Organic Concepts

BASIC OF REACTION MECHANISM OF ORGANIC COMPOUNDS   Section - 1

Reaction of organic compounds can takes place in one step or in many step depending upon nature of reactants and reaction conditions and also on nature of reactants and their functional group. These chemical reactions involve breaking and making of the bonds that hold together the atoms of reactant and product molecules.

In one step reactions, breaking and making of the bonds takes place simultaneous at the same instant. A one step reaction is represented as : Reactant(s) $\longrightarrow$ Transition State $\longrightarrow$ Product(s)

A many steps reaction involve a time gap between bond breaking and bond making and it results in formation of an additional species called as reactive intermediate :

Reactant(s) $\longrightarrow$ Transition State $\longrightarrow$ Reactive intermediate [Step 1]
State 1

Reactive intermediate $\longrightarrow$ Transition State $\longrightarrow$ Product(s) [Step 2]
State 2
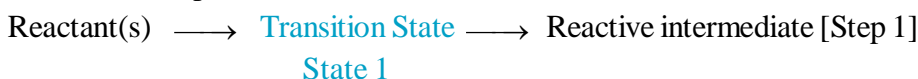
In two steps reaction one of the step is slow step and other one is fast step. The slowest step of many step reaction is called as rate determining step (RDS).

Nature of reaction intermediate formed depends upon type of bond breaking. Bond breaking can be homolytically or heterolytically as illustrated below.
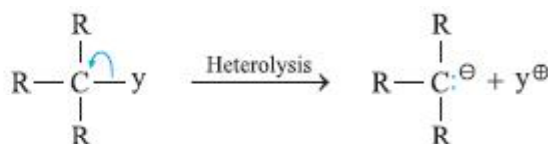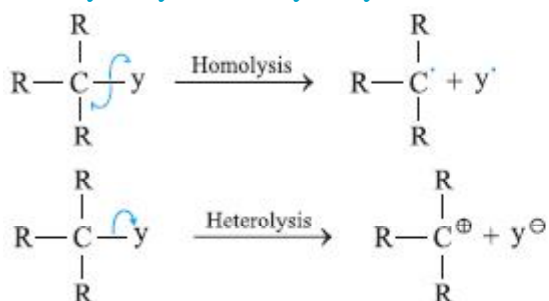
The chemical reactions that involve only homolytic bond cleavage are called as free radical reactions and those reactions that involve heterolytic bond cleavage are termed as ionic reactions.

The products of bond breaking, shown above are not stable in the usual sense and cannot be isolated for prolonged study. Such species are reffered to as reactive intermediates, and are believed to be transient intermediates in many reactions. The general structures and names of four such intermediates are given below.
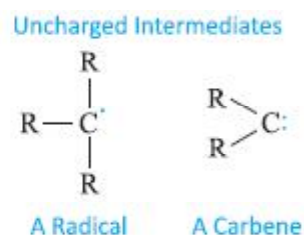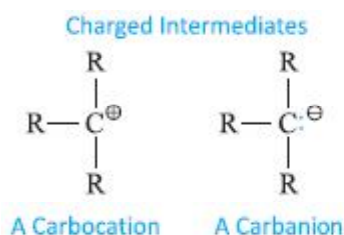
The shapes ideally assumed by these intermediates becomes important when considering the stereochemistry of reactions in which they play a role. A simple tetravalent compounds like methane, CH_4 has a tetrahedral configuration.

Carbocations have only three bonds to the charge bearing carbon, so it adopts a planar trigonal configuration.

Carbanions are pyramidal in shape but these species invert rapidly at room temperature, passing through a higher energy planar form in which the electron pair occupies a p-orbital. Radicals are intermediate in configuration, the energy difference between pyramidal and planar forms being very small. Generally most of the free radicals adopts a planar trigonal configuration. The shape of carbenes is planar, however, the valance electron distribution varies.

You have already studied detailed aspect of these intermediates in 'IOC' chapter.

Note : CF_3 radical is essentially pryamidal in shape. Less % of *s*-character of orbital help in stabilization of free radical.

Note : Types of particular intermediate depends upon the type of carbon atom bearing charge. The stability of charged intermediate is inversely releated to its charge density. The delocalisation of charge decreases charge density hence increases stability. The presence of electron releasing group increases stability of both free radical and carbocations. While presence of electron withdrawing group increases stability of carbanion.
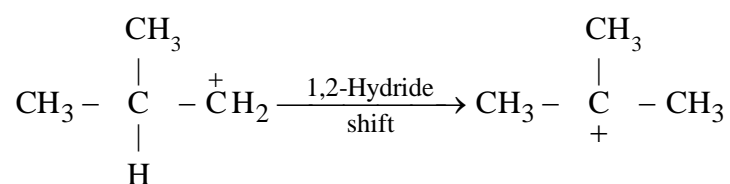
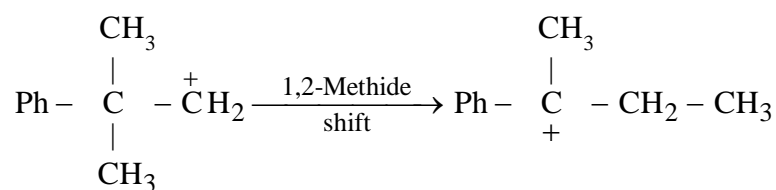Alkyl carbocations are stabilized by hyper conjugation.

Note : Hyperconjugation involve formation of 3C-2e bond.

Allylic and benzylic free radical, carbocation and carbanion are stabilized by resonance due to presence of conjugation.

Intermediate	Stability order
Free radical	tert-butyl > 1° benzyl ≈ 1° allyl > 3° alkyl > 2° alkyl > 1° alkyl > methyl
Carbocation	tert-butyl > 1° benzyl ≈ 1° allyl > 3° alkyl > 2° alkyl > 1° alkyl > methyl
Carbanion	1° benzyl > 1° allyl > methyl > 1° alkyl > 2° alkyl > 3° alkyl

Note : A carbocation of lower stability can rearrange to a carbocation of higher stability by 1,2-hybride, methide or phenide shift, if possible.

$$CH_3 - \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}} - \overset{+}{C}H_2 \xrightarrow[\text{shift}]{\text{1,2-Hydride}} CH_3 - \underset{\underset{+}{}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$$

$$\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{Ph-C}}-\overset{+}{C}H_2 \xrightarrow[\text{shift}]{\text{1,2-Methide}} Ph-\underset{+}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_3$$

Alkyl carbocation having cyclo alkyl group (with number of carbon atoms less than six) may undergo ring expansion because organic compound having five or six membered ring are more stable.

2° carbocation   2° carbocation   3° carbocation
(Five membered ring)   (Six membered ring)   (Six membered ring)
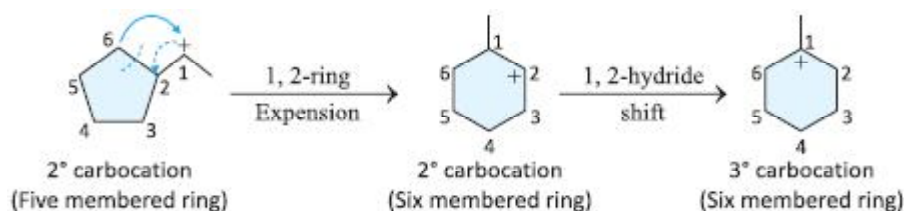
Such type of rearrangement is generally not observed in carbanion and free radicals.

The ionic organic reactions involve the bonding of a nucleophile (electron rich) to an electrophile (electron deficient). While free radical reactions involve the bonding of a free radical to a radical or neutral molecule.

Electrophile : An electron deficient atom, ion or molecule that has an affinity for an electron pair, and will bond to a Lewis base or nucleophile.

Nucleophile : An atom, ion or molecule that has an electron pair that may be donated in bonding to an electrophile (or Lewis acid)
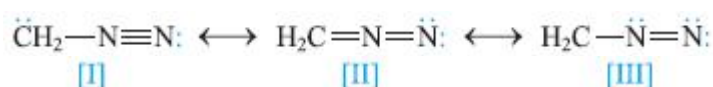
REVIEW EXERCISE

In the Chapter, "Introduction to Organic Chemistry", you have already learned about details of above basic concepts (Electrical effects, intermediates formed while visualising reaction mechanisms) and their simple uses in Section – 5 & 6. Before moving forward, please solve the following 'Review Exercise' so that you are not only able to review basic fundamental but also consolidate your understanding.

1.   What is the formal charge of oxygen in each of the following Lewis structures?

   (A) $CH_3\ddot{O}:$ (B) $(CH_3)_2\ddot{O}:$ (C) $(CH_3)_3O:$
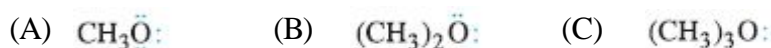
2.   Consider structural formulas I, II, and III :

$$\ddot{C}H_2 - N \equiv N: \longleftrightarrow H_2C = N = \ddot{N}: \longleftrightarrow H_2C - \ddot{N} = \ddot{N}:$$
$$[I] \qquad\qquad [II] \qquad\qquad [III]$$

   (A)   Are I, II and III constitutional isomers, or are they resonance forms ?
   (B)   Which structure have a negatively charged carbon?
   (C)   Which structure have a positively charged carbon ?
   (D)   Which structure have a positively charged nitrogen?
   (E)   Which structures have a negatively charged nitrogen ?
   (F)   Which is a more stable structure?
   (G)   Which structure have nucleophilic carbon?
   (H)   Which structures have electrophilic carbon?
   (I)   What is the CNN geometry in each structure according to VSEPR?

   Species [I], [II] and [III] have same molecular formula, the same atomic positions, and the same number of electrons. They differ only in the arrangement of their electrons.

NOW ATTEMPT REVIEW EXERCISE BEFORE PROCEEDING AHEAD IN THIS EBOOK

Classification of Organic Chemical Reactions :

1. Classification by Structural Change : On the basis of structural changes reactions of organic compounds are of following types.
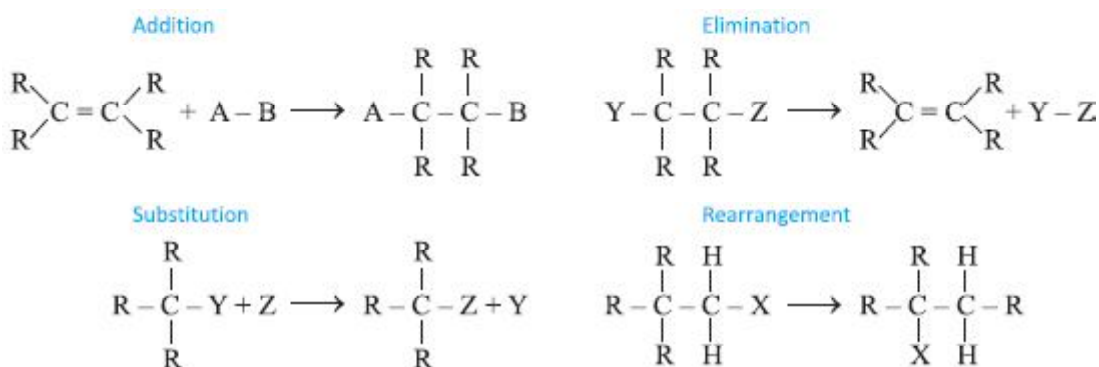
2. **Classification by Functional Group :** Functional groups are atoms or small groups of atoms (usually two to four) that exhibit a characteristic reactivity when treated with certain reagents.

A particular functional group will almost always display its characteristic chemical behaviour when it is present in a compound. The following table summarizes the general chemical behaviour of the common functional groups.

For reference, the alkanes provide a background of behaviour in the absence of more localized functional groups.

Functional Class	Formula	Characteristic Reactions
Alkanes	$C - C, C - H$	Substitution (of H, commonly by Cl or Br) Combustion (conversion to CO_2 and H_2O)
Alkenes	$C = C - C - H$	Addition and Substitution (of H)
Alkynes	$C \equiv C - H$	Addition and Substitution of (H)
Alkyl Halides	$H - C - C - X$	Substitution (of H) and Elimination (of HX)
Alcohols	$H - C - C - O - H$	Substitution (of H) ; Substitution (of OH) Elimination (of HOH) ; Oxidation (elimination of 2H)
Ethers	$(\alpha) \underset{H}{C} - O - R$	Substitution (of OR) ; Substitution (of $\alpha - H$)
Amines	$C - NH - R$	Substitution (of H) ; Addition (to N) ; Oxidation (of N)
Benzene Ring	C_6H_6	Substitution (of H)
Aldehydes	$(\alpha) \underset{H}{C} - \overset{O}{\underset{\|}{C}} - H$	Addition and Substitution (of H or $\alpha - H$)
Ketones	$(\alpha) \underset{H}{C} - \overset{O}{\underset{\|}{C}} - R$	Addition and Substitution (of H or $\alpha - H$)
Carboxylic Acids	$(\alpha) \underset{H}{C} - COOH$	Substitution (of H or $\alpha - H$) ; Substitution (of OH) ; Addition (to C = O)
Carboxylic Derivatives	$(\alpha) \underset{H}{C} - \overset{O}{\underset{\|}{C}} - Z$ $(Z = OR, Cl, NHR, etc.)$	Substitution (of Z) ; Substitution (of $\alpha - H$) Addition (to C = O)

Illustration - 1 *Some chemical reactions are shown below classify each as Addition, Elimination, Substitution.*
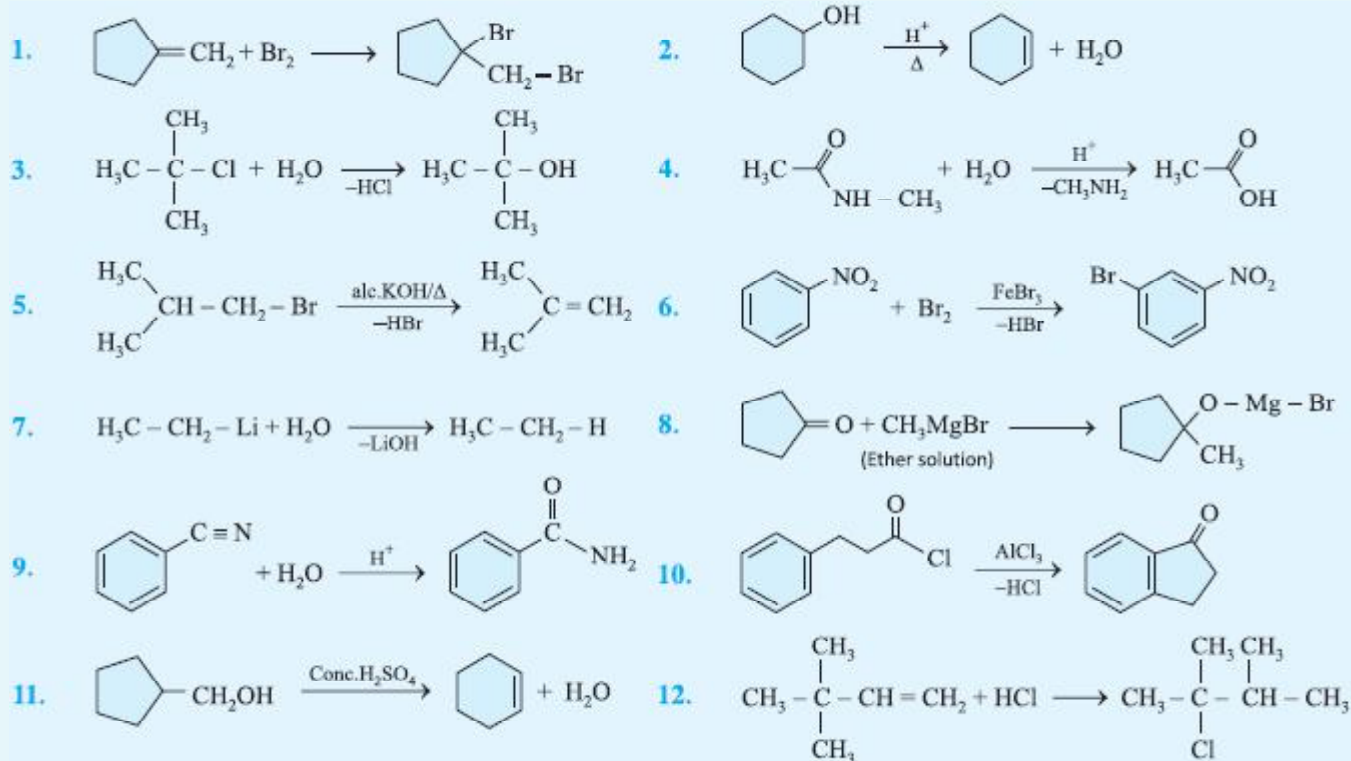
SOLUTION :

Addition : 1, 8, 9, 12
Elimination : 2, 5, 11
Substitution : 3, 4, 6, 7, 10

Organic Compounds having multiple bonds ($C = C$, $C \equiv C$, $C = O$, $C \equiv N$) undergoes addition reactions. Thus reaction 1, 8, 9 and 12 are addition reactions.

Reactions of organic compound that results in formation of multiple bonds ($C = C$, $C \equiv C$) are elimination reactions.
Thus reaction 2, 5 and 11 are elimination reactions.

Reaction in which one of the atom or group (H, halogen, OH etc.) is replaced by other substituent is called as substitution reaction. Thus reaction

3 [Cl is replaced by OH]

4 [CH_3NH is replaced by OH]

6 [H is replaced by Br]

7 [Li is replaced by H]

10 [Cl is replaced by acyl group] are substitution reactions.

Reaction 10 : Ring closure

Reaction 11 : Ring expansion

Reaction 12 : Rearrangement

3. Oxidation and Reduction Reactions :

Organic reactions can also be classified by oxidation-reduction terminology.

Carbon atoms may have any oxidation state from -4 (e.g. CH_4) to $+4$ (e.g. CO_2), depending upon their substituents. Fortunately, we need not determine the absolute oxidation state of each carbon atom in a molecule, but only the change in oxidation state of those carbons involved in a chemical transformation. To determine whether a carbon atom has undergone a redox change during a reaction, we simply note any changes in the number of H bonded to carbon and the number of bonds to more electronegative atoms such as O, N, F, Cl, Br, I, and S that has occurred. Bonds to other carbon atoms are ignored.

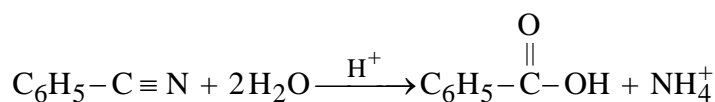This count should be conducted for each carbon atom undergoing any change during a reaction.

(i) If the number of hydrogen atoms bonded to a carbon increases, and/or if the number of bonds to more electronegative atoms decreases, the carbon in question has been reduced (i.e. it is in a lower oxidation state).

$$CH_3 - CH = O \xrightarrow{\text{NaBH}_4} CH_3 - CH_2 - OH$$
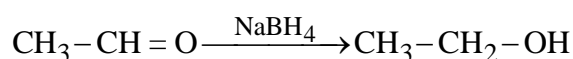
(ii) If the number of hydrogen atoms bonded to a carbon decreases, and/or of the number of bonds to more electronegative atoms increases, the carbon in question has been oxidized (i.e. it is in a higher oxidation state).

$$CH_3 - CH_2 - OH \xrightarrow[\text{H}^+]{\text{K}_2\text{Cr}_2\text{O}_7} CH_3 - COOH$$
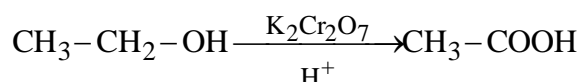
(iii) If there has been no change in the number of such bond, then the carbon in question has not changed its oxidation state. In the hydrolysis reaction of a nitrile shown below, the carbon atom of –CN group has not changed its oxidation state.

$$C_6H_5 - C \equiv N + 2H_2O \xrightarrow{\text{H}^+} C_6H_5 - \overset{\overset{\displaystyle O}{\|}}{C} - OH + NH_4^+$$

Oxidizing Agents

	Reagent	Functions Oxidized
1.	$KMnO_4$	Aldehyde to carboxylic acids 1°-primary alcohols to carboxylic acids and 2°-alcohols to ketones Alkynes to carboxylic acid ; Alkene to carboxylic acid or ketone Alkenes to vicinal diols [If $KMnO_4$ is cold and alkaline]
2.	OsO_4	Alkenes to vicinal diols
3.	H_2CrO_4 (Jone's reagent)	1°-alcohols to carboxylic acids ; Aldehydes to carboxylic acids. 2°-alcohols to ketones (It does not oxidise $C = C$ bond)
4.	PCC Pyridinium chlorochromate $ClCrO_3C_5H_5NH$	1°-alcohols to aldehydes 2°-alcohols to ketones (It does not oxidise $C = C$ bond)

	Reagent	Functions Oxidized
5.	HIO_4	vicinal-glycols to carbonyl compounds
6.	LTA [Lead tetra acetate] $Pb(CH_3COO)_4$	vicinal-glycols to carbonyl compounds
7.	Peroxy acids (RCO_3H) CH_3COOOH	Alkene to epoxides ; ketones to esters
8.	Ozone (O_3)/Zn	Cleaves alkenes to keto & oxidises alkynes to diketo compounds
9.	SeO_2	$\alpha - C - H$ of aldehyde to α-ketoaldehyde $\alpha - C - H$ of alkene to allylic alcohols
10.	Tollen's reagent	Aldehyde to carboxylic acids
11.	MnO_2	1°(allylic or benzylic) alcohol to aldehyde 2°(allylic or benzylic) alcohol to ketone

Reducing Agents

	Reagent	Functions Reduced
1.	H_2/catalyst H_2/Pt or Pd or Ni	Alkenes to alkane ; Alkynes to alkane ; Aldehydes to alcohols ; Ketones to alcohols ; Nitro compounds to amines ; Ester to 1° alcohol; Nitriles to amines
2.	H_2/poisoned catalyst (Lindlar's catalyst)	Alkynes to alkene ; Acyl chlorides to aldehydes (syn addition)
3.	$NaBH_4/H_2O$	Aldehydes to 1°-alcohols, Ketones to 2°-alcohols
4.	$LiAlH_4$/Ether	Aldehydes to 1°-alcohols, Ketones to 2°-alcohols, carboxylic acids to 1°-alcohols, Esters to 1°-alcohols, epoxides to alcohols, nitriles to amines, amides to amines, halides to alkanes.
5.	DIBAL-H Di-isobutyl aluminium hydride	Acid chlorides to aldehydes, nitriles to aldehydes, esters to aldehydes
6.	Diborane	Carboxylic acid to 1°-alcohols, aldehydes to 1°-alcohols, Ketones to 2°-alcohols, nitriles to amines, esters to 1°-alcohols
7.	Zn-Hg/conc. HCl	Aldehydes to alkanes, Ketones to alkanes
8.	NH_2NH_2/alc. KOH/glycol	Aldehydes to alkanes, Ketones to alkanes
9.	Na or Li/NH_3 (ℓ)	Alkynes to alkene (anti addition), benzene to cyclohexa-1, 4-diene
10.	Sn/HCl	Nitro compounds to amines, nitriles to imines
11.	Red P/HI/Δ	Aldehydes to alkanes, ketones to alkanes, carboxylic acid to alkanes Alcohols to alkanes
12.	H_2/Pd-C/MeOH	Specially reduces unsaturated compounds to saturated ; does not reduce majority of other functional groups.

Illustration - 2 *Consider the following four addition reactions involving the same starting material, cyclohexene. Identify in which reaction carbon in question has been reduced or oxidized or has not changed its oxidation state.*
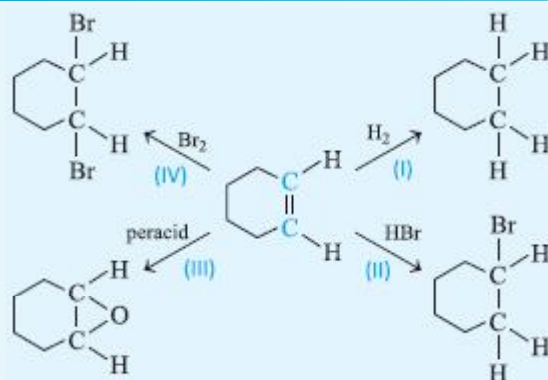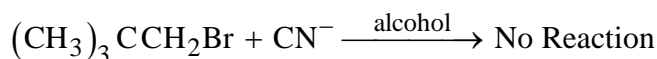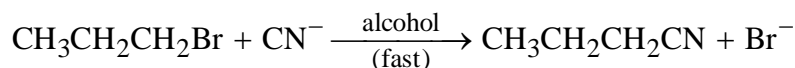

SOLUTION :

In the addition of hydrogen both carbon atoms are reduced, and the overall reaction is termed a reduction (I). Peracid does epoxidation (III) and addition of Br_2 (IV) oxidize both carbon atoms, so this will be oxidation (IV). The addition of HBr in (II) reduces one of the double bond carbon atoms and oxidizes the other ; consequently, there is no overall redox change in the substrate molecule (II).

The Variables of Organic Reactions :

The various important properties and characteristics of a reaction that may be observed and/or measured as the reaction proceeds are listed below.

1. **Reactant Structure :** Variation in the structure of the reactant may have a marked influence on the course of a reaction, even though the functional group is unchanged. Thus, reaction of 1-bromopropane with sodium cyanide proceeds smoothly to yield butanenitrile, whereas 1-bromo-2, 2-dimethylpropane fails to give any product and is recovered unchanged. In contrast, both alkylbromides form Grignard reagents (RMgBr) on reaction with magnesium.

$$CH_3CH_2CH_2Br + CN^- \xrightarrow[\text{(fast)}]{\text{alcohol}} CH_3CH_2CH_2CN + Br^-$$

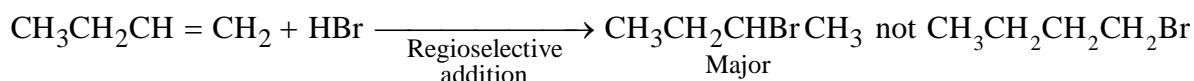$$\left(CH_3\right)_3 CCH_2Br + CN^- \xrightarrow{\text{alcohol}} \text{No Reaction}$$

2. **Reagent Characteristics :** The minor changes in a reagent may lead to a significant change in the course of a reaction. For example, 2-bromopropane gives a substitution reaction with sodium methylthiolate (CH_3SNa) but undergoes elimination on treatment with sodium methoxide (CH_3ONa).
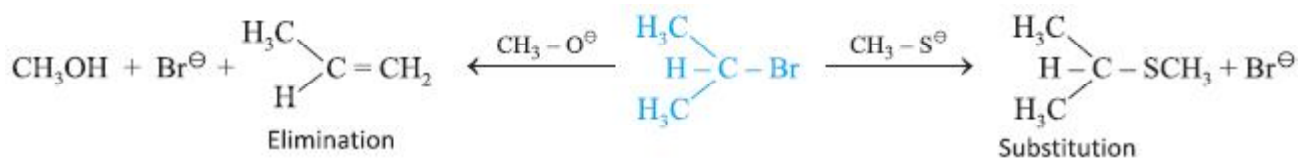
3. **Product Selectivity :**

    (A) **Regioselectivity :** It is often the case that addition and elimination reactions may, in principle, proceed to more than one product. Thus 1-butene might add HBr to give either 1-bromobutane or 2-bromobutane, depending on which carbon of the double bond receives the hydrogen and which the bromine. If one possible product out of two or more is formed preferentially, the reaction is said to be regioselective.

$$CH_3CH_2CH = CH_2 + HBr \xrightarrow[\text{addition}]{\text{Regioselective}} \underset{\text{Major}}{CH_3CH_2CHBr\,CH_3} \text{ not } CH_3CH_2CH_2CH_2Br$$

Simple substitution reactions are not normally considered regioselective, since by definition only one consti -tutional product is possible. However, rearrangements are known to occur during some reactions.

(B) Stereoselectivity : If the reaction's products are such that stereoisomer may be formed ; a reaction that yield one stereoisomer preferentially is said to be stereoselective. In the addition of bromine to cyclohexene, for example, cis and trans-1, 2-dibromocyclohexane are both possible products of the addition. Since the trans-isomer is the only isolated product, due to *anti-addition*, this reaction is stereoselective.

In the partial hydrogenation of 2-butyne using Lindlar's catalyst, *cis* and *trans*-2-butene are both possible products of the addition. Since the cis-isomer is the only product obtained, due to *syn*-addition, this reac-tion is also sterco-selective.
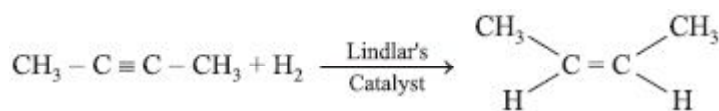
(C) Stereospecifically : This term is applied to cases in which stereoisomeric reactants behave differently in a given reaction. Examples

(i) Formation of different stereoisomeric products, as in the reaction of stereoisomeric 2-butene isomer with Br_2/CCl_4, shown in the following diagram.
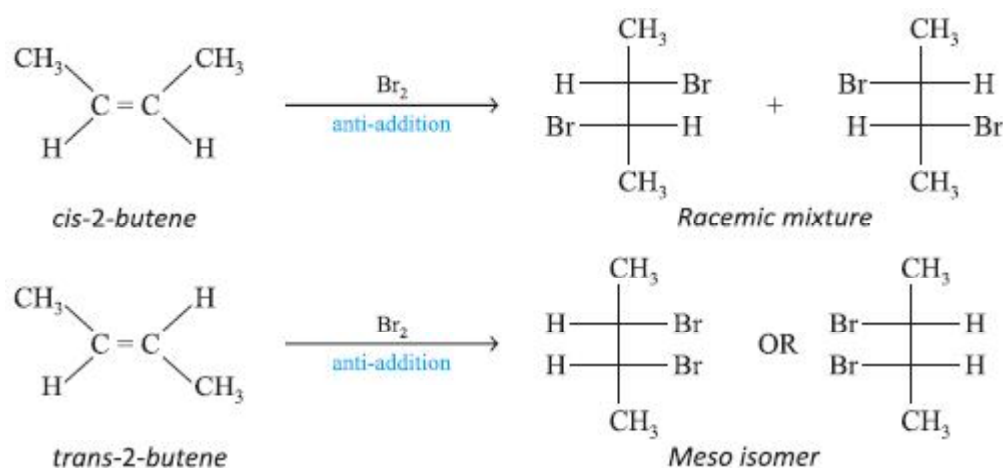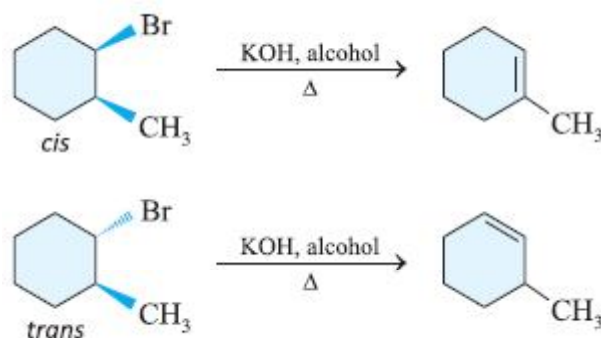
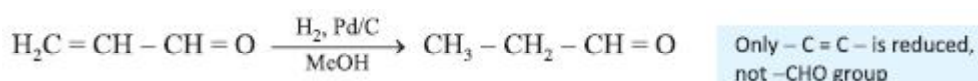Here, the *cis*-isomer gives the racemic mixture and *trans*-isomer produces *meso*-isomers of 2, 3-dibromo butane.

(ii) Different rates of reaction, as in the base-induced elimination of cis & trans-4-tert-butylcyclohexylbromide.

(iii) Different reaction paths leading to different products, as in the base-induced elimination of cis & trans-2-methylcyclohexyl bromide.
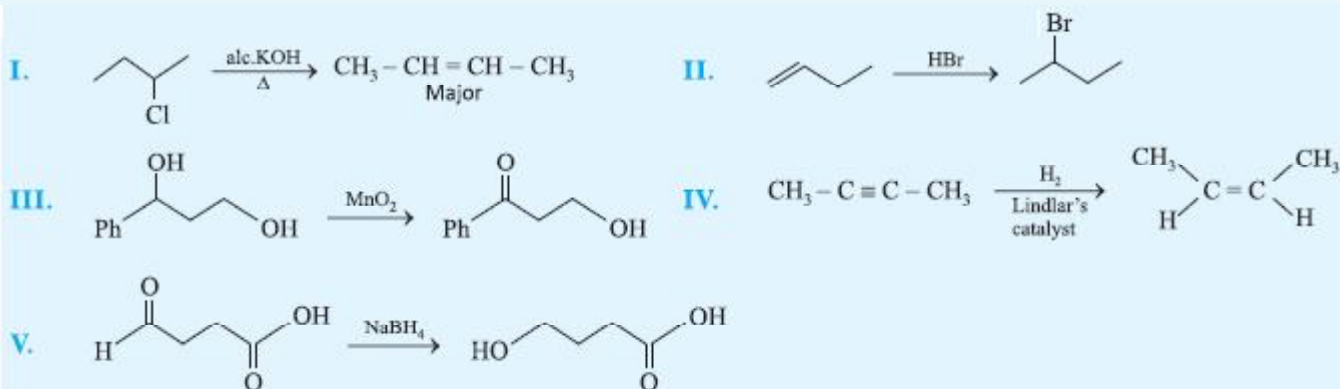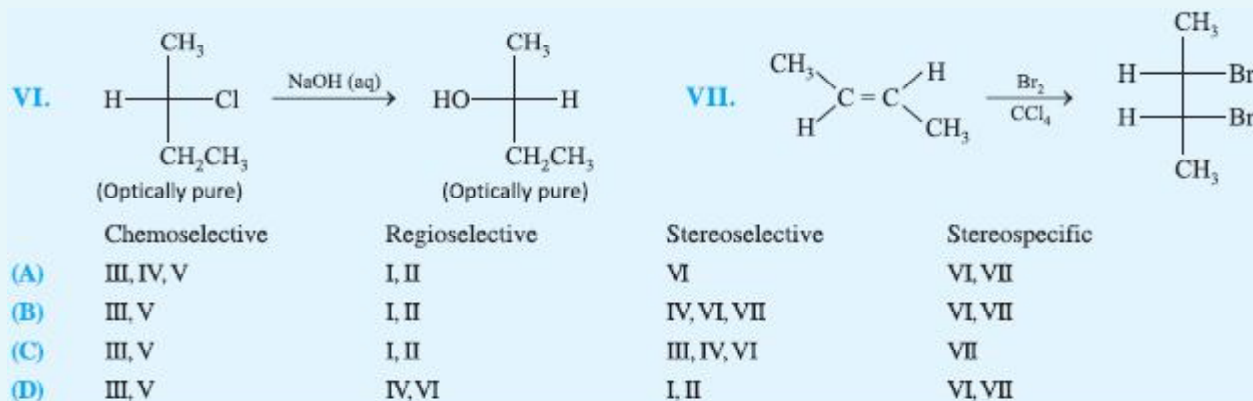

Note : A reaction in which a reagent selectively reacts with one of the functional group of a poly functional group compound is called as Chemoselective reaction.

$$H_2C = CH - CH = O \xrightarrow[\text{MeOH}]{H_2, \text{Pd/C}} CH_3 - CH_2 - CH = O \qquad \text{Only} - C = C - \text{is reduced, not } -CHO \text{ group}$$

Illustration - 3   *Consider the following reactions and identify their correct classification.*

	Chemoselective	Regioselective	Stereoselective	Stereospecific
(A)	III, IV, V	I, II	VI	VI, VII
(B)	III, V	I, II	IV, VI, VII	VI, VII
(C)	III, V	I, II	III, IV, VI	VII
(D)	III, V	IV, VI	I, II	VI, VII

SOLUTION : (B)

I and II are regioselective reaction.

In I and II two structural isomers of the product can be formed but only one isomer is formed as an exclusive product or in major amount hence these two reactions are regioselective reaction.

III and V are chemoselective. In III MnO_2 acts as an oxidising agent and it selectively oxidise only allylic or benzylic C – OH bond to C = O bond. So this reaction is chemoselective. Similarly $NaBH_4$ is selectively reduces aldehyde to alcohols not carboxylic acid.

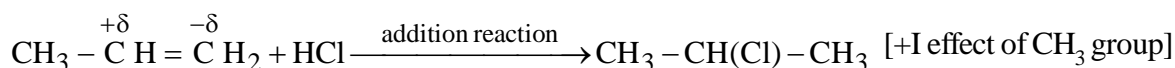IV is stereoselective because only one stereoisomer of the product is formed.

VI and VII are stereoselective as well as stereospecific because a particular stereoisomeric reactant reacts to give a particular stereoisomers of the product.
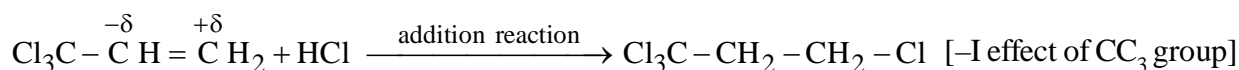
4. **Factors that Influence Reactions :** Some of the most important factors that influence reactions are as follows.

   (A) **Energetics :** The potential energy of a reacting system changes as the reaction progresses. The overall change may be exothermic (energy is released) or endothermic (energy must be added) and there is usually an activation energy requirement as well. As a rule, compounds constructed of strong covalent bonds are more stable than compounds incorporating one or more relatively weak bonds.
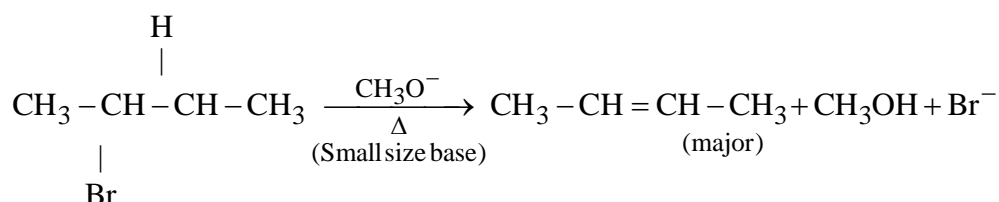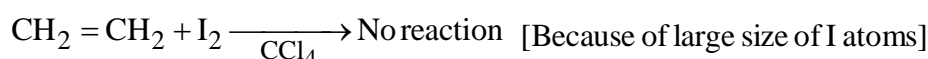
   $$CH_2 = CH_2 + H_2 \longrightarrow CH_3 — CH_3 \; ; \Delta H < 0 \text{ [Addition reaction]}$$

   $$CH_3 — CH_2 — Cl \xrightarrow[\Delta]{\text{alc.KOH}} CH_2 = CH_2 \; ; \Delta H > 0 \text{ [Elimination reaction]}$$
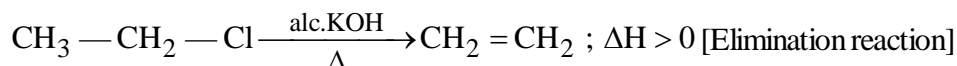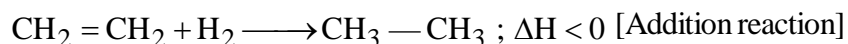
   (B) **Electronic Effect :** The distribution of electrons at sites of reaction (functional groups) is a particularly important factor. The charge distribution in a molecule is usually discussed with respect to two interacting effects such as inductive effect and resonance effect. [As discussed in chapter IOC]
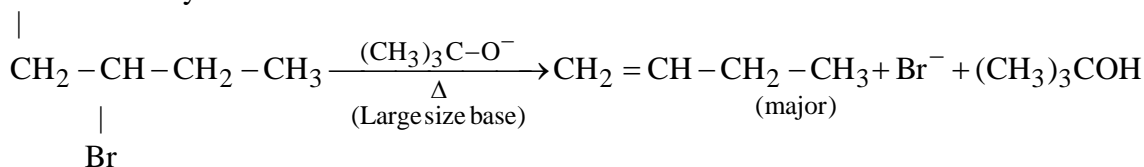
   $$CH_3 - \overset{+\delta}{C}H = \overset{-\delta}{C}H_2 + HCl \xrightarrow{\text{addition reaction}} CH_3 - CH(Cl) - CH_3 \text{ [+I effect of } CH_3 \text{ group]}$$

$$\overset{-\delta}{Cl_3C - \overset{}{C}} H = \overset{+\delta}{\overset{}{C}} H_2 + HCl \xrightarrow{\text{addition reaction}} Cl_3C - CH_2 - CH_2 - Cl \quad [\text{–I effect of } CC_3 \text{ group}]$$

(C)   **Steric Effect :** Atoms occupy space, when they are crowded together, vander Waals repulsions produce an unfavourable steric hinderance. Steric hinderance may influence conformational equilibria, as well as destabilizing transition states of reactions.

$$CH_2 = CH_2 + Cl_2 \xrightarrow[CCl_4]{} Cl - CH_2 - CH_2 - Cl$$

$$CH_2 = CH_2 + I_2 \xrightarrow[CCl_4]{} \text{No reaction} \quad [\text{Because of large size of I atoms}]$$

$$CH_3 - \underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{CH}} - CH - CH_3 \xrightarrow[\Delta]{CH_3O^-} CH_3 - CH = CH - CH_3 + CH_3OH + Br^-$$
$$\text{(Small size base)} \qquad \text{(major)}$$

$$\text{H} \leftarrow \text{Sterically unhindered H atom}$$
$$\underset{\underset{Br}{|}}{\overset{|}{CH_2}} - CH - CH_2 - CH_3 \xrightarrow[\Delta]{(CH_3)_3C-O^-} CH_2 = CH - CH_2 - CH_3 + Br^- + (CH_3)_3COH$$
$$\text{(Large size base)} \qquad \text{(major)}$$

(D)   **Solvent Effect :** Most reactions are conducted in solution, not in a gaseous state. The solvent selected for a given reactions may exert a strong influence on its course. Remember, solvents are chemicals and most undergo chemical reaction under the right conditions.

For example nitrobenzene can be used as solvent for F.C. acylation reaction of aromatic compounds although it is also an aromatic compound because -NO$_2$ group deactivates benzene ring for electrophilic substitution reaction. *You will study role of solvent in later reac -tions.*

Stability :

Common use of the term stability implies an object, system or situation that is likely to remain unchanged for a significant period of time. In chemistry, however, we often refer to two kinds of stability.

Thermodynamic Stability : Thermodynamic stability refers to the potential energy of a compound relative to a reference state. It is related to the bond energies of its constituent atoms. For exothermic reactions we may say that the products are thermodynamically more stable than the reactants. The opposite would be true for endothermic reactions.

Chemical Stability : The chemical stability refers to resistance of a compound or mixture of compounds to chemical change (reaction) with a variety of reagents. It is related to the activation energy barrier it presents to possible chemical change.
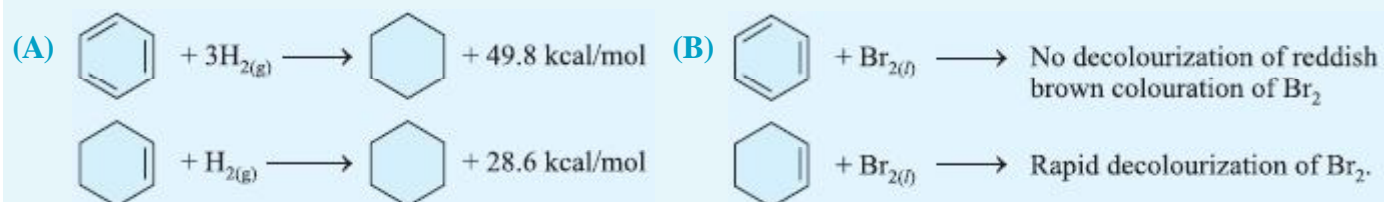
For example, benzene is thermodynamically unstable compared with elemental carbon and hydrogen, but it is chemically stable under normal laboratory conditions, even when mixed with some reactive compounds such as bromine.

Note : Compounds or mixtures that are chemically unstable are often called labile.

Kinetic Vs Thermodynamic Control :

In some reactions different products are formed at different temperature depending upon kinetics and thermodynamics of the reaction. At low temperature, the products are formed irreversibly and reflect rates of the two competing reaction. This is termed as *kinetic control* and product formed is called as *kinetically controlled product* i.e. product that has higher rate of formation. At higher temperatures, equilibrium is established between the products, and the thermodynamically favoured product dominates (product stable at higher temperature). In the case it is called as *thermodynamic control* and product is called as *thermodynamically controlled product*. For illustration refer Chapter hydrocarbon, reactions of conjugated dienes

Illustration - 4   *Consider the following reactions of benzene and cyclohexene as given below. Identify thermodynamically stable and chemically stable reactant.*

(A) $\bigcirc + 3H_{2(g)} \longrightarrow \bigcirc + 49.8$ kcal/mol   (B) $\bigcirc + Br_{2(l)} \longrightarrow$ No decolourization of reddish brown colouration of Br_2

$\bigcirc + H_{2(g)} \longrightarrow \bigcirc + 28.6$ kcal/mol $\bigcirc + Br_{2(l)} \longrightarrow$ Rapid decolourization of Br_2.

SOLUTION :

From heats of hydrogenation we find that cyclohexene has a potential energy roughly 28.6 kcal/mol higher than cyclohexane, whereas benzene is 48.9 kcal/mol above cyclohexane. We conclude from these measurments that both cyclohexene and benzene are thermodynamically less stable than cyclohexane, and that benzene is thermodynamically less stable than cyclohexene. We know, however, that the chemical reactivity of these unsaturated compounds does not reflect this stability order. cyclohexene reacts rapidly with bromine, whereas benzene is relatively inert to bromine (in the absence of catalyst and/or heat).The chemical reactivity of benzene is therefore less than the reactivity of cyclohexene, and we may say that benzene is chemically more stable than cyclohexene -at least toward the reagent noted here.
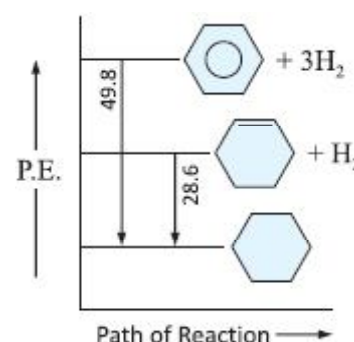
Just as a chain is no stronger than its weakest link, a molecule may be rendered chemically unstable by one weak bond. We see this in the chemical behaviour of peroxides (R–O–O–R). The O–O bond is less than half as strong as a C–C bond, and peroxides are notoriously unstable, decomposing via alkoxy radicals (R–O) on mild heating.
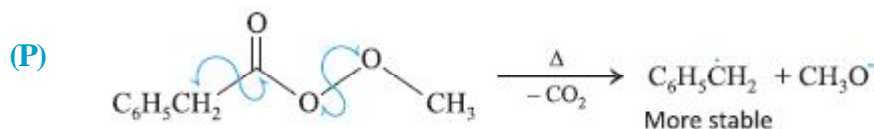
Illustration - 5 *Different possible thermal decomposition pathways for peroxyesters are shown below. Match each pathway from List I with an appropriate structure from List II and select the correct answer using the code given below the lists.*
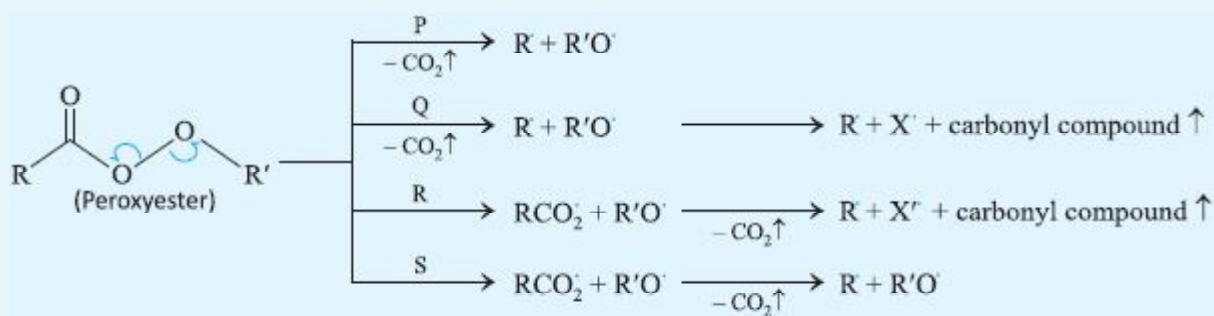
List - I   **List - II**

(P) Pathway P   1.

(Q) Pathway Q   2.

(R) Pathway R   3.

(S) Pathway S   4.

Codes :

	P	Q	R	S			P	Q	R	S
(A)	1	3	4	2		(B)	2	4	3	1
(C)	4	1	2	3		(D)	3	2	1	4

SOLUTION : (A)

(P)

(Q)

$$C_6H_5CH_2 \cdot \overset{O}{\underset{||}{C}} - O - O - \overset{CH_3}{\underset{CH_2C_6H_5}{\overset{|}{C}}} - CH_3 \xrightarrow[-CO_2]{\Delta} C_6H_5\dot{C}H_2 + \underset{C_6H_5CH_2}{\overset{CH_3}{\diagdown}} \overset{CH_3}{\diagup} O \cdot \longrightarrow C_6H_5\dot{C}H_2 + CH_3COCH_3\uparrow$$

Carbonyl compound

(R)

$$C_6H_5 \cdot \overset{O}{\underset{||}{C}} - O - O - \overset{CH_3}{\underset{C_6H_5}{\overset{|}{C}}} - CH_3 \xrightarrow{\Delta} \overset{O}{\underset{||}{C_6H_5 - C}} - O \cdot + \underset{C_6H_5}{\overset{CH_3}{\diagdown}} \overset{CH_3}{\diagup} O \cdot \longrightarrow \dot{C}_6H_5 + CH_3COCH_3\uparrow$$

$$C_6H_5\dot{} \xleftarrow{-CO_2\uparrow}$$

Carbonyl compound

(S)

$$C_6H_5 \cdot \overset{O}{\underset{||}{C}} - O - O - CH_3 \xrightarrow{\Delta} \overset{O}{\underset{||}{C_6H_5 - C}} - O \cdot + CH_3O\cdot$$

$$C_6H_5\dot{} \xleftarrow{-CO_2\uparrow}$$
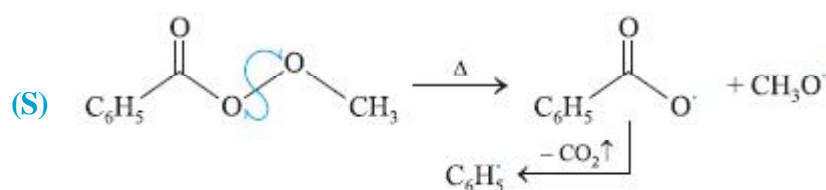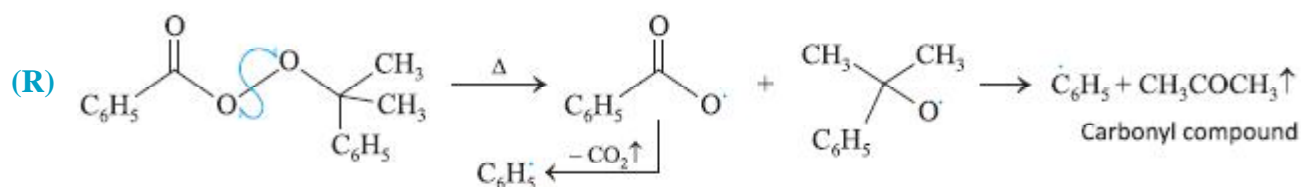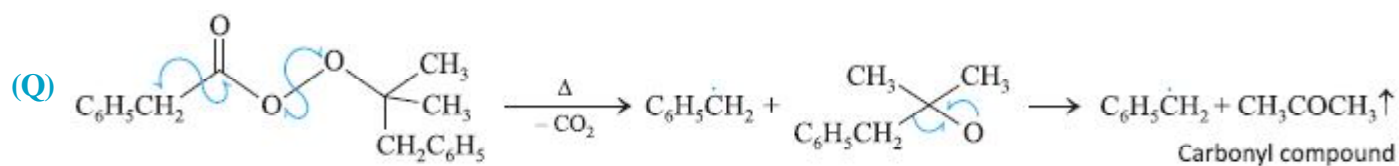
Note :   Other radical initiators are given below.

$$CH_3 - \overset{CH_3}{\underset{CH_3}{\overset{|}{C}}} - O - O - \overset{CH_3}{\underset{CH_3}{\overset{|}{C}}} - CH_3 \xrightarrow[hv]{\Delta} 2CH_3 - \overset{CH_3}{\underset{CH_3}{\overset{|}{C}}} - O\cdot \quad ; \quad CH_3 - \overset{CN}{\underset{CH_3}{\overset{|}{C}}} - N = N - \overset{CN}{\underset{CH_3}{\overset{|}{C}}} - CH_3 \xrightarrow[hv]{\Delta} 2CH_3 - \overset{CN}{\underset{CH_3}{\overset{|}{C}}}\cdot + N_2$$

t-butyl peroxide   Azobisisobutyronitrile [AIBN]
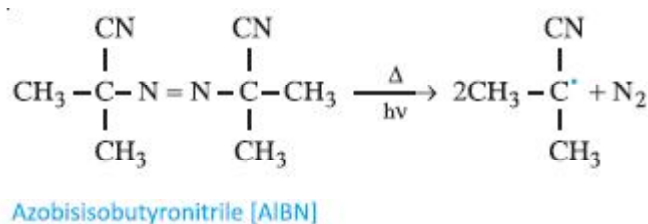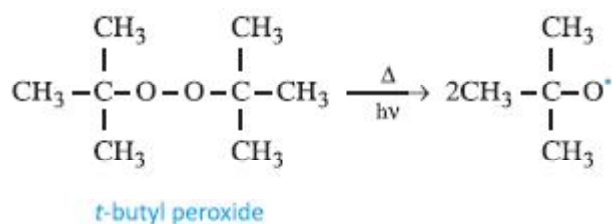
REACTION MECHANISM (A Detailed view)   Section - 2

Let us now discuss the mechanisms of Substitution, Addition and Elimination Reactions in detail.

2.A Substitution (Displacement) Reaction :

The replacement of an atom or group from a molecule by a different atom or group is called as substitution reaction.

$$RH + X_2 \longrightarrow RX + HX$$

$$RX + NaOH(aq) \longrightarrow ROH + NaX$$

$$C_6H_6 + RCl \xrightarrow{AlCl_3} C_6H_5R + HCl$$
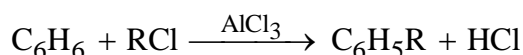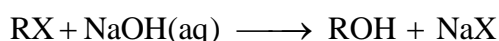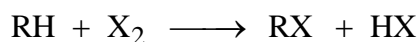
These reactions are further divided into three types depending upon the type of attacking reagent.

(a)   Free - radical   **(b)**   Nucleophilic   **(c)**   Electrophilic

Mechanism of Substitution Reactions :

(a)   Free Radical Substitution : It is free radical reaction and involve homolytic cleavage of bonds.

Consider halogenation in alkanes :

It is supposed to proceed via the *Free Radical Chain Mechanism* involving the following three steps.

(i)   Initiation : $Cl - Cl \xrightarrow[\text{homolysis}]{h\nu} Cl^\circ + Cl^\circ$

   Chlorine free radicals

(ii)   Propagation : $CH_4 + Cl^\circ \longrightarrow CH_3^\circ + H - Cl$

   Methyl free radicals

$$CH_3^\circ + Cl - Cl \xrightarrow{h\nu} CH_3 - Cl + Cl^\circ$$

   Chlorine free radicals
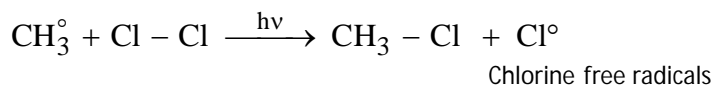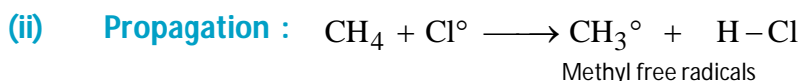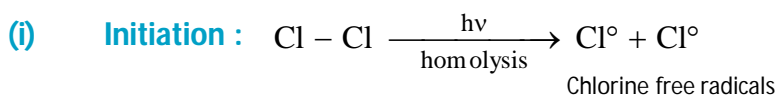
The chlorine and methyl free radicals generated above, repeat these steps and thereby set up a chain of reactions. Other propagation steps are also possible and may occur.

$$CH_3Cl + Cl^\circ \longrightarrow ClCH_2^\circ + HCl$$

$$ClCH_2^\circ + Cl - Cl \longrightarrow CH_2Cl_2 + Cl^\circ$$
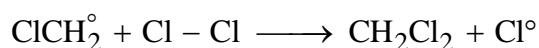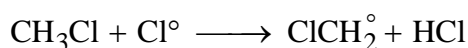
(iii)   Termination :

The reaction stops after some time due to consumption of reactants and (or) due to the following side reactions.

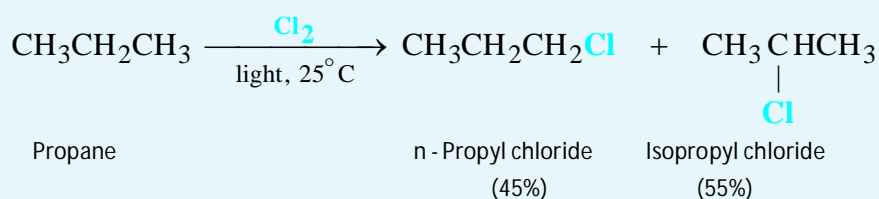The possible chain terminating steps are :

$$Cl^{\circ} + Cl^{\circ} \longrightarrow Cl - Cl \quad ; \quad \overset{\circ}{CH_3} + \overset{\circ}{CH_3} \longrightarrow CH_3 - CH_3$$

$$\overset{\circ}{CH_3} + Cl^{\circ} \longrightarrow CH_3 - Cl$$
$$\text{Halogenated alkane}$$
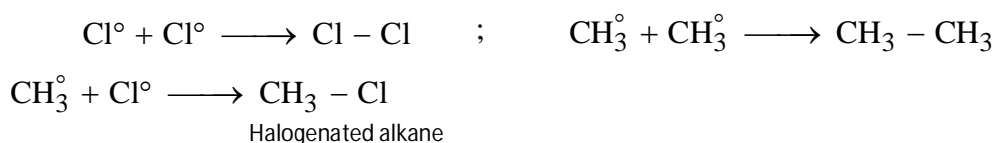
The above mechanism justifies the formation of ethane, which is actually isolated as a by product during chlorination of methane.
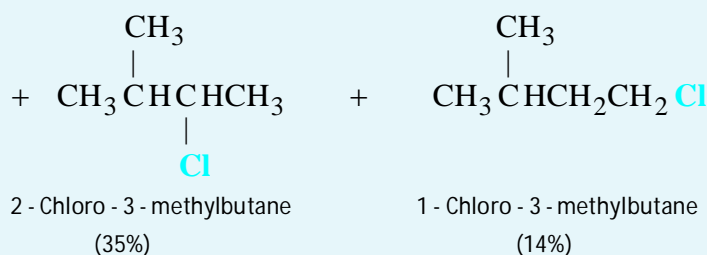
Note : **(i)** Rate of reaction of Halogens with alkanes, follows the order : $F_2 > Cl_2 > Br_2 > I_2$
Fluorination is too violent to be controlled, while Iodination is very slow and a reversible reaction. Iodination can be carried out in the pressure of oxidizing agents such as HIO_3 or HNO_3.

$$CH_4 + I_4 \rightleftharpoons CH_3I + HI \quad ; \quad HIO_3 + 5HI \longrightarrow 3I_2 + 3H_2O$$
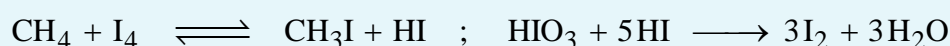
(ii) Chlorination of most alkanes whose molecules contain more than two carbon atoms gives a mixture of isomeric monochloro products (as well as more highly chlorinated compounds). Some examples are given below. The percentages given are based on the total amount of monochloro products formed in each reaction. The number of mono-halogenated products formed are equal to the number of different type of H-atoms.

$$CH_3CH_2CH_3 \xrightarrow[\text{light, } 25^{\circ}C]{Cl_2} CH_3CH_2CH_2Cl \quad + \quad CH_3\underset{|}{\overset{}{C}}HCH_3$$
$$\underset{Cl}{|}$$

Propane	n - Propyl chloride (45%)	Isopropyl chloride (55%)

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{light, } 25°C]{Cl_2} CH_3CH_2CH_2CH_2Cl \quad + \quad CH_3 - \underset{|}{CH} - CH_2 - CH_3$$
$$\underset{Cl}{|}$$

n-Butane	n - Butyl chloride (28%)	sec - Butyl chloride (72%)

$$\overset{\overset{CH_3}{|}}{CH_3\underset{}{C}H_2CH_3} \xrightarrow[\text{light, } 25^{\circ}C]{Cl_2} \overset{\overset{CH_3}{|}}{CH_3\underset{}{C}HCH_2Cl} \quad + \quad \overset{\overset{CH_3}{|}}{CH_3\underset{\underset{Cl}{|}}{C}CH_3}$$

Isobutane	Isobutyl chloride (63%)	tert - Butyl chloride (37%)

$$\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{CH_3\,C\,CH_2CH_3}} \xrightarrow[300^{\circ}C]{Cl_2} \overset{\overset{CH_3}{|}}{ClCH_2\,CHCH_2CH_3} \quad + \quad \overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{CH_3\,C\,CH_2CH_3}}$$

2 - Methylbutane	1 - Chloro - 2 - methylbutane (28%)	2 - Chloro - 2 - methylbutane (23%)

$$\text{+} \quad \underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{CH_3\,CHCHCH_3}} \quad \text{+} \quad \underset{}{\overset{\overset{\displaystyle CH_3}{|}}{CH_3\,CHCH_2CH_2\,\textbf{Cl}}}$$

2 - Chloro - 3 - methylbutane   1 - Chloro - 3 - methylbutane

(35%)   (14%)

➤ The ratios of products that we obtain in chlorination reactions of higher alkanes are not identical with what we would except if all the hydrogen atoms of the alkane were equally reactive. We find that there is a correlation between reactivity of different hydrogen atoms and the type of hydrogen atom ($1°$, $2°$ or $3°$) being replaced. The tertiary hydrogen atoms of an alkane are most reactive, secondary hydrogen atoms are next most reactive, and primary hydrogen atoms are the least reactive.

(iii) Bromine is less reactive toward alkanes in general than chlorine, but bromine is more selective in the site of attack when it does react. Bromine shows a much greater ability to discriminate among the different types of hydrogenatoms.

The reaction of isobutane and bromine, for example, gives almost exclusive replacement of the tertiary hydrogen atom.

$$\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{CH_3\!-\!C\!-\!CH_3}} \xrightarrow[\text{light, } 25°C]{\textbf{Br}_2} \underset{\underset{\displaystyle \textbf{Br}}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{CH_3\!-\!C\!-\!CH_3}} \;+\; \underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{CH_3\,CH_2\textbf{Br}}}$$

(~ 99%)   (Trace)
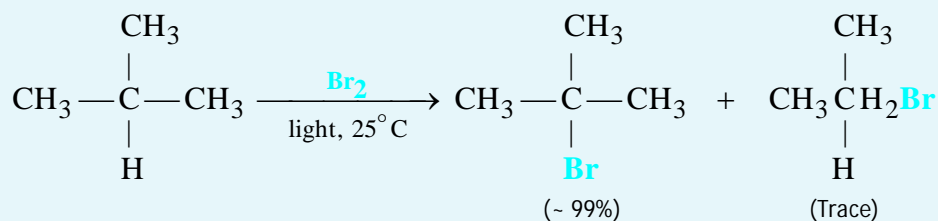
Thus bromination is highly selective reaction.

(iv) Relative rate of substitution of H-atoms of alkane in free radical halogenation is :

$$F_2 \;\Rightarrow\; 3°H \;:\; 2°H \;:\; 1°H \;;\; 1.4:1.2:1$$
$$Cl_2 \;\Rightarrow\; 3°H \;:\; 2°H \;:\; 1°H \;;\; 5:3.8:1$$
$$Br_2 \;\Rightarrow\; 3°H \;:\; 2°H \;:\; 1°H \;;\; 1600:82:1$$
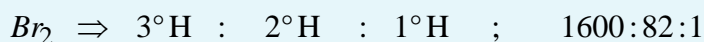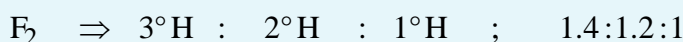
(v) Fluorine, being much more reactive than chlorine, is even less selective than chlorine. Because the energy of activation for the abstraction of any type of hydrogen by a fluorine atom is low, there is very little difference in the rate at which a $1°$, $2°$ or $3°$ hydrogen reacts with fluorine. Reactions of alkanes with fluorine give (almost) the distribution of products that we would expect if all of the hydrogens of the alkane were equally reactive.

Illustration - 6 *The relative reactivity of* $1° : 2° : 3°$ *hydrogen to chlorination is* $1 : 3.8 : 5$*. Calculate the percentage of all the monochlorinated products obtained from 2-methylbutane.*

SOLUTION :

$$\overset{1°}{H_3C} - \overset{3°}{CH_2} - \overset{2°}{CH} - \overset{1°}{CH_3}$$
$$| $$
$$\underset{1°}{CH_3}$$
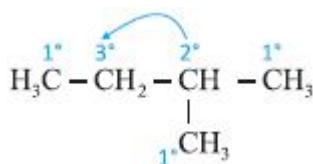
Observe that 2-Methyl butane has $9 - 1°$ H-atoms (6-H atoms are of one type and 3-H atoms are of other type).

Hence products are :   **Relative Amounts**

I. $CH_3 - CH - CH_2CH_2Cl$ $\equiv 3 \times 1 = 3$
$$| $$
$$CH_3$$

II. $CH_3 - CH - CH_2CH_3$ $\equiv 6 \times 1 = 6$
$$| $$
$$CH_2Cl$$
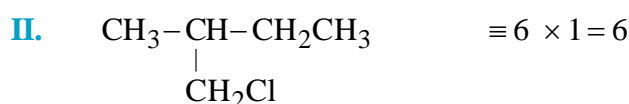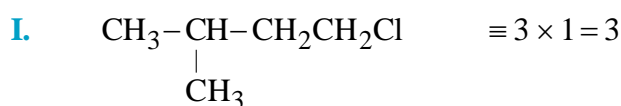
(Reactivity order of $1° : 2° : 3° \equiv 1 : 3.8 : 5$)

Observe that there are $2 - 2°$ H-atoms ; accordingly the product is :

$$Cl$$
$$| $$
III. $CH_3 - CH - CH - CH_3$ $\equiv 2 \times 3.8 = 7.6$
$$| $$
$$CH_3$$
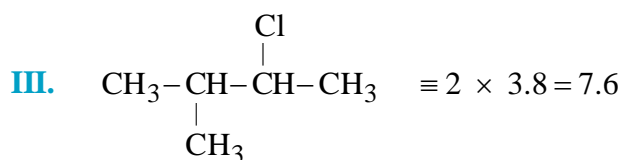
Finally there is only $1 - 3°$ H-atom.

Relative Amounts

$$Cl$$
$$| $$
IV. $CH_3 - C - CH_2CH_3$ $\equiv 1 \times 5 = 5$
$$| $$
$$CH_3$$
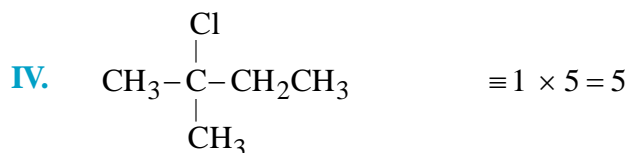
Hence percentages of products are :

(i) $\dfrac{3}{21.6} \times 100 = 13.89$

(ii) $\dfrac{6}{21.6} \times 100 = 27.78$

(iii) $\dfrac{7.6}{21.6} \times 100 = 35.18$

(iv) $\dfrac{5}{21.6} \times 100 = 23.15$

Note : This is true only for chlorination. Bromination is highly selective i.e. $3°$ bromides are the absolute major product.

Allylic substitution :

Alkenes show substitution at allylic position when they react with low concentration of Cl_2 at $500°C - 600°C$ along with addition product.

$$CH_3CH = CH_2 + Cl_2 \xrightarrow[\text{(gas phase)}]{500°C - 600°C} CH_2 - CH = CH_2$$
$$| $$
$$Cl$$

Allyl chloride
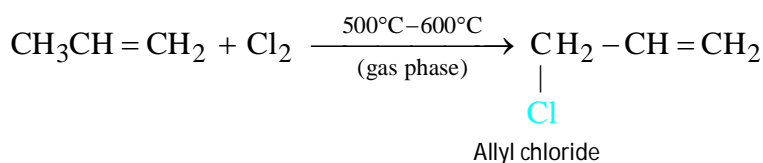
Note that at low temperature and absence of light in liquid phase alkenes show addition reaction. Alkenes show allylic substitution is presence of NBS in CCl_4 (N-bromosuccinimide). NBS is highly selective brominating reagent at allylic position in alkenes, α-carbon to benzene ring (benzylic position) and α-carbon to $-C \equiv C$ and carbonyl group.

Note :

(Markovnikov and Anti addition)
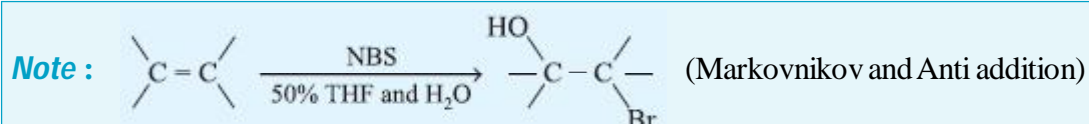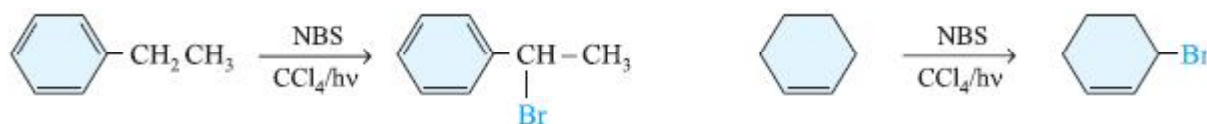
Mechanism

NBS reacts usually in presence of non-polar solvent, CCl_4. NBS is very slightly soluble in CCl_4, which ensure that low concentration of bromine needed to avoid addition reaction is maintained. The reaction is catalysed by sunlight or heat.

$$Br° + CH_3CH = CH_2 \longrightarrow \overset{\circ}{C}H_2 - CH = CH_2 + HBr$$
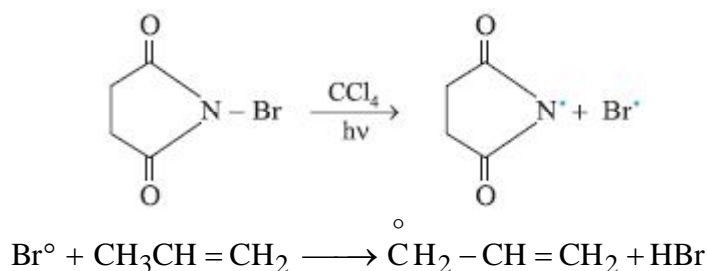
H–Br is taken up by NBS to avoid addition across double bond.

$$\overset{.}{C}H_2 - CH = CH_2 + Br_2 \longrightarrow BrCH_2 - CH = CH_2 + Br°$$
allyl bromide
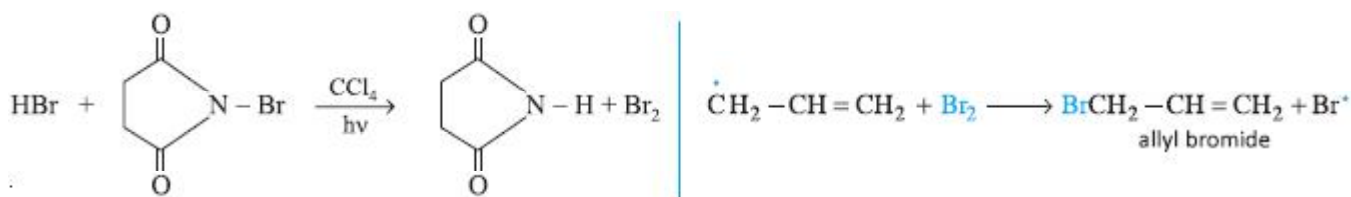
Note : ➤ NBS provides a low concentration of bromide and use up the HBr formed (avoiding addition reaction)

➤ In case of unsymmetric allylic intermediates, allylic rearrangement takes place to give mixture of two products.

Organic Concepts   **Vidyamandir Classes**
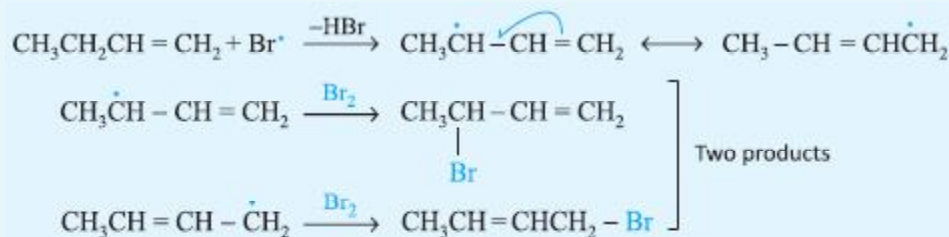
(b) Nucleophillic Substitution Reactions :

1. Aliphatic Nucleophilic Substitution Reactions :

It proceeds by ionic mechanism. On the basis of time of bond cleavage and bond formation, a nucleophilic substitution reaction can takes place by two different mechanisms.

They are divided into two categories :

(i) $S_N 2$ mechanism :

These are Bimolecular reactions. When rate of reaction depends upon concentration of both substrate (organic compound) and the nucleophile, the reaction is said to follow bimolecular mechanism (path) and is represented as $S_N 2$.

Consider the alkaline hydrolysis of CH_3Cl :

$$H_3 C^{\delta+} - Cl^{\delta-} + OH^- \longrightarrow H_3 C - OH + Cl^-$$
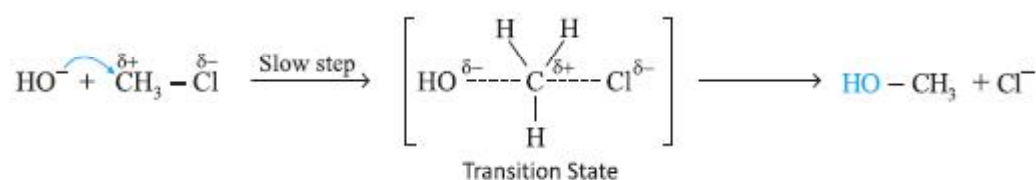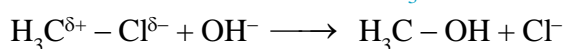
The nucleophile OH^- attacks from the opposite side of Cl atom, and a transition state results where both OH^- and Cl⁻ are partially bonded to carbon atom, to form a pentavalent activated complex known as transition state (T.S) in the slow step. The transition state then gives the product and the halide ion. $S_N 2$ reaction mechanism is one step reaction mechanim.

(ii) $S_N 1$ mechanism :

These are Unimolecular reactions. When the rate of nucleophillic substitution depends only on the concentration of the substrate, the reaction is said to follow unimolecular path and is represented by $S_N 1$.

Consider hydrolysis of tertiary butyl bromide :

It follows two steps process :

➤   Heterolytic fission forming carbonium ion.

$$\left(CH_3\right)_3 - C - X \xrightarrow{\text{slow step}} \left(CH_3\right)_3 - C^+ + X^-$$
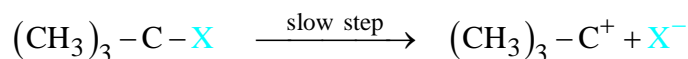
➤   Attack of nucleophilic on planar carbonium ion.

$$\left(CH_3\right)_3 - C^+ + \underset{(Nu^-)}{OH^-} \xrightarrow{\text{fast step}} \left(CH_3\right)_3 - C - OH$$
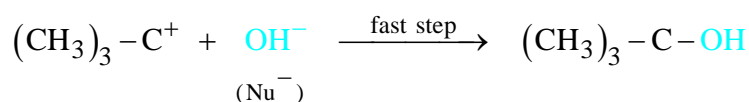
Note 1 : ➤ Stronger is the nucleophile, more is the chance of S_N2 mechanism.

(*large and easily polarised groups are stronger nucleophiles* : HS^-, I^-, CH_3COO^-)

➤ Higher is the concentration of nucleophile, higher is the rate of S_N2 mechanism.

➤ 1° Alkyl Halides (RX) will always follow S_N2 path (absence of steric hindrance).

➤ 2° Alkyl Halides will follow S_N2 in presence of stronger nucleophile and non-ionising aprotic polar solvents (such as acetone, DMSO).

Note 2 : ➤ 3° Alkyl Halides (RX) will always follow S_N1 path (greater stability of 3° Alkyl carbocations).

➤ 2° Alkyl Halides will follow S_N1 path when ionising solvents such as H_2O or EtOH are used.

If H_2O acts as reagent :

$$(CH_3)_3 - C^+ + \underset{(Nu^-)}{HOH} \xrightarrow{\text{fast step}} \underset{\text{Protonated alcohol}}{(CH_3)_3 - C - OH_2} \xrightarrow{-H} (CH_3)_3 - C - OH$$
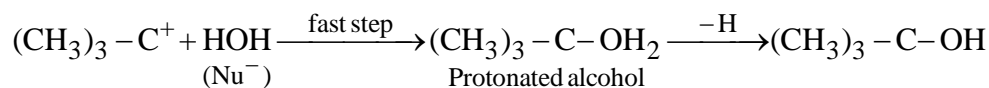
➤ Polarising medium such as water, alcohols favour heterolytic fission and hence favour S_N1. These solvents after ionising the substrate act as nucleophiles in fast step. This is referred to as solvolysis (S_N1). In solvolysis, we have to visualise rearrangement to get the most stable carbocations (*Also refer to addition & elimination reactions involving carbocations*).

➤ Adjacent $C = C$ or $C = 0$ π system increase the rate of $S_N 2$ reaction by stabilizing the transition state.

➤ Adjacent $C = C$ π system increase the rate $S_N 1$ reactions by stabilizing the carbocation.

➤ Among the fastest of all $S_N 2$ reactions are those where the leaving group is adjacent to a carbonyl group.

i.e.   or
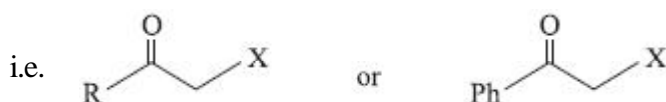
➤ Bicyclo bridge head 3° alkyl halide does not react with nucleophiles either by $S_N 1$ or by $S_N 2$.

Bicyclo bridge head
3° alkyl halide

It does not react by $S_N 1$ because the carbocation cannot become planar, nor by $S_N 2$ because the nucleophile cannot approach the carbon atom from the opposite side.

Note 3 : ➤ Ease of S_N1 mechanism : benzyl > allyl > 3° > 2° > 1° > methyl
(*It depends upon stability of carbonium ion*).

➤ Ease of S_N2 mechanism : $\alpha -$ halocarbonyl > benzyl $\approx$ methyl > allyl > 1° > 2° > 3°
(*It depends upon ease of attack of nucleophile ; steric factors*).

➤ There are three outcomes for a reaction at an asymmetric carbon atom and these are inversion, retention and racemisation. Consider the replacement of a group X by Y in the following reaction :
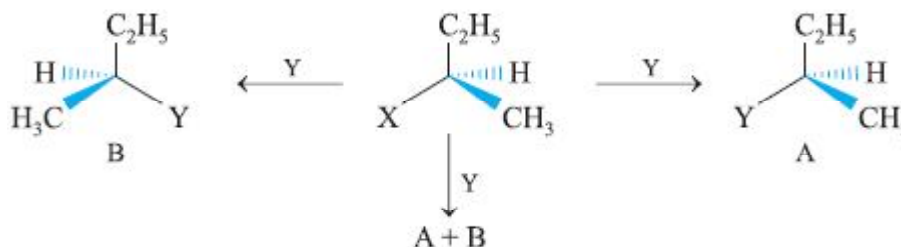
If (A) is the only compound obtained, the process is called retention of configuration.

If (B) is the only compound obtained, the process is called inversion of configuration.

If a 50 : 50 mixture of the above two is obtained then the process is called racemisation and the product is optically inactive, as one isomer will rotate light in the direction opposite to another.

➤ Retention : Retention of configuration is the preservation of integrity of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation. It is also the configurational correlation when a chemical species X Cabc is converted into the chemical species Y Cabc having the same relative configuration.
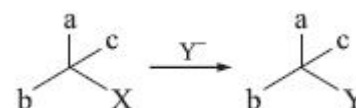
In general, if during a reaction, no bond to the stereocentre is broken, the product will have the same general configuration of groups around the stereocentre as that of reactant. Such a reaction is said to proceed with retention of the configuration.

(−)-2-Methylbutan-1-ol   (−)-1-Chloro-2-methylbutane
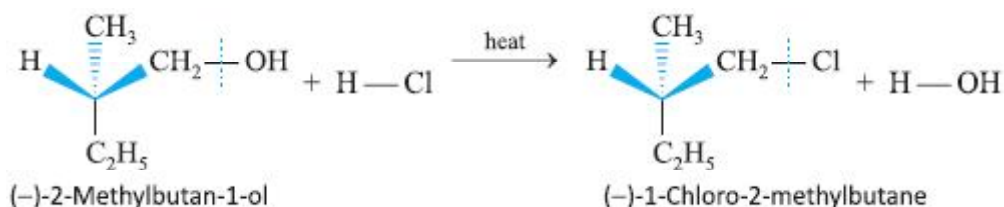
Note 4 : In S_N2 mechanism, Nu^- attacks from back side i.e., side opposite to halide atom.

optically active   Transition state   optically active
optically pure   inversion in configuration
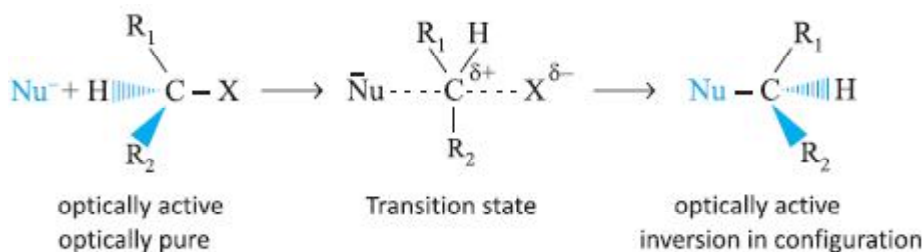
This means in $S_N 2$ mechanism, the inversion of configuration takes place i.e., spatial arrangements of four different substituents around chiral carbon atom get changed. In $S_N 2$ path, the nucleophile attacks the substrate from back side and forms an intermediary transition state giving a molecule with opposite configuration. This means that there is complete inversion which is also referred to as *Walden Inversion*. Since

Nu^- attacks α – carbon from back, the steric hindrance around α – carbon is the key to an effective S_N2 attack. Note that hindrance is almost negligible around $1°\,\alpha - C -$ atom. Therefore S_N2 reaction is stereoselective as well as stereospecific. Note that only one stereoisomer is formed.

Note 5 : In S_N1 mechanism, first carbonium ion is formed which is sp^2 hybridised and planar.
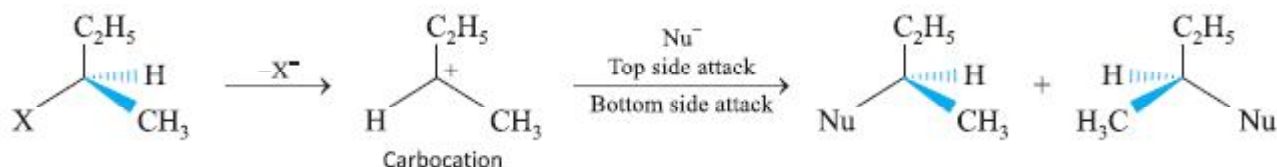
Hence in S_N1 path, a racemic mixture (product) is expected. However on analysing the products, one observes that only 90 – 95% racemization occurs. The above discussion (Note 4 & 5) provides a strong evidence for S_N1 and S_N2 mechanisms.

Note 6 : The nature of solvent also affects the mechanism of the reaction.

➤   A polarising (ionising) solvent (water, alcohols, acids) favours S_N1 path because of :

   (i)   the formation of carbonium ions is easy as the ions formed are easily solvated.

   (ii) Nu^- are also solvated (stabilised) in polaring solvents.

   The ionising power of solvent depends upon its dielectric constant. e.g., the order of ionising power of some solvents is : $H_2O > HCOOH > CH_3OH > C_2H_5OH > CH_3COOH$ (*Such solvents are also called as Protic Solvents*).

➤   A Non-ionising solvent such as DMSO (Dimethyl Sulphoxide) : $(CH_3)_2\,SO$

   or   DMF : Dimethyl Formamide : $H - CON(CH_3)_2$ or Acetone favour S_N2 path because :

   (i)   the formation of carbonium ions is not possible as such solvents does not stabilise anions effectively.

   (ii)   the strength of nucleophile is increased as it being an anion is not solvated.

   (*Such solvents are also called as Aprotic Solvents*)

Note 7 : **Nature of leaving group (i.e. halide ion) :**

A good leaving group is one, which is able to stabilise itself. It is observed that a weak base is a good leaving group. Among halide ions, I^- weakest base and hence a good leaving group. A good leaving group, however cannot decide whether a given reaction will be S_N1 or S_N2. A good leaving group will enhance the rate of both S_N1 or S_N2 reactions. Among halide ions, I^- (weak base : conjugated base of strong acid, HI) is best leaving group. [Nature of living group : $I^- > Br^- > Cl^- \gg F^-$] Other good leaving group are : sulphonates such as tosylates or mesylates.
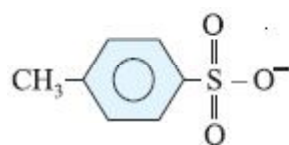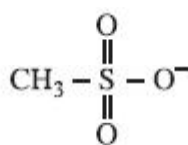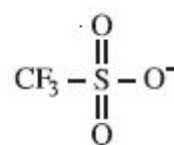
***Note* 8 :** For a given alkyl group, the reactivity of the halide, $R - X$, follow the same order in both S_N1 and S_N2 mechanism.

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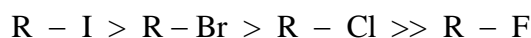
Ambient Nucleophiles

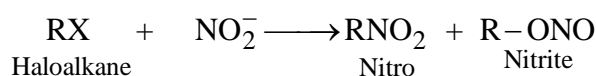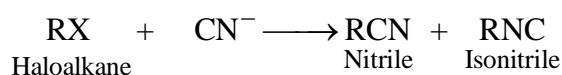A nucleophile which can attack a substrate through two possible sites.

e.g.   Cyanide ion (CN^-) : can attack through 'C' or 'N' atom
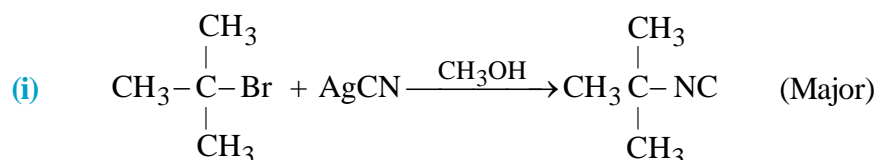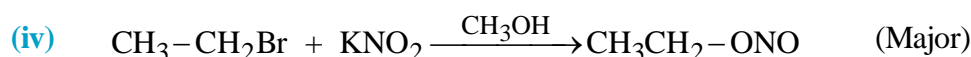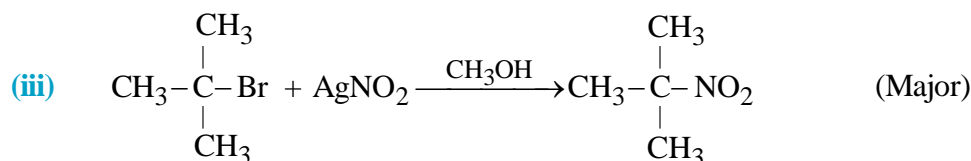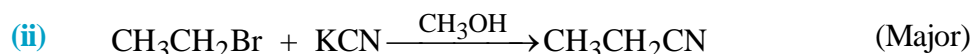
Nitrite (NO_2^-) : can attrack through 'N' or 'O' atom
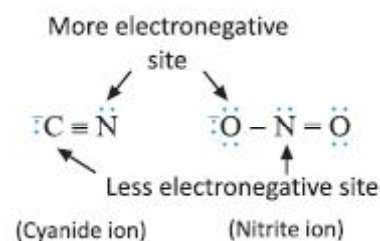
It is important to note that the atom of the ambient nucleophile, which attacks the electrophilec site depends upon the nature of the attacking reagent.

➤   It KCN (Ionic) is there, then the attack takes place from the carbon side. This can be understood by observing the structure of ^-CN which suggests the greater electron density over carbon making it better nucleophilic site.

➤   It AgCN (covalent) is there then the attack takes place from nitrogen side (having lone pair). Since AgCN is covalent therefore we do not expect free ^-CN ion, so the attack takes place from the lone pair of nitrogen only.

➤   If KNO_2 (Ionic) is there, then the attack takes place from oxygen side. In NO_2^- ion, negative charge of oxygen makes it a better donor as compared with the lone pair of nitrogen.

➤   If $AgNO_2$ (Covalent) is there, then the attack takes place from nitrogen side. This time there is a competition between the lone pair of nitrogen and oxygen. Nitrogen being less electronegative comes out as a better nucleophilic site.

$$\underset{\text{Haloalkane}}{RX} \quad + \quad CN^- \longrightarrow \underset{\text{Nitrile}}{RCN} \; + \; \underset{\text{Isonitrile}}{RNC}$$

$$\underset{\text{Haloalkane}}{RX} \quad + \quad NO_2^- \longrightarrow \underset{\text{Nitro}}{RNO_2} \; + \; \underset{\text{Nitrite}}{R-ONO}$$

Consider the following reactions :

(i)

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - Br \; + \; AgCN \xrightarrow{CH_3OH} CH_3 \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - NC \qquad \text{(Major)}$$

(ii) $CH_3CH_2Br + KCN \xrightarrow{CH_3OH} CH_3CH_2CN$ (Major)

(iii) $CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - Br + AgNO_2 \xrightarrow{CH_3OH} CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - NO_2$ (Major)

(iv) $CH_3 - CH_2Br + KNO_2 \xrightarrow{CH_3OH} CH_3CH_2 - ONO$ (Major)

Summary of structural variations and nucleophilic substitution.

Substrate (Electrophile)	Me — X	R⌒X	R₂CHX	R₃CX	Neopentyl
	Methyl	Primary	Secondary	Tertiary	Neopentyl
S_N1 mechanism	Bad	Bad	Poor	Excellent	Bad
S_N2 mechanism	Excellent	Good	Poor	Bad	Bad

Substrate (Electrophile)	Allylic	Benzylic	α-alkoxy	α-carbonyl (Primary)	α-carbonyl (Tertiary)
	Allylic	Benzylic	α-alkoxy (adj. lone pair)	α-carbonyl (Primary)	α-carbonyl (Tertiary)
S_N1 mechanism	Good	Good	Good	Bad	Bad
S_N2 mechanism	Good	Good	Okay but S_N1 better	Excellent	Possible

Neighbouring group participation Reaction Mechanism :

Some compounds having a substituent with lone pair or π – electron at the carbon next to the reaction centre [at β carbon atom of leaving group] undergoes nucleophilic substitution reaction by a mechanism known as neighbouring group participation (NGP). These substituents are called as neighbouring groups.

Consider the following reaction :

$Ph\overset{\ddot{S}}{\diagdown}\diagup Cl + ROH \longrightarrow Ph\overset{\ddot{S}}{\diagdown}\diagup OR + HCl$

NGP is two step reaction mechanism.
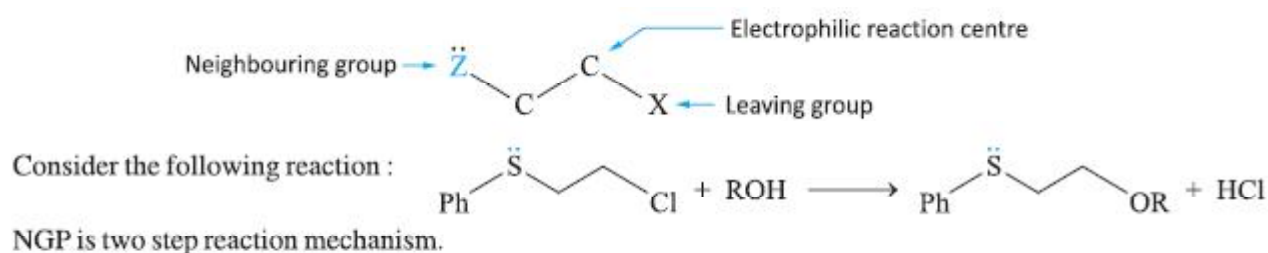
First Step :   It is intramolecular nucleophilic attack of neighbouring group through its lone pair electron or π – bond electron.

Three membered ring intermediate
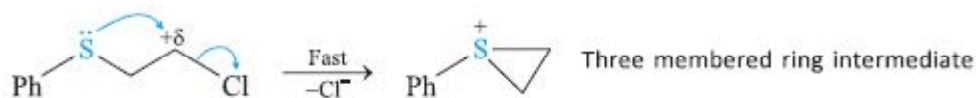
Second Step :   It is intermolecular nucleophilic attack of attacking nucleophile on three membered ring intermediate.
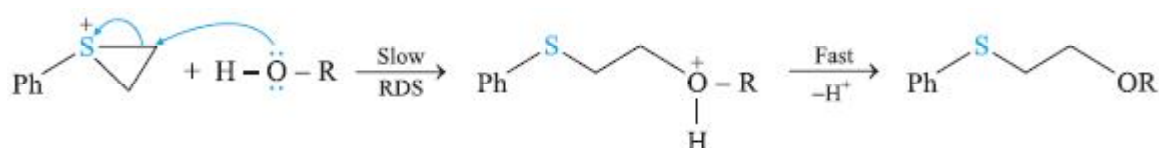
It is understood from reaction mechanism that NGP is two successive S_N2 reactions on reaction centre. The involvement of neighbouring group increase the rate of the substitution reaction.

reacts with water 600 times faster than

reacts with water 3000 times faster than

As you know, S_N2 reactions go with inversion but nucleophilic substitution by NGP on stereogenic centre proceed with retention of configuration of stereogenic centre [Because of two successive S_N2 reactions on same chiral carbon atom]

trans isomer

Reaction goes with retention at C1

cis isomer

Reaction goes with inversion at C1 because NGP is not possible due to *cis* configuration of neighbouring group
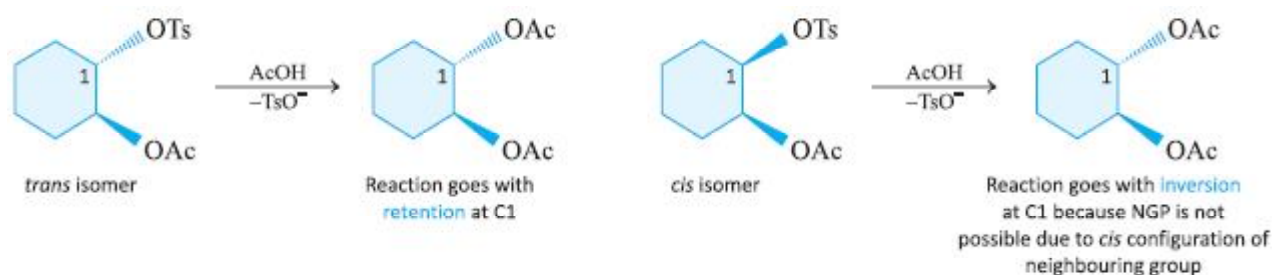
Note :
➤ Retention of configuration in nucleophilic substitution reaction, is an indication of neighbouring group participation.

➤ Sulphides, esters, carboxylate, ethers and amines, phenyl groups can assist substitution reactions through NGP

➤ Intramolecular reactions (including participation of a neighbouring group) that give three, five, or six membered rings are usually faster than intermolecular reactions.

➤ In some cases there may be rearrangement during nucleophilic substitution reaction by NGP mechanism.

Illustration - 7   *Find the major product of the reaction given* :
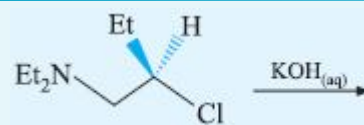
SOLUTION :

It is neighbouring group participation (NGP) reaction in which a three membered cyclic intermediate is formed in first step of reaction (intramolecular $S_N 2$ attack).

In second step there is further $S_N 2$ attack on least hindered carbon atom of three membered cyclic intermediate.
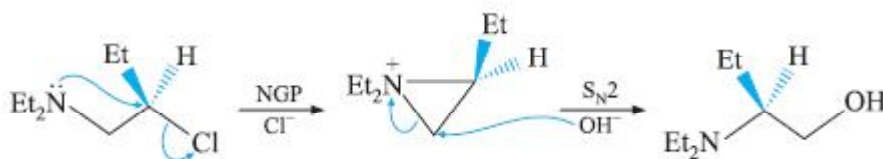
Illustration - 8   *Identify the product(s) formed in each of the following reactions, Identify the paths as* $S_N 1$ or $S_N 2$?
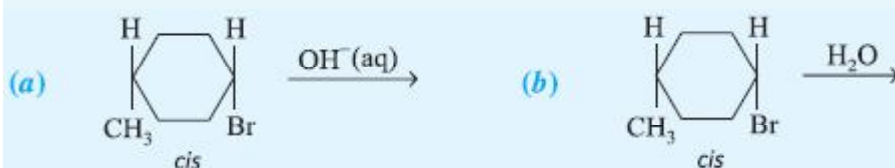
SOLUTION :

(a) OH^- (aq) is a strong Nu^-, will initiate an $S_N 2$ attack in cyclo alkyl bromide (*in* $2°$ *cycloalkyl halides, the steric hindrance is not very high unlike in* $2°$ *alkyl halides*). OH^- will attack α – carbon from the side opposite to Br -atom resulting in the formation *of trans* product (*equivalent to Walden inversion in optically active compounds*). This illustrates stereo-selective and stereo – specific aspect.
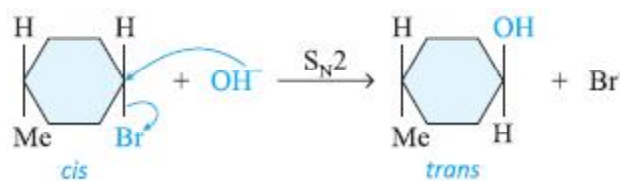
(b) H_2O (a weak Nu^-) being highly polarising will favour $S_N 1$ path (solvolysis).
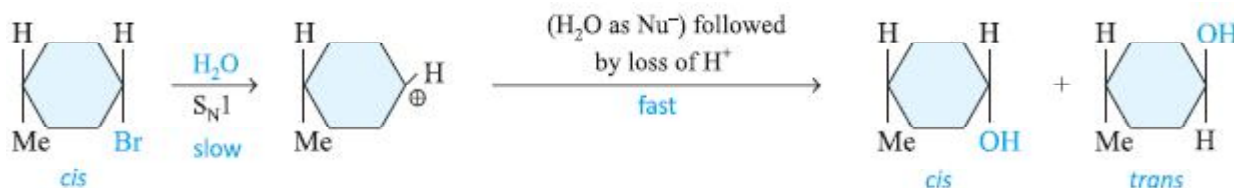
Note that the Carbocation is planar, hence Nu^- an attack it from two sides giving a mixture of two products.

Illustration - 9 / *Answer the following questions with proper explanation :*

(i) *KI in acetone, undergoes* $S_N 2$ *reaction with each of P, Q, R and S. Compare their relative rates.*

[P] $CH_3 - Cl$ [Q] $\text{(CH}_3\text{)}_2\text{CH–Cl}$ [R] allyl chloride [S] phenacyl chloride (PhCOCH$_2$Cl)

(ii)

$$\begin{array}{c} Br \\ H \underset{MeO}{\overset{}{\rule{0pt}{0pt}}}\!\!\!-\!\!\!\!\begin{array}{c} Ph \\ \hline \\ H \end{array} \\ Ph \end{array} \xrightarrow[acetone]{NaI} product.$$
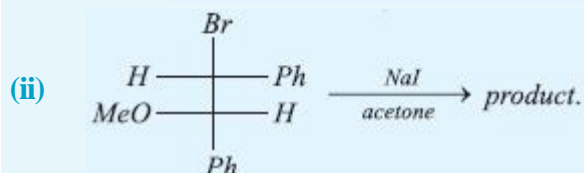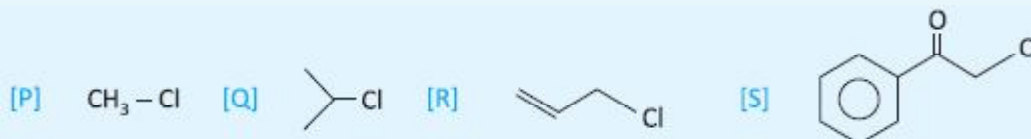
SOLUTION :

(i) In $S_N 2$ reactions, apart from strength of Nucleophile the steric factors are very important for the rate of reaction.

But in special cases, where $\alpha-$carbon having a strongly electron withdrawing group (EWG), rate of $S_N 2$ is very fast as in option [S]. The relative rates of $S_N 2$ are as follows :

S (PhCOCH$_2$Cl, $\delta+$) > P ($CH_3 - Cl$, Methyl, Least hindered) > R (Allylic) > Q (2°)

$\delta+$ is high due to $-I$ effect of carbonyl group

Methyl — Least hindered

Allylic — $\delta+$ is lesser as compared to methyl

$2°$ — Most hindered
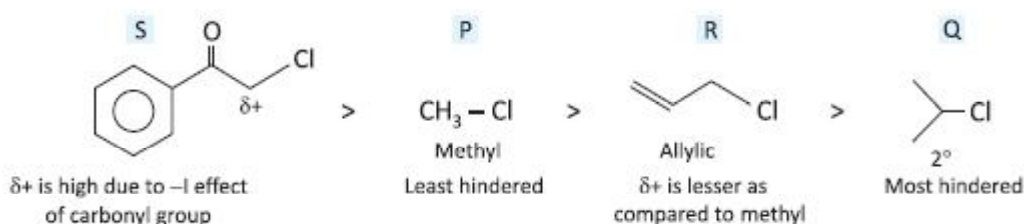
(ii) It is NGP reaction so there is retention in configuration of chiral carbon atom.

In this reaction I^- can attack as nucleophile on benzylic C atom having Br atom. But lone pair electron of oxygen of methoxy group will attack intramolecularly so reaction proceed by NGP reaction mechanism. The configuration of chiral carbon atom remain unchanged

$$\begin{array}{c} I \\ H \!-\!\!\!-\!\!\!\!\begin{array}{c} \\ \hline \\ \end{array}\!\!\!-\!\!\! Ph \\ MeO \!-\!\!\!-\!\!\!\!\begin{array}{c} \\ \hline \\ \end{array}\!\!\!-\!\!\! H \\ Ph \end{array}$$
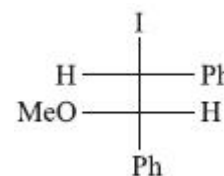
Illustration - 10 / *What are the minor and major products, when the following compound undergoes hydrolysis in aqueous acetone?*

$$CH_3 - O \text{—} \underset{}{\boxed{}} \text{—} \underset{H}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} \text{—} \underset{Cl}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} \text{—} \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} \text{—} \boxed{} \text{—} NO_2$$
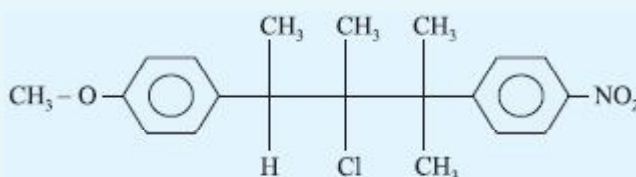
SOLUTION :

Hydrolysis in aqueous acetone will involve solvolysis (S_N1).
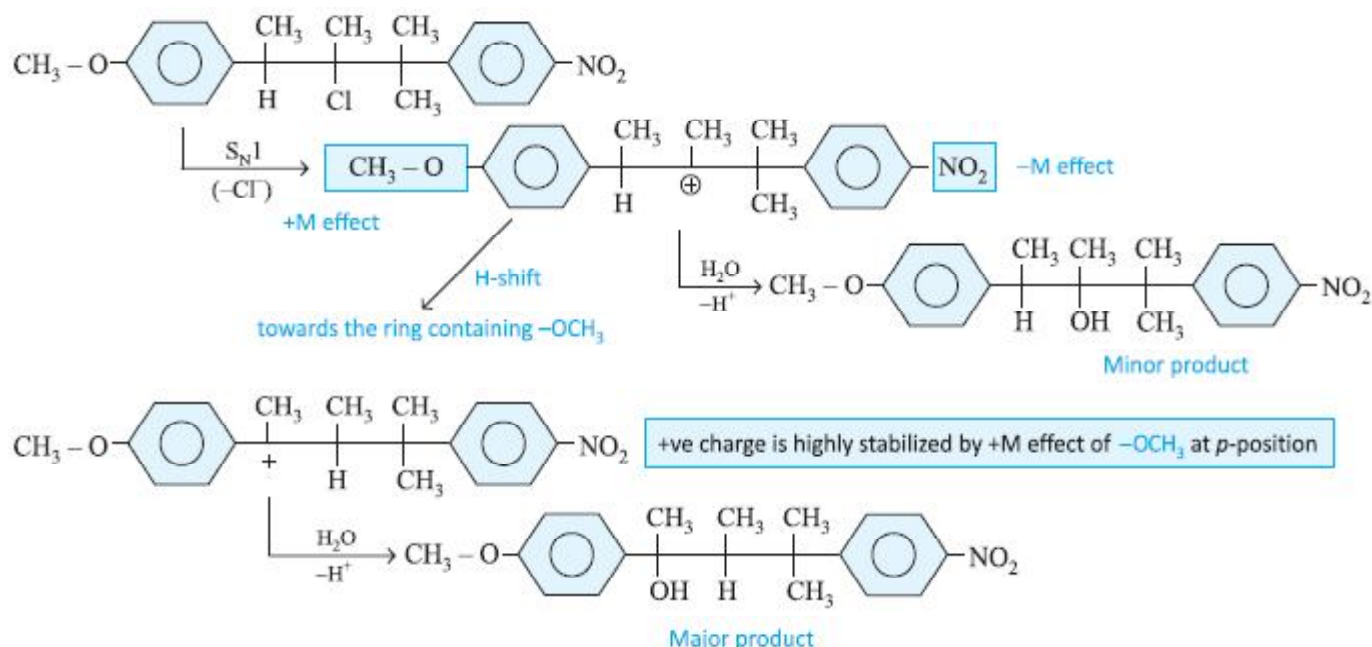
II. Aromatic Nucleophilic Substitution Reaction : Activated S_N2

In general, nucleophilic substitution is not possible on unsaturated carbon atom under normal reaction conditions. This is because of an increase in bond dissociation energy of C – X bond due to resonance. Visualise the case of Aromatic Halides and Vinyl Halides.


$$R - \overset{\frown}{CH} = CH \overset{\frown}{\underset{}{-}} \ddot{Cl}: \longleftrightarrow R - \overset{\ominus}{CH} - CH = \overset{\oplus}{Cl}$$
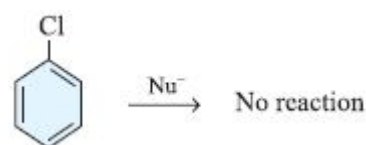
However, if a deactivating group (EWG) is present in the ring, it can "activate" the ring for nucleophilic substitution reaction by the withdrawal of benzene ring $\pi e^- s$ towards itself.
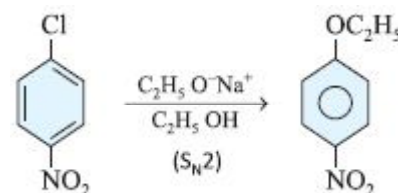
Aryl halide also undergoes nucleophilic substitution reaction under vigorous reaction conditions i.e. at high temperature and high pressure by using stronger nucleophiles such as RO^-, NH_2^-, R^- etc., or in presence of KNH_2.

On the basis of relative reactivity towards nucleophile, aryl halides are classified as follows.
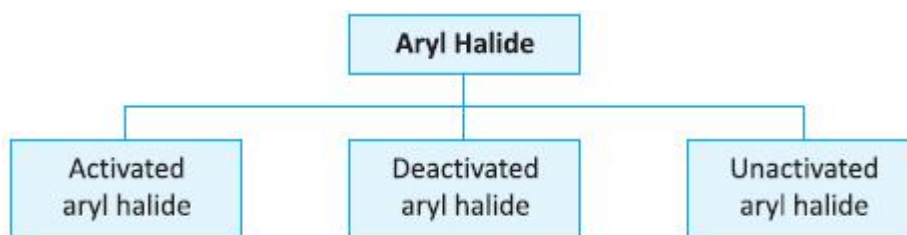
Activated aryl halide :

Aryl halide having EWG on ortho and/or para positions.

Deactivated aryl halide:

Aryl halide having ERG on any positions.
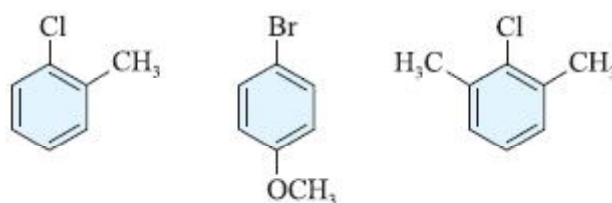
Unactivated aryl halide :

Unsubstituted aryl halide or aryl halide having EWG on meta position.
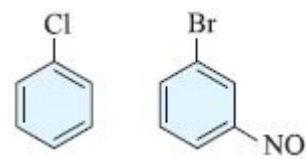
Note :
- ➤ Activated aryl halides means aryl halides activated for nucleophilic substitution reactions and de-activated aryl halides means less reactive (de-activated) for nucleophilic substitution reaction.
- ➤ EWG-Electron withdrawing group ; ERG – Electron releasing group.
- ➤ The EWG must be present at '*o*' or '*p*' position w.r.t. the substituent (to be undergone nucleophilic substitution).
- ➤ Any substituent that deactivates the benzene ring towards electrophilic substitution, activates the same ring towards nucleophilic substitution.
- ➤ "To be replaced" substituent must be a weaker base as compared to the attacking nucleophile.

Activated aryl halide undergoes nucleophilic substitution reaction by two step reaction mechanism called as addition-elimination reaction mechanism under proper reaction condition.

Consider the following reaction :
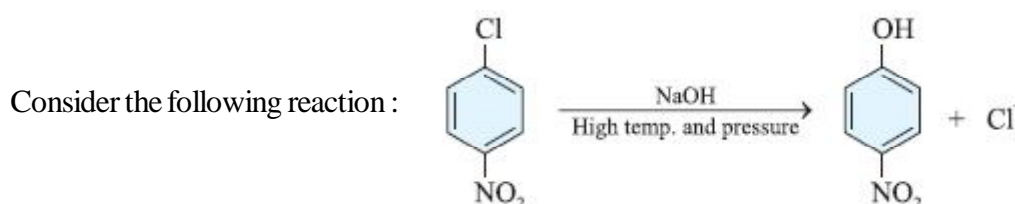
The generally accepted mechanism for the reaction is as shown below :

➤   Attack of the strong nucleophile on the halogen substituted aromatic carbon forming an anionic intermediate (Cyclohexadienyl anion).

➤   Loss of the leaving group, the halide ion restores the aromaticity.

1st Step : Intermediate (Cyclohexadienyl anion) carbanion — Resonance stabilization of cyclohexadienyl anion by a nitro group

2nd Step : Intermediate (Cyclohexadienyl anion) carbanion
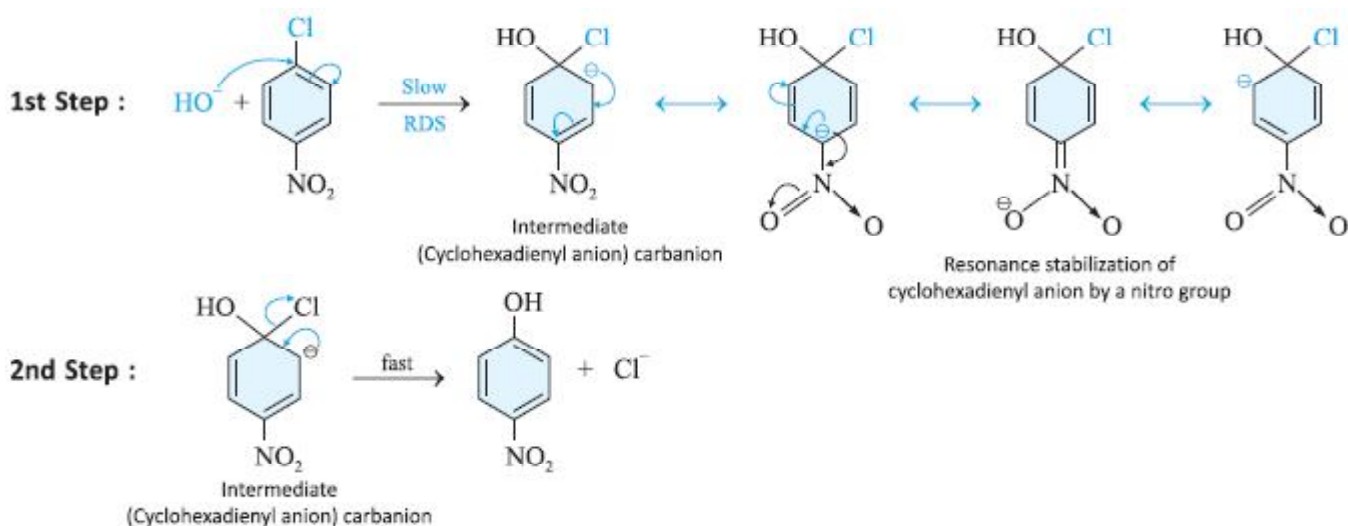
➤   Kinetics of the reaction are observed to be second order.

➤   The addition step (step – 1) is the rate determining step (Loss of aromaticity).

➤   Nucleophilic substitution, and therefore reaction rate, is facilitated by the presence of a strong electron withdrawing group ortho or para to the site of substitution, which stabilize the cyclohexadienyl anion through resonance.

➤   Aryl halide reactivity order : $Ar – F > Ar – Cl > Ar – Br > Ar – I$ (Note the contrast to simple nucleophilic substitution).

➤   The more electronegative the group the greater the ability to attract electrons which increase the rate of formation of cyclohexadienyl anion.

This addition-elimination reaction mechanism is a bimolecular nucleophilic substitution reaction mechanism represented as $S_N 2$ Ar. [Aromatic bimolecular nucleophilic substitution]

Note : Presence of EWG on ortho and/or para position increase rate of reaction because intermediate carbanion is stabilized by EWGs

Order of reactivity :
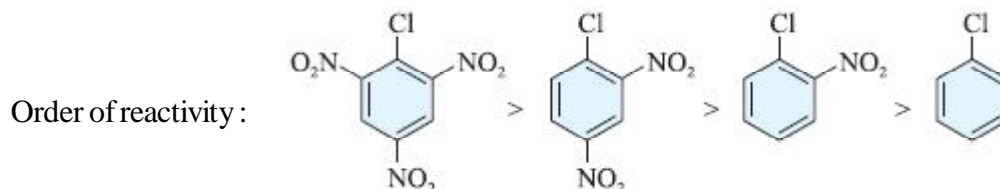
Note :   Deactivated and unactivated aryl halides undergoes nucleophilic substitution under proper reaction conditions by elimination-addition reaction mechanism [Benzyne reaction mechanisms].

Illustration - 11 *Explain the formation of products in the reaction given below.*
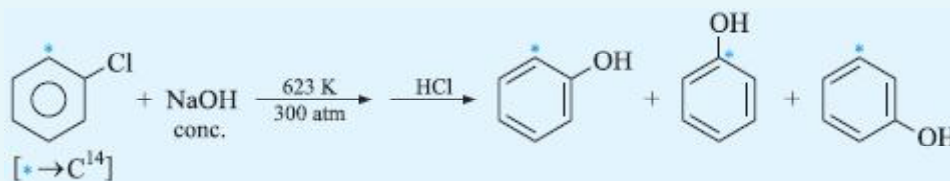
SOLUTION :

Under normal reaction conditions chlorobenzene is inert towards nucleophilic substitution reaction. But in presence of drastic reaction conditions (high temperature and high pressure) it under goes nucleophilic substitution reaction by elimination-addition reaction mechanism or benzyne reaction mechanism. Benzyne reaction mechanism is two steps reaction mechanism.
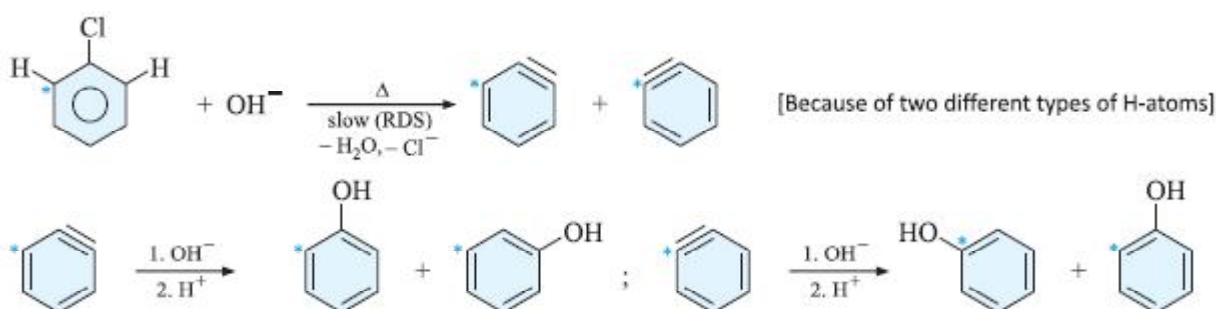
First step : Elimination of HCl (1, 2-elimination)
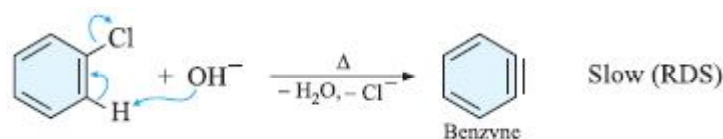
Second step : Addition of OH^-
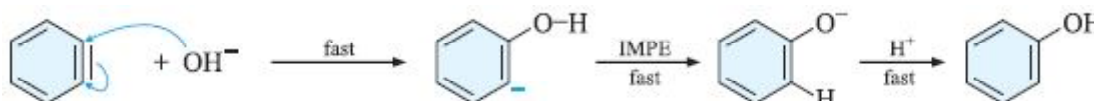
For the reaction given in question

Note : Benzyne is symmetrical intermediate hence nucleophile can attack on any carbon atom of $C \equiv C$ of benzyne

NOW ATTEMPT IN-CHAPTER EXERCISE-B BEFORE PROCEEDING AHEAD IN THIS EBOOK

(c) Electrophillic Substitution (S_E)

Substitution in benzene and its derivatives follows electrophillic substitution mechanism. Important S_E reactions include halogenation, nitration, sulphonation, Friedal Craft alkylation and acylation. The mechanisms proceeds via the following three steps :

1. **Formation of Electrophile (E^+)**

   (a) Chlorination (Bromination), Alkylation and Acylation of benzene

   In each of these reactions, in anhydrous $AlCl_3$, being a Lewis acid, helps in the generation of the electrophile.

   $$Cl - Cl \ + AlCl_3 \ \longrightarrow Cl^+ + AlCl_4^-$$
   $$\text{Chlorinium ion}$$

   $$CH_3 - Cl \ + AlCl_3 \ \longrightarrow CH_3^+ + AlCl_4^-$$
   $$\text{Alkyl carbocation}$$

   $$CH_3COCl - AlCl_3 \ \longrightarrow CH_3 \overset{+}{C}O + AlCl_4^-$$
   $$\text{Acyl carbocation}$$
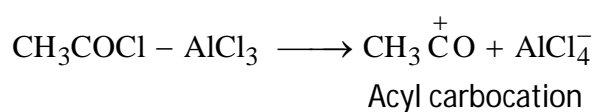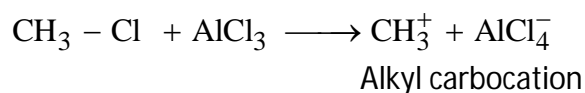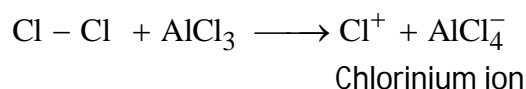
   (b) In the case of Nitration, NO_2^+ (Nitronium ion) is produced by the acid-base reaction of H_2SO_4 and HNO_3, as shown below. H_2SO_4 acts as Bronsted acid (Proton donor) and HNO_3 acts as Bronsted base (Proton acceptor).

   Step - 1　$\underset{\text{Proton donor}}{HO_3SO - H} + \underset{\text{Proton acceptor}}{H - \overset{..}{\underset{..}{O}} - NO_2} \ \rightleftharpoons \ H - \overset{H}{\underset{..}{\overset{|}{\underset{..}{O}}}}{}^+ - NO_2 + HSO_4^-$

   Step - 2　$H - \overset{H}{\overset{|}{\underset{..}{O}}}{}^+ - NO_2 \ \rightleftharpoons \ \underset{\text{Nitronium ion (a very strong electrophile)}}{NO_2^+ + H_2O}$
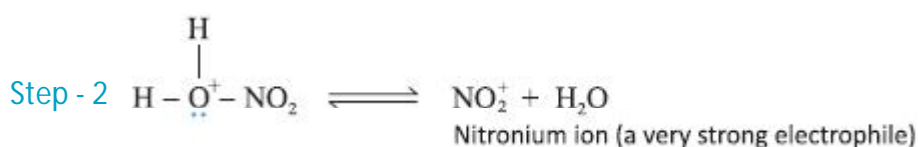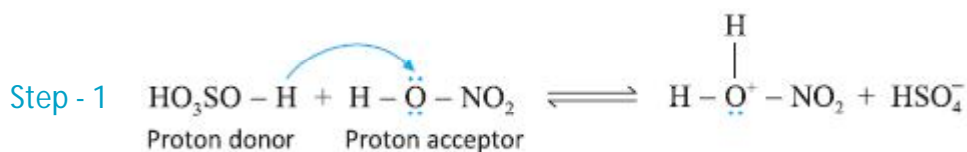
   Note : In sulphonation SO_3 acts as an electrophile.

2. **Formation of Intermediate (Arenium ion) :**

   E^+ attacks benzene due to nucleophillic character of ring and via Electromeric effect. This results in the formation of a complex (an intermediate) known as arenium ion, in which one of the carbons is sp^3 hybridised.
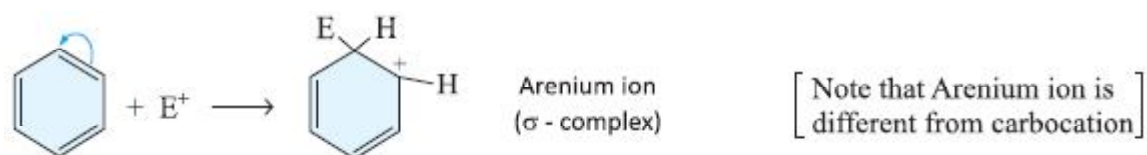
   The arenium ion is resonance stabilized.
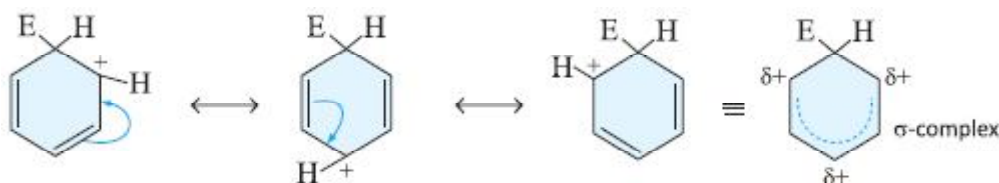
The σ complex does not have an Aromatic character because delocalisation of electrons stops at sp³ hybridised carbon.

3. Elimination of proton

In order to restore the Aromatic character, the σ complex release a proton.

$AlCl_4^-$ (in case of halogenation, alkylation, and acylation) and HSO_4^- (in case of nitration) abstracts a proton from the sp³ hybridised carbon atom to give monosubstituted benzene derivative.
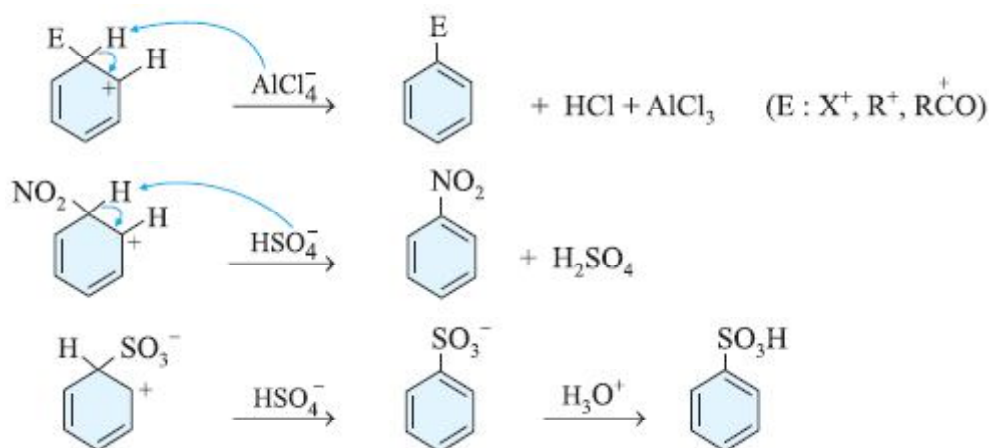
Note 1 : The number of products formed on monosubstitution is equal to the number of different types of H atoms in the substrate.

Note 2 : In benzene derivatives $(C_6H_5 - G),$ the functional group G can also be classified on basis of their polar nature as : Activating or Deactivating.

The various groups are classified as electron donating and electron withdrawing. Those that withdraw electrons inductively (polar effect) are said to exert a –I effect and those that withdraw electron conjugatively are said to exert a –M effect. Similarly +I and +M effect terms are used for electron donating.

➤ An activating group (an electron donating group via mesomeric effect) is one which makes benzene *more reactive* (nucleophillic) than benzene itself. Such groups are : –NH₂, –OH, –OR etc. *Note that these group exert –I effect over the ring, but in these cases +M effect > –I effect.*

➤ A de-activating group (an electron withdrawing group via mesomeric effect) is one which makes benzene *less reactive* (nucleophillic) than benzene itself. Such groups are –COOH, –C = O,–CHO, NO₂, –CN etc. *Note that these group exert –I effect over the ring, which makes these even more strongly deactivating.*

➤ The halogens exert a very strong –I effect over the ring which outweighs their +M effect, hence these are weakly deactivating groups. Note that these are weakly ortho & para directing due to +M effect.

➤ The alkyl group are weakly activating due to only +I effect. They are ortho & para directing because of hyperconjugation effect (explained below).

In toluene, $-CH_3$ has weak $+I$ effect and considered to be a weaker activating group ; still it is an *o/p* directing group for incoming electrophiles. It is due to hyperconjugation. Let us visualize hyperconjugation in toluene.
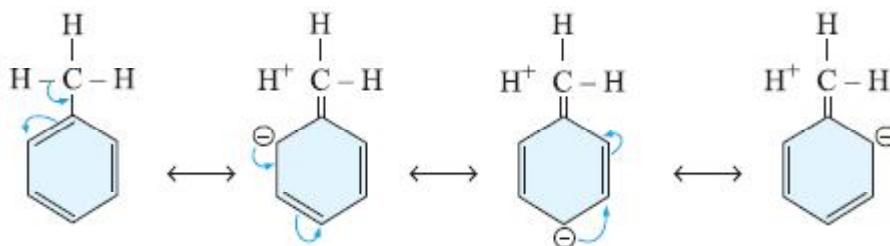
More is the number of $H-C$ bonds $(\alpha-H)$ attached to the unsaturated system, more is the probability of electron release by this effect.

In the given reaction, which is the major product (A) or (B)?
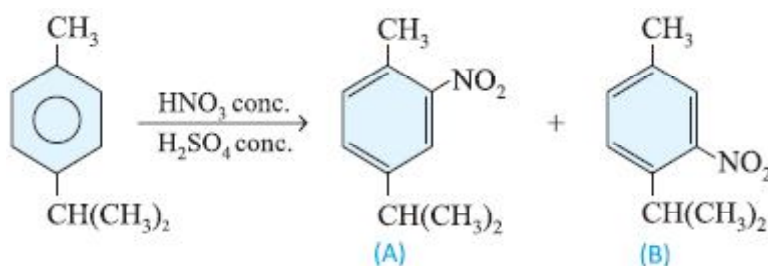
Answer is obviously (A) since $-CH_3$ is more activating than $-CH(CH_3)_2$ as the former has '3' $\alpha-H$ whereas latter has only '1' $\alpha-H$.

Orientation of Electrophilic Substitution in Benzene :

A typical electrophilic substitution reaction in benzene can be represented as :

If there is already a substituent attached to the benzene ring (as a substrate), the incoming electrophile may be directed to '*o*', '*m*' or '*p*' positions (w.r.t. the substituent) based on the stability of $\sigma-$ complex (arenium ion) formed as an intermediate.

Consider the following reaction :
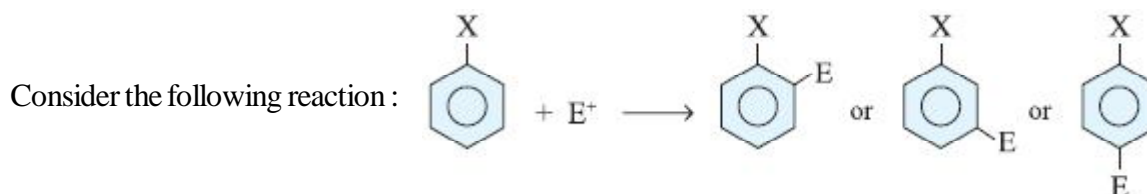
Out of the above shown products, which will form to what extent depends on the "behavior" of the substituent already attached to benzene ring. We can draw the intermediate arenium ion formed during the above electrophilic substitution reaction based on the position of the electrophilic attack and then look at the stability of the intermediate formed.
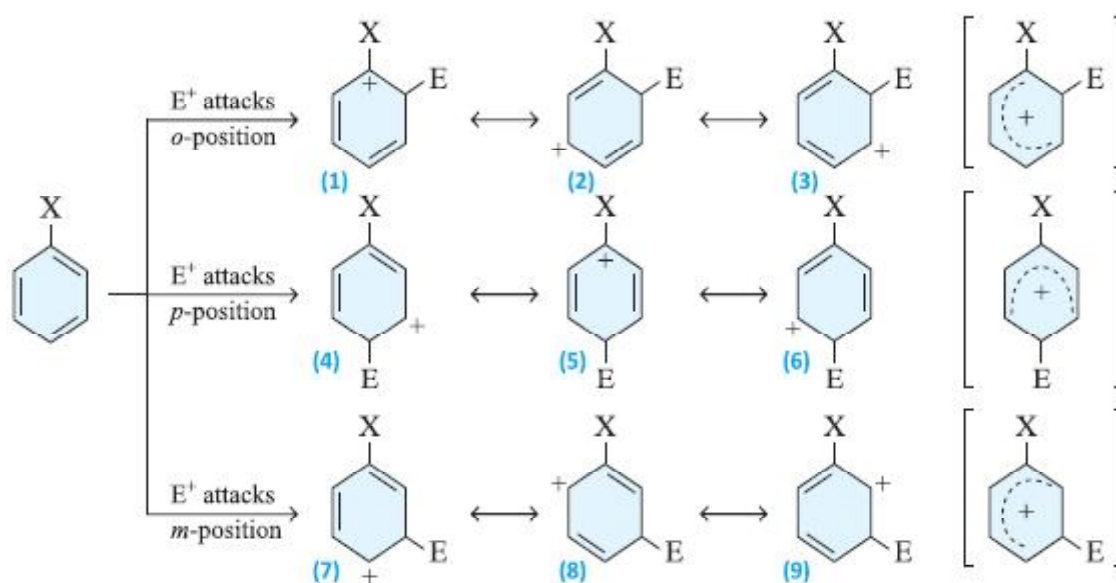

The product formed will depend on the stability of the resonance hybrid as per the "behavior" of substituent 'X'.

(i) If 'X' has +I effect or electron donating effect (+R) e.g. $-CH_3$ group, it will stabilize the carbocation

$-CH_3$ can also stabilise the carbocation through hyperconjugation).

Thus, (1) and (5) will be the most stable resonating structures.

$\Rightarrow$ '*o*'/ '*p*' isomer will be formed in greater amount.
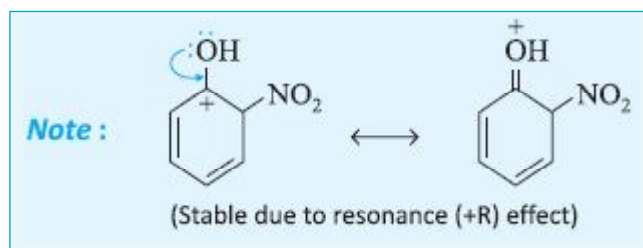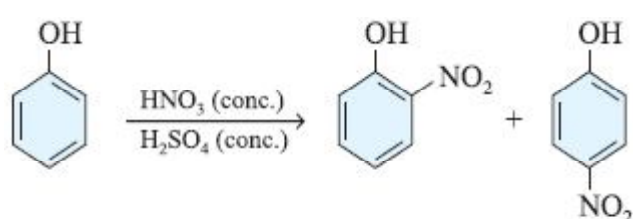
(ii) If 'X' has a –I effect (e.g. $-\overset{+}{N}R_3$) or electron withdrawing effect (e.g. $-NO_2$), it will destabilise the carbocation. Clearly, the destabilizing effect will be much lesser in case of (7), (8) and (9) as compared to the 'o' and 'p' resonating structures.
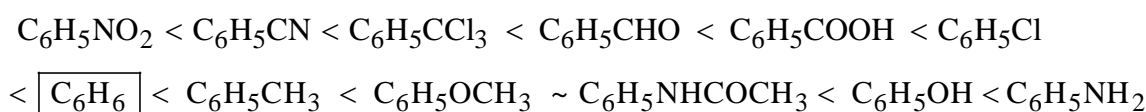
$\Rightarrow$ 'm' isomer will be formed
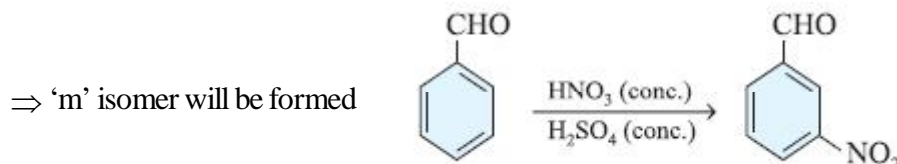
Note : Electrophilic substitution is quite interesting in case of halo benzenes. $(-I)$ effect of halogens exceed their (+M) effect, the overall effect of the substituent is deactivating but still it is o, p-directing.
[Remember : All groups that donate electrons by resonance are otho-para director]

As a special case consider hyperconjugation in benzotrichloride.
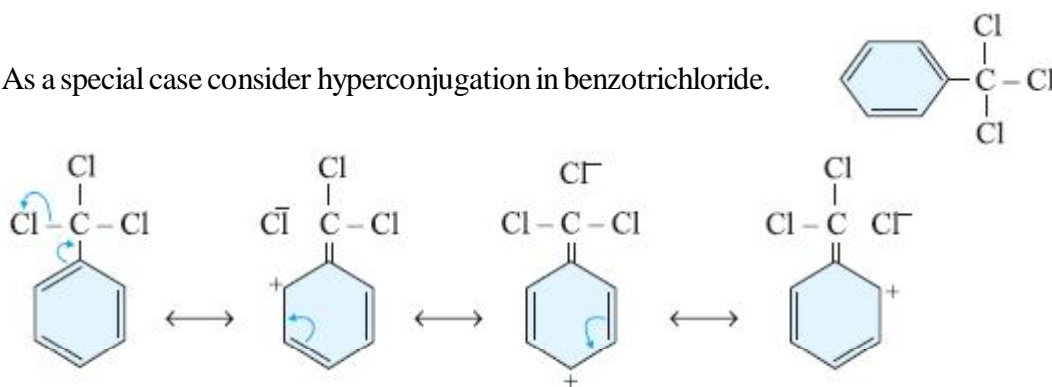
It means, $-CCl_3$ is a strong m-directing group. Such type of hyperconjugation is known as Reverse Hyperconjugation.

Note 1 : The presence of activating groups in benzene ring increases the ease of electrophillic substitution, whereas the deactivating groups do just the opposite. Observe the ease of S_E reaction in various substituted benzenes.

$$C_6H_5NO_2 < C_6H_5CN < C_6H_5CCl_3 < C_6H_5CHO < C_6H_5COOH < C_6H_5Cl$$

$$< \boxed{C_6H_6} < C_6H_5CH_3 < C_6H_5OCH_3 \sim C_6H_5NHCOCH_3 < C_6H_5OH < C_6H_5NH_2$$

Note 2 : **(i)** In Friedal Craft (F.C.)alkylation, rearrangement in carbocation takes place to give most stable carbocation via hydride (H^-) or methide (CH_3^-) shift.

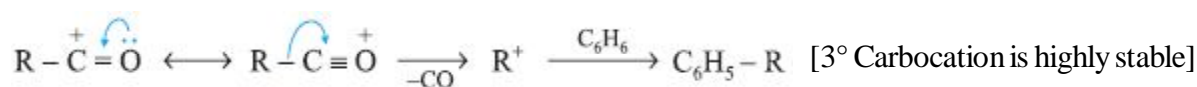**(ii)** In F.C. alkylation, poly alkylation may occur as alkyl groups are 'o' & 'p' directing.
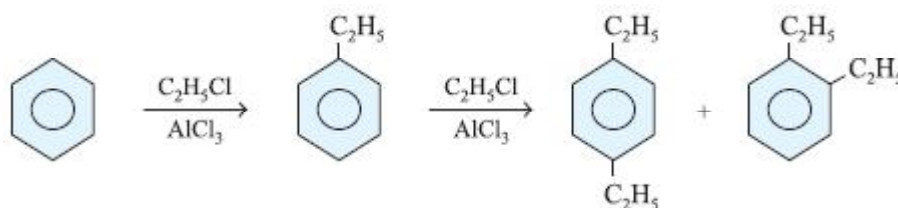
(iii) Mono substituted benzene having strongly deactivating groups such as $-NO_2, -SO_3H$ and $-CN$ do not give F.C. alkylation.

**(iv)** There is no rearrangement in acyl carbocation (RCO) as it is resonance stabilised due to oxygen atom.

$$R - \overset{+}{C} = \overset{..}{O} \longleftrightarrow R - C \equiv \overset{+}{O}$$

(v) In F.C. acylation, there is no change of poly acylated product formation as $-COR$ group deativates the ring.

(vi) In F.C. acylation, if alkyl group (R) in $R\overset{+}{C}O$ is 3°, alkylation occurs as follows :

$$R - \overset{+}{C} = \overset{..}{O} \longleftrightarrow R - C = \overset{+}{O} \xrightarrow[-CO]{} R^+ \xrightarrow{C_6H_6} C_6H_5 - R \quad [\text{3° Carbocation is highly stable}]$$

(vi) Mono substituted benzene having strongly activating groups such as $-NH_2$ and $-OH$ do not prefer F.C. alkylation as $AlCl_3$ being acidic coordinate with these groups.
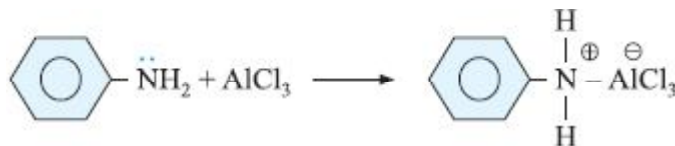
Now this +ve charge over nitrogen atom deactivates the benzene ring.

In Friedel-Craft acylation reaction, phenolic ether reacts rapidly with the AlX_3 catalyst to form complex.

$$Ph - OCH_3 + AlX_3 \longrightarrow Ph(CH_3)O \rightarrow AlX_3 \longleftrightarrow Ph(CH_3)O - AlX_3$$
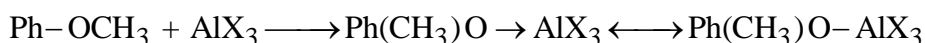
Illustration - 12 *For the reaction given in below, explain why different products are obtained when different amounts of AlBr₃ catalyst are used.*


SOLUTION :

In Friedal-Craft acylation reaction, phenolic ether reacts rapidly with the AlX_3 catalyst to form complex.

$$Ph - OCH_3 + AlX_3 \longrightarrow Ph(CH_3)O \rightarrow AlX_3 \longleftrightarrow Ph(CH_3)O - AlX_3$$
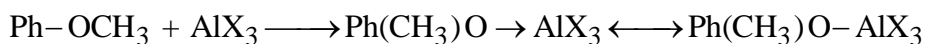
The adduct of phenolic ether and AlX_3 is much less reactive than benzene or phenolic ether in electrophilic aromatic substitution reactions because, as show in above equation, the oxygen electrons are delocalized onto the electron-deficient aluminium. Because of their delocalization away from the benzene ring, these electrons are less available for resonance stabilization of the carbocation. Intermediate formed within the ring during Friedal-Crafts acylation.
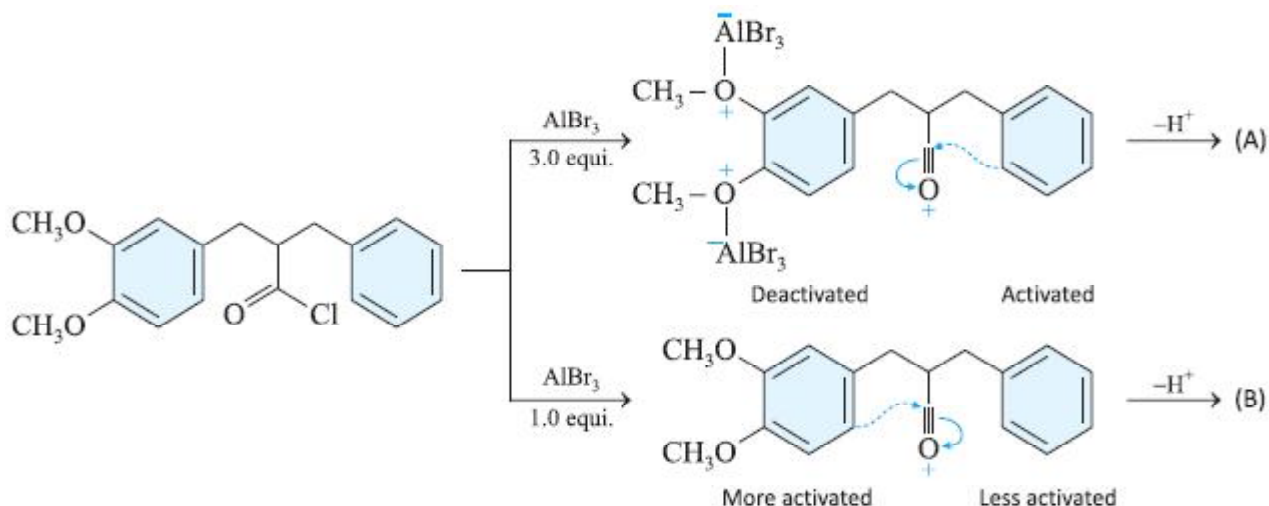

Note 3 : Orientation in Disubstituted Benzene :

1. When the two substituents are so situated that their influence reinforces at a point, further substitution can be predicted without any difficulty.
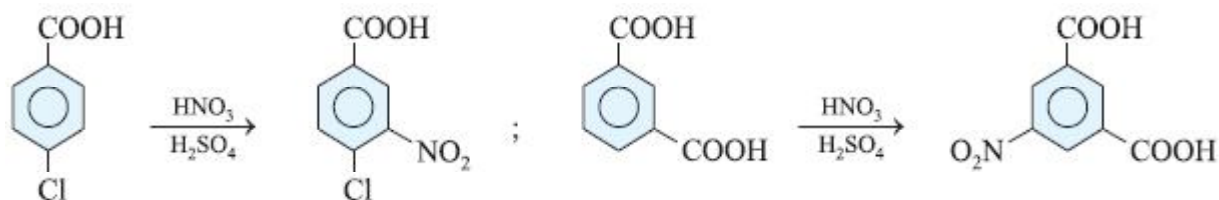
2. When both groups are activating, further substitution is controlled by the stronger activating group.

3. When one substituent is meta-directing and the other is o, p-directing, but they are situated meta to each other the third substituent goes otho to the meta directing group. This is known as ortho effect.
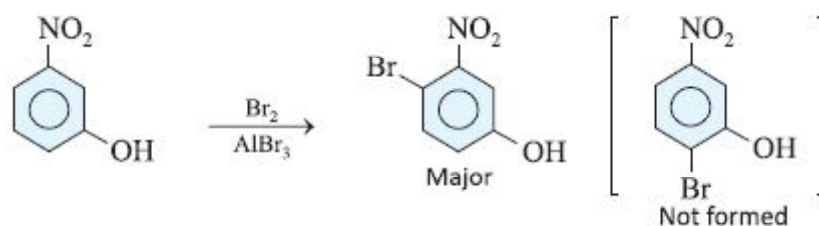
Note 4 : During intramolecular S_E reaction electrophile attack on *ortho*-position of existing substituents. It is a cyclization reaction. Five membered or six membered cyclic product is formed. Observe the following in tramolecular F.C. alkylation.
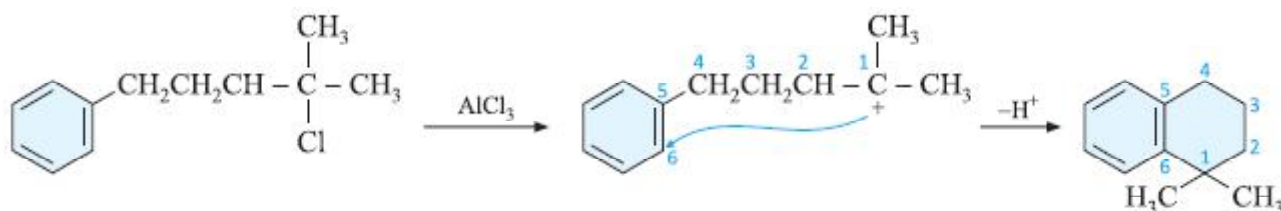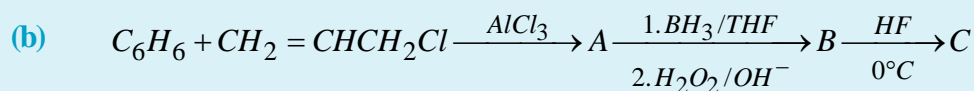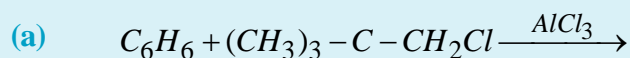

Directive influence of substituents on Benzene

The following table illustrates the directive influence of various functional groups over benzene for second substitution.

o, p-directing Groups					m-directing Groups	
Very Strongly activating	Strongly activating	Moderatly activating	Weakly activating	Deactivating	Very strongly deactivating	Strongly deactivating
+I & +M	−I << +M	−I < +M	+I < +H	+M < −I	−I & −M	−M(Less)
	−NH₂	−NHCOR	−CH₃	−F	−NO₂	−COOH
	−OH	−OCOR	−CR₃ (+I only)	−Cl	−CN	−COOR
−O⁻	−OR	−OCOPh	−CHR₂	−I	−SO₃H	−COOPh
	−NHR	−Ph	−CH₂R	−CH₂Cl (+H & −I)	−CHO	−CONH₂
	−NR₂	−CH = CH₂			−COR	−CCl₃
					−N⁺R₃	−CF₃

Note : ➤ $-\overset{+}{N}H_3$ is strongly deactivating and both '*p*' and '*m*' directing. Think it in terms of –I effort NOT –M. Remember it as a fact.

➤ $-NO$ group shows both $-M$ as well as $+M$ effect and it is weakly deactivating but *o, p*-directing.

**Illustration - 13** *Give the products in each of the following reactions.*

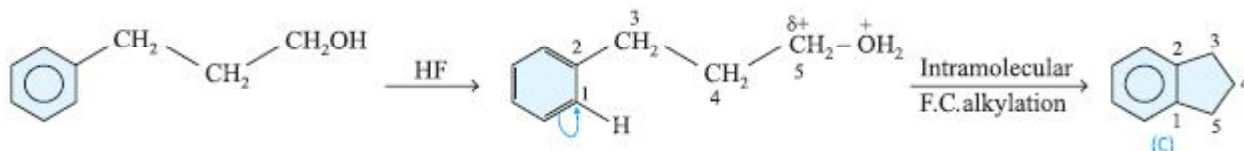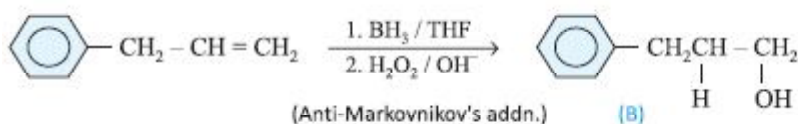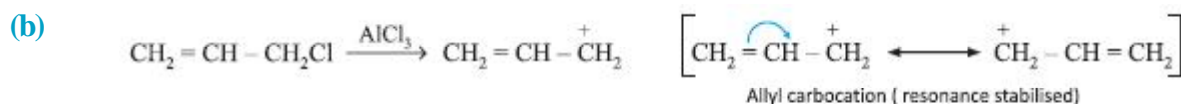(a) $C_6H_6 + (CH_3)_3 - C - CH_2Cl \xrightarrow{AlCl_3}$

(b) $C_6H_6 + CH_2 = CHCH_2Cl \xrightarrow{AlCl_3} A \xrightarrow[2.H_2O_2/OH^-]{1.BH_3/THF} B \xrightarrow[0°C]{HF} C$

SOLUTION :

(a) This reaction is an illustration of Friedel – Craft alkylation (S_E reaction).

1° carbocation (unstable) → 3° carbocation (highly stable)
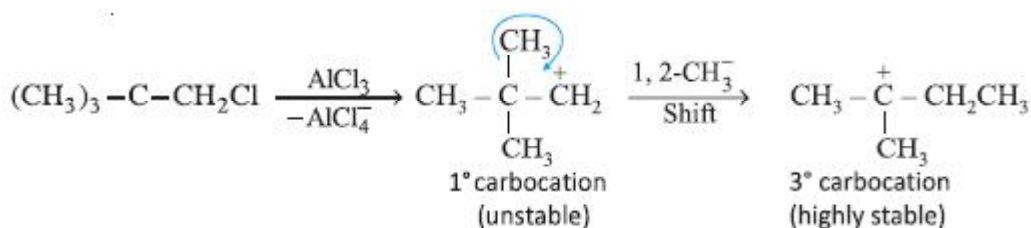
Now it is simply F.C. alkylation. *Here we have visualized the formation of $1°C^+$ as there is no other pathway.*
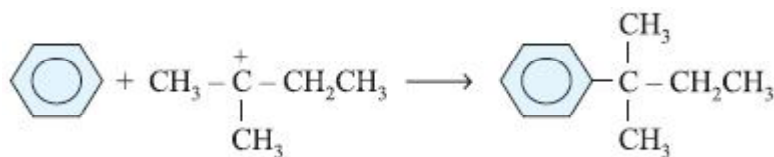

Note : In S_E reaction involving carbocation (Friedal Craft alkylation), a stable carbocation is to be taken as an attacking Electrophile (i.e. visualise rearrangement).
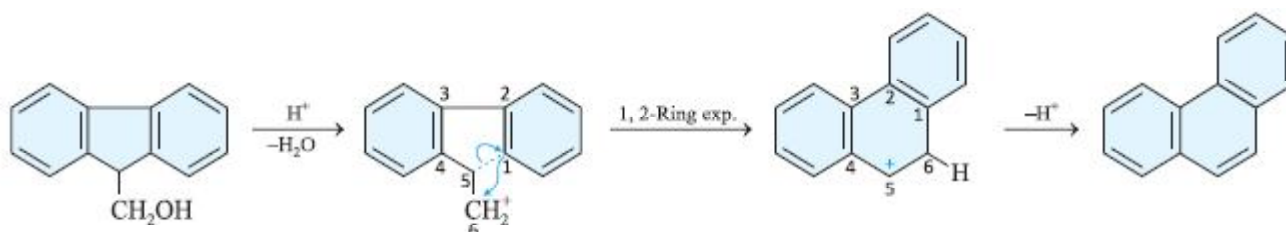
(b)

Allyl carbocation (resonance stabilised)

(A)

(Anti-Markovnikov's addn.)   (B)

Intramolecular F.C. alkylation   (C)

Note : Observe that Friedel –Craft Alkylation can also be achieved with ROH/HF or $RCH = CH_2/$ HF at very low temperature.
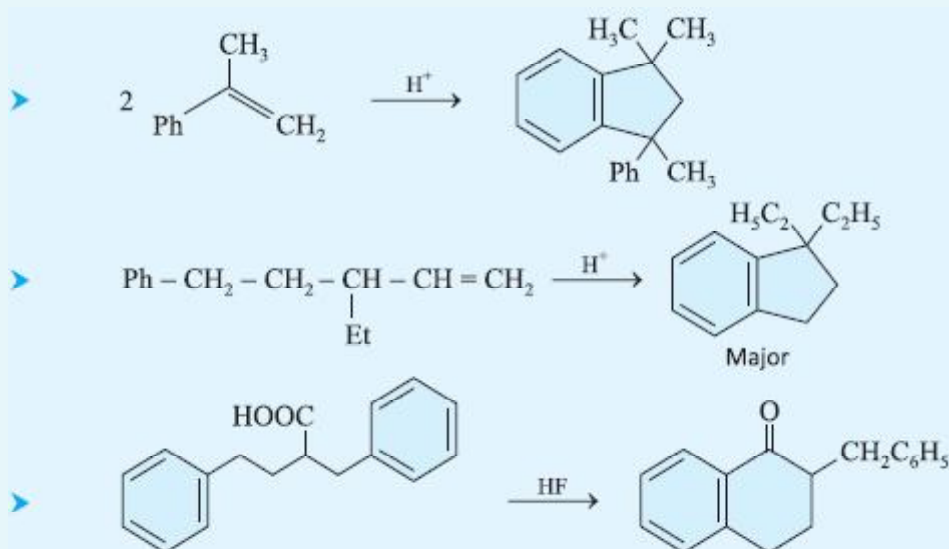
Illustration - 14 *Identify the product and propose the mechanism :*
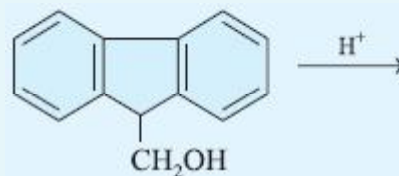
SOLUTION :

Try yourself : Propose the mechanism for the following reaction :

NOW ATTEMPT IN-CHAPTER EXERCISE-C BEFORE PROCEEDING AHEAD IN THIS EBOOK
NOW ATTEMPT PRACTICE EXERCISE-I BEFORE PROCEEDING AHEAD IN THIS EBOOK

2.B   Addition Reactions

Reactions in which atoms or groups of atoms are added to a molecule are called addition reactions. Usually such reactions take place in unsaturated compounds containing double and triple covalent bonds.

These are also classified into three types depending upon type of attacking reagent.

(a)   Electrophillic

(b)   Free radical

(c)   Nucleophillic

Mechanism of Addition Reactions :

(a)   Electrophillic Addition Reactions :

Alkenes are $\pi\,e^-$ rich so are prone to be attacked by an electrophile, so predominantly undergo electrophile addition reaction i.e. it gets converted to a saturated compound by undergoing addition reaction, initiated by attack of electrophile. Electrophilic addition on alkenes proceed through following mechanisms :

Mechanism I :

$$R - CH = CH_2 \xrightarrow[\text{Slow}]{E^+} R - \overset{+}{C}H - CH_2 - E \xrightarrow[\text{Fast}]{Nu^-} R - \underset{|}{\overset{Nu}{\underset{|}{C}}}H - CH_2 - E$$

Specific Features :

Electrophile causes shifting of $\pi -$ bond (i.e. electromeric effect) in a manner so as to form a stable carbocation.

Carbocation intermediate may rearrange if possible. Racemisation is possible as carbocation is involved and it is planar intermediate.
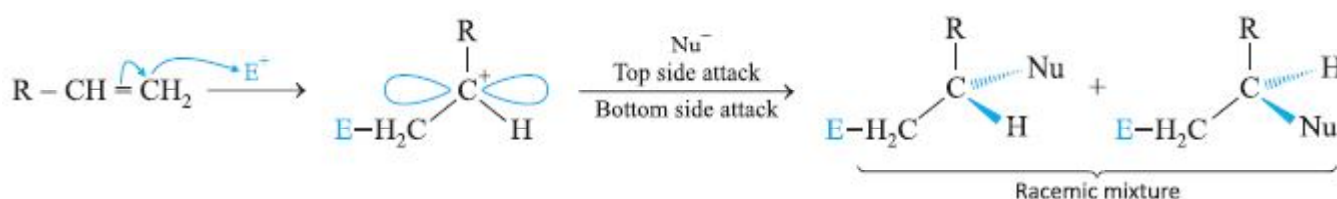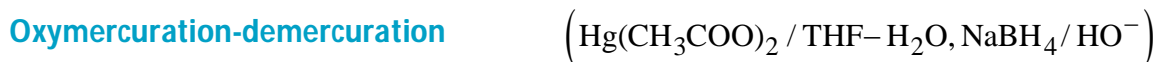

It's a Markovnikov's addition i.e. nucleophile gets attached to the carbon, where most stable carbocation is favoured, after rearrangement (if possible). Addition of HX, H^+ / H_2O follows above mechanism.

Mechanism II :
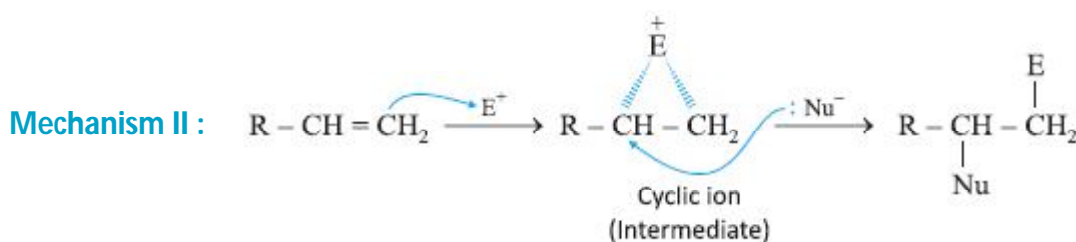
Specific features :

(i)   Electrophile causes polarization of π and e^- density to form a cyclic ion.

(ii)   No rearrangement, as carbocation is not involved.

(iii) Nucleophile attacks cyclic ion in an anti manner i.e. it attacks cyclic ion from the opposite side of attached E in order to avoid steric and electrostatic repulsion.

(iv)   It's a Markovnikov's addition i.e. the nucleophile attacks cyclic ion on the carbon where a stable carbocation is possible, i.e. a carbon attached to stabilising alkyl groups (+I, +H)

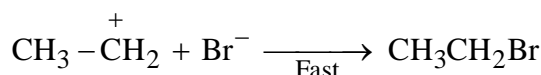Following reactions proceeds through above mechanism :

Oxymercuration-demercuration $\left(Hg(CH_3COO)_2 / THF- H_2O, NaBH_4 / HO^-\right)$

Addition of Halogen $[X_2 / CCl_4, X_2 / H_2O]$
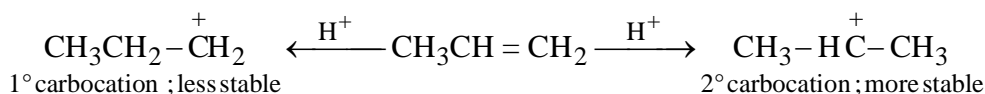
Addition of HA :

Consider addition of HBr to ethylene :

Step 1 :   Electrophile (H^+) attacks the $C = C$ bond via electromeric effect, (+E effect). Seeing the incoming electrophile (H^+), electromeric shift (effect) occurs, and π electron cloud is displaced towards one of the carbon atoms.

$$CH_2 = CH_2 \; + \; \overset{\delta+}{H} - \overset{\delta-}{Br} \xrightarrow{\text{Slow}} \; H - CH_2 - \overset{+}{CH_2} \; + \; Br^- \quad \text{(Carbocation)}$$

Step 2 :   Nucleophile (Br^-) adds to the carbonium ion :

$$CH_3 - \overset{+}{CH_2} \; + \; Br^- \xrightarrow{\text{Fast}} \; CH_3CH_2Br$$

In case of $CH_3CH = CH_2$ (i.e., unsymmetrical alkenes), electromeric shift can occur in either direction to give two carbocations.
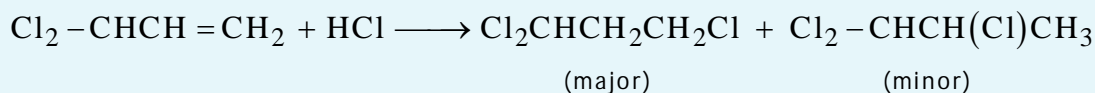
$$\underset{\substack{1° \text{ carbocation ; less stable}}}{CH_3CH_2 - \overset{+}{CH_2}} \xleftarrow{\;\; H^+ \;\;} CH_3CH = CH_2 \xrightarrow{\;\; H^+ \;\;} \underset{\substack{2° \text{ carbocation ; more stable}}}{CH_3 - \overset{+}{HC} - CH_3}$$

Hence the major product formed is $CH_3 - HC(Br) - CH_3$. This is in accordance with Markonikov's addition. In addition reactions of alkenes with HX and H_2O / H^+, the same mechanism is followed.

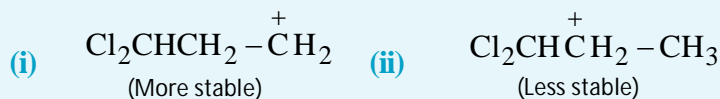➤   Reactivity of Halogen acids for addition reaction : $HI > HBr > HCl$

Such addition reactions are referred to as regioselective reactions.

Note :   If an electron withdrawing group is present at one end of the alkene, then the addition is reversed. For example consider addition of HCl to 3, 3-Dichloro propene.
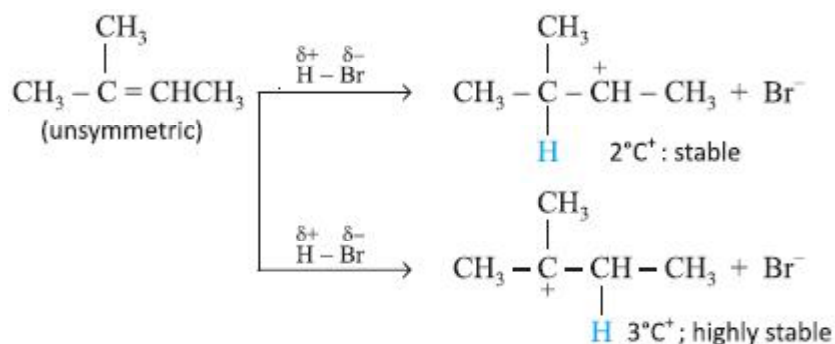
$$Cl_2 - CHCH = CH_2 + HCl \longrightarrow \underset{\text{(major)}}{Cl_2CHCH_2CH_2Cl} \; + \; \underset{\text{(minor)}}{Cl_2 - CHCH(Cl)CH_3}$$

The reason for this is the stability of intermediate carbonium ion. –I effect of the Cl atoms decreases stability of carbonium. Try to compare the two possible carbonium ions formed.
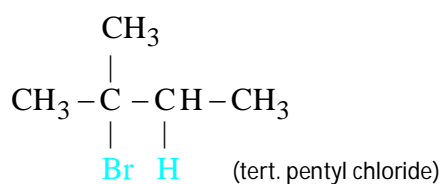
(i) $\underset{\text{(More stable)}}{Cl_2CHCH_2 - \overset{+}{C}H_2}$ **(ii)** $\underset{\text{(Less stable)}}{Cl_2CH\overset{+}{C}H_2 - CH_3}$

In (i), two Cl atoms are at a greater distance from C^+ site, whereas in (ii), two Cl atoms are nearer to C^+ site. Hence –I effect de-stabilises the carboction. (ii) to a much greater extent than it does in (i), and hence the major product is with respect to intermediate (carbocation) (i).

Observe the following addition of HBr in 2-Methyl-2-butene.

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CHCH_3 \xrightarrow{\overset{\delta+\ \ \delta-}{H-Br}} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{+}{C}H-CH_3 + Br^-$$

(unsymmetric)   2°C⁺ : stable

$$\xrightarrow{\overset{\delta+\ \ \delta-}{H-Br}} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{+}{C}}-\overset{\underset{\displaystyle H}{|}}{C}H-CH_3 + Br^-$$

3°C⁺ ; highly stable

Now the major product eventually will be :
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-\overset{\underset{\displaystyle H}{|}}{C}H-CH_3$$
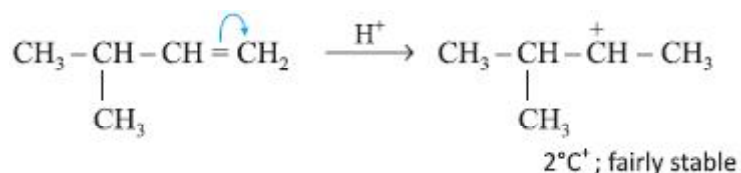
(tert. pentyl chloride)

So let us red line Markonikov's rule as : "Electrophillic addition to a carbon - carbon double bond involves the intermediate formation of the most stable carbocation".
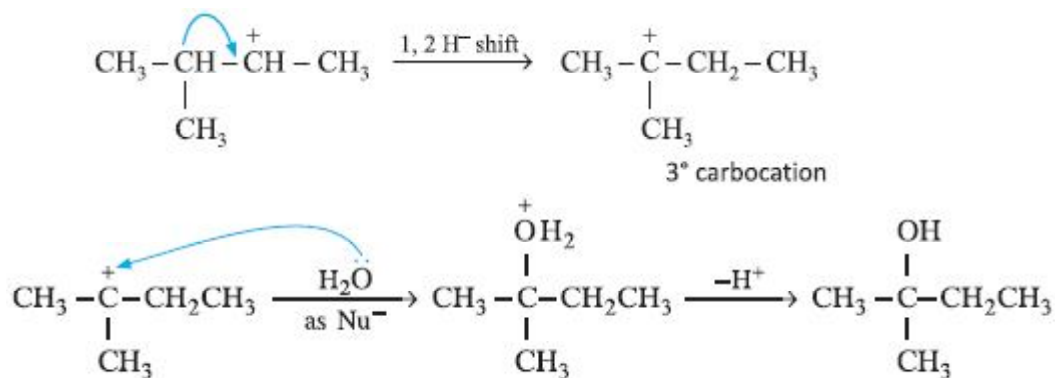
Rearrangement in addition reaction

Observe the following example of hydration of alkene in acidic medium carefully.

$$CH_3-\overset{\underset{\displaystyle CH_3}{|}}{C}H-CH=CH_2 \xrightarrow[H_2O]{H^+} ?$$
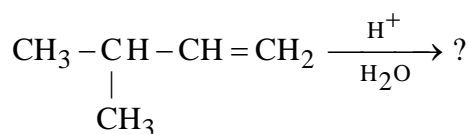
First visualise formation of initial carbocation via electromeric effect.

$$CH_3-\overset{\underset{\displaystyle CH_3}{|}}{C}H-CH=CH_2 \xrightarrow{H^+} CH_3-\overset{\underset{\displaystyle CH_3}{|}}{C}H-\overset{+}{C}H-CH_3$$

2°C⁺ ; fairly stable

Now H⁻ (hydride) from the adjacent 3° carbon occurs to give more stable 3° carbocation.

$$CH_3-\overset{\underset{\displaystyle CH_3}{|}}{C}H-\overset{+}{C}H-CH_3 \xrightarrow{1,2\ H^-\ shift} CH_3-\overset{\overset{+}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_3$$

3° carbocation

$$CH_3-\overset{\overset{+}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2CH_3 \xrightarrow[\text{as } Nu^-]{H_2O} CH_3-\overset{\overset{\overset{+}{O}H_2}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2CH_3 \xrightarrow{-H^+} CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2CH_3$$
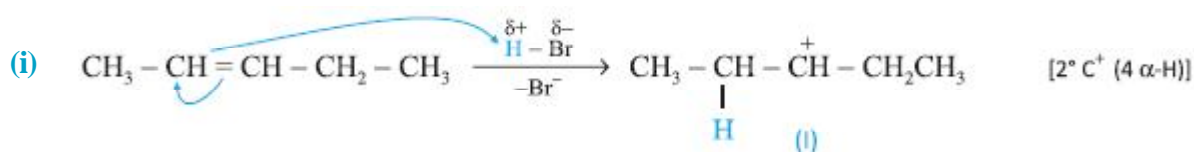
So, you have observed a rearrangement in addition reaction to give the most stable carbocation.

Illustration - 15 *Predict the major products in the following reactions :*

(i) $CH_3 - CH = CH - CH_2 - CH_3 \xrightarrow{HBr}$

(ii) (phenyl)$-\underset{\underset{Me}{|}}{C} = CH - CH_3 \xrightarrow[H^+]{H_2O}$
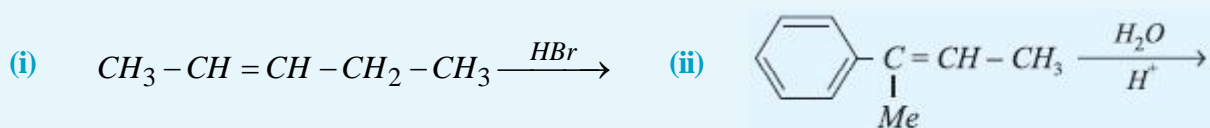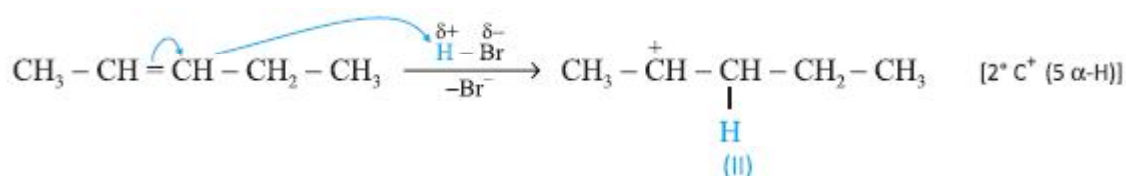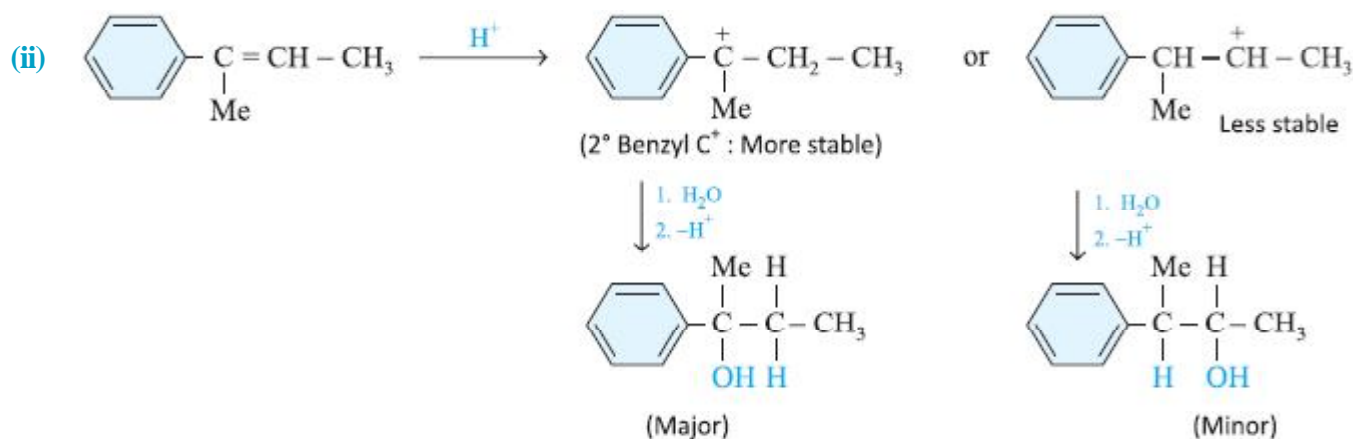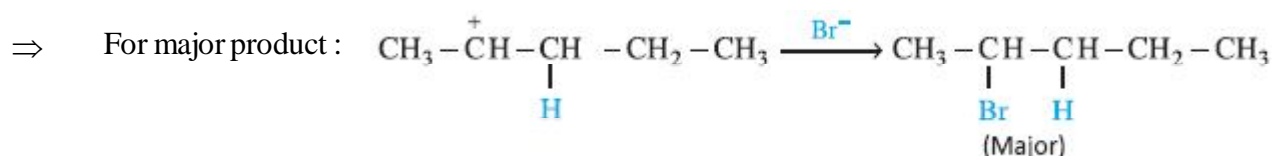
SOLUTION :

In all the given reactions, visualise the addition across the π bond (starting with addition of an electrophile) through more stable carbocation.

(i) $CH_3 - CH = CH - CH_2 - CH_3 \xrightarrow[-Br^-]{\overset{\delta+}{H} - \overset{\delta-}{Br}} CH_3 - \underset{\underset{H}{|}}{CH} - \overset{+}{CH} - CH_2CH_3$ [2° C^+ (4 α-H)]

(I)

or

$CH_3 - CH = CH - CH_2 - CH_3 \xrightarrow[-Br^-]{\overset{\delta+}{H} - \overset{\delta-}{Br}} CH_3 - \overset{+}{CH} - \underset{\underset{H}{|}}{CH} - CH_2 - CH_3$ [2° C^+ (5 α-H)]

(II)

Note : (II) is more stable than (I) due to more number of $\alpha - H$ available for hyperconjugation.

$\Rightarrow$ For major product : $CH_3 - \overset{+}{CH} - \underset{\underset{H}{|}}{CH} - CH_2 - CH_3 \xrightarrow{Br^-} CH_3 - \underset{\underset{Br}{|}}{CH} - \underset{\underset{H}{|}}{CH} - CH_2 - CH_3$

(Major)

(ii) (phenyl)$-\underset{\underset{Me}{|}}{C} = CH - CH_3 \xrightarrow{H^+}$ (phenyl)$-\underset{\underset{Me}{|}}{\overset{+}{C}} - CH_2 - CH_3$ or   (phenyl)$-\underset{\underset{Me}{|}}{CH} - \overset{+}{CH} - CH_3$

(2° Benzyl C^+ : More stable)   Less stable

1. H_2O
2. $-H^+$

(phenyl)$-\underset{\underset{OH}{|}}{\overset{\overset{Me}{|}}{C}} - \underset{\underset{H}{|}}{C} - CH_3$

(Major)

1. H_2O
2. $-H^+$

(phenyl)$-\underset{\underset{H}{|}}{\overset{\overset{Me}{|}}{C}} - \underset{\underset{OH}{|}}{C} - CH_3$

(Minor)

➤ **Addition of X_2 in CCl_4 :**

Addition of Halogens (X_2) in CCl_4 follows the mechanism involving cyclic intermedimate.

(i)

Cyclic bromonium ion
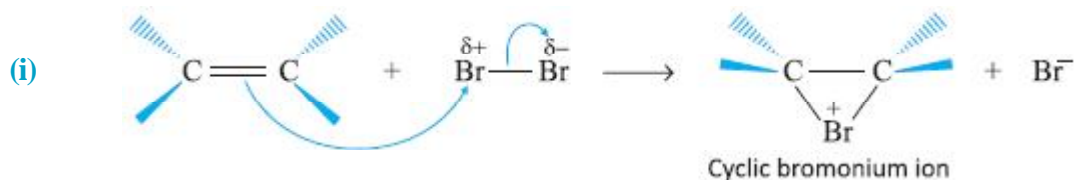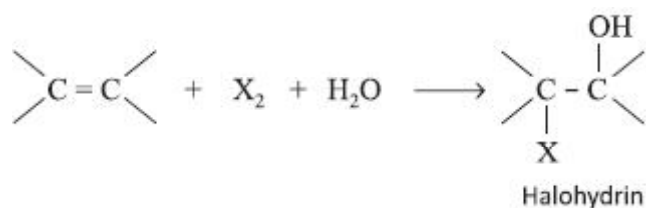
The bromine molecule is polarised when it approaches alkene. It then transfers a +ve Br atom (an electrophile) to form a cyclic bromonium ion.

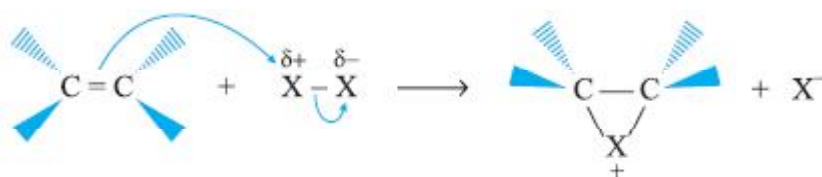**(ii)**

A Dibromide (An anti-addition)
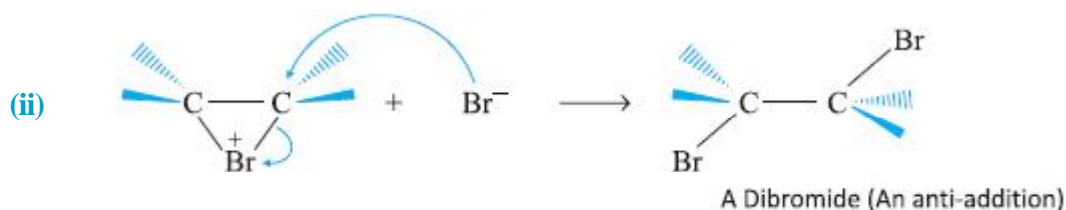
The bromide ion (Br^-) attacks one of the carbon like an attack in S_N2 reaction, which results in opening of ring to give viccinal dibromide.

➤ **Addition of X_2 in H_2O :** ($\equiv HO^-X^+$)

Halohydrin

The first step is same as for halogens (Br_2) shown above.

In next step, instead of bromide ion, H_2O acts as a nucleophile and attacks a carbon of the ring forming protonated halohydrin.

Protonated halohydrin
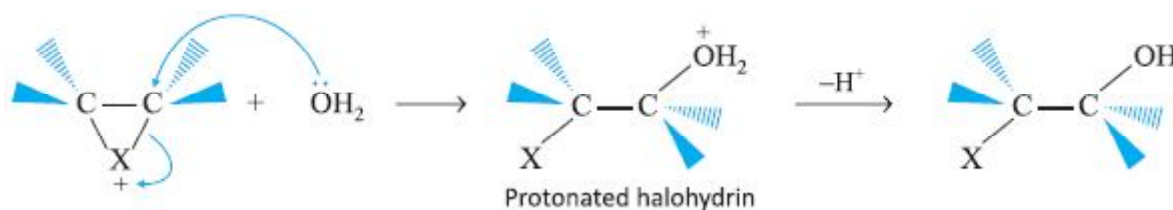
In the given example, the structure of the product tells us that what attacks the more highly substituted carbon.

$$(CH_3)_2 \, C = CH_2 \xrightarrow[H_2O]{Br_2} (CH_3)_2 \, \underset{\underset{OH}{|}}{C} - CH_2Br$$
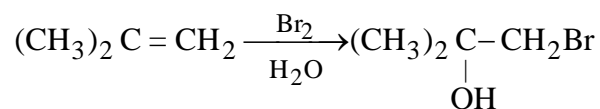
2 - Methylpropene   1 - Bromo- 2 - methyl- 2 - propanol (Major)

This suggests that, as water attacks the bromonium ion, positive charge develops on the carbon from which the bromine departs. The transition state has some of the character of a carbocation. We know that more substituted carbocation are more stable than less substituted ones ; therefore, when the bromonium ion ring opens, it does so by breaking the bond between bromine and the more substituted carbon.

More stable transition state; has some of the character of a tertiary carbocation

Less stable transition state; has some of the character of a primary carbocation
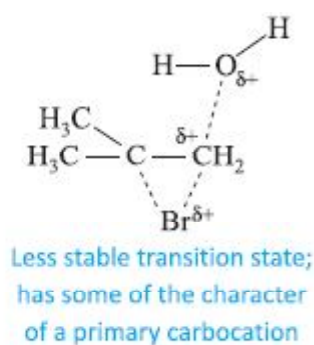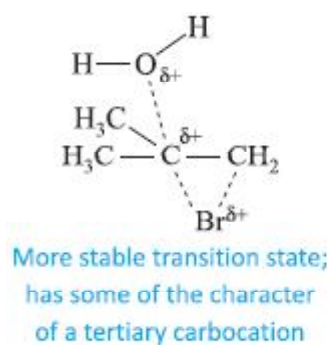
➤ The above additions are region-selective as one of the product dominates over the other.

➤ Whereas, the addition of Br_2 in CCl_4 and hydroxylation are sterco-specific and sterco-selective reactions as illustrated by following examples.

Maleic acid (*cis*-isomer)

Meso isomer

Fumaric acid (*trans*-isomer)

Racemic mixture

cis-2-butene → Br$_2$ anti-addition → Racemic mixture

trans-2-butene → Br$_2$ anti-addition → Meso isomer
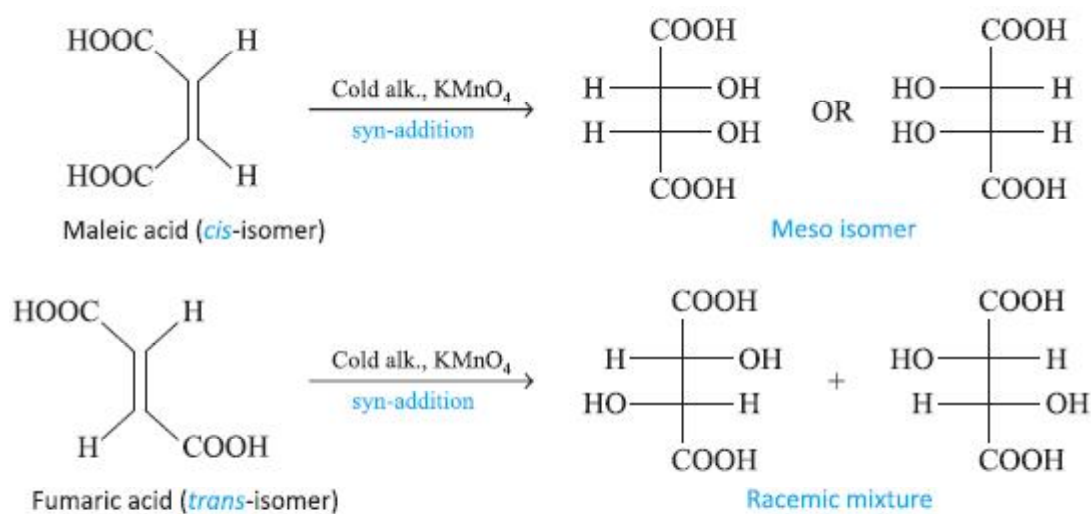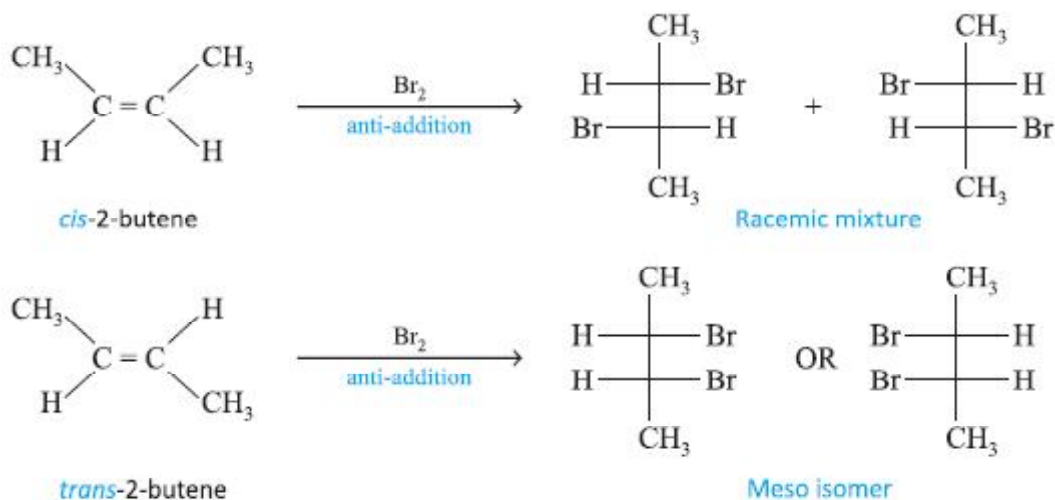
Note : Both-*cis*-2-pentene and *trans*-2-pentene on reaction will Br$_2$ form racemic mixture, as there will not be any plane of symmetry in both cases.


Illustration - 16 *When 3-Buten-2-ol reacts with HBr, two isomeric products are obtained. Explain with proper mechanism.*

SOLUTION :

Usually alcohols do not give nucleophilic substitution, as OH^-, the leaving group is poor being strong base. However, in presence of H^+ ions, 2° and 3° alcohols give S_N1 type of nucleophilic substitution as H_2O (weak base) is now the good leaving group.
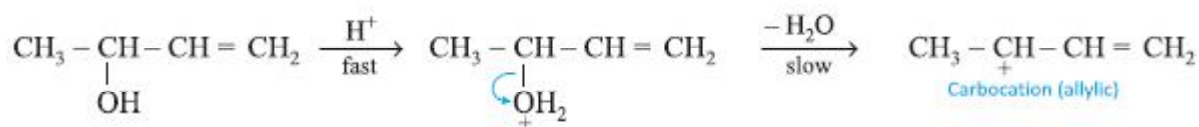
Allylic carbocations are resonance stabilised.
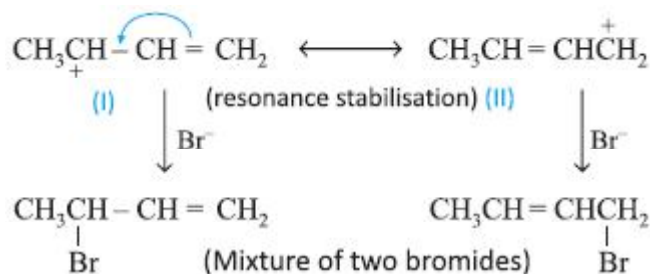
➤ Note that in the above question H^+ attacks on the lone pair in preference to π – bond. If H^+ attacks π – bond, the intermediate formed is : $CH_3CH(OH) - \overset{+}{C}HCH_3,$ which is less stable as compared to

$$CH_3 - \overset{+}{CH} - CH = CH_3$$
Carbocation (allylic)

➤ If both lone pair and π – bond are in conjugation with each other, then H^+ attacks on π – bond to give a stable carbocation.
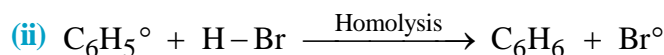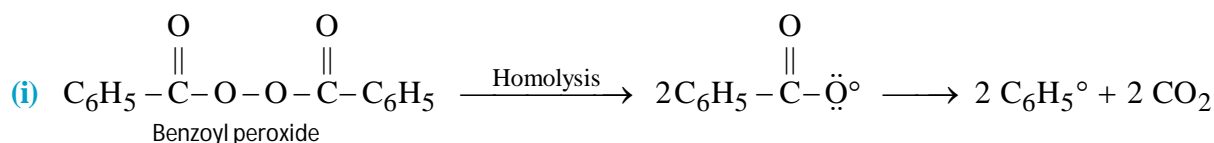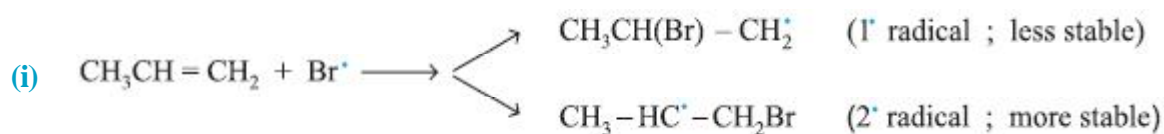
$$CH_2 = CH - \overset{..}{O} - CH_3 \xrightarrow{\ H^+\ } CH_3 - \overset{+}{CH} \overset{\frown}{-} \overset{..}{O} - CH_3 \longleftrightarrow CH_3CH = \overset{+}{O} - CH_3$$
Resonance stabilised
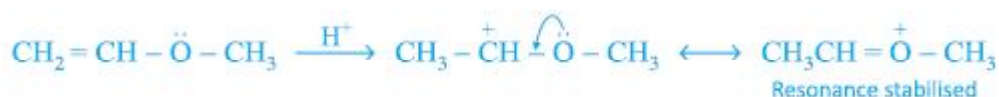
(b) Free radical addition

In the presence of peroxide, addition of HBr follows Anti-Markonikov's addition (Peroxide or Kharash effect).

Consider addition of HBr in propene in presence of Benzoyl peroxide. The following *free radical chain mechanism* has been proposed :
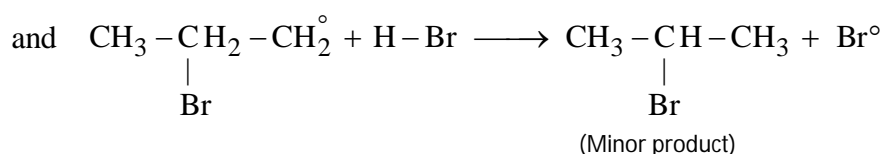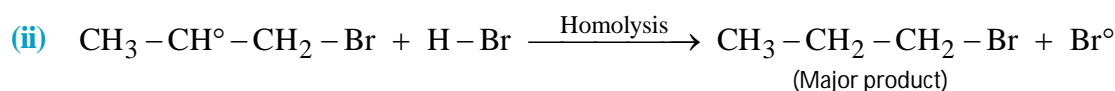
Chain initiation :

(i) $C_6H_5 - \overset{\overset{O}{\|}}{C} - O - O - \overset{\overset{O}{\|}}{C} - C_6H_5 \xrightarrow{\text{Homolysis}} 2C_6H_5 - \overset{\overset{O}{\|}}{C} - \overset{..}{O}° \longrightarrow 2\ C_6H_5° + 2\ CO_2$

Benzoyl peroxide

(ii) $C_6H_5° + H - Br \xrightarrow{\text{Homolysis}} C_6H_6 + Br°$

Chain Propagation Step :

(i) $CH_3CH = CH_2 + Br^· \longrightarrow$

$CH_3CH(Br) - CH_2^·$ (I° radical ; less stable)

$CH_3 - HC^· - CH_2Br$ (2° radical ; more stable)

Recall stability of free radicals via Hyperconjugation effect.

(ii) $CH_3 - CH° - CH_2 - Br + H - Br \xrightarrow{\text{Homolysis}} CH_3 - CH_2 - CH_2 - Br + Br°$
(Major product)

and $CH_3 - \underset{\underset{Br}{|}}{CH_2} - CH_2° + H - Br \longrightarrow CH_3 - \underset{\underset{Br}{|}}{CH} - CH_3 + Br°$
(Minor product)

Note : HCl and HI do not add similarly in the presence of peroxides because one of the step of chain propagation steps becomes endothermic. The reaction with $H-Cl$ fails because of higher $H-Cl$ bond energy, which prevents its cleavage by the free radical [step (ii)]. The $H-I$ bond is weaker, but iodine free radicals com -bine to form iodine molecules instead of adding to the double bond.

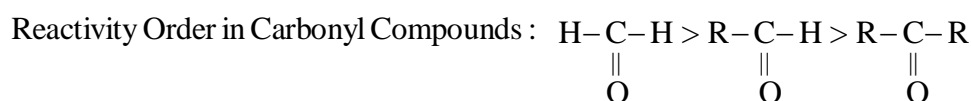NOW ATTEMPT IN-CHAPTER EXERCISE-D BEFORE PROCEEDING AHEAD IN THIS EBOOK

(c) Nucleophilic Addition Reaction

Consider the addition of CN^- to aldehydes and ketones.

➤ In presence of CN^- (nucleophile), π e's of $>C^{\delta+}=O^{\delta-}$ bond are shifted towards more electrone-gative oxygen atom via –E effect).
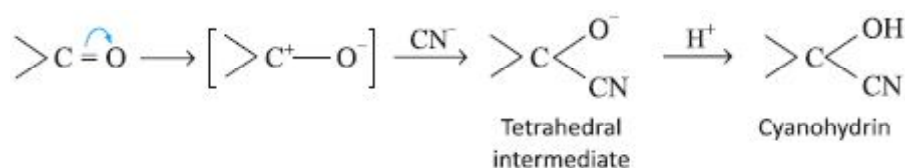
Presence of EWG increase reactivity while presence of ERG decrease reactivity towards nucleo-philic addition reactions.

Reactivity Order in Carbonyl Compounds :

$$\underset{O}{\overset{\|}{H-C-H}} > \underset{O}{\overset{\|}{R-C-H}} > \underset{O}{\overset{\|}{R-C-R}}$$

Addition of Grignard Reagent with carbonyl compounds follows the above mechanism. The conden-sation reactions (to be studied later) usually follow nucleophilic addition reaction pathway.

2.C Elimination Reactions :

These reactions involve loss of atoms or group of atom from a molecule to form multiple bonds.
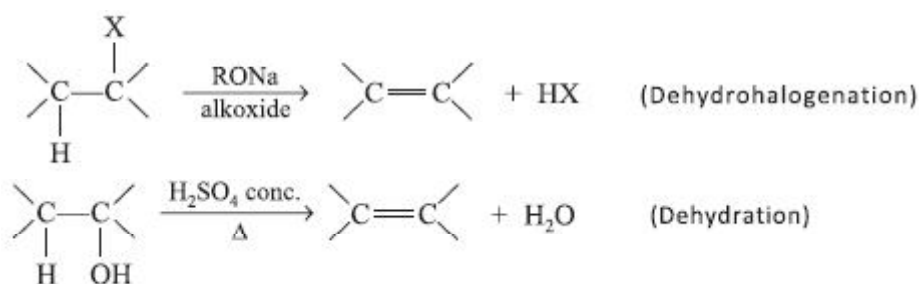
Mechanism of elimination reactions :

**(a) Dehydrohalogenation of alkyl halides :** It can be achieved by E1 (unimolecular) or E2 (bimolecular) path.

E2 Elimination : It is one step reaction mechanism.

Consider elimination in tertiary butyl bromide by ethoxide ion.

➤ Base (B^-)is this case is ethoxide, $C_2H_5O^-$ or (ethanolic KOH : OH^- as base or NH_2^-) which forms a transition state with alkyl halides as shown below (just like an S_N2 path). Ethoxide EtO^- attacks β-proton (H), and abstracts it.
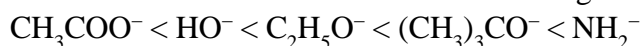

(A Transition State)
BF : Bond forming
BB : Bond breaking
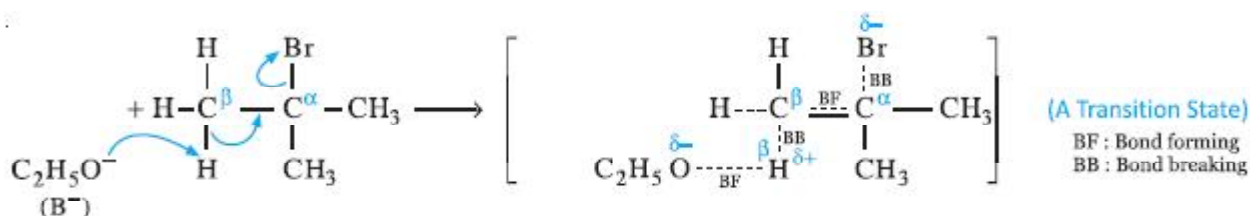
Observe that the reaction is bimolecular i.e., it follows E2 path, just like S_N2 path.
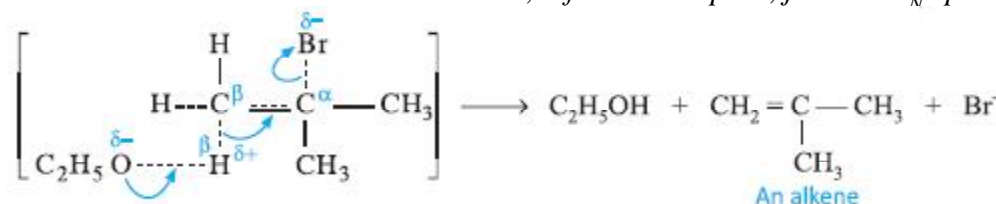
An alkene

Note 1 : ➤ Since all nucleophiles are good bases, S_N2 products also follow along with E2 products.
➤ 3° and 2° alkyl halides give alkene (E2) as major product.
➤ 1° alkyl halides give S_N2 as major product. (Williamson's synthesis of ethers)
➤ 1° alkyl halides, however give alkenes with strong and sterically (bulky) hindered bases such as tert. butoxide.

**Note 2 :** ➤ The reaction rate of elimination increases with increasing strength of the base :
$$CH_3COO^- < HO^- < C_2H_5O^- < (CH_3)_3CO^- < NH_2^-$$
➤ The ease of elimination follows : 3° > 2° > 1° (alkyl halides)
➤ The elimination occurs more easily when the halides are already unsaturated. e.g., elimination occurs readily in
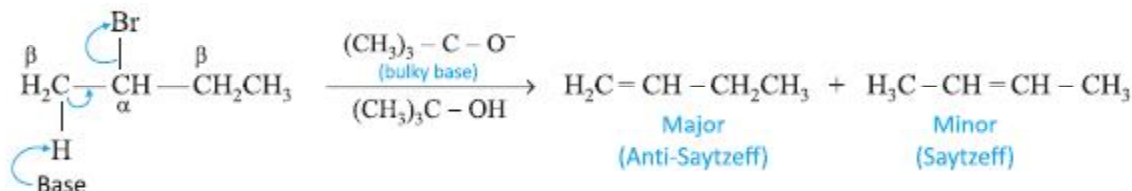$$CH_2 = CH - CH_2CH_2Br \text{ than in } CH_3CH_2CH_2CH_2Br.$$
Visualise the product on elimination. (a conjugated diene is formed)
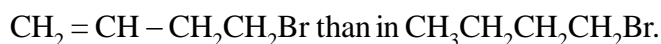
Note 3 : **(Orientation of products)**
➤ Two different alkenes may be formed when there are two β-hydrogen atoms. The major is one having more alkylation about the double bond (in accordance with Zaitsev Rule or Saytzeff Rule). It is also a regio-selective reaction.
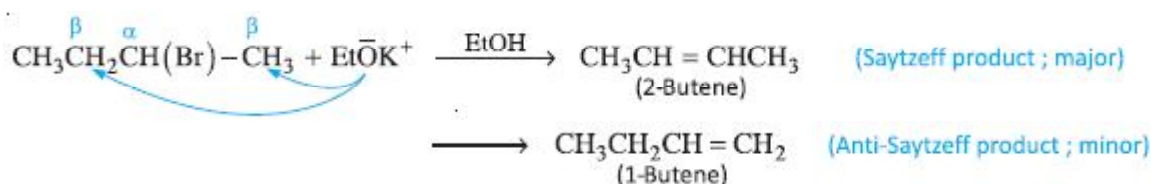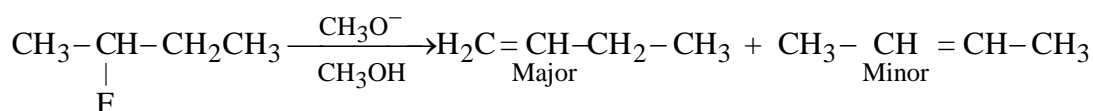
This is referred to as *Saytzeff Rule*. The exception to Saytzeff rule comes when a large (bulky) and strong bases such as teritary butoxide are used, then due to steric hindrance (in base) less substituted alkene (Anti-saytzeff product) is formed. It is also known as Hoffmann's product.

$$H_2C-CH-CH_2CH_3 \xrightarrow[\substack{(CH_3)_3C-OH}]{\substack{(CH_3)_3-C-O^- \\ \text{(bulky base)}}} H_2C=CH-CH_2CH_3 + H_3C-CH=CH-CH_3$$

Major (Anti-Saytzeff)   Minor (Saytzeff)

➤ Note that Saytzeff's (Zaitsev) rule is not used in cases, where alkyl halide has double bond or benzene ring. In such cases, conjugated double bonds have a greater stability (including conjugation with benzene ring).
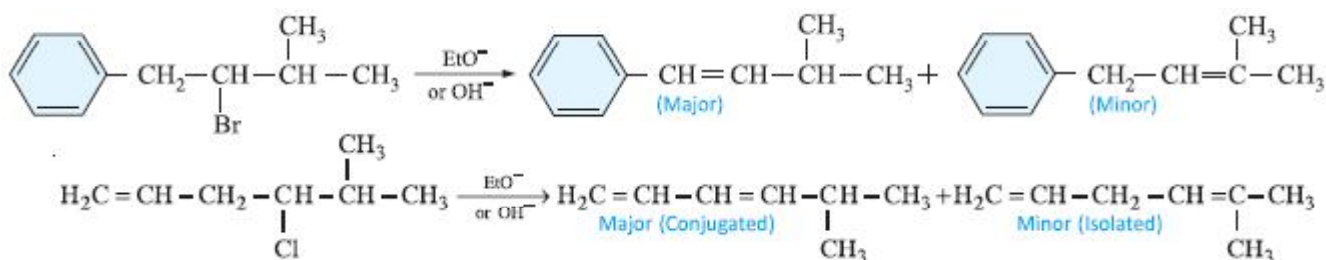

➤ In case of alkyl fluorides, the product of E2 reaction is also Anti-Zaitsev. F^- is a poor leaving group, so remember it as a fact that Zaitsev product is minor.
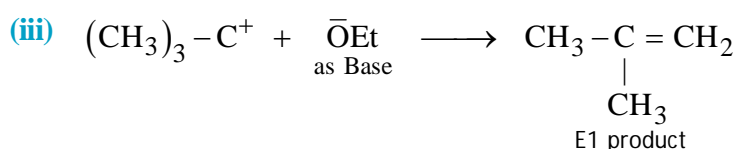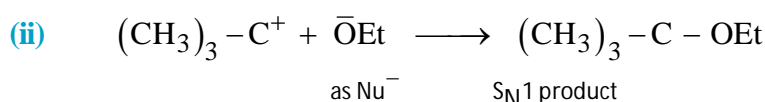
$$CH_3-CH-CH_2CH_3 \xrightarrow[CH_3OH]{CH_3O^-} \underset{\text{Major}}{H_2C=CH-CH_2-CH_3} + \underset{\text{Minor}}{CH_3-CH=CH-CH_3}$$
$$\underset{F}{|}$$

E2 An anti Elimination :

In the following substrate, observe that there are two βH-atoms. H^1 atom is anti to Br atom and H^2 atom is in the same plane as that of Br atom. Note that E2 is an *anti-elimination*, which means β hydrogen and the leaving halogen atom (Br) must leave from opposite planes. In the following Illustration, observed that product formed is not a Saytzeff product. Which justifies the concept of *anti-elimination*.
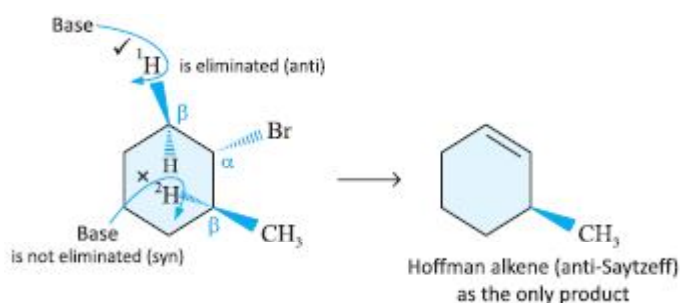
E1 Elimination : Its is a two steps reaction mechanism.

Elimination may take a different path (*E1 path is just like* S_N1 *path*). Consider the elimination of $(CH_3)_3 - C - Br$ via E1 as :

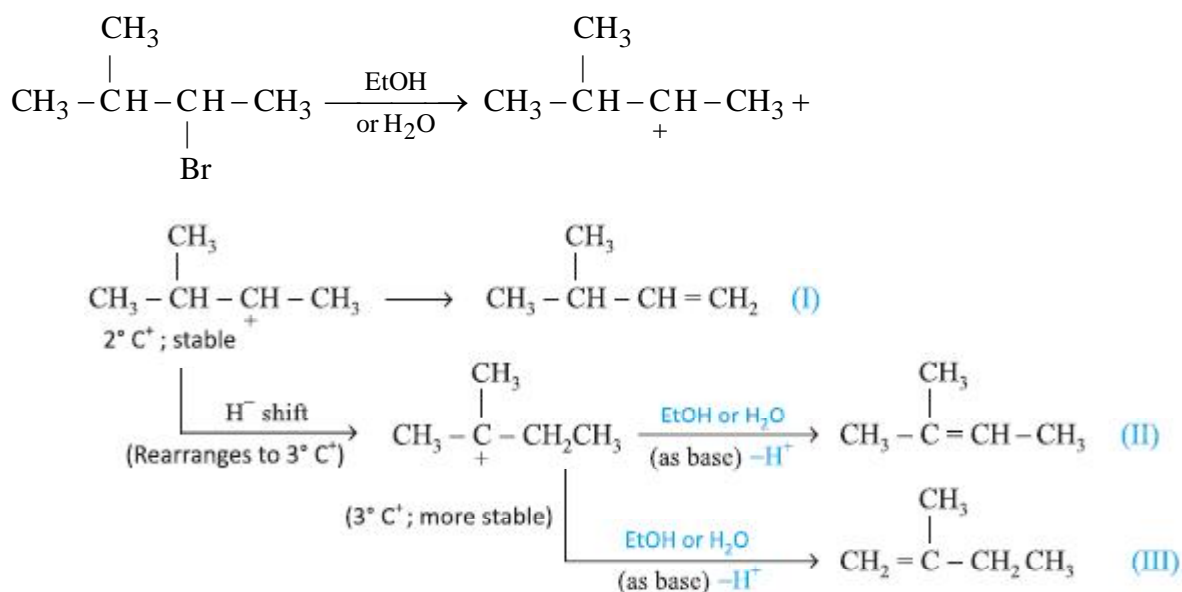**(i)** $\qquad (CH_3)_3 - C - Br \longrightarrow (CH_3)_3 - C^+ + Br^-$

(ii) $\qquad (CH_3)_3 - C^+ + \overline{O}Et \longrightarrow (CH_3)_3 - C - OEt$
$\qquad\qquad\qquad\quad$ as Nu$^-$ $\qquad\qquad$ S_N1 product

(iii) $(CH_3)_3 - C^+ + \underset{\text{as Base}}{\overline{O}Et} \longrightarrow CH_3 - \underset{\underset{CH_3}{|}}{C} = CH_2$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ E1 product

➤ This means E1 path will always accompany S_N1 and usually S_N1 product dominate over E1 product. Note that usually a good base is always a good Nucleophile and vice-versa except among halide ions. (I^- is a good nucleophile, but weaker base and F^- is a poor nucleophile, but stronger base). Hence we should visualize above elimination via E2 path, using strong bases and slightly polarised (weak) nucleophiles.
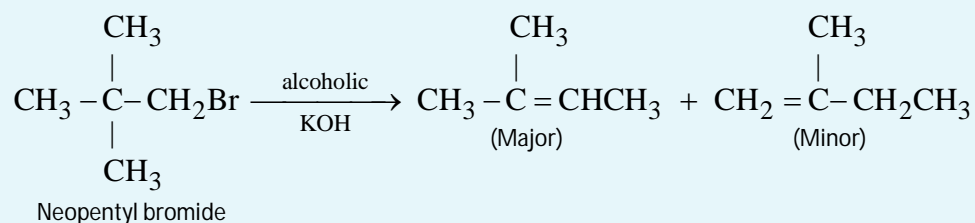
$\quad (RO^-, OH_{abc}^-, NH_2^-)$

➤ In such unimolecular reactions (i.e., in E1 and S_N1), wherever structure permits, rearrangement occurs, since reactivity depends upon stability of carbocations.

E1 is observed when using weak bases which are usually polarizing. ($H_2O, EtOH$)

$$CH_3 - \underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}H} - CH - CH_3 \xrightarrow[\text{or } H_2O]{EtOH} CH_3 - \overset{\overset{CH_3}{|}}{C}H - \underset{+}{C}H - CH_3 +$$

$$CH_3 - \underset{\underset{\text{2° C}^+; \text{ stable}}{}}{\overset{\overset{CH_3}{|}}{C}}H - \underset{+}{C}H - CH_3 \longrightarrow CH_3 - \overset{\overset{CH_3}{|}}{C}H - CH = CH_2 \quad (I)$$

$$\xrightarrow[\text{(Rearranges to 3° C}^+\text{)}]{H^- \text{ shift}} CH_3 - \underset{+}{\overset{\overset{CH_3}{|}}{C}} - CH_2CH_3 \xrightarrow[\text{(as base)} -H^+]{EtOH \text{ or } H_2O} CH_3 - \overset{\overset{CH_3}{|}}{C} = CH - CH_3 \quad (II)$$

$$\text{(3° C}^+; \text{ more stable)} \xrightarrow[\text{(as base)} -H^+]{EtOH \text{ or } H_2O} CH_2 = \overset{\overset{CH_3}{|}}{C} - CH_2CH_3 \quad (III)$$

The product I, II and III are formed. Product (II) is most stable and major product. In the above path, we also expect S_N1 product, as H_2O and EtOH are also weak nucleophiles. At low temperature, S_N1 product usually dominate and at high temperature, E1 product dominate.

Note :   E1 elimination also occurs in cases where there is no β-hydrogen. Visualise rearrangement via CH_3^- (methide) shift.

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2Br \xrightarrow[\text{KOH}]{\text{alcoholic}} CH_3 - \underset{\underset{(Major)}{}}{\overset{\overset{CH_3}{|}}{C}} = CHCH_3 \ + \ CH_2 = \underset{\underset{(Minor)}{}}{\overset{\overset{CH_3}{|}}{C}} - CH_2CH_3$$

Neopentyl bromide

(E2 is not possible & S_N2 is also not possible)

A double bond in a six-membered ring is usually more stable in an endocylic position than in an exocyclic position.

Illustration - 17   *Visualise both* $E1$ *and* $E2$ *paths for dehydrohalogenation of* 1-*Bromo*-1-*methyl cyclohexane.*
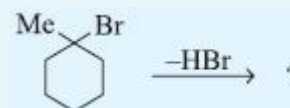
SOLUTION :   **E1 path :**   First step is similar to that of S_N1 path.
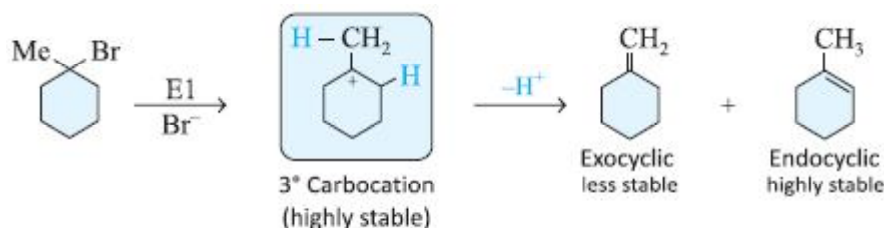
It can give two E1 products losing a proton to base being used for dehydrobromination.

E2 path :

Base (such as RO^- or alcoholic $KOH \equiv OH^-$ as base) abstracts a $\beta - H$ atom which simultaneously results in loss of Br^- ion in a bimolecular (E2) path. Note that in given case orientation of product is important as there are two $\beta - H$ atoms.
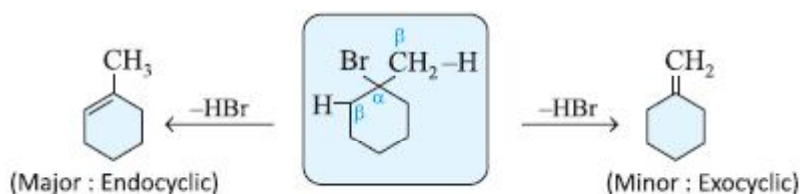
If we take $(CH_3)_3 CO^-$ as a base, the products ratio will get reversed.

Note : Just by change E1 and E2 both give same products. It is not necessary that two paths give the same products. Usually dehydrohalogenation occurs via E2 pathways as S_N1 always competes with E1 at normal temperature.

**Illustration - 18** *Predict the product (X) of the following reaction :*
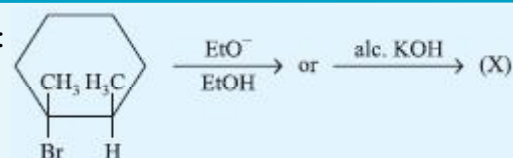
SOLUTION :

Clearly the given reaction involves dehydrohalogenation of alkyl halides and under the given condition, $3°$ cycloalkyl halide will follow E2 path. Now E2 mechanism involves β – elimination of hydrogen, so we need to keep one thing in mind that the $\beta - H$ to be removed should be present in an *anti-position* (or exactly opposite position) w.r.t the bromine atom. In other words, E2 mechanism involves "anti-elimination".
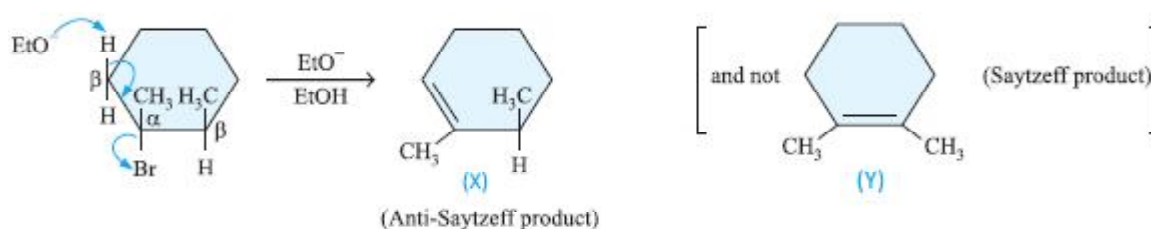
Hence in this question, product (X) will be the less stable anti-Saytzeff (Hoffmann's product). The more stable Saytzeff's product (Y) would have formed if the substrate was as shown in reaction :
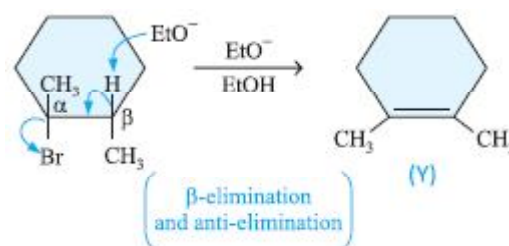
E1 versus E2

➤ With respect to the substrate, the reacitivity of both E1 ad E2 increases from $1°$, $2°$ and to $3°$ alkyl halides. Note that reactivity of E2 increases due to greater stability of more highly branched alkenes formation (Saytzeff Rule) ; whereas the reactivity of E1 increases because of the greater stability of carbocations in rate determining step.

➤ The rate of E2 is proportional to concentration and strength of the base, whereas rate of E1 is independent of nature of base.

➤ For a given substrate, E2 is the path for dehydrohalogenation in presence of more concentrated base or a strong and slightly polarised base (RO^-, NH_2^-, OH^- ions).

➤ E1 path is followed by $2°$ and $3°$ alkyl halides in presence of weak bases such as alcohols i.e. basically when base is the solvent.
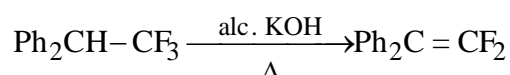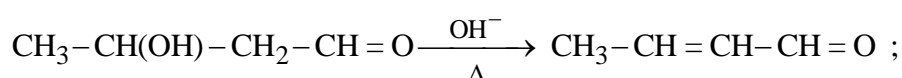
Summary of S_N1, S_N2, E1, and E2 reactions :

CH_3X	RCH_2X [1°]	R_2CHX [2°]	R_3C-X [3°]
S_N2	S_N2 and E2 Bimolecular reactions	S_N2 or E2	S_N1 and E1 or E2
Gives S_N2 reactions only	Gives mainly S_N2 except with a hindered strong base [e.g., tert. butoxide [$(CH_3)_3CO^-$], or using strong base such as alcoholic KOH via E2 path.	Gives mainly S_N2 with weak bases (e.g., I^-, CN^- and RCO_2^-) and mainly E2 with strong bases (e.g., RO^- $(CH_3)_3CO^-$, NH_2^-, OH^-)	No S_N2 reaction. In polarising solvent, it gives S_N1/E1, and at lower temperature S_N1 is favored. When a strong base (e.g., RO^-, OH^-) is used, E2 occurs with a minor product via E1

Mechanism	Substrate Preference	No. of Steps (intermediate)	Rate Law	Stereochemistry	Regio-chemistry	Preferred Temperature	Preferred Solvent
S_N2	Methyl > 1° > 2°	1 (none)	k[RX][Nu]	Inversion at reaction center	-	Low	Depends on charge type
S_N1	3° or resonance stabilized > 2° ; good leaving group	2 (carbocation)	k[RX]	Racemization at reaction centre	-	Low	High ionization power
E2	Accessible β-hydrogen	1 (none)	k[RX][B]	Anti-elimination	Depends on late ness of transition state	High	Depends on charge type
E1	Same as S_N1 must have a β-hydrogen	2 (carbocation)	k[RX]	-	Most stable alkene	High	High ionization power
E1cB	Must have acidic β-hydrogen	2 (carbanion)	k[RX][B]	-	-	High	Basic
E_i	Must have internal base located near β-hydrogen	1 (none)	k[RX]	Syn-elimination	Often gives least hindered alkene	High	Little or no effect

ElcB is a rare mechanism of β – elimination reaction of organic compound having poor leaving group and more acidic β – Hydrogen atom.
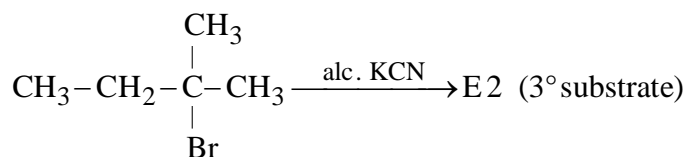
$$CH_3-CH(OH)-CH_2-CH=O \xrightarrow[\Delta]{OH^-} CH_3-CH=CH-CH=O \; ;$$

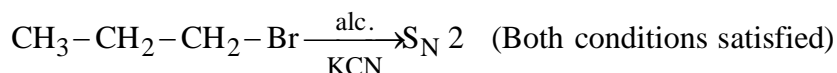$$Ph_2CH-CF_3 \xrightarrow[\Delta]{alc.\ KOH} Ph_2C=CF_2$$

Conditions for $S_N 2$ reaction :

Steric hinderance should be minimum, so usually $1°$ and $2°$ substrate show $S_N 2$ reactions. Hence it is not possible for $3°$ substrate to show $S_N 2$ reactions.

Nucleophilic should act as a pure nucleophile i.e. the basic nature of nucleophile should not dominate over its nucleophilic character.
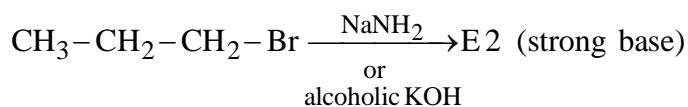
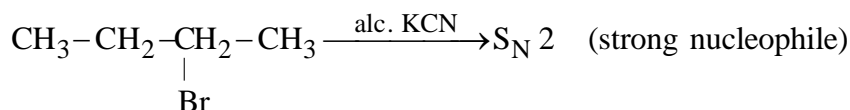If any (or both) of the above two conditions are violated, it results in E2 reaction.

$$CH_3-CH_2-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow{\text{alc. KCN}} E\,2 \ (3°\,\text{substrate})$$

$3°$ alkyl halide

$$CH_3-CH_2-CH_2-Br \xrightarrow[\text{KCN}]{\text{alc.}} S_N\,2 \ (\text{Both conditions satisfied})$$

$1°$ alkyl halide

$$CH_3-CH_2-CH_2-Br \xrightarrow[\underset{\text{alcoholic KOH}}{\text{or}}]{NaNH_2} E\,2 \ (\text{strong base})$$

$1°$ alkyl halide

$$CH_3-CH_2-\underset{\underset{Br}{|}}{CH_2}-CH_3 \xrightarrow{\text{alc. KCN}} S_N\,2 \ (\text{strong nucleophile})$$

$2°$ alkyl halide

Illustration - 19 *Give major and minor products when each of the given compounds (bromides) reacts with aqueous KOH. Also identify the path (S_N1 or S_N2).*

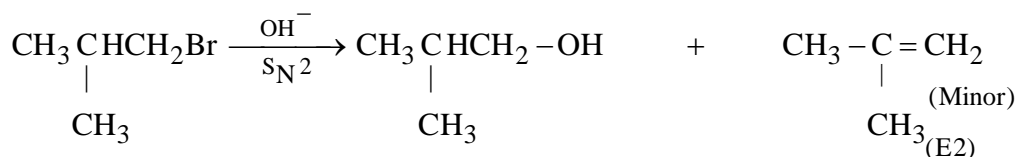**(A)** $CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2Br$

(B) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{Br}{|}}{C}H-CH_3$

(C) $\overset{CH_2CH_2Br}{\underset{Me}{}}$

(D) $\overset{Br}{\underset{CH_3}{}}$
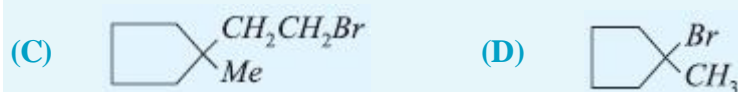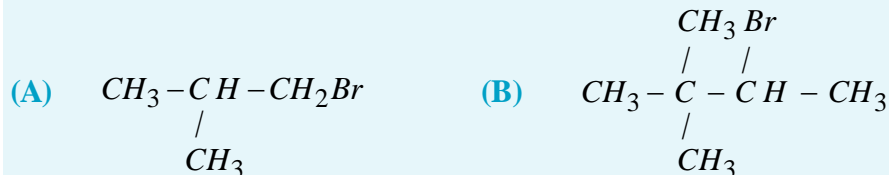
SOLUTION :

(A) Note that aq. KOH $\equiv$ OH$^-$ as Nu$^-$ and alc. KOH $\equiv$ OH$^-$ as base.

$$CH_3\overset{\mid}{\underset{\underset{\textstyle CH_3}{\mid}}{C}H} - CH_2Br \xrightarrow[KOH]{aq.}$$
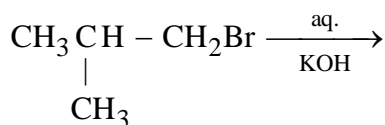
Observe that substrate is 1° halide and OH$^-$ is a strong Nu$^-$. Hence product will be via S$_N$2 path (1° halides have no hindrance to Nucleophilic attack).
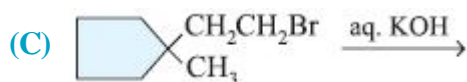
$$CH_3\underset{\underset{\textstyle CH_3}{\mid}}{C}HCH_2Br \xrightarrow[S_N2]{OH^-} CH_3\underset{\underset{\textstyle CH_3}{\mid}}{C}HCH_2-OH \quad + \quad CH_3-\underset{\underset{\textstyle CH_3}{\mid}}{C}=CH_2$$
$$\text{(Minor)}$$
$$\text{(E2)}$$

Note : S$_N$1 path is not favoured as 1° carbocation is weakly stable.

(B) Observe that substrate is 2° halide, and reagent is aq. KOH. Aqueous solution i.e. H$_2$O is a strong polarising solvents, hence S$_N$1 path will be followed.
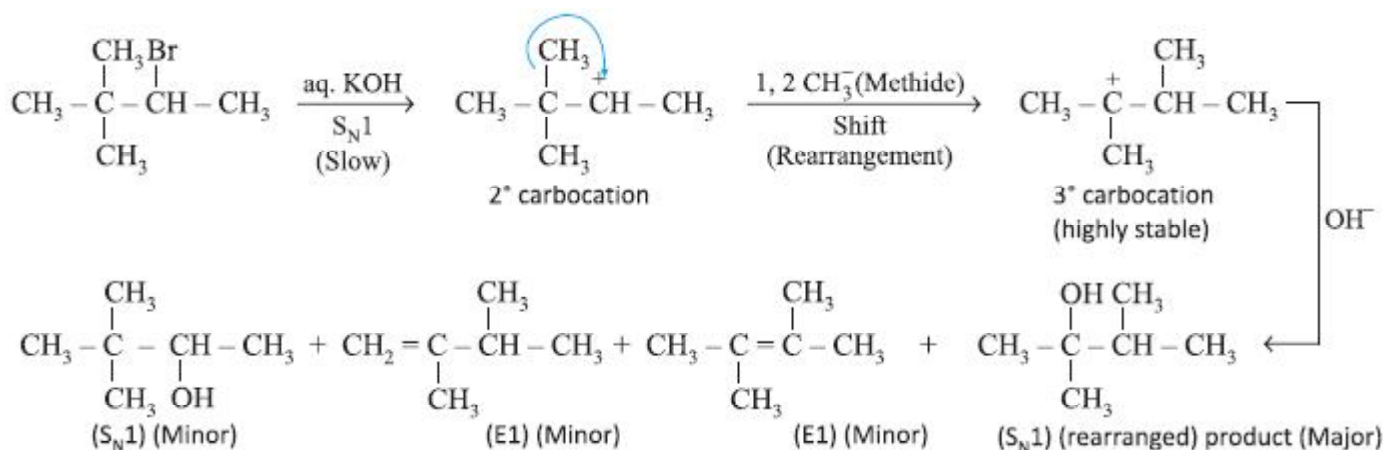
Note that due to strong hindrance, S$_N$ 2 will not be possible.

(C)

Observe that substrate is 1° [as in (A)], so S$_N$2 path is followed.
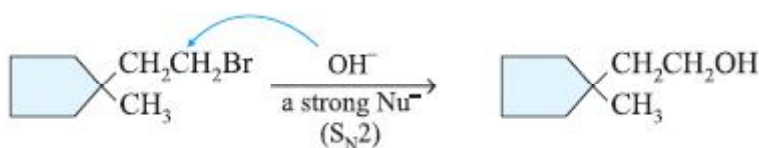
Note that S$_N$1 Path will not occur as 1° carbocation is weakly stable.
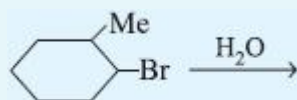
(D)
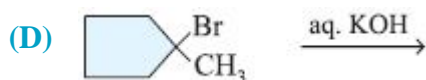
Observe that substrate is 3°, so S_N1 path will be favoured as intermediate will be highly stable 3° carbocation.
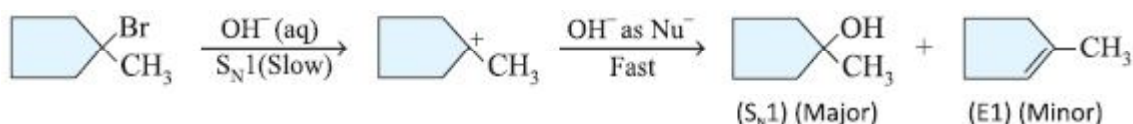

Note that in 3° halides, S_N2 is not possible due to steric hindrance.

Illustration - 20 *Give the major and minor products in the following reaction.*

SOLUTION :

Note that H_2O is a strong ionising solvent (protic) and a weaker nucleophile. Substrate is 2° halide and aqueous medium serves as polarising (protic polar) solvent favouring S_N1 path. This is an illustration of solvolysis.

The minor product is formed as follows :
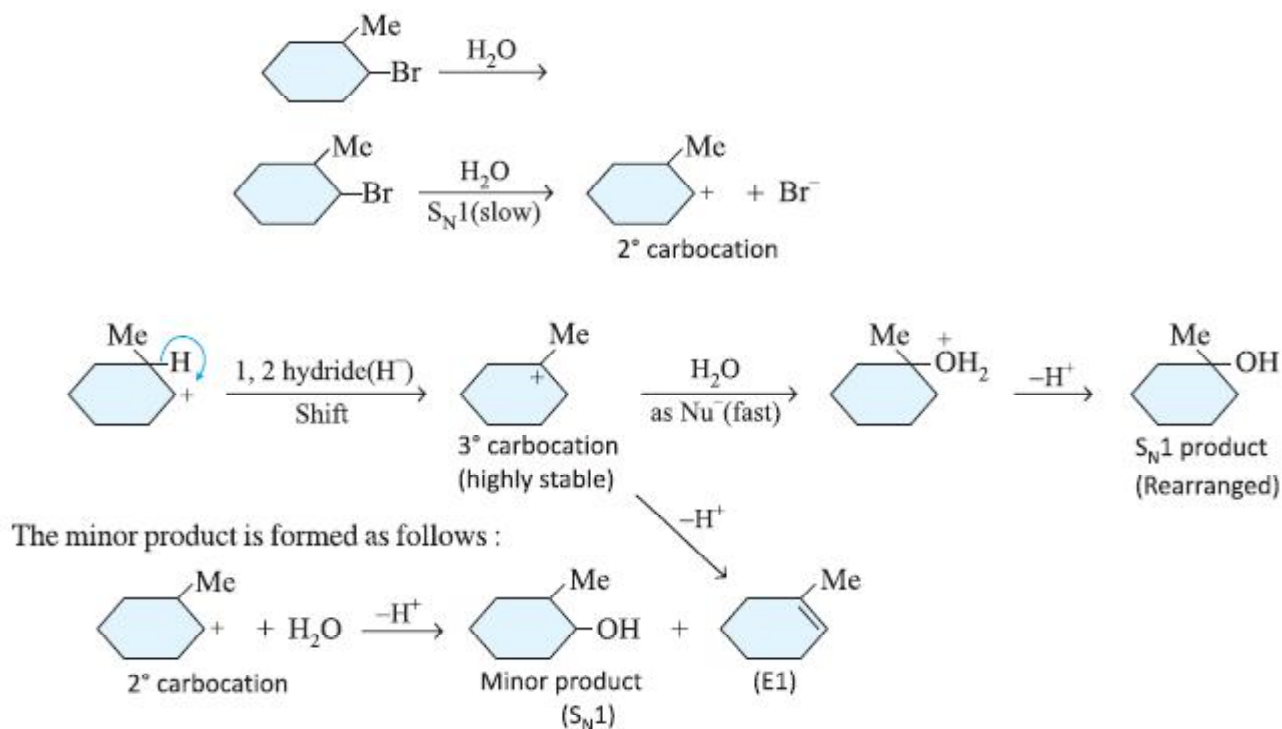
Illustration - 21 *Identify various products obtained when* 1 - *Bromomethyl cyclohexene undergoes solvolysis in the presence of* C_2H_5OH. *Propose a proper mechanism and identify the type of paths* (*mechanism*).

SOLUTION :

1-Bromomethylcyclohexene $\xrightarrow{C_2H_5OH}$?

(i) C_2H_5OH is a weakly polarising (protic polar) solvent which favours S_N1 type of path giving carbocations as intermediate. in slow (RDS) step.

(ii) $C_2H_5\overset{..}{O}H$ serves as a weak nucleophile in the fast step to give ethers as S_N1 products.
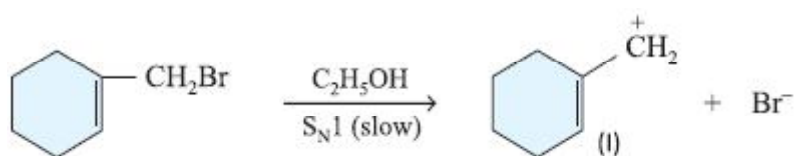
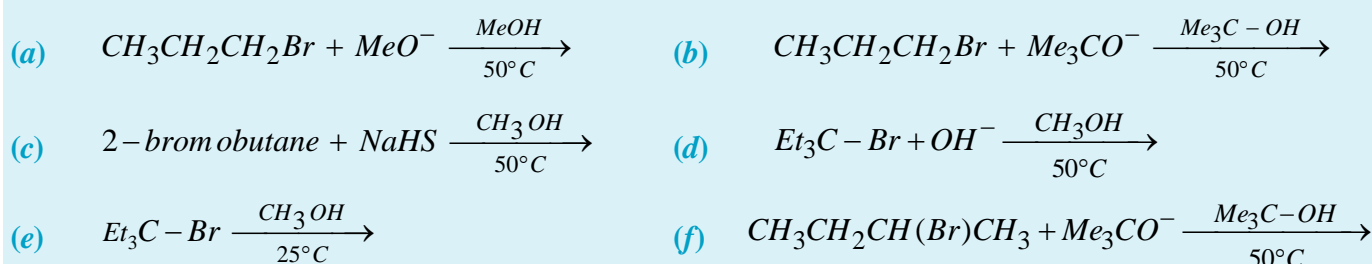Note that the carbocation formed is resonance stabilised (Allylic type).

Product: I (S_N1)

Product: II (S_N1)
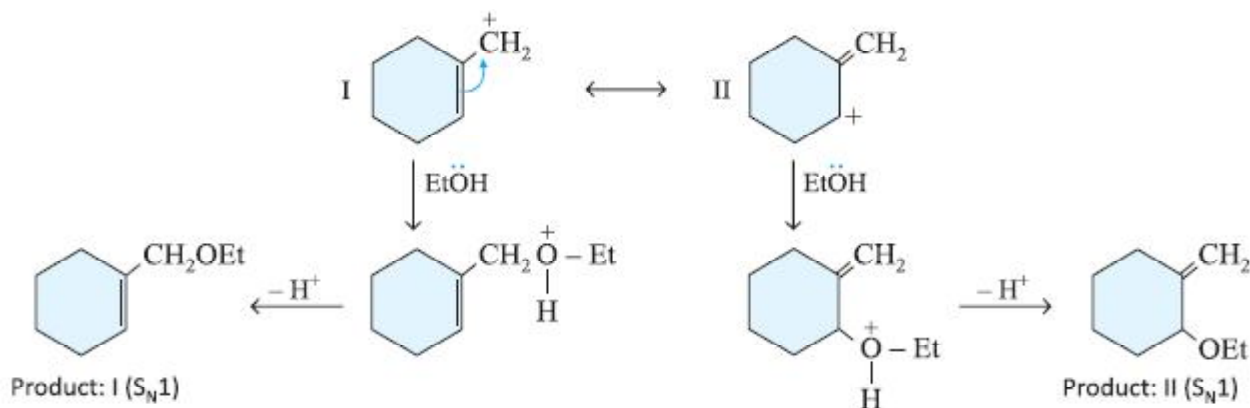
Note : S_N1 path (products) is usually competed by E1 path (products), since carbocations can loose a proton to give alkene (E1) as product.


II :
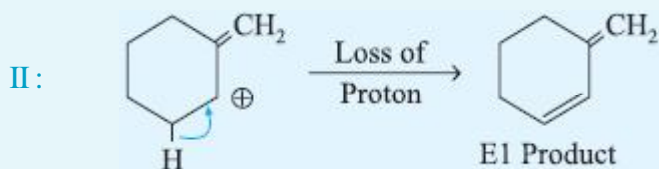
E1 Product

Observe that :

1. Intermediate : I cannot loose proton.

2. Usually S_N1 products are formed at normal room temperature. Here as a special case, E1 is very important as a conjugated diene is formed which is highly stable (due to resonance).

3. If instead of C_2H_5OH, we use aqueous solution of KOH, the reaction will be faster and instead of ethers, alcohols are formed as S_N1 products. However E1 product will remain same.

Illustration - 22 *Give the products (s) that can be formed in each of the following reactions. Also identify the path (S_N1, S_N2, E1, or E2) in each case.*

(a) $CH_3CH_2CH_2Br + MeO^- \xrightarrow[50°C]{MeOH}$

(b) $CH_3CH_2CH_2Br + Me_3CO^- \xrightarrow[50°C]{Me_3C-OH}$

(c) $2-bromobutane + NaHS \xrightarrow[50°C]{CH_3OH}$

(d) $Et_3C-Br + OH^- \xrightarrow[50°C]{CH_3OH}$

(e) $Et_3C-Br \xrightarrow[25°C]{CH_3OH}$

(f) $CH_3CH_2CH(Br)CH_3 + Me_3CO^- \xrightarrow[50°C]{Me_3C-OH}$

SOLUTION :

(a) The substrate is a 1° halide. The attacking species is CH_3O^-, a strong base (but not a hindered one) and a good nucleophile. So we should visualise an S_N2 reaction mainly, and the major product should be $CH_3CH_2CH_2OCH_3$.
A minor product might be $CH_3CH=CH_2$ by an E2 pathway.

(b) Again the substrate is a 1° halide, but the reagent is $(CH_3)_3CO^-$, is a strong and hindered base. We should expect, therefore, the major product to be $CH_3CH=CH_2$ by an E2 path, and a minor product to be $CH_3CH_2CH_2OC(CH_3)_3$ by an S_N2 path. Note that here a β-H is abstract which is not sterically hindered.

(c) The reactant is 2-bromobutane, a 2° halide, and one in which the leaving group is attached to a chiral centre. The reagent is HS^-, a strong nucleophile, but a weak base. We should expect mainly an S_N2 reaction, causing an inversion of configuration at the chiral centre and giving an inverted stereoisomer.
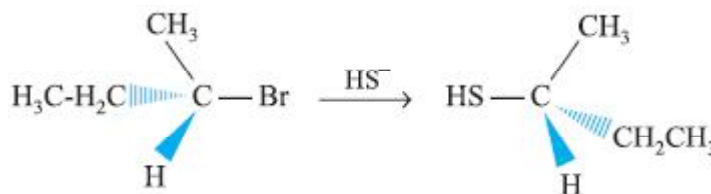

(d) The base/nucleophile is OH^-, a strong base and a strong nucleophile. However, the substrate is a 3°halide; therefore, we should not expect an S_N2 reaction. The major product should be $CH_3CH=C(CH_2CH_3)_2$ via E2 reaction. At this higher temperature, and in the presence of a strong base, we should not expect an appreciable amount of the S_N1 product, $CH_3OC(CH_2CH_3)_3$, however we can expect the product :
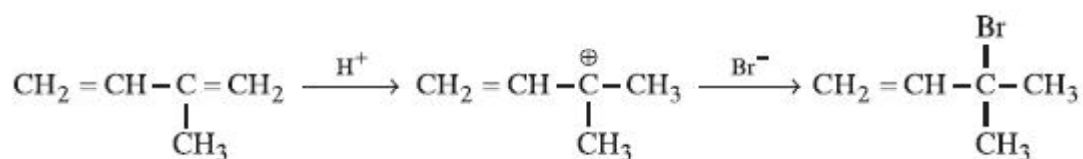
$CH_3CH=C(CH_2CH_3)_2$ via E1 also.

(e)   This is solvolysis; the reagent is simply the solvent, CH_3OH, which is a weak base (therefore, no E2 reaction) and a poor nucleophile. The substrate is tertiary (Therefore, no S_N2 reaction). At this lower temperature we should expect mainly an S_N1 pathway leading to $CH_3OC(CH_2CH_3)_3$. A minor product, by an E1 path would be : $CH_3CH = C(CH_2CH_3)_2$.

(f)   Refer (b), $(CH_3)_3\,CO^-$ will abstract less hindered $\beta - H$ to give 1-Butene as major product (Anti-Saytzeiffs product).

Illustration - 23 *Find the product* (A) *and* (B) :
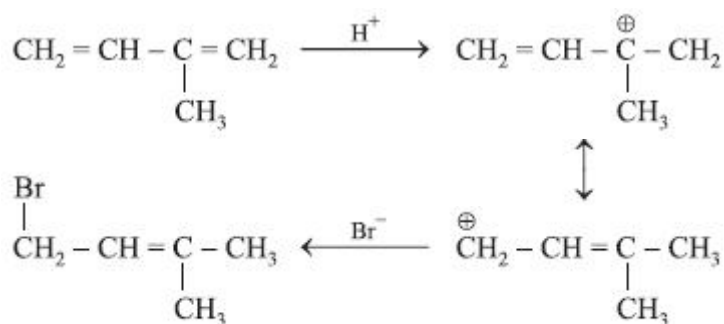
$$CH_2 = CH - \underset{\underset{CH_3}{|}}{C} = CH_2 \xrightarrow[0°C]{HBr} (A)$$

$$\xrightarrow[65°C]{HBr} (B)$$
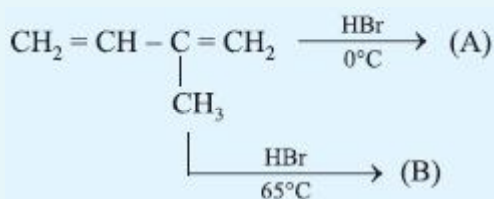
SOLUTION :
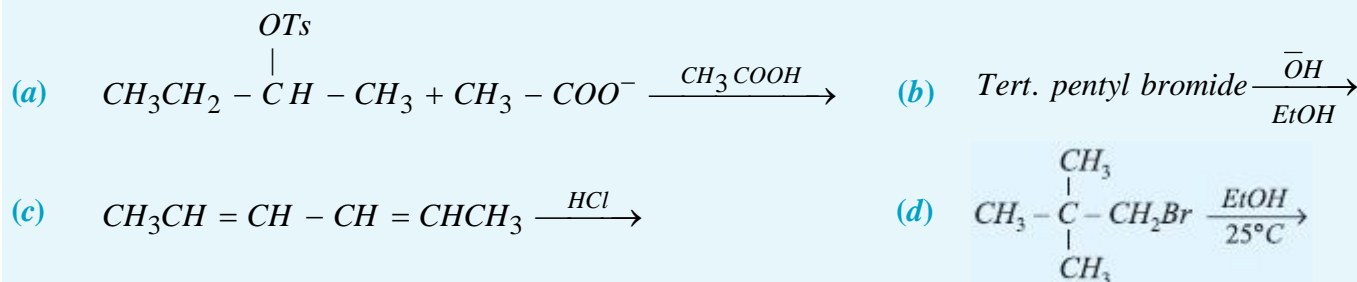
At $0°C$, product will be controlled kinetically i.e. according to stability of intermediate, $\therefore$ 1, 2-addition.

$$CH_2 = CH - \underset{\underset{CH_3}{|}}{C} = CH_2 \xrightarrow{H^+} CH_2 = CH - \overset{\oplus}{\underset{\underset{CH_3}{|}}{C}} - CH_3 \xrightarrow{Br^-} CH_2 = CH - \overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_3$$

At $65°C$, product will be controlled thermodynamically i.e. according to the stability of products, $\therefore$ 1, 4-addition.

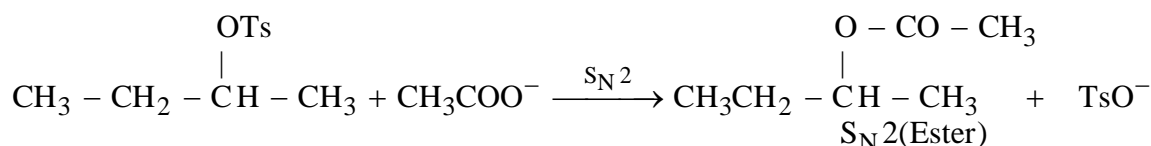$$CH_2 = CH - \underset{\underset{CH_3}{|}}{C} = CH_2 \xrightarrow{H^+} CH_2 = CH - \overset{\oplus}{\underset{\underset{CH_3}{|}}{C}} - CH_2$$

$$\updownarrow$$

$$\overset{\overset{Br}{|}}{CH_2} - CH = \underset{\underset{CH_3}{|}}{C} - CH_3 \xleftarrow{Br^-} \overset{\oplus}{CH_2} - CH = \underset{\underset{CH_3}{|}}{C} - CH_3$$

Illustration - 24   *What are the major/minor products obtained in each of the following reactions. Also identify paths.*
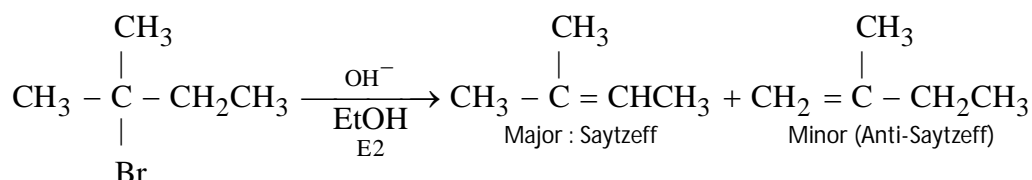
(a)
$$CH_3CH_2 - \overset{\overset{\displaystyle OTs}{|}}{C}H - CH_3 + CH_3 - COO^- \xrightarrow{CH_3COOH}$$

(b) *Tert. pentyl bromide* $\xrightarrow[EtOH]{\overline{O}H}$

(c)
$$CH_3CH = CH - CH = CHCH_3 \xrightarrow{HCl}$$

(d)
$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2Br \xrightarrow[25°C]{EtOH}$$

SOLUTION :

(a) Note that substrate is 2° and CH_3COO^- is a weak base, so elimination is not possible. However CH_3COO^- acts a good Nu^- to give S_N2 product as major. Also observe that TsO^-, tosylate is a very good learing group.

$$CH_3 - CH_2 - \overset{\overset{\displaystyle OTs}{|}}{C}H - CH_3 + CH_3COO^- \xrightarrow{S_N2} CH_3CH_2 - \underset{S_N2(Ester)}{\overset{\overset{\displaystyle O - CO - CH_3}{|}}{C}H - CH_3} \quad + \quad TsO^-$$

There may be minor, E2 product.

(b) Note that alc. $KOH \equiv \overline{O}H$ as a base. Here, substrate is 3° and $\overline{O}H$ a good $\overline{Nu}$ and a good base, will give E2 products (S_N2 will not be possible due to steric factors at $3° - \alpha - carbon$)

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}} - CH_2CH_3 \xrightarrow[\underset{E2}{EtOH}]{OH^-} \underset{\text{Major : Saytzeff}}{CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CHCH_3} + \underset{\text{Minor (Anti-Saytzeff)}}{CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH_2CH_3}$$

$$\left[\begin{array}{l} \text{E1 is also possible along with} \\ \text{small amount of alcohol and} \\ \text{ether via } S_N1 \end{array} \right]$$

(c) $CH_3CH = CH - CH = CHCH_3 \xrightarrow[Cl^-]{H^+}$ Visualise electrophilic addition in alkenes.

$$CH_3CH = CH - CH = CHCH_3 \xrightarrow{H^+} CH_3CH_2 - \overset{+}{C}H - CH = CHCH_3$$
$$\text{Allylic Carbocation}$$

$$CH_3CH_2\overset{+}{C}H \overset{\frown}{-} CH = CH - CH_3 \longleftrightarrow CH_3CH_2 - CH = CH - \overset{+}{C}H - CH_3$$

(I) $\downarrow Cl^-$ (Resonance stabilised) $\downarrow Cl^-$ (II)

$$CH_3CH_2 - \underset{\underset{Cl}{|}}{CH} - CH = CH - CH_3 \qquad CH_3CH_2 - CH = CH - \underset{\underset{Cl}{|}}{CH}CH_3 \quad \text{(Two products)}$$
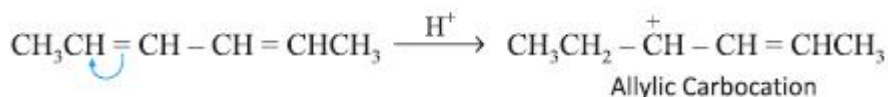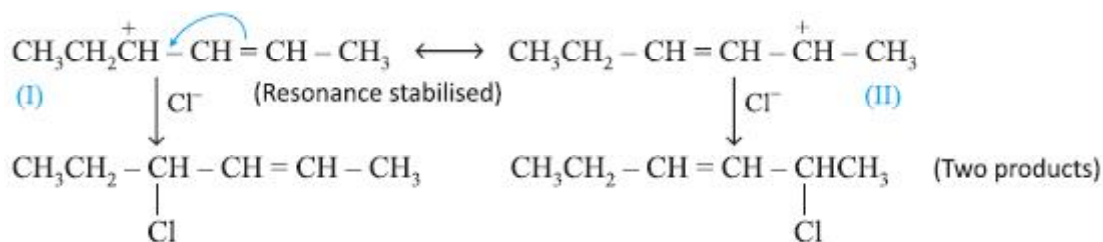
This is referred to as conjugate (E^+) addition in dienes.

Note :   If electromeric effect in diene occurs as follow, another (minor) addition product can be formed.

$$CH_3CH \overset{\frown}{=} CH - CH = CHCH_3 \xrightarrow{\overset{+}{H}} CH_3\overset{+}{C}H - CH_2 - CH = CHCH_3 \xrightarrow{Cl^-} CH_3CH - \underset{\underset{Cl}{|}}{CH_2}CH = CHCH_3$$
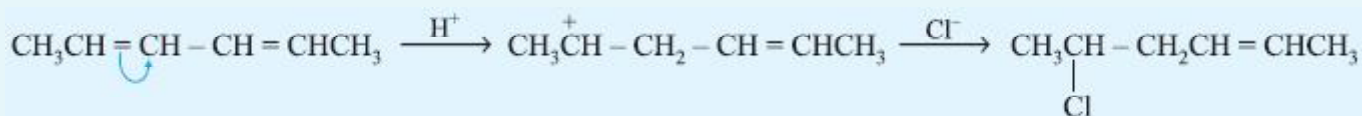
(d)   Clearly it will follow S_N1 path as C_2H_5OH is a polarising solvent and weak nucleophile.

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2Br \xrightarrow{S_N1} CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \overset{+}{C}H_2 \xrightarrow[\text{shift}]{CH_3^-} CH_3 - \overset{+}{\underset{\underset{CH_3}{|}}{C}} - CH_2CH_3$$

$1°C^+$: Less stable $3°C^+$: More stable
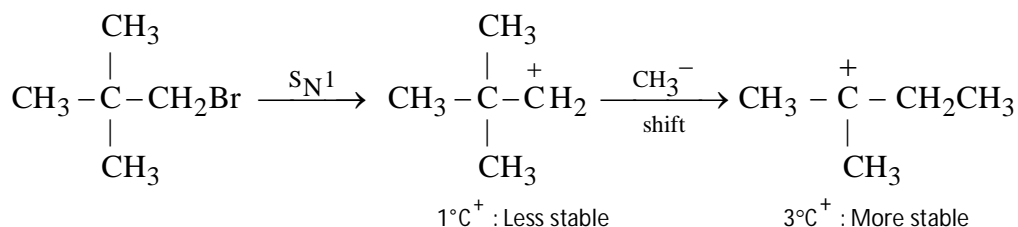
Accordingly 3° carbocation can give both S_N1 (Major) and E1 (Minor) products.

$$CH_3 - \underset{\underset{CH_3}{|}}{C} = CHCH_3 \longleftarrow \boxed{CH_3 - \overset{+}{\underset{\underset{CH_3}{|}}{C}} - CH_2CH_3} \xrightarrow[-H^+]{Et\ddot{O}H} CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{OEt}{|}}{C}} - CH_2CH_3$$

E1   (Minor) S_N1 (Major)
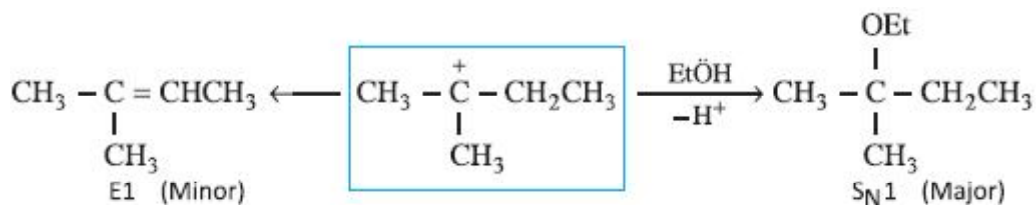
(b)   Dehydration of Alcohols
It can also be achieved via E1 or E2 paths.

E1 path :

Consider Dehydration in tertiary butyl alcohol

Step 1 :   *Formation of Oxonium ion* :

In this reaction, first conc. H_2SO_4 gives a proton (H^+). The electrophile (H^+) attacks oxygen atom (−OH) containing lone pairs of electrons to form an unstable intermediate called as oxonium ion (protonated alcohol).

Oxonium ion
(protonated alcohol)
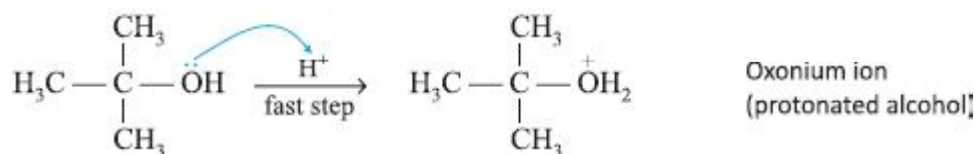
Step 2 : *Formation of Carbocation* :

The oxonium ion (being unstable) loses a water molecule to give a carbocation.

carbocation
(more stable than oxonium)
(Unimolecular ; E1)
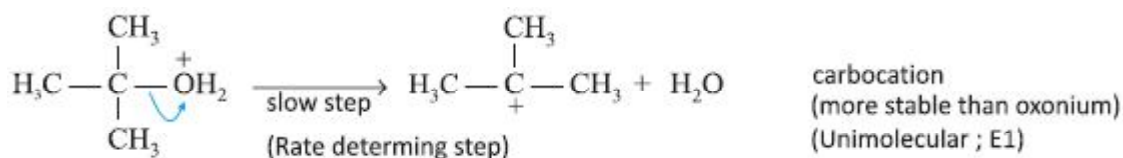
Step 3 : *Elimination of Proton* :
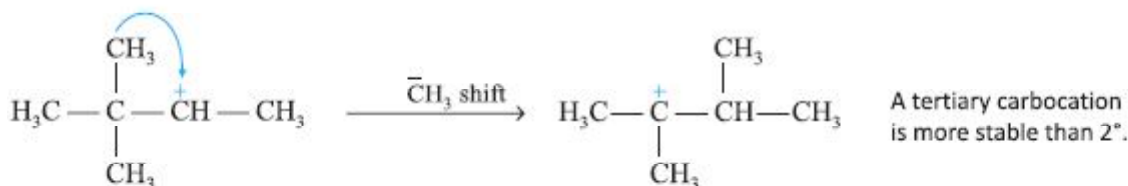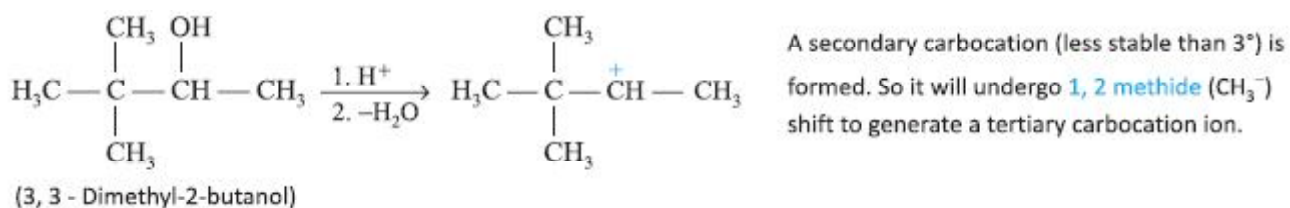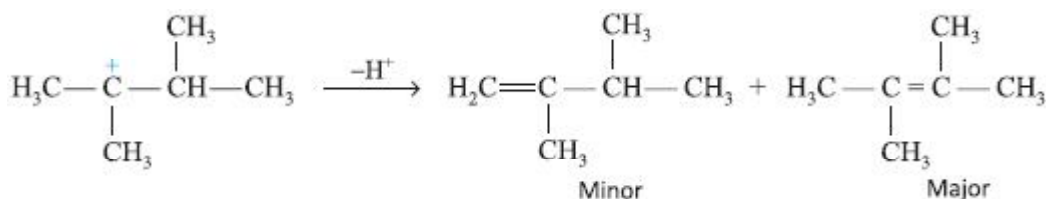
This carbocation loses a proton to give an alkene at 170°C.

An alkene is formed and water accepts a proton (H^+) to give H_3O^+.

Note 1 :

➤ The important intermediate in this reaction is carbocation ion. So you have to check its stability, while proposing the mechanism. In the above case, the carbocation ion formed is tertiary butyl carbocation, which being a tertiary ion is highly stable (Recall the stability of carbonium ions). In other case, you have to make *proper rearrangements* for the stability of carbonium ion.

For example consider Dehydration of the following alcohol :

A secondary carbocation (less stable than 3°) is formed. So it will undergo 1, 2 methide (CH_3^-) shift to generate a tertiary carbocation ion.

(3, 3 - Dimethyl-2-butanol)

A tertiary carbocation is more stable than 2°.

In Dehydration of alcohols, Saytzeff rule is always obeyed, unlike in dehydrohalogenation.

Note 2 :

In alcohols having cycloalkyl radicals, ring expansion occurs and cycloalkenes are formed. For example consider following dehydration.
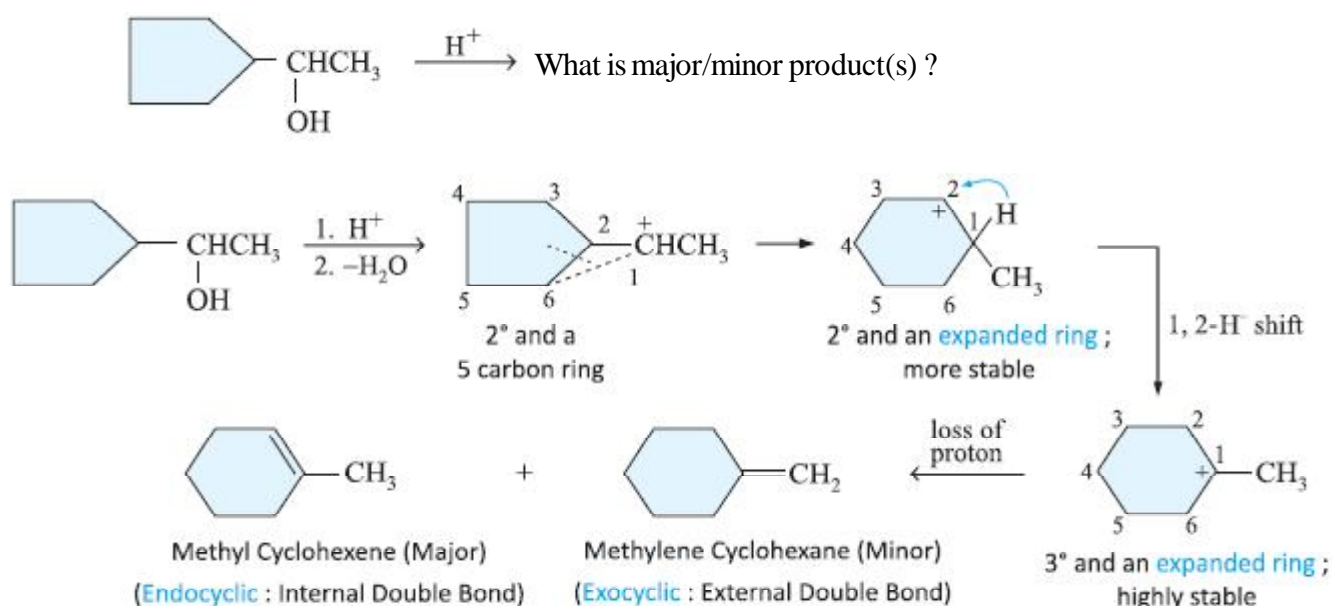
E2 path :

The E1 mechansim is clearly followed by secondary (2°) and tertiary (3°) alcohols as the corresponding carbocations are stable and hence are formed. Primary alcohols do not prefer E1 path as the corresponding (1°) carbocations are not formed, being poorly stable. These alcohols follow E2 dehydration as follows :

After protonation of –OH group (similar to E1 path) in step-1, a primary protonated alcohol reacts with the conjugate base of mineral acid (HSO_4^-) by β-elimination (similar to E2 elimination in halides by RO^-).

$$RCH_2CH_2OH \xrightarrow{H_2SO_4} RCH_2CH_2\overset{+}{O}H_2 + HSO_4^-$$
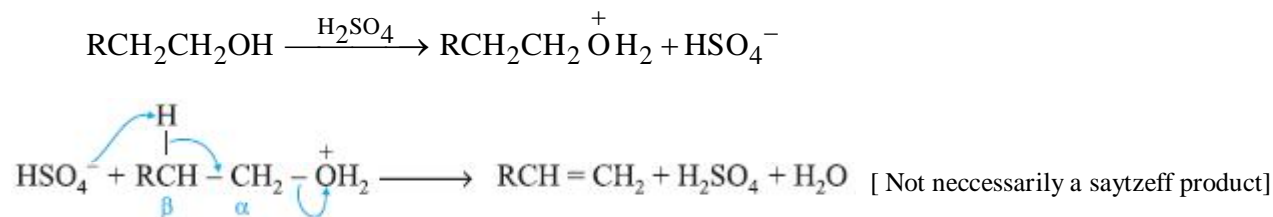
Note: **(i)** E2 products always accomany S_N2 products (just like in case of alkyl halides) since steric hinderance is absent at 1° α-carbon. HSO_4^- can attack 'α – C' to give alkyl sulphate ester.

$$RCH_2 - CH_2 - \overset{+}{O}H_2 + HSO_4^- \longrightarrow RCH_2CH_2OSO_3H + H_2O$$
$$\text{(Alkyl sulphate ester)}$$
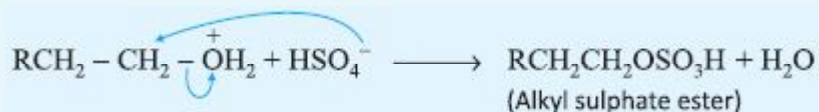
(ii) In this reaction, we can also expect an ether to be formed if a second alcohol molecule makes an S_N2 attack at 1° α-carbon.

$$RCH_2CH_2 - \overset{+}{O}H_2 + \overset{..}{O}HCH_2CH_2R \longrightarrow RCH_2CH_2OCH_2CH_2R + H_2O + H^+$$
$$\text{(an ether)}$$

Hence acid-catalysed dehydration involving 1° alcohols is not a good method to prepare alkenes.

(iii) Alcohols cannot show E2 reactions with bases, as –OH will be a poor leaving group. So we use acid catalysed dehydration (as above i.e., E1). But to prepare alkenes from 1° alcohols, E1 is not a good method. So an alternative method is first convert alcohol to alkyl sulphonate and then carry out E2 with sterically hindered base such as tert. butoxide

$$RCH_2CH_2OH \xrightarrow[\text{Pyridine}]{p-CH_3-C_6H_4-SO_2Cl} RCH_2CH_2O - Ts + HCl$$

$$Ts : tosyl \equiv CH_3 - C_6H_4 - SO_2 -$$

$$RCH_2CH_2OTs \xrightarrow[\text{E2}]{R'O^-/R'OH} RCH = CH_2 + \bar{O}Ts$$
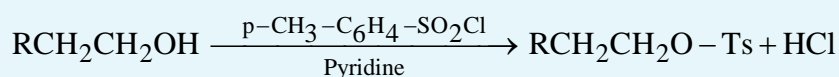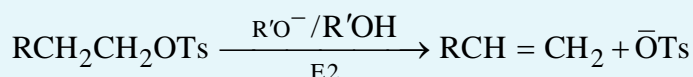
$$\text{(TsO}^- \text{: Tosylate : a very good leaving group)}$$
$$\text{(R' 3° alkyl group)}$$

Note : Although dehydration of Primary Alcohols is an E2 reaction, the product in most of the cases is identical to the product that could be obtained if a carbocation has been formed in an E1 reaction and then had rearranged. This can be explained as per the following reaction mechanism :
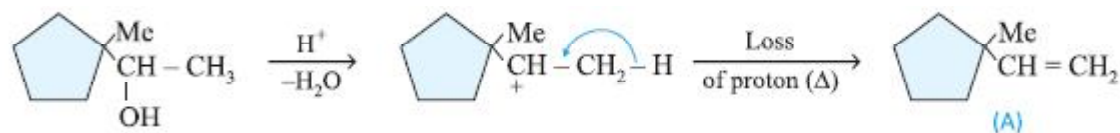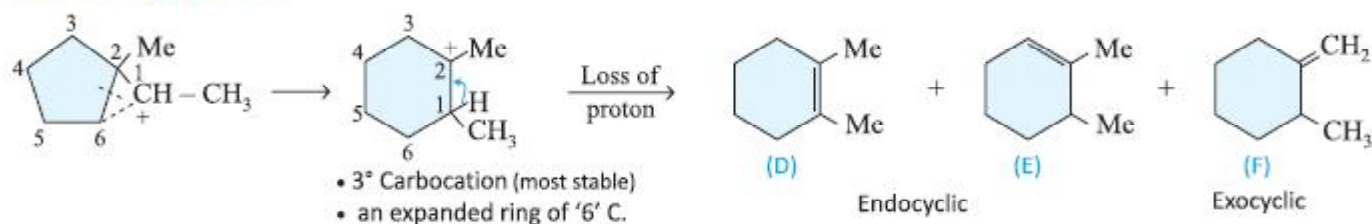
$$CH_3 - CH_2 - CH_2 - CH_2 - OH \xrightarrow[\Delta]{H_2SO_4} CH_3 - CH_2 - CH = CH_2 \xrightarrow{H^+} CH_3 - CH_2 - \overset{+}{C}H - CH_3 \;(2°)$$
$$\text{1 - butanol} \qquad \text{(E2)} \qquad \text{1-Butene}$$
$$\Big\downarrow -H^+$$
$$CH_3 - CH = CH - CH_3 \;\; \text{2-Butene}$$
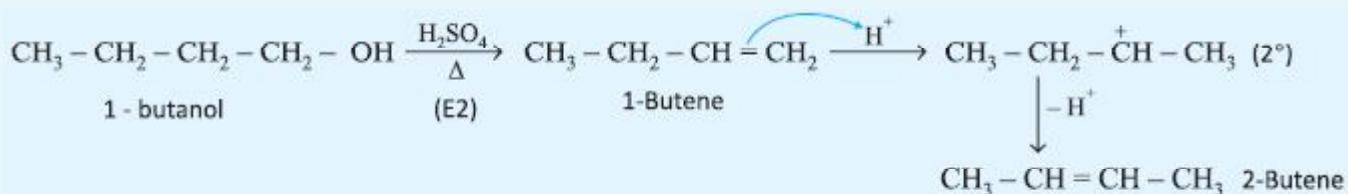
Illustration - 25 *What are the major and minor products obtained when the given compound is dehydrated is presence of heated conc.H_2SO_4?*
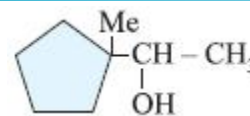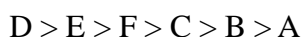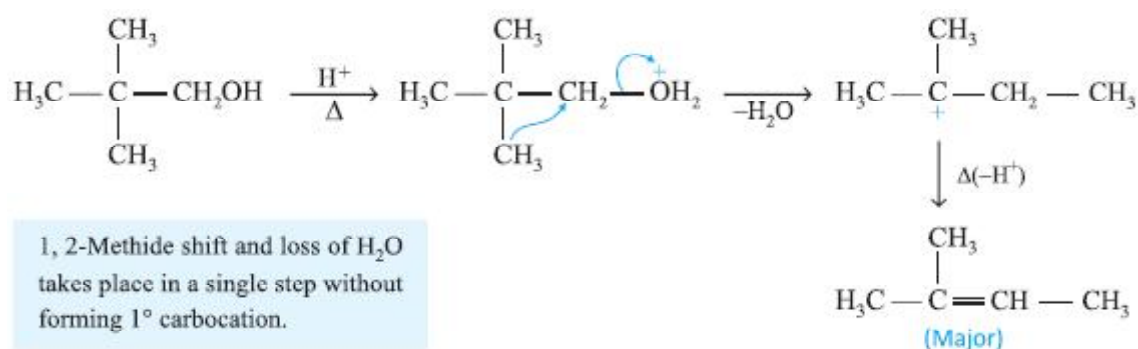
SOLUTION :
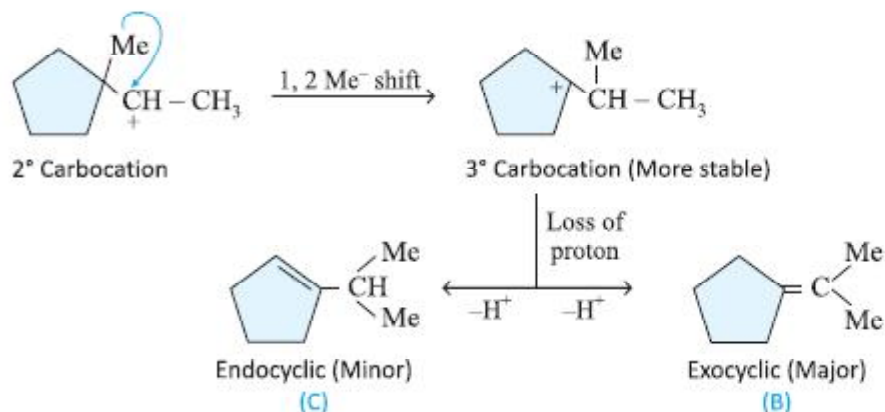
Visualise ring expansion

The six different Alkenes (A, B, C, D, E and F) are the possible products. The order of stability of these alkenes is in order :

$$D > E > F > C > B > A$$ Hence major is D and minor is E (second important product).

Note : **(i)** In such reaction i.e., involving carbocations, always visualise the most stable carbocation (visualise rearrangement or ring expansion) and then proceed.

(ii) Usually endocyclic cycloalkenes are more stable, but watch for special case (as above) considering stability via Hyperconjugation.

(iii) In $1°$ alcohols with β – carbon being $3°$ or $4°$, E1 elimination occurs as follows. In such cases E2 can not occur due to steric factor or absence of $\beta - H$.

1, 2-Methide shift and loss of H_2O takes place in a single step without forming 1° carbocation.

IN - CHAPTER EXERCISE - E

1. Give the mechanistic symbols ($S_N 1, S_N 2, E 1, E 2$) that are most consistent with each of the following statements :

   (A) Methyl halides react with sodium ethoxide in ethanol only by this mechanism.

   (B) Unhindered primary halides react with sodium ethoxide in ethanol mainly by this mechanism.

   (C) When cyclohexyl bromide is treated with sodium ethoxide in ethanol, the major product is formed by this mechanism.

   (D) The substitution product obtained by solvolysis of tert-butyl bromide in ethanol arises by this mecha-nism.

   (E) In ethanol that contains sodium ethoxide, tert-butyl bromide reacts mainly by this mechanism.

   (F) These reaction mechanisms represent concerted processes.

   (G) Reactions proceeding by these mechanisms are stereospecific.

   (H) These reaction mechanisms involve carbocation intermediates.

   (I) These reaction mechanisms are the ones most likely to have been involved when the products are found to have a different carbon skeleton from the substrate.

   (J) Alkyl iodides reacts faster than alkyl bromides in reactions that proceed by these mechanism.

NOW ATTEMPT PRACTICE EXERCISE-II BEFORE PROCEEDING AHEAD IN THIS EBOOK

SUBJECTIVE SOLVED EXAMPLES

Example - 1   *Arrange the following in increasing order of stability on the basis of resonance :*
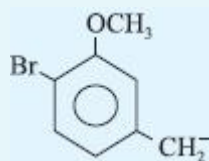
(A)   **(i)**   **(ii)**

(iii)   **(iv)**

(B)   **(i)** $\overset{-}{C}H_2-CH=CH-CH=\overset{\oplus}{O}-CH_3$ **(ii)** $CH_2=CH-\overset{-}{C}H-CH=\overset{\oplus}{O}-CH_2$

(iii) $\overset{-}{C}H_2-\overset{\oplus}{C}H-CH=CH-O-CH_3$ **(iv)** $CH_2=CH-\overset{-}{C}H-\overset{\oplus}{C}H-O-CH_3$

(C)   **(i)** $CH_2=CH-CH=CH-\overset{\oplus}{C}H_2$ **(ii)** $CH_2=CH-\overset{\oplus}{C}H-CH=CH_2$

(iii) $CH_2=CH-\overset{\oplus}{C}H-\overset{-}{C}H-\overset{\oplus}{C}H_2$ **(iv)** $\overset{\oplus}{C}H_2-CH=CH-\overset{-}{C}H-\overset{\oplus}{C}H_2$

(D)   **(i)** $CH_2=CH-CH=CH-CH=CH_2$ **(ii)** $CH_2=CH-\overset{\oplus}{C}H-CH=CH-\overset{-}{C}H_2$

(iii) $\overset{\oplus}{C}H_2-CH=CH-CH=CH-\overset{-}{C}H_2$
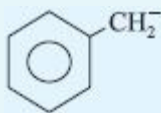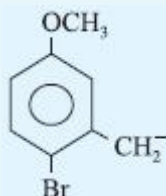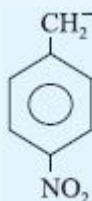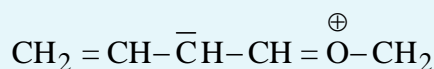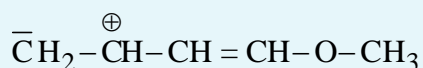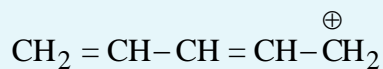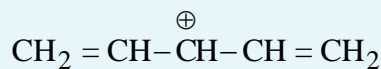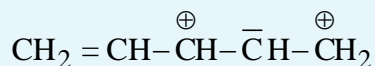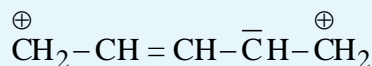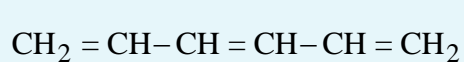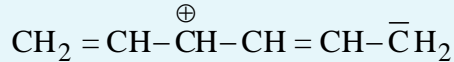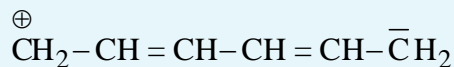
SOLUTION :

(A)   (i) < (iv) < (ii) < (iii)

In (iii) there is strong $-M$ effect of NO_2.

In (ii) and (iv) $-I$ effect of Br and OCH_3 are prominent.

In (i) delocalization due to only phenyl ring is there.

(B)   (iii) < (iv) < (ii) < (i)

(i) and (ii) should have more stability as compared to (iii) and (iv) because of more number of covalent bonds.

Also (i) has got $1°$ carbanion whereas (ii) has got $2°$ carbanion. Hence (ii) < (i)

In (iv), carbocation is close to oxygen hence it is more stable due to the lone pairs on oxygen. $\therefore$ (iv) > (iii).

(C) (ii) > (i) > (iii) > (iv)

(i) and (ii) should have greater stability as compared to (iii) and (iv) because of greater number of covalent bonds.

Also (ii) has got $2°$ carbocation whereas (i) has $1°$ carbocation.

(iii) has unlike charges close to each other but (iv) has no such factor.

(D) (iii) < (ii) < (i)

(i) is most stable due to maximum number of covalent bonds.

(ii) has got $2°$ carbocation whereas (iii) has got $1°$ carbocation. Hence (ii) > (iii).

Example - 2 *7-bromo-1, 3, 5-cycloheptatriene exists as ionic species in aqueous solution while 5-bromo-1, 3-cyclopentadiene doesn't ionise even in presence of* Ag^+ *(aq). Explain.*

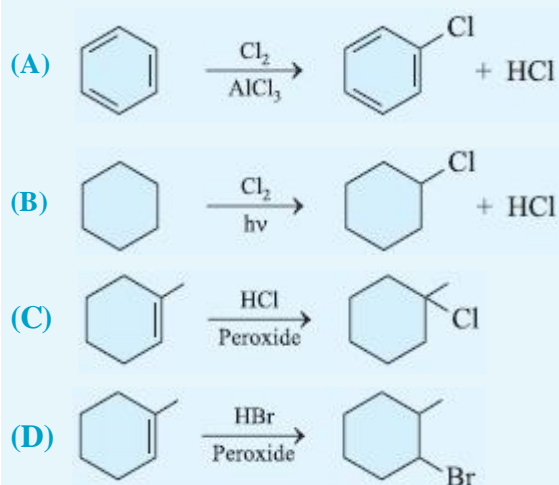**SOLUTION :**
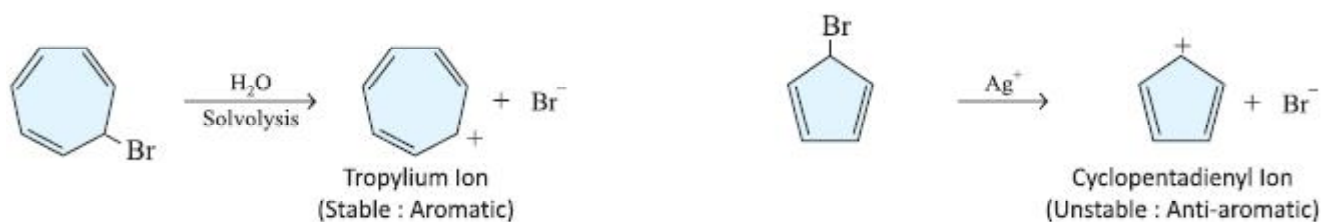
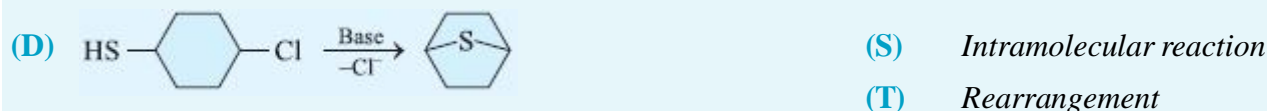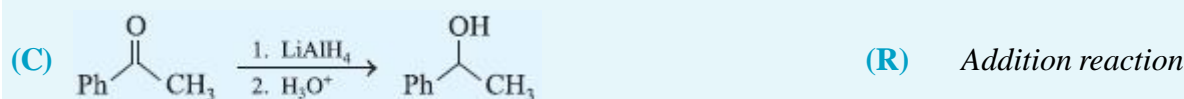**Example - 3** *MATCH THE FOLLOWING :*

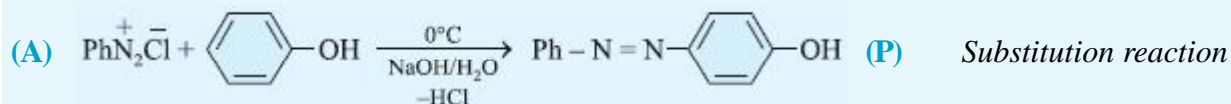| Column 1 [Reactions]	Column 2 [Type of reaction]
(A)	**(P)** *Electrophilic Substitution*
(B)	**(Q)** *Free radical substitution*
(C)	**(R)** *Electrophilic addition*
(D)	**(S)** *Free radical addition*

SOLUTION :　[A-P]　[B-Q]　[C-R]　[D-S]

Benzene is an aromatic compound and aromatic compounds undergoes electrophilic substitution reactions. Cyclohexane is a saturated aliphatic hydrocarbon and it undergoes free radical substitution reaction in presence of light.

1-Methyl cyclohexene is unsaturated hydrocarbon and it undergoes electrophilic addition reactions. But addition of HBr in presence of peroxide takes place by free radical addition reaction mechanism.

Example - 4　　*MATCH THE FOLLOWING* :

Column 1 [Reactions]	**Column 2 [Type of reaction]**

(A) $PhN_2^+\bar{Cl} + \langle \rangle - OH \xrightarrow[\substack{NaOH/H_2O \\ -HCl}]{0°C} Ph-N=N-\langle \rangle-OH$ 　(P) *Substitution reaction*

(B) $CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2OH \xrightarrow[-H_2O]{Conc.\ H_2SO_4} CH_3 - \underset{\underset{CH_3}{|}}{C} = CH - CH_3$　(Q) *Elimination reaction*

(C) $\underset{Ph}{\overset{O}{\|}}\underset{CH_3}{} \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4} \underset{Ph}{\overset{OH}{}}\underset{CH_3}{}$　(R) *Addition reaction*

(D) $HS-\langle \rangle-Cl \xrightarrow[-Cl^-]{Base} \langle S \rangle$　(S) *Intramolecular reaction*

　　　　　　　　　　　　　　　　　　　　　　　　　(T) *Rearrangement*
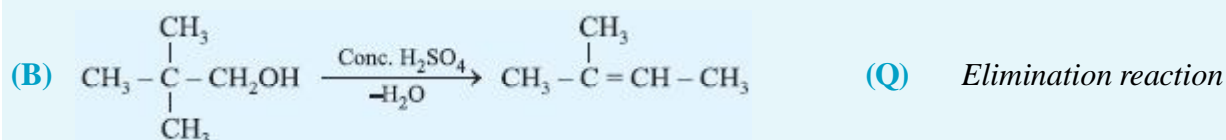
SOLUTION :　[A-P]　[B-Q, T]　　[C-R]　　[D-P, S]

Derivative of benzene undergoes electrophilic substitution reactions. Alcohols on heating with conc. H_2SO_4 undergoes dehydration (elimination reaction). In this case alcohol is primary alcohol without β-hydrogen atom hence it dehydrated by E1 reaction through formation of carbocation. Primary carbocation formed will rearrange to more stable 3° carbocation.

Reduction of ketone is an addition reaction.

When attacking nucleophile and leaving group are part of same substrate then reaction is intramolecular reaction.

Example - 5 *Consider reactions* 1 *through* 6. *Those carbon atoms undergoing change, as part of a functional group, are coloured. In the cases shown, each carbon atom has either been reduced or oxidized. Your job is to identify the change in oxidation state that has occured for each of the colored carbons.*

1. $CH_3CH = CH_2 \xrightarrow{Br_2} CH_3CHBrCH_2Br$

2. $CH_3CH = CH_2 \xrightarrow[\text{2. } H_2O_2, NaOH]{\text{1. } B_2H_6} CH_3CH_2CH_2OH$

3. $CH_3CH_2CH = O \xrightarrow{NaBH_4} CH_3CH_2CH_2OH$

4. $CH_3CH_2CH = O \xrightarrow[H_2O,\ pH > 8]{Ag^+} CH_3CH_2CO_2H$

5. $CH_3COCH_2CO_2H \xrightarrow{Heat} CH_3COCH_3 + CO_2$

6. $H_2C = C(OH)C_2H_5 \xrightarrow{tautomerization} H_3CCOC_2H_5$

SOLUTION :

Addition of electronegative atom to carbon is oxidation. Removal of hydrogen atom from carbon is also oxidation. While addition of hydrogen atom or removal of electronegative atom result in reduction of carbon. So in reaction :
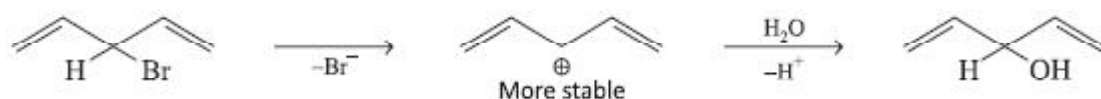
(1) Both carbon atoms are oxidized   (2) One is reduced, other is oxidized
(3) Carbon is reduced   (4) Carbon is oxidized
(5) One is reduced, other is oxidized   (6) One is reduced, other is oxidized

Example - 6 *Explain why the doubly allylic alkyl halide* (A) *undergoes much more rapid solvolysis in aqueous acetone than compound* (B). *Also then explain why compound* (C). *Which is also a doubly allylic alkyl halide, is solvolytically inert.*
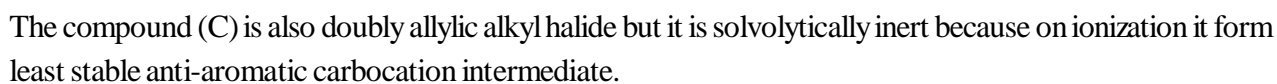
(A)   (B)   (C)
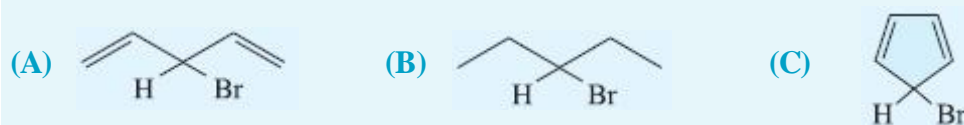
SOLUTION :

Solvolysis reaction is nucleophilic substitution reaction in which both nucleophile and solvent are same chemical species e.g. hydrolysis reaction. Generally solvolysis reactions of alkyl halides are proceed by S_N1 reaction mechanism. The doubly allylic halide (A) easily undergoes solvolysis reaction because allylic carbocation is resonance stabilized.
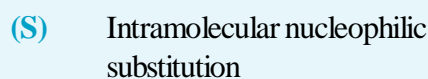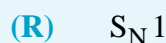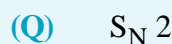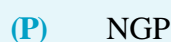
The compound (C) is also doubly allylic alkyl halide but it is solvolytically inert because on ionization it form least stable anti-aromatic carbocation intermediate.

Example - 7   MATCH THE COLUMN :

Column 1 [Reactions]   **Column 2 [Reaction mechanism]**

(A)   (P)   NGP

(B)   (Q) $S_N 2$

(C)   (R) $S_N 1$

(D)   (S)   Intramolecular nucleophilic substitution

SOLUTION :   [A-r][B-q, s][C-q][D-p,s]

Lone pair of electron on adjacent carbon atom of reaction centre stabilize carbocation so reaction proceed by $S_N 1$.

$S_N 2$ reactions adjacent $\overset{}{>}C = O$ groups are usually fast due to neighbouring group participation.
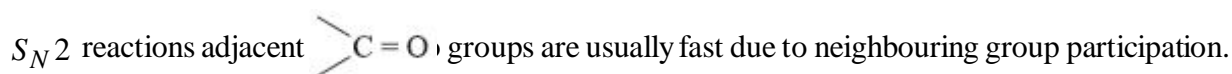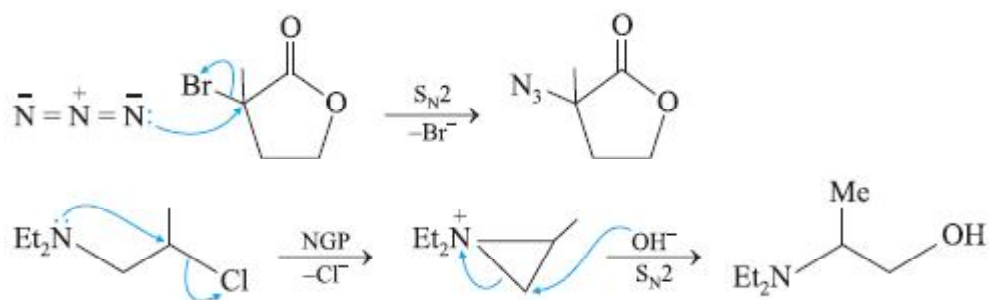
Observe the rearrangement in NGP.

NOW ATTEMPT OBJECTIVE WORKSHEET TO COMPLETE THIS EBOOK

SOLUTIONS TO REVIEW EXERCISE

1. If bonds formed by an atom are more or less than its valency, it has some charge called as formal charge.
Formal charge = Valence electrons in isolated atom – No. of bonds formed – No. of unshared electron
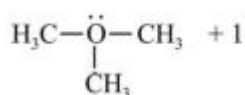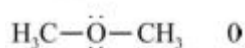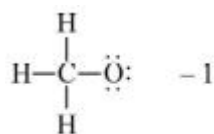
2. A, B and C are resonance forms of diazomethylene (CH_2N_2)
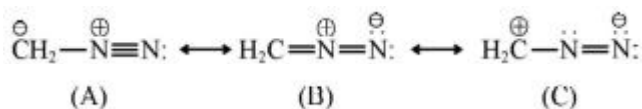
The structure (C) is least stable due to incomplete octet. But structure (B) is most stable because negative charge is on more electronegative atom.

The structure (A) contains nucleophilic carbon atom while structuere (C) contains electrophilic carbon atom. Both (A) and (B) have linear geometry while (C) has bent geometry. This is an example of how VSEPR can fail when comparing resonance structures.

IN - CHAPTER EXERCISE - E

1.   **(A)**   Methyl halides are unhindred and react rapidly by the S_N2 mechanism.

      (B)   Sodium ethoxide is a good nucleophile and will react with unhindered primary alkyl halides by the S_N2 mechanism.

      (C)   Cyclohexyl bromide is a secondary halide and will reacts with a strong base (sodium ethoxide) predominatly by the E2 mechanism.

      (D)   The tertiary halide tert-butyl bromide will undergo solvolysis by the S_N1 mechanism.

      (E)   The presence of the strong base sodium ethoxide will cause the E2 mechanism to predominate.

      (F)   Concerted reactions are those that occur in a single step. The bimolecular mechanisms S_N2 and E2 represent concerted processes.

      (G)   In a stereospecific reaction, stereoisomeric reactants yield products that are stereoisomers of each other. Reactions that occur by the S_N2 and E2 mechanisms are stereospecific.

      (H)   The unimolecular mechanisms S_N1 and E1, involve the formation of carbocation intermediates.

      (I)   Rearrangements are possbile when carbocations are intermediates in a reaction. Thus reactions occuring by the S_N1 and E1 mechanisms are most likely to have a rearranged carbon skeleton.

      (J)   Iodide is a better leaving group than bromide, and alkyl iodides react faster than alkyl bromides by any of the four mechanisms S_N1, S_N2, E1 and E2.

My Chapter Notes