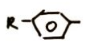
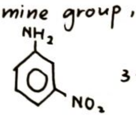
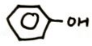
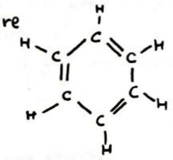
ARENES - AROMATIC HYDROCARBONS

NAMING BASED ON BENZENE

- → 
  phenyl (prefix)
  benzene (suffix)
- → with amine group, use prefix
  ↳ 
  3-nitrophenylamine
- → 
  phenol (suffix)

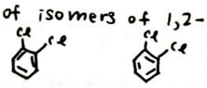
BENZENE

- → starting material for aromatic materials
- → carcinogen
- → colourless liquid, sweet odour, flammable.
- → empirical formula → CH, molecular formula → C_6H_6
- → kekule's Structure



↳ problems :

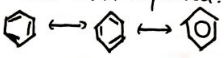
① → absence of isomers of 1,2-dichlorobenzene



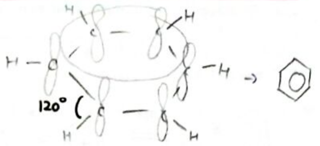
→ couldn't separate

② → low reactivity
- if C=C bonds present = similar to alkenes
- benzene did not readily undergo electrophilic addition

③ → C–C bond lengths were similar (shows one type of bond)

④ → ring more thermodynamically stable than expected.
- benzene = resonance hybrid 

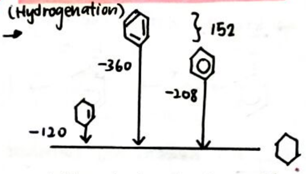
ARRANGEMENT OF e^- IN BENZENE

→ 

- → planar hexagonal ring
- → sp^2 hybridisation, 3 σ bonds
- → 2p orbital above & below plane.
- → orbitals overlap, forms ring
- → overlap produces system of π-bonds
- → e^- delocalised.

THERMODYNAMIC EVIDENCE

(Hydrogenation)

→ 

- → Expected $-360\ kJ\,mol^{-1}$, but benzene releases only $208\ kJ\,mol^{-1}$
- → it is $152\ kJ\,mol^{-1}$ more stable
  ↳ delocalisation energy (energy to overcome delocalised πe^- system)
- → ∴ benzene less reactive than alkenes.

THERMODYNAMIC EVIDENCE

(Bond enthalpies)

→ Theoretical value

$$\begin{tikzcd} 6C(s) + 3H_2(g) \arrow[r, "\Delta H_f"] \arrow[d, "+4290"'] & C_6H_6(g) \\ 6C(g) + 3H_2(g) \arrow[r, "+1308"] & 6C(g) + 6H(g) \arrow[u, "-5352"'] \end{tikzcd}$$

$$\Delta H_f = 4290 + 1308 - 5352$$
$$= +246\ kJ\,mol^{-1}$$

Benzene stable ∵ forms strong bonds. ∴ release energy ∴ no need to give so much

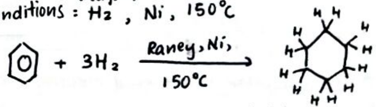
- → In practice $+163\ kJ\,mol^{-1}$ only.
- → difference due to resonance energy.

COMBUSTION

- → C:H ratio ↑ compared to alkenes
- → smoky flame
  ↳ C atoms stay as carbon & form soot

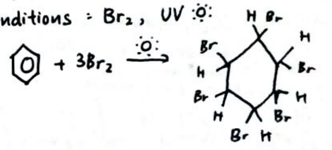
ADDITION REACTION

- → Benzene does not go through addition easily ∵ ring of delocalised πe^- would be broken & requires ↑ energy.
- → Conditions : H_2 (reagent), Ni, 150°C



cyclohexane

- → Free radical reaction
  Conditions : Br_2, UV ☼



1,2,3,4,5,6 – hexachlorocyclohexane

ARENES-AROMATIC HYDROCARBONS

ELECTROPHILIC SUBSTITUTION REACTIONS

- → Electropliles attack high e⁻ density in ring
- → Catalyst needed since Ea ↑

NITRATION

→ Conditions : conc HNO_3 (reagent), conc
catalyst → H_2SO_4, heat under reflux
55°C
* >65°C further substitution occurs.

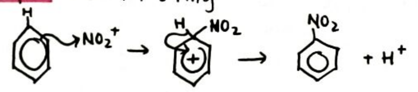
→ **Step 1** - Generate electrophile (acid-base)

$H_2SO_4 + HNO_3 \longrightarrow HSO_4^- + NO_2^+ + H_2O$

↑ weak acid ∴ cannot dissociate fully

↑ new electrophile (nitronium ion)

→ **Step 2** - Attack the ring



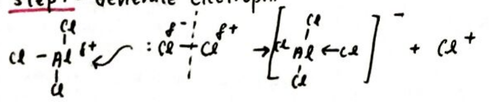
→ **step 3** - Regenerate the catalyst

$H^+ + HSO_4^- \rightarrow H_2SO_4$

→ overall : $C_6H_6 + HNO_3 \longrightarrow C_6H_6NO_2 + H_2O$

HALOGENATION

- → Cl_2 non-polar ∴ not good electrophile.
- → Halogen carrier (catalyst) polarises halogen
- → Reagents : Cl_2, halogen carrier ($FeCl_3$, $FeBr_3$, aluminium bromide.)
- → Conditions : Heat under reflux.
- → **Step 1** - Generate electrophile



→ $AlCl_3 + Cl_2 \rightarrow AlCl_4^- + Cl^+$

→ **Step 2**: Attack the ring.

→ **Step 3** : Regenerate catalyst

$H^+ + AlCl_4^- \rightarrow HCl + AlCl_3$

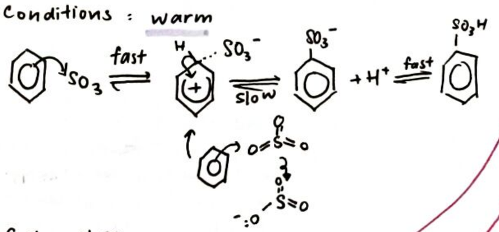
→ overall: $C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$

SULFONATION

→ Reagents : fuming sulfuric acid (SO_3 solution + H_2SO_4)

→ Conditions : warm

→



→ $C_6H_6 + H_2SO_4 \longrightarrow C_6H_5SO_3H + H_2O$

FRIEDEL CRAFTS REACTIONS

- → catalyst used to ↑ +ve nature of electrophile
- → $AlBr_3$ acts as Lewis Acid (lp e⁻ acceptor & helps break C-Br bond.
- → in dry ether

ALKYLATION

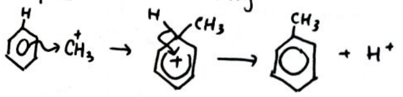
→ Reagents : haloalkane, anhydrous Aluminium Bromide.

→ Conditions : room temp, dry inert Solvent (ether)
* for ethyl; heat under reflux.

→ **step 1** - Generate electrophile.

$AlBr_3 + CH_3Br \rightarrow AlBr_4^- + \overset{+}{C}H_3$
(accepts lp of Br)

→ **Step 2** - Attack the ring.



methylbenzene

→ **step 3** - Regenerate the catalyst

$H^+ + AlBr_4^- \rightarrow HBr + AlBr_3$

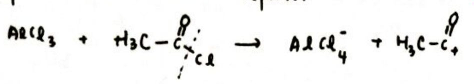
→ overall : $C_6H_6 + CH_3Br \longrightarrow C_6H_5CH_3 + HBr$

* ACYLATION, HALOGENATION, ALKYLATION = catalyst works the same way.

ARENES-AROMATIC HYDROCARBON

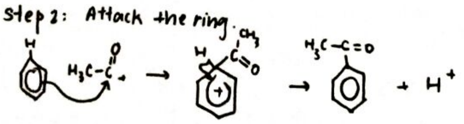
ACYLATION

- $AlCl_3$ catalyst acts in the same way with alkylation
- Reagents : acyl chloride ($R-COCl$), anhydrous $AlCl_3$
- Conditions : reflux 50°C, dry inert solvent (ether)
- Step 1 : Generate the electrophile.



$$AlCl_3 + H_3C-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow AlCl_4^- + H_3C-\overset{O}{\overset{\|}{C}}{}^+$$

- Step 2 : Attack the ring.



- Step 3 - Regenerate the catalyst

$$H^+ + AlCl_4^- \rightarrow HCl + AlCl_3$$

- Overall : $C_6H_6 + CH_3COCl \rightarrow C_6H_5COCH_3 + HCl$.

FURTHER SUBSTITUTION OF BENZENE

e⁻ releasing

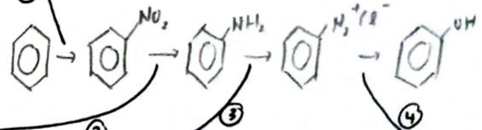
e⁻-withdrawing

Eg.	OH, CH_3	NO_2
e⁻ density	↑	↓
Ease of substitution	Easier	Harder
position	2, 4, 6	3, 5

- Substitution of nitrobenzene is more difficult than w/ benzene. NO_2 is e⁻ withdrawing, directs to 3 position. produces 1, 3 disubstituted product } & vice versa.

PHENOL

- aromatic alcohol
- used in production of plastics, antiseptics, resins for paints.
- synthesised in a multi-stage process.



- nitration of benzene (electrophilic substitution)
  - conc. nitric acid, conc H_2SO_4
  - reflux 55°C
  - $C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$

- Reduction of nitrobenzene
  - tin + conc. HCl
  - reflux.
  - $C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$

- Diazotisation of phenylamine. (diazotisation)

  - nitrous acid (HNO_2), HCl
  - below 10°C
  - $C_6H_5NH_2 + HNO_2 + HCl \rightarrow C_6H_5N_2^+Cl^- + 2H_2O$

- Substitution
  - water
  - warm above 10°C
  - $C_6H_5N_2^+Cl^- + H_2O \rightarrow C_6H_5OH + N_2 + HCl$.

PHENOL & WATER

- phenol = weak acid.
- aromatic ring weakens O-H & stabilises anion formed.
- $C_6H_5OH_{(aq)} \rightleftharpoons \underset{\text{(stable)}}{C_6H_5O^-_{(aq)}} + H^+_{(aq)}$

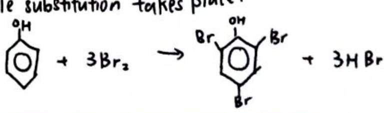
PHENOL & NaOH

(acid base)

- $C_6H_5OH_{(aq)} + NaOH_{(aq)} \rightarrow \overset{\text{sodium phenoxide}}{C_6H_5O^-Na^+_{(aq)}} + H_2O_{(l)}$
  ↑ (ionic & water soluble)

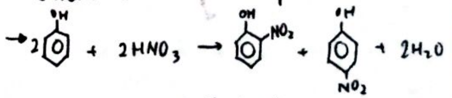
PHENOL & BROMINE

- reacts readily w/ out catalyst
- multiple substitution takes place.



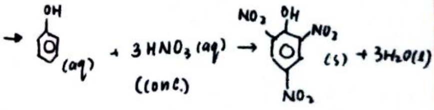
NITRATION OF PHENOL

- Reagents : dilute nitric acid (HNO_3)
- Conditions : room temp.



2-nitrophenol + 4-nitrophenol

OR



2, 4, 6, - trinitrophenol

* 2 moles of reagent

- ARENES -
METHYLBENZENE

REACTIONS

→ 

, contains benzene ring & methyl side chain

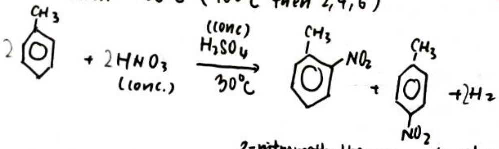
∴ undergo :
- → electrophilic substitutions of benzene
- → reactions of alkanes.

→ substitution takes place @ 2-, 4-

NITRATION

→ Reagent : conc HNO_3, conc H_2SO_4

→ Condition : 30°C (100°C then 2,4,6)

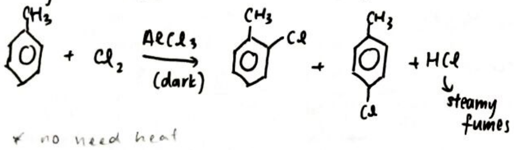


2-nitromethylbenzene 4-nitromethylbenzene

→ lower temp used ∴ methylbenzene more reactive than benzene

HALOGENATION
(of ring)

→ Reagent : Cl_2 , $AlCl_3$ (in the dark)

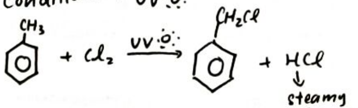
→ 

* no need heat

HALOGENATION
(of side chain)

→ Reagents : Cl_2

→ Conditions : UV ☼

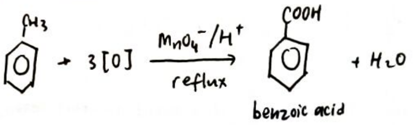
→ 

→ mono, di, tri depends on amount of halogen.

OXYDATION OF SIDE CHAIN

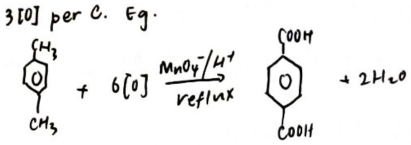
→ Reagent : acidified $KMnO_4$ (dichromate not strong enough)

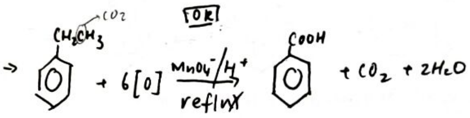
→ Condition : reflux.



benzoic acid

→ 3[O] per C. Eg.

→ 

→ 

Comparison:

		 CH_3	 OH
Halogenation	→ Cl_2, $AlCl_3$, heat under reflux	→ Cl_2, $AlCl_3$ (dark)	→ Cl_2
Nitration	→ conc HNO_3, conc H_2SO_4, heat under reflux 55°C	→ conc HNO_3, conc H_2SO_4, heat under reflux 30°C	→ HNO_3 (aq)

e^- density of ring ↑
∴ more reactive