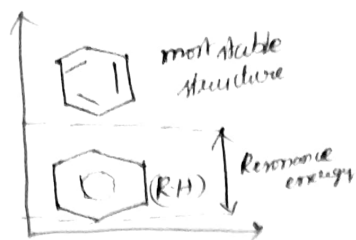


BENZENE

Resonance energy of benzene : potential energy diff b/w most stable & real structure



36 kcal is resonance energy of benzene

61 kcal/mol for naphthalene

84 kcal/mol for phenanthracene

→ It does not decolourize $\text{Br}_2/\text{H}_2\text{O}$ (&c) alk. KMnO_4 , can't undergo polymerisation and oxidation under normal conditions, undergo E^+ substitution rather than addition and is a stable molecule.

→ Stability and structure of benzene was explained by 2 theories

(a) Resonance (&c) valence bond theory

(b) Molecular orbital theory.

Hybrid : pure orbital

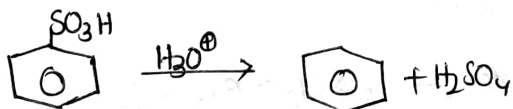
18 : 12

① Preparation:

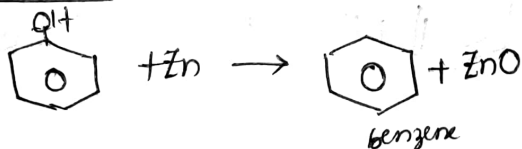
i) from acetylene



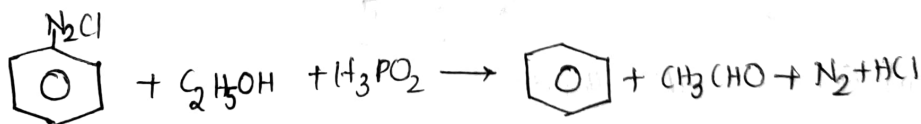
ii) Decarboxylation



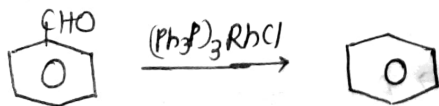
iii) reduction



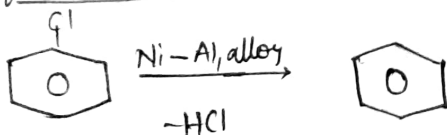
iv) from benzene diazonium chloride:



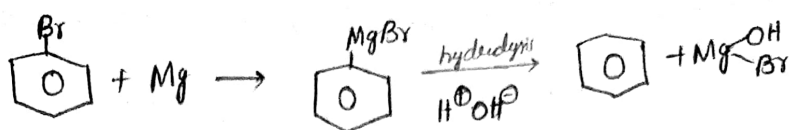
v) from benzaldehyde:



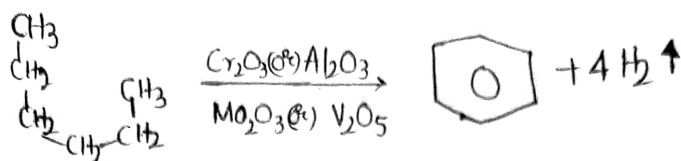
vi) from chlorobenzene:



Vii) from Grignard reagent:



Viii) Aromatisation:



II Physical properties:

→ colourless liquid (or) solids with corresponding different aromas, benzene is insoluble in water but soluble in organic solvents, aromatic hydrocarbons are highly inflammable with sooty flame.
b.p of benzene is 80°C

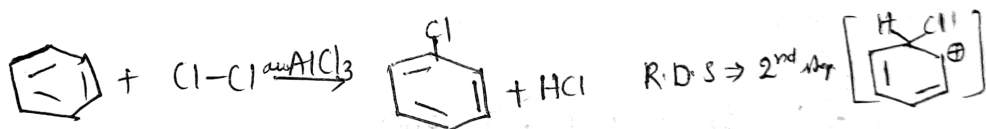
III Chemical properties:

→ Benzene and its derivatives undergo E^+ subⁿ. but addⁿ under special condition.

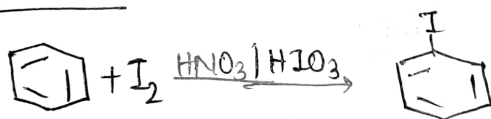
i) Halogenation

Presence of Anhydrous AlCl_3 (or) FeCl_3

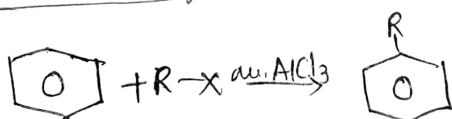
$\text{E}^+ - \text{X}^+$, reactivity order — $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$



ii) Iodination



iii) Friedel craft alkylation:



reactivity order $\text{R}-\text{F} > \text{R}-\text{Cl} > \text{R}-\text{Br} > \text{R}-\text{I}$
 $\text{E}^+ - \text{R}^+$

Alkylating agents

a) $\text{R}-\text{X}$ / Lewis acid

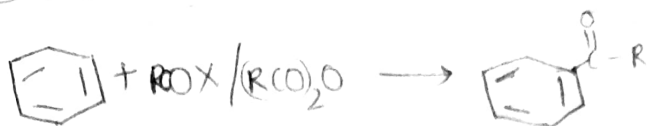
b) alkene / protonic acid

c) $\text{R}-\text{OH} / \text{H}^+$

d) HF

→ Rearrangement possible

iv) Friedel-Crafts acylation:



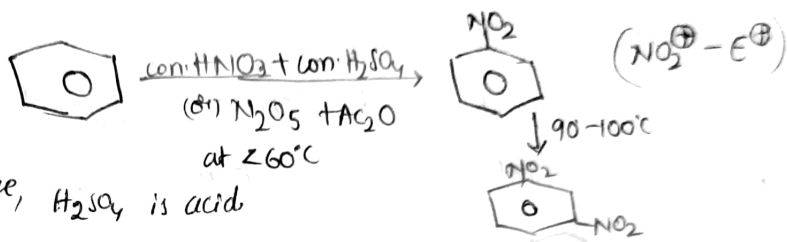
Reagents are: (i) $R-CO-X$, (ii) $R-COOH / (R-CO)_2O$ or $CH_2=C=O$ (ketene - Lewis acid)

No rearrangement.

Limitations - i) with $(CH_3)_3C-COCl / AlCl_3$ only alkylation because $(CH_3)_3C^+$ reacts with Lewis acid.

ii) with aniline no alkylation because $(-NH_2)$ reacts with Lewis acid. Deactivating groups like $-CHO$, $-NO_2$, $-COOH$, etc. are attached to aromatic ring no alkylation because R^+ is weak electrophile.

v) Nitration:



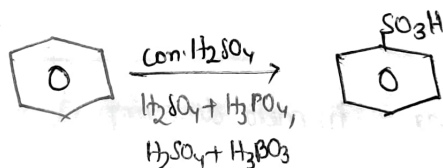
HNO_3 is base, H_2SO_4 is acid

total no. of ions = 4

Agents are i) $con. HNO_3$, ii) $con. HNO_3 + CH_3COOH$, iii) N_2O_5 / CCl_4 ,
 (or) $(CH_3CO)_2O$

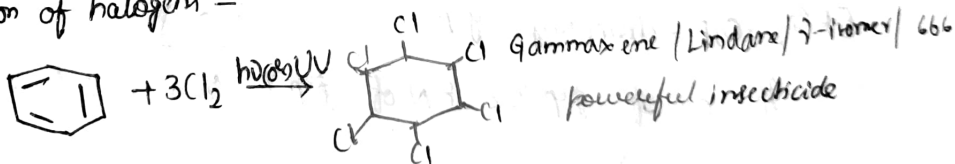
iv) Acylnitrate / ester

vi) Sulphonation:

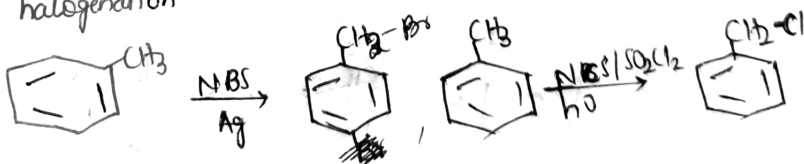


⇒ Addition reactions

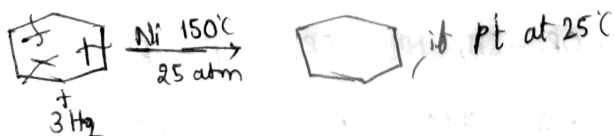
addition of halogens -



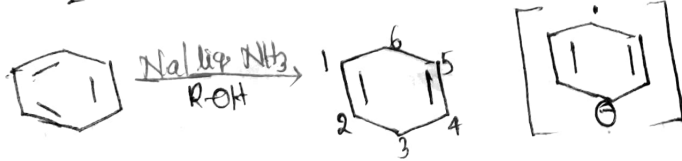
side chain halogenation
 (free radical sub^m)

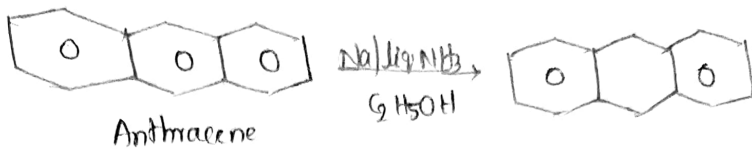
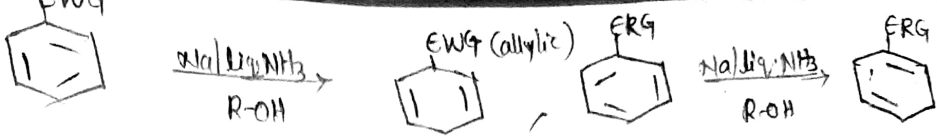


Reductions:

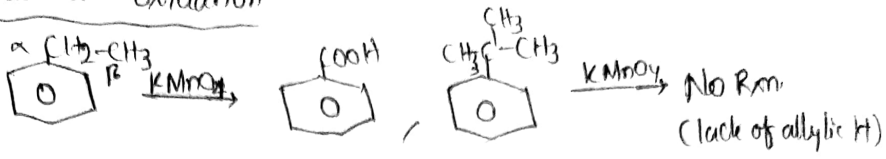


Birch reduction

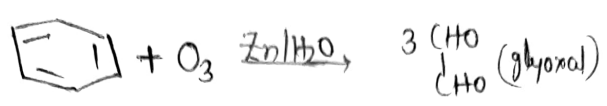




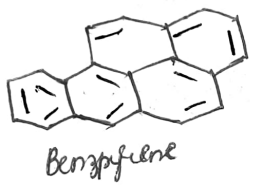
Side chain oxidation



OZONOLYSIS



Carcinogenity: C_6H_6 & several polynuclear hydrocarbon are formed due to incomplete combustion of tobacco, coal, petroleum etc. they undergo various biochemical change in human body leads cancer.



Orientation of electrophile in mono substituted benzene:

① Activity effect -

- i) Ortho, para directing
- ii) meta directing

Case I: In , if E.N of group X > E.N of group Y it acts as ERG, (O,p-directing group) Ex:

Case II: If E.N of group X < E.N of group Y then it acts as EWG, (meta-directing) Ex:



- EX: $-R, -OH, -OR, -SH, -NH_2, -SR, -NHR, -NR_2, -CH_2R, -C_6H_5, -X, -CH_2OH, -CH_2Cl, -CH_2NH_2, -CH_2CN, -CH_2COOH, -CH=CH-COOH, -CH=CH_2$ etc.

Class-I \Rightarrow groups release e^- to benzene ring makes unstable to attack of electrophile. O,p-directing & being activating group.

Class - II (Meta directing)

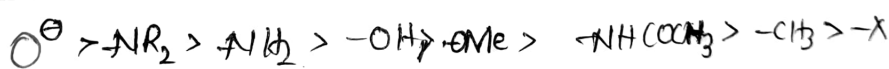
Ex: $-\text{NO}_2$, $-\text{SO}_3\text{H}$, $-\text{SOCl}$, $-\text{COR}$, $-\text{C}(=\text{O})\text{COOH}$, $-\text{CX}_3$, $-\text{N}^+\text{H}_3$, $-\text{N}^+\text{HR}_2$, $-\text{N}^+\text{R}_3$, etc.

with draw e^- particularly from O, p-positions, there by meta position is more e^- density hence these grps are called meta directing grps or being deactivating grps.

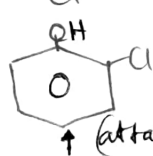
Effect of react	Substituent	Effect of orientation
① Very strong activating groups	Ex: $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{OH}$	O, p-directing
② Strongly activating groups	Ex: $-\text{NHCOR}$, $-\text{OR}$, $-\text{OCOR}$	O, p-directing
③ Activating groups	Ex: $-\text{R}$, $-\text{Ar}$, $-\text{CH}=\text{CH}_2$	O, p-directing
④ deactivating grps	Ex: $-\text{X}$, $-\text{CH}_2\text{X}$, $-\text{NO}$, $-\text{SOCH}_3$, $-\text{CH}=\text{CH}-\text{COOH}$, $-\text{CH}=\text{CH}_2$, $-\text{CHO}$	O, p directing
⑤ Strongly deactivating grps	Ex: $-\text{CHO}$, $-\text{COR}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{COCl}$, $-\text{CN}$, $-\text{SO}_3\text{H}$	meta directing
⑥ Very strongly deactivating grps	$-\text{CF}_3$, $-\text{NO}_2$, $-\text{N}^+\text{R}_3$, $-\text{N}^+\text{H}_3$	meta directing

\Rightarrow Orientation of electrophile in di or poly substituted benzene:

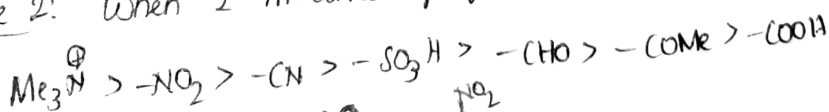
Case I - when 2 O, p-directing the directivity order follows as

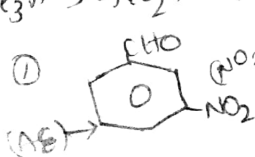


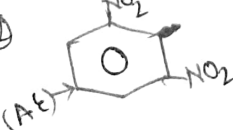
Ex: ①  $\text{NH}_2 > \text{Cl}$

②  $-\text{OH} > -\text{Cl}$

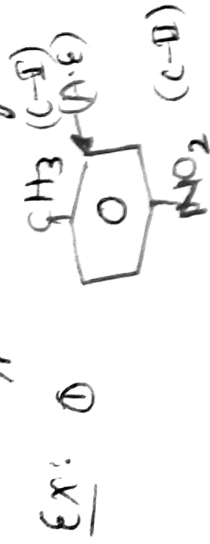
Case 2: When 2 m-directing grps belong then order is



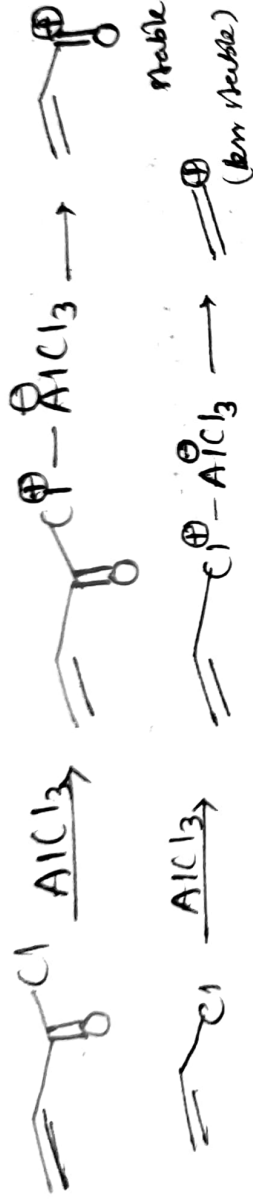
Ex: ①  (NE) $\text{CHO} > \text{NO}_2$

②  (AE) $\text{NO}_2 > \text{NO}_2$

Case 3: When 2 groups of different directive influences the group belonging to o,p-directing takes higher priority



Friedel craft alkylation



∴ Vinyl halides does not undergo friedel craft alkylation.



Reactivity towards friedel craft alkylation

Ozonolysis

