

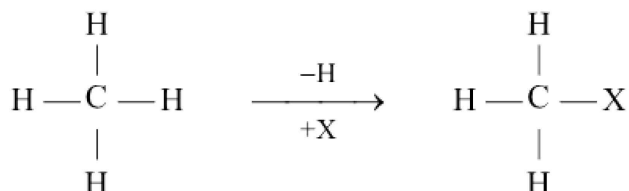
Chapter

10

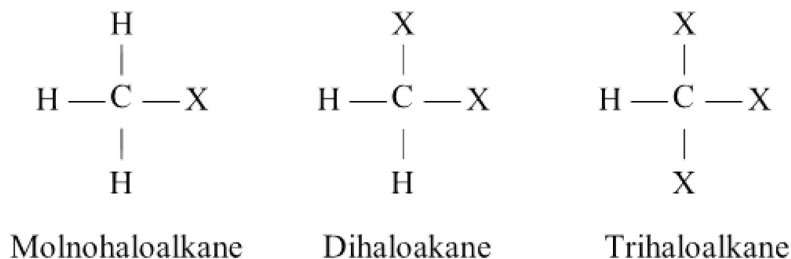
ALKYL HALIDES

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 halogen atoms, are called trihaloalkanes. If many halogen atoms are present in an alkane, it is called polyhaloalkanes.



MONOHALOALKANES

Monohaloalkanes are also called alkyl halides. They have general formula $\text{R} - \text{X}$ or $\text{C}_n\text{H}_{2n+1} \text{X}$.

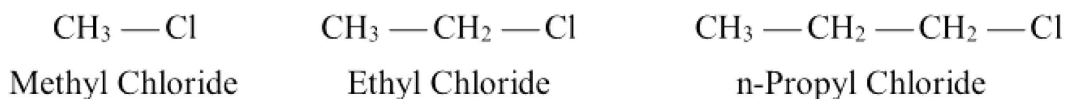
X represents to F, Cl, Br or I.

Classification of Monohaloalkanes or Alkyl Halides:

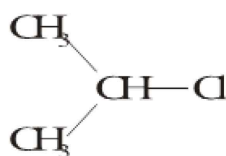
Alkyl halides are classified as follows:

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.,

**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.,



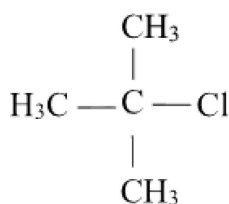
Sec propyl chloride (iso propyl chloride)



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.,

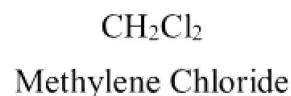
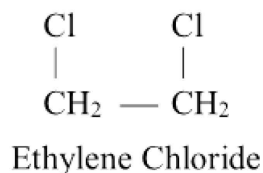
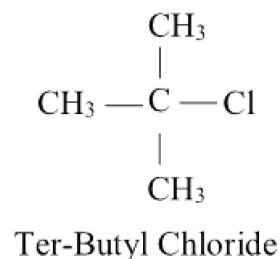
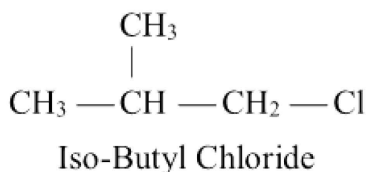
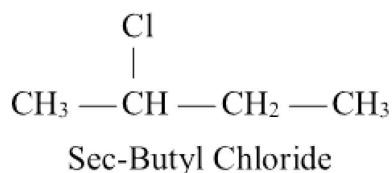
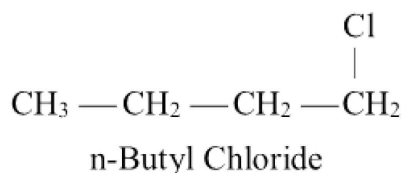


ter-butyl chloride

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.

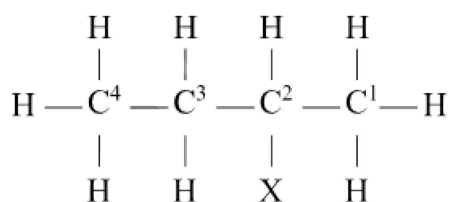




(b) IUPAC Nomenclature:

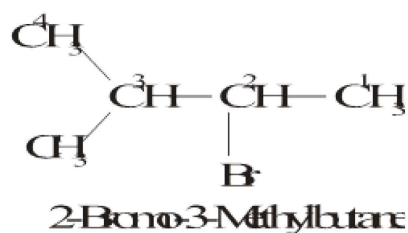
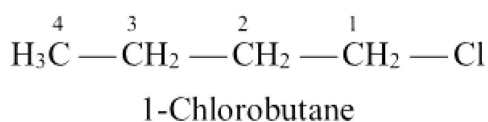
The systematic names given to alkyl halides follow the underlying rules.

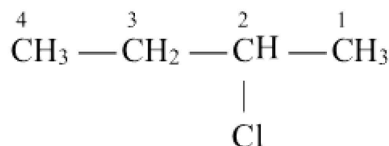
- (1) Select the longest continuous carbon chain and consider the compound to have been derived from this structure.
- (2) Number the carbon atoms in the chain so that the carbon atom bearing the functional group (F, Cl, Br, I) gets the lowest possible number, e.g.,



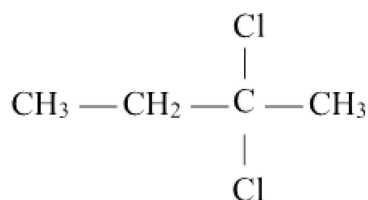
- (3) If the same alkyl substituent occurs more than once on the chain, the prefix di, tri and so on are used before the name of the alkyl group.
- (4) The positions of the substituents are indicated by the appropriate numbers separated by commas. If the same substituent occurs twice or more on the same carbon atom, the numbers is repeated.

Examples which follow the above mentioned rules:

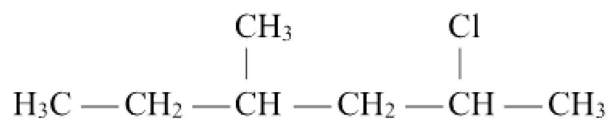




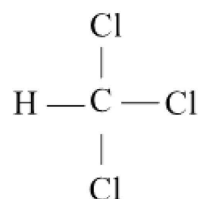
2-Chlorobutane



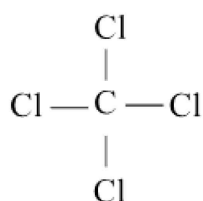
2,2-Dichlorobutane



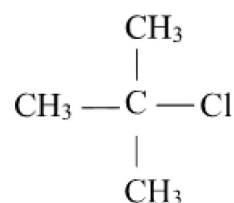
2-Chloro-4-Methylhexane



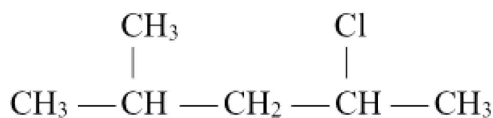
Trichloromethane



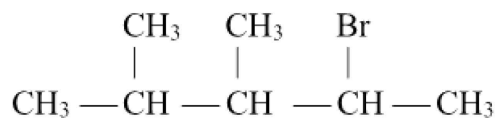
Tetrachloromethane



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.

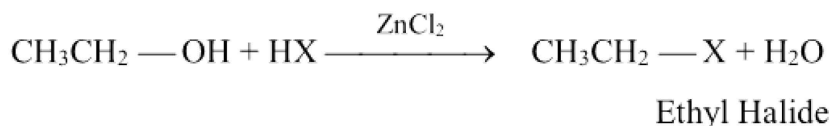


(2) From Alcohol:

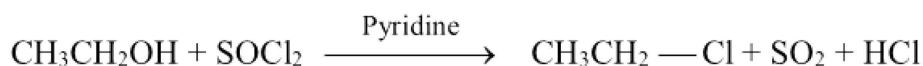
Different methods are used for the preparation of alkyl halides from alcohol.

(a) Reaction of Alcohols with Halogen Acids:

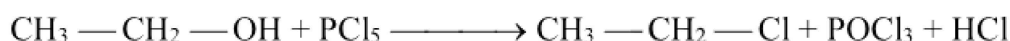
Alcohols may be converted to the corresponding alkyl halides by the action of halogen acid in the presence of ZnCl_2 which acts as a catalyst.

**(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-products (HCl , SO_2) are gases, which escape leaving behind the pure product.

**(c) Reaction of Alcohol with PX_3 or PX_5 :**

Phosphorus trihalides or phosphorus pentahalides react with alcohols to replace $-\text{OH}$ group by a halo group.



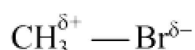
Phosphorus Oxytrichloride

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.

**Reactivity of Alkyl Halides:**

An alkyl halide molecule ($\text{R} - \text{X}$) 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.



There are two main factors which govern the reactivity of $\text{R} - \text{X}$ bond.

These are:

- (i) $\text{C} - \text{X}$ bond energy (ii) $\text{C} - \text{X}$ Bond polarity

Bond Energies:

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

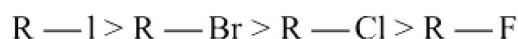
**Bond Polarity:**

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.

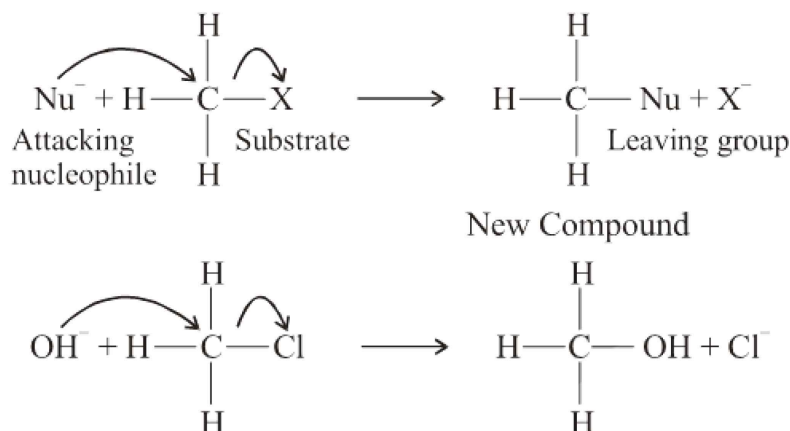
REACTIONS OF ALKYL HALIDES

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
$\text{C}_2\text{H}_5\text{O}^-$	Ethoxide ion	Cl^-	Chloride ion
HS^-	Hydrogen sulphide ion	Br^-	Bromide ion
SCN^-	Thiocyanate ion	$\ddot{\text{N}}\text{H}_3$	Ammonia
$\text{H}_2\ddot{\text{O}}:$	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.



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 .

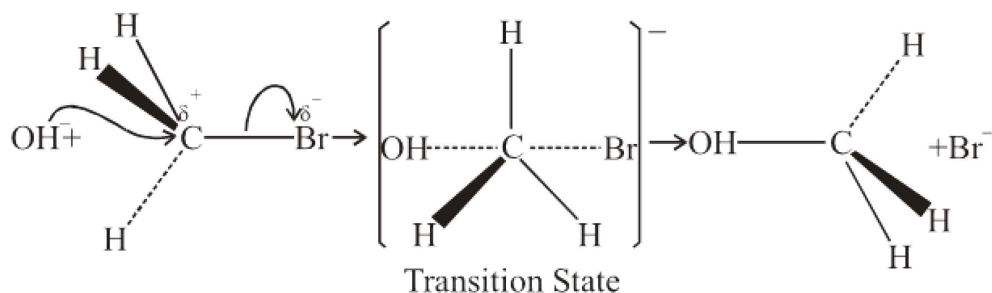
Nucleophilic substitution reaction on alkyl halides involve two main processes, the breakage of $C-X$ bond and the formation of $C-Nu$ bond. The mechanism of the nucleophilic substitution reaction depends upon the timing of these two processes. If the two processes occur simultaneously the mechanism 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.



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.

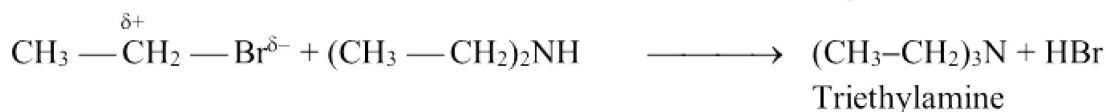
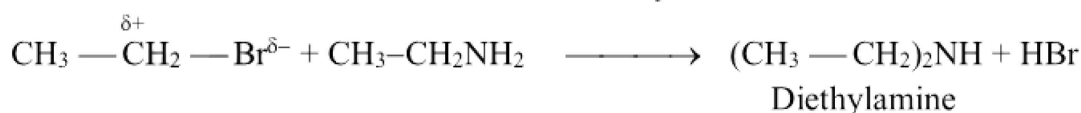
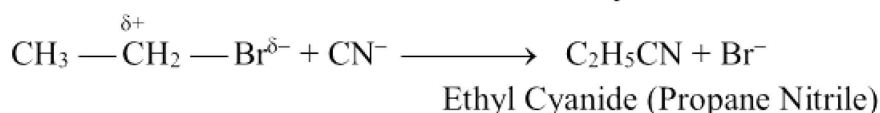
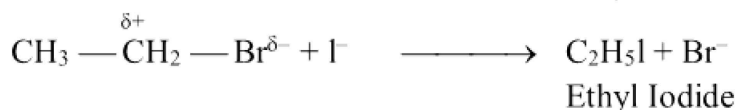
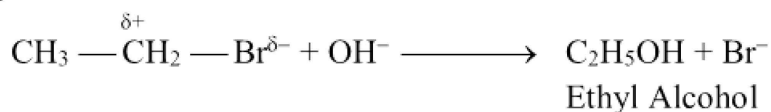
Kinetic studies of the reactions involving S_N2 mechanism have shown that the rates of such reactions depend upon the concentrations of alkyl halide as well as the attacking Nucleophile. Mathematically, the rate can be expressed as.

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

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

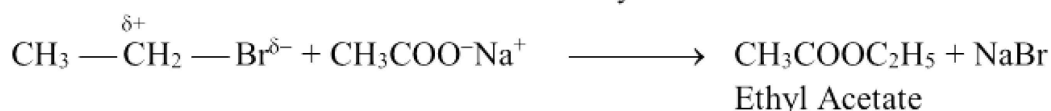
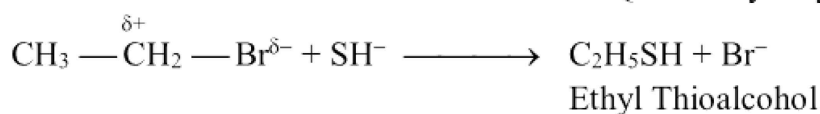
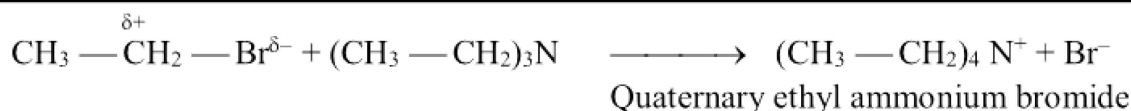
Among the alkyl halides, the primary alkyl halides always follow S_N2 mechanism whenever they are attacked by nucleophiles.

Examples of S_N2 Reactions:



Why primary alkyl halides give S_N2 reactions?

- (1) **Sterric Hinderance:** In primary alkyl halides, small groups are attached 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.

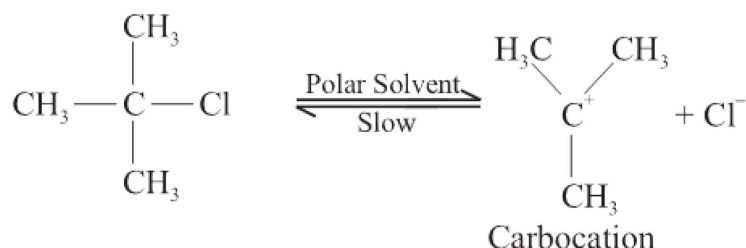


(2) Nucleophilic Substitution Unimolecular S_N1:

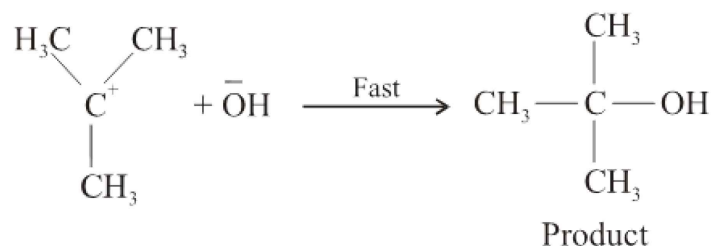
Tertiary alkyl halides when attacked by a nucleophile, undergo S_N1 mechanism. Ter-alkyl halide is highly branched substrate. When a nucleophile attacks it, it has difficulty to approach to the central carbon, due to steric hindrance. The polar solvent present in medium, promotes the ionization of substrate, 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:

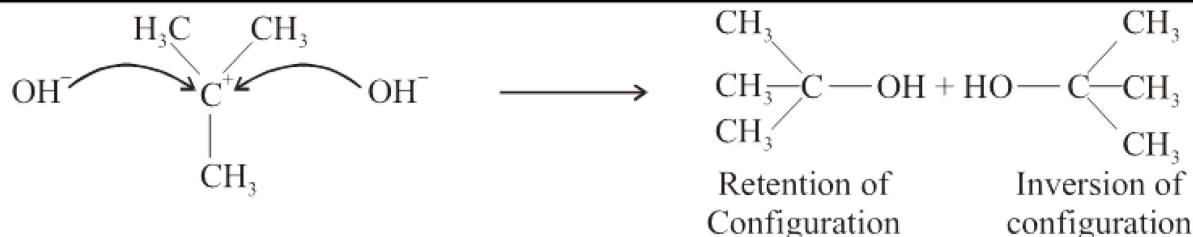


Second Step:



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 has already gone, so the question of the direction of the attack does not arise. Moreover, the intermediate carbocation is a planar species 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 $\text{S}_{\text{N}}1$ 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 $\text{S}_{\text{N}}2$ or $\text{S}_{\text{N}}1$ mechanism depends upon the nature of solvent used and nature of alkyl group present in it. Polar solvents promote the ionization and $\text{S}_{\text{N}}1$ reaction occurs. If alkyl group are bulky $\text{S}_{\text{N}}1$ reaction takes place in two steps and if alkyl groups are smaller in size, $\text{S}_{\text{N}}2$ reaction occur in single step.

Why tertiary alkyl halides give $\text{S}_{\text{N}}1$ reaction?

- (1) **Steric 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.

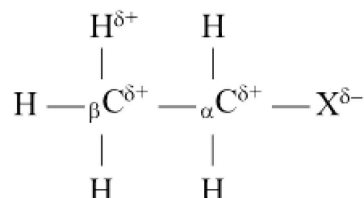
DIFFERENCE BETWEEN $\text{S}_{\text{N}}2$ AND $\text{S}_{\text{N}}1$ MECHANISM

$\text{S}_{\text{N}}1$ – Reactions	$\text{S}_{\text{N}}2$ – Reactions
(1) $\text{S}_{\text{N}}1$ – stands for substitution nucleophilic unimolecular reactions. (2) $\text{S}_{\text{N}}1$ reactions is completed in two steps. (3) Alkyl halide first ionizes to form carbonium ion. $\text{R}_3\text{C} - \text{X} \longrightarrow \text{R}_3\text{C}^+ + \text{X}^-$ It is a slow step and rate-determining step. Second step involves the attacking of nucleophile to form product. $\text{R}_3\text{C}^+ + \text{Nu}^- \longrightarrow \text{R}_3\text{C} - \text{Nu}$ (4) $\text{S}_{\text{N}}1$ reactions are generally given by tertiary 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. (6) It is favoured in polar solvent.	(1) $\text{S}_{\text{N}}2$ – stands for substitution nucleophilic bimolecular reactions. (2) $\text{S}_{\text{N}}2$ – reactions is completed in one step. (3) Formation of new bond and breakage of old bonds takes place simultaneously. $\text{Nu}^- + \text{R} - \text{CH}_2 - \text{X} \longrightarrow \text{R} - \text{CH}_2 - \text{Nu} + \text{X}^-$ (4) $\text{S}_{\text{N}}2$ reactions are generally given by primary alkyl halides. (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 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.”

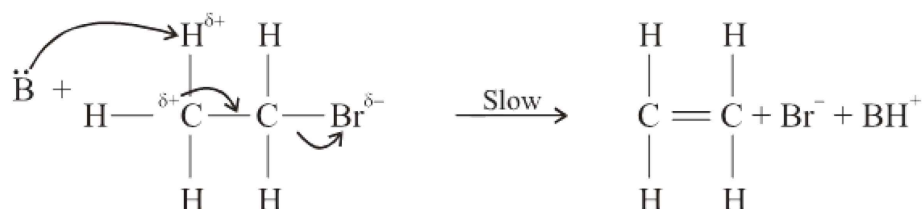


With the elimination at 1, 2 position double bond is formed.

There are two mechanisms for elimination reactions.

E₂-Mechanism:

In E₂ 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.,



E₂-mechanism is analogous to S_N2 mechanism. Rate of reaction depends upon the concentration of base as well as concentration of substrate.

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

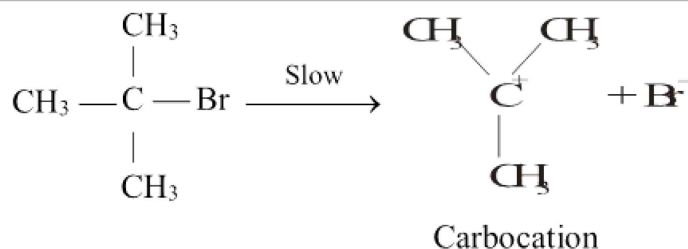
According to above reaction.

$$\text{Rate} \propto [\text{B}] [\text{CH}_3 - \text{CH}_2 - \text{Br}]$$

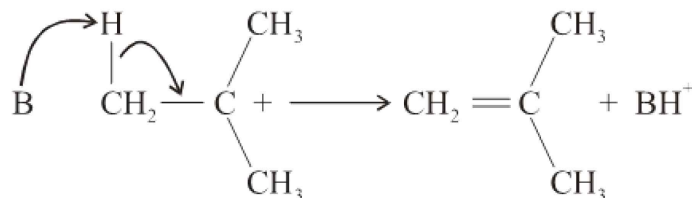
Rate of reaction depends upon concentrations of two molecules so it is called E₂-reaction, primary alkyl halides usually undergo E₂-mechanism. Like S_N2 reactions, the molecularity of E₂ reaction is two and they are second order reactions.

E₁-Mechanism:

E₁ 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 sp³ – hybridized which changes to sp² – hybridization after the removal of halogen atom. Carbocation has planar geometry with the angle of 120°.



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.

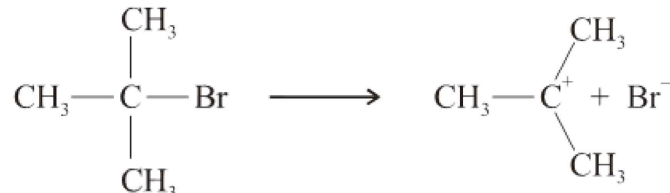
$$\text{Rate} \propto [\text{Substrate}]$$

$$\text{or Rate} \propto [(\text{CH}_3)_3\text{C} - \text{Br}]$$

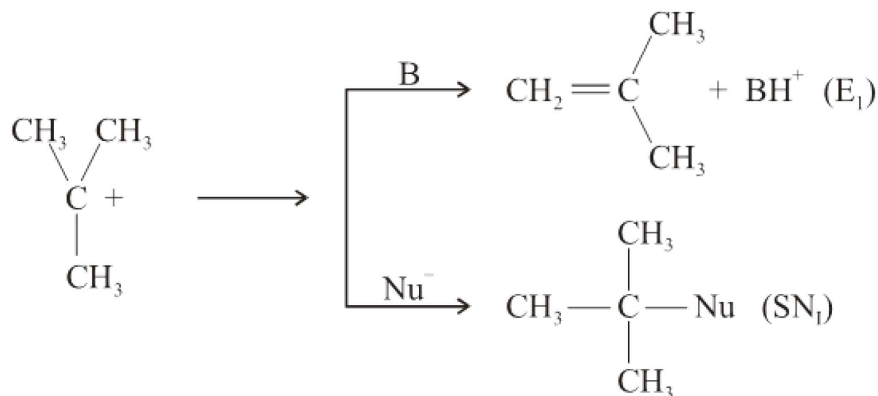
The rate of reaction depends upon the concentration of one molecule so it is unimolecular reaction E_1 -reaction.

DIFFERENCE IN MECHANISM OF $\text{S}_{\text{N}}1$ AND E_1

In $\text{S}_{\text{N}}1$ and E_1 first step or formation of carbocation is same.



In second step, in S_{N} mechanism, another nucleophile attack on carbocation whereas in E_1 -reaction base attack on β -hydrogen.



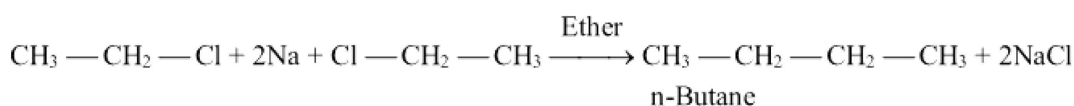
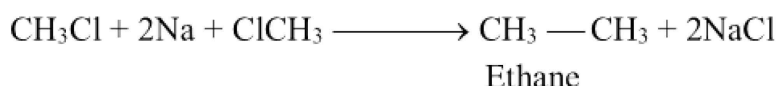
So elimination can be a troublesome side reaction during substitution of tertiary alkyl halides.

Primary alkyl halides follow E₂-mechanism whereas tertiary alkyl halides follow E₁-mechanism.

SOME MORE REACTIONS OF ALKYL HALIDES

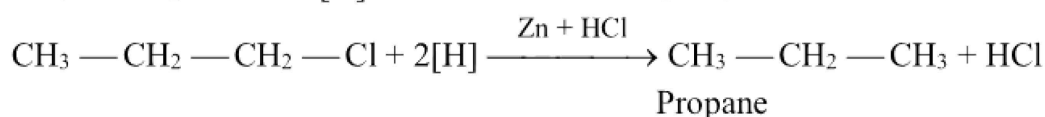
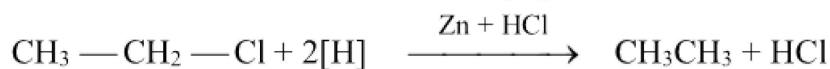
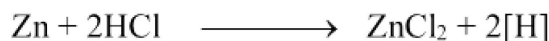
(1) Wurtz Reaction:

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



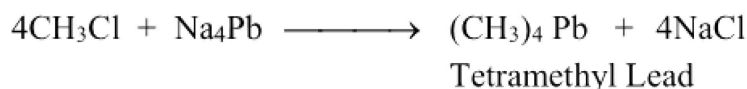
(2) Reduction of Alkyl Halides:

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



(3) Reaction with Sodium Lead Alloy (Na₄Pb):

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.

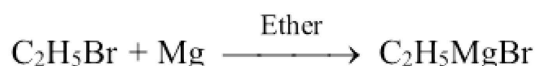
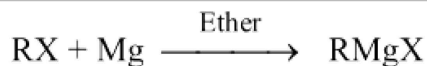


“Alkyl halides reacts with metal in dry ether to form an organometallic compound called Grignard’s Reagent.” This reagent was first of all prepared by Victor Grignard in 1900. The general formula of Grignard’s reagent is RMgX or alkyl or aryl magnesium halide.

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).



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:

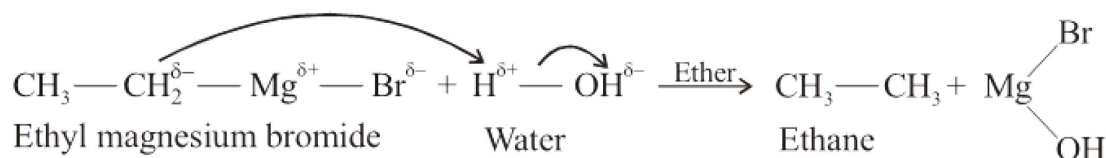


REACTIONS OF GRIGNARD'S REAGENT

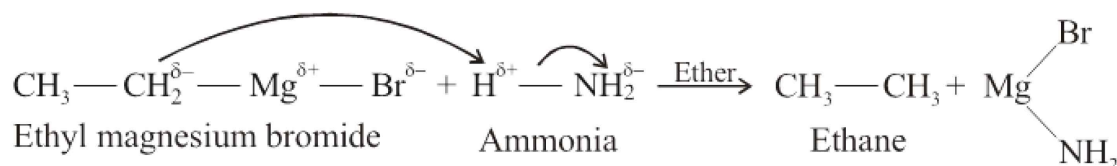
(1) Reaction with Active Hydrogen Compounds (Formation of Hydrocarbons):

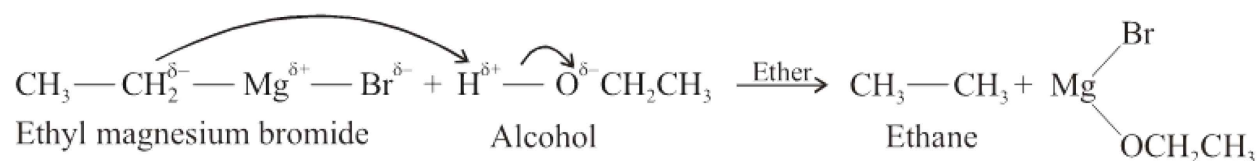
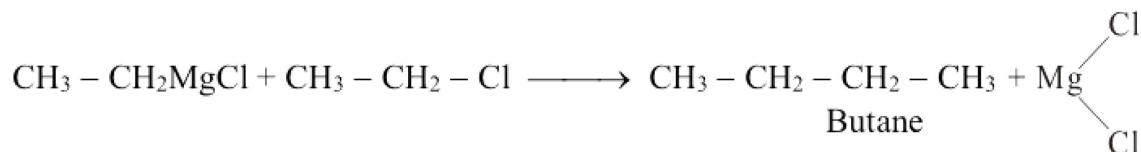
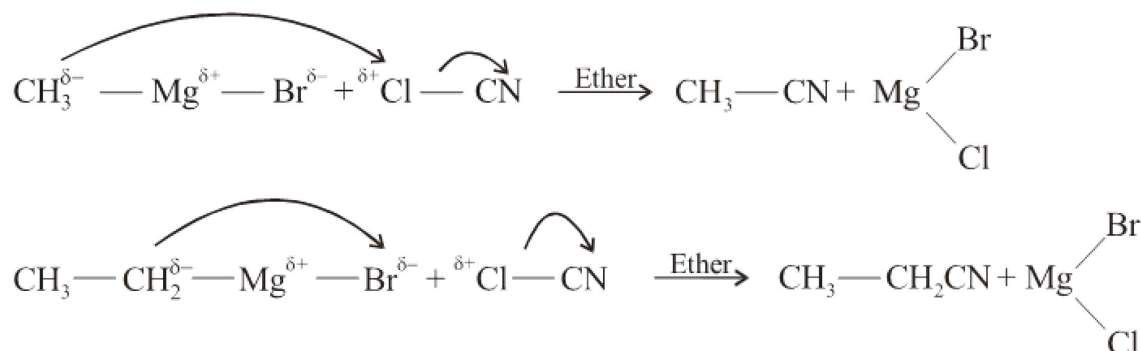
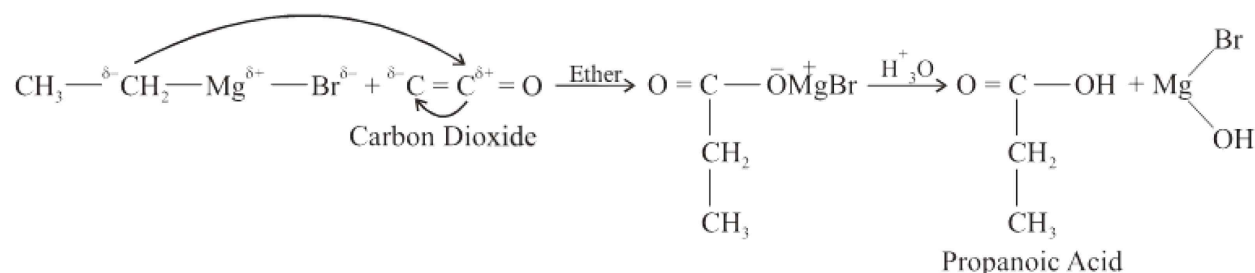
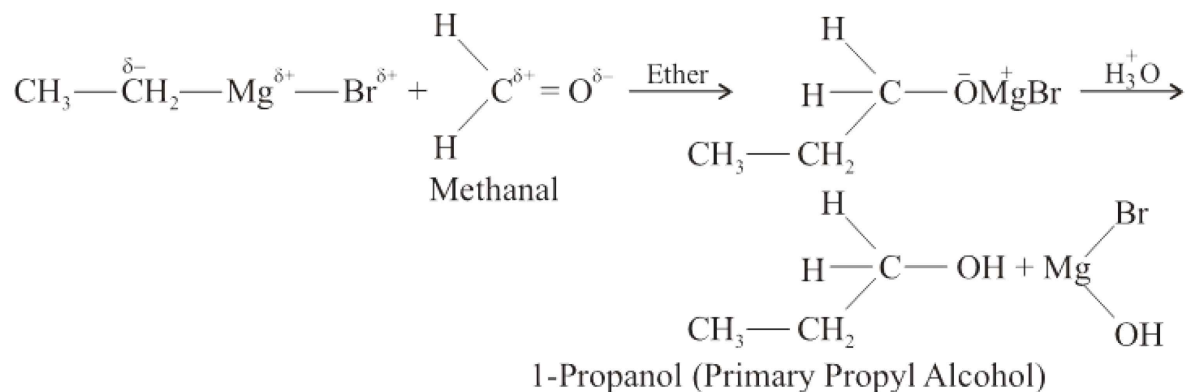
Compounds like water, ammonia or alcohol in which hydrogen is attached with highly electronegative element, easily dissociate as proton are known as active hydrogen compounds.

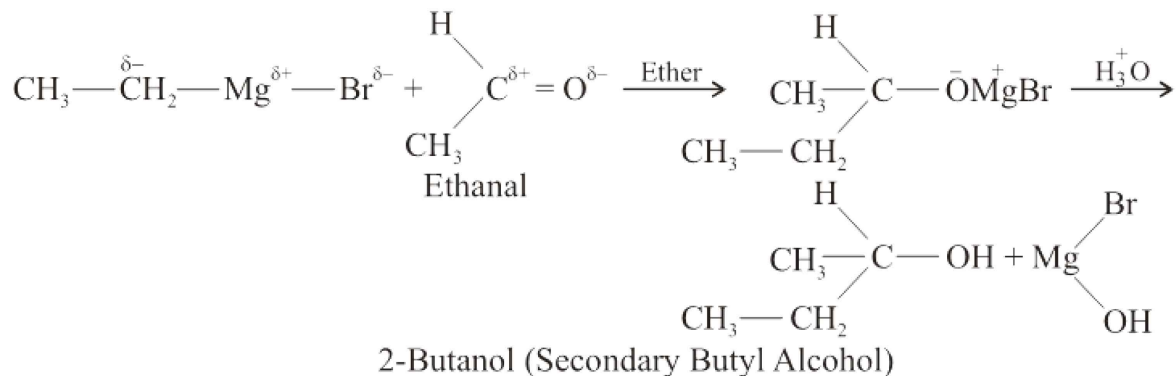
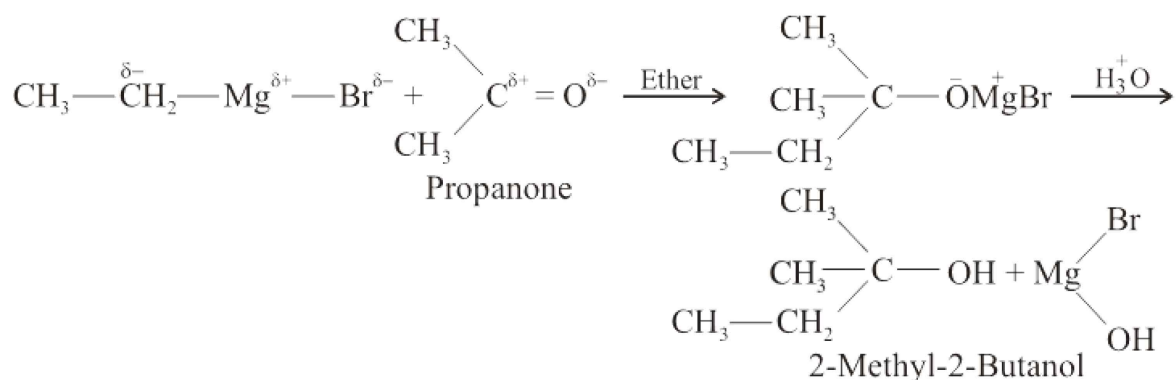
(i) With Water:



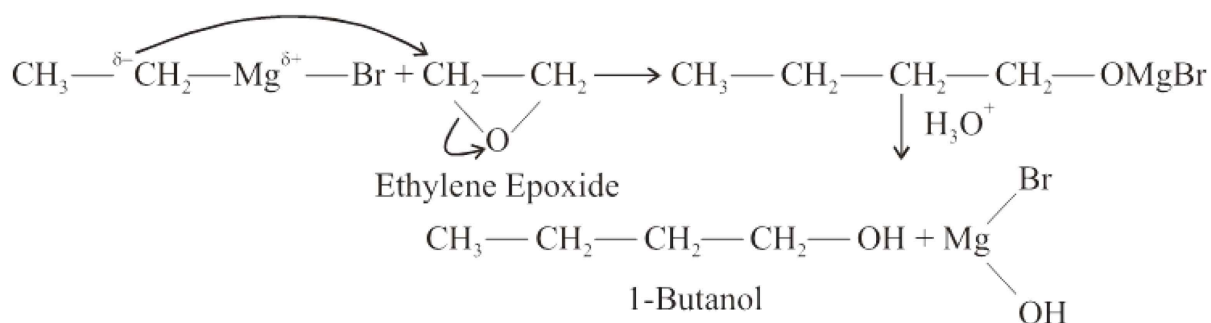
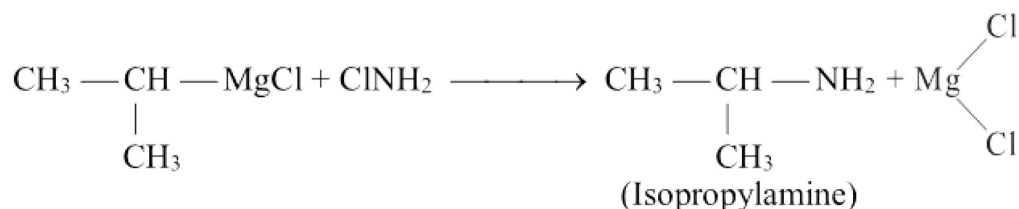
(ii) With Ammonia:



(iii) With Alcohols:**(iv) With Alkyl Halides:****(2) Reaction with Cyanogen Chloride (Formation of Cyanides):****(3) Addition of CO₂ (Formation of Carboxylic Acid):****(4) Reaction with Formaldehyde:**

(5) Reaction with Acetaldehyde:**(6) Reaction with Propane (Acetone):****(7) Reaction with Epoxides (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 _N 1	(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) Propanoic 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 alkyl halides
(c) Tertiary alkyl 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, 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
- (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) H₂O (b) H₂S
(c) BF₃ (d) NH₃

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.

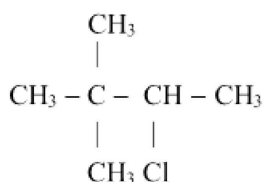
Q.6 Give IUPAC names to the following compounds.**Ans.**

$\begin{array}{c} \text{CH}_3 - \text{CH}(\text{CH}_3) - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	2-Chloro, 4-methyl pentane
$\begin{array}{c} \text{C}_2\text{H}_5 - \text{CH} - \text{CH} - \text{C}_2\text{H}_5 \\ \quad \\ \text{CH}_3 \quad \text{Cl} \end{array}$	3-Chloro, 4-methyl hexane
$\begin{array}{c} (\text{C}_2\text{H}_5)_2\text{CH} - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	3-Chloro, 4-ethyl hexane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{Cl} \\ \\ \text{CH}_3 \end{array}$	1-Chloro, 2, 2-dimethyl propane
$(\text{CH}_3)_2\text{CHBr}$	2-Bromo propane
$(\text{CH}_3)_2\text{CH} - \text{CH}_2 - \text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{Cl}$	1-Chloro, 2-ethyl, 4-methyl pentane
CBr_4	Tetra Bromo methane
$\begin{array}{c} \text{H}_2\text{C} - \text{CH}_2 \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	1, 2-dichloroethane
CH_2Cl_2	Dichloromethane (Methylene di-chloride)
$(\text{CH}_3)_3\text{C} - \text{CH}_2 - \text{CH}_2 - \text{Br}$	1-Bromo, 3, 3-dimethyl butane
$\begin{array}{c} (\text{CH}_3)_2\text{CH} - \text{CH}_2 - \text{C}(\text{CH}_3)_3 \\ \\ \text{Cl} \end{array}$	3-Chloro, 2, 2, 4-trimethyl pentane
$\begin{array}{c} (\text{CH}_3)_2\text{C} - \text{C}(\text{CH}_3)_2 \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	2, 3-Dichloro, 2, 3-dimethyl butane
$(\text{CH}_3\text{CH}_2)_3\text{CBr}$	3-Bromo, 3-ethyl pentane

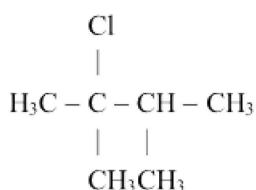
Q.7 Draw all the possible structures that have the molecular formula $C_6H_{13}Cl$. Classify each as primary, secondary or tertiary chloride. Give their names according to IUPAC system.

Ans.

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



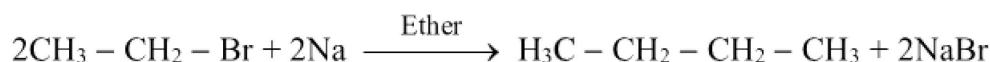
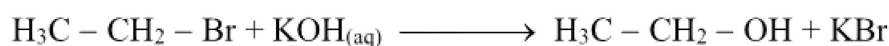
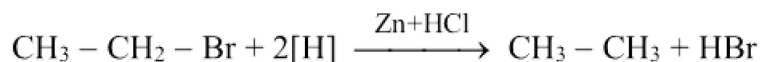
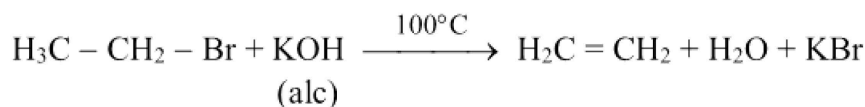
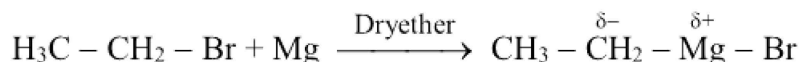
2-Chloro-3, 3 dimethyl butane Secondary

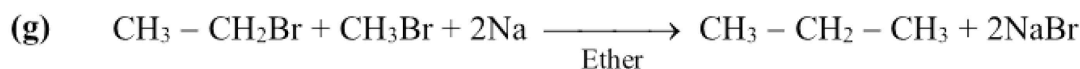
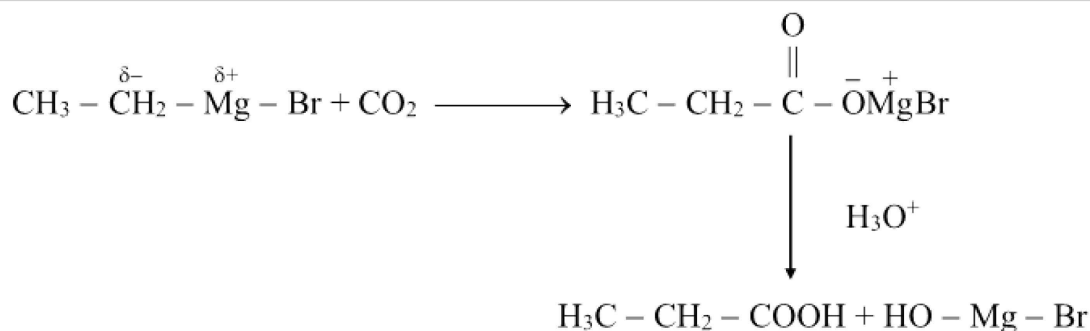


2-Chloro, 2, 3-dimethylbutane Tertiary chloride

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:****(b) Ethyl alcohol:****(c) Ethyl cyanide:****(d) Ethane:****(e) Ethene:****(f) Propanoic acid:**



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:**

