Electrophilic Aromatic Substitution Reactions Part-2

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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 Halogenation, Friedel-Craft's alkylation/acylation

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Electrophilic aromatic substitution

An atom appended to the aromatic ring, usually hydrogen, is replaced by an electrophile.

Type

- Nitration
- Halogenation
- Sulfonation
- Acylation and alkylating *Friedel-Crafts reactions.*

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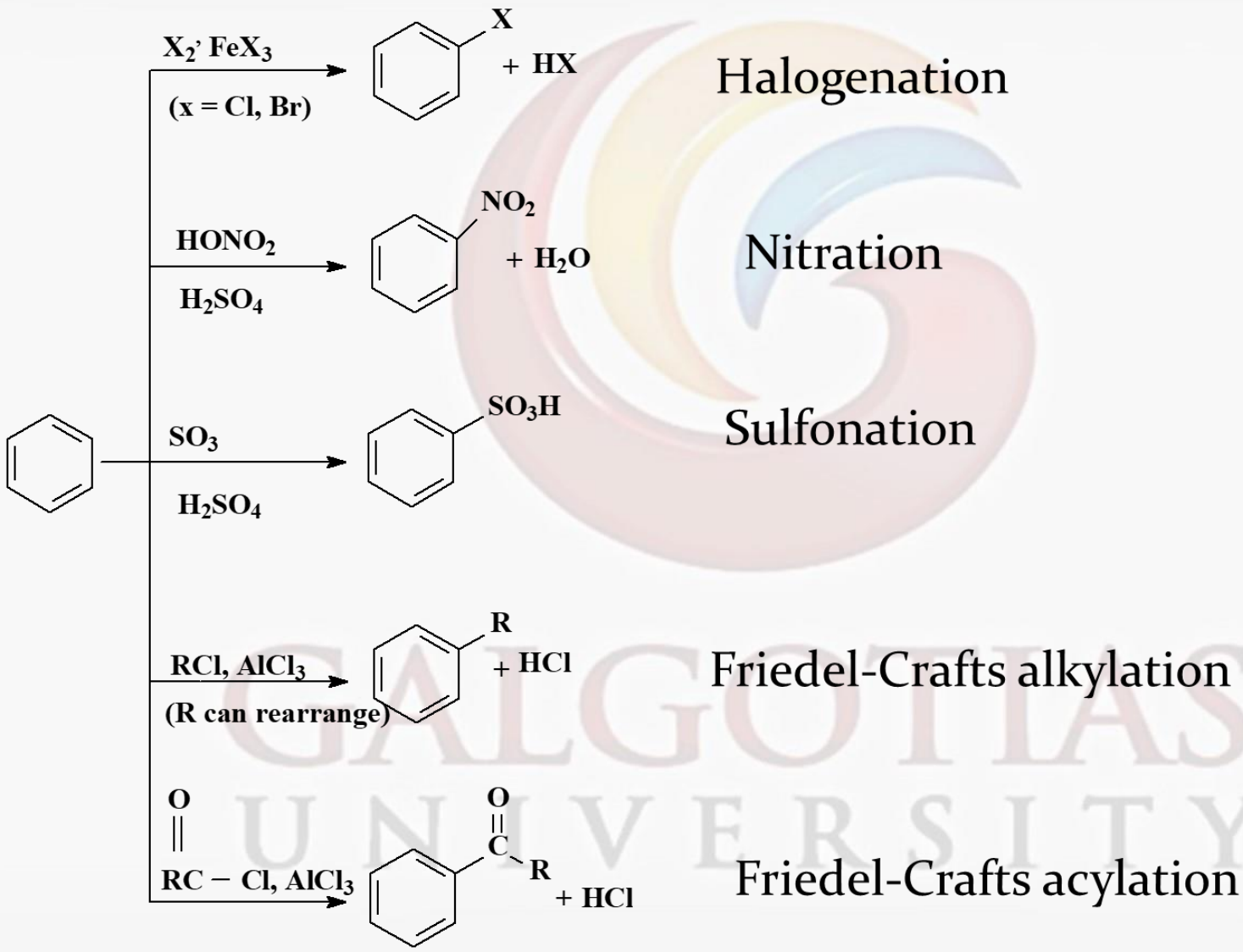
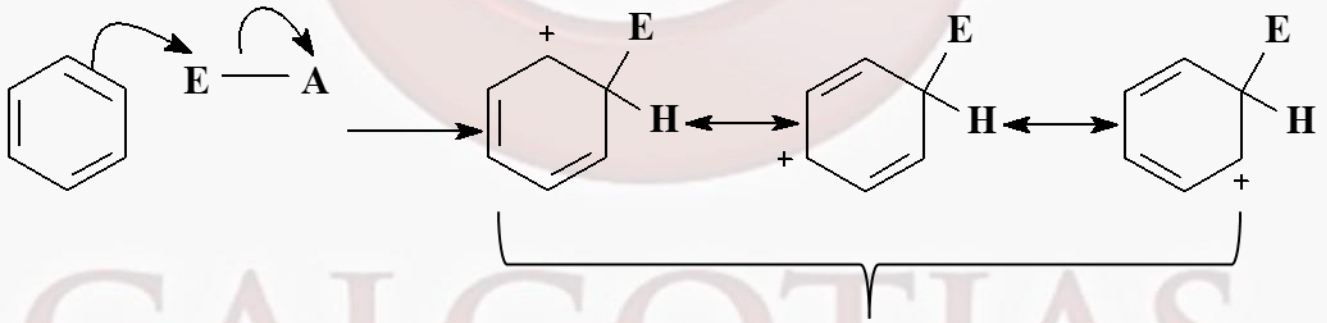

X2, FeX3
(x = Cl, Br)
X
+ HX
Halogenation
HONO2
H2SO4
NO2
+ H2O
Nitration
SO3
H2SO4
SO3H
Sulfonation
RCl, AlCl3
(R can rearrange)
R
+ HCl
Friedel-Crafts alkylation
O
RC − Cl, AlCl3
O
C
R
+ HCl
Friedel-Crafts acylation

Mechaniism of EAS: arenium ions

Step 1



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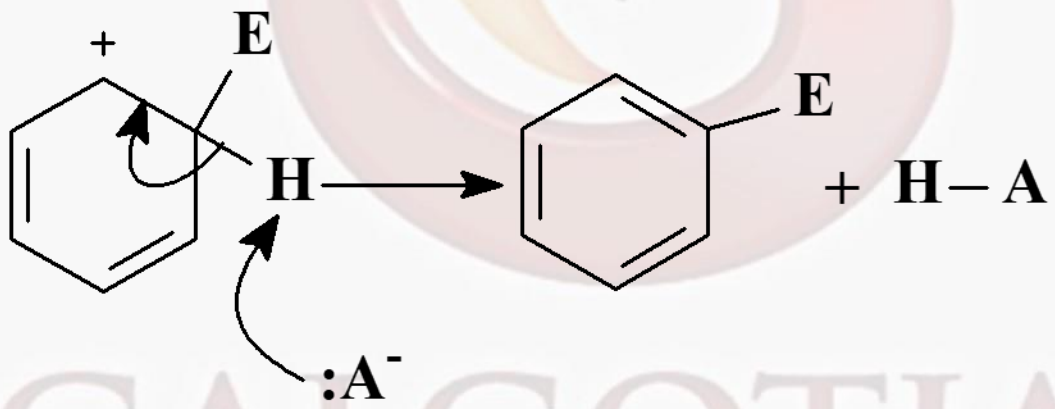
Mechaniism of EAS: arenium ions

Step 2



The proton is removed by any of the bases, for example by the anion derived from the electrophile

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Halogenation of benzene

- Benzene does not react with Br_2 or CL_2 unless a Lewis acid is present in mixture
- Lewis acid is an electron-pair acceptor
- Lewis acids most commonly used to effect bromination and chlorination reactions are $FeCl_3$, $FeBr_3$ and $AlCl_3$

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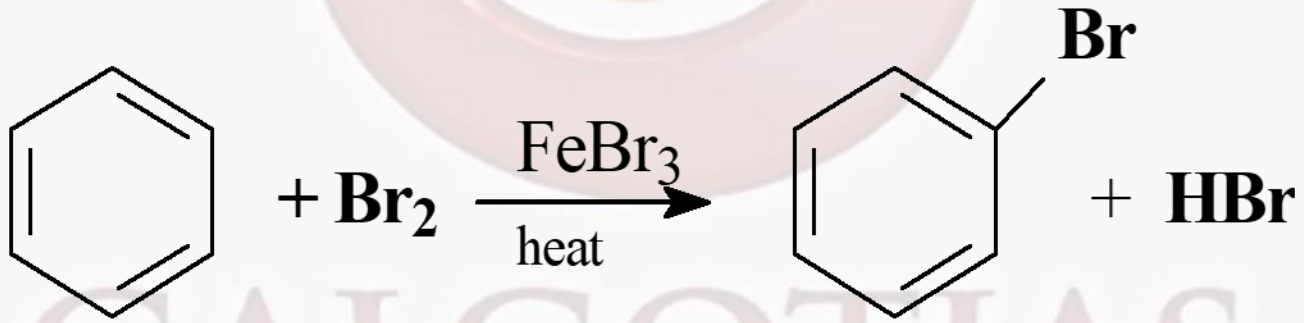
Bromination of benzene



Bromobenzene (75%)

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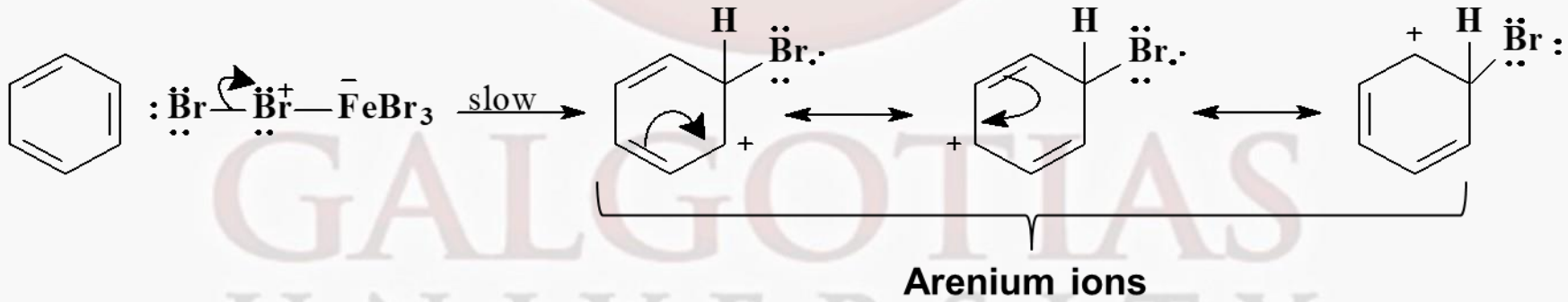
Electrophilic Aromatic Bromination

Step 1

Bromine combines with FeBr3 to form acomplex that dissocates to form apostive bromine ion and FeBr4-

Step 2



Positive bromine ion is attacked by benzene to form an arenium ion

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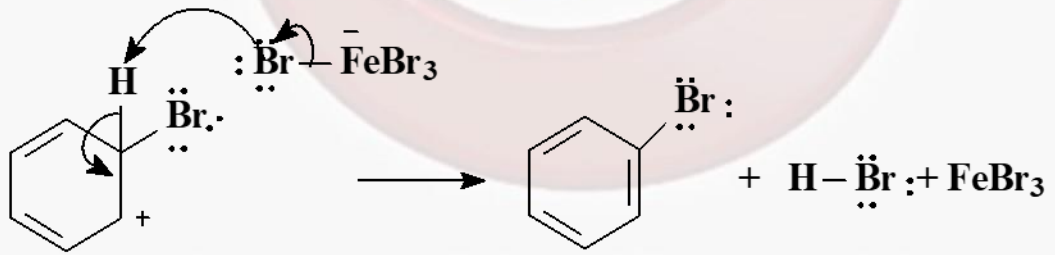
Electrophilic Aromatic Bromination

Step 3



Proton is removed from the arenium ion to become bromobenzene

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FRIDEL CRAFT REACTIONS

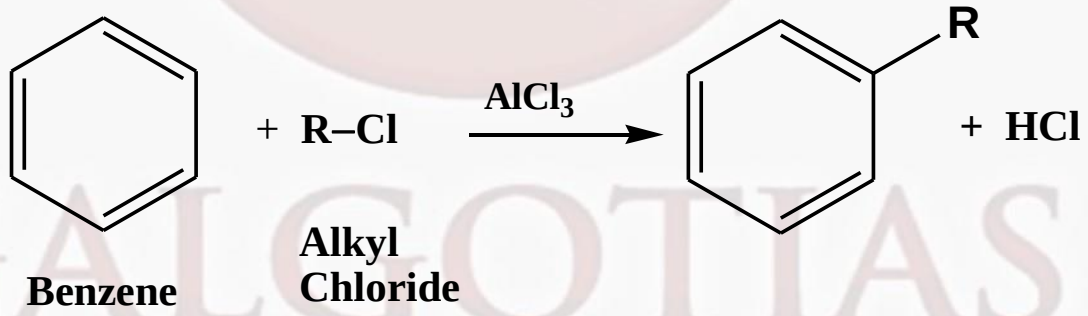
These are of two types-

(a) Fridel Craft Alkylation Reaction

(b) Fridel Craft Acylation Reaction

(a) FRIDEL CRAFTS ALKYLATION REACTION

The reaction of benzene with alkyl bromides or chlorides in the presence of a Lewis acid catalyst (such as $FeCl_3$ or $AlCl_3$) leads to the formation of alkyl benzenes.



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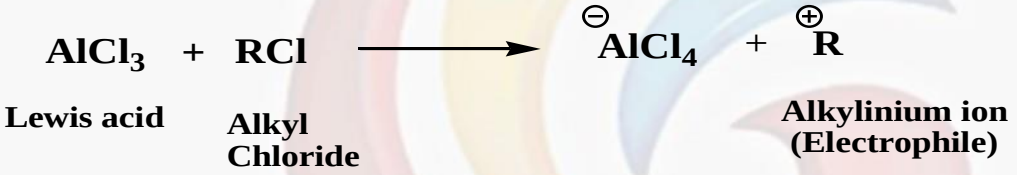
MECHANISM

STEP I

Generation of electrophile (Alkyl carbocation ion)

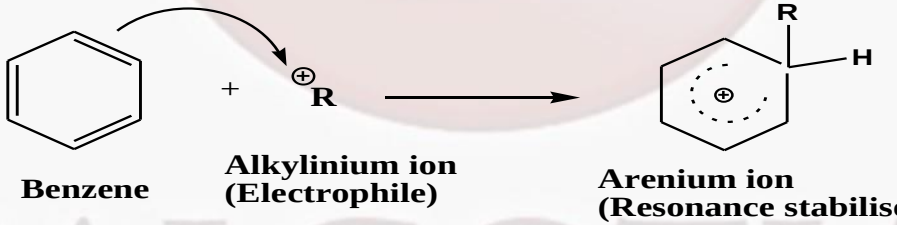
The Lewis acid enhances the electrophilic character on carbon of alkyl group to facilitate formation of electrophile.



STEP II

Attack of Alkylium ion (electrophile) on benzene

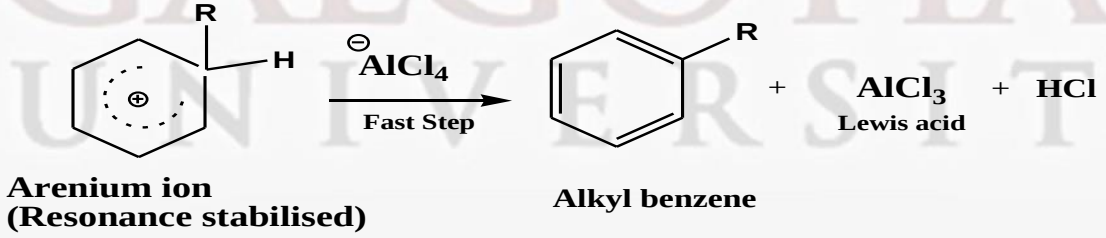
This is the rate determining step of the reaction; and arenium ion is formed as intermediate.



STEP III

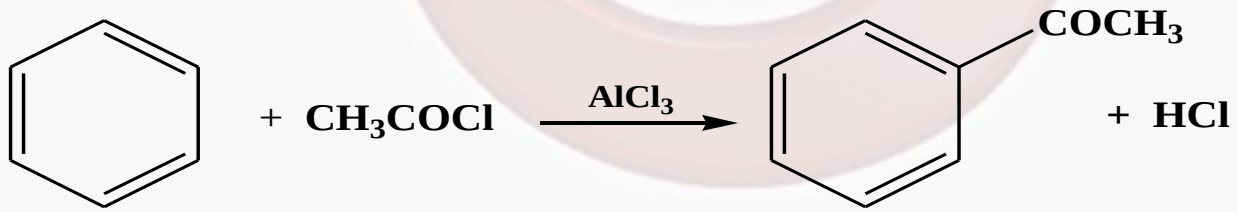
Formation of product (Alkylbenzene)

Alkylbenzene is formed by the loss of proton from intermediate (Arenium ion)



(b) **FRIDEL CRAFTS ACYLATION REACTION**

The reaction of benzene with acyl halide or acid anhydride in the presence of a Lewis acid catalyst (such as $FeCl_3$ or $AlCl_3$) results in the introduction of an acyl group (RCO^-) in the benzene ring and formation of an arylketone as product.



Benzene **Acetyl Chloride** **Acetophenone**

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MECHANISM

STEP I

Generation of electrophile (Acylium ion)

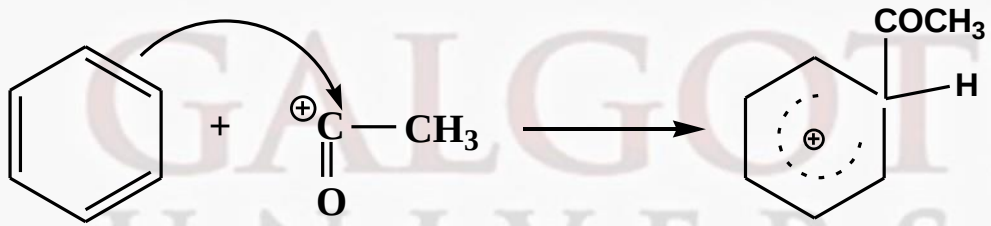
The Lewis acid forms a complex with acid chloride which dissociates further to generate acylium ion (electrophile).

Lewis acid **Acetyl Chloride** **Acyliumion (Electrophile)**

STEP II

Attack of Acylium ion (electrophile) on benzene

This is the rate determining step of the reaction; and arenium ion is formed as intermediate



Benzene **Arenium ion (Resonance stabilised)**

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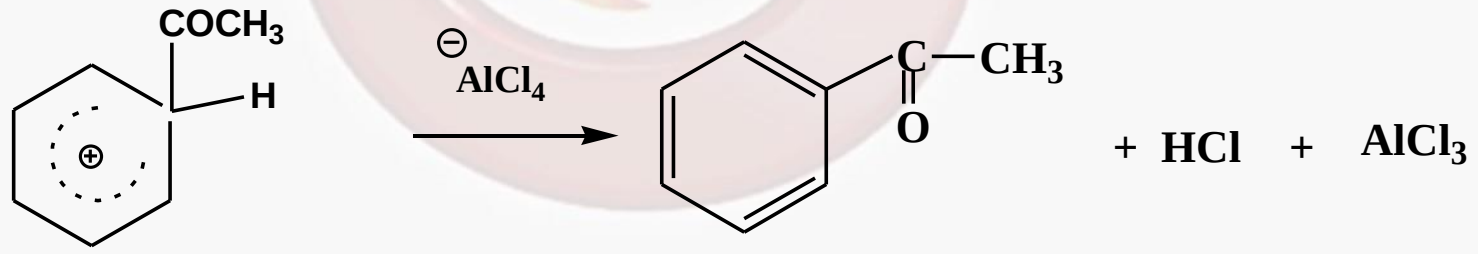
STEP III

Formation of product (Acetophenone)

Acyllbenzene (Acetophenone) is formed by the loss of proton from intermediate (Arenium ion)



Arenium ion
(Resonance stabilised)

Acetophenone

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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).
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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.
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Thank You

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