21 HALOGENOALKANES

Student Learning Outcomes [C-12-D-30 to C-12-D-37]

- Classify haloalkanes based on the type of halogen atom and its position in the carbon chain, and explain how the molecular structure affects their reactivity.
- Explain the organic functional groups involved in a simple haloalkane synthesis and predict the major product(s) based on the reaction conditions.

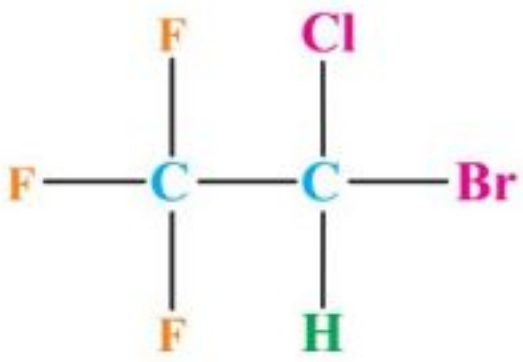
  This includes:

  a. the free-radical substitution of alkanes by Cl or Br in the presence of ultraviolet light, exemplified by the reactions of ethane.

  b. electrophilic addition of an alkene with a halogen, X_2, or hydrogen halide, $HX_{(g)}$ at room temperature.

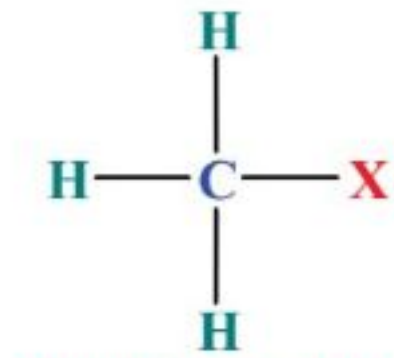
  c. substitution of alcohol, e.g. by reaction with HX or KBr with H_2SO_4 or H_3PO_4; or with PCl_3 and heat; or with PCl_5; or with $SOCl_2$.
- Describe nucleophilic substitution reactions specifically:
  a. the reaction with $NaOH_{(aq)}$ and heat to produce an alcohol
  b. the reaction with KCN in ethanol and heat to produce a nitrile
  c. the reaction with NH_3 in ethanol heated under pressure to produce an amine
  d. the reaction with aqueous silver nitrate in ethanol as a method of identifying the halogen present, exemplified by bromoethane
- Describe the elimination reaction with NaOH in ethanol and heat to produce an alkene as exemplified by bromoethane.
- Describe the production of halogenoarenes, i.e., the reaction of benzene with Cl_2 and Br_2 in the presence of a catalyst.
- Compare the reactivity of halogenoalkanes and halogenoarenes using chloroethane and chlorobenzene as examples.
- Predict the major product(s) based on the reaction conditions and the molecular structure of the halogenoalkane.
- Analyze the mechanism and products of a reaction pathway involving a halogenoalkane and use retrosynthesis to deduce the starting materials.

Halogenoalkanes are very useful in daily life, primarily due to their specialized chemical stability. In the past, chlorofluorocarbons (CFCs) were used as **refrigerants** and aerosol propellants, though these are being replaced by eco-friendly alternatives such as Freons. In medicine, halogenated compounds serve as powerful anesthetic agents. Furthermore, they are vital intermediates in manufacturing **polymers**, such as PVC (polyvinyl chloride) for piping and PTFE (Teflon) for non-stick cookware.

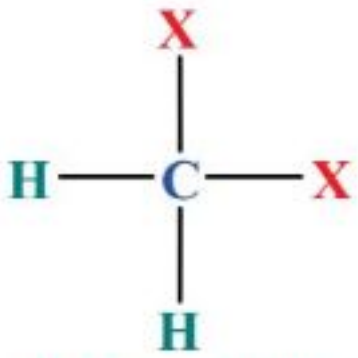


Halothane is a halogenated hydrocarbon widely used as a powerful inhalation **anesthetic**. It induces a reversible loss of consciousness during surgeries. Previously, chloroform and other chlorinated anesthetics were used, which are banned now due to their toxicity and safetyconcerns.

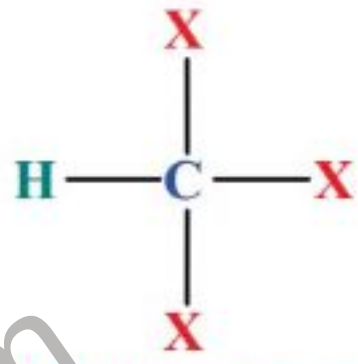
A halogenoalkane is formed when one or more hydrogen atoms of an alkane are replaced by halogen atoms. They may be mono, di, tri or poly halogenoalkanes depending upon the number of halogen atoms (-x) present in the molecule.



Monohalogenoalkane



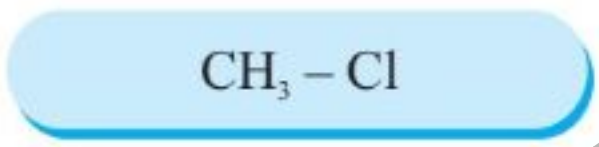
Dihalogenoalkane



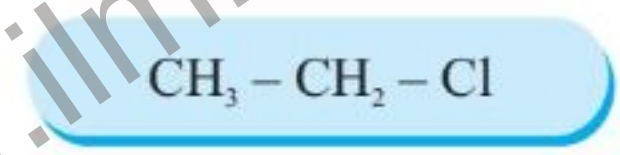
Trihalogenoalkane

Among these, monohalogenoalkanes are also called alkyl halides. Their general formula is R – X, where R may be methyl, ethyl, propyl, etc., and X represents halogen atoms (F, Cl, Br, I). Monohalogenoalkane or alkyl halides are further classified into primary, secondary and tertiary monohalogenoalkanes depending upon the type of carbon atom bearing the halogen atom.

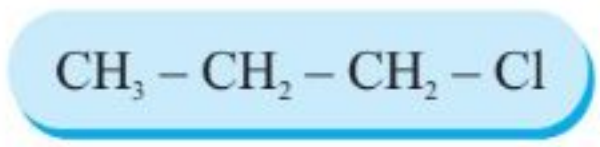
In a primary halogenoalkane, the halogen atom is attached with a carbon which is further attached to one or no carbon atom e.g.



chloromethane

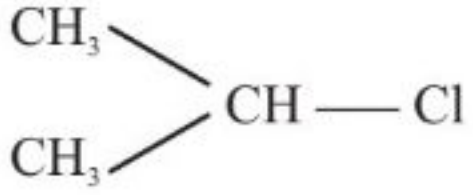


chloroethane

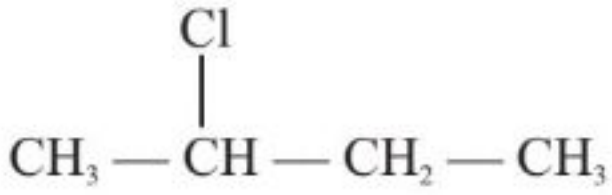


1-chloropropane

Secondary halogenoalkanes are those in which the halogen atom is attached with a carbon atom which is further attached to two other carbon atoms directly.

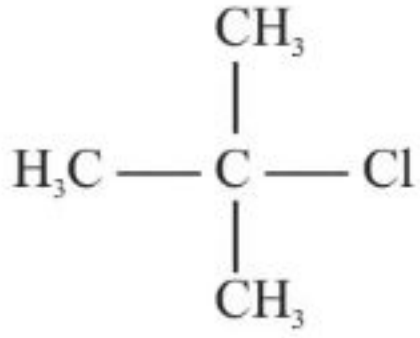


2-chloropropane



2-chlorobutane

In a **tertiary halogenoalkane**, the halogen atom is attached to a carbon atom which is further attached to three carbon atoms directly.



2-chloro-2-methylpropane

Quick Check 21.1

a) Write down the IUPAC name of the compound, $(CH_3)_2CH\text{-}CH_2\text{-}Cl$

b) Draw all possible structures of a compound having the molecular formula $C_5H_{11}Cl$. Classify each as primary, secondary or tertiary chloride.

21.1 PREPARATION OF HALOGENOALKANES

(i) Halogenoalkanes can be prepared by the halogenation of alkanes in the presence of light.

$$\underset{\text{ethane}}{CH_3—CH_3} + Cl_2 \xrightarrow{\text{light}} \underset{\text{chloroethane}}{CH_3—CH_2—Cl} + HCl$$

(ii) They can also be prepared by the electrophilic addition of hydrogen halides to alkenes.

$$\underset{\text{ethene}}{H_2C=CH_2} + HBr \longrightarrow \underset{\text{bromoethane}}{CH_3—CH_2—Br}$$

(iii) Alcohols may be converted to the corresponding alkyl halides by the action of halogen acid in the presence of $ZnCl_2$ which acts as a catalyst.

$$\underset{\text{ethanol}}{CH_3—CH_2—OH} + HCl \xrightarrow{ZnCl_2} \underset{\text{chloroethane}}{CH_3—CH_2—Cl} + H_2O$$

(iv) Alcohols also react with thionyl chloride in pyridine as a catalyst to give alkyl chlorides. This method is especially useful since the by-products (HCl and SO_2) are gases which go off leaving behind the pure product.

$$\underset{\text{ethanol}}{CH_3—CH_2—OH} + SOCl_2 \xrightarrow{\text{pyridine}} \underset{\text{chloroethane}}{CH_3—CH_2—Cl} + SO_2 + HCl$$

(v) Phosphorus trihalides or phosphorus pentahalides react with alcohols to replace – OH group by a halo group.

$$\underset{\text{ethanol}}{3CH_3—CH_2—OH} + PBr_3 \longrightarrow \underset{\text{bromoethane}}{3CH_3—CH_2—Br} + H_3PO_3$$

$$\underset{\text{ethanol}}{CH_3—CH_2—OH} + PCl_5 \longrightarrow \underset{\text{chloroethane}}{CH_3—CH_2—Cl} + POCl_3 + HCl$$

(vi) Alcohols can be converted to halogenoalkanes by reacting with potassium bromide and an acid like sulphuric acid (H_2SO_4) or phosphoric acid (H_3PO_4). This method is commonly used to prepare bromoalkanes and iodoalkanes. The acid first reacts with potassium bromide to give hydrogen bromide which then further reacts with alcohols to give bromoalkanes.

$$\underset{\text{ethanol}}{CH_3—CH_2—OH} + KBr + H_2SO_4 \longrightarrow \underset{\text{bromoethane}}{CH_3—CH_2—Br} + H_2O + KHSO_4$$

Phosphoric acid is preferably used to prepare iodoalkanes because it is a weak oxidizing agent and less likely to oxidize iodide ions to iodine.

MORE INFO

Interesting Information

Bromoethane is naturally emitted primarily by **marine algae and phytoplankton such as trichodesmium**. These organisms convert seawater bromide into volatile organobromides. Once in the atmosphere, bromoethane contributes to the global bromine cycle and plays a role in stratospheric ozone depletion.

Quick Check 21.2

a) Give two methods to convert methanol into chloromethane.
b) Give reactions of propanol with $SOCl_2$ and PBr_3.
c) Can we prepare fluoromethane using methane and fluorine gas?

21.2 REACTIVITY OF HALOGENOALKANES

A halogenoalkane molecule (R – X) consists of two parts, an alkyl group with a partial positive charge on the carbon atom attached to halogen atom and the halide atom with a partial negative charge. Experiments have shown that the strength of carbon halogen bond is the main factor which decides the reactivity of haloalkanes. The weaker bond will be more easily broken and make the molecule more reactive. **Table 21.1** shows the bond energies of C – X bonds in alkyl halides.

The strength of the bonds shows that iodo compounds (with the weakest bonds) would be the most reactive halogenoalkanes, while fluoro compounds will be the least reactive i.e., the order of reactivity of halogenoalkanes should be:

$$R - I > R - Br > R - Cl > R - F$$

In fact, the C – F bond is so strong that fluoroalkanes do not react under ordinary conditions. Some other factors which may affect the reactivity of halogenoalkanes are, bond polarity, steric hindrance, inductive effect, etc.

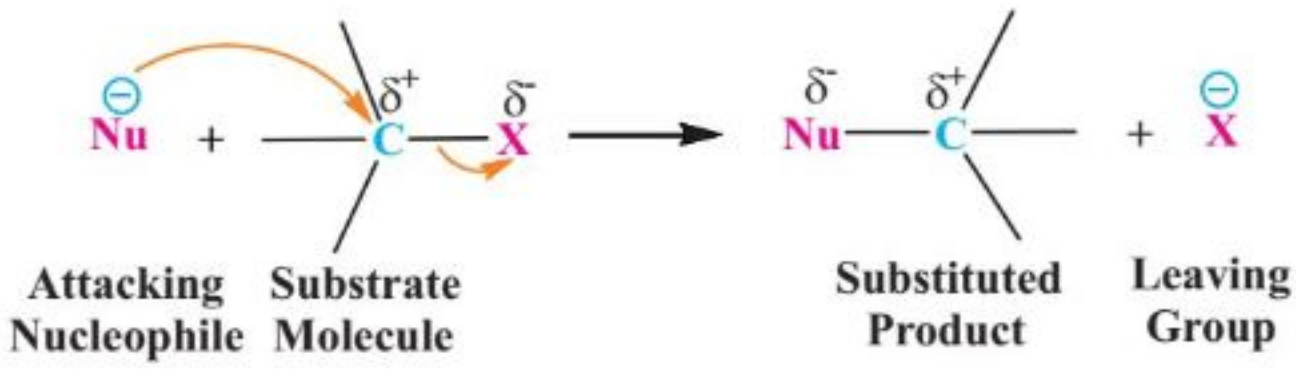
Table 21.1 Bond energies of different C-X bonds

Bond	Bond Energy (kJ/mol)
C – F	467
C – Cl	346
C – Br	290
C – I	228

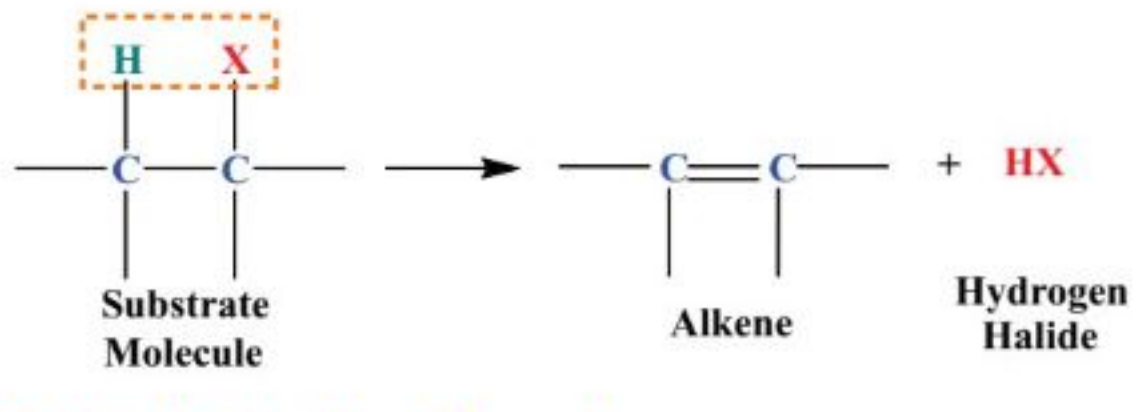
21.3 REACTIONS OF HALOGENOALKANES

The C-X bond in halogenoalkanes is polar due to the difference of electronegativity between C and the halogen atom. The carbon of C-X acts as an electrophilic centre, which can be attacked by a nucleophile. Alternatively, the hydrogen attached to the carbon atom may be attacked by a base. These two possibilities result in two types of reaction of halogenoalkanes

a) Those reactions in which the halogen is replaced by some other atom or a group (nucleophilic substitution, or S_N reactions).



b) Those that involve the removal of HX from halogenoalkanes (elimination, or E reactions), results in the formation of alkenes.



21.3.1 Nucleophilic Substitution Reactions

Alkyl halides may undergo nucleophilic substitution reactions in two different ways:

a. Nucleophilic Substitution Bimolecular (S_N2)

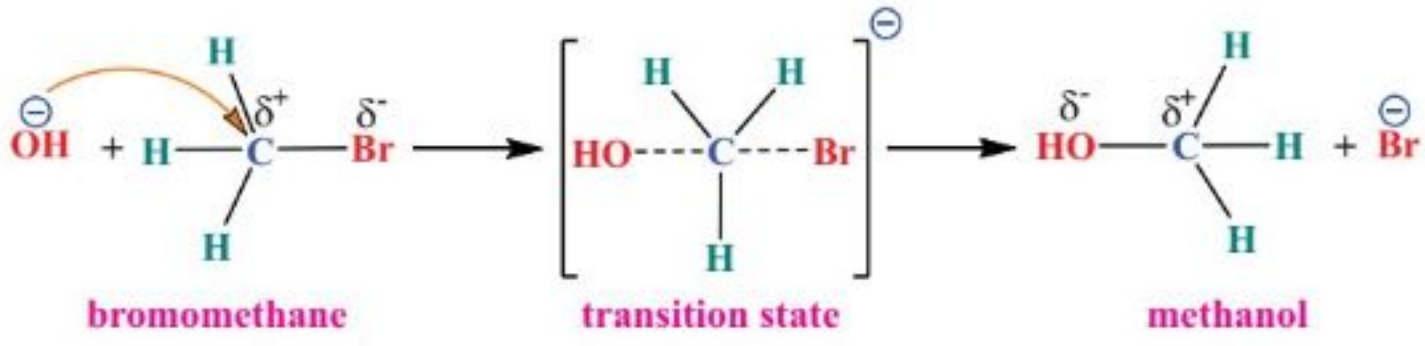
b. Nucleophilic Substitution Unimolecular (S_N1)

Nucleophilic substitution reactions on alkyl halides involve two main processes, the departure of leaving group (breaking of C – X bond) and the attack of nucleophile (the formation of C – Nu bond). If the two processes occur simultaneously in single step the mechanism is called S_N2. But if the two changes occur in two separate steps, i.e., the bond breaks in first step followed by the formation of a new bond in second step, then the mechanism is called S_N1.

i) Nucleophilic Substitution Bimolecular (S_N2)

This is a single step mechanism. As soon as the nucleophile starts attacking the electrophilic carbon of the substrate, the bond with which the leaving group is attached, starts breaking. In other words, the extent of bond formation is equal to the extent of bond breaking.

Another important feature of this mechanism is the direction of the attack of the attacking nucleophile. It attacks from the side which is opposite to the leaving group. The attack of the nucleophile and the departure of the leaving group, everything occurs at the same time.



Since in this mechanism, the reaction takes place in only one step, which is also a rate-determining step and two molecules are participating in this step, it is a bimolecular reaction.

Kinetic studies of the reactions involving S_N2 mechanism have shown that the rates of such reactions depend upon both the concentrations of alkyl halide and the attacking nucleophile. Mathematically, the rate can be expressed as:

Rate = k [Alkyl halide]^1[Nucleophile]^1 order = 1 + 1 = 2

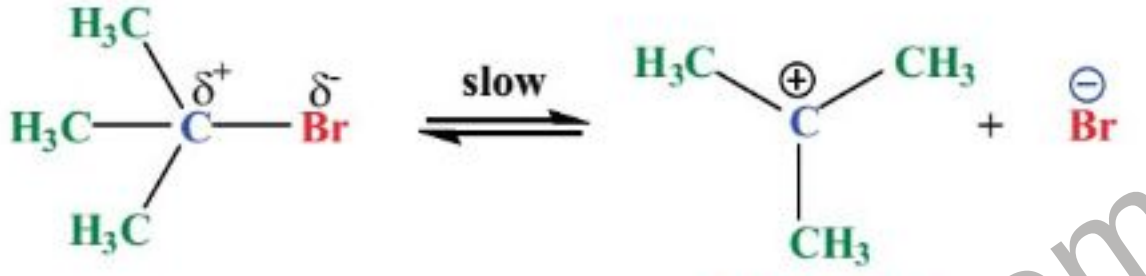
A typical S_N2 reaction is a second order reaction.

Among the monohalogenoalkanes, primary monohalogenoalkanes always follow S_N2 mechanism whenever they are attacked by nucleophiles. This is due to steric reasons, as in primary monohalogenoalkanes the substrate carbon is attached with hydrogen atoms or only one carbon atom, the nucleophile can approach and attack the electrophilic carbon easily.

ii) Nucleophilic Substitution Unimolecular (S_N1)

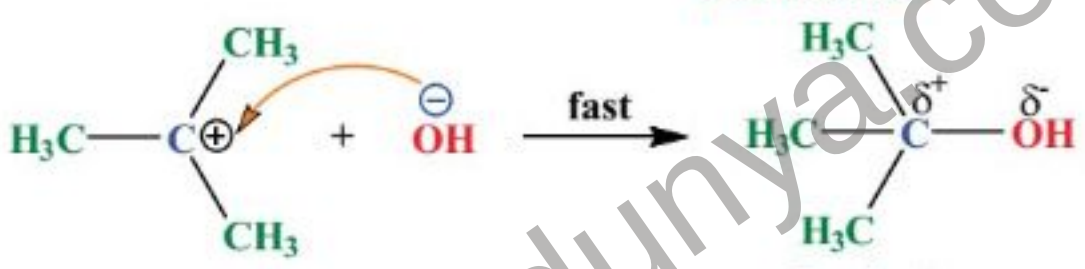
This type of mechanism involves two steps. The first step is the reversible ionization of the alkyl halide in the presence of aqueous acetone or aqueous ethyl alcohol. This step provides a carbocation as an intermediate. In the second step, this carbocation is attacked by the nucleophile to give the product.

First Step:



Carbocation

Second Step:



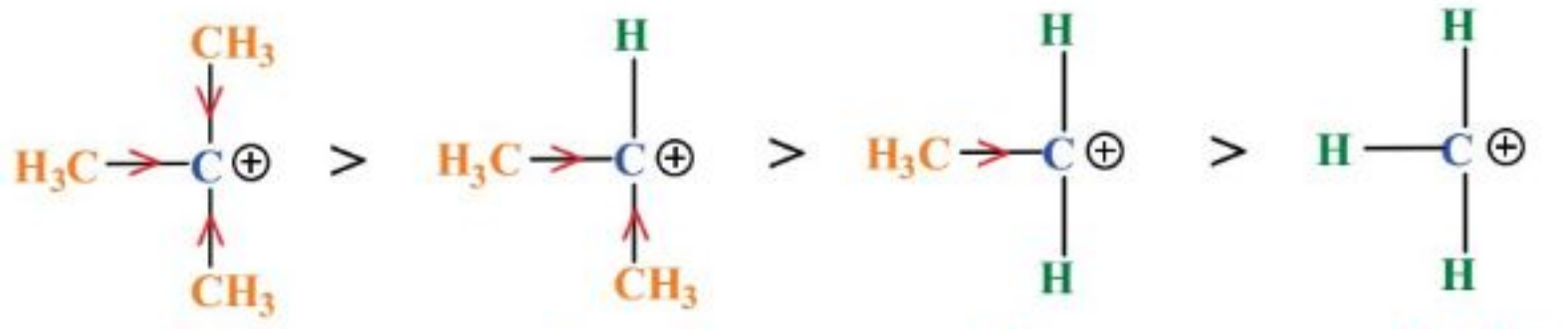
Product

Since the first step involves the breaking of a covalent bond so it is a slow step as compared to the second step, which involves the energetically favourable combination of ions. The first step is, therefore, called the rate-determining step. The mechanism is called unimolecular because only one molecule takes part in the rate-determining step.

Reactions involving S_N1 mechanism show first order kinetics and the rates of such reactions depend only upon the concentration of the alkyl halide. The rate equation of such reactions can be written as follows:

Rate = k [Alkyl halide]

Tertiary monohalogenoalkanes always follow S_N1 mechanism whenever they are attacked by a nucleophile, the major reason is the formation of the stable tertiary carbocation. Moreover three bulky groups attached with the electrophilic carbon prevent the attacking nucleophile to attack from the backside of leaving group. The substrate molecule thus prefers to follow the S_N1 mechanism.



Decreasing stability order of carbocations due to decrease in positive inductive effect (+I).

The mechanism shows that a carbocation is formed in the rate-determining step, so, the more stable the carbocation, the more easily it is formed. Tertiary carbocations are more stable than secondary carbocations which are in turn, more stable than the primary carbocations.

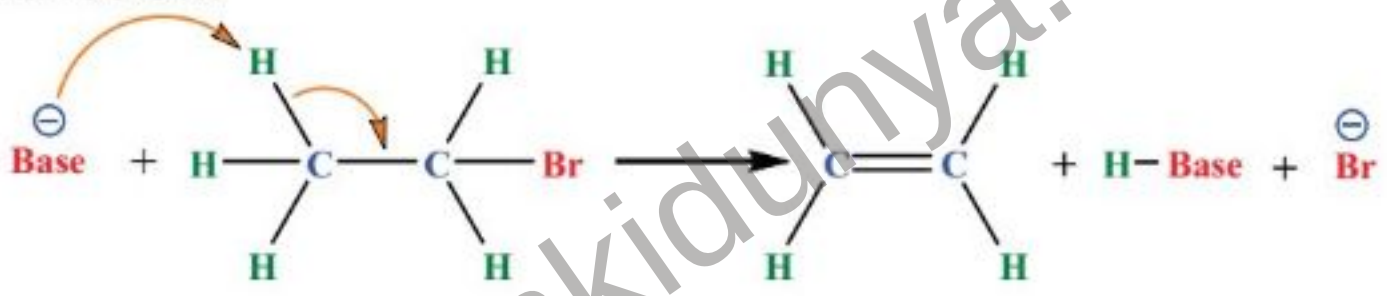
A secondary halogenoalkane can undergo both S_N2 and S_N1 reaction mechanism, depending upon the nature of solvent.

21.3.2 β-Elimination Reactions

β-elimination is a reaction in which a hydrogen atom attached to the β-carbon of the alkyl halide and the halogen atom on the adjacent carbon atom are removed from a halogenoalkane. This reaction occurs when a base attacks the β-bhydrogen atom of the halogenoalkane. The removal of the halogen takes place either simultaneously or after the removal of the hydrogen atom. Thus, an alkene molecule is obtained instead of a substitution product. These reactions take place simultaneously with substitution reactions and often compete with them. Like nucleophilic substitution, the elimination reactions can follow two types of mechanism; E2 or E1.

Elimination Bimolecular (E2)

In E2 mechanism, the base attacks the β hydrogen atom and the leaving group leaves at the same time with the formation of a carbon-carbon double bond. The single step E2 elimination mechanism is given below.



bromoethane **ethene**

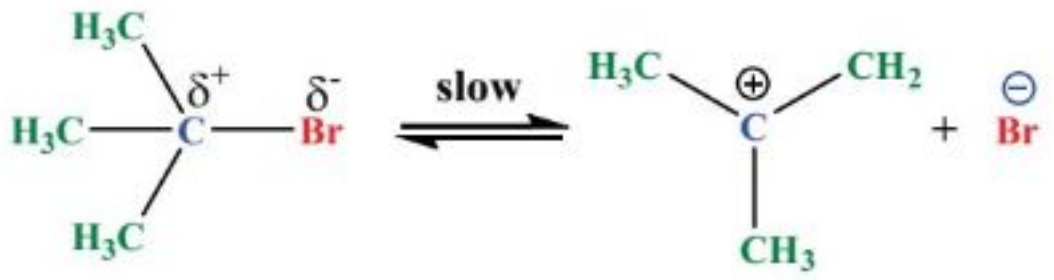
E2 reaction is bimolecular and the rate of this reaction depends upon the concentrations of the alkyl halide and the base.s Like S_N2 reactions, the molecularity of E2 reactions is also two and these reactions show second order kinetics.

Rate = k [Alkyl halide]^1[Base]^1 Order = 1 + 1 = 2

Elimination Unimolecular (E1)

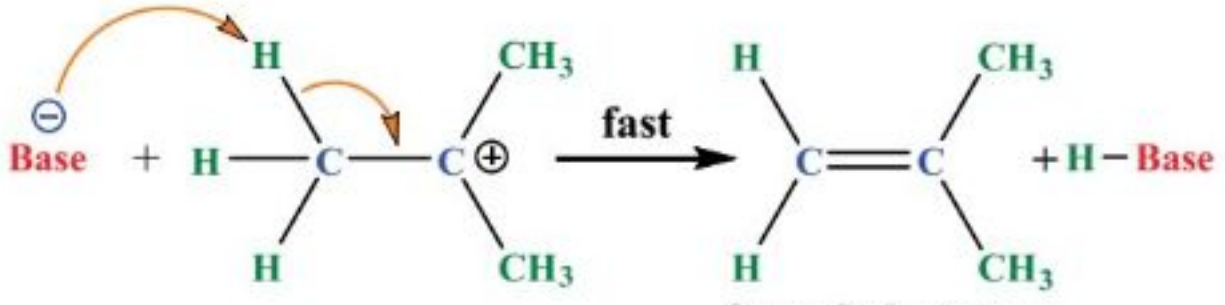
In E1 mechanism, like S_N1 mechanism, the first step is the slow ionization of the substrate to give a carbocation. In the second step, the base attacks the β-hydrogen atom to give an alkene as a product.

Step - 1



2-bromo-2-methylpropane **3^0 carbocation**

Step - 2



2-methylpropene

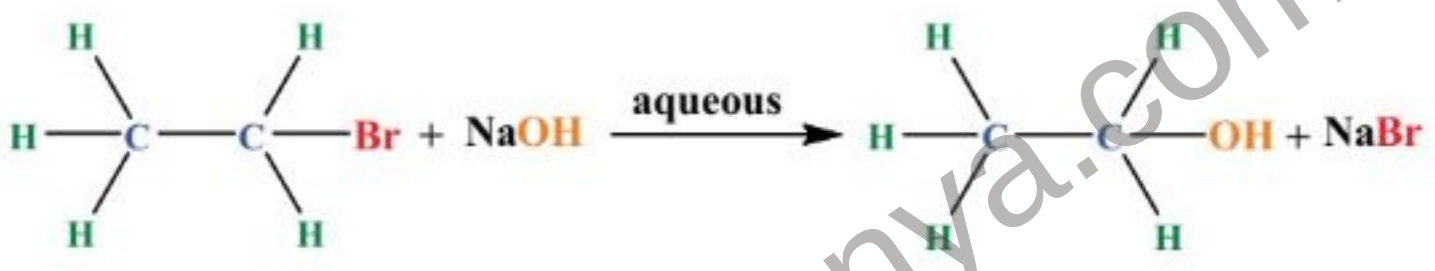
E1 mechanism is a unimolecular mechanism and the rate of the reaction depends only upon the concentration of the alkyl halide molecule. Primary halogenoalkanes generally follow E2 mechanism whereas tertiary halogenoalkanes follow E1 mechanism. However, secondary halogenoalkanes can show both E2 and E1 reactions according to the choice of the solvent.

21.4 EXAMPLES OF REACTIONS OF HALOGENOALKANES

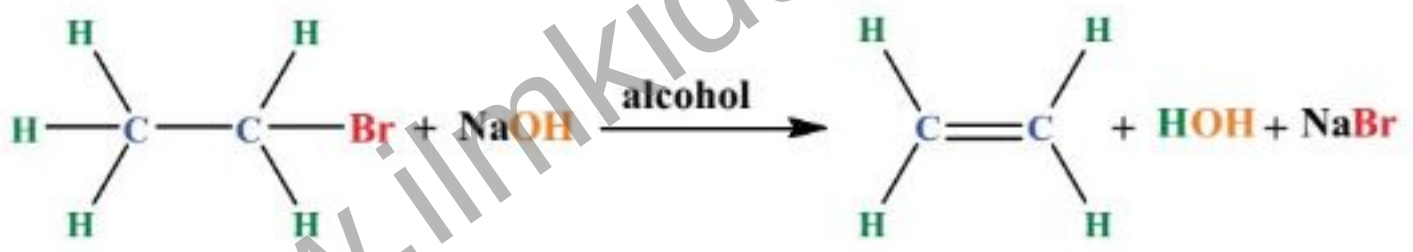
I. With Sodium Hydroxide

A halogenoalkane reacts with aqueous sodium hydroxide to give both substitution and elimination products depending upon the reaction conditions. Hydroxide ion is both a good nucleophile and a good base. So, when it attacks as a nucleophile, it replaces the halogen atom of the halogenoalkane to form a substitution product, alcohol. As a base, it removes both the β-hydrogen atom and the halogen atom to give an elimination product, an alkene. The reaction takes place at higher temperature under reflux conditions to avoid the loss of volatile products. Bromoethane reacts with aqueous sodium hydroxide to give ethanol as well as ethene.

Substitution Reaction



bromoethane ethanol



bromoethane ethene

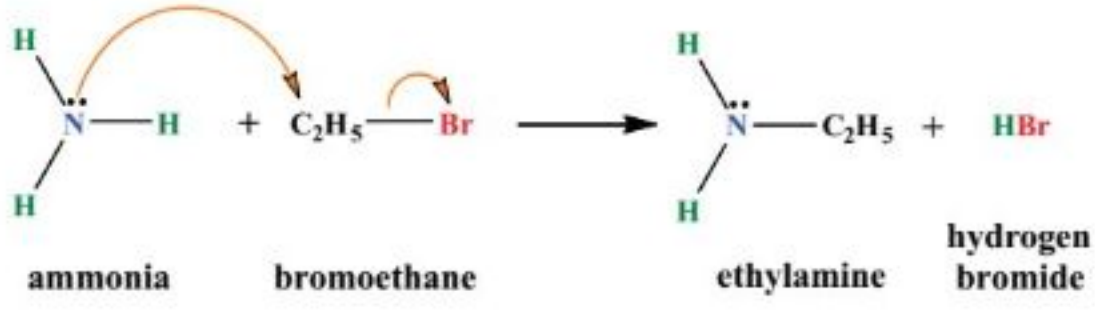
ii. Reactions of Halogenoalkanes with KCN

Since cyanide ion (CN^-) is a strong nucleophile but a weak base so it reacts with halogenoalkanes to give substitution product, a nitrile. The reaction is typically carried out by heating the halogenoalkane with an ethanolic solution of potassium cyanide under reflux. Bromoethane reacts with potassium cyanide to give propane nitrile.

bromoethane propanenitrile

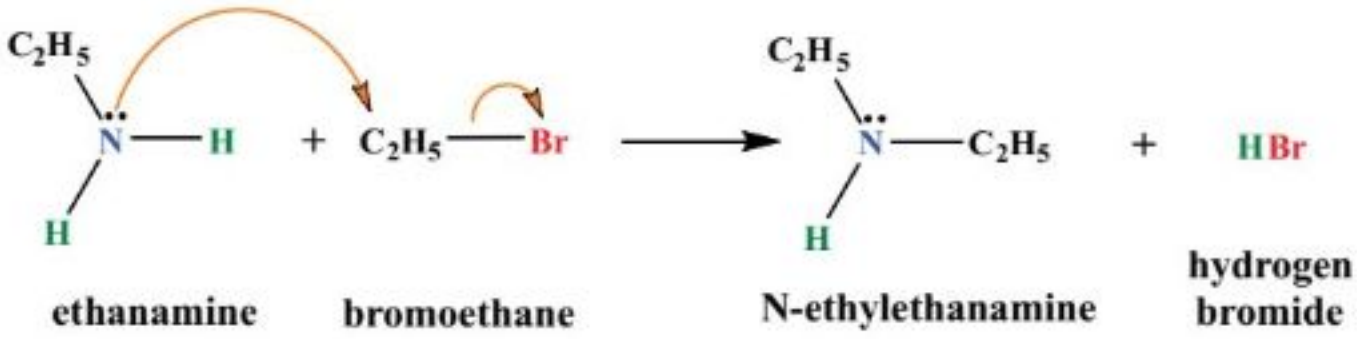
iii. Reactions of Halogenoalkanes with Ammonia

Ammonia is a good nucleophile and it reacts with halogenoalkanes a favourably. Different types of amines can be produced if the amounts of halogenoalkane and ammonia are carefully controlled.



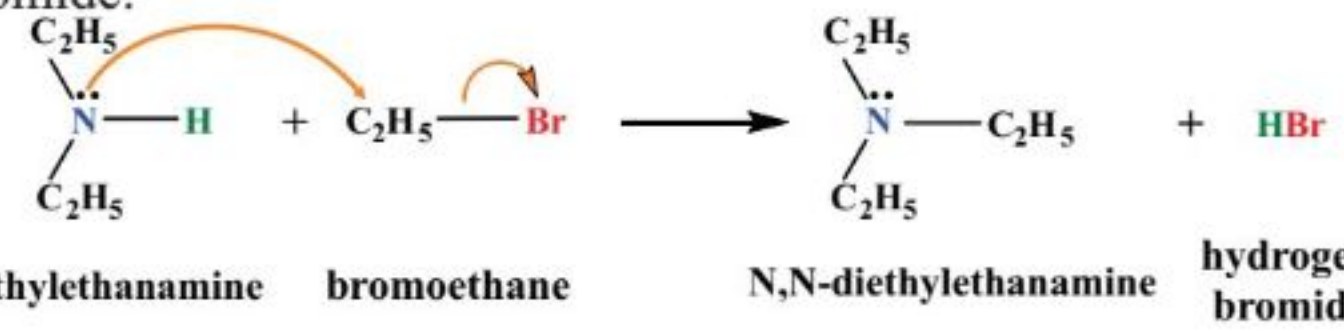
ammonia bromoethane ethylamine hydrogen bromide

Since ethanamine is also a nucleophile, it can compete with ammonia to react with alkyl halide to give diethyl amine.



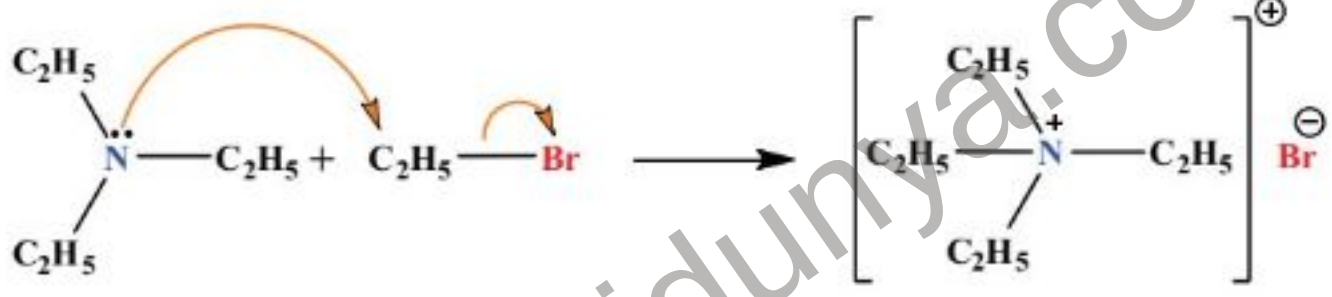
ethanamine bromoethane N-ethylethanamine hydrogen bromide

N-ethylethanamine will act as a nucleophile and will attack on another bromoethane molecule to form hydrogen bromide.



N-ethylethanamine bromoethane N,N-diethylethanamine hydrogen bromide

If a large excess of bromoethane is used, the reaction may proceed to give quaternary ammonium salt as the final product.



N,N-diethylethanamine bromoethane N,N,N-triethylethanaminebromide

iv. Reactions of Halogenoalkanes with Aqueous Silver Nitrate

This reaction is carried out in a mixture of water and ethanol, the alcohol in this mixture helps to dissolve the halogenoalkane. Water reacts with halogenoalkane as a nucleophile replacing the halide ion.

haloethane ethanol

The released halide ion then reacts with silver nitrate to give a precipitate with a characteristic colour corresponding to the halide ion present. Thus, the reaction helps to detect the halide ion present in halogenoalkanes.

$Ag^+ + Cl^- \longrightarrow AgCl$ **(White ppt)**

$Ag^+ + Br^- \longrightarrow AgBr$ **(Cream yellow ppt)**

$Ag^+ + I^- \longrightarrow AgI$ **(Bright Yellow ppt)**

Comparing the rates of formation of silver halides in this reaction gives us a clue about the different reactivities of halides. The quicker the precipitate appears, the more reactive is the halogenoalkane. An iodoalkane produces a precipitate very quicker than bromoalkane. A chloroalkane, however, reacts very slowly.

Quick Check 21.3

a) Why halogenoalkanes are considered as very reactive class of organic compounds?

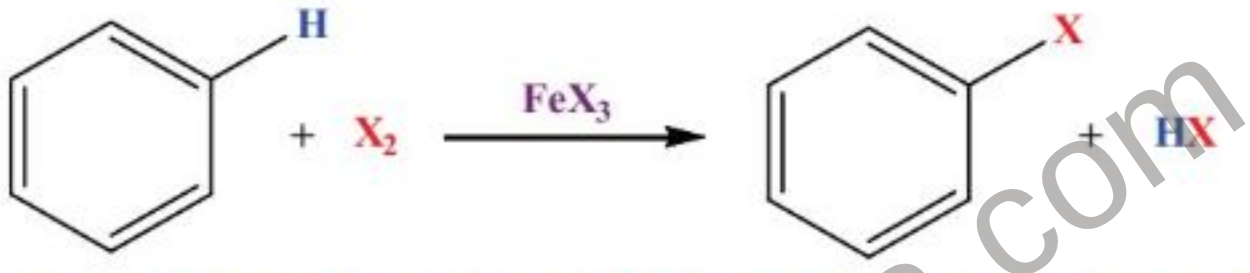
b) Complete the following equation. $C_2H_5Br + CH_3COONa \longrightarrow$

c) How will you convert ethane into ethanol and ethene?

d) Give the reaction of bromopropane with KCN. Is this a substitution reaction or an elimination reaction? Name the main product of this reaction.

21.5 HALOGENOARENES

Halogenoarenes like chlorobenzene and bromobenzene are prepared by reacting benzene with either chlorine or bromine in the presence a of catalyst, anhydrous $FeCl_3$ or $FeBr_3$. The reaction is called electrophilic aromatic substitution reaction and is typically carried out at room temperature.

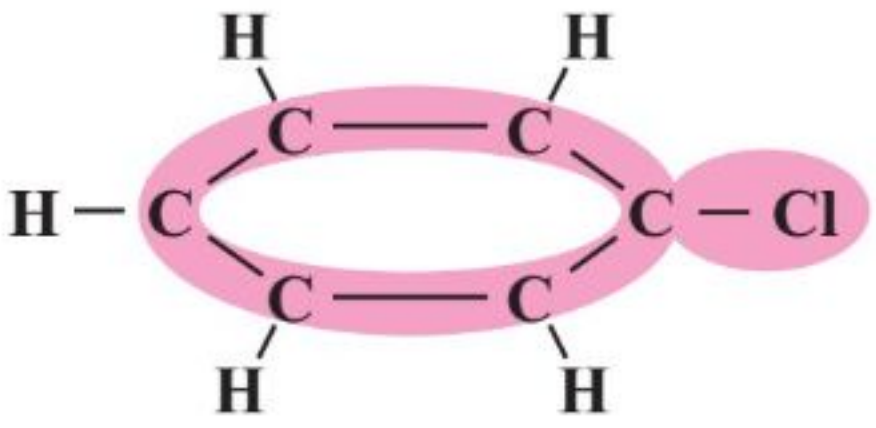


21.5.1 Comparison of Reactivities of Halogenoalkanes and Halogenoarenes

Halogenoalkanes are aliphatic organic compounds in which halogen atom is attached with an alkyl group. Owing to the difference in the electronegativity values of carbon and halogen a partial positive charge is developed on the carbon atom attached to the halogen making it an electrophile. This electrophilic carbon atom invites nucleophiles to attack on it giving a vast body of reactions called nucleophilic substitution reactions.

The attack by bases on the hydrogen atom attached with the carbon atom adjacent to it gives another important class of reactions called elimination reactions. These reactions have been discussed in detail previously.

However, in halogenoarenes, the electron pair on the chlorine atom is delocalised due to the involvement of the chlorine lone pair with the aromatic ring as shown below. The carbon-halogen bond is stronger due to the partial double-bond character, resulting from this delocalisation. The strength of C—Cl bond, thus increases making it difficult to break. Consequently, the halogenoarenes, are less reactive and synthetically less useful.



Quick Check 21.4

a) What is the role of iron halide in the preparation of halogenoarene?
b) Chlorobenzene does not react with NaOH under normal conditions, but chloroethane does; explain why?
c) Can chlorobenzene undergo elimination? Explain why or why not?

MORE INFO Interesting Information

Some halogen compounds like DDT have been used as pesticides, but their persistence in the environment has led to restrictions or banning of their use in developed countries. Because DDT is a cheap and effective mosquito control agent, some developing countries have experienced a sharp increase in malaria deaths following its removal from stores. It is therefore, advised to restrict its use for environmental protection.

Exercise

Q1. MULTIPLE CHOICE QUESTIONS:

1 Encircle The Correct Answer.

I) Which of the following compound is a primary halogenoalkane?

a) 1-bromo-2,2-dimethyl propane
b) 2-bromo-3-methyl butane
c) 2-bromopropane
d) 2-bromo-2-methyl propane

II) The reactivity order of halogenoalkanes for a particular alkyl group is:

a) Fluoride > Chloride > Bromide > Iodide
b) Chloride > Bromide > Fluoride > Chloride
c) Iodide > Bromide > Chloride > Fluoride
d) Bromide > Iodide > Chloride > Fluoride

III) S_N2 reactions can be best carried out with:

a) Primary halogenoalkanes
b) Secondary halogenoalkanes
c) Tertiary halogenoalkanes
d) Halogenoarenes

IV) Elimination bimolecular reactions involve:

a) First order kinetics
b) Second order kinetics
c) Third order kinetics
d) Zero order kinetics

V) For which mechanisms, the first step involved is the same:

a) E1 and E2
b) E2 and S_N2
c) S_N1 and E2
d) E1 and S_N1

VI) Halogenoalkanes are considered to be very reactive compounds towards nucleophiles, because:

a) They have an electrophilic carbon

b) They have an electrophilic carbon and a good leaving group

c) They have an electrophilic carbon and a bad leaving group

d) They have a nucleophilic carbon and a good leaving group

VII) 2-chloropropane will follow which mechanism when it reacts with aqueous KOH resulting in the formation of an alcohol.

a) S_N1 b) S_N2

c) Mixed S_N1 and S_N2 d) E1

VIII) Which one of the following is not a nucleophile?

a) H_2O b) H_2S

c) BF_3 d) NH_3

IX) When aqueous solution of alkyl halides are reacted with $AgNO_3$, the most rapid ppt. formation occurs with:

a) fluoroalkane b) chloroalkane

c) bromoalkane d) iodoalkane

X) The rate of E1 reaction depends upon:

a) The concentration of the substrate

b) The concentration of the base

c) The concentrations of substrate as well as base

d) Neither the concentration of substrate nor the base

Q2. SHORT ANSWER QUESTIONS

a) Why halogenoalkanes are known to be very reactive compounds?

b) Why fluoroalkanes rarely undergo nucleophilic substitution reactions?

c) Why primary halogenoalkanes undergo substitution reactions by S_N2 mechanism?

d) Does 1-bromo-2,2-dimethylpropane undergo elimination reaction or not? Justify.

e) Why tertiary halogenoalkanes undergo elimination reaction by E1 mechanism?

f) Hydroxide ion is a good base as well as a good nucleophile. Justify.

g) What is the role of iron chloride ($FeCl_3$) during the chlorination of benzene?

h) Which among haloalkanes or haloarenes, is more reactive towards nucleophiles?

i) Write the equation for the reaction of 1-chloropropane with $AgNO_3$.

Q3. CONSTRUCTED RESPONSE QUESTIONS

a) Predict the mechanism which the chloroalkane will adopt while giving nucleophilic substitution reactions.

b) Why nucleophilic substitution and elimination reactions of haloalkanes proceed together under similar conditions?

c) It is difficult for chlorobenzene to undergo nucleophilic substitution reactions but it is easier for it to undergo electrophilic substitution reactions. Give reasons.

d) Differentiate between E2 and E1 reactions. Draw a table for your response.

e) Why does CH_3-CH_2-I give a precipitate with aqueous silver nitrate earlier than CH_3-CH_2-Cl?

DESCRIPTIVE QUESTIONS

Q4. Describe how substitution of alcohol with following reagents help to synthesize halogenoalkanes

i) KBr with H_2SO_4

ii) $SOCl_2$/Pyridine

iii) PCl_3

iv) PCl_5

Q5. Describe nucleophilic substitution reactions of halogenoalkane starting from bromoethane with following reagents:

i) Aqueous NaOH

ii) Ethanolic KCN

iii) Ethanolic NH_3

Q6. Compare the reactivity of halogenoalkanes and halogenoarenes using chloroethane and chlorobenzene as examples.

Q7. Describe the S_N1 and S_N2 mechanisms of nucleophilic substitution in halogenoalkanes.