrides may be prepared. The latter, however, on distillation decompose, giving a mixture of the simple anhydrides.



$$2\begin{matrix}C_2H_3O\\ C_5H_9O\end{matrix}\Big\rangle O = \begin{matrix}C_2H_3O\\ C_2H_3O\end{matrix}\Big\rangle O + \begin{matrix}C_5H_9O\\ C_5H_9O\end{matrix}\Big\rangle O.$$

Anhydrides may also be prepared by the action of $POCl_3$ on the potassium salt of the acid in presence of excess of the latter, the reaction occurring in two phases:

$$2CH_3.COOK + POCl_3 = 2CH_3.COCl + KPO_3 + KCl.$$
$$CH_3.COOK + C_2H_3OCl = (C_2H_3O)_2O + KCl.$$

In addition to the reactions described under the Preparation, the anhydrides undergo the following changes:

1. With HCl, HBr, and HI they give, on heating, the acid chloride and free acid,

$$(CH_3CO)_2O + HCl = CH_3COCl + CH_3.COOH.$$

2. With Cl they form acid chloride and chlorinated acid,

$$(CH_3CO)_2O + Cl_2 = CH_3COCl + CH_2Cl.COOH.$$

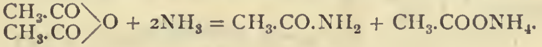
3. With Na amalgam they are reduced to aldehydes.

PREPARATION 12.

Acetamide.—The acid amides, or simply amides, correspond to the amines, being ammonia in which hydrogen is replaced by acid radicals, and, like the amines, exist in the form of primary secondary and tertiary amides. The following methods are used for obtaining the amides, in addition to that described under the preparation :

1. The action of ammonia on the acid chlorides or anhydrides (see Prep. 98, p. 209).

$$CH_3.CO.Cl + 2NH_3 = CH_3.CO.NH_2 + NH_4Cl.$$



$$\left.\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\right\rangle O + 2NH_3 = CH_3.CO.NH_2 + CH_3.COONH_4.$$

2. The action of ammonia on the esters (see Prep. 26, p. 102).

$$CH_3.COOC_2H_5 + NH_3. = CH_3.CONH_2 + C_2H_5OH.$$

3. Partial hydrolysis of the cyanides by conc. hydrochloric or sulphuric acid,

$$CH_3 CN + H_2O = CH_3.CONH_2.$$

The alkyl amides or substituted ammonias, with both acid and alkyl radicals, also exist, and are formed by the first two of the above reactions and by heating the salt of the amine (see Prep. 54, p. 151).

$$CH_3.CO.Cl + NH_2C_2H_5 = \underset{\text{Acetethylamide.}}{CH_3.CO.NHC_2H_5} + HCl.$$

$$\underset{\text{Aniline acetate.}}{CH_3.COOH.NH_2C_6H_5} = \underset{\text{Acetanilide.}}{CH_3.CONH.C_6H_5} + H_2O.$$

With the exception of formamide, which is a viscid liquid, the majority of these compounds are crystalline solids. The lower members are soluble in water, and they all dissolve in alcohol or ether. Many of them distil without decomposition. They are neutral substances uniting with both mineral acids and a few of them with caustic alkalis and alkaline alcoholates to form compounds which are rapidly decomposed by water.

The hydrogen of the amido-group is also replaceable by metals, and derivatives of acetamide of the following formulæ are known :

$$CH_3CONHNa,\ CH_3.CONHAg,\ (CH_3.CO.NH)_2Hg.$$

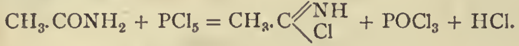
They are converted by nitrous acid into the organic acid, and in the case of substituted amides into nitrosamides,

$$CH_3CONH_2 + HNO_2 = CH_3.CO.OH + N_2 + H_2O.$$
$$\underset{\text{Acetanilide.}}{CH_3.CO.NHC_6H_5} + HNO_2 = \underset{\text{Nitrosoacetanilide.}}{CH_3.CO.N(NO).C_6H_5} + H_2O.$$

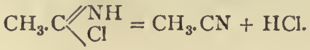
With the latter class of substituted amides, PCl_5 forms the imidochlorides, a reaction which is usually formulated in two steps,

$$CH_3.CO.NHC_6H_5 + PCl_5 = CH_3.CCl_2.NHC_6H_5 + POCl_3.$$
$$CH_3.CCl_2.NHC_6H_5 = CH_3CCl : NC_6H_5 + HCl.$$

The substituted amides give both imidochloride and the cyanide with PCl_5,



$$CH_3.CONH_2 + PCl_5 = CH_3.C\begin{matrix}\diagup NH\\ \diagdown Cl\end{matrix} + POCl_3 + HCl.$$



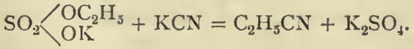
$$CH_3.C\begin{matrix}\diagup NH\\ \diagdown Cl\end{matrix} = CH_3.CN + HCl.$$

PREPARATION 13

Acetonitrile.—The various reactions by which the nitriles or alkyl cyanides are obtained have already been mentioned in one or other of the previous notes, but they may be recapitulated.

1. By the action of KCN on the alkyl iodide or alkyl potassium sulphate,

$$C_2H_5I + KCN = C_2H_5CN + KI.$$



$$SO_2\begin{matrix}\diagup OC_2H_5\\ \diagdown OK\end{matrix} + KCN = C_2H_5CN + K_2SO_4.$$

2. By the action of PCl_5 (as well as P_2O_5) on the amide,

$$CH_3.CONH_2 + PCl_5 = CH_3CN + POCl_3 + 2HCl.$$

3. By heating the aldoxime with acetic anhydride,

$$CH_3.CH : NOH + (CH_3CO)_2O = CH_3CN + 2CH_3.COOH.$$

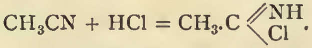
They are compounds which are, for the most part, insoluble in water, possess an ethereal smell, have a neutral reaction, and may be distilled.

The fact that they are eminently unsaturated compounds is evidenced by their general behaviour towards a great variety of reagents.

1. On reduction they give the primary amine (Mendius),

$$CH_3CN + 2H_2 = CH_3CH_2NH_2.$$

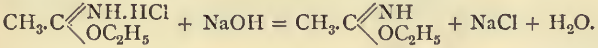
2. With HCl, HBr, and HI they form imidohalides (Wallach),



$$CH_3CN + HCl = CH_3.C\Big\langle\begin{array}{l}NH\\ Cl\end{array}.$$

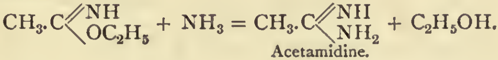
3. With alcohol and HCl they form the hydrochloride of the imidoethers, from which caustic alkali liberates the base (Pinner),

$$CH_3CN + C_2H_5OH + HCl = CH_3.C\Big\langle\begin{array}{l}NH.HCl\\ OC_2H_5\end{array}.$$



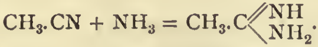
$$CH_3.C\Big\langle\begin{array}{l}NH.HCl\\ OC_2H_5\end{array} + NaOH = CH_3.C\Big\langle\begin{array}{l}NH\\ OC_2H_5\end{array} + NaCl + H_2O.$$

These imidoethers unite with ammonia and amines and form the amidines,



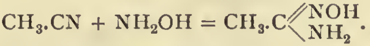
$$CH_3.C\Big\langle\begin{array}{l}NH\\ OC_2H_5\end{array} + NH_3 = \underset{\text{Acetamidine.}}{CH_3.C\Big\langle\begin{array}{l}NH\\ NH_2\end{array}} + C_2H_5OH.$$

4. The latter are also formed by the direct action of ammonia on the cyanide,



$$CH_3.CN + NH_3 = CH_3.C\Big\langle\begin{array}{l}NH\\ NH_2\end{array}.$$

5. Hydroxylamine unites with the cyanides, forming amidoximes,



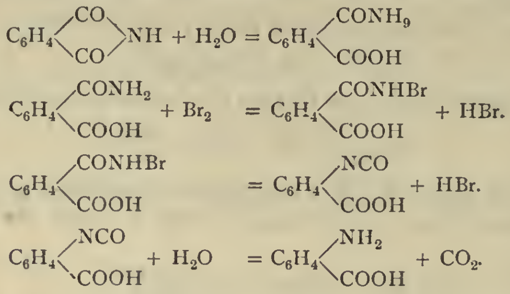
$$CH_3.CN + NH_2OH = CH_3.C\Big\langle\begin{array}{l}NOH\\ NH_2\end{array}.$$

6. With H_2S the thiamides are formed,

$$CH_3.CN + H_2S = CH_3.CS.NH_2.$$

PREPARATION 14

Methylamine Hydrochloride.—This reaction, which yields the primary amine, is applicable, not only to the aliphatic, but also to the aromatic amides. The formation of anthranilic acid from phthalimide is a process of technical importance. By the action of bromine and caustic potash, phthalaminic acid is first formed, which then yields the amino-acid,



$$C_6H_4\left\langle\begin{array}{l}CO\\CO\end{array}\right\rangle NH + H_2O = C_6H_4\left\langle\begin{array}{l}CONH_9\\COOH\end{array}\right.$$

$$C_6H_4\left\langle\begin{array}{l}CONH_2\\COOH\end{array}\right. + Br_2 = C_6H_4\left\langle\begin{array}{l}CONHBr\\COOH\end{array}\right. + HBr.$$

$$C_6H_4\left\langle\begin{array}{l}CONHBr\\COOH\end{array}\right. = C_6H_4\left\langle\begin{array}{l}NCO\\COOH\end{array}\right. + HBr.$$

$$C_6H_4\left\langle\begin{array}{l}NCO\\COOH\end{array}\right. + H_2O = C_6H_4\left\langle\begin{array}{l}NH_2\\COOH\end{array}\right. + CO_2.$$

The primary amines may also be obtained by the following reactions :

1. Action of alcoholic ammonia on the alkyl iodides and nitrates,

$$C_2H_5I + NH_3 = C_2H_5NH_2 + HI. \quad \text{(Hofmann.)}$$

Secondary and tertiary amines are also formed (see p. 156),

$$C_2H_5ONO_2 + NH_3 = C_2H_5NH_2 + HNO_3. \quad \text{(Wallach.)}$$

2. Reduction of the following classes of compounds :

nitro-compounds
cyanides
oximes
phenylhydrazones

$$C_2H_5NO_2 + 3H_2 = C_2H_5NH_2 + 2H_2O. \quad \text{(V. Meyer.)}$$

$$C_2H_5CN + 2H_2 = C_2H_5CH_2NH_2. \quad \text{(Mendius.)}$$

$$CH_3.CH{:}NOH + 2H_2 = CH_3.CH_2.NH_2 + H_2O. \quad \text{(Goldschmidt.)}$$

$$CH_3.CH{:}N.NHC_6H_5 + 2H_2 = CH_3.CH_2.NH_2 + C_6H_5.NH_2. \quad \text{(Tafel.)}$$

3. Hydrolysis of the isocyanides with conc. HCl, which occurs in two steps :

$$C_2H_5NC + H_2O = C_2H_5NH.COH$$
$$C_2H_5NH.COH + H_2O = C_2H_5NH_2 + HCO.OH.$$

The three classes of aliphatic amines (primary, secondary, and tertiary) may be distinguished by their behaviour with nitrous acid and alkyl iodide. The primary amine is decomposed with HNO_2, forming the alcohol, and nitrogen is evolved,

$$C_2H_5NH_2 + HNO_2 = C_2H_5OH + N_2 + H_2O.$$

The secondary amine forms the nitrosamine, insoluble in water

$$(C_2H_5)_2NH + HNO_2 = \underset{\text{Diethylnitrosamine.}}{(C_2H_5)_2N.NO} + H_2O.$$

The tertiary amine is unacted on by nitrous acid, but, unlike the other two, unites with an alkyl iodide and forms the quaternary ammonium iodide (Hofmann),

$$(C_2H_5)_3N + CH_3I = \underset{\text{Triethylmethylammonium iodide.}}{(C_2H_5)_3NCH_3I.}$$

The behaviour of nitrous acid with the aromatic amines is somewhat different (See Preps. 60, p. 157, and 62, p. 161).

The primary amines may also be distinguished from secondary and tertiary amines by the isocyanide reaction (p. 150), which consists in heating the amine with a little chloroform and alcoholic potash solution. An intolerable odour of isocyanide is emitted,

$$C_2H_5NH_2 + CHCl_3 + 3KOH = C_2H_5NC + 3KCl + 3H_2O.$$

PREPARATION 15.

Ethyl Acetate.—Esters may be obtained by the direct action of the alcohol on the acid as in the case of methyl oxalate. (Prep 26, p. 101). A certain quantity of ethyl acetate is also obtained from ethyl alcohol and acetic acid, but the action, which is a *reversible* one, stops when a certain proportion of the constituents have combined (p. 234). It is represented thus :

$$C_2H_5OH + CH_3.COOH \rightleftarrows CH_3.COOC_2H_5 + H_2O,$$

which signifies that the ester and water react and regenerate alcohol and acid, whilst the reverse process is in operation. By removing the water as it is formed by means of sulphuric acid or by distillation, this condition of equilibrium is disturbed and the reaction is completed. This does not, however, explain the fact, first discovered by Scheele and afterwards investigated by Fischer and Speier (see Prep. 99, p. 209), that a very limited quantity of conc. sulphuric or hydrochloric acid will produce the same result. According to Henry the reaction with HCl takes place in several steps,

$$CH_3.COOH + C_2H_5OH = CH_3C(OH)_2OC_2H_5.$$
$$CH_3.C(OH)_2OC_2H_5 + HCl = CH_3C(OH)ClOC_2H_5 + H_2O.$$
$$CH_3.C(OH)ClOC_2H_5 = CH_3.COOC_2H_5 + HCl.$$

Other methods for the preparation of esters are by the action of alcohol on the acid chloride or anhydride (see Reactions, p. 75), or by boiling up the dry powdered silver salt of the acid with the alkyl iodide,

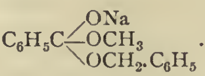
$$CH_3.COOAg + C_2H_5I = CH_3.COOC_2H_5 + AgI.$$

The esters are, for the most part, colourless liquids or solids of low m. p., with a fruity smell and insoluble in water. They are hydrolysed by potash (most readily with alcoholic potash) and give amides with ammonia,

$$CH_3.COOC_2H_5 + NH_3 = \underset{\text{Acetamide.}}{CH_3.CONH_2} + C_2H_5OH.$$

PREPARATION 16.

Ethyl Acetoacetate.—The explanation of the manner in which this substance is produced has been given in the account of the preparation. The result was arrived at, not by the isolation of the intermediate compound formed by the union of ethyl acetate with sodium ethylate, but by analogy with the behaviour of benzoic methyl ester with sodium benzylate, which gave the same additive product as that obtained by combining benzoic benzyl ester with sodium methylate, showing that such combinations could occur,



$$C_6H_5C\begin{cases}ONa\\OCH_3\\OCH_2.C_6H_5\end{cases}.$$

Also by the fact that sodium only attacks ethyl acetate in presence of ethyl alcohol, although the quantity of the latter may be very minute. Similar reactions have been effected with either metallic sodium or sodium ethylate by Claisen,

W. Wislicenus and others, of which the following examples must suffice;

$$\underset{\text{Benzoic ester.}}{C_6H_5COOC_2H_5} + \underset{\text{Acetic ester.}}{CH_3.COOC_2H_5} = \underset{\text{Benzoylbenzoic ester.}}{C_6H_5CO.CH_2.COOC_2H_5} + C_2H_5OH.$$

$$\underset{\text{Formic ester.}}{HCOOC_2H_5} + \underset{\text{Acetic ester.}}{CH_3.COOC_2H_5} = \underset{\text{Formylacetic ester.}}{H.CO.CH_2.COOC_2H_5} + C_2H_5OH.$$

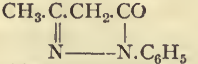
$$\underset{\text{Oxalic ester.}}{C_2H_5OCO.COOC_2H_5} + \underset{\text{Acetic ester.}}{CH_3.COOC_2H_5} = \underset{\text{Oxalylacetic ester.}}{C_2H_5OCO.CO.CH_2.COOC_2H_5} + C_2H_5OH.$$

From this it would appear that *condensation* might always be effected between an ester on the one hand and a compound containing the group $CH_2.CO$ on the other. This seems very generally to be the case, and Claisen has succeeded in producing condensation products between esters and ketones or aldehydes containing this group. (See Prep. 100, p. 212.)

The formula for ethyl acetoacetate would imply the properties of a ketone, a view which is borne out by its reduction to a hydroxy-acid,

$$\underset{\beta\text{-Hydroxybutyric ester.}}{CH_3.CHOH.CH_2.COOC_2H_5},$$

and by its behaviour with phenylhydrazine and hydroxylamine. The latter reactions give rise to the formation of the usual phenylhydrazone and oxime, whilst a molecule of alcohol is also removed resulting in a closed chain, in the former case phenylmethylpyrazolone, and in the latter methylisoxazolone being formed,



$$\begin{array}{l} CH_3.C.CH_2.CO \\ \quad \| \qquad\quad | \\ \quad N\text{——}N.C_6H_5 \end{array}$$

Phenylmethylpyrazolone.

$$\begin{array}{l} CH_3.C.CH_2.CO \\ \quad \| \qquad\quad | \\ \quad N\text{——}O \end{array}$$

Methylisoxazolone.

The "methylene" group (CH_2) standing between two CO groups, such as occurs in acetoacetic ester, is characterised by certain properties, which are shared by all compounds of similar structure, viz., by their behaviour towards nitrous acid, diazobenzene salts, and metallic sodium or sodium alcoholate.

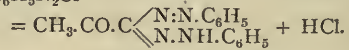
The first reaction leads to the formation of isonitrosoacetone,

$$CH_3.CO.CH_2.COOC_2H_5 + HNO_2 = CH_3.CO.CH{:}NOH + CO_2 + C_2H_5OH.$$

The second yields, in acetic acid solution, *formazyl* derivatives,

$$CH_3.CO.CH_2.COOC_2H_5 + C_6H_5N_2Cl = CH_3.CO.CH{:}N.NH.C_6H_5 + H_2O + CO_2 + C_2H_5OH + HCl.$$

$$CH_3.CO.CH{:}N.NHC_6H_5 + C_6H_5N_2Cl$$



$$= CH_3.CO.C\begin{matrix}\diagup N{:}N.C_6H_5 \\ \diagdown N.NH.C_6H_5\end{matrix} + HCl.$$

Acetyl diphenyl formazyl.

The third is capable of the utmost variety, since the sodium in the sodium compound may be removed by the action of:

1. Iodine, which leads to the formation of acetosuccinic ester,

$$\begin{array}{l} CH_3.CO.CHNa.COOC_2H_5 \\ CH_3.CO.CHNa.COOC_2H_5 \end{array} + I_2 = \begin{array}{l} CH_3.CO.CH.COOC_2H_5 \\ \qquad\quad\;\; | \\ CH_3.CO.CH.COOC_2H_5 \end{array} + 2NaI.$$

Acetosuccinic ester.

2. Alkyl iodide, whereby two atoms of hydrogen may be *successively* replaced by the same or different radicals,

$$CH_3.CO.CHNa.COOC_2H_5 + CH_3I = CH_3.CO.CH(CH_3)COOC_2H_5 + NaI.$$

$$CH_3.CO.CNa(CH_3).COOC_2H_5 + CH_3I = CH_3.CO.C(CH_3)_2.COOC_2H_5 + NaI.$$

3. Acid chloride, which is of similar character to the foregoing process, but gives rise in some cases to the simultaneous formation of two isomeric compounds, a fact which at one time threw considerable doubt on the ketonic character of acetoacetic ester. Thus chloroformic ester and sodium acetoacetic ester produce the following two derivatives, of which the second predominates:

$CH_3.CO.CH(CO_2C_2H_5)_2.$ Acetylmalonic ester.

$CH_3.C(OCO_2C_2H_5){:}CH.CO_2C_2H_5.$ β-Carboxethylacetoacetic ester.

The synthetic capabilities of this compound are not yet exhausted. Acetoacetic ester and its alkyl derivatives undergo decomposition in two ways, according to whether dilute alkalis and acids or, on the other hand, strong alkalis are employed.

1. With *dilute* aqueous or alcoholic caustic alkalis, or baryta, or sulphuric acid, a ketone is formed (ketonic decomposition),

$$CH_3.CO.CH_2.COOC_2H_5 + H_2O = CH_3.CO.CH_3 + CO_2 + C_2H_5OH.$$

2. Concentrated alcoholic potash decomposes the ester into two molecules of acid (acid decomposition),

$$CH_3.CO.CH_2.COOC_2H_5 + 2H_2O = CH_3.COOH + CH_3.COOH + C_2H_5OH.$$

If the alkyl derivatives of the ester are employed, it is possible to effect the synthesis of a series of ketones and saturated aliphatic acids, according to whether the one or other reaction is used.

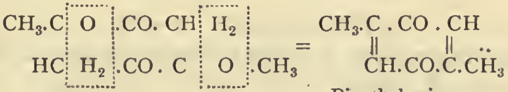
Of the other synthetic processes which have been studied in connection with this substance, the following may be mentioned :

1. The monoalkyl derivatives yield with nitrous acid the isonitroso-derivative, from which the ortho-diketone may be obtained (v. Pechmann),

$$CH_3.CO.CH(CH_3).COOC_2H_5 + HNO_2 = CH_3.CO.C:(NOH).CH_3 + C_2H_5OH + CO_2$$

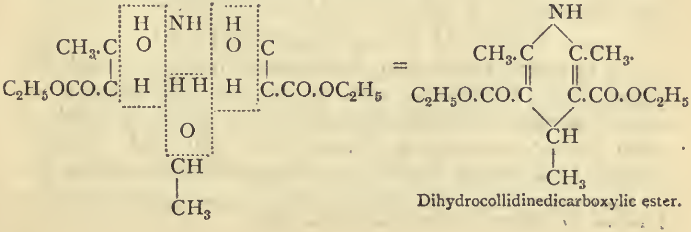
$$CH_3.CO.C:(NOH).CH_3 + H_2O = CH_3.CO.\underset{\text{Diacetyl.}}{CO.CH_3} + NH_2OH.$$

These compounds readily condense, forming derivatives of quinone,



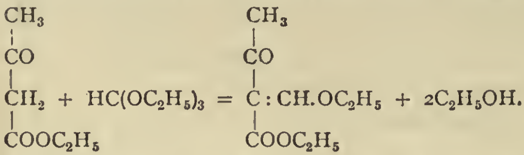
Dimethyl quinone.

2. Aldehyde-ammonias and acetoacetic ester yield pyridine derivatives (Hantzsch),



Dihydrocollidinedicarboxylic ester.

3. Orthoformic ester and acetoacetic ester in presence of acetic anhydride form a hydroxymethylene ester (Claisen),



$$\begin{array}{l}CH_3\\ |\\ CO\\ |\\ CH_2\\ |\\ COOC_2H_5\end{array} + HC(OC_2H_5)_3 = \begin{array}{l}CH_3\\ |\\ CO\\ |\\ C:CH.OC_2H_5\\ |\\ COOC_2H_5\end{array} + 2C_2H_5OH.$$

4. The derivatives of acetosuccinic ester are very numerous the compound lending itself readily to the formation of *heterocyclic* compounds (pyrrole, furfurane, thiophene, pyridine, &c., derivatives).

The impartial way in which acetoacetic ester was found to behave, sometimes playing the part of a hydroxy-compound, sometimes that of a ketone, has led to much discussion on the merits of the formulæ proposed by Geuther and Frankland,

$$\underset{\text{Geuther's formula.}}{CH_3.C(OH):CH.COOC_2H_5.} \qquad \underset{\text{Frankland's formula.}}{CH_3.CO.CH_2.COOC_2H_5.}$$

From its physical properties and from its close analogy with compounds which are known in both *desmotropic* forms, there is now little doubt that the liquid is a mixture of both compounds, the proportion of each being determined by temperature and other conditions. It is a typical example of *tautomerism.*[1]

PREPARATIONS 17—18.

Monochloracetic Acid and Monobromacetic Acid.—The action of chlorine on the aliphatic acids takes place in presence of sunlight, also on the addition of small quantities of the "halogen-carriers," iodine, sulphur, and red phosphorus. By the action of iodine, ICl is formed, which decomposes more readily than the molecule of chlorine, and hydriodic acid is liberated,

$$CH_3.COOH + ICl = CH_2Cl.COOH + HI.$$

The hydriodic acid is then decomposed by chlorine, and ICl regenerated. Phosphorus acts by forming the chloride of phosphorus from which the acid chloride is produced, which is more readily attacked by chlorine than the acid. Sulphur behaves in a similar fashion, sulphur chloride converting the

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[1] For a full discussion of the subject of tautomerism, see the author's *Organic Chemistry for Advanced Students*, E. Arnold, London.

acid into the acid chloride. Bromine in presence of phosphorus forms in the same way, first, the acid bromide, and in the second stage of the reaction, the bromine substitution product. The bromine in all cases attaches itself to the *a*-carbon (*i.e.*, next the carboxyl). Where no free hydrogen exists in this position, as in trimethylacetic acid, no substitution occurs. Iodine can be introduced by the action of KI on the bromine derivative,

$$CH_2Br.COOH + KI = CH_2I.COOH + KBr.$$

Monohalogen derivatives may also be obtained from the unsaturated acids by the action of the hydracids (HCl, HBr, HI). In this case the halogen attaches itself to the carbon farthest from the carboxyl. Thus acrylic acid gives with HBr the β-bromopropionic acid,

$$CH_2{:}CH.CO.OH + HBr = CH_2Br.CH_2.COOH.$$

The action of the hydracids, PCl_5 and PBr_5, on the hydroxy-acids also yields the halogen derivatives,

$$CH_3.CH(OH).COOH + HBr. = CH_3.CHBr.COOH + H_2O.$$
$$CH_3.CH(OH).COOH + 2PCl_5 = CH_3.CHCl.COCl + 2POCl_3 + 2HCl.$$

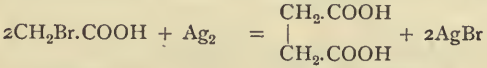
In the latter case the acid chloride must be subsequently decomposed by water to obtain the acid.

The increase in the number of halogen atoms in the acid raises the boiling point as well as the strength of the acid as determined by its dissociation constant K.

	B.P.	K.
Acetic acid	118°	·0018
Monochloracetic acid . . .	185°	·155
Dichloracetic acid	190°	5·14
Trichloracetic acid	195°	121

Some of the transformations of monohalogen acids are illustrated by the following equations :

$$CH_2Cl.COOH + H_2O = CH_2OH.COOH + HCl.$$
$$CH_2Cl.COOH + KCN = CH_2CN.COOH + KCl$$
$$CH_2Cl.COOH + 2NH_3 = CH_2NH_2.COOH + NH_4Cl.$$

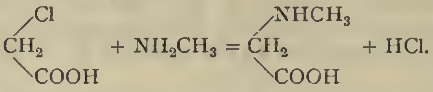


$$2CH_2Br.COOH + Ag_2 = \begin{array}{l} CH_2.COOH \\ | \\ CH_2.COOH \end{array} + 2AgBr$$

$$CH_2I.CH_2COOH + KOH = CH_2{:}CH.COOH + KI + H_2O.$$

PREPARATIONS 19—20.

Glycocoll.—By the action of primary and secondary amines, corresponding amino-acids are formed. Chloracetic acid and methylamine yield sarcosine,

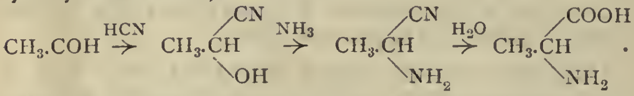


$$\mathrm{CH_2}\left\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{COOH}\end{matrix}\right. + \mathrm{NH_2CH_3} = \mathrm{CH_2}\left\langle\begin{matrix}\mathrm{NHCH_3}\\ \mathrm{COOH}\end{matrix}\right. + \mathrm{HCl}.$$

The amino-acids are further obtained by the reduction (Zn and HCl) of nitro-, oximino- and cyano-acids, thus :

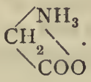
$$\mathrm{CH_2(NO_2).COOH + 3H_2 = CH_2(NH_2)COOH + 2H_2O},$$
$$\mathrm{CH_3.C(NOH).COOH + 2H_2 = CH_3.CH(NH_2).COOH + H_2O},$$
$$\mathrm{CN.COOH + 2H_2 = CH_2(NH_2).COOH},$$

and by the action of NH_3 on the cyanhydrin of aldehydes and ketones, or simply of ammonium cyanide. The product is then hydrolysed with HCl,



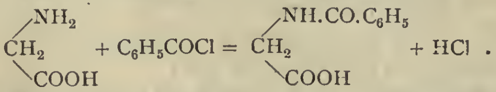
$$\mathrm{CH_3.COH} \xrightarrow{\mathrm{HCN}} \mathrm{CH_3.CH}\left\langle\begin{matrix}\mathrm{CN}\\ \mathrm{OH}\end{matrix}\right. \xrightarrow{\mathrm{NH_3}} \mathrm{CH_3.CH}\left\langle\begin{matrix}\mathrm{CN}\\ \mathrm{NH_2}\end{matrix}\right. \xrightarrow{\mathrm{H_2O}} \mathrm{CH_3.CH}\left\langle\begin{matrix}\mathrm{COOH}\\ \mathrm{NH_2}\end{matrix}\right. .$$

The amino-acids are crystalline compounds usually of a sweet taste and soluble in water. They are neutral compounds, from which it may be assumed that an inner ammonium salt is formed—



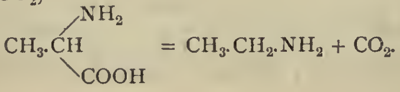
$$\mathrm{CH_2}\left\langle\begin{matrix}\mathrm{NH_3}\\ \mathrm{COO}\end{matrix}\right\rangle .$$

By the action of an acid chloride on the amino-acid, the hydrogen of the amino-group may be replaced by an acid radical. Hippuric acid has been synthesised in this way.



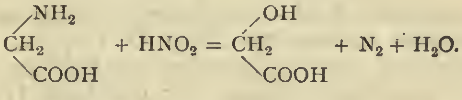
$$\mathrm{CH_2}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{COOH}\end{matrix}\right. + \mathrm{C_6H_5COCl} = \mathrm{CH_2}\left\langle\begin{matrix}\mathrm{NH.CO.C_6H_5}\\ \mathrm{COOH}\end{matrix}\right. + \mathrm{HCl}\ .$$

The amino-acids are not acted on by a hot solution of caustic alkali, but on fusion with caustic soda or potash, yield the amine and CO_2,



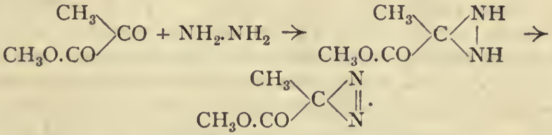
$$\mathrm{CH_3.CH}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{COOH}\end{matrix}\right. = \mathrm{CH_3.CH_2.NH_2 + CO_2}.$$

With nitrous acid the hydroxy-acid is formed,

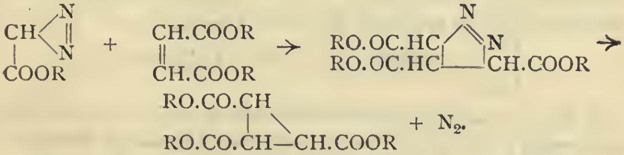


PREPARATION 21.

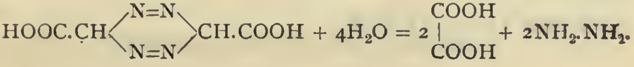
Diazoacetic Ester.—The primary amines of the aliphatic series differ from those of the aromatic group in the fact that the former yield no diazo-compounds with nitrous acid. It is otherwise with the amino-esters, the ester group probably furnishing the acid character (represented by the nucleus in the aromatic series) necessary to give stability to the compound. It should be pointed out that the two classes of compounds have not an identical structure. The formation of diazoacetic ester from pyruvic ester and hydrazine and subsequent oxidation with mercuric oxide indicates that both nitrogen atoms are attached to carbon,



In addition to the reactions described in the preparation diazoacetic ester unites with unsaturated acids and forms cyclic compounds. Fumaric ester, for example, combines in the following way:—

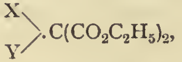


When bisdiazoacetic ester is heated with water or dilute acid it breaks up into hydrazine and oxalic acid,



PREPARATION 22—23.

Ethylmalonic Acid.—Like acetoacetic ester (see p. 83), diethylmalonate contains the group $CO.CH_2.CO$. By the action of sodium or sodium alcoholate, the hydrogen atoms of the methylene group are successively replaceable by sodium. The sodium atoms are in turn replaceable by alkyl or acyl groups. Thus, in the present preparation, ethyl malonic ester is obtained by the action of ethyl iodide on the monosodium compound. If this substance be treated with a second molecule of sodium alcoholate and a second molecule of alkyl iodide, a second radical would be introduced, and a compound formed of the general formula



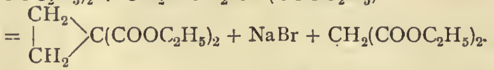
$$\left.\begin{matrix}X\\Y\end{matrix}\right>.C(CO_2C_2H_5)_2,$$

in which X and Y denote the same or different radicals.

These compounds yield, on hydrolysis, the free acids, which, like all acids containing two carboxyl groups attached to the same carbon atom, lose CO_2 on heating. Thus, ethyl malonic acid yields butyric acid. In this way the synthesis of monobasic acids may be readily effected. Malonic ester, moreover, may be used in the preparation of cyclic compounds as well as of tetrabasic and also dibasic acids of the malonic acid series (Perkin). To give one illustration: malonic ester, and ethylene bromide in presence of sodium alcoholate, yield trimethylene dicarboxylic ester and tetramethylene tetracarboxylic ester. The first reaction takes place in two steps,

$$CHNa(COOC_2H_5)_2 + C_2H_4Br_2 = CH_2Br.CH_2.CH(COOC_2H_5)_2 + NaBr.$$

$$CHNa(COOC_2H_5)_2 + CH_2BrCH_2\ CH(COOC_2H_5)$$



$$= \left.\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right>C(COOC_2H_5)_2 + NaBr + CH_2(COOC_2H_5)_2.$$

In the second step a second molecule of sodium malonic ester exchanges its sodium with the substituted malonic ester and a second molecule of NaBr is then removed.

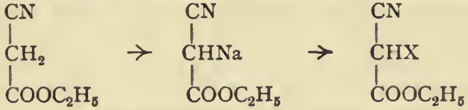
The formation of the tetracarboxylic ester occurs simultaneously,

$$2CHNa(COOC_2H_5)_2 + C_2H_4Br_2$$
$$= (COOC_2H_5)_2CH.CH_2.CH_2.CH(COOC_2H_5)_2 + 2NaBr$$

The free acid derived from the ester by hydrolysis loses two molecules of CO_2 on heating, and gives adipic acid,

$$(COOH)_2CH.CH_2.CH_2.CH(COOH)_2 \\ = COOH.CH_2.CH_2.CH_2.CH_2.COOH + 2CO_2.$$

Cyanacetic ester has similar properties to malonic ester, inasmuch as the methylene hydrogen is replaceable by sodium and thus by alkyl groups.



$$\begin{array}{c} CN \\ | \\ CH_2 \\ | \\ COOC_2H_5 \end{array} \rightarrow \begin{array}{c} CN \\ | \\ CHNa \\ | \\ COOC_2H_5 \end{array} \rightarrow \begin{array}{c} CN \\ | \\ CHX \\ | \\ COOC_2H_5 \end{array}$$

PREPARATION 24.

Trichloracetic Acid.—This acid may also be obtained by direct substitution of acetic acid by chlorine (Dumas) (see Prep. 17, p. 87). The oxidation of the corresponding aldehyde is, however, the more convenient method. Trichloracetic acid decomposes with alkalis on heating into carbon dioxide and chloroform,

$$CCl_3.COOH = CHCl_3 + CO_2.$$

The reaction resembles the formation of methane from sodium acetate when heated with soda-lime.

On reduction with sodium or potassium amalgam, trichloracetic acid is converted into acetic acid (Melsens),

$$CCl_3.COOH + 3H_2 = CH_3.COOH + 3HCl.$$

Dichloracetic acid may also be obtained from chloral by the action of potassium cyanide and water,

$$CCl_3COH + H_2O + KCN = CHCl_2.COOH + KCl + HCN.$$

Whereas mono- and tri-chloracetic acid are solid, dichloracetic acid is a liquid at the ordinary temperature.

PREPARATION 25.

Oxalic Acid.—The preparation of oxalic acid by the action of nitric acid on sugar was introduced by Scheele, and was used for some time as a technical process. The vanadium pentoxide acts as carrier of oxygen, being alternately reduced to tetroxide and re-oxidised. The present commercial method is to heat sawdust with a mixture of caustic potash and soda on iron plates to 200—220°, and to lixiviate the product with water. The acid is precipitated as the calcium salt, which is then decomposed with sulphuric acid.

PREPARATION 27.

Glyoxylic and Glycollic Acids.—The process of electrolytic reduction has been applied successfully to a large number of organic compounds, and has not only been found to have definite practical advantages in many cases over other methods, but, on account of the ease with which it may be controlled, has elucidated the various stages in the mechanism of some of the more complex changes. The reduction of nitro-compounds is illustrated in Preps. 49 and 50. The reduction of organic acids, ketones and carbonyl compounds generally has been developed by Tafel and others, and in these cases it is found advantageous to use a mercury or lead electrode. An essential feature of the process is a clean metallic surface at the cathode and the absence of foreign metallic impurities. The reduction of the carbonyl group proceeds in three steps:

$$
\begin{aligned}
&>CO + 2H = \overset{\vee}{C}(OH) - \overset{\vee}{C}(OH)\\
&>CO + 2H = \;>CHOH\\
&>CO + 4H = \;>CH_2 + H_2O.
\end{aligned}
$$

PREPARATION 28.

Palmitic Acid.—This acid, together with stearic and oleic acids, in the form of the glycerides, are the chief constituents of fats. Palmitin (glyceride of palmitic acid) is also found in certain vegetable oils like palm and olive oil. The acid occurs also as the cetyl ester in spermaceti and as the myricyl ester in bees-wax. It may be obtained from oleic acid by fusion with potash,

$$C_{18}H_{34}O_2 + 5O + 5KOH = C_{16}H_{31}O_2K + 2K_2CO_3 + 4H_2O.$$

In the analysis of oils and fats, where the quantity of fatty acid is the chief object of the determination, it is customary to hydrolyse the substance with a standard solution of *alcoholic* potash in place of aqueous potash, and to estimate the excess of free alkali with standard acid, using phenolphthalein as indicator. The difference gives the amount of alkali neutralised by the fatty acid (see p. 210).

PREPARATION 29.

Formic Acid.—In addition to the method described, the acid is formed in the decomposition of chloral (see p. 9), chloroform (see Prep. 8, p. 71), by the action of conc. HCl on the isocyanides,

$$C_2H_5NC + 2H_2O = C_2H_5NH_2 + HCO.OH,$$

by the decomposition of aqueous hydrocyanic acid, which yields the ammonium salt,

$$HCN + 2H_2O = HCOONH_4,$$

and by the oxidation of methyl alcohol with potassium bichromate and sulphuric acid. It is present in the sting of ants and nettles, and is also occasionally found among the products of bacterial fermentation of polyhydric alcohols and carbohydrates. The commercial method is to act on solid NaOH with CO under pressure and at a temperature of about 100° :

$$CO + NaOH = HCOONa.$$

The calcium salt is used in the preparation of aldehydes by heating it with the calcium salt of a higher aliphatic acid,

$$(HCOO)_2Ca + (CH_3.COO)_2Ca = 2CH_3CO.H + 2CaCO_3.$$

The reducing action of formic acid and formates on metallic salts may be ascribed to the presence of the aldehyde group (OH)CH:O in the acid.

PREPARATION 30.

Allyl Alcohol.—Note the difference produced by the change in the relative quantities of glycerol and oxalic acid, and the temperature at which the reaction is brought about. In the case of formic acid, it is the oxalic acid alone which undergoes decomposition, and theoretically a small quantity of glycerol will effect the decomposition of an unlimited amount of oxalic acid. But at the higher temperature it is the glycerol which yields the main product. Allyl alcohol being an unsaturated compound, forms additive compounds with halogens and halogen acids. With permanganate solution it may be converted into glycerol,

$$CH_2{:}CH.CH_2OH + H_2O + O = CH_2OH.CHOH.CH_2OH.$$

On oxidation with silver oxide it yields the corresponding aldehyde (acrolein) and the acid (acrylic acid).

PREPARATION 31

Isopropyl Iodide.—The replacement of hydroxyl by iodine in the action of phosphorus and iodine on alcohols has already been described (see Prep. 6, p. 68), but here the presence of an excess of hydriodic acid, which is due to the action of water on the phosphorus iodide,

$$PI_3 + 3H_2O = P(OH)_3 + 3HI,$$

exerts in addition a reducing action on certain of the hydroxyl groups. By diminishing the proportion of phosphorus and iodine to glycerol, the reaction may be interrupted at an earlier stage, when allyl iodide is formed. This is probably due to the splitting off of iodine from propenyl tri-iodide,

$$CH_2I.CHI.CH_2I = CH_2{:}CH.CH_2I + I_2.$$

On the other hand a larger proportion of phosphorus and iodine or conc. hydriodic acid will reduce allyl iodide to propylene,

$$CH_2{:}CH.CH_2I + HI = CH_2{:}CH.CH_3 + I_2.$$

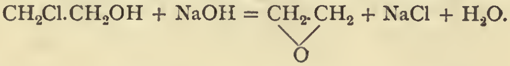
The action of hydriodic acid on glycerol is typical of the polyhydric alcohols. Hydriodic acid converts erythritol into secondary butyl iodide, and mannitol into secondary hexyl iodide. The normal iodides are never formed.

PREPARATION 32.

Epichlorhydrin.—It is a noteworthy fact that although hydrochloric acid can replace hydroxyl by chlorine in the case of the monohydric alcohols, the number of hydroxyl groups which are substituted in the case of polyhydric alcohols is strictly limited. Like glycerol, ethylene glycol gives a chlorhydrin,

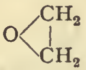
$$CH_2OH.CH_2OH + HCl = CH_2OH.CH_2Cl + H_2O.$$

The remaining hydroxyls can always be replaced by chlorine by the action of PCl_5. The chlorhydrins may also be obtained by the action of HOCl on the olefines. It is a general property of these compounds to form the oxide when heated with caustic alkalis. Ethylene chlorhydrin gives ethylene oxide in this way,

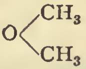


$$CH_2Cl.CH_2OH + NaOH = \underset{\diagdown O \diagup}{CH_2.CH_2} + NaCl + H_2O.$$

Compounds like ethylene oxide and epichlorhydrin may be regarded as inner ethers,



Ethylene oxide.

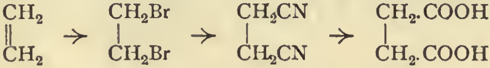


Dimethyl ether.

These oxides are easily decomposed. With water, ethylene oxide forms glycol; with hydrochloric acid, the chlorhydrin; with hydrocyanic acid, the cyanhydrin. Epichlorhydrin behaves similarly.

PREPARATION 33.

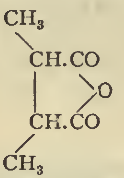
Succinic Acid.—Tartaric acid, like malic acid, is converted into succinic acid on reduction with HI, and the relationship of these three acids is thereby established. The constitution of succinic acid itself has been determined by its synthesis from ethylene (Maxwell Simpson). Ethylene unites with bromine, forming ethylene bromide, which yields ethylene cyanide with potassium cyanide. The latter is then hydrolysed.



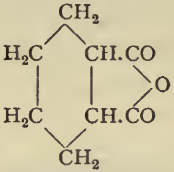
$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} \rightarrow \begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} \rightarrow \begin{array}{l} CH_2CN \\ | \\ CH_2CN \end{array} \rightarrow \begin{array}{l} CH_2.COOH \\ | \\ CH_2.COOH \end{array}$$

It is an interesting fact, not yet fully explained, that the alkyl succinic acids give anhydrides more readily than succinic acid, and the greater the number of alkyl groups, the more readily is the anhydride produced. Thus the anhydride of tetramethyl succinic acid is so stable that it is not decomposed by water.

The symmetrical dialkyl succinic acids exist in two forms, each yielding a separate anhydride. From their similarity to the anhydrides of hexahydrophthalic acid, they are distinguished as cis- and trans-compounds (see Notes on Prep. 37, p. 265).



Dimethylsuccinic anhydride.

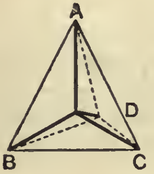


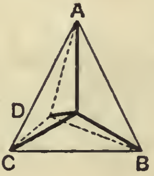
Hexahydrophthalic anhydride.

PREPARATION 34.

Ethyl Tartrate.—The speculations of Pasteur (1860) on the cause of the optical activity and hemihedry of tartaric acid and its salts, and of Wislicenus (1873) on the existence of three lactic acids, have developed in the hands of Van't Hoff and Le Bel (1874) into the present theory of stereo-chemistry or atomic space arrangement. Optical activity is found to be invariably associated with the presence in the substance of an *asymmetric* carbon atom, *i.e.* one linked to four different groups. Now every asymmetric (unsymmetrical) object like a hand or foot has its fellow; but the two do not precisely overlap, and every substance containing an asymmetric carbon atom, round which the four groups are distributed, not, as usually represented, in one plane, but in space of three dimensions, is capable of existing in two forms, which correspond to a left and right hand, or to an object and its reflected image.

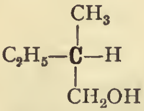
This is represented by making the carbon atom the centre of a tetrahedron and attaching the four different groups to the four solid angles. The two forms will then appear as in the Fig., in which ABCD represent four different groups. When





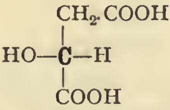
using actual models, it will be found that they cannot be turned so as to coincide until two of the groups in one model have been interchanged.

The main difference between two such substances lies in their action on polarised light, the one turning it to the right (dextro-rotatory) and the other to the left (laevo-rotatory), when in the liquid or dissolved state. Although every optically active substance contains at least one asymmetric carbon atom like amyl alcohol and malic acid, or two like tartaric acid (the asymmetric carbon is represented in heavy type),



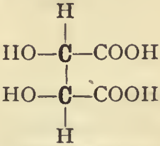
$$\begin{array}{c} CH_3 \\ | \\ C_2H_5-\mathbf{C}-H \\ | \\ CH_2OH \end{array}$$

Active amyl alcohol.



$$\begin{array}{c} CH_2.COOH \\ | \\ HO-\mathbf{C}-H \\ | \\ COOH \end{array}$$

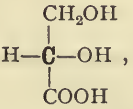
Malic acid.



$$\begin{array}{c} H \\ | \\ HO-\mathbf{C}-COOH \\ | \\ HO-\mathbf{C}-COOH \\ | \\ H \end{array}$$

Tartaric acid.

the converse does not always hold; for there are many compounds which possess an asymmetric carbon atom and show no rotation. The cause of this may be, either that the substance is a mixture of equal quantities of the two forms, which by having opposite rotations neutralise each other's effect as in the case of racemic acid, which consists of equal quantities of dextro- and laevo-tartaric acid and produces what is termed "external compensation," or the two similar asymmetric carbon atoms exist within the same molecule and neutralise each other's effect by "internal compensation," as in the case of mesotartaric acid. External compensation is generally exhibited by artificially prepared compounds as distinguished from natural products. Thus, glyceric acid from glycerol is inactive, though it contains an asymmetric carbon atom,



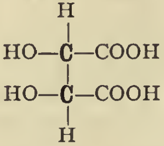
$$\begin{array}{c} CH_2OH \\ | \\ H-\mathbf{C}-OH \\ | \\ COOH \end{array},$$

because it consists of a mixture of dextro- and laevo-glyceric acid in equal quantities, whereas tartaric acid, which occurs in grapes, malic acid, which is obtained from mountain ash berries, and also the sugars, terpenes, alkaloids, and a number of other natural products are all active. One of the great achievements of Pasteur in this line of research was the separation of inactive "externally compensated" compounds into their active components or "optical antipodes" or "enantiomorphs." One method of separation is described in Prep. 35. For details of other methods a book on stereo-chemistry must be consulted.

On the formation of ethyl tartrate, see notes on Prep. 15, p 247. Ethyl tartrate may also be obtained by the method described in Prep. 99, which rather curtails the operation and does not necessitate the use of more than half the quantity of ethyl alcohol required by the earlier process.

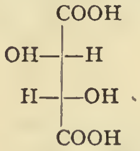
PREPARATION 35.

Racemic and Mesotartaric Acids.—These two acids represent two inactive types of compounds containing *asymmetric* carbon atoms (see above). Apart from certain well-marked differences in physical properties they also differ in one important feature ; racemic acid can be resolved into its optical enantiomorphs, whereas mesotartaric acid cannot. The latter belongs to what is termed the inactive indivisible type. If we examine the structural formula of tartaric acid it will be seen that it possesses two asymmetric carbon atoms, denoted in the formula by thick type.



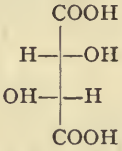
$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{HO{-}}\mathbf{C}\mathrm{{-}COOH} \\ | \\ \mathrm{HO{-}}\mathbf{C}\mathrm{{-}COOH} \\ | \\ \mathrm{H} \end{array}$$

Each asymmetric carbon atom is attached to similar groups. Let us suppose that each asymmetric carbon with its associated groups produces a certain rotation in a given direction. We may imagine the following combinations of two similar asymmetric groups. Both produce dextro-rotation, or both produce laevo-rotation. They will represent the dextro and laevo enantiomorphs, and the mixture of the two will produce inactive racemic acid. Racemic acid is said to be inactive by *external compensation.* Suppose, finally, that the two asymmetric groups produce rotation in opposite directions. They will neutralise one another. The resulting compound will be inactive by *internal compensation.* Such a compound cannot be resolved by any process into its active components. The above compounds may be represented by the following projection formulæ, in which the groups must be assumed to occupy three-dimensional space (the asymmetric carbon atoms being denoted by cross-lines),



$$\begin{array}{c} COOH \\ OH-|-H \\ H-|-OH \\ COOH \end{array}$$

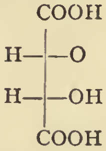
d. Tartaric acid.



$$\begin{array}{c} COOH \\ H-|-OH \\ OH-|-H \\ COOH \end{array}$$

l. Tartaric acid.

Racemic acid.



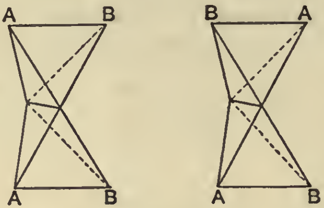
$$\begin{array}{c} COOH \\ H-|-O \\ H-|-OH \\ COOH \end{array}$$

Mesotartaric acid.

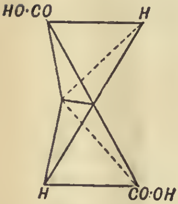
The conversion of active tartaric acid into the inactive forms is known as *racemisation*, and according to Winther is effected by the interchange of the groups round each asymmetric carbon atom successively so that part of the active acid is first converted into mesotartaric acid, which then passes into the laevo variety.

PREPARATION 37.

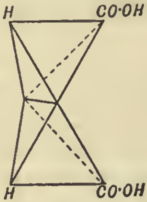
Citraconic and Mesaconic Acid.—The theory of Le Bel and Van't Hoff has been extended to unsaturated compounds like fumaric and maleic and the above two acids, which form isomeric pairs. These two pairs of acids bear a close resemblance. It has already been observed in the course of the preparation that citraconic is readily converted into mesaconic acid. Moreover, they both yield pyrotartaric acid, on reduction, but only one, citraconic acid, forms an anhydride. Maleic acid in the same way is easily converted into fumaric acid by bromine, both maleic and fumaric acid yield succinic acid on reduction, but only maleic acid forms an anhydride. The explanation is as follows: in each pair of compounds there exists two carbon atoms linked to one another by a double bond and each attached to two different groups. Van't Hoff refers the isomerism of each pair to a space arrangement, which may be represented by supposing two tetrahedra to be joined by a common edge. As the centre of each tetrahedron is occupied by a carbon atom, and the four bonds are directed towards the four corners of the tetrahedron, this space arrangement will correspond to a doubly-linked carbon. If the two spare corners of each tetrahedron are now occupied by different groups, it is possible to produce two forms by transposing one pair of groups. Supposing A and B to represent two different groups, the above forms will result.



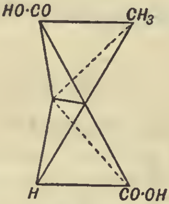
The two pairs of acids will be represented as follows :—



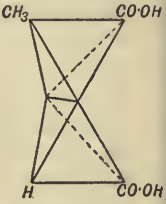
Fumaric acid.



Maleic acid.



Mesaconic acid.



Citraconic acid.

Isomerism in this case is not characterised by optical activity, as the groups lie in one plane and no structural asymmetry is possible ; but is exhibited by such physical differences as solubility, melting-point, electrical conductivity, and by the fact that in the case of dibasic acids only one of the pair yields an anhydride. Maleic and citraconic acid form anhydrides, but fumaric and mesaconic acid do not. In the case of the acids which form anhydrides, the carboxyl groups are supposed to be nearer together, *i.e.* on the same side (*cis*) of the molecule, in the other case on opposite sides (*trans*) of the molecule. Maleic and citraconic are "cis" acids, fumaric and mesaconic are "trans" acids. The following table gives the various physical properties, solubility, melting-point, and dissociation constant K of the two pairs of acids.

	S.	M.P.	K.
Maleic	very soluble.	130°	1·17
Fumaric	much less soluble.	sublimes at 200°	·093
Citraconic . . .	very soluble.	80°	·340
Mesaconic . . .	much less soluble.	202°	·079

PREPARATION 38.

Urea.—In addition to the method described in the preparation, urea may be obtained by the oxidation of anhydrous potassium ferrocyanide with potassium bichromate (Williams), or manganese dioxide at a red heat, or by the action of permanganate on a cold solution of potassium cyanide (Volhard). It has been synthesised by the action of ammonia on (1) phosgene, (2) urethane, (3) chloroformic ester, and (4) ethyl carbonate.

1. $COCl_2 + 4NH_3 = NH_2.CO.NH_2 + 2NH_4Cl.$
2. $NH_2.COOC_2H_5 + NH_3 = NH_2.CO.NH_2 + C_2H_5OH.$
3. $ClCOOC_2H_5 + 3NH_3 = NH_2.CO.NH_2 + C_2H_5OH + NH_4Cl.$
4. $CO(OC_2H_5)_2 + 2NH_3 = NH_2.CO.NH_2 + 2C_2H_5OH.$

also (5) by the action of dilute acid on cyanamide, and (6) by heating guanidine with dilute sulphuric acid or baryta.

5. $CNNH_2 + H_2O = NH_2.CO.NH_2.$
6. $NH : C(NH_2)_2 + H_2O = NH_2.CO.NH_2 + NH_3.$

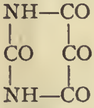
The synthesis of urea by Wöhler in 1828 is usually regarded as a turning-point in the history of organic chemistry, when organic compounds ceased to be merely products of a vital force, associated with living animals and plants. They now assumed for the first time an independent *rôle* as substances capable of synthesis by ordinary chemical means. In point of fact this is not strictly true, for Scheele had prepared oxalic acid, only previously known in wood sorrel and other plants, from cane sugar, and Döbereiner had obtained the formic acid of ants by the oxidation of tartaric acid. The formation of urea offers an interesting example of intramolecular change of which many cases are now known. See the formation of benzidine from hydrazobenzene (Prep. 51, p. 148) and aminoazobenzene from diazoaminobenzene (Prep. 70, p. 172).

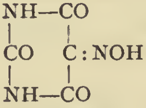
PREPARATION 39.

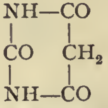
Thiocarbamide.—This is an example of a reversible reaction, in which either ammonium-thiocyanate or thiourea when heated yields the same equilibrium mixture. It may be shown by melting a little thiourea for a minute, when the presence of thiocyanate is indicated by the addition of $FeCl_3$.

PREPARATION 41.

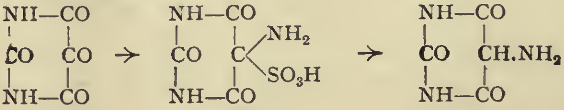
Alloxan.—The decomposition of uric acid into alloxan and area renders the constitution of alloxan of value in elucidating the structure of uric acid. The constitution is derived from the following facts: Alloxan is decomposed with caustic soda or potash into mesoxalic acid and urea, and with hydroxylamine it combines to form violuric acid, which points to the presence of a ketone group (Baeyer). Barbituric acid and nitrous acid also give violuric acid, and seeing that barbituric acid has been synthesised from malonic acid and urea by the action of phosphorus oxychloride (Grimaux), it is unquestionably malonyl urea. The relationship of these substances must therefore be represented as follows:


Alloxan.

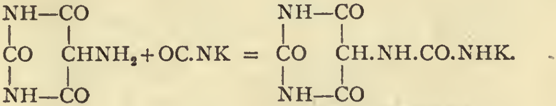

Violuric acid.


Barbituric acid.

A renewed interest attaches to alloxan since E. Fischer's discovery of the new synthesis of uric acid. The steps in the synthesis are briefly the following. Alloxan and ammonium sulphite form thionuric acid, which is decomposed by hydrochloric or sulphuric acid into uramil.


Alloxan. Thionuric acid Uramil.

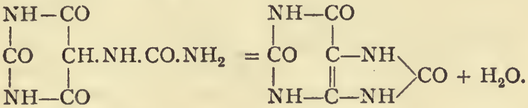
Uramil and potassium cyanate unite to form potassium pseudourate,



$$\begin{array}{l} NH-CO \\ | \quad\;\; | \\ CO \quad CHNH_2 \end{array} + OC.NK = \begin{array}{l} NH-CO \\ | \quad\;\; | \\ CO \quad CH.NH.CO.NHK. \end{array}$$
$$\begin{array}{l} | \quad\;\; | \\ NH-CO \end{array} \qquad\qquad \begin{array}{l} | \quad\;\; | \\ NH-CO \end{array}$$

Potassium pseudourate.

When free pseudouric acid is heated with 20 per cent. hydrochloric acid it yields uric acid,

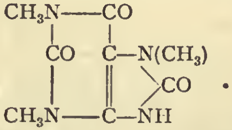


Pseudouric acid. Uric acid.

Other synthetic methods are also known for which a book of reference must be consulted.

PREPARATION 42.

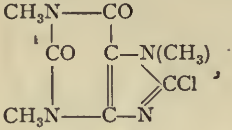
Caffeine.—The close relationship existing between uric acid and caffeine has long suggested the possibility of converting uric acid, a comparatively plentiful material, into caffeine, an important and costly drug, occurring only in small quantities in tea and coffee. The problem has been solved by E. Fischer, who has succeeded in synthesising caffeine in a variety of ways. Fischer found that by using the same series of processes as described above in the synthesis of uric acid, but substituting dimethylalloxan for alloxan, and methylamine sulphite for ammonium sulphite, trimethyl uric acid is formed, and is identical with hydroxycaffeine,

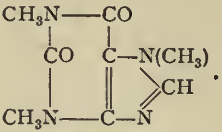


Trimethyl uric acid (Hydroxycaffeine).

Hydroxycaffeine is converted into caffeine by acting upon it with a mixture of phosphorus pentachloride and oxychloride.

This forms chlorocaffeine, which is then reduced with hydriodic acid to caffeine,


Chlorocaffeine.


Caffeine.

The same result may be obtained in a simpler way by methylating uric acid, and converting it into trimethyluric acid and then into caffeine ; or by preparing the mono- and di-methyl derivatives of uric acid, reducing these to the corresponding mono- and di-methylxanthines and introducing additional methyl groups into the product.

PREPARATION 44.

Tyrosine, Leucine.—It has long been known that mineral acids and alkalis possess the property of breaking up albuminoid substances and resolving them into the simpler amino-acids. The recent introduction by Fischer of a method of separating the amino-acids by converting them into volatile esters followed by fractional distillation *in vacuo* has led to the recognition of the wide distribution of such acids as alanine, serine, and phenylalanine, and to the discovery of two cyclic acids, pyrrolidine-carboxylic acid and hydroxypyrrolidine carboxylic acid. The following is a list of amino-acids from albuminoid substances which have been separated by fractional distillation of their esters under reduced pressure :

Ethyl ester.	b. p.	Pressure in mm.
Glycocoll	51·5—52·5°	10
Alanine	48·5°	10
Aminoisovaleric acid . .	63·5°	8
Leucine	83·5°	12
Aspartic acid	126·5°	11
Glutamic acid	139—140°	10
Phenylalanine	143°	10

PREPARATION 45.

Grape-sugar.—Although grape-sugar yields neither a bisulphite compound nor gives Schiff's reaction under ordinary conditions, its properties are for the most part those of an aldehyde. In addition to its reducing action on copper and silver salts, and its combination with phenylhydrazine, it forms an oxime with hydroxylamine and a cyanhydrin with hydrocyanic acid. On reduction it gives the hexahydric alcohol *sorbitol*, and, on oxidation, the corresponding monobasic acid, *gluconic acid*, and the dibasic acid, *saccharic acid*,

$CH_2OH(CHOH)_4COOH.$ Gluconic acid.

$COOH(CHOH)_4COOH.$ Saccharic acid.

The presence of five hydroxyl groups in glucose is determined by the existence of a pentacetyl derivative. These and other facts, which cannot be discussed in detail, have led to the adoption of the present formula. The discovery of the optical antipode of grape-sugar (which is dextro-rotatory) has determined the present name of dextro-glucose to distinguish it from laevo-glucose, which is laevo-rotatory. For the synthesis of these two sugars and the other mono-saccharoses, a text-book must be consulted.

The other common sugars, which reduce alkaline copper sulphate, are fructose (laevulose), galactose, maltose and milk-sugar, the two latter being disaccharoses. They are most readily identified by the microscopic appearance and melting-point of their phenylosazones. Cane-sugar is readily distinguished from the majority of the common sugars by its indifference towards alkaline copper sulphate, until previously boiled with a few drops of dilute sulphuric acid. It is then inverted and gives the reactions for glucose and fructose.

PREPARATION 46.

Bromobenzene.—The replacement of hydrogen by the halogens Cl and Br, in the nucleus of aromatic hydrocarbons, is assisted by the presence of a "halogen carrier," the action of which has been referred to in the Note on the preparations of chlor- and brom-acetic acids, p. 252. Iodine, iron, iron and aluminium chlorides and bromides, the aluminium-mercury couple, and pyridine all behave in this way. The action of iodine has already been explained on p. 252. Iron and its salts are supposed to act by alternately passing from the ferrous to the ferric state, the ferric salt delivering up its halogen in the nascent state,

$$2FeBr_2 + Br_2 = 2FeBr_3.$$
$$FeBr_3 = FeBr_2 + Br.$$

The action of aluminium and its compounds is not fully understood. Pyridine probably acts by the intermediate formation of the perbromide, as explained.

Unless a large excess of the hydrocarbon is present, the action of the halogen will effect the substitution of a second atom of hyrogen. By increasing the proportion of halogen, all the hydrogen may be ultimately replaced by chlorine or bromine. The second halogen atom enters the ortho- and para-positions, never the meta. Another kind of compound is obtained if the halogen is allowed to act in presence of sunlight. In the case of benzene, the additive compounds, benzene hexachloride and hexabromide, are then formed. They are very unstable compounds, and readily give off hydrochloric and hydrobromic acid. If boiled with alcoholic potash they are decomposed, forming trichloro- and tribromo-benzene,

$$C_6H_6Cl_6 + 3KOH = C_6H_3Cl_3 + 3KCl + 3H_2O.$$

If chlorine and bromine are allowed to act upon an aromatic hydrocarbon like toluene, which has a side-chain, substitution may occur in the nucleus or the side-chain, according to the conditions. Generally speaking, in the cold and in presence of a "halogen carrier," nuclear substitution occurs, but at a high temperature the halogen passes into the side-chain (see Prep. 86, p. 194).

The halogen derivatives of the aromatic hydrocarbons, like those of the aliphatic series, are colourless liquids or solids, denser than water, and possessing an agreeable smell, unless the side-chain is substituted. The latter substances can often be distinguished by their irritating action on the eyes and mucous membrane of the nose (see Prep. 86, p. 194).

The halogen in the aromatic nucleus is much more firmly fixed than in the case of the aliphatic compounds, *e.g.* bromobenzene is quite unaffected by most of the reagents which act upon ethyl bromide. The presence of *nitro*-groups, however, disturbs this stability, and the halogen in a substance like dinitrochlorobenzene is readily replaced by hydroxyl with potash, or by NH_2 with ammonia. When the halogen is in the side-chain, the substance behaves like an aliphatic compound.

PREPARATION 47.

Ethyl Benzene.—"Fittig's reaction," so-called from its discoverer, is analogous to the synthetical method employed by Wurtz for the preparation of the aliphatic hydrocarbons, as in the formation of butane from ethyl bromide,

$$2C_2H_5Br + 2Na = C_4H_{10} + 2NaBr.$$

In the case of the aromatic hydrocarbons, a second side-chain may be introduced from a dibromo-derivative either simultaneously with the first, or subsequently by a repetition of the process. Both dibromobenzene and monobromotoluene may be converted into xylene.

$$C_6H_4Br_2 + 2CH_3I + 4Na = C_6H_4(CH_3)_2 + 2NaBr + 2NaI.$$
$$C_6H_4BrCH_3 + CH_3I + 2Na = C_6H_4(CH_3)_2 + NaI + NaBr.$$

The action also takes place between aromatic hydrocarbons substituted either in the nucleus or side-chain. Bromobenzene yields diphenyl, whereas benzyl bromide yields dibenzyl,

$$2C_6H_5Br + 2Na = C_6H_5.C_6H_5 + 2NaBr.$$
$$2C_6H_5CH_2Br + 2Na = C_6H_5.CH_2.CH_2.C_6H_5 + 2NaBr.$$

This reaction does not, however, occur with the same readiness in all cases, nor does it always yield exclusively the anticipated product. Para-bromotoluene and sodium give tolyl phenyl methane and dibenzyl as well as ditolyl (Weiler). Again, *p*-bromotoluene gives a good yield of *p*-xylene, the ortho-compound reacts sluggishly, whilst the meta-derivative gives no xylene. Occasionally the action is vigorous, and has to be moderated by dilution with an indifferent solvent. At other times it is sluggish and has to be promoted by raising the temperature. Often the addition of a little ethyl acetate will start the decomposition. For the synthesis of some of the aromatic hydrocarbons, it is preferable to use the Friedel-Crafts' reaction (see Prep. 102, p. 214).

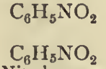
PREPARATION 48

Nitrobenzene.—The formation of nitro-compounds, by the action of strong nitric acid on the hydrocarbon, is a distinctive property of aromatic compounds, although recent researches have shown that dilute nitric acid under pressure will convert some of the paraffins, especially the tertiary hydrocarbons, into mono- and di-nitro-derivatives. The production of nitro-compounds is usually effected by strong or fuming nitric acid, or solid potassium nitrate, in presence of conc. sulphuric acid. Where the action is vigorous, as in the case of the phenols, it is necessary to use moderately dilute acid. The number of hydrogen atoms replaceable by the nitro-group (NO_2) is limited. In benzene the first nitro-group is introduced with great ease, the second less readily, and the third with some difficulty. The position taken up by the nitro-groups may be briefly stated as follows: When a negative group (nitro, carboxyl, cyanogen, aldehyde) is already present, the nitro-group enters the meta-position to the first group. In the presence of other groups (alkyl, hydroxyl, halogen, amino), the nitro-group attaches itself to both ortho- and para-positions. Benzoic acid and benzaldehyde give, on nitration, mainly meta-compounds, whereas toluene, phenol, and aniline form simultaneously ortho- and para-derivatives.

Nitro-compounds have often a yellow or red colour, are with difficulty or not at all volatile, possess a much higher boiling-point than the corresponding halogen derivatives, and are denser than water, and insoluble in that liquid.

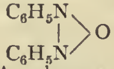
PREPARATIONS 49—51.

Azoxybenzene, Azobenzene, Hydrazobenzene.—Nitro-compounds yield a series of reduction products according to the nature of the reducing agent. Alkaline reducing agents: sodium methylate, zinc dust and caustic soda, stannous chloride and caustic soda, produce azoxy, azo- and hydrazo-compounds.



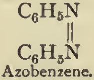
$$\begin{array}{c}C_6H_5NO_2\\ C_6H_5NO_2\end{array}$$

Nitrobenzene.



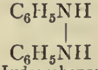
$$\left.\begin{array}{c}C_6H_5N\\ |\\ C_6H_5N\end{array}\right>O$$

Azoxybenzene.



$$\begin{array}{c}C_6H_5N\\ \|\\ C_6H_5N\end{array}$$

Azobenzene.



$$\begin{array}{c}C_6H_5NH\\ |\\ C_6H_5NH\end{array}$$

Hydrazobenzene.

The sodium methylate acts as a reducing agent by taking up oxygen and forming sodium formate.

In the preparations, the nitrobenzene is converted by successive steps into azoxy-, azo- and hydrazo-benzene; but, by suitably modifying the conditions, the intermediate steps may be omitted. Thus, nitrobenzene may be converted with alcoholic caustic soda and zinc dust directly into hydrazobenzene.

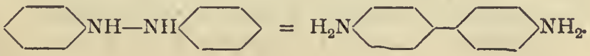
If the reduction of nitrobenzene takes place in neutral solution with zinc dust and water in presence of a little calcium or ammonium chloride, or with aluminium-mercury couple and water, β-phenylhydroxylamine is formed (see Prep. 52, p. 148).

$$C_6H_5NO_2 + 2H_2 = C_6H_5NHOH + H_2O.$$

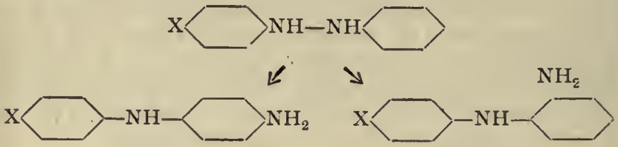
Reduction in acid solution produces an amine (see Prep. 53, p. 149). The mechanism of the change, although giving rise to such different products when carried out in alkaline, neutral, or acid solution, is not essentially different in the three cases. The first reduction product is nitrosobenzene, C_6H_5NO, followed by that of β-phenylhydroxylamine. In alkaline solution the two compounds unite with elimination of water to form azoxybenzene, which may undergo further reduction in a normal fashion giving rise to azo- and hydrazo-benzene. In acid solution, on the other hand, phenylhydroxylamine does not combine with nitrosobenzene and can then undergo further reduction. The reduction of nitrobenzene in alkaline and neutral solution is also effected, as already described, by electrolysing the liquid in contact with the negative electrode. If the process is conducted in presence of concentrated sulphuric acid *p*-aminophenol is obtained (Gattermann). The latter is produced by intramolecular change from phenylhydroxylamine, which is first formed,

$$C_6H_5NHOH = OHC_6H_4NH_2.$$

Azobenzene, though not a colouring matter, may be regarded as the mother substance of the large family of azo-colours, which are, however, prepared by a totally distinct method, viz., by the action of a diazo-salt on a phenol or base (see Prep. 62, p. 163). The intramolecular change from hydrazobenzene to benzidine is one of great technical importance. The change occurs by the transfer of the link between the two nitrogen atoms to the two carbon atoms in the *para*-position,



If one of the nuclei of hydrazobenzene is already substituted in the *para*-position, the reaction may give rise to diphenylamine derivatives, which are known as ortho- or para-semidines (Jacobson),



Para-semidine. Ortho-semidine.

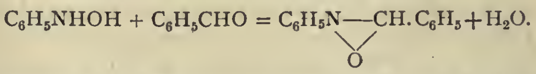
Benzidine and its homologues are used in the manufacture of valuable azo-colours, *congo-red*, *benzopurpurin*, &c. (see p. 291).

PREPARATION 52.

Phenylhydroxylamine.—The necessity for conducting the reduction of nitrobenzene in neutral solution has been explained in the previous note. In addition to the reagent named in the preparation, the aluminium-mercury couple in presence of water or ammonium sulphide in alcoholic solution may be also used. The conversion of nitrobenzene into *p*-aminophenol on electrolysis in acid solution will also be evident from the fact that phenylhydroxylamine readily undergoes isomeric change. Phenylhydroxylamine reacts with nitrous acid, forming a nitroso-derivative,

$$C_6H_5NHOH + HNO_2 = C_6H_5N(NO)OH + H_2O.$$

It also condenses with aldehydes in the following way :



$$C_6H_5NHOH + C_6H_5CHO = C_6H_5\underbrace{N—CH}_{O}.C_6H_5 + H_2O.$$

Nitrosobenzene, which shares the general character of nitroso-compounds in giving rise to a green vapour or solution, is readily reduced to phenylhydroxylamine and aniline. It condenses with amino-compounds, yielding azo- or diazo-derivatives.

$$C_6H_5NO + H_2N.C_6H_5 = C_6H_5N = N.C_6H_5 + H_2O.$$
$$C_6H_5NO + H_2N.OH = C_6H_5N = N.OH + H_2O.$$

PREPARATION 53.

Aniline.—The reduction of a nitro-compound in an acid solution is a very general method for preparing primary amines. For laboratory purposes it is customary to use tin and hydrochloric or a solution of stannous chloride crystals ($SnCl_2+2H_2O$) in conc. hydrochloric acid or zinc dust and acetic acid. The manufacture of aniline on the industrial scale is effected by means of iron borings and hydrochloric acid ; but of the latter only a fraction of the theoretical quantity, required by the equation $Fe + 2HCl = FeCl_2 + H_2$, is employed. The main reaction is probably represented by the following equation,

$$C_6H_5NO_2 + 2Fe + 4H_2O = C_6H_5NH_2 + Fe_2(OH)_6.$$

When the base is volatile in steam, as in the present case, the simplest method of separation is to add an excess of alkali and to distil in steam. Otherwise the base may be separated by shaking out with ether, or the tin may be precipitated in the warm solution by H_2S and the filtrate evaporated to dryness. If the compound contains more than one nitro-group, the reduction is carried out with one of the above reducing agents in the manner described, but if it is necessary to reduce only one of the nitro-groups, it is effected by the action of H_2S in presence of ammonia (see Prep. 58, p. 154). Another method, which may also be used for determining the number of nitro-groups, is to prepare an alcoholic solution of the nitro-compound, and to add an alcoholic solution of the calculated quantity of stannous chloride. In this way the reduction of the groups may be carried out in succession and estimated.

The aromatic amines are colourless liquids or solids, which may be distilled without decomposition. Although they form salts with acids, they are much weaker bases than the aliphatic amines owing to the negative character of the phenyl group, The salts have an acid reaction to litmus, whilst the free bases are neutral. The *neutralisation* of an aromatic base by acid is usually determined by the use of methyl violet, magenta, or congo-red paper. The first is turned green, the second colourless, and the third blue by free acid.

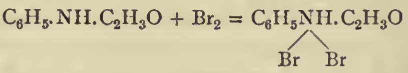
Aromatic amines, containing the amino-group in the side-chain, have the basic character and properties of aliphatic amines.

PREPARATIONS 54—55.

Acetanilide, Bromacetanilide.—Primary and secondary bases form acetyl derivatives with acetic acid, acetyl chloride, or acetic anhydride (see Reactions, pp. 76, 77). Tertiary bases are unacted on in this way. As the acetyl derivatives are much less volatile than the original bases, the method is frequently used for separating a tertiary base from mixtures containing the other two (see Prep. 59, p. 156). The anilides are very stable compounds ; they can be distilled, as a rule, without decomposition, and may be directly brominated, chlorinated and nitrated. In these reactions, either the ortho- or para- or both derivatives are formed. The remaining hydrogen atom of the amino-group may be replaced by (1) a second acid radical, by the action of acetic anhydride, (2) sodium, by the action of the metal, (3) a nitroso-group, with nitrous acid, and (4) chlorine or bromine, by the action of hypochlorous or hypobromous acid.

$C_6H_5N(CO.CH_3)_2$	Diacetanilide.
$C_6H_5NNa.CO.CH_3$	Sodium acetanilide.
$C_6H_5N(NO)CO.CH_3$	Nitrosoacetanilide.
$C_6H_5NCl.CO.CH_3$	Acetchloranilide.

The mechanism of the change effected in producing substitution products by halogens appears to occur in two steps, the first being the addition of a molecule of halogen, probably to the nitrogen, the second being an isomeric change accompanied (if water is present) by the elimination of halogen acid.



$$C_6H_5.NH.C_2H_3O + Br_2 = C_6H_5\underset{Br\ \ Br}{N}H.C_2H_3O$$

$$C_6H_5NHBr_2.C_2H_3O = C_6H_4BrNH.C_2H_3O.HBr.$$

All the anilides are hydrolysed by strong mineral acids or alkalis and the acid radical removed (see also Beckmann's reaction, Prep. 100, p. 212).

Formanilide is a *tautomeric* compound, *i.e.*, it reacts as though it possessed the alternative formulæ,

$$C_6H_5N{:}CH(OH) \qquad C_6H_5NH.CO.H,$$

for it yields two isomeric ethers, the one, by the action of methyl iodide on the silver salt, and the other by the action of methyl iodide on the sodium compound (Comstock). Acetanilide is known in pharmacy as antifebrin, and is used as an antipyretic.

PREPARATIONS 57—58.

m-Dinitrobenzene.—In the Notes on Prep. 48, p. 274, it is mentioned that the second nitro-group enters the meta-position to the first. This is usually the case where two acid groups are successively introduced into the hydrocarbon. Thus, benzenedisulphonic acid, obtained by heating benzene sulphonic acid (see Prep. 74, p. 177) with fuming sulphuric acid, is a meta-compound.

m-Nitraniline.—The reduction product of *m*-dinitrobenzene is naturally *m*-nitraniline. The *o*- and *p*-nitranilines can be obtained by acting upon aniline or, preferably, acetanilide, with fuming nitric acid.

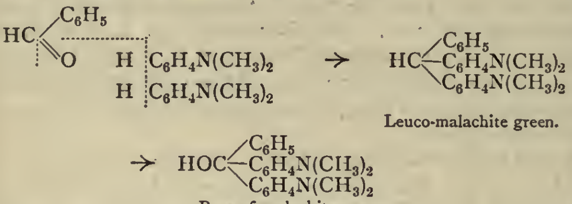
Whereas the first nitro-group of a tri- or di-nitro derivatives is rapidly and completely reduced by ammonium sulphide, the second is very slowly attacked. The rate of change appears to be determined mainly by the acidic nature of the molecule as a whole, the halogens and carboxyl playing a similar *rôle* to that of the nitro-group. In all these cases hydroxylamine compounds are produced as intermediate products.

PREPARATION 59.

Dimethylaniline.—It is a well-known fact that the alkyl halides convert the primary amines into secondary and tertiary bases (Hofmann). The formation of dimethylaniline is probably due to the action of CH_3Cl, which is formed, as an intermediate product, by the action of hydrochloric acid on the methyl alcohol. There is always a small quantity of monomethylaniline, $C_6H_5NHCH_3$, produced at the same time. The three bases cannot well be separated by fractional distillation, as their boiling points lie too near together,

Aniline	180°.
Methylaniline	192°.
Dimethylaniline	192°.

It is for this reason that the action of acetic anhydride is utilised, which only unites with the primary and secondary base. Dimethylaniline is a weak base, which, like aniline, is neutral to litmus, but gives no stable salts. It is used in the preparation of malachite green (benzaldehyde green) by heating together dimethylaniline, benzaldehyde, and solid zinc chloride. The product (leuco-malachite green) is then oxidised with lead peroxide and hydrochloric acid (see p. 216),



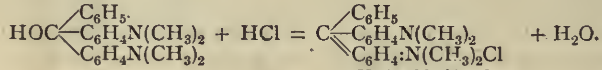
$$HC\left\langle\begin{array}{l}C_6H_5\\O\end{array}\right. \quad \begin{array}{l}H\\H\end{array}\begin{array}{l}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{array} \rightarrow HC\left\langle\begin{array}{l}C_6H_5\\C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{array}\right.$$

Leuco-malachite green.

$$\rightarrow HOC\left\langle\begin{array}{l}C_6H_5\\C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{array}\right.$$

Base of malachite green.

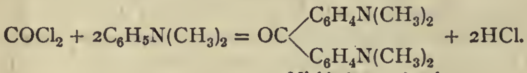
The latter, in presence of the hydrochloric acid, is converted into the hydrochloride,



$$HOC\left\langle\begin{array}{l}C_6H_5\\C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{array}\right. + HCl = C\left\langle\begin{array}{l}C_6H_5\\C_6H_4N(CH_3)_2\\C_6H_4{:}N(CH_3)_2Cl\end{array}\right. + H_2O.$$

Hydrochloride of malachite green.

Dimethylaniline is also used for the preparation of tetramethyldiaminobenzophenone (Michler's compound), which forms the basis of many colouring matters, and is obtained by acting upon dimethylaniline with phosgene (see p. 314),



$$COCl_2 + 2C_6H_5N(CH_3)_2 = OC\left\langle\begin{array}{l}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{array}\right. + 2HCl.$$

Michler's compound.

PREPARATION 60.

Nitrosodimethylaniline.—It is a peculiarity of the tertiary aromatic amines, which distinguish them from the corresponding aliphatic compounds, that they are capable of reacting with nitrous acid. Here the nitroso-group replaces hydrogen in the para-position to the dimethylamino-group.

The substances, thus formed, are bases, and form salts with acids, which dissolve in water with a yellow colour. The solubility of the hydrochloride of the nitroso-bases in water distinguishes them from the nitrosamines of the secondary bases, which are insoluble.

Nitrosodimethylaniline is readily oxidised to nitrodimethylaniline.

It is an interesting fact that the nitrosamines of the secondary bases undergo molecular change when acted on with alcoholic hydrochloric acid. The nitroso-group is thereby transferred to the para-position in the nucleus (O. Fischer),

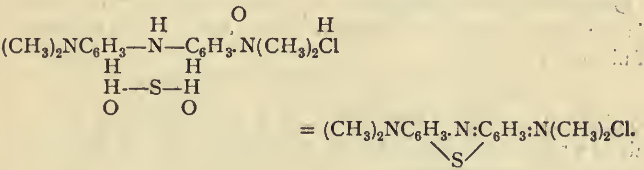
$$C_6H_5N(NO)CH_3 = NO.C_6H_4.NHCH_3.$$

The para-nitroso derivatives of both secondary and tertiary amines are decomposed with caustic soda into nitrosophenol and alkylamine.

The formation of methylene blue may be explained as follows: By the action of ammonium sulphide on nitrosodimethylaniline, the nitroso-group is reduced to an amino-group. Two molecules of *p*-aminodimethylaniline then combine with the elimination of ammonia to form a diphenylamine derivative,

$$(CH_3)_2NC_6H_4\,\boxed{NH_2\quad H}\,HNC_6H_4N(CH_3)_2$$
$$= (CH_3)_2NC_6H_4.NH.C_6H_4N(CH_3)_2.$$

The sulphur of the hydrogen sulphide then enters the molecule under the oxidising influence of the ferric chloride, forming a thiodiphenylamine derivative,

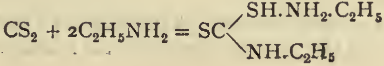


$$\begin{array}{l}\qquad\qquad\quad H\qquad\quad O\qquad\quad H\\(CH_3)_2NC_6H_3—N—C_6H_3.N(CH_3)_2Cl\\\qquad\qquad H\qquad\quad H\\\qquad\qquad H—S—H\\\qquad\qquad O\qquad\quad O\end{array}$$
$$= (CH_3)_2NC_6H_3.N:C_6H_3:N(CH_3)_2Cl.\atop \diagdown S\diagup$$

Methylene blue

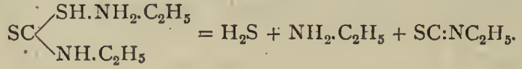
PREPARATION 61.

Thiocarbanilide, Thiocarbimide, Triphenylguanidine.—Whereas carbon bisulphide reacts with aromatic amino-compounds yielding a thiocarbanilide, with primary aliphatic amines the reaction takes a different course and thiocarbamates are produced,



$$CS_2 + 2C_2H_5NH_2 = SC\begin{array}{l}\diagup SH.NH_2.C_2H_5\\ \diagdown NH.C_2H_5\end{array}$$

The product can, however, be converted into the mustard oil by treatment with a metallic salt which removes hydrogen sulphide.



$$SC\begin{cases} SH.NH_2.C_2H_5 \\ NH.C_2H_5 \end{cases} = H_2S + NH_2.C_2H_5 + SC{:}NC_2H_5.$$

Among the reactions appended to this preparation, the formation of phenylcarbimide from phenyl mustard oil is described. It should be noted that phenyl carbimide, like the thiocarbimide, unites with ammonia, amines, and more especially with alcohols and phenols. The bases yield urea derivatives; the alcohols and phenols form urethanes.

$C_6H_5N{:}CO + NH_3 = C_6H_5NH.CO.NH_2$ Phenyl urea.
$C_6H_5N{:}CO + NH_2CH_3 = C_6H_5NH.CO.NHCH_3$ Methyl phenyl urea.
$C_6H_5N{:}CO + C_2H_5OH = C_6H_5NH.CO.OC_2H_5$ Phenyl urethane
$C_6H_5N{:}CO + C_6H_5OH = C_6H_5NH.CO.OC_6H_5$ Phenyl carbamic phenyl ester.

The latter two reactions are frequently used for detecting the presence of a hydroxyl group (Goldschmidt).

PREPARATION 62.

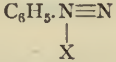
Diazobenzene Sulphate.—Whereas nitrous acid immediately decomposes the primary aliphatic amines with evolution of nitrogen,

$$CH_3NH_2 + HNO_2 = CH_3OH + N_2 + H_2O,$$

no nitrogen is evolved if nitrous acid is allowed to act upon a salt of a primary aromatic amine *in the cold.* The solution then contains a diazo-salt, which is readily soluble in water. It may already have been observed that in the salts of diazobenzene, the radical, diazobenzene, $C_6H_5N_2$, plays the part of ammonium, NH_4, in the ammonium salts. Diazobenzene chloride, nitrate, sulphate, &c., correspond to ammonium chloride, nitrate, and sulphate.

$C_6H_5N_2.Cl$	$NH_4.Cl.$
$C_6H_5N_2.NO_3$	$NH_4.NO_3.$
$C_6H_5N_2.SO_4H$	$NH_4.SO_4H.$

The hydrate of diazobenzene, $C_6H_5N_2.OH$, which would be analogous to NH_4OH, is also known as an unstable oil. Considerations of this kind have suggested the alternative formula,

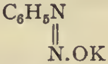


$$\begin{array}{rl} C_6H_5. & N\equiv N \\ & | \\ & X \end{array}$$

in which X stands for the acid radical (Blomstrand). The nitrogen which combines with the acid radical is thereby quinquivalent, as in the ammonium salts. On the other hand, diazobenzene hydrate forms two isomeric potassium salts, one of which is obtained by adding caustic potash to diazobenzene chloride. This compound is unstable, and unites in the ordinary way with phenols to form hydroxyazobenzene derivatives (see Reaction 6, p. 163). The second one, which is obtained by heating the first to 130° with caustic potash, is very stable, and does not combine directly with phenols (Schraube and Schmidt). Other derivatives of diazobenzene exist in two forms, such as the cyanide and sulphite. The difference has been explained in two ways. According to one theory, the two potassium compounds represent two different space configurations similar to that of citraconic and mesaconic acid (see p. 266) and the oximes (see p. 301), and are distinguished by the terms 'syn and 'anti' (Hantzsch).

$$\begin{array}{r} C_6H_5N \\ \| \\ KO.N \end{array}$$

Syn-benzene diazotate of potassium.



$$\begin{array}{l} C_6H_5N \\ \| \\ N.OK \end{array}$$

Anti-benzene diazotate of potassium.

The second theory ascribes the difference to structural arrangement, and the compounds are termed diazo- and isodiazo-compounds (Bamberger).

$C_6H_5N{:}NOK.$
Benzene diazotate of potassium.

$C_6H_5NK.NO.$
Benzene isodiazotate of potassium.

It is now generally admitted that the diazo-salts of the stronger acids, which have only one representative, are most satisfactorily represented by the "diazonium," or Blomstrand formula, and the salts are known as diazonium salts.

A few of the numerous changes which the diazonium salts undergo are illustrated in the series of reactions which follow the preparation, and are among the most important in organic chemistry. Some of these reactions are carried out on a larger scale in Preps. 63—69. It will there be noticed that it is unnecessary, as a rule, to isolate the diazonium salt, but that the substance is prepared in solution, and is decomposed by the specific reagent.

With few exceptions, all aromatic compounds which contain a nuclear amino-group may be diazotised. At the same time there are notable differences in the ease with which the process is effected.

PREPARATION 63.

Toluene from Toluidine.—It is often desirable to obtain the hydrocarbon from the base. The process of diazotisation offers the only convenient method. The diazonium salt may be reduced by alcohol (Reaction 1, p. 162) or, as in the present instance, by sodium stannite. Less direct methods are the conversion of the diazonium compound into (1) the hydrazine (see p. 174), (2) the acid and distillation with lime (p. 200), (3) the halogen derivative and reduction with sodium amalgam, or, finally (4) the phenol and distillation with zinc dust.

PREPARATION 64.

***p*-Cresol.**—This reaction resembles that of nitrous acid on an aliphatic primary amine; but the liquid requires to be warmed.

PREPARATIONS 65—66.

p-Chlorotoluene, p-Bromotoluene.—The action of cuprous chloride, bromide, and cyanide on diazonium chlorides was discovered by Sandmeyer, and is known as 'Sandmeyer's reaction.'

$$\begin{aligned} C_6H_5N_2.Cl &= C_6H_5Cl + N_2. \\ C_6H_5N_2.Br &= C_6H_5Br + N_2. \\ C_6H_5N_2.CN &= C_6H_5CN + N_2. \end{aligned}$$

Some of the cuprous chloride compounds of the diazonium salts have been isolated and analysed, and correspond to the formula $C_6H_5N_2Cl.Cu_2Cl_2$ (Hantzsch). The formation of a crystalline copper compound is rendered very evident in the present preparation. A modification of Sandmeyer's reaction is the introduction of precipitated metallic copper in place of the cuprous salt (Gattermann).

The preparation of potassium iodide-starch paper is made by dipping strips of filter paper into a thin solution of starch paste to which a little potassium iodide has been added, and drying the paper.

The oxidation of a side-chain by means of permanganate solution is one which is commonly employed where the acid is required. The monohalogen derivatives are readily oxidised in this way, but greater difficulty is experienced if two halogen atoms or other acid groups are present. The dichlorotoluenes, for example, are only slowly attacked.

PREPARATION 67.

Iodosotoluene.—The most interesting of the compounds belonging to this group, which were carefully investigated by V. Meyer, is the substance prepared by shaking a mixture of iodosobenzene and iodoxybenzene (obtained by the oxidation of the iodoso-compound) with moist silver oxide. Diphenyliodonium oxide is thus produced, which in basic properties resembles ammonium hydrate,

$$C_6H_5IO + C_6H_5IO_2 + AgOH = (C_6H_5)_2I.OH + AgIO_3.$$

With hydriodic acid it forms the iodide, $(C_6H_5)_2I.I$.

PREPARATION 69.

Diazoaminobenzene.—Diazoamino-compounds are also formed by the action of diazonium salts on primary and secondary amines of both the aliphatic and aromatic series. The method given in the preparation must then be modified. The diazonium salt is first prepared, and the amine stirred in with the addition of sodium acetate. The sodium combines with the mineral acid, liberating the weaker acetic acid, which thereby assists the separation of the diazoamino-compound. Compounds of the following formulæ have been prepared in this way.

$C_6H_5N{:}N.NHC_6H_4.CH_3$	Diazobenzene-aminotoluene.
$C_6H_5N{:}N.NHC_2H_5$	Diazobenzene-ethylamine.
$C_6H_5N{:}N.N(CH_3)_2$	Diazobenzene-dimethylamine.
$C_6H_5N{:}N.NC_5H_{10}$	Diazobenzene-piperidine.

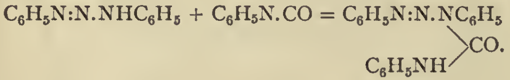
The last compound has been utilised for the preparation of fluorobenzene, and its congeners by the action of conc. hydrofluoric acid,

$$C_6H_5N{:}N.C_5H_{10} + 2HF = C_6H_5F + N_2 + C_5H_{10}NH.HF.$$

Diazoaminobenzene undergoes the following reactions :—

1. The hydrogen of the imino-group may be replaced by acid and alkyl radicals. In the latter case the sodium compound is treated with an alkyl iodide.

2. Phenyl carbimide forms a urea derivative,



$$C_6H_5N{:}N.NHC_6H_5 + C_6H_5N.CO = \begin{matrix} C_6H_5N{:}N.NC_6H_5 \\ C_6H_5NH \end{matrix} \Big\rangle CO.$$

3. With strong hydrochloric acid, decomposition into diazonium salt and amine takes place,

$$C_6H_5N{:}N.NHC_6H_5 + HCl = C_6H_5N_2.Cl + C_6H_5NH_2.$$

If nitrous acid is added, the second molecule of base is also converted into diazobenzene chloride. In presence of cuprous chloride, chlorobenzene is formed.

4. On boiling with water, diazoaminobenzene decomposes into phenol and base,

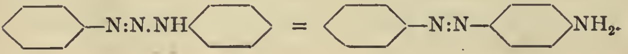
$$C_6H_5N{:}N.NH.C_6H_5 + H_2O = C_6H_5OH + C_6H_5NH_2 + N_2.$$

5. On reduction, it splits up into phenylhydrazine and aniline,

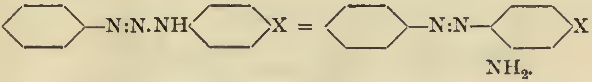
$$C_6H_5N{:}N.NHC_6H_5 + 2H_2 = C_6H_5NH.NH_2 + C_6H_5NH_2.$$

PREPARATION 70.

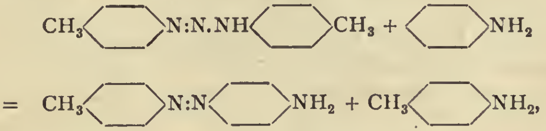
Aminoazobenzene.—The conversion of diazoaminobenzene into aminoazobenzene resembles the formation of benzidine from hydrazobenzene (see p. 148). The diazo-nitrogen seizes on the carbon of the nucleus in the para-position to the amino-group,



If the para-position is already occupied, the nitrogen takes the ortho-position to the amino-group,



but the reaction only takes place readily where the para-position is free. The manner in which the change is brought about has not been satisfactorily explained, although from the fact that *p*-diazoaminotoluene yields, on warming with aniline hydrochloride, *p*-toluene azoaminobenzene and *p*-toluidine,

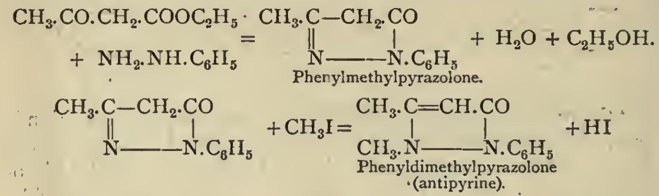


it would appear as if the hydrochloride of the base were the chief factor in the decomposition, and that the change was rather *inter-* than *intra*-molecular. Aminoazobenzene, under the name of *aniline yellow*, has been used as a colouring matter. Its chief technical application at present is in the manufacture of a class of dark blue colours, known as *indulines*. On reduction with tin and hydrochloric acid, it decomposes into two molecules of base, aniline and *p*-phenylenediamine, a reaction which is shared by most of the azo-compounds (see p. 176),

$$C_6H_5N{:}N.C_6H_4NH_2 = C_6H_5NH_2 + NH_2C_6H_4NH_2.$$

Preparation 71.

Phenylhydrazine, Phenylmethylpyrazolone. — The use of phenylhydrazine or, in some cases *p*-bromo- or *p*-nitrophenylhydrazine, as a reagent for the detection of aldehydes and ketones, has been illustrated in the reactions on p. 70. One of its most important technical uses is in the preparation of antipyrine, in which the product, obtained by the action of phenylhydrazine on ethyl acetoacetate, is acted upon with methyl iodide. The two reactions are represented as follows :—

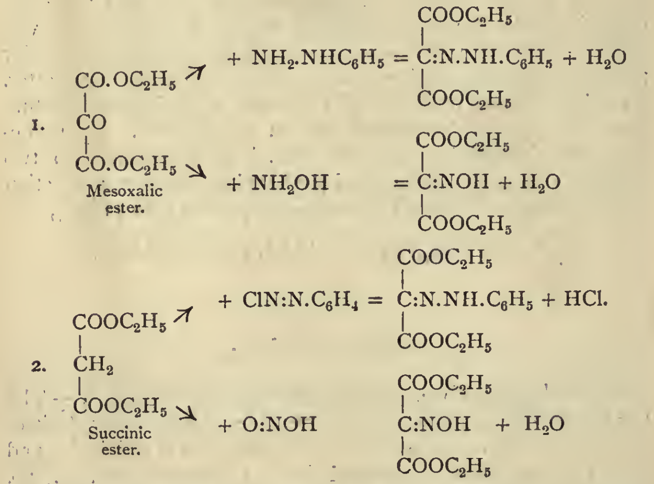


Phenylmethylpyrazolone.

Phenyldimethylpyrazolone (antipyrine).

The variety of syntheses into which phenylhydrazine enters cannot be described here; but reference must be made to the text-book.

It should be noted that the action of phenylhydrazine on the ketone group, and of diazobenzene salts on the methylene group situated between two CO groups, are analogous to that of hydroxylamine and nitrous acid upon these two groups, of which the following are examples :—



1\. Mesoxalic ester.

2\. Succinic ester.

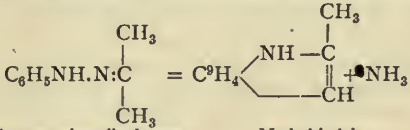
$$\begin{array}{l}\mathrm{CO.OC_2H_5}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{CO.OC_2H_5}\end{array} + \mathrm{NH_2.NHC_6H_5} = \begin{array}{l}\mathrm{COOC_2H_5}\\ |\\ \mathrm{C{:}N.NH.C_6H_5}\\ |\\ \mathrm{COOC_2H_5}\end{array} + \mathrm{H_2O}$$

$$\begin{array}{l}\mathrm{CO.OC_2H_5}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{CO.OC_2H_5}\end{array} + \mathrm{NH_2OH} = \begin{array}{l}\mathrm{COOC_2H_5}\\ |\\ \mathrm{C{:}NOH}\\ |\\ \mathrm{COOC_2H_5}\end{array} + \mathrm{H_2O}$$

$$\begin{array}{l}\mathrm{COOC_2H_5}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{COOC_2H_5}\end{array} + \mathrm{ClN{:}N.C_6H_4} = \begin{array}{l}\mathrm{COOC_2H_5}\\ |\\ \mathrm{C{:}N.NH.C_6H_5}\\ |\\ \mathrm{COOC_2H_5}\end{array} + \mathrm{HCl.}$$

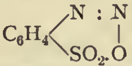
$$\begin{array}{l}\mathrm{COOC_2H_5}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{COOC_2H_5}\end{array} + \mathrm{O{:}NOH} \quad \begin{array}{l}\mathrm{COOC_2H_5}\\ |\\ \mathrm{C{:}NOH}\\ |\\ \mathrm{COOC_2H_5}\end{array} + \mathrm{H_2O}$$

Phenylhydrazine has been used in the synthesis of indole derivatives. The hydrazones of aldehydes and ketones containing a methyl group are decomposed on heating with zinc chloride, indoles being formed with elimination of ammonia. (E. Fischer.)


Acetone-phenylhydrazone. Methyl indole.

PREPARATION 72.

Sulphanilic Acid.—The acid characters of this substance, which is both base and acid, are more prominently developed than the basic character. Nevertheless it reacts with nitrous acid like a primary amine, and forms a diazonium salt, which has the following constitution (see Prep. 62, p. 161) :—


Diazobenzene sulphonic acid.

The formation of suphanilic acid is probably preceded by the sulphonation of the amino-group,

$$C_6H_5NH.SO_3H.$$

A compound of this character has been obtained which decomposes with acids into *o*- and *p*-aminosulphonic acid by a process of intramolecular change (Bamberger). The fact of the para-compound being exclusively formed at the higher temperature may account for the production of this substance in the present preparation.

PREPARATION 66.

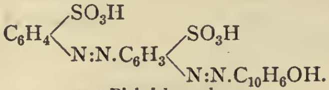
Methyl Orange.—The first point to notice in this reaction is that the diazonium salt forms no diazoamino-compound with the dimethylaniline, but at once produces an azo-compound. This is always the case with tertiary amines, some secondary amines like diphenylamine and the phenols. The reaction may be regarded as typical of the formation of all azo-colouring matters. At least two substances are requisite in this process; on the one hand an aromatic compound containing an amino-group in the nucleus, and, on the other, a base or phenol

The first is diazotised and combined or coupled with the second. The coupling takes place, in the case of amines, in a faintly acid or neutral solution, in the case of phenols, in an alkaline solution (see Reaction 6, p. 163). In all cases the diazo-group seizes upon the carbon in the para-position to the amino- or hydroxyl group of the coupled nucleus. When the para-position is already appropriated, the ortho-position serves as a link, but no coupling ever occurs in the meta-position. The sulphonic acid derivatives of the base or phenol are frequently preferable to the unsubstituted compound. The dyes formed have in consequence of the presence of the SO_3H group an acid character, which renders them capable of forming soluble sodium salts, and adapts them better for dyeing purposes. When an azo-compound is formed by coupling the diazo-compound with a primary amine, the new product is capable of being diazotised and coupled a second time. Thus a tetrazo-compound is formed containing a double diazo-group –N:N–. Aminoazobenzene, when diazotised, forms diazo-azobenzene with nitrous acid, which, like a simple diazo-compound, reacts with the phenols,

$$C_6H_5N{:}N.C_6H_4NH_2HCl + HNO_2 = C_6H_5N{:}N.C_6H_4N_2.Cl + 2H_2O.$$

$$C_6H_5N{:}N.C_6H_4N_2.Cl + C_6H_5ONa \\ = C_6H_5N{:}N.C_6H_4N{:}N.C_6H_4OH + NaCl.$$

If aminoazobenzene is sulphonated with fuming sulphuric acid, and the product again diazotised and coupled with β-naphthol, *Biebrich scarlet* is formed,

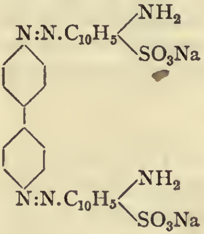


$$C_6H_4\begin{cases}SO_3H \\ N{:}N.C_6H_3\begin{cases}SO_3H \\ N{:}N.C_{10}H_6OH.\end{cases}\end{cases}$$

Biebrich scarlet.

If in the last phase the different sulphonic acids of β-naphthol are employed, various shades of red, known as *Croceins*, are produced. Thus it appears that the colour deepens from orange to red with the introduction of a second azo-group.

This is not the only method of forming tetrazo-compounds. Each amino-group of a diamine may be diazotised and coupled. Benzidine and its homologues, which have been utilised in this way, have a special value for the cotton dyer, as the shades produced are not only very brilliant, but, unlike the majority of colouring matters, are *substantive colours*, *i.e.*, possess the property of attaching themselves to the cotton fibre without the aid of a mordant. *Congo reds* and *benzopurpurins* are combinations of benzidine and its homologues with the sulphonic acids of naphthol and naphthylamine. The following is the constitution of Congo red, the simplest of these compounds, which is used in the form of its sodium salt :—



Attention should be drawn to the fact that azobenzene, although a brightly coloured substance, is without dyeing properties, *i.e.*, it is not a colouring matter, whereas aminoazobenzene and methyl orange are true dyes. They all three contain the azo-group (–N:N–), called by Witt a *chromophore*, united to two aromatic nuclei ; but in the case of aminoazobenzene and methyl orange, one of these nuclei contains a basic group, NH_2 or $N(CH_3)_2$. It will also have been observed that the combinations with phenols likewise result in the production of colouring matters. It would appear, therefore, as if there were at least two essentials to a dye, a fundamental or mother substance like azobenzene, termed a *chromogenic* compound, and an amino- or hydroxyl group, called an *auxochrome*. The same thing has been observed in the case of other colouring matters (see Note on Prep. 103, p. 313).

Most of the azo-colours split at the double link, on reduction with stannous chloride and hydrochloric acid, forming two molecules of base. Methyl orange yields sulphanilic acid and dimethyl *p*-phenylenediamine,

$$SO_3H.C_6H_4N{:}N.C_6H_4N(CH_3)_2 + 2H_2$$
$$= SO_3H.C_6H_4NH_2 + NH_2C_6H_4N(CH_3)_2.$$

PREPARATION 74.

Potassium Benzenesulphonate.—The formation of sulphonic acids by the action of sulphuric acid, &c., on the aromatic hydrocarbon is a special property of aromatic hydrocarbons, although, in a few cases, paraffins have been found to react in a similar manner. The process is called "sulphonation." In place of conc. sulphuric acid, fuming sulphuric acid, *i.e.*, an acid containing varying proportions of sulphur trioxide (see Prep. 109, p. 226), and, occasionally, chlorosulphonic acid, $ClSO_2OH$, are used. In the two latter cases sulphones are sometimes formed as a by-product,

$$2C_6H_6 + SO_3 = (C_6H_5)_2SO_2 + H_2O.$$
$$2C_6H_6 + ClSO_2OH = (C_6H_5)_2SO_2 + HCl + H_2O.$$

The sulphonic acids are also obtained by the oxidation of thiophenols, a reaction which, at the same time, indicates their constitution,

$$C_6H_5SH + O_3 = C_6H_5.SO_3H.$$

The majority of aromatic sulphonic acids are very soluble in water, and are difficult to obtain in the crystalline form. On the other hand, the sodium or potassium salts generally crystallise well, and it is customary to prepare them by pouring the sulphonic acid directly after sulphonation into a strong solution of sodium or potassium chloride (Gattermann).

The sulphonic acids decompose on heating into the hydrocarbon and SO_3. This reaction is greatly facilitated by heating with conc. hydrochloric acid to 150—180° (Jacobsen), or by passing superheated steam into the sulphonic acid mixed with moderately strong sulphuric acid (Armstrong).

This method is sometimes used for separating hydrocarbons, one of which is more easily sulphonated than another. The sulphonic acid is separated from the unchanged hydrocarbon, and the hydrocarbon is then regenerated from the sulphonic acid.

The salts of the sulphonic acids undergo the following reactions :—

1. By fusion with caustic alkalis, phenols are prepared (see Preps. 106 and 219),

$$C_6H_5SO_3Na + NaOH = C_6H_5OH + Na_2SO_3.$$

2. By distillation with potassium cyanide, the nitriles are obtained,

$$C_6H_5SO_3K + KCN = C_6H_5CN + K_2SO_3.$$

3. By fusion with sodium formate, the sulphonic group is replaced by carboxyl,

$$C_6H_5SO_3Na + HCOONa = C_6H_5COONa + NaHSO_3.$$

4 By the action of phosphorus pentachloride the sulphonic chloride is obtained,

$$C_6H_5SO_3K + PCl_5 = C_6H_5SO_2Cl + POCl_3 + KCl.$$

PREPARATION 75.

Benzenesulphonic Chloride.—The sulphonic chlorides differ from the carboxylic chlorides in being very slowly decomposed by water. They react, however, in an analogous fashion with alcohols, phenols, and amines in presence of caustic soda.

The behaviour of primary, secondary, and tertiary amines has been suggested as a basis of separation of these three classes of compounds. The primary amines usually form compounds with the sulphonic chloride, which dissolve in caustic soda ; the derivatives of the secondary amine are insoluble, whereas the tertiary amines do not react with the sulphonic chloride (Hinsberg). The method cannot always be employed.

On reduction of the sulphonic chloride with zinc dust and water, the zinc salt of the sulphinic acid is formed,

$$2C_6H_5SO_2Cl + 2Zn = (C_6H_5SO_2)_2Zn + ZnCl_2.$$

The acid is separated from the zinc salt by boiling with sodium carbonate, filtering from zinc carbonate, and decomposing the soluble sodium salt with sulphuric acid, which precipitates the sulphinic acid.

The sulphinic acids are unstable compounds. They are readily oxidised to sulphonic acids ; on fusion with alkalis they are converted into the hydrocarbon and alkaline sulphite,

$$C_6H_5.SO_2Na + NaOH = Na_2SO_3 + C_6H_6,$$

on reduction they form thiophenols,

$$C_6H_5.SO_2H + 2H_2 = C_6H_5SH + 2H_2O.$$

PREPARATION 76.

Phenol.—Fusion of the alkali salt of the sulphonic acid with caustic soda or potash is a common method for preparing phenols (see Prep. 106, p. 219). Phenols correspond in constitution to the tertiary alcohols of the aliphatic series, but differ in their more negative character. The phenols dissolve in caustic alkalis, forming alkaline phenates, which are, however, decomposed by carbon dioxide. In this way a phenol may be separated from an acid. The solution in caustic soda is saturated with carbon dioxide, and the phenol is then extracted with ether or filtered off. The entrance of nitro-groups into the nucleus converts phenols into strong acids (see Preps. 79 and 80).

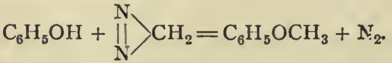
The various reactions which the phenols undergo are illustrated in Preps. 79—84.

The technical method for obtaining phenol is by shaking out with caustic soda the "middle oil" of the coal-tar distillate, after some of the naphthalene has crystallised out. The phenol dissolves in the alkali, and is then removed from insoluble oils. The alkaline liquid is acidified, the phenol separated, distilled, and finally purified by freezing.

PREPARATION 77.

Anisole.—The preparation of anisole from phenol is analogous to Williamson's synthesis of the ethers (see p. 236), but the ethers of phenol cannot be obtained by the action of the alcohol on the phenol in presence of sulphuric acid. This reaction can, however, be effected in the case of the naphthols (see p. 316).

Another method of replacing hydrogen by methyl, in addition to the use of alkyl halide and alkyl sulphate, is by the action of diazomethane on the phenol :



$$C_6H_5OH + \begin{matrix} N \\ \| \\ N \end{matrix}\!\!>CH_2 = C_6H_5OCH_3 + N_2.$$

The methyl group in anisole can be split off, and the phenol regenerated by heating with HCl or HI,

$$C_6H_5OCH_3 + HI = CH_3I + C_6H_5OH.$$

The latter reaction has been made the basis of a quantitative method for determining the number of methoxyl groups (OCH_3) present in a compound (Zeisel, see p. 220).

PREPARATION 78.

Hexahydrophenol.—The method of Sabatier and Senderens for the reduction of organic compounds is very generally applicable. It consists in passing the vapour of the organic compound mixed with hydrogen over finely divided metals, especially nickel, as in the example given. Aldehydes and ketones are reduced to alcohols, olefines to paraffins, and, in the aromatic series, hydrogen is taken up in the nucleus and hydrocyclic compounds result. The hydrocarbons form cycloparaffins; the phenols, cyclic alcohols; the bases, cyclic amines, &c.

PREPARATION 79.

o- and p-Nitrophenol.—The action of nitric acid on phenol is much more energetic than it is in the case of benzene. To obtain the mono-derivatives, the acid has, in consequence, to be diluted.

The entrance of the nitro-group renders the phenol more strongly acid, so that the nitrophenols, unlike the phenols, form stable salts with alkaline carbonates. It should be noted that the nitro-group enters the ortho- and para-position, but not the meta-position to the OH group, according to the general rule explained on p. 274. Moreover, the ortho-compound is more volatile than the para-compound. Compare *o*- and *p*-hydroxybenzaldehyde (Prep. 83, p. 188).

PREPARATION 80.

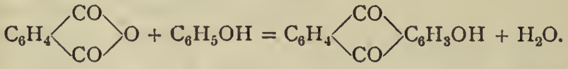
Picric Acid.—The presence of three nitro-groups converts the phenol into a strong acid. Picryl chloride, which is formed by the action of PCl_5 on the acid, behaves like an acid chloride, is decomposed by water and alkalis and forms picramide or trinitraniline with ammonia,

$$C_6H_2(NO_2)_3Cl + NH_3 = C_6H_2(NO_2)_3NH_2 + HCl.$$

Note that the three nitro-groups occupy meta-positions in regard to one another; ortho- or para-positions in reference to the hydroxyl group.

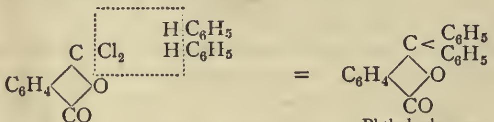
PREPARATIONS 81—82.

Phenolphthalein.—The action of phthalic anhydride on phenol takes place in two ways. When equal molecules of the substance react in presence of conc. sulphuric acid, hydroxyanthraquinone is formed (Baeyer),



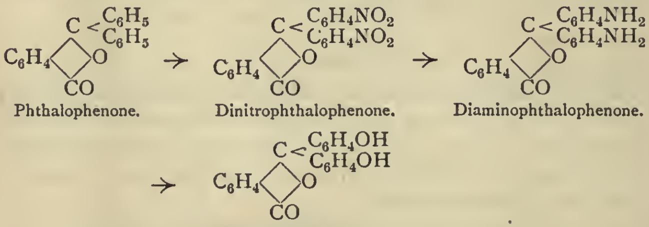
$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O + C_6H_5OH = C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>C_6H_3OH + H_2O.$$

It is by a similar process that alizarin has been synthesised with the object of ascertaining its constitution (see Notes on Prep. 110, p. 316). When two molecules of phenol and one molecule of phthalic anhydride are heated together with conc. sulphuric acid, then phenolphthalein is formed (Baeyer). Its constitution has been determined by its synthesis from phthalyl chloride and benzene by means of the "Friedel-Crafts' reaction" (see Notes on Prep. 100, p. 309). Phthalyl chloride and benzene yield in presence of $AlCl_3$ phthalophenone,



Phthalophenone.

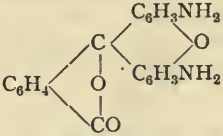
Phthalophenone is then converted successively into dinitro-, diamino-, and, finally, by the action of nitrous acid, into dihydroxyphthalophenone or phenolphthalein,



Phthalophenone. Dinitrophthalophenone. Diaminophthalophenone.

Phenolphthalein.

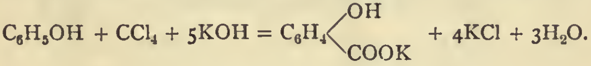
An important group of colouring matters, known as the "rhodamines," is obtained from phthalic anhydride and *m*-aminophenol and its derivatives. They have a constitution similar to that of fluorescein. The simplest of these compounds is represented by the following formula :—



Rhodamine.

PREPARATION 83.

Salicylaldehyde, p-Hydroxybenzaldehyde.—"Reimer's reaction" for the preparation of hydroxyaldehydes from phenols is applicable to a very large number of monohydric and polyhydric phenols. The substitution of two H atoms by two aldehyde groups sometimes occurs, as in the case of resorcinol. An analogous reaction is that of caustic potash and carbon tetrachloride on phenol, which yields chiefly *p*-hydroxybenzoic acid,



$$C_6H_5OH + CCl_4 + 5KOH = C_6H_4{<}\begin{array}{l}OH\\COOK\end{array} + 4KCl + 3H_2O.$$

PREPARATION 84.

Salicylic Acid.—The reaction was discovered by Kolbe, and is known as "Kolbe's synthesis." It will have been observed that it takes place in two steps. Sodium phenylcarbonate is first formed, which then undergoes intramolecular change with the production of sodium salicylate (Schmidt). The technical process is carried out in autoclaves, in which carbon dioxide is passed into the sodium phenate under pressure at 120—130°. It is a curious fact that the use of potassium phenate yields, especially at a high temperature (220°), almost exclusively the *p*-hydroxybenzoate of potassium.

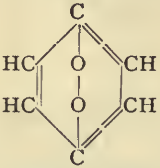
The above reaction may be applied in the case of other phenols.

PREPARATION 85.

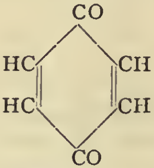
Quinone and Quinol.—Quinone, which was originally obtained by the oxidation of quinic acid (the acid associated with quinine in cinchona bark), is now prepared from aniline. The aniline, in process of oxidation to quinone, appears to pass through the following intermediate stages,

$$C_6H_5NH_2 \rightarrow C_6H_5N{<}^{H_2}_{O} \rightarrow C_6H_5NH.OH \rightarrow C_6H_4{<}^{NH_2}_{OH} \rightarrow C_6H_4.O_2.$$

The aniline is first oxidised to phenylammonium oxide, which changes into phenylhydroxylamine. The latter also undergoes intramolecular change, being converted into *p*-aminophenol, which is finally oxidised to quinone (Bamberger). It may also be obtained by the oxidation of para-derivatives of aniline, such as *p*-phenylenediamine, sulphanilic acid, *p*-aminophenol, &c. Other amino-compounds and phenols yield corresponding quinones, and it can even be prepared from an amino-compound or phenol, if an alkyl group occupies the para-position, as in the case of mesidine, which loses a methyl group and yields *m*-xyloquinone. Quinone is sometimes regarded as a superoxide (Graebe), sometimes as a para-diketone (Fittig).

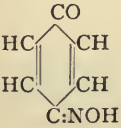


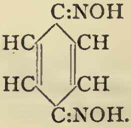
Superoxide formula.



Diketone formula.

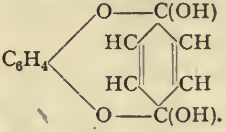
The facts in favour of the first are that quinone, like a peroxide, has a strong oxidising action, that on reduction it yields, not a glycol, but a dihydroxybenzene; moreover, with PCl_5 instead of a tetra-chloro-derivative, a dichlorobenzene is formed. In favour of the ketone structure is the formation of a mono- and di-oxime (Goldschmidt),





Phenylhydrazones are not formed, as phenylhydrazine acts as a reducing agent and produces quinol.

The constitution of quinhydrone, the intermediate product formed by the reduction of quinone or oxidation of quinol, is represented by the formula,



For the formation of dimethylquinone, see p. 251.

PREPARATION 86.

Benzyl Chloride.—The action of chlorine on *boiling* toluene is quite distinct from the action which occurs in the cold or in presence of a "halogen carrier" (see pp. 252, 271). In the present instance substitution takes place in the side-chain. It is a curious fact, however, that chlorine produced by electrolysis in presence of boiling toluene mainly enters the nucleus.

By prolonged action all three hydrogen atoms of the side-chain may be replaced, and the following compounds obtained:—

$C_6H_5CH_2Cl$	Benzyl Chloride.
$C_6H_5CHCl_2$	Benzal Chloride.
$C_6H_5CCl_3$	Benzotrichloride.

Hydrocarbons containing the halogen in the side-chain may be generally, though not invariably distinguished, by their irritating action on the eyes and mucous membrane of the nose, from those in which the halogen is present in the nucleus. Moreover, the halogen in the side-chain is much more readily substituted or removed than when it occurs in the nucleus. In this respect the above compounds resemble the members of the aliphatic series (alkyl and alkylene halides). Benzyl chloride is decomposed by water, ammonia, and potassium cyanide, forming benzyl alcohol, benzyl cyanide, and benzylamine.

$$C_6H_5CH_2Cl + H_2O = \underset{\text{Benzyl alcohol.}}{C_6H_5CH_2OH} + HCl.$$

$$C_6H_5CH_2Cl + KCN = \underset{\text{Benzyl cyanide.}}{C_6H_5CH_2CN} + KCl.$$

$$C_6H_5CH_2Cl + 2NH_3 = \underset{\text{Benzylamine.}}{C_6H_5CH_2NH_2} + NH_4Cl.$$

It is also much more easily oxidised than toluene to benzoic acid,

$$C_6H_5CH_2Cl + O_2 = C_6H_5COOH + HCl.$$

Benzal chloride and benzotrichloride are also decomposed by water, the former in presence of calcium carbonate, and the latter at a high temperature, yielding, in the one case, benzaldehyde, and in the other, benzoic acid,

$$C_6H_5CHCl_2 + H_2O = \underset{\text{Benzaldehyde.}}{C_6H_5COH} + 2HCl.$$

$$C_6H_5CCl_3 + 2H_2O = \underset{\text{Benzoic acid.}}{C_6H_5CO.OH} + 3HCl.$$

PREPARATION 87.

Benzyl alcohol may be also obtained by the action of caustic potash on benzaldehyde (see Reaction 4, p. 197). This reaction is specially characteristic of cyclic-compounds containing an aldehyde-group in the nucleus, although some of the higher aliphatic aldehydes behave in a similar fashion (Cannizzaro),

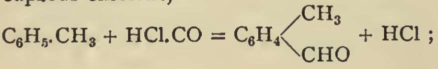
$$2C_6H_5COH + KOH = \underset{\text{Benzyl alcohol.}}{C_6H_5CH_2OH} + \underset{\text{Potassium benzoate.}}{C_6H_5COOK.}$$

Benzyl alcohol has the properties of an aliphatic alcohol, and not those of a phenol. On oxidation, it gives benzaldehyde and benzoic acid, and it forms benzyl esters with acids or acid chlorides,

$$\underset{\text{Benzyl benzoate.}}{C_6H_5CO.OCH_2.C_6H_5.}$$

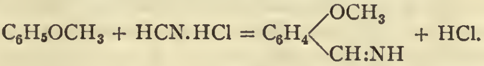
PREPARATION 88.

Benzaldehyde.—The aldehydes of the aromatic series may also be obtained by the oxidation of a methyl side-chain with chromium oxychloride. The solid brown product, $C_6H_5CH_3(CrO_2Cl_2)_2$, formed by adding CrO_2Cl_2 to toluene, dissolved in carbon bisulphide, is decomposed with water, and benzaldehyde separates out (Etard). Other methods for preparing aromatic aldehydes are (1) the Friedel-Crafts reaction, in which a mixture of carbon monoxide and hydrogen chloride are passed into the hydrocarbon in presence of aluminium chloride and a little cuprous chloride,



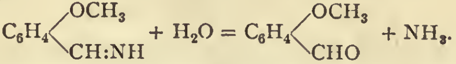
$$C_6H_5.CH_3 + HCl.CO = C_6H_4\left\langle\begin{matrix}CH_3\\CHO\end{matrix}\right. + HCl;$$

(2) also by passing a mixture of hydrogen cyanide and hydrogen chloride into a phenol ether in presence of $AlCl_3$,



$$C_6H_5OCH_3 + HCN.HCl = C_6H_4\begin{cases}OCH_3\\CH{:}NH\end{cases} + HCl.$$

The product is then hydrolysed with hydrochloric acid (Gattermann),

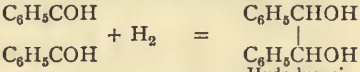


$$C_6H_4\begin{cases}OCH_3\\CH{:}NH\end{cases} + H_2O = C_6H_4\begin{cases}OCH_3\\CHO\end{cases} + NH_3.$$

(3) Grignard's reaction can also be used for preparing aromatic aldehydes (p. 308).

The numerous reactions which benzaldehyde undergoes are described in this preparation, and in some of the subsequent ones (see Preps. 93–97).

On reduction, benzaldehyde yields, in addition to benzyl alcohol, a pinacone known as *hydrobenzoin*,



$$\begin{matrix}C_6H_5COH\\C_6H_5COH\end{matrix} + H_2 = \begin{matrix}C_6H_5CHOH\\ |\\ C_6H_5CHOH\end{matrix}$$

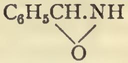
Hydrobenzoin.

PREPARATION 89.

***α*- and *β*-Benzaldoximes.**—The existence of two isomeric benzaldoximes was first observed by Beckmann in 1889, who explained their relation by a difference in structure.

$C_6H_5CH{:}NOH$

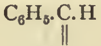
α-Benzaldoxime.



β-Benzaldoxime.

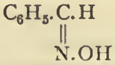
In the following year Hantzsch and Werner published their theory, by which the greater number of isomeric oximes both of aldehydes and ketones have found a satisfactory explanation.

These compounds were not structurally but stereo-isomeric, the relation being similar to that which exists between fumaric, maleic or mesaconic and citraconic acids (p. 265), or again between the two diazotates of potassium (p. 283), and which may be represented as follows :



$$\begin{matrix}C_6H_5.C.H\\ \|\\ HO.N\end{matrix}$$

α-Benzaldoxime.



$$\begin{matrix}C_6H_5.C.H\\ \|\\ N.OH\end{matrix}$$

β-Benzaldoxime.

It will be easily understood from these formula why the β-compound should yield benzonitrile with acetic anhydride whilst the α-compound does not. The proximity of hydrogen and hydroxyl in the former case facilitates the formation and elimination of water. In this way the configuration of most of the aldoximes may be ascertained.

PREPARATION 90.

Benzoic Acid.—The oxidation of the side-chains in aromatic hydrocarbons is a matter of considerable interest, as illustrating the difference of stability of the side-chain and nucleus, and also the influence which the relative positions of the side-chains, where more than one is present, exert in presence of oxidising agents.

The oxidation of the side-chain of an aromatic hydrocarbon, when more than one is present, takes place in successive steps. Thus, mesitylene is converted into the following compounds on oxidation.

$$\begin{tikzcd} & C_6H_3(CH_3)_2CO.OH & \text{Mesitylenic acid.} \\ \text{Mesitylene, } C_6H_3(CH_3)_3 \arrow[ur] \arrow[r] \arrow[dr] & C_6H_3CH_3(CO.OH)_2 & \text{Uvitic acid.} \\ & C_6H_3(CO.OH)_3 & \text{Trimesic acid.} \end{tikzcd}$$

The reagents usually employed are (1) chromic acid or potassium bichromate and sulphuric acid, (2) dilute nitric acid and (3) potassium permanganate in alkaline or neutral solution. The action of these upon the side-chain, when more than one side-chain is present, depends upon their relative position. Thus, for example, potassium bichromate and sulphuric acid either does not act, or completely destroys the compound when the side-chains occupy the ortho-position (Fittig), whereas the para- and meta-compounds yield the corresponding carboxylic acids. This is true also of substituted hydrocarbons with one side-chain; thus with nitric acid *m*- and *p*-nitrotoluene give *m*- and *p*-nitrobenzoic acid, whilst the ortho-compound is either unattacked or destroyed. If, however, the substituent is a halogen and the oxidising agent nitric acid, the meta-compound is least, and the para-compound most acted on. Dilute nitric acid or alkaline permanganate are most serviceable for oxidising side-chains where only one side-chain is to be converted into carboxyl on account of their less energetic action.

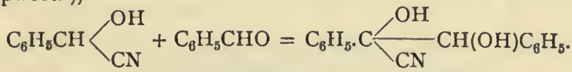
The oxidation of a halogen-substituted side-chain by the usual oxidising agents is much more readily accomplished than that of a simple alkyl group. A similar case is that of naphthalene tetrachloride, $C_{10}H_8Cl_4$, which, though an additive compound, is much more readily converted into phthalic acid than naphthalene itself.

PREPARATION 91.

m-Nitro-, m-Amino-, m-Hydroxy-benzoic Acids.—This series of compounds merely furnishes an exercise in the processes previously described and illustrates the application of the same reactions in the case of a substituted benzene derivative containing a nitro-group. It also illustrates the manner in which meta-compounds of benzoic acid may be indirectly prepared where a direct method is inapplicable.

PREPARATION 93.

Benzoin.—As a small quantity of potassium cyanide is capable of converting a large quantity of benzaldehyde into benzoin, the action of the cyanide has been explained as follows: The potassium cyanide first reacts with the aldehyde and forms a cyanhydrin, which then condenses with another molecule of aldehyde, hydrogen cyanide being finally eliminated (Lapworth),



$$C_6H_5CH\left\langle\begin{matrix}OH\\ CN\end{matrix}\right. + C_6H_5CHO = C_6H_5.C\left\langle\begin{matrix}OH\\ CN\end{matrix}\right.\!\!-\!CH(OH)C_6H_5.$$
$$= C_6H_5.CO.CH(OH).C_6H_5 + HCN.$$

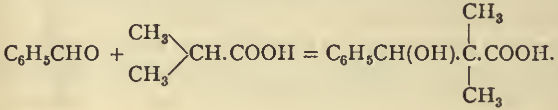
The same reaction occurs with other aromatic aldehydes (anisaldehyde, cuminol, furfurol, &c.).

Benzoin yields hydrobenzoin on reduction with sodium amalgam, and desoxybenzoin, $C_6H_5CO.CH_2.C_6H_5$, when reduced with zinc and hydrochloric acid.

The latter, which contains the group $CO.CH_2.C_6H_5$, behaves like malonic ester, the hydrogen of the methylene group being replaceable by sodium, and hence by alkyl groups.

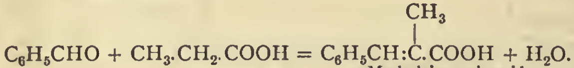
PREPARATION 94.

Cinnamic Acid.—The reaction, which takes place when an aldehyde (aliphatic or aromatic) acts on the sodium salt of an aliphatic acid in presence of the anhydride, is known as "Perkin's reaction," and has a very wide application. According to the result of Fittig's researches on the properties of the unsaturated acids described below, the reaction occurs in two steps. The aldehyde forms first an additive compound with the acid, the aldehyde carbon attaching itself to the α-carbon (*i.e.*, next the carboxyl) of the acid. A saturated hydroxy-acid is formed, which is stable, if the α-carbon is attached to only one atom of hydrogen, as in the case of isobutyric acid,



$$C_6H_5CHO + \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH.COOH = C_6H_5CH(OH).\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}.COOH.$$

If, as in acetic and propionic acids, the group CH_2 is present in the α-position, water is simultaneously split off, and an unsaturated acid results,



$$C_6H_5CHO + CH_3.CH_2.COOH = C_6H_5CH:\overset{\displaystyle CH_3}{C}.COOH + H_2O.$$

α-Methylcinnamic acid.

That α-methylcinnamic acid is formed and not phenylisocrotonic acid according to the equation,

$$C_6H_5CHO + CH_3.CH_2.COOH = \underset{\text{Phenylisocrotonic acid.}}{C_6H_5CH:CH.CH_2.COOH} + H_2O,$$

follows from Fittig's researches, and depends upon the marked difference exhibited by the two principal groups of unsaturated acids, viz., the *αβ* acids, which have the double link between the first and second carbon from the carboxyl, and *βγ* acids, in which the double link lies between the second and third carbons. Methylcinnamic acid belongs to the first group, whereas phenylcrotonic acid belongs to the second group.

It may be noted in passing that this reaction bears a close resemblance to that studied by Claisen, which occurs in presence of caustic soda solution between aldehydes or ketones on the one hand, and compounds containing the group

$CH_2.CO$. Benzaldehyde and acetone combine under these conditions to form benzylidene- and dibenzylidene-acetone,

$$C_6H_5COH + CH_3.CO.CH_3 = \underset{\text{Benzylidene acetone.}}{C_6H_5CH{:}CH.CO.CH_3}.$$

$$2C_6H_5COH + CH_3.CO.CH_3 = \underset{\text{Dibenzylidene acetone.}}{C_6H_5CH{:}CH.CO.CH{:}CH.C_6H_5}.$$

All the unsaturated acids have the following properties in common. They form additive compounds with nascent hydrogen, halogen acids, and the halogens. On oxidation with alkaline permanganate in the cold, they take up two hydroxyl groups to form a dihydroxy-derivative, and, on further oxidation, ultimately divide at the double link. Cinnamic acid may be taken by way of illustration. On reduction it forms phenylpropionic acid, with hydrobromic acid, *β*-bromophenylpropionic acid (the bromine attaching itself to the *β*-carbon, see p. 253), with bromine *αβ*-dibromophenylpropionic acid, on oxidation with permanganate, phenylglyceric acid and then benzaldehyde and benzoic acid,

$$C_6H_5CH{:}CH.CO.OH + H_2 = \underset{\text{Phenylpropionic acid.}}{C_6H_5CH_2.CH_2.CO.OH}.$$

$$C_6H_5CH{:}CH.CO.OH + HBr = \underset{\text{Phenyl }\beta\text{-bromopropionic acid.}}{C_6H_5CHBr.CH_2.CO.OH}.$$

$$C_6H_5CH{:}CH.CO.OH + Br_2 = \underset{\text{Phenyl }\alpha\beta\text{-dibromopropionic acid.}}{C_6H_5CHBr.CHBr.CO.OH}.$$

$$C_6H_5CH{:}CH.CO.OH + H_2O + O = \underset{\text{Phenylglyceric acid.}}{C_6H_5CHOH.CHOH.CO.OH}.$$

$$C_6H_5CH{:}CH.CO.OH + 2O_2 = \underset{\text{Benzaldehyde.}}{C_6H_5COH} + 2CO_2 + H_2O.$$

The chief difference between the two groups of *αβ* and *βγ* unsaturated acids lies in the behaviour of the additive compounds which they form with hydrobromic acid and bromine.

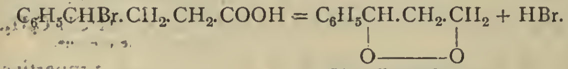
In the case of the *αβ* acids, the hydrobromide of the acid, on boiling with water, yields the corresponding *β* hydroxy-acid, and, on boiling with alkalis, a mixture of the original acid and the unsaturated hydrocarbon, formed by the elimination of carbon dioxide and hydrobromic acid,

1. $C_6H_5CHBr.CH_2.COOH + H_2O = \underset{\beta\text{-Oxyphenyl-propionic acid.}}{C_6H_5CHOH.CH_2.COOH} + HBr.$

2. $C_6H_5CHBr.CH_2.COOH + NaOH = \underset{\text{Cinnamic acid.}}{C_6H_5CH{:}CH.COOH} + NaBr + H_2O.$

3. $C_6H_5CHBr.CH_2.COOH + NaOH = \underset{\text{Styrene.}}{C_6H_5CH{:}CH_2} + CO_2 + NaBr + H_2O.$

The hydrobromides of $\beta\gamma$ unsaturated acids like β-phenylcrotonic acid behave quite differently. On boiling with water, lactones are formed, *i.e.*, inner anhydrides of oxy-acids,



$$C_6H_5CHBr.CH_2.CH_2.COOH = C_6H_5\underset{\overset{|}{O}}{CH}.CH_2.\underset{\overset{|}{O}}{CH_2} + HBr.$$

Phenylbutyrolactone.

The readiest method for distinguishing a $\beta\gamma$-acid, especially of the aliphatic series, is to heat the acid with a mixture of equal volumes of conc. sulphuric acid and water to about 140°. The lactone is formed if a $\beta\gamma$-acid is present, whereas an $\alpha\beta$-acid remains unchanged. By diluting, neutralising with sodium carbonate, and extracting with ether, the lactone is separated, the $\alpha\beta$-acid remaining in solution.

An interesting relation exists between the two groups of acids. It has been found that, on heating $\beta\gamma$-acids with caustic soda solution, a shifting of the double link on the $\alpha\beta$-position takes place,

$$C_6H_5\underset{\gamma}{CH}:\underset{\beta}{CH}.\underset{\alpha}{CH_2}.COOH = C_6H_5CH_2.\underset{\beta}{CH}:\underset{\alpha}{CH}.COOH.$$

PREPARATION 95.

Hydrocinnamic Acid.—The preparation illustrates the use of sodium amalgam as a reducing agent. It should be noted that hydrocinnamic acid may be also obtained from malonic ester by acting upon the sodium compound with benzyl chloride, then hydrolysing and removing carbon dioxide,

$$C_6H_5CH_2Cl + NaCH(COOC_2H_5)_2 \rightarrow C_6H_5CH_2.CH(COOC_2H_5)_2$$
$$\rightarrow C_6H_5CH_2.CH(COOH)_2 + C_6H_5CH_2.CH_2COOH.$$

PREPARATION 96.

Mandelic Acid.—The reaction furnishes a simple and general method for obtaining hydroxy-acids from aldehydes or ketones by the aid of the cyanhydrin. The formation of the cyanhydrin may be effected in the manner described or by the action of hydrochloric acid on a mixture of the aldehyde or ketone with potassium cyanide, or, as in the case of the sugars, by the use of liquid hydrocyanic acid and a little ammonia, Mandelic acid was originally derived from bitter almonds, and can be obtained by the action of baryta on amygdalin, the glucoside of bitter almonds, which breaks up into glucose and mandelic acid. Mandelic acid contains an asymmetric carbon atom, and is capable, therefore, of being resolved into optical enantiomorphs (p. 262). This has been effected by fractional crystallisation of the cinchonine salt, from a solution of which the dextro-rotatory component first separates. Another method, known as the biochemical method, is to cultivate certain low organisms in a solution of a salt of the acid when one of the components is destroyed or assimilated. Thus ordinary green mould (*penicillium*) assimilates and removes the lævo component, leaving a dextro-rotatory solution. These two methods, together with the separation of the enantiomorphous crystalline forms described on p. 123, comprise the three classical methods devised by Pasteur for resolving inactive substances into their active components. Mandelic acid may also be resolved by partial hydrolysis of its esters by the ferment "lipase" (Dakin) and also by the partial esterification of the acid with an active alcohol such as menthol (Marckwald).

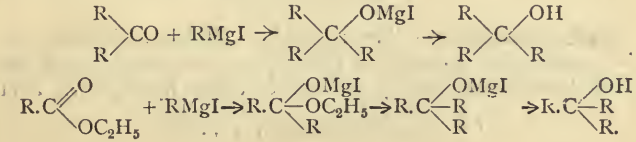
PREPARATION 97.

Phenylmethylcarbinol.—The method of Grignard, of which this preparation serves as an illustration, has received a very wide application. The following is a brief and incomplete list of these reactions, in which the organic radical (R) represents within certain wide limits both an alkyl and aryl group:

Hydrocarbons. The magnesium compound is decomposed by water,

$$RMgI + H_2O = R.H + MgI(OH).$$

Alcohols may be obtained from aldehydes, ketones, esters, acid chlorides, and anhydrides,



$$\substack{R\diagdown\\ R\diagup}CO + RMgI \rightarrow \substack{R\diagdown\\ R\diagup}C\substack{\diagup OMgI\\ \diagdown R} \rightarrow \substack{R\diagdown\\ R\diagup}C\substack{\diagup OH\\ \diagdown R}$$

$$R.C\substack{\diagup\!\!\diagup O\\ \diagdown OC_2H_5} + RMgI \rightarrow R.C\substack{\diagup OMgI\\ -OC_2H_5\\ \diagdown R} \rightarrow R.C\substack{\diagup OMgI\\ -R\\ \diagdown R} \rightarrow R.C\substack{\diagup OH\\ -R\\ \diagdown R.}$$

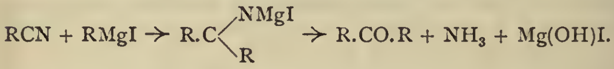
Aldehydes can be prepared from dimethylformamide,

$$HCO.NRR + RMgI \rightarrow HCR(OMgI)NRR \rightarrow RCHO + NHRR + Mg(OH)I,$$

and from formic and orthoformic ester,

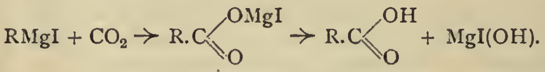
$$HCO.OC_2H_5 + RMgI \rightarrow RCHO + MgI.OC_2H_5.$$

Ketones may be obtained from cyanogen, cyanides, or amides,



$$RCN + RMgI \rightarrow R.C\begin{matrix} \diagup NMgI \\ \diagdown R \end{matrix} \rightarrow R.CO.R + NH_3 + Mg(OH)I.$$

Acids are produced by passing carbon dioxide into the ether solution of the magnesium alkyl compound,



$$RMgI + CO_2 \rightarrow R.C\begin{matrix} \diagup OMgI \\ \diagdown\!\!\diagdown O \end{matrix} \rightarrow R.C\begin{matrix} \diagup OH \\ \diagdown\!\!\diagdown O \end{matrix} + MgI(OH).$$

In addition to the above, Grignard's reagent has been utilised in preparing olefines, ethers, ketonic esters, hydroxy-acids, quinols, amides, hydroxylamines, &c., for details of which books of reference must be consulted.[1]

PREPARATION 98.

Benzoyl Chloride.—The formation of esters by the action of benzoyl chloride or other acid chloride on an alcohol or phenol in presence of caustic soda is known as the "Schotten-Baumann reaction." The reaction may also be employed in the preparation of derivatives of the aromatic amines containing an acid radical, like benzanilide, $C_6H_5NH.CO.C_6H_5$,

$$C_6H_5COCl + NH_2.C_6H_5 + NaOH = C_6H_5CO.NHC_6H_5 + NaCl + H_2O.$$

PREPARATION 99.

Ethyl Benzoate.—The method of Fischer and Speier for the preparation of esters, by boiling together the acid with the alcohol containing about 3 per cent. of either hydrochloric acid

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[1] Schmidt, Ahrens' *Vorträge*, 1905, **10**, 68.

or conc. sulphuric acid, can be adopted in the majority of cases with good results, and has many advantages over the old method of passing hydrochloric acid gas into a mixture of the alcohol and acid until saturated. Read Notes on Prep. 15, p. 247.

PREPARATION 100.

Acetophenone.—The "Friedel-Crafts' reaction," of which this preparation is a type, consists in the use of anhydrous aluminium chloride for effecting combination between an aromatic hydrocarbon or its derivative on the one hand, and a halogen (Cl or Br) compound on the other. The reaction is always accompanied by the evolution of hydrochloric or hydrobromic acid, and the product is a compound with $AlCl_3$, which decomposes and yields the new substance on the addition of water. This reaction has been utilised, as in the present case, (1) for the preparation of ketones, in which an acid chloride (aliphatic or aromatic) is employed,

$$C_6H_6 + Cl.CO.CH_3 = \underset{\text{Acetophenone.}}{C_6H_5.CO.CH_3} + HCl.$$

$$C_6H_6 + Cl.CO.C_6H_5 = \underset{\text{Benzophenone.}}{C_6H_6.CO.C_6H_6} + HCl.$$

If a substituted aromatic hydrocarbon is used, the ketone group then enters the para-position, or, if this is occupied, the ortho-position. Substituted aromatic acid chlorides may also be used, and if the acid is dibasic and has two carboxyl chloride groups, two molecules of the aromatic hydrocarbon may be attached. If phosgene is used with two molecules of benzene, benzophenone is obtained,

$$2C_6H_6 + Cl_2CO = \underset{\text{Benzophenone.}}{C_6H_5.CO.C_6H_5} + 2HCl.$$

(2) This reaction may be modified by decreasing the proportion of the hydrocarbon, and an acid chloride is then formed,

$$C_6H_6 + ClCOCl = \underset{\text{Benzoyl chloride.}}{C_6H_5.COCl} + HCl.$$

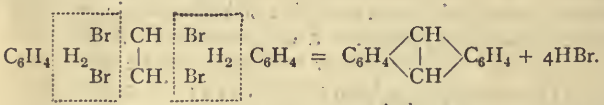
(3) With an aromatic hydrocarbon and a halogen derivative of an aliphatic hydrocarbon or aromatic hydrocarbon substituted in the side-chain, new hydrocarbons may be built up (see Prep. 102, p. 214),

$$C_6H_6 + C_2H_5Br = \underset{\text{Ethylbenzene.}}{C_6H_5.C_2H_5} + HBr.$$

$$C_6H_6 + ClCH_2.C_6H_5 = \underset{\text{Diphenylmethane.}}{C_6H_5.CH_2.C_6H_5} + HCl.$$

$$3C_6H_6 + CHCl_3 = \underset{\text{Triphenylmethane.}}{CH(C_6H_5)_3} + 3HCl.$$

Anthracene has been synthesised from tetrabromethane and benzene by this method,



Anthracene.

(4) Amides may be prepared by the use of chloroformamide,

$$C_6H_6 + ClCONH_2 = C_6H_5.CO.NH_2 + HCl.$$

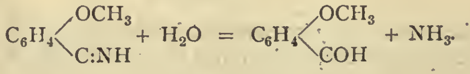
The chloroformamide is obtained by passing HCl gas over heated cyanuric acid (Gattermann),

$$HOCN + HCl = Cl.CONH_2.$$

(5) Hydroxyaldehydes have been obtained indirectly by the use of the crystalline compound HCl,HCN (which hydrochloric acid forms with hydrocyanic acid) acting upon a phenol ether,

$$C_6H_5OCH_3 + HCl.HCN = C_6H_4\begin{cases}OCH_3\\CH{:}NH.\end{cases}$$

The aldime is subsequently hydrolysed with dilute sulphuric acid (Gattermann),



$$C_6H_4\begin{cases}OCH_3\\C{:}NH\end{cases} + H_2O = C_6H_4\begin{cases}OCH_3\\COH\end{cases} + NH_3.$$

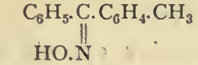
In addition to the Friedel-Crafts' reaction the aromatic ketones may be obtained by distilling the calcium salt of the aromatic acid or a mixture of the salts of an aromatic and aliphatic acid. The reaction is precisely analogous to the process used for the preparation of aliphatic ketones,

$$2C_6H_5COOca' = \underset{\text{Benzophenone.}}{C_6H_5CO.C_6H_5} + CaCO_3.$$

$$C_6H_5COOca' + CH_3COOca' = \underset{\text{Acetophenone.}}{C_6H_5.CO.CH_3} + CaCO_3.$$

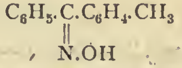
They possess the usual properties of ketones of the aliphatic series (see p. 69), which are illustrated by the various reactions described at the end of this preparation.

A special interest attaches to the oximes of those ketones which contain two different radicals linked to the CO group. Many of these substances exist in two isomeric forms, which are readily converted into one another. Phenyltolylketoxime exists in two forms and benzildioxime in three forms, which cannot be explained by structural differences of constitution. They must therefore represent different space configurations of a type analogous to that of citraconic and mesaconic acid (Hantzsch, see p. 265). They are distinguished by the terms "syn" and "anti," corresponding to "cis" and "trans" among the unsaturated acids. "Anti" signifies away from the group, the name of which follows; "syn" signifies the position near that group (see pp. 283 and 301),



$$\begin{array}{l} C_6H_5.C.C_6H_4.CH_3 \\ \quad\;\; \| \\ HO.N \end{array}$$

Syn-Phenyltolylketoxime.



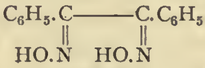
$$\begin{array}{l} C_6H_5.C.C_6H_4.CH_3 \\ \quad\;\; \| \\ \quad\;\; N.OH \end{array}$$

Anti-Phenyltolylketoxime.

Benzil forms three dioximes which are distinguished by the names "syn," "anti," and "amphi."

$$\begin{array}{l} C_6H_5C.C.C_6H_5 \\ \quad\;\;\; \|\;\; \| \\ HO.N\;N.OH \end{array}$$

anti.



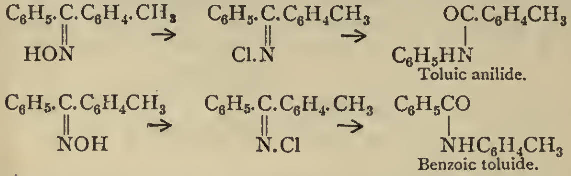
$$\begin{array}{l} C_6H_5.C\text{———}C.C_6H_5 \\ \qquad\;\; \| \qquad\quad \| \\ HO.N \quad HO.N \end{array}$$

amphi.

$$\begin{array}{l} C_6H_5.C\text{————}C.C_6H_5 \\ \qquad\;\; \| \qquad\quad\;\; \| \\ \qquad N.OH\;\; HO.N \end{array}$$

syn.

The action of PCl_5 on these substances, known as Beckmann's reaction, is of great importance in distinguishing the different forms of ketoximes. The two isomeric phenyltolylketoximes yield two different amides,



$$C_6H_5.\underset{\underset{HON}{\|}}{C}.C_6H_4.CH_3 \rightarrow C_6H_5.\underset{\underset{Cl.N}{\|}}{C}.C_6H_4CH_3 \rightarrow \underset{\underset{C_6H_5HN}{|}}{OC}.C_6H_4CH_3$$

Toluic anilide.

$$C_6H_5.\underset{\underset{NOH}{\|}}{C}.C_6H_4CH_3 \rightarrow C_6H_5.\underset{\underset{N.Cl}{\|}}{C}.C_6H_4.CH_3 \quad \underset{\underset{NHC_6H_4CH_3}{|}}{C_6H_5CO}$$

Benzoic toluide.

Toluic anilide, on hydrolysis, forms toluic acid and aniline, whereas benzoic toluide yields benzoic acid and toluidine. It follows therefore that, in the original compound, the first contains the hydroxyl nearer the phenyl group and the second nearer the tolyl group.

For further details on the stereoisomerism of nitrogen compounds, the text-book must be consulted.

PREPARATION 101.

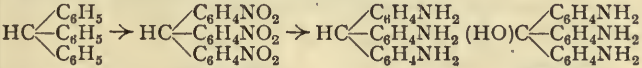
Diphenylmethane.—This reaction is analogous to that of aluminium chloride on a mixture of benzene and benzyl chloride referred to in the notes on Prep. 100, p. 310. The reaction is also effected by the use of zinc dust or finely-divided copper (Zincke).

PREPARATION 102.

Triphenylmethane.—This is another example of the "Friedel-Crafts'" reaction, which has already been referred to in the notes on Prep. 100, p. 309.

The synthesis of pararosaniline from triphenylmethane is one which has gone far to solve the problem of the constitution of the important class of triphenylmethane colouring matters.

Rosaniline or magenta was originally obtained by oxidising with arsenic acid a mixture of aniline with *o*- and *p*-toluidine. The product was then lixiviated and treated with common salt, which converted the arsenate into the hydrochloride of rosaniline. Pararosaniline was prepared in a similar way from a mixture of aniline and *p*-toluidine. The series of reactions by which triphenylmethane is converted into pararosaniline may be represented as follows :—



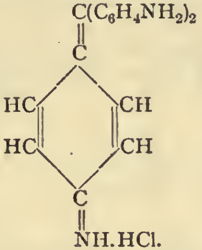
$$HC\begin{cases}C_6H_5\\C_6H_5\\C_6H_5\end{cases}\rightarrow HC\begin{cases}C_6H_4NO_2\\C_6H_4NO_2\\C_6H_4NO_2\end{cases}\rightarrow HC\begin{cases}C_6H_4NH_2\\C_6H_4NH_2\\C_6H_4NH_2\end{cases}\quad (HO)C\begin{cases}C_6H_4NH_2\\C_6H_4NH_2\\C_6H_4NH_2\end{cases}$$

Triphenylmethane. Trinitro-triphenylmethane. Paraleucaniline. Pararosaniline base.

By the action of hydrochloric acid on the base, the hydrochloride of pararosaniline is formed, which is the soluble colouring matter,

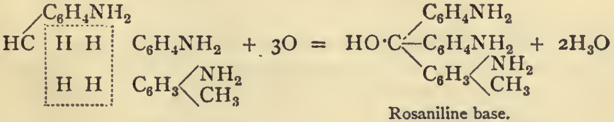
$$HO.C(C_6H_4NH_2)_3 + HCl = C(C_6H_4NH_2)_3Cl + H_2O.$$

The constitution of the hydrochloride is doubtful; but the so-called *quinonoid* structure, by which the substance is represented as a derivative of quinone, is generally accepted,



Pararosaniline hydrochloride.

The formation of rosaniline from a mixture of aniline, *o*- and *p*-toluidine is represented by assuming that the methyl-group of *p*-toluidine acts as the link which connects the nuclei of aniline and *o*-toluidine.

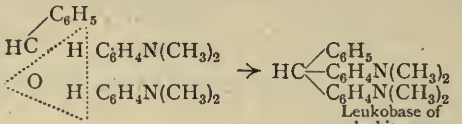


$$HC\begin{cases}C_6H_4NH_2\\ \boxed{\begin{matrix}H & H\\ H & H\end{matrix}}\end{cases}\begin{matrix}C_6H_4NH_2\\ C_6H_3\begin{cases}NH_2\\CH_3\end{cases}\end{matrix} + 3O = HO\cdot C\begin{cases}C_6H_4NH_2\\C_6H_4NH_2\\C_6H_3\begin{cases}NH_2\\CH_3\end{cases}\end{cases} + 2H_2O$$

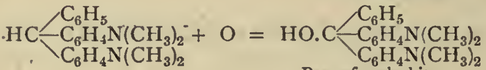
Rosaniline base.

PREPARATION 103.

Benzaldehyde Green.—The formation of malachite green (benzaldehyde green) by the action of benzaldehyde upon dimethylaniline in presence of zinc chloride, and subsequent oxidation of the product, may be interpreted on similiar lines, and has already been referred to. (See notes on Prep. 59, p. 279).



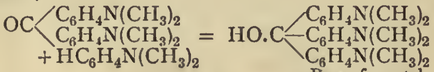
Leukobase of malachite green.



$$\mathrm{HC}\left\langle\begin{matrix}C_6H_5\\C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{matrix}\right. + O = \mathrm{HO.C}\left\langle\begin{matrix}C_6H_5\\C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{matrix}\right.$$

Base of malachite green.

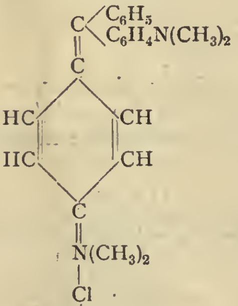
The preparation of "crystal violet" from Michler's compound and dimethylaniline in presence of $POCl_3$ may be explained in a similar fashion,



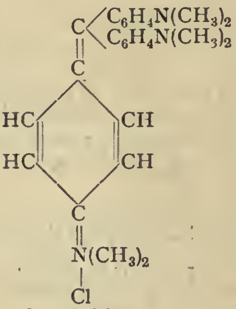
$$\mathrm{OC}\left\langle\begin{matrix}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{matrix}\right. + HC_6H_4N(CH_3)_2 = \mathrm{HO.C}\left\langle\begin{matrix}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{matrix}\right.$$

Base of crystal violet.

The constitution of the hydrochlorides of malachite green and crystal violet will appear as follows:—



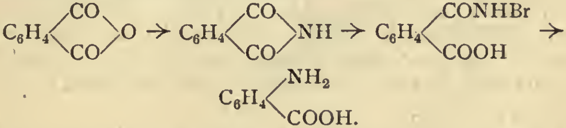
Malachite green.



Crystal violet.

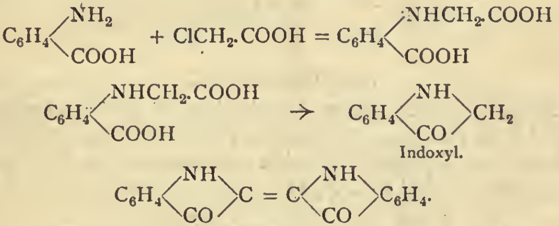
Preparation 104.

Phthalic Acid. In the formation of phthalic acid by the oxidation of naphthalene with sulphuric acid, the mercuric sulphate acts as a catalyst. The latter reagent has been used successfully in other oxidising processes, although the manner of its action is not yet explained. The formation of phthalic acid from naphthalene represents the initial stage in the manufacture of artificial indigo from coal-tar. The subsequent processes consist in converting the acid into the anhydride by sublimation, the anhydride into phthalimide by the action of ammonia gas, and the phthalimide into anthranilic acid by the action of sodium hypobromite (Hofmann's reaction, see p. 80).



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O \rightarrow C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH \rightarrow C_6H_4\left\langle\begin{matrix}CONHBr\\COOH\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}NH_2\\COOH.\end{matrix}\right.$$

The anthranilic acid is then converted into indigo by combining it with chloracetic acid and fusing the product with caustic alkali, which gives indoxyl and finally indigo by oxidation,



$$C_6H_4\left\langle\begin{matrix}NH_2\\COOH\end{matrix}\right. + ClCH_2.COOH = C_6H_4\left\langle\begin{matrix}NHCH_2.COOH\\COOH\end{matrix}\right.$$

$$C_6H_4\left\langle\begin{matrix}NHCH_2.COOH\\COOH\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}NH\\CO\end{matrix}\right\rangle CH_2$$

Indoxyl.

$$C_6H_4\left\langle\begin{matrix}NH\\CO\end{matrix}\right\rangle C = C\left\langle\begin{matrix}NH\\CO\end{matrix}\right\rangle C_6H_4.$$

Indigo.

PREPARATIONS 105 and 106.

Naphthalenesulphonate of Sodium. β-Naphthol.—The formation of the sulphonic acid of naphthalene and the corresponding phenol by fusion with caustic soda is analogous to that of benzene sulphonic acid and phenol (see Prep. 74, p. 177, and 76, p. 179. It should be noted that naphthalene forms two series of mono-derivatives distinguished as *a* and *β* compounds. By the action of sulphuric acid on naphthalene, both *a* and *β* sulphonic acids are formed. At a lower temperature (100°) the product consists mainly of the *a* compound ; at a higher temperature (170°) of the β compound. β-Naphthol and its derivatives are used for the preparation of azo-colours (see Reaction 6, p. 163), and for that of β-naphthylamine. The latter is obtained by the action of ammonia under pressure on β-naphthol,

$$C_{10}H_7OH + NH_3 = C_{10}H_7NH_2 + H_2O.$$

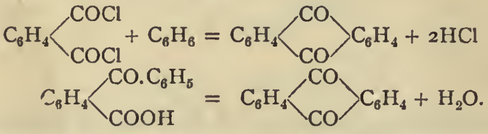
This reaction is resorted to for the reason that naphthalene forms only the α-nitro-compound with nitric acid. The method, similar to that used for preparing aniline from nitrobenzene, cannot, therefore, be employed for the production of β-naphthylamine. α-Naphthol is mainly used for the manufacture of yellow and orange colours (Martius and naphthol yellow) by the action of nitric acid, and are similar in constitution to picric acid (see Prep. 107).

The naphthols differ from the phenols of the benzene series in forming ethers after the manner of aliphatic alcohols, viz., by the action of sulphuric acid on a mixture of the naphthol and the alcohol, which the other phenols do not,

$$C_{10}H_7OH + CH_3OH = \underset{\text{Naphthyl methyl ether.}}{C_{10}H_7OCH_3} + H_2O$$

PREPARATION 108.

Anthraquinone.—The constitution of anthraquinone is derived from various syntheses, such as the action of zinc dust on a mixture of phthalyl chloride and benzene, or by heating benzoyl benzoic acid with P_2O_5,



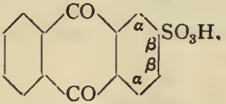
$$C_6H_4\left\langle\begin{matrix}COCl\\COCl\end{matrix}\right. + C_6H_6 = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4 + 2HCl$$

$$C_6H_4\left\langle\begin{matrix}CO.C_6H_5\\COOH\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4 + H_2O.$$

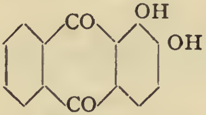
Unlike benzoquinone, it is not reduced by sulphur dioxide (see Prep. 85, p. 193). Heated with HI or zinc dust it is converted into anthracene.

PREPARATION 110.

Alizarin.—The first synthesis of alizarin is due to Graebe and Liebermann (1868). The present method was discovered simultaneously by these chemists and by Perkin. By the action of fuming sulphuric acid on anthraquinone, the main product is β-anthraquinone monosulphonic acid,

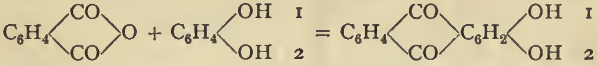


By fusion of the sodium salt with caustic soda and potassium chlorate, the hydroxyl groups enter the *a* and β position. The constitution of alizarin is therefore



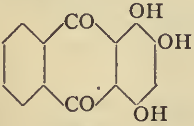
Alizarin.

The constitution has been determined by its synthesis from phthalic anhydride and catechol in presence of concentrated sulphuric acid (Baeyer),

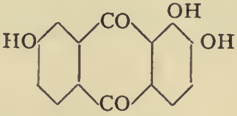


$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O + C_6H_4\left<\begin{matrix}OH & 1\\OH & 2\end{matrix}\right. = C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>C_6H_2\left<\begin{matrix}OH & 1\\OH & 2\end{matrix}\right.$$

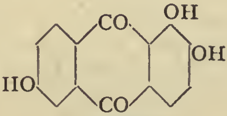
Other colouring matters have been obtained by the oxidation of alizarin (purpurin), and by fusion of the disulphonic acids of anthraquinone with caustic soda (anthrapurpurin and flavopurpurin). It is an interesting fact that, among the numerous di- and poly-hydroxyanthraquinones, only those which have the two hydroxyls in the *a*β position are colouring matters (Liebermann and Kostanecki),



Purpurin.



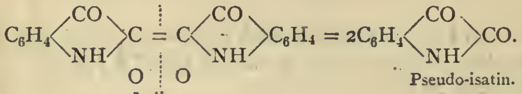
Anthrapurpurin.



Flavopurpurin.

PREPARATION 111.

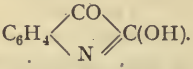
Isatin.—The formation of isatin from indigo may be represented as follows :—



Indigo.

Pseudo-isatin.

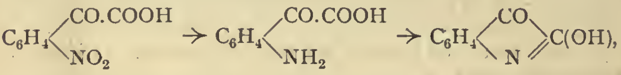
This compound represents the unstable pseudo- or lactam-form, and passes into the stable or lactim-form (Baeyer),



Isatin (stable form).

There exists, however, some uncertainty as to which formula represents the stable form. Derivatives of both forms are known, and the compound offers an example of *tautomerism* (see Notes on Preps. 16, p. 252), or, as it has been also termed, *pseudomerism.*

The constitution of isatin has been determined by its synthesis from *o*-nitrophenylglyoxylic acid,



which passes on reduction into the amino-compound, the latter forming the anhydride or isatin (Claisen).

PREPARATION 112.

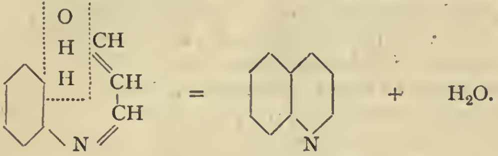
Quinoline.—The formation of quinoline by "Skraup's reaction" may be explained as follows: The sulphuric acid converts the glycerol into acrolein, which then combines with the aniline to form acrolein-aniline. The latter on oxidation with nitrobenzene yields quinoline.

$$CH_2OH.CHOH.CH_2OH = CH_2:CH.COH + 2H_2O$$

Acrolein.

$$C_6H_5NH_2 + OCH.CH:CH_2 = C_6H_5N:CH.CH:CH_2 + H_2O$$

Acrolein aniline.



Quinoline.

The reaction is a very general one, and most of the primary aromatic amines and their derivatives can be converted into quinoline derivatives, provided that one ortho-position to the amino-group is free. *o*-Aminophenol, for example, yields *o*-hydroxyquinoline in the same way,

o-Aminophenol. *o*-Hydroxyquinoline.

PREPARATION 113.

Quinine Sulphate.—Quinine belongs to the group of "vegetable bases" or alkaloids. These substances are widely distributed among different orders of plants, and are usually colourless, odourless, and crystalline solids. A few, however, are liquids (conine and nicotine), and possess an unpleasant smell. There is no general method by which the alkaloids can be isolated from the plants in which they are found. They usually exist in combination with acids, such as malic, lactic, and other common vegetable acids. Frequently the acid present is peculiar to the plant in which it occurs. Quinine and the other cinchona alkaloids are found in combination with quinic acid, morphine with meconic acid, aconitine with aconitic acid, &c. A common method for separating the alkaloid is to add an alkali. If the base is volatile in steam, like conine, it is distilled with water; if, as generally happens, the substance is non-volatile, it is extracted by means of a suitable volatile solvent, such as ether, chloroform, alcohol, amyl alcohol, &c. The solvent is then distilled off, and the alkaloid, which remains, is either crystallised or converted into a crystalline salt.

The alkaloids are strong bases, which turn red litmus blue, and are very slightly soluble in water. They form soluble salts and double salts with platinic and auric chlorides. The principal general reagents for the alkaloids are:

1. A solution of iodine in potassium iodide, which forms a reddish-brown precipitate of the periodides.

2. A solution of phosphomolybdic acid in nitric acid, which gives yellow precipitates of different shades.

3. A solution of potassium mercuric iodide, which forms white or yellowish-white precipitates.

The constitution of quinine is not yet elucidated. Its relationship to quinoline has long been known, since it gives this substance on distillation with caustic potash (Gerhardt).

PREPARATION 114.

Phenylmethyltriazole Carboxylic Acid.—The mother substance of this compound is a triazole, viz., pyrro-*αβ*-diazole, which is one of four isomeric compounds:

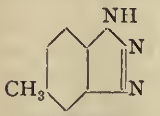
Pyrro-*αα′*-diazole.

Pyrro-*αβ*-diazole.

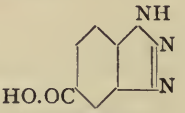
Pyrro-*αβ′*-diazole.

Pyrro-*ββ′*-diazole.

Pyrro-*αβ*-diazole was first obtained by the oxidation of azimidotoluene, which in turn was prepared by the action of nitrous acid on *o*-toluylenediamine,



Azimidotoluene.



Azimidobenzoic acid.

Triazoledicarboxylic acid

Pyrro-*αβ*-diazole.

It is a colourless oil, b. p. 280°, with the properties of a weak secondary base, dissolving in acids, and forming easily hydrolysable salts.

The reaction described in this preparation is of a general character, and furnishes a useful method for preparing members of this series of heterocyclic compounds. Diazobenzolimide condenses in a similar fashion with ketones (acetophenone) and dibasic esters (malonic ester) as well as with ketonic esters, as in the present case. These substances possess the usual properties of cyclic compounds ; carboxyl may be removed as CO_2, and alkyl side-chains oxidised to carboxyl ; they may be sulphonated and nitrated, and the nitro-group reduced to an amino-group ; the phenyl group attached to the nitrogen may also be removed by oxidation. Thus, phenylmethyltriazole carboxylic acid loses CO_2 on heating, and on oxidation the methyl group becomes carboxyl and can also be removed in the same way. The resulting product is phenyl triazole. The properties of the individual triazoles are influenced, like other cyclic compounds, by the groups attached to the nucleus, and to some extent also by the basic character of the mother substance.

HINTS ON THE INVESTIGATION OF ORGANIC SUBSTANCES

Provide yourself with a good book of reference, or chemist's pocket book which contains tables of physical constants.

Homogeneity.—Determine if the substance is homogeneous.

A Liquid.—If it is a liquid, distil a few c.c. from a miniature distilling flask with a long side-tube, but no condenser, or with the apparatus shown in Fig. 86, in which the condensing surface is supplied by an inner tube through which water percolates.[1]

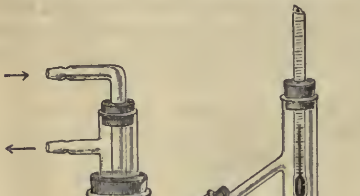


Fig. 86.

Use a thermometer and collect the distillate in a test-tube. Note the boiling-point, and observe if it fluctuates or remains constant and if any solid residue remains. A low boiling-point generally denotes a low molecular weight. A portion distilling in the neighbourhood of 100° may indicate the presence of water.

It is useful to shake a known volume (5 c.c.) of the liquid with an equal volume of water and to note if the substance dissolves, or if any marked change in the volume of the liquid occurs. A convenient apparatus for this

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[1] This apparatus can also be used as reflux condenser or for collecting evolved gas if the side piece is furnished with a delivery tube dipping under water or mercury.

purpose is shown in Fig. 87, which is merely a small and narrow, graduated cylinder holding 10 c.c.[1] The solubility of a portion of the liquid is an indication of the presence of a mixture. Furthermore, the specific gravity of the insoluble portion (its floating or sinking in the water) will be roughly indicated and should be noted.

A Solid.—If the substance is a solid, examine a few particles on a slide under the microscope, or, better still, recrystallise a little if possible and notice if the crystals appear similar in shape. If it is a mixture, try to separate the constituents by making a few trials with different solvents, water, alcohol, ether, benzene, petroleum spirit, ethyl acetate, acetic acid, etc. If it appears homogeneous, determine the melting-point, the sharpness of which will be a further confirmation. If it turns out to be a mixture, it must be further treated in the manner described under "mixtures" (p. 343).

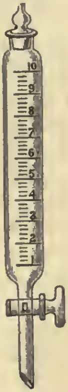

FIG. 87.

The Action of Heat.—We will assume in the first place that the substance is homogeneous and consists of a single individual. Heat a portion on platinum foil and notice if it volatilises, chars, or burns with a clear, luminous, non-luminous (aliphatic), or smoky (aromatic) flame. Determine the nature of the residue, if any, when the carbon has burnt away.

Metal or *metallic oxide* or *carbonate* may indicate the presence of an organic acid, phenate, or double salt of a base.

Sulphate, *sulphite*, or *sulphide* may indicate a sulphate, sulphonate, mercaptan, or bisulphite compound of an aldehyde or ketone.

Cyanide may indicate a cyanide or ferrocyanide, etc.

Heat a little of the substance in a small, hard-glass tube and observe whether the substance melts, chars, explodes, sublimes, or volatilises; whether an inflammable gas, water, etc., is evolved; also notice the smell.

Carbohydrates, polyhydric alcohols, higher organic acids (*e.g.*, stearic), dibasic and hydroxy-acids (*e.g.*, tartaric), certain amides (*e.g.*, oxamide), alkaloids, and azo and other organic colours char

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[1] Both pieces of apparatus (Figs. 86 and 87) can be obtained from Mr. O. Baumbach, 10, Lime Grove, Oxford Street, Manchester.

and give off water or (if nitrogen is present) ammonia or basic constituents. But a great number of common organic compounds are volatile without decomposition.

The Elements.—Test for nitrogen,[1] sulphur, and halogens. If none of these are found, carbon and hydrogen are present and, if the substance has given off water or is soluble in water, it may be assumed that oxygen is present as well. The action of sodium on the substance, if liquid, or on its solution in benzene or ligroin, if solid, should be tried in the apparatus, Fig. 86, and the gas evolved tested for hydrogen, which if present, may indicate hydroxyl, ketone, or ester groups.

The presence of nitrogen may indicate an *ammonium salt*, *organic base* (*amine* or *alkaloid*), *amino-acid*, *amide*, *cyanide*, iso*cyanide*, *oxime*, *nitroso-* or *nitro-compound*, *azo-compound*, etc.

The presence of sulphur may indicate a *sulphate of an organic base*, *alkyl sulphate*, *sulphite*, *sulphide*, *mercaptan*, *sulphonic acid*, *bisulphite compound of aldehyde or ketone*.

The presence of a halogen may indicate a *haloid salt of a base*, *alkyl*, *alkylene*, *or aryl halide*, *acid halide*, *haloid derivative of an aldehyde or acid.* Some substances. like *mustard oils*, *amino-sulphonic acids* and *thioamides*, contain both nitrogen and sulphur.

Solubility.—Try if the substance dissolves in hot or cold water. Apart from the salts of organic bases and acids, many of which are very soluble in water, the solubility of simple organic substances is generally determined by the presence of the OH group (including CO.OH and SO_2.OH groups) and to some extent by the NH_2 group. The greater the proportion of OH groups to carbon, the greater, as a rule, is the solubility in water. The lower alcohols, methyl, ethyl and propyl alcohols, are miscible with water; normal butyl and *iso*butyl alcohols (fermentation) dissolve in about 10 parts of water at the ordinary temperature ; amyl alcohol (fermentation) in about 40 parts of water. The first two may be separated from solution by the addition of solid potassium carbonate. The addition of common salt is sufficient to

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[1] It is sometimes difficult to detect nitrogen by the sodium test. The result should not be regarded as conclusive, especially if the substance is volatile, unless it has been dropped in small quantities at a time into the melted metal, which should be heated in a hard-glass tube clamped in a retort-stand. Special care must be used with nitro-compounds, which may explode and shatter the tube.

separate the last three (propyl, butyl, and amyl). The polyhydricalcohols, glycol, glycerol, and mannitol, and also substances like the sugars are extremely soluble, for the proportion of OH groups to carbon is high. Ordinary phenol requires for solution 15 parts of water, whereas the di- and tri-hydric phenols readily dissolve. The same applies to acids. The lower monobasic aliphatic acids (formic, acetic, propionic, and normal butyric) are easily soluble in water, whereas *iso*butyric requires 3 parts and valeric about 30 parts of water. The last three separate from water on the addition of salt. The dibasic and hydroxy-acids, where the proportion of carbon is small (succinic, tartaric, and citric), are naturally more soluble than the monobasic acids having the same number of carbon atoms.

The majority of aromatic acids are not very soluble in water at the ordinary temperature, for the proportion of carbon to carboxyl is high; the hydroxy- and polybasic and also amino-acids are more soluble than the unsubstituted monobasic acids (or, if substituted, where the substituents are halogens or nitro-groups, which diminish, as a rule, the solubility). One thousand parts of water dissolve about 2½ parts of benzoic, 2¼ parts of salicylic, 8 parts of phthalic, and 159 parts of mandelic acid. Acids such as gallic and tannic acids are readily soluble in water.

The sulphonic acids and also many of their salts are very soluble.

The lower aliphatic amines and amides are soluble in water, but not the higher members, nor the simple aromatic amines; but some diamines, amino-phenols and amino-acids are moderately soluble. Many of these soluble compounds may be extracted with ether after salting-out (adding common salt to saturation). If the substance is soluble in water, it may be one of the above-named compounds, or a lower aldehyde or ketone, or a bisulphite compound of these substances, or the salt of a base or acid.

The following is a list of the more soluble organic compounds their boiling-points, melting-points and solubilities, which are roughly indicated by the letters *s.* (soluble in cold water) *h.s.* (soluble in hot water).

Soluble Liquids and Solids.

	Soluble.	Melting-point.	Boiling-point.
Alcohols—			
Methyl (p. 67)	s.	—	66
Ethyl (p. 49)	,,	—	78
n-Propyl	,,	—	97
i- ,,	,,	—	85
n-Butyl	,,	—	117
i- ,,	,,	—	108
Allyl (p. 109)	,,	—	97
Benzyl (p. 195)	,,	—	207
Glycol	,,	—	197
Glycerol (p. 106)	,,	—	290
Aldehydes—			
Formaldehyde	s.	—	−21
Acetaldehyde (p. 64)	,,	—	21
,, ammonia	,,	decomp.	—
Chloral	,,	—	96
Chloral hydrate (p. 99)	,,	57	97
Butyl chloral hydrate	,,	78	decomp.
Acrolein	,,	—	52
Ketones—			
Acetone (p. 69)	s.	—	56
Methyl ethyl ketone	,,	—	81
Bisulphite compounds of aldehydes and ketones	,,	decomp.	—
Acids—			
Formic (p. 106)	s.	—	100
Acetic (p. 74)	,,	—	119
Propionic	,,	—	140
n-Butyric (p. 98)	,,	—	163
i- ,,	,,	—	155
Chloracetic (p. 87)	,,	62	186
Dichloracetic	,,	—	190
Trichloracetic (p. 99)	,,	52	195
Bromacetic (p. 89)	,,	50	208
Aminoacetic (Glycocoll) (p. 90)	,,	236	—
Aminocaproic (Leucine) (p. 133)	h.s.	66	—
Acrylic	s.	10	140
Glycollic (p. 102)	,,	80	decomp.
Lactic	,,	—	—
Glyoxylic acid (p. 102)	,,	—	decomp.
Pyruvic (p. 124)	,,	—	165
Oxalic (p. 100) (anhydrous)	,,	98	—
Malonic (p. 97)	,,	132	decomp.
Ethyl malonic	,,	112	,,
Succinic (p. 113)	,,	180	forms anhyd.
Malic (p. 112)	,,	100	decomp.
Tartaric (p. 114)	,,	169	,,
Citric (p. 124)	,,	154	,,
Citraconic (p. 125)	,,	80	anhyd.
Benzoic (p. 302)	h.s.	122	—
o-Chlorobenzoic	,,	137	—
o-Bromobenzoic	,,	150	—

SOLUBLE LIQUIDS AND SOLIDS (*continued*).

	Soluble.	Melting-point	Boiling-point.
Acids—			
o-Hydroxybenzoic (Salicylic) (p. 190)	h.s.	155	anhyd.
m- ,,	,,	200	—
p- ,,	,,	210	—
o-Aminobenzoic (Anthranilic)	,,	144	—
m- ,,	,,	174	—
p- ,,	,,	187	—
o-Toluic	,,	102	—
m- ,,	,,	110	—
p- ,, (p. 170)	,,	179	—
Gallic	s.	222	—
Tannic	,,	decomp.	—
Mandelic (p. 205)	,,	118	—
Benzilic (p. 203)	h.s.	150	—
Cinnamic (p. 204)	,,	133	—
Hydrocinnamic (p. 204)	,,	47	—
Phthalic (p. 217)	,,	213	anhyd.
Benzene sulphonic (p. 177)	s.	51	—
α-Naphthalene sulphonic	,,	90	—
β- ,, (p. 218)	,,	160	—
β-Naphthol 6. sulphonic	,,	125°	—
,, 6.8. disulphonic G	,,	—	—
,, 3.6. ,, R	,,	—	—
Sulphanilic (p. 175)	h.s.	decomp.	—
Alkyl acid sulphates (p. 50)	s.	,,	—
Sulphonal	h.s.	126	—
Phenols—			
Phenol (p. 179)	h.s.	43	181
Catechol	s.	104	245
Resorcinol	,,	118	276
Quinol (p. 193)	,,	169	subl.
Orcinol (cryst.)	,,	56	—
,, (anhyd.)	,,	107	—
Pyrogallol	,,	132	293
Phloroglucinol	,,	217	subl.
p-Aminophenol (p. 146)	h.s.	184	—
α-Naphthol	,,	95	—
β- ,, (p. 219)	,,	122	—
Carbohydrate—			
Glucose (p. 135)	s.	146	—
Galactose	,,	163	—
Lævulose	,,	95	—
Cane-sugar	,,	160	—
Lactose	,,	205	—
Maltose	,,	—	—
Dextrin	,,	—	—
Starch	h.s.	—	—
Glucosides—			
Amygdalin	s.	200	—
Arbutin	h.s.	187	—
Helicin	,,	175	—
Salicin	,,	201	—

Soluble Liquids and Solids (*continued*).

	Soluble.	Melting-point.	Boiling-point.
Bases—			
Methylamine (p. 80)	s.	—	gas
Dimethylamine	,,	—	,,
Trimethylamine	,,	—	,,
Ethylamine	,,	—	19
Diethylamine	,,	—	57
Urethane	,,	52	180
Benzylamine	,,	—	183
o-Phenylenediamine	h.s.	102	—
m- ,, (p. 155)	,,	63	—
p- ,, (p. 173)	,,	147	—
p-Aminophenol (p. 149)	,,	184	—
Pyridine	s.	—	116
Caffeine (p. 131)	,,	234	—
Amides and Cyanides—			
Formamide	s.	—	192
Acetamide (p. 77)	,,	82	222
Urea (p. 126)	,,	132	decomp.
Thiourea (p. 128)	h.s.	172	—
Succinimide	s.	126	—
Benzamide (p. 209)	h.s.	128	—
Formanilide	,,	46	—
Acetanilide (p. 151)	,,	112	—
Acetonitrile (p. 79)	s.	—	82
Salts of bases and acids.			
Acid anhydrides and *chlorides* dissolve gradually on warming and yield the acid.			

The above preliminary investigation will determine the further course of investigation, but the following rough plan may serve as a guide.

§ I. SINGLE SUBSTANCE SOLUBLE IN WATER :—

1. **Contains only Carbon, Hydrogen and Oxygen.**—The number of such substances, as seen from the above table, is comparatively small. It may be an *alcohol*, *aldehyde* or *ketone* of low molecular weight, *acid*, *phenol*, *carbohydrate* or *glucoside*.

Acids.—Make a solution (if not already dissolved) and test with litmus. If the liquid is acid, a free *acid* is probably present. If the liquid is neutral and a metal has been found, a metallic salt is probably present. If the liquid is alkaline, it may be the alkaline salt of a phenol or an alkaline cyanide, both of which are hydrolysed in solution. The separation and identification of the acid is not a very simple matter. If the acid is an aromatic or an aliphatic acid of high molecular weight, in short, any acid which either does not appear in the table or is marked as only soluble in hot water, a few drops of conc. hydrochloric acid will usually precipitate it, and it may then be filtered, or removed with ether, and its melting-point determined. If no precipitate is formed, but the solution turns brown on the addition of an alkali, tannic or gallic acid may be present. If the acid is volatile and has a distinctive smell (formic, acetic, butyric, etc.), the solution should be acidified with sulphuric acid and distilled. The distillate will contain the free acid, which will probably have a distinctive smell. Individual tests may then be directly applied, but it is preferable to neutralise the distillate with caustic soda and evaporate to dryness on the water-bath, so as to obtain the sodium salt before testing. The free acid may be soluble and non-volatile, like oxalic, tartaric, succinic, citric, etc., and then special tests must be applied (see tests for these acids).

Phenols.—If it is a free phenol, ether will extract it from its aqueous solution. If it is present in alkaline solution, the solution should first be saturated with carbon dioxide. (N.B.—The alkaline solutions of catechol, quinol and pyrogallol darken rapidly in the air.) The following tests should then be applied.

Ferric chloride reaction.—Dissolve a drop of the free phenol in water and add a drop of *neutral* ferric chloride. A green (catechol), blue (orcinol, pyrogallol) or purple (phenol, resorcinol) colouration is produced, which is often destroyed by acid or alkali. Quinol is oxidised to quinone, and turns brown (p. 193). The naphthols give precipitates of dinaphthol (p. 220).

Schotten-Baumann reaction (p. 209).—This may be applied to the pure phenol in order to obtain the benzoyl derivative, and the melting-point determined, or the acetyl derivative may be prepared by boiling for a minute with acetic anhydride with the same object.

The action of bromine water (p. 180), Liebermann's nitroso-reaction (p. 180) and the phenolphthalein reaction (p. 186), using conc. sulphuric acid or zinc chloride, may also be applied.

Alcohols.—It may be a liquid alcohol (methyl, ethyl, propyl, etc., glycerol, benzyl) or a solution of it in water. In the former case its boiling-point will have already been determined. It may be further identified (1) by converting it into the benzoic ester by the Schotten-Baumann reaction, and determining the boiling-point or melting-point; (2) by oxidation with excess of bichromate mixture (10 grams of $K_2Cr_2O_7$ in 100 c.c. dilute sulphuric acid, 1 : 3 by volume). The alcohols are boiled for some time with reflux condenser, and the product distilled, neutralised with alkali and evaporated on the water-bath and the sodium salts tested. Glycerol will be identified by its viscid character and reactions (p. 106). If the alcohol is in aqueous solution, it should first be fractionated and potassium carbonate added to the distillate, when the alcohol will separate. Glycerol or glycol in aqueous solution may be separated by evaporation on the water-bath.

Aldehydes and Ketones are detected in the first instance by: (1) Shaking with a cold saturated solution of sodium bisulphite (see Reaction 2, p. 67). (2) Adding to the aqueous solution *p*-bromo- or *p*-nitro-phenylhydrazine acetate solution (see Reaction 2, p. 70).

The aldehyde may be distinguished from the ketone by its reducing action on alkaline copper sulphate, ammonia-silver nitrate and by Schiff's test (see Reactions, p. 67).

Carbohydrates will char on heating, and give off water and emit a smell of burnt sugar. The substance is tested with alkaline copper sulphate, ammonia-silver nitrate, phenylhydrazine acetate or Molisch's test (see p. 136). Cane-sugar will not respond to these reactions until it has been boiled for a few minutes with a few drops of dilute sulphuric acid and inverted (see Prep. and Notes). Special tests may then be applied to identify the particular sugar. A few glucosides are soluble in water, and give the sugar reactions after boiling with dilute acid.

2. **Contains Nitrogen.**—First test the original solid or liquid by heating in a hard-glass tube with soda-lime (p. 2), and notice if the smell is that of ammonia (ammonia salt, amide or cyanide), an amine (amine or amino-acid) or a pyridine base (alkaloid).

Dissolve the substance in water, add caustic soda solution and warm.

Ammonium or amine salts, if present, emit the smell of ammonia or amine; if the salt of an insoluble organic base is present (*amine*, *alkaloid*), it may be precipitated as a liquid or solid. Salts of aliphatic bases and bases such as benzylamine and piperidine are neutral; salts of aromatic bases (amino-group in the nucleus) are acid. A soluble organic base (lower amine, benzylamine, pyridine) will be detected by its smell. Most aromatic amino-compounds and alkaloids are insoluble in water. Some aromatic diamines and aminophenols are moderately soluble. The nature of the amine, whether primary, secondary, or tertiary, should then be investigated as described under § II. 2.

Amino-acids of both the aliphatic and aromatic series will also come under this head. Substances like glycocoll, alanine, etc., are very soluble in water, giving neutral solutions, and may be identified by means of the copper salt (see p. 91). Amino-acids of the aliphatic series also evolve nitrogen when treated with sodium nitrite and hydrochloric acid, and give off amines when heated with soda-lime. Amino-acids of the aromatic series may be diazotised and coupled with phenols, like aromatic amines (see p. 151).

Amides and Cyanides.—Many amides and a few cyanides are soluble in water. They are decomposed by hot concentrated aqueous or alcoholic caustic soda solutions, by concentrated hydrochloric acid or sulphuric acid (equal vols. of acid and water) on long reflux boiling. In the first case, ammonia is evolved; in the latter two cases, salts of ammonia are formed, which yield ammonia on heating with excess of caustic soda. Anilides behave similarly, but aniline in place of ammonia is liberated and must be looked for. Some amides are difficult to hydrolyse with any of these reagents. In such cases, gently heating with a mixture of one volume of conc. sulphuric acid and two volumes of ethyl alcohol will yield the ester of the acid and ammonium sulphate. The ester can then be separated by adding a little water and extracting with ether, and can be hydrolysed and the organic acid identified (see p. 333), whilst the aqueous solution, after driving off dissolved ether, will give the smell of ammonia on warming with excess of alkali.

3. **Contains Halogen.**—It may be a *halogen acid* (*e.g.*, chloracetic acid) or its salt, or the *hydrochloride of a base* or *amino-acid*, or a *substituted aldehyde* (chloral, butyl chloral). If it is a free halogen acid, the solution will have an acid reaction, and the solution will remain clear on adding caustic soda. If it is the hydrochloride of a base, it will give a precipitate with

$AgNO_3$, and the addition of caustic soda will cause the base to separate (if insoluble) as solid or liquid, or, if the base is volatile, will produce a strong ammoniacal smell. The further examination of the base is the same as that described under § I, 2. Acid chlorides are usually insoluble in water, but rapidly decompose, and may pass into solution as the free acid, giving at the same time free hydrochloric acid.

4. **Contains Sulphur.**—It may be the *sulphate of a base*, in which case the solution will give a precipitate with barium chloride, and the process of examination is that described under § I, 2. Heat with dilute hydrochloric acid. The *bisulphite compound* of an aldehyde or ketone will be decomposed and sulphur dioxide evolved. An *alkyl acid sulphate* will also be decomposed, and free sulphuric acid will be found in solution (see Reaction, p. 54). Distil with dilute sulphuric acid, and test the distillate for volatile aldehyde or ketone. *p*.-Bromo- and *p*-nitro-phenylhydrazine are useful reagents (see § I, 1). An acid ester of sulphuric or sulphurous acid will also be decomposed by dilute sulphuric acid, and the distillate may be tested for an alcohol. If it is an *aromatic sulphonic acid*, it may be distilled in steam with the addition of conc. sulphuric acid, when the hydrocarbon will distil (p. 292), or fused with caustic potash, when the phenol will be obtained (p. 179). *Thiourea* will also appear under this head, and should be looked for. Heat a little of the substance to the melting-point for a minute, and test for thiocyanate with HCl and $FeCl_3$.

§ II. SINGLE SUBSTANCES, INSOLUBLE OR SLIGHTLY SOLUBLE IN HOT OR COLD WATER.—This category includes the majority of organic compounds.

1. Contains only Carbon and Hydrogen, or Carbon, Hydrogen, and Oxygen.

Liquids.—It may be a *hydrocarbon* (paraffin, olefine, aromatic) *higher alcohol* (*e.g.*, amyl alcohol), *aldehyde* (*e.g.*, benzaldehyde) *ketone* (*e.g.*, acetophenone) *acid* (*e.g.*, valeric acid), *ether*, *ester*, *phenol* (*e.g.*, carvacrol) *phenol ether* (*e.g.*, anisole).

Hydrocarbons.—The action of sodium when testing for the elements will already have indicated the hydrocarbon by its inertness. The immediate decolourisation of bromine water will identify it as an unsaturated hydrocarbon. A paraffin may be distinguished from an aromatic hydrocarbon by treating the liquid with a mixture of concentrated sulphuric and nitric acids. (p. 142). The product is then poured into water. If the product sinks as a yellow liquid or solid it is probably a nitro-compound and the original hydrocarbon is aromatic. If it floats unchanged on the surface of the water, it is probably a paraffin. An aromatic hydrocarbon also dissolves in fuming sulphuric acid on warming and shaking and does not separate on pouring the solution into water. A paraffin is unacted on and separates on the surface. There is also a marked difference in the smell of the two classes of hydrocarbons.

Higher Alcohols and Phenol.—The substance will react with metallic sodium yielding hydrogen, with phosphorus pentachloride giving HCl. It can be identified by its boiling point and by the b.p. or m.p. of the benzoic ester (p. 208). In the case of a phenol it will possess a phenolic smell and may give a distinctive colour reaction with $FeCl_3$ (p. 180).

Aldehydes and Ketones.—The usual tests are applied (p. 330).

Acids.—The number of liquid, insoluble acids is very limited and is confined to the aliphatic series. They possess distinctive b.p.'s and smells and dissolve readily in a solution of sodium carbonate.

Ethers and Phenol Ethers have usually a pleasant odour and if the methyl or ethyl ether is present are decomposed on heating with strong hydriodic acid. The evolved gas passed into alcoholic silver nitrate will give a precipitate as in Zeisel's method (p. 220).

Esters possess a fruity smell and usually distil without decomposition. Boil with reflux for 5 minutes on the water-bath a few c.c. of the liquid with 3 to 4 volumes of a ten per cent. solution of caustic potash in methyl alcohol and pour into water. Notice if the liquid dissolves and has lost the odour of the ester. An ester will be completely hydrolysed, and if the alcohol is soluble in water a clear solution will be obtained. If the alcohol is volatile and the solution neutralised with sulphuric acid and evaporated on the water-bath, the alkali salt of the organic acid mixed with potassium sulphate will be left and the acid may be investigated as described under §I. If it is required to ascertain the nature of the alcohol in the ester, hydrolysis must be effected with a strong *aqueous* solution of caustic potash

($1KOH,3H_2O$). Then distil the liquid, using a thermometer. The alcohol, if volatile, will pass into the receiver, whilst the acid remains as the potassium salt in the vessel. The boiling point will give some indication of the former. The distillate should be fractionated and dehydrated with solid potassium carbonate. Its boiling-point and that of the benzoic ester is then determined.

Glycerides.—If the substance is a liquid fat or oil (*i.e.* non-volatile, which decomposes on heating, turning brown and evolving the smell of acrolein) then the hydrolysis is effected with methyl-alcoholic potash as described. After hydrolysis, the alcohol is driven off on the water-bath, the residue dissolved in water, and the organic acid set free with hydrochloric acid. The acid if solid is filtered, if liquid extracted with ether, or if soluble and volatile (butyric acid) distilled and the remaining liquid neutralised and evaporated to dryness. The glycerol is then extracted with alcohol and the alcoholic solution evaporated on the water-bath. The tests for glycerol may then be applied (p. 106). The following is a table of common insoluble liquids with their boiling-points and specific gravities. Where the temperature is not indicated the specific gravity has been determined at 0°.

ORGANIC LIQUIDS, INSOLUBLE IN WATER.

(Containing C and H or C, H, and O.)

		Boiling-point.	Sp. gr.	*t.*
Hydrocarbons—				
n-Pentane	Present in Petrol, Petroleum, Ether, and Ligroin	39	0·626	17
i- ,,		30	0·638	14
n-Hexane		72	0·660	20
n-Heptane		97	0·712	16
n-Octane		124	0·708	12
Petroleum (lamp oil)		150—300	0·803 0·822	Amer. Russ.
i-Amylene		25	0·680	—
Benzene (p. 136)		80	0·880	20
Toluene (p. 163)		110	0·865	20
Ethyl benzene (p. 141)		136	0·867	20
o-Xylene		142	0·865	20
m- ,,		139	0·863	20
p- ,,		138	0·869	20
Cumene (Isopropyl benzene)		152	0·880	—
Pseudocumene		166	0·861	—
Mesitylene		164	0·855	20

ORGANIC LIQUIDS, INSOLUBLE IN WATER (*continued*).

	Boiling-point.	Sp. gr.	*t.*
Hydrocarbons (continued)—			
Cymene	175	0·853	20
Turpentine oil (Pinene)	155—160	0·865 –0·870	—
Lemon oil (Limonene)	160—165	0·858 –c.861	—
Alcohols—			
i-Amyl (p. 69)	131	0·812	20
Octyl	190	0·830	16
Linalol	198	0·868	15
Benzyl (p. 195)	206	1·043	20
Aldehydes—			
Paraldehyde (p. 67)	124	0·990	20
Citral	229	0·897	—
Benzaldehyde (p. 196)	179	1·045	20
Cuminaldehyde	237	0·983	—
Anisaldehyde	248	1·122	20
Cinnamic aldehyde	247	1·049	20
Salicylaldehyde (p. 188)	196	1·122	20
Ketones—			
Methyl nonyl ketone	225	0·829	17
Acetophenone (p. 210) (m.p. 20°)	202	1·032	—
Carvone	224	0·953	15
Acids—			
i-Valeric	176	0·947	—
Caproic	205	0·945	—
Anhydrides—			
Acetic (p. 76)	138	1·08	15
Phenols—			
Phenol (p. 179) (m.p. 43°)	182	1·070	20
o-Cresol (m.p. 31°)	191	1·037	20
m- ,,	202	1·033	20
p- ,, (p. 164)	202	1·033	20
Guaiacol (m.p. 30°)	205	1·12	—
Carvacrol	236	0·985	15
Eugenol	248	1·09	18
Isoeugenol	260	1·08	16
Ethers and Phenol Ethers—			
Ethyl ether (p. 59)	35	0·713	15
Amyl ,,	176	0·800	—
Methylal	42	0·850	20
Acetal	104	0·831	20
Anisole (p. 181)	154	0·988	20
Phenetole	172	0·973	15
Anethole	232	1·022	20
Safrole	232	1·114	—
Esters—			
Methyl formate	32	0·900	—
,, acetate	57	0·904	20

ORGANIC LIQUIDS, INSOLUBLE IN WATER (*continued*).

	Boiling-point.	Sp. gr	*t.*
Esters (continued)—			
Methyl propionate	79	0·937	—
,, butyrate	102	0·896	20
,, *i*-valerate	117	0·879	20
,, succinate	198	1·126	15
,, tartrate	280	1·340	—
,, benzoate	199	1·086	20
,, salicylate	224	1·182	—
Ethyl formate	54	0·906	20
,, acetate (p. 81)	77	0·900	20
,, acetoacetate (p. 83)	181	—	—
,, propionate	99	1·029	20
,, butyrate	120	0·896	—
,, *i*-valerate	135	0·889	20
,, oxalate	186	0·866	20
,, malonate (p. 96)	198	1·080	20
,, succinate	216	1·076	—
,, tartrate (p. 115)	decomp.	1·072	—
,, benzoate (p. 209)	213	1·047	20
,, salicylate	227	1·184	—
n-Propyl formate	81	0·918	—
i- ,, ,,	71	0·882	—
n- ,, acetate	101	0·885	20
,, propionate	122	0·901	—
,, butyrate	143	0·893	—
,, benzoate	229	1·031	—
n-Butyl formate	107	0·910	—
i- ,, ,,	98	0·900	—
n- ,, acetate	125	0·866	—
i- ,, propionate	136	0·887	—
,, butyrate	157	0·887	—
,, *i*-valerate	169	0·873	—
i-Amyl formate	123	0·880	20
,, acetate	139	0·856	20
,, propionate	160	0·887	—
,, butyrate	178	0·882	—
,, *i*-valerate	190	0·870	—
,, benzoate	261	1·004	—
,, salicylate	270	—	—
Glyceryl triacetate	258	1·155	—
,, trioleate	decomp.	0·91	—
Phenyl acetate	195	1·093	—
Benzyl acetate	206	1·057	16
,, benzoate (m.p. 20°)	323	1·114	—

Solids.—It may be a *hydrocarbon* (*e.g.*, paraffin wax, naphthalene) *higher alcohol* (*e.g.*, cetyl alcohol) ; *aldehyde* (*e.g.*, *p*-hydroxybenzaldehyde) *ketone* and *quinone* (*e.g.*, benzophenone, camphor) *acid* (higher fatty, *e.g.*, palmitic acid or aromatic acid) *ester* (of glycerol, phenols or aromatic alcohols) *phenol* (*e.g.*, thymol).

The process of investigation is similar to that described in the preceding section.

Acids.—A free acid may be at once identified by its solubility in a solution of sodium carbonate and by being reprecipitated by concentrated hydrochloric acid. If a metal has been discovered in the preliminary examination, a careful examination must be made for an organic acid. As the substance is insoluble in water the metal will probably not be an alkali metal. Boil the substance with sodium carbonate solution. The sodium salt of the acid passes into solution and the metallic carbonate is precipitated. Filter; boil the filtrate with a slight excess of nitric acid, add excess of ammonia and boil until neutral, tests may then be applied in order to identify one of the common acids and the m.p. determined; but beyond this it is impossible to carry the investigation in a limited time.

INSOLUBLE SOLIDS.

(Containing C and H, or C, H, and O.)

	Melting-point.
Hydrocarbons—	
Paraffin wax	45—60
Naphthalene (p. 216)	80
Anthracene (p. 225)	217
Phenanthrene	99
Stilbene	125
Alcohols—	
Cetyl Alcohol	50
Menthol	42
Aldehydes—	
Vanillin	81
Piperonal	37
Ketones—	
Benzophenone	48
Benzil (p. 202)	95
Benzoin (p. 203)	137
Camphor	175
Quinones—	
Benzoquinone (p. 192)	116
o-Naphthaquinone	125
β- „	115—120 decomp.
Anthraquinone (p. 225)	285
Phenanthraquinone	205
Acids—	
Palmitic (p. 104)	62
Stearic	69
Benzoic (p. 199)	122
o-Hydroxybenzoic (p. 190)	155
m- „ (p. 201)	200
p- „	210
Acids—(continued)	
Anisic	184
o-Toluic	102
m- „	110
p- „ (p. 170)	179
Phenyl acetic	76
o-Phthalic (p. 217)	213
m- „ (isophthalic	subl.
p- „ (terephthalic) (p. 171)	„
Anhydrides—	
Benzoic	42
Phthalic (p. 218)	128
Phenols—	
o-Cresol	31
p- „ (p. 164)	36
Thymol	44
α-Naphthol	95
β- „ (p. 219)	122
Esters—	
Methyl oxalate (p. 101)	54
Cetyl palmitate (Spermaceti)	53
Myricyl palmitate (Bees wax)	62—65
Glyceryl tripalmitate (Palmitin) (p. 104)	62
Glyceryl tristearate (Stearin)	71
Phenyl benzoate	69
„ salicylate	43
Benzyl benzoate	21
„ salicylate	—

2. Contains Nitrogen.

Organic base.—If it is a *base* or *amine*, amino-phenol or amino-acid, it will probably dissolve in dilute hydrochloric acid and yield a chloroplatinate with platinic chloride. Some aromatic bases like diphenylamine are not very soluble in dilute acids. Amino-phenols and acids may be extracted with ether from an acid solution to which ammonia has been added till faintly acid and then sodium acetate. Many amines and amino-phenols give quinones on oxidation with potassium bichromate and sulphuric acid having a characteristic smell (p. 192). Many of the common *alkaloids* when dissolved in hydrochloric acid (avoid excess) give a brown amorphous precipitate with iodine solution and respond to other general reactions for the alkaloids (see p. 320). To identify the individual alkaloid, special tests must be applied.

Primary, *secondary*, and *tertiary amines* may be distinguished as follows: To a solution of the base in dilute hydrochloric acid add a few drops of sodium nitrite solution. In the case of primary aliphatic amines, a rapid evolution of nitrogen will at once occur; a primary aromatic amine at first gives a clear solution of the diazonium-salt, which evolves nitrogen and turns darker on warming. The effervescence, due to the liberation of nitrous fumes, is easily distinguished from that of nitrogen, which goes on uninterruptedly, even when the liquid is removed from the flame.

After the solution of the diazonium salt has been decomposed by warming, the phenol which has been produced may be extracted with ether, the ether evaporated, and the phenol identified by special tests. A solution of the diazonium salt, when poured into a solution of β-naphthol in caustic soda, will usually give a red azo-colour. The original amine, if liquid, may sometimes be identified by warming with a little acetyl chloride and converting it into the solid acetyl derivative, which is recrystallised and the melting-point determined (see Reaction 3, p. 76).

In the case of a secondary base, the above treatment with hydrochloric acid and sodium nitrite will give an insoluble nitrosamine (liquid or solid), which is frequently yellow. It may be separated by ether and, after removing the ether, tested by Liebermann's nitroso-reaction (see Reaction 3, p. 159). Nitrous acid has no action on tertiary aliphatic amines, but forms nitroso-bases with tertiary aromatic amines (see p. 157), which dissolve in water in presence of hydrochloric acid, with which they form soluble hydrochlorides. Tertiary amines also combine with methyl iodide on warming (see Reaction, p. 157), but not with acetyl chloride. Primary amines give the carbamine reaction (p. 150), and unite with carbon bisulphide (p. 159).

Oximes.—It should be remembered that oximes act as bases as well as acids, and dissolve in both caustic alkalis and acids. On reduction in acid solution (with tin or zinc) they yield amines.

Cyanides and Amides are hydrolysed by caustic potash (aqueous or, better, alcoholic), conc. hydrochloric or sulphuric acid as mentioned previously under § I, 2. It should be mentioned that some amides are attacked only with difficulty, and must then be treated as described under § I, 2.

Nitro-compounds are frequently yellow or orange in colour. Heated with stannous chloride in conc. HCl or zinc dust and glacial acetic acid they dissolve and remain in solution on the addition of water. The base which is thus formed may be separated by adding an excess of caustic soda until the metallic oxide dissolves and then shaking out with ether. When the ether is removed, the base remains. If liquid, the base should be converted into the acetyl derivative by warming with acetyl chloride for a few minutes and pouring into water. The free base or solid acetyl derivative, as the case may be, should be recrystallised and the melting-point determined. It can also be diazotised and coupled with β-naphthol.

Alkyl Nitrates are hydrolysed like other esters, and yield alcohol and nitric acid (p. 82).

Nitro-phenols and Nitro-acids dissolve in caustic alkalis as a rule with a deep yellow or orange colour. On reduction with stannous chloride or zinc dust, as described above, they yield the amino-derivatives. In the case of the amino-phenol, the solution is made alkaline with caustic soda, saturated with CO_2, salt added and extracted with ether. In the case of the amino-acid, the method used is that described under Prep. 91 (p. 201).

Azo- and Azoxy-compounds. Both classes of compounds are usually highly coloured and are rapidly decolorised by warming with a solution of stannous chloride and hydrochloric acid, forming amino-compounds (see Reactions, pp. 173, 177).

INSOLUBLE SUBSTANCES.

(Containing C, H, and N or C, H, O, and N.)

	Melting-point.	Boiling-point.
Bases (primary)—		
Aniline (p. 149)	—	182
o-Nitraniline	71	—
m- ,, (p. 154)	114	—
p- ,, (p. 153)	147	—
o-Chloraniline	—	207
m- ,,	—	230
p- ,,	70	230
o-Bromaniline	31	251
m- ,,	18	251
p- ,, (p. 152)	63	—
o-Toluidine	—	197
m- ,,	—	199
p- ,,	45	198
1-3-4-Xylidine	—	215
1-2-4-5-Cumidine	63	234
p-Hydroxyaniline(*p*-aminophenol)	184	—
Anisidine	—	226
Phenetidine	—	228
α-Naphthylamine	50	—
β- ,,	112	—
Benzidine (p. 148)	122	—
o-Tolidine	128	—
o-Phenylenediamine	102	—
m- ,, (p. 155)	63	—
p-Phenylenediamine (p. 173)	147	—
p-Dimethylphenylenediamine (p. 177)	41	—
Phenylhydrazine (p. 173)	23	241
Bases (secondary)—		
Methylaniline	—	191
Ethylaniline	—	206
Benzylaniline	33	298
Diphenylamine	54	—
Methyldiphenylamine	—	292
Phenyl β-naphthylamine	108	—
Piperidine	—	105
Conine	—	166
Bases (tertiary)—		
Dimethylaniline (p. 156)	—	192
Diethylaniline	—	213
Dimethyl *o*-toluidine	—	183
,, *p*- ,,	—	208
α-Picoline	—	129
Quinoline (p. 230)	—	239
Antipyrine	113	—
The alkaloids	—	—

	Melting-point.	Boiling point.
Aminophenols—		
p-Aminophenol (p. 149)	184	—
o-Methylaminophenol (Metol)	87	—
p-Methylaminophenol (Ortol)	80	—
2-4-Diaminophenol (Amidol)	decomp.	—
Cyanhydrins and *Oximes*—		
Benzaldehyde cyanhydrin (p. 206)	10	decomp.
Acetoxime (p. 71)	60	—
α-Benzaldoxime (p. 197)	35	—
β-Benzaldoxime (p. 197)	130	—
Acetophenoneoxime (p. 211)	60	—
Cyanides and *Amides*—		
Succinamide	—	decomp.
Phenyl cyanide	—	191
p-Tolyl cyanide (p. 169)	29	218
Oxamide (p. 102)	decomp.	—
Benzamide (p. 209)	128	—
Hydrobenzamide (p. 196)	110	—
Salicylamide	142	—
Formanilide	46	—
Acetanilide (p. 151)	112	—
Methylacetanilide	102	—
Propionanilide	92	—
Benzanilide	163	—
Oxanilide	245	—
o-Acetotoluide	110	—
p- ,,	153	—
Diphenylurea	235	—
Triphenyl guanidine (p. 160)	143	—
α-Acetnaphthalide	159	—
β- ,,	132	—
Amino-acids—		
Hippuric acid	187	—
Uric acid	decomp.	—
Anthranilic acid	144	—
Nitro-compounds—		
Nitrobenzene (p. 142)	—	210
m-Dinitrobenzene (p. 154)	90	—

INSOLUBLE SUBSTANCES (*continued*).

	Melting-point.	Boiling-point.
Nitro-compounds (continued).		
Trinitrobenzene . .	122	—
o-Nitrotoluene . .	—	223
m- ,, . .	—	230
p- ,, . .	54	238
1-2-4-Dinitrotoluene	71	—
α-Nitronaphthalene	61	—
o-Nitracetanilide .	78	—
p- ,, (p. 153)	207	—
Nitro-phenols, Aldehydes and *Acids*—		
o-Nitrophenol (p. 183)	45	—
m- ,, . .	96	—
p- ,, (p. 183)	114	—
Trinitrophenol (p. 185)	122	—
Nitroanisole . . .	—	—
m-Nitrobenzaldehyde	58	—
o-Nitrobenzoic acid	148	—
m- ,, (p. 200)	141	—
p-Nitrobenzoic acid	238	—
1-2-4-Dinitrobenzoic acid	179	—
1-3-5-Dinitrobenzoic acid	205	—
Nitroso-compounds—		
p-Nitrosodimethylaniline (p. 157) .	85	—
p-Nitrosodiethylaniline	84	—
Nitroso-β-naphthol	106	—
Alkyl Nitrites and *Nitrates*—		
Ethyl nitrite . . .	—	16
,, nitrate . . .	—	86
Amyl nitrite (p. 69)	—	95
,, nitrate . . .	—	147
Azo- and *Azoxy-compounds*—		
Azoxybenzene (p. 143)	36	—
Azobenzene (p. 145)	68	—
Hydrazobenzene (p. 146)	125	—
Diazoaminobenzene (p. 171)	98	—
Aminoazobenzene (p. 172)	127	—

3. **Contains Halogen.**—Halogen compounds may be *alkyl*, *alkylene*, *aryl* or *acid halides* or *halogen acids* (*e.g.*, ethyl bromide, ethylene bromide, bromobenzene, benzoyl chloride, or chlorobenzoic acid).

Alkyl, *Alkylene and Aryl Halides* are usually liquids or solids specifically heavier than water and with a sweet penetrating smell, or if aromatic compounds substituted in the side-chain, they have a sharp penetrating smell and attack the eyes. They are for the most part colourless, but the bromine and iodine compounds usually acquire a brown colour on standing. Iodoform is naturally yellow. In the case of alkyl and alkylene halides and aromatic compounds substituted in the side-chain, alcoholic silver nitrate will, on warming, yield silver halide. Strong methyl-alcoholic potash will, with the same compounds, produce olefines and acetylenes (p. 64). The experiment should be tried with the apparatus Fig. 86, and the gas collected and tested. Aromatic compounds substituted in the nucleus are not, as a rule, acted on by these reagents unless nitro-groups are also present; many of these react with magnesium in presence of dry ether (p. 206).

INSOLUBLE SUBSTANCES.

(Containing C, H and halogens or C, H, O and halogens.)

	Melting-point.	Boiling-point.
Alkyl, Alkylene, and Aryl Halides—		
Methyl iodide (p. 68)	—	43
Ethyl bromide (p. 54)	—	38
Ethyl iodide	—	72
n-Propyl chloride	—	44
,, bromide	—	71
,, iodide	—	102
i- ,, chloride	—	36
,, bromide	—	60
,, iodide	—	89
n-Butyl chloride	—	77
,, bromide	—	100
,, iodide	—	130
i- ,, chloride	—	68
,, bromide	—	92
,, iodide	—	120
i-Amyl chloride	—	100
,, bromide	—	120
,, iodide	—	148
Allyl bromide	—	71
,, iodide	—	101
Methylene chloride	—	41
,, bromide	—	58
Ethylene chloride	—	84
Ethylidene ,,	—	58
Ethylene bromide (p. 62)	—	131
Ethylidene bromide	—	109
Chloroform (p. 70)	—	61
Bromoform	—	151
Iodoform	119	—
Carbon tetrachloride	—	76
Benzyl chloride (p. 194)	—	176
Benzal ,,	—	204
Benzotrichloride	—	213
Chlorobenzene	—	132
Bromobenzene (p. 140)	—	155
Iodobenzene	—	188
o-Dichlorobenzene	—	179
p- ,,	53	173
Alkyl, Alkylene, and Aryl Halides (continued)—		
o-Dibromobenzene	—	225
p-Dibromobenzene	89	218
o-Chlorotoluene	—	157
m- ,,	—	156
p- ,, (p. 165)	—	160
o-Bromotoluene	—	182
m- ,,	—	184
p- ,, (p. 167)	28	185
α-Chloronaphthalene	—	263
β-Chloronaphthalene	56	265
α-Bromonaphthalene	—	279
β-Bromonaphthalene	59	282
Phenols—		
Trichlorophenol	68	—
Tribromophenol	95	—
Acid Chlorides—		
Acetyl chloride (p. 74)	—	55
Benzoyl ,, (p. 208)	—	198
Acids—		
o-Chlorobenzoic	137	—
m- ,,	153	—
p- ,, (p. 166)	236	—
o-Bromobenzoic	147	—
m- ,, (p. 201)	155	—
p- ,,	251	—
Esters—		
Methyl chloroformate	—	71
Methyl chloracetate	—	130
,, bromacetate	—	144
Ethyl chloroformate	—	94
,, chloracetate	—	143
,, bromacetate	—	159

Acid Chlorides and Bromides are also specifically heavier than water, but reveal their presence by fuming in moist air. They are decomposed by water more or less rapidly, and give the corresponding acid and hydrochloric acid, which may be tested for. They are also acted on rapidly by strong ammonia, and give the amide, the melting-point of which may be ascertained (p. 209).

Halogen Acids and *Esters.*—Most of the insoluble halogen acids belong to the aromatic series, and have a distinctive melting-point. For further confirmation, they may be converted into the acid chloride and amide. Insoluble esters containing halogens may belong to both series, and the acid and alcohol must then be separated and separately investigated.

4. The following among the more common organic substances contain sulphur or sulphur and nitrogen in addition to carbon, hydrogen and oxygen.

INSOLUBLE SUBSTANCES.

(Containing C, H, and S or C, H, O, S, and N.)

	Melting-point.	Boiling-point.		Melting-point.	Boiling-point.
Sulphides—			*Thiocyanates*—		
Allyl sulphide . .	—	140	Allyl thiocyanate .	—	151
Benzyl ,, . .	49	—	Phenyl ,, (p. 160)	—	222
Sulphonic Acids—			*Thioamides*—		
Sulphobenzoic acid	decomp.	—	Thiocarbamide (p. 128)	175	—
Sulphanilic acid (p. 175)	,,	—	Thiocarbanilide (p. 159)	151	—
Naphthionic acid .	,,	—	*Sulphonamides*—		
β-Naphthylamine sulphonic acid .	,,	—	Benzenesulphonamide (p. 179)	150	—
β-Naphthylamine disulphonic acid .	,,	—	Benzenesulphonanilide (p. 179) . .	110	—
R acid . .	,,	—			
G ,, . .	,,	—			
Sulphates—					
Methyl sulphate	—	187			
Ethyl ,, .	—	208			

Mixtures.—A preliminary investigation carried out as described on p. 322 will determine roughly if the substance is a mixture. Before proceeding to identify the substances present, it is essential that they should first be separated. This may be a long and difficult operation, but the following methods may lead to the desired result.

If the substance cannot be satisfactorily separated by fractional distillation (if a liquid) or by crystallisation (if a solid), shake with caustic soda solution. This will dissolve the acid or phenol, and the insoluble constituent may be removed mechanically or, if volatile, by distillation in steam, by extraction with ether or, if solid, by filtration.

Acid and *Phenol*, if present together, may be separated by adding sodium bicarbonate in excess and extracting with ether, or by dissolving in caustic soda solution, saturating with carbon dioxide and then extracting with ether. The ether extracts the phenol, which is insoluble in sodium carbonate, leaving the acid.

Ester and *Hydrocarbon* may be separated by hydrolysis, which decomposes the ester, but not the hydrocarbon.

Paraffin and *Aromatic Hydrocarbon* may be separated by the action of fuming sulphuric acid, which forms the sulphonic acid with the aromatic hydrocarbon. The product is poured into water. The sulphonic acid dissolves readily in water, whereas the paraffin is insoluble.

Amine or *Base* may be separated from the majority of insoluble organic substances by shaking it with dilute hydrochloric acid, with which it forms the soluble hydrochloride.

Aldehyde or *Ketone* may be separated from the other constituents by shaking the liquid, which should be free from water, with a saturated solution of sodium bisulphite, and decanting or filtering the liquid residue. If the liquid is soluble in water, like ethyl alcohol, it may precipitate the bisulphite of sodium. This is prevented by adding a little ether before introducing the bisulphite into the liquid.

In separating two liquids in a test-tube, for example, an ethereal from an aqueous solution, either the ether may be decanted or it may be desirable to withdraw the lower aqueous layer. This is done by sucking the liquid into a small pipette furnished with a mouth-piece of rubber tubing, which may be nipped when the requisite quantity is removed. The pipette is then withdrawn, keeping the rubber tube tightly closed, and the liquid transferred to another test-tube. It is often advisable to adopt this method previous to decanting the top layer, which is much more effectively separated from a small than from a large quantity of the aqueous layer.

I.—TABLE OF THE ATOMIC WEIGHTS OF THE ELEMENTS.

O = 16.

Element.	Symbol.	Atomic Weight.	Element.	Symbol.	Atomic Weight.
Aluminium	Al.	27·1	Neon	Ne.	20
Antimony	Sb.	120·2	Nickel	Ni.	58·7
Argon	Ar.	39·9	Niobium	Nb.	94
Arsenic	As.	75	Nitrogen	N.	14·01
Barium	Ba.	137·4	Osmium	Os.	191
Beryllium	Be.	9·1	Oxygen	O.	16
Bismuth	Bi.	208	Palladium	Pd.	106·5
Boron	B.	11	Phosphorus	P.	31
Bromine	Br.	79·96	Platinum	Pt.	194·8
Cadmium	Cd.	112·4	Potassium	K.	39·15
Caesium	Cs.	133	Radium	Ra.	225
Calcium	Ca.	40·1	Rhodium	Rh.	103
Carbon	C.	12	Rubidium	Rb.	85·5
Cerium	Ce.	140·25	Ruthenium	Ru.	101·7
Chlorine	Cl.	35·45	Scandium	Sc.	44·1
Chromium	Cr.	52·1	Selenium	Se.	79·2
Cobalt	Co.	59	Silicon	Si.	28·4
Copper	Cu.	63·6	Silver	Ag.	107·93
Fluorine	F.	19	Sodium	Na.	23·05
Gallium	G.	70	Strontium	Sr.	87·6
Germanium	Ge.	72·5	Sulphur	S.	32·06
Gold	Au.	197·2	Tantalum	Ta.	181
Helium	He.	4·0	Tellurium	Te.	127·6
Hydrogen	H.	1·008	Thallium	Tl.	204·1
Indium	In.	115	Thorium	Th.	232·5
Iodine	I.	126·97	Tin	Sn.	119
Iridium	Ir.	193	Titanium	Ti.	48·1
Iron	Fe.	55·9	Tungsten	W.	184
Lanthanum	La.	138·9	Uranium	U.	238·5
Lead	Pb.	206·9	Vanadium	V.	51·2
Krypton	Kr.	81·8	Xenon	X.	128
Lithium	Li.	7·03	Ytterbium	Yb.	173
Magnesium	Mg.	24·36	Yttrium	Y.	89
Manganese	Mn.	55	Zinc	Zn.	65·4
Mercury	Hg.	200	Zirconium	Zr.	90·6
Molybdenum	Mo.	96			

VAPOUR TENSION OF WATER FROM 5° TO 20°.

t	Tension.	*t*	Tension.	*t*	Tension.	*t*	Tension.
5·0	6·507	9·0	8·548	13·0	11·137	17·0	14·395
·1	·552	·1	·606	·1	·210	·1	·486
·2	·597	·2	·664	·2	·283	·2	·578
·3	·643	·3	·722	·3	·356	·3	·670
·4	·689	·4	·781	·4	·430	·4	·763
·5	·736	·5	·840	·5	·505	·5	·856
·6	·782	·6	·899	·6	·580	·6	·950
·7	·829	·7	·959	·7	·655	·7	15·044
·8	·876	·8	9·019	·8	·731	·8	·139
·9	·924	·9	·079	·9	·807	·9	·234
6·0	·971	10·0	140	14·0	·884	18·0	·330
·1	7·020	·1	·201	·1	·960	·1	·427
·2	·068	·2	·262	·2	12·038	·2	·524
·3	·117	·3	·324	·3	·116	·3	·621
·4	·166	·4	·386	4	·194	·4	·719
·5	·215	·5	·449	·5	·273	·5	·818
·6	·265	·6	·512	·6	·352	·6	·917
·7	·314	·7	·575	·7	·432	·7	16·017
·8	·365	·8	·639	·8	·512	·8	·117
·9	·415	·9	·703	·9	·593	·9	·218
7·0	·466	11·0	·767	15·0	·674	19·0	·319
·1	·517	·1	·832	·1	·755	·1	·421
·2	·568	·2	·897	·2	·837	·2	·523
·3	·620	·3	·962	·3	·920	·3	·626
·4	·672	·4	10·028	·4	13·003	·4	·730
·5	·725	·5	·095	·5	·086	·5	·834
·6	·777	·6	·161	·6	·170	·6	·939
·7	·830	·7	·228	·7	·254	·7	17·044
·8	·883	·8	·296	·8	·339	·8	·150
·9	·937	·9	·364	·9	·424	·9	·256
8·0	·991	12·0	·432	16·0	·510	20·0	·363
·1	8 045	·1	·501	·1	·596	·1	·471
·2	·100	·2	·570	·2	·683	·2	·579
·3	·155	·3	·639	·3	·770	·3	·688
·4	·210	·4	·709	·4	·858	·4	·797
·5	·266	·5	·780	·5	·946	·5	·907
·6	·321	·6	·850	·6	14·035	·6	18·018
·7	·378	·7	·921	·7	·124	·7	·129
·8	·434	·8	·993	·8	·214	·8	·241
·9	491	·9	11·065	·9	·304	·9	353

VAPOUR TENSION OF CAUSTIC POTASH SOLUTIONS FROM 10°—20°.

t	$30KOH.$ $100H_2O.$	$40KOH.$ $100H_2O.$	$49KOH.$ $100H_2O.$
10·0	7·31	6·50	5·62
10·5	7·56	6·72	5·81
11·0	7·82	6·95	6·01
11·7	8·19	7·28	6·29
12·1	8·41	7·47	6·46
12·5	8·63	7·67	6·63
13·0	8·92	7·93	6·86
13·5	9·22	8·19	7·00
13·95	9·49	8·44	7·30
14·5	9·83	8·74	7·56
15·15	10·25	9·11	7·88
15·30	10·35	9·20	7·96
16·0	10·82	9·62	8·33
16·35	11·07	9·85	8·53
17·0	11·54	10·26	8·88
17·5	11·91	10·59	9·17
18·0	12·29	10·93	9·47
18·5	12·69	11·29	9·78
19·0	13·09	11·65	10·09
19·4	13·41	11·93	10·33
20 0	13·93	12·40	10·75
20·25	14·15	12·59	10·91

II.—TABLE OF SPECIFIC GRAVITY AND PERCENTAGE OF SULPHURIC ACID IN AQUEOUS SOLUTION. (Kolbe.)

Sp. gr. at 15° *compared with water at* 0° = 1.

Degrees Beaumé.	Sp. gr. $d = 15/0$.	100 parts by weight contain H_2SO_4.	Degrees Beaumé.	Sp. gr. $d = 15/0$.	100 parts by weight contain H_2SO_4.
1	1·007	1·9	34	1·308	40·2
2	1·014	2·8	35	1·320	41·6
3	1·022	3·8	36	1·332	43
4	1·029	4·8	37	1·345	44·4
5	1·037	5·8	38	1·357	45·6
6	1·045	6·8	39	1·370	46·9
7	1·052	7·8	40	1·383	48·3
8	1·060	8·8	41	1·397	49·8
9	1·067	9·8	42	1·410	51·2
10	1·075	10·8	43	1·424	52·6
11	1·083	11·9	44	1·438	54·0
12	1·091	13	45	1·453	55·4
13	1·100	14·1	46	1·468	56·9
14	1·108	15·2	47	1·483	58·3
15	1·116	16·2	48	1·498	59·6
16	1·125	17·3	49	1·514	61
17	1·134	18·5	50	1·530	62·5
18	1·142	19·6	51	1·540	64
19	1·152	20·8	52	1·563	65·5
20	1·162	22·1	53	1·580	67
21	1·171	23·3	54	1·597	68·6
22	1·180	24·5	55	1·615	70
23	1·190	25·8	56	1·634	71·6
24	1·200	27·1	57	1·652	73·2
25	1·210	28·4	58	1·671	74·7
26	1·220	29·6	59	1·691	76·4
27	1·231	30·9	60	1·711	78·1
28	1·241	32·2	61	1·732	79·9
29	1·252	33·4	62	1·753	81·7
30	1·263	34·7	63	1·774	84·1
31	1·274	36	64	1·796	86·5
32	1·285	37·4	65	1·81	89·7
33	1·297	38·8	66	1·842	100

II.—Table of Specific Gravity and Percentage of H_2SO_4 in Concentrated Sulphuric Acid. (Lunge and Naef.)

Sp. gr. at 15° compared with water at 4° = 1.

Per cent. H_2SO_4.	Sp. gr. $d = 15/4$.	Per cent. H_2SO_4.	Sp. gr. $d = 15/4$
90	1·3185	96	1·8406
91	1·8241	97	1·8410
92	1·8294	98	1·8412
93	1·8339	99	1·8403
94	1·8372	100	1·8384
95	1·8390		

IV.—Table of Specific Gravity and Percentage of Nitric Acid in Aqueous Solution. (Kolbe.)

Sp. gr. at 15° compared with water at 0° = 1.

Sp. gr. at 15°.	Percentage HNO_3.	Sp. gr. at 15°.	Percentage HNO_3.	Sp. gr. at 15°.	Percentage HNO_3.	Sp. gr. at 15°.	Percentage HNO_3.
1·530	100	1·451	77·6	1·363	58	1·237	37·95
1·529	99·5	1·445	76	1·358	57	1·225	36
1·523	97·9	1·442	75	1·353	56·1	1·218	35
1·516	96	1·438	74	1·346	55	1·211	33·8
1·514	95·2	1·435	73	1·341	54	1·198	32
1·509	94	1·432	72·4	1·339	53·8	1·102	31
1·506	93	1·429	71·2	1·335	53	1·185	30
1·503	92	1·423	69·9	1·331	52·3	1·179	29
1·499	91	1·419	69·2	1·323	51	1·172	28
1·495	90	1·414	68	1·317	49·9	1·166	27
1·494	89·5	1·410	67	1·312	49	1·157	25·7
1·488	88	1·405	66	1·304	48	1·138	23
1·486	87·4	1·400	65	1·298	47·1	1·120	20
1·482	86·1	1·395	64	1·295	46·6	1·105	17·4
1·478	85	1·393	63·6	1·284	45	1·089	15
1·474	84	1·386	62	1·274	43·5	1·077	13
1·470	83	1·381	61·2	1·264	42	1·067	11·4
1·467	82	1·374	60	1·257	41	1·045	7·2
1·463	80·9	1·372	59·6	1·251	40	1·022	4
1·460	80	1·368	58·8	1·244	39	1·010	2
1·456	79						

V.—TABLE OF SPECIFIC GRAVITY AND PERCENTAGE OF HYDROCHLORIC ACID IN AQUEOUS SOLUTION.

Sp. gr. at 15°.	Percentage HCl.	Sp. gr. at 15°.	Percentage HCl.	Sp. gr. at 15°.	Percentage HCl.	Sp. gr. at 15°.	Percentage HCl.
1·007	1·5	1·055	11·0	1·116	23·1	1·175	34·7
1·010	2·2	1·060	12	1·125	24·8	1·180	35·7
1·014	2·9	1·067	13·4	1·134	26·6	1·185	36·8
1·019	3·8	1·075	15	1·143	28·4	1·190	37·9
1·022	4·5	1·083	16·5	1·150	29·7	1·194	38·6
1·029	5·8	1·091	18·1	1·152	30·2	1·199	39·8
1·031	6·2	1·094	18.6	1·159	31·5	1·202	40·5
1·036	7·3	1·100	19·9	1·161	32	1·205	41·2
1·044	8·9	1·105	20·9	1·166	33	1·210	42·4
1·052	10·4	1·108	21·5	1·171	33·9	1·212	43

VI.—TABLE OF SPECIFIC GRAVITY AND PERCENTAGE OF CAUSTIC POTASH IN AQUEOUS SOLUTION.

Sp. gr. at 15°.	Percentage of KOH.	Sp. gr. at 15°.	Percentage of KOH.	Sp. gr. at 15°.	Percentage of KOH.	Sp. gr. at 15°.	Percentage of KOH.
1·009	1	1·166	19	1·374	37	1·590	54
1·017	2	1·177	20	1·387	38	1·604	55
1·025	3	1·188	21	1·400	39	1·618	56
1·033	4	1·198	22	1·412	40	1·630	57
1·041	5	1·209	23	1·425	41	1·642	58
1·049	6	1·220	24	1·438	42	1·655	59
1·058	7	1·230	25	1·450	43	1·667	60
1·065	8	1·241	26	1·462	44	1·681	61
1·074	9	1·252	27	1·475	45	1·695	62
1·083	10	1·264	28	1·488	46	1·705	63
1·092	11	1·276	29	1·499	47	1·718	64
1·101	12	1·288	30	1·511	48	1·729	65
1·110	13	1·300	31	1·525	49	1·740	66
1·119	14	1·311	32	1·539	50	1·754	67
1·128	15	1·324	33	1·552	51	1·768	68
1·137	16	1·336	34	1·565	52	1·780	69
1·146	17	1·349	35	1·578	53	1·790	70
1·155	18	1·361	36				

VII.—TABLE OF SPECIFIC GRAVITY AND PERCENTAGE OF CAUSTIC SODA IN AQUEOUS SOLUTION.

Sp. gr. at 15°.	Percentage of NaOH.	Sp. gr. at 15°.	Percentage of NaOH.	Sp. gr. at 15°.	Percentage of NaOH.	Sp. gr. at 15°.	Percentage of NaOH.
1 012	1	1·213	19	1·405	37	1·580	54
1·023	2	1·225	20	1·415	38	1·591	55
1·035	3	1·236	21	1·426	39	1·601	56
1·048	4	1·247	22	1·437	40	1·611	57
1·058	5	1·258	23	1·447	41	1·622	58
1·070	6	1·269	24	1·457	42	1·633	59
1·081	7	1·279	25	1·468	43	1·643	60
1·092	8	1·290	26	1·478	44	1·654	61
1·103	9	1·300	27	1·488	45	1·666	62
1·115	10	1·310	28	1·499	46	1·674	63
1·126	11	1·321	29	1·509	47	1·684	64
1·137	12	1·332	30	1·519	48	1·695	65
1·148	13	1·343	31	1·529	49	1·705	66
1·159	14	1·353	32	1·540	50	1·715	67
1·170	15	1·363	33	1·550	51	1·726	68
1·181	16	1·374	34	1·560	52	1·737	69
1·192	17	1·384	35	1·570	53	1·748	70
1·202	18	1·395	36				

VIII.—TABLE OF SPECIFIC GRAVITY AND PERCENTAGE OF AMMONIA IN AQUEOUS SOLUTION.

Sp. gr. at 14° *compared with water at* 14° = 1.

Sp. gr.	Percentage of NH_3.	Sp. gr.	Percentage of NH_3.	Sp. gr.	Percentage of NH_3.	Sp. gr.	Percentage of NH_3.
·884	36	·905	27	·931	18	·963	9
·886	35	·907	26	·934	17	·967	8
·888	34	·910	25	·938	16	·970	7
·890	33	·913	24	·941	15	·974	6
·892	32	·916	23	·944	14	·979	5
·895	31	·919	22	·948	13	·983	4
·897	30	·922	21	·952	12	·987	3
·900	29	925	20	·955	11	·991	2
·902	28	·928	19	·959	10	·995	1

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