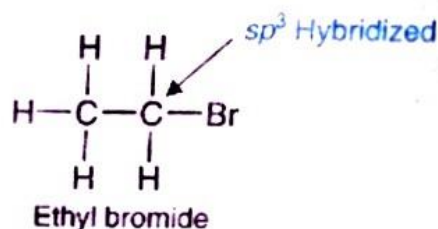
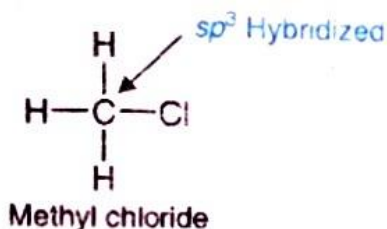


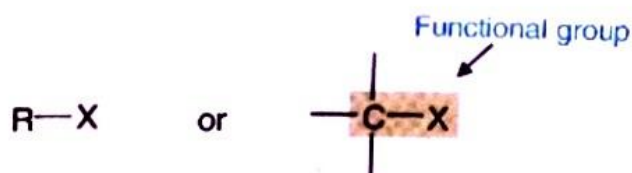
Alkyl Halides

(Nucleophilic Substitution and Elimination Reactions)

Alkyl halides are compounds in which a halogen atom is bonded to sp^3 hybridized Carbon



They have the general formula :



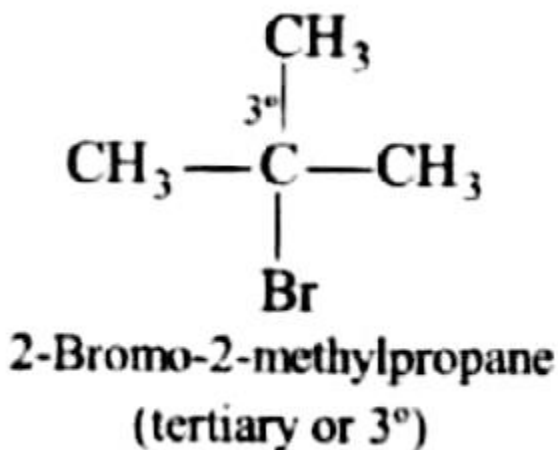
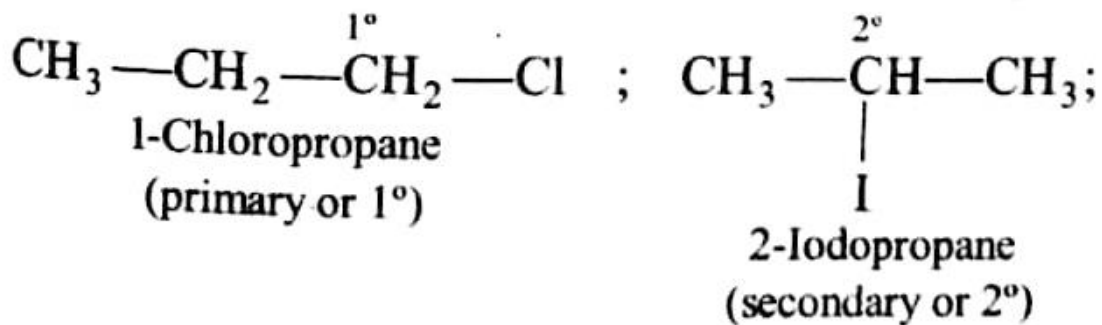
Where R=alkyl group : X=Cl, Br, I, or F, The halogen atom bonded to sp^3 hybridized carbon is the functional group of alkyl halides.

Classification

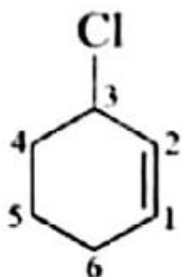
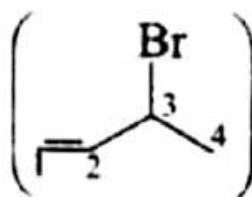
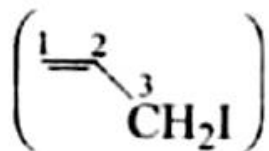
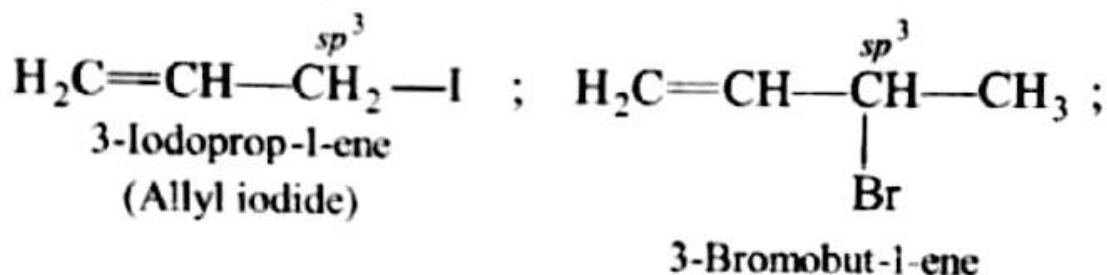
Monohalogen compounds may further be classified according to the **nature of C-X bond** in haloalkanes and haloalkenes particularly to the hybridization of the carbon atom to the halogen.

(A) Compounds containing C-X bond, where carbon is sp^3 –hybridized.

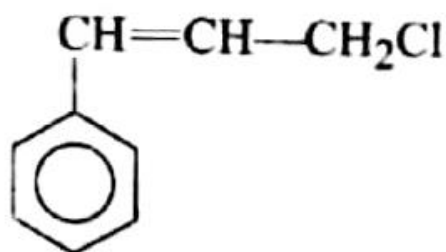
(i) Alkyl halides or Haloalkanes: In alkyl halides, the halogen atom is bonded to an alkyl group. The homologous series is represented by $C_nH_{2n+1}X$. They are further classified as primary (1°), secondary (2°) and tertiary (3°) halides depending upon where the halogen atom is attached to a primary, secondary or tertiary carbon atom. Examples are:



(ii) Allylic halides: In these halides, the halogen atom is attached to allylic carbon (C=C-C-X), i.e., carbon atom next to C=C. Examples are:



3-Chlorocyclohex-1-ene
 $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{Br}$
 1-Bromobut-2-ene
 (Crotyl bromide)



3-Chloro-1-phenylprop-1-ene
 (Cinnamyl chloride)

Allylic halides may be primary, secondary or tertiary.

(iii) Benzylic halides: In these halides, the halogen atom

atom is attached to a benzylic carbon ($C_6H_5\overset{\bullet}{C}H_2-$, $C_6H_5\overset{\bullet}{C}H<$ or $C_6H_5\overset{\bullet}{C}<$), i.e., the carbon atoms of the side chain carrying the aryl group. Examples are:

Benzyl chloride ; Benzal chloride;
Benzo trichloride ; β -Phenyl ethyl bromide etc.

(B) Compounds containing C-X bond, where carbon is sp^2 -hybridized.

(i) Arylhalides: In these halides, the halogen atom is directly attached to the carbon atom of an aromatic ring. These halides are also called haloarenes. Examples are:

Chlorobenzene : Bromobenzene ;

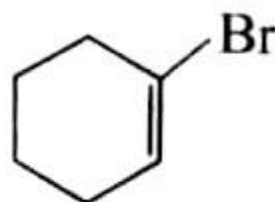
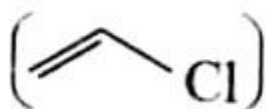
Iodobenzene : 2-Chlorotoluene;

3-Bromotoluene : 4-Bromotoluene

(ii) Vinylic halides: In these halides, the halogen atom is attached to vinylic carbon ($C=C-X$), i.e., one of the carbon atoms of $C=C$. Examples are:



Chloroethene
(Vinyl chloride)

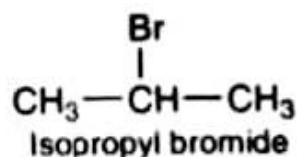
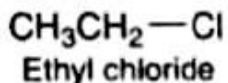
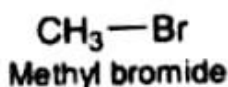


1-Bromocyclohex-1-ene

NOMENCLATURE

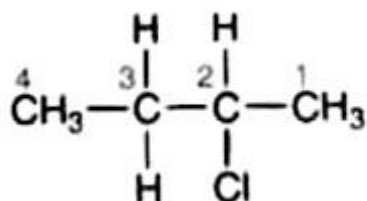
Alkyl halides are named in two ways :

(1) Common System. In this system the alkyl group attached to the halogen atom is named first. This is then followed by an appropriate word chloride, bromide, or fluoride. Notice that the common names of alkyl halides are TWO-WORD names.



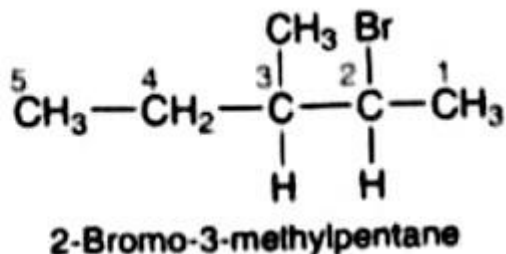
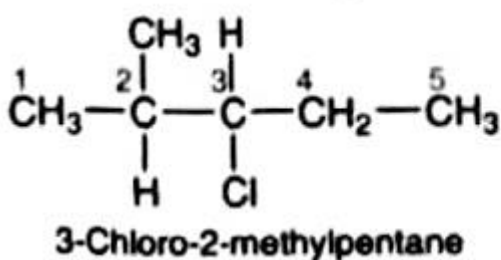
(2) IUPAC System. The IUPAC names of alkyl halides are obtained by using the following rules:

Rule 1. The longest continuous chain of carbon atoms is chosen as the parent. If the parent chain has no branching alkyl groups, the position of the halogen atom is given by a number that corresponds to the carbon atom to which it is attached. The carbon chain is numbered so that the carbon atom bearing the halogen atom has the lowest number.

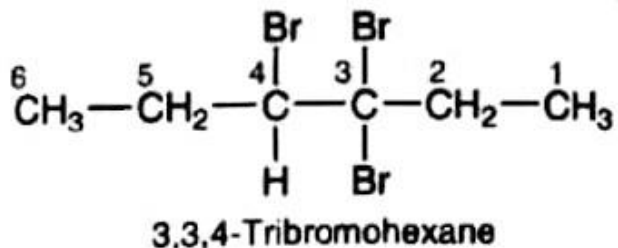
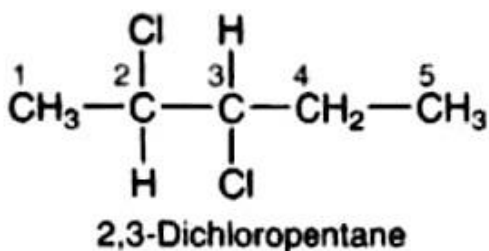


This is 2-chlorobutane,
not 3-chlorobutane

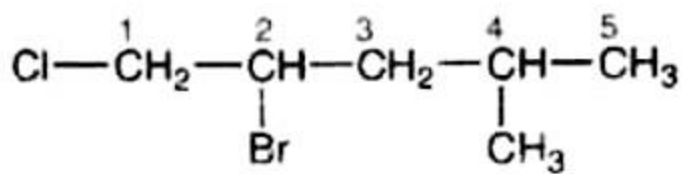
Rule 2. If the parent chain has branching alkyl groups, number the chain from the end nearer the first substituent, regardless of whether it is an alkyl group or a halogen atom.



Rule 3. If the compound contains two or more halogen atoms of the same type, they are indicated with the prefixes di-, tri-, etc. Each halogen atom is given a number that corresponds to its position in the parent chain.

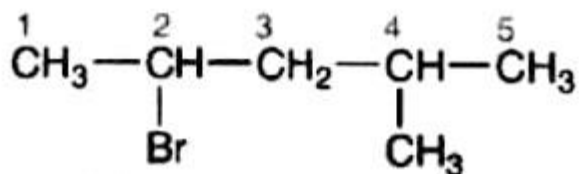


Rule 4. If a compound contains different halogen atoms, they are numbered according to their positions on the chain and listed in alphabetical order.



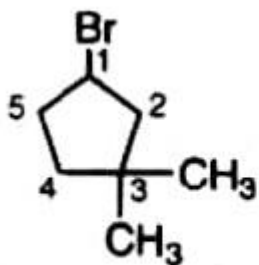
2-Bromo-1-chloro-4-methylpentane

Rule 5. If the chain can be numbered from either end based on the location of the substituents, begin at the end nearer the substituent that has alphabetical precedence, whether it is an alkyl group or a halogen atom

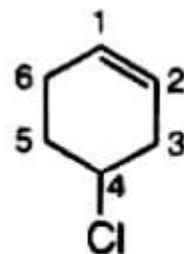


2-Bromo-4-methylpentane

Rule 6. Halocycloalkanes are numbered from the carbon atom bearing the halogen atom unless another group such as a double bond takes precedence. Carbon atom in the ring are numbered to give the lower numbers to the substituents



1-Bromo-3,3-dimethylcyclopentane



4-Chlorocyclohexene

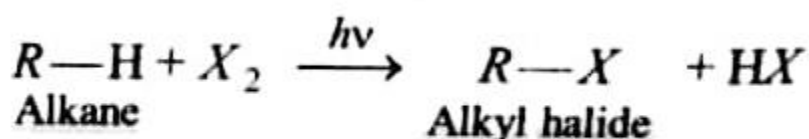
GENERAL METHODS OF PREPARATION OF MONOHALOGEN DERIVATIVES OR ALKYL HALIDES

The following general methods are used for the preparation of alkyl halides.

1. From alkanes : Direct halogenation of alkanes in presence of sunlight, heat or suitable catalyst yields alkyl halides. Chlorination is fast, bromination is slow while direct iodination is not possible as the reaction is reversible and highly endothermic. (However, iodination can be done in presence of oxidising agents such as HNO_3 , or iodic acid, HIO_3).

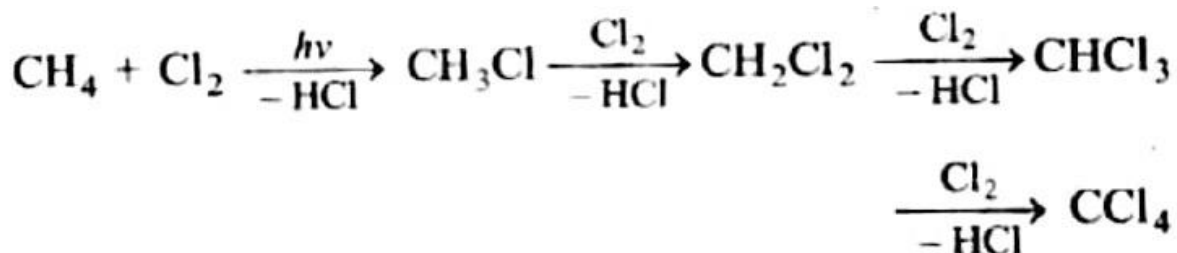
The reactivity of the alkanes follows the following order:

Tertiary alkane > Secondary alkane > Primary alkane

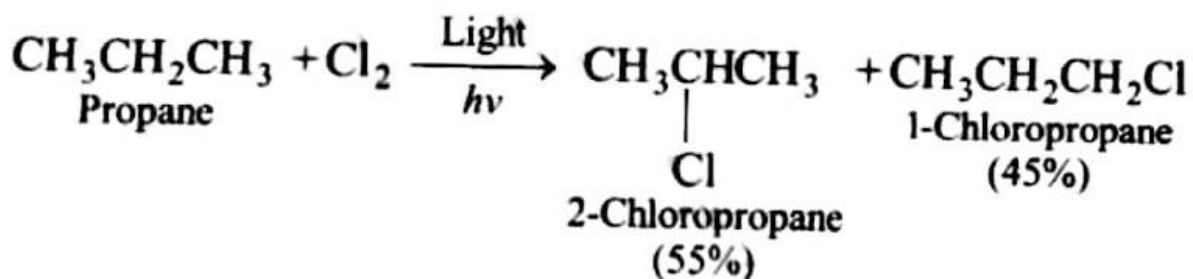
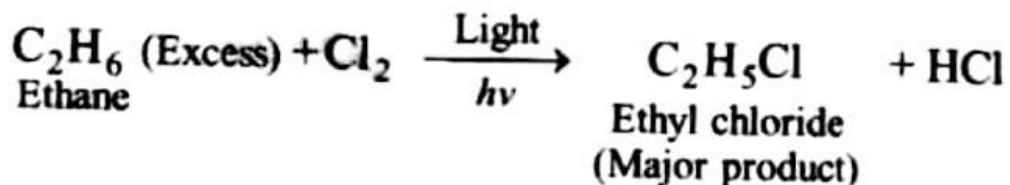
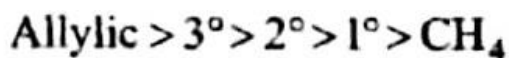


Direct halogenation proceeds through free radical mechanism : Direct halogenation does not form pure monohalogen derivatives but a mixture of polyhalogen derivatives is always obtained. For example, methane reacts with chlorine in presence of diffused sunlight or at

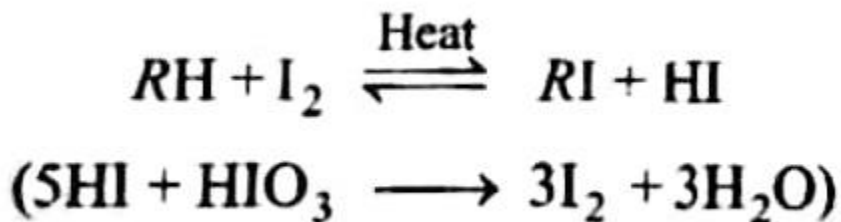
250-400°C to form a mixture of methyl chloride, methylene chloride, chloroform and carbon tetrachloride..



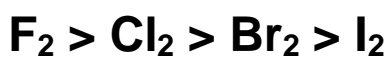
This method is, thus not used in laboratory because it is not easy to separate the individual members from the mixture. However, it is the most important commercial method for obtaining alkyl halides because alkanes are available in large amounts from petroleum and natural gas. If the conditions are well maintained especially the ratio of halogen and alkane, the halogenation may be suppressed beyond monosubstituted product. The displacement of H from hydrocarbon is in the order:



Similarly, bromination takes place, but not so vigorous as chlorination. However, iodination can be done by heating with iodine in the presence of oxidising agents such as conc. HNO₃ or HIO₃, (to oxidise HI formed during the reaction to iodine), and hence, shift the equilibrium in the forward reaction.

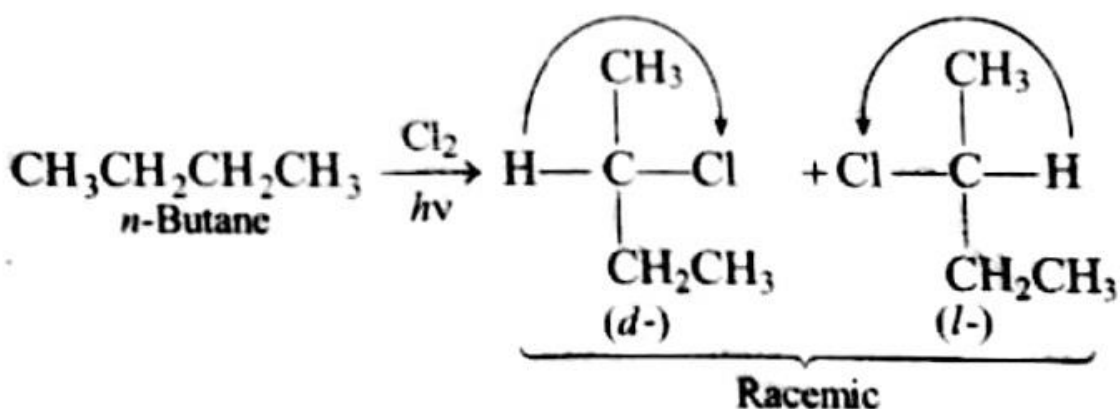


The reactivity of halogens decreases in the order

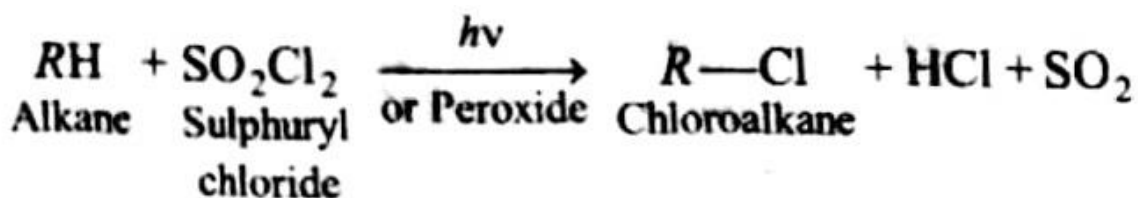


Bromination of alkanes is less exothermic than chlorination and so with fluorination. Iodine is unique as its reaction with alkanes is endothermic.

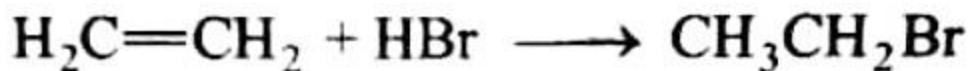
Chlorination of n-alkanes (C₄ and above) gives a mixture of *d*- and *l*- optical isomers, i. e., racemic mixture (optically inactive).



Alkane can react with sulphuryl chloride only in presence of light and traces of organic peroxide.

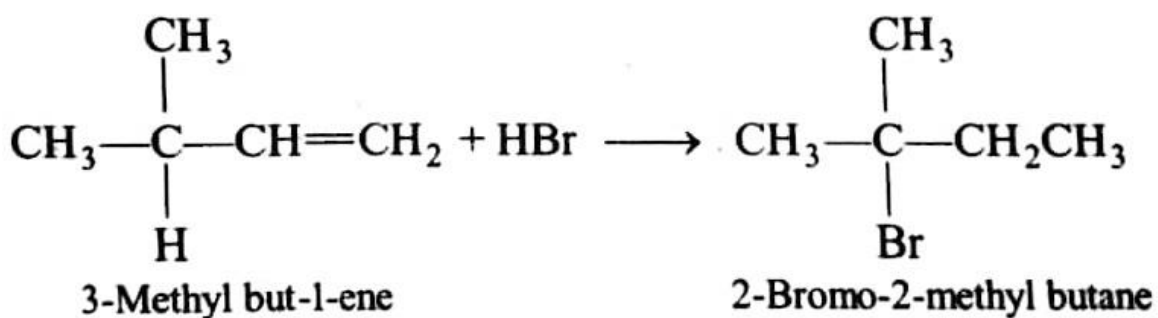
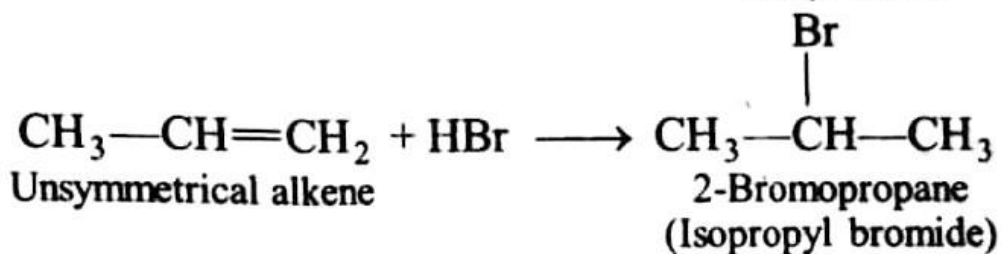
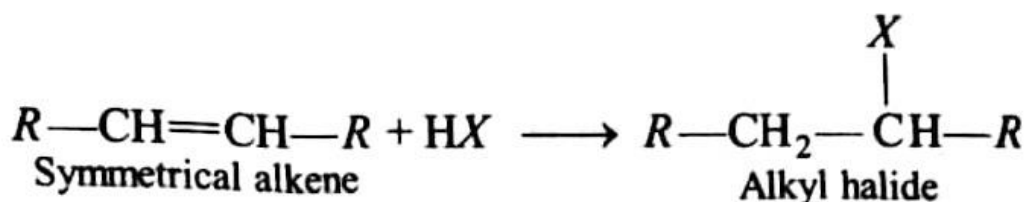


2. From alkenes : Halogen acids (HCl, HBr, HI) react readily with alkenes to form Alkyl halides. The order of reactivity of halogen acids is:

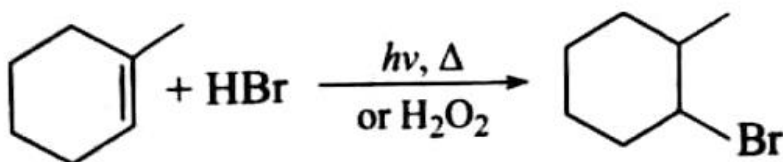
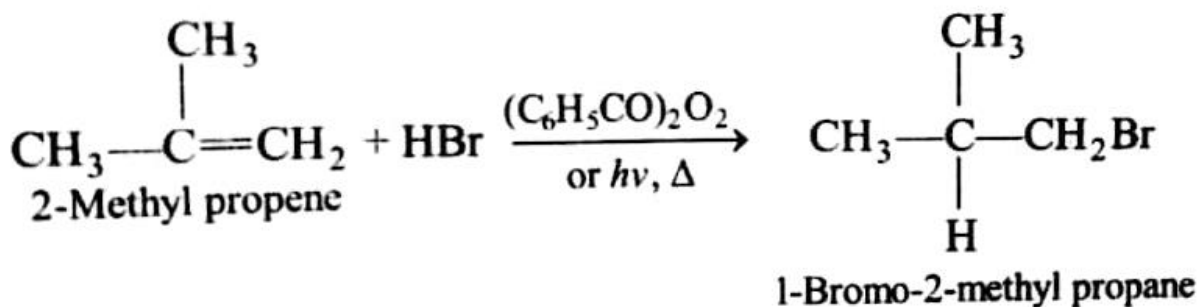
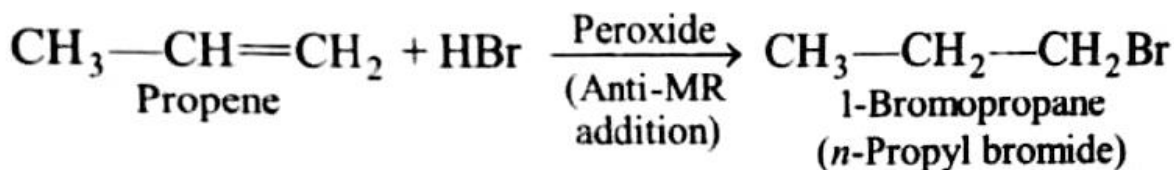


The unsymmetrical alkenes follow **Markownikoff's rule** during addition forming secondary or tertiary alkyl halides predominantly through the formation of most stable carbocation. Addition occurs through electrophilic attack.

However, in presence of light, heat or peroxide (R-O-O-R), such as benzoyl peroxide (C₆H₅CO-O-O-COC₆H₅), the HBr addition follows anti-Markownikoff's rule (**peroxide effect or Kharasch effect**) and form primary or normal alkyl bromides. Such an addition follows free radical mechanism. This method is well suited for the industrial preparation of alkyl halides as the lower alkenes are obtained during cracking of petroleum products.



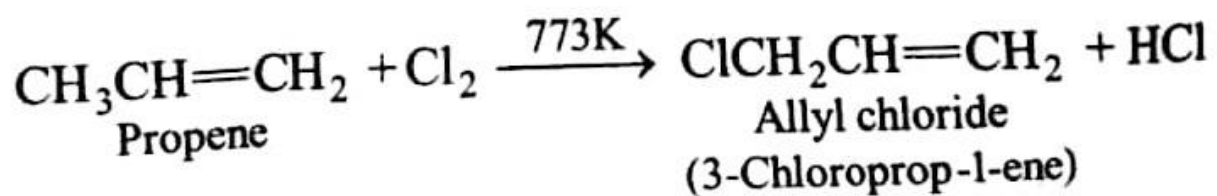
This can be explained by **1,2-Hydride shift** to attain greater stability of carbocation -



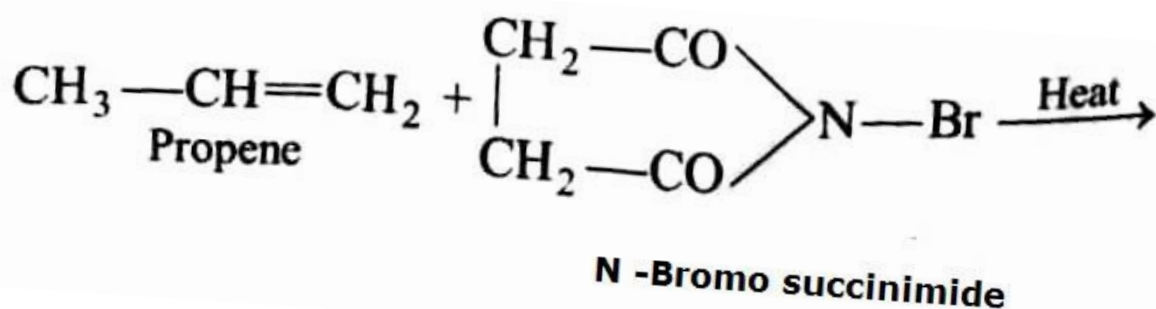
It may be noted that the peroxide effect applies to the **addition of HBr only** and not to the addition of HCl or HI.

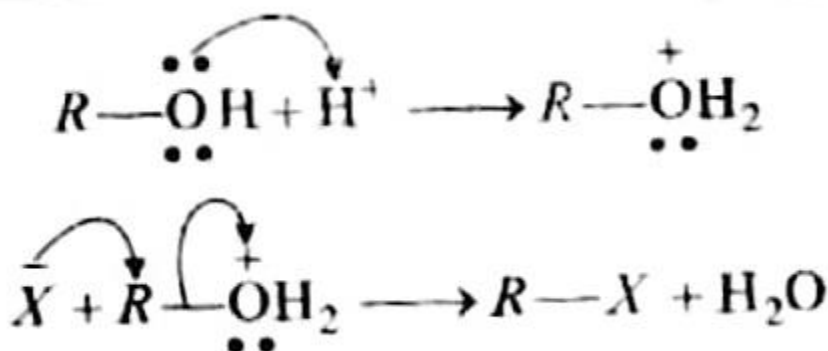
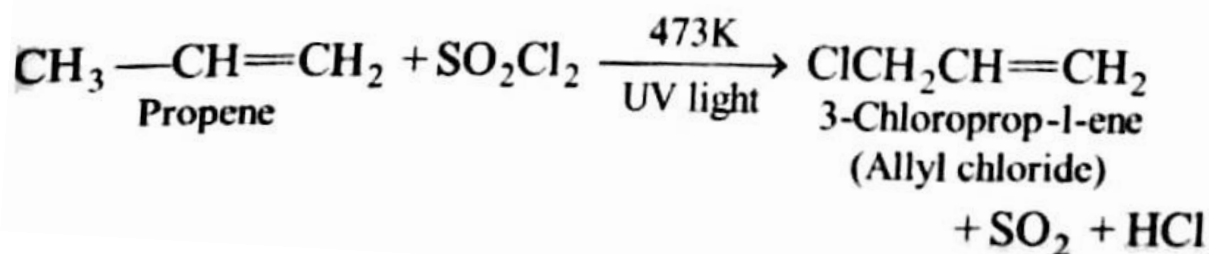
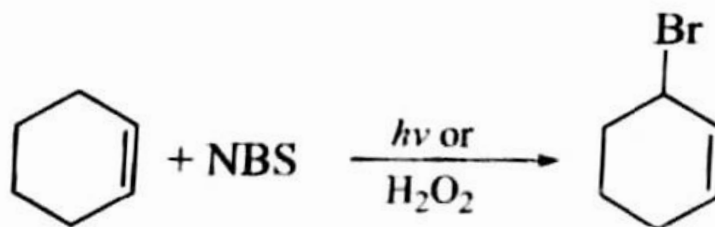
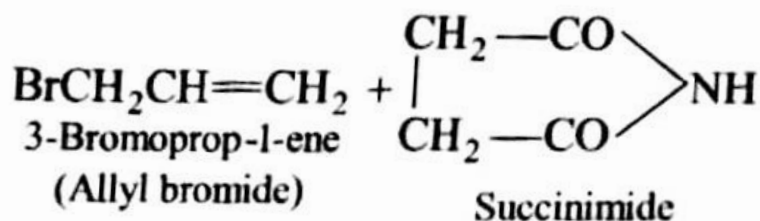
Allylic substitution

When alkenes are heated with Cl, or Br, at a high temperature of about 773K, the hydrogen atom of the allylic carbon (i.e., carbon atom next to the double bonds) is substituted with the halogen atom without breaking the double bond (allylic substitution) and forms allyl halide. For example,



The allylic substitution can also be carried out by heating the alkene with N-bromo succinimide (NBS) or sulphuryl chloride (SO₂Cl₂) at 473K in presence of light and traces of organic peroxides such as benzoyl peroxide.

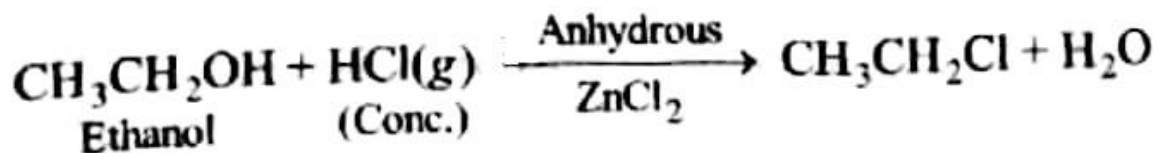




Since, the nucleophilicity (i.e., tendency to donate electron pair to the carbon) of halide ions decreases in the order, $\text{I}^- > \text{Br}^- > \text{Cl}^-$ the order of reactivity of the halogen acids decreases in the same order, i.e.,



(a) Alkyl chlorides are obtained by passing hydrogen chloride (gas) through alcohol in presence of anhydrous zinc chloride (Lewis acid).

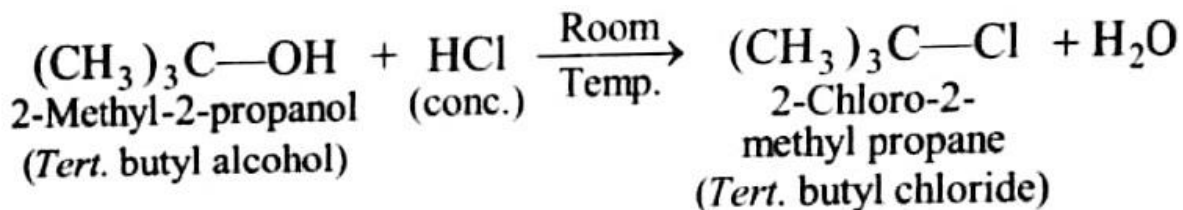


This mixture (1 : 1) of conc. HCl and anhyd. ZnCl₂, is called **Lucas reagent**.

The yield can be improved when the vapours of alcohol and HCl are passed over alumina at 623K.

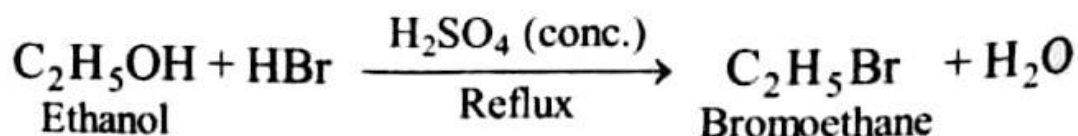
It must be noted that 1° and 2° alkyl chlorides are prepared from their respective alcohols by using HCl gas and anhydrous ZnCl₂, (**Groove's process**).

Tertiary alcohols are very reactive and therefore, they react readily with conc. HCl even in the absence of ZnCl₂.

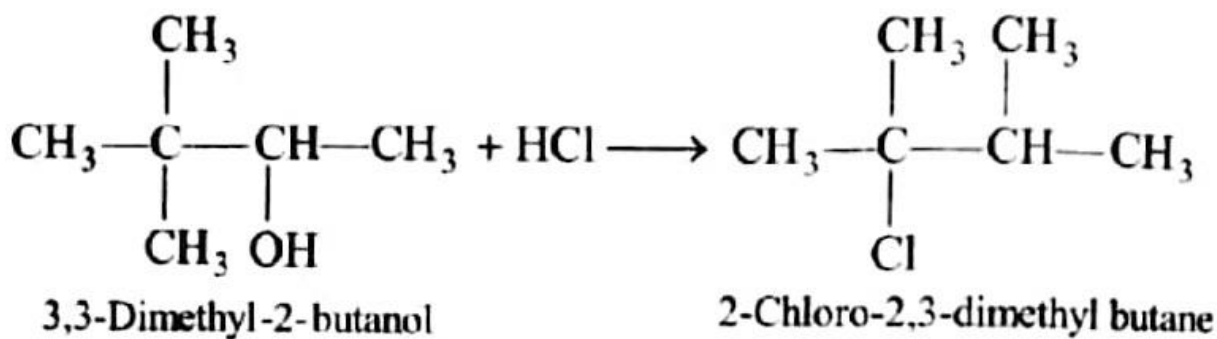


1° alcohols follow S_N² path while 2° and 3° alcohols S_N¹ path (proceeds through most stable carbocation intermediate).

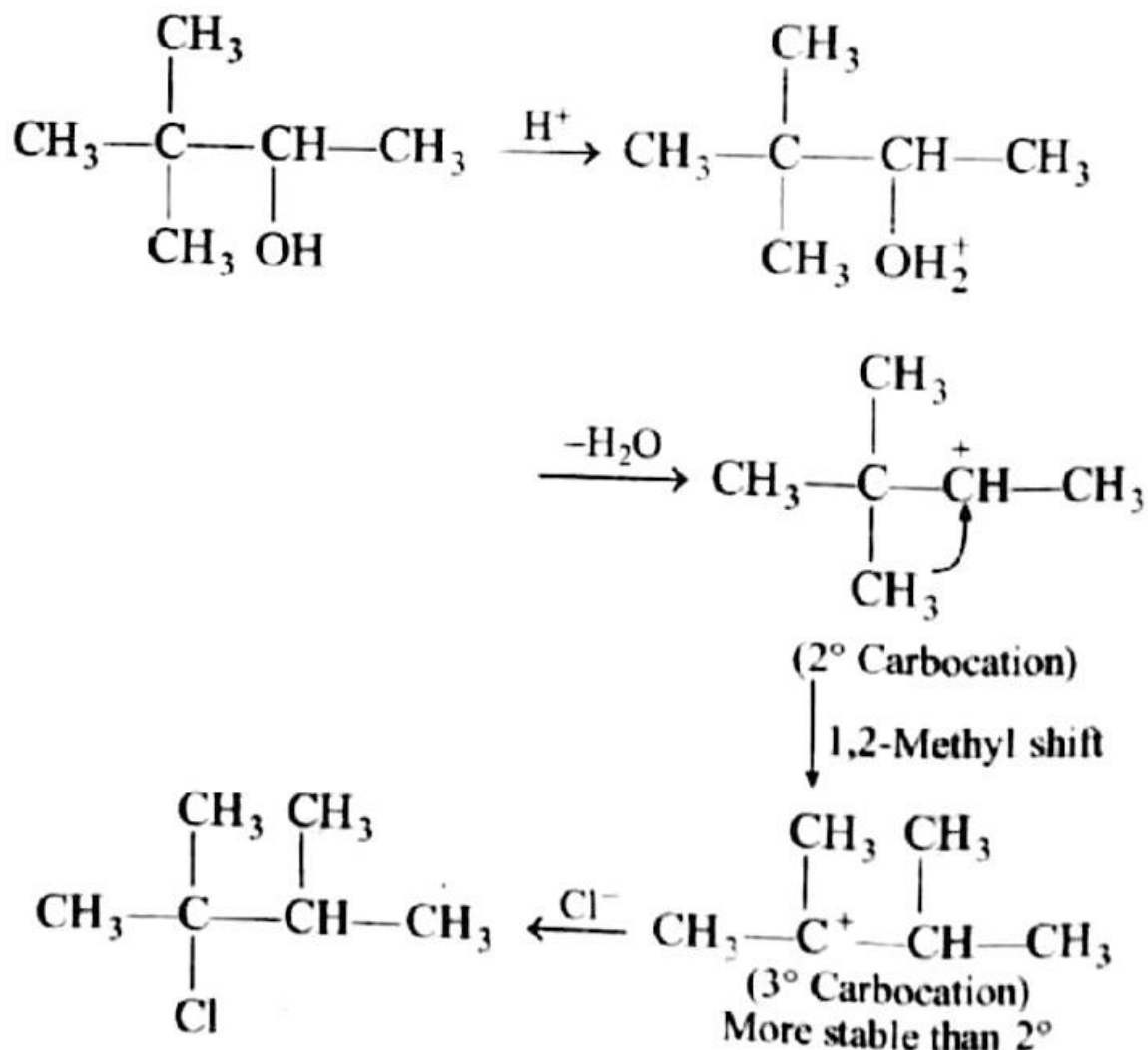
(b) Alkyl bromides are obtained in a similar manner by refluxing the alcohol with constant boiling HBr (48%) in presence of a little concentrated sulphuric acid. These are also obtained when the alcohol is heated with potassium bromide in presence of conc. H_2SO_4 in excess (**Lab method**).



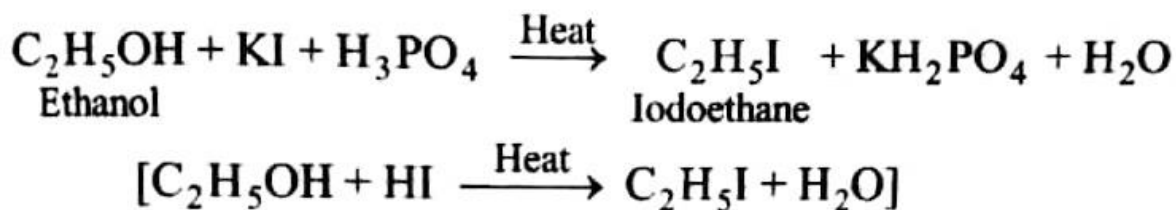
In case of higher alcohols, there can be 1,2-methyl (CH_3^-) or 1,2-hydride (H^-) shift to form more stable carbocation.



This is due to **1,2 – Methyl shift**



(c) Alkyl iodides are prepared by refluxing alcohol with excess of HI (57%). These are also obtained when the alcohol is heated with potassium iodide in presence of phosphoric acid

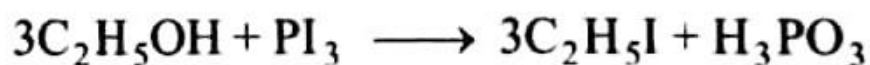
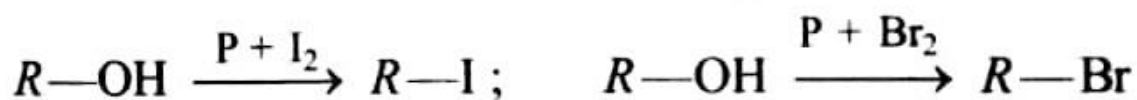


(ii) Action of phosphorus halides : Action of phosphorus halides on alcohols converts them readily into alkyl halides.



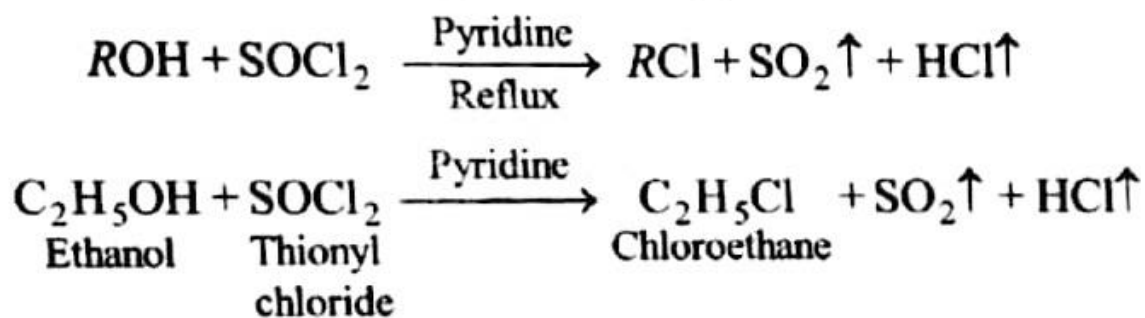
The alkyl chlorides are formed by the action of PCl_3 or PCl_5 on alcohols.

In the case of preparation of alkyl bromides and iodides, PBr_3 or PI_3 required for the reaction is generally produced in situ by the action of red phosphorus on bromine or iodine. Thus, the overall reaction may be depicted as:



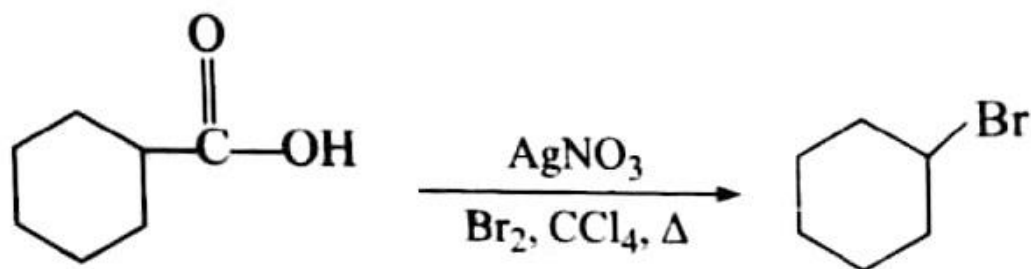
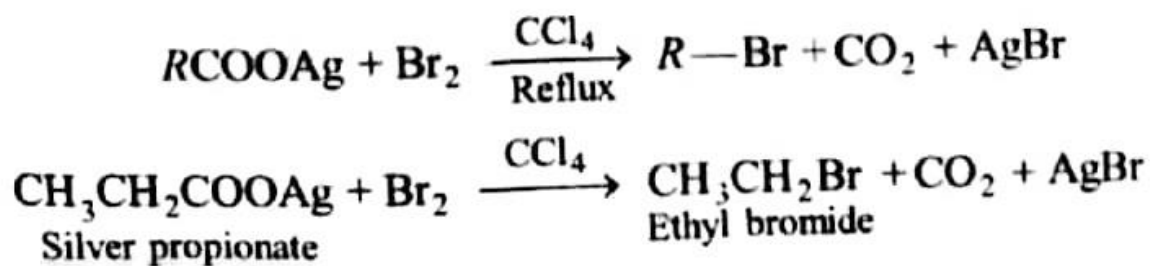
The method gives good yield of primary alkyl halides but poor yields of secondary and tertiary alkyl halides because secondary and tertiary alcohols on heating forms alkenes. The method is useful for preparing lower alkyl bromides and iodides in the **laboratory**.

(iii) Action of thionyl chloride (Darzen's method) : Alkyl chlorides are prepared when thionyl chloride and alcohols are refluxed in presence of pyridine.



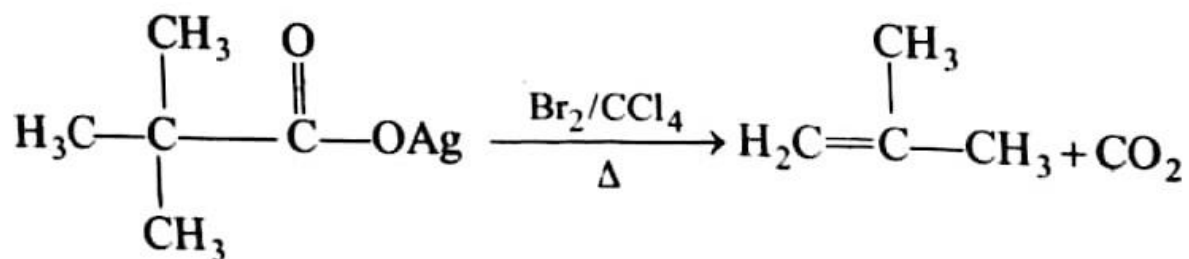
This method is widely used for the preparation of alkyl chlorides only as it has advantage over phosphorus chloride because the byproducts sulphur dioxide and hydrogen chloride are gases which can be easily removed from the reaction mixture. Bromides and iodides are not prepared by this method, because thionyl bromide is unstable and thionyl iodide does not exist.

4. From silver salts of fatty acids: Alkyl chlorides or alkyl bromides are prepared by the action of chlorine or bromine in CCl₄, on silver salt of the fatty acids. This reaction is called **Borodine-Hunsdiecker reaction or Hunsdiecker reaction.**

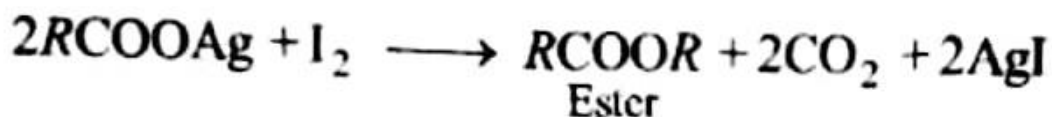


This reaction gives the product with one carbon atom less than the fatty acid and the yield of halide is $1^\circ > 2^\circ > 3^\circ$.

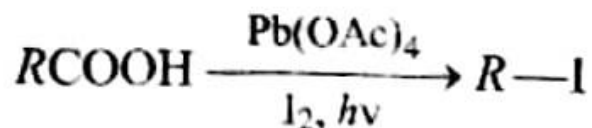
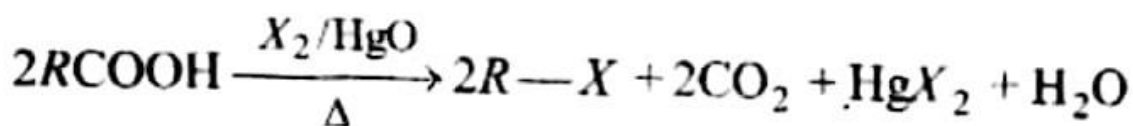
If R group is 3° , then alkene is produced as major product in this reaction



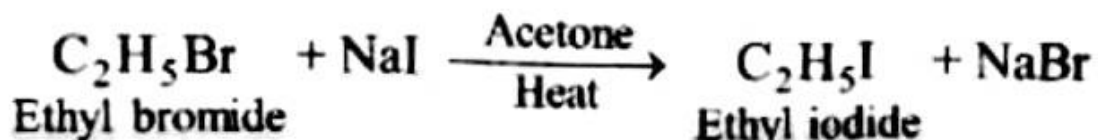
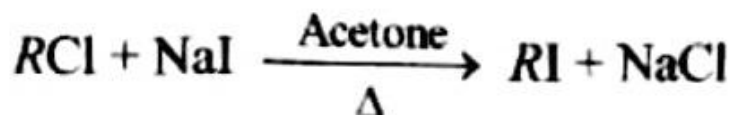
But iodine forms ester instead of alkyl halide and is called **Birnbaum-Simonini reaction**.



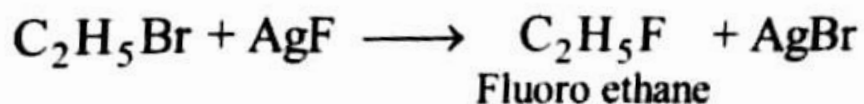
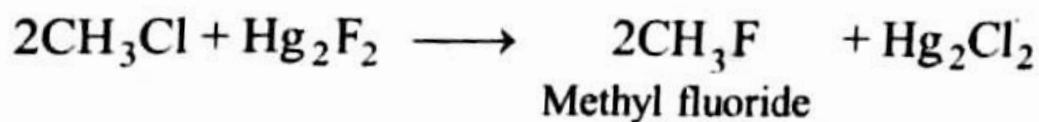
One useful modification of this reaction is the use of HgO or Pb(OAc)₄ in place of silver salt to form alkyl halides.



5. By halide exchange method: This is a convenient method for the preparation of alkyl iodides. The corresponding alkyl bromides or chlorides are heated with a solution of sodium iodide in acetone or methanol.



This reaction is called **Finkelstein reaction**. Even alkyl fluorides which cannot be prepared by the above methods may be obtained from corresponding chlorides by the action of mercurous fluoride or antimony trifluoride or AsF_3 or AgF , etc. , (**Swarts reaction**).



6. By Rydons method: An alcohol on heating with halogen in presence of triphenyl phosphate $(\text{PhO})_3\text{PO}$ produces alkyl halides.

