

ALKYL HALIDES

Alkyl halides or haloalkanes are the derivatives of alkanes which are obtained by replacing one or more hydrogen atoms of the alkanes by halogen atoms. Haloalkanes with one, two, three or more halogen are called mono, di, tri or polyhaloalkanes. If in a dihaloalkane the halogens are attached to carbon atoms of adjacent positions in the carbon chain, the dihaloalkane is called vicinal dihaloalkane. If attached to same carbon atom, the dihaloalkane is called geminal dihaloalkane.

Mono haloalkanes are classified into three types- primary(1°), secondary(2°) and tertiary(3°) depending on whether the carbon atom to which the halogen is bonded contains one, two or three alkyl substituents e.g., Methyl halide is also a primary mono haloalkane.

Nomenclature: In IUPAC system, an alkyl halide is considered to be a halo derivative of alkane.

$\text{CH}_3\text{-Cl}$ Chloromethane $\text{CH}_3\text{-CH}_2\text{-I}$ Iodoethane

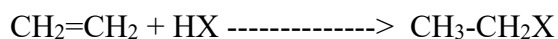
$\text{CH}_3\text{-CHBr-CH}_3$ 2-Bromopropane

$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Br}$ 1-Bromobutane.

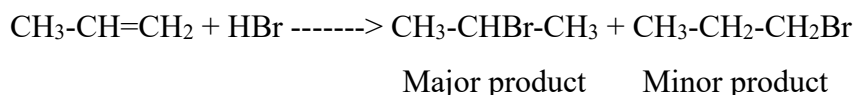
Methods of preparation:

- I. a. By addition of HX to alkene:

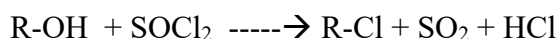
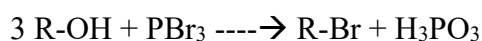
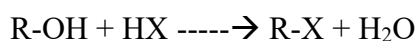
An alkene can be converted to the corresponding alkyl halide by combining with hydrogen halides i.e. HCl, HBr or HI.



b. With non-symmetrical alkene, two isomeric products can form in accordance with Markownikoff's rule. Thus

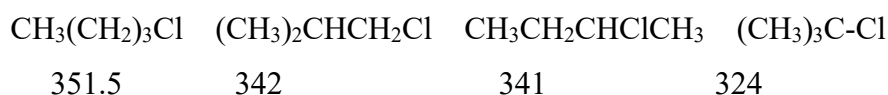


- II. From alcohols: The -OH group of an alcohol can be converted to halogen as follows:



PHYSICAL PROPERTIES:

- 1) The melting and boiling points of haloalkanes are higher than the corresponding alkanes due to their higher molecular mass and polarity compared to the alkanes. For the same alkyl groups, the melting and boiling points of haloalkanes vary in the order $R-I > R-Br > R-Cl > R-F$.
- 2) Haloalkanes are polar, but are insoluble in water as their inability to break the hydrogen bond network in water.
- 3) For isomeric alkyl halides, the boiling points decrease with branching. This is because with branching the surface area of the alkyl halide decreases and hence van der Waals force of attraction decreases. Thus, boiling points (in K) are



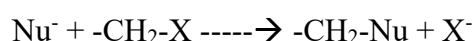
CHEMICAL PROPERTIES:

Because of the presence of polar C-X bond, alkyl halides are very reactive. They undergo the following reactions:

- I) Nucleophilic substitution reactions.
- II) Elimination reactions and
- III) Reaction with metals.

I) Nucleophilic substitution reactions:

As C-X bond in alkyl is polar, a number of nucleophilic reagents can therefore, attack at the C-atom in alkyl halides and replace the halide ion. These reactions are called nucleophilic substitution reactions.

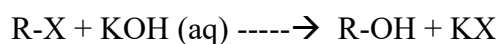


Such reactions can follow either of two mechanisms.

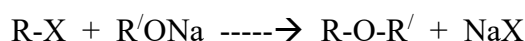
- A) Bimolecular nucleophilic substitution (S_N^2) mechanism or
- B) Unimolecular nucleophilic substitution (S_N^1) mechanism.

Some examples of S_N reactions:

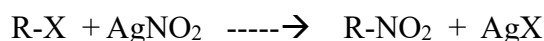
- 1) Substitution by hydroxyl group; Hydrolysis reaction: Alkaline hydrolysis of alkyl halide produces alcohol.



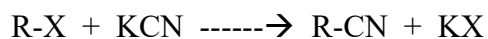
- 2) Substitution by alkoxy group; Williamson ether synthesis: On reacting an alkyl halide with sodium alkoxide, an ether is formed.



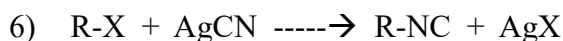
- 3) Substitution by nitro group: When alkyl halide is heated with silver nitrite, a nitroalkane is formed.



- 4) Substitution by cyanide group: When alkyl halide is heated with alcoholic solution of KCN, alkanenitrile is produced.

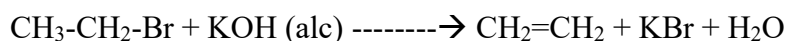


- 5) Substitution by isocyanide group: On heating alkyl halide with silver cyanide, alkyl isocyanide is formed.



II) Elimination reactions

A reaction involving the loss of two atoms or groups from a molecule, without there being substituted by other atoms or groups is known as elimination reaction. E g



Such reactions can follow either of two mechanisms.

A) Unimolecular elimination, E₁ mechanism

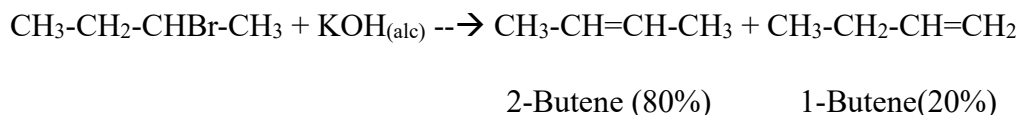
According to this mechanism, in the first step a halide ion is eliminated from the alkyl halide to form a carbocation. In the second step, a beta hydrogen is eliminated from the carbocation to produce an alkene.

B) Bimolecular elimination, E₂ mechanism.

According to this mechanism, the base abstracts a proton from the beta- carbon atom and simultaneously halide ion departs from the alpha- carbon along with bonding electron to produce an alkene.

Saytzeff rule: Orientation of double bond in elimination reactions:

This rule states that if an alkyl halide (or alcohol) is capable of forming double bond in any one of the two possible directions, it invariably yields the alkene which has the greater number of substituents across the double bond i.e. the more substituted alkene is preferably formed. For instance, dehydrobromination of 2- bromo butane gives 2 -butene as the major product.

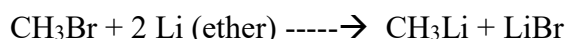


ELIMINATION VERSUS SUBSTITUTION:

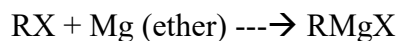
- 1) Structure of the haloalkane: A substrate with several branches will prefer to undergo elimination reaction.
- 2) Nature of nucleophile/ base: A bulky nucleophile favours elimination reactions.
- 3) Temperature: Higher temperature favours elimination reactions.

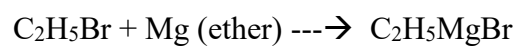
III. REACTION WITH METALS:

Most of the alkyl halides react with certain active metals to produce organometallic compounds. E.g.



An important class of organometallic compounds known as Grignard reagents (RMgX) are prepared by treating haloalkanes with Mg- metal in ether.





Wurtz reaction: Haloalkanes on treatment with Na in ether are converted to alkanes with double the number of carbon atoms.

