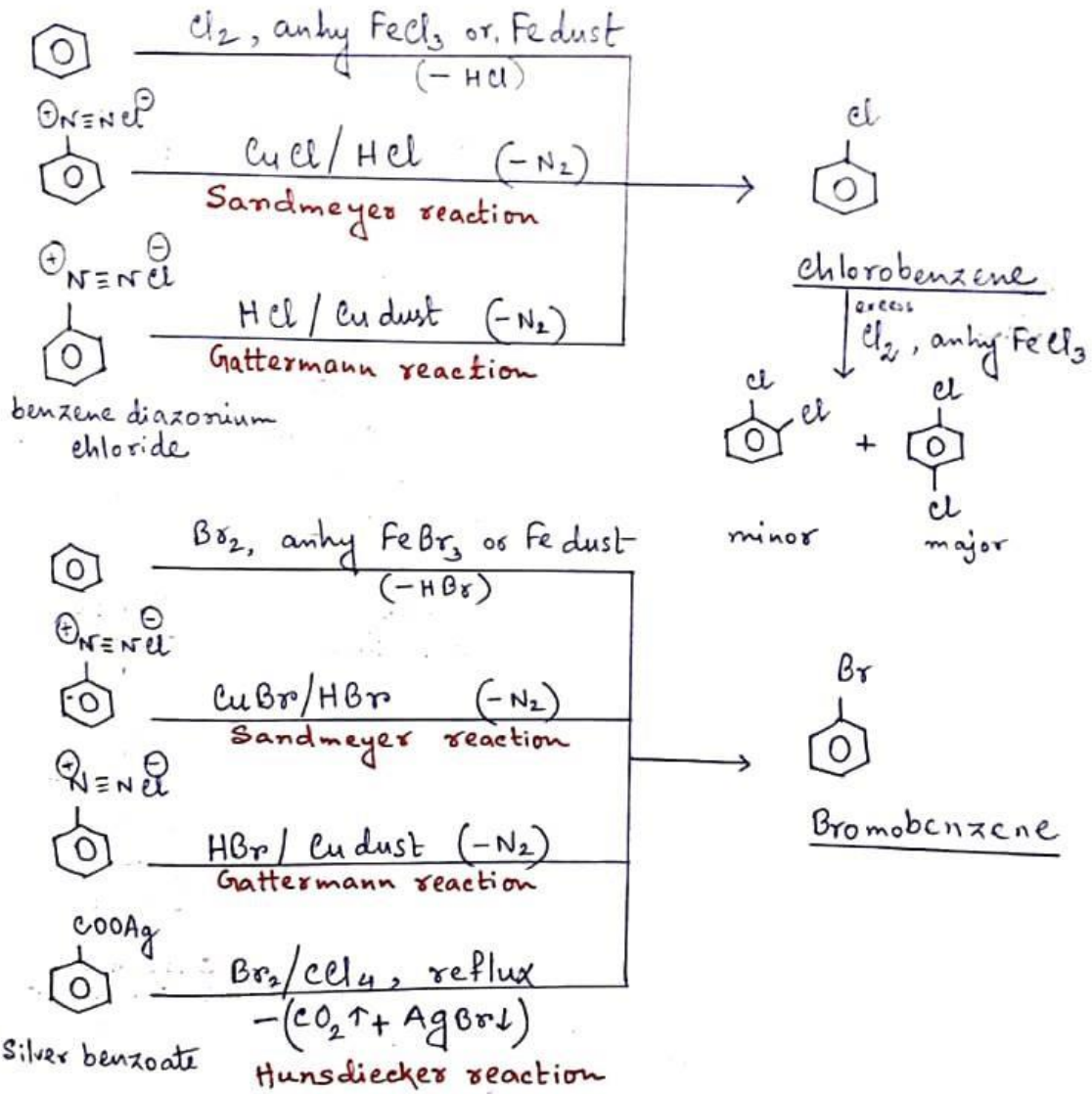
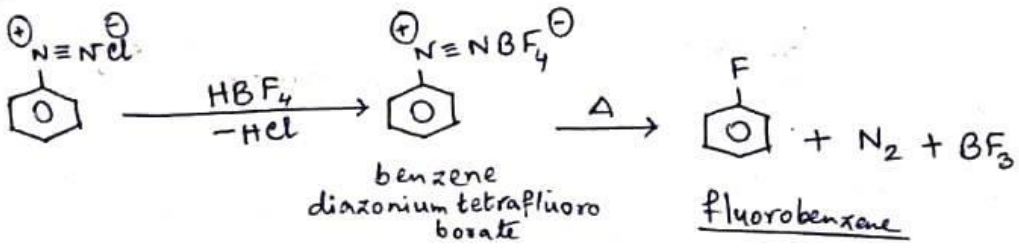
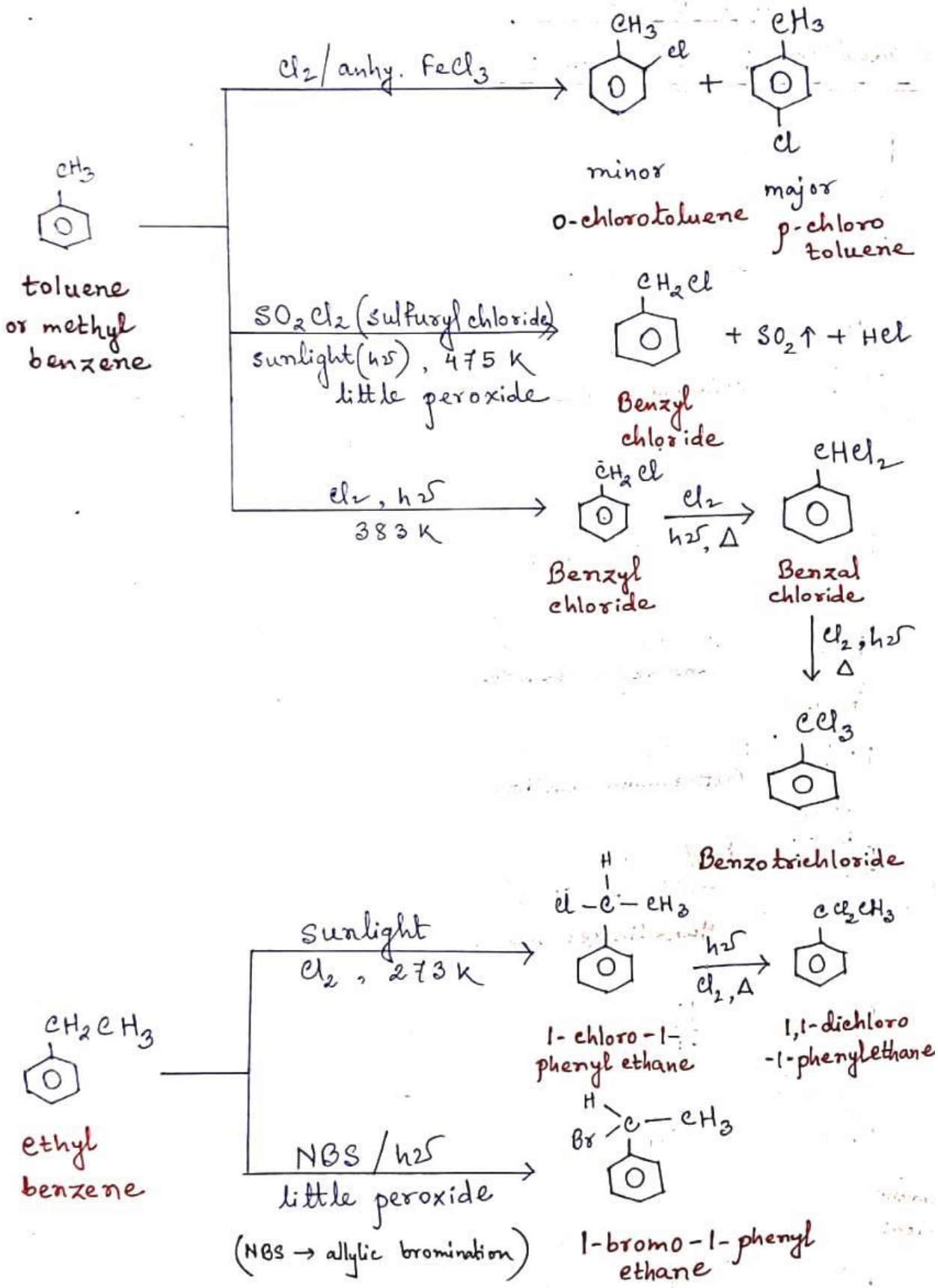
Haloarenes

• Preparation of haloarenes :

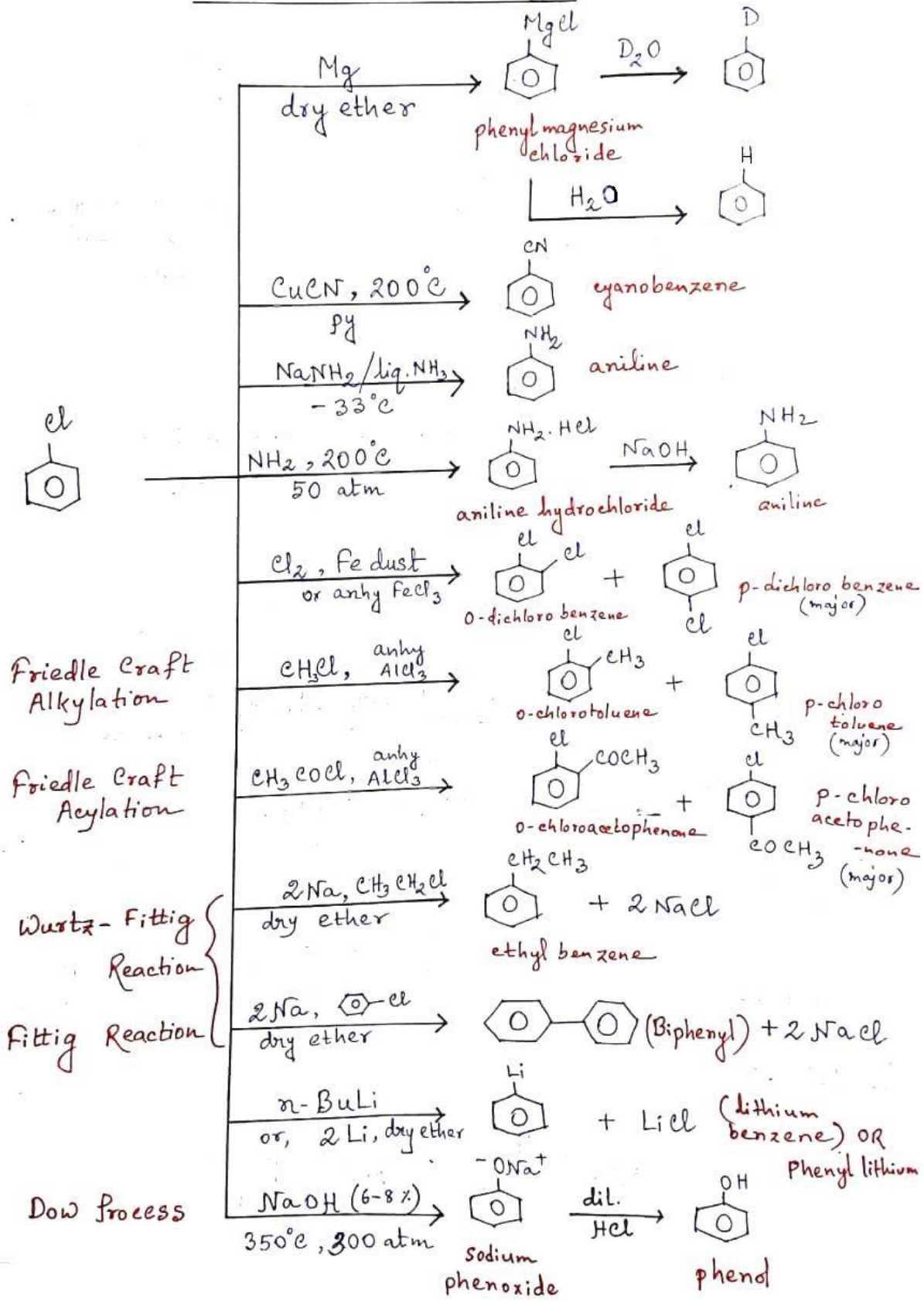


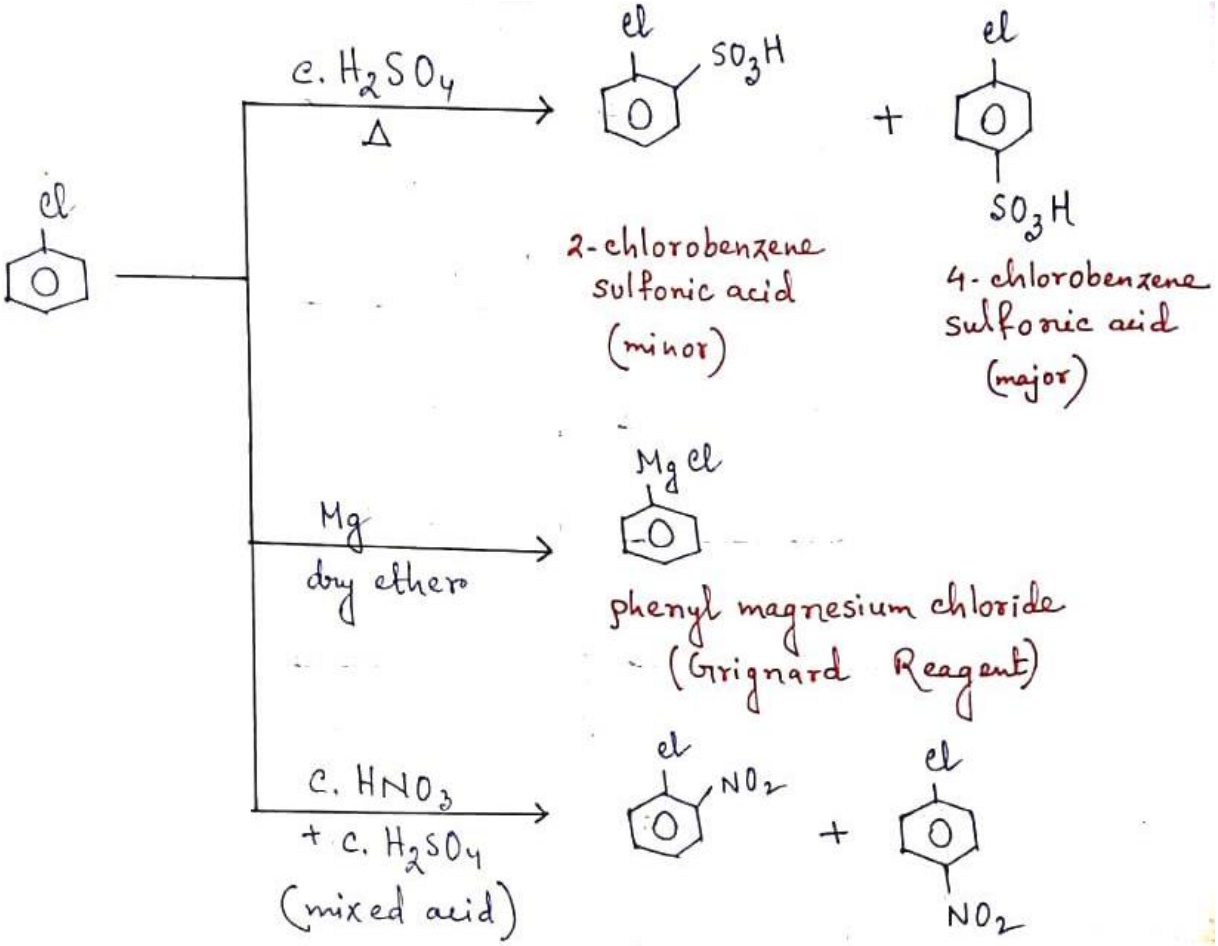
Schiemann Reaction:



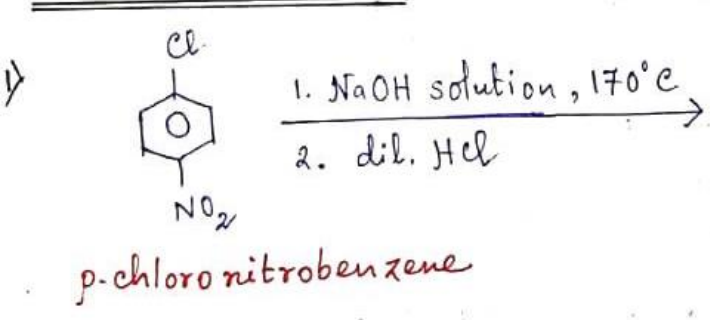

toluene
or methyl benzene
Cl2/ anhy. FeCl3
minor
o-chlorotoluene
major
p-chloro toluene
SO2Cl2 (sulfuryl chloride)
sunlight(hν), 475 K
little peroxide
+ SO2↑ + HCl
Benzyl chloride
Cl2, hν
383 K
Benzyl chloride
Cl2
hν, Δ
Benzal chloride
Cl2, hν
Δ
Benzotrichloride
ethyl benzene
Sunlight
Cl2, 273 K
1- chloro-1- phenyl ethane
hν
Cl2, Δ
1,1-dichloro -1-phenylethane
NBS / hν
little peroxide
(NBS → allylic bromination)
1-bromo-1-phenyl ethane

• Reactions of Haloarenes •

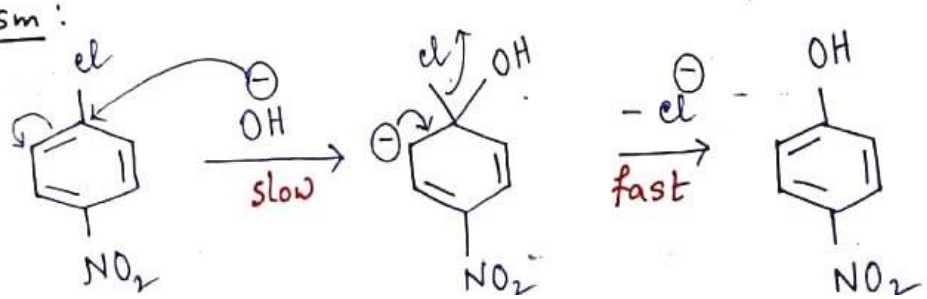




More Reactions :

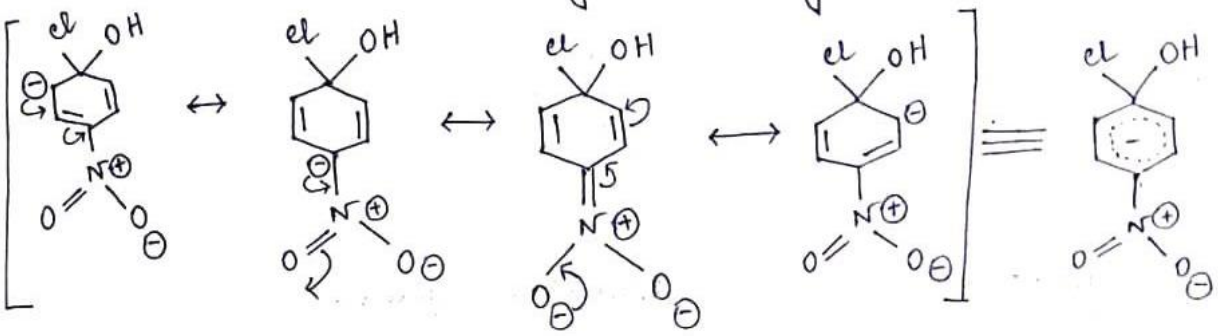


Mechanism :

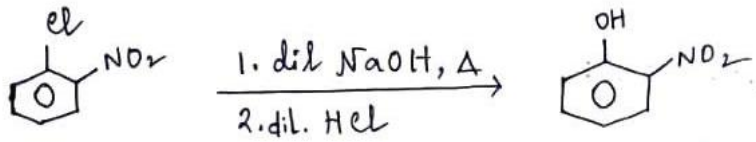


This reaction undergoes through S_NAr mechanism.
(S_NAr → Aromatic nucleophilic substitution)

The intermediate carbanion stabilizes through the formation of the following resonating structures.

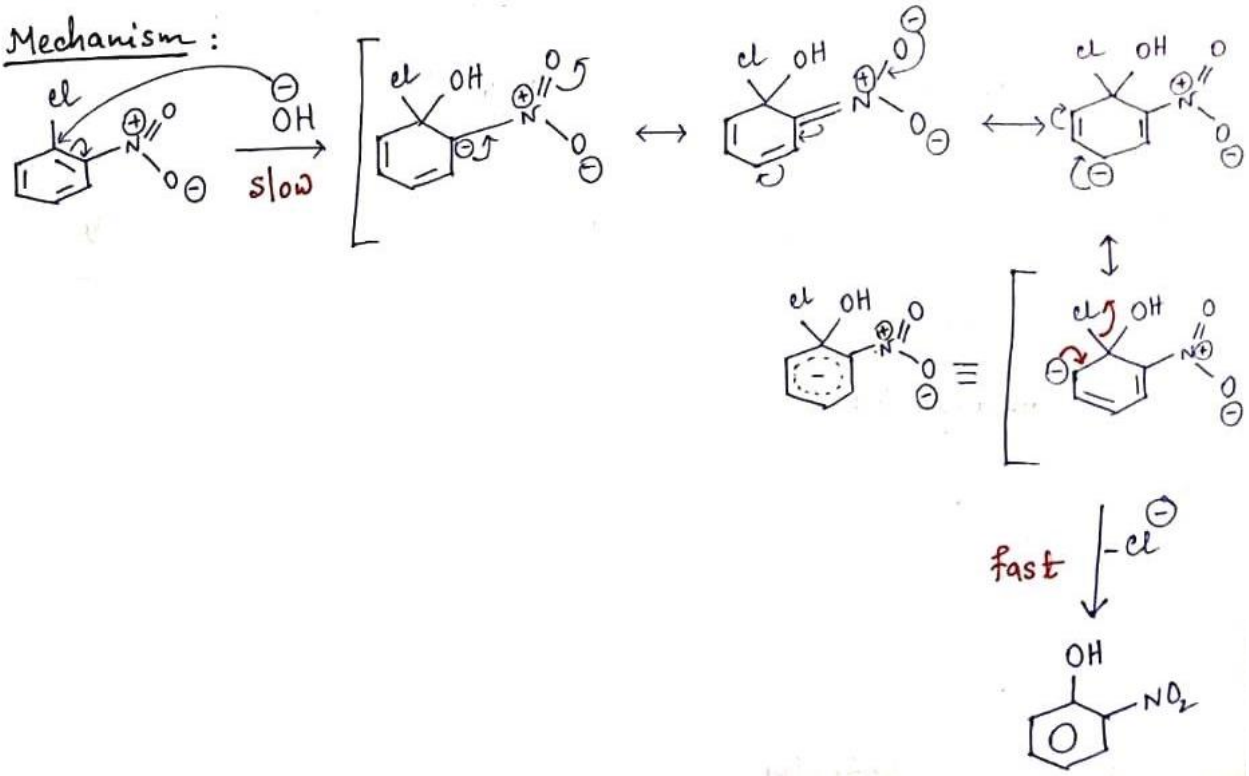


2)

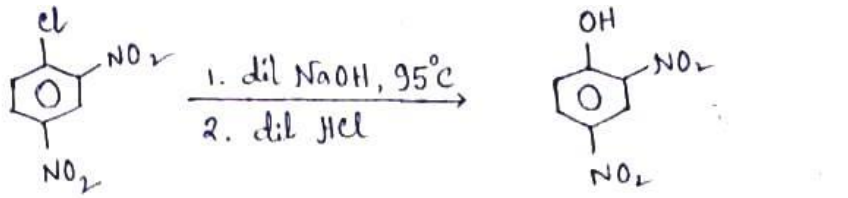


o-chloronitrobenzene → o-nitrophenol

Mechanism:

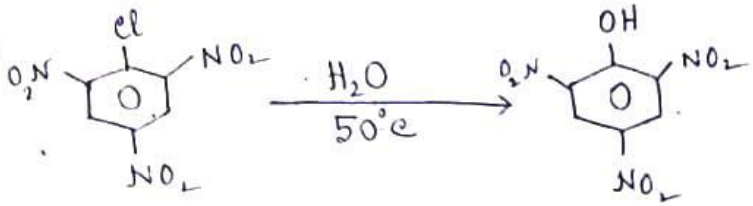


3)



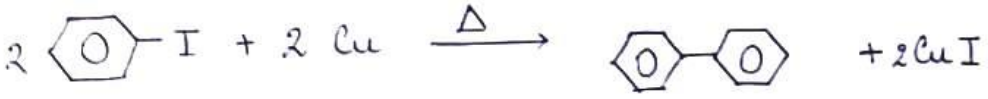
2,4-dinitrochloro benzene — 2,4-dinitrophenol

4)



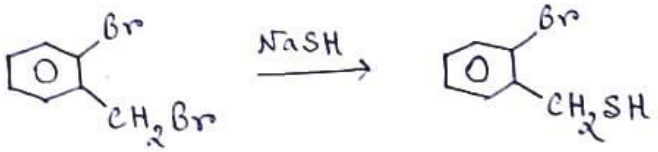
2,4,6-trinitro chlorobenzene — 2,4,6-trinitrophenol

5) Ullmann Reaction :



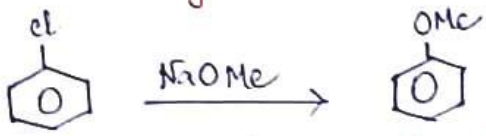
Iodobenzene — Biphenyl

6)



o-bromobenzyl bromide — o-bromobenzyl thiol

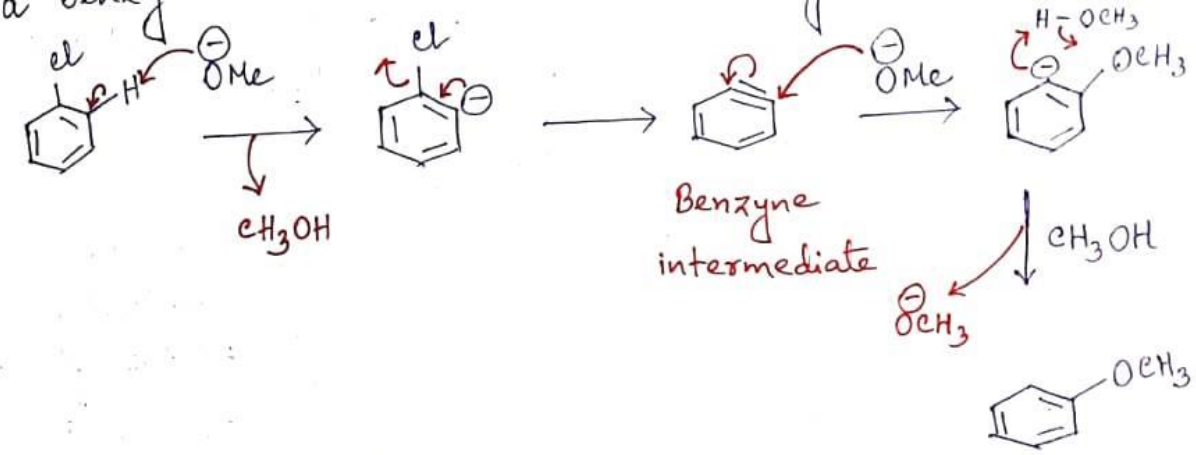
7)



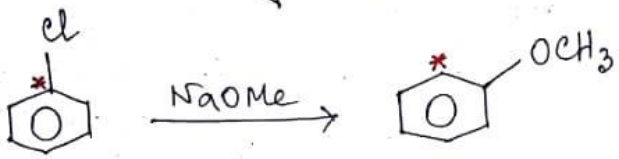
Anisole

Chlorobenzene is inert towards most form of nucleophilic substitution as C–Cl bond is strong and dissociation of Cl^- is therefore not very likely.

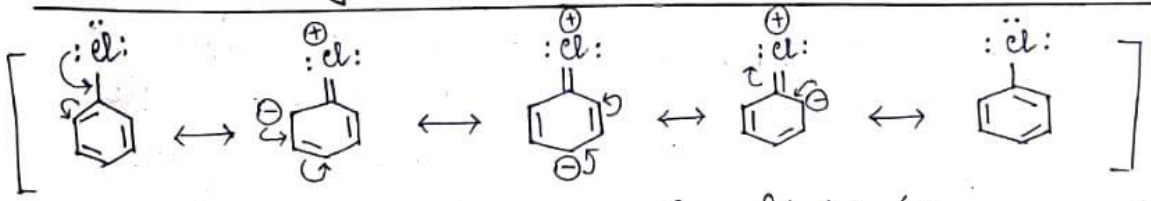
This reaction actually goes through the formation of a benzyne intermediate followed by E, cb mechanism.



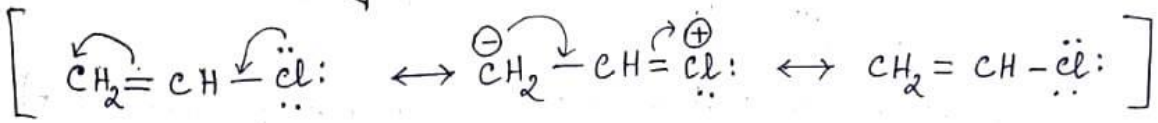
This reaction mechanism can be proved by isotope labelling (C^{13}).



8) Reason of very low reactivity of aryl and venyl halide:



Resonating structures of aryl halide (chloro benzene)



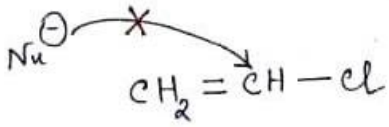
Resonating structures of venyl chloride

i) In aryl halide, the lone pairs of electrons on halogen atom are in conjugation with the π-electrons of benzene ring and stabilize through the formation of the resonating structures. (Same for venyl halide)

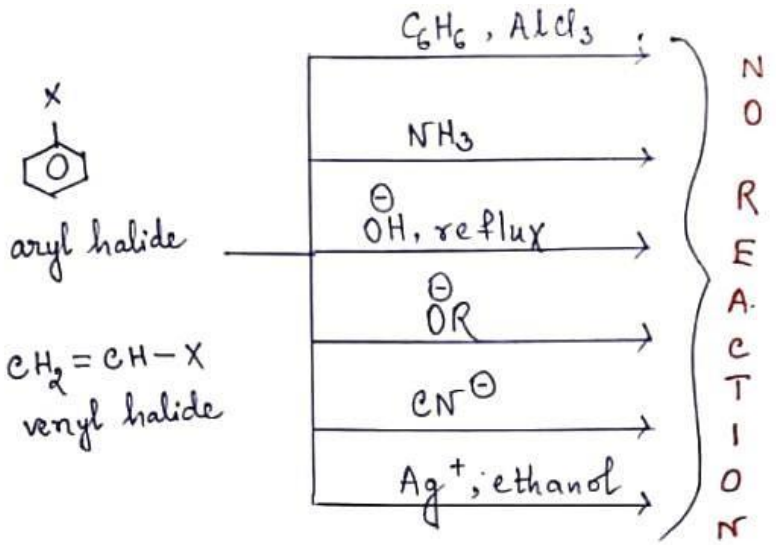
ii) Because of resonance, C–Cl bond gets partial double bond charecter and gets very strong that can not undergo S_N1 and S_N2 reaction.

iii) In case of alkyl halide, the C atom of C–X is sp^3 hybridised where as in case of aryl halide or venyl halide C atom is sp^2 hybridised. As the sp^2 hybrid orbital having more s charecter (33.33%.) is smaller in size than sp^3 hybrid orbital having less s charecter (25%.), C–X bond of aryl or venyl halide formed by (sp^2 – p) overlapping is small in length and stronger than C–X bond of alkyl halide formed by (sp^3 – p) overlapping. So they can not partieipate in S_N1 or S_N2 reaction mechanism.

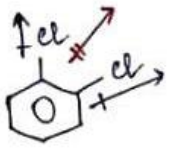
iv) Benzene ring of aryl halide or double bond of venyl halide are electron rich, therefore they repulse and restrict the backside attack of electron rich nucleophile. As a result S_N2 mechanism does not take place



v) Aryl or venyl cation (after elimination of halogen atom) can not stabilize through resonance because the (+)ve charge and double bond are not in conjugation.

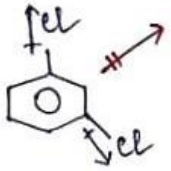


9) Dipole moment :



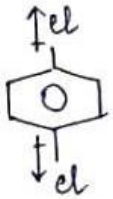
o-dichlorobenzene

$\mu = 2.54$ D



m-dichloro benzene

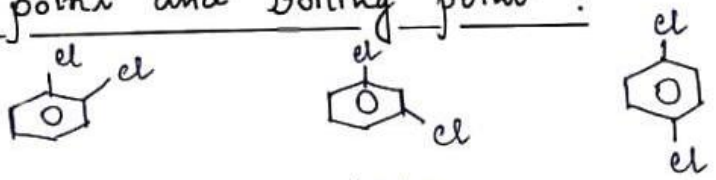
$\mu = 1.72$ D



p-dichloro benzene

$\mu = 0$ D

10) Melting point and Boiling point :



Boiling Pt :	453 K	446 K	448 K
Melting Pt :	256 K	249 K	325 K

Boiling points of these three isomers are almost same but melting point of p-isomer is much higher than o- and m-isomers. The molecules of p-isomers are closely packed in crystal lattice due to their balanced or regular shape. As a result intermolecular force of attraction between them is very high and higher energy is required to break the crystal lattice. So melting point of p-isomer is very higher than the other isomers.