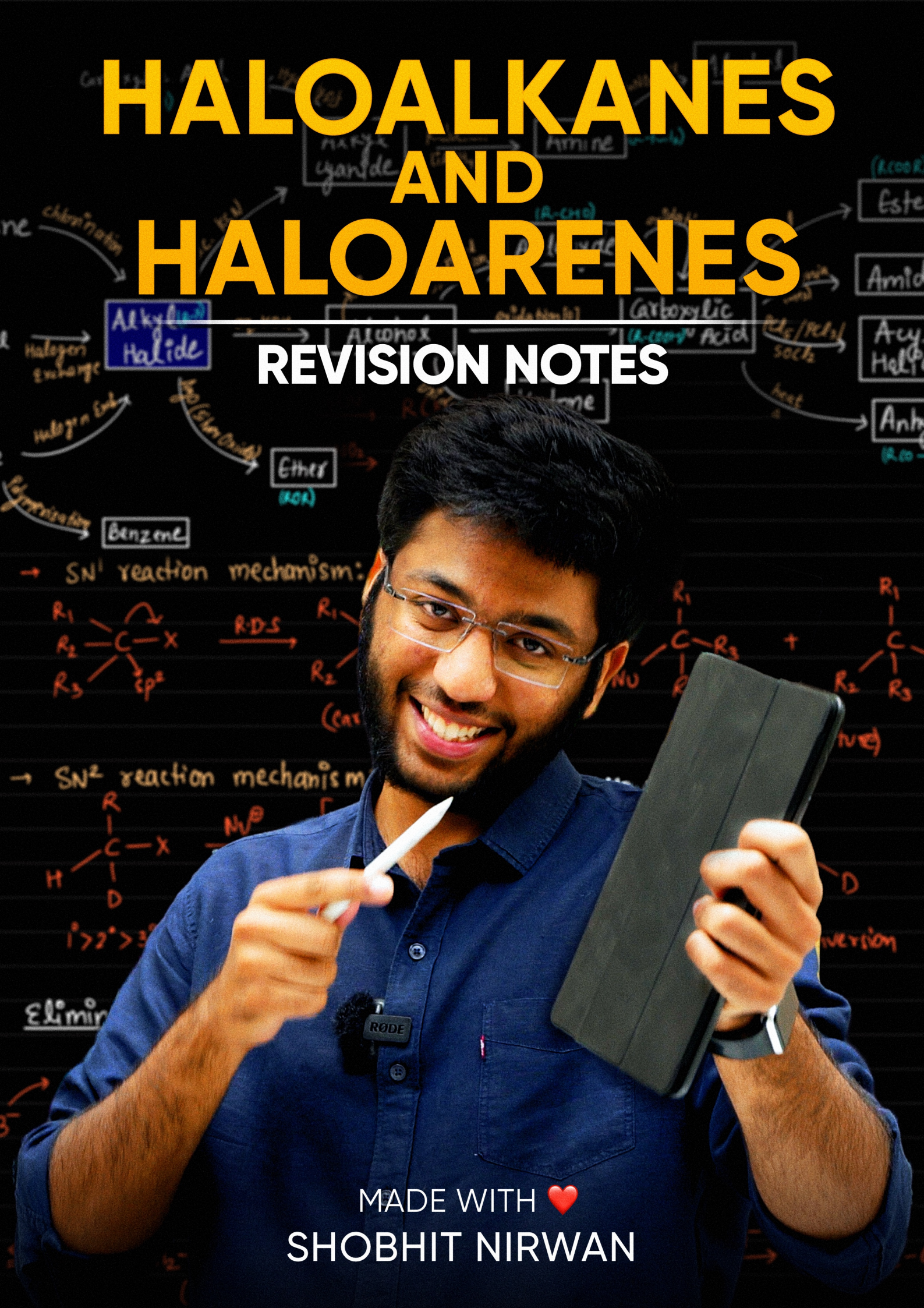
HALOALKANES AND HALOARENES

REVISION NOTES



MADE WITH ❤️

SHOBHIT NIRWAN

NAME REACTIONS OF THIS CHAPTER

[1] **Finkelstein Reaction:** (Alkyl halide preparation)

$$R-X + Na-I \longrightarrow R-I + NaX \quad [X = Cl, Br]$$

[This reaction can be favoured in forward direction by precipitating NaX with dry acetone. Acc. to Le Chatlier's Principle]

[2] **Swartz Reaction:**

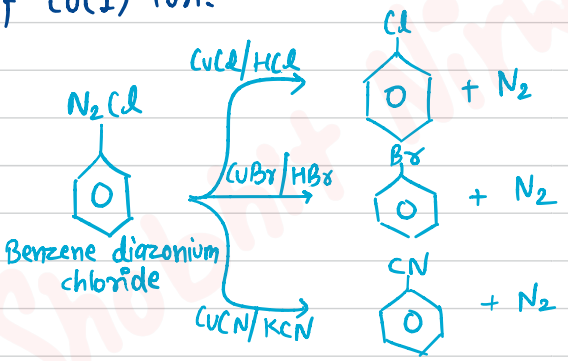
$$R-X + \text{Metallic floride} \longrightarrow R-F + AgX$$

$(X = Cl, Br)$ [AgF, Hg_2F_2, CoF_2, SbF_3]

finkelstein and swartz Rxn ⇒ Halogen exchange rxn

[3] **Sandmayer's Reaction:**

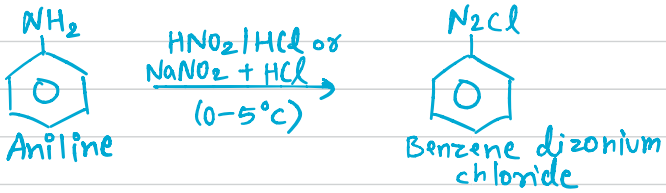
Cl, Br and CN → can be easily introduced in the benzene ring of benzene diazonium salt in presence of Cu(I) ion.



(Kuch kaam Ki Baat)

K³B: **Diazotization Reaction:** (How this Benzene diazonium chloride is formed)

Diazonium ($C_6H_5N_2Cl$) is prepared by treating ice cold solution of Aniline in excess dilute HCl with aq. soln of $NaNO_2$ at low temperature.



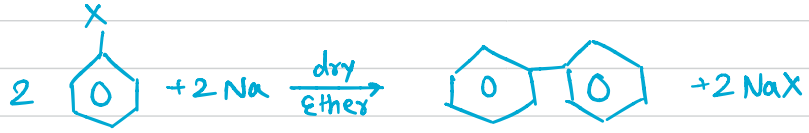
[4] **Wurtz Reaction:**

$$R-X + 2Na + X-R \xrightarrow[\text{ether}]{\text{dry}} R-R + 2NaX$$

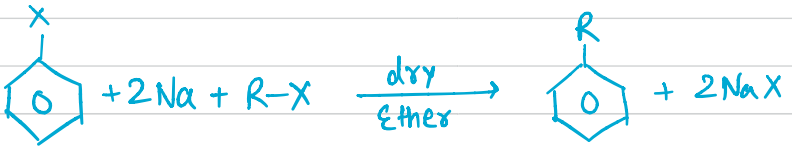
eg: $CH_3-CH_2-Br + 2Na + Br-CH_2-CH_3 \xrightarrow{\text{Dry ether}} CH_3-CH_2-CH_2-CH_3 + 2NaBr$

eg: $2CH_3-X + 2Na \xrightarrow{\text{dry ether}} CH_3-CH_3 + 2NaX$

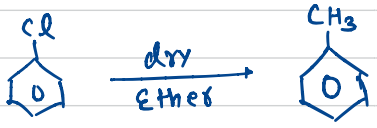
[5] **Fittig's Reaction:**



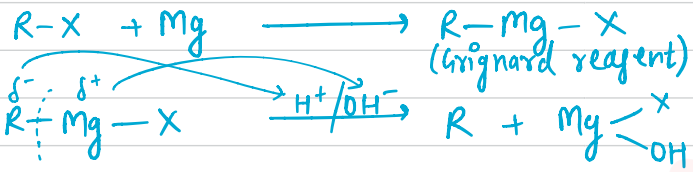
[6] **Wurtz-Fittig's Reaction:**



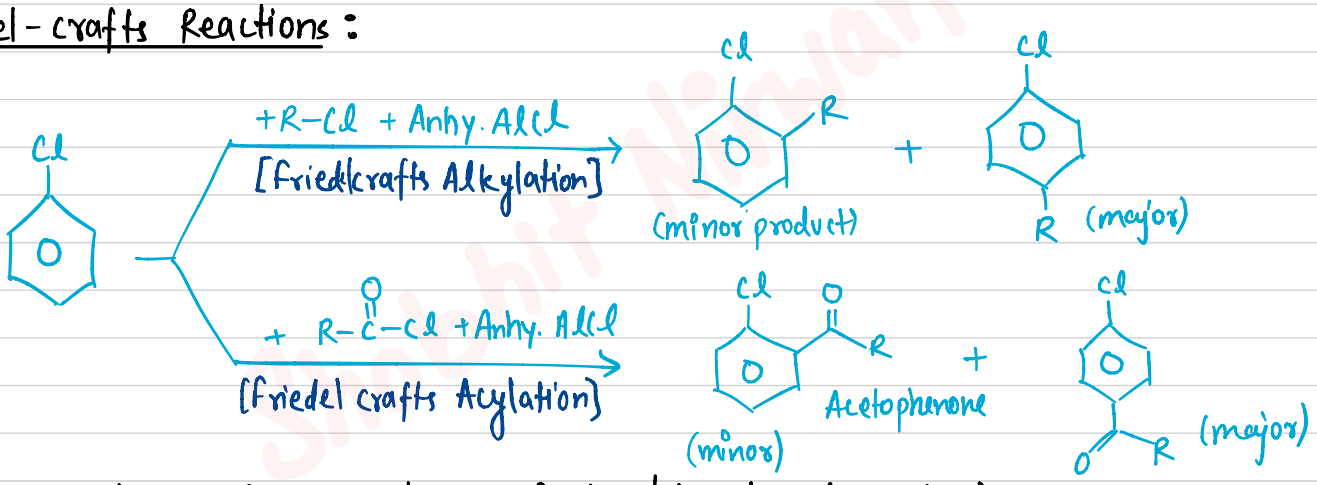
eg: $CH_3-Cl + 2Na +$



[7] **Reaction with Metal (Grignard reagent):**



[8] **Friedel-crafts Reactions:**



[9] **Saytzaff Rule:** (zaitser rule / β-elimination / dehydrohalogenation)

Rule: More alkyl group containing alkene is major product.

eg: $CH_3-\underset{\beta}{CH}(Br)-\underset{\alpha}{CH_2}-\underset{\beta}{CH_2}-CH_3$ $\xrightarrow[KOH]{\text{Ethanoic}}$ $CH_2=CH-CH_2-CH_2-CH_3$

$CH_3-CH=CH-CH_2-CH_3$ (Major Product)

∵ 2 alkyl group

Note: Now we'll use these Name reactions further in these notes by mentioning only name of the reaction.

PREPARATIONS

HALOALKANES

[1] From Alcohols:

→ Luca's test (Luca's reagent = Conc. HCl + Anhy. $ZnCl_2$)

$$R-OH + HCl \xrightarrow{ZnCl_2} R-Cl + H_2O$$

→ Darzen's test (best process as SO_2 and HCl is released as gas)

$$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$$

Thionyl chloride

→ $R-OH + NaBr + H_2SO_4 \longrightarrow R-Br + NaHSO_4 + H_2O$

→ $3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$

[Boric acid]

→ $R-OH \xrightarrow[X_2 = Br_2, I_2]{\text{red } P/X_2} R-X$

→ $R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$

[2] From Hydrocarbons:

→ From Alkanes:

(i) $RH + X_2 \xrightarrow{h\nu} R-X + HX$

(ii) $CH_3-CH_2-CH_2-CH_3 \xrightarrow{Cl_2} Cl-CH_2-CH_2-CH_2-CH_3 + CH_3-CHCl-CH_2-CH_3$

two type of H_s so 2 product will be there with Cl on diff. position.

→ From Alkenes:

(i) Add^n of Hydrogen Halide: (only Br, Cl, I)

$$>C=C< + HX \longrightarrow >C(H)-C(X)<$$

eg: $CH_3-CH=CH_2 + HCl \longrightarrow CH_3-\underset{Cl}{CH}-\underset{H}{CH_2}$

(ii) Add^n of Halogens:

$$H_2C=CH_2 + Br_2 \xrightarrow{CCl_4} Br_2-CH_2-CH_2-Br$$

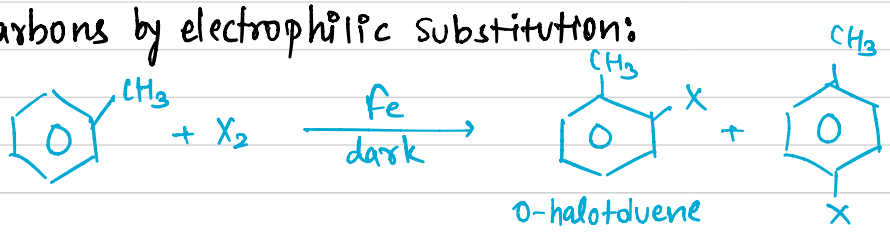
add^n of Br in CCl_4 to alkene give reddish brom fumes help in detach of =/- bonds.

[3] From Halogen Exchange:

By finkelstein and swartz reaction (mentioned earlies)

HALOARENES

[1] From hydrocarbons by electrophilic substitution:

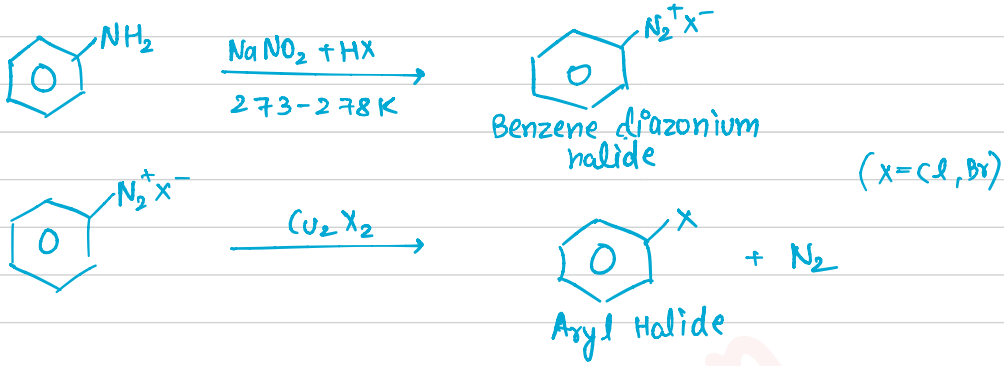


o-halotoluene

p-halotoluene

[2] From amines by sandmeyer's Reaction:

(i)



(X = Cl, Br)

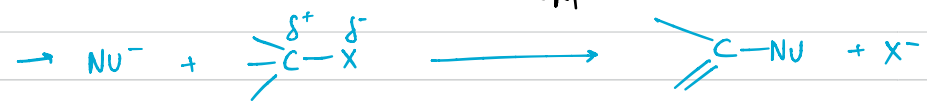
Aryl Halide

(ii) If Iodine, then no Cu required:

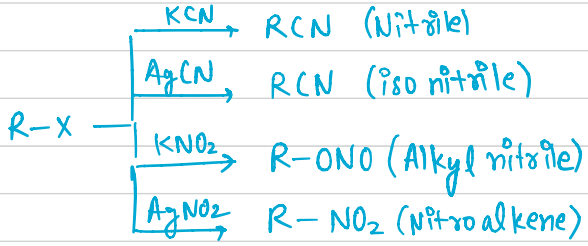
CHEMICAL REACTIONS

HALOALKANES

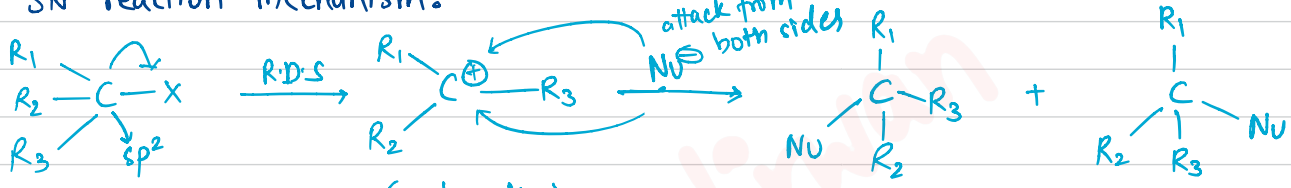
[1] Nucleophilic substitution — S_N2 / S_N1



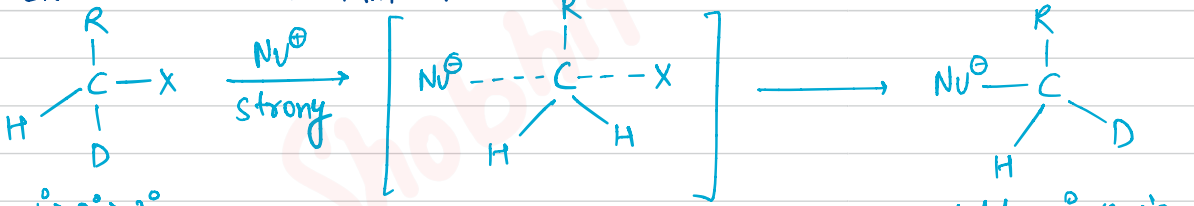
→ other rx^{n}s in table 10.4, but main ↓



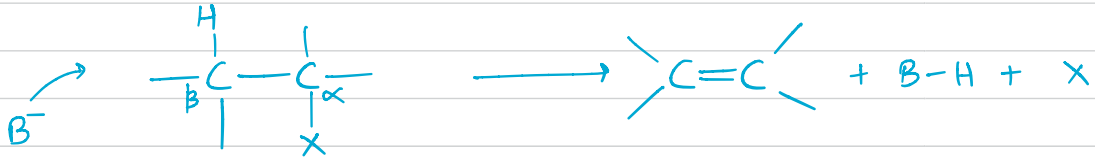
→ S_N1 reaction mechanism:



→ S_N2 reaction mechanism:



[2] Elimination Reaction:



B = Base , X = leaving group

eg: $H_3C-CH_2-CH=CH-CH_3$ (81%) ← $^{OH^-}$ $H_3C-CH_2-CH_2-CH(Br)-CH_2(H)$ $\xrightarrow{OH^-}$ $H_3C-CH_2-CH_2-CH_2=CH$ (19%)

[3] Reaction with metals:

→ Grignard Reagent
→ Wurtz Reaction

[both mentioned earlier]

HALOARENES

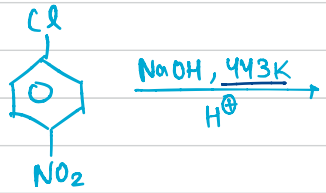
[1] Nucleophilic Substitution:

→ Chlorobenzene ⟶ Phenol (Dow's Process)

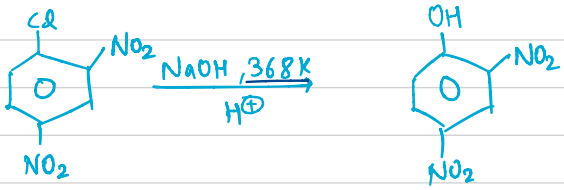
→ This process is very costly, so alternatively we add (NO_2) so at less temp it is affordable.

And, if we add more NO_2 grps ⇒ temp ↓ and rxn easily occurs.

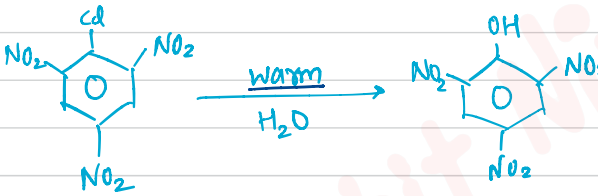
i.e.



add more NO_2 :

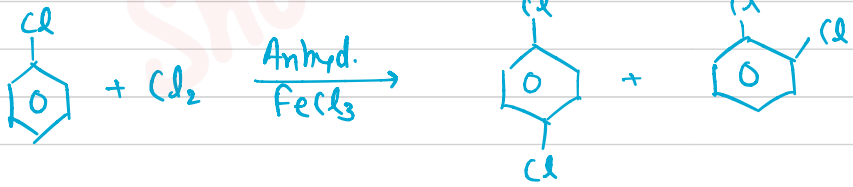


add more NO_2 :

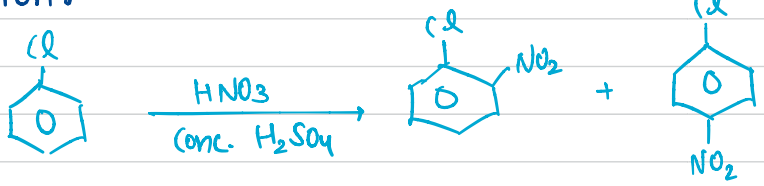


[2] Electrophilic Substitution Rxn: (all 'Para' products → major)

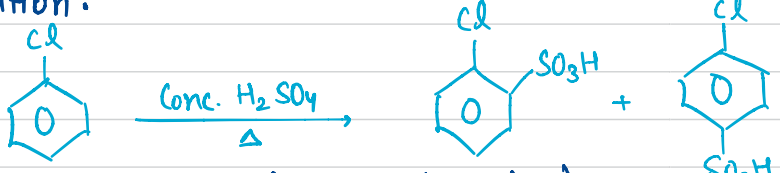
→ Halogenation:



→ Nitration:



→ Sulphonation:



→ friedel crafts Rxn (mentioned earlier)

[3] Reaction with metals:

→ Wurtz fitig (mentioned earlier)

→ fitig

PHYSICAL PROPERTIES

i) They are colourless
ii) Polar but insoluble in water
iii) Soluble in org. solvents
iv) Polarity → R-F > R-Cl > R-Br > R-I
v) Boiling point ∝ Molecular wt. → R-F < R-Cl < R-Br < R-I

vi) Melting Point (seen by symmetry)