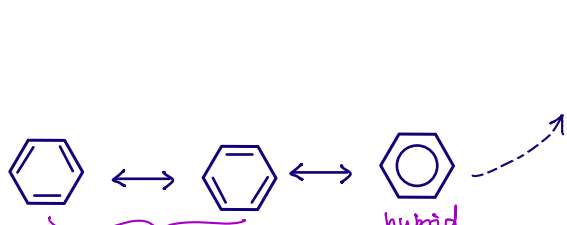
# Arenes

## BENZENE




delocalisation → planar; π cloud e⁻ above and below benzene ring

Resonance structures

hybrid resonance structure

gives extra stability to ring

**Physical properties:**

① Non-polar — only weak dispersion forces between molecules
⇓
low melting and boiling points, volatile and flammable

② soluble in non-polar solvents like $CCl_4$, insoluble in $H_2O$

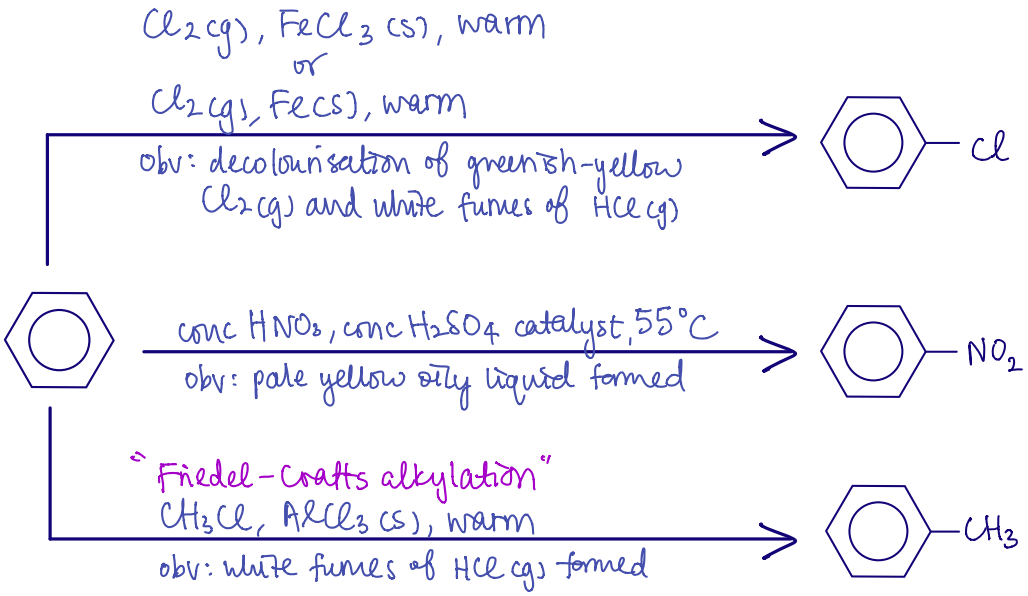
③ Benzene is a colourless liquid at room temperature

preferentially undergoes electrophilic substitution to preserve aromaticity & stability

its stability also makes it less susceptible to attack by electrophiles than C=C bonds in alkenes — requires stronger electrophiles for rx

## REACTIONS INVOLVING BENZENE – ELECTROPHILIC SUBSTITUTION

Generation of electrophile



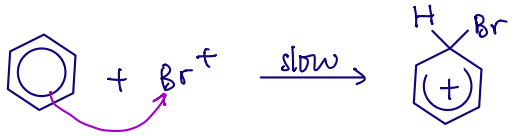
# MECHANISM OF ELECTROPHILIC SUBSTITUTION

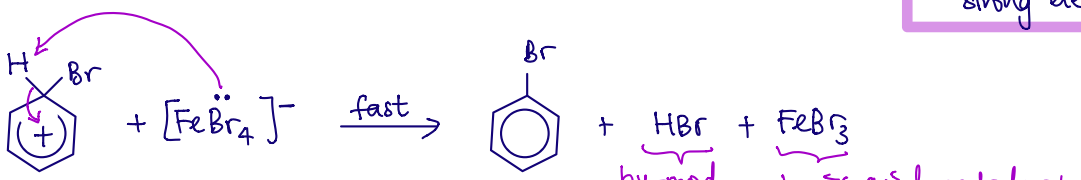
$C_6H_{12}(l) + Br_2(l) \xrightarrow[\text{warm}]{FeBr_3(s)} C_6H_{11}Br + HBr$

$FeBr_3 + Br_2 \longrightarrow Br^+ + [FeBr_4]^-$

strong electrophile generated

* Reaction only occurs in anhydrous conditions! $H_2O$ will compete with $Br_2$ for $FeBr_3$ as an acceptor of a lone pair of electrons. This prevents the formation of strong electrophile $Br^+$.

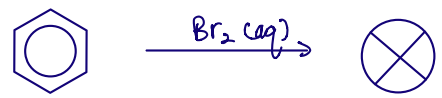


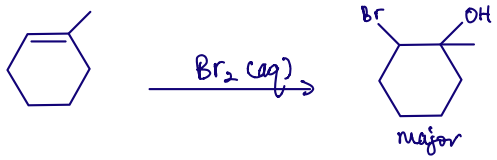

* Notes:

- $H_2SO_4$ is a stronger Lewis acid than $HNO_3$, thus $H_2SO_4$ protonates $HNO_3$ to generate $NO_2^+$.
- $-NO_2$ is electron-withdrawing, and deactivates the benzene ring. More rigorous conditions are required for further nitration.
- $-NO_2$ is a 3-directing substituent — further groups added to benzene ring are added at $C_3$. (KIV)

* Note: Use $Br_2(aq)$ as a distinguishing test between alkenes and arenes.
Eg. Add $Br_2(aq)$ dropwise with shaking to 1 $cm^3$ of 1-methylcyclohexene and benzene.



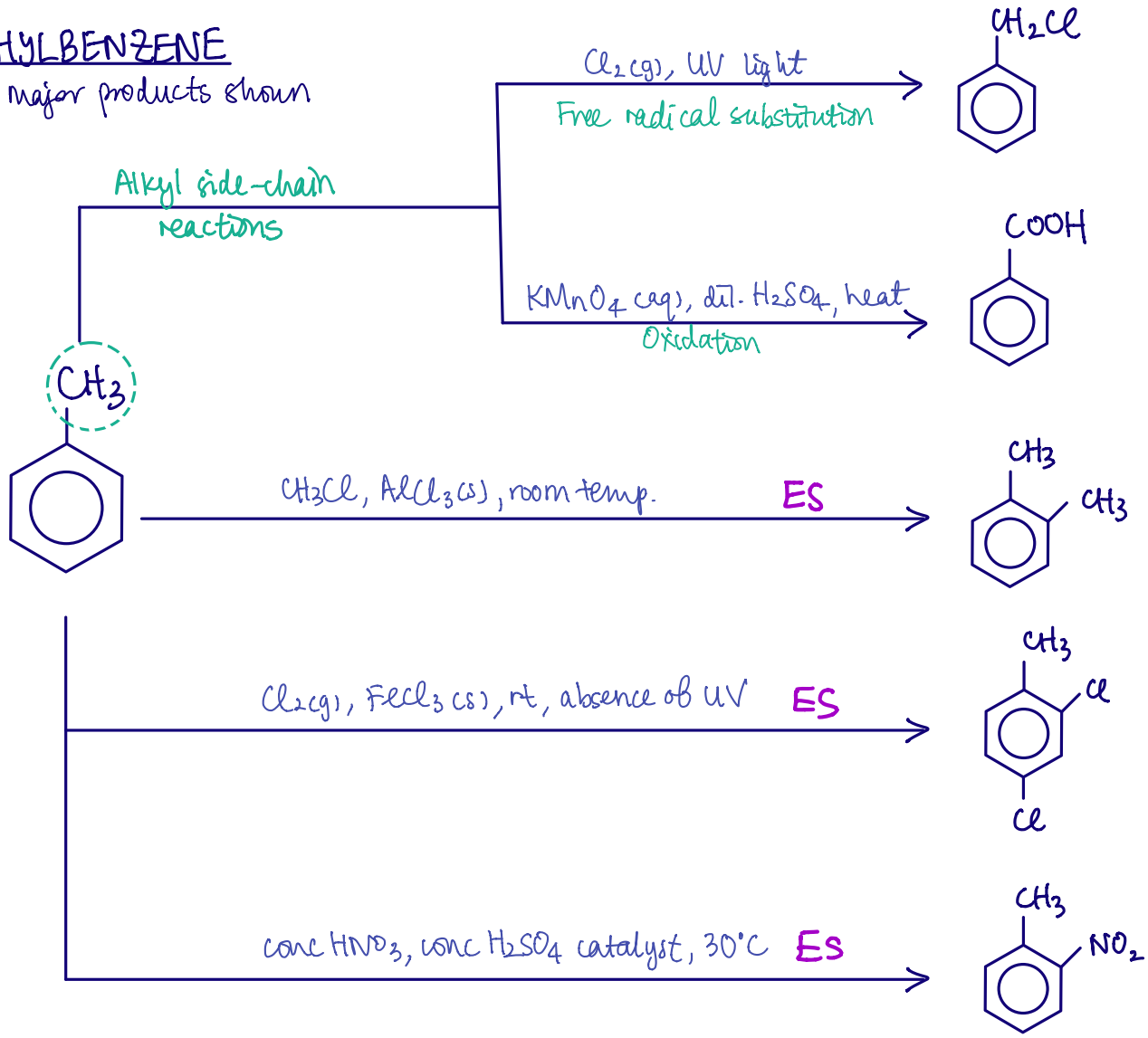

no reaction — Yellow-orange $Br_2(aq)$ not decolourised.




Yellow-orange $Br_2(aq)$ is decolourised.

# METHYLBENZENE

*only major products shown



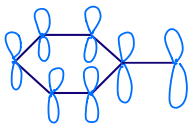

* Note: because $-CH_3$ is electron-donating, it ↑ electron density of the benze ring, thus it is an activating substituent. Therefore, conditions for electrophilic substitution are milder than for benzene.

## EFFECTS OF SUBSTITUENTS ON BENZENE RING

① Inductive effect — electron-donating substituents increase electron density of the benzene ring through the sigma bond. (eg. $-CH_3$, $-OH$, $-NH_2$) They are activating.

— conversely, electron-withdrawing substituents reduce electron density (eg. $-Br$, $-CHO$, $-NO_2$). They are deactivating.

② Resonance effect —



substituents with a lone pair of electrons residing in the p orbital can donate them into the benzene ring via resonance through the π bond (delocalisation of $e^-$). (eg. $-I$, $-OH$, $-NH_2$)

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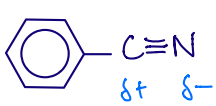
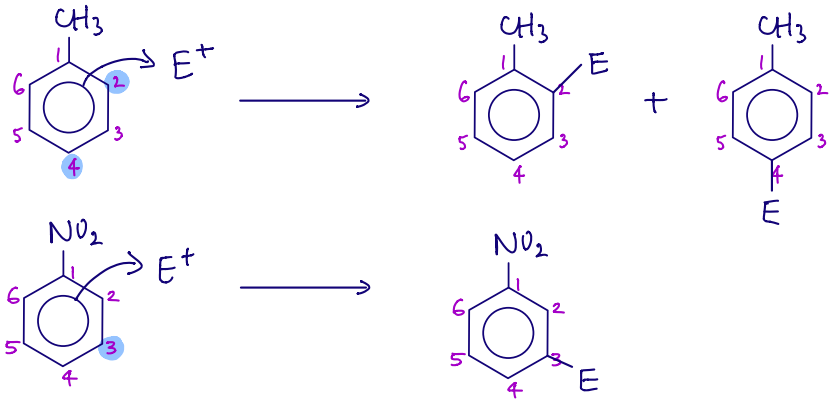



Electronegative substituents can withdraw electrons from the benzene ring via resonance through the π bond. (eg. $-COOH$, $-CN$, $-CHO$)

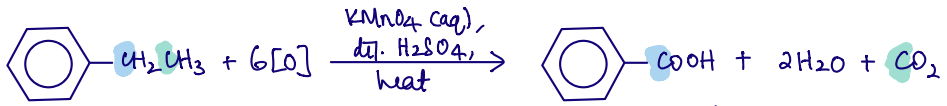
③ Activating groups and halogens are 2,4-directing, while deactivating groups are 3-directing.

| Substituent | Effect on benzene ring to electrophilic attack | Effect on position of electrophilic attack |
|---|---|---|
| $-R$ (alkyl group) | Activating | 2,4-directing |
| $-OH$, $-OR$, $-NH_2$, $-NHR$, $-NR_2$ | Strongly activating | 2,4-directing |
| $-Cl$, $-Br$, $-I$ | Deactivating | 2,4-directing |
| $-CHO$, $-COR$, $-CO_2H$, $-CO_2R$, $-NH_3^+$, $-NO_2$, $-CN$ | Strongly deactivating | 3-directing |



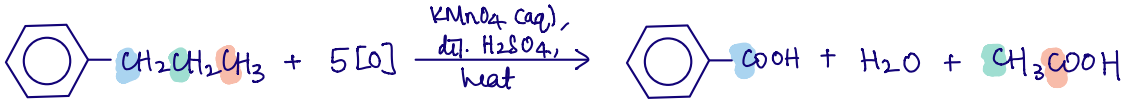

## SIDE-CHAIN OXIDATION

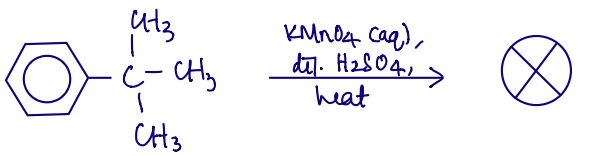
All alkyl groups except 3° side chains will get oxidised to $-COOH$.

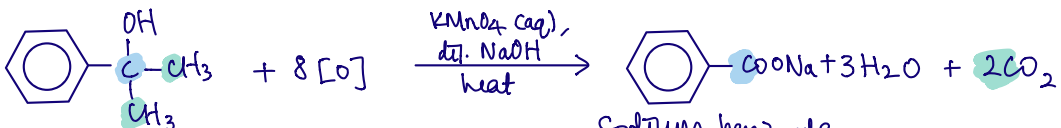



Benzoic acid (white ppt)

Purple $KMnO_4$ is decolourised. White ppt of benzoic acid is formed.




Sodium benzoate (soluble in $H_2O$)

Purple $KMnO_4$ is decolourised. Brown ppt of $MnO_2$ (s) is formed.