(2) By Alcohols → Alkyl halide can be prepared by four processes :-

Alcohol

- Reaction with HX in presence of Anhy $ZnCl_2$ | H_2SO_4
- Reaction with PX_3 | PCl_5
- Reaction with X_2 in presence of Red P
- Reaction with $SOCl_2$

a) Preparation of R-X by alcohol & HX :→ When alcohol (aliphatic which may be 1° or 2° or 3°) react with HX in presence of Anhy $ZnCl_2$ and H_2SO_4 it form alkyl halide

$$R-\overset{\delta-}{O}H + H\overset{\delta+}{X} \xrightarrow[\text{Conc } H_2SO_4]{\text{Anhy. } ZnCl_2} R-X + H_2O$$

$$C_2H_5OH + HCl \xrightarrow{\text{Anhy } ZnCl_2} C_2H_5Cl + H_2O.$$

$HCl + ZnCl_2$ is called Lucas reagent which is used to distinguish 1°, 2° & 3° Alcohols.

b) $$C_2H_5OH + KBr + H_2SO_4 \longrightarrow C_2H_5Br + KHSO_4 + H_2O.$$

OR $$KBr + H_2SO_4 \longrightarrow HBr + KHSO_4$$

$$C_2H_5OH + HBr \xrightarrow{\Delta} C_2H_5Br + H_2O.$$

$$C_2H_5OH + KI + H_2SO_4 \longrightarrow C_2H_5I + KHSO_4 + H_2O.$$

OR $$KI + H_2SO_4 \longrightarrow HI + KHSO_4$$

$$C_2H_5OH + HI \longrightarrow C_2H_5I + H_2O.$$

Reactivity of HX → HI > HBr > HCl.

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Reaction mechanism

- Protonation

$CH_3-CH_2 + \ddot{O}-H + H^+ \longrightarrow CH_3-CH_2-\overset{+}{O}(H)-H$

- formation of carbocation:-

$CH_3-CH_2-\overset{+}{O}(H)-H \longrightarrow CH_3-\overset{\oplus}{C}H_2 + H_2O$

- Nucleophilic attack:-

$CH_3-\overset{\oplus}{C}H_2 + Cl^- \longrightarrow CH_3-CH_2-Cl$

The reaction is nucleophilic substitution reaction which has gone through the formation of carbocation so 3° alcohol > 2° alcohol > 1° Alcohol. for their reactivity.

Note :- 3° Alcohol can react with HX without Anhy $ZnCl_2$ also, because by +I effect & by hyperconjugation 3° carbocation is more stable.

II. Aromatic halide or aryl halide can not be prepared by this method.

- By PX_3 / PCl_5 :-

When alcohol (1° Aliphatic) react with PCl_3 / PBr_3 & PCl_5 it give R-X.

$3\,CH_3-CH_2-OH + PCl_3 \longrightarrow 3\cdot CH_3-CH_2-Cl + H_3PO_3$

$3\,CH_3-CH_2-OH + PBr_3 \longrightarrow 3\cdot CH_3-CH_2-Br + H_3PO_3$

$3\,CH_3-CH_2-OH + PI_3 \longrightarrow 3\cdot CH_3-CH_2-I + H_3PO_3$

Note: Although PBr_3 & PI_3 are not so stable so PCl_3 is the main reaction.

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• $CH_3-CH_2-OH + PCl_5 \longrightarrow CH_3-CH_2-Cl + POCl_3 + HCl$.

With X_2 & Red P: When alcohol react with X_2 (Cl/Br) in presence of red phosphorus it gives R-X.

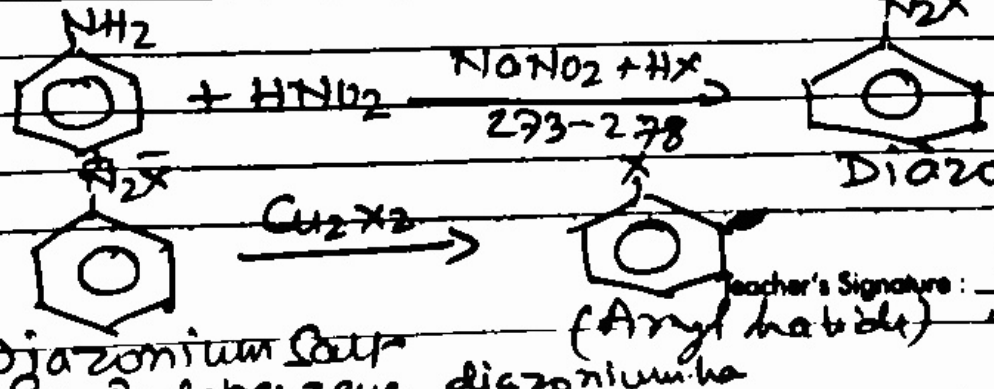
$$CH_3-CH_2-OH + X_2 \xrightarrow{\text{Red P}} CH_3-CH_2-X$$

Where $X_2 = Cl_2/Br_2$.

• With $SOCl_2$:- When alcohol react with $SOCl_2$ it form R-Cl and SO_2 & HCl, in this reaction byproducts are gases so it escape automatically, hence we don't have to separate byproduct from main product, so this method is highly preferred for the preparation of R-Cl.

$$CH_3-CH_2-OH + SOCl_2 \longrightarrow CH_3-CH_2-Cl + SO_2\uparrow + HCl\uparrow$$

(3) By Sandmayer reaction :- When primary or 1° amine dissolved in mineral acid (HX) is treated with Sodium nitrite at very low temperature i.e 273K to 278K it form Benzene diazonium halide, this reaction is called diazotisation reaction, further when treated with Cu_2X_2 it form aryl halide & N_2 will be liberated.



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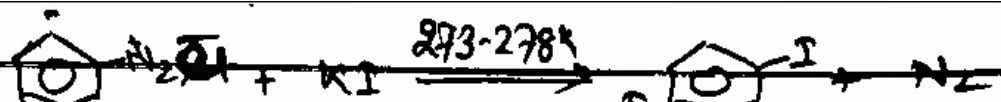

(4) By halogen exchange method:- There are two methods viz i) Finkelstein reaction in which we can prepare alkyl Iodide & ii) Swarf reaction in which we can prepare alkyl fluorides.

(a) Finkelstein reaction:-

$$R-X + NaI \xrightarrow{\text{Dry acetone}} R-I + NaX.$$

Here X = Cl, Br, so I^- can replace Cl^- / Br^- from reactant to form R-I. It is a kind of halogen exchange type reaction. NaI is soluble in acetone, but NaCl & NaBr formed will be precipitated out.

(b) Swarf reaction:

When alkyl chloride or bromide is heated with AgF or Hg_2F_2 or CoF_3 or SbF_3 (Metallic fluorides), then alkyl fluoride is formed due to halogen exchange method. This reaction is called Swarf reaction.

$$CH_3-Br + AgF \xrightarrow{\Delta} CH_3-F + AgBr.$$

$$CH_3-Cl + AgF \xrightarrow{\Delta} CH_3-F + AgCl.$$