Aromatic Hydrocarbons
(Also called Arenes)

- They possess an 'Aroma' or fragrance
- They possess a ringed structure that resembles that of benzene.

Benzene, C_6H_6

⇒ It is made up of 92.3% of Carbon by mass
7.7% of Hydrogen

Ratio of C : H = $\frac{92.3}{12\text{ (Molar mass of C)}} : \frac{7.7}{1\text{ (Molar mass of H)}}$

$= 7.7 : 7.7$

$= 1 : 1$

∴ Empirical formula = CH

Molecular formula = $(CH)_n$

Relative Molecular mass = $(12+1)_n = 13n$

Experimental mol. mass = 78

∴ $13n = 78$

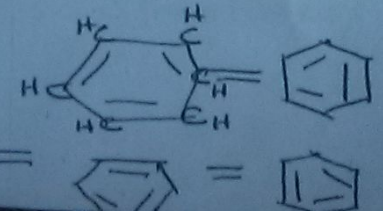
∴ $n = 78/13 = 6$

∴ Molecular formula of Benzene = C_6H_6

Indicating:

A high degree of unsaturation (greater than that of alkenes & alkynes)

A high carbon content



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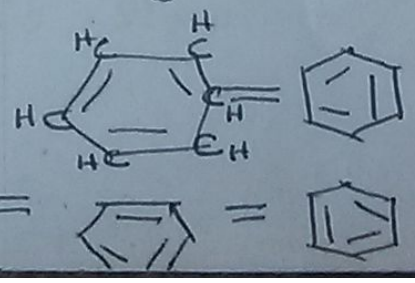
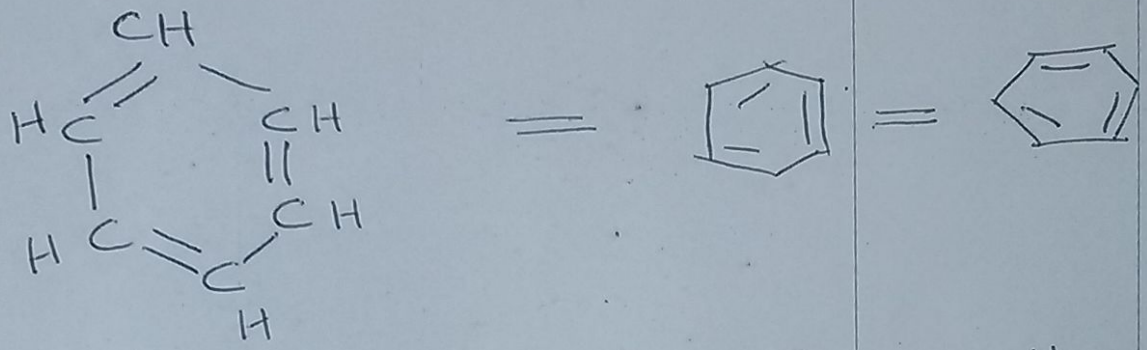
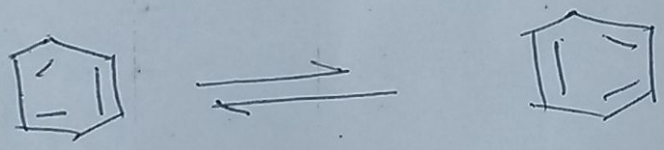


⇒ Kekulé formula for Benzene

- He 1st suggested that C_6H_6 should be an aromatic ring
- Each C atom is joined to two other C atoms and to one H atom by covalent bonds
- It is a cycloalkene with three alternating double bonds.



- He later proposed that benzene alternated between two structures.



Indicating: (π but not σ)

- Double bonds are mobile (labile) ie can be moved from one position to another
- benzene is an equilibrium mixture.

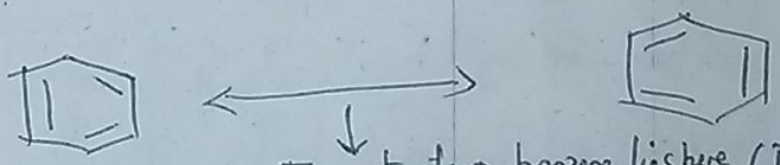
Resonance Theory

A phenomenon whereby a molecule can be represented by 2 or more structures which have the same arrangement of their atoms but different arrangement of their electrons (again π e⁻ and not σ e⁻).

Benzene can be represented by various alternative structures in which the true structure (called 'Resonance Hybrid') lies somewhere between the alternative structures (I and II)

ie True structure = Resonance Hybrid (most stable)
other alternative structures = Canonical forms.

The relative contribution of each canonical forms to the resonance hybrid depends upon its energy content (the lesser the energy, the greater the stability, $E \propto \frac{1}{\text{stability}}$)



(I) ↓ True struct. of benzene lies here (II)
Represents a resonance hybrid between the 2 structures (≃ 80% contribution)

Both (I) and (II) have equal energy content
Both I and II are Kekulé's structures/ Kekulé's canonical forms.

Other Canonical forms:

higher energy content

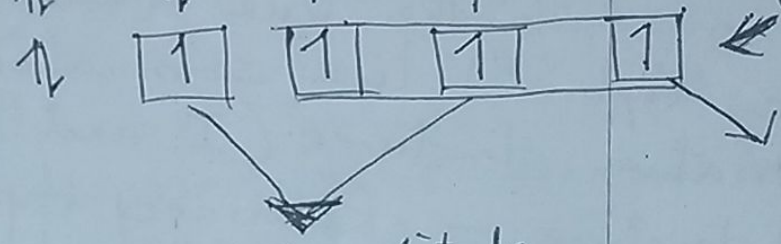
(III) (IV) (V)

(III – V) are Dewar's structures (contribute 20%).

⇒ Hybridization & Molecular Orbital Image

C(6) – $1s^2$ $2s^2$ $2p_x^1$ $2p_y^1$ $2p_z^0$ (Ground state)

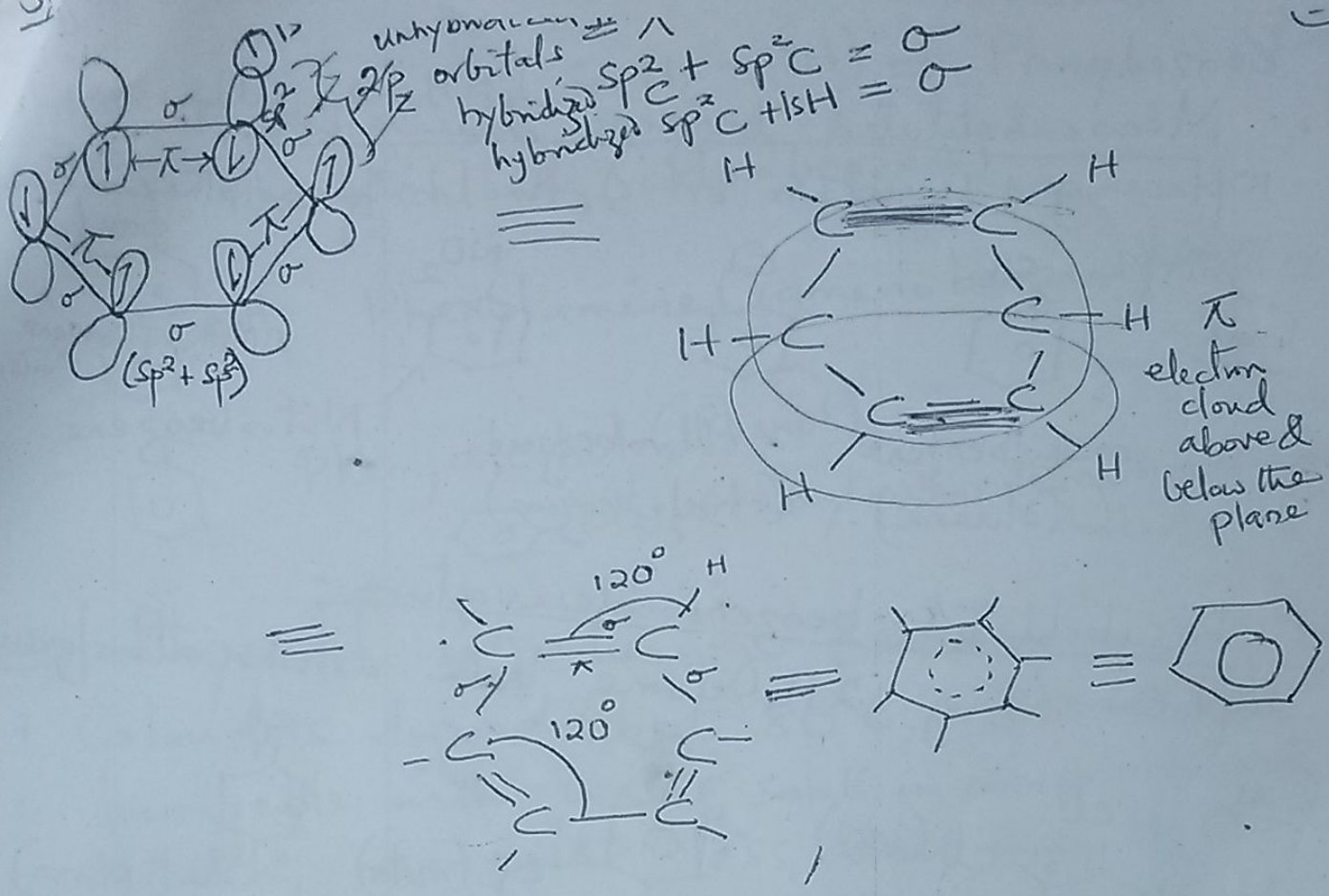
(On excitation)



Unhybridized p_z orbitals

S & 2p orbitals hybridize = sp^2 hybrid orbitals

- sp^2 hybrid orbitals will combine with 1s of H = σ
  Since there are 6 C atoms; 6C atoms ~~having~~ (sp^2 hybrid orbitals) will combine with 6 1s H = 6σ bonds. All atoms in one plane. Also sp^2 of 1C + sp^2 of 2nd C = σ (6C = 6σ; end to end combination)
- The unhybridized p_z orbitals of 6C atoms overlap sideways @ right angle to the plane to form π bonds.
- Electron cloud is above and below the plane of the ring, forming a delocalized π electrons orbitals around the ring.



Benzene is therefore
- C_6H_6 (all Hydrogen are equivalent)
- cyclic & planar, bond angle 120°
- Unsaturated ($4n + 2$) π electrons (Huckel's rule)
- Each C atom is sp^2 hybridized (σ) ~~and Pz~~
- ~~unhybridized~~. ~~It~~
- There is conjugation (= — = — = —)
- The π electrons are labile and could be found in any part of the electron cloud
- electrons do not maintain a permanent position (only σ electrons does) ~~not~~

= delocalization of electrons

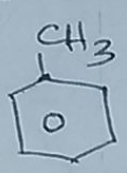
Delocalization of electrons in an aromatic ring confers a great stability on benzene. (Compounds that obey Huckel's rule have special stability.)

⇒ Nomenclature

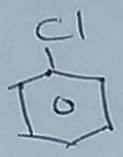
Its derivatives are named as derivatives of Ce
benzene.

- **Monosubstituted benzene derivatives:** replacing 1 H atom on C_6H_6 with another atom/group.

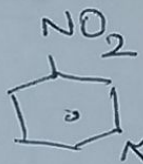
Egs



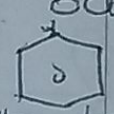
methylbenzene (Toluene)



chlorobenzene (halobenzene)



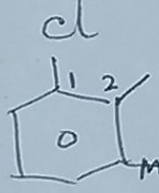
Nitrobenzene



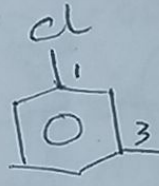
Methoxybenzene (Anisole)

- **Disubstituted benzene derivatives:** replacement of 2H atoms with another atoms/groups

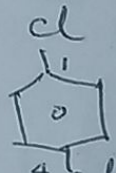
Egs



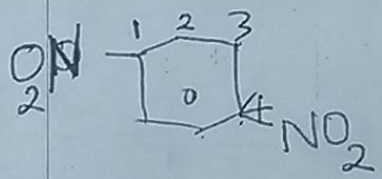
1,2-dichloro benzene (o-Dichloro benzene)



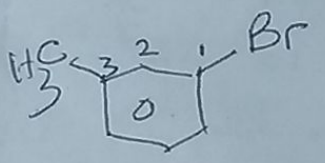
1,3-dichloro benzene (m-Dichloro benzene)



1,4-dichloro benzene (p-Dichloro benzene)

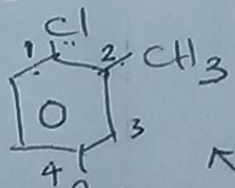


1,4-dinitrobenzene

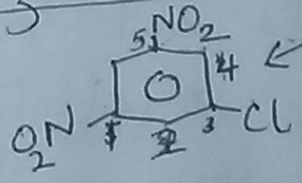


1-Bromo-3-methylbenzene

- **Trisubstituted benzene derivatives** (o, m & p not applicable here)



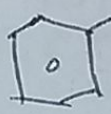
4-Bromo-1-chloro-3-methylbenzene



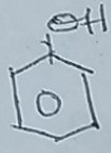
3-chloro-1,5-dinitrobenzene

Generally, C_6H_5 ($C_6H_6 - 1H$) = Phenyl

Phenyl chloride (chlorobenzene)



Phenylamine (aminobenzene)/Aniline



Phenyalcohol (Phenol)

(Phenylmethoxide/methoxybenzene/Anisole

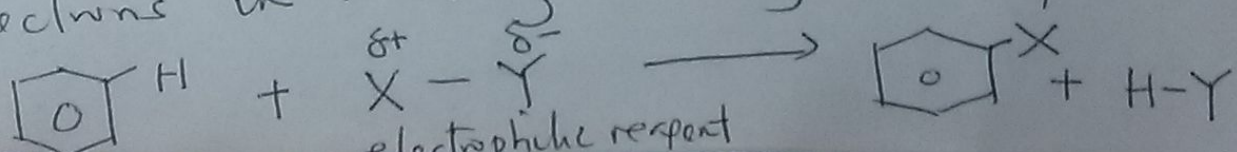
⇒ Physical Properties of Benzene.

- Colourless liquid (bpt 80°C, mpt 55°C)
- Immiscible with water, soluble in non-polar solvents
- Volatile, non-polar, less dense than H_2O
- A useful organic solvent, though highly carcinogenic/highly toxic
- Like all aromatic compounds, it burns with a smoky luminous flame (as a result of high carbon content).

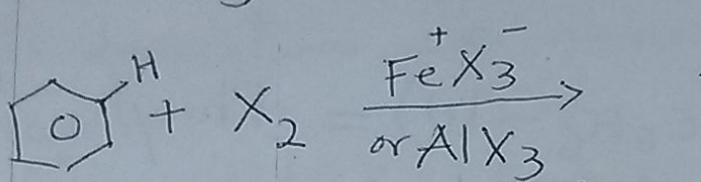
⇒ Reactions

They undergo electrophilic aromatic substitution reactions (ie substitute H atom(s) with electrophiles).

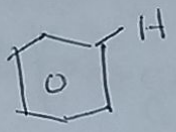
Electrophiles are electron deficient species (positively charged) which have affinity for the π electrons in a benzene ring (nucleophile)



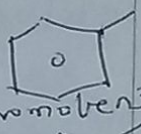
① Halogenation



$$+ X_2 \xrightarrow[\text{or } AlX_3]{Fe^{+}X_3^{-}} \text{(catalyst)} \quad + HX$$

eg 

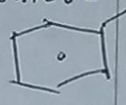
$$+ Br_2 \xrightarrow{FeBr_3}$$



Bromobenzene

$$+ HBr$$

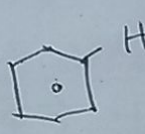
$$Cl_2 \text{ or } FeCl_3 \xrightarrow{AlCl_3}$$



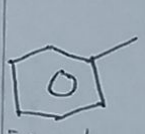
$$+ HCl$$

Phenylchloride

② Nitration



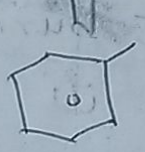
$$+ \underset{(HNO_3)}{H\overset{-}{O}-\overset{+}{N}O_2} \xrightarrow[\text{conc. } H_2SO_4]{\triangle}$$



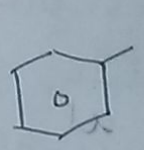
$$+ H_2O$$

Nitrobenzene

③ Sulphonation



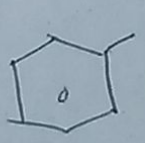
$$+ \underset{(H_2SO_4)\ \text{Conc}}{H\overset{-}{O}-\overset{+}{S}O_3H} \longrightarrow$$



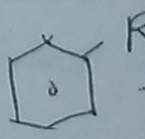
$$+ H_2O$$

Benzenesulphonic acid

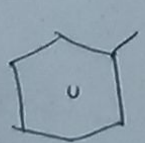
④ Friedel Crafts's alkylation



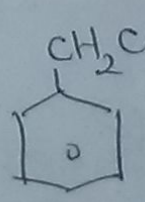
$$+ \underset{\text{(Alkylhalide)}}{\overset{+}{R}X^{-}} \xrightarrow[0^\circ C]{AlCl_3}$$



$$+ HX$$

eg 

$$+ \underset{\text{(Ethyl chloride) or chloroethane}}{CH_3CH_2Cl} \xrightarrow[0^\circ C]{AlCl_3}$$



$$+ HCl$$

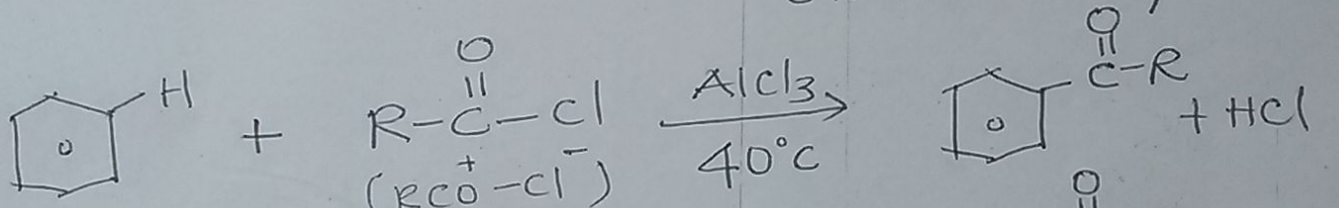
Ethylbenzene or Phenylethane

Friedel Crafts Acylation

Egs of acylating agents:

- $R-\overset{O}{\overset{\|}{C}}-Cl$ (Acid chloride) eg CH_3COCl = Acetyl chloride (Ethanoyl or Acetyl chloride)
- RCOOH (Acid eg $CH_3\overset{O}{\overset{\|}{C}}-OH$ = Ethanoic acid
- $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R = (RCO)_2O$ = $CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 = (CH_3CO)_2O$

= Acetic anhydride or Ethanoic anhydride



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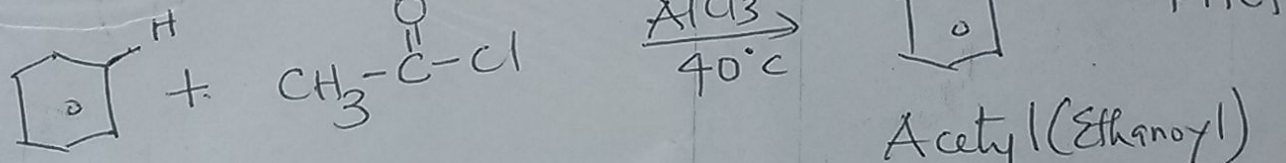
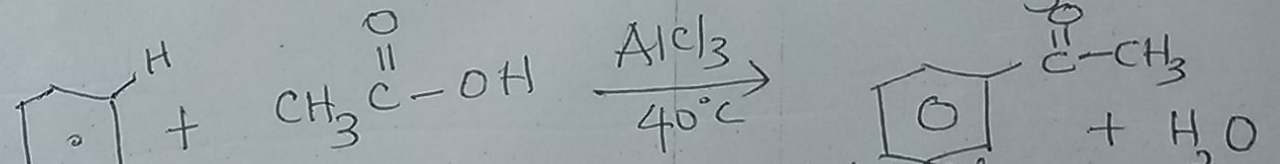


Acetyl (Ethanoyl) benzene



Acetylbenzene

Acetylbenzene Ethanoic acid