

Unit: Haloalkane

- General formula: $C_n H_{2n+1} X$ where $X = F, Cl, Br, I$
 $n = \text{no. of atoms}$
- Representative formula: $R-X$

Saturated hydrocarbon from which atleast one hydrogen is replaced by halogen atom is called haloalkane. Depending on no. of halogen atoms present, haloalkanes are classified as monohaloalkane, or dihaloalkane or trihaloalkane or polyhaloalkane.

* classification of monohaloalkane:-

①

↳

Depending on nature of carbon to which halogen atom is attached, monohaloalkanes are of following three types

① primary haloalkane (pri.) Eg CH_3-CH_2-Cl

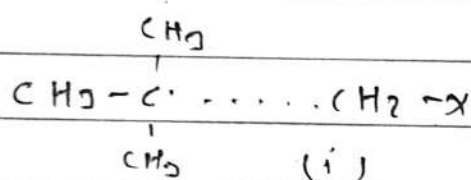
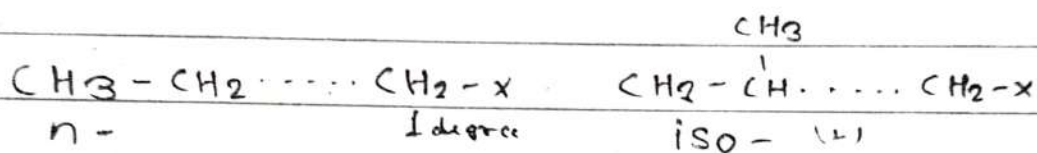
② Secondary haloalkane (sec.) Eg. $CH_3-\underset{\substack{| \\ F}}{CH}-CH_3$

③ Tertiary haloalkane (Tert). Eg $CH_3-\underset{\substack{| \\ CH_3}}{C}-Br$

* Nomenclature:-

→ Common System:-

In this system halogen compounds are named as alkyl halide. In case of complex molecule prefix like n-, iso-, neo-, or sec-, tert etc is used to show nature of carbon chain or nature of carbon to which halogen compound atom is attached respectively



neo-

→ Iupac Name:-

Formula	Common Name	Iupac Name
① $\text{CH}_3 - \text{F}$	Methyl fluoride	Fluoromethane
② $\text{CH}_3 - \text{CH}_2 - \text{Cl}$	Ethyl chloride	Chloroethane.
③ $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{Br}$	n-propyl bromide	1-Bromopropane
④ $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH} - \text{I} \end{array}$ or $\begin{array}{c} \text{I} \\ \\ \text{CH}_3 - \text{CH} - \text{CH}_3 \end{array}$	sec-propyl iodide iso-propyl iodide	2-Iodopropane.

⑤ $\text{CH}_3 - \overset{\text{CH}_3}{\underset{|}{\text{CH}}} - (\text{CH}_2 - \text{Cl})$ iso-Butyl chloride 1-chloro-2-methylpropane

⑥ $\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{|}{\text{C}}} - \text{Br}$ tert-Butyl bromide 2-bromo-2-methylpropane

⑦ $\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{|}{\text{C}}} - \text{CH}_2 - \text{I}$ neo-pentyl iodide 1-iodo-2,2-dimethylpropane

⑧ CHCl_3 chloroform Trichloromethane

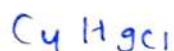
⑨ CHI_3 Iodoform Tri-iodomethane

⑩ CCl_4 carbon tetrachloride Tetrachloromethane

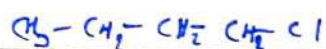
Isomerism

Organic compound having same molecular formula but different structural formula and properties are called isomers and this phenomenon is called Isomerism.

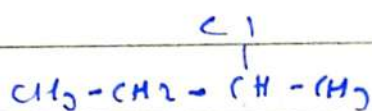
Haloalkane shows following two isomerism



2. position isomerism

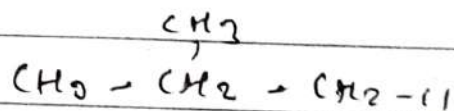
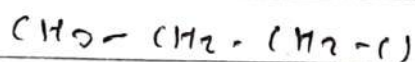
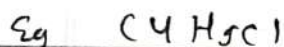


1-chlorobutane



2-chlorobutane.

1. chain isomerism



* General method of preparation

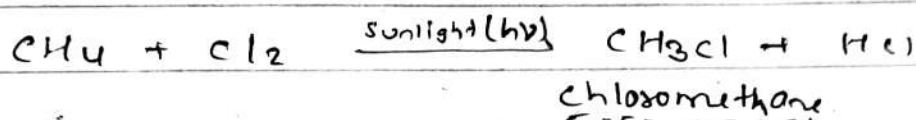
(i) From alkane:- (Halogenation)

When alkane is treated with Halogen in presence of sunlight or heat or suitable catalyst, haloalkane is formed.
(Halogenation)

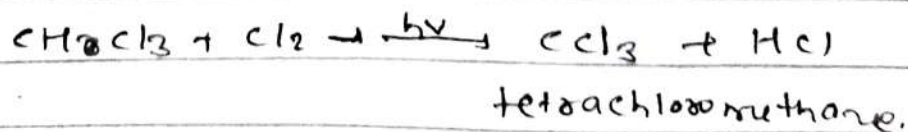
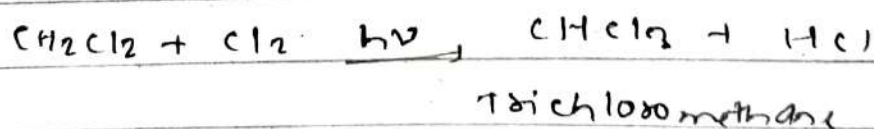
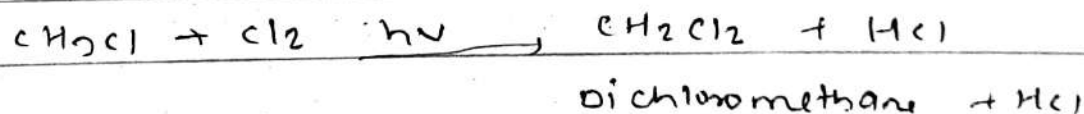
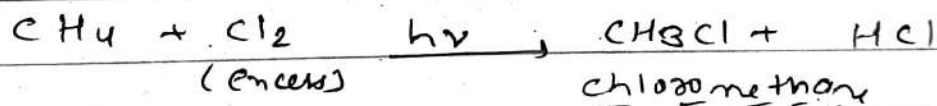


* Chlorination:-

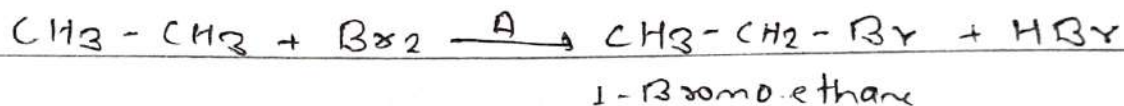
When alkane is treated with limited chlorine in presence of sunlight, chloroalkane is formed.



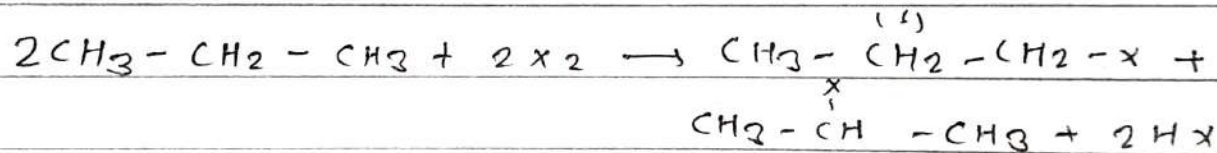
When alkane is treated with excess chlorine in presence of sunlight, mixture of mono, di, tri and poly chloro alkane is formed.



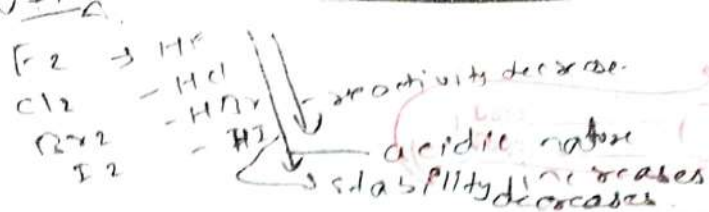
* Bromination :-



* Note :-



When alkane containing different nature of hydrogen and carbon is treated with halogen then respective haloalkanes are formed.

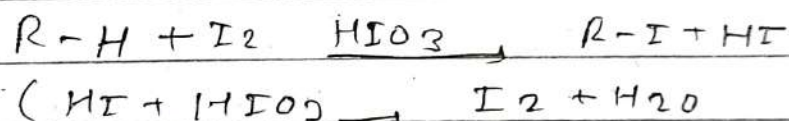


* Iodination:-

Direct Iodination of alkane is not possible because iodine is least reactive among the halogens and the hydrogen iodide formed is strong reducing agent which reduces Iodo alkane to alkane.



Iodination of alkane is carried out in presence of oxidizing agent like Iodic Acid (HIO_3) or conc. (HNO_3) because it oxidizes hydrogen Iodide (HI) to Iodine and also increases the rate of forward reaction.

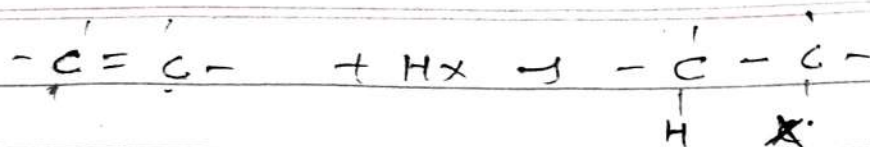


* Fluorination:-

Direct fluorination of alkane is not possible due to very high affinity of fluorine for hydrogen.

2. From alkene:-

When alkene is treated with hydrogen halide ($\text{HX} = \text{HF}, \text{HCl}, \text{HBr}$) Haloalkane is formed.



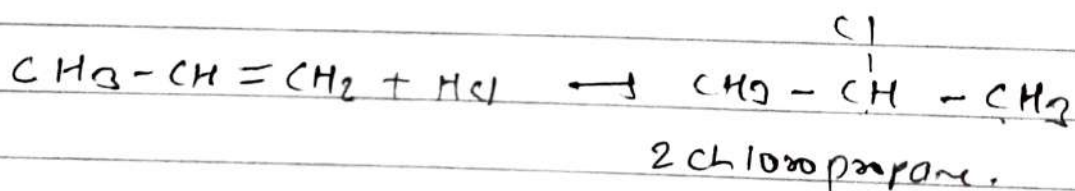
Haloalkane.



↓ Chloroethane.

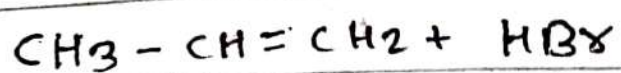
* Markovnikov's rule:-

Adding of hydrogen halide to unsymmetric alkene takes place according to markovnikov's rule which states that hydrogen of hydrogen halide get attached to that doubly bonded carbon atom which has more no. of hydrogen atoms.

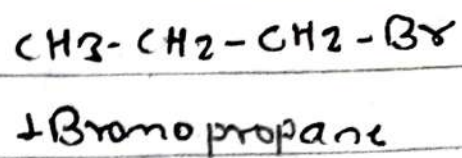


* Anti-Markovnikov's rule:-

Addition of hydrogen bromide to unsymmetric alkene in presence of organic peroxide takes place opposite to markovnikov's rule that is hydrogen of hydrogen bromide get attach to that doubly bonded carbon atom which has less number of hydrogen atom. It is called anti markovnikov's rule or peroxide effect or Kharasch effect.



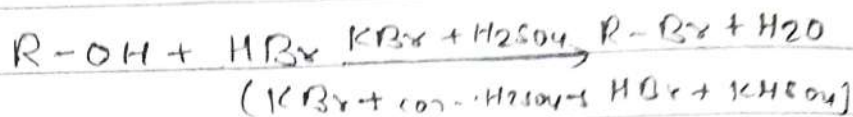
organic
Peroxide



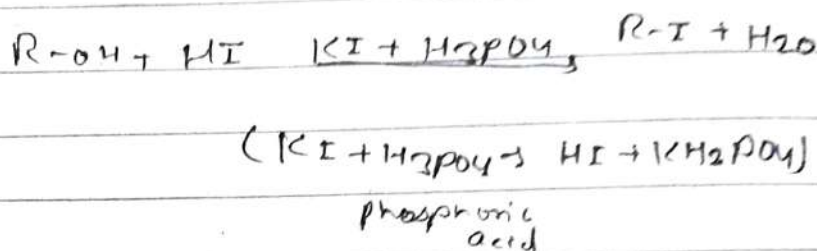
H_2PO_4
phosphoric
acid

H_3PO_3
phosphorous
acid

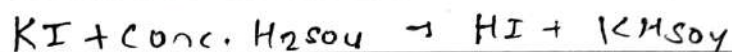
Bromoalkane:



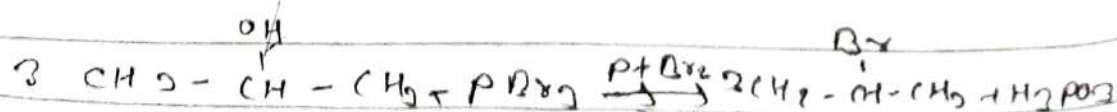
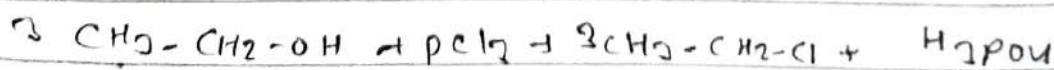
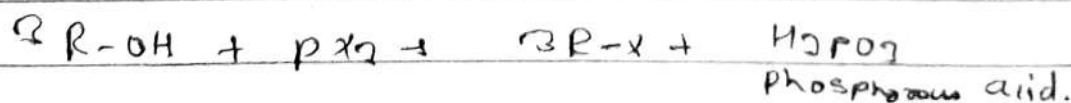
Iodoalkane:



for the preparation of hydrogen iodide, conc. H_2SO_4 cannot be used instead of phosphoric acid because conc. H_2SO_4 oxidise hydrogen Iodide (HI) to Iodine.

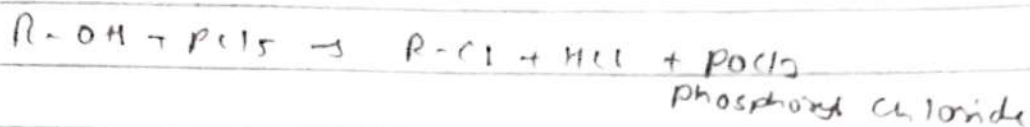
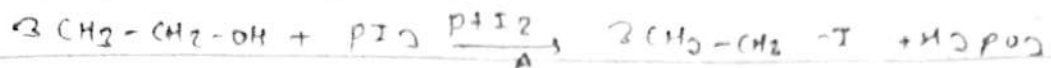


By reaction with phosphorous halide



common name ~~acetone~~
acetone \rightarrow propanone

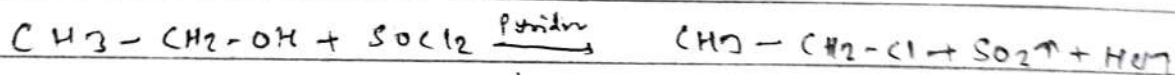
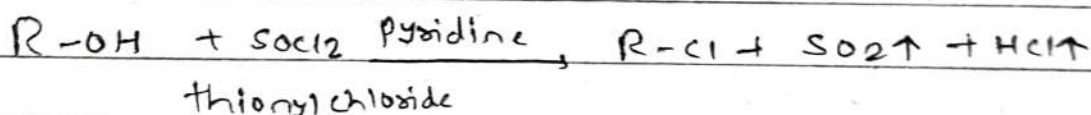
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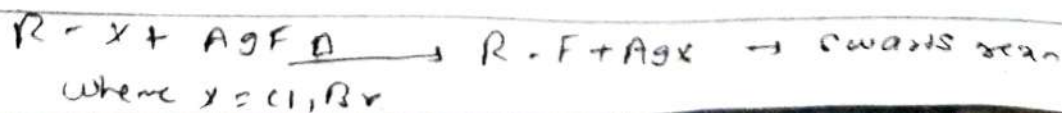
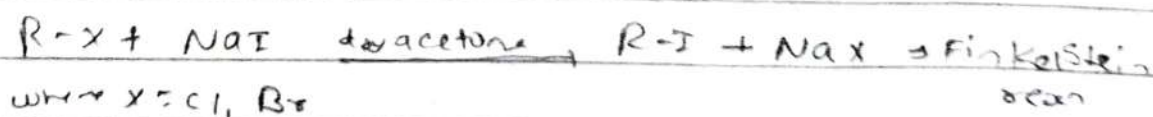
3/11 © By reaction with thionyl chloride:-

when alcohol

is treated with thionyl chloride in presence of pyridine, chloroalkane is formed. This reaction is preferred for the preparation of chloroalkane because the side product form are gases and escaped out ^{leaving} ~~living~~ behind pure chloroalkane.



④ By halogen exchange method:-



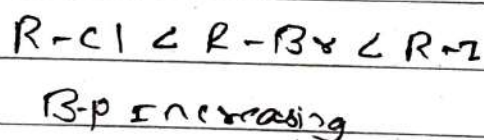
* physical properties of haloalkane.

① physical state:-

lower member of haloalkane like $\text{CH}_3\text{-Cl}$, $\text{CH}_3\text{-Br}$, $\text{C}_2\text{H}_5\text{-Cl}$ etc are colourless gas. Higher members are oily liquid and more higher members are solid.

② Boiling point:-

Haloalkane shows following order of their boiling point.



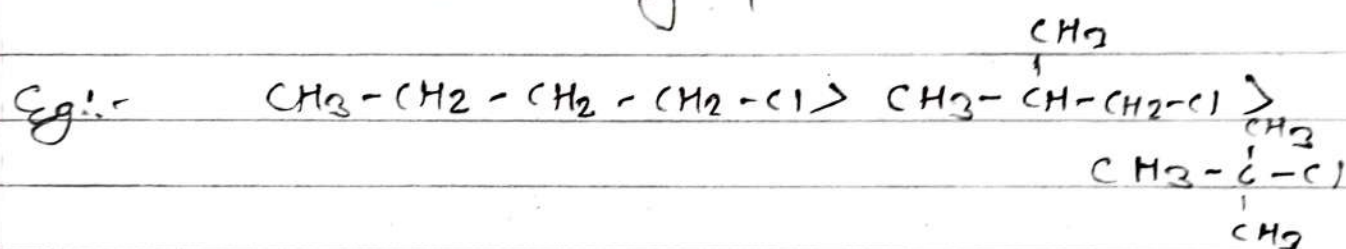
It is because as mass and ~~volume~~ size of halogen atom increases, vander waal's force of attraction also increases.

Q. Between chloroethane and Bromoethane, which one will have high boiling point and why?

⇒ Bromoethane has high boiling point than chloroethane size and mass of bromine is higher than chlorine so, vander waal's

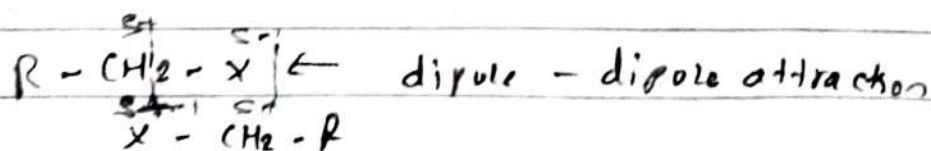
force of attraction is higher in bromoethane than chloroethane

In case of isomeric haloalkane as branching increases boiling point decreases because increase in branching tends the molecule to be spherical with less contact surface area as a result intermolecular force of attraction decreases which in turn decreases the boiling point



(ii) i-haloalkane > 2-haloalkane > 3-haloalkane

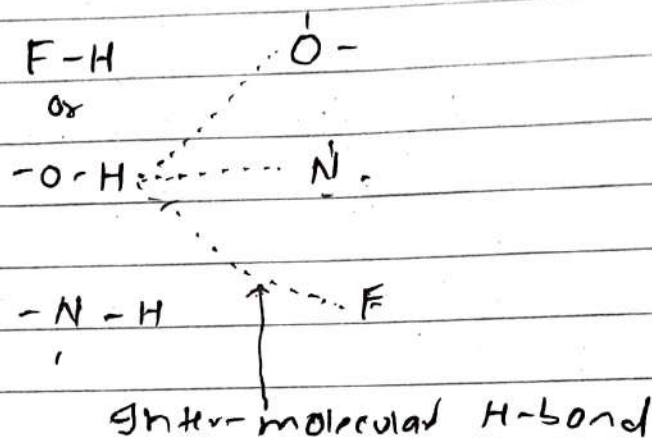
Haloalkane have high boiling point than alkane having comparable molecular mass because haloalkanes are polar molecules & show dipole-dipole attraction



③ Solubility:-

Halobalkanes are insoluble in water because they cannot form intermolecular H-bond with water.

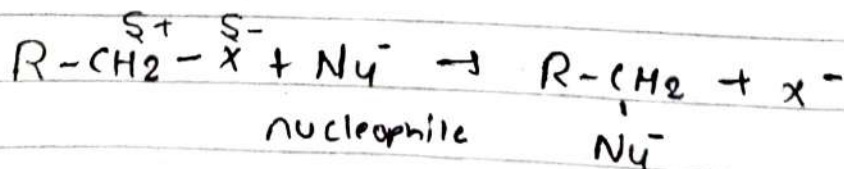
Capable Hydrogen



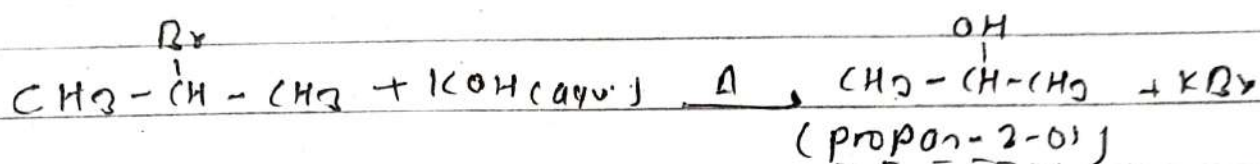
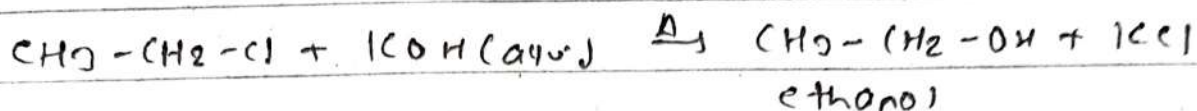
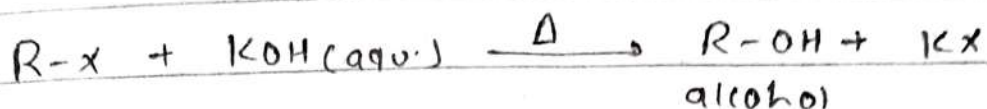
Chemical properties of halobalkane:-

① Nucleophilic substitution reaction:-

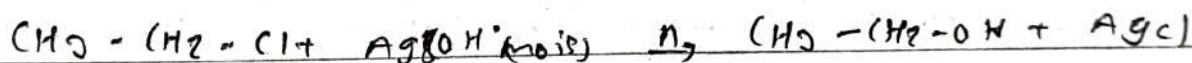
→ Reaction is initiated by nucleophile. It is characteristic reaction of halobalkane and occurs easily because halobalkane is polar molecule which makes attack of nucleophile easier.



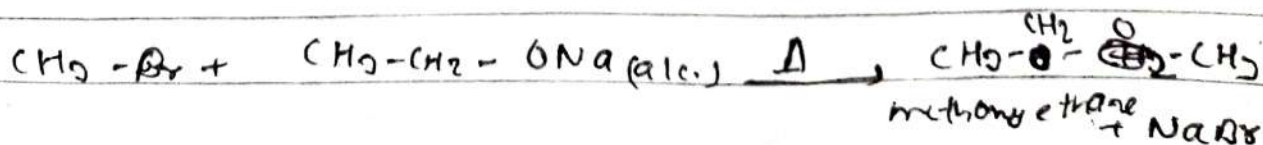
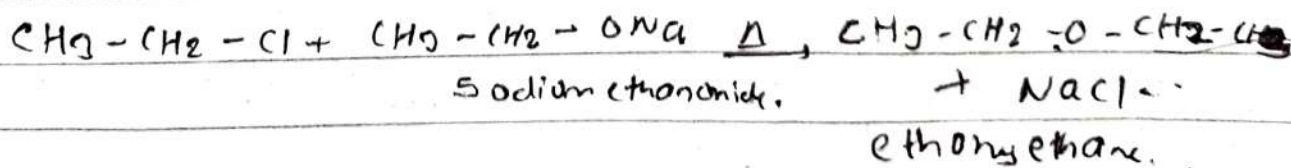
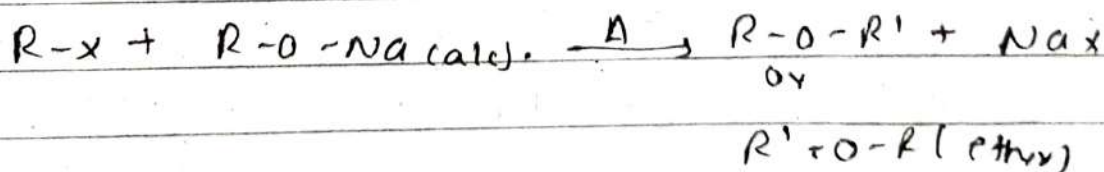
- (i) Reaction with aqueous alkali like KOH , NaOH gives alcohol



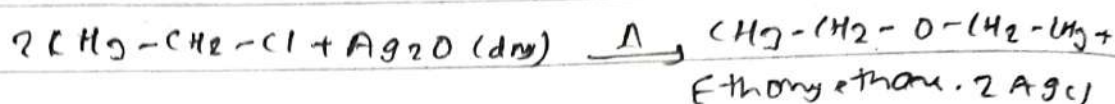
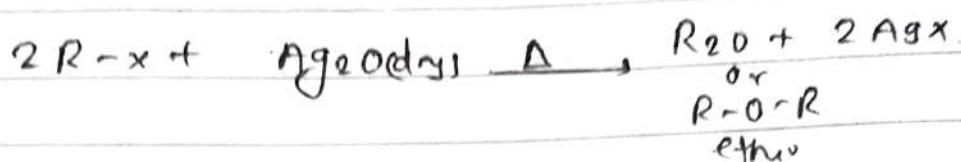
- (ii) Reaction with moist silver hydronide gives alcohol



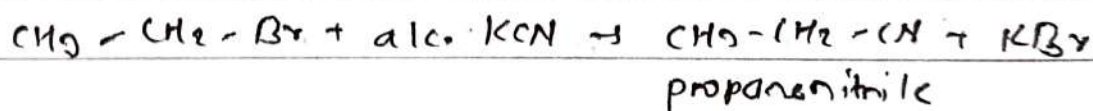
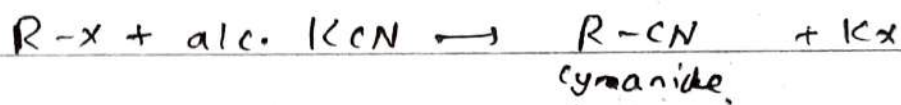
- (iii) Reaction with alcoholic sodium alkoxide (RONa) gives ether



(iv) Reaction with dry silver oxide (Ag_2O) gives ether



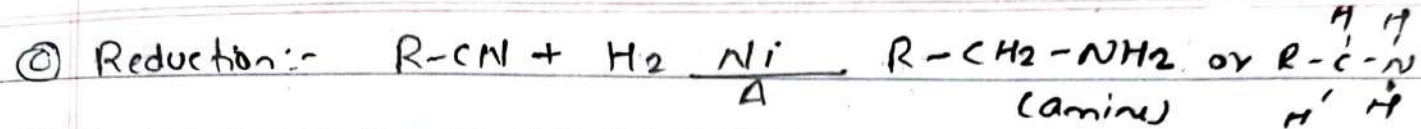
// (v) Reaction with alcoholic potassium cyanide (KCN)



Application of alkane nitrile

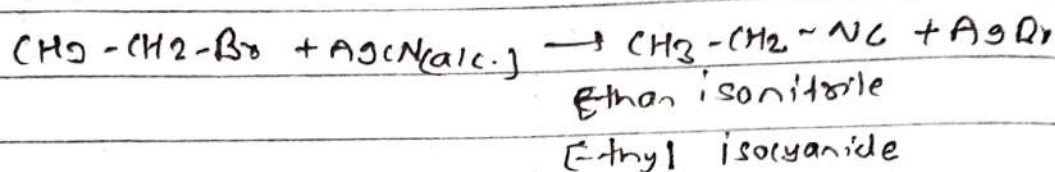
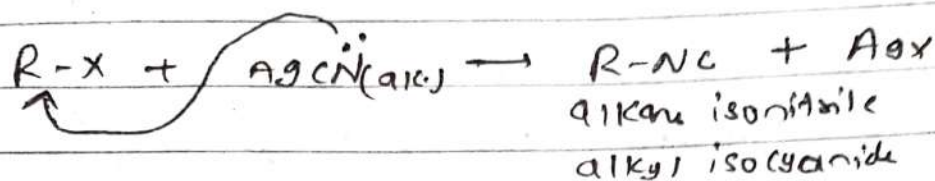
(a) partial hydrolysis: $\text{R-CN} + \text{H}_2\text{O} \xrightarrow{\text{conc. HCl}} \text{R-C(=O)NH}_2$
amide

(b) complete hydrolysis: $\text{R-CN} + \text{H}_2\text{O} \xrightarrow[\text{H}^+]{\text{dil. HCl}} \text{R-COOH}$
carboxylic acid





Reaction with alcoholic silver cyanide (AgCN)



NOTE

- ② isocyanide is formed because the bond between silver and carbon in AgCN is covalent so the lone pair of electron on nitrogen makes attack on haloalkane

③ Ambident nucleophile:-

The group like CN, NO₂ which can make attack through two different atoms during reaction is called ambident nucleophile (ambident group)

Note

Eg

CN

-CN: cyanide

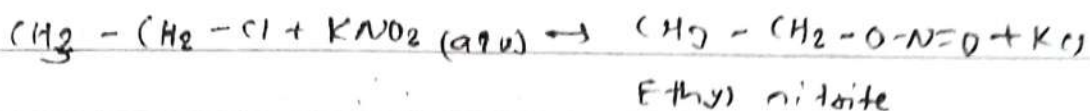
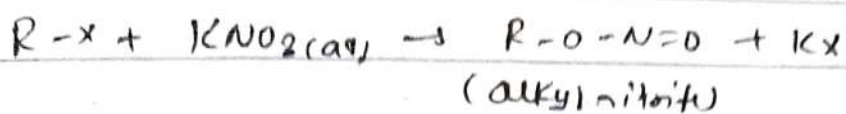
-NC: isocyanide

NO₂

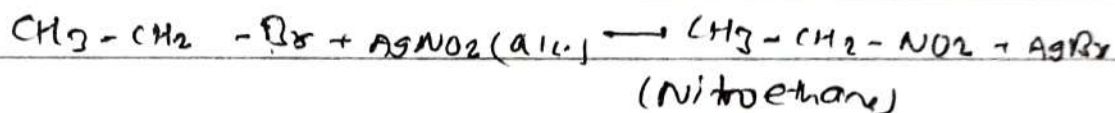
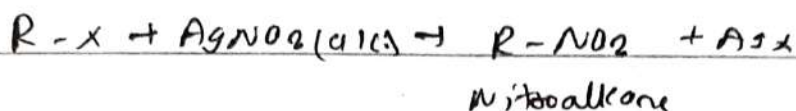
-N=O nitro
→ O

-O-N=O nitrite

(vii) Reaction with aqueous potassium nitrite (KNO_2 ; K^+ , $-\text{O}-\text{N}=\text{O}$)



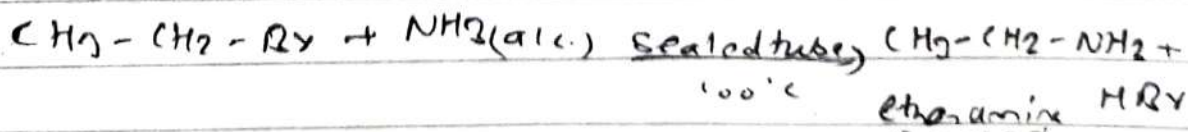
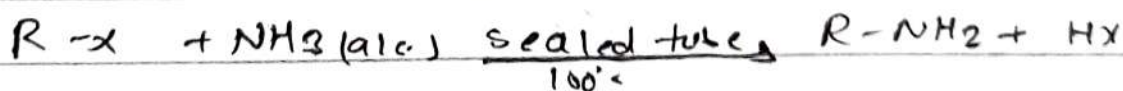
(viii) Reaction with alcoholic silver nitrite (AgNO_2 ; $\text{Ag}-\text{O}-\text{N}=\text{O}$)



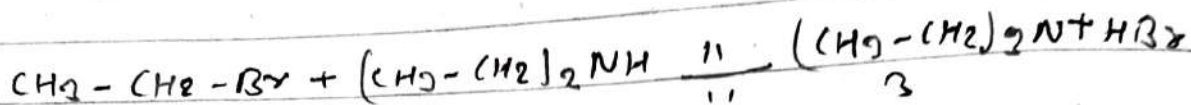
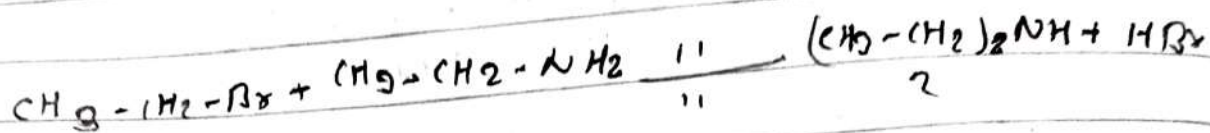
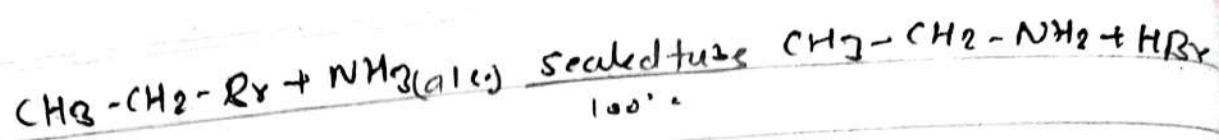
(ix) Reaction with alc. ammonia :-

when haloalkane

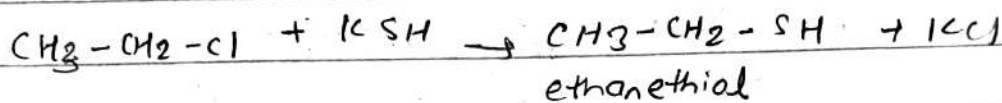
is treated with ammonia in a sealed tube at 100°C temperature, amine is formed



if haloalkane is in excess mixture of primary secondary and tertiary amine is formed

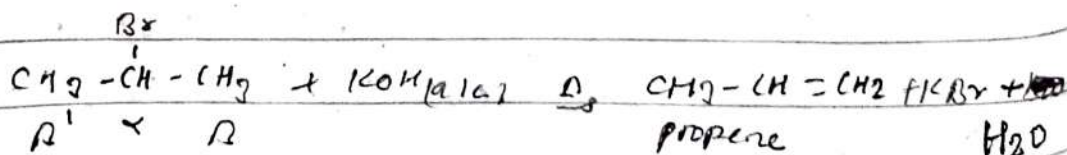
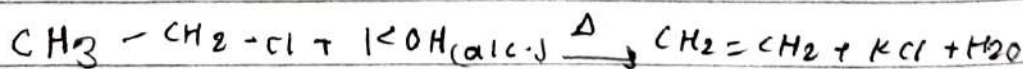


⑩ Reaction with potassium hydrogen sulphide



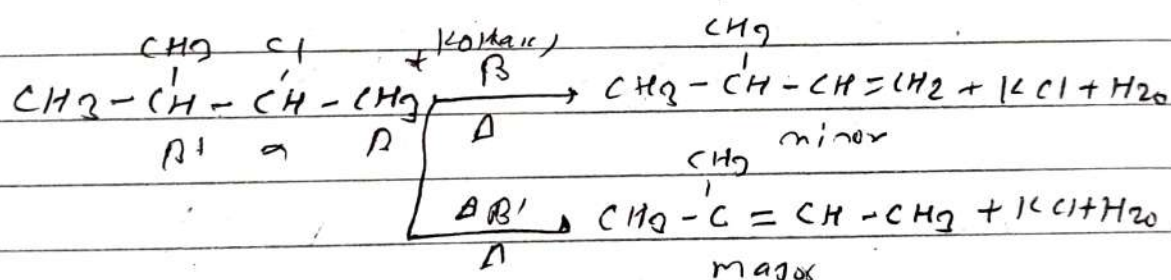
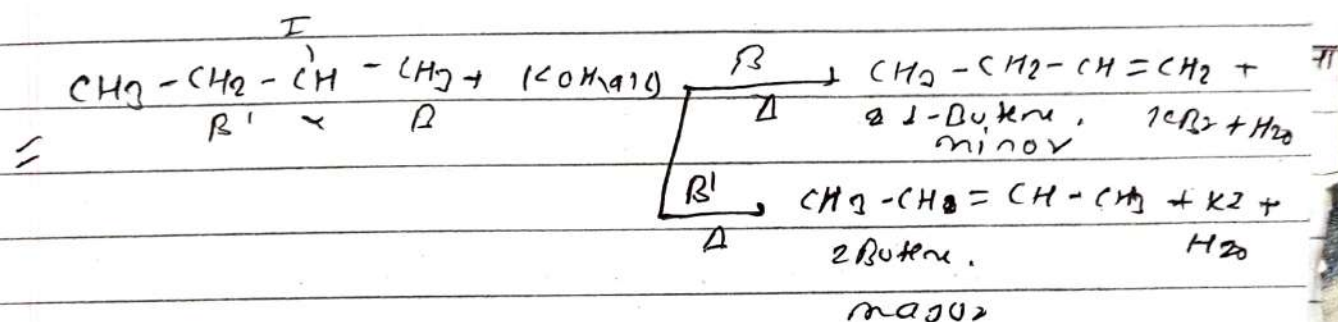
⑪ Reaction with alcoholic alkali (Dehydrohalogenation rxn. - Elimination rxn) :-

When haloalkane is heated with ~~sodium~~ alcoholic alkali like KOH, NaOH, it under goes Dehydrohalogenation rxn producing alkene. Since Hydrogen is replaced from β -carbon, it is also called β -elimination reaction.



* Saytzeff's rule:-

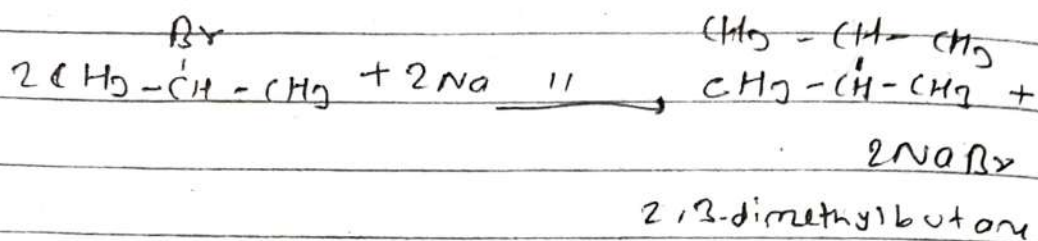
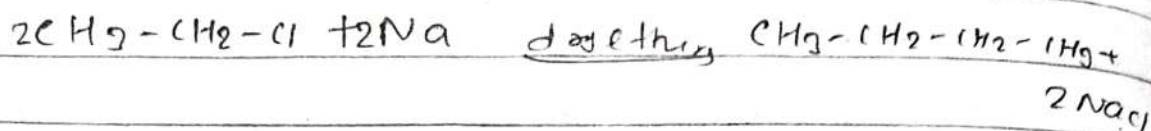
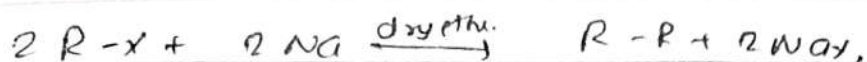
During dehydrohalogenation reaction that alkene is measure product which contains more number of alkyl group directly attach to the doubly bonded carbon atom



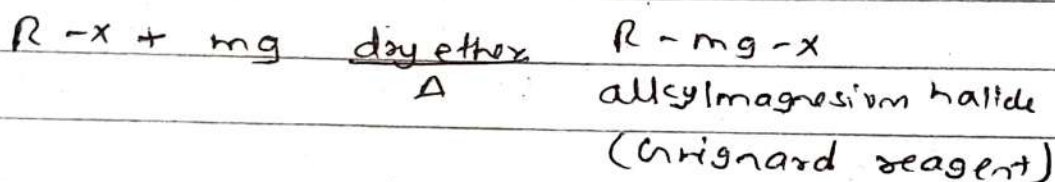
③ Reaction with metal

① Reaction with sodium metal (Wurtz reaction):-

When haloalkane is treated with sodium metal in presence of dry ether, alkane with double the no. of carbon atoms than haloalkane is formed. This reaction is called wurtz reaction



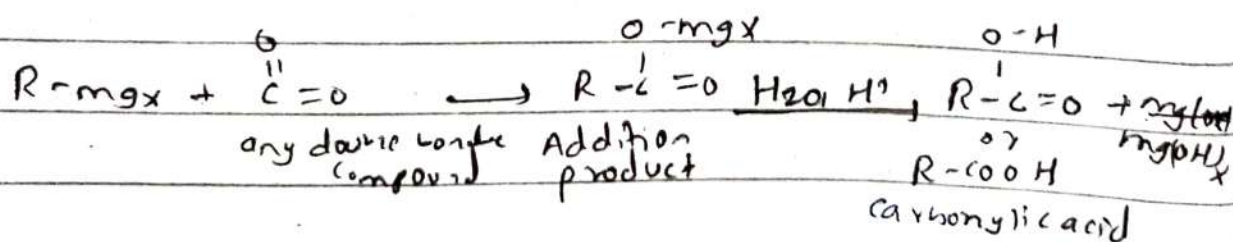
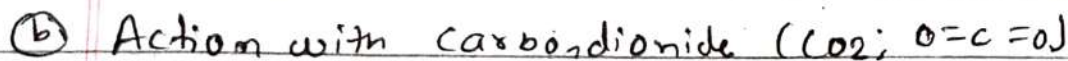
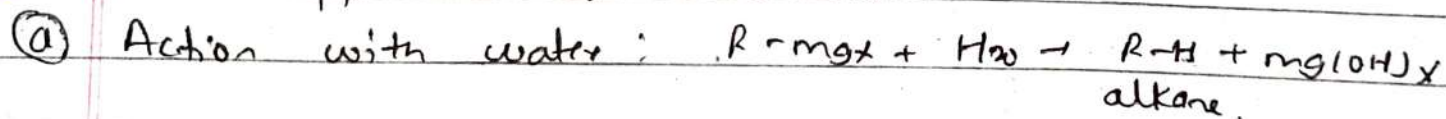
// ③ ii Reaction with magnesium metal



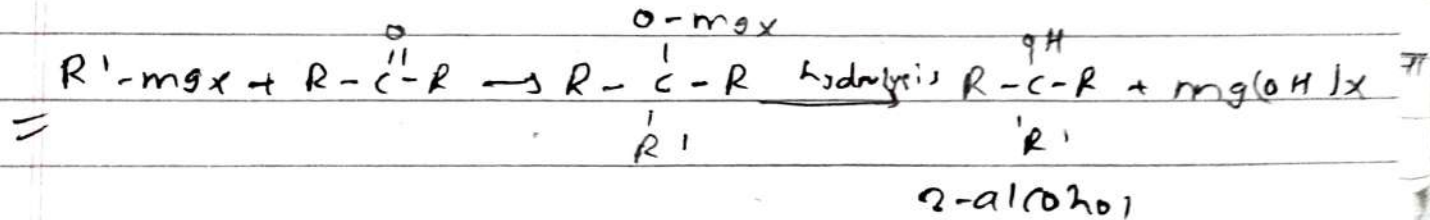
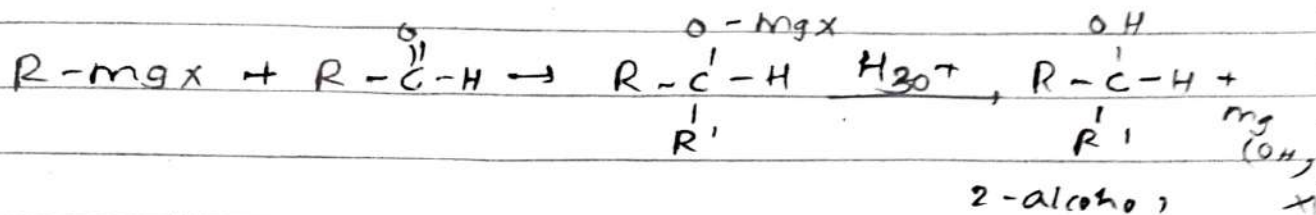
Note.

$R-MgX$ does not exist in polar solvent like water

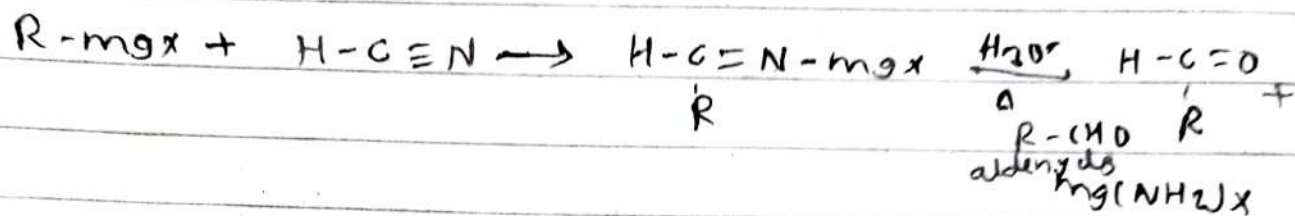
→ Application of Grignard



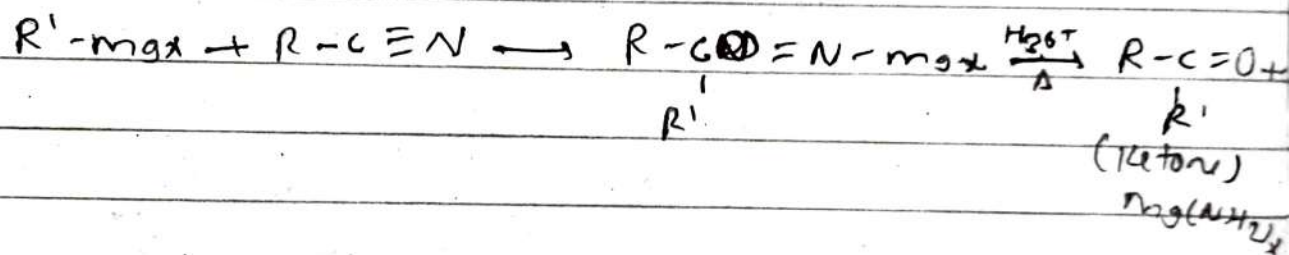
② Action with aldehyde ($R-CHO$) and Ketone ($R-COR$)



✓ (d) Action with hydrogen cyanide (HCN)

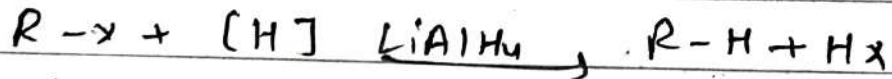
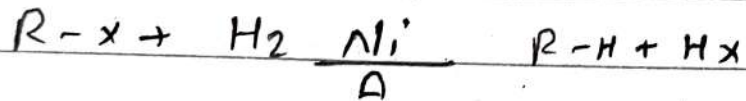


✓ (e) Action with alkane nitrile (R-CN)



✓ (u) Reduction :- when haloalkane is treated with hydrogen gas in presence of Ni or Pt or Pd as catalyst or treated with nascent hydrogen obtained from Zn/HCl or $Zn/NaOH$ or Sn/HCl or $Ni-Al/NaOH$ or $H_2/Red\ phosphorus$ or $NaBH_4$ (sodium borohydride) or $LiAlH_4$ (Lithium

aluminium) or $(C_2H_5OH + Na)$ etc. alkane is formed.

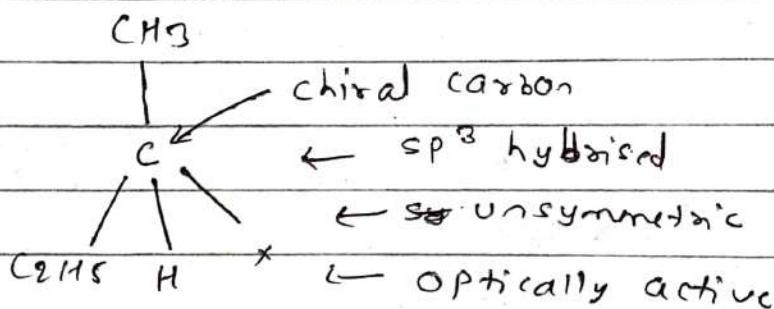


Stereoisomerism:

Organic compounds having same molecular formula and structural formula but different spatial arrangement of atom or group of atom is called stereoisomers and this phenomenon is called stereoisomerism.

* plane polarised light (PPL): Beam of light having oscillation in one plane.

* chiral carbon / chiral centre :-



Optically active compound :-

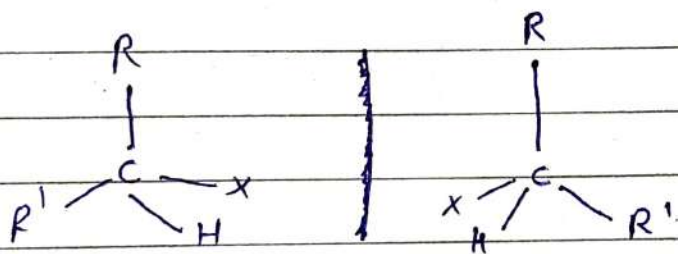
The compound whose solution rotate the plane of plane polarised light (PPL) when it is passed through it is called optically active compound. If it rotate PPL to right, it is called dextrorotatory. It is represented by d or $(+)$. If it rotate PPL to left, it is called laevorotatory, it is denoted by

l or \odot (-) .

* Enantiomer:-

Stereoisomer which are non-superimposable mirror image are called Enantiomers.

Enantiomers are optically active. They rotate p.p.L to equal extent but in opposite direction so, equimolar mixture of Enantiomer is optically inactive. and Such mixture is called racemic mixture.



Ques

Mechanism for Nucleophilic substitution reaction:-

Nucleophilic Substitution reaction proceeds through following two mechanism

1. S_N1 :- Substitution Nucleophilic Unimolecular (Unimolecular Nucleophilic Substitution)

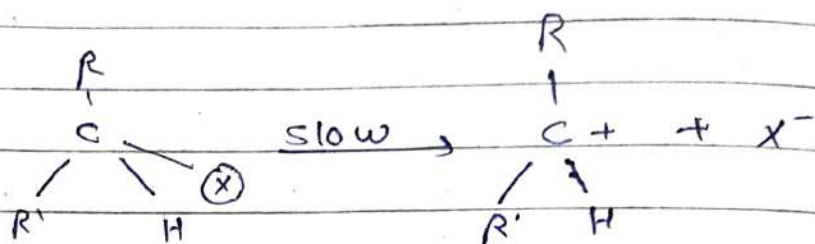
- It follows first order reaction.
- It occurs in two steps.
- The reactivity for haloalkane by S_N1

mechanism is

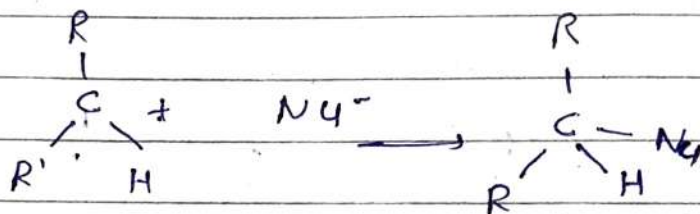
1-haloalkane < 2-haloalkane < 3-haloalkane

Mechanism:

Step-I



Step-II



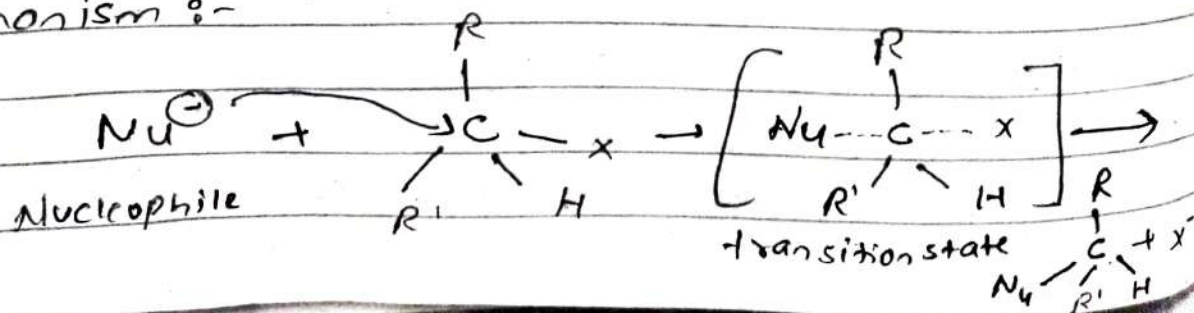
2. SN^2 :- Substitution Nucleophilic Bimolecular
(Bimolecular Nucleophilic Substitution)

- It follows ~~2~~ Second order reaction.
- It occurs in single step
- The reactivity order for haloalkane by SN^2 mechanism is

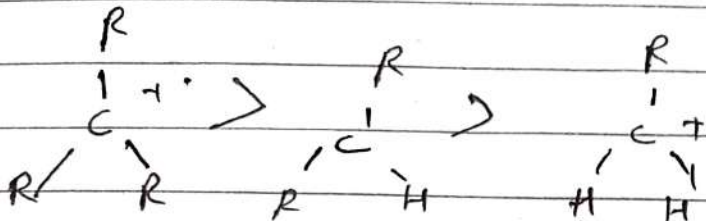
1-haloalkane > 2-haloalkane > 3-haloalkane

- It proceeds with inversion in configuration.

Mechanism :-



Not



stability decreasing.