Preparation of R-x from alcohols (R-OH)

This method is preferred over other methods because alcohol (R-OH) is cheap and easily available and it is easier to break the R — OH bond.

- 1. By the action of halogen acids (H-X)
- 2. By the action of Phosphorus halides PX_3 and PX_5
- 3. By the action of SO_2Cl_2 (Thionyl Chloride)

1. By the action of H-X:

$$R-OH + H-X \longrightarrow R-X + H_2O$$

Reactivity of halogen acids in the above reaction

$$\boxed{HI > H-Br > H-Cl}$$

Because the order of nucleophilicity of halide ions is $I^- > Br^- > Cl^-$

Reactivity of alcohols with halogen acids is

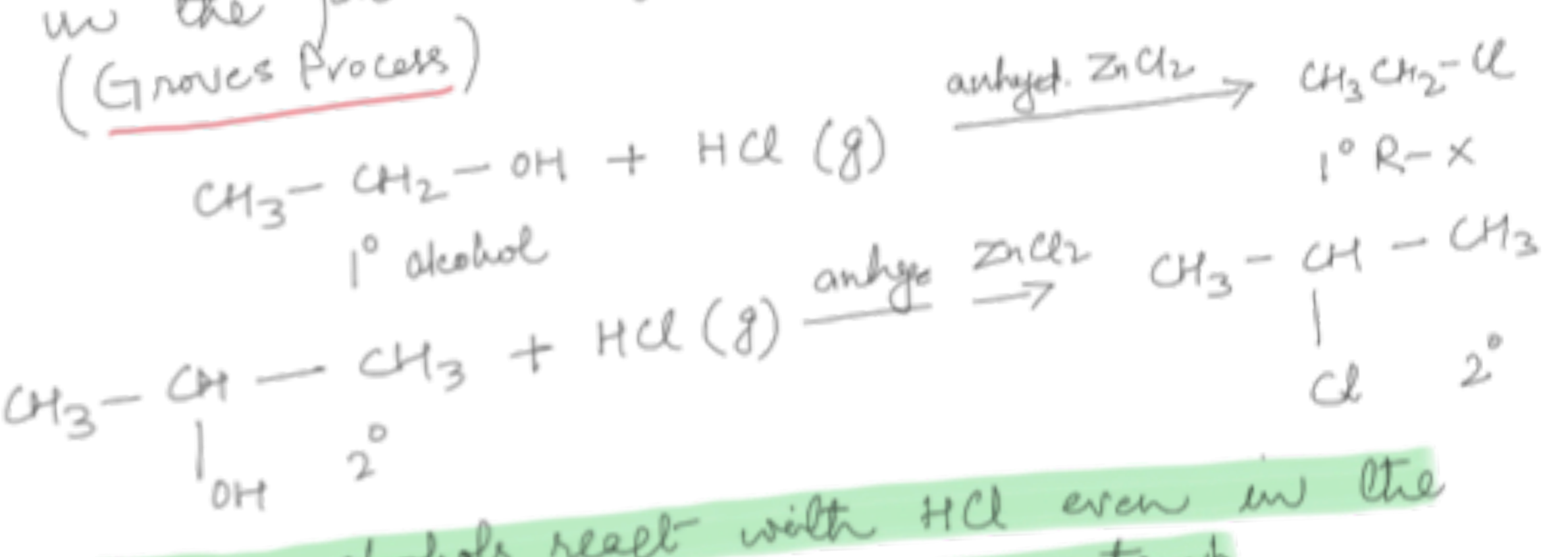
$$\boxed{3^\circ > 2^\circ > 1^\circ}$$

Because the order of stability of incipient Carbocation in the transition state is

$$3^\circ > 2^\circ > 1^\circ$$

Chloroalkanes or Alkyl Chlorides:

Primary and secondary alkyl halides are prepared by passing HCl gas through a suitable alcohol in the presence of anhydrous zinc chloride ($ZnCl_2$) (Groves Process)



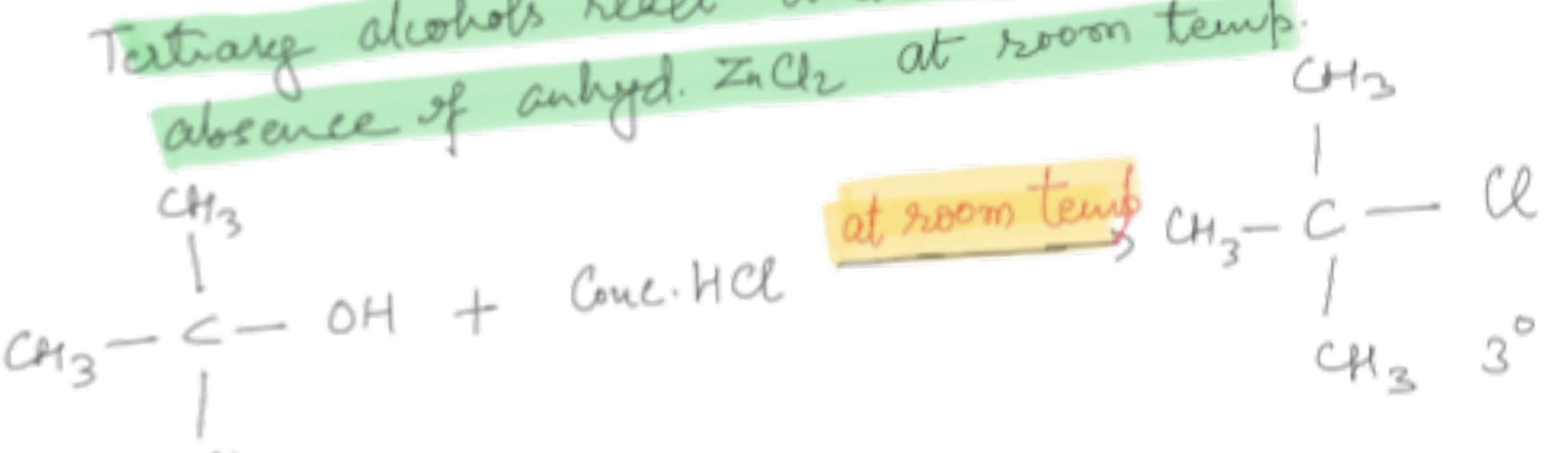
$$CH_3-CH_2-OH + HCl(g) \xrightarrow{\text{anhyd. } ZnCl_2} CH_3CH_2-Cl$$

1° alcohol, 1° R-X

$$CH_3-\underset{\substack{|\\OH}}{CH}-CH_3 + HCl(g) \xrightarrow{\text{anhyd. } ZnCl_2} CH_3-\underset{\substack{|\\Cl}}{CH}-CH_3$$

2°, 2°

Tertiary alcohols react with HCl even in the absence of anhyd. $ZnCl_2$ at room temp.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH + \text{Conc. } HCl \xrightarrow{\text{at room temp}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl$$

3°

Bromoalkanes Bromoalkanes are obtained by refluxing a suitable alcohol with constant boiling HBr (48%) in presence of a small amount of H_2SO_4 as catalyst

$$CH_3-CH_2-OH + HBr \xrightarrow[\text{Reflux}]{H_2SO_4} CH_3-CH_2-Br + H_2O$$

HBr can be generated in situ:

$$KBr + H_2SO_4 \xrightarrow{\Delta} KHSO_4 + HBr$$

Iodoalkanes: Iodoalkanes are prepared by refluxing a suitable alcohol with constant boiling HI (57%).

$$CH_3-CH_2-OH + HI \xrightarrow{\text{Reflux}} CH_3-CH_2-I + H_2O$$

HI may also be prepared in situ

$$KI^{(s)} + H_3PO_4^{(l)} \longrightarrow HI(g) + KH_2PO_4(s)$$

[with KI, H_2SO_4 being an oxidising acid is not used as it oxidises the HI formed back to I_2

step 1. $2KI + H_2SO_4 \longrightarrow 2HI + K_2SO_4$

step 2. $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$

H_3PO_4 is a non-oxidising acid, it does not react further with HI]

By the action of PX_3, PX_5 on alcohols:

Chloroalkanes:

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

$$3ROH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

Bromoalkanes and Iodoalkanes are prepared by the action of PBr_3 and PI_3 respectively on suitable R-OH

PBr_3 and PI_3, being unstable are generally prepared in situ

$$P_4 + 6Br_2 \longrightarrow 4PBr_3$$

$$P_4 + 6I_2 \longrightarrow 4PI_3$$

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

$$3CH_3-OH + PI_3 \longrightarrow 3CH_3-I + H_3PO_3$$

PBr_5 and PI_5 are highly unstable hence not used in this reaction. (PI_5 not formed)

3. $R-OH + SOCl_2$ (Thionyl Chloride)

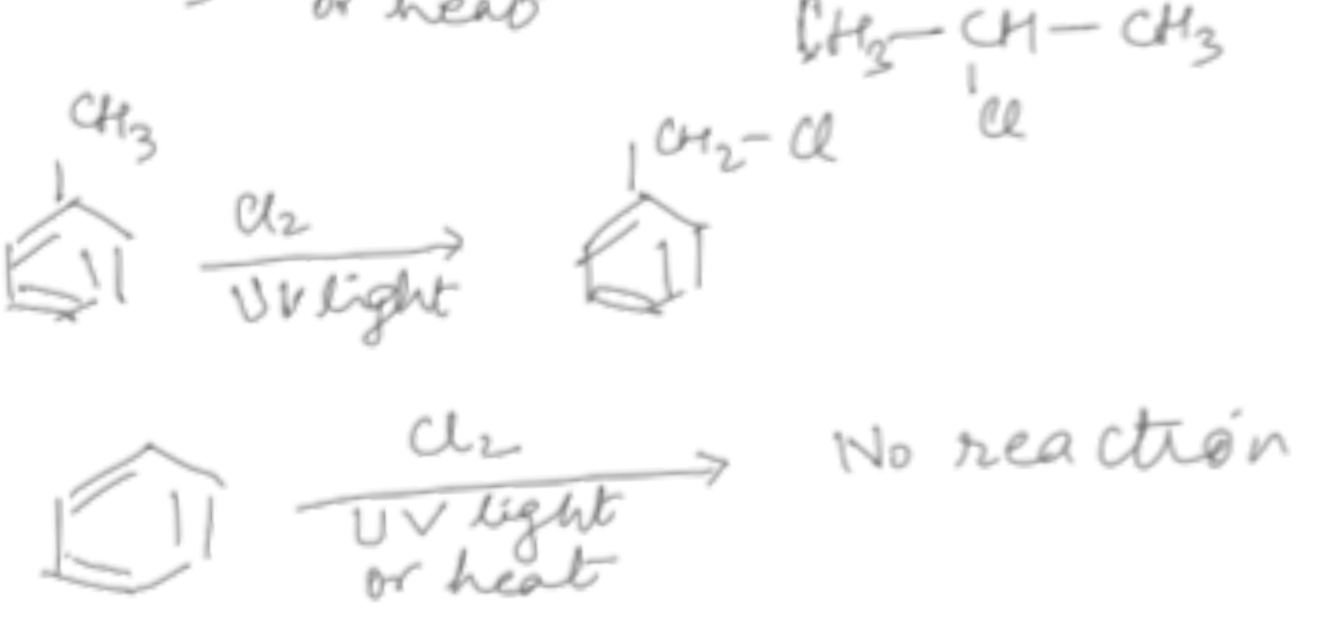
$$CH_3CH_2-OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3-CH_2-Cl + SO_2\uparrow + HCl\uparrow$$

Purest form of R-Cl is obtained because othe two products are escapable gases. This is the reason this method is preferred over HX, PX_3, PX_5.

Preparation of R-X from hydrocarbons by halogenation

(i) Free radical Chlorination and Bromination of alkanes gives a mixture of mono- and polyhaloalkanes. This method is not very useful as separation of the mixture is very difficult.

$$CH_3-CH_2-CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3-CH_2-CH_2-Cl,\ CH_3-\underset{\substack{|\\Cl}}{CH}-CH_3$$



No reaction

Allylic halogenation: Cl_2, Br_2 when heated to 773K, substitution at allylic Carbon takes place:

$$CH_3-CH=CH_2 + Cl_2 \xrightarrow{773K} \underset{\substack{|\\Cl}}{CH_2}-CH=CH_2 + HCl$$

Iodination is reversible: $CH_4 + I_2 \rightleftharpoons CH_3-I + HI$

It may be carried out in the presence of oxidising agents — HIO_3, HNO_3, HgO.

Flourination with pure F_2 gas occurs explosively. Indirect method for flourination is employed. (Swarts Reaction)

(ii) From alkenes

(a) By addition of H-X: HCl, HBr and HI add across double bond in accordance with Markownikov's rule

$$CH_2=CH-CH_3 + H-I \longrightarrow \underset{\text{Minor}}{CH_3-CH_2-CH_2-I} + \underset{\text{major}}{CH_3-\underset{\substack{|\\I}}{CH}-CH_3}$$

In presence of peroxides, H-Br adds accross double bond of the alkene giving anti-Markownikov's product (Kharasch effect or peroxide effect) Also known as Anti-Markownikov's addition.

$$CH_3-CH=CH_2 + H-Br \xrightarrow{\text{Peroxide}} \underset{\text{major product}}{CH_3-CH_2-CH_2-Br}$$

(b) by addition of X_2 (Cl_2, Br_2)

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

Reddish brown colour of Br_2 in CCl_4 is discharged. Reaction is used as test for unsaturation.

$$CH_2=CH_2 + Cl_2 \xrightarrow{CCl_4} \underset{\substack{|\\Cl}}{CH_2}-\underset{\substack{|\\Cl}}{CH_2}$$

Halogen exchange

(i) **Finkelstien Reaction:** R-I is prepared by the reaction of R-Cl and R-Br with NaI in dry acetone. This reaction is known as F. R^{xn}.

$$R-Br + NaI \xrightarrow{\text{dry acetone}} R-I + NaBr$$

Being less soluble than NaI in dry acetone, NaCl and NaBr are precipitated driving the reaction to the forward [Le-Chatlier Principle).

(ii) **Swarts Reaction:** Alkyl Flourides are prepared by heating R-Cl or R-Br in the presence of metallic flourides — AgF, Hg_2F_2, CoF_2 or SbF_3. The reaction is known as Swarts reaction

$$H_3C-Br + AgF \longrightarrow CH_3-F + AgBr$$