CH 15 Halogenoalkane

Saturday, July 26, 2025 4:03 PM

$\boxed{\text{Chap } 13, 14, 15, 29}$ Test in next week saturday

$-\overset{|}{\underset{|}{C}}-X$ $X = Cl, Br, I$

Reactivity of C–X Bond

F E.N

Cl > Br > I

Cl → more E.N I → less E.N

$H_3\overset{+\delta}{C}-\overset{-\delta}{Cl}$ methyl chloride

$H_3\overset{+\delta}{C}-\overset{-\delta}{Br}$ " Bromide

$H_3\overset{+\delta}{C}-\overset{-\delta}{I}$ " Iodide

When bond length is bigger, it can easily be broken.

Reactivity of the halogen increases down the group. C–I bond needs less energy to break as compared to C–Cl and C–Br because C–I bond length is bigger.

Here polarity is not deciding the reactivity. Bond energy is deciding the reactivity.

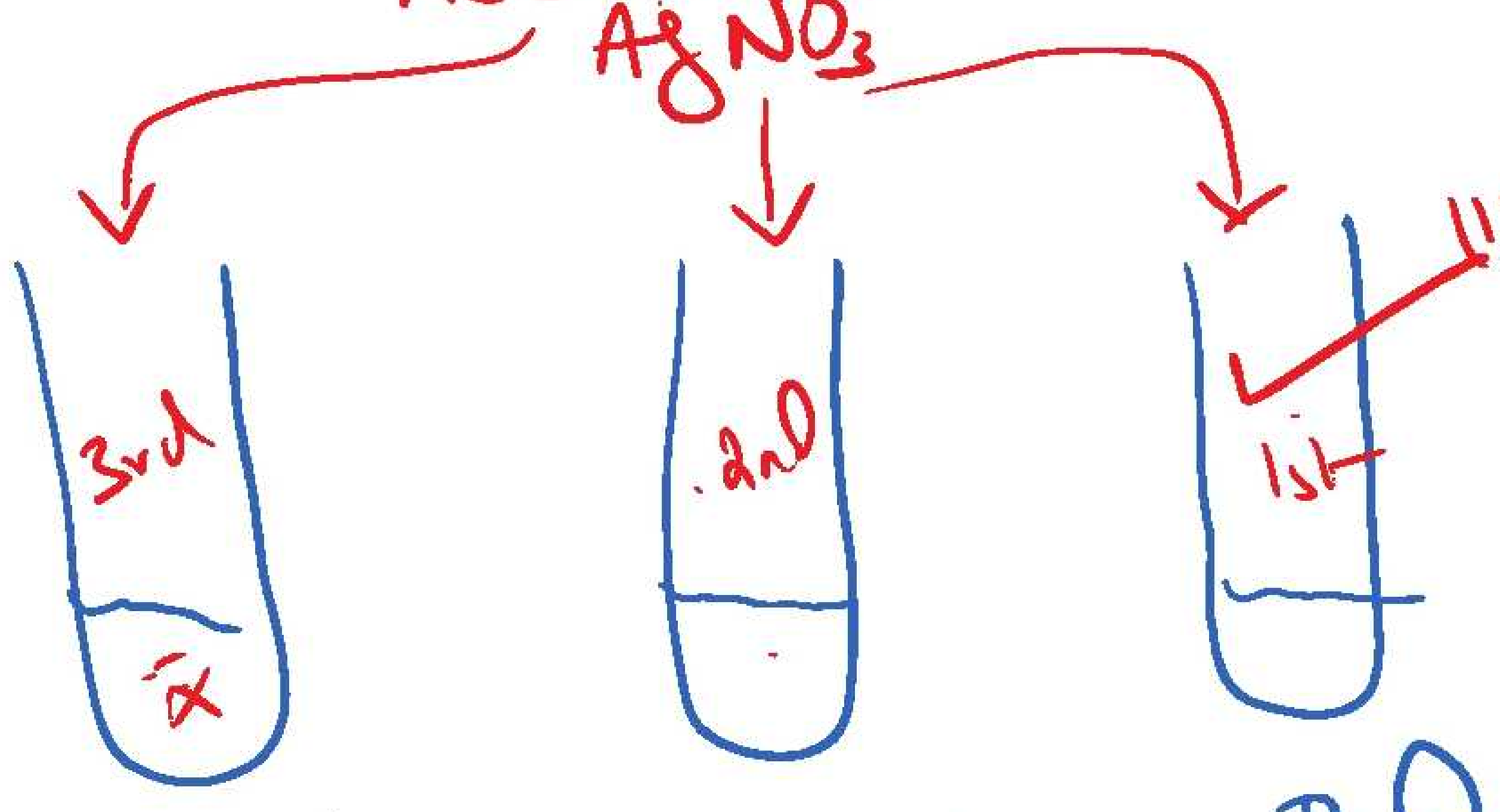
Reactivity order for the halogenoalkane

$CH_3-I > CH_3-Br > CH_3-Cl$

$AgNO_{3(aq)}$

$Ag^+ + NO_3^-$

Acidified $AgNO_3$ + HNO_3



C–Cl

Hydrolysis reaction

(1) C–X Bond breaks

X^- ions released into solution

$AgX_{(s)}$

Chlorobutane Bromobutane Iodobutane

AgCl white ppt (3rd) Cream ppt (2nd) Yellow ppt (1st)

$AgBr$ AgI

$CH_3-I > CH_3-Br > CH_3-Cl$

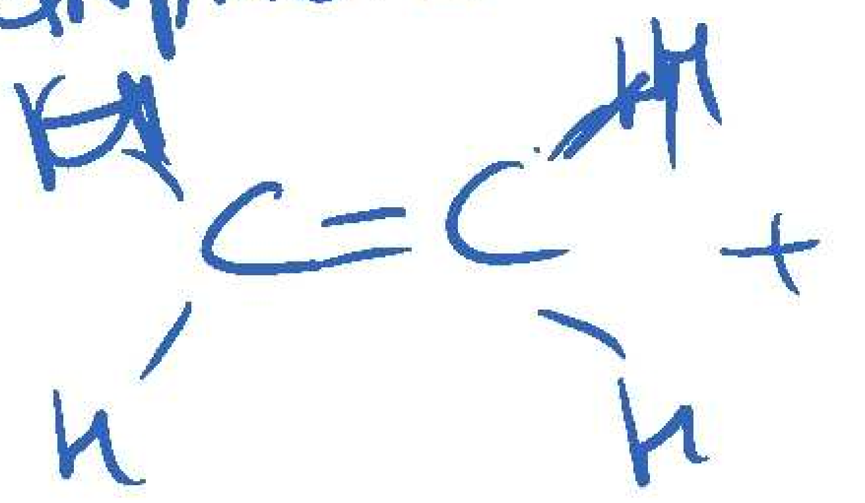
Preparation of Halogenoalkane

① $CH_4 + \dot{Cl} \longrightarrow \boxed{CH_3Cl}$

Free Radical reaction of alkane

Its not a good method, multiple products are formed.

② Electrophilic addition reaction



$+ HCl \longrightarrow \underline{CH_3-CH_2-Cl}$

③ Substitution Reactions of Alcohol

(HCl, PCl_3, PCl_5, $SOCl_2$)

(i) With HCl

HCl Cant be use directly due to its toxicity

It can be prepared indirectly

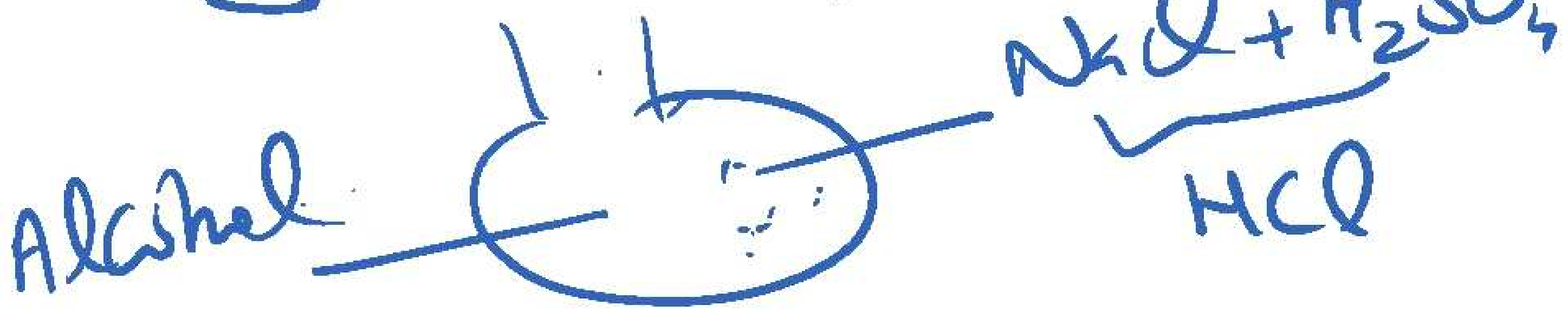
$NaCl + H_2SO_4 \longrightarrow HCl + NaHSO_4$

$CH_3-CH_2-OH + \underbrace{\overset{HCl}{NaCl + H_2SO_4}}_{\text{in situ}} \longrightarrow CH_3-CH_2-Cl$

KBr / H_3PO_4 KBr / H_2SO_4

$NaBr / H_3PO_4$ $NaBr / H_2SO_4$

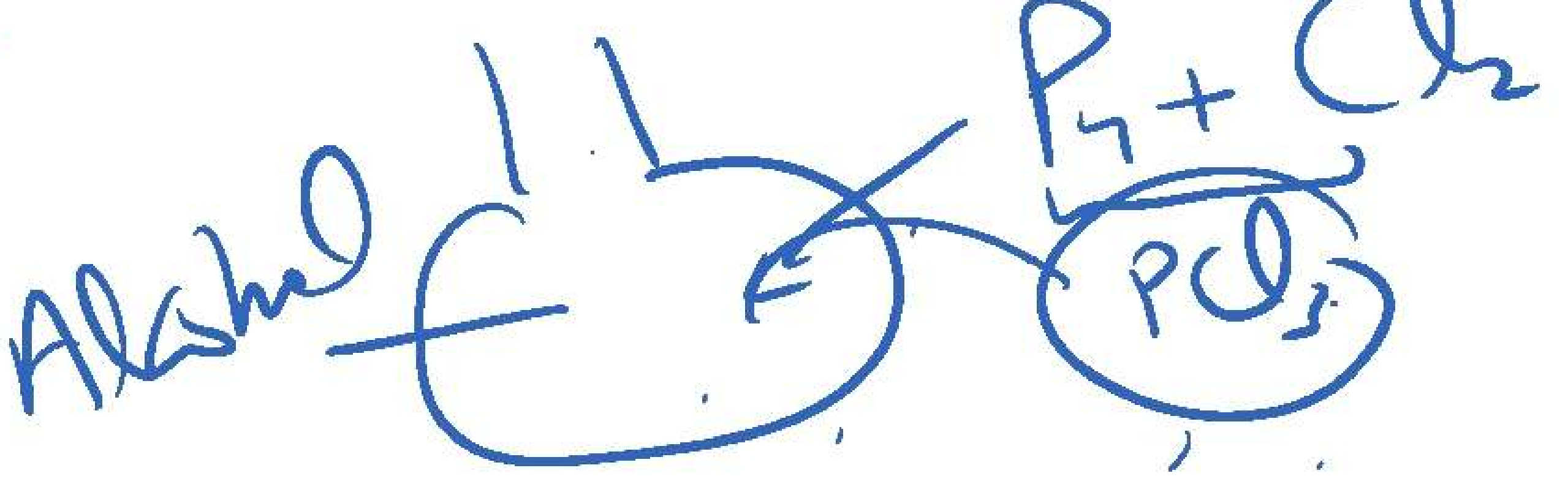
When toxic reagent is not used directly but its reactant are used in reaction mixture to produce this toxic reagent is called Sith



and toxic gas)

(ii) with PCl_3 (highly volatile

$$CH_3-CH_2-OH + \xrightarrow[\text{heat}]{\overset{PCl_3}{P_4 + Cl_2}} \underline{CH_3-CH_2-Cl + \overset{\text{phosphorous acid}}{H_3PO_3}}$$

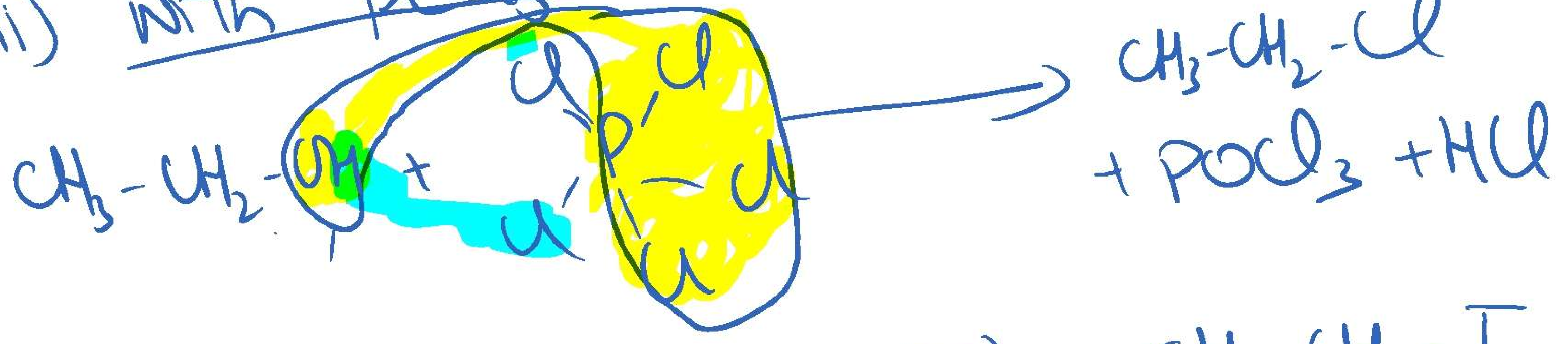


H_3PO_3

CH_3-CH_2-OH
$CH_3-CH_2-OH + PCl_3 \longrightarrow$
CH_3-CH_2-OH

CH_3-CH_2-Cl
$CH_3-CH_2-Cl + H_3PO_3$
CH_3-CH_2-Cl

(iii) with PCl_5



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

$$CH_3-CH_2-OH + PI_3 \longrightarrow CH_3-CH_2-I$$

$$PBr_3 \longrightarrow CH_3-CH_2-Br$$

(iv) with $SOCl_2$

$$CH_3-CH_2-OH + SOCl_2 \xrightarrow[\text{temp}]{\text{room}} CH_3-CH_2-Cl + SO_2 + HCl$$

Best Method to prepare haloalkane with $SOCl_2$ is a best method

→ SO_2 & HCl gases will evaporated leaving CH_3-CH_2-Cl in pure form

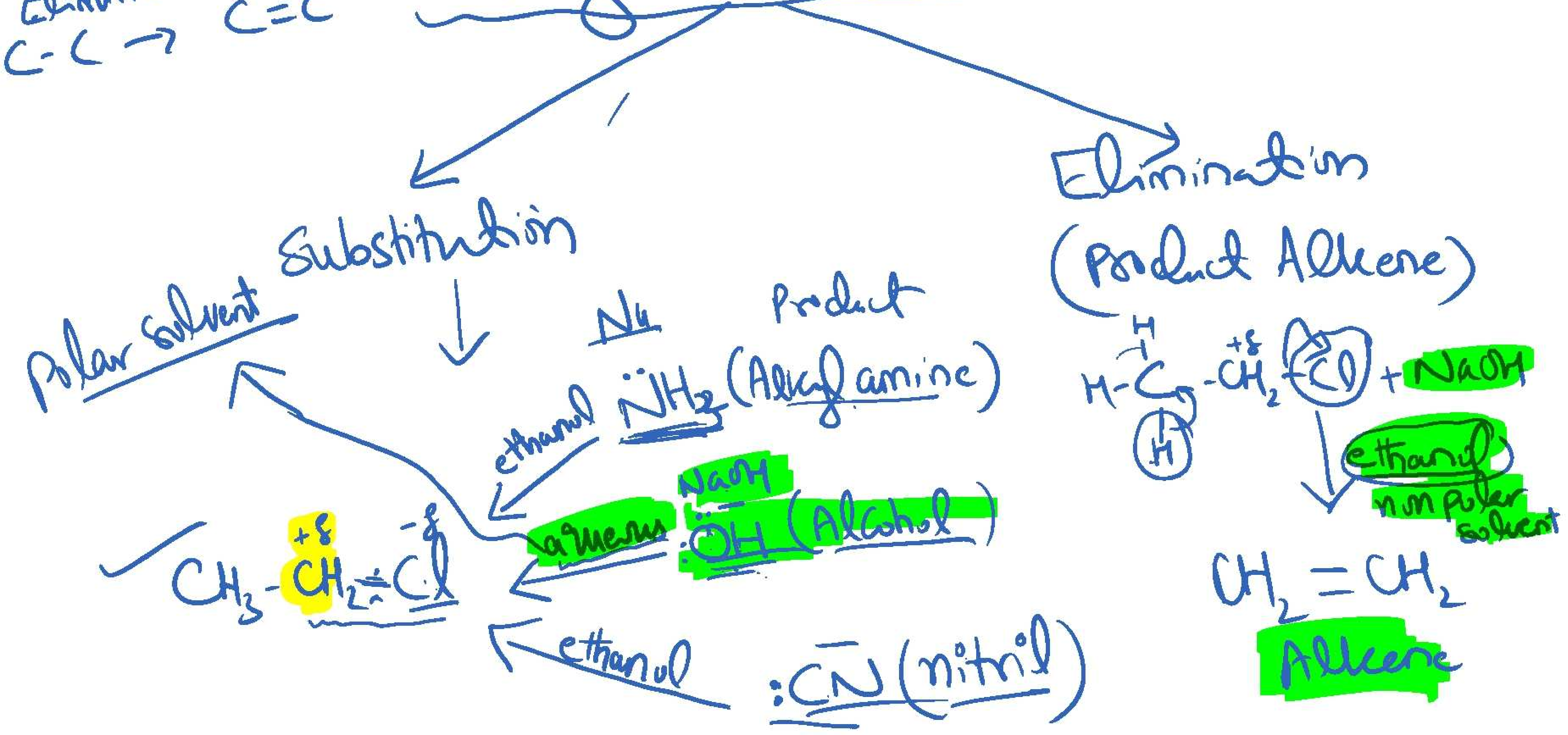
→ No need to apply separation technique

→ Reaction taking place at room temp so it is cost effective.

Primary Halogenoalkane	Secondary Halogenoalkane	Tertiary Halogenoalkane

Addition
$C=C \rightarrow C-C$
Elimination
$C-C \rightarrow C=C$

Halogenoalkane Reactions



Nucleophilic Substitution Reaction

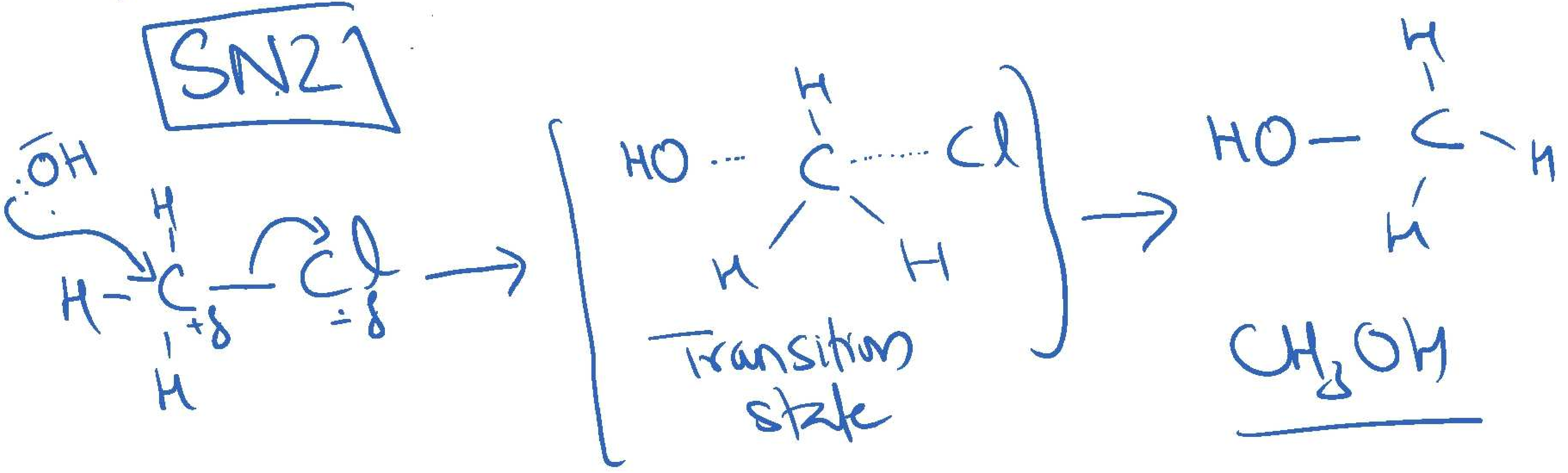
SN2 — rate

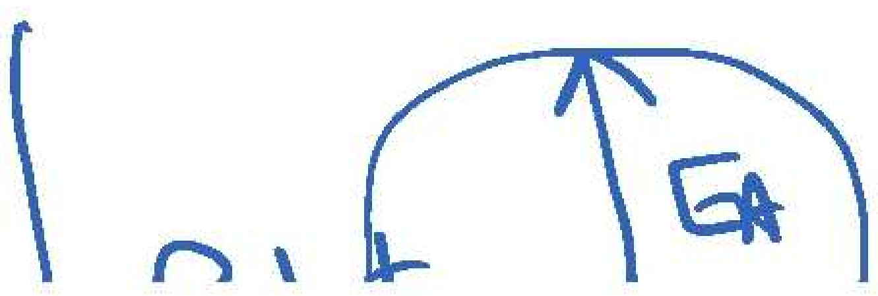
- → Primary halogenoalkane
- → Single step mechanism
- → Rate ∝ [:Nu] [R-X] (Primary halogenoalkane)

SN1

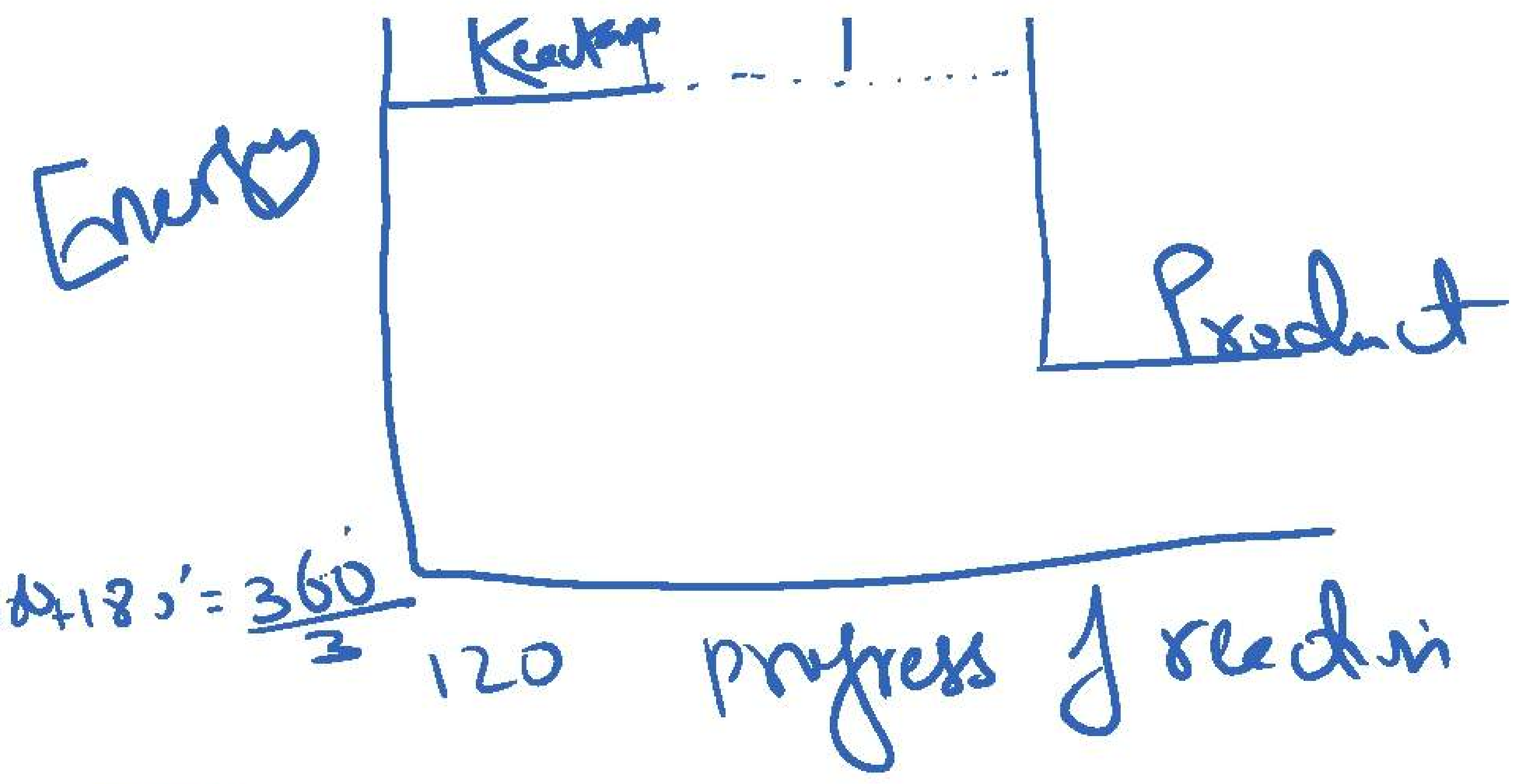
- → Tertiary halogenoalkane
- → 2 step mechanism
- → Rate ∝ [Tertiary halogenoalkane]

$\boxed{SN2}$

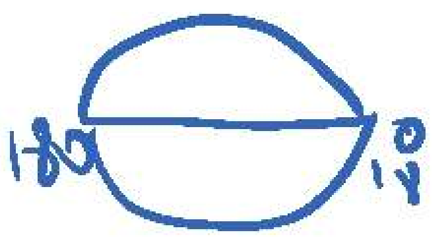




Single hump because it single



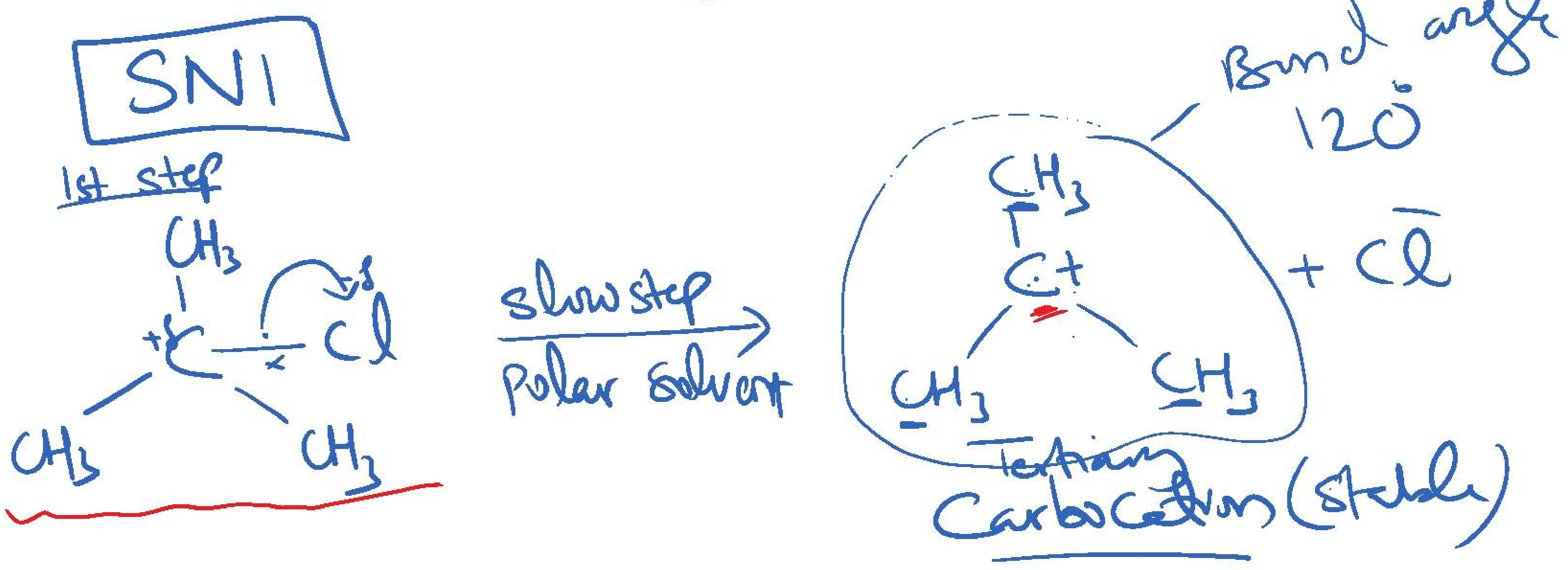
Step mechanism



$180+180 = \frac{360}{3}$ 120

SN1

1st step

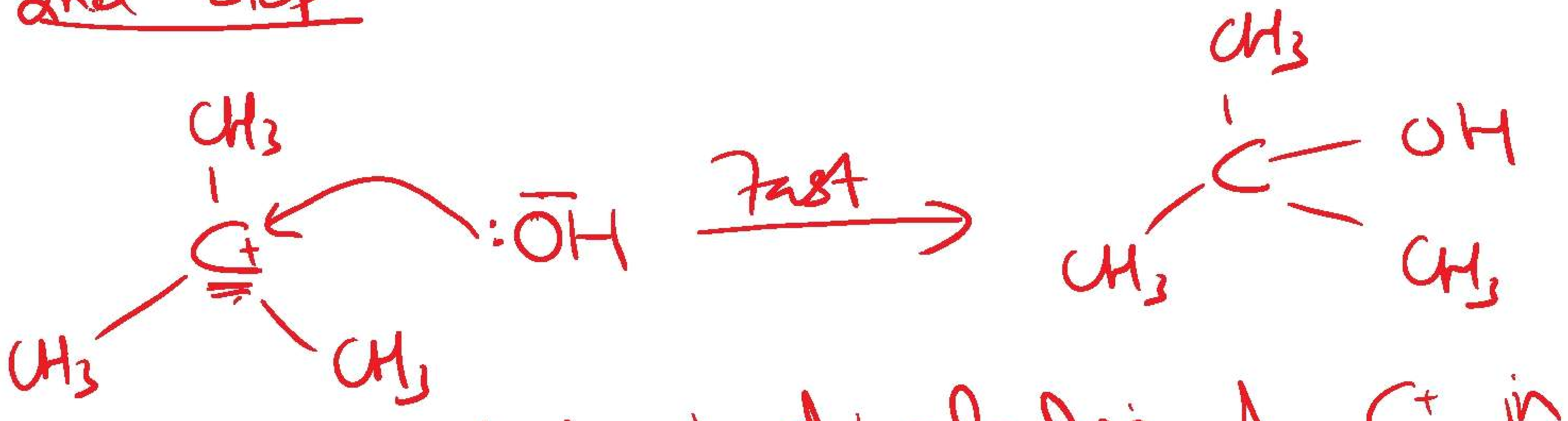


→ There are big groups around tertiary C so Nu will not attack from any side so Cl must be removed.

→ Bond breaking is always rate determining step means it will always be slow.

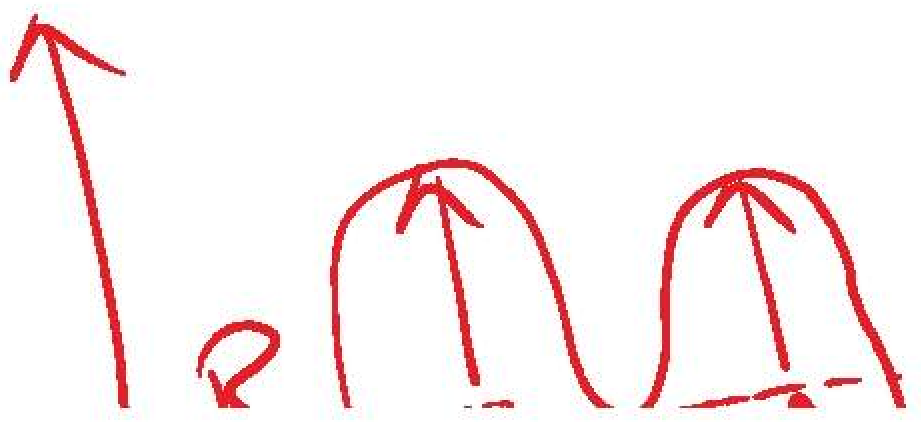
→ Polar solvent + part will bonded with -ive part of halogenoalkane and -ive part of the solvent will bonded with +ive part of halogenoalkane.

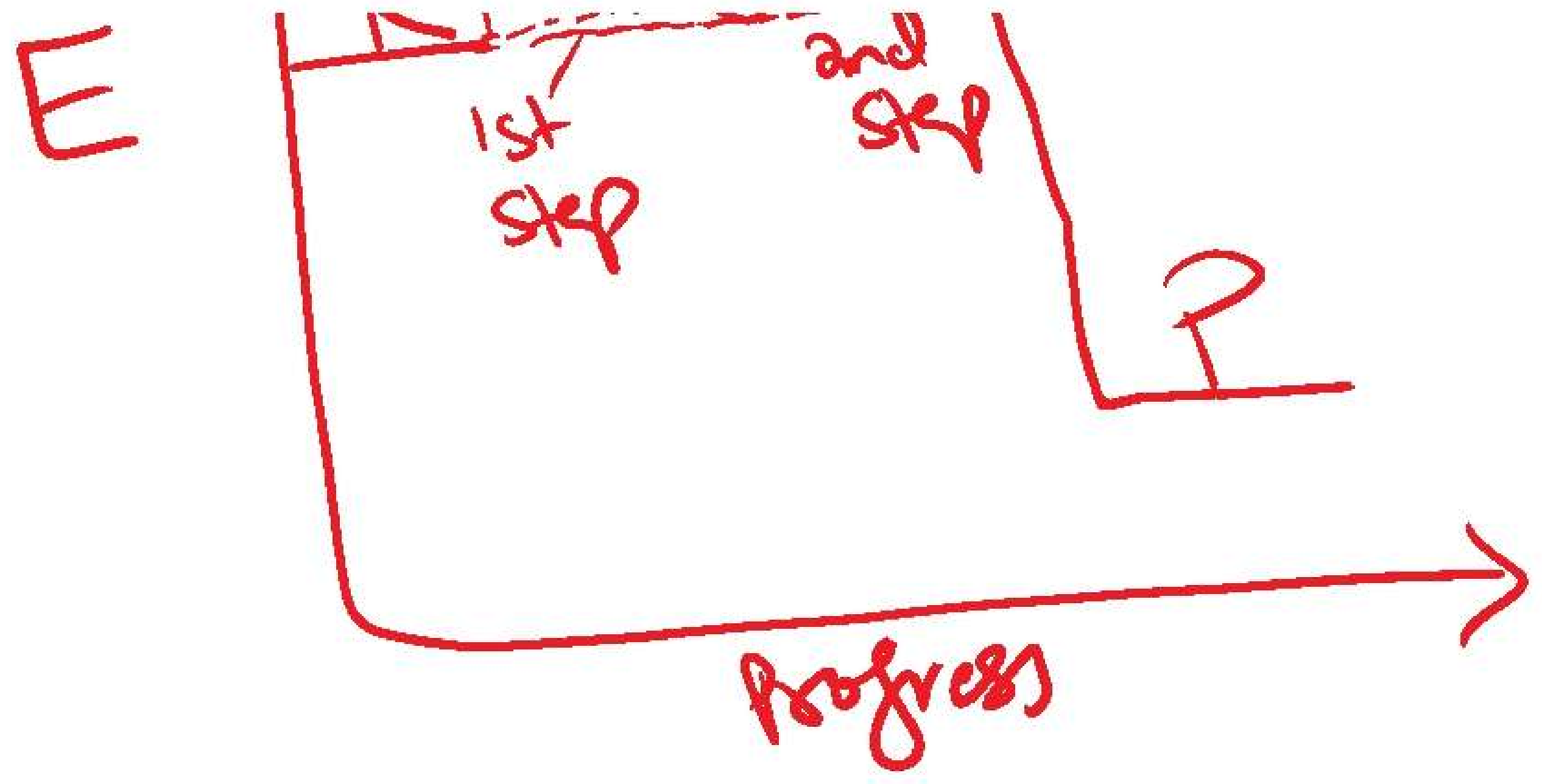
2nd step



HW to detect hybridization of C⁺ in tertiary

Rate of reaction ∝ [Tert: halogenoalkane]





Substitution of halogenoalkane require Polar solvent

① Reaction with Aqueous Alkali (:$\bar{O}H$

SN2 $CH_3-CH_2-Cl + \underset{(aq)}{NaOH} \xrightarrow[\text{reflux}]{\text{heat under}} CH_3-CH_2-OH + NaCl$ ethanol.

(ionic) → $CH_3-CH_2-Cl + \underset{(aq)}{:\bar{O}H} \xrightarrow[\text{reflux}]{\text{heat under}} CH_3-CH_2-OH + \underset{(aq)}{\bar{Cl}}$

Condition for this (1) Aqueous NaOH/KOH

(2) Heat under reflux

H–O–H

ionic Nu

(i) $CH_3-CH_2-Cl + \underset{(aq)}{\overset{NaOH}{:\bar{O}H}} \xrightarrow[\text{reflux}]{\text{faster heat under}} CH_3-CH_2-OH + \bar{Cl}$ Alcohol

Nucleophile

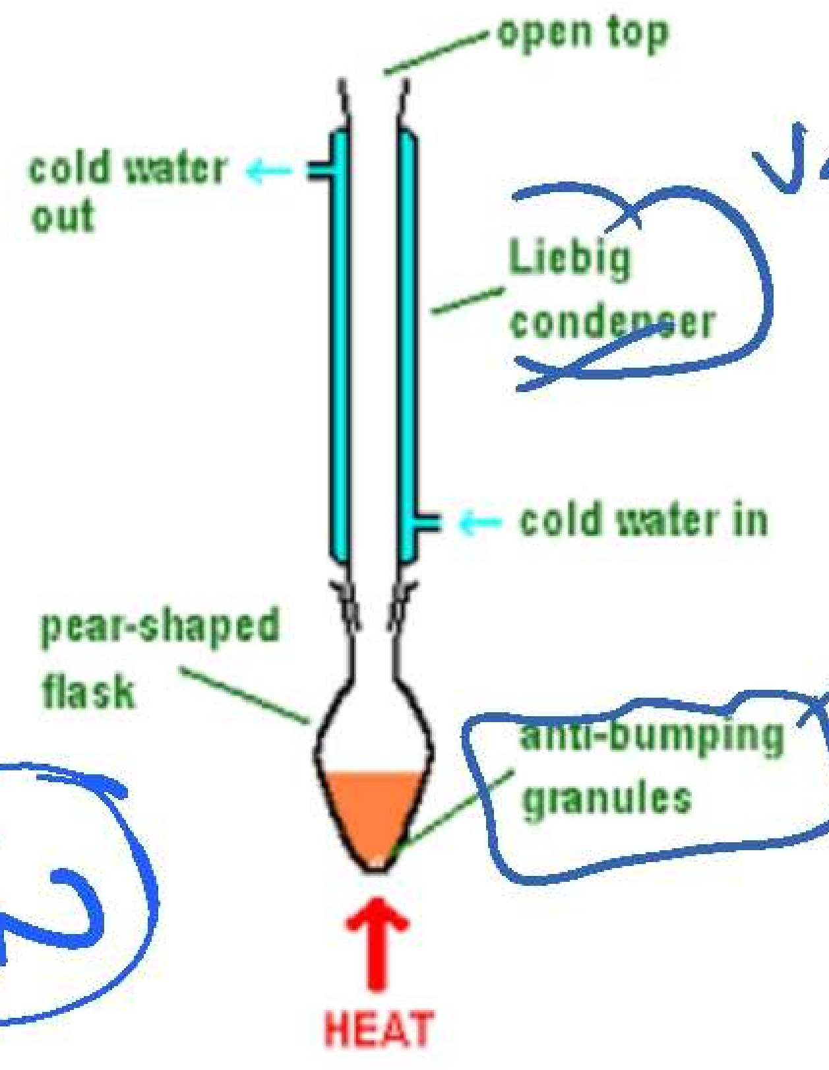
(ii) $CH_3-CH_2-Cl + \boxed{H_2\ddot{O}:} \xrightarrow[\text{slow}]{} CH_3-CH_2-OH$

neutral nucleophile

$\bar{O}H$ is stronger Nu than H_2O

Heat Under Reflux

organic compound reactions too slow, low B.P and are volatile



vapour → liquid

To prevent the formation of large gas bubbles that cause violent boiling

$:\bar{CN}$ (ionic)

$\overset{+}{K}\bar{CN}$ $\overset{+}{Na}\bar{CN}$

→ Nitrile

(2) with $\underline{KCN}$/$\underline{NaCN}$ (Metal cyanide

$:\bar{C}\equiv N$
Nucleophile

(in. ethanol) reaction condition

$$\underbrace{CH_3CH_2}_{2C}Cl + \boxed{\underset{(alco)}{KCN}} \xrightarrow[reflux]{heat} \underbrace{CH_3CH_2}_{3C}CN$$

nitrile

Reaction with nitril increases chain length.

3) Reaction with ethanolic $\underline{NH_3}$ (gas)
(Heat under Pressure)

$$CH_3-CH_2-Cl + \underset{excess}{\ddot{N}H_3}(alco) \xrightarrow[under\ pressure]{heat} \underset{Base}{CH_3-CH_2-\ddot{N}H_2} + \underset{Acid}{\underline{HCl}}$$

Nucleophile

ethyl amine

$$NH_3 + HCl \rightarrow \underline{NH_4Cl}$$

But if NH_3 not in excess

$$\times \quad \underset{Base}{CH_3-CH_2-NH_3} + \underset{Acid}{HCl} \longrightarrow \underset{Salt}{CH_3-CH_2-\overset{+}{N}H_3\bar{Cl}}$$

Base	**Nucleophile**
always attack on hydrogen H^+	always attack on $C^{+\delta}$ (carbocation)

$\bar{O}H$ Nu
$\bar{O}H$ Base

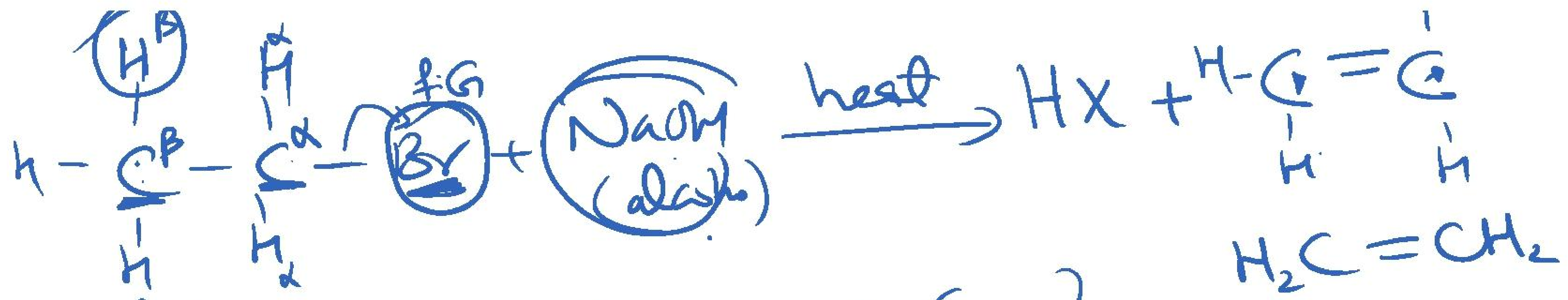
Elimination Reaction

Removal of atoms from adjacent carbon atoms resulting in the formation of Alkene.

→ loss of small molecule such as ~~HCl~~ HX/ H_2O

→ In case of halogenoalkane small molecule is HX.

H



$H_2C=CH_2$

Imp [H is removed from β C
X is removed from α C]

Q.1 $\boxed{?} \xleftarrow[\text{alch}]{\overline{OH}} CH_3-CH_2-Cl \xrightarrow[(aq)]{\overline{OH}} \boxed{\text{Alcoho}}$

Q.2 2-Chlorobutane when reacted with alcoholic KOH will give you how many isomeric products?

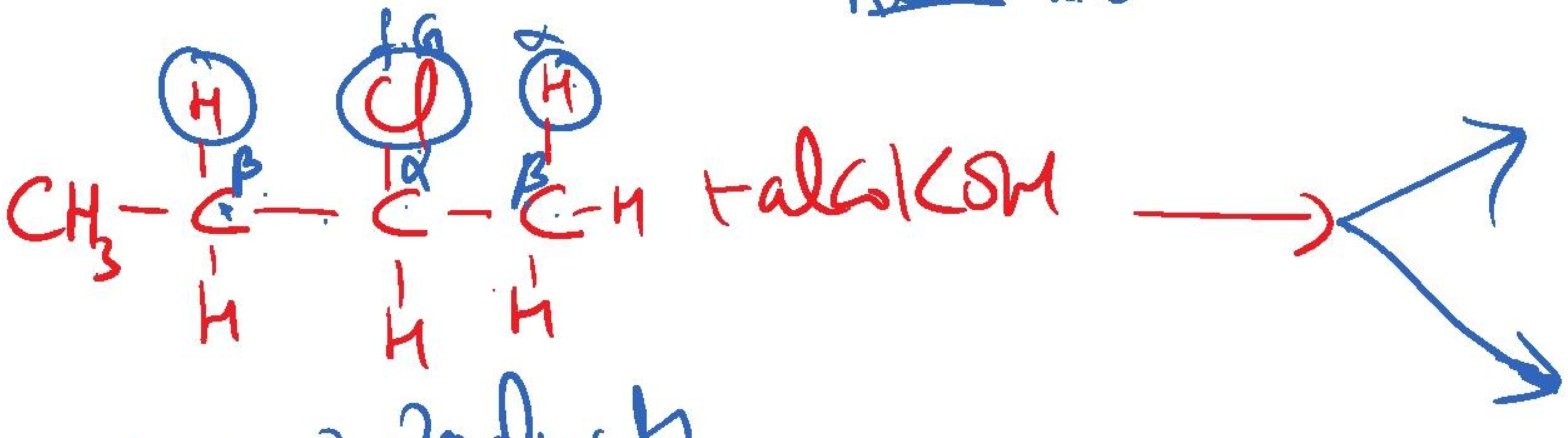
$\overline{OH}_{\text{alcoholic}}$

~~elimination Reaction~~

Alkene and HCl

α C → remove Cl

β C → H



③ ~~$CH_3=CH_2$~~$-CH=CH_2$

But-1-ene

$CH_3-CH=CH-CH_3$

But-2-ene.

Ans 3 Products