Preparation of Haloalkane – 2

From Alcohols.

$$R-OH \xrightarrow[\text{OR } PCl_5 \text{ OR } PCl_3 \text{ OR } SOCl_2]{\text{Conc HCl/Anhyd } ZnCl_2} R-Cl$$

i) Conc HCl / Anhyd $ZnCl_2$ (Luca's Reagant)

$$R-\ddot{O}H + \underset{\text{Conc}}{HCl} \xrightarrow[ZnCl_2]{\text{Anhyd}} R-Cl + H_2O$$

Mechanism.

$$R-\ddot{O}H + ZnCl_2 \longrightarrow R-\overset{+}{O}(H)-\overset{\ominus}{Z}nCl_2$$

$$\downarrow$$

$$R^+ + \overset{\ominus}{Z}nCl_2(OH)$$

R^+ : Carbocation, sp^2 hybridised

$Cl^\ominus$ can attack from upside or downside

Retention + Inversion ⇒ Racemic Mixture

$$R^+ \xrightarrow{Cl^\ominus} R-Cl$$

$$\xrightarrow{H^+} H_2O + ZnCl$$

(S_N1 Mechanism)

Rate ∝ stability of Carbocation

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

Lucas Test → distinguishes $1^\circ, 2^\circ, 3^\circ$ alcohol.

$$R\text{-}OH + \underset{\text{Conc}}{HCl} \xrightarrow[ZnCl_2]{\text{Anhyd}} R\text{-}Cl\downarrow + H_2O$$

white ppt

3° alcohol ⟶ R-Cl↓ immediately
white ppt

2° alcohol ⟶ R-Cl↓ in 5-10 mins
white ppt

1° alcohol ⟶ R-Cl↓ not observed at
white ppt Room Temperature
(only at higher temp)

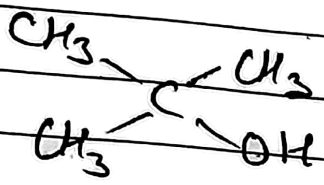
Q) Give a chemical test to distinguish between propan-2-ol and ethanol.

Ans CH_3-CH_2-OH
ethanol (1° alcohol) → No white ppt at Room Temp

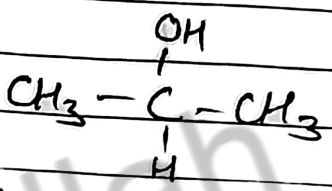
$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$
propan-2-ol (2° alcohol) → white ppt after 5-10 mins

Q) Which of the following gives Lucas Test positive?

a) CH_3-CH_2-OH

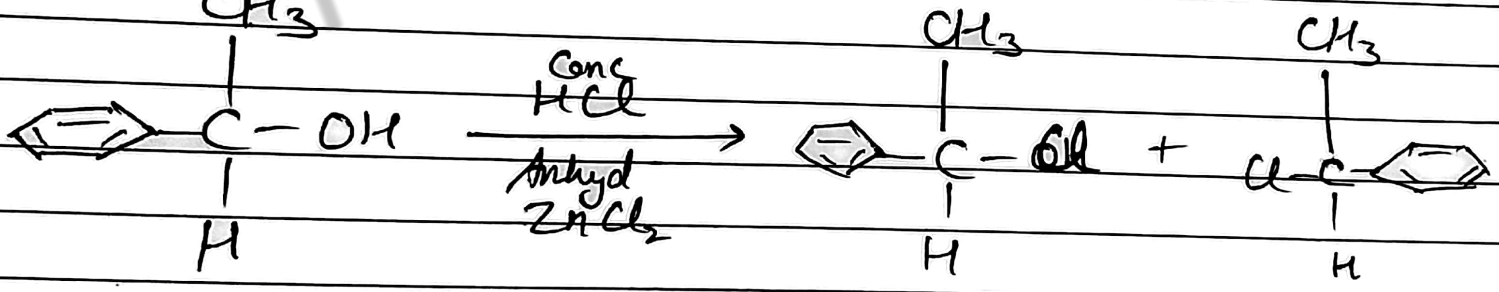
b) 

c) 

d) 

Ans) b & c (c → as  very stable carbocation)

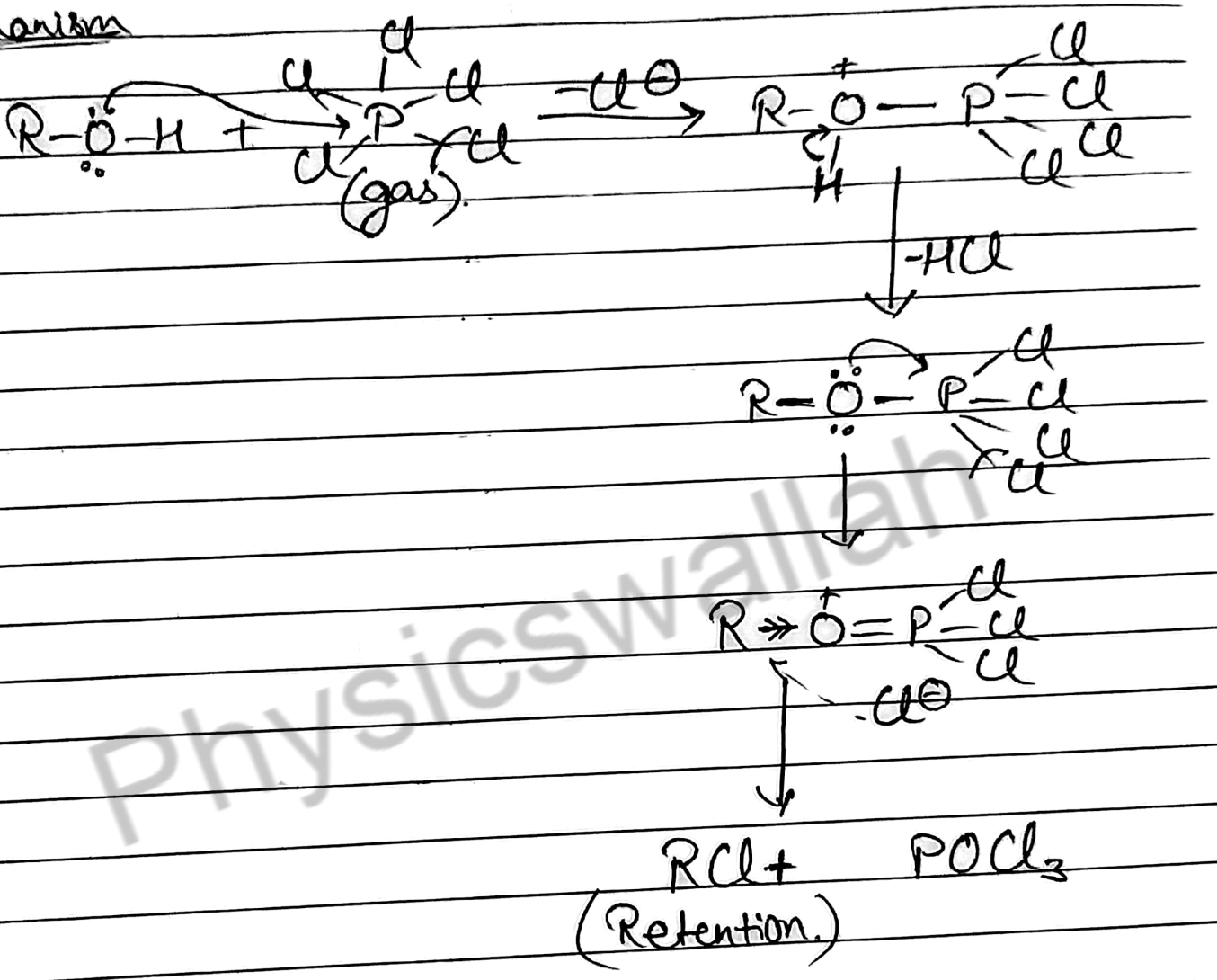
Q) What are the products formed.



ii) PCl_5

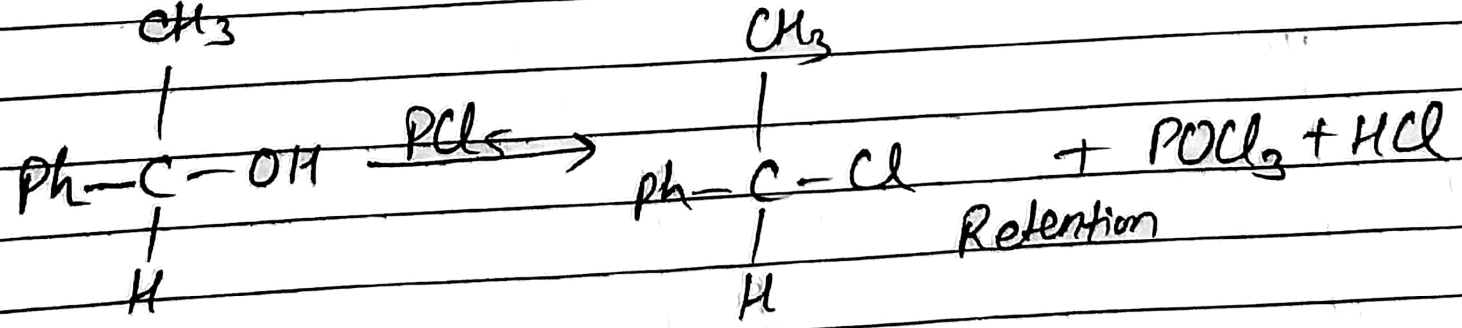
$$R-\ddot{O}-H + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

Mechanism



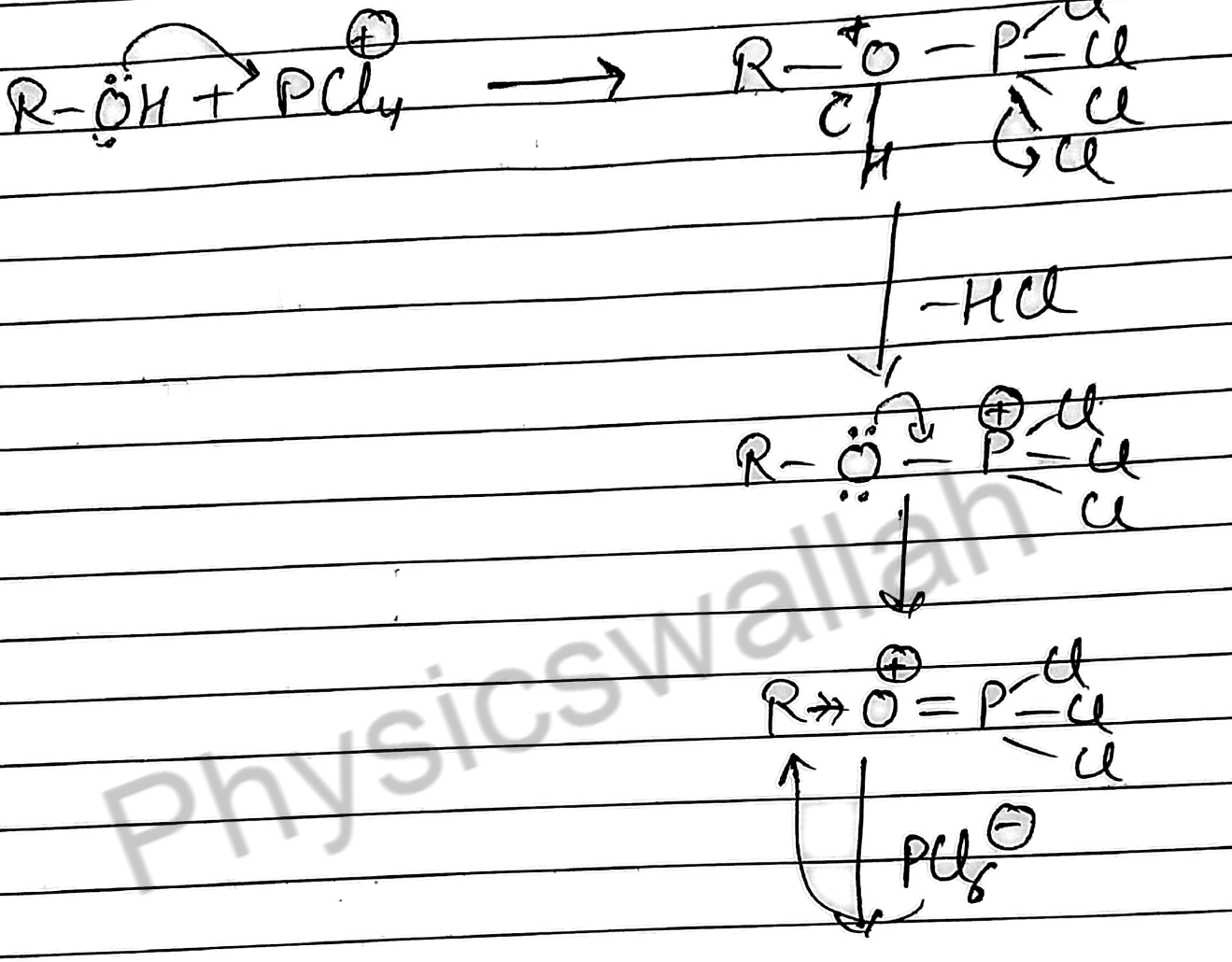
RCl + $POCl_3$

(Retention)



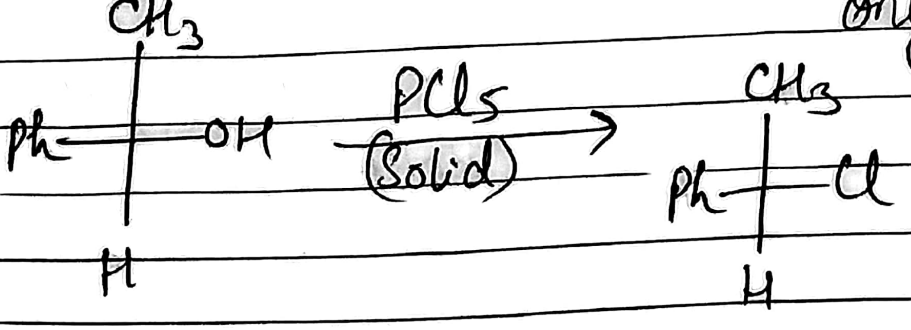
If Solid PCl_5 is given ⇒ Inversion occurs.

Mechanism. Solid $PCl_5 \rightarrow PCl_4^{+} + PCl_6^{\ominus}$



$R\text{-}Cl + POCl_3$

Inversion attack occurs from other side only

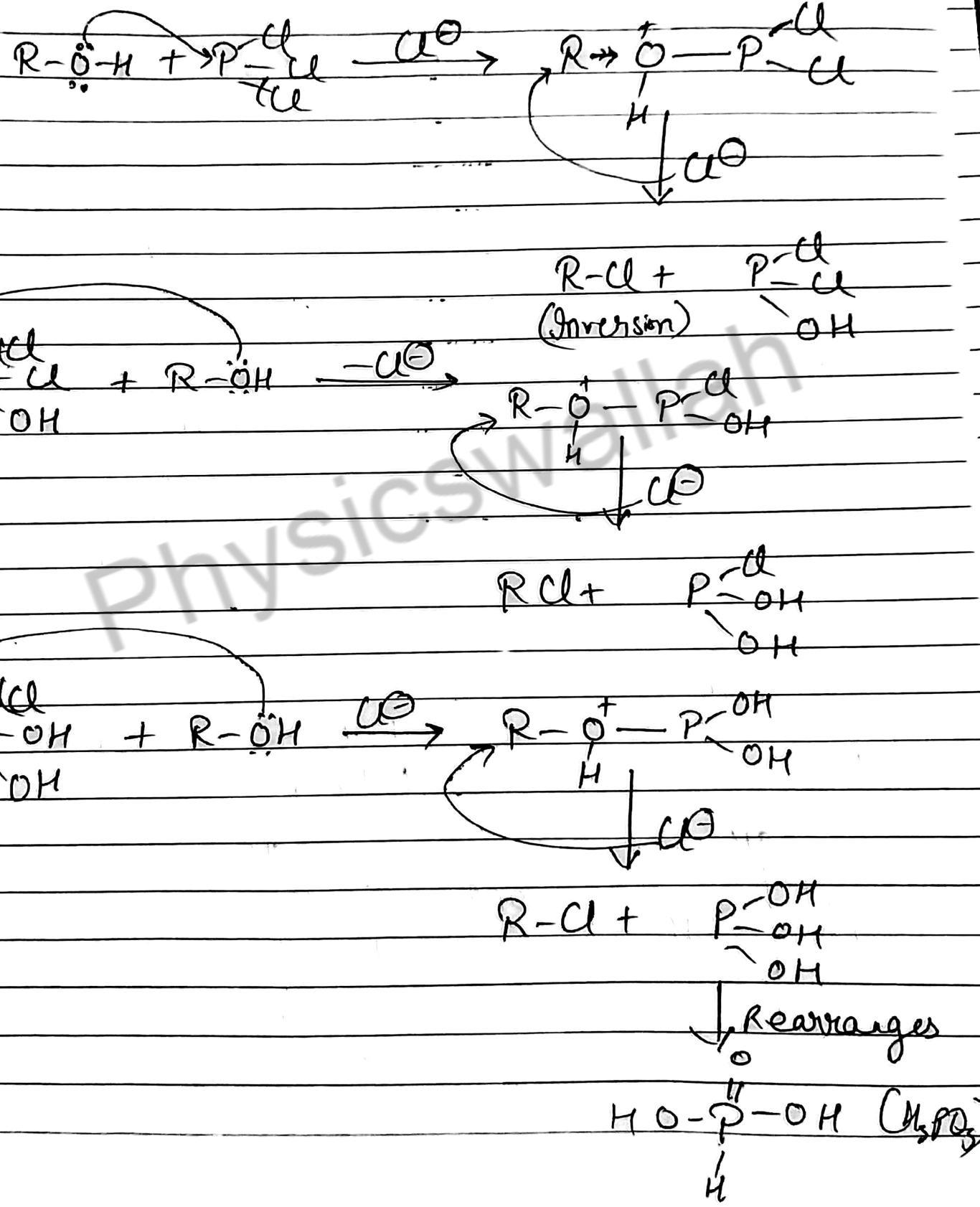


(PBr_5 & PI_5 do not exist)

iii) PCl_3

$$3R-OH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

Mechanism:



$$R-OH \xrightarrow[\text{or } P+Br_2\ (PBr_3)]{P+I_2\ (PI_3)} \begin{matrix} R-I \\ \text{or} \\ R-Br \end{matrix}$$

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$

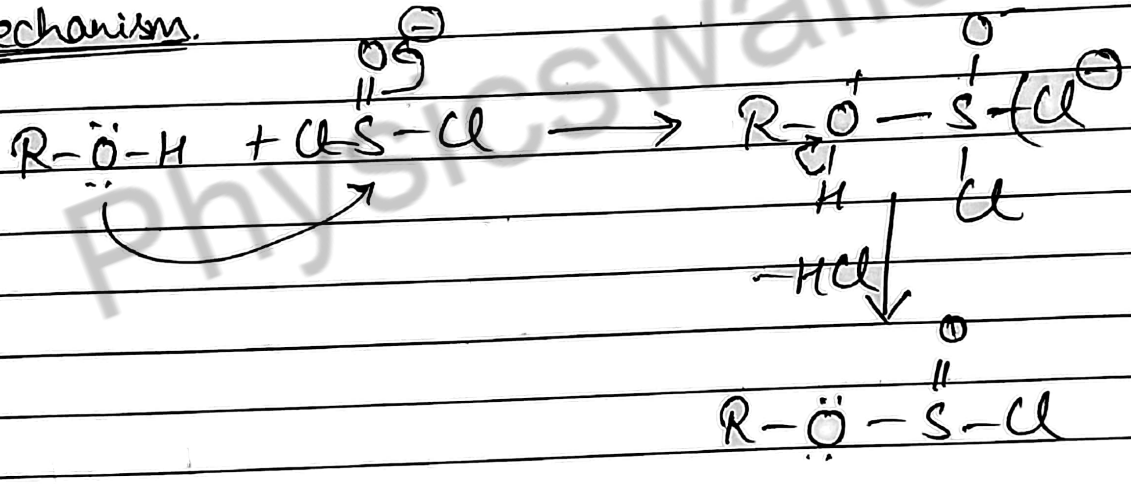
$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$

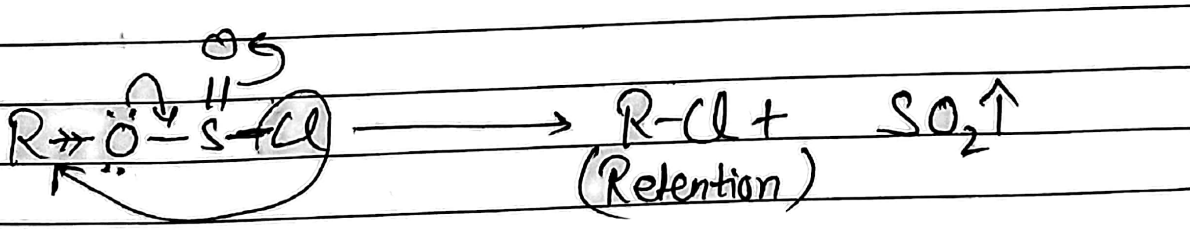
iv) $SOCl_2$ (Best Method to obtain good yield)
(Darzen's Method)

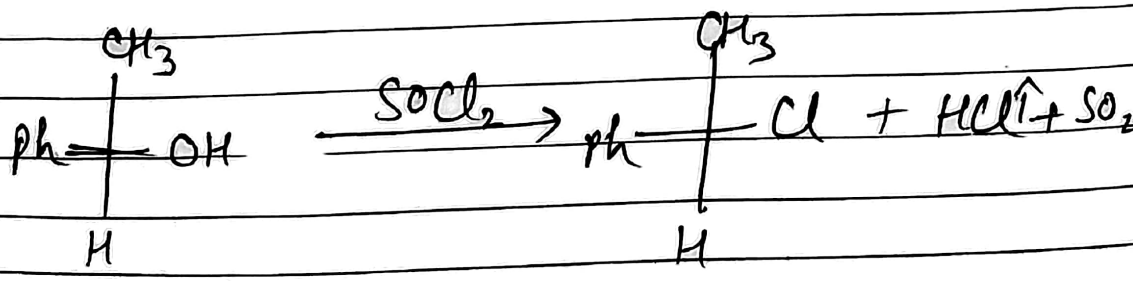
$$R-OH + SOCl_2 \longrightarrow RCl + SO_2\uparrow + HCl\uparrow$$

(By products are gaseous & escapes)

Mechanism.







Summary:

① $R-OH + \underset{Conc}{HCl} \xrightarrow[ZnCl_2]{Anhyd} R-Cl + H_2O$

$3° > 2° > 1°$ (Racemic Mixture)

② $R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$

Retention → if PCl_5 gas

Inversion → if PCl_5 solid

③ $3R-OH + PCl_3 \longrightarrow 3R-Cl + H_3PO_3$

(Inversion)

④ $R-OH + SOCl_2 \longrightarrow R-Cl + SO_2\uparrow + HCl\uparrow$

Retention