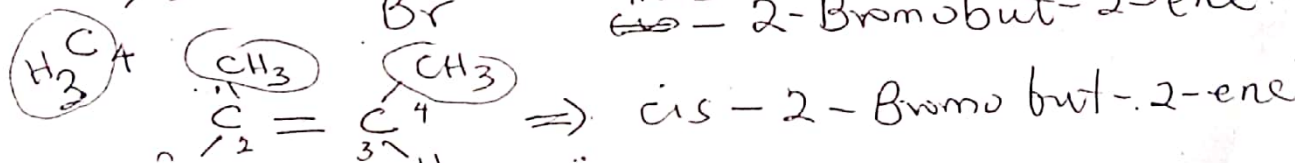
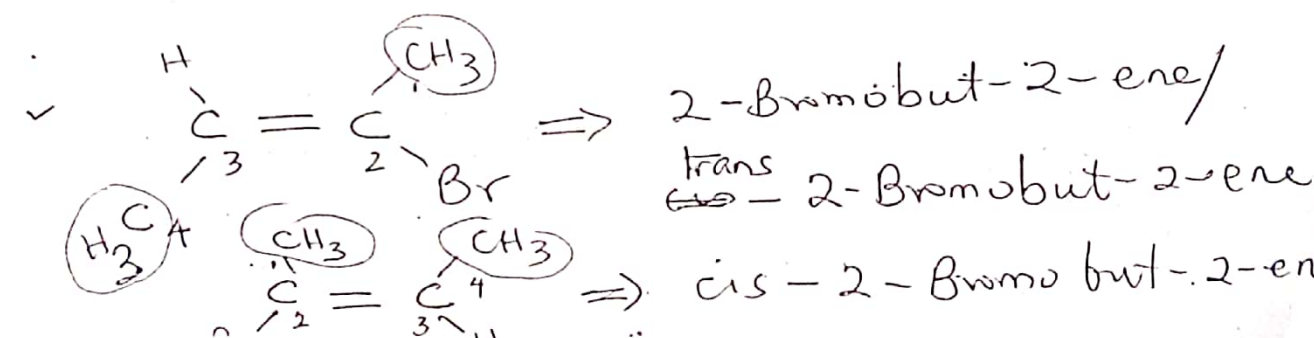
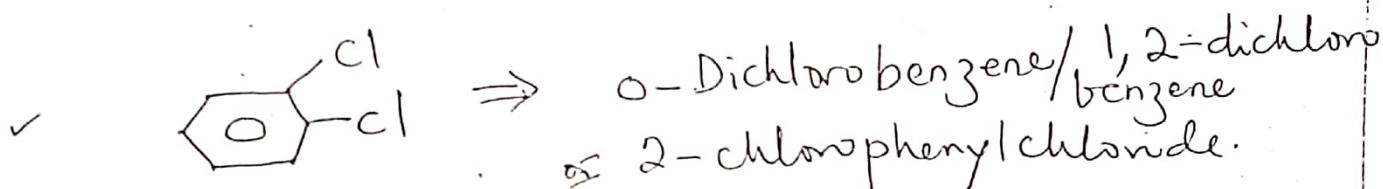
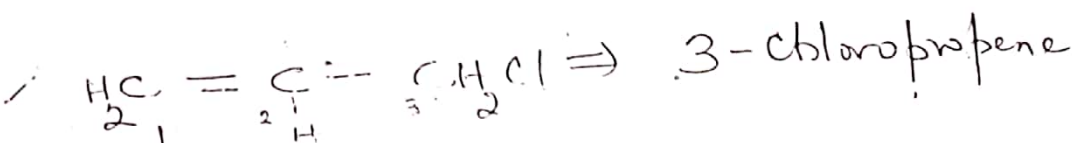
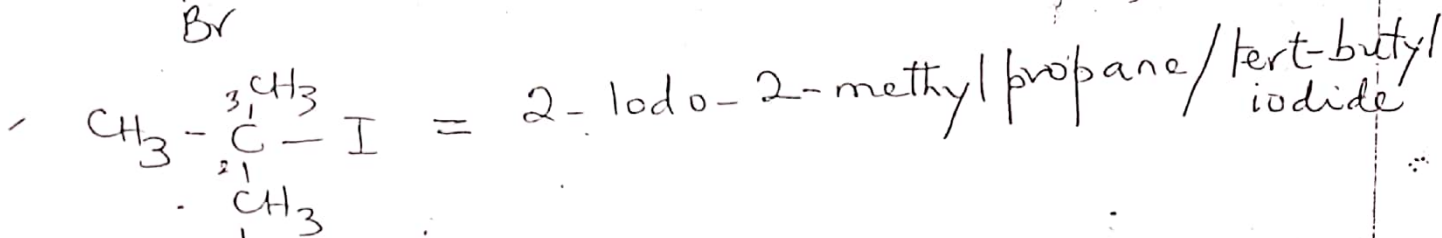
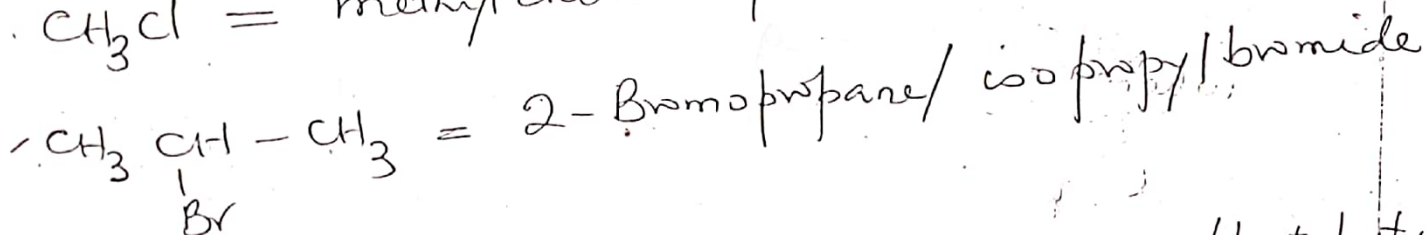
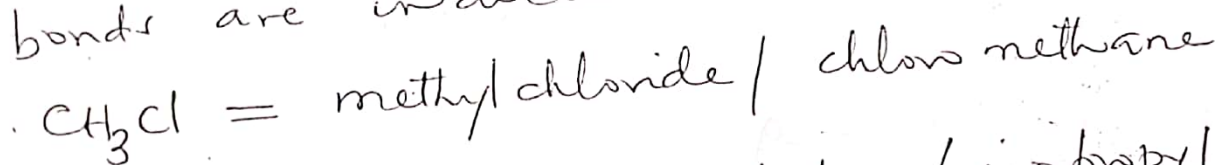


# ALKYL HALIDES / HALO COMPOUNDS / HALO HYDROCARBONS / HALO ALKANES (RX) ALKENES

- They are derivatives of alkanes/alkenes
- General formula for haloalkanes  $C_nH_{2n+1}X$  or simply  $R-X$  ( $R = \text{alkyl}$ ,  $X = \text{halogen}$ )
- May be aliphatic, straight, branched, aromatic

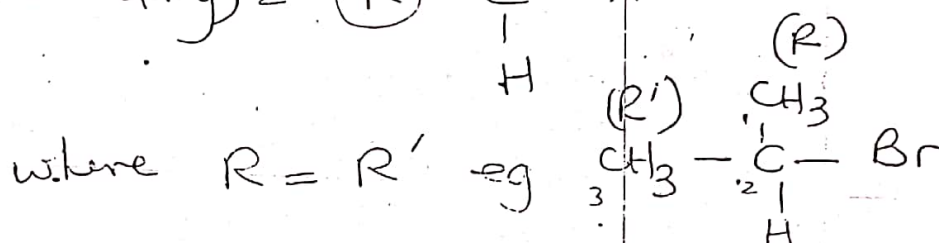
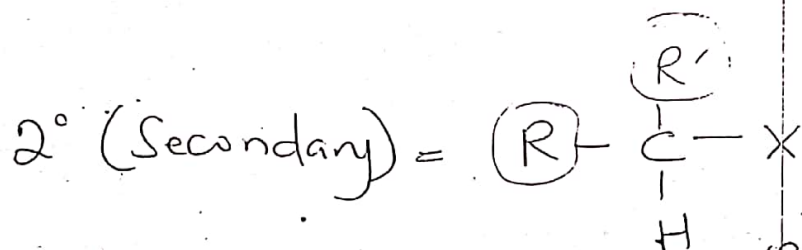
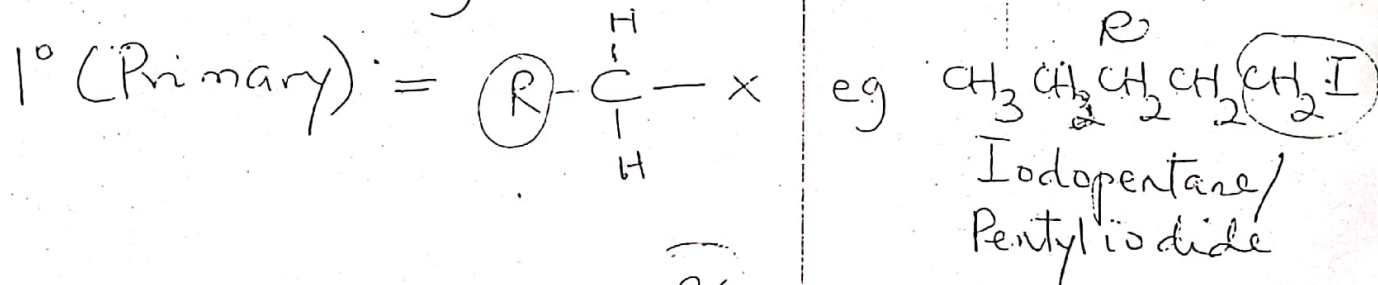
## Nomenclature

⇒ They are named as derivatives of corresponding alkanes. Positions of substituent(s) and multiple bonds are indicated.



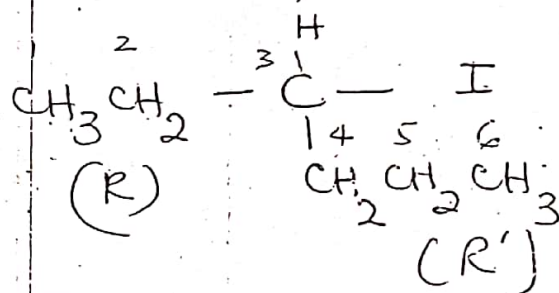
⇒ Classification

Depends on the no of R groups attached to the C bearing the X atom

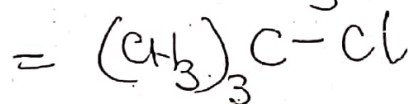
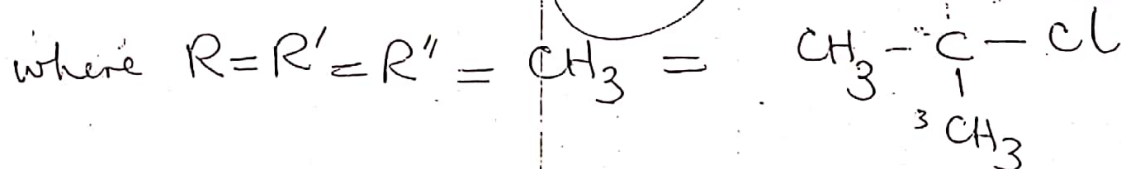
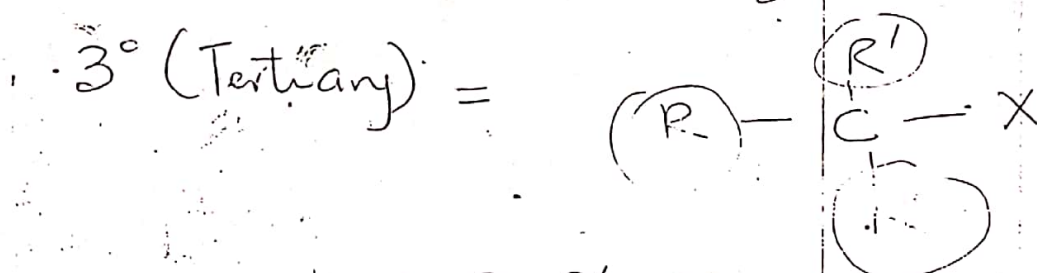


(2-Bromopropane)

where  $\text{R} \neq \text{R}'$  eg



3-Iodohexane



= Tert-butyl chloride

or 2-chloro-2-methylpropane

## Physical Properties

• Most are liquids, except halomethanes (apart from iodomethane) are gases. Fluoroethane and chloroethane are also gases.

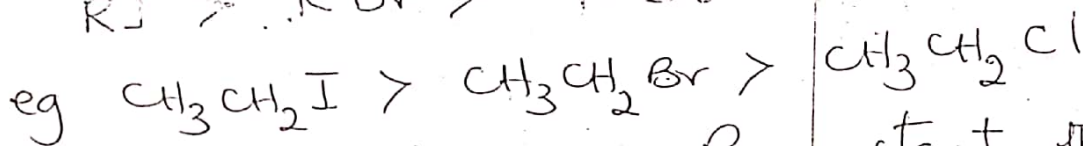
• They are polar in nature (i.e.  $\mu \neq 0$ )

$$\begin{array}{c} \delta^+ \quad \quad \delta^- \\ R - X \end{array} / \begin{array}{c} \delta^+ \quad \quad \delta^- \\ R - X \end{array} / \begin{array}{c} \delta^+ \quad \quad \delta^- \\ R - X \end{array}$$

i.e. X (Grp 7) is more electronegative than C (Grp 14)  
Recall electronegativity increases from left  $\rightarrow$  right of a periodic table and decreases down a group ( $F \gg Cl > Br > I$ ).

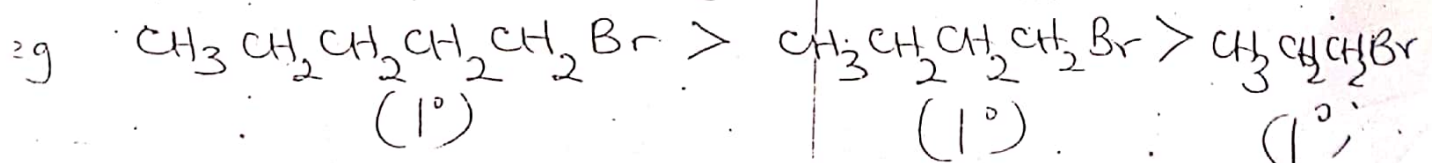
Because of their polar nature, they have higher boiling points, melting points and densities than their corresponding alkanes/alkynes. These parameters increase with increase in RMM.

Their bpts, mpts. and densities increase if:  
1) for same R groups, diff X atoms

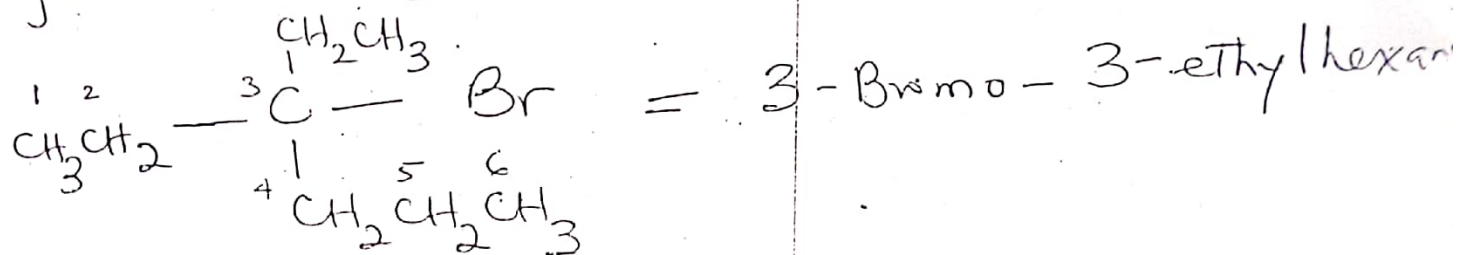
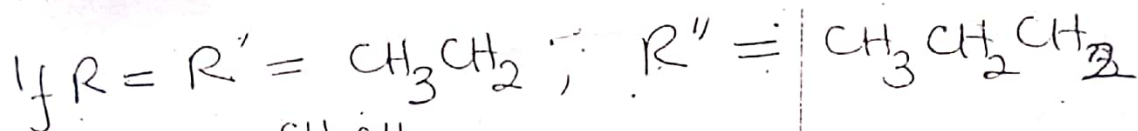


As RMM of X increases, R constant, the parameters increase.

2) diff R groups, same X, parameters also increase i.e. As chain length increases, bpt/mpt also increases

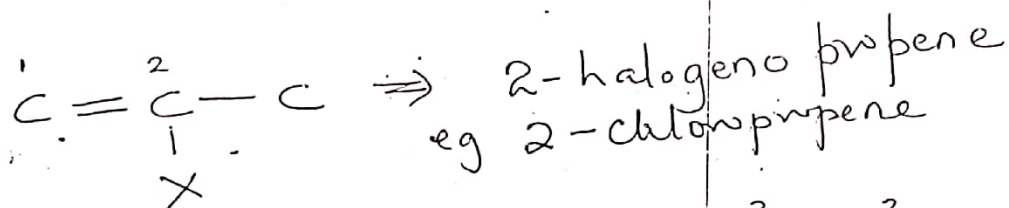




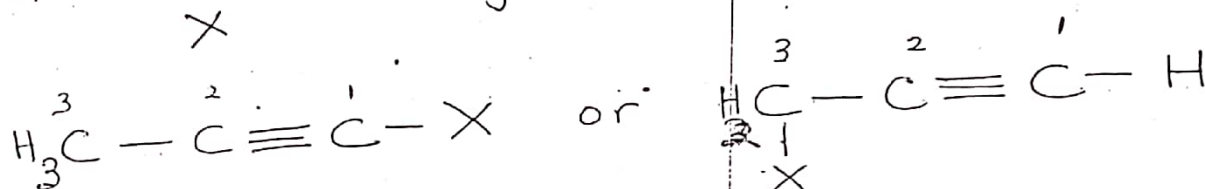


⇒ Unsaturated alkyl halides

Posses  $=$  or  $\equiv$  bonds



eg 2-chloropropene



Halogeno propyne

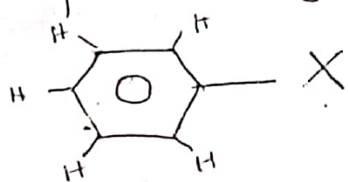
eg Iodopropyne

3-halogeno propyne


eg 3-Bromopropyne

⇒ Aryl halides (Ar-X)

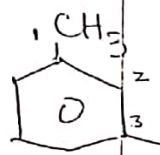
X is directly attached to an aromatic ring (ie X replaces 1 of the H atoms on eg a benzene ring)



(Ar)X eg  $\text{C}_6\text{H}_5\text{X}$

eg  (Monosubstituted benzene)

Phenyl chloride/  
chlorobenzene



3-chloromethylbenzene

or 3-chlorotoluene

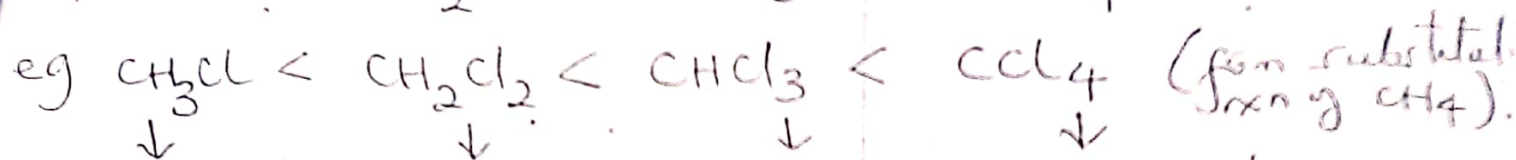
or m-chlorotoluene

or Toluyl chloride

(Disubstituted benzene)

(X-C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>)

ii) Keeping R constant and increasing the no. of X atoms, decreases bpts/mps/densities.



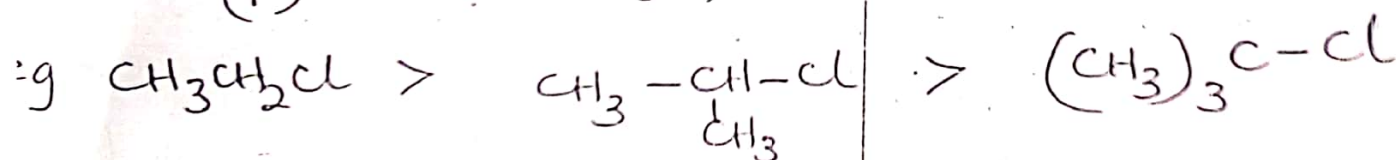
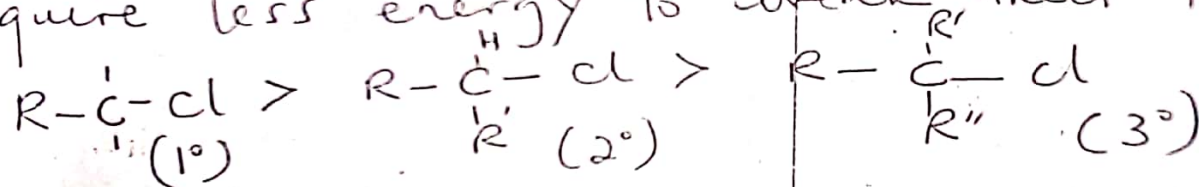
↓  
chloromethane  
(methyl chloride)

↓  
dichloromethane  
(carbon dichloride)

↓  
trichloromethane  
(chloroform)

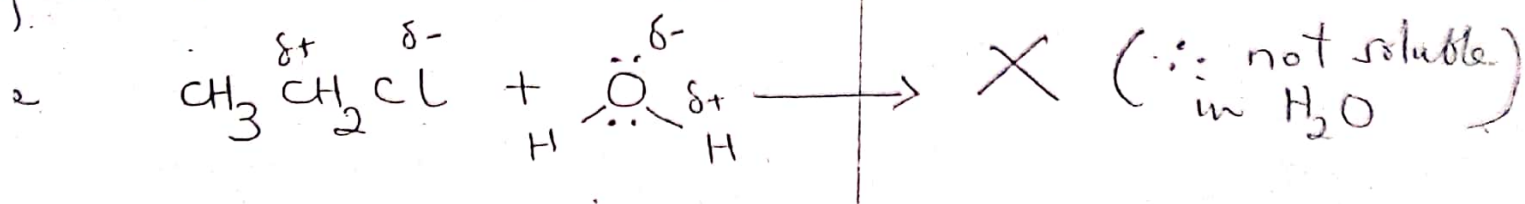
↓  
tetrachloromethane  
(carbon tetrachloride)

i) Changing from  $1^\circ \rightarrow 2^\circ \rightarrow 3^\circ$  RX, bpt/mps/density decreases (becoming more compact and  $\therefore$  require less energy to break their lattice)



They are water-insoluble (though polar) but soluble in organic solvents eg.  $Et_2O$ ,  $CHCl_3$ ,  $CH_2Cl_2$ ,  $CCl_4$ .  $\therefore$  they do not

form H-bonds with water



## Questions

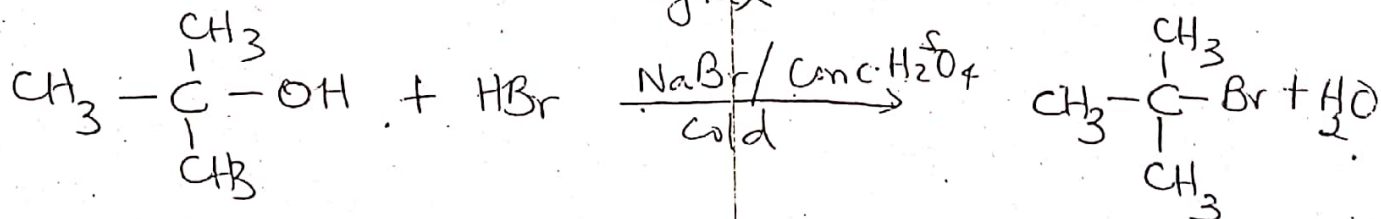
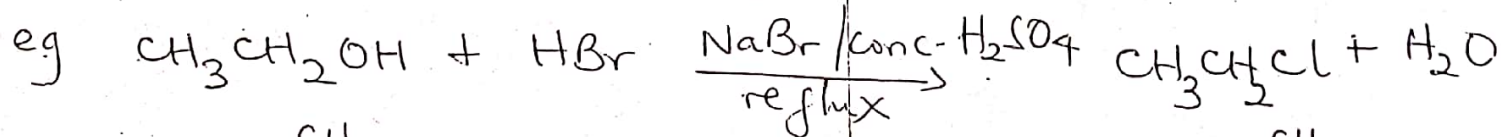
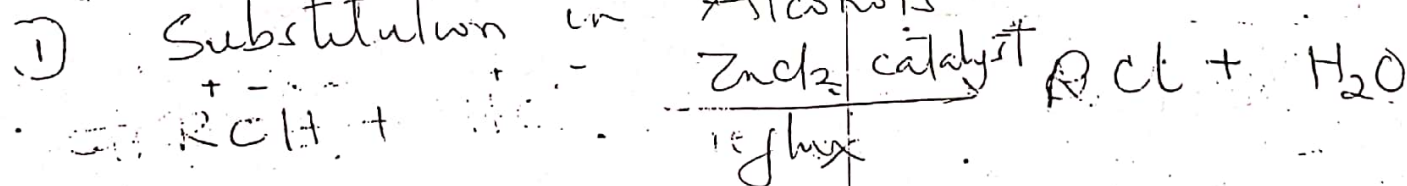
2) Predict the following compound which will have the highest b.p. / melting point / density for the following pairs:

- iodobutane and iodopentane
- 2-chlorobutane and 2-bromobutane
- 2-chloropropane and 2-chloro-2-methylpropane
- chloroform and iodoform
- cis-2-bromobut-2-ene and trans-2-bromobut-2-ene

3) Bromopropane, though a polar compound, does not dissolve in water. Explain.

⇒ Synthetic methods of Preparation of Rx

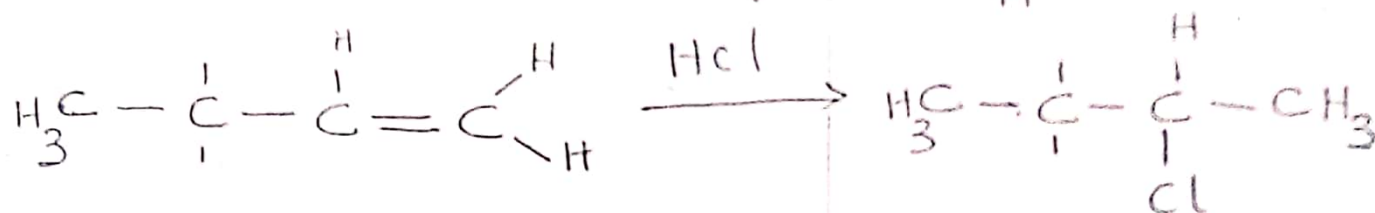
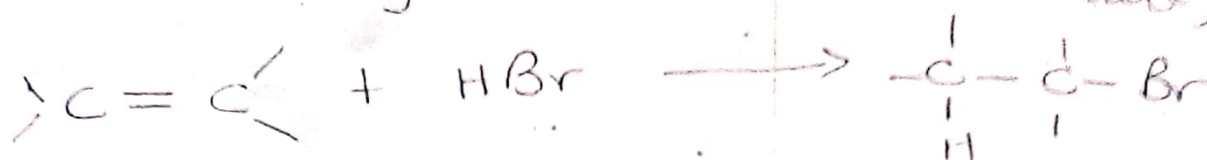
1) Substitution in Alcohols



Ease of substitution  $3^\circ OH > 2^\circ OH > 1^\circ OH$   
 $\downarrow$  cold  $\qquad \qquad \qquad \downarrow$  hot



9 Addition of HX to alkenes (Markovnikov's rule)



⇒ Reactions

2 major types:

• Nucleophilic substitution Reactions

- Nucleophilic substitution unimolecular ( $S_N^1$ )
- Nucleophilic substitution bimolecular ( $S_N^2$ )

Elimination Reactions

- Elimination Unimolecular ( $E1$ )
- Elimination bimolecular ( $E2$ )

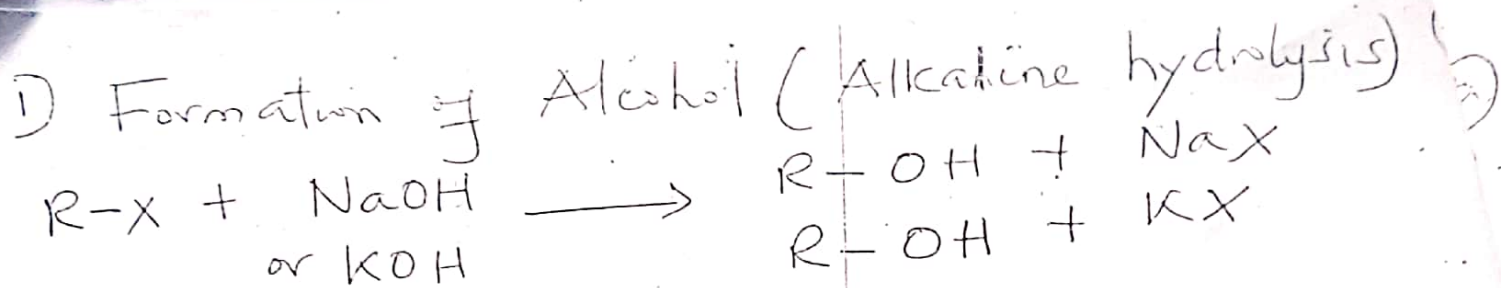
Ⓐ Nucleophilic Substitution Reactions

Nucleophiles (groups rich in electron, highly electronegative) displaces X atoms in  $R-X$

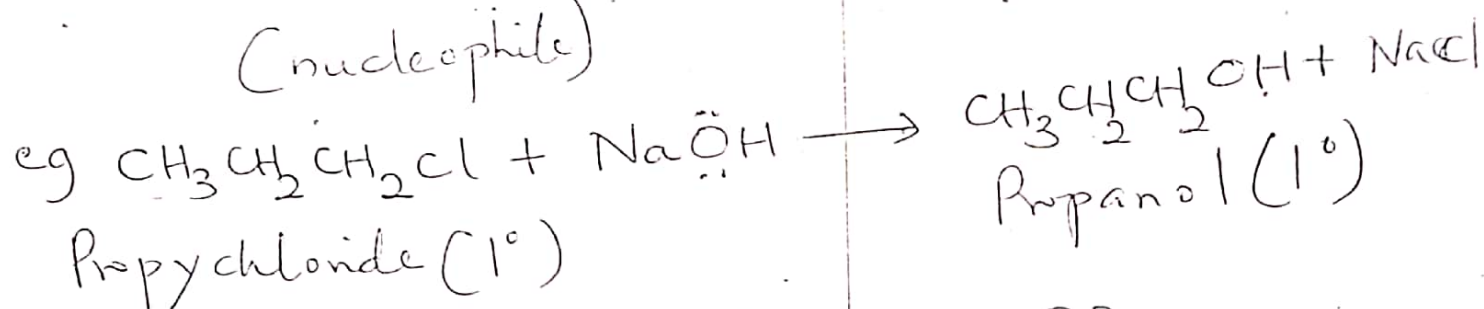
Eg. of Nucleophiles —  $\ddot{O}H^-$ ,  $\ddot{O}R^-$ ,  $\text{C}\equiv\text{N}^-$ ,

$\text{NH}_2^-$  leading to formation of  $ROH$ s,  $RORS$ ,  $RCN$  and  $RNH_2$  respectively

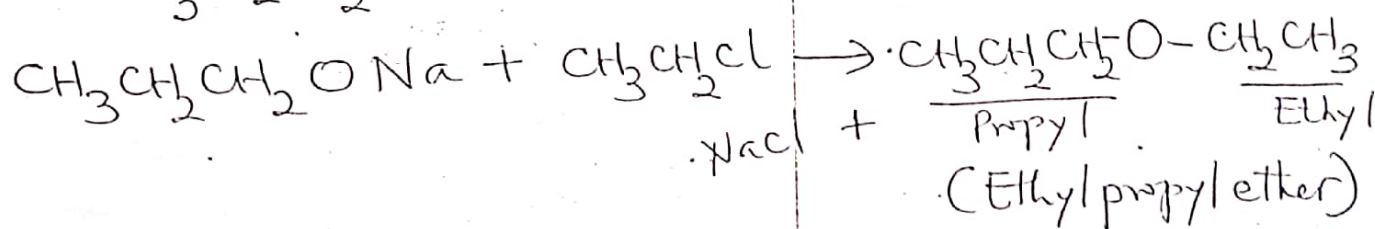
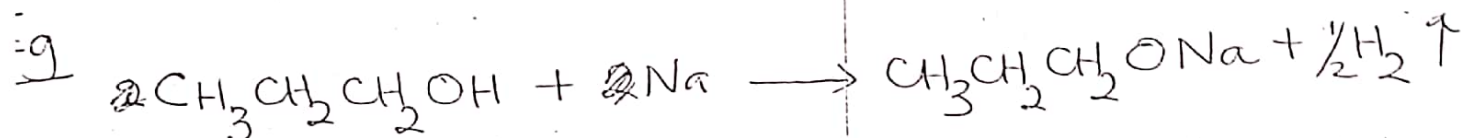
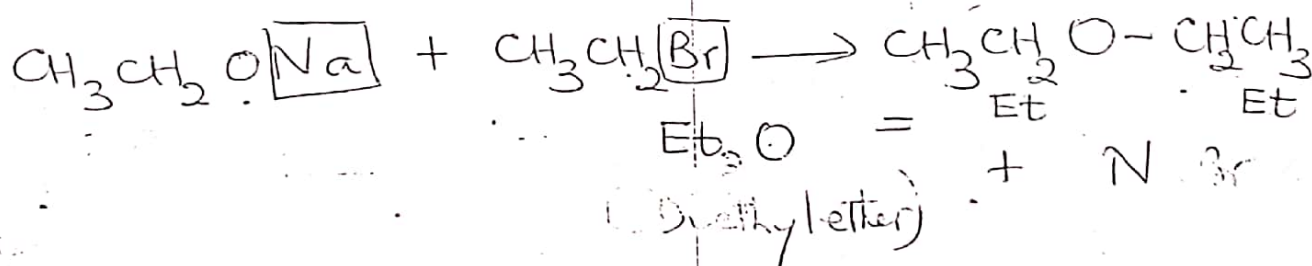
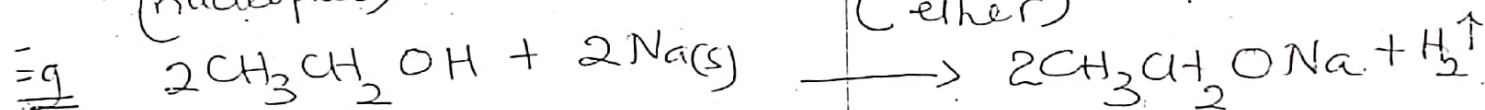
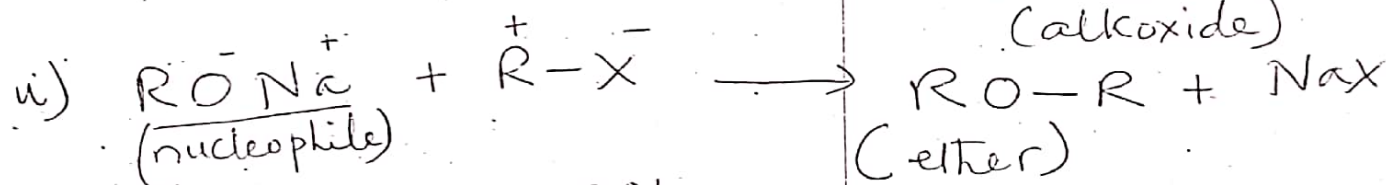
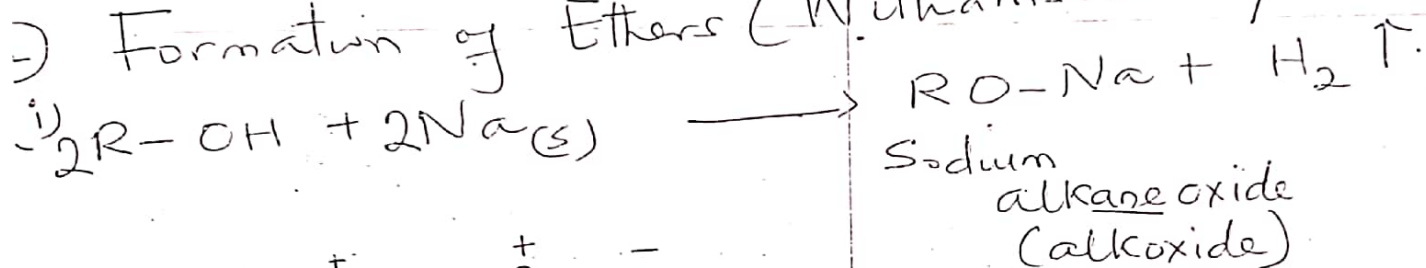
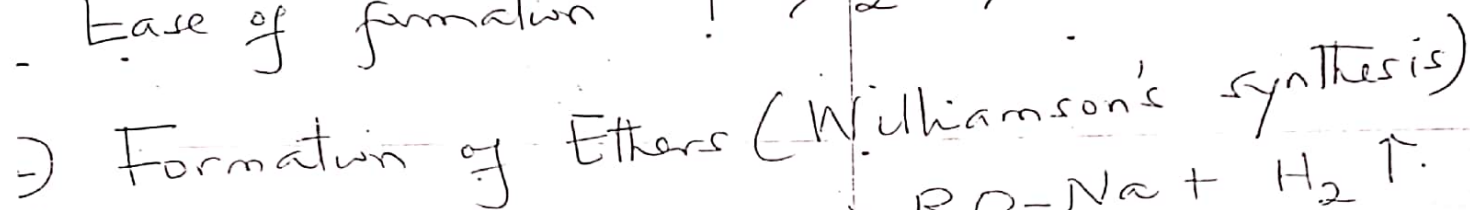
(alcohols) (ethers)  
(nitriles)  
(amines)



(nucleophile)

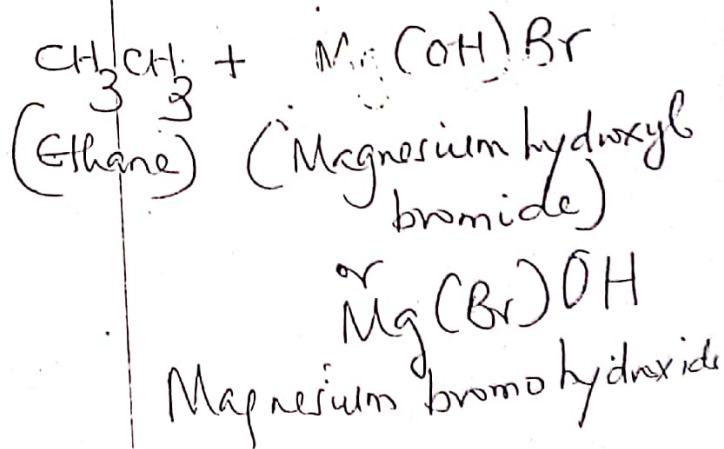
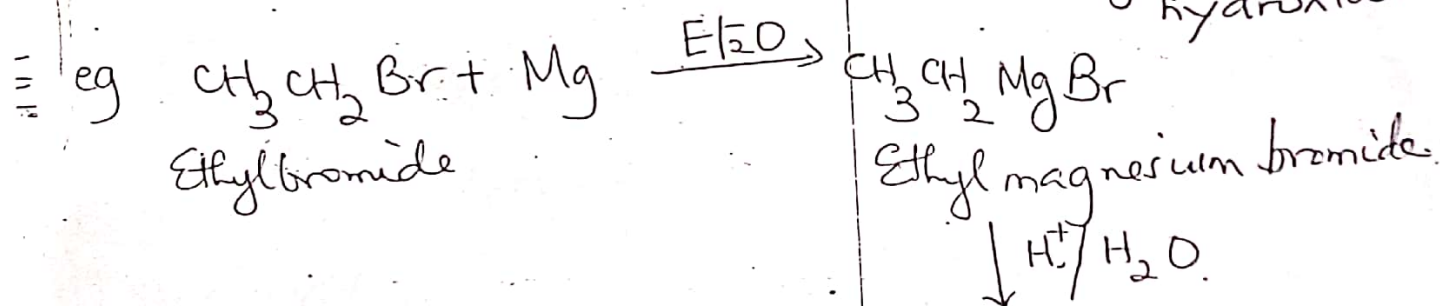
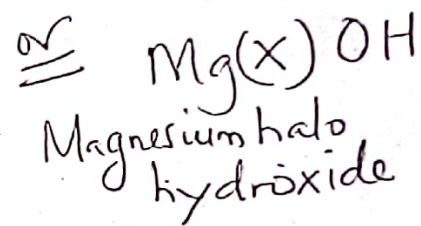
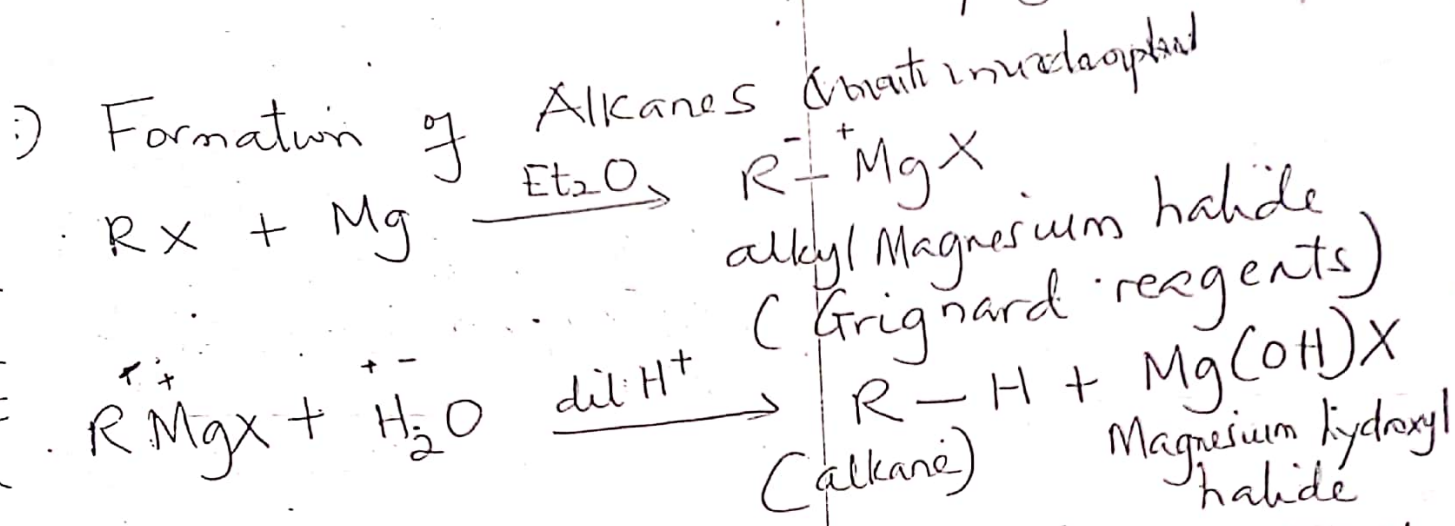
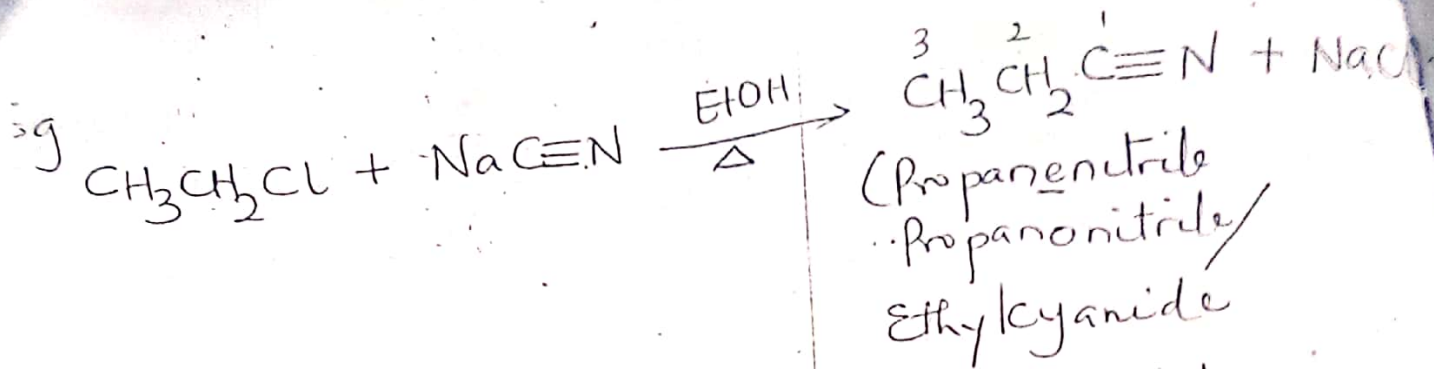


Ease of formation  $1^\circ > 2^\circ > 3^\circ$

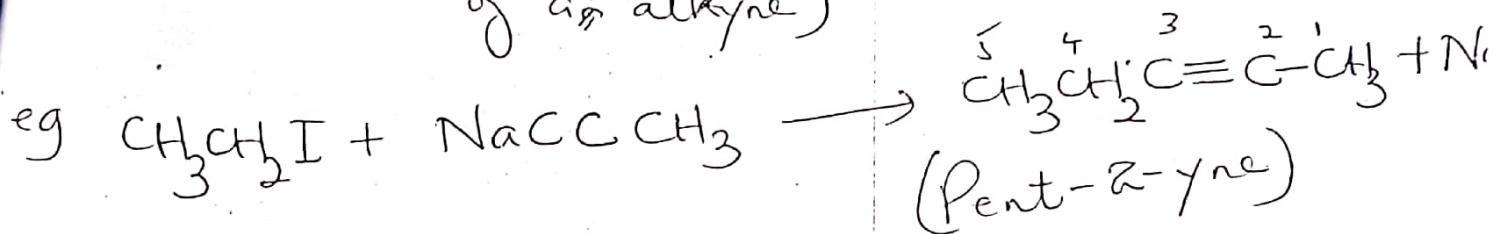
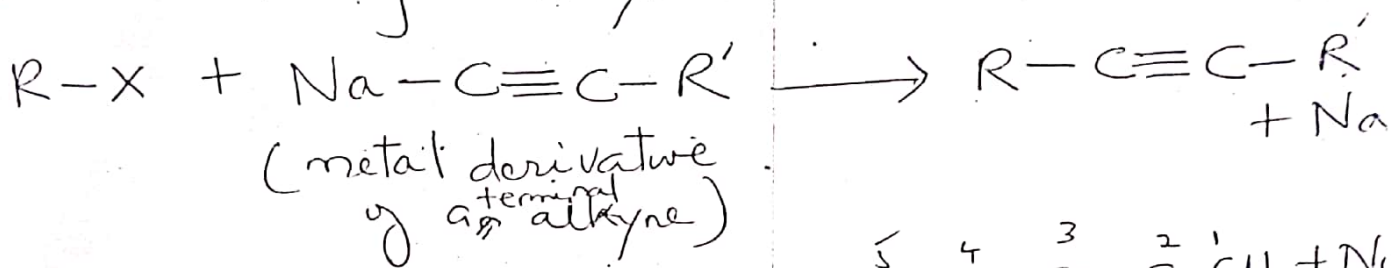




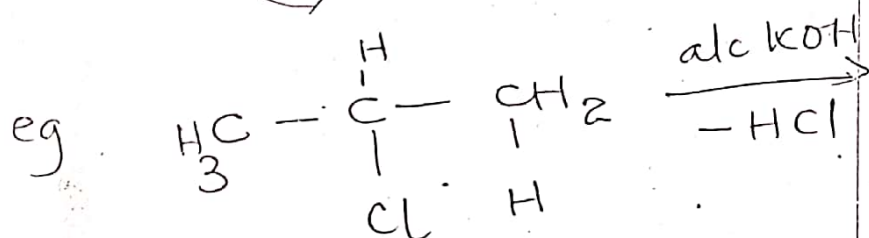
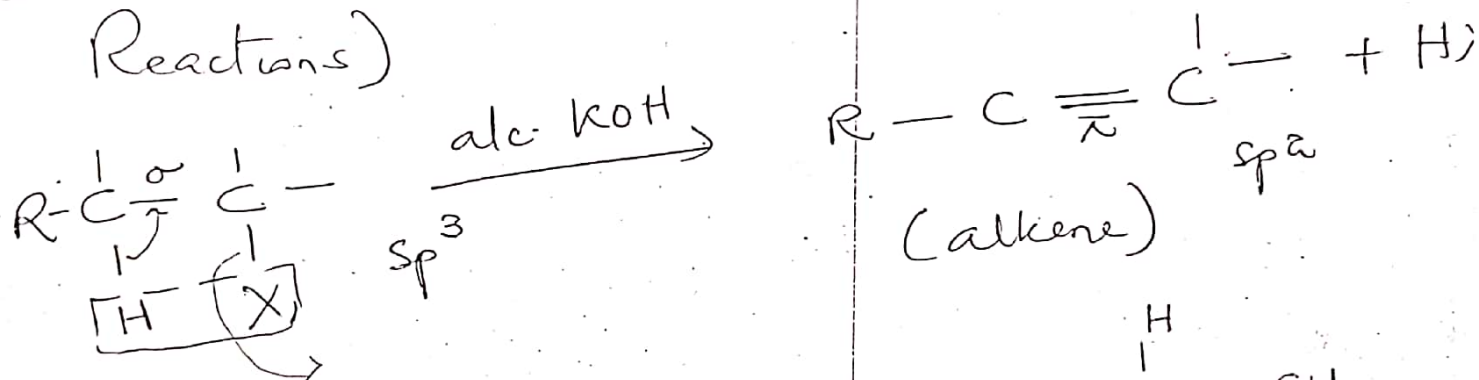




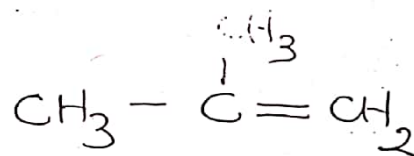
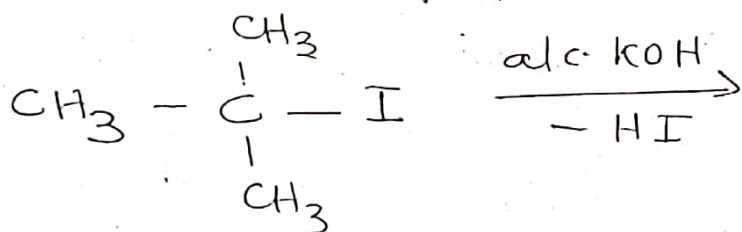
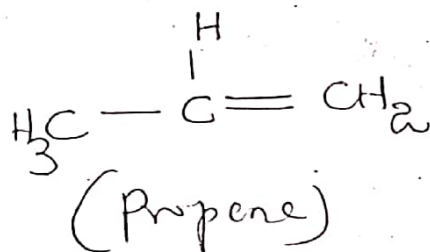
## 1) Formation of Alkynes



## B) Elimination Reactions (Dehydrohalogenation Reactions)



(Propyl 2-chloro propane)



Ease;  $3^\circ > 2^\circ > 1^\circ$  RX.