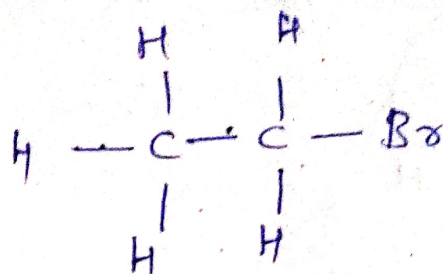
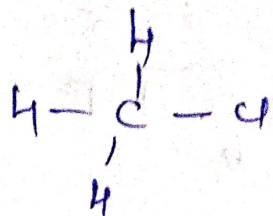


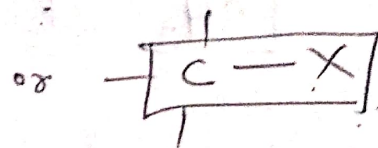
UNIT-III - ALKYLE HALIDES

→ These are the compound in which halide is attached to the carbon.

e.g.

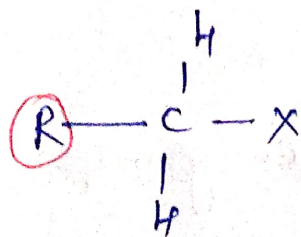


so general formula is

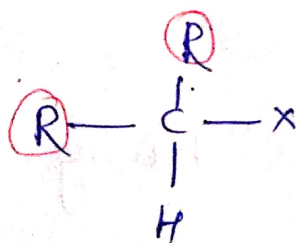


$\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{F}$ etc.

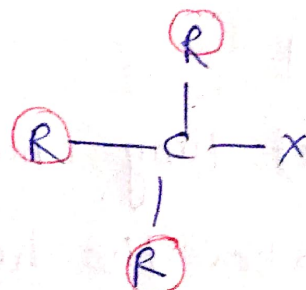
→ They are classified as primary, secondary & 3° depending on carbon atom at which they attached.



1^o carbon



2^o (Secondary)



Tertiary (3°)

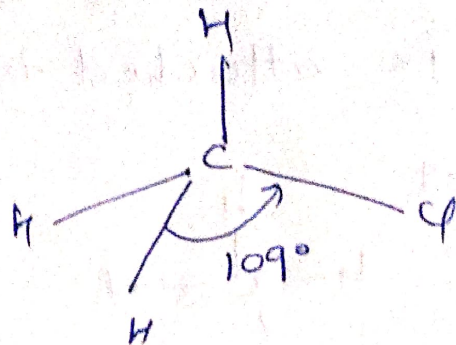
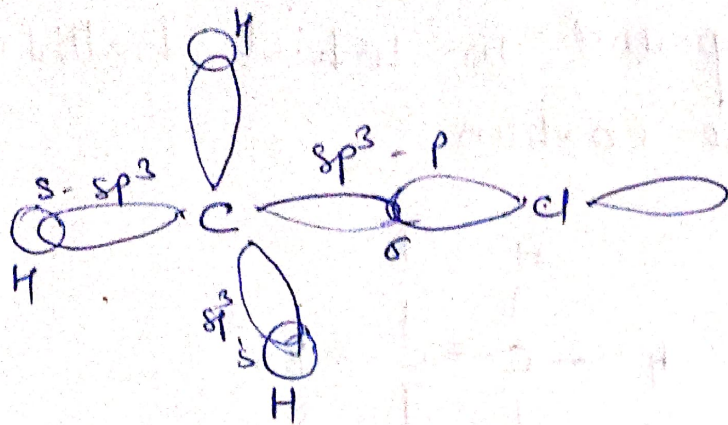
STRUCTURE

→ for example CH_3Cl .

→ The carbon atom is sp^3 hybridized.

→ The C-Cl bond forms by overlapping of sp^3 orbital of carbon & half filled or p-orbital

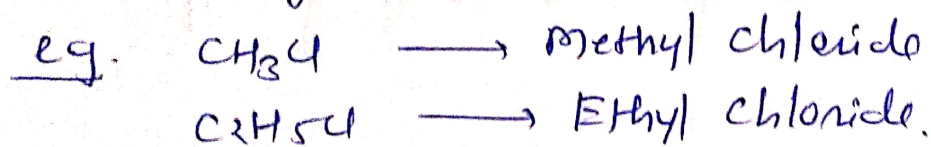
of chlorine atom.



Nomenclature

COMMON SYSTEM:

- Alkyl group name at first & then halogen atom.



IUPAC

- Select long chain of 'C' having halogen group
- Number the halogen.
- Name the halogen first as. chloro, fluoro, bromo.

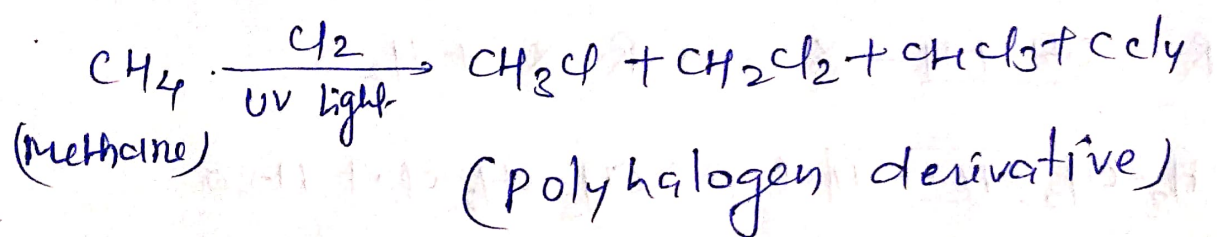
position + halogen + carbon chain + suffix
(no. of C)



Method of Preparation

- ① Halogenation of alkane
- ② Addition of halogen acid to alkene
- ③ Action of halogen acid to alcohol
- ④ Action of phosphorus halide to alcohol
- ⑤ Halogen exchange reaction.

① Halogenation of alkane

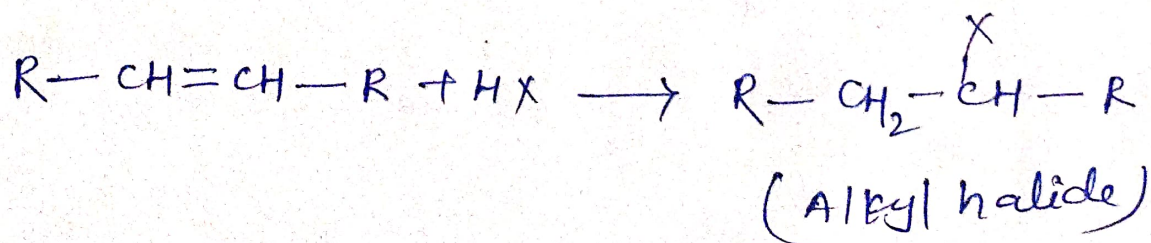


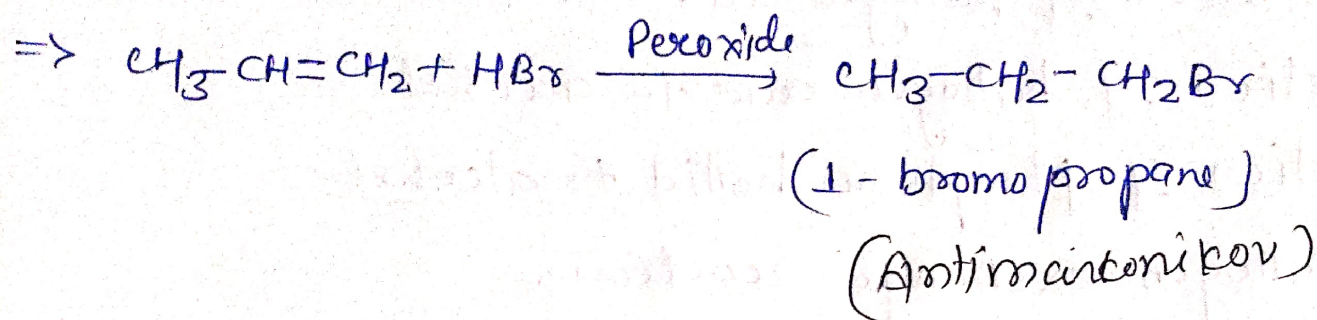
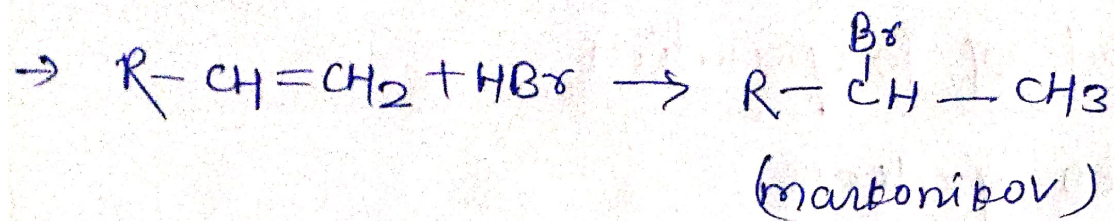
* This method is not used in lab as there is difficulty to separate it.

② Addition of halogen acid to Alkene

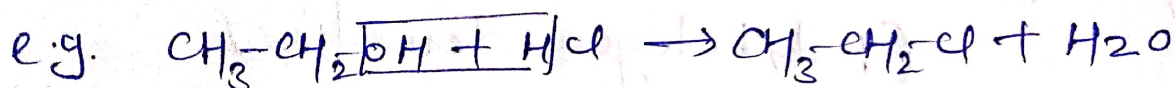
→ Halogen acid (HCl , HBr , HI) added to alkenes to give "alkyl halides"

→ It follows Markovnikov's rule except HBr , that follows Anti-Markovnikov's rule, in presence of (R-O-O-R) .

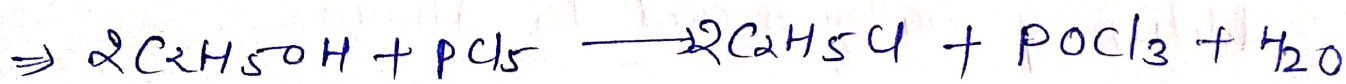
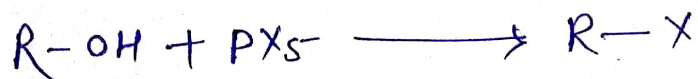




③ Action of halogen Acid on Alcohols



④ Action of phosphorus Halide on alcohols



PHYSICAL PROPERTY OF ALKYL HALIDE

1) H_2O Insoluble, Soluble in Organic solvent.

2) Alkyl bromide & $R-I$ are denser than H_2O

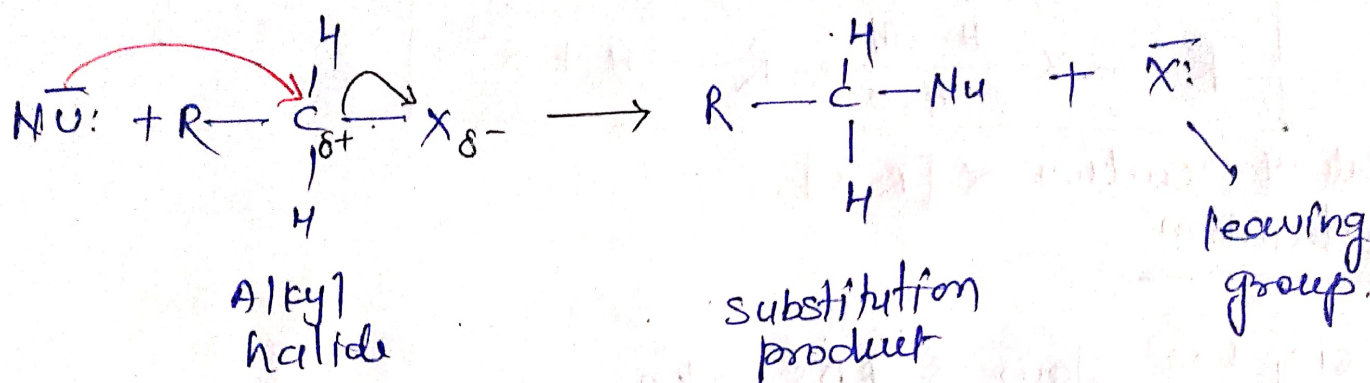
$R-Cl$ & $R-F$ are lighter than H_2O .

Chemical Property

(A) SUBSTITUTION REACTION

→ C-halogen bond in alkyl halide is "polar" due to Δ high electro-negativity of halogen atom relative to carbon.

→ 'C' is good target for nucleophilic attack.



Types of Substitution Reaction

SN1

* Unimolecular

* ~~single~~ ² step reaction

* favored by polar solvent

* It has transition state an intermediate

Carbocation ion.

* Rate depends only on R-X con^n .

* Reaction occurs in weak base

* Rate depends on $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\text{-X}$

SN2

* Bimolecular

Single

* ~~2~~ step reaction.

* favored by ~~non~~-polar aprotic

* It has transition state

* Rate depends on R-X + Nucleophile both.

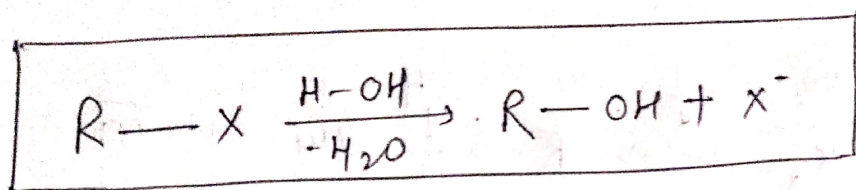
* C^- strong base

* $1^\circ > 2^\circ > 3^\circ > \text{CH}_3\text{X}$

SN1- Reaction

- Unimolecular ~~sub~~ Nucleophilic substitution reaction.
- Its rate determining step depends on 1 molecule.
- first order reaction.

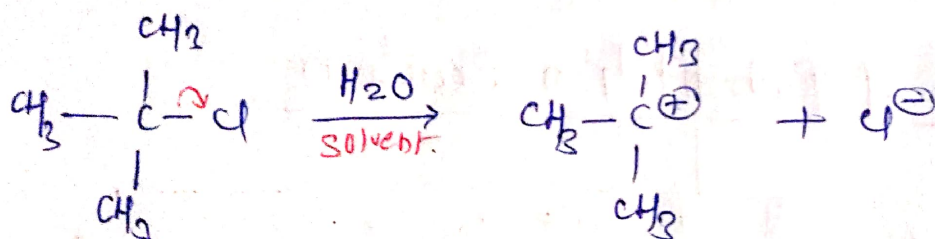
e.g. Hydrolysis of alkyl halide



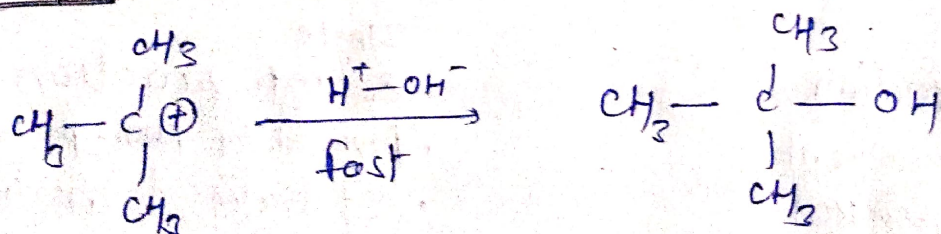
* Rate of reaction $\propto [R-X]$

Mechanism

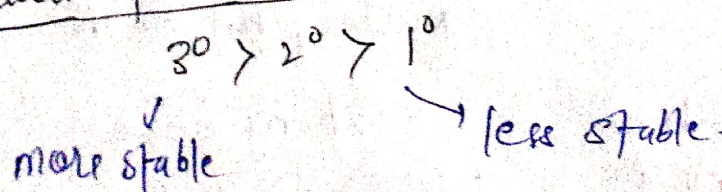
Step I: Slow & RDS Step.



Step II



Reactivity order (carbocation)



Property / factor of SN¹ Reaction

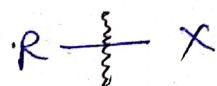
① Unimolecular

→ depends only on R-X

→ Rate of reaction $\propto [R-X]$ so follow first order kinetic.

② Solvent: Polar protic solvent

Polar = break $R-\overset{\text{|||}}{\underset{\text{|||}}{X}}$ due to dielectric property.

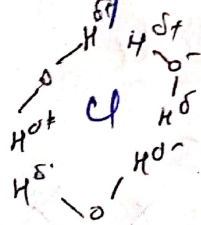
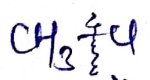


(dielectric)

Prop. of H_2O

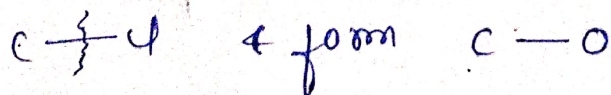
Protic → c have proton.

e.g.



due to protic property
halide ion entrapped
by H_2O molecule &
it will not be free for
reaction back to
carbocation

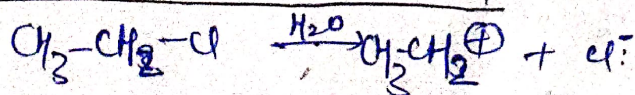
③ Exothermic reaction



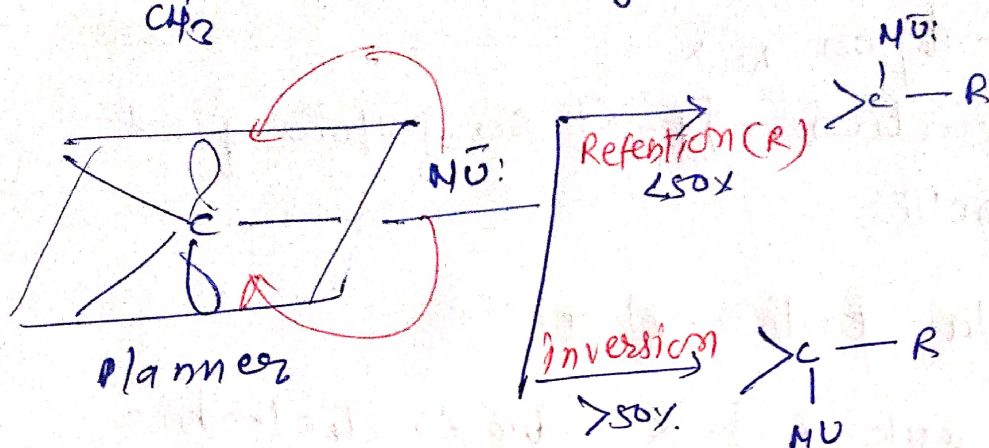
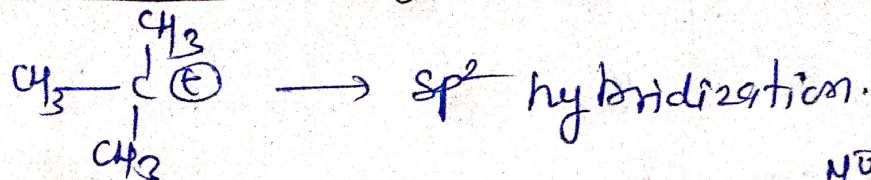
→ Energy of C-O bond is more compared to C-Cl

→ It is performed on low temp.

④ carbocation will form



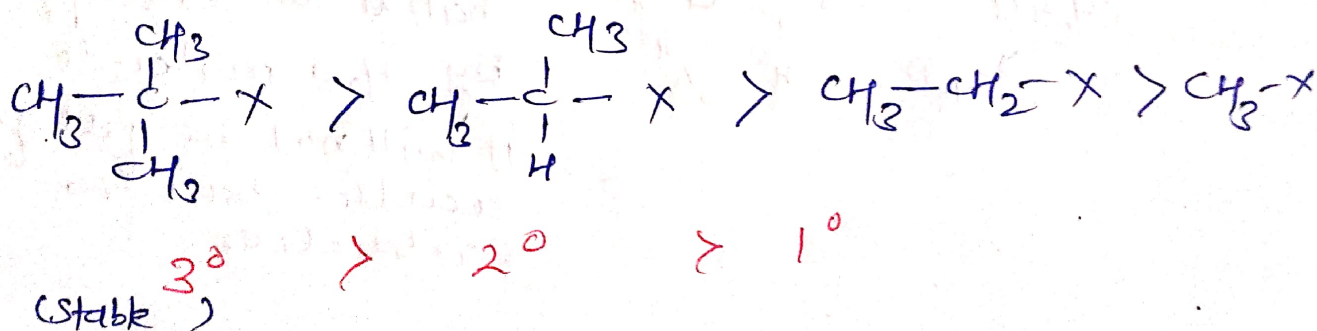
⑤ Stereochemistry of S_N1



So form a mixture called "Racemic mixture"

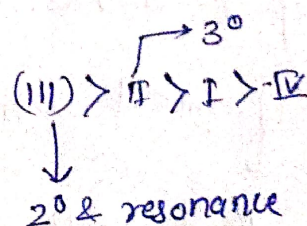
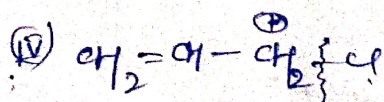
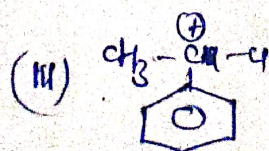
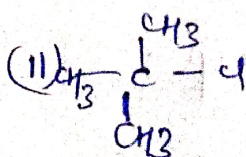
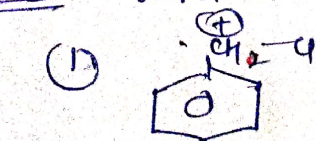
FACTORS AFFECTING RATE OF S_N1

① Nature of alkyl halide

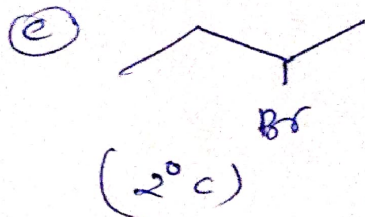
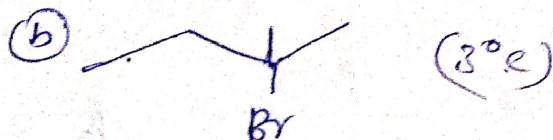
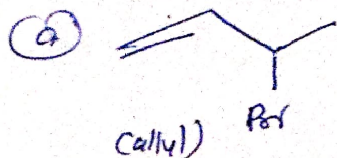


$\rightarrow 3^\circ$ will give more reaction as compared to 2° & 1°

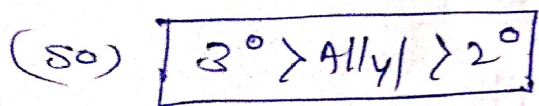
e.g. which one is more stable



e.g. Stability

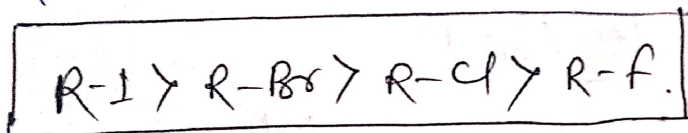


(d) all



② Nature of leaving group

→ Rate of reaction ↑ which group easily leave.



③ Nature of solvent

solvent → S_N1 = polar-protic

S_N2 = non-polar / polar-aprotic

solvent have dielectric property

1) H_2O - 80

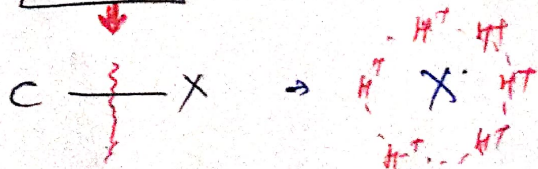
2) C_2H_5OH - 35

3) CH_3COOH - 5

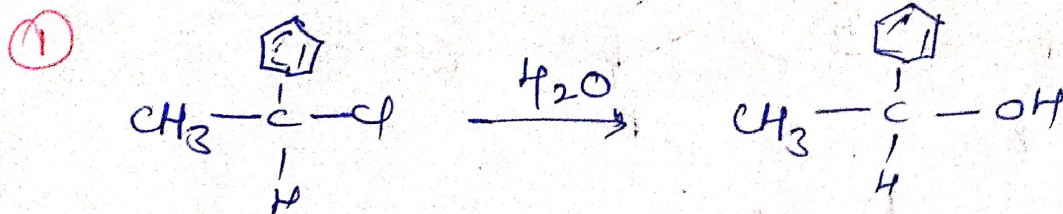
dielectric property
reduce the force b/w
 $C-X$

Polar

Protic

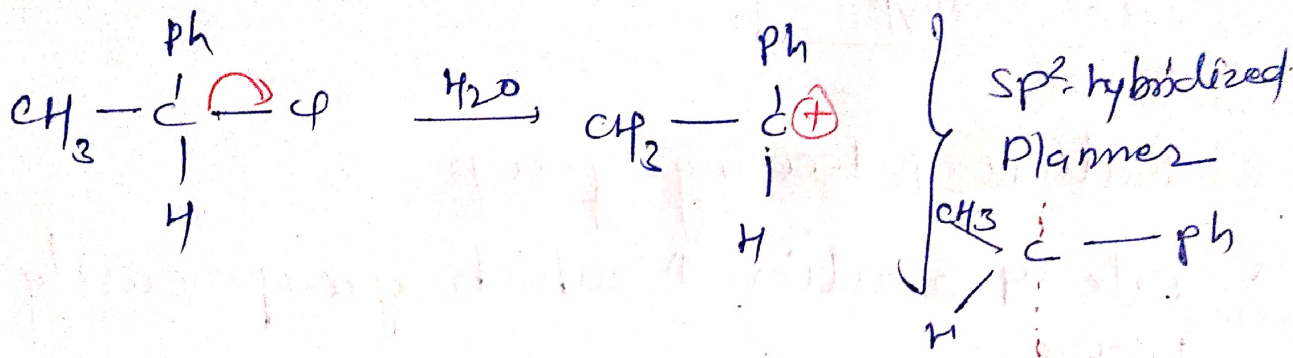


Ex. of S_N1

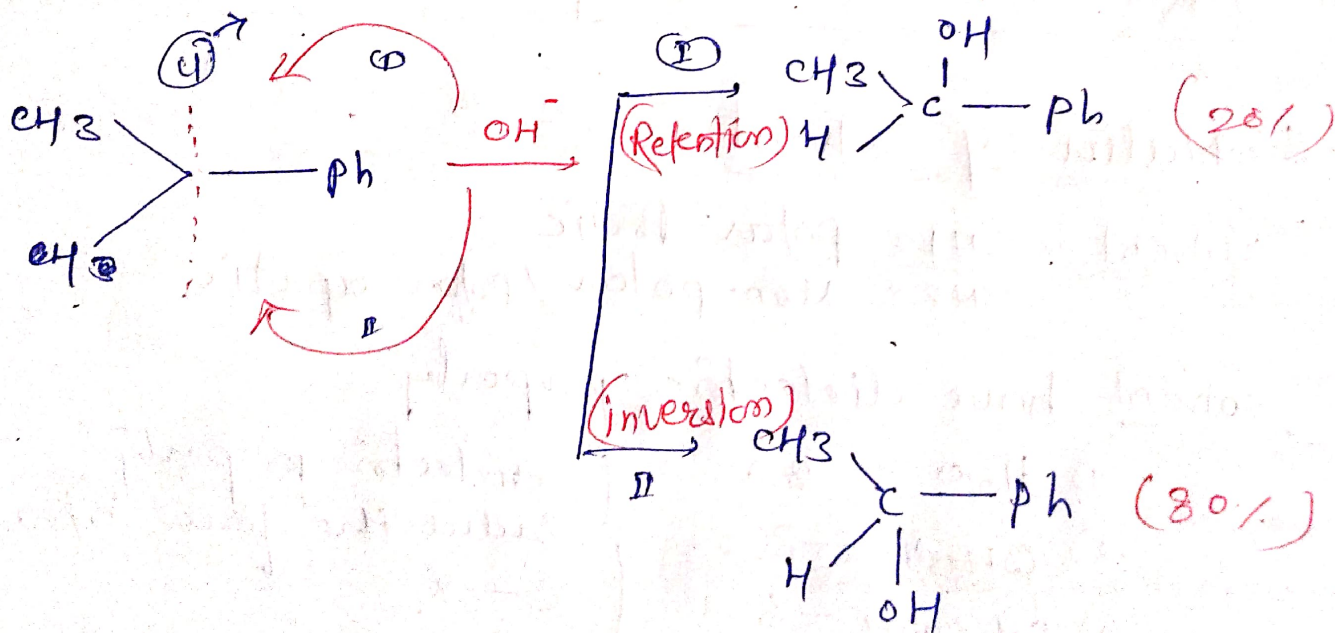


Mechanism

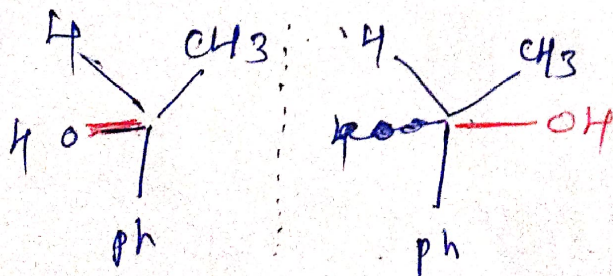
Step 1: formation of carbocation



Step 2: Attack of Nucleophile (OH^-)

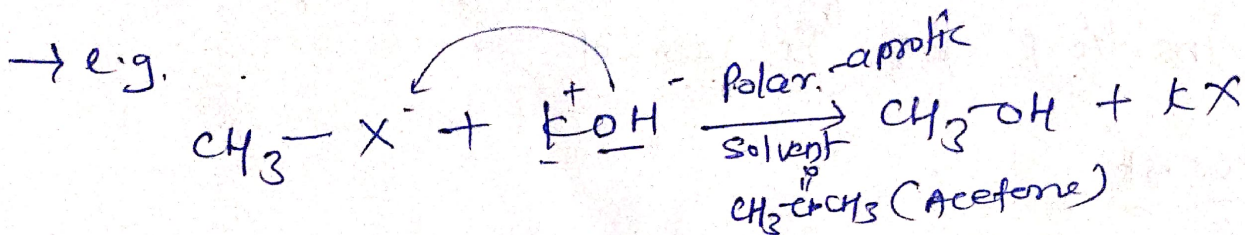


$\Rightarrow$ Both are enantiomer also as form mirror image



SN2 Reaction

(Substitution Nucleophilic, Bimolecular)
 → No carbocation will form.



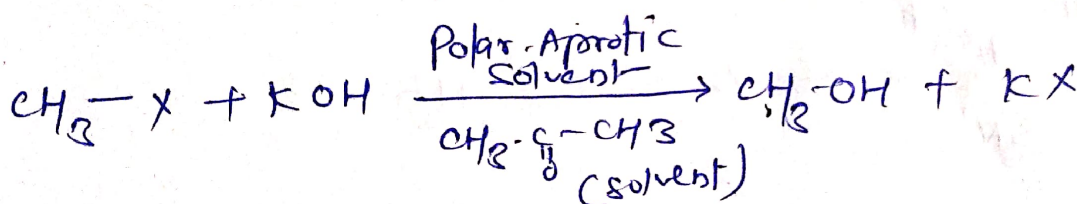
→ In this a transition state will form

→ Single step reaction

→ follow 2° kinetic, $\text{Rate} \propto [\text{R-X}] [\text{Nu}]$

→ Reactivity order is $1^\circ > 2^\circ > 3^\circ$

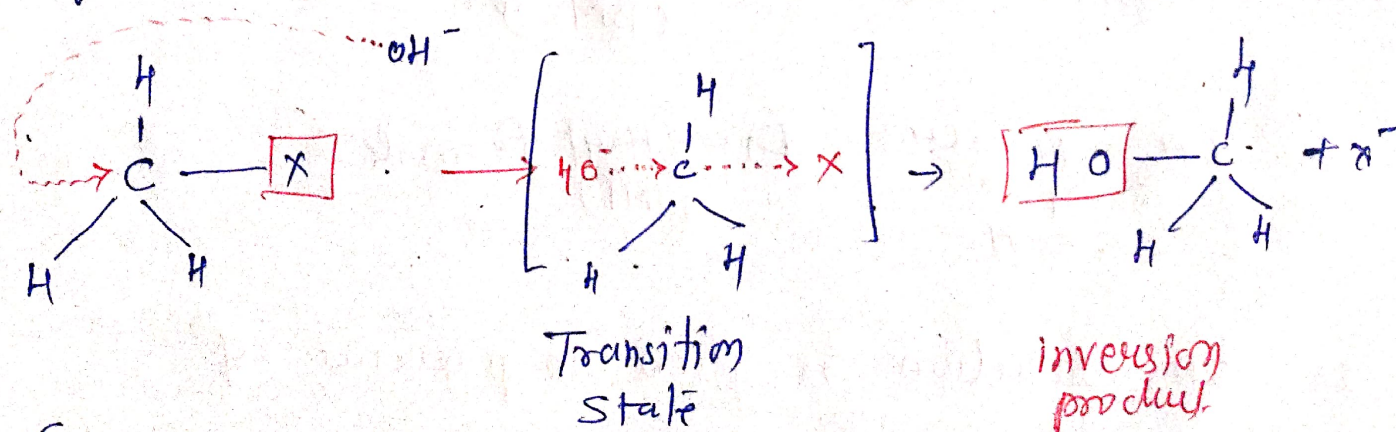
Reaction



Solvent
$\text{CH}_3-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_3$ (acetone)
$\text{CH}_3-\overset{\text{O}}{\underset{\text{ }}{\text{S}}}-\text{CH}_3$ dimethyl sulfoxide (DMSO)
$\text{O}=\text{C}-\text{H}$ $\text{CH}_3-\text{N}(\text{CH}_3)-\text{CH}_3$ dimethyl formide DMF

Mechanism

In SN2, Nu⁻ will attack from backside on 'C' of alkyl halide → C further form a transition state
 C further give inversion product

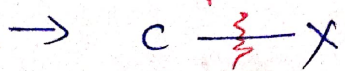


(Rear side attack of OH⁻)

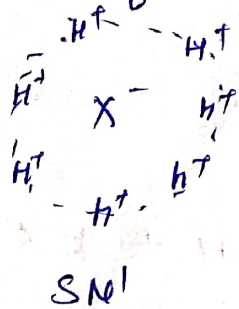
Property of SiH_2

- ① single step reaction
- ② No. carbocation formation, instead of that transition state is formed.
- ③ Solvent

→ Polar-aprotic solvent e.g. $\text{CH}_3-\overset{\text{O}}{\parallel}-\text{CH}_3$

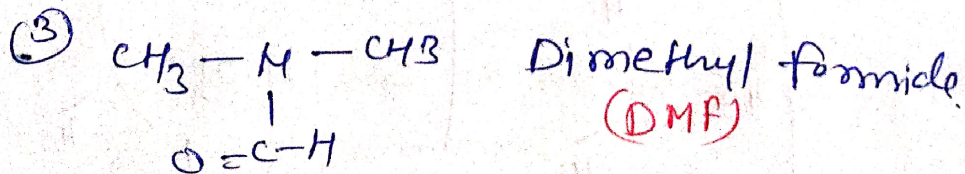
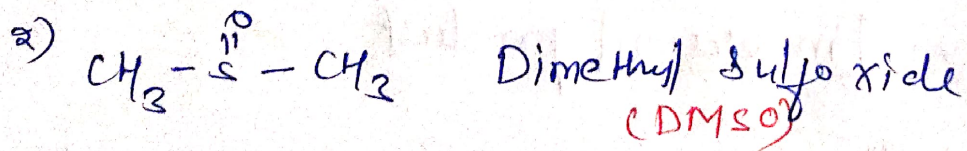
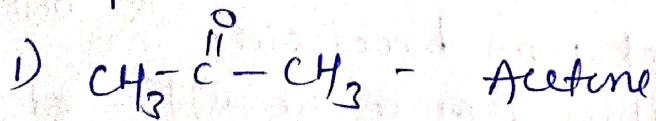


→ here no. proton is present so halide ion remain free to react $\approx K^+$



SN²

Eg. of solvent



So SH_2 reaction is given in presence of above solvent.

Stereochemistry of S_N2

→ In S_N2 only inversion product will form.

Factor Affecting to S_N2 reaction

① Nature of alkyl halide

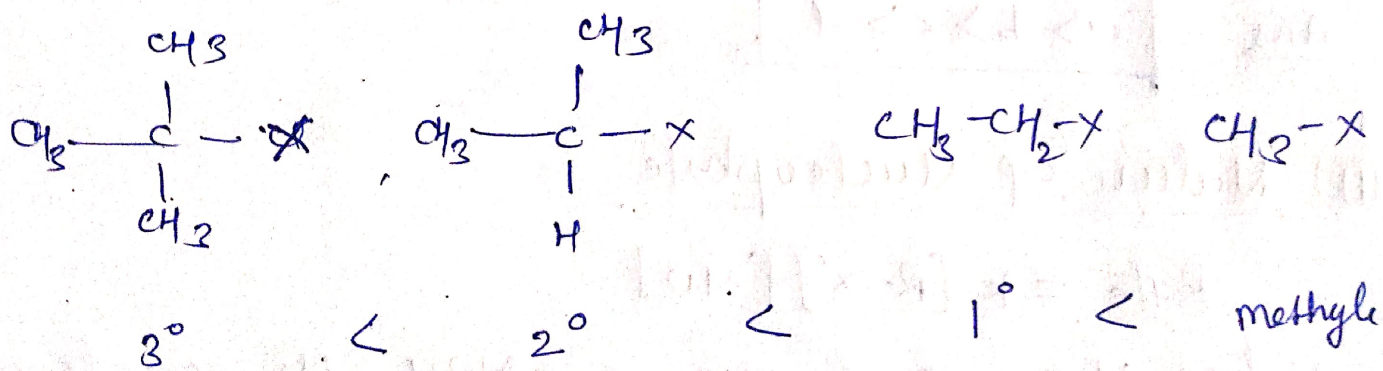
$$\text{Rate of reaction} \propto \frac{1}{\text{steric hinderance}}$$

* steric hinderance : presence of ligands surrounding the given atom in molecule.

→ It prevent the reaction.

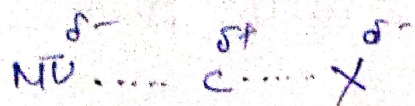
→ more ligand $\propto$ more hinderance.

→ so in 3° halide steric hinderance is more there for Nu^- will not easily attack in 3° .

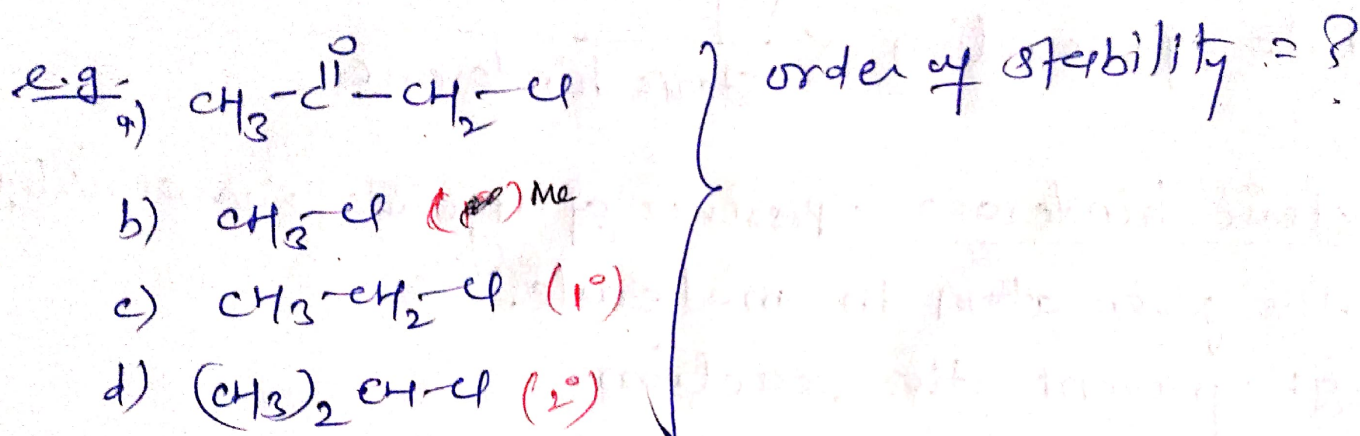


so in substitution 2, rear attack is not possible in 3° . therefore in methyl or 1° have is more chances for S_N2 reaction.

(I) Stability of transition state



If C is bonded π more electron withdrawing group then stability of compound will $\uparrow$.
 stability $\uparrow \rightarrow$ rate of $\text{S}_\text{N}2 \uparrow$ > steric hindrance.



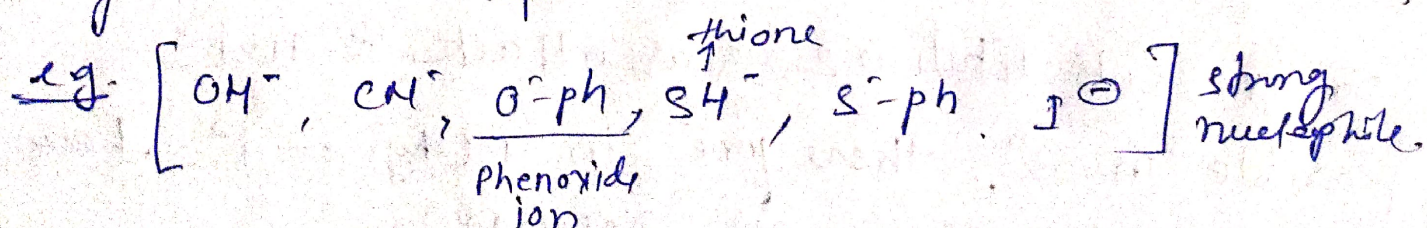
here (a) have electron withdrawing group dominate to stability by 10,000 time.

so
 Ans: $\boxed{\text{a} > \text{b} > \text{c} > \text{d}}$

(II) Nature of Nucleophile

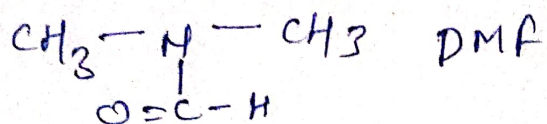
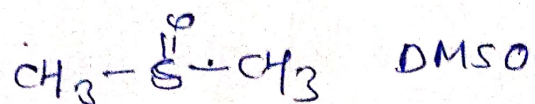
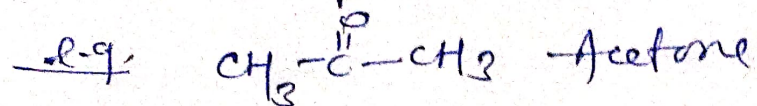
$$\text{Rate} = k [\text{R-X}] [\text{Nu}]$$

Higher the con° of Nu $\rightarrow$ more $\text{S}_\text{N}2$ reaction.

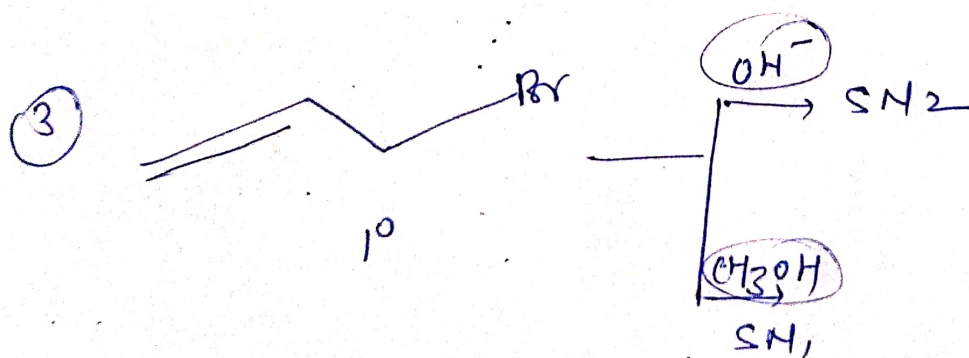
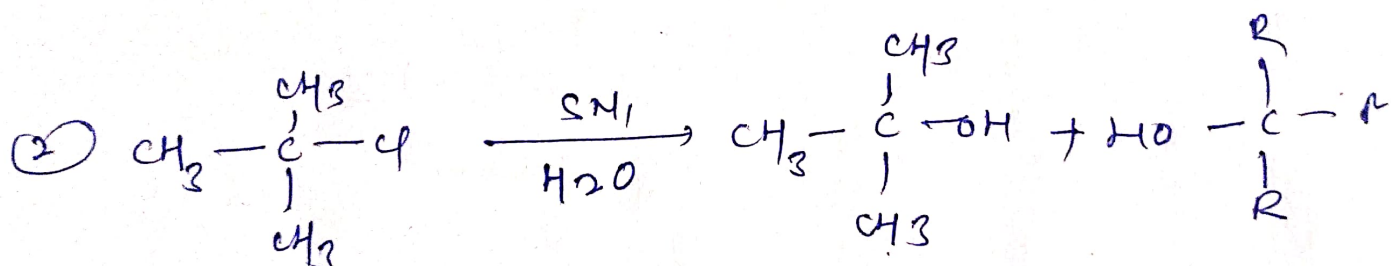
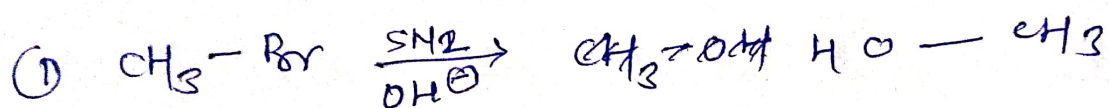


(IV) Nature of solvent

→ Polar - Aprotic



e.g. Exercise



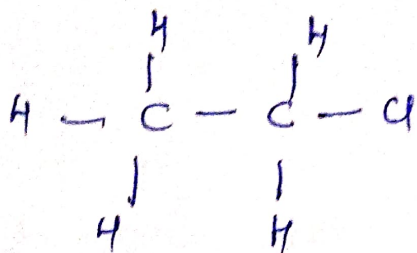
④

Structure and Uses of Ethylchloride

→ General formula → C_2H_5Cl

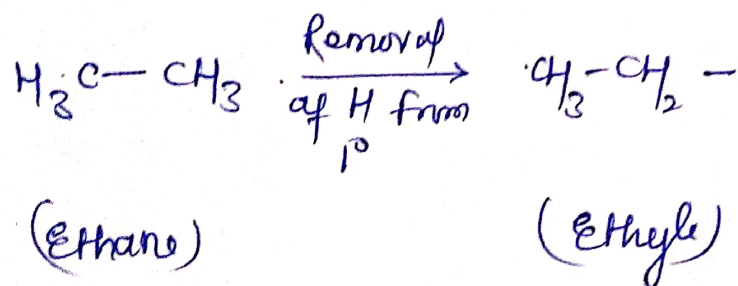
→ Comm. Name: chloroethane, / monochloroethane.

→ It's a colourless, flammable gas or refrigerated liquid with a faintly sweet odour.

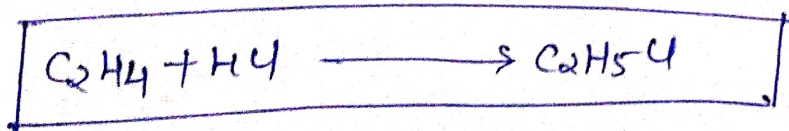


→ Ethyl carbon atoms are sp^3 hybridized.

⇒ formation of ethyl group



⇒ Preparation



⇒ Uses

- 1) Used as refrigerant, an aerosol spray propellant,
- 2) Used as anaesthetics
- 3) In industry used to make ethylcellulose from cellulose
- 4) Act as ~~car~~ depressant.

→ Used for temporary relief of minor sports injury.

→ E.C. is a cooling substance that is applied to skin.

→ It is used to prevent pain caused by injection and minor surgical procedure.

Side effect

→ cutaneous sensitization may occur.

→ It is a toxin for liver & kidney on long exposure.

⇒ Precaution

→ Flammable :- Don't use in presence of flame.

→ Do not spray in eyes.

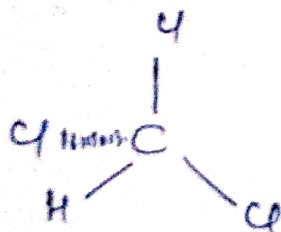
CHLOROFORM (CHCl_3)

- It is one carbon compound.
- It is a methane in which 3-H is replaced by Cl.
- Initially it is employed as ideal anaesthetics.
- first prepared in 1831.

⇒ Properties of CHCl_3

- 1) colourless.
- 2) Sweet smelling
- 3) Non-inflammable
- 4) Boiling point $\rightarrow 61.2^\circ\text{C}$
- 5) insoluble in H_2O

Structure



⇒ Chemical property of chloroform

a) Reaction with NaOH



$\downarrow$
(Sodi formate)

b) Oxidation of CHCl_3



Uses of CFCs

- 1) Used as anaesthetics, primarily during root canal procedure in dentistry.
- 2) Utilized in production of R-22 Freon refrigerant.
- 3) Used as indirect food additive in food packaging material for adhesive component.

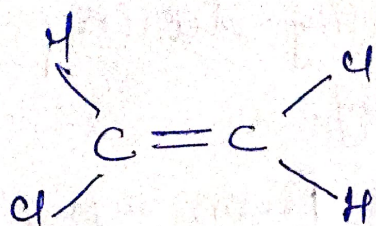
Side effect

- 1) Progressive central nervous system depression.
- 2) Chronic exposure leads to defect in blood, liver and kidney.

Trichloroethylene

- first prepared in 1864.
- Man. made compound
- formula $\rightarrow C_2HCl_3$
- It can be released into environment by evaporation from adhesive glue, paint, coatings and other chemical during their production.
- IUPAC $\rightarrow$ Trichloromethane

structure , C_2HCl_3

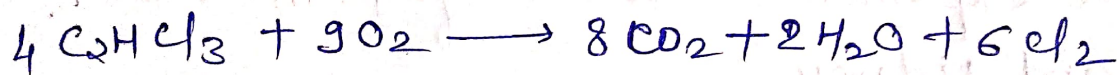


(1,2, trichloro ethane)

chemical property of C_2HCl_3

⇒ Oxidation

→ It goes to combustion reaction forming CO_2 , H_2O & Cl^- .



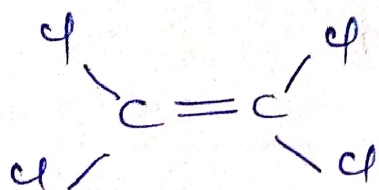
Uses

- 1) Used in anaesthesia for its analgesic property.
- 2) Used as solvent to remove grease from fabricated metal parts & some textiles.
- 3) Ingredient in adhesive, pain remover, type - writer correction fluid etc.

Tetrachloroethylene

- Volatile chlorinated organic hydrocarbon
- widely used as a solvent
- chemical formula $\rightarrow C_2Cl_4$
- Introduced in 1925

Structure C_2Cl_4



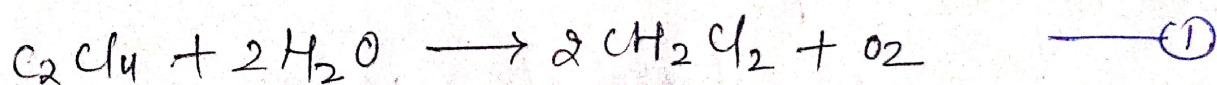
1, 2 tetrachloro ethylene
ethane.

Property

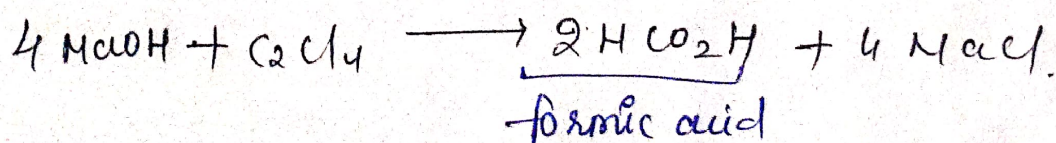
- $\Rightarrow$ odour $\rightarrow$ ethereal odour / sweat odour
- $\Rightarrow$ Appearance $\rightarrow$ colourless volatile liquid
- $\Rightarrow$ Solubility $\rightarrow$ Soluble in H_2O
- $\Rightarrow$ Non-inflammable
- $\Rightarrow$ liquid at room temperature

chemical property

① C_2Cl_4 dissolved in H_2O to form dichloromethane & O_2 .



②



Uses

- 1) Used as a cleaning solvent
 - 2) Chemical precursor for fluorocarbons
 - 3) It act as an anthelmintic for treatment of hook worm infestation.
 - 4) Used in transformers.
 - 5) Used as paint remover, ink, adhesive formulation.
 - 6) cooling gas in aerosol formation.
-

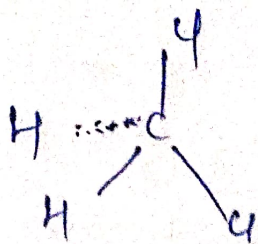
Dichloromethane

- Also called methylene chloride.
- Source : → Naturally from - Volcano, macro algae
- Majority is due to industrial emissions.
- formula : → $\boxed{\text{CH}_2\text{Cl}_2}$

Property

- colourless liquid
- sweet, penetrating ether like smell.
- volatile in nature
- Generally non combustible, but combustible on higher temp.
- It may produce toxic flame fumes.

Structure



Uses

- 1) As solvent in food technology.
- 2) Used in aerosol formation.
- 3) Used as degreasing agent.
- 4) Used in electronic manufacturing.

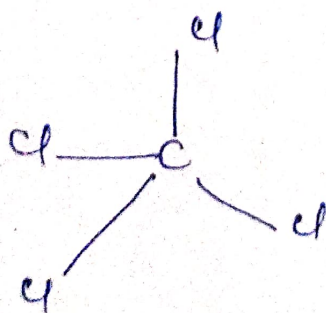
Tetrachloromethane, (CCl₄)

- Carbon tetrachloride, also k/as tetrachloromethane.
- CCl₄
- Under standard condition it is colourless liquid.

Properties

- colourless
- sweet odour
- M.P. = -22.93°C
- Soluble in H₂O
- It can be crystalizes in a monoclinic crystal lattice.

Structure



Uses

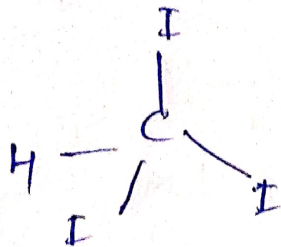
- 1) As a chlorine source in a reaction k/as Appel Reacⁿ
- 2) Used in proton NMR Spectroscopy.

* Appel reaction ∴ Reaction in which alcohol convert into alkyl chloride using "tri-phenyl phosphine"

Iodoform

- It is also known as tri-iodo-methane.
- Chemical formula → CHI_3
- It is highly inflammable
- It is volatile
- m.p. = 121°C
- It is a skin friendly chemical.

Structure



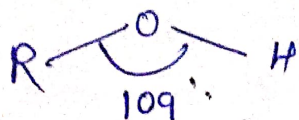
(Carbon tri-iodide)

Uses

- 1) Antiseptic to treat minor conditions.
- 2) Used in disinfectant products.
- 3) Sterilization of surgical instrument
- 4) It helps removing ear hair for dogs & cats.
- 5) Used in hospitals.

Alcohols

→ Alcohol is any organic compound in which the hydroxyl functional group ($-OH$) is bound to a saturated carbon atom.



Qualitative test

→ These tests are used to identify the presence of alcohol in a particular solution.

⇒ Following types of test.

(1) Sodium metal test

(2) Ester test

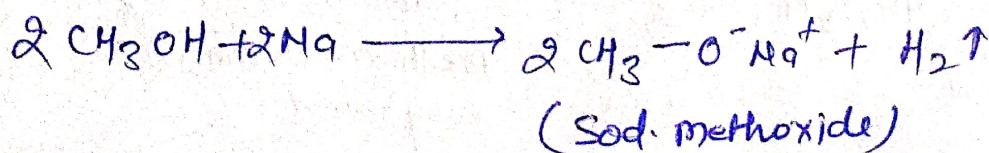
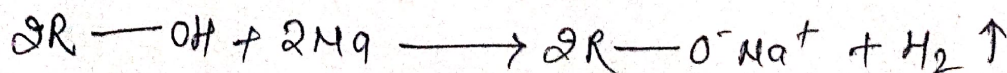
(3) Ceric ammonium nitrate test

(4) Acetyl chloride test

(5) Iodoform test.

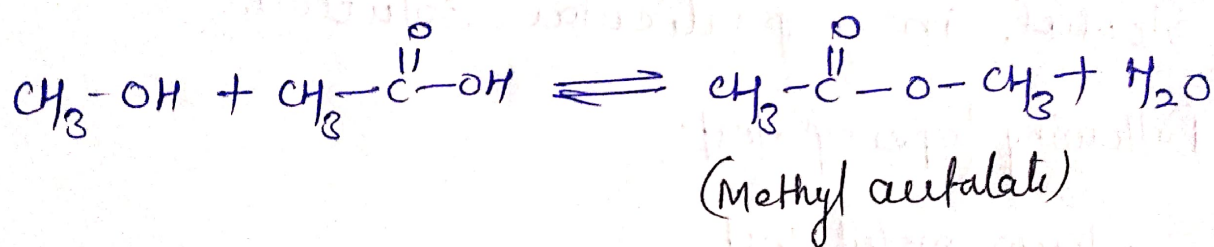
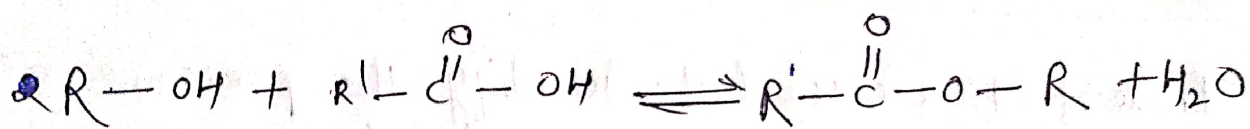
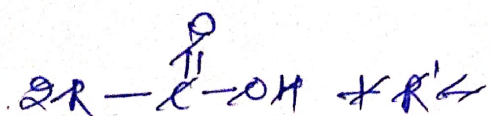
(1) Sodium metal test-

→ Alcohol reacts with dry Na metal & liberates H_2 gas that can be observed in form of effervescence.



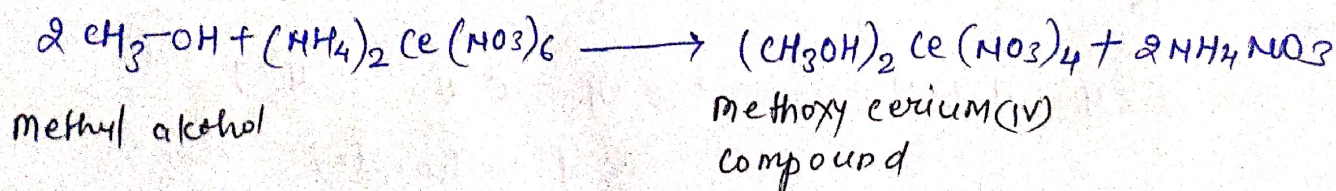
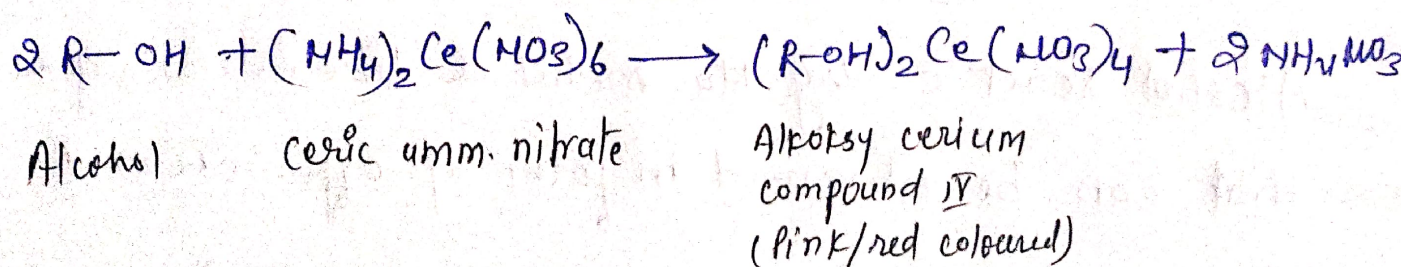
(2) Ester test

- Alcohol react w- COOH to form fruity smelling compound called "Ester".
- This reaction is called esterification.
- Catalysed by $\text{con}^n \text{H}_2\text{SO}_4$



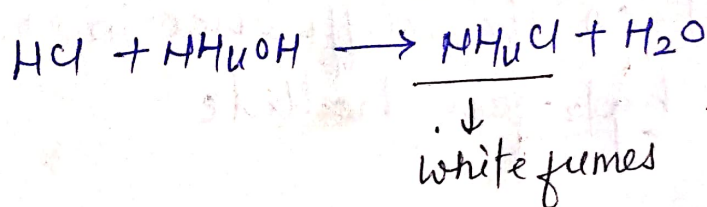
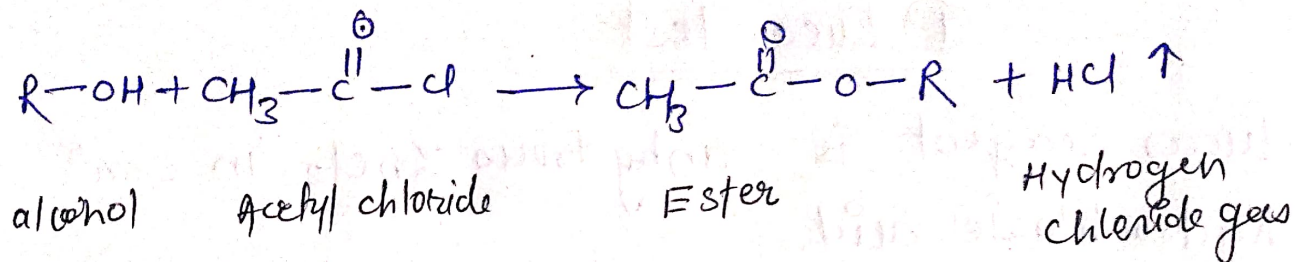
(3) Ceric Ammonium nitrate test

Alcohols react w- ceric ammonium nitrate to form a red coloured Alkoxy cerium compound.



④ Acetyl chloride test

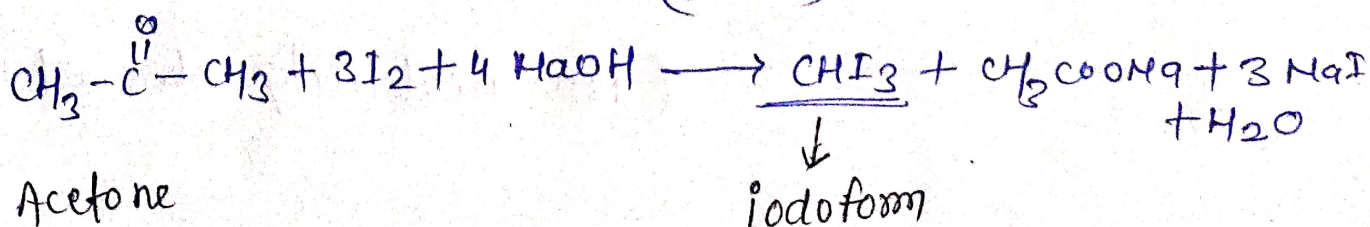
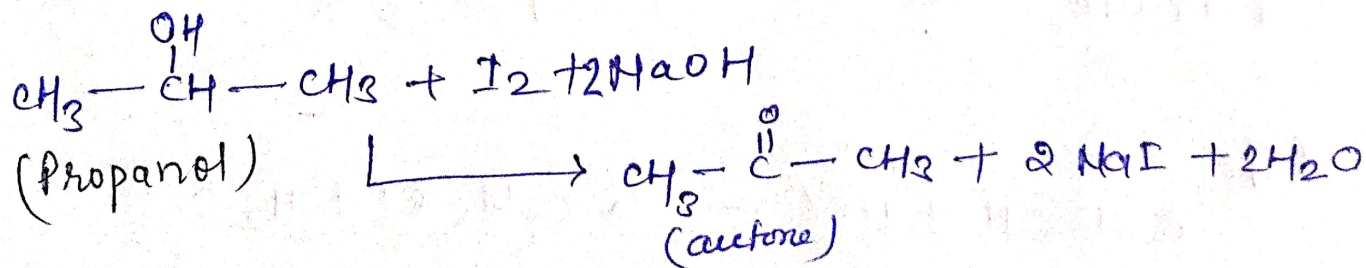
- * Alcohol react $\bar{c}$ acetyl chloride to form ester and give out HCl gas.
- * HCl gas when react $\bar{c}$ NH_4OH give white fumes.



⑤ Iodoform test

→ This test is given by acetaldehyde, all methyl ketones & all alcohol containing $\text{CH}_3\text{-CH-OH}$ group.

→ when alcohol react $\bar{c}$ / warmed $\bar{c}$ NaOH solution and iodine $\rightarrow$ A yellow precipitate forms.



Test to differentiate Primary, secondary and tertiary alcohol.

① Lucas test

② Victor Meyer test

① Lucas test

→ Lucas reagent is anhydrous ZnCl_2 in conⁿ hydrochloric acid.

→ It is based on the difference in reactivity of alcohol & hydrogen halide.

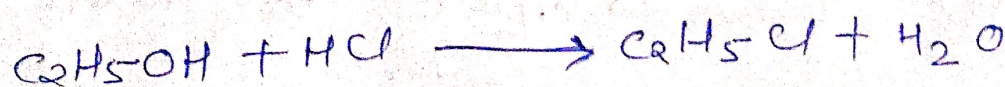
→ It follows the $\text{S}_\text{N}1$ reaction.

① Test for Primary Alcohol

→ When Lucas reagent is added to 1° alcohol, there is no change observed in the solution, rather it remains colourless.

→ The solution is then heated for 30-45 minutes and an oily layer is formed.

e.g.

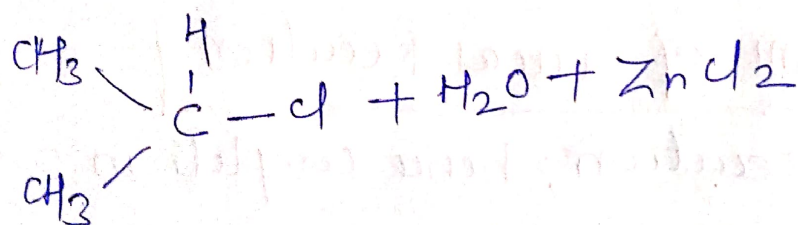
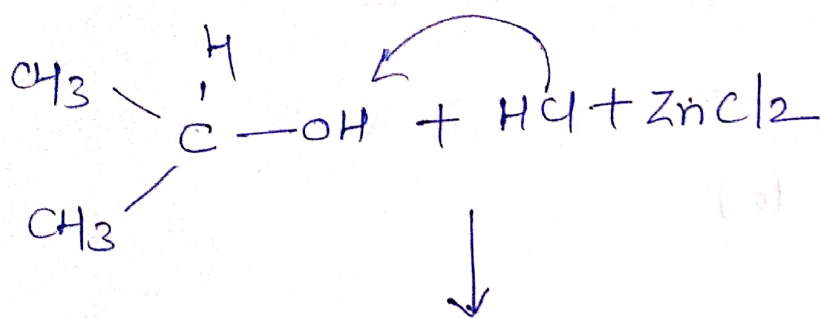
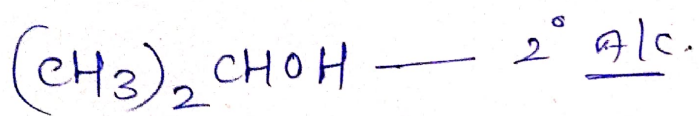


(no turbidity observed)

② Test for Secondary alcohol

2° alcohol + Lucas reagent

- ↓
- 1) Oily layer is formed in 2-4 minutes.
 - 2) Turbidity is observed.

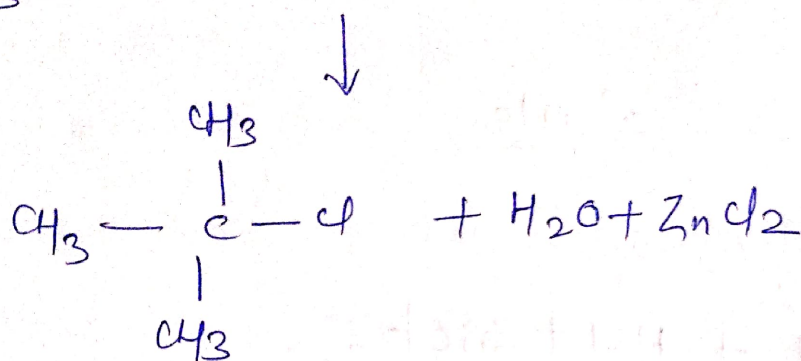
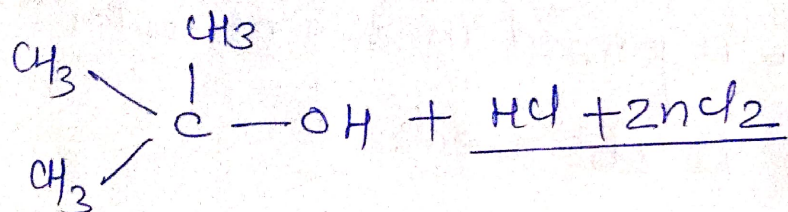


(propyl chloride)

* Propyl chloride is responsible for turbidity in solⁿ.

(3) Test for tertiary alcohols

→ 3° alcohol quickly form an oily layer & turbidity is also observed.

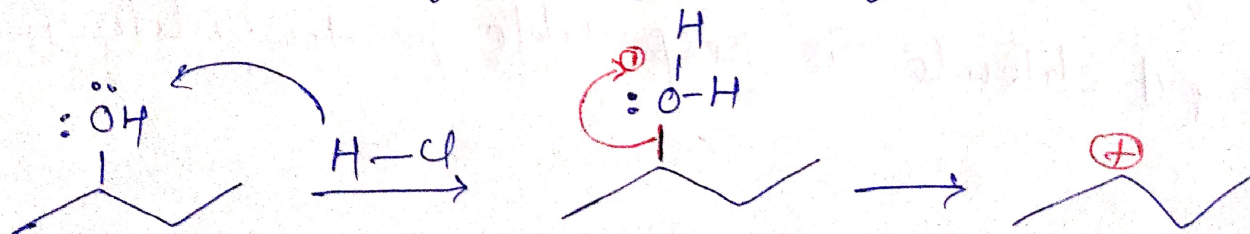


(tert) chloride

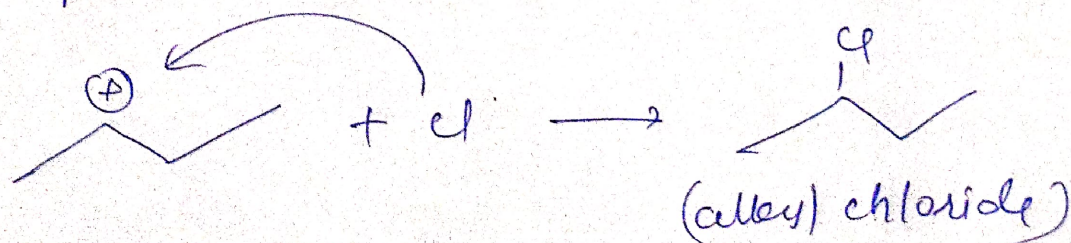
Mechanism of Lucas Reaction

* It follows S_N1 reaction; hence complete in 2 steps.

(I) Protonation of hydroxyl group & formation of



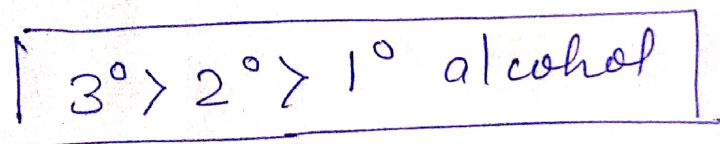
(II) Attack of Cl on carbocation.



Observation

Type of alcohol	Observation
Primary	no change in sol. upon heating an oily layer is formed.
Secondary	solution turn turbid, oily layer formed (3-5 min)
Tertiary	Turbid solution, oily layer is formed.

* Rate of reaction is according to Carbocation stability



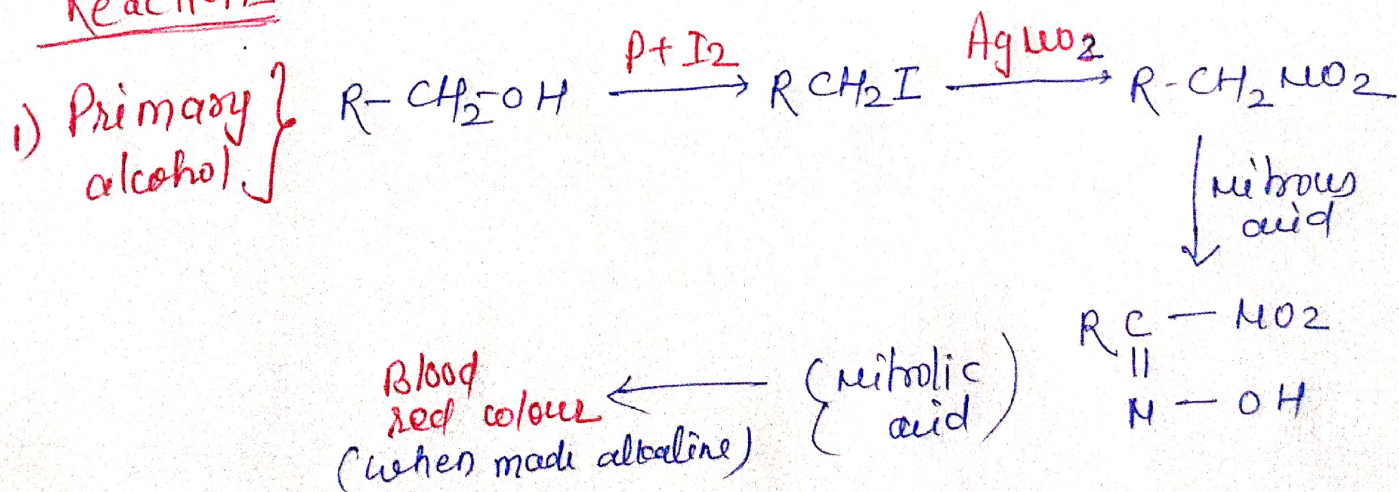
Victor Meyer test

→ In this method $1^\circ, 2^\circ, 3^\circ$ alcohol are subjected to series of chemical analysis. & colour of resulting solution is observed.

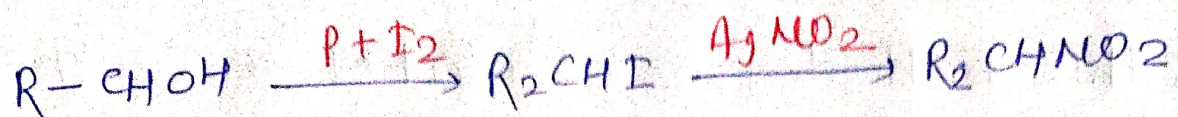
Steps

- 1) Alc. is treated w/ I_2 in presence of red-phosphorus to obtain iodo alkane.
- 2) Iodo alkane reacts w/ alc. $AgNO_3$ to obtain nitro-alkane.
- 3) Nitro-alkane is treated w/ nitrous acid $(HNO_2 + HCl)$ & resulting soln made alkaline.
- 4) Colour observed
 - a) Primary alcohol → Red blood colour
 - b) Secondary alcohol → blue colour
 - c) Tertiary alcohol → no. colour.

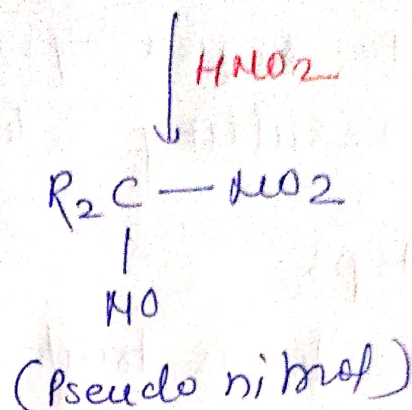
Reactions



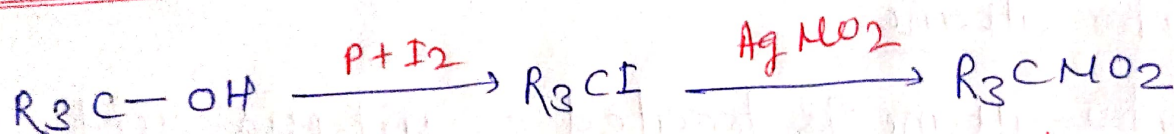
Secondary



Blue colour
w/ alkali



Tertiary



↓
(no reaction)