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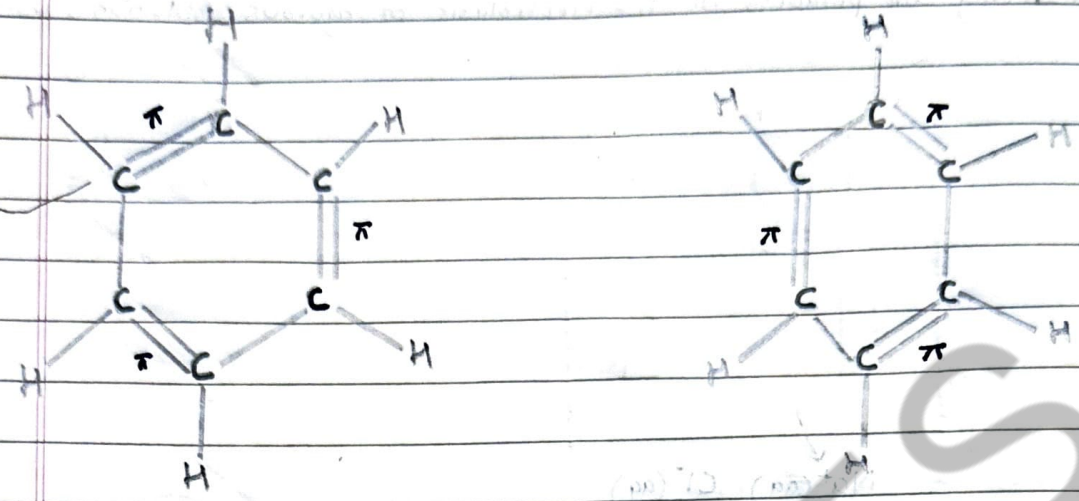
Benzene and its compounds



→ This phenomenon where we have alternating double bonds and single bonds is called: CONJUGATION

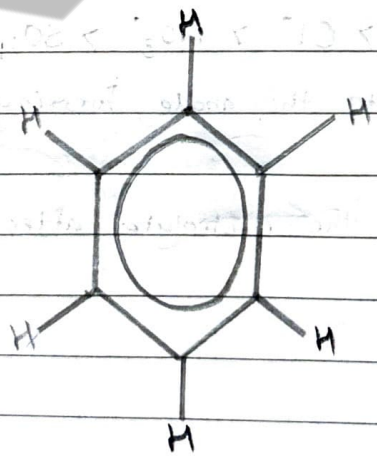
→ In both structures we can see that the π bond can be formed at any place, ∴ these are called RESONANCE STRUCTURES

  → both structures are unstable and keep switching amongst each other.

  → this makes the π bond to keep shifting, which spreads evenly in all 6 bonds.

  → all carbon - carbon bonds are of same strength and same length.

→ The resultant structure for these resonance structures is:



→ The circle signifies the even spread of π electrons

★ remember ★

sp^3 : 4σ bonds → bond angle : 109.5°

sp^2 : 3σ and 1π bonds → bond angle : 120°

sp : 2σ and 2π bonds → bond angle : 180°

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⇒ Some conclusions based on the structure of benzene

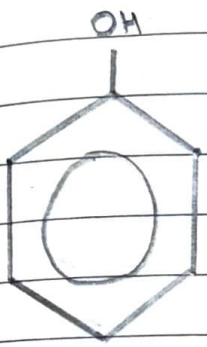
→ All carbon atoms are sp^2 hybridized

→ All bond angles are 120°, thus the molecule is planar

→ The benzene ring is very stable because the delocalised π-electron cloud is spread over the entire ring.

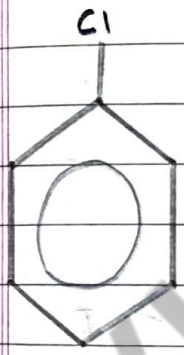
→ benzene has a very low negative charge density.

⇒ Common Aryl compounds



phenol

substitute OH

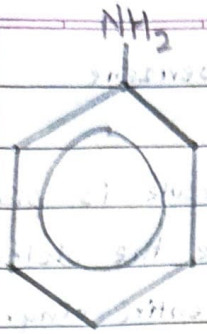


chloro benzene

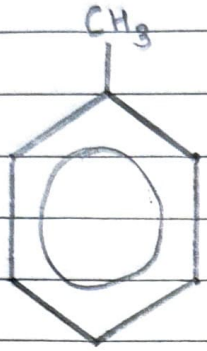
substitute Cl

Nitro benzene

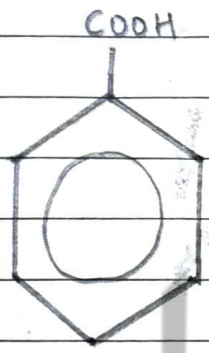
Substitute NO_2



phenylamine
Substitute NH_2

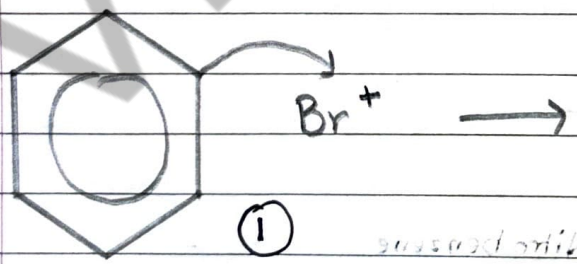


Methyl benzene
Substitute CH_3



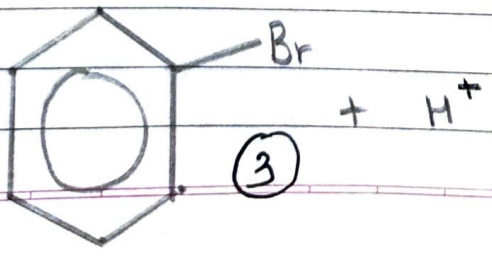
Benzoic Acid
Substitute COOH

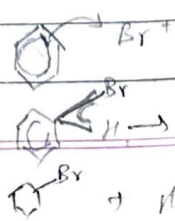
⇒ Electrophilic Substitution



This is planar T
all carbons sp^2 hybridized

This is not planar T
as one carbon is sp^3 hybridized





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⇒ Important reactions of benzene

1. Halogenation of benzene
   - → Reagent - X_2 (Br_2, Cl_2 etc.)
   - → Conditions (catalyst) - $AlCl_3$ / $FeCl_3$ / $FeBr_3$
   - → example: benzene + Br_2
     - → $Br_2 + AlBr_3 \rightarrow [AlBr_3Br]^- + Br^+$
     - → Br^+ + 
     - →  + H^+ / $H^+ + [AlCl_3Br]^- \rightarrow AlCl_3 + HBr$
   - → Electrophilic Substitution

2. Nitration of benzene
   - → Reagent - concentrated HNO_3 $H^+ + NO_3^-$
   - → Condition - 55°C
   - → Catalyst - Concentrated H_2SO_4
   - → example: benzene + HNO_3
     - → $HNO_3 + 2H_2SO_4 \rightarrow 2HSO_4^- + NO_2^+ + H_3O^+$
     - → NO_2^+ + 
     - →  + H^+ / $2HSO_4^- + H^+ \rightarrow 2H_2SO_4$
   - → Electrophilic Substitutions

3. Alkylation of benzene
   - → Reagent - RCl, where R is the alkyl (hydrocarbon) group
   - → Catalyst - $AlCl_3$
   - → example: CH_3CH_2Cl + benzene
     - → $CH_3CH_2Cl + AlCl_3 \rightarrow (AlCl_4)^- + CH_3CH_2^+$
     - → $CH_3CH_2^+$ + 
     - →  + H^+ / $H^+ + [AlCl_4]^- \rightarrow AlCl_3 + HCl$
   - → Electrophilic Substitution

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4. Acylation of benzene

→ Reagent : Acyl Chloride $C(=O)-Cl$

→ Catalyst : $AlCl_3$

→ example : $CH_3-C(=O)-Cl$ + benzene (ethanoyl chloride)

→ $CH_3COCl + AlCl_3 \rightarrow [AlCl_4]^- + CH_3CO^+$

→ $CH_3CO^+ +$  →

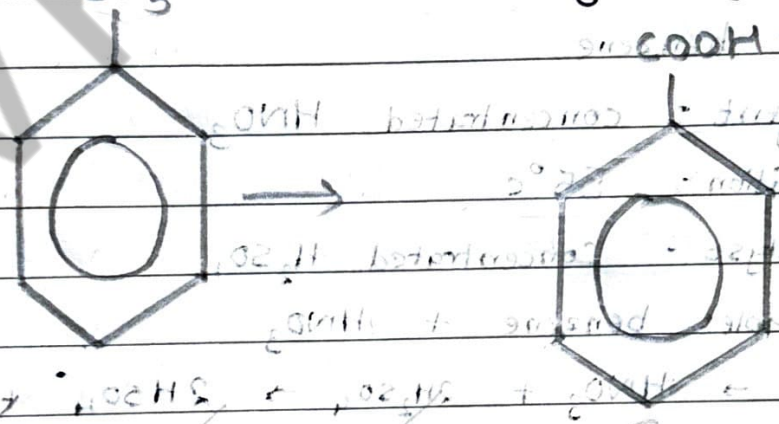
→  $CH_3CO + H^+ / [AlCl_4]^- + H^+ \rightarrow HCl + AlCl_3$

5. Oxidation of side chains on the benzene ring

→ Reagent : concentrated, acidified $KMnO_4$

→ Condition : heat

CH_3 → side chain (always alkyl group)



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⇒ Activating and deactivating groups. (Used to substitute more groups)

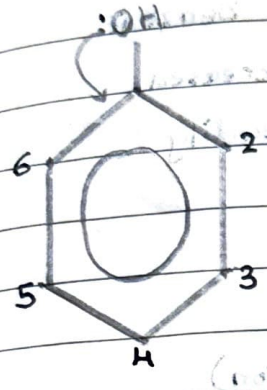
→ activating groups donate electrons to the benzene ring

ex. OH, CH_3, NH_2, Cl

→ deactivating groups remove electrons from the benzene ring

ex. NO_2, NH_3^+, COOH, CN

→ Activating Groups:

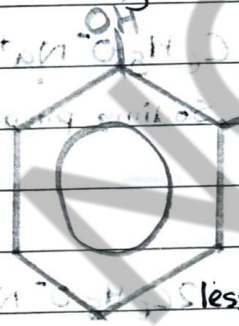


→ when it is an activating group the new group can be added to 2, 4 or 6.

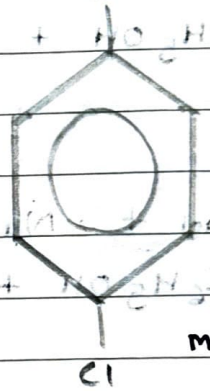
→ It is most stable when it is farthest from the previously added/substituted group.

→ Electrophilic Substitution

→ adding Cl^+ Isomers

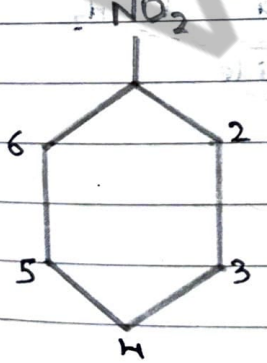


less stable



most stable

→ Deactivating Groups:

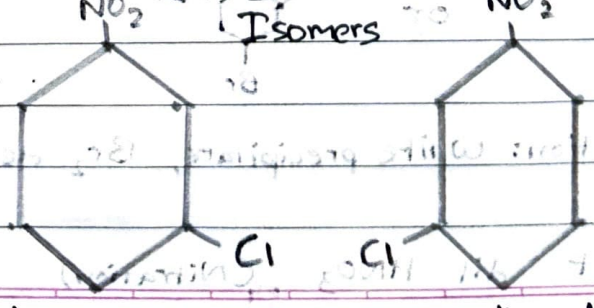


→ when it is deactivating group the new group can be substituted only at 3 ~~and~~ or 5.

→ Electrophilic Substitution

→ substituting Cl^+

Isomers



both are equally stable as the distance from NO_2 is same.

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⇒ Phenol

→ phenol is insoluble, as the benzene is a very big compound it disrupts the H-bonding.

→ phenol is weakly acidic

→ $C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$

→ it partially dissociates, and is proton donor

→ because of lack of lone pair on OH

→ phenol is a lot more reactive than benzene

→ negative charge density is increased

→ it activates 2, 4 and 6 very readily

→ Reactions

1. Phenol + NaOH (neutralisation reaction)

$C_6H_5OH + NaOH \rightarrow C_6H_5O^-Na^+ + H_2O$

Sodium phenoxide

2. Phenol + Na

$2C_6H_5OH + 2Na \longrightarrow 2C_6H_5O^-Na^+ + H_2$

Sodium phenoxide

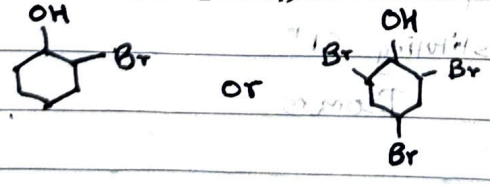
Comparing with

ethanol + Na

$2CH_3CH_2OH + Na \rightarrow 2CH_3CH_2O^-Na^+ + H_2$

Sodium ethoxide

3. Phenol + Br_2 (aq) (Bromination)



observation: white precipitate, Br_2 decolourises

4. Phenol + dil HNO_3 (Nitration)