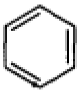
UNIT-IV:BENZENE AND ITS REACTIVITY(9 Hrs.)

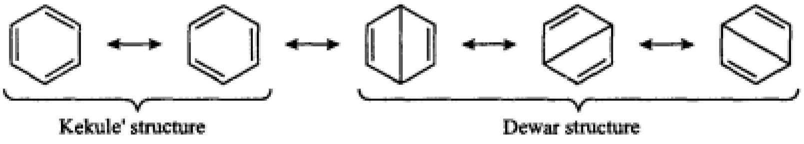
Structure of Benzene – Preparation - polymerization of acetylene and decarboxylation- Properties - mechanism of electrophilic aromatic substitution of Friedel- Craft's alkylation and acylation. halogenation and nitration.

Structure of Benzene: Bonding and Resonance

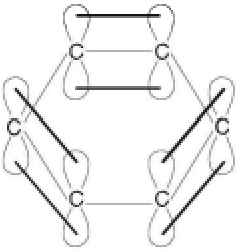
Benzene: C_6H_6, planar hexagonal ring.



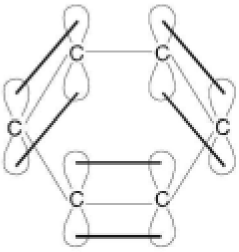
Real structure: resonance hybrid, delocalized π cloud above and below plane.



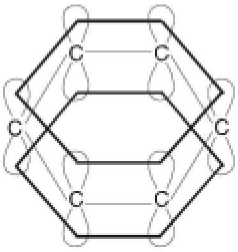
(a)



(b)

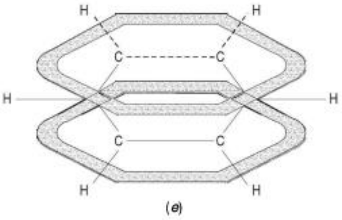


(c)

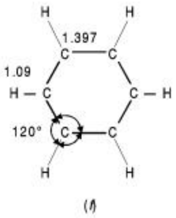


(d)

Orbital structure. Structure of benzene can be best described by using the orbital concept. Each carbon atom in benzene is sp^2 hybridized and thus forms three bonds, two with adjacent carbon atoms and one with hydrogen. Thus, all the six carbons and six hydrogen atoms lie in the same plane and the angle between two adjacent & bonds is 120° Each carbon is still left with an unhybridized p-orbitals lying above and below the plane of benzene ring. Each one of these p-orbitals overlap sideways on either sides to form two sets of π-electron clouds. [Figs. (b) and (c)]. π electrons are delocalized as these can move over all the six carbon atoms [Fig. (d)]. As a result of this delocalization two continuous ring like electron clouds one above and the other below the plane of carbon atoms [Fig. (e)] are formed. Bond angles and bond lengths in the molecule of benzene are depicted in [Fig. (/)].



(e)



(f)

Experimental Evidence:

Bond lengths: All C–C equal (1.39 Å) by X-ray diffraction.

Hydrogenation energies: Cyclohexatriene would release ~360 kJ/mol; benzene releases ~208 kJ/mol

→ resonance energy ~152 kJ/mol.

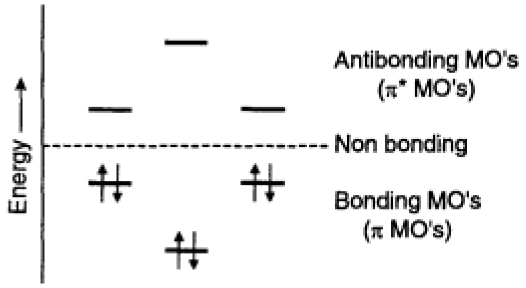
Spectroscopy: NMR shows ring current, equal deshielding.

Molecular Orbital Description:

6 p-orbitals overlap, forming 6 π MOs.

Energy levels: three bonding (π_1, π_2, π_3), three antibonding (π^*).

Filling: 6 π electrons fully occupy bonding orbitals.



Physical Properties

Non-polar liquid, bp = 80 °C, mp = 5.5 °C.

Insoluble in water, soluble in organic solvents.

Density: 0.88 g/cm^3.

Toxic, carcinogenic; handle with care.

Preparation of Benzene

1. From Acetylene (Polymerization)

$$C_2H_2 \xrightarrow{\text{[red hot Fe tube, 600 °C]}} C_6H_6$$

(acetylene)

Mechanism: trimerization via radical intermediates.

Formation of the First Radical

Acetylene molecules are activated by either high temperature, UV irradiation, or catalytic surfaces, resulting in the formation of a carbon-cantered acetylene radical

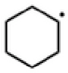
$CH{\equiv}CH \rightarrow \cdot C{\equiv}CH$

The acetylene radical reacts with another acetylene molecule to form a butadiyne-type radical intermediate $\cdot CH = C\text{-}C{\equiv}CH$

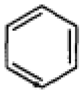
The butadiyne-type radical intermediate reacts with a third acetylene molecule to form a six-carbon linear radical

$CH{\equiv}CH + \cdot CH = C\text{-}C{\equiv}CH \rightarrow \cdot CH_2\text{-}CH = CH\text{-}CH{=}CH\text{-} CH_2 \cdot$

The six-carbon radical undergoes intramolecular radical cyclization, forming a cyclohexatriene radical intermediate



further The cyclohexatriene radical intermediate undergoes hydrogen shifts and electron rearrangement, resulting in aromatization and formation of the benzene ring

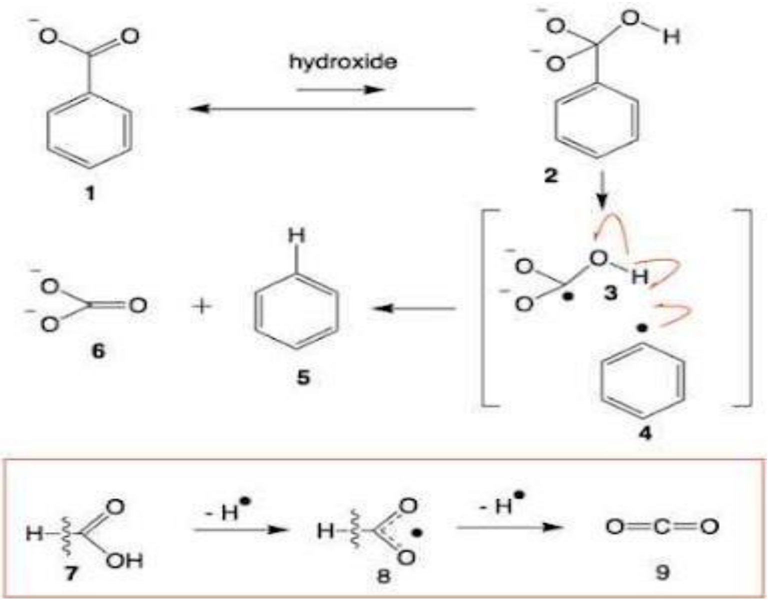


2. Decarboxylation of Benzoic Acid

   $C_6H_5COONa + NaOH \xrightarrow{[CaO, \Delta]} C_6H_6 + Na_2CO_3$

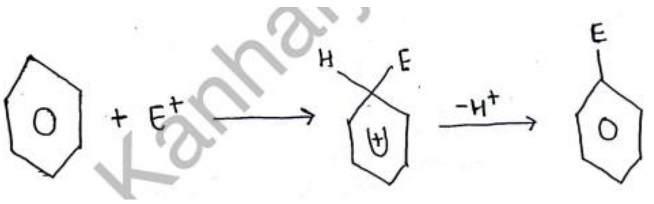
   Mechanism: carboxylate → carbanion → decarboxylation.

   addition of hydroxide to the carbonyl group of the benzoate anion 1 occurs to form adduct 2. Bond dissociation of 2 leads to phenyl radical 4 and radical 3

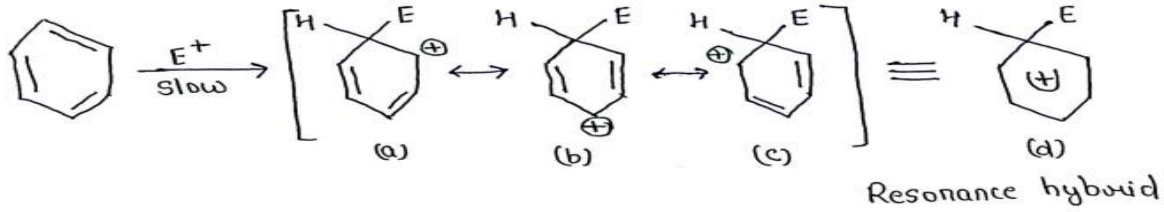


Electrophilic Substitution Mechanism:

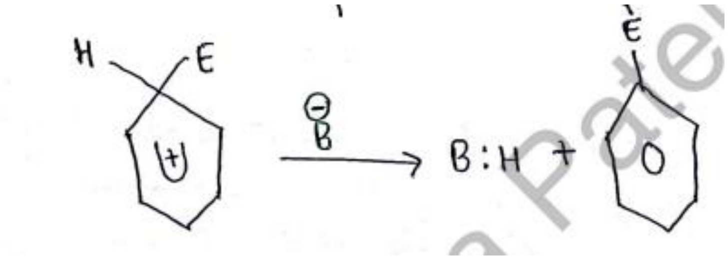
Electrophilic substitution is a type of replacement reaction where a hydrogen atom or any other radical attached to a benzene nucleus is replaced by an electrophilic reagent. The mechanism of all electrophilic substitution reactions is approximately the same. When an electrophilic reagent approaches a benzene ring, the equal distribution of electron density in the ring is disturbed. This disturbance leads to the formation of two centers: one with high electron density (δ-) and another with low electron density (δ+).The electrophile, being electron-deficient, links with the carbon atom that has high electron density (δ-), forming an intermediate compound. This intermediate compound then loses a proton (H+) in the presence of a base, resulting in the formation of a mono-substituted compound is formed. Electrophilic Substitution is a bimolecular (E2) reaction in which formation of intermediate Compound is a rate determining step



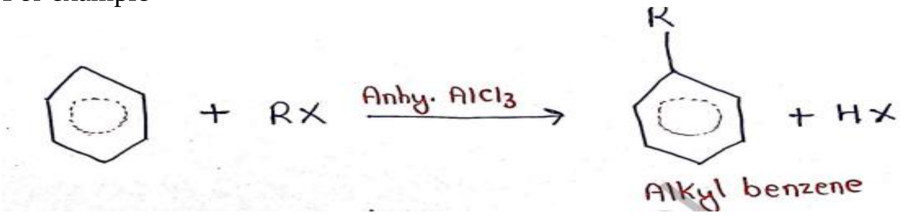
This reaction takes place in two steps :-
(i) In first step electrophilic reagent attacks any Carbon of benzene ring and forms intermediate Complex which is a resonance hybrid of a,b and c.



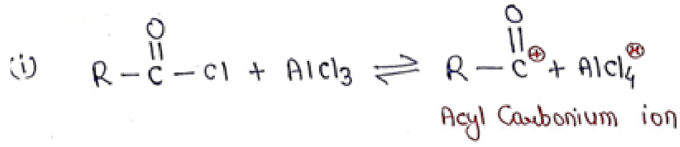
Out of 6π-electrons of benzene ring, 2π electrons are used in bond formation with electrophilic reagent and remaining 4π electrons are delocalized on 5 Carbon atoms. delocalized positive charge remains on all five Carbon atoms (d) and thus, intermediate Compound is formed.
And (ii) In Second step this intermediate Compound in presence of any base loses proton and change into benzenoid form a substitution product is formed



Friedel - Grafts alkylation:
In this reaction reacted with an aromatic hydrocarbon is an alkyl halide in the presence of anhydrous aluminum chloride.
For example



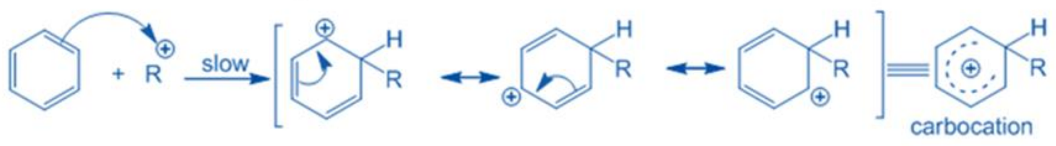
Mechanism:
The reaction begins with the generation of an electrophile, an alkyl carbocation. This occurs when the alkyl halide (R-Cl) reacts with a Lewis acid, such as anhydrous aluminum chloride ($AlCl_3$). The Lewis acid accepts the lone pair of electrons from the chlorine atom, forming a complex that facilitates the departure of the chloride ion, leaving behind a carbocation (R^+) and a tetra chloroaluminate anion ($AlCl_4^-$).



$$\text{(i)}\quad R-\overset{\overset{O}{\|}}{C}-Cl + AlCl_3 \rightleftharpoons R-\overset{\overset{O}{\|}}{C}{}^{\oplus} + AlCl_4^{\ominus}$$

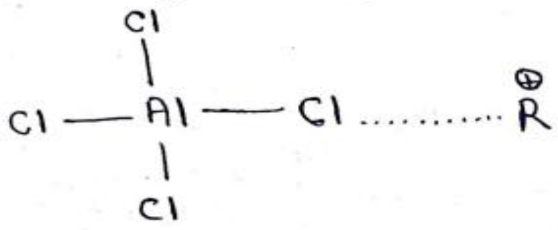
Acyl Carbonium ion

The generated carbocation (R+), acting as an electrophile, attacks the electron-rich aromatic ring. This step is typically the slow, rate-determining step of the reaction. The π electrons of the aromatic ring attack the carbocation, forming a new C-C bond and disrupting the aromaticity of the ring, leading to the formation of a resonance-stabilized carbocationic intermediate known as a sigma complex or arenium ion. This intermediate is stabilized by resonance, with the positive charge delocalized over the ring.



A proton is removed from the arenium ion, restoring the aromaticity of the ring and forming the alkylbenzene product, while also regenerating the Lewis acid catalyst.

It is also possible that the free alkyl Carbonium may not exist. Complexes of alkyl chloride and the aluminum chloride may be the actual attacking reagent.



Aluminium chloride - alkyl chloride Complex

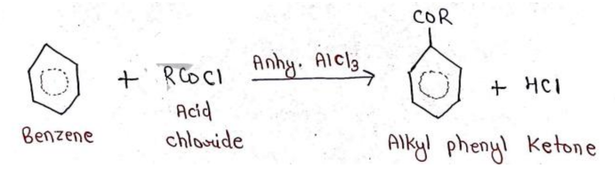
Limitation of Friedel Craft alkylation

- Vinyl and aryl halides do not generate stable carbocations. As a result, they are ineligible for use in the Friedel-Crafts alkylation procedure.
- Aromatic rings with deactivating groups may not be ideal for Friedel-Crafts alkylation because the deactivating groups remove the electron density from the benzene ring, making a nucleophilic attack on the benzene ring impossible.
- The aniline amine group interacts with anhydrous aluminum chloride to generate a compound that deactivates the ring. As a result, the response is incomplete.
- Alkylation occurs on the benzene ring when it combines with an alkyl halide in the presence of anhydrous Lewis acid, however, polyalkylation may occur due to the activating nature of the alkyl group. To avoid this problem, a considerable amount of aromatic samples must be taken.
- The Lewis acid catalyst $AlCl_3$ frequently binds with aryl amines, rendering them inactive.
- Isomerization and disproportionation can occur in the presence of excess catalysts and at high temperatures.

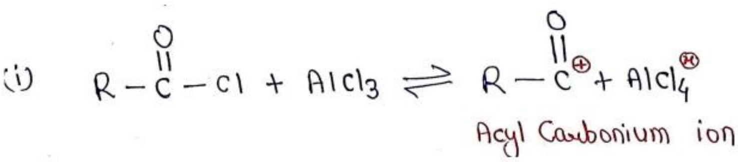
Friedel - Crafts Acylation :

In this reaction an aromatic hydrocarbon reacts with an acid halide or acid anhydride in the Presence of anhydrous aluminum chloride to form alkyl aryl ketone.

for example

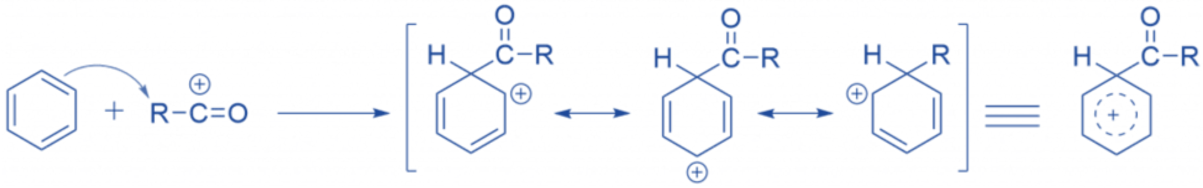


In this reaction, Lewis's acid $AlCl_3$ polarizes the acid chloride to form also Known electrophilic an acyl Carbonium ion.

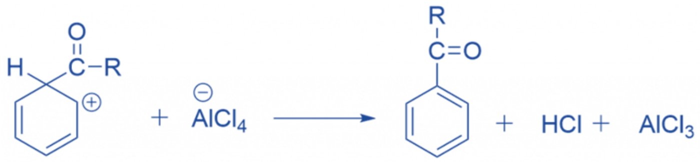


$$(i)\quad R-\overset{O}{\overset{\|}{C}}-Cl + AlCl_3 \rightleftharpoons R-\overset{O}{\overset{\|}{C}}{}^{\oplus} + AlCl_4^{\ominus}$$

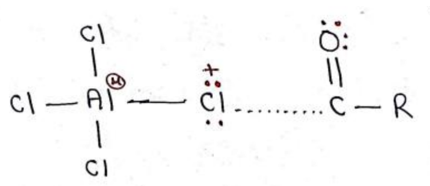
This ion as the acylium ion makes attack an on the benzene nucleus. When RCO^+ attacks an aromatic ring, an arenium ion or sigma complex is formed. Another carbon in this arenium ion has gone through sp3 hybridization. This arenium ion achieves stability in a resonance configuration. Because electron delocalization occurs at the sp3 hybridized carbon,' the aromatic property of the sigma complex or intermediate ion' is lost.



The intermediate complex is now deprotonated, restoring the ring's aromaticity. A chloride ion extracts the proton from the complexed Lewis acid, creating HCl. The $AlCl_3$ catalyst has been regenerated.



In this reaction, instead of RCO^+, the actual attacking reagent may be the acyl chloride aluminum chloride Complex.



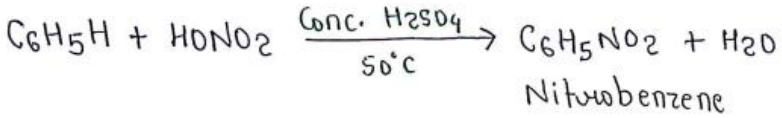
Aluminium chloride · acyl chloride Complex

Limitation of Friedel Craft acylation

- Acylation can only produce ketones. Because of the reaction circumstances, HCOCl decomposes into CO and HCl.
- The Lewis acid catalyst AlCl3 frequently binds with aryl amines, rendering them inactive.
- Instead of the required ring acylation, amines, and alcohols can produce competing N or O acylation.
- Because they are the least reactive, compounds like mono halo benzenes do not respond or participate in the Friedel-Crafts acylation reaction.

Nitration :-

On heating benzene with mixture of Conc. HNO_3 and Conc. H_2SO_4 (nitrating mixture), nitrobenzene is formed



$$C_6H_5H + HONO_2 \xrightarrow[50^\circ C]{Conc.\ H_2SO_4} C_6H_5NO_2 + H_2O$$

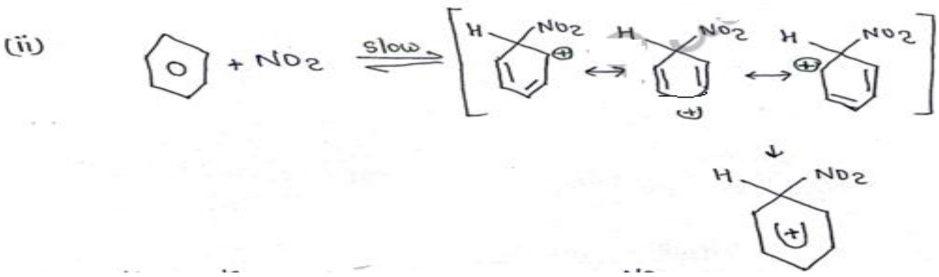
Nitrobenzene

Mechanism :- This reaction takes place by electrophilic nitronium ion (NO^+_2).

Nitric acid $HONO_2$ reacts with sulfuric acid (H_2SO_4) to generate the nitronium ion (NO^+_2), which is the active electrophile in this reaction.

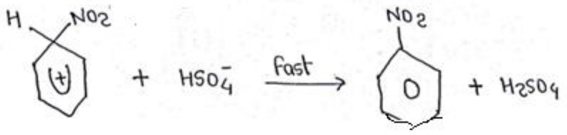
$$\text{(i)}\quad HONO_2 + 2H_2SO_4 \rightleftharpoons H_3\overset{+}{O} + 2HSO_4^- + NO_2^+$$

The nitronium ion (NO^+_2) attacks the electron-rich benzene ring in a slow, rate-determining step, forming a resonance-stabilized carbocation intermediate known as the arenium ion or sigma complex. This involves the breaking of aromaticity in the benzene ring.



A base, typically the bisulfate ion (HSO_4^-) from the sulfuric acid, rapidly removes a proton from the arenium ion. This step restores the aromaticity of the ring and forms nitrobenzene, along with regenerating sulfuric acid.

iii)



Halogenation :-

When aromatic hydrocarbons react with halogen at room temperature in dark and in presence of any halogen Carrier ($AlCl_3$, BF_3 Iron, J_2,etc.) aryl halide is formed. For example: benzene forms chlorobenzene with chlorine in presence of halogen carrier

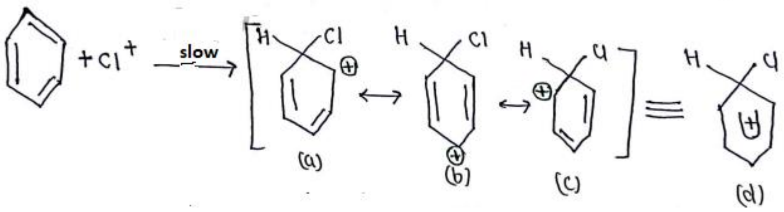
$$C_6H_6 + Cl_2 \xrightarrow{AlCl_3} C_6H_5Cl + HCl$$

If halogen is in excess, Further halogenation proceeds and mixture of 0- and P-dichlorobenzene is formed.

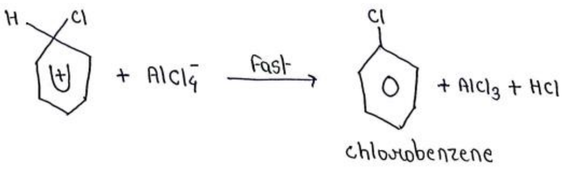
Mechanism :- Halogenation takes place by electrophilic reagent chloronium ion or in general halonium ion. chlorine molecule reacts with Catalyst with Catalyst and Cl^+ is formed

$$Cl_2 + AlCl_3 \rightleftharpoons AlCl_4^- + Cl^+$$

(ii) chloronium ion attacks on double bond of benzene ring an addition product Carbocation is formed. It is hybrid of 3 structures (a. b and c) a resonance



In presence of $AlCl_3$, Carbocation loses one proton and now Structure becomes Chlorobenzene



Unit 4: Benzene and its Reactivity

Long Answer Questions (10 Marks)

1. Explain the structure of benzene and its resonance properties.
2. Describe the mechanism of electrophilic aromatic substitution with examples of Friedel-Crafts alkylation and acylation.
3. Discuss the polymerization of acetylene and its role in organic chemistry.

4. Explain the decarboxylation of benzene derivatives with examples.
5. Discuss the electrophilic aromatic substitution reactions with a focus on nitration and halogenation.

Short Answer Questions (5 Marks)

1. What is the mechanism of Friedel-Crafts alkylation?
2. Write a short note on the polymerization of acetylene.
3. Discuss the halogenation reaction of benzene.
4. What is the decarboxylation of benzene derivatives?
5. Explain the concept of aromaticity and its importance in organic chemistry.