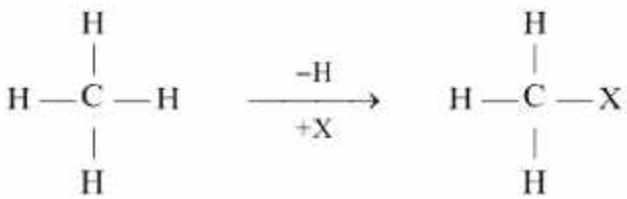
Chapter

10

ALKYL HALIDES

INTRODUCTION

"If hydrogen atom of alkane is replaced by a halogen atom, the product formed is called haloalkane." e.g.,



Alkanes having one halogen atom are called monohaloalkane, having two halogen atoms are called dihaloalkane, having three halogan atoms, are called trihaloalkanes. If many halogen atoms are present in an alkane, it is called polyhaloalkanes.



Molnohaloalkane Dihaloakane Trihaloalkane

MONOHALOALKANES

Monohaloalkanes are also called alkyl halides. They have general formula R – X or C_nH_{2n+1} X.

X represents to F, Cl, Br or l.

Classification of Monohaloalkanes or Alkyl Halides:

Alkyl halides are classified as follows:

Primary Alkyl Halides:

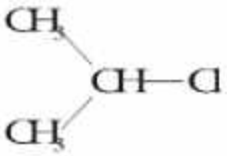
"In a primary alkyl halide, halogen atom is attached with a carbon which is further attached to one or no carbon atoms" e.g.,

$CH_3—Cl$ $CH_3—CH_2—Cl$ $CH_3—CH_2—CH_2—Cl$

Methyl Chloride Ethyl Chloride n-Propyl Chloride

Secondary Alkyl Halides:

"Secondary alkyl halides are those, in which halogen atom is attached with a carbon atom which is further attached to two other carbon atoms directly." e.g.,



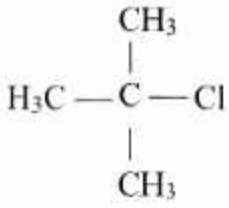
Sec propyl chloride (iso propyl chloride)



Sec-butyl chloride

Tertiary Alkyl Halides:

"In tertiary halides, halogen atom is attached to a carbon which is further attached to three carbon atoms directly" e.g.,



ter-butyl chloride

NOMENCLATURE OF ALKYL HALIDES (R-X)

(a) Common Names:

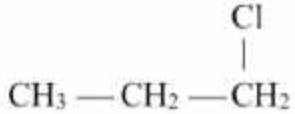
In this method of nomenclature, name of alkyl group is written first and connected with the given halide. For examples.

$CH_3—Cl$

Methyl Chloride

$CH_3—CH_2—Cl$

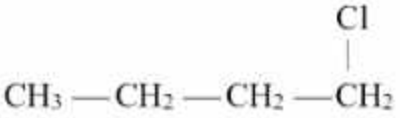
Ethyl Chloride



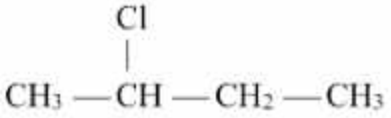
n-Propyl Chloride



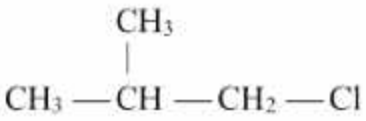
Iso-Propyl Chloride



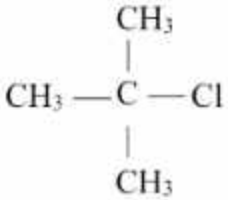
n-Butyl Chloride



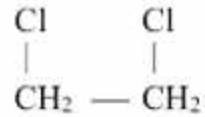
Sec-Butyl Chloride



Iso-Butyl Chloride



Ter-Butyl Chloride



Ethylene Chloride

CH_2Cl_2

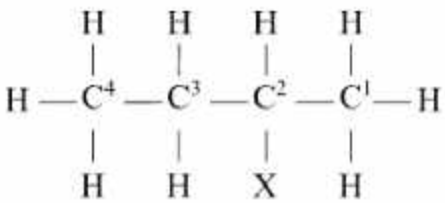
Methylene Chloride

(b) IUPAC Nomenclature:

The systematic names given to alkyl halides follow the underlying rules.

(1) Select the longest continuous carbon chain and consider the compound to have been derived from this structure.

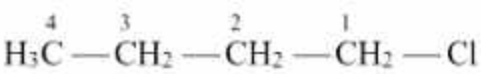
(2) Number the carbon atoms in the chain so that the carbon atom bearing the functional group (F, Cl, Br, I) gets the lowest possible number, e.g.,



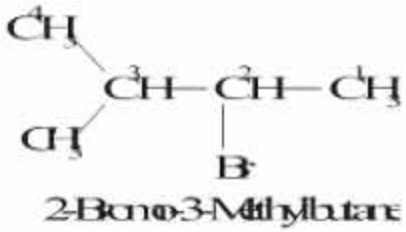
(3) If the same alkyl substituent occurs more than once on the chain, the prefix di, tri and so on are used before the name of the alkyl group.

(4) The positions of the substituents are indicated by the appropriate numbers separated by commas. If the same substituent occurs twice or more on the same carbon atom, the numbers is repeated.

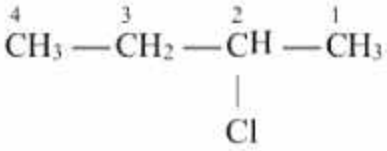
Examples which follow the above mentioned rules:



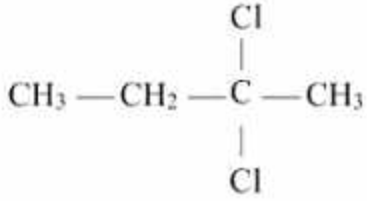
1-Chlorobutane



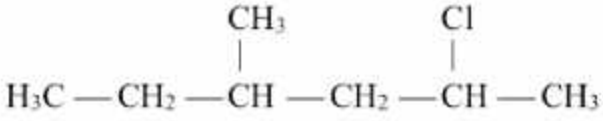
2-Bromo-3-Methylbutane



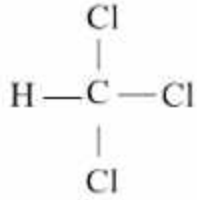
2-Chlorobutane



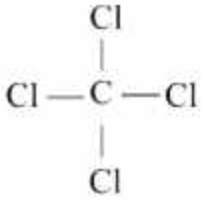
2,2-Dichlorobutane



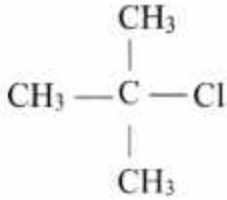
2-Chloro-4-Methylhexane



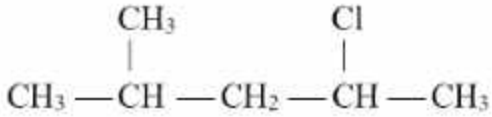
Trichloromethane



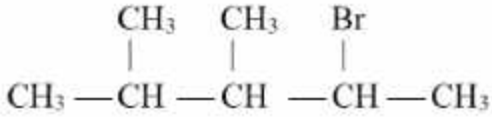
Tetrachloromethane



2-Chloro-2-Methylpropane



2-Chloro-4-Methylpentane



2-Bromo-3, 4-Dimethylpentane

PREPARATION OF ALKYL HALIDES

(1) From Alkanes:

When alkene is treated with halogen acids, an alkyl halide is produced.



Ethylene

The order of addition of halogen acids is.

$$HI > HBr > HCl$$

(2) From Alcohol:

Different methods are used for the preparation of alkyl halides from alcohol.

(a) Reaction of Alcohols with Halogen Acids:

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 catlyst.

$$CH_3CH_2 — OH + HX \xrightarrow{ZnCl_2} CH_3CH_2 — X + H_2O$$

Ethyl Halide

(b) Reaction of Alcohol with Thionyl Chloride:

Alcohols also react with thionyl chloride in pyridine as a solvent to give alkyl chlorides. This method is especially useful since the by-produces (HCl, SO_2) are gases, which escape leaving behind the pure product.

$$CH_3CH_2OH + SOCl_2 \xrightarrow{Pyridine} CH_3CH_2 — Cl + SO_2 + HCl$$

(c) Reaction of Alcohol with PX_3 or PX_5:

Phosphorus trihalides or phosphorus pentahalides react with alcohols to replace —OH group by a halo group.

$$3CH_3 — CH_2 — OH + PBr_3 \longrightarrow 3CH_3 — CH_2 — Br + H_3PO_3$$

$$CH_3 — CH_2 — OH + PCl_5 \longrightarrow CH_3 — CH_2 — Cl + POCl_3 + HCl$$

Phosphorus Oxytrichloride

Preparation of Alkyl Iodide:

An excellent method for the preparation of simple alkyl iodide is the treatment of alkyl chloride or alkyl bromide with sodium iodide. This method is particularly useful because alkyl iodides cannot be prepared by the direct iodination of alkanes.

$$RCl + NaI \longrightarrow RI + NaCl$$

$$RBr + NaI \longrightarrow RI + NaBr$$

Reactivity of Alkyl Halides:

An alkyl halide 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.

$$CH_3^{\delta+} — Br^{\delta-}$$

There are two main factors which govern the reactivity of R — X bond.

These are:

(i) C — X bond energy (ii) C — X Bond polarity

Bond Energies:

The following table shows the bond energies of C — X bonds in alkylk halides.

Bond	Bond Energy (kJ/Mole)
C — F	467
C — Cl	346
C — Br	290
C — I	228
C — H	413

The strength of the bonds show that iodo compound (with the weakest bonds) would be the most reactive while fluoro compound will be the least reactive i.e., the order of reactivity of alkyl halides should be.

$$R — I > R — Br > R — Cl > R — F$$

Bond Polarity:

Table – Electronegativity (E.N) of some elements are give below

Element	E.N	Element	E.N
F	4.0	I	2.5
Cl	3.0	H	2.1
Br	2.8	C	2.5

The greatest electronegativity difference exists between carbon fluorine atoms in alkyl fluorides. If an electrophile is the attacking reagent then this difference suggests that alkyl fluorides would be the most reactive one. On the same lines, alkyl iodides should be the least reactive alkyl halides.

In the light of the above discussion, it is clear that the two factors mentioned above predict different types of behaviour about the reactivity of alkyl halides. Experiments have shown that the strength of carbon halogen bond is the main factor which decides the reactivity of alkyl halides.

So the overall order of reactivity of alkyl halides for a particular alkyl group is.

Iodide > Bromide > Chloride > Fluoride

In fact the C — F bond is so strong that alkyl fluorides do not react under ordinary conditions.

REACTIONS OF ALKYL HALIDES

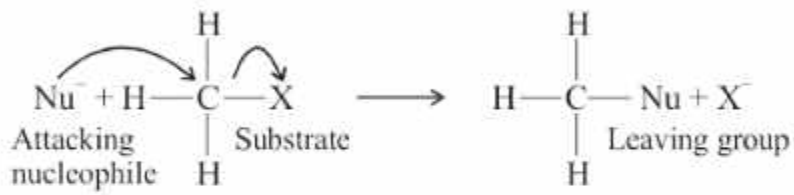
The reactions of alkyl halides fall into two categories.

(1) Those reactions in which the nucleophile of a substrate is replaced by another nucleophile (nucleophilic substitution, or S_N, reactions).

(2) Those reactions that involve the elimination of HX from the alkyl halide (elimination, or E, reactions).

Nucleophilic Substitution Reactions:

"The reactions in which nucleophile of a substrate is replaced by another nucleophile, are called nucleophilic substitution reactions".





Attacking Nucleophile:

Nucleophile means nucleus loving. It donates a pair of electron to species which are electron deficient. It may be neutral or negatively charged. A strong nucleophile can replace a weak nucleophile.

Some examples of nucleophiles are given below.

HO^-	Hydroxide ion	NH_2^-	Amino group
$C_2H_5O^-$	Ethoxide ion	Cl–	Chloride ion
HS^-	Hydrogen sulphide ion	Br^-	Bromide ion
SCN^-	Thiocyanate ion	$\ddot{N}H_3$	Ammonia
$H_2\ddot{O}:$	Water		

Substrate Molecule:

"Molecule at which a nucleophile attacks is called substrate." For example, alkyl halide is a substrate. The carbon of alkyl halide acts as electrophilic centre. Due to greater electronegativity of halogen, C —X bond is highly polar.

$$R^{\delta+} — X^{\delta-}$$

Leaving Group:

Leaving group is also a nucleophile. It is called leaving group because it departs with an unshared pair of electrons. If we wish S_N reaction to proceed in the forward direction, the incoming nucleophile must be stronger than the departing one. Cl^-, Br^-, I^-, HSO_4^- are good leaving groups. Poor leaving groups are OH^-, OR^- and NH_2^-. Iodide ion is a good nucleophile as well as a good leaving group.

MECHANISM OF NUCLEOPHILE SUBSTITUTION REACTIONS

Alkyl halides may undergo nucleophilic reaction in two different ways.

(1) Nucleophilic substitution bimolecular S_N2.

(2) Nucleophilic substitution unimolecular S_N1.

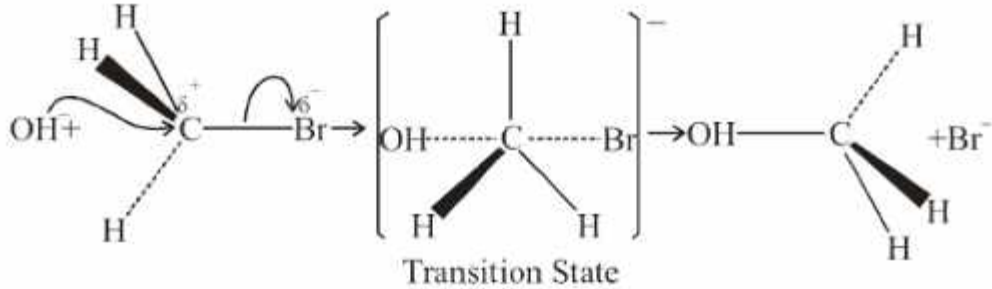
Nucleophilic substitution reaction on alkyl halides involve two main processes, the breakage of C — X bond and the formation of C — Nu bond. The mechanism of the nucleophilic substitution reaction depends upon the timing of these two processes. If the two processes occur simultaneously the mechanism is called S_N2. If the bond breaks first followed by the formation of a new bond, the mechanism is called S_N1.

(1) Nucleophilic Substitution Bimolecular S_N2:

This is a single step reaction. 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 breakage.

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.

In order to give to the nucleophile enough room to attack, the substrate carbon atom changes its state of hybridization from tetrahedral sp^3 to planar sp^2. The attack of the nucleophile, the change in the state of hybridization and the departure of the leaving group, every thing occurs at the same time.



Transition State

During the reaction, the configuration of the alkyl halide molecule gets inverted. This is called inversion of configuration.

Molecularity of a reaction is defined as the number of molecules taking part in the rate determining step. Since in this mechanism, the reaction takes place only in one step which is also a rate-determining step and two molecules are participating in this step, so it is called a bimolecular reaction.

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

$$\text{Rate} = k[\text{Alkyl halide}]^1\,[\text{Nucleophile}]^1$$

Since the exponents of the concentration terms in the above expression are unity, so the order of a typical S_N2 reaction will be $1 + 1 = 2$.

Among the alkyl halides, the primary alkyl halides always follow S_N2 mechanism whenever they are attacked by nucleophiles.

Examples of S_N2 Reactions:

$$CH_3-\overset{\delta+}{C}H_2-Br^{\delta-} + OH^- \longrightarrow C_2H_5OH + Br^-$$
Ethyl Alcohol

$$CH_3-\overset{\delta+}{C}H_2-Br^{\delta-} + I^- \longrightarrow C_2H_5I + Br^-$$
Ethyl Iodide

$$CH_3-\overset{\delta+}{C}H_2-Br^{\delta-} + CN^- \longrightarrow C_2H_5CN + Br^-$$
Ethyl Cyanide (Propane Nitrile)

$$CH_3-\overset{\delta+}{C}H_2-Br^{\delta-} + NO_2^- \longrightarrow C_2H_5NO_2 + Br^-$$
Nitroethane

$$CH_3-\overset{\delta+}{C}H_2-Br^{\delta-} + CH_3O^- \longrightarrow CH_3-CH_2-O-CH_3 + Br^-$$
Ethyl Methyl Ether

$$CH_3-\overset{\delta+}{C}H_2-Br^{\delta-} + NH_3 \longrightarrow C_2H_5-NH_2 + HBr$$
Ethylamine

$$CH_3-\overset{\delta+}{C}H_2-Br^{\delta-} + CH_3\text{–}CH_2NH_2 \longrightarrow (CH_3-CH_2)_2NH + HBr$$
Diethylamine

$$CH_3-\overset{\delta+}{C}H_2-Br^{\delta-} + (CH_3-CH_2)_2NH \longrightarrow (CH_3\text{–}CH_2)_3N + HBr$$
Triethylamine

Why primary alkyl halides give S_N2 reactions?

(1) Sterric Hinderance: In primary alkyl halides, small groups are attacked to α-carbon atom. The attack of the nucleophile is possible from the backside.

(2) Stability of Carbonium Ion: Primary carbonium ion is unstable due to less hyperconjugation structures.

$$CH_3-\overset{\delta+}{C}H_2-Br^{\delta-} + (CH_3-CH_2)_3N \longrightarrow (CH_3-CH_2)_4\,N^+ + Br^-$$

Quaternary ethyl ammonium bromide

$$CH_3-\overset{\delta+}{C}H_2-Br^{\delta-} + SH^- \longrightarrow C_2H_5SH + Br^-$$

Ethyl Thioalcohol

$$CH_3-\overset{\delta+}{C}H_2-Br^{\delta-} + CH_3COO^-Na^+ \longrightarrow CH_3COOC_2H_5 + NaBr$$

Ethyl Acetate

(2) Nucleophilic Substitution Unimolecular S_N1:

Tertiary alkyl halides when attached by a nucleophile, undergo S_N1 mechanism. Ter-alkyl halide is highly branched substrate. When a nucleophile attack on it, it has difficulty to approach to the central carbon, due to stearic hindrence. The polar solvent present in medium, promote the ionization of substrate, so the mechanism involves two steps.

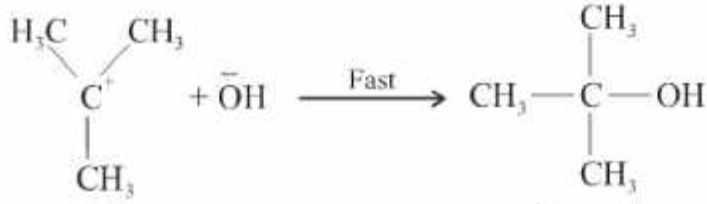
The first step is the reversible ionization of the alkyl halide in the presence of an aqueous acetone or an aqueous ethyl alcohol. This step provides a carbocation as an intermediate. In the second step this carbocation is attacked by the nucleophile to give the product.

First Step:



Carbocation

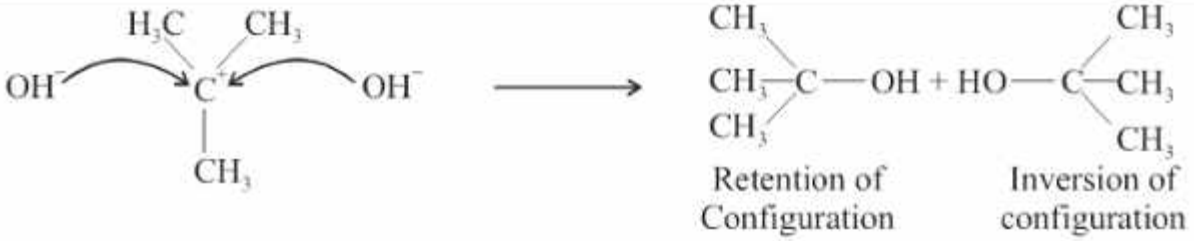
Second Step:



Product

Since the first step involves the breakage 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.

In S_N1 mechanism, the nucleophile attacks when the leaving group had already gone, so the question of the direction of the attack does not arise. Moreover, the intermediate carbocation is a planar specie allowing the nucleophile to attack on it from both the directions with equal ease. We, therefore, observe 50% inversion of configuration and 50% retention of configuration.



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.

$$\text{Rate} = k[\text{Alkyl Halide}]$$

Secondary alkyl halides may undergo S_N2 or S_N1 mechanism depends upon the nature of solvent used and nature of alkyl group present in it. Polar solvents promote the ionization and S_N1 reaction occurs. If alkyl group are bulky S_N1 reaction takes place in two steps and if alkyl groups are smaller in size, S_N2 reaction occur in single step.

Why tertiary alkyl halides give S_N1 reaction?

(1) **Sterric Hinderance:** In tertiary alkyl halides α-carbon atom is attached to three bulky alkyl groups besides a H-atom. The attack of the nucleophile is difficult from the backside. Hence, both the molecules cannot take part in the same step. The reaction takes place in two steps. In the first step carbonium ion is formed.

(2) **Stability of Carbonium Ion:** Tertiary carbonium ion is very stable due to number of hyperconjugation structure.

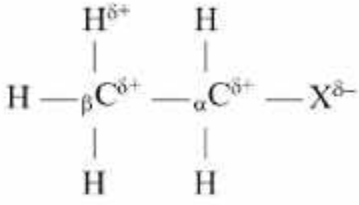
DIFFERENCE BETWEEN S_N2 AND S_N1 MECHANISM

SN_1 – Reactions	SN_2 – Reactions
(1) S_N1 – stands for substitution nucleophilic unimolecular reactions.	(1) S_N2 – stands for substitution nucleophilic bimolecular reactions.
(2) S_N1 reactions is completed in two steps.	(2) S_N2 – reactions is completed in one step.
(3) Alkyl halide first ionizes to form carbonium ion. $R_3C—X \longrightarrow R_3C^+ + X^-$ It is a slow step and rate-determining step. Second step involves the attacking of nucleophile to form product. $R_3C^+ + Nu^- \longrightarrow R_3C—Nu$	(3) Formation of new bond and breakage of old bonds takes place simultaneously. $Nu^- + R—CH_2—X \longrightarrow R—CH_2—Nu + X^-$
(4) SN_1 reactions are generally given by tertiary alkyl halides.	(4) S_N2 reactions are generally given by primary alkyl halides.
(5) The attacking nucleophile have equal chance to attack on both sides of the planar carbocation. 50% inversion and 50% retention of configuration.	(5) The attacking nucleophile attacks from backside i.e., which is opposite to the side to which the leaving group (X^-) is bonded. 100% inversion of configuration.
(6) It is favoured in polar solvent.	(6) It is favoured in non-polar solvent.

β-ELIMINATION REACTION IN ALKYL HALIDES

In alkyl halides, bond between α-carbon and halogen is polar. (Carbon at which halogen is attached is called α-carbon). This effect goes to β-carbon and hydrogen present at β-carbon also becomes acidic.

"If we react a base with alkyl halides, hydrogen is eliminated from β-carbon and halogen is eliminated from α-carbon and such reactions are called elimination reactions or β-elimination or 1-2 elimination reactions."



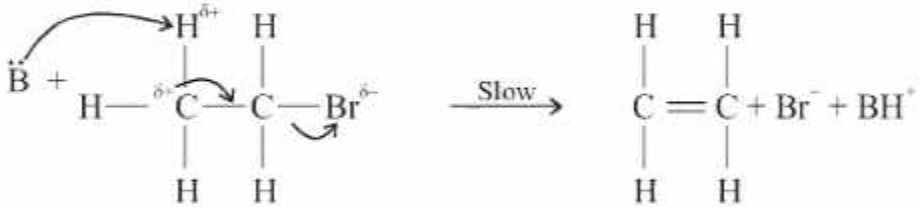
$$B + H—CH_2—CH_2—X \longrightarrow CH_2 = CH_2 + BH^+ + X^-$$

With the elimination at 1, 2 position double bond is formed.

There are two mechanisms for elimination reactions.

E_2-Mechanism:

In E_2 mechanism, base attaches on the β-hydrogen and halogen is removed in a single step. Hydrogen atom, which is attached to β-carbon atom is called β-hydrogen. e.g.,



E_2-mechanism is analogous to S_N2 mechanism. Rate of reaction depends upon the concentration of base as well as concentration of substrate.

Rate α [Base] [Substrate]

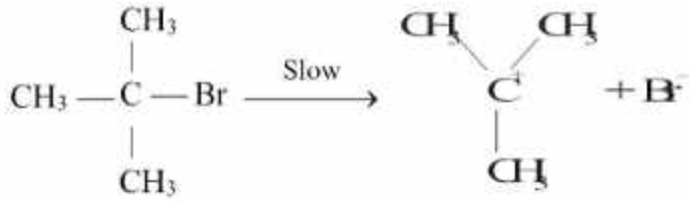
According to above reaction.

Rate α [B] [$CH_3—CH_2—Br$]

Rate of reaction depends upon concentrations of two molecules so it is called E_2-reaction, primary alkyl halides usually undergo E_2-mechanism. Like S_N2 reactions, the molecularity of E_2 reaction is two and they are second order reactions.

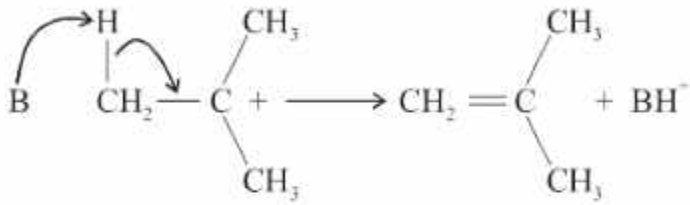
E_1-Mechanism:

E_1 mechanism takes place in two step. In first step carbocation is formed under the influence of base. It is slow step and rate determining step. Tertiary carbon is sp^3 – hybridized which changes to sp^2 – bybridization after the removal of halogen atom. Carbocation has planer geometry with the angle of 120°.



Carbocation

Second step is fast. In this step, base acts on β-hydrogen and double bond between two carbon atoms is formed.



The rate of reaction depends upon slow step or upon the concentration of substrate only.

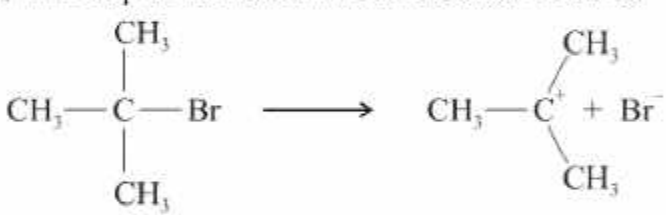
$$\text{Rate} \propto [\text{Substrate}]$$

or $$\text{Rate} \propto [(CH_3)_3C—Br]$$

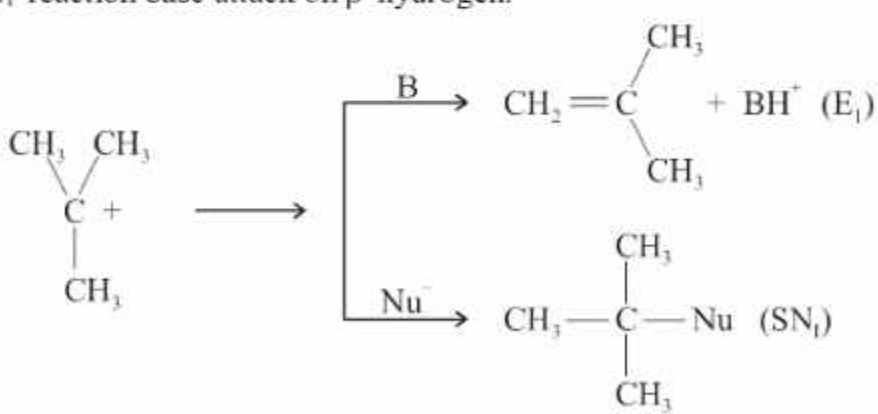
The rate of reaction depend upon the concentration of one molecule so it is unimolecular reaction E_1-reaction.

DIFFERENCE IN MECHANISM OF SN_1 AND E_1

In S_N1 and E_1 first step or formation of carbocation is same.



In second step, in SN mechanism, another nucleophile attack on carbonation whereas in E_1-reaction base attack on β-hydrogen.



So elimination can be a troublesome side reaction during substitution of tertiarty alkyl halides.

Primary alkyl halides follow E_2-mechanism whereas tertiary alkyl halides follow E_1-mechanism.

SOME MORE REACTIONS OF ALKYL HALIDES

(1) Wurtz Reaction:

Alkyl halides react with sodium in ether solvent to give alkanes. The reaction is particularly useful for the preparation of symmetrical alkanes.

$$CH_3Cl + 2Na + ClCH_3 \longrightarrow \underset{\text{Ethane}}{CH_3 — CH_3} + 2NaCl$$

$$CH_3 — CH_2 — Cl + 2Na + Cl — CH_2 — CH_3 \xrightarrow{\text{Ether}} \underset{\text{n-Butane}}{CH_3 — CH_2 — CH_2 — CH_3} + 2NaCl$$

(2) Reduction of Alkyl Halides:

Alkyl halides can be reduced by nascent hydrogen which may be generated either by Zn/HCl or Zn – Cu couple and alochol.

$$Zn + 2HCl \longrightarrow ZnCl_2 + 2[H]$$

$$CH_3 — CH_2 — Cl + 2[H] \xrightarrow{Zn + HCl} CH_3CH_3 + HCl$$

$$CH_3 — CH_2 — CH_2 — Cl + 2[H] \xrightarrow{Zn + HCl} \underset{\text{Propane}}{CH_3 — CH_2 — CH_3} + HCl$$

(3) Reaction with Sodium Lead Alloy (Na_4Pb):

Methyl chloride and ethyl chloride react with sodium lead alloy giving tetramethyl lead and tetraethyl lead respectively. These compounds are important anti-knock agents and are used in gasoline.

$$4CH_3Cl + Na_4Pb \longrightarrow \underset{\text{Tetramethyl Lead}}{(CH_3)_4 Pb} + 4NaCl$$

$$4CH_3CH_2 — Cl + Na_4Pb \longrightarrow \underset{\text{Tetraethyl Lead}}{(CH_3 — CH_2)_4Pb} + 4NaCl$$

"Alkyl halides reacts with metal in dry ether to form an organometallic compound called Grignard's Reagent." This reagent was first of all prepared by Victor Grignard in 1900. The general formula of Grignard's reagent is RMgX or alkyl or aryl magnesium halide.

Grignard Reagent is important in synthesis of organic compounds. Due to its importance in synthesis Victor Grignard was awarded a Nobel Prize of chemistry in 1912.

Preparation of Grignard Reagents:

Grignard reagents are prepared by the reaction of magnesium metal with alkyl halides in the presence of dry ether (alcohol free, moisture free).

$$RX + Mg \xrightarrow{\text{Ether}} RMgX$$

$$C_2H_5Br + Mg \xrightarrow{\text{Ether}} C_2H_5MgBr$$

It is important that all the reactants must be absolutely dry and pure because Grignard Reagents are so reactive that they may react with moisture or any impurity present.

Structure and Reactivity:

The electronegativity of carbon is 2.5 while that of Mg is 1.2. Due to greater difference of electronegativity bond between carbon and metal is highly polar in nature.



Alkyl carbon has partial negative charge and acts as base as well as nucleophilic site. The negative charge present on alkyl group makes it highly reactive toward electrophilic centre.

Alkyl iodide > Alkyl bromide > Alkyl chloride

For a particular halogen, order of reactivity with respect to alkyl group is as follows:

$CH_3X > C_2H_5X > C_3H_7X$

REACTIONS OF GRIGNARD'S REAGENT

(1) Reaction with Active Hydrogen Compounds (Formation of Hydrocarbons):

Compounds like water, ammonia or alcohol in which hydrogen is attached with highly electronegative element, easily dissociate as proton are known as active hydrogen compounds.

(i) With Water:

$$CH_3-\overset{\delta-}{C}H_2-Mg^{\delta+}-Br^{\delta-} + H^{\delta+}-OH^{\delta-} \xrightarrow{\text{Ether}} CH_3-CH_3 + Mg(Br)(OH)$$

Ethyl magnesium bromide — Water — Ethane

(ii) With Ammonia:

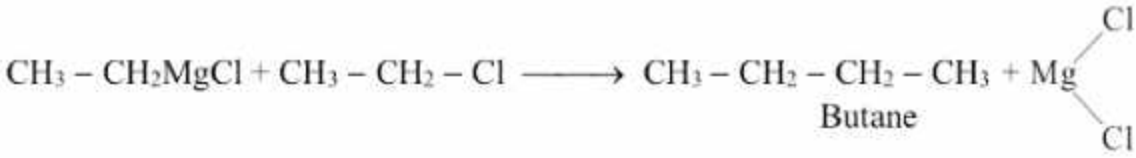
$$CH_3-\overset{\delta-}{C}H_2-Mg^{\delta+}-Br^{\delta-} + H^{\delta+}-NH_2^{\delta-} \xrightarrow{\text{Ether}} CH_3-CH_3 + Mg(Br)(NH_2)$$

Ethyl magnesium bromide — Ammonia — Ethane

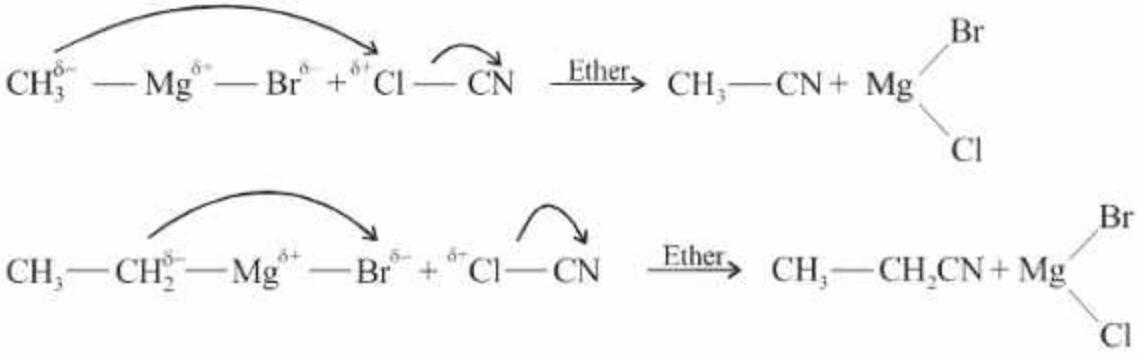
(iii) With Alcohols:



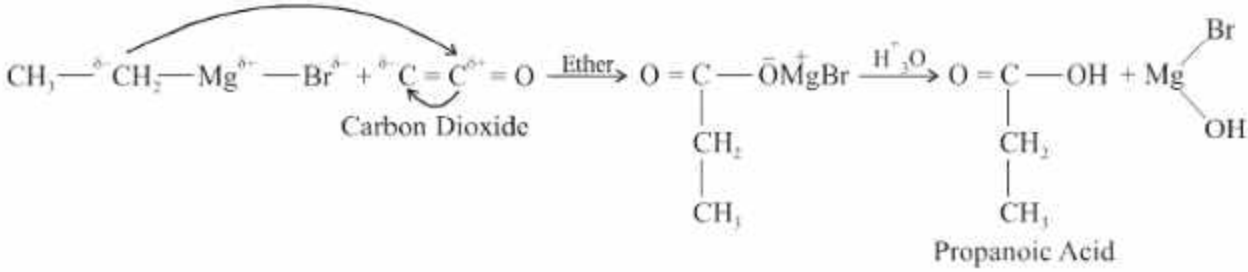
(iv) With Alkyl Halides:



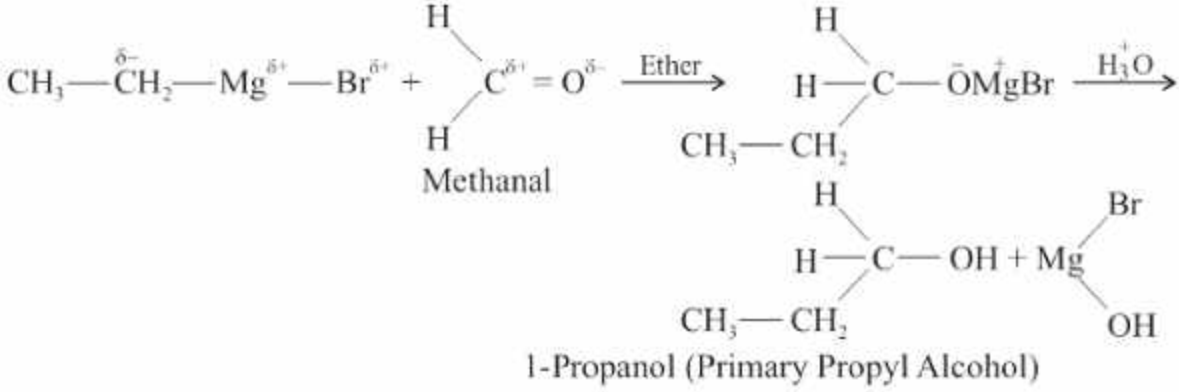
(2) Reaction with Cyanogen Chloride (Formation of Cyanides):



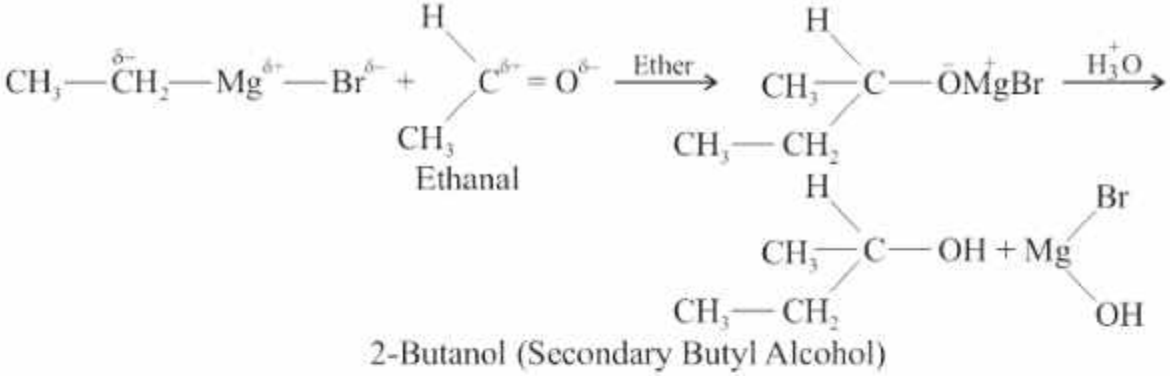
(3) Addition of CO_2 (Formation of Carboxylic Acid):



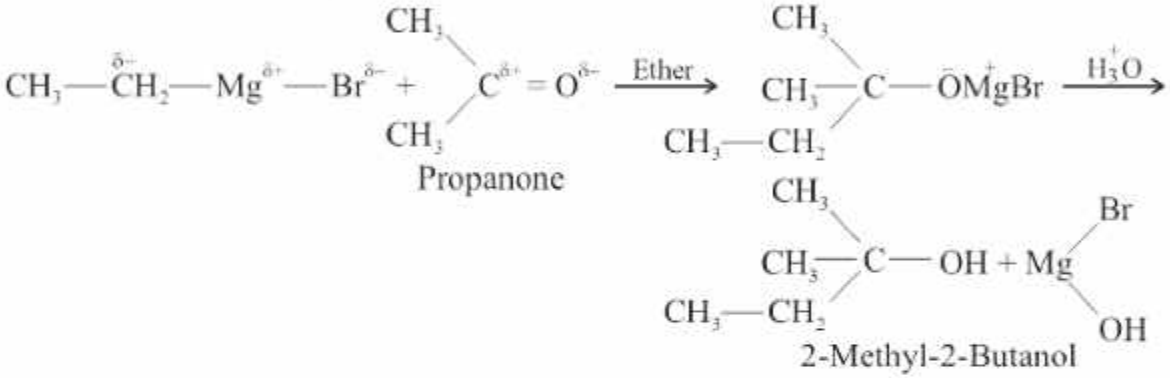
(4) Reaction with Formaldehyde:



(5) Reaction with Acetaldehyde:

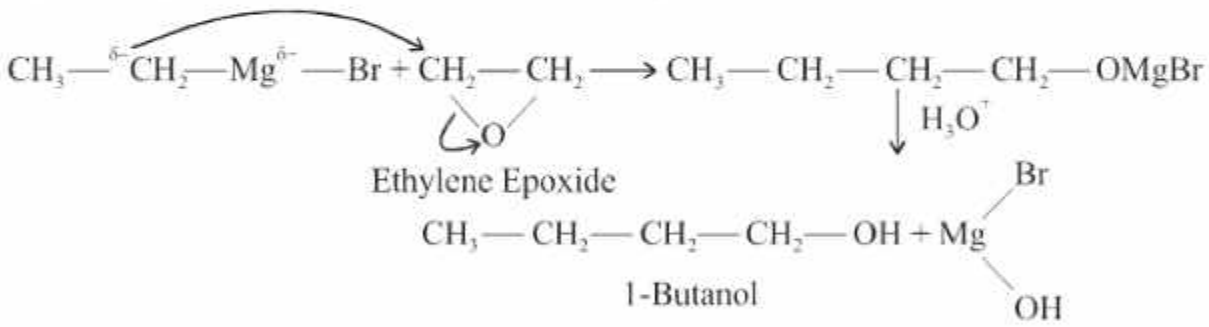


(6) Reaction with Propane (Acetone):

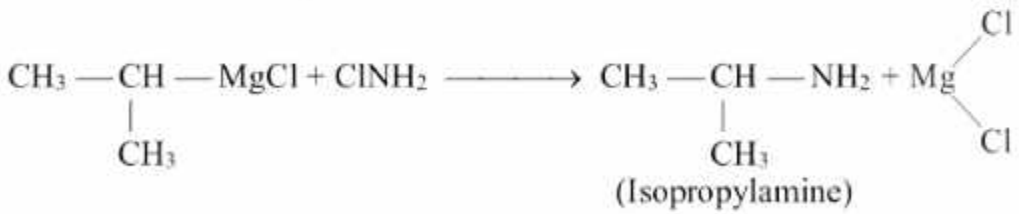


(7) Reaction with Expoxides (Formation of Primary Alcohol):

Ethylene oxide undergoes cleavage at carbon oxygen bond when treated with Grignard reagent to form primary alcohol with higher number of carbon atoms.



(8) Reaction with $ClNH_2$:



EXERCISE

Q.1 Fill in the blanks:

(i) In tertiary alkyl halides the halogen atom is attached to a carbon which is further attached to ———— carbon atoms directly.

(ii) The best method for the preparation of alkyl halides is the reaction of ———— with inorganic reagents.

(iii) An alkyl group with a partial positive charge on the carbon atom is called ———— centre.

(iv) The mechanism is called ———— if it involves one molecule in the rate-determining step.

(v) Molecularity of a reaction is defined as the number of molecules taking part in the ————.

(vi) The molecularity of E-2 reactions is always two and the reactions show ———— order kinetics.

(vii) Wurtz synthesis is useful for the preparation of ———— alkanes.

(viii) Grignard reagents are prepared by the reaction of magnesium metal with alkyl halides in the presence of ————.

ANSWERS

(i)	three	**(ii)**	alcohol	**(iii)**	electrophile
(iv)	E1 and S_N1	**(v)**	R.D.S	**(vi)**	second
(vii)	higher	**(viii)**	anhydrous ether		

Q.2 Indicate True or False:

(i) In secondary alkyl halides, the halogen atom is attached to a carbon which is further attached to two carbon atoms directly.

(ii) Alcohols react with thionyl chloride in ether as solvent to give alkyl halides.

(iii) Order of reactivity of alkyl halides for a particular alkyl group is:

Iodide > Bromide > Chloride > Fluoride

(iv) In S_N2 reactions the attacking nucleophile always attacks from the side in which the leaving group is attached.

(v) Methylmagnesium iodide on hydrolysis yields ethyl alcohol.

(vi) Primary, secondary and tertiary amines react with Grignard reagents in the same way.

(vii) The reactions of secondary alkyl halides may follow both S_N1 and S_N2 mechanisms.

(viii) S_N1 mechanism is a one stage process involving a simultaneous bond breakage and bond formation.

(ix) In β-elimination reactions, the two atoms or groups attached to two adjacent carbon atoms are lost under the influence of an electrophile.

(x) The reactivity order of alkyl halides is determined by the strength of carbon-halogen bond.

ANSWERS

(i)	True	**(ii)**	False	**(iii)**	True	**(iv)**	False	**(v)**	False
(vi)	False	**(vii)**	True	**(viii)**	False	**(ix)**	False	**(x)**	True

Q.3 Multiple choice questions. Encircle the correct answer:

(i) In primary alkyl halides, the halogen atom is attached to a carbon which is further attached to how many carbon atoms:

(a) Two **(b)** Three

(c) One **(d)** Four

(ii) The reactivity order of alkyl halides for a particular alkyl group is:

(a) Fluoride > Chloride > Bromide > Iodide

(b) Chloride > Bromide > Fluoride > Iodide

(c) Iodide > Bromide > Chloride > Fluoride

(d) Bromide > Iodide > Chloride > Fluoride

(iii) When CO_2 is made to react with ethyl magnesium iodide, followed by acid hydrolysis, the product formed is:

(a) Propane **(b)** Propanic acid

(c) Propanal **(d)** Propanol

(iv) Grignard reagent is reactive due to:

(a) The presence of halogen atom **(b)** The presence of Mg atom

(c) The polarity of C – Mg bond **(d)** None of the above

(v) S_N2 reactions can be best carried out with:

(a) Primary alkyl halides **(b)** Secondary alkhyl halides

(c) Tertiary alkhyl halides **(d)** All the three

(vi) Elimination bimolecular reactions involve:

(a) First order kinetics **(b)** Second order kinetics

(c) Third order kinetics **(d)** Zero order kinetics

(vii) 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

(viii) Alkyl halides are considered to be very reactive compounds towards nucleophiles, becuase:

(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 nulceophilic carbon and a good leaving group

(ix) The rate of E1 reaction depends upon:

(a) The concentration of substrate

(b) The concentration of nucleophile

(c) The concentration of substrate as well as nulceophile

(d) None of the above

(x) Which one of the following is not a nucleophile:

(a) H_2O **(b)** H_2S

(c) BF_3 **(d)** NH_3

ANSWERS

(i)	(c)	**(ii)**	(c)	**(iii)**	(b)	**(iv)**	(c)	**(v)**	(a)
(vi)	(b)	**(vii)**	(d)	**(viii)**	(b)	**(ix)**	(a)	**(x)**	(c)

Q.4 Define alkyl halide. Which is the best method of preparing alkyl halide?

Ans. **Alkyl Halide:** Halogen derivatives of alkanes are called haloalkanes. They may be mono, di, tri or poly haloalkanes depending upon the no of halogen atoms present in the molecule. Among these, monohaloalkanes are also called **alkyl halides**.

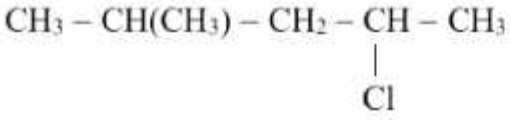
Method of preparation see in text book.

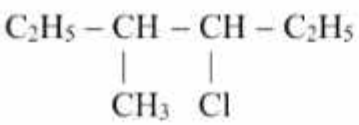
Q.5 Write down a method for the preparation of ethyl magnesium bromide in the laboratory?

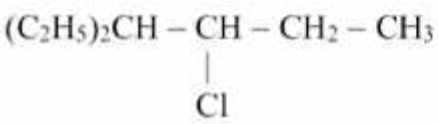
Ans. See in text book.

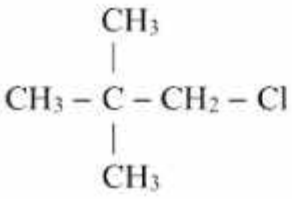
Q.6 Give IUPAC names to the following compounds.

Ans.

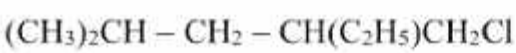

2-Chloro, 4-methyl pentane

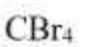

3-Chloro, 4-methyl hexane

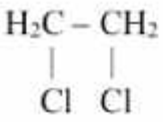

3-Chloro, 4-ethyl hexane

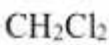

1-Chloro, 2, 2-dimethyl propane

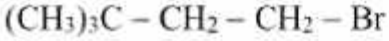

2-Bromo propane

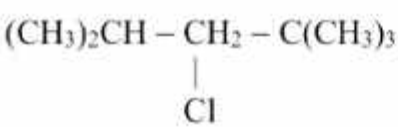

1-Chloro, 2-ethyl, 4-methyl pentane

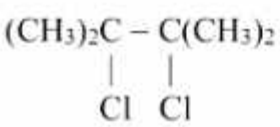

Tetra Bromo methane


1, 2-dichloroethane


Dichloromethane (Methylene di-chloride)


1-Bromo, 3, 3-dimethyl butane


3-Chloro, 2, 2, 4-trimethyl pentane

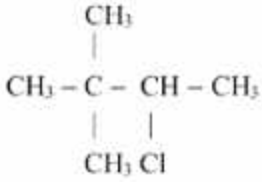

2, 3-Dichloro, 2, 3-dimethyl butane


3-Bromo, 3-ethyl pentane

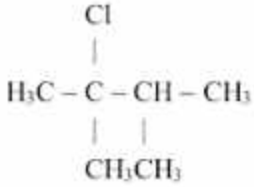
Q.7 Draw all the possible structures that have the molecular formula $C_6H_{13}Cl$. Classify each as primary, secondary or tertiary chloride. Give their names according to IUPAC system.

Ans.

Structure	IUPAC Name	Type of Chloride
$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-Cl$	1-Chlorohexane	Primary chloride
$H_3C-CH_2-CH_2-CH_2-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_3$	2-Chlorohexane	Secondary chloride
$H_3C-CH_2-CH_2-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_2-CH_3$	3-Chlorohexane	Secondary chloride
$H_3C-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-Cl$	1-Chloro, 2-Methylpentane	Primary chloride
$H_3C-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-Cl$	1-Chloro, 3-Methylpentane	Primary chloride
$H_3C-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-CH_2-Cl$	1-Chloro, 4-Methylpentane	Primary chloride
$H_3C-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_3$	2-Chloro, 4-Methylpentane	Secondary chloride
$H_3C-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_2-CH_3$	3-Chloro, 2-Methylpentane	Secondary chloride
$H_3C-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-CH_3$	2-Chloro, 3-Methylpentane	Secondary chloride
$H_3C-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-Cl$	1-Chloro, 2, 3-Dimethylbutane	Primary chloride
$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}-CH_2-CH_2-Cl$	1-Chloro-3, 3 dimethyl butane	Primary



2-Chloro-3, 3 dimethyl butane — Secondary



2-Chloro, 2, 3-dimethylibutane — Tertiary chloride

Q.8 Using ethyl bromide as a starting material how would you prepare the following compounds. Give also the inorganic reagents and conditions necessary to carry out these reactions:

(a) n-butane **(b) Ethyl alcohol**

(c) Ethyl cyanide **(d) Ethane**

(e) Ethene **(f) Propanoic acid**

(g) Propane

Ans.

(a) n-butane:

$$2CH_3 - CH_2 - Br + 2Na \xrightarrow{\text{Ether}} H_3C - CH_2 - CH_2 - CH_3 + 2NaBr$$

(b) Ethyl alcohol:

$$H_3C - CH_2 - Br + KOH_{(aq)} \longrightarrow H_3C - CH_2 - OH + KBr$$

(c) Ethyl cyanide:

$$CH_3 - CH_2 - Br + KCN \longrightarrow H_3C - CH_2 - CN + KBr$$

(d) Ethane:

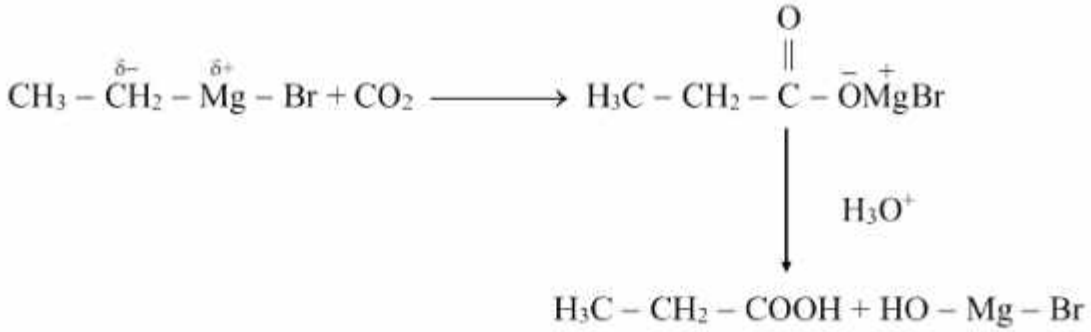
$$CH_3 - CH_2 - Br + 2[H] \xrightarrow{Zn+HCl} CH_3 - CH_3 + HBr$$

(e) Ethene:

$$H_3C - CH_2 - Br + KOH \xrightarrow[(alc)]{100^\circ C} H_2C = CH_2 + H_2O + KBr$$

(f) Propanoic acid:

$$H_3C - CH_2 - Br + Mg \xrightarrow{\text{Dryether}} CH_3 - \overset{\delta-}{CH_2} - \overset{\delta+}{Mg} - Br$$



(g) $CH_3 - CH_2Br + CH_3Br + 2Na \xrightarrow[\text{Ether}]{} CH_3 - CH_2 - CH_3 + 2NaBr$

Q.9 Write a detailed note on the mechanism of nucleophilic substitution reactions.

Ans. Detailed question. See text book.

Q.10 What do you understand by the term β-elimination reaction? Explain briefly the two possible mechanisms of β-elimination reaction.

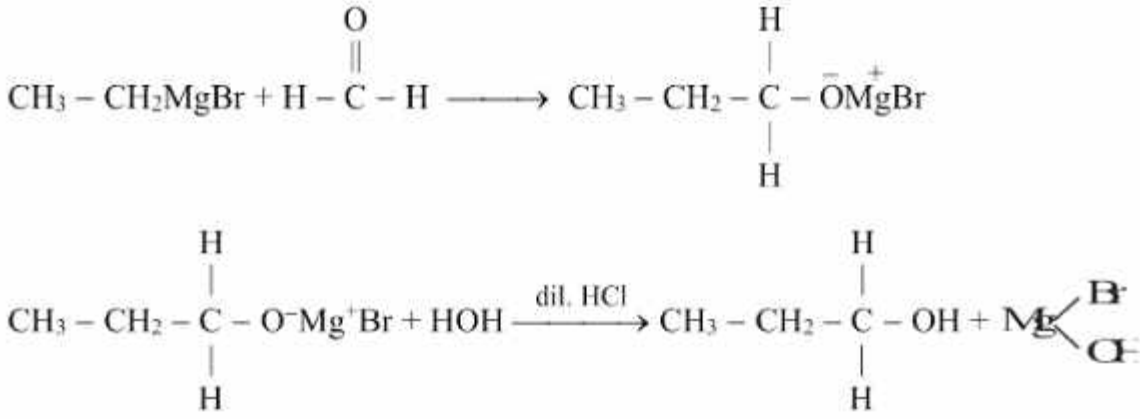
Ans. **β-elimination Reaction:** It can be define as:

During nucleophilic substitution reactions, when attacking nucleophile attacks the electrophilic hydrogen atom attached to the β-carbon of the alkyl halide and we get an alkene instead of substitution product then such type of reaction is called as β-elimination reaction.

Q.11 What products are formed when the following compounds are treated with ethyl-Mg-bromide, followed by hydrolysis in the presence of an acid?

Ans.

(a) HCHO:



(b) **$CH_3-\overset{\overset{O}{\|}}{C}-H$:**

$$CH_3-CH_2MgBr + CH_3-\overset{\overset{O}{\|}}{C}-H \longrightarrow CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-\overset{-}{O}\overset{+}{M}gBr$$

$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-\overset{-}{O}\overset{+}{M}gBr + \overset{+}{H}\overset{-}{O}H \xrightarrow[HCl]{dil.} CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-OH + \overset{Cl^-}{\underset{Br^-}{Mg^{++}}}$$

(c) **CO_2:**

$$CH_3-CH_2MgBr + O=C=O \longrightarrow CH_3-CH_2-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{M}gBr$$

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{M}gBr + H_2O \xrightarrow{dil.\ HCl} CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH + \overset{Br^-}{\underset{Cl^-}{Mg^{++}}}$$

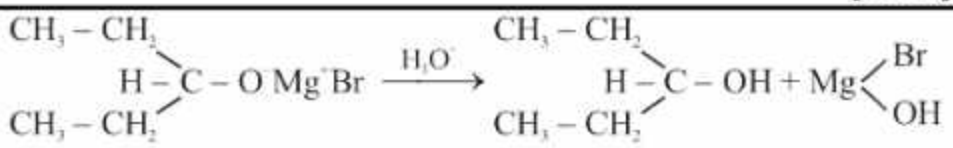
(d) **$(CH_3)_2CO$:**

$$CH_3-CH_2MgBr + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{-}{O}\overset{+}{M}gBr$$

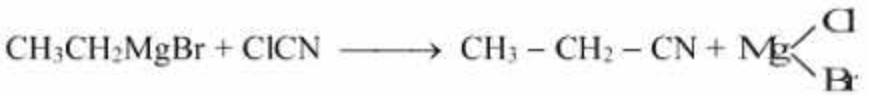
$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O^-Mg^+Br + H_2O \xrightarrow{dil.\ HCl} CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH + \overset{Br^-}{\underset{Cl^-}{Mg^{++}}}$$

(e) **$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$:**

$$CH_3-CH_2-MgBr + \underset{CH_3-CH_2}{\overset{H}{\diagdown}\!\!\diagup}C=O \xrightarrow{Ether} \underset{CH_3-CH_2}{\overset{CH_3-CH_2}{\diagdown}\!\!\diagup}H-C-\overset{-}{O}\overset{+}{M}gBr$$



(f) ClCN:



Q.12 How will you carry out the following conversions?

(i) $CH_4 \longrightarrow CH_3CH_2COOH$

(ii) $CH_3 - CH_3 \longrightarrow (CH_3 - CH_2)_4N^+Br^-$

(iii) $CH_2 = CH_2 \longrightarrow CH_3 - CH_2 - CH_2 - CH_2 - OH$

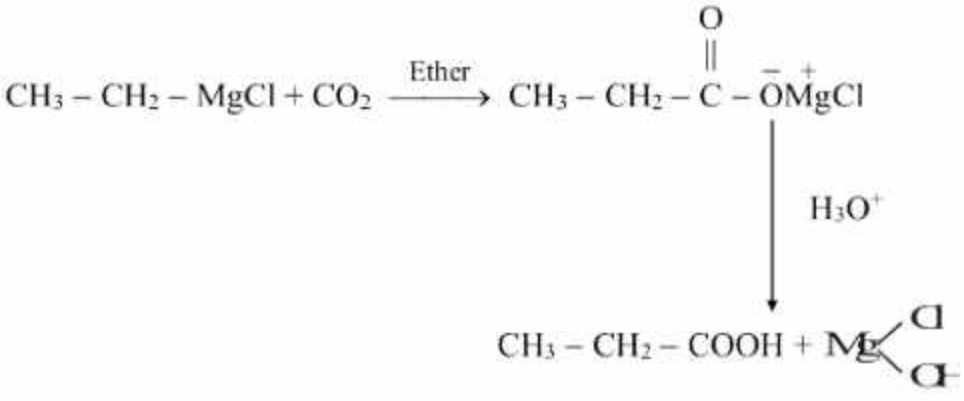
(iv) $CH_3CH_2CH_2Cl \longrightarrow CH_3 - CH = CH_2$

(v) $CH_3COOH \longrightarrow CH_3CH_2COOH$

Ans.

(i) $CH_4 \longrightarrow CH_3CH_2COOH$

Step Involved:

1. $CH_4 + Cl_2 \xrightarrow{hv} CH_3 - Cl + HCl$
2. $2CH_3 - Cl + 2Na \longrightarrow CH_3 - CH_3 + 2NaCl$
3. $CH_3 - CH_3 + Cl_2 \xrightarrow{hv} CH_3 - CH_2 - Cl + HCl$
4. $CH_3 - CH_2 - Cl + Mg \xrightarrow{\text{Dry ether}} CH_3 - CH_2 - MgCl$
5. 

(ii) $\mathbf{CH_3 - CH_3 \longrightarrow (CH_3 - CH_2)_4N^+Br^-}$

By Hoffman's reaction:

Steps Involved:

1. $CH_3 - CH_3 + Br_2 \xrightarrow{hv} CH_3 - CH_2 - Br + HBr$
2. $CH_3 - CH_2 - Br + NH_3 \longrightarrow CH_3 - CH_2 - NH_2 + HBr$
3. $CH_3 - CH_2 - NH_2 + CH_3 - CH_2 - Br \longrightarrow (CH_3 - CH_2)_2NH + HBr$
4. $(CH_3 - CH_2)_2NH + CH_3 - CH_2 - Br \longrightarrow (CH_3 - CH_2)_3N + HBr$
5. $(CH_3 - CH_2)_3N + CH_3 - CH_2 - Br \longrightarrow [(CH_3 - CH_2)_4N^+]Br^-$

(iii) $\mathbf{CH_2 = CH_2 \longrightarrow CH_3 - CH_2 - CH_2 - CH_2 - OH}$

Steps Involved:

1. $CH_2 = CH_2 + HCl \longrightarrow CH_3 - CH_2 - Cl$
2. $2CH_3 - CH_2 - Cl + 2Na \longrightarrow CH_3 - CH_2 - CH_2 - CH_3 + 2NaCl$
3. $CH_3 - CH_2 - CH_2 - CH_3 + Cl_2 \longrightarrow CH_3 - CH_2 - CH_2 - CH_2 - Cl + HCl$
4. $CH_3-CH_2-CH_2-CH_2-Cl+KOH_{(aq)} \longrightarrow CH_3-CH_2-CH_2-CH_2-OH+KCl$

(iv) $\mathbf{CH_3CH_2CH_2Cl \longrightarrow CH_3 - CH = CH_2}$

Steps Involved:

$$CH_3 - CH_2 - CH_2 - Cl + KOH \xrightarrow{100^\circ C,\ \text{alcohol}} CH_3 - CH = CH_2 + H_2O + KCl$$

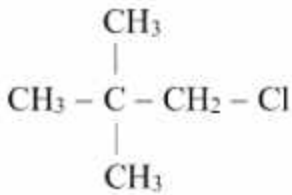
(v) $\mathbf{CH_3COOH \longrightarrow CH_3CH_2COOH}$

Steps Involved:

1. $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$
2. $2CH_3COONa + 2H_2O \xrightarrow{\text{Elctrolysis}} CH_3 - CH_3 + 2CO_2 + 2NaOH + H_2$
3. $CH_3 - CH_3 + Cl_2 \xrightarrow{hv} CH_3 - CH_2 - Cl + HCl$
4. $CH_3 - CH_2 - Cl + Mg \xrightarrow{\text{Ether}} CH_3 - CH_2 - Mg - Cl$
5. $CH_3 - CH_2 - Mg - Cl + CO_2 \xrightarrow{\text{Ether}} CH_3 - CH_2 - \underset{\underset{O}{\|}}{C}O\overset{+}{M}gCl \xrightarrow{H_3\overset{+}{O}} CH_3 - CH_2 - COOH + Mg\begin{matrix}Cl\\Cl\end{matrix}$

DO YOU KNOW?

(1) Formula of neo pentyl chloride is:



(2) CH_2I_2 is called methylene di iodide.

(3) Order of reactivity of alkyl halides is:

$$RI > R - Br > R - Cl > R - F$$

(4) Those species which are electron deficient and accept the electron pairs to form the covalent bond is called "electrophiles".

(5) The species which have the tendency to donate the electrons are called nucleophiles.

(6) S_N2 reaction is bi molecular where S_N1 is uni-molecular.

(7) Primary alkyl halides give S_N2 reaction.

(8) Tertiary alkyl halides give S_N1 reaction.

(9) Tertiary carbonium ions are more stable than the primary carbonium ions.

(10) Grignarid's reagents react with Formaldehyde and epoxides to form primary alcohols.

(11) Grignard's reagent (R – Mg – X) was discovered by victor Grignard in 1902 and he got the Nobel Prize in 1912.

(12) Ketones react with Grignard's reagent to form tertiary alcohols.

CHAPTER 10

ALKYL HALIDE

MULTIPLE CHOICE QUESTIONS

1. Which of the following alkyl halide is the most reactive towards the attacking nucleophile:

(a) CH_3F **(b)** CH_3Cl

(c) CH_3Br **(d)** CH_3I

2. Which of the following is not nucleophile:

(a) H_2O **(b)** H_2S

(c) BF_3 **(d)** NH_3

3. Carbocation is a/an:

(a) Electrophile **(b)** Nucleophile

(c) Free radical **(d)** Group of atoms

4. 1-bromobutane on reaction with alcoholic potassium hydroxide gives:

(a) 1-butanol **(b)** 1-butene

(c) 2-butene **(d)** 1-butyne

5. S_N2 reaction can be best carried out with:

(a) Primary alkyl halide **(b)** Secondary alkyl

(c) Tetiary alkyl halide **(d)** All of above

6. For which mechanism the first step involved is the same:

(a) E_1 and E_2 **(b)** E_2 and SN_2

(c) SN_1 and E_2 **(d)** E_1 and SN_1

7. In the transition state of S_N2 mechanism reaction with alkhyl halides, which of the following orbital hybridization is involved:

(a) sp^3 **(b)** sp^2

(c) sp **(d)** dsp^2

8. Which of the following factors does not affect the S_N1 rate is:

(a) Nucleophilicity of the attacking nucleophile

(b) Stability of the carbonium ion

(c) Solvent system

(d) The nature of leaving group

9. In β-elimination reaction, nucleophile attacks on:

(a) α-hydrogen **(b)** β-hydrogen

(c) Hydrogen **(d)** α-carbon

10. The substances which donates a pair of electron to electrophile are called:

(a) Electrophile **(b)** Nucleophile

(c) Lewis acid **(d)** Dibasic acid

11. Which one the following will be present at the position of letter B

$$C_2H_5Br \xrightarrow[\text{Alcohol}]{KOH} A \xrightarrow{H_2/Pt} B$$

(a) Ethyl alcohol **(b)** Acetaldehyde

(c) Ethene **(d)** Ethane

12. In unimolecular reactions, the reaction completes in:

(a) One step **(b)** Two steps

(c) Three steps **(d)** None of these

13. Grignard's reagent reacts to form alkane with:

(a) Water **(b)** Ammonia

(c) Ethanol **(d)** All of these

14. Grignard's reagents produce primary alcohol with:

(a) Formaldehyde **(b)** Epoxide

(c) Acetaldehyde **(d)** Both (a) and (b)

15. Carbanians are:

(a) Electrophile **(b)** Nucleophile

(c) Free radical **(d)** Group of atoms

16. Which substance is used to convert alcohol to alkyl halide:

(a) $SOCl_2$ **(b)** PCl_3

(c) $HCl + ZnCl_2$ **(d)** All of these

17. Ethyl bromide when reduced with nascent hydrogen the product will be:

(a) Ethyl alcohol **(b)** Ethane

(c) Butane **(d)** Propane

18. When bromomethane is hydrolyzed by aqueous NaOH solution which ion brings about the first stage of substitution:

(a) Na^+ **(b)** OH^-

(c) Anyone **(d)** No reaction

19. In primary alkyl halide the halogen atom is attached to a carbon which is further attached to how many carbon atoms:

(a) One **(b)** Two

(c) Three **(d)** Nil

20. Which one of the following is not associated with S_N2 mechanism:

(a) 100% inversion of configuration

(b) 2^{nd} order kinetics

(c) Tetiary alkyl halides

(d) Change of hybridization from sp^3 to sp^2 in transition state

21. Grignard reagent is reactive due to:

(a) The presence of halogen atom **(b)** The presence of Mg atom

(c) The polarity of C – Mg bond **(d)** Electrophilic carbon

22. Reaction of C_2H_5MgBr with CO_2 is an example of:

(a) Electrophilic substitution **(b)** Nucleophilic substitution

(c) Electrophilic addition **(d)** Nucleophilic addition

23. Which one of the following is not a nucleophile:

(a) $CH_3 - NH_2$ **(b)** $CH_2 = CH_2$

(c) OH^- **(d)** $\bar{C}H_3$

24. Acetic acid can be obtained from CH_3MgI by treatment with:

(a) H_2O **(b)** $ClNH_2$

(c) CO_2 **(d)** HCHO

answers

1.	(d)	**2.**	(c)	**3.**	(a)	**4.**	(b)	**5.**	(a)
6.	(d)	**7.**	(b)	**8.**	(a)	**9.**	(b)	**10.**	(b)
11.	(d)	**12.**	(b)	**13.**	(d)	**14.**	(d)	**15.**	(b)
16.	(d)	**17.**	(b)	**18.**	(d)	**19.**	(a)	**20.**	(c)
21.	(c)	**22.**	(d)	**23.**	(d)	**24.**	(c)		

SOLVED EXERCISE

Q.1 Fill in the blanks:

(i) In tertiary alkyl halides the halogen atom is attached to a carbon which is further attached to ———— carbon atoms directly.

(ii) The best method for the preparation of alkyl halides is the reaction of ———— with inorganic reagents.

(iii) An alkyl group with a partial positive charge on the carbon atom is called ———— centre.

(iv) The mechanism is called ———— if it involves one molecule in the rate-determining step.

(v) Molecularity of a reaction is defined as the number of molecules taking part in the ————.

(vi) The molecularity of E-2 reactions is always two and the reactions show ———— order kinetics.

(vii) Wurtz synthesis is useful for the preparation of ———— alkanes.

(viii) Grignard reagents are prepared by the reaction of magnesium metal with alkyl halides in the presence of ————.

answers

(i)	three	**(ii)**	alcohol	**(iii)**	electrophile
(iv)	E1 and E_N1	**(v)**	R.D.S	**(vi)**	second
(vii)	higher	**(viii)**	anhydrous ether		

Q.2 Indicate True or False:

(i) In secondary alkyl halides, the halogen atom is attached to a carbon which is further attached to two carbon atoms directly.

(ii) Alcohols react with thionyl chloride in ether as solvent to give alkyl halides.

(iii) Order of reactivity of alkyl halides for a particular alkyl group is:

Iodide > Bromide > Chloride > Fluoride

(iv) In S_N2 reactions the attacking nucleophile always attacks from the side in which the leaving group is attached.

(v) Methylmagnesium iodide on hydrolysis yields ethyl alcohol.

(vi) Primary, secondary and tertiary amines react with Grignard reagents in the same way.

(vii) The reactions of secondary alkyl halides may follow both S_N1 and S_N2 mechanisms.

(viii) S_N1 mechanism is a one stage process involving a simultaneous bond breakage and bond formation.

(ix) In β-elimination reactions, the two atoms or groups attached to two adjacent carbon atoms are lost under the influence of an electrophile.

(x) The reactivity order of alkyl halides is determined by the strength of carbon-halogen bond.

answers

(i)	True	**(ii)**	False	**(iii)**	True	**(iv)**	False	**(v)**	False
(vi)	False	**(vii)**	True	**(viii)**	False	**(ix)**	False	**(x)**	True

Q.3 Multiple choice questions. Encircle the correct answer:

(i) In primary alkyl halides, the halogen atom is attached to a carbon which is further attached to how many carbon atoms:

(a) Two **(b)** Three

(c) One **(d)** Four

(ii) The reactivity order of alkyl halides for a particular alkyl group is:

(a) Fluoride > Chloride > Bromide > Iodide

(b) Chloride > Bromide > Fluoride > Iodide

(c) Iodide > Bromide > Chloride > Fluoride

(d) Bromide > Iodide > Chloride > Fluoride

(iii) When CO_2 is made to react with ethyl magnesium iodide, followed by acid hydrolysis, the product formed is:

(a) Propane **(b)** Propanic acid

(c) Propanal **(d)** Propanol

(iv) Grignard reagent is reactive due to:

(a) The presence of halogen atom **(b)** The presence of Mg atom

(c) The polarity of C – Mg bond **(d)** None of the above

(v) S_N2 reactions can be best carried out with:

(a) Primary alkyl halides **(b)** Secondary alkhyl halides

(c) Tertiary alkhyl halides **(d)** All the three

(vi) Elimination bimolecular reactions involve:

(a) First order kinetics **(b)** Second order kinetics

(c) Third order kinetics **(d)** Zero order kinetics

(vii) 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

(viii) Alkyl halides are considered to be very reactive compounds towards nucleophiles, becuase:

(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 nulceophilic carbon and a good leaving group

(ix) The rate of E1 reaction depends upon:

(a) The concentration of substrate

(b) The concentration of nucleophile

(c) The concentration of substrate as well as nucleophile

(d) None of the above

(x) Which one of the following is not a nucleophile:

(a) H_2O **(b)** H_2S

(c) BF_3 **(d)** NH_3

answers

(i)	(c)	**(ii)**	(c)	**(iii)**	(b)	**(iv)**	(c)	**(v)**	(a)
(vi)	(b)	**(vii)**	(d)	**(viii)**	(b)	**(ix)**	(a)	**(x)**	(c)

Q.4 Define alkyl halide. Which is the best method of preparing alkyl halide?

Ans. **Alkyl Halide:** Halogen derivatives of alkanes are called haloalkanes they may be mono, di, tri or poly haloalkanes depending upon the no of halogen atoms present in the molecule. Among these, monohaloalkanes are also called **alkyl halides**.

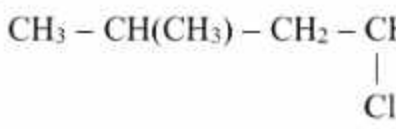
Method of preparation see in text book.

Q.5 Write down a method for the preparation of ethyl magnesium bromide in the laboratory?

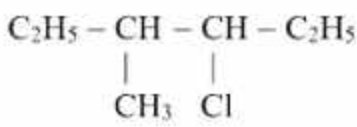
Ans. See in text book.

Q.6 Give IUPAC names to the following compounds.

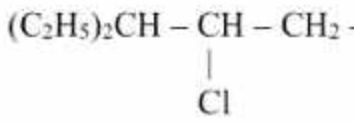
Ans.



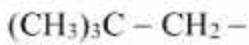
2-chloro, 4-methyl pentane



3-chloro, 4-methyl hexane



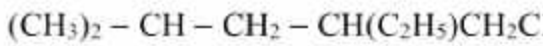
3-chloro, 4-ethyl hexane



1-chloro, 2-methyl propane



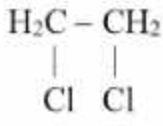
2-bromo propane



1-chloro, 2-ethyl, 4-methyl pentane



Tetra bromo methane



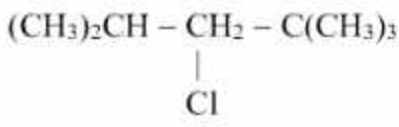
1, 2-dichloroethane



Dichloromethane (Methylene di-chloride)



1-bromo, 3, 3-dimethyl butane



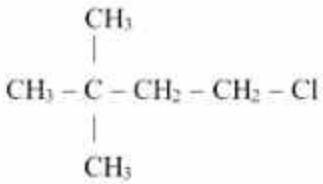
3-chloro, 2, 2, 4-trimethyl pentane

$(CH_3)_2C(Cl) - C(Cl)(CH_3)_2$	2, 3-dichloro, 2, 3-dimethyl butane
$(CH_3CH_2)_3CBr$	3-bromo, 3-ethyl pentane

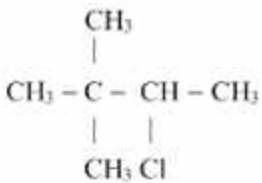
Q.7 Draw all the possible structures that have the molecular formula $C_6H_{13}Cl$. Classify each as primary, secondary or tertiary chloride. Give their names according to IUPAC system.

Ans.

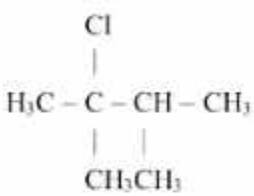
Structure	IUPAC Name	Type of Chloride
$H_3C - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - Cl$	1-chlorohexane	Primary chloride
$H_3C - CH_2 - CH_2 - CH_2 - CH(Cl) - CH_3$	2-chlorohexane	Secondary chloride
$H_3C - CH_2 - CH_2 - CH(Cl) - CH_2 - CH_3$	3-chlorohexane	Secondary chloride
$H_3C - CH_2 - CH_2 - CH(CH_3) - CH_2 - Cl$	1-chloro, 2-methylpentane	Primary chloride
$H_3C - CH_2 - CH(CH_3) - CH_2 - CH_2 - Cl$	1-chloro, 3-methylpentane	Primary chloride
$H_3C - CH(CH_3) - CH_2 - CH_2 - CH_2 - Cl$	1-chloro, 4-methylpentane	Primary chloride
$H_3C - CH(CH_3) - CH_2 - CH(Cl) - CH_3$	2-chloro, 4-methylpentane	Secondary chloride
$H_3C - CH(CH_3) - CH(Cl) - CH_2 - CH_3$	3-chloro, 2-methylpentane	Secondary chloride
$H_3C - CH(Cl) - CH(CH_3) - CH_2 - CH_3$	2-chloro, 3-methylpentane	Secondary chloride
$H_3C - CH(CH_3) - CH(CH_3) - CH_2 - Cl$	1-chloro, 2, 3-dimethylbutane	Primary chloride



1-chloro-3, 3 dimethyl butane — Primary



2-chloro-3, 3 dimethyl butane — Secondary



2-chloro, 2, 3-dimethylibutane — Tertiary chloride

Q.8 Using ethyl bromide as a starting material how would you prepare the following compounds. Give also the inorganic reagents and conditions necessary to carry out these reactions:

(a) n-butane **(b) Ethyl alcohol**

(c) Ethyl cyanide **(d) Ethane**

(e) Not present in book **(f) Ethene**

(g) Propanoic acid **(h) Propane**

Ans.

(a) n-butane:

$$2CH_3 - CH_2 - Br + 2Na \xrightarrow{\text{Ether}} H_3C - CH_2 - CH_2 - CH_3 + 2NaBr$$

(b) Ethyl alcohol:

$$H_3C - CH_2 - Br + KOH_{(aq)} \longrightarrow H_3C - CH_2 - OH + KBr$$

(c) Ethyl cyanide:

$$H_3C - CH_2 - Br + KCN \longrightarrow H_3C - CH_2 - CN + KBr$$

(d) Ethane:

$$CH_3 - CH_2 - Br + 2[H] \xrightarrow{Zn+HCl} CH_3 - CH_3 + HBr$$

(f) Ethene:

$$H_3C - CH_2 - Br + KOH \xrightarrow[(alc)]{100^\circ C} H_2C = CH_2 + H_2O + KBr$$

(g) Propanoic acid:

(i) $H_3C - CH_2 - Br + Mg \xrightarrow{Dry\ ether} CH_3 - \overset{\delta-}{C}H_2 - \overset{\delta+}{M}g - Br$

(ii) $CH_3 - \overset{\delta-}{C}H_2 - \overset{\delta+}{M}g - Br + CO_2 \longrightarrow H_3C - CH_2 - \underset{\|}{\overset{O}{C}} - \overset{-}{O}\overset{+}{M}gBr$

$\downarrow H_3O^+$

$H_3C - CH_2 - COOH + HO - Mg - Br$

Q.9 Write a detailed note on the mechanism of nucleophilic substitution reactions.

Ans. Detailed question. See text book.

Q.10 What do you understand by the term β-elimination reaction? Explain briefly the two possible mechanisms of β-elimination reaction.

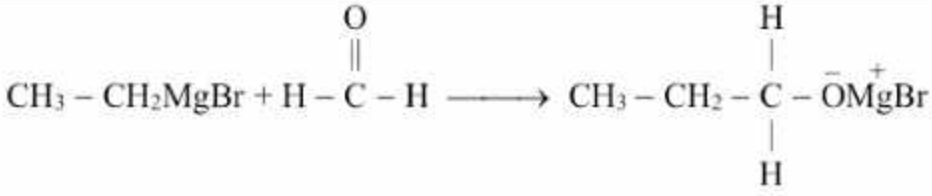
Ans. **β-elimination Reaction:** It can be defined as:

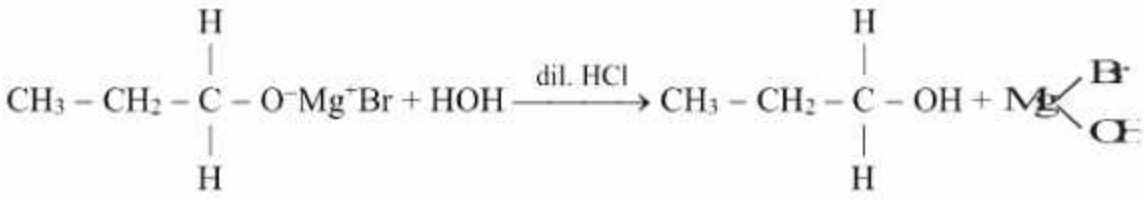
During nucleophilic substitution reactions, when attacking nucleophile attacks the electrophilic hydrogen atom attached to the β-carbon of the alkyl halide and we get an alkene instead of substitution product then such type of reaction is called as β-elimination reaction.

Q.11 What products are formed when the following compounds are treated with ethyl-Mg-bromide, followed by hydrolysis in the presence of an acid?

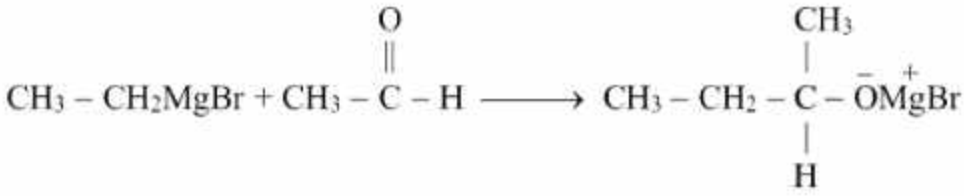
Ans.

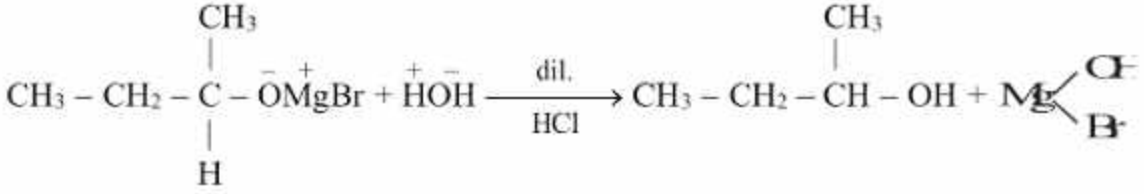
(a) HCHO:



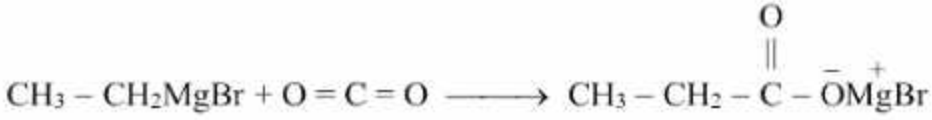


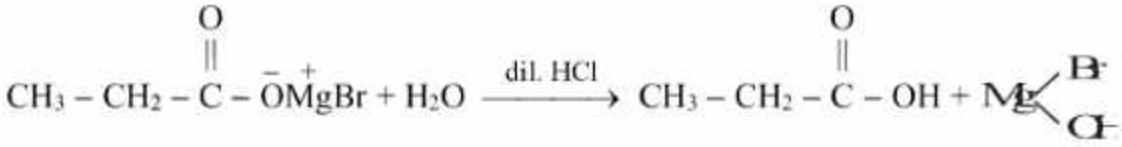
(b) **$CH_3-\overset{\overset{O}{\|}}{C}-H$:**



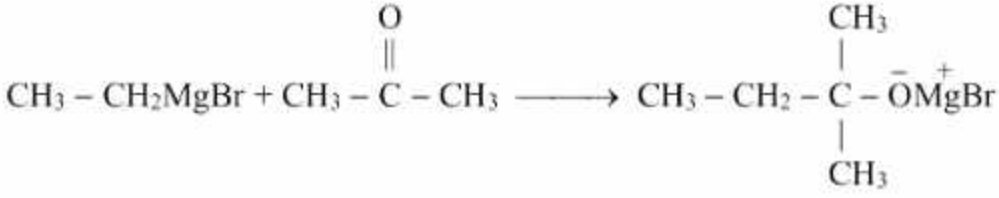


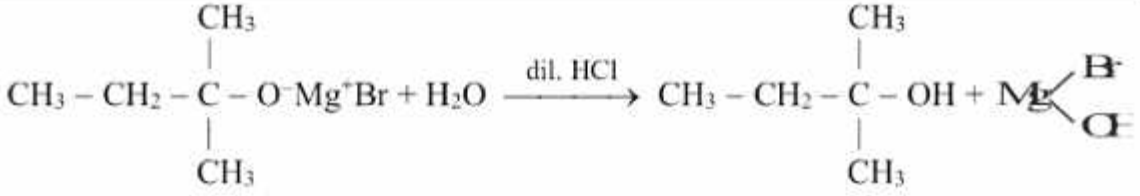
(c) **CO_2:**



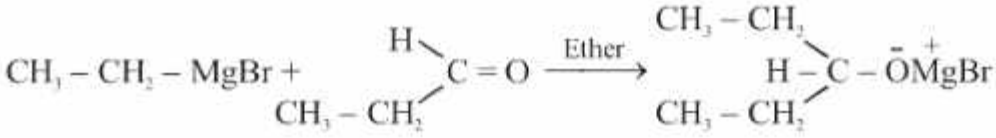


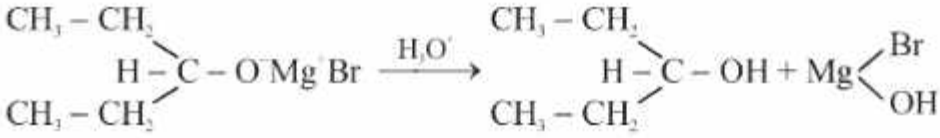
(d) **$(CH_3)_2CO$:**



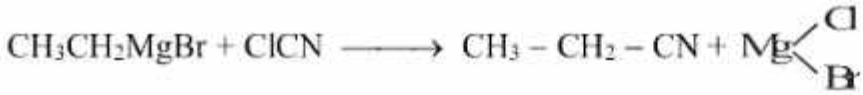


(e) **$CH_3 - CH_2 - \overset{\overset{O}{\|}}{C} - H$:**





(f) **ClCN:**



Q.12 **How will you carry out the following conversions?**

(i) $CH_4 \longrightarrow CH_3CH_2COOH$

(ii) $CH_3 - CH_3 \longrightarrow (CH_3 - CH_2)_4N^+Br^-$

(iii) $CH_2 - CH_2 \longrightarrow CH_3 - CH_2 - CH_2 - CH_2 - OH$

(iv) $CH_3CH_2CH_2Cl \longrightarrow CH_3CH_2COOH$

Ans.

(i) $CH_4 \longrightarrow CH_3CH_2COOH$

Step Involved:

1. $CH_4 + Cl_2 \xrightarrow{hv} CH_3 - Cl + HCl$
2. $2CH_3 - Cl + 2Na \longrightarrow CH_3 - CH_3 + 2NaCl$
3. $CH_3 - CH_3 + Cl_2 \xrightarrow{hv} CH_3 - CH_2 - Cl + HCl$

4. $CH_3 - CH_2 - Cl + Mg \xrightarrow{\text{Dry ether}} CH_3 - CH_2 - MgCl$

5. $CH_3 - CH_2 - MgCl + CO_2 \xrightarrow{\text{Ether}} CH_3 - CH_2 - \underset{\underset{\displaystyle O}{\|}}{C} - \overset{-}{O}\overset{+}{M}gCl \xrightarrow{H_3O^+} CH_3 - CH_2 - COOH + Mg\begin{matrix} Cl \\ Cl \end{matrix}$

(ii) $\mathbf{CH_3 - CH_3 \longrightarrow (CH_3 - CH_2)_4N^+Br^-}$

By Hoffman's reaction:

Steps Involved:

1. $CH_3 - CH_3 + Br_2 \xrightarrow{hv} CH_3 - CH_2 - Br + HBr$
2. $CH_3 - CH_2 - Br + NH_3 \longrightarrow CH_3 - CH_2 - NH_2 + HBr$
3. $CH_3 - CH_2 - NH_2 + CH_3 - CH_2 - Br \longrightarrow (CH_3 - CH_2)_2NH + HBr$
4. $(CH_3 - CH_2)_2NH + CH_3 - CH_2 - Br \longrightarrow (CH_3 - CH_2)_3N + HBr$
5. $(CH_3 - CH_2)_3N + CH_3 - CH_2 - Br \longrightarrow [(CH_3 - CH_2)_4N^+]Br^-$

(iii) $\mathbf{CH_2 = CH_2 \longrightarrow CH_3 - CH_2 - CH_2 - CH_2 - OH}$

Steps Involved:

1. $CH_2 = CH_2 + HCl \longrightarrow CH_3 - CH_2 - Cl$
2. $2CH_3 - CH_2 - Cl + 2Na \longrightarrow CH_3 - CH_2 - CH_2 - CH_3 + 2NaCl$
3. $CH_3 - CH_2 - CH_2 - CH_3 + Cl_2 \longrightarrow CH_3 - CH_2 - CH_2 - CH_2 - Cl + HCl$
4. $CH_3 - CH_2 - CH_2 - CH_2 - Cl + KOH_{(aq)} \longrightarrow CH_3 - CH_2 - CH_2 - CH_2 - OH + KCl$

(iv) $\mathbf{CH_3CH_2CH_2Cl \longrightarrow CH_3 - CH = CH_2}$

Steps Involved:

$CH_3 - CH_2 - CH_2 - Cl + KOH \xrightarrow{100^\circ C,\ \text{alcohol}} CH_3 - CH = CH_2 + H_2O + KCl$

(v) $\mathbf{CH_3COOH \longrightarrow CH_3CH_2COOH}$

Steps Involved:

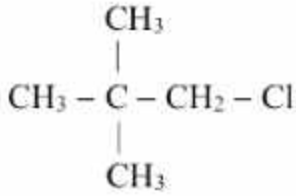
1. $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$
2. $2CH_3COONa + 2H_2O \xrightarrow{\text{Elctrolysis}} CH_3 - CH_3 + 2CO_2 + 2NaOH + H_2$
3. $CH_3 - CH_3 + Cl_2 \xrightarrow{hv} CH_3 - CH_2 - Cl + HCl$

4. $CH_3 - CH_2 - Cl + Mg \xrightarrow{\text{Ether}} CH_3 - CH_2 - Mg - Cl$

5. $CH_3 - CH_2 - Mg - Cl + CO_2 \xrightarrow{\text{Ether}} CH_3 - CH_2 - C(=O)\overset{-}{O}\overset{+}{M}gCl \xrightarrow{H_3\overset{+}{O}} CH_3 - CH_2 - COOH + Mg(Cl)(Cl)$

DO YOU KNOW?

1. Formula of neo pentyl chloride is:



2. CH_2I_2 is called methylene di iodide.
3. Order of reactivity of alkyl halides is:

$$RI > R - Br > R - Cl > R - F$$

4. Those species which are electron deficient and accept the electron pairs to form the covalent bond is called "electrophiles".
5. The species which have the tendency to donate the electrons are called nucleophiles.
6. S_N2 reaction is bi molecular where S_N1 is uni-molecular.
7. Primary alkyl halides give S_N2 reaction.
8. Tertiary alkyl halides give S_N1 reaction.
9. Tertiary carbonium ions are more stable than the primary carbonium ions.
10. Grignard's reagents react with Formaldehyde and epoxides to form primary alcohols.
11. Grignard's reagent (R – Mg – X) was discovered by Victor Grignard in 1902 and he got the Nobel Prize in 1912.
12. Ketones react with Grignard's reagent to form tertiary alcohols.

SHORT QUESTIONS

Q.1 What is order of reactivity of HX with ethene?

Ans. Ethene reacts with HX to form ethyl halide.

$$CH_2 = CH_2 + HX \longrightarrow CH_3 - CH_2X$$

The order of reactivity of HX is given below.

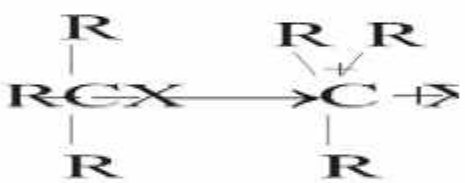
$$HI > HBr > HCl > HF$$

Q.2 What is substrate?

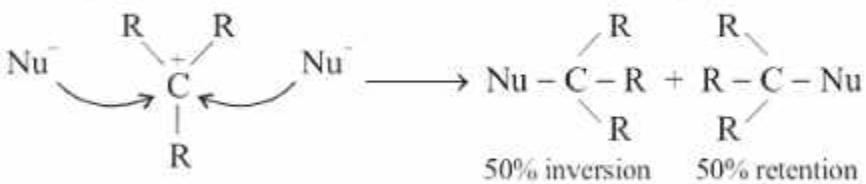
Ans. The molecule at which another substance attacks is called substrate. For example, when a nucleophile attacks on RX, the alkyl halide is substrate. When enzyme reacts with any species, it is also called substrate.

Q.3 In tertiary alkyl halides, S_N1 reaction takes place but not S_N2 reaction why?

Ans. In tertiary alkys halide, a nucleophile cannot attack directly at the electrophilic centre due to stearic hindrance. First of all ionization of alkylhalide takes place and carbocation is formed.



Now nucleophile can attack from either side of carbon plane.



Q.4 Why reaction of ethylbromide with OH^- nucleophile is S_N2?

Ans. Reaction of ethyl bromide with OH^- is S_N2 because it is bimolecular reaction. The rate of reaction depends upon the concentration of nucleophile as well as substrate.

$$CH_3 - CH_2 - Br + OH^- \longrightarrow CH_3 - CH_2OH + Br^-$$

$$\text{Rate} = K[CH_3CH_2Br][OH^-]$$

Q.5 Secondary alkyl halides undergo S_N1 or S_N2 reactions, while primary alkyl halides have S_N2 and tertiary alkyl halides have SN_1 reactions, why?

Ans. In secondary alkyl halides two alkyl group are attacked with α-carbon.

$$R - \underset{\displaystyle X}{\underset{|}{CH}} - R$$

The reaction kinetic depends upon the size of alkyl group and nature of solvent used.

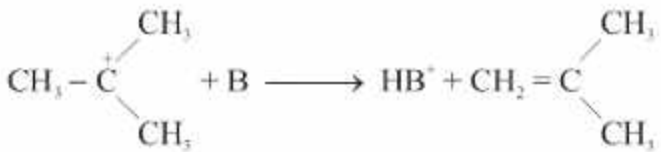
If alkyl groups have higher size, S_N1 reaction takes places due to stearic hindrance. This reaction takes place in two steps. Polar solvent also favours S_N1 mechanism. If alkyl groups have smaller size than S_N2 reaction takes place in single step. Non-polar solvent also favours the S_N2 mechanism.

Q.6 First step of E_1 and S_N1 mechanism is same but second is different. Explain it.

Ans. In E_1 or S_N1 first step is formation of carbocation.



Second step of E_1:



Second step of S_N1:

