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Electrophilic Aromatic Substitution Reactions

Part-1

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Learning outcome

After studying this lecture, you shall be able to:

- ❖ Explain electrophilic aromatic substitution reactions
- ❖ Types of electrophilic aromatic substitution reactions
- ❖ Mechanism of Nitration, Sulphonation

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❖ ELECTROPHILIC SUBSTITUTION REACTION

When a substitution reaction involves the attack by an electrophile, the reaction is referred to as electrophilic reaction. For example: the bromination of benzene in the presence of FeBr_3 or AlCl_3 .

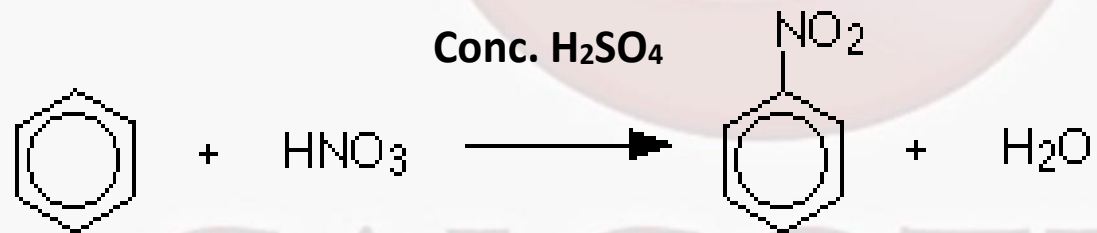


There are various reactions which undergo electrophilic substitution reaction. Such as-

- (i) Nitration
- (ii) Sulphonation
- (iii) Halogenation
- (iv) Friedel Crafts reaction

(I) NITRATION

Benzene is converted into nitrobenzene by its treatment with conc. nitric acid in the presence of conc. sulfuric acid as catalyst.



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MECHANISM

STEP- I

Formation of the electrophile

The electrophile is the "nitronium ion" or the "nitryl cation", NO_2^+ . This is formed by reaction between the nitric acid and the sulphuric acid.



Nitronium ion

STEP- II

Attack of electrophile (nitronium ion) on benzene

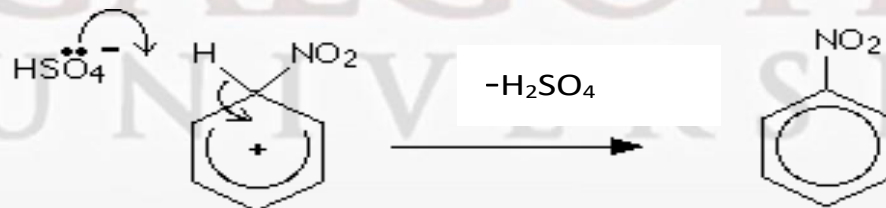
Nitronium ion attacked on benzene ring and forms an intermediate known as arenium ion or Benzenonium ion (resonance stabilized). This is the rate determining (slow step) step of the reaction.



STEP- III

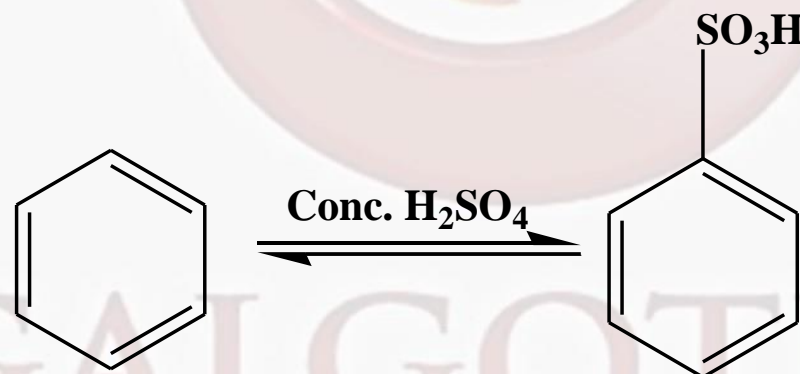
Formation of product (Nitrobenzene)

The intermediate (arenium ion) undergoes loss of proton with simultaneous formation of product.



(ii) SULPHONATION

The reaction of benzene with fuming sulfuric acid or oleum ($\text{H}_2\text{S}_2\text{O}_7$ or mixture of H_2SO_4 & SO_3) leads to the formation of benzene sulphonic acid.



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MECHANISM

STEP -I

Formation of the electrophile

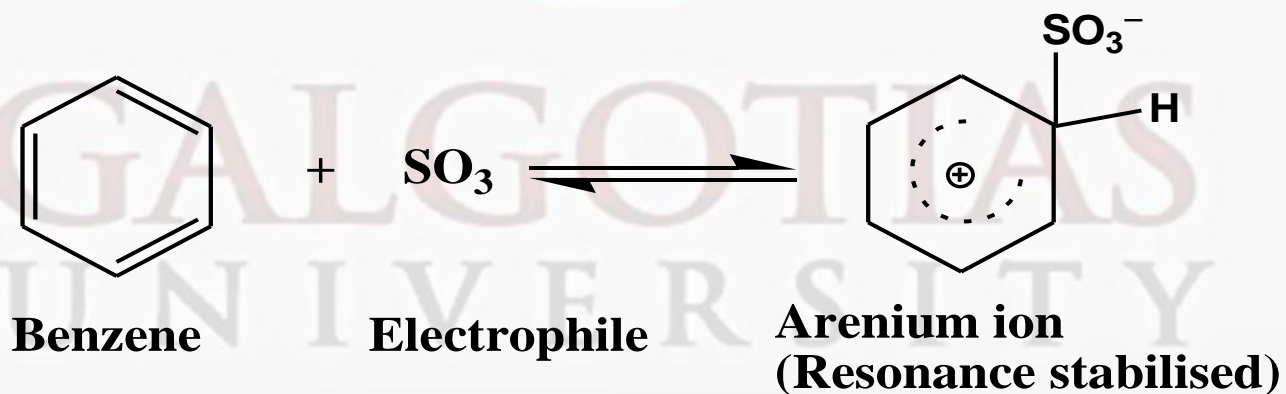
The active electrophile SO_3 is present in Conc. H_2SO_4 and may be formed as follows



STEP -II

Attack of electrophile on benzene

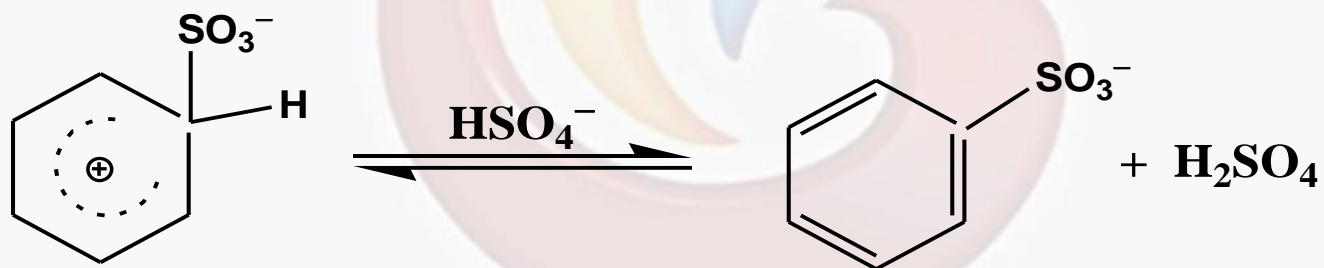
The electrophile SO_3 attacks on benzene to give resonance stabilized Arenium ion.



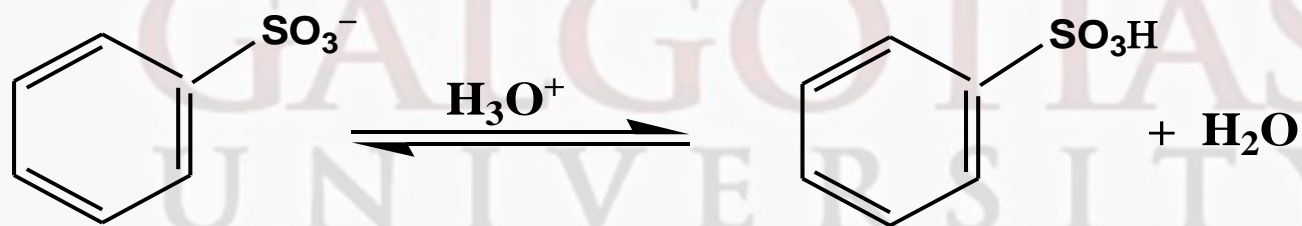
STEP III

Formation of product

The intermediate (arenium ion) undergoes loss of proton with simultaneous formation of product.



**Arenium ion
(Resonance stabilised)**



MECHANISM

STEP -I

Formation of the electrophile

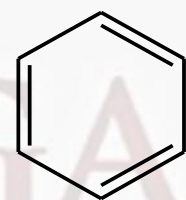
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STEP -II

Attack of electrophile on benzene

The electrophile SO_3 attacks on benzene to give resonance stabilized Arenium ion.

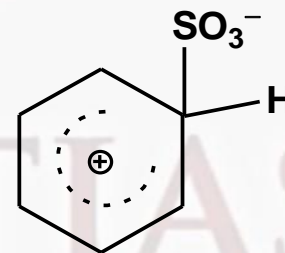
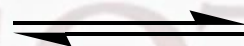


Benzene

+



Electrophile



**Arenium ion
(Resonance stabilised)**

References

1. Morrison, R. N. & Boyd, R. N. *Organic Chemistry*, Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
1. Finar, I. L. *Organic Chemistry (Volume 1)*, Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
2. Finar, I. L. *Organic Chemistry (Volume 2: Stereochemistry and the Chemistry of Natural Products)*, Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
3. Eliel, E. L. & Wilen, S. H. *Stereochemistry of Organic Compounds*, Wiley: London, 1994.
4. Kalsi, P. S. *Stereochemistry Conformation and Mechanism*, New Age International, 2005.
5. McMurry, J.E. *Fundamentals of Organic Chemistry*, 7th Ed. Cengage Learning India Edition, 2013.

School of Basic and Applied Sciences

Course Code : BSCC2001

Course Name: Organic Chemistry I

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Thank You

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