Akhtar Saleem Sandhu
M.Sc Chemistry PUNJAB University, Lahore
Scientific Assistant SA-1 (PAEC)

Chapter 5

Unsaturated Hydrocarbons

CHAPTER'S SUMMARY

Unsaturated hydrocarbons are those compounds of carbon and hydrogen which contain fewer than maximum number of hydrogen atoms and thus their chemical affinity is not fully satisfied. Instead, they have carbon-carbon multiple bonds and have a tendency to add reagents such as hydrogen, halogens, hydrogen halides, etc., to form saturated compounds.

ALKENES

Alkenes, also known as olefins, are the unsaturated hydrocarbons which contain a carbon-carbon double bond in their molecules and can be represented by the general formula C_nH_{2n}.

Nomenclature

Alkenes, like alkanes, are named either by common (or trivial) names, or according to the IUPAC system. The common names of alkenes are derived by replacing the ending *-ane* of the name of the alkane having the same number of carbon atoms by *-ylene*. According to the IUPAC system, the alkenes are named by replacing the ending *-ane* of the name of the corresponding alkanes by *-ene*. However, in this case, alkenes have to follow certain rules which are similar in many respects to those used for naming the alkanes.

Preparation of Alkenes

The principal source of alkenes also is petroleum from which these are obtained by fractionation. However, alkenes can also be prepared from other compounds, mostly saturated, by the following methods, essentially involving elimination reactions:

1. Dehydrohalogenation of alkyl halides either by treatment with a strong base, such as sodium ethoxide, or by heating at high temperature (300–400°C).

2. Dehydration of alcohols by heating with an acid, such as sulfuric acid.

3. Dehalogenation of *vic*-dihalides by treatment with zinc dust in an anhydrous solvent, such as methanol or acetic acid.

4. Pyrolysis of esters of carboxylic acids, xanthate esters or tertiary amine oxides (pyrolytic eliminations).

5. Thermal decomposition of quaternary ammonium hydroxides (Hofmann reaction).

6. Treatment of an aldehyde or a ketone with Wittig reagent, phosphorus ylide (Wittig reaction).

7. Controlled hydrogenation of alkynes by using either Lindlar's catalyst or sodium in liquid ammonia.

Physical Properties of Alkenes

The physical properties of alkenes are essentially similar to those of the corresponding alkanes. At room temperature, the alkenes containing up to 4 carbon atoms are gases, alkenes with 5 to 17 carbon atoms are volatile liquid, and those containing 18 or more carbon atoms are solid. 1-Alkenes, like *n*-alkanes, show regular changes in their physical properties with the number of carbon atoms. They are insoluble in water, but quite soluble in solvents of low polarity. Alkenes are also less dense than water.

Relative Stability of Alkenes

Different alkenes have different relative stability, as determined from their heats of combustion, which depend on the position of the double bond in the molecule, and the number, nature and relative positions of the substituents on the double-bonded carbon atoms. In general, the greater the number of alkyl groups attached to the double bond, the greater the stability of the alkene. The relative stability of alkenes may be explained on the basis of steric effect and hyperconjugation.

Reactions of Alkenes

Alkenes generally undergo two types of reactions: (i) Addition reactions due to the carbon-carbon double bond. These may involve electrophilic addition or free-radical addition. (ii) Substitution reactions due to the alkyl group (if any) present in the molecule. These are essentially the reactions discussed in the case of alkanes. Some of the important reactions are summarized here:

1. Hydrogenation. Alkenes can be hydrogenated in the presence of a catalyst, usually Raney nickel, to produce alkanes. Since catalytic hydrogenation is an exothermic process, it can be used to determine the relative stability of alkenes, by measuring the heat of hydrogenation, i.e., the amount of heat evolved when one mole of an alkene is hydrogenated.

2. Addition of hydrogen halides. Alkenes add hydrogen halides, either by passing a dry gaseous hydrogen halide directly into an alkene or by using a moderately polar solvent, such as acetic acid or alcohol, to form haloalkanes. The reaction follows Markovnikov's rule. However, the addition of hydrogen bromide to an alkene in the presence of a peroxide follows anti-Markovnikov's rule.

3. Hydration. Alkenes on hydration can add a molecule of water across the double bond to form alcohols. Hydration of alkenes may be brought about in different ways: (i) Treatment of alkene with cold conc. H_2SO_4, followed by heating with water. (ii) Direct addition of water to the double bond in the presence of an acid catalyst such as H_2SO_4. (iii) Reaction of alkenes with mercuric acetate in a mixture of THF and water, followed by reduction by sodium borohydride in aq. NaOH (oxymercuration-demercuration). (iv) Treatment of alkenes with diborane, followed by oxidation with alkaline hydrogen peroxide (hydroboration-oxidation.)

The first three methods result in the Markovnikov's addition of water to an alkene, whereas the fourth method results in the anti-Markovnikov's addition of water to the double bond.

4. Addition of halogens. Alkenes can readily add a molecule of chlorine or bromine in an inert solvent such as CCl_4 at room temperature to give *vic*-dichlorides or dibromides. At high temperature (400–600°C), the product that is obtained is that of substitution, rather than addition.

5. Addition of hypohalous acids. Alkenes react with an aqueous solution of a halogen to form halohydrin which in fact involves the Markovnikov's addition of hypohalous acid across the double bond.

6. Oxidation. Alkenes react with various oxidizing agents to yield different types of oxidation products, depending on the nature of the oxidizing agent, the reaction conditions and the extent of oxidation. (i) Alkenes on treatment with organic peracids, e.g., peracetic acid, are converted to epoxides (epoxidation) which on acid-catalysed hydrolysis yield glycols. The overall reaction gives the product of *anti*-hydroxylation. (ii) A direct *syn*-hydroxylation of an alkene can be achieved either by the use of OsO_4, followed by treatment with $NaHSO_3$, or by the controlled use of cold dilute alkaline solution of $KMnO_4$ which usually ends up in the cleavage of the alkene at the position of the double bond. (iii) Treatment of alkenes with ozone (ozonolysis) forms ozonides which on hydrolysis yield carbonyl compounds, involving overall the cleavage of the molecule at the position of the double bond.

Oxidation of alkenes with $KMnO_4$ or ozone can be thus used to locate the position of the double bond in a molecule.

7. Polymerization. Alkenes undergo polymerization to yield a variety of industrially important polymers.

8. Addition of carbenes. When an alkene is heated with a mixture of diiodomethane and zinc-copper couple in anhydrous ether, a cyclopropane is formed, which involves the addition of methylene across the double bond.

9. Isomerization. Alkenes may undergo isomerization when heated at a very high temperature (500–700°C), or at a lower temperature (200–300°C) in the presence of a catalyst, such as $AlCl_3$.

ALKYNES

Alkynes are the unsaturated hydrocarbons that contain a triple bond in their molecules, and can be represented by the general formula C_nH_{2n-2}.

Nomenclature

Simple alkynes are usually named as the derivatives of acetylene, the parent member of the family. The more complicated alkynes are named according to the IUPAC system following the same rules as employed for alkenes, except that the ending *-ane* of the name of the corresponding alkane is replaced by *-yne*, instead of *-ene*.

Preparation of Alkynes

Acetylene itself is of great importance due to its high heat of combustion. The oxyacetylene torch is commonly used for the welding and cutting of metals. Acetylene is prepared on industrial scale by the reaction of calcium carbide (CaC_2) with water. The other alkynes can be prepared either by introducing a carbon-carbon triple bond in a molecule, e.g., by dehydrohalogenation of *vic*-dihalides, or by increasing the size of a molecule that already contains a triple bond, e.g., by the alkylation of a terminal alkyne.

Physical Properties of Alkynes

The physical properties of alkynes, in general, are essentially the same as those of the corresponding alkenes.

Reactions of Alkynes

Alkynes resemble alkenes in most of their reactions, except that an alkyne can add two molecules of the reagents in a step-wise manner, but by selecting suitable conditions it is possible to restrict the reaction to the addition of only one molecule of the reagent to get an alkene. However, due to the acidic nature of the acetylenic hydrogen, alkynes also undergo certain reactions that are not commonly observed with alkenes. Some of the common reactions of alkynes are summarized below:

1. Hydrogenation. An alkyne can add either one molecule of hydrogen to form an alkene or two molecules of hydrogen to produce an alkane; the extent of hydrogenation depends on the conditions and the catalyst employed.

2. Addition of halogens. Halogens (chlorine or bromine) can add to an alkyne to form either a dihaloalkene or a tetrahaloalkane, depending on whether one or two molecules of the halogen are used.

3. Addition of hydrogen halides. Alkynes can react with hydrogen halides (HBr and HCl) to form either haloalkenes or gem-dihaloalkanes, following the Markovnikov's rule. However, in the presence of peroxides, the addition of HBr follows the anti-Markovnikov's rule.

4. Hydration. Alkynes add one molecule of water in the presence of H_2SO_4 and mercuric sulfate at about 60°C to yield an aldehyde or a ketone, through the intermediate formation of vinylic alcohol.

5. Oxidation. On treatment with neutral $KMnO_4$ or ozone, alkynes undergo oxidation to yield 1,2-dicarbonyl compounds. However, the oxidation reaction can be carried on further to yield the cleavage products.

6. Hydroboration. Alkynes react with diborane, followed either by pyrolysis to yield cis alkenes, or by oxidation to yield aldehydes or ketones.

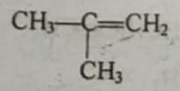
7. Formation of metal acetylides. Due to the acidic nature of acetylenic hydrogen, acetylene or a terminal alkyne can easily form metal alkynides which can react with a number of reagents to yield a variety of products.

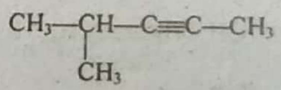
8. Polymerization. Alkynes undergo polymerization under different conditions to yield a variety of industrially important polymers.

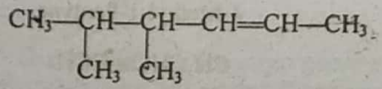
9. Isomerization. Alkynes isomerize under the influence of either an acidic or a basic catalyst.

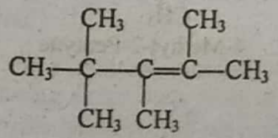
ANSWERS TO EXERCISES

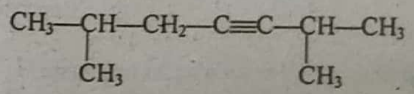
1. (*a*) 2-Isopropyl-1-pentene.
   (*b*) 3-Ethyl-2-methyl-3-heptene.
   (*c*) 3-Ethyl-4-isopropyl-1-heptene.
   (*d*) 4,4,5-Trimethyl-2-hexyne.
   (*e*) 6-Isopropyl-4-nonyne.
   (*f*) 3,4-dimethylcyclopentene.
   (*g*) 1-Propynylcyclobutane.
   (*h*) 3-(2-Propynyl)cyclohexene.
   (*i*) 1-Hexen-5-yne.
   (*j*) 4-Isopropenyl-1,6-heptadiyne.

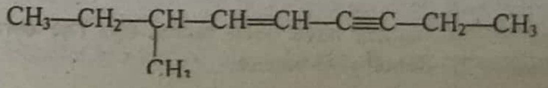
2. (*a*)

$CH_3-\underset{CH_3}{C}=CH_2$

(*b*)

$CH_3-\underset{CH_3}{CH}-C\equiv C-CH_3$

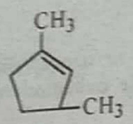
(*c*)

$CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH=CH-CH_3$

(*d*)

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_3}{C}=\overset{CH_3}{C}-CH_3$

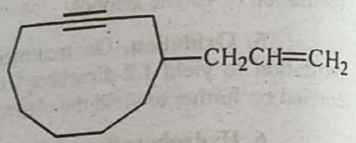
(*e*)

$CH_3-\underset{CH_3}{CH}-CH_2-C\equiv C-\underset{CH_3}{CH}-CH_3$

(*f*)

$CH_3-CH_2-\underset{CH_3}{CH}-CH=CH-C\equiv C-CH_2-CH_3$

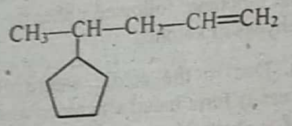
(g)



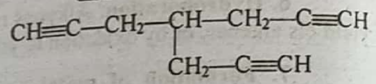
(h)



(i)



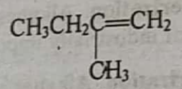
(j)



$CH\equiv C-CH_2-\underset{CH_2-C\equiv CH}{CH}-CH_2-C\equiv CH$

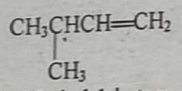
3. (i) C_5H_{10},

$CH_3CH_2CH_2CH{=}CH_2$
1-pentene



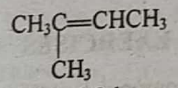
$CH_3CH_2\underset{CH_3}{C}{=}CH_2$

2-Methyl-1-butene



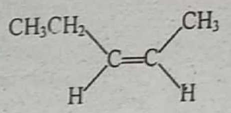
$CH_3\underset{CH_3}{C}HCH{=}CH_2$

3-Methyl-1-butene

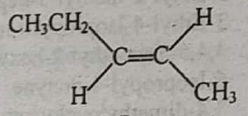


$CH_3\underset{CH_3}{C}{=}CHCH_3$

2-Methyl-2-butene



cis-2-Pentene



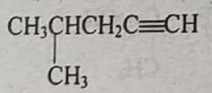
trans-2-Pentene

(ii) C_6H_{10},

$CH_3CH_2CH_2CH_2C\equiv CH$
1-Hexyne

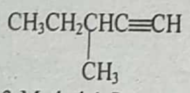
$CH_3CH_2CH_2C\equiv CCH_3$
2-Hexyne

$CH_3CH_2C\equiv CCH_2CH_3$
3-Hexyne



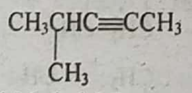
$CH_3\underset{CH_3}{C}HCH_2C\equiv CH$

4-Methyl-1-Pentyne



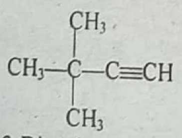
$CH_3CH_2\underset{CH_3}{C}HC\equiv CH$

3-Methyl-1-Pentyne



$CH_3\underset{CH_3}{C}HC\equiv CCH_3$

4-Methyl-2-Pentyne



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-C\equiv CH$

3,3-Dimethyl-1-butyne

4. *(a)* Trivial and IUPAC names have been mixed up. The correct name is tetramethylethylene or 2,3-dimethyl-2-butene.

(b) The name has been based on the wrong parent name. The correct name is 3,3-dimethyl-1-butene.

(c) The numbering has been started from the wrong side of the double bond. The correct name is 1-methylcyclopentene.

(d) Isobutylene is not a parent name according to the IUPAC system. The correct name is 2-methyl-2-butene.

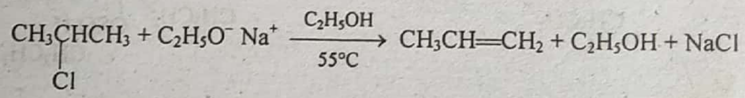
(e) The methyl group at position 1 has not been included in the parent chain. The correct name is 2-heptyne.

(f) The numbering has been started from the wrong end of the chain. The correct name is 4-methyl-2-pentyne.

5. *(a)* $CH_3CH_2CH_2Cl + C_2H_5O^-Na^+ \xrightarrow[55°C]{C_2H_5OH} CH_3CH{=}CH_2 + C_2H_5OH + NaCl$

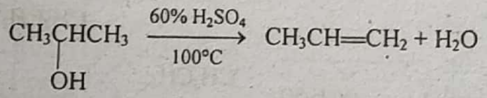
(b) $CH_3CH_2CH_2OH \xrightarrow[180°C]{\text{conc. } H_2SO_4} CH_3CH{=}CH_2 + H_2O$

(c)



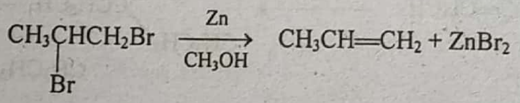
$CH_3\underset{Cl}{C}HCH_3 + C_2H_5O^- Na^+ \xrightarrow[55°C]{C_2H_5OH} CH_3CH{=}CH_2 + C_2H_5OH + NaCl$

(d)



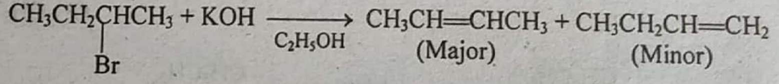
$CH_3\underset{OH}{C}HCH_3 \xrightarrow[100°C]{60\%\ H_2SO_4} CH_3CH{=}CH_2 + H_2O$

(e)



$CH_3\underset{Br}{C}HCH_2Br \xrightarrow[CH_3OH]{Zn} CH_3CH{=}CH_2 + ZnBr_2$

6.



$CH_3CH_2\underset{Br}{C}HCH_3 + KOH \xrightarrow[C_2H_5OH]{} \underset{\text{(Major)}}{CH_3CH{=}CHCH_3} + \underset{\text{(Minor)}}{CH_3CH_2CH{=}CH_2}$

7. The stability of the given alkenes decreases in the following order: 2,3-dimethyl-2-butene > 2-methyl-2-pentene > *trans*-3-hexene > *cis*-3-hexene > 1-hexene.

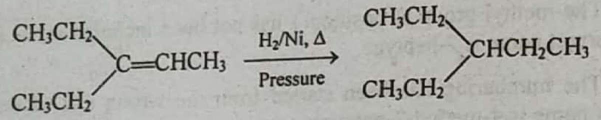
The relative stability of alkenes can be determined practically by measuring either their heats of combustion or their heats of hydrogenation. The larger the heat evolved on combustion or hydrogenation, the less the stability of the alkene.

8. (a) Preparation of an alkene by the dehydration of an alcohol proceeds through a carbocation which usually undergoes rearrangement to lead to a mixture of elimination products. Although the preparation of alkenes by the dehydrohalogenation of alkyl halides is also accompanied by the substitution

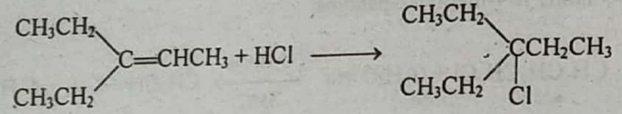
product but this can be minimized by using potassium *t*-butoxide as a base for the elimination. I would therefore prefer dehydrohalogenation of an alkyl halide in this case.

(b) In both the cases (*i* and *ii*), the second compound is a better starting material because the first compound in each case, having β-hydrogen at more than one position will give a mixture of alkenes.

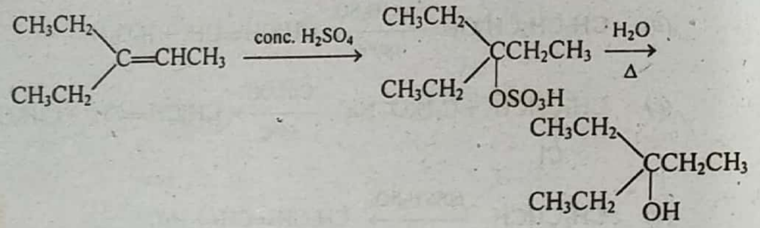
9. *(a)*



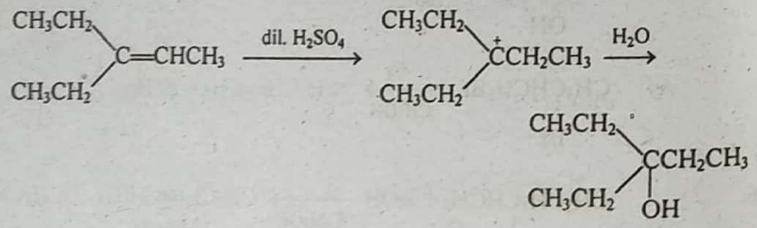
(b)



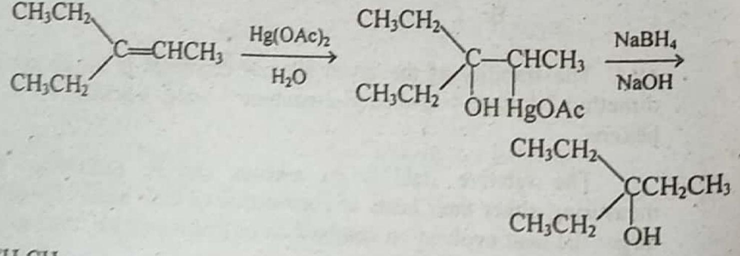
(c)



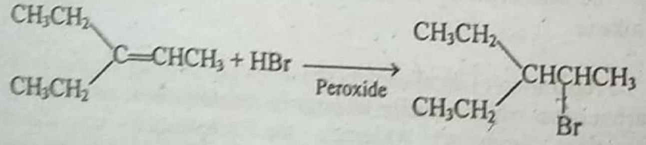
(d)



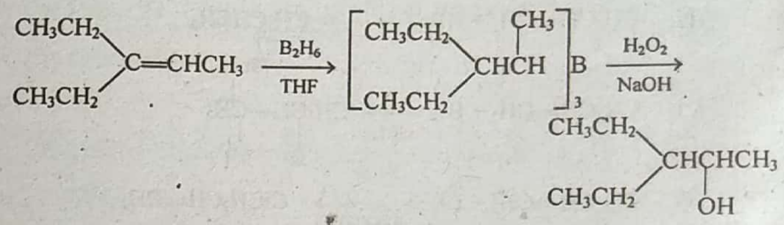
(e)



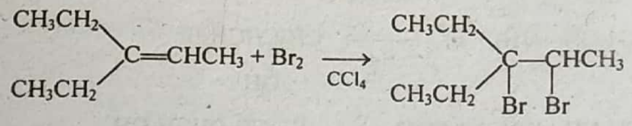
(f)



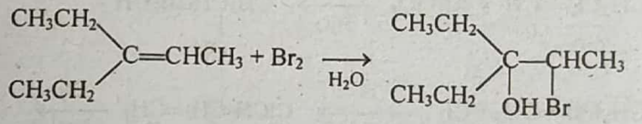
(g)



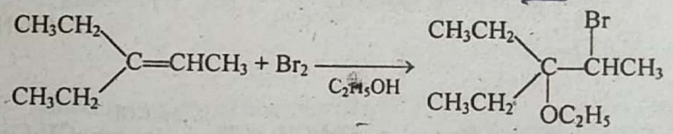
(h)



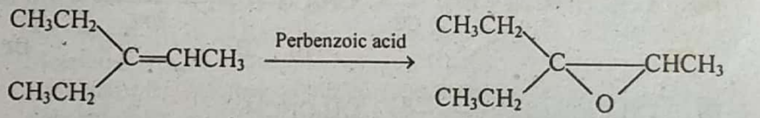
(i)



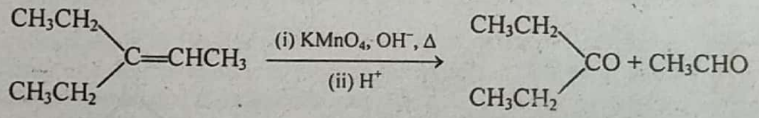
(j)



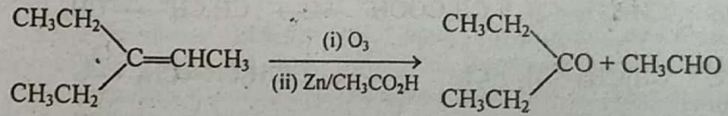
(k)



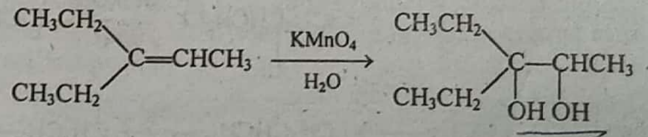
(l)



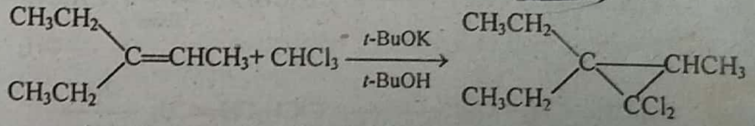
(m)



(n)

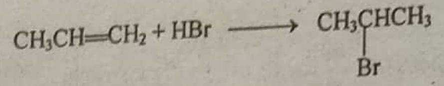


(o)



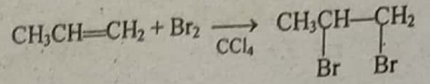
10. *(a)* $CH_3CH{=}CH_2 + H_2 \xrightarrow[\text{Pressure}]{\text{Ni, }\Delta} CH_3CH_2CH_3$

(*b*)



$$CH_3CH{=}CH_2 + HBr \longrightarrow CH_3\underset{Br}{CH}CH_3$$

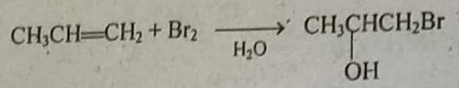
(*c*)



$$CH_3CH{=}CH_2 + Br_2 \xrightarrow[CCl_4]{} CH_3\underset{Br}{CH}{-}\underset{Br}{CH_2}$$

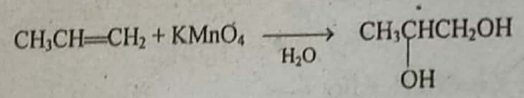
(*d*) $CH_3CH{=}CH_2 + Cl_2 \xrightarrow[400\text{-}600°C]{} ClCH_2CH{=}CH_2$

(*e*)



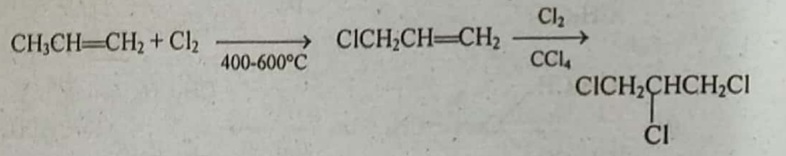
$$CH_3CH{=}CH_2 + Br_2 \xrightarrow[H_2O]{} CH_3\underset{OH}{CH}CH_2Br$$

(*f*)



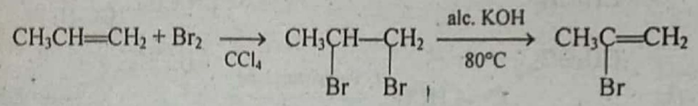
$$CH_3CH{=}CH_2 + KMnO_4 \xrightarrow[H_2O]{} CH_3\underset{OH}{CH}CH_2OH$$

(*g*)



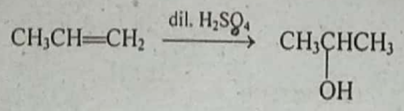
$$CH_3CH{=}CH_2 + Cl_2 \xrightarrow[400\text{-}600°C]{} ClCH_2CH{=}CH_2 \xrightarrow[CCl_4]{Cl_2} ClCH_2\underset{Cl}{CH}CH_2Cl$$

(*h*)



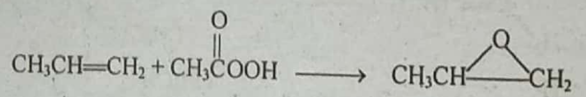
$$CH_3CH{=}CH_2 + Br_2 \xrightarrow[CCl_4]{} CH_3\underset{Br}{CH}{-}\underset{Br}{CH_2} \xrightarrow[80°C]{alc.\ KOH} CH_3\underset{Br}{C}{=}CH_2$$

(*i*)



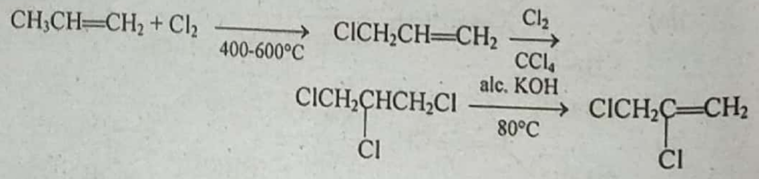
$$CH_3CH{=}CH_2 \xrightarrow{dil.\ H_2SO_4} CH_3\underset{OH}{CH}CH_3$$

(*j*)



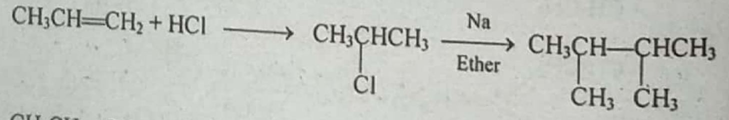
$$CH_3CH{=}CH_2 + CH_3\overset{O}{\overset{\|}{C}}OOH \longrightarrow CH_3CH\overset{O}{—}CH_2$$

(*k*)



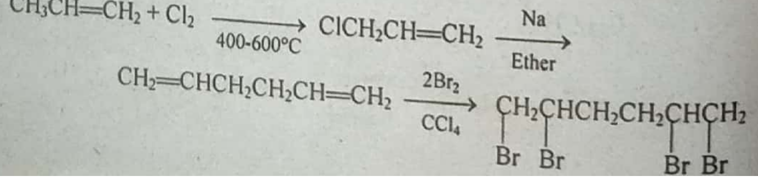
$$CH_3CH{=}CH_2 + Cl_2 \xrightarrow[400\text{-}600°C]{} ClCH_2CH{=}CH_2 \xrightarrow[CCl_4]{Cl_2}$$
$$ClCH_2\underset{Cl}{CH}CH_2Cl \xrightarrow[80°C]{alc.\ KOH} ClCH_2\underset{Cl}{C}{=}CH_2$$

(*l*)



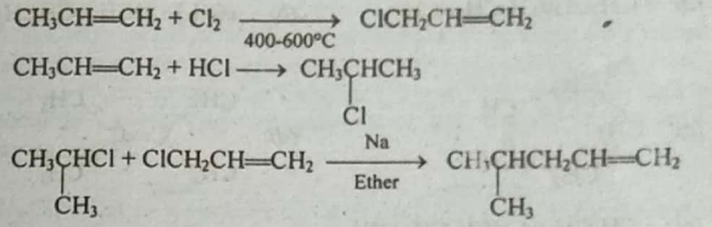
$$CH_3CH{=}CH_2 + HCl \longrightarrow CH_3\underset{Cl}{CH}CH_3 \xrightarrow[Ether]{Na} CH_3\underset{CH_3}{CH}{-}\underset{CH_3}{CH}CH_3$$

(*m*)



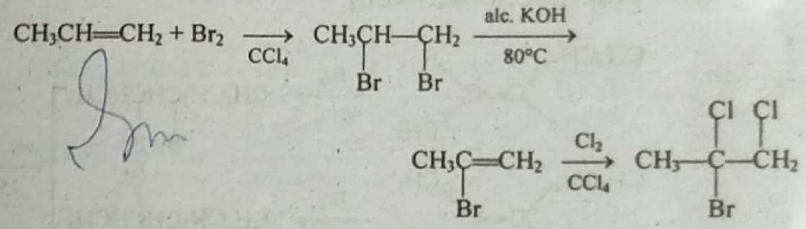
$$CH_3CH{=}CH_2 + Cl_2 \xrightarrow[400\text{-}600°C]{} ClCH_2CH{=}CH_2 \xrightarrow[Ether]{Na}$$
$$CH_2{=}CHCH_2CH_2CH{=}CH_2 \xrightarrow[CCl_4]{2Br_2} \underset{Br}{CH_2}\underset{Br}{CH}CH_2CH_2\underset{Br}{CH}\underset{Br}{CH_2}$$

(*n*)



$$CH_3CH{=}CH_2 + Cl_2 \xrightarrow[400\text{-}600°C]{} ClCH_2CH{=}CH_2$$
$$CH_3CH{=}CH_2 + HCl \longrightarrow CH_3\underset{Cl}{CH}CH_3$$
$$CH_3\underset{CH_3}{CH}Cl + ClCH_2CH{=}CH_2 \xrightarrow[Ether]{Na} CH_3\underset{CH_3}{CH}CH_2CH{=}CH_2$$

(*o*)



$$CH_3CH{=}CH_2 + Br_2 \xrightarrow[CCl_4]{} CH_3\underset{Br}{CH}{-}\underset{Br}{CH_2} \xrightarrow[80°C]{alc.\ KOH}$$
$$CH_3\underset{Br}{C}{=}CH_2 \xrightarrow[CCl_4]{Cl_2} CH_3{-}\overset{Cl}{\underset{Br}{C}}{-}\overset{Cl}{CH_2}$$

(*p*) $CH_3CH{=}CH_2 + Cl_2 \xrightarrow[400\text{-}600°C]{} ClCH_2CH{=}CH_2 \xrightarrow[Ether]{Na}$ $CH_2{=}CHCH_2CH_2CH{=}CH_2$

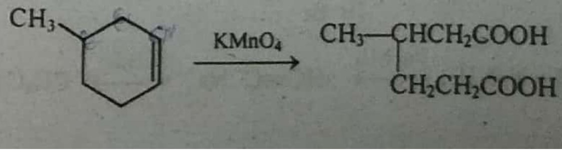
11\. Molecular weight of bromine (Br_2) = 160
Amount of Br_2 in 1000 ml of 0.1 molar solution = 16 g
Amount of Br_2 in 14.7 ml of 0.1 molar solution = 0.2352 g
Molecular weight of the cyclic alkene, $C_{10}H_{16}$ = 136
Amount of Br_2 reacting with 0.20 g of the cyclic alkene = 0.2352 g
Amount of Br_2 reacting with 136 g of the cyclic alkene = 160 g.

So, 1 mole of Br_2 has reacted with 1 mole of the cyclic alkene. This means that only one double bond is present in the molecule of alkene, and the hydrogen deficiency shows that the alkene is bicyclic.

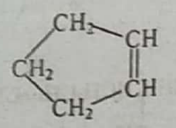
12\. Since the alkene consumes only 1 mole of hydrogen in the presence of a catalyst to form a saturated alkane (*n*-hexane), it contains only one double bond. On vigorous oxidation with $KMnO_4$ an alkene undergoes cleavage at the position of the double bond to yield carboxylic acids. Since in this case only one three-carbon carboxylic acid is formed, the hexene is cleaved at half point. So, the alkene is 3-hexene,

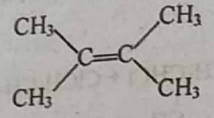
$$CH_3CH_2CH{=}CHCH_2CH_3 \xrightarrow{KMnO_4} 2CH_3CH_2COOH$$

13\. Under the conditions of the exercise the given compound A could be obtained from 4-methylcyclohexene.

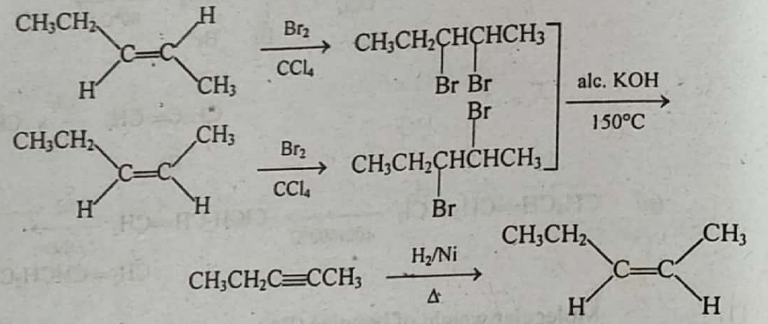


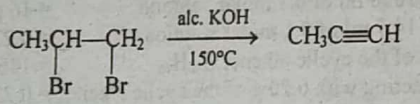
14. (a) $CH_3CH_2CH_2CH{=}CH_2$ (b) $(CH_3)_2CHCH{=}CHCH_3$

(c)


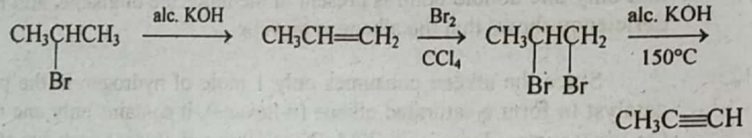
(d)


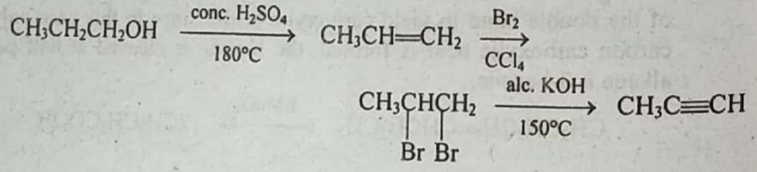
(e) $CH_3CH{=}CHCH_2CH{=}CH_2$

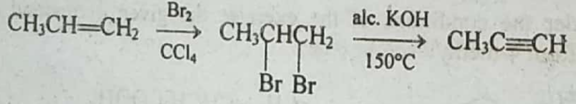
15.


16. (a)

$CH_3\underset{Br}{CH}-\underset{Br}{CH_2} \xrightarrow[150°C]{\text{alc. KOH}} CH_3C\equiv CH$

(b) $CH_3CH_2CHCl_2 \xrightarrow[150°C]{\text{alc. KOH}} CH_3C\equiv CH$

(c)

$CH_3\underset{Br}{CH}CH_3 \xrightarrow{\text{alc. KOH}} CH_3CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} CH_3\underset{Br}{CH}\underset{Br}{CH_2} \xrightarrow[150°C]{\text{alc. KOH}} CH_3C\equiv CH$

(d)

$CH_3CH_2CH_2OH \xrightarrow[180°C]{\text{conc. } H_2SO_4} CH_3CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} CH_3\underset{Br}{CH}\underset{Br}{CH_2} \xrightarrow[150°C]{\text{alc. KOH}} CH_3C\equiv CH$

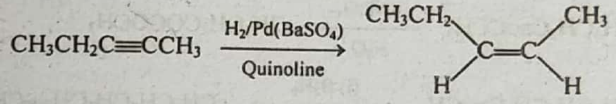
(e)

$CH_3CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} CH_3\underset{Br}{CH}\underset{Br}{CH_2} \xrightarrow[150°C]{\text{alc. KOH}} CH_3C\equiv CH$

(f) $HC\equiv CH + NaNH_2 \xrightarrow{\text{liq. } NH_3} HC\equiv C^- Na^+ \xrightarrow{CH_3Br} CH_3C\equiv CH$

17. In this reaction acetylide anion is formed as an intermediate which reacts with the alkyl halide in an S_N2 type reaction. A tertiary alkyl halide is not a suitable substrate for the S_N2 reaction. Moreover, a tertiary alkyl halide in the presence of a strong base like acetylide anion undergoes elimination, rather than substitution. I would therefore prefer the combination *(b)* for the preparation of the given alkyne.

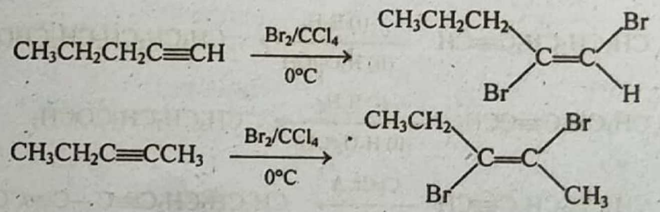
$$(CH_3)_3CC\equiv CH \xrightarrow[\text{liq. } NH_3]{NaNH_2} (CH_3)_3CC\equiv C^- Na^+ \xrightarrow{CH_3CH_2Br} (CH_3)_3CC\equiv CCH_2CH_3$$

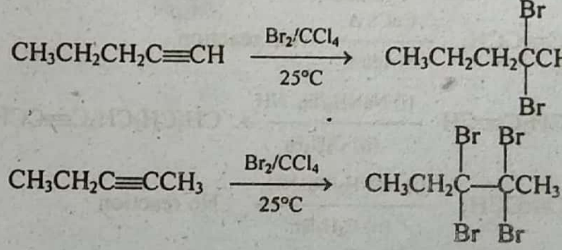
18. (a) $CH_3CH_2CH_2C\equiv CH \xrightarrow[\text{Quinoline}]{H_2/Pd(BaSO_4)} CH_3CH_2CH_2CH{=}CH_2$



(b) $CH_3CH_2CH_2C\equiv CH \xrightarrow{H_2/Pt} CH_3CH_2CH_2CH_2CH_3$

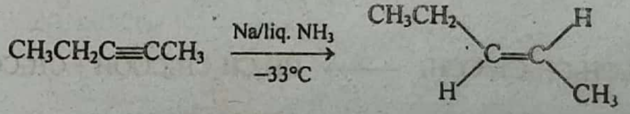
$CH_3CH_2C\equiv CCH_3 \xrightarrow{H_2/Pt} CH_3CH_2CH_2CH_2CH_3$

(c)


(d)

$CH_3CH_2CH_2C\equiv CH \xrightarrow[25°C]{Br_2/CCl_4} CH_3CH_2CH_2\overset{Br}{\underset{Br}{C}}CHBr_2$

$CH_3CH_2C\equiv CCH_3 \xrightarrow[25°C]{Br_2/CCl_4} CH_3CH_2\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}CH_3$

(e) $CH_3CH_2CH_2C\equiv CH \xrightarrow[-33°C]{\text{Na/liq. } NH_3} CH_3CH_2CH_2CH{=}CH_2$



(f) $CH_3CH_2CH_2C\equiv CH \xrightarrow{HBr/HgBr_2} CH_3CH_2CH_2CBr_2CH_3$

$CH_3CH_2C\equiv CCH_3 \xrightarrow{HBr/HgBr_2} CH_3CH_2CH_2CBr_2CH_3$

(g) $CH_3CH_2CH_2C\equiv CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} CH_3CH_2CH_2COCH_3$

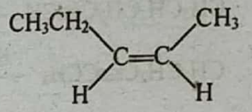
$CH_3CH_2C\equiv CCH_3 + H_2O \xrightarrow[HgSO_4]{H_2SO_4} CH_3CH_2CH_2COCH_3$

(h) $CH_3CH_2CH_2C\equiv CH \xrightarrow[H_2O]{KMnO_4} CH_3CH_2CH_2COCHO$

$CH_3CH_2C\equiv CCH_3 \xrightarrow[H_2O]{KMnO_4} CH_3CH_2COCOCH_3$

(i) $CH_3CH_2CH_2C\equiv CH \xrightarrow[\text{(ii) } CH_3COOH]{\text{(i) } B_2H_6} CH_3CH_2CH_2CH{=}CH_2$

$CH_3CH_2C\equiv CCH_3 \xrightarrow[\text{(ii) } CH_3COOH]{\text{(i) } B_2H_6}$



(j) $CH_3CH_2CH_2C\equiv CH \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6} CH_3CH_2CH_2CH_2CHO$

$CH_3CH_2C\equiv CCH_3 \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6} CH_3CH_2CH_2COCH_3$

(k) $CH_3CH_2CH_2C\equiv CH \xrightarrow[\text{Pyridine}]{CuCl,\ \Delta} CH_3CH_2CH_2C\equiv C{-}C\equiv CCH_2CH_2CH_3$

$CH_3CH_2C\equiv CCH_3 \xrightarrow[\text{Pyridine}]{CuCl,\ \Delta}$ No reaction

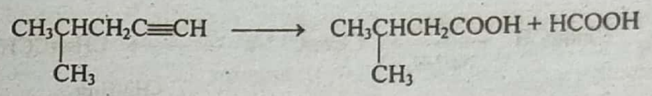
(l) $CH_3CH_2CH_2C\equiv CH \xrightarrow[\text{(ii) } C_2H_5Br]{\text{(i) } NaNH_2/\text{liq. } NH_3} CH_3CH_2CH_2C\equiv CCH_2CH_3$

$CH_3CH_2C\equiv CCH_3 \xrightarrow[\text{(ii) } C_2H_5Br]{\text{(i) } NaNH_2/\text{liq. } NH_3}$ No reaction

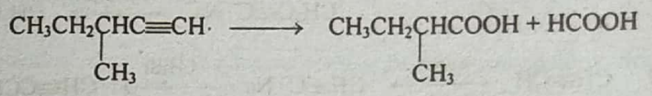
19. $CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[\text{(iii) } H_2O_2]{\text{(i) } O_3 \text{ (ii) } H_2O} CH_3CH_2CH_2CH_2COOH +$ HCOOH

$CH_3CH_2CH_2C\equiv CCH_3 \longrightarrow CH_3CH_2CH_2COOH + CH_3COOH$

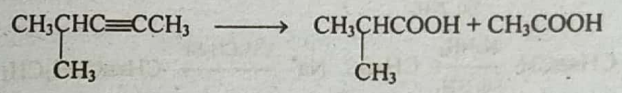
$CH_3CH_2C\equiv CCH_2CH_3 \longrightarrow 2CH_3CH_2COOH$



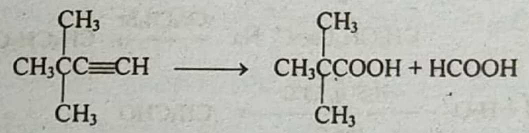
$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2C\equiv CH \longrightarrow CH_3\underset{CH_3}{\underset{|}{C}}HCH_2COOH + HCOOH$



$CH_3CH_2\underset{CH_3}{\underset{|}{C}}HC\equiv CH \longrightarrow CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCOOH + HCOOH$



$CH_3\underset{CH_3}{\underset{|}{C}}HC\equiv CCH_3 \longrightarrow CH_3\underset{CH_3}{\underset{|}{C}}HCOOH + CH_3COOH$

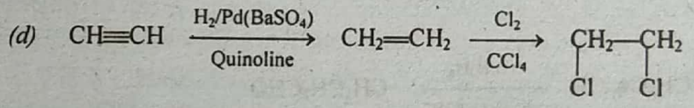


$CH_3\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}C\equiv CH \longrightarrow CH_3\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}COOH + HCOOH$

20. (a) $HC\equiv CH \xrightarrow{H_2/Pt} CH_3CH_3$

(b) $HC\equiv CH \xrightarrow[\text{Quinoline}]{H_2/Pd(BaSO_4)} CH_2{=}CH_2$

(c) $CH\equiv CH \xrightarrow{HBr/HgBr_2} CH_3CHBr_2$



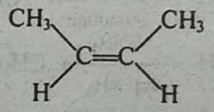
(d) $CH\equiv CH \xrightarrow[\text{Quinoline}]{H_2/Pd(BaSO_4)} CH_2{=}CH_2 \xrightarrow[CCl_4]{Cl_2} \underset{Cl}{\underset{|}{C}}H_2{-}\underset{Cl}{\underset{|}{C}}H_2$

(e) $CH\equiv CH \xrightarrow[\text{liq. } NH_3]{NaNH_2} CH\equiv C^-\ Na^+ \xrightarrow{CH_3CH_2Br} CH\equiv CCH_2CH_3$

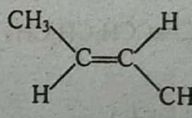
(f) $CH\equiv CH \xrightarrow[\text{liq. } NH_3]{NaNH_2} CH\equiv C^-\ Na^+ \xrightarrow{CH_3Br} CH\equiv CCH_3 \xrightarrow[\text{liq. } NH_3]{NaNH_2}$

$CH_3C\equiv C^-\ Na^+ \xrightarrow{CH_3Br} CH_3C\equiv CCH_3$

(g) $CH_3C\equiv CCH_3$ (From f) $\xrightarrow[\text{Quinoline}]{H_2/Pd(BaSO_4)}$



(h) $CH_3C\equiv CCH_3 \xrightarrow[-33°C]{Na/\text{liq. } NH_3}$



(i) $CH\equiv CH \xrightarrow[\text{liq. } NH_3]{NaNH_2} CH\equiv C^-\ Na^+ \xrightarrow{CH_3CH_2CH_2Br} CH\equiv CCH_2CH_2CH_3$

(j) $$CH\equiv CH \xrightarrow[\text{liq. }NH_3]{NaNH_2} CH\equiv C^-Na^+ \xrightarrow{CH_3Br} CH\equiv CCH_3 \xrightarrow[\text{liq. }NH_3]{NaNH_2} CH_3C\equiv C^-Na^+ \xrightarrow{CH_3CH_2Br} CH_3C\equiv CCH_2CH_3$$

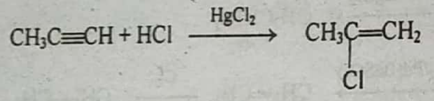
(k) $$CH\equiv CH \xrightarrow[\text{liq. }NH_3]{NaNH_2} CH\equiv C^-Na^+ \xrightarrow{CH_3Br} CH\equiv CCH_3$$

(l) $$CH\equiv CH \xrightarrow[\text{liq. }NH_3]{NaNH_2} CH\equiv C^-Na^+ \xrightarrow{CH_3CH_2Br} CH\equiv CCH_2CH_3 \xrightarrow[\text{liq. }NH_3]{NaNH_2} CH_3CH_2C\equiv C^-Na^+ \xrightarrow{CH_3CH_2Br} CH_3CH_2C\equiv CCH_2CH_3$$

(m) $$CH\equiv CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4,\ 60^\circ C} CH_3CHO$$

(n) $$CH\equiv CH + HCl \xrightarrow{HgCl_2} CH_2{=}CHCl$$

21. (a) $$CH_3C\equiv CH \xrightarrow[\text{Quinoline}]{H_2/Pd(BaSO_4)} CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3CHBrCH_3$$

(b) 

$$CH_3C\equiv CH + HCl \xrightarrow{HgCl_2} CH_3C(Cl){=}CH_2$$

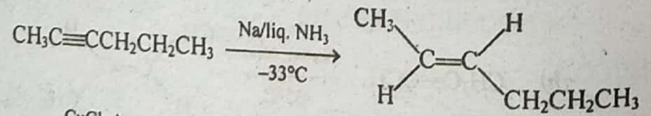
(c) $$CH_3C\equiv CH \xrightarrow[\text{(ii) }H_2O_2/OH^-]{\text{(i) }B_2H_6} CH_3CH_2CHO$$

(d) $$CH_3C\equiv CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4,\ 60^\circ C} CH_3COCH_3$$

(e) $$CH_3C\equiv CH \xrightarrow[\text{Pyridine}]{CuCl,\ \Delta} CH_3C\equiv C{-}C\equiv CCH_3 \xrightarrow{H_2/Pt} CH_3(CH_2)_4CH_3$$

(f) $$CH_3C\equiv CH \xrightarrow[\text{Quinoline}]{H_2/Pd(BaSO_4)} CH_3CH{=}CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3CH_2CH_2Br$$

$$CH_3C\equiv CH \xrightarrow[\text{liq. }NH_3]{NaNH_2} CH_3C\equiv C^-Na^+ \xrightarrow{CH_3CH_2CH_2Br}$$



(g) $$CH_3C\equiv CH \xrightarrow[\text{Pyridine}]{CuCl,\ \Delta} CH_3C\equiv C{-}C\equiv CCH_3$$

22. The sample of 2-pentyne containing 1-pentyne as impurity is treated with an ammoniacal solution of silver nitrate whereby 1-pentyne forms a precipitate which can be removed by filtration. 2-Pentyne does not react with the reagent and remains intact.

23. (a) 1-Butyne forms a precipitate with an ammoniacal solution of silver nitrate, whereas 2-butyne does not.

(b) 1-Hexene decolorises a red solution of Br_2 in CCl_4, whereas cyclohexane does not.

(c) Propyne forms a precipitate with an ammoniacal solution of silver nitrate, whereas propene does not.

(d) Isobutylene dissolves in 65% H_2SO_4, whereas isobutane does not.

(e) 1-Pentene dissolves in conc. H_2SO_4, whereas *n*-pentane does not.

(f) 2-Pentyne decolorises a red solution of Br_2 in CCl_4 at room temperature, whereas *n*-pentane does not.

(g) 1-Pentyne forms a precipitate with an ammoniacal solution of silver nitrate, whereas 1-pentene does not.

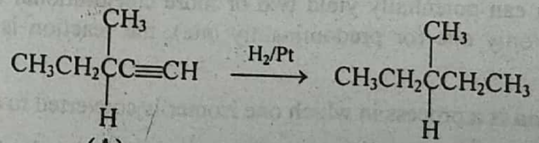
24. The unknown compound is treated with ammoniacal solution of silver nitrate. If it forms a precipitate, it is 1-pentyne, and if it does not, then its possibility of being 1-pentyne is ruled out. Similarly the characteristic tests of other compounds are also performed one by one.

If it is 1,3-pentadiene (a conjugated diene), it should undergo Diels-Alder reaction to form an adduct with a dienophile, such as maleic anthydride, to give a new solid product, as determined by its melting point.

2-Pentyne should consume two equivalent of hydrogen in the presence of a catalyst, whereas the alkenes consume only one.

Trimethylethylene and 3,3-dimethyl-l-butene dissolve in 65% H_2SO_4, whereas 1-pentene and 2-pentene dissolve in 85% H_2SO_4. Out of these two pairs, 3,3-dimethyl-l-butene and 1-pentene on oxidative degradation with $KMnO_4$ evolve CO_2 which turns lime water milky.

If the unknown compound does not respond to any of the above tests, then it is *n*-pentane.

25. 

$$CH_3CH_2C(CH_3)(H)C\equiv CH \xrightarrow{H_2/Pt} CH_3CH_2C(CH_3)(H)CH_2CH_3$$

(A) (B)

26. *(a)* **Electrophile** (electron-loving) is a species that accepts an electron-pair from an attacking nucleophile.

(b) **Nucleophile** (nucleus-loving) is a species with an electron-pair that tends to attack an electron-deficient centre.

(c) **Substitution** is a reaction in which an atom or a group in a molecule is replaced by another atom or group.

(d) **Elimination** is a reaction in which two atoms or groups are removed from adjacent carbon atoms in a molecule to create a double bond.

(e) **Markovnikov's rule** states that in the addition of a hydrogen halide to a carbon-carbon double bond of an unsymmetrical alkene, the hydrogen atom attaches itself to the carbon atom of the double bond that already holds greater number of hydrogens.

(f) **Hofmann rule** states that in the thermal decomposition of quaternary ammonium hydroxides (Hofmann reaction), that alkene is formed predominantly which is least substituted.

(g) **Saytzeff rule** states that in an elimination reaction, the most highly substituted alkene is formed predominantly.

(h) **Raney nickel** is a catalyst which is specially prepared by the treatment of a nickel-aluminium alloy with conc. aq. sodium hydroxide which dissolves aluminium leaving nickel in a finely divided porous form.

(i) **Lindlar's catalyst** is a finely divided palladium metal deposited on barium sulphate and then poisoned by treatment with quinoline.

(j) **Hydration** is a process in which a molecule of water is added across a double bond to form alcohol.

(k) **Epoxidation** is a process in which an alkene is converted to epoxide by treatment with an organic peracid.

(l) **Hydroxylation** is a process in which two hydroxy groups are added across a double bond to form a glycol.

(m) **Ozonolysis** is the reaction of ozone with an alkene to form an ozonide.

(n) A reaction is **stereospecific** when a particular compound reacts in such a way that it gives a specific stereoisomeric form of the product.

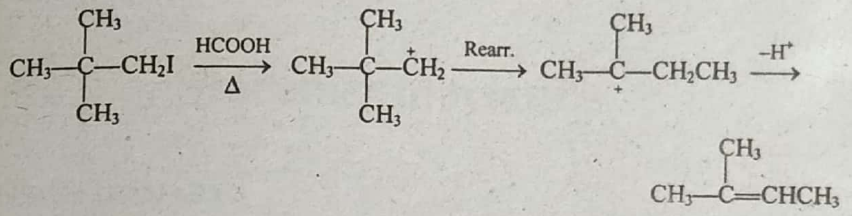
(o) If a reaction can potentially yield two or more constitutional isomers but actually produces only one (or predominantly one), the reaction is said to be **regioselective**.

(p) **Isomerization** is a process in which one isomer is converted to another.

(q) **Polymerization** is a process in which small organic molecules (monomers) combine together to form a large molecule (polymer).

(r) **Principle of microscopic reversibility** states that in a reversible reaction the forward and the reverse reactions follow exactly the same path.

27. *(a)* On heating in the presence of formic acid, neopentyl iodide ionizes to produce neopentyl carbocation which is a primary carbocation. It rearranges to the more stable tertiary carbocation which then leads to the given product.



(b) Ethanolic potassium hydroxide is a reagent which is used for the dehydrohalogenation of an alkyl halide to form an alkene. For the dehydrohalogenation of an alkyl halide, a hydrogen β to the halogen is necessary, which is not available in neopentyl chloride. So, neopentyl chloride does not react with alc. KOH and is recovered unchanged.

(c) 2-Butene is more stable, and is at a lower energy than 1-butene. It therefore requires more energy of activation than 1-butene to form the same carbocation. This is why the reaction of 1-butene with HCl is faster than that of 2-butene.

Chapter 6

Stereoisomerism

CHAPTER'S SUMMARY

The compounds which possess the same molecular formula but different structures are called isomers and the phenomenon is known as **isomerism**. There are two main types of isomerism: (i) constitutional isomerism and (ii) stereoisomerism. The constitutional isomerism is shown by the compounds that have the same molecular formula but different connectivity, i.e., the sequence in which the atoms are bonded to each other in the molecule. It is further subdivided into skeletal isomerism, functional isomerism and positional isomerism. The stereoisomerism is exhibited by the compounds that have the same connectivity but different arrangement of the atoms in space. It is subdivided into conformational isomerism and configurational isomerism. The latter is further subdivided into optical isomerism and geometrical isomerism.

CONFORMATIONAL ISOMERISM

Conformational isomerism is a phenomenon in which the stereoisomers are interconvertible simply by the rotation of one part of the molecule with respect to the other about a single bond. The structures of such stereoisomers are called conformations and the compounds which are represented by these conformations are called conformational isomers or simply conformers or rotamers. The study of the consequences of the energy changes accompanying the rotation of the groups about single bonds is known as conformational analysis.

Conformations of ethane and propane. Although rotation about a carbon-carbon single bond gives rise to an infinite number of conformations, each of ethane and propane has two main conformations, i.e., staggered conformation (having lowest energy) and eclipsed conformation (having highest energy). The energy difference between staggered and eclipsed conformations of ethane is 12.5 kJ/mol, whereas that of propane is 14.2 kJ/mol.

Conformations of *n*-butane. The principal conformations of *n*-butane are: anti-staggered (having lowest energy), gauche-staggered, partially eclipsed and fully eclipsed (having highest energy). The energy difference of the gauche-staggered conformation from the anti-staggered conformation is 3.5 kJ/mol, whereas that of the partially eclipsed conformation is 15.9 kJ/mol and that of the fully eclipsed conformation is 18.8 kJ/mol.

Conformations of cyclohexane. Cyclohexane has two main conformations, i.e., the chair and the boat conformations. The chair conformation is more stable than the boat conformation by about 27.2 kJ/mol; more than 99% of cyclohexane therefore exists in the chair conformation. The C—H bonds of the chair form of cyclohexane can be divided into two sets of six bonds each, called the axial bonds and the equatorial bonds; each carbon possesses one axial and one equatorial bond. Substitution at the equatorial position of cyclohexane is energetically more favourable than at the axial position.

OPTICAL ISOMERISM

Optical activity. Optical activity is the property possessed by a compound of rotating the plane of polarization of light when the compound is placed in its path. If the compound rotates the plane of polarization in the clockwise direction, facing the beam, it is called dextrorotatory and if it rotates the plane in the counter-clockwise direction, it is called levorotatory. The angle through which the plane of polarization is rotated, is referred to as optical rotation and is expressed by the symbol α. The observed optical rotation is related to a very useful physical property known as specific rotation, [α], of an optically active compound as follows:

$$[\alpha]_{\lambda}^{t} = \frac{\alpha}{l \times c}(\textit{solvent})$$

where, [α] is the specific rotation, *t* is the temperature at which the measurement is made, λ is the wavelength of the light used, α is the observed optical rotation, *l* is the path-length in decimeters and *c* is the concentration of the solution in g/ml.

Chirality and optical activity. A carbon atom that has all the four different groups attached to it, is called a chiral carbon atom. If two stereoisomers are related to each other as our right hand to the left hand, i.e., they are nonsuperimposable mirror reflection of each other, they are said to have 'handedness'. A molecule that has handedness is said to be chiral, and the property of having handedness is called chirality. A chiral molecule is always optically active. The two stereoisomers that have handedness are called enantiomers. The enantiomers have identical physical and chemical properties, but they rotate the plane of polarization in opposite directions, to the same extent. The stereoisomers that are not enantiomers are called diastereomers. The diastereomers behave like different compounds.

The stereoisomers which differ in their behaviour toward the plane-polarized light are called optical isomers, and the phenomenon is known as **optical isomerism**.

Relative and absolute configuration. The configurations of optical isomers are mostly expressed by Fischer projections. A compound is assigned D or L configuration if it is correlated to D or L-glyceraldehyde, respectively, and is termed as the relative configuration of the compound. The absolute configuration of a chiral carbon atom is determined by applying the Cahn-Ingold-Prelog system of nomenclature. According to this system, a compound is designated as *R* if the sequence of the substituents on its chiral carbon atom is clockwise in order of decreasing priority, keeping the substituent the lowest priority away from the viewer. A counter-clockwise sequence of substituents in the same order of priority will assign the configuration *S* t compound.

The racemate. An equimolar mixture of a pair of enantiomers is called a racemate, and does not show optical activity. Whenever a symmetrical substance is used for the preparation of a chiral compound, a racemate is obtained. However, a racemic mixture can be separated into optically active enantiomers by several methods. Conversion of an optically active compound (either enantiomer) into an equimolar mixture of its enantiomers, i.e., the racemate, is known as racemization.

Compounds with more than one chiral carbon atom. The stereoisomers containing more than one chiral carbon atom may be mutually enantiomers, diastereomers or meso forms. The stereoisomers which are not enantiomers are diastereomers, and behave like different compounds; they differ in their physical properties. Any stereoisomer that has a plane of symmetry passing through it, is called meso isomer, and does not show optical activity.

Chirality and symmetry. In spite of the presence of chiral carbon atoms, a molecule will be achiral (not chiral) if it has any of the elements of symmetry, such as (i) plane of symmetry, (ii) centre of symmetry or (iii) alternating axis of symmetry.

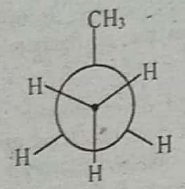
On the other hand, a molecule may not have any chiral carbon atom, but still be chiral if it has two mutually perpendicular planes such that none of the planes is a plane of symmetry.

GEOMETRICAL ISOMERISM

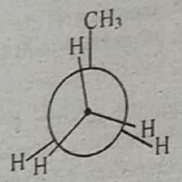
The presence of a double bond in a molecule gives rise to a new type of stereoisomerism called **geometrical isomerism** or **cis-trans isomerism**. A molecule is designated as *cis* if the two similar substituents on the two double-bonded carbon atoms are on the same side of the plane of the double bond, and *trans* if they are on the opposite sides. However, the geometrical isomers can be assigned a more clear configuration by using the Cahn-Ingold-Prelog system of nomenclature. According to this system, if the groups of higher priority on each of the double-bonded carbon atoms are on the same side of the plane of the double bond, the molecule is designated as *Z*, and if on opposite sides, then it is designated as *E*.

Determination of configuration of geometrical isomers. The configuration of geometrical isomers can be determined by using different methods which depend on the nature of the compound. Some of the more generally applied methods include: (i) cyclization, (ii) correlation with compounds of known configuration, (iii) measurement of dipole moment, and (iv) some other methods based on spectroscopic study and physical properties.

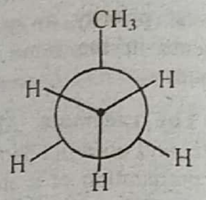
ANSWERS TO EXERCISES



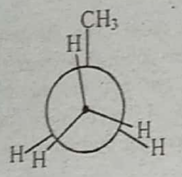
1
Staggered



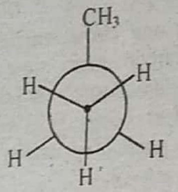
2
Eclipsed



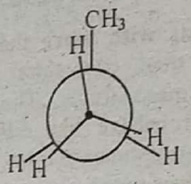
3
Staggered



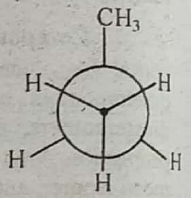
4
Eclipsed



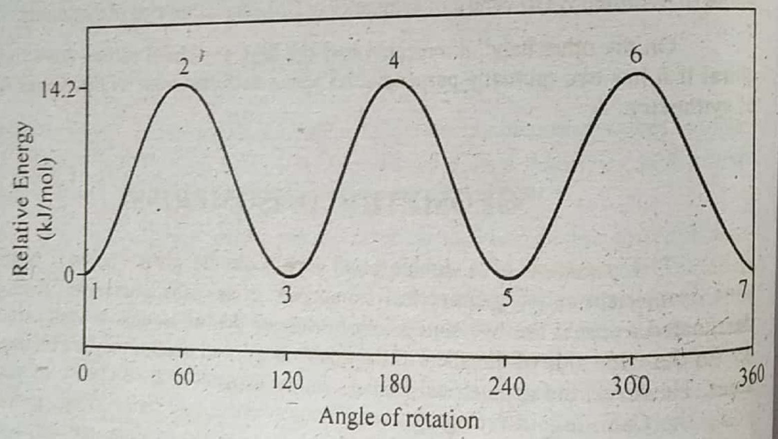
5
Staggered



6
Eclipsed



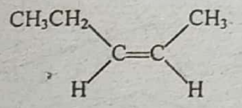
7
Staggered



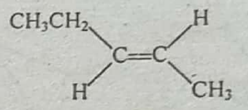
2. A planer cyclopentane molecule would have a bond angle of 108° which is so close to the normal tetrahedral angle that almost no angle strain is expected. However, it will have all the ten hydrogen atoms eclipsed that will cause a significant torsional strain. The molecule finds it energetically favourable to twist somewhat to adopt an envelope shape in which one carbon of the ring is out of the plane of the other four. The hydrogens of the out-of-plane methylene group are almost staggered with respect to those of its neighbouring methylene groups. The envelope structure of cyclopentane is dynamic in the sense that each carbon of the ring gets out of the plane of the ring turn by turn. The additional angle strain involved in the envelope structure is more than compensated by the reduction in the torsional strain and the molecule becomes more stable.

---

3. (a)



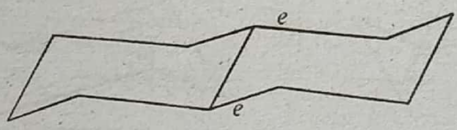
cis



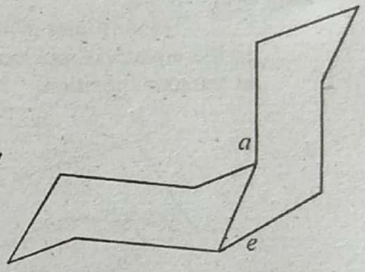
trans

Trans isomer is more stable because it is more symmetrical and the interaction between two large groups is minimum.

(b)



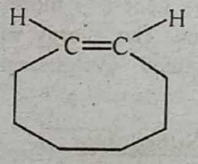
trans



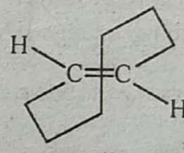
cis

Trans isomer is more stable because in this case the two rings are joined through two equatorial bonds, whereas in the cis isomer the two rings are joined through one equatorial and one axial bond.

(c)



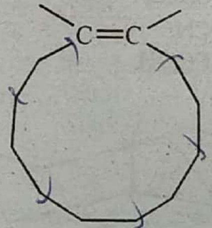
cis



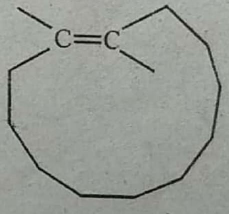
trans

Cis isomer is more stable because the trans isomer would be highly strained molecule.

(d)



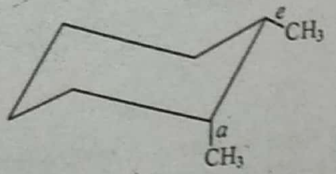
cis



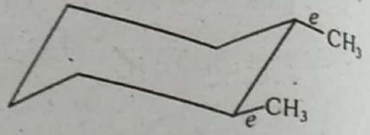
trans

Trans isomer is more stable because with this ring size both geometrical isomers are possible without involving any strain. It therefore follows the general rule of stability, 'the trans isomer is generally more stable than the cis isomer'.

(e)



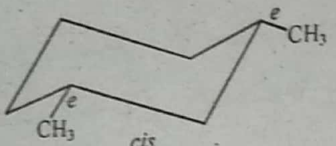
cis



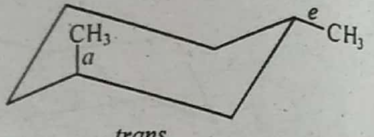
trans

Trans isomer is more stable because in this case both methyl groups can be at the equatorial positions, whereas in the cis isomer one methyl group has to be at the axial position.

(f)



cis



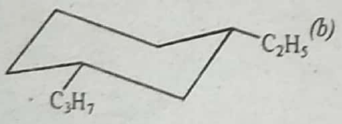
trans

Cis isomer is more stable because in this case both methyl groups can be at the equatorial positions, whereas in the trans isomer one methyl group has to be at the axial position.

4. Equatorially substituted cyclohexanes are generally more stable than the corresponding axially substituted cyclohexanes. The energy difference (ΔG°) between the two conformations of substituted cyclohexane for various substituents is as follows:

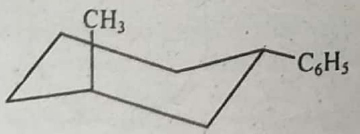
Substituent	**ΔG° (kJ/mol)**	**Substituent**	**ΔG° (kJ/mol)**
F	1.4	$CH_2CH_2CH_3$	8.3
Cl	2.5	$CH(CH_3)_2$	9.2
Br	2.5	$C(CH_3)_3$	23.0
I	2.3	C_6H_5	13.4
OH	4.6	$C{\equiv}CH$	2.1
CH_3	7.5	CN	1.2
CH_2CH_3	8.0	COOH	6.2

(a)



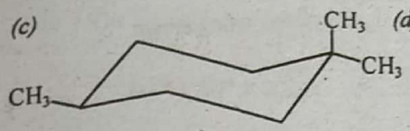
$$\Delta G^\circ = -8.0 - 8.3 = -16.3 \text{ kJ/mol}$$

(b)



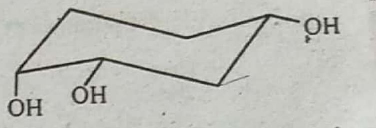
$$\Delta G^\circ = 7.5 - 13.4 = -5.9 \text{ kJ/mol}$$

(c)



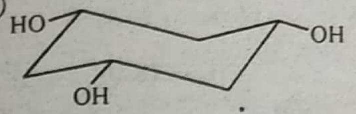
$$\Delta G^\circ = 7.5 - (7.5 \times 2) = -7.5 \text{ kJ/mol}$$

(d)



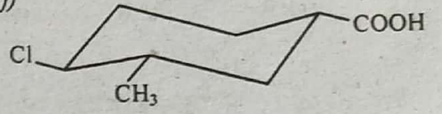
$$\Delta G^\circ = 4.6 - (4.6 \times 2) = -4.6 \text{ kJ/mol}$$

(e)



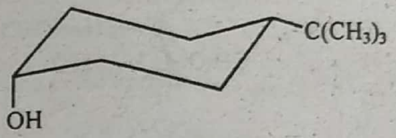
$$\Delta G^\circ = -4.6 \times 3 = -13.8 \text{ kJ/mol}$$

(f)



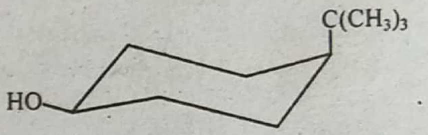
$$\Delta G^\circ = -6.2 - 7.5 - 2.5 = -16.2 \text{ kJ/mol}$$

5.



(A)

$$\Delta G^\circ = 4.6 - 23 = -18.4 \text{ kJ/mol}$$



(B)

$$\Delta G^\circ = 23.0 - 4.6 = 18.4 \text{ kJ/mol}$$

The conformation A is more stable than B by an amount of about 36.8 kJ/mol. This difference in energy is sufficient to make *cis*-4-*tert*-butylcyclohexanol to exist almost exclusively in conformation A.

6.

Chiral	**Achiral**
(c) Shoe	(a) Pencil
(g) Ear	(b) Book
(h) Foot	(d) Cup
(i) Person	(e) Fork
(m) Football (laced)	(f) Kitchen knife
(n) Screw	(j) Egg
(o) Spiral staircase	(k) Funnel
	(l) Spoon (plane)

80 +
20 −
40 ±
60 +

7. (a) The optically active compound contains 80% (+)enantiomer and 20% (−)enantiomer. This means that its mixture is 40% racemic and 60% pure (+)enantiomer, i.e., the compound is 60% optically pure.

$$\text{Optical purity (OP)} = \frac{\alpha_{obs}}{[\alpha]} \times 100 \text{ percent}$$

$$\alpha_{obs} = \frac{OP \times [\alpha]}{100} = \frac{60 \times (+80^\circ)}{100} = +48^\circ$$

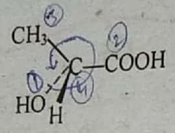
(b) Optical purity (OP) = $\frac{\alpha_{obs}}{[\alpha]} \times 100$ percent

$= \frac{+40°}{+50°} \times 100 = 80\%$

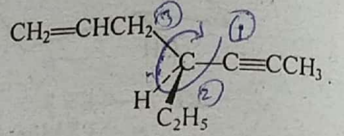
The compound is 80% optically pure. This means that its mixture is 20% racemic and 80% pure (+)enantiomer. In other words, it contains 10% (–)enantiomer and 90% (+)enantiomer. So, the impurity is 10%.

8. (a) R (b) R (c) S (d) S (e) S (f) S

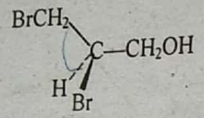
9. (a)



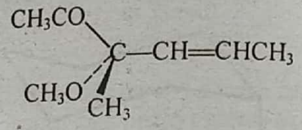
(b)



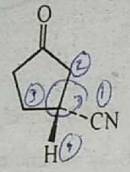
(c)



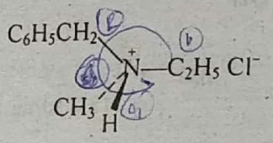
(d)



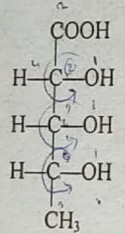
(e)

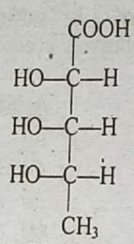


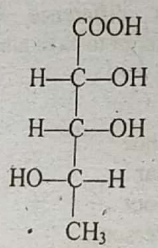
(f)

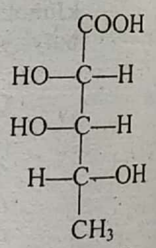


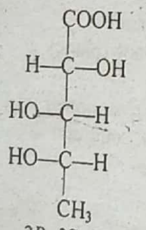
10.

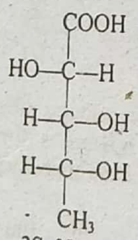

2R, 3R, 4R

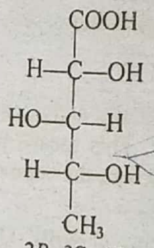

2S, 3S, 4S

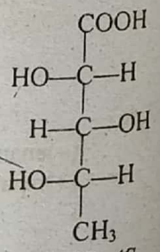

2R, 3R, 4S


2S, 3S, 4R

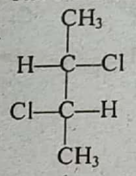

2R, 3S, 4S

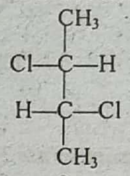

2S, 3R, 4R

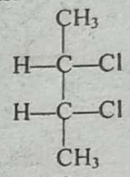

2R, 3S, 4R


2S, 3R, 4S

11. (a) The stereostructures are written in Fischer projections:


1


2

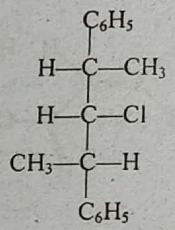

3

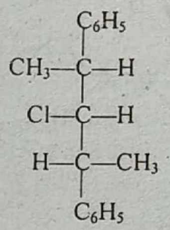
1 and 2 are enantiomers.

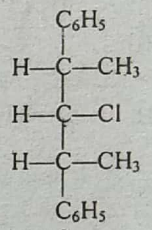
1 and 3 are diastereomers, as are 2 and 3. 3 $\frac{380}{100}$

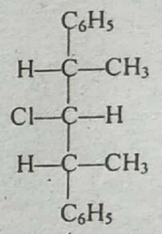
1 and 2 are optically active, whereas 3 is the meso form.

(b)


1


2


3

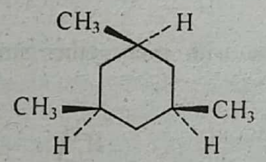

4

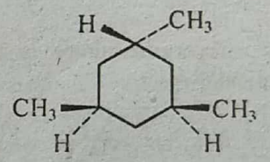
1 and 2 are enantiomers.

1 and 3 are diastereomers, as are 1 and 4, 2 and 3, 2 and 4, and 3 and 4.

1 and 2 are optically active, whereas 3 and 4 are meso forms.

(c)

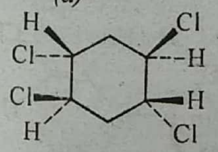

1

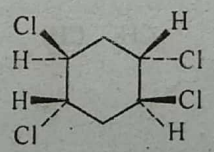

2

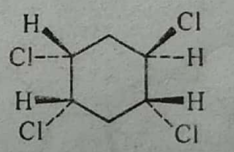
1 and 2 are diastereomers.

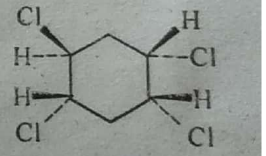
Both are meso forms, and therefore optically inactive.

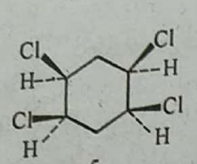
(d)


1

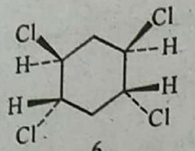

2


3

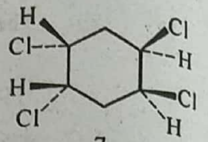

4



5



6



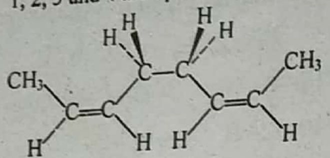
7

1 and 2 are enantiomers, as are 3 and 4.

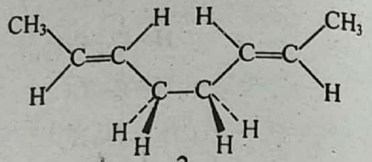
All other pairings: 1 and 3, 1 and 4, 1 and 5, 1 and 6, 1 and 7, 2 and 3, 2 and 4, 2 and 5, 2 and 6, 2 and 7, 3 and 5, 3 and 6, 3 and 7, 4 and 5, 4 and 6, 4 and 7, 5 and 6, 5 and 7, and 6 and 7 are diastereomeric.

1, 2, 3 and 4 are optically active, while 5, 6 and 7 are meso forms.

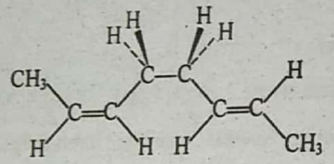
(e)



1



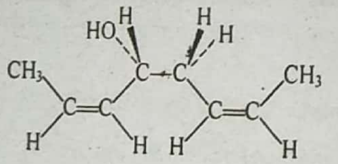
2



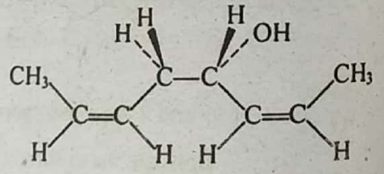
3

Every structure is diastereomeric with every other structure. All are optically inactive.

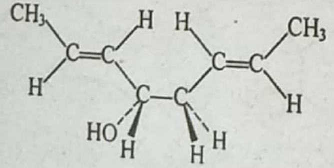
(f)



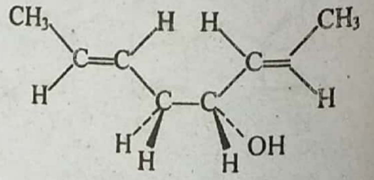
1



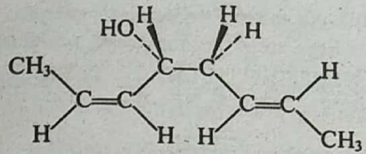
2



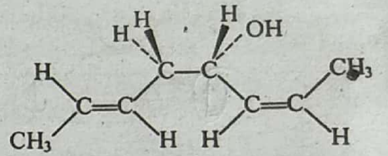
3



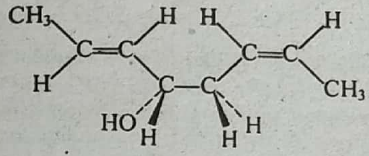
4



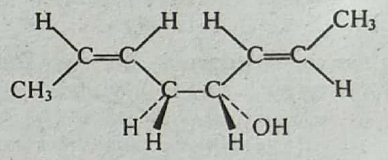
5



6



7

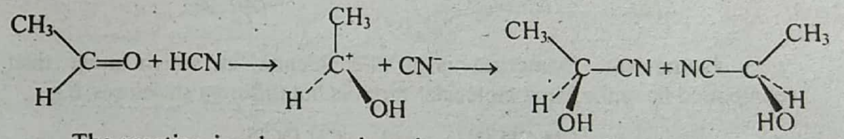


8

1 and 2 are enantiomers, as are 3 and 4, 5 and 6, and 7 and 8.

All other pairings: 1 and 3, 1 and 4, 1 and 5, 1 and 6, 1 and 7, 1 and 8, 2 and 3, 2 and 4, 2 and 5, 2 and 6, 2 and 7, 2 and 8, 3 and 5, 3 and 6, 3 and 7, 3 and 8, 4 and 5, 4 and 6, 4 and 7, 4 and 8, 5 and 7, 5 and 8, 6 and 7, and 6 and 8 are diastereomeric.

All are optically active.

12. 

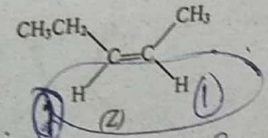
The reaction involves a carbocation as an intermediate, which is a planer molecule. In the second step, CN^- can attack from either side of the plane of the carbocation with equal possibility, to produce a racemic mixture which does not show optical activity. The product of the reaction therefore will not show optical activity.

13. In a molecule having a plane of symmetry, one half of the molecule is the mirror reflection (enantiomeric) of the other half. If one half of the molecule rotates the plane of polarization in one direction, the other half will rotate it in the opposite direction to the same extent. The net result is that the rotation due to one half of the molecule is cancelled by the other half, and the molecule as a whole does not show optical activity.

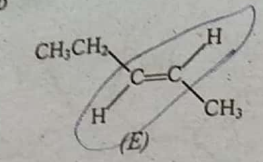
14. Chiral structures: *c*, and *e*.
Achiral structures: *a*, *b*, and *d*.

15. *(a)* Diastereomers *(b)* Diastereomers
(c) Enantiomers *(d)* Enantiomers
(e) Diastereomers

16. (a)

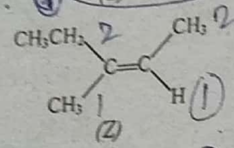


(Z)

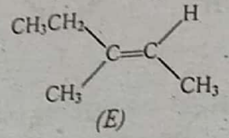


(E)

(b)

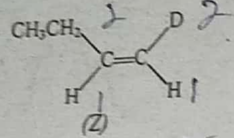


(Z)

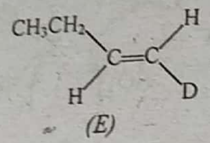


(E)

(c)

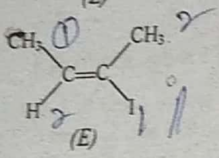


(Z)

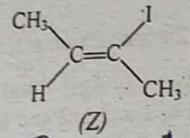


(E)

(d)

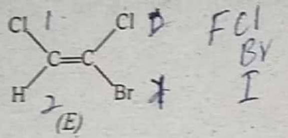


(E)

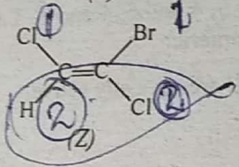


(Z)

(e)



(E)

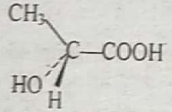


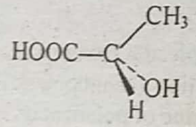
(Z)

7. (a) **Isomerism.** Isomerism is a phenomenon in which more than one compound have the same molecular formula but different structures, e.g.,

CH_3CH_2OH and CH_3OCH_3

(b) **Chirality.** Chirality is the property possessed by a molecule of having handedness (nonsuperimposability on its mirror reflection), e.g., lactic acid has chirality.





(c) **Connectivity.** Connectivity is the sequence in which the atoms are bonded to each other in a molecule, e.g., ethanol and dimethyl ether have different connectivity, whereas the two enantiomers of lactic acid have the same connectivity.

(d) **Stereocentre.** If we interchange any two atoms or groups of atoms bonded tetrahedrally to a central atom and we get a new stereoisomer, the central atom is called stereocentre. If the new stereoisomer is an enantiomer of the original molecule, the stereocentre is a chiral centre, e.g., in lactic acid. In fact, if an atom is bonded tetrahedrally to four different atoms or groups of atoms, it is called a

chiral centre. Not all stereocentres are chiral centres but all chiral centres are stereocentres.

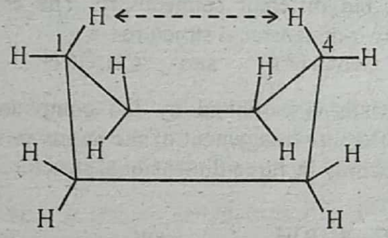
(e) **Racemate.** An equimolar mixture of a pair of enantiomers, e.g., that of lactic acid, is called a racemate or a racemic mixture.

(f) **Resolution.** Separation of a racemic mixture into enantiomeric components is called resolution, e.g., separation of *dl*-lactic acid into *d*- and *l*-lactic acids. Various methods are available for the resolution of racemic mixtures (see the *Textbook*).

(g) **Elements of symmetry.** These are the characteristics present in a molecule which make the molecule symmetric, e.g., plane of symmetry, centre of symmetry and alternating axis of symmetry. If any one of these elements of symmetry is present in a molecule, the molecule will not show optical activity.

(h) **Puckered.** Cycloalkanes usually adopt a nonplanar structure to relieve off their angle strain. This nonplanar structure is known as the puckered structure, e.g., the chair or the boat structure of cyclohexane.

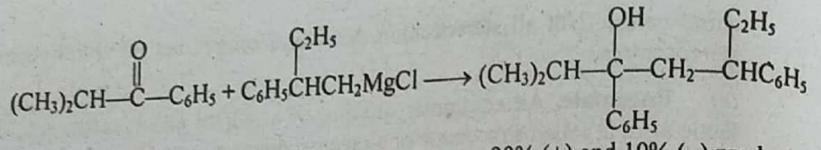
(i) **Flagpole interaction.** In the boat conformation of cyclohexane, the two hydrogens emerging upward on C_1 and C_4 are close enough to each other to cause nonbonded van der Waals repulsion, as shown below. This repulsion is called 'flagpole' interaction.



(j) **Time-average plane.** The carbon atoms of the chair conformation of cyclohexane lie in two parallel planes, 0.5 Å apart, each plane containing three alternate carbon atoms. However, the chair structure of cyclohexane is dynamic in the sense that the two planes of the ring are continuously interchanging. At room temperature this interchange of the two planes is so rapid that it appears to be planar. This is why that the plane of the cyclohexane ring is said to be the 'time-average' plane.

(k) **Restricted rotation.** Generally one part of an organic molecule rotates freely about a single bond with respect to the other part of the molecule. However, this rotation can be restricted by certain structural features in the molecule, e.g., a double bond or substitution of large groups in all the ortho positions of a biphenyl molecule. The rotation is then said to be restricted.

(l) **Asymmetric synthesis.** It is the creation of a new chiral centre by the use of a chiral reagent or a chiral catalyst. The product obtained in this case has one optical isomer in excess, e.g.,

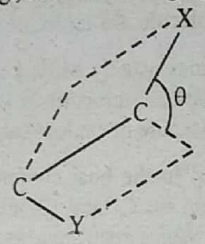


$$(CH_3)_2CH\!-\!\overset{O}{\overset{\|}{C}}\!-\!C_6H_5 + C_6H_5\overset{C_2H_5}{\overset{|}{C}}HCH_2MgCl \longrightarrow (CH_3)_2CH\!-\!\underset{C_6H_5}{\underset{|}{\overset{OH}{\overset{|}{C}}}}\!-\!CH_2\!-\!\overset{C_2H_5}{\overset{|}{C}}HC_6H_5$$

90% (+) and 10% (−) product

(m) **Energy barrier.** It is the amount of energy which has to be supplied for the conversion of one stereoisomer to another. For example, the energy barrier for the conversion of the staggered conformation of ethane to its eclipsed conformation is 12.5 kJ/mol.

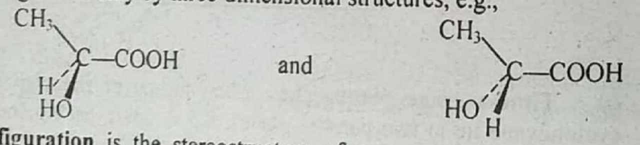
(n) **Dihedral angle.** It is the angle between the planes of two bonds on adjacent carbon atoms, e.g., in the following figure, θ is the dihedral angle.



18. *(a)* **Constitutional isomerism** is shown by the compounds that have the same molecular formula but different connectivity. The constitutional isomers are distinguishable by two-dimensional structures, e.g.,

CH_3CH_2OH and CH_3OCH_3

Stereoisomerism is exhibited by the compounds that have the same connectivity but different arrangement of the atoms in space. The stereoisomers can be distinguished only by three-dimensional structures, e.g.,



(b) **Configuration** is the stereostructure of a compound, which cannot be converted to its stereoisomer without breaking and making the bonds, e.g., the stereostructure of lactic acid.

Conformation is the stereostructure of a compound which can be converted to its stereoisomer simply by rotation about a bond, e.g., the stereostructure of ethane.

(c) **Enantiomers** are the stereoisomers which are nonsuperimposable mirror reflection of each other, e.g., the stereoisomeric structurės of lactic acid.

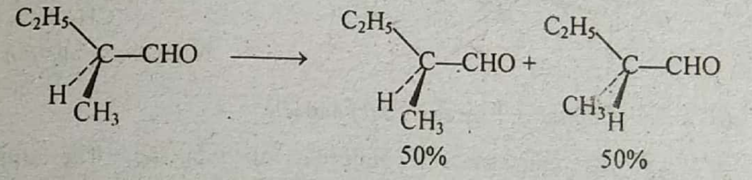
Diastereomers are the stereoisomers which are not enantiomers, e.g., the two geometrical isomers.

(d) **Optical rotation** is the angle through which the plane of polarization of light is rotated when it passes through the solution of an optically active compound. On the other hand, **specific rotation** is the observed optical rotation divided by the pathlength taken in dm and the concentration of the sample solution taken in g/ml, i.e.,

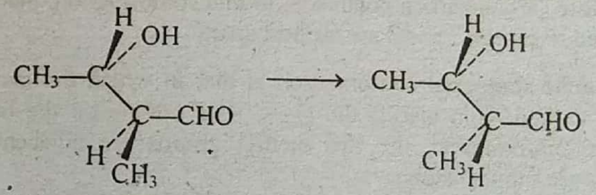
$$[\alpha]_\lambda^t = \frac{\alpha}{l \times c} \text{ (solvent)}$$

where, t is the temperature at which the measurement is made and λ is the wavelength of the light used.

(e) **Racemization** is the conversion of an optically active compound (either enantiomer) into an equimolar mixture of its enantiomers.



Epimerization is the inversion of configuration at one chiral carbon atom of a compound having more than one chiral carbon atom.

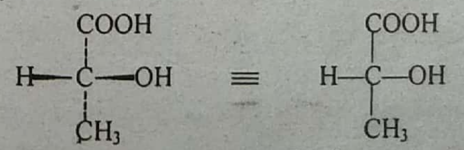


(f) **Mirror plane** and **plane of symmetry** are the same thing. It is an imaginary plane that bisects a molecule in such a way that the two halves of the molecule are mirror reflection of each other, e.g., in *meso*-tartaric acid.

(g) **Racemic form** is an equimolar mixture of a pair of enantiomers. It does not show optical activity because one enantiomer cancels the optical rotation due to the other, e.g., 50/50 mixture of (+)- and (−)-lactic acids.

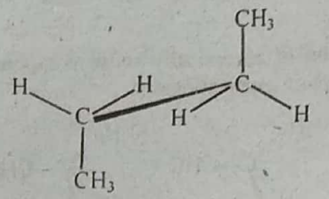
Meso form is an optical isomer which has a plane of symmetry. It is optically inactive because one half of the molecule cancels the optical rotation due to the other half, e.g., *meso*-tartaric acid.

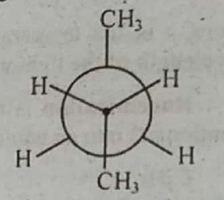
(h) **Fischer projection** is a way of representing a tetrahedral carbon atom on paper. In this way, the two bonds of the tetrahedral carbon atom projecting forward from the plane of the paper are represented by horizontal lines, while the two bonds projecting backward from the plane of the paper are represented by vertical lines, the tetrahedral carbon itself lying in the plane of the paper, as shown below:



Fischer projection

Newman projection is a way of expressing a conformation on paper. In this way, we imagine ourselves viewing the molecule from one end directly along the carbon-carbon bond axis. The front carbon atom is represented by a point from where the three remaining bonds emerge. The rear carbon atom is represented by a circle with its bonds originating from the edge of the circle, as shown below:



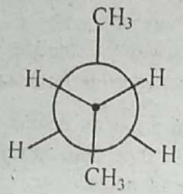


Newman projection

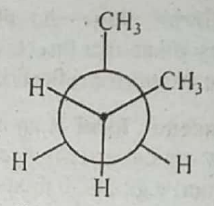
(i) See *Chapter 4*, Exercise 32 *(k)* and *(j)*.

(j) Let us consider the molecule of *n*-butane. The **anti-staggered** conformation is that in which the carbon-methyl bond on one carbon atom bisects the H—C—H angle on the other carbon atom, when the molecule is viewed along the middle carbon-carbon bond axis. In this conformation, the two methyl groups attached to carbon 2 and 3 are farthest apart.

The **gauche-staggered** conformation is that in which the carbon-methyl bond on one carbon atom bisects the H—C—CH_3 angle on the other carbon atom. In this conformation, the two methyl groups are adjacent. The two conformations are shown below:



Anti-staggered



Gauche-staggered

(k) **Centre of symmetry** is a point within a molecule from which if a line is drawn on one side and extended to an equal distance on the opposite side, it encounters identical environments, e.g., in 2,4-dimethylcyclobutane-1,3-dicarboxylic acid.

Axis of symmetry of a molecule is that axis about which when the molecule is rotated through certain angle, we obtain a structure whose reflection from a plane perpendicular to the axis is indistinguishable from the original molecule, e.g., in 1,2,3,4-tetramethylcyclobutane.

Chapter 7

Alkyl Halides

CHAPTER'S SUMMARY

A functional group is an atom or a group of atoms that defines the structure of a particular family of organic compounds and also determines their properties, e.g., —OH is the functional group of alcohols and phenols, and —COOH is the functional group of carboxylic acids.

Organohalogen Compounds

Compounds in which one or more halogen atoms are bonded to carbon are known as organohalogen compounds. These are named as alkanes with the halogen atoms being considered as substituents, arranged alphabetically, and their positions indicated by numbers using the principle of lowest numbers.

ALKYL HALIDES

Monohaloalkanes are usually called **alkyl halides** and are classified according to the nature of the alkyl group to which the halogen atom is attached.

Preparation of Alkyl Halides

Alkyl halides can be prepared by various methods as follows:

1. By the reaction of alkanes with halogens (chlorine or bromine) either by heating at 250–400°C or under the influence of light.

2. By the addition of hydrogen halides to alkenes either by passing dry gaseous hydrogen halide directly into the alkene or by using a moderately polar solvent to dissolve both the polar hydrogen halide and the nonpolar alkene.

3. By the treatment of alcohols either with halogen acids or with thionyl chloride or phosphorus halide.

4. By the decomposition of silver salts of carboxylic acids by chlorine or bromine in carbon tetrachloride solution.

5. An alkyl iodide is often prepared from the corresponding alkyl bromide or chloride by treatment with sodium iodide in acetone.

Physical Properties of Alkyl Halides

The lower members, i.e., methyl chloride, methyl bromide and ethyl chloride are gases, whereas methyl iodide and majority of higher members are sweet-smelling liquids. In general, for a given halogen, the boiling point rises with increasing number of carbon atoms, and for a given alkyl group, it increases with increasing atomic weight of the halogen. Branching in the molecule lowers the boiling point. The density of iodo, bromo, and polychloro compounds is higher than that of water. Alkyl halides are generally insoluble in water, but soluble in organic solvents.

Reactions of Alkyl Halides

Alkyl halides are extremely important organic compounds because they undergo a variety of organic reactions leading to the synthesis of a large number of organic compounds. Some of the more important reactions of alkyl halides are given below:

1. **Substitution.** Alkyl halides undergo a variety of substitution reactions in which halogen is replaced by various nucleophiles.

2. **Elimination.** Alkyl halides on boiling with ethanolic potassium hydroxide undergo dehydrohalogenation to form alkenes.

3. **Reduction.** Alkyl halides are reduced to alkanes by various reducing agents, such as dissolving metals (zinc in aq. acid, zinc in alkali or Zn/Cu couple in ethanol), lithium aluminium hydride or sodium borohydride, or on catalytic hydrogenolysis.

4. **Reaction with metals.** Alkyl halides react with almost all metals in dry ether to produce a broad class of compounds generally called organometallic compounds.

5. **Wurtz reaction.** Alkyl halides react with sodium in ether to form higher alkanes.

6. **Friedel-Crafts reaction.** Alkyl halides are used for the introduction of alkyl group into the benzene ring in the presence of $AlCl_3$.

7. **Rearrangement.** Alkyl halides on heating at about 300°C undergo rearrangement.

ALIPHATIC NUCLEOPHILIC SUBSTITUTION

The aliphatic nucleophilic substitution reactions are of a fairly broad nature and are generally represented as:

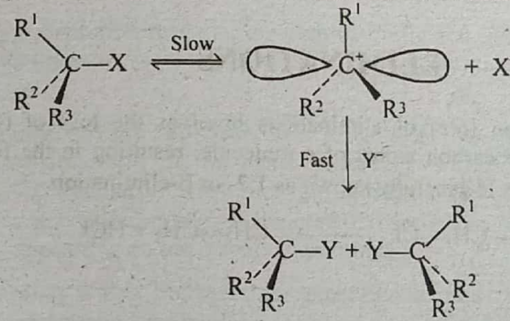
$$\underset{\text{Nucleophile}}{Y:} + \underset{\text{Substrate}}{R\text{—}X} \longrightarrow \underset{\text{Product}}{R\text{—}Y} + \underset{\text{Leaving group}}{X:}$$

Mechanism

The mechanism of a reaction is the actual pathway through which the reaction proceeds, i.e., which bonds are broken, which are formed, and in what order; how many steps are involved and what is the relative rate of each step, etc.

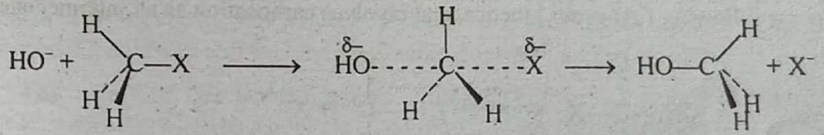
For an aliphatic nucleophilic substitution reaction, several pathways are possible, depending on the nature of the substrate, the nucleophile, and the leaving group, and the reaction conditions including the solvent used. However, the most common mechanisms are S_N1 and S_N2.

The S_N1 mechanism. It is a two-step unimolecular mechanism following first-order kinetics, and involves the intermediate formation of a carbocation.



If we start with an optically active substrate, the product is a racemic mixture.

The S_N2 mechanism. It is a one-step bimolecular mechanism following second-order kinetics, and involves inversion of configuration.



Transition state

Reactivity

The reactivity and the mechanism of an aliphatic nucleophilic substitution reaction depends on the nature of (i) the substrate, (ii) the nucleophile, (iii) the leaving group and (iv) the solvent.

The effect of the substrate. The primary alkyl substrates generally react by the S_N2 mechanism, whereas the tertiary alkyl substrates react by the S_N1 mechanism. The secondary alkyl substrates could proceed either by S_N1 or S_N2 or both mechanisms, depending on the reaction conditions. The rate of the S_N1 reaction increases as we change the substrate from primary to tertiary. On the other hand, the rate of the S_N2 reaction decreases as the number of alkyl groups surrounding the central carbon atom increases.

The effect of the nucleophile. The rate of the S_N1 reaction is not influenced by the nucleophile because the nucleophile is not involved in the rate-determining step (first step) of this reaction. On the other hand, the rate of the S_N2 reaction increases with the nucleophilicity of the nucleophile.

The effect of the leaving group. Both S_N1 and S_N2 reactions are favoured by a better leaving group. Since the leaving group comes off along with its bonding electron pair, the group that can better accommodate the electron pair is a better leaving group. However, a poor leaving group, like OH, may be converted to a good leaving group either by protonation or by converting it to tosylate.

The effect of the solvent. The S_N1 reaction in which a carbocation is formed in the rate-determining step, is more favourable in polar solvents. For S_N2 reactions, the reaction in which charges are created in the transition state, is favoured by increasing the polarity of the solvent, whereas the reaction in which charges are either destroyed or dispersed in the transition state, is favoured by decreasing the solvent polarity.

ELIMINATIONS

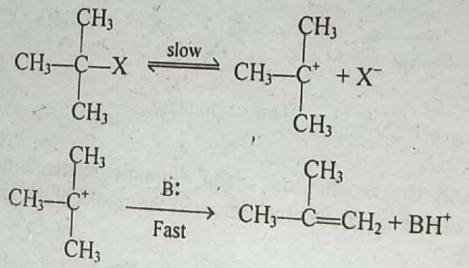
The most common form of eliminations involves the loss of two atoms (or groups) from the adjacent carbon atoms of a molecule, resulting in the formation of a multiple bond. The process is generally known as 1,2- or β-elimination.

$$CH_3—CH_2—Cl \longrightarrow CH_2{=}CH_2 + HCl$$

Mechanism

Of all the possible mechanistic pathways usually available for the β-eliminations, E1 and E2 which are closely related to the S_N1 and S_N2 mechanisms, are most common.

The E1 mechanism. The E1 reaction, like S_N1, is a two-step unimolecular process following first-order kinetics, and involves carbocation as an intermediate.

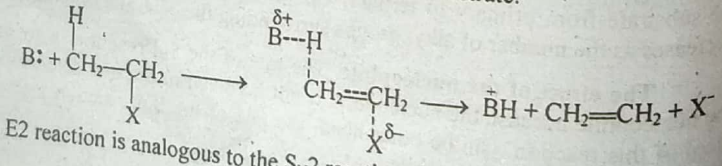


$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—X \xrightleftharpoons{\text{slow}} CH_3—\underset{CH_3}{\overset{CH_3}{C^+}} + X^-$$

$$CH_3—\underset{CH_3}{\overset{CH_3}{C^+}} \xrightarrow[\text{Fast}]{B:} CH_3—\overset{CH_3}{C}{=}CH_2 + BH^+$$

The E1 reaction is thus analogous to the S_N1 reaction and often competes with it.

The E2 mechanism. It is a one-step bimolecular mechanism following second-order kinetics and requires antiperiplanar geometry of the substrate.



$$B\!: + \overset{H}{CH_2}—\underset{X}{CH_2} \longrightarrow \underset{\overset{\vdots}{X}{}^{\delta-}}{\overset{\overset{\delta+}{B}\text{---}H}{CH_2{=}{=}{=}CH_2}} \longrightarrow \overset{+}{B}H + CH_2{=}CH_2 + X^-$$

The E2 reaction is analogous to the S_N2 reaction and often competes with it.

Orientation of Double Bond

If the substrate contains β-hydrogens at more than one position, more than one olefinic product are possible. Which olefinic product dominates depends on various factors. In general, the E1 reaction follows the Saytzeff rule, i.e., the most highly substituted olefin dominates. In the case of E2 reaction, if the substrate contains an uncharged leaving group (that comes off as a negative ion), the Saytzeff rule is generally followed, as in the case of E1 reaction, and if the substrate contains a charged leaving group (that comes off as a neutral molecule), the Hofmann rule is followed, i.e., the least highly substituted olefin dominates.

Reactivity

Like substitution reaction, the pathway followed by an elimination reaction and its rate, in addition to its competition with the substitution reaction, also depends on various factors.

The effect of the substrate. Like substitution, the elimination reaction proceeds by E1 mechanism when the substrate is tertiary, while with a primary substrate it proceeds by E2 mechanism. However, unlike substitution, E2 mechanism is also often observed with tertiary substrates. In the case of a secondary substrate the mechanism may be E1 or E2, depending on the reaction conditions.

Crowding within the substrate generally favours elimination over substitution, whether the mechanism is unimolecular (E1 vs S_N1) or bimolecular (E2 vs S_N2).

The effect of the base. The reaction is elimination or substitution depends on the fact that whether the attacking reagent is a better base or a better nucleophile. When the base is weak or in low concentration, E1 mechanism is observed with tertiary and in some cases with secondary substrates. If a strong base or a higher concentration of the base is used, E2 pathway will become favourable even with a tertiary substrate.

The effect of the leaving group. Like substitutions, a better leaving group favours E1 pathway, whereas a poor leaving group favours E2 mechanism.

The effect of the solvent. Like substitution, E1 mechanism is favoured by polar solvents, while in nonpolar solvents the reaction will tend to proceed by E2 mechanism.

In a bimolecular reaction, elimination (E2) is favoured more than substitution by decreasing the solvent polarity.

The effect of temperature. An increase in temperature will favour elimination more than substitution, whether the mechanism is unimolecular or bimolecular.

GRIGNARD REAGENTS

Grignard reagents are alkylmagnesium halides, RMgX.

Preparation of Grignard Reagents

Grignard reagents are generally prepared by stirring a solution of an alkyl halide in dry ether in contact with magnesium turnings for 6–8 hours.

Reactions of Grignard Reagents

Grignard reagents are highly reactive species. They react with numerous inorganic and organic reagents to produce a wide variety of organic compounds. Some of the more important reactions of Grignard reagents are given below:

1. Reaction with active hydrogen compounds. Grignard reagents can readily react even with weak acids like water, alcohol and amine, whereby the alkyl group of the Grignard reagent is quantitatively converted to the corresponding alkane.

2. Reaction with carbonyl compounds. Since the alkyl-magnesium bond in Grignard reagents is polar, the addition of RMgX to the polar carbonyl group occurs in such a way that MgX adds to the more electronegative oxygen atom and R to the less electronegative carbon atom of the carbonyl group, resulting in the formation of a new carbon-carbon bond. Thus, with suitable variation of the carbonyl compound, a wide variety of organic compounds can be prepared.

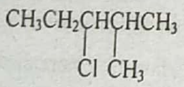
3. Reaction with nitriles. Grignard reagents add to nitriles to produce ketones through the intermediate formation of ketimines.

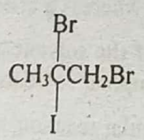
4. Reaction with oxygen. Grignard reagents react with oxygen at a low temperature (–70°C) to produce hydroperoxides. The reaction is very vigorous at room temperature, and the product is an alcohol.

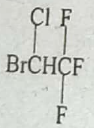
5. Displacement reactions. Grignard reagents provide a very good nucleophile $(R:^-)$ which can bring about displacement reactions on alkyl halides or alkyl sulfonates. Grignard reagents also react with small-ring cyclic ethers to produce primary alcohols containing two or three carbon atoms more than the alkyl group of the Grignard reagent.

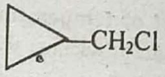
6. Reaction with halogenated ethers. Grignard reagents can react with α-monochloro ethers to give higher ethers.

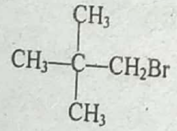
ANSWERS TO EXERCISES

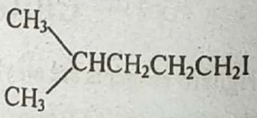
1. (a) (i) 
$\mathrm{CH_3CH_2\underset{Cl}{CH}\underset{CH_3}{CH}CH_3}$

(ii) 
$\mathrm{CH_3\overset{Br}{\underset{I}{C}}CH_2Br}$

(iii) 
$\mathrm{Br\overset{Cl}{CH}\overset{F}{\underset{F}{C}}F}$

(iv) 

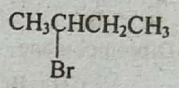
(v) 
$\mathrm{CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2Br}$

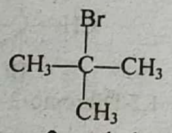
(vi) 

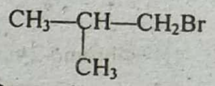
(b) (i) 2-Chloro-4-iodo-3-methylpentane
(ii) 4,4-Difluoro-2,2-dimethylhexane

(iii) 2,3-Dibromo-2,3-dimethylbutane
(iv) 1,2-Dichloro-1,1-difluoro-2,2-diiodoethane
(v) Chlorocyclohexylmethane or Cyclohexylmethyl chloride

(c) (i) $\mathrm{CH_3CH_2CH_2CH_2Br}$
1-Bromobutane

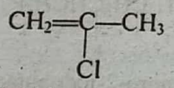

$\mathrm{CH_3\underset{Br}{CH}CH_2CH_3}$
2-Bromobutane

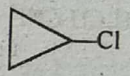

$\mathrm{CH_3{-}\overset{Br}{\underset{CH_3}{C}}{-}CH_3}$
2-Bromo-2-methylpropane


$\mathrm{CH_3{-}\underset{CH_3}{CH}{-}CH_2Br}$
1-Bromo-2-methylpropane

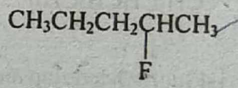
(ii) $\mathrm{ClCH{=}CH{-}CH_3}$
1-Chloropropene

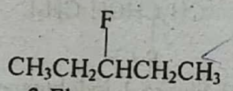
$\mathrm{CH_2{=}CH{-}CH_2Cl}$
3-Chloropropene

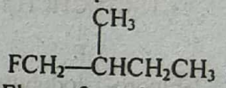

$\mathrm{CH_2{=}\underset{Cl}{C}{-}CH_3}$
2-Chloropropene

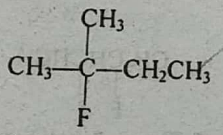

Chlorocyclopropane

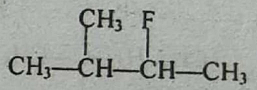
(iii) $\mathrm{CH_3CH_2CH_2CH_2CH_2F}$
1-Fluoropentane

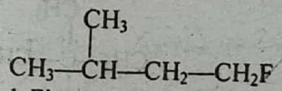

$\mathrm{CH_3CH_2CH_2\underset{F}{CH}CH_3}$
2-Fluoropentane

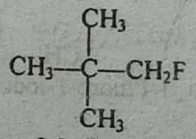

$\mathrm{CH_3CH_2\overset{F}{CH}CH_2CH_3}$
3-Fluoropentane

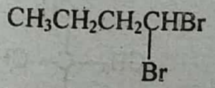

$\mathrm{FCH_2{-}\overset{CH_3}{CH}CH_2CH_3}$
1-Fluoro-2-methylbutane

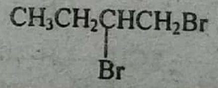

$\mathrm{CH_3{-}\overset{CH_3}{\underset{F}{C}}{-}CH_2CH_3}$
2-Fluoro-2-methylbutane

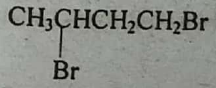

$\mathrm{CH_3{-}\overset{CH_3}{CH}{-}\overset{F}{CH}{-}CH_3}$
2-Fluoro-3-methylbutane


$\mathrm{CH_3{-}\overset{CH_3}{CH}{-}CH_2{-}CH_2F}$
1-Fluoro-3-methylbutane

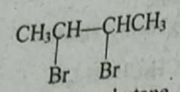

$\mathrm{CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2F}$
1-Fluoro-2,2-dimethylpropane

(iv) 
$\mathrm{CH_3CH_2CH_2\underset{Br}{CH}Br}$
1,1-Dibromobutane

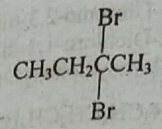

$\mathrm{CH_3CH_2\underset{Br}{CH}CH_2Br}$
1,2-Dibromobutane


$\mathrm{CH_3\underset{Br}{CH}CH_2CH_2Br}$
1,3-Dibromobutane

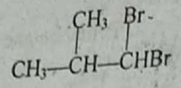
$\mathrm{BrCH_2CH_2CH_2CH_2Br}$
1,4-Dibromobutane


$CH_3\underset{Br}{C}H-\underset{Br}{C}HCH_3$

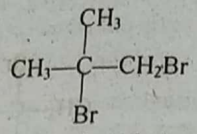
2,3-Dibromobutane


$CH_3CH_2\overset{Br}{\underset{Br}{C}}CH_3$

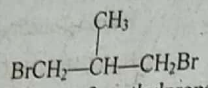
2,2-Dibromobutane


$CH_3-\overset{CH_3}{C}H-\overset{Br}{C}HBr$

1,1-Dibromo-2-methylpropane

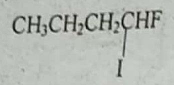

$CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_2Br$

1,2-Dibromo-2-methylpropane

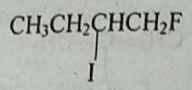

$BrCH_2-\overset{CH_3}{C}H-CH_2Br$

1,3-Dibromo-2-methylpropane

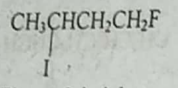
(v)


$CH_3CH_2CH_2\underset{I}{C}HF$

1-Fluoro-1-iodobutane


$CH_3CH_2\underset{I}{C}HCH_2F$

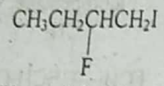
1-Fluoro-2-iodobutane


$CH_3\underset{I}{C}HCH_2CH_2F$

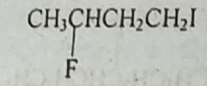
1-Fluoro-3-iodobutane

$ICH_2CH_2CH_2CH_2F$

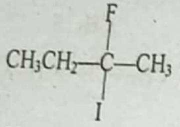
1-Fluoro-4-iodobutane


$CH_3CH_2\underset{F}{C}HCH_2I$

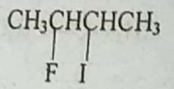
2-Fluoro-1-iodobutane


$CH_3\underset{F}{C}HCH_2CH_2I$

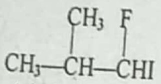
3-Fluoro-1-iodobutane


$CH_3CH_2-\overset{F}{\underset{I}{C}}-CH_3$

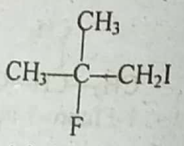
2-Fluoro-2-iodobutane


$CH_3\underset{F}{C}H\underset{I}{C}HCH_3$

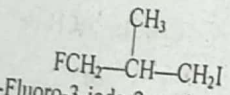
2-Fluoro-3-iodobutane


$CH_3-\overset{CH_3}{C}H-\overset{F}{C}HI$

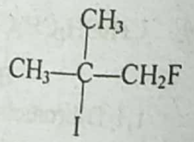
1-Fluoro-1-iodo-2-methylpropane


$CH_3-\overset{CH_3}{\underset{F}{C}}-CH_2I$

2-Fluoro-1-iodo-2-methylpropane


$FCH_2-\overset{CH_3}{C}H-CH_2I$

1-Fluoro-3-iodo-2-methylpropane


$CH_3-\overset{CH_3}{\underset{I}{C}}-CH_2F$

1-Fluoro-2-iodo-2-methylpropane

2\. (i) $C_2H_6 + Cl_2 \xrightarrow{h\nu,\ 25°C} C_2H_5Cl + HCl$

$C_2H_5Cl + NaI \xrightarrow[\text{Acetone}]{} C_2H_5I + NaCl$

(ii) $CH_2{=}CH_2 + HI \longrightarrow CH_3CH_2I$

(iii) $CH{\equiv}CH + H_2 \xrightarrow[\text{Quinoline}]{Pd(BaSO_4)} CH_2{=}CH_2$

$CH_2{=}CH_2 + HI \longrightarrow CH_3CH_2I$

(iv) $C_2H_5OH + HI \longrightarrow I^- + C_2H_5\overset{+}{O}H_2 \longrightarrow C_2H_5I + H_2O$

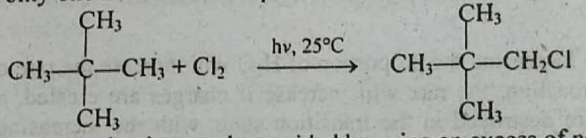
(v) $C_2H_5Br + NaI \xrightarrow[\text{Acetone}]{} C_2H_5I + NaBr$

(vi) $C_2H_5COOH \xrightarrow{AgOH} C_2H_5COOAg + H_2O$

$C_2H_5COOAg + Br_2 \xrightarrow[CCl_4]{} C_2H_5Br + CO_2 + AgBr$

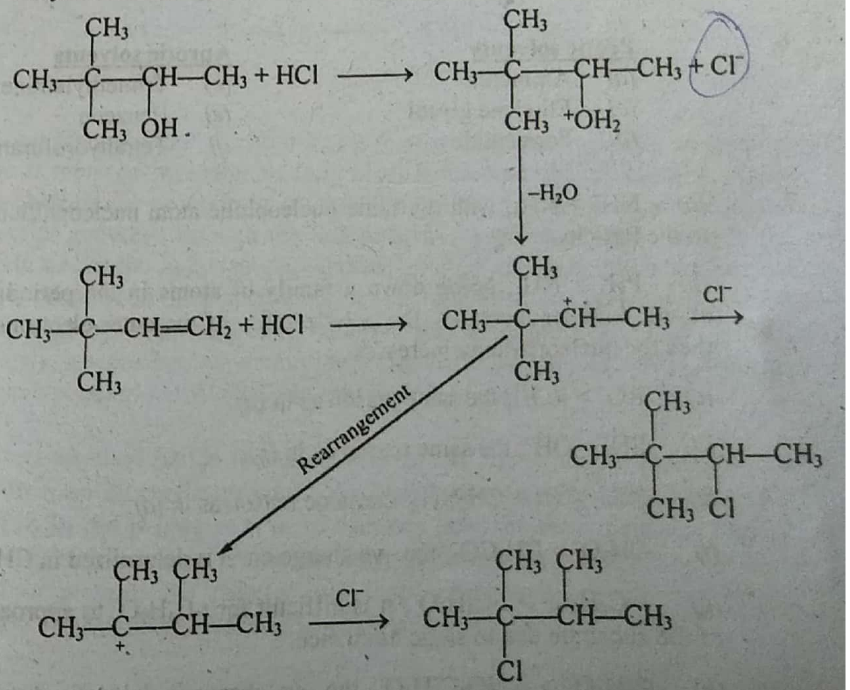
$C_2H_5Br + NaI \xrightarrow[\text{Acetone}]{} C_2H_5I + NaBr$

3\. Since neopentane has only one type of hydrogens, its chlorination will yield only one monochloroneopentane.


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 + Cl_2 \xrightarrow{h\nu,\ 25°C} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Cl$$

Polychlorination can be avoided by using an excess of neopentane.

4\.


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{OH}{C}H-CH_3 + HCl \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{^+OH_2}{C}H-CH_3 + Cl^-$$

$$\xrightarrow{-H_2O} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{+}{C}H-CH_3 \xrightarrow{Cl^-} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{Cl}{C}H-CH_3$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH{=}CH_2 + HCl \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{+}{C}H-CH_3$$

$$\xrightarrow{\text{Rearrangement}} CH_3-\overset{CH_3}{\underset{+}{C}}-\overset{CH_3}{C}H-CH_3 \xrightarrow{Cl^-} CH_3-\overset{CH_3}{\underset{Cl}{C}}-\overset{CH_3}{C}H-CH_3$$

5. For the mechanism, kinetics and stereochemistry of S_N1 and S_N2 reactions, see the *Textbook*.

(a) Since S_N1 reaction involves the intermediate formation of a carbocation, there is a possibility of rearrangement. On the other hand, there is no possibility of rearrangement in S_N2 reaction.

(b) As R changes from CH_3 through C_2H_5, *iso*-C_3H_7 to *tert*-C_4H_9, the rate of the S_N1 reaction increases, whereas that of the S_N2 reaction decreases.

(c) The rate of both S_N1 and S_N2 reactions increase as X changes from Cl through Br to I.

(d) (i) The rate of both S_N1 and S_N2 reactions increases as we increase the concentration of the substrate, RX.

(ii) The rate of S_N2 reaction increases with the increasing concentration of the nucleophile, $[OH^-]$, whereas the concentration of the nucleophile has no effect on the rate of S_N1 reaction because it is not involved in the rate-determining step of this reaction.

(iii) Increase of temperature will increase the rate of both S_N1 and S_N2 reactions.

(iv) Increasing the proportion of H_2O will increase the rate of S_N1 reaction. For S_N2 reaction, the rate will increase if charges are created, and decrease if charges are destroyed in the transition state, with the increasing proportion of H_2O; however the effect is small.

6.

Protic solvents	**Aprotic solvents**
(a) Ammonia	*(b)* Trimethylamine
(c) Ethylene glycol	*(e)* Benzene
(d) Formamide	*(f)* Tetrahydrofuran

7. *(a)* $NH_2^- > NH_3$; with the same nucleophilic atom nucleophilicity corresponds to the basicity.

(b) $PH_3 > NH_3$; going down a family of atoms in the periodic table, as the atomic number increases, the polarizability of the outer electrons increases and thus the nucleophilicity increases.

(c) $RO^- > ROH$; the same reason as in *(a)*.

(d) $SH^- > OH^-$; the same reason as in *(b)*.

(e) $(CH_3)_2NH > CH_3NH_2$; the same reason as in *(a)*.

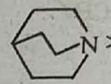
(f) $CH_3O^- > CH_3CO_2^-$; the –ve charge on O is delocalized in $CH_3CO_2^-$.

(g) *n*-$C_4H_9O^-$ > *t*-$C_4H_9O^-$; it is difficult for *t*-$C_4H_9O^-$ to approach carbon atom of the substrate due to steric hindrance.

(h) $C_6H_5O^- > p\text{-}NO_2C_6H_4O^-$, the –ve charge is delocalized

than in the former.

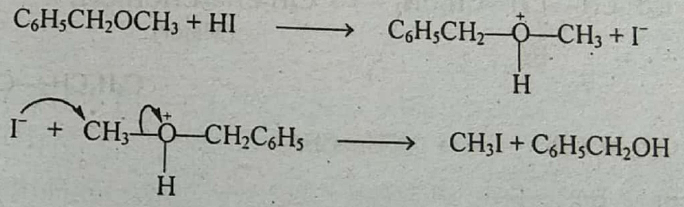
(i) $C_6H_5O^- > C_6H_5OH$; the same reason as in *(a)*.

(j) 

> $(C_2H_5)_3N$; both are tertiary amines but the bonds in quinuclidine are tied up on the backside; it therefore involves less steric hindrance than triethylamine.

8. Both reactions proceed through S_N2 mechanism. In reaction (i), the substrate contains β hydrogens. It therefore also gives E2 product (an olefin) in addition to the S_N2 product (an ether). In reaction (ii), the substrate has no β-hydrogen, and it gives only the substitution product, i.e., ether. The reaction (ii) is therefore expected to give better yield.

9. In this reaction the substrate is first protonated by HI to convert the leaving group into a better leaving group. Then the nucleophilic iodide ion (I^-) may attack the methyl carbon or the benzylic carbon to bring about the substitution reaction. Since the methyl carbon is more electrophilic than the benzylic carbon, the nucleophile preferably attacks the methyl group to yield methyl iodide and benzyl alcohol.

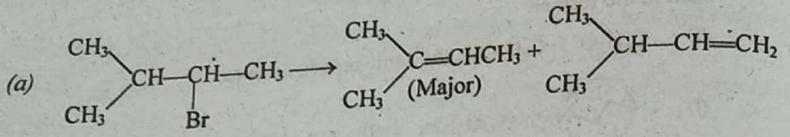


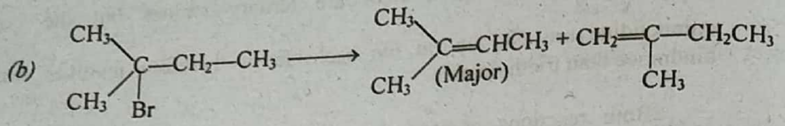
$$C_6H_5CH_2OCH_3 + HI \longrightarrow C_6H_5CH_2\text{—}\underset{\displaystyle H}{\overset{+}{O}}\text{—}CH_3 + I^-$$

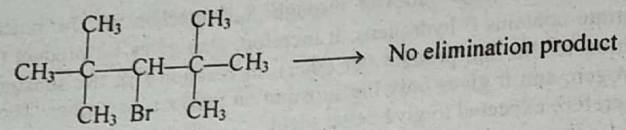
$$I^- + CH_3\text{—}\underset{\displaystyle H}{\overset{+}{O}}\text{—}CH_2C_6H_5 \longrightarrow CH_3I + C_6H_5CH_2OH$$

10. If an alkyl chloride (or bromide) is treated with sodium iodide in acetone, chloride is replaced by iodide to form alkyl iodide and sodium chloride. Since sodium chloride (or bromide) is insoluble in acetone, it will form a precipitate. The reaction proceeds through the S_N2 pathway. A primary alkyl halide is the best substrate for the S_N2 reaction, whereas a tertiary alkyl halide is the poorest substrate. Thus, when these alkyl chlorides (or bromides) are treated with sodium iodide in acetone, a primary alkyl chloride will give the precipitate of NaCl immediately, a secondary alkyl chloride will give the precipitate slowly, whereas a tertiary alkyl chloride will not form the precipitate at all.

11. When an alkyl halide is treated with alc. KOH, it mainly undergoes E2 reaction to form an olefin, provided that a β hydrogen is present in the alkyl halide. If hydrogen is present at more than one position, more than one olefinic product may be formed in proportion corresponding to their stability. If no β hydrogen is present, the reaction will not occur. A small amount of the substitution product may be formed in a side reaction.

(a)


(b)


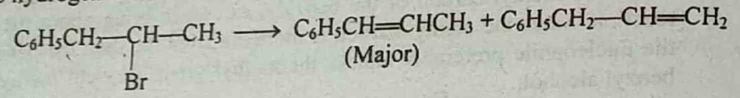
(c)


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{Br}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \longrightarrow$ No elimination product

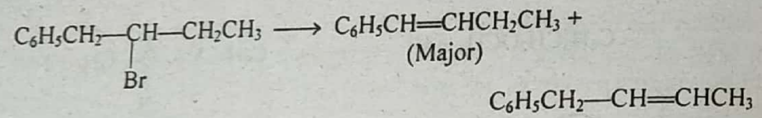
No β hydrogen is available.

(d) $C_6H_5CH_2Br \longrightarrow$ No elimination product

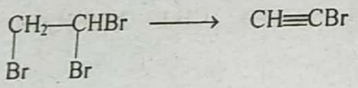
No β hydrogen is available.

(e)


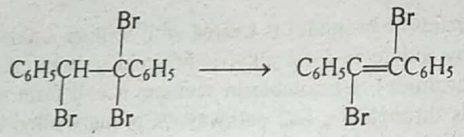
$C_6H_5CH_2-\underset{Br}{CH}-CH_3 \longrightarrow \underset{(Major)}{C_6H_5CH{=}CHCH_3} + C_6H_5CH_2-CH{=}CH_2$

(f)


$C_6H_5CH_2-\underset{Br}{CH}-CH_2CH_3 \longrightarrow \underset{(Major)}{C_6H_5CH{=}CHCH_2CH_3} + C_6H_5CH_2-CH{=}CHCH_3$

(g)


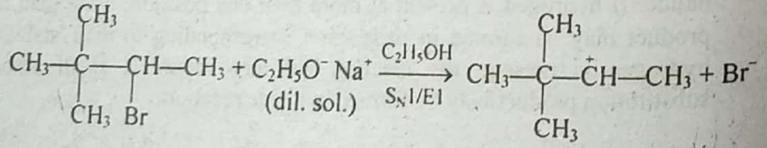
$\underset{Br}{CH_2}-\underset{Br}{CHBr} \longrightarrow CH{\equiv}CBr$

(h)


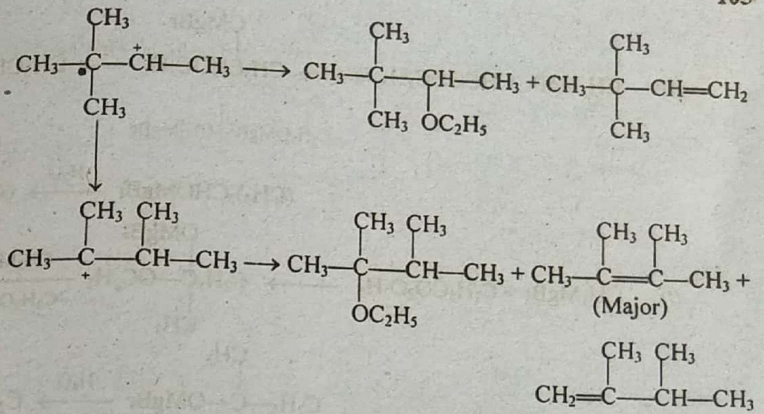
$C_6H_5\underset{Br}{CH}-\overset{Br}{\underset{Br}{C}}C_6H_5 \longrightarrow C_6H_5\underset{Br}{C}{=}\overset{Br}{C}C_6H_5$

12. In a reaction involving isopropyl bromide as a substrate the following members of the given pairs give the larger substitution to elimination ratio:

(a)	I^-	(b)	H_2O
(c)	CH_3S^-	(d)	$C_2H_5O^-$
(e)	$(CH_3)_3P$	(f)	H_2O (as solvent)
(g)	50°C	(h)	—OTs (as nucleofuge)

13. (a)


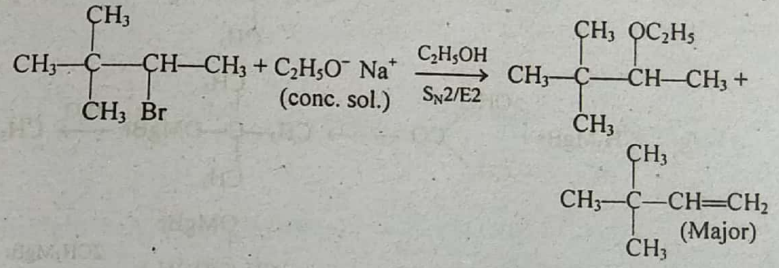
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{Br}{CH}-CH_3 + \underset{\text{(dil. sol.)}}{C_2H_5O^-\,Na^+} \xrightarrow[S_N1/E1]{C_2H_5OH} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{+}{C}H-CH_3 + Br^-$



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{+}{C}H-CH_3 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{OC_2H_5}{CH}-CH_3 + CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH{=}CH_2$

$\downarrow$

$CH_3-\overset{CH_3}{\underset{+}{C}}-\overset{CH_3}{CH}-CH_3 \longrightarrow CH_3-\overset{CH_3}{\underset{OC_2H_5}{C}}-\overset{CH_3}{CH}-CH_3 + \underset{(Major)}{CH_3-\overset{CH_3}{C}{=}\overset{CH_3}{C}-CH_3} + CH_2{=}\overset{CH_3}{C}-\overset{CH_3}{CH}-CH_3$

(b)


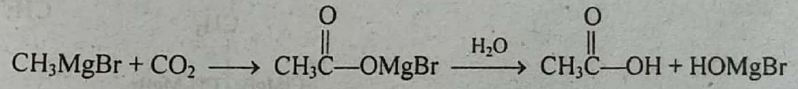
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{Br}{CH}-CH_3 + \underset{\text{(conc. sol.)}}{C_2H_5O^-\,Na^+} \xrightarrow[S_N2/E2]{C_2H_5OH} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{OC_2H_5}{CH}-CH_3 + \underset{(Major)}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH{=}CH_2}$

14. (a) $I^- > Br^- > Cl^- > CH_3CO_2^- > CH_3O^- > HO^- > H^-$

(b) $OTs^- > H_2O > p\text{-}O_2NC_6H_4O^- > C_6H_5O^-$

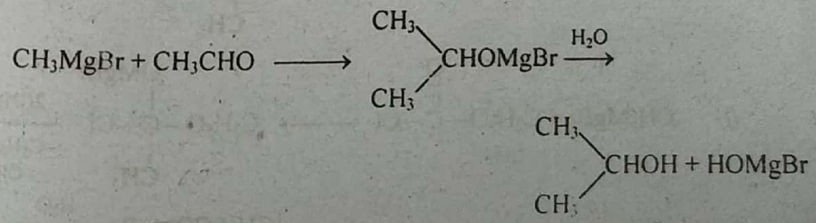
15. (a) $CH_3MgBr + NH_3 \longrightarrow CH_4 + H_2NMgBr \xrightarrow{CH_3MgBr}$

$CH_4 + HN(MgBr)_2 \xrightarrow{CH_3MgBr} CH_4 + N(MgBr)_3$

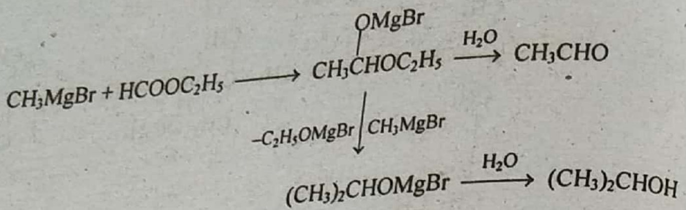
(b)


$CH_3MgBr + CO_2 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-OMgBr \xrightarrow{H_2O} CH_3\overset{O}{\overset{\|}{C}}-OH + HOMgBr$

(c) $CH_3MgBr + HCHO \longrightarrow CH_3CH_2OMgBr \xrightarrow{H_2O} CH_3CH_2OH + HOMgBr$

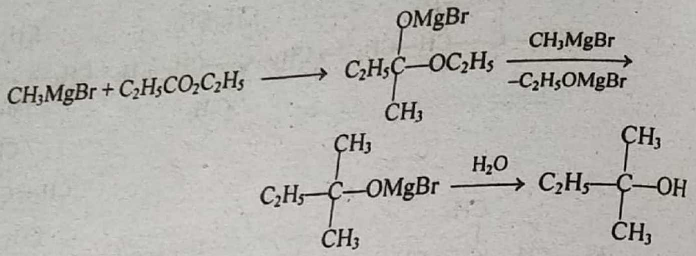
(d)


(e)



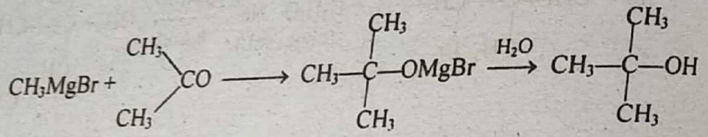
$$CH_3MgBr + HCOOC_2H_5 \longrightarrow CH_3\overset{OMgBr}{\overset{|}{C}}HOC_2H_5 \xrightarrow{H_2O} CH_3CHO$$
$$\Big\downarrow {\scriptstyle -C_2H_5OMgBr \;|\; CH_3MgBr}$$
$$(CH_3)_2CHOMgBr \xrightarrow{H_2O} (CH_3)_2CHOH$$

(f)



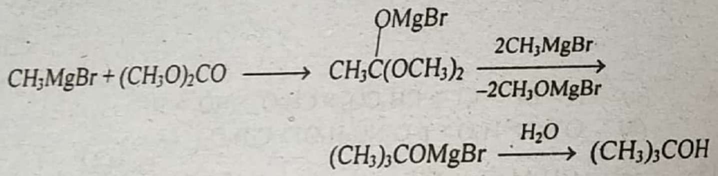
$$CH_3MgBr + C_2H_5CO_2C_2H_5 \longrightarrow C_2H_5\overset{OMgBr}{\underset{CH_3}{C}}{-}OC_2H_5 \xrightarrow[-C_2H_5OMgBr]{CH_3MgBr}$$
$$C_2H_5{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OMgBr \xrightarrow{H_2O} C_2H_5{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH$$

(g)



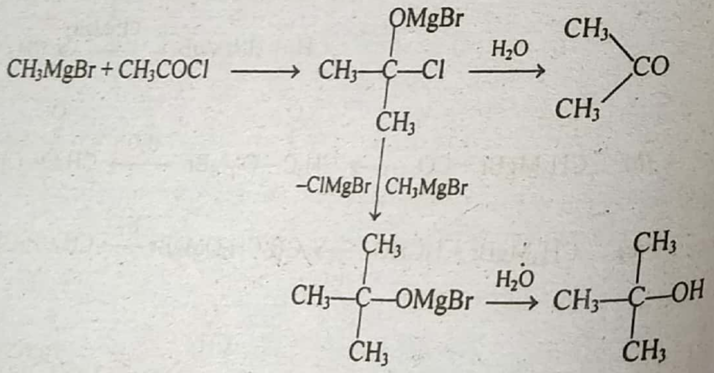
$$CH_3MgBr + \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO \longrightarrow CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OMgBr \xrightarrow{H_2O} CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH$$

(h)



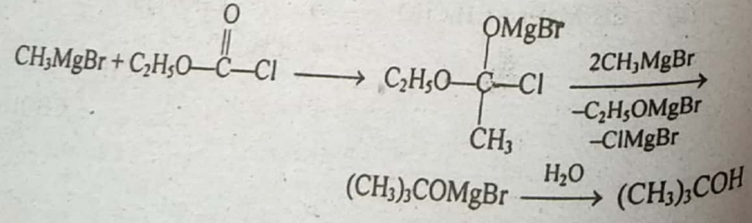
$$CH_3MgBr + (CH_3O)_2CO \longrightarrow CH_3\overset{OMgBr}{\overset{|}{C}}(OCH_3)_2 \xrightarrow[-2CH_3OMgBr]{2CH_3MgBr}$$
$$(CH_3)_3COMgBr \xrightarrow{H_2O} (CH_3)_3COH$$

(i)



$$CH_3MgBr + CH_3COCl \longrightarrow CH_3{-}\overset{OMgBr}{\underset{CH_3}{C}}{-}Cl \xrightarrow{H_2O} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO$$
$$\Big\downarrow {\scriptstyle -ClMgBr \;|\; CH_3MgBr}$$
$$CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OMgBr \xrightarrow{H_2O} CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH$$

(j)

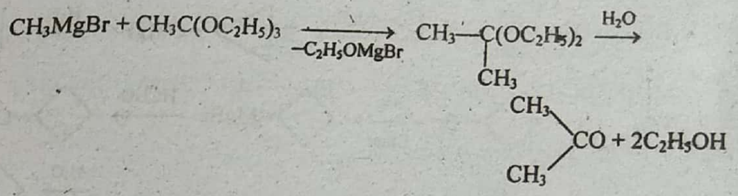


$$CH_3MgBr + C_2H_5O{-}\overset{O}{\overset{\|}{C}}{-}Cl \longrightarrow C_2H_5O{-}\overset{OMgBr}{\underset{CH_3}{C}}{-}Cl \xrightarrow[\substack{-C_2H_5OMgBr\\-ClMgBr}]{2CH_3MgBr}$$
$$(CH_3)_3COMgBr \xrightarrow{H_2O} (CH_3)_3COH$$

(k) $CH_3MgBr + HC(OC_2H_5)_3 \xrightarrow[-C_2H_5OMgBr]{} CH_3CH(OC_2H_5)_2 \xrightarrow{H_2O}$

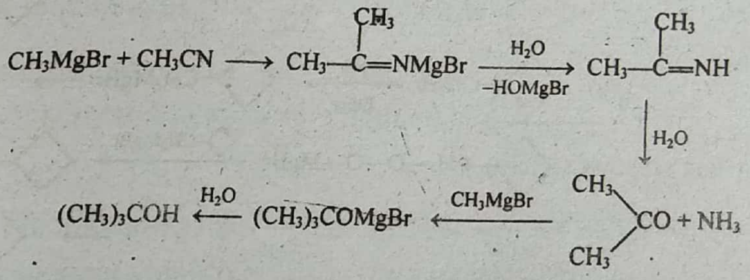
$CH_3CHO + 2C_2H_5OH$

(l)



$$CH_3MgBr + CH_3C(OC_2H_5)_3 \xrightarrow[-C_2H_5OMgBr]{} CH_3{-}\underset{CH_3}{C}(OC_2H_5)_2 \xrightarrow{H_2O}$$
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + 2C_2H_5OH$$

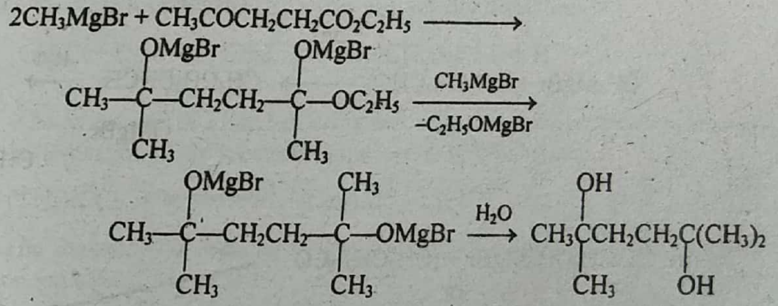
(m)



$$CH_3MgBr + CH_3CN \longrightarrow CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}NMgBr \xrightarrow[-HOMgBr]{H_2O} CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}NH$$
$$\Big\downarrow {\scriptstyle H_2O}$$
$$(CH_3)_3COH \xleftarrow{H_2O} (CH_3)_3COMgBr \xleftarrow{CH_3MgBr} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + NH_3$$

(n) $CH_3MgBr + O_2 \longrightarrow CH_3OOMgBr \xrightarrow{H_2O} CH_3OOH + HOMgBr$

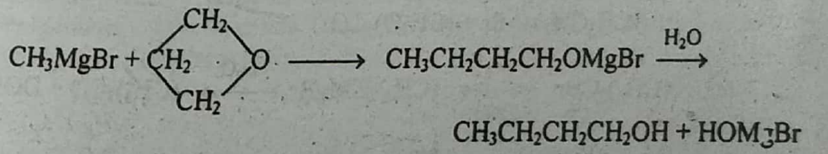
(o)



$$2CH_3MgBr + CH_3COCH_2CH_2CO_2C_2H_5 \longrightarrow$$
$$CH_3{-}\overset{OMgBr}{\underset{CH_3}{C}}{-}CH_2CH_2{-}\overset{OMgBr}{\underset{CH_3}{C}}{-}OC_2H_5 \xrightarrow[-C_2H_5OMgBr]{CH_3MgBr}$$
$$CH_3{-}\overset{OMgBr}{\underset{CH_3}{C}}{-}CH_2CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OMgBr \xrightarrow{H_2O} CH_3\overset{OH}{\underset{CH_3}{C}}CH_2CH_2\underset{OH}{C}(CH_3)_2$$

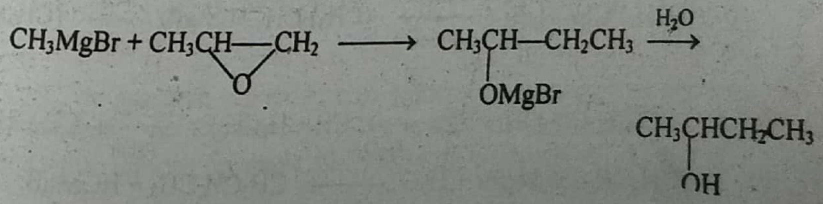
(p) $CH_3MgBr + CH_3CH_2OTs \longrightarrow CH_3CH_2CH_3 + TsOMgBr$

(q)



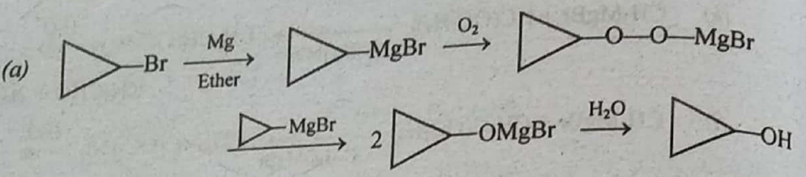
$$CH_3MgBr + \text{(CH}_2\text{–CH}_2\text{–CH}_2\text{–O ring)} \longrightarrow CH_3CH_2CH_2CH_2OMgBr \xrightarrow{H_2O}$$
$$CH_3CH_2CH_2CH_2OH + HOMgBr$$

(r)

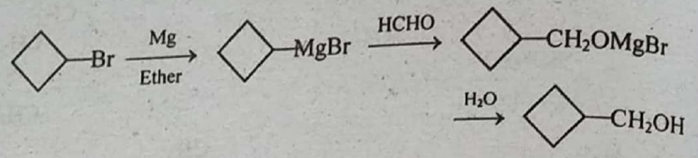


$$CH_3MgBr + CH_3\underset{\diagdown O \diagup}{CH{-}CH_2} \longrightarrow CH_3\underset{OMgBr}{CH}{-}CH_2CH_3 \xrightarrow{H_2O}$$
$$CH_3\underset{OH}{C}HCH_2CH_3$$

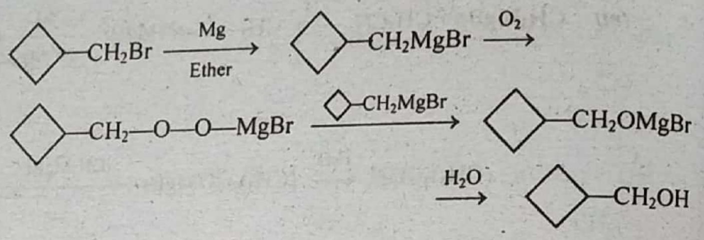
16. (a)



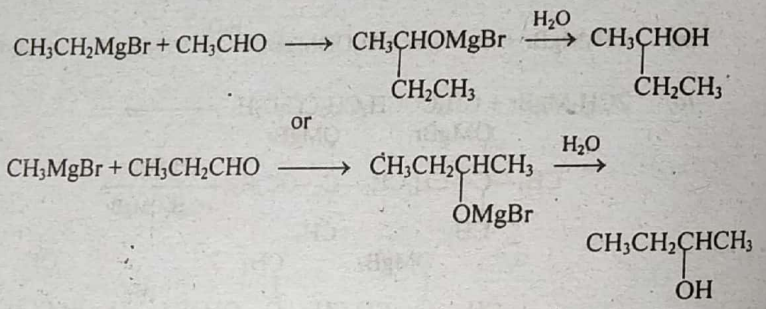
(b) (i)



(ii)



(c)



$$CH_3CH_2MgBr + CH_3CHO \longrightarrow \underset{CH_2CH_3}{CH_3CHOMgBr} \xrightarrow{H_2O} \underset{CH_2CH_3}{CH_3CHOH}$$

or

$$CH_3MgBr + CH_3CH_2CHO \longrightarrow \underset{OMgBr}{CH_3CH_2CHCH_3} \xrightarrow{H_2O} \underset{OH}{CH_3CH_2CHCH_3}$$

(d) $CH_3CH_2MgBr + (CH_3CH_2)_2CO$

or

$2CH_3CH_2MgBr + CH_3CH_2CO_2CH_3 \longrightarrow (CH_3CH_2)_3COH$

or

$3CH_3CH_2MgBr + (CH_3O)_2CO$

(e) $(CH_3)_3CBr \xrightarrow[Ether]{Mg} (CH_3)_3CMgBr \xrightarrow{D_2O} (CH_3)_3CD + DOMgBr$

(f) $(CH_3)_2CHCH_2Br \xrightarrow[Ether]{Mg} (CH_3)_2CHCH_2MgBr \xrightarrow{D_2O} (CH_3)_2CHCH_2D$

17. (a) $CH_3CH_2CH_2OH + HBr \xrightarrow[-H_2O]{} CH_3CH_2CH_2Br \xrightarrow[Ether]{Mg} CH_3CH_2CH_2MgBr$

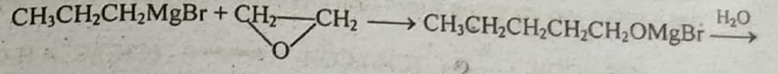
$CH_3CH_2CH_2MgBr + H_2O \longrightarrow CH_3CH_2CH_3 + HOMgBr$

(b) $CH_3CH_2CH_2OH + HBr \longrightarrow CH_3CH_2CH_2Br + H_2O$

$2CH_3CH_2CH_2Br + 2Na \longrightarrow CH_3CH_2CH_2CH_2CH_2CH_3 + 2NaBr$

(c) $CH_3CH_2CH_2OH + HBr \longrightarrow CH_3CH_2CH_2Br + H_2O$

(d) $CH_3CH_2CH_2OH + HBr \xrightarrow[-H_2O]{} CH_3CH_2CH_2Br \xrightarrow[Ether]{Mg} CH_3CH_2CH_2MgBr$



$CH_3CH_2CH_2CH_2CH_2OH + HOMgBr$

(e) $CH_3CH_2CH_2OH + HBr \xrightarrow[-H_2O]{} CH_3CH_2CH_2Br \xrightarrow{KCN} CH_3CH_2CH_2CN$

(f) $CH_3CH_2CH_2OH + Na \longrightarrow CH_3CH_2CH_2O^- Na^+$

$CH_3CH_2CH_2OH + HBr \xrightarrow[-H_2O]{} CH_3CH_2CH_2Br \xrightarrow{CH_3CH_2CH_2O^- Na^+}$

$CH_3CH_2CH_2OCH_2CH_2CH_3$

(g) $CH_3CH_2CH_2OH + HBr \xrightarrow[-H_2O]{} CH_3CH_2CH_2Br \xrightarrow[Ether]{Mg} CH_3CH_2CH_2MgBr$

$CH_3CH_2CH_2MgBr + D_2O \longrightarrow CH_3CH_2CH_2D + DOMgBr$

18. (a) Iodide is a better nucleophile than chloride and is also a better leaving group. So it readily replaces Cl^-, and is also readily displaced.

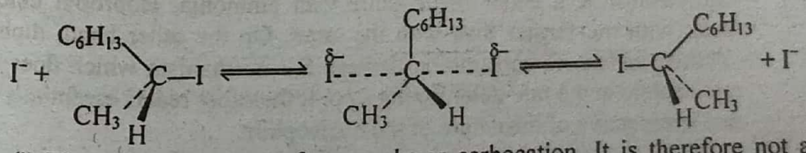
$$CH_3Cl + I^- \xrightarrow[-Cl^-]{} CH_3I \xrightarrow{H_2O} CH_3OH + I^- + H^+$$

(b) The hydrolysis of *t*-butyl chloride proceeds through S_N1 mechanism which involves ionization of the substrate in the rate-determining step.

$$(CH_3)_3CCl \rightleftharpoons (CH_3)_3C^+ + Cl^-$$

The ionization is retarded by the addition of sodium chloride due to the common ion effect.

(c) The reaction of 2-iodooctane with KI in acetone proceeds through S_N2 mechanism which involves inversion of configuration. The product is therefore the enantiomer of the substrate. Thus, the reaction leads to the racemic mixture which shows no optical activity.



(d) (i) The substrate cannot form a planar carbocation. It is therefore not a suitable substrate for S_N1 reaction. It is also not suitable for S_N2 reaction because it hinders the attack by the nucleophile from the backside.

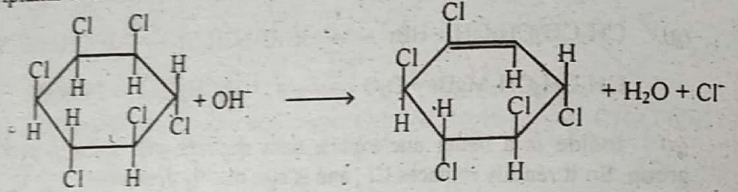
(ii) The substrate is a primary alkyl halide. It is therefore not a suitable substrate for S_N1 reaction. It is also not suitable for S_N2 reaction because the attack by the nucleophile from the backside is sterically hindered.

(e) *t*-Butyl alcohol has a very poor leaving group (OH^-) and does not ionize easily. However, HCl protonates the hydroxyl group of the alcohol to convert it into a better leaving group which then makes the substrate to ionize easily.

$$(CH_3)_3COH \xrightarrow[-Cl^-]{HCl} (CH_3)_3C\overset{+}{O}H_2 \rightleftharpoons (CH_3)_3C^+ + H_2O$$

$$(CH_3)_3C^+ \xrightarrow{Cl^-} (CH_3)_3CCl$$

(f) Basic dehydrohalogenation of an alkyl halide proceeds through E2 mechanism which requires trans periplanar geometry of the halide and the β hydrogen. The structure A has no β hydrogen trans periplanar to any chloride. However, the structure B does have a chloride and β hydrogen that are trans periplanar to each other. It can, therefore, easily undergo E2 reaction.



(g) The formation of *t*-butyl ethyl ether from *t*-butyl bromide follows S_N1 mechanism in which the rate-determining step involves the ionization of the substrate, and the nucleophile is not involved in this step. The rate of the reaction is, therefore, not affected by changing the nucleophile.

$$(CH_3)_3CBr \underset{Slow}{\rightleftharpoons} (CH_3)_3C^+ + Br^-$$

$$(CH_3)_3C^+ + C_2H_5OH \text{ (or } C_2H_5ONa) \xrightarrow[Fast]{} (CH_3)_3COC_2H_5$$

(h) The substitution reaction of isopropyl chloride with diethylamine or with ammonia proceeds through S_N2 mechanism in which the substrate is attacked by a nucleophile in the only step which is the rate-determining step. The rate of the reaction therefore depends on the nucleophilicity of the nucleophile. Since diethylamine is a better nucleophile than ammonia, isopropyl chloride reacts faster with the former than with the latter. On the other hand, diphenylmethyl chloride undergoes substitution through S_N1 mechanism which does not involve nucleophile in the rate-determining step. It therefore reacts essentially at the same rate irrespective of the nature of the nucleophile.

(i) The alkyl halide in ethereal solution must react with magnesium on the surface of solid magnesium. The magnesium metal that provides the surface for the reaction to occur must therefore remain even after the reaction ceases.

Chapter 8

Aromatic Hydrocarbons

CHAPTER'S SUMMARY

The aromatic hydrocarbons include benzene and those compounds of carbon and hydrogen that resemble benzene in their chemical behaviour.

Structure of Benzene

The structure of benzene was established on the basis of the following facts:

1. Elemental analysis and molecular weight determination show that the molecular formula of benzene is C_6H_6.

2. Benzene is not oxidized by aq. $KMnO_4$, neither it adds bromine in CCl_4. It is also not hydrogenated even in the presence of a catalyst except at a high temperature and pressure. This behaviour of benzene is not consistent with an unsaturated molecule, despite its hydrogen deficiency index of four.

3. However, benzene does react with bromine, but the reaction involves substitution, rather than addition. As a result of this substitution reaction only one monobromobenzene is formed, indicating that all the six hydrogen atoms in the benzene molecule are equivalent. It forms three isomeric dibromobenzenes.

4. The substitution product can undergo further substitution of the same kind, indicating that the characteristics of the benzene ring remain intact after the substitution reaction, i.e., the benzene ring resists destruction. This is why it does not give addition reaction which would destroy the ring system. This means that the benzene ring is very stable. The extent of its stability can be estimated from its resonance energy. Its resonance energy is 150.5 kJ/mol.

5. In view of the above facts the structure of benzene can be represented by a regular hexagon containing a circle inside it, as follows:

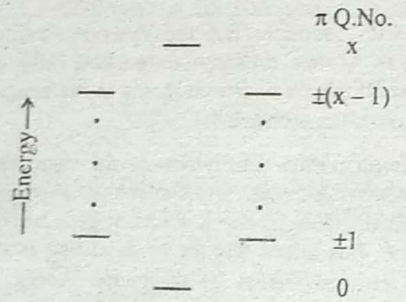
The structure can be explained both by the resonance method as a resonance hybrid of the Kekule's canonical structures and by the molecular orbital method according to which benzene has a closed shell of delocalized π electrons.

Aromaticity

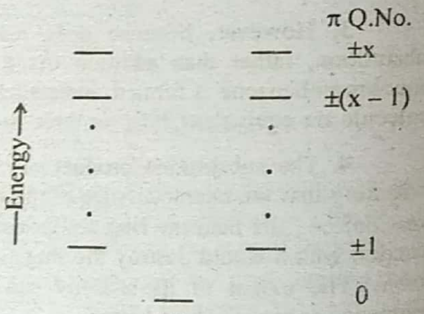
The term aromaticity is associated with the cyclic compounds having a completely filled shell of π molecular orbitals.

To account for the stability of benzene and some of the other annulenes (cyclic compounds having alternating single and double bonds), Eric Huckel carried out a series of mathematical calculations and developed a rule known as the **Huckel's (4n + 2) π electrons rule** which states, "the planar rings will be particularly stable and hence aromatic if the number of π electrons in their cyclic conjugated system is (4n + 2), where n = 0, 1, 2, 3, and so on". Huckel showed that this rule has a bearing on the filling up of the various shells of the π molecular orbitals.

Huckel discovered that there are two distinct patterns of π molecular orbital energy levels which are based on the number of atoms constituting the ring system. A planar regular polygon with even number of atoms, such as benzene, can form even number of π molecular orbitals that will follow a pattern in which there is a single lowest-lying π molecular orbital followed by higher π molecular orbitals in degenerate pairs until there is a single highest-lying π molecular orbital as shown in (a). The middle degenerate pair (if any) is nonbonding, the lower π molecular orbitals are bonding, and the higher ones are antibonding. A planar regular polygon with odd number of atoms can form an odd number of π molecular orbitals that will follow a π molecular orbital energy level pattern in which there is a single π molecular orbital at the lowest energy level, above which the π molecular orbitals are in degenerate pairs, as shown in (b). The lower degenerate pairs are bonding, and the higher ones are antibonding. There is no nonbonding π molecular orbital in this pattern.



(a)



(b)

If electrons are filled into the π molecular orbitals of any of the two patterns, a closed-shell structure (all electrons paired) similar to that of benzene will result only when the total number of π electrons is 2, 6, 10, 14, etc., i.e., (4n + 2), where n = 0, 1, 2, 3, etc. If the number of π electrons is 4, 8, 12, 16, etc., i.e. 4n, the last occupied shell will have its degenerate π molecular orbitals filled with only one electron each, with their spins parallel. In other words, it will have an open-shell structure and therefore would not be expected to have the special stability associated with benzene.

It has been found that the cyclic conjugated polyenes (C_nH_n) are stabilized as compared to the open-chain conjugated polyenes (C_nH_{n+2}) if the number of the π electrons is (4n + 2), and destabilized if the number of the π electrons is 4n. In the former case the planar cyclic conjugated polyenes are said to be aromatic, whereas in the latter case they are called antiaromatic. (A species is antiaromatic if it has electrons in antibonding π molecular orbitals or if it has half-filled bonding or nonbonding π molecular orbitals, provided it is planar). A cyclic conjugated polyene showing neither stabilization nor destabilization is known as nonaromatic. Various cyclic systems have been studied by the Huckel's (4n + 2) π electrons rule and found as follows:

Aromatic

Benzene
[14] Annulene
Cyclopropenyl cation
Cycloheptatrienyl cation
Cyclooctatetraenyl dication
Azulene
Anthracene
[10] Annulene
[18] Annulene
Cyclopentadienyl anion
Cyclononatetraenyl anion
Cyclooctatetraenyl dianion
Naphthalene
Phenanthrene
Pyrene (in this case the Huckel's rule applies to the peripheral π electrons).

Antiaromatic

Cyclobutadiene
Cyclopentadienyl cation
Cyclononatetraenyl cation
Cyclopropenyl anion
Cycloheptatrienyl anion

Nonaromatic

Cyclooctatetraene (because it is not planar)

Thus, for a compound to be aromatic its molecule must fulfil the following requirements:

(a) It must have a planar regular cyclic structure.
(b) It must obey Huckel's rule, i.e., it must have (4n + 2) π electrons.
(c) Every atom of the ring must be sp^2 hybridized to permit delocalization of the π electrons through its unhybridized *p* orbitals.

Nomenclature

The nomenclature of the aromatic hydrocarbons and their derivatives is more complex than that of the aliphatic compounds. Each type of compound is named in its own way.

Natural Sources of Aromatic Hydrocarbons

The main natural sources of benzene and other simple aromatic hydrocarbons are coal and petroleum. These simple aromatic hydrocarbons are then used as the main starting materials for nearly all aromatic compounds.

Preparation of Aromatic Hydrocarbons

The aromatic hydrocarbons containing both the aromatic and the aliphatic components, such as in ethylbenzene, are commonly known as **arenes**. They are generally prepared either by the introduction of an alkyl group into the benzene ring, or by converting the substituent already present in the benzene ring into an alkyl group. Some of the methods generally used for the preparation of aromatic hydrocarbons are given below:

1. Cyclohexane and its derivatives are dehydrogenated to aromatic compounds either catalytically at an elevated temperature or on oxidation with sulfur or selenium.

2. Cyclohexene obtained from Diels-Alder reaction can be dehydrogenated catalytically at an elevated temperature to yield the aromatic ring.

3. Alkanes containing a chain of six or more carbon atoms undergo dehydrogenation with cyclization to form aromatic hydrocarbons when heated at an elevated temperature under pressure in the presence of a metal oxide.

4. An alkyl group can be introduced into the benzene ring by its treatment with an alkyl halide in the presence of a Lewis acid (Friedel-Crafts reaction).

5. An arene can be prepared by warming an ethereal solution of a mixture of alkyl and aryl halides with sodium (Wurtz-Fittig reaction).

6. Arenes may also be prepared by the reaction between an alkyl halide and a Grignard reagent.

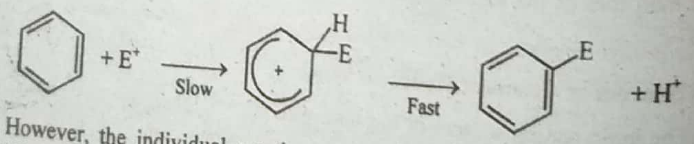
7. Biphenyl and its derivatives may be prepared by the reaction of aryl iodide with copper powder in boiling nitrobenzene.

Physical Properties of Aromatic Hydrocarbons

The physical properties of aromatic hydrocarbons are almost similar to those of the corresponding cycloalkanes. The boiling points of the aromatic hydrocarbons increase fairly regularly with the molecular weights, but the freezing points depend on the symmetry of the molecules. The aromatic hydrocarbons are less dense than water. They burn with a luminous smoky flame, whereas the aliphatic hydrocarbons burn with a bluish non-smoky flame.

Electrophilic Aromatic Substitution

Due to its unusual stability, benzene undergoes substitution reactions such as nitration, halogenation, alkylation, acylation and sulfonation, all following the same general mechanism.



However, the individual reactions may differ from each other in the way the electrophile is produced

The electrophilic aromatic substitution reactions are also given by the substituted benzenes. In this case, the rate of the reaction and the orientation of the second substituent is influenced by the substituent already present in the benzene ring. In general, the electron-donating groups increase the rate of the substitution reaction and direct the second substituent to the ortho and para positions. On the other hand, the electron-withdrawing groups decrease the rate of the reaction, and are meta-directing. This influence of the group already present in the benzene ring on the reactivity and orientation in an electrophilic substitution reaction can be explained either on the basis of the charge distribution over the ring, or on the basis of the relative arenium ion stability. The net influence of some important groups on the reactivity of the aromatic ring and orientation in an electrophilic substitution reaction is summarized as follows:

Ortho/para-directing

Strongly activating:	O^-, OH, NH_2, NHR, NR_2
Moderately activating:	OR, OCOR, NHCOR
Weakly activating:	R, Ar

Meta-directing

Weakly deactivating:	X (*o/p*-directing), CH_2X
Moderately deactivating:	CN, CHO, COR, CO_2H, CO_2R, SO_3H, $CONH_2$, CHX_2
Strongly deactivating:	NO_2, $\overset{+}{N}H_3$, $\overset{+}{N}R_3$, CX_3

Electrophilic aromatic substitution is very useful for introducing a functional group into an aromatic ring. However, we have to keep in mind the reactivity and the directive influence of various groups while planning a synthetic scheme.

Reactions of Aromatic Hydrocarbons

Aromatic hydrocarbons generally consist of two parts: (i) aromatic nucleus and (ii) aliphatic side-chain. They are therefore expected to show reactions typical of each part.

1. Nitration. Nitration of aromatic hydrocarbons is most commonly carried out by a mixture of conc. HNO_3 and conc. H_2SO_4.

2. Halogenation. Aromatic compounds are halogenated on treatment with a halogen in the presence of a Lewis acid.

3. Friedel-Crafts reaction. An alkyl or an acyl group can be introduced into an aromatic ring by its treatment with an alkyl halide or an acid halide, respectively, in the presence of a Lewis acid.

4. Sulfonation. Sulfonic acid group (SO_3H) can be introduced into an aromatic ring by its treatment with a slight excess of conc. H_2SO_4 or fuming sulfuric acid (H_2SO_4 + SO_3).

5. Nucleophilic aromatic substitution. An aryl halide can undergo displacement of the halide ion by a nucleophile provided that the ring contains strong electron-withdrawing groups ortho or para to the halide.

6. Addition reactions. Benzene ring can be hydrogenated either completely on treatment with H_2 in the presence of a catalyst at an elevated temperature and pressure or partially on treatment with an alkali metal in ammonia in the presence of ethanol.

Benzene can also add three molecules of Cl_2 or Br_2 under the influence of light.

7. Oxidation. Benzene ring can be oxidized on treatment either with air in the presence of V_2O_5 at 450°C or with ozone.

8. Reactions of the side-chain. Reactions of the aliphatic side-chain of an arene are essentially those of the aliphatic hydrocarbons.

(i) Halogenation of the side-chain. When an arene is treated with chlorine or bromine under free-radical conditions ($h\nu$ or Δ), halogenation takes place in the aliphatic side-chain, preferentially at the α-position.

(ii) Oxidation of the side-chain. The alkyl side-chain of an arene is converted to the carboxylic acid group (COOH) on treatment with alkaline $KMnO_4$.

POLYCYCLIC AROMATIC HYDROCARBONS

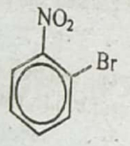
The polycyclic aromatic hydrocarbons contain two or more benzene rings fused together at ortho positions so that the adjacent rings have a common carbon-carbon bond, e.g., naphthalene, anthracene and phenanthrene.

The major source of the fused-ring aromatic hydrocarbons is coal tar, though they may also be prepared by the cyclization of benzene derivatives, followed by catalytic dehydrogenation to obtain the desired aromatic system.

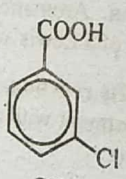
The fused-ring aromatic hydrocarbons undergo the reactions usually given by benzene. However, these are generally more reactive than benzene in both the substitution and the addition reactions. The general order of reactivity is: anthracene > phenanthrene > naphthalene > benzene.

ANSWERS TO EXERCISES

1. (a) *(a)*

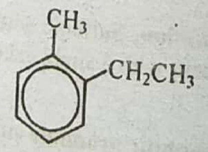


(b)

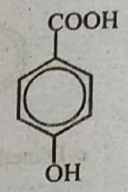


(c)

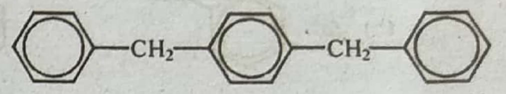
(d)



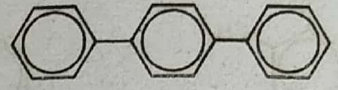
(e)



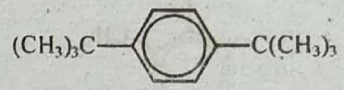
(f)



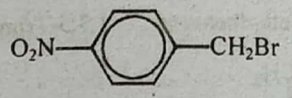
(g)



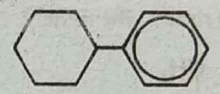
(h)



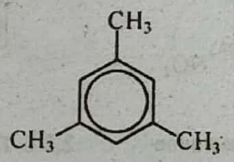
(i)



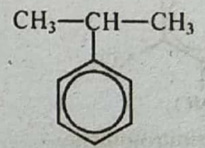
(j)



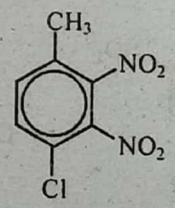
(k)



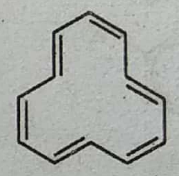
(l)



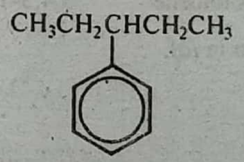
(m)



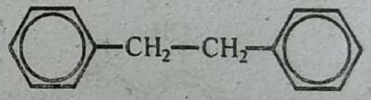
(n)



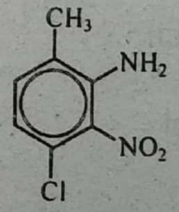
(o)



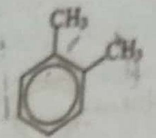
(p)

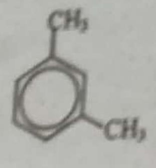


(q)



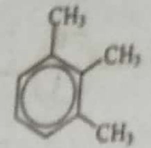
(b) (a)

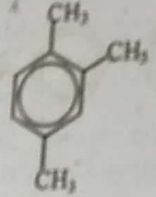

o-Dimethylbenzene

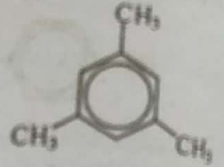

m-Dimethylbenzene


p-Dimethylbenzene

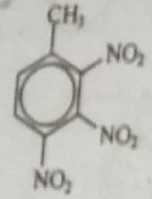
(b)

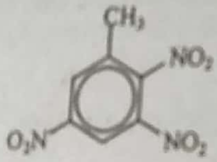

1,2,3-Trimethylbenzene

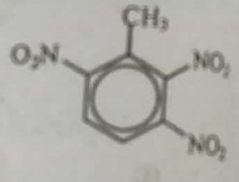

1,2,4-Trimethylbenzene

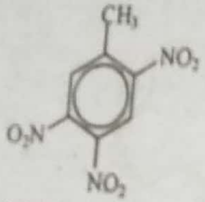

1,3,5-Trimethylbenzene

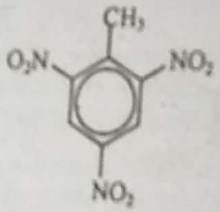
(c)

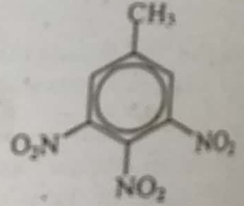

2,3,4-Trinitrotoluene


2,3,5-Trinitrotoluene


2,3,6-Trinitrotoluene

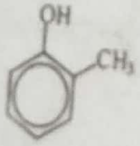

2,4,5-Trinitrotoluene

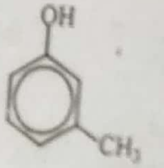

2,4,6-Trinitrotoluene


3,4,5-Trinitrotoluene

(d) Xylenes are dimethylbenzenes shown in (a).

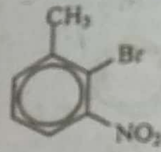
(e)

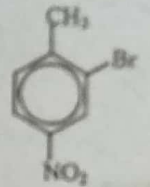

o-Cresol

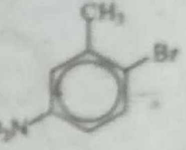

m-Cresol

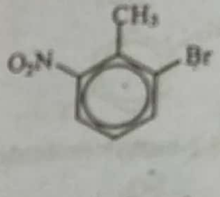

p-Cresol

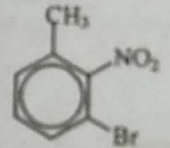
(f)

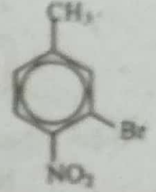

2-Bromo-3-nitrotoluene

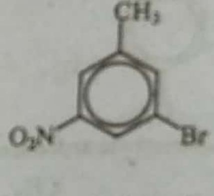

2-Bromo-4-nitrotoluene

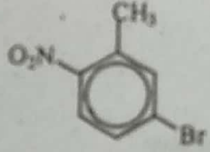

2-Bromo-5-nitrotoluene

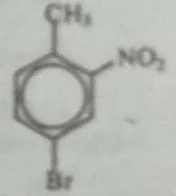

2-Bromo-6-nitrotoluene

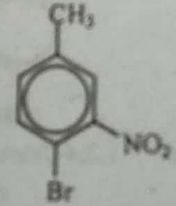

3-Bromo-2-nitrotoluene


3-Bromo-4-nitrotoluene

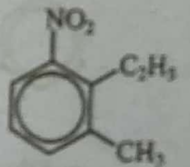

3-Bromo-5-nitrotoluene

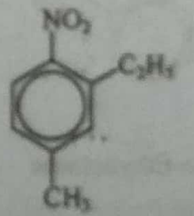

5-Bromo-2-nitrotoluene

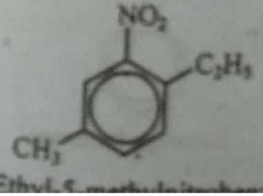

4-Bromo-2-nitrotoluene

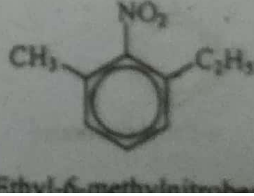

4-Bromo-3-nitrotoluene

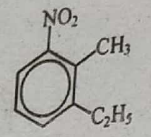
(g)


2-Ethyl-3-methylnitrobenzene

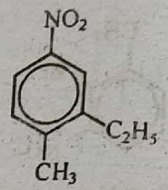

2-Ethyl-4-methylnitrobenzene


2-Ethyl-5-methylnitrobenzene

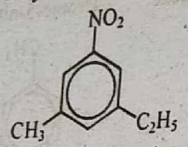

2-Ethyl-6-methylnitrobenzene



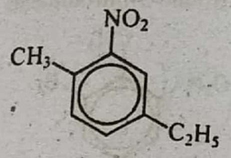
3-Ethyl-2-methylnitrobenzene



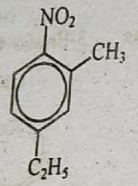
3-Ethyl-4-methylnitrobenzene



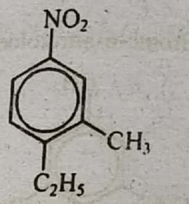
3-Ethyl-5-methylnitrobenzene



5-Ethyl-2-methylnitrobenzene

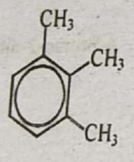


4-Ethyl-2-methylnitrobenzene

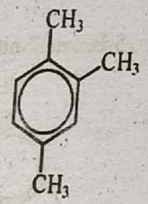


4-Ethyl-3-methylnitrobenzene

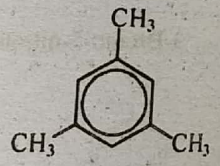
(c)



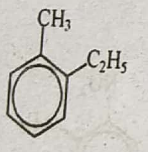
1,2,3-Trimethylbenzene



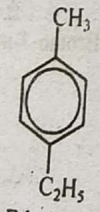
1,2,4-Trimethylbenzene



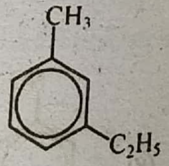
1,3,5-Trimethylbenzene



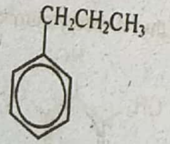
o-Ethyltoluene



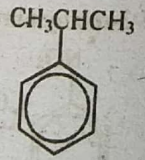
p-Ethyltoluene



m-Ethyltoluene



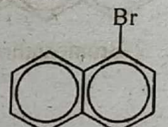
n-Propylbenzene



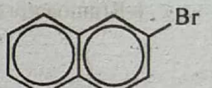
Isopropylbenzene

2. (a) Triphenylmethane
(b) *p*-*n*-Propyltoluene
(c) 1,1,3,3-Tetramethylbutylbenzene
(d) *t*-Butylbenzene
(e) 1,2,4-Trimethylbenzene
(f) 4-Bromo-2,6-dimethylbenzaldehyde
(g) 2-*p*-Nitrophenylbutane
(h) 2-Bromo-1-ethyl-4-methylbenzene or 3-Bromo-4-ethyltoluene
(i) 2-Bromo-4-chloro-6-iodophenol
(j) *p*-Isopropylchlorobenzene (*p*-Chlorocumene)

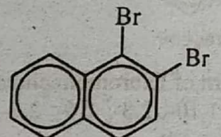
3. **Naphthalenes**



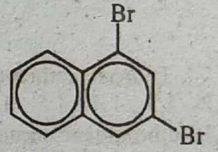
1-Bromonaphthalene



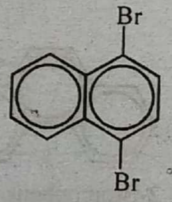
2-Bromonaphthalene



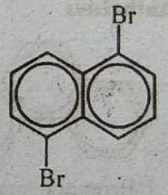
1,2-Dibromonaphthalene



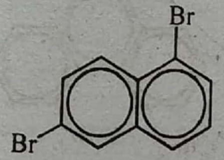
1,3-Dibromonaphthalene



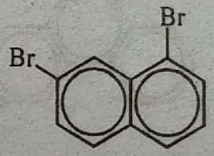
1,4-Dibromonaphthalene



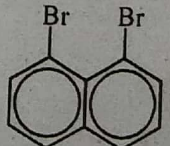
1,5-Dibromonaphthalene



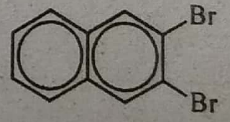
1,6-Dibromonaphthalene



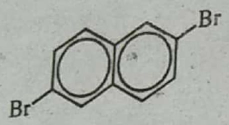
1,7-Dibromonaphthalene



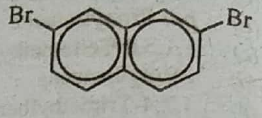
1,8-Dibromonaphthalene



2,3-Dibromonaphthalene

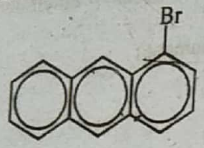


2,6-Dibromonaphthalene

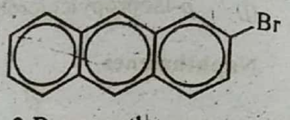


2,7-Dibromonaphthalene

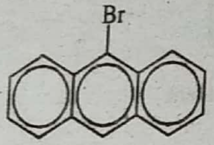
Anthracenes



1-Bromoanthracene



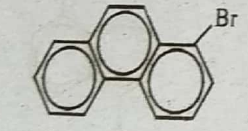
2-Bromoanthracene



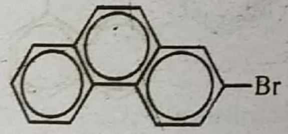
9-Bromoanthracene

Dibromoanthracenes follow the pattern of Dibromonaphthalenes. They are: 1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 1,8-, 1,9-, 1,10-, 2,3-, 2,6-, 2,7-, 2,9-, 2,10- and 9,10-dibromoanthracenes.

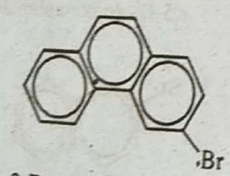
Phenanthrenes



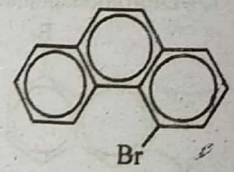
1-Bromophenanthrene



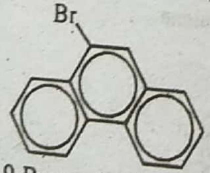
2-Bromophenanthrene



3-Bromophenanthrene



4-Bromophenanthrene



9-Bromophenanthrene

Dibromophenanthrenes follow the pattern of dibromoanthracenes. They are: 1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 1,8-, 1,9-, 1,10-, 2,3-, 2,4-, 2,5-, 2,6-, 2,7-, 2,9-, 2,10-, 3,4-, 3,5-, 3,6-, 3,9-, 3,10-, 4,5-, 4,9-, 4,10- and 9,10-dibromophenanthrenes.

4. **Monobromo- derivatives**

(a) 5, *(b)* 2, *(c)* 2, *(d)* 3, *(e)* 3, *(f)* 2.

Dibromo- derivatives

(a) 11, *(b)* 5, *(c)* 5, *(d)* 5, *(e)* 5, *(f)* 4.

5. (a) The isomer giving only one dibromonitrobenzene is *p*-dibromobenzene, whereas the isomer giving two dibromonitrobenzenes is *o*-dibromobenzene and that giving three dibromonitrobenzenes is *m*-dibromobenzene.

(b) On nitration, each bottle will give a different number of tribromonitrobenzenes, as follows:

Tribromobenzene	No. of tribromonitrobenzenes
1,2,3-Tribromobenzene	Two
1,2,4-Tribromobenzene	Three
1,3,5-Tribromobenzene	One

6. (a) *(a)* $\Delta H = 231.5 - 208.0 = 23.5$ kJ/mol.
(b) $\Delta H = 119.5 - 231.5 = -112.0$ kJ/mol.

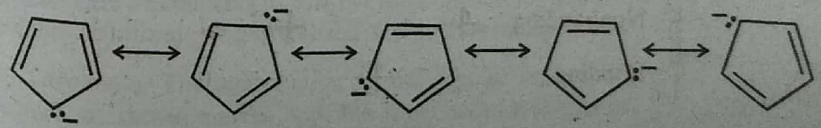
(b) Resonance energy $= (4 \times 97) - 422 = -34$ kJ/mol.
The negative value of the resonance energy implies that not only is there no resonance stabilization, but that cyclooctatetraene is probably more strained because of the four double bonds.

7. An alkane is generally more stable than the corresponding alkene. Thus, when propene adds bromine, it is converted to propane derivative which is accompanied by the evolution of heat. On the other hand, cyclohexadiene is less stable than benzene, as can be seen from the *Fig. 8.1* in the *Textbook*. Since addition of one molecule of bromine to benzene leads to a cyclohexadiene derivative, it is accompanied by the absorption of heat.

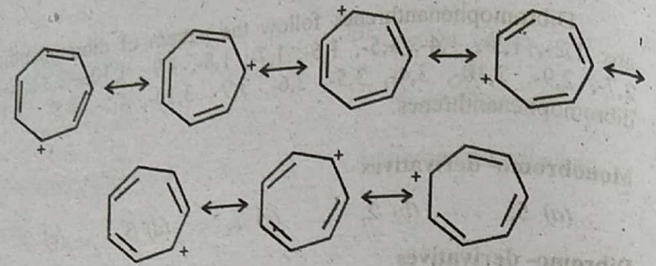
8. (a) *(a)* [6] Annulene, [10] annulene, [14] annulene and [18] annulene.

(b) $C_9H_9^-$

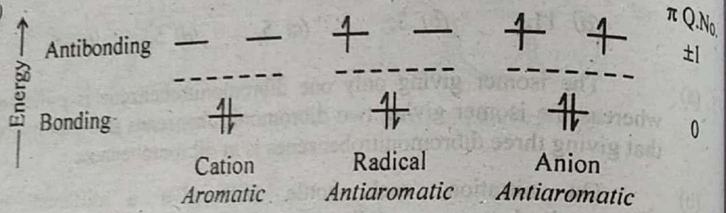
(b) *(a)*



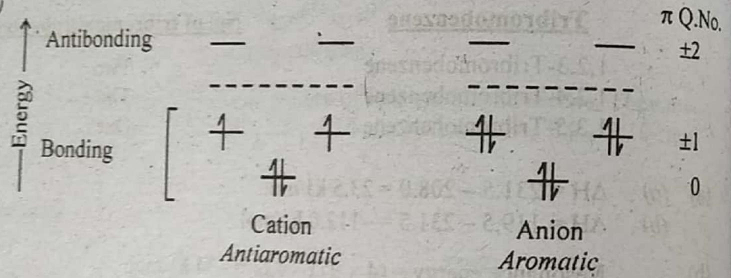
(b)



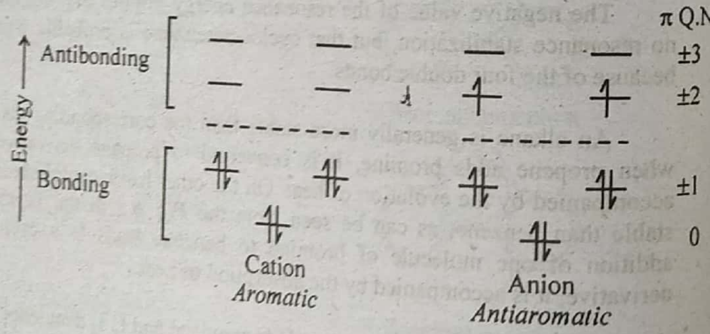
9. (a) (a)



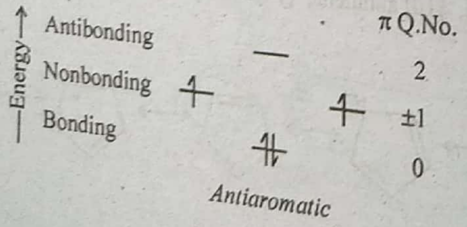
(b)



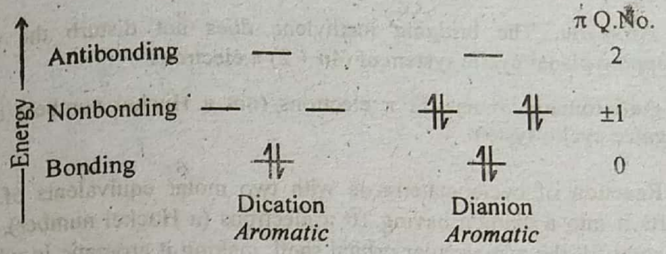
(c)



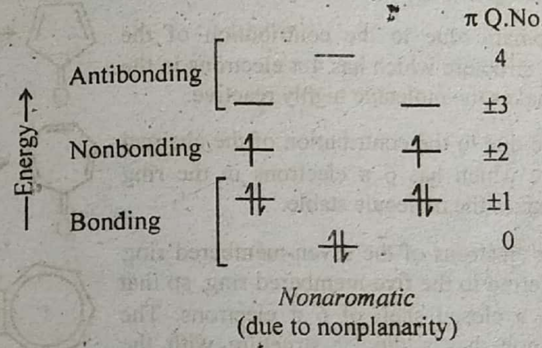
(d)



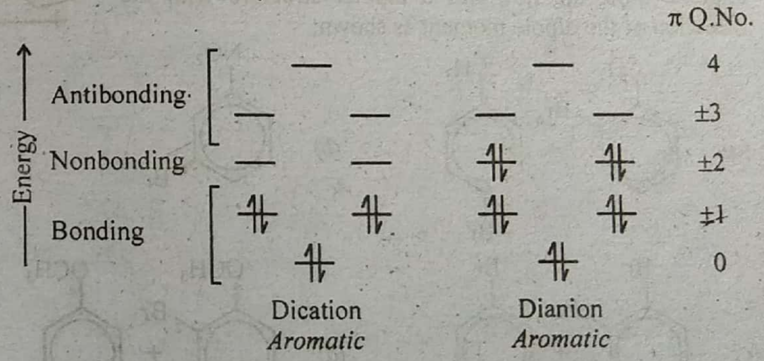
(e)



(f)



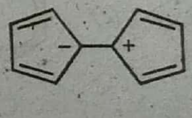
(g)



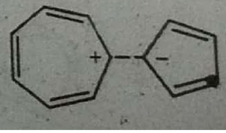
(b) *(a)* Nonaromatic. Due to the sp^3 hybridization of the two common carbon atoms, no ring has a completely overlapping cyclic system of π electrons.

(b) Nonaromatic. One of the carbon atoms of the ring is sp^3 hybridized, and thus prevents a completely overlapping cyclic system of π electrons.

(c) Nonaromatic. It has one of the resonance structures as shown. In this structure one ring stabilizes the molecule, while the other ring destabilizes it. The net result is that the molecule is neither stabilized nor destabilized, and is thus nonaromatic.



(d) Aromatic. The contribution of the dipolar resonance structure, as shown, makes both the rings acquire aromatic character.

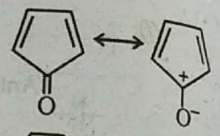


(e) Aromatic. The bridging methylene does not disturb the completely overlapping planar cyclic system of (4n + 2) π electrons.

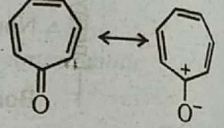
(f) Antiaromatic. It has 12 π electrons (not a Huckel number) in a planar conjugated cyclic system.

10.(a) Reaction of cyclooctatetraene with two molar equivalents of potassium converts it into a dianion having 10 π electrons (a Huckel number), enough to completely fill the π molecular orbital shell, making it aromatic in which all the hydrogen atoms are equivalent, like those of benzene.

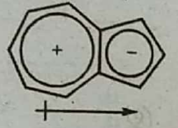
(b) *(a)* It is antiaromatic due to the contribution of the charged resonance structure which has 4 π electrons in the ring system, and makes the molecule highly reactive.



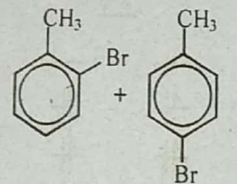
(b) It is aromatic due to the contribution of the charged resonance structure which has 6 π electrons in the ring system, and thus makes the molecule stable.



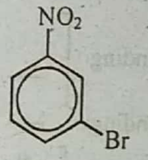
(c) One of the π electrons of the seven-membered ring of azulene is transferred to the five-membered ring, so that each ring acquires a closed shell of 6 π electrons. The azulene molecule now has a dipolar structure with the direction of the dipole moment as shown:



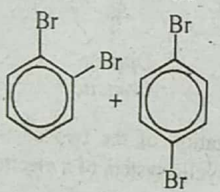
11. (a) *(a)*



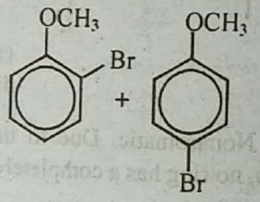
(b)



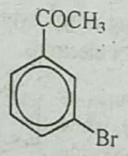
(c)



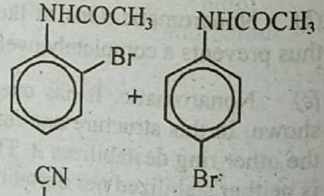
(d)



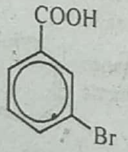
(e)



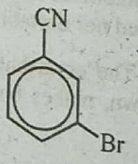
(f)



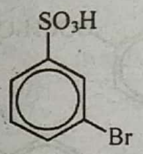
(g)



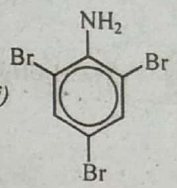
(h)



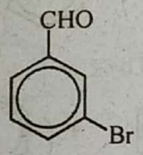
(i)



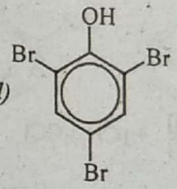
(j)



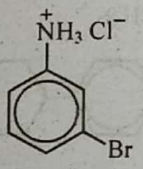
(k)



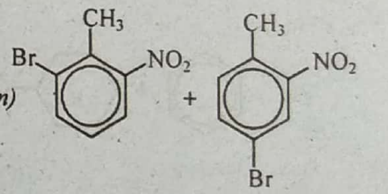
(l)



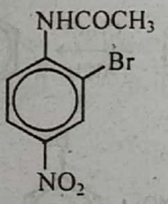
(m)



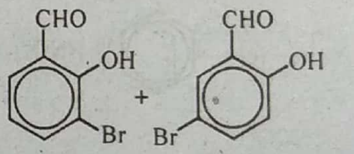
(n)



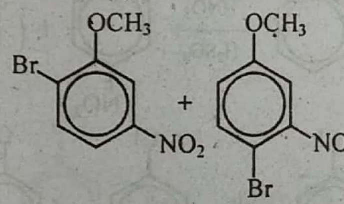
(o)



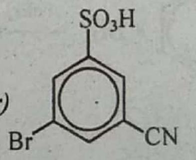
(p)



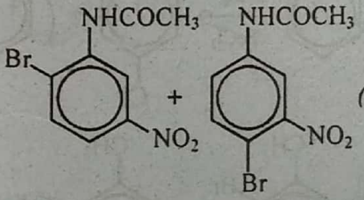
(q)



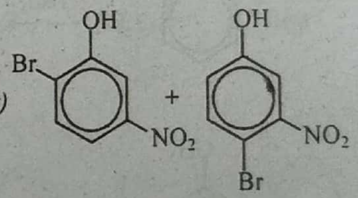
(r)



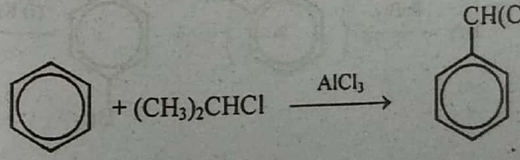
(s)



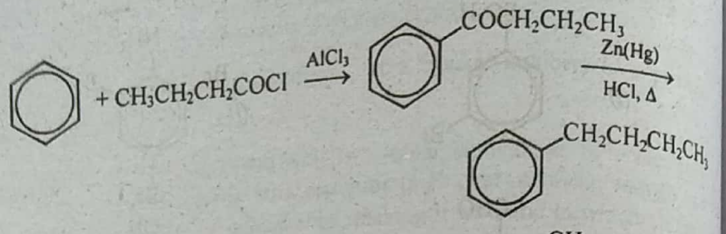
(t)



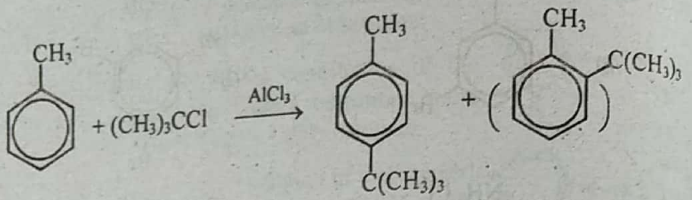
(b) *(a)*



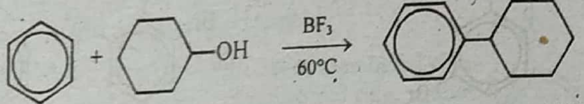
(b)



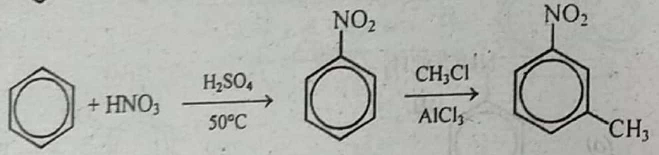
(c)



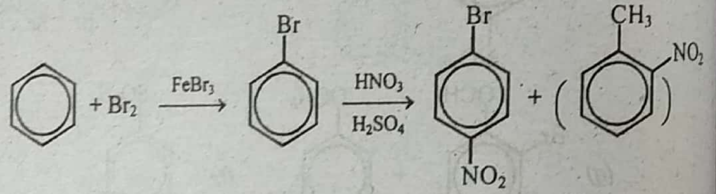
(d)



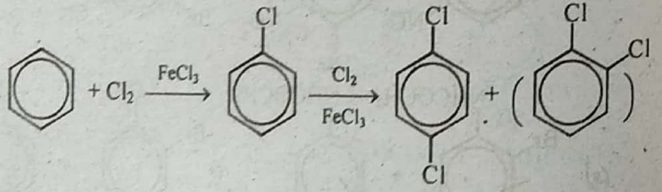
(e)



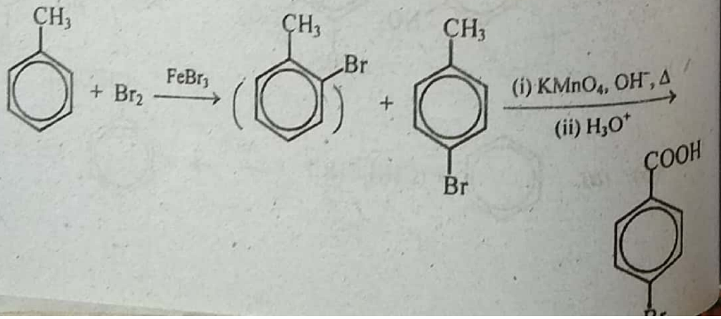
(f)



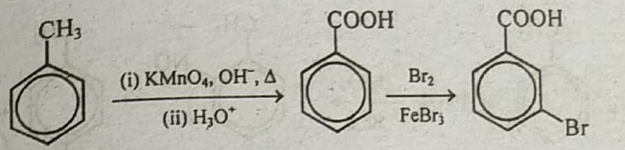
(g)



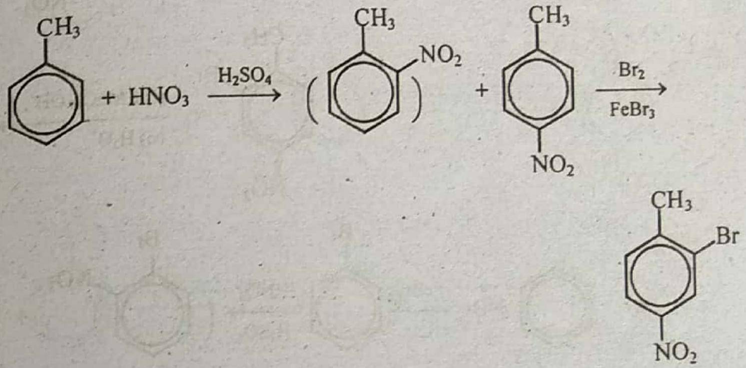
(h)



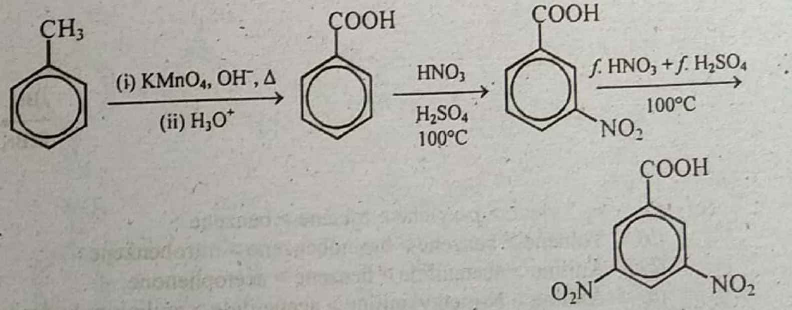
(i)



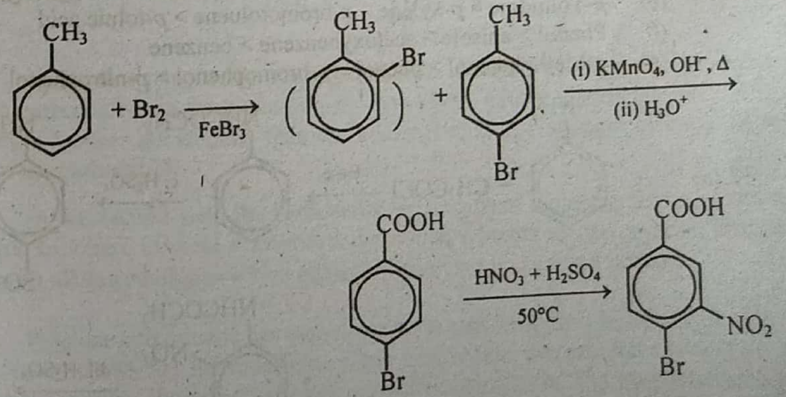
(j)



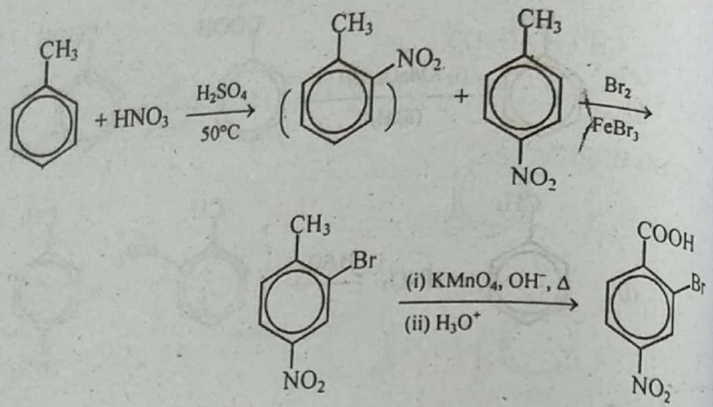
(k)



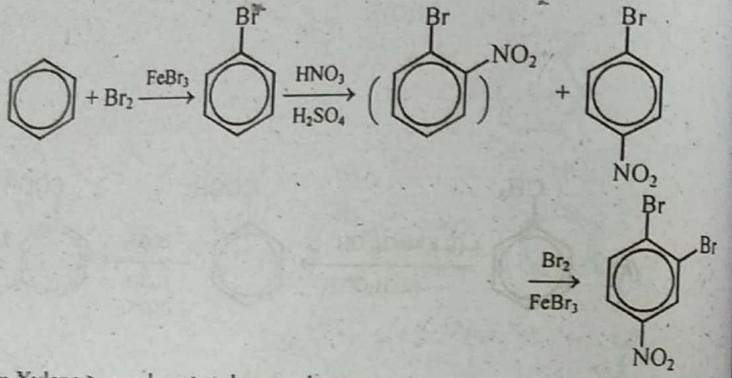
(l)



(m)



(n)



(c) (a) *m*-Xylene > *p*-xylene > toluene > benzene

(b) Toluene > benzene > bromobenzene > nitrobenzene

(c) Aniline > acetanilide > benzene > acetophenone

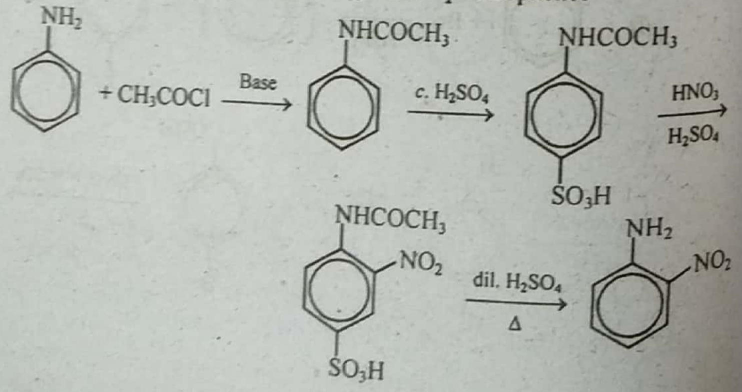
(d) Aniline > N-methylaniline > acetanilide > anilinium hydrogen sulfate

(e) *p*-Toluidine > *p*-xylene > *p*-bromotoluene > *p*-toluic acid

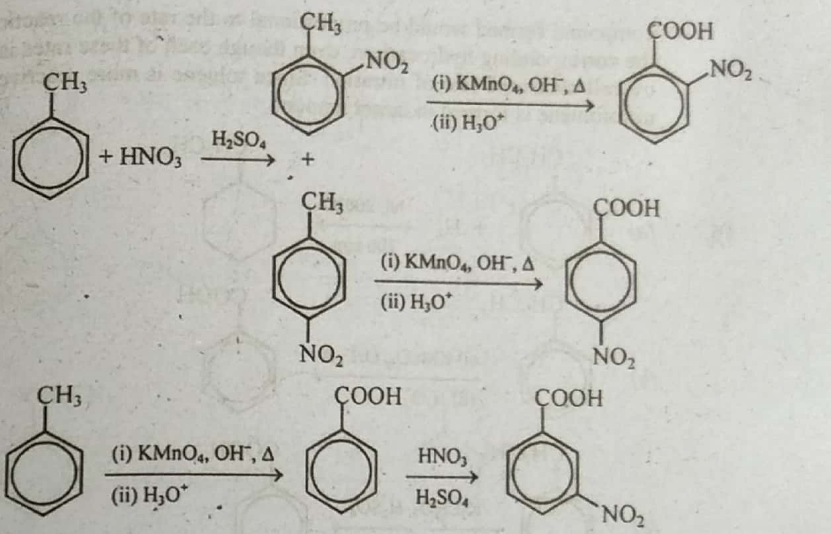
(f) Phenol > anisole > acetoxybenzene > benzene

(g) *p*-Methylphenol > phenol > *p*-bromophenol > *p*-nitrophenol

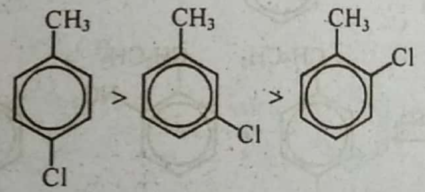
12.(a)



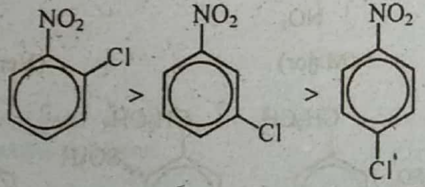
(b)



13. (a)



(b)



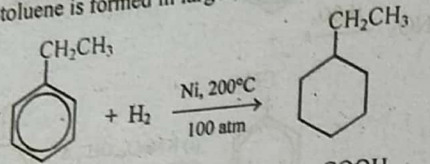
14. In the first step, both types of reactions involve the attack of an electrophile on a carbon atom to form a cationic intermediate, except that the aromatic ring, being a weaker nucleophile than the alkene, requires a stronger electrophile to form the carbocation.

In the second step, the carbocation arising from the aromatic ring loses a proton to a base to yield a substitution product, whereas the carbocation formed from an alkene combines with a nucleophile to give an addition product.

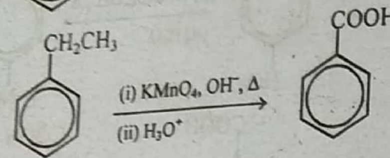
15. Benzene and toluene undergo nitration at a rate which is independent of the concentration of the hydrocarbons. This means that the rate-determining step does not involve the attack of NO_2^+ on these compounds. The rate-determining step then must be the formation of the nitronium ion.

Nitration of an equimolal mixture of benzene and toluene would not give an equimolal mixture of nitrobenzene and nitrotoluene. The amount of each nitro compound formed would be proportional to the rate of the reaction of NO_2^+ with the corresponding hydrocarbon, even though each of these rates is faster than the overall measured rate of nitration. Since toluene is more reactive than benzene, nitrotoluene is formed in larger amount.

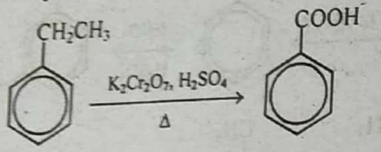
16. (a)



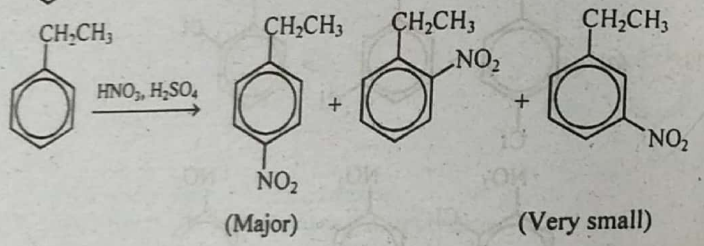
(b)



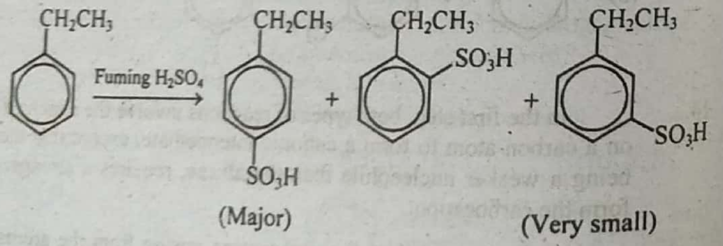
(c)



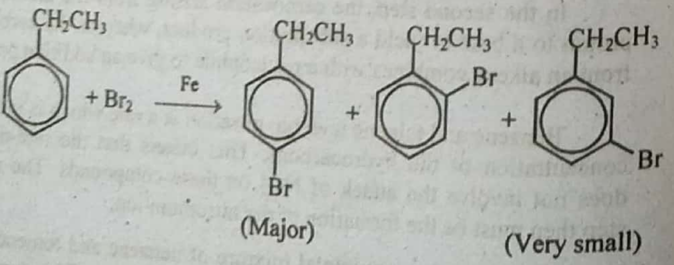
(d)



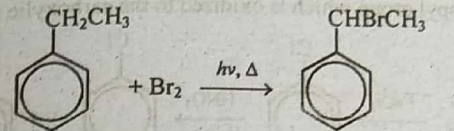
(e)



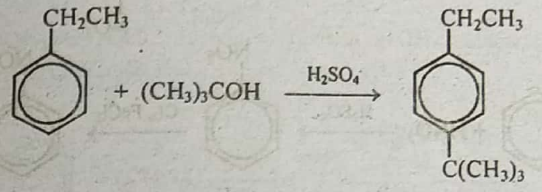
(f)



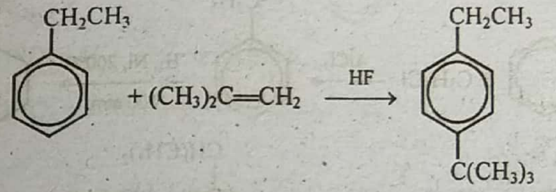
(g)



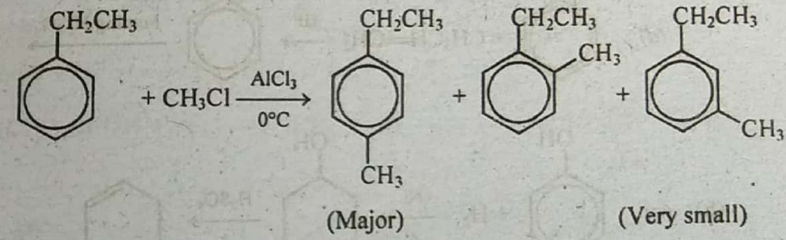
(h)



(i)



(j)



17. (a) Benzene dissolves in fuming H_2SO_4 due to protonation, whereas cyclohexane does not.

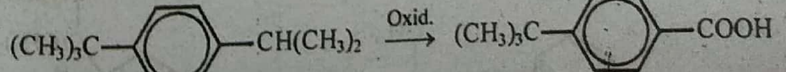
(b) Cyclohexene adds a molecule of Br_2 in CCl_4 and thus discharges its colour; benzene does not react with Br_2 under these conditions.

(c) Toluene is oxidized to benzoic acid by alkaline $KMnO_4$ and thus discharges its colour; benzene is not oxidized under such mild conditions.

(d) Ethylbenzene is oxidized to benzoic acid by alkaline $KMnO_4$ and thus discharges its colour; chlorobenzene does not discharge the colour of $KMnO_4$. These can also be distinguished by elemental analysis.

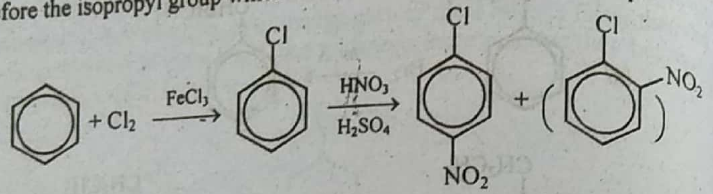
(e) 1-Phenylcyclohexene decolorizes Br_2 in CCl_4 as in (b), whereas cyclohexylbenzene does not.

18.

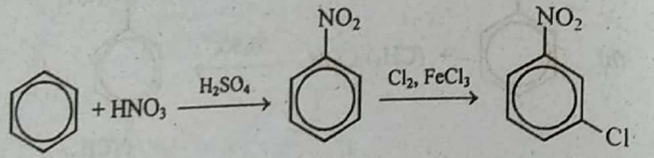


Since *t*-butyl group does not contain hydrogen at the benzylic carbon atom, which is required for initial oxidation of the side chain, it is not oxidized. It is therefore the isopropyl group which is oxidized to the carboxylic group.

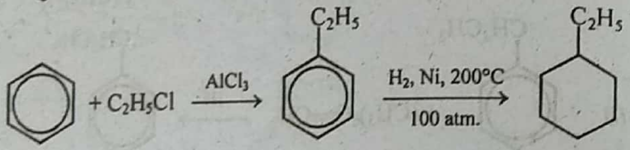
19. (a) *(a)*



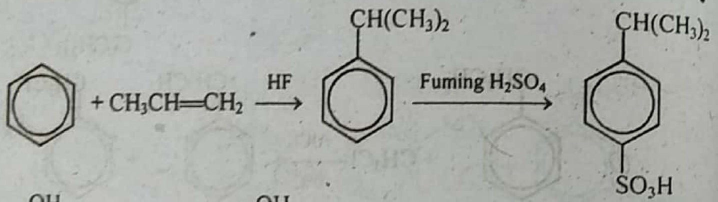
(b)



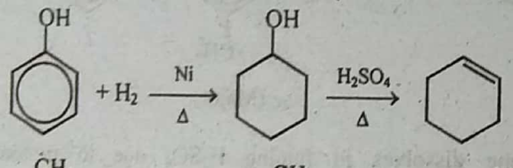
(c)



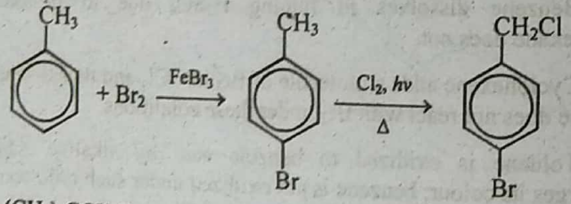
(d)



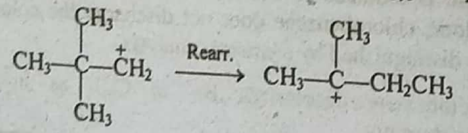
(b) *(a)*



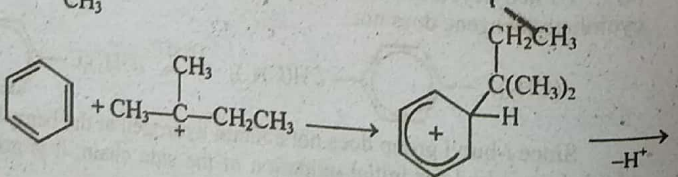
(b)

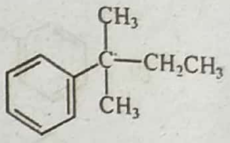


20. *(a)* $(CH_3)_3CCH_2Br + AlCl_3 \longrightarrow (CH_3)_3C\overset{+}{C}H_2 + Br\bar{A}lCl_3$



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{+}{C}H_2 \xrightarrow{\text{Rearr.}} CH_3-\underset{+}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3$$

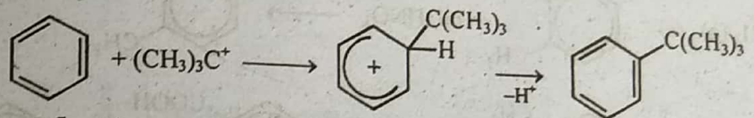




$Br\bar{A}lCl_3 + H^+ \longrightarrow HBr + AlCl_3$

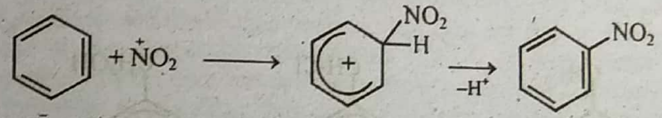
(b) $(CH_3)_3C-OH \xrightarrow{H_2SO_4} (CH_3)_3C-\overset{+}{O}H_2 + HSO_4^-$

$(CH_3)_3C-\overset{+}{O}H_2 \xrightarrow[-H_2O]{} (CH_3)_3C^+$



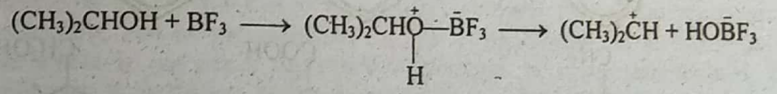
$HSO_4^- + H^+ \longrightarrow H_2SO_4$

(c) $HNO_3 + HNO_3 \longrightarrow H_2O + \overset{+}{N}O_2 + NO_3^-$

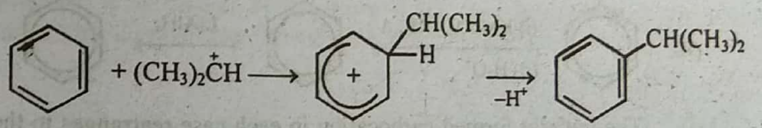


$NO_3^- + H^+ \longrightarrow HNO_3$

(d)

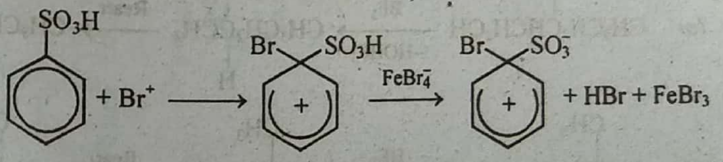


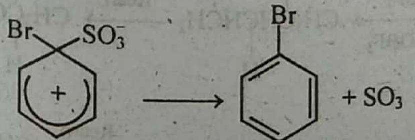
$$(CH_3)_2CHOH + BF_3 \longrightarrow (CH_3)_2CH\underset{\underset{H}{|}}{\overset{+}{O}}-\bar{B}F_3 \longrightarrow (CH_3)_2\overset{+}{C}H + HO\bar{B}F_3$$



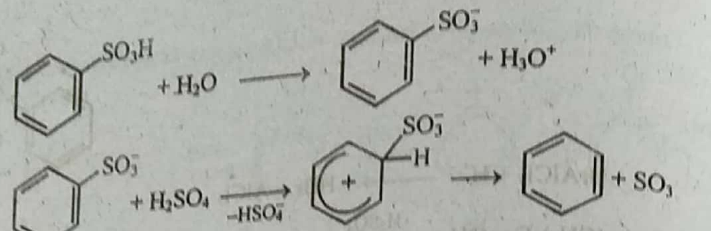
$HO\bar{B}F_3 + H^+ \longrightarrow H_2O{:}BF_3$

(e) $Br_2 + FeBr_3 \longrightarrow Br^+ + FeBr_4^-$



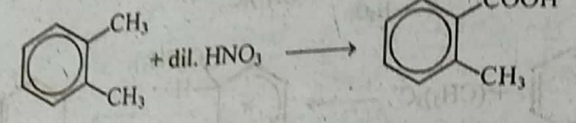


(f)

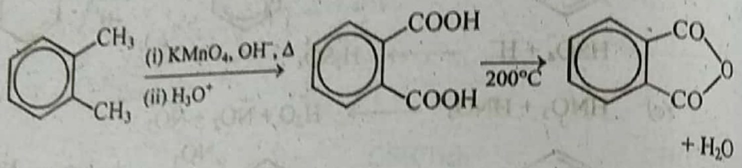


$$\mathrm{SO_3 + HSO_4^- + H_3O^+ \longrightarrow 2H_2SO_4}$$

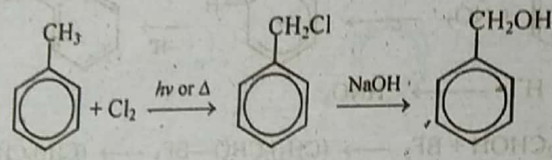
21. (a) (a)



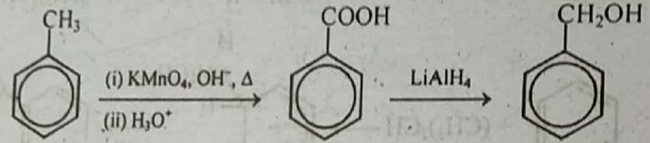
(b)



(b) (i)

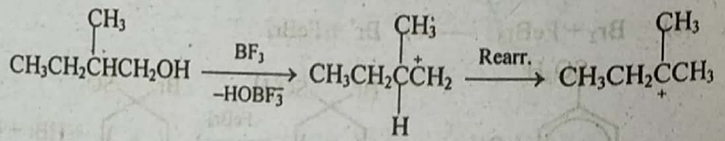


(ii)



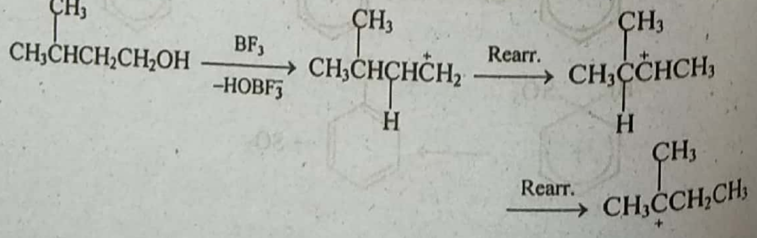
22. (i) The initially formed carbocation in each case rearranges to the same more stable tertiary carbocation as follows:

(a)



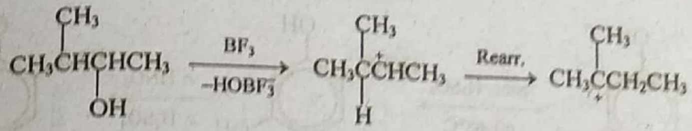
$$\mathrm{CH_3CH_2\overset{CH_3}{C}HCH_2OH \xrightarrow[-HOBF_3^-]{BF_3} CH_3CH_2\underset{H}{\overset{CH_3}{C}}\overset{+}{C}H_2 \xrightarrow{Rearr.} CH_3CH_2\underset{+}{\overset{CH_3}{C}}CH_3}$$

(b)



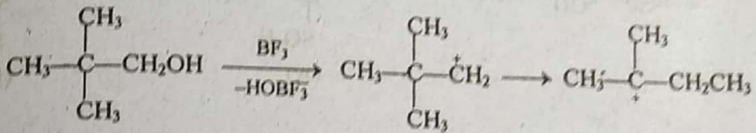
$$\mathrm{CH_3\overset{CH_3}{C}HCH_2CH_2OH \xrightarrow[-HOBF_3^-]{BF_3} CH_3\overset{CH_3}{C}H\underset{H}{C}H\overset{+}{C}H_2 \xrightarrow{Rearr.} CH_3\underset{H}{\overset{CH_3}{C}}\overset{+}{C}HCH_3 \xrightarrow{Rearr.} CH_3\underset{+}{\overset{CH_3}{C}}CH_2CH_3}$$

(c)



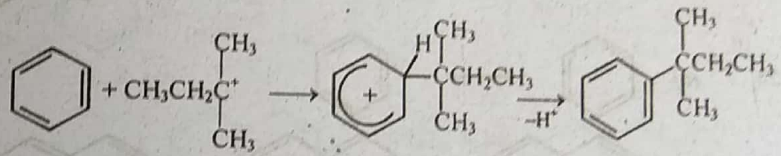
$$\mathrm{CH_3\overset{CH_3}{C}H\underset{OH}{C}HCH_3 \xrightarrow[-HOBF_3^-]{BF_3} CH_3\underset{H}{\overset{CH_3}{C}}\overset{+}{C}HCH_3 \xrightarrow{Rearr.} CH_3\underset{+}{\overset{CH_3}{C}}CH_2CH_3}$$

(d)

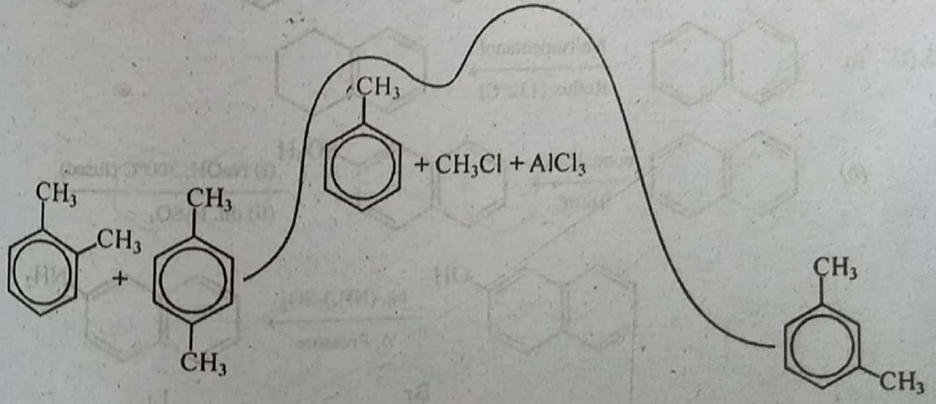


$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2OH \xrightarrow[-HOBF_3^-]{BF_3} CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\overset{+}{C}H_2 \longrightarrow CH_3{-}\underset{+}{\overset{CH_3}{C}}{-}CH_2CH_3}$$

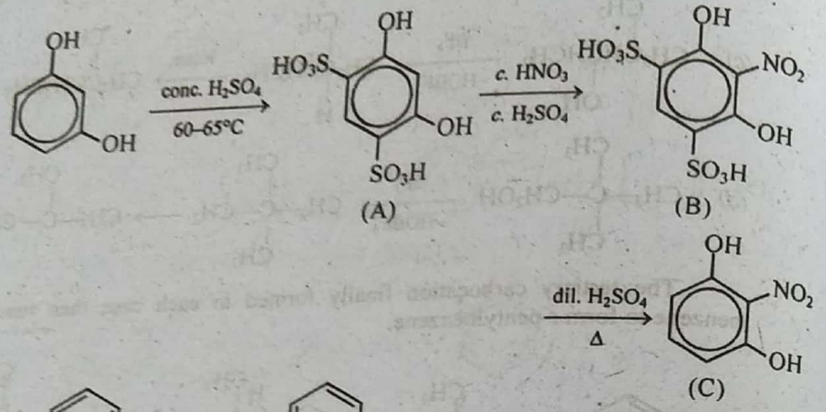
The tertiary carbocation finally formed in each case then reacts with benzene to form *t*-pentylbenzene.



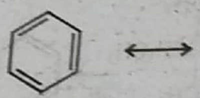
(ii) In the reaction of toluene with methyl chloride in the presence of $AlCl_3$, *o*- and *p*-xylenes are the kinetic products, i.e., they are formed faster, whereas *m*-xylene is the thermodynamic product, i.e., it is more stable. The lower temperature (0°C) does not provide sufficient energy of activation required for the formation of *m*-xylene; only *o*- and *p*-xylenes are formed, which require less energy of activation. At higher temperature (80°C), the energy of activation is available for the formation of all the xylenes. Moreover, the process of alkylation is reversible, and *o*- and *p*-xylenes are easily dealkylated but *m*-xylene being more stable is not easily dealkylated. Therefore, at higher temperature, the equilibrium is in favour of the more stable *m*-xylene which is the principal product. This will be clear from the following energy diagram:



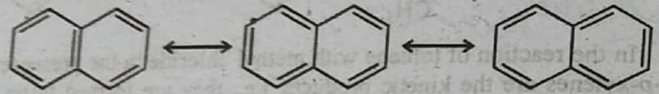
23.



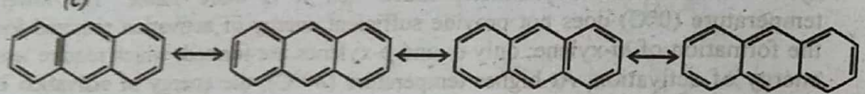
24. (a)



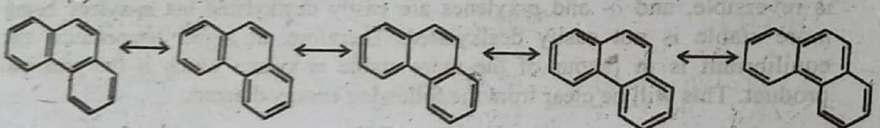
(b)



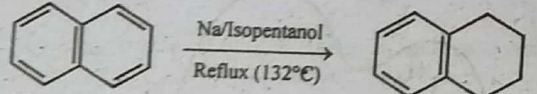
(c)



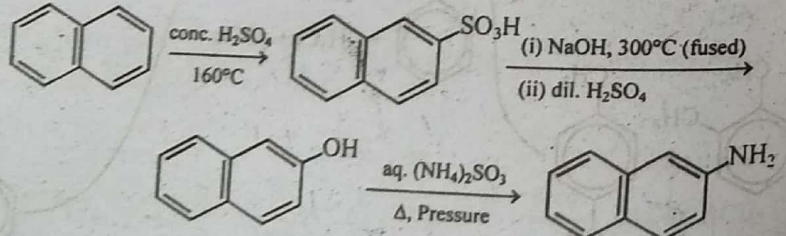
(d)



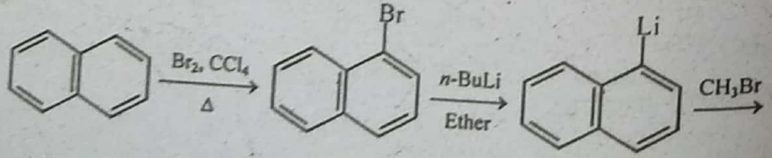
25.(i) (a)

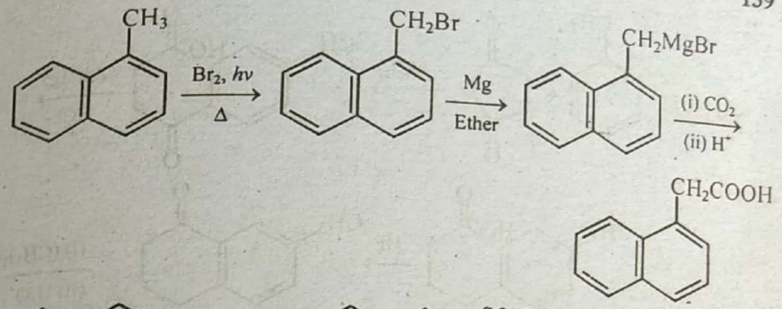


(b)

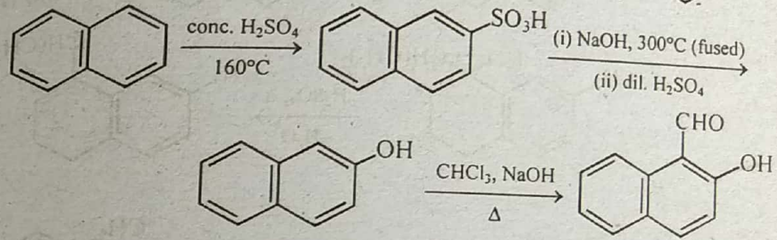


(c)

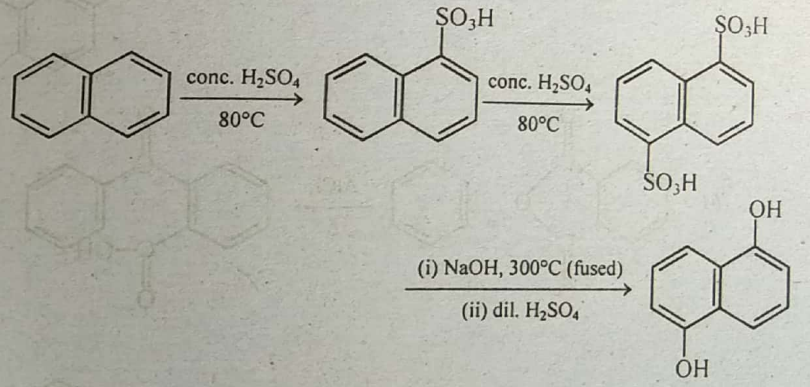




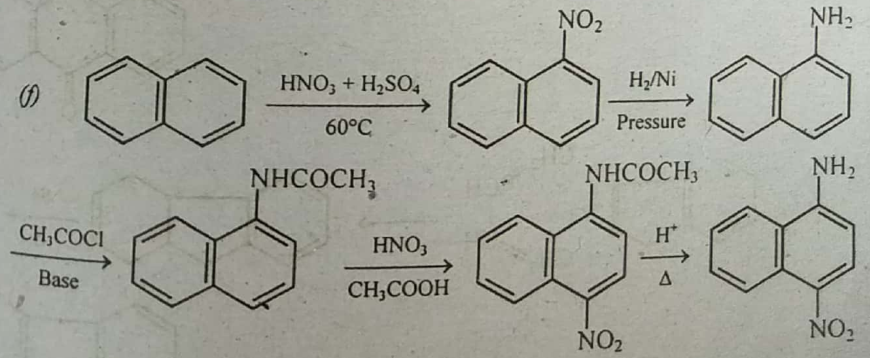
(d)



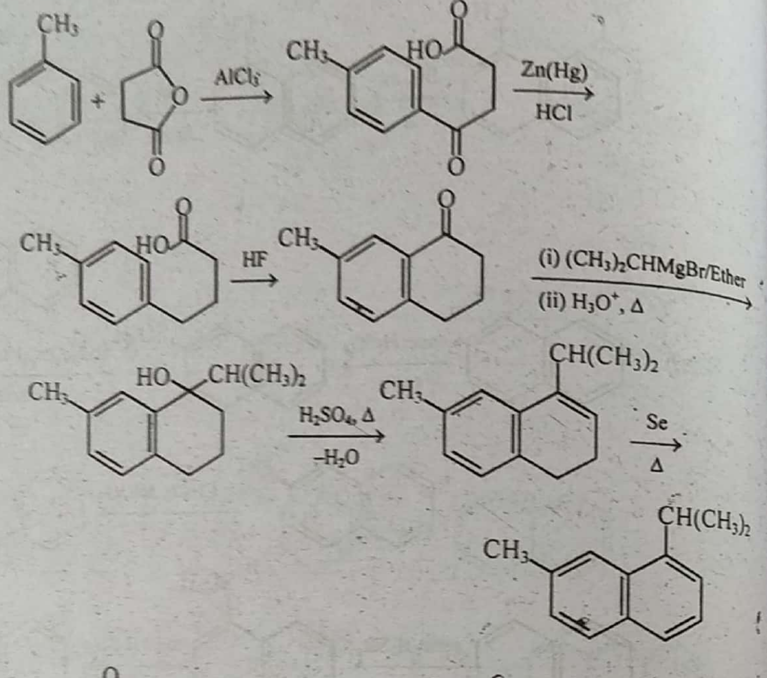
(e)



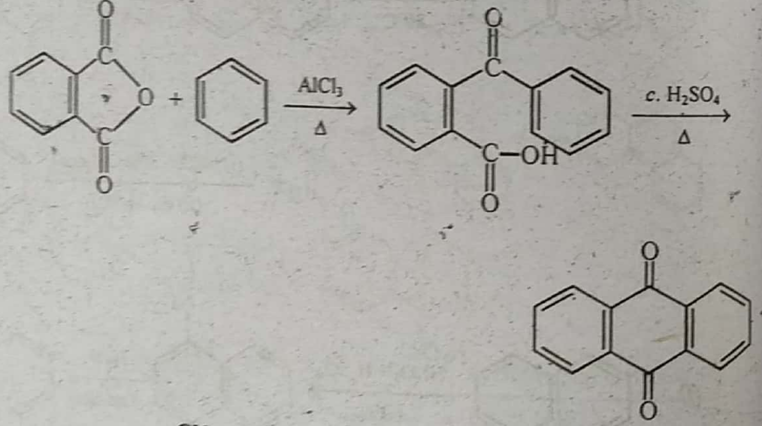
(f)



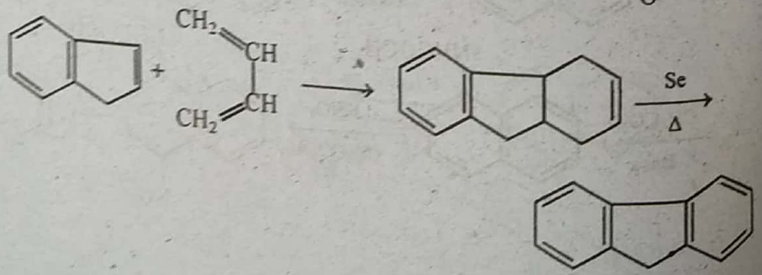
(ii) (a)



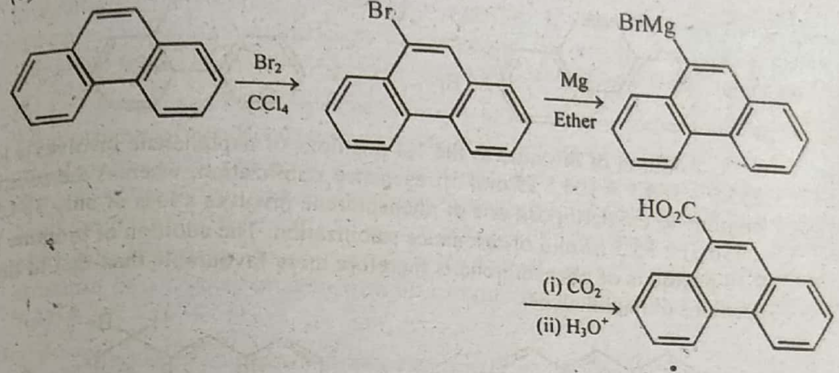
(b)



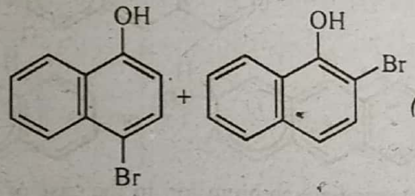
(c)



(d)

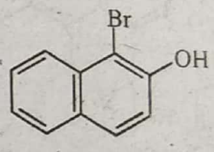


(iii) (a)

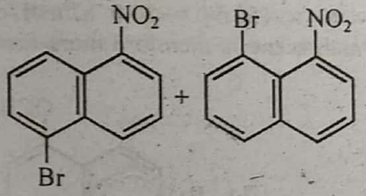


(Major)

(b)

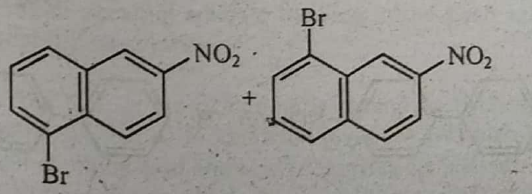


(c)

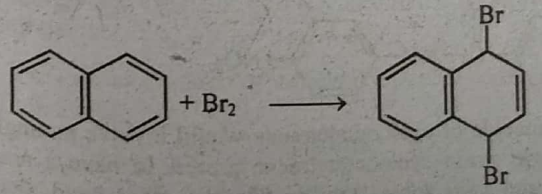


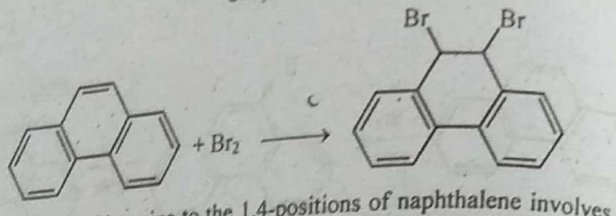
(Major)

(d)



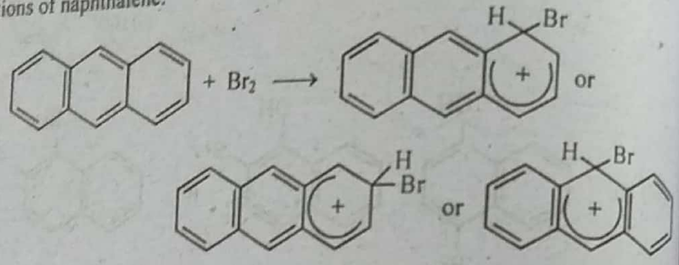
26. (a)





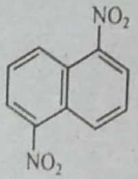
Addition of bromine to the 1,4-positions of naphthalene involves a loss of 255.0 – 150.5 = 104.5 kJ/mol of resonance stabilization, whereas the addition of bromine to the 9,10-positions of phenanthrene involves a loss of only 384.5 – (2 × 150.5) = 83.5 kJ/mol of resonance stabilization. The addition of bromine to the 9,10-positions of phenanthrene is therefore more favourable than that to the 1,4-positions of naphthalene.

(b)

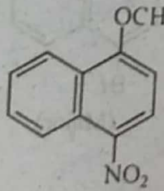


The formation of the intermediate arenium ion in the case of bromination of anthracene at 1- or 2-position involves a loss of 351.0 – 255.0 = 96.0 kJ/mol of resonance stabilization, whereas in the case of bromination at 9-position it involves a loss of only 351.0 – (2 × 150.5) = 50.0 kJ/mol of resonance stabilization. The bromination of anthracene is therefore more favourable at 9-position than at 1- or 2-position.

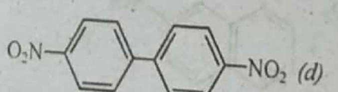
27. (a) A;



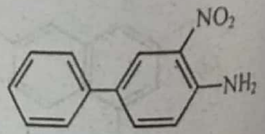
(b) B;



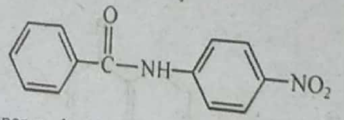
(c) A;



(d) B;



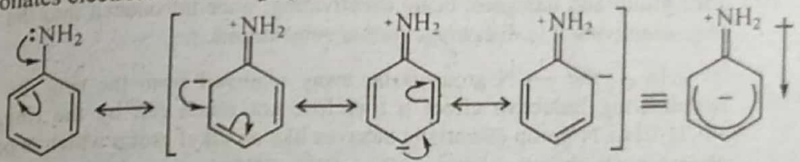
(e) B;



28. (a) A planar molecule of cyclooctatetraene would involve an angle strain. To overcome this angle strain cyclooctatetraene prefers to have a nonplanar tub-shaped molecule and gain some stability. On the other hand, the dianion of cyclooctatetraene has special stability associated with the closed shell of π molecular orbitals having a delocalized system of 10 (4n + 2) π electrons. This special stabilization is sufficient to overcome the angle strain of a planar octagonal ring. The dianion of cyclooctatetraene is therefore a planar molecule.

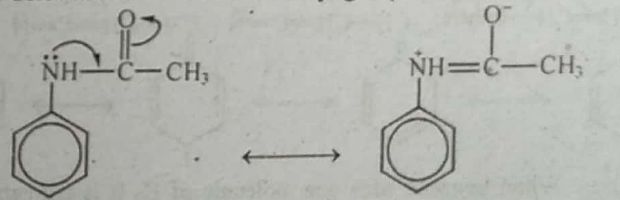
(b) As explained in (a), cyclooctatetraene has a tub-shaped molecule in which the p orbitals of one C=C are not coplanar with those of a neighbouring C=C, and therefore there can be no effective overlap between them for delocalization. The molecule, in fact, has an alternating system of single and double bonds with bond lengths of 1.50 Å and 1.35 Å, respectively. On the other hand, the dianion of cyclooctatetraene has a delocalized system of ten π electrons in a planar structure of a regular octagon with all carbon-carbon bonds of equal lengths of 1.41 Å.

(c) Although nitrogen withdraws electrons from the ring by inductive effect, it donates electrons to the ring by resonance effect as follows:



Since the resonance effect is stronger than the inductive effect in the case of aniline, the direction of the dipole moment is toward the ring.

(d) The electron pair of nitrogen which activates the ring by resonance effect is also partially delocalized toward the carbonyl group of acetanilide.



It therefore does not activate the ring to the same extent as in aniline, toward electrophilic substitution.

(e) The NH_2 group of aniline is strongly activating and ortho/para-directing. Therefore, aniline on bromination gives 2,4,6-Tribromoaniline. Since nitration is brought about by acid, the acid protonates the NH_2 group to $^+NH_3$ group which is deactivating and meta-directing. Nitration of aniline therefore gives m-nitroaniline.

(f) The rate of nitration of aromatic compounds depends on the formation of NO_2^+ from HNO_3.

$$HONO_2 + HNO_3 \rightleftharpoons H_2O + NO_2^+ + NO_3^-$$

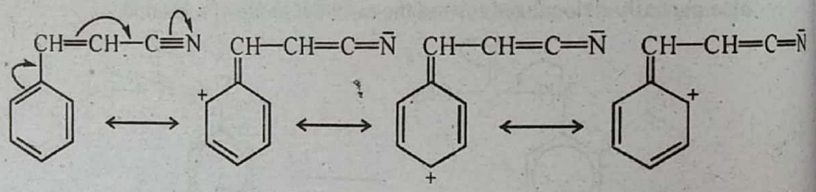
The addition of NO_3^- retards the formation of NO_2^+, by the common ion effect, and thus retards the nitration of aromatic compounds. On the other hand, H_2SO_4, being a stronger acid, easily protonates HNO_3 to facilitate the formation of NO_2^+, and thus accelerates the process of nitration:

$$HONO_2 + H_2SO_4 \rightleftharpoons H_2O + NO_2^+ + HSO_4^-$$

(g) Although the positions 4 and 6 of *m*-xylene are the most active sites in the ring for further alkylation but these are sterically hindered, particularly when a large alkyl group is to be introduced. If *m*-xylene is initially alkylated by the tertiary butyl group at these positions, it undergoes dealkylation (a tertiary alkyl group is most easily cleaved) to be realkylated at thermodynamically more stable position, e.g., position 5 in this case. Thus, *m*-xylene reacts with *t*-butyl chloride in the presence of $AlCl_3$ to give 5-*t*-butyl-1,3-dimethylbenzene.

(h) Since an alkyl group is activating, once it is introduced into an aromatic ring it activates the ring to facilitate further alkylation. On the other hand, the nitro group and halogens, being deactivating, once introduced into the aromatic ring, deactivate it to discourage further substitution.

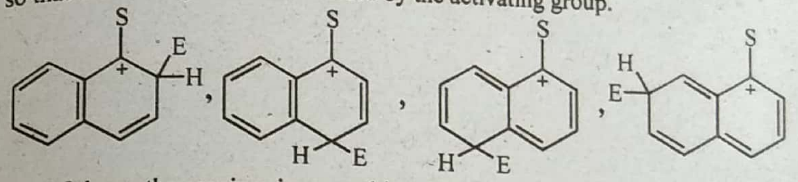
(i) In A, the —CN group is far away removed from the ring. Its electron-withdrawing inductive effect is therefore not much felt by the ring, and the $—CH_2CH_2CN$ group essentially behaves like an alkyl group which is ortho/para-directing. On the other hand, in B, —CH═CHCN group deactivates the ring by resonance effect, and it deactivates the ortho and para positions more than the meta position. It is therefore meta-directing and undergoes nitration at meta position.



(j) When benzene adds one molecule of H_2 it is converted to more reactive 1,3-cyclohexadiene. Further addition of H_2 would therefore preferably occur in 1,3-cyclohexadiene until fully saturated molecule of cyclohexane is obtained involving the addition of three molecules of H_2. Each molecule of benzene will consume three molecules of H_2 before another molecule of benzene starts reacting. In this way, 2/3 of benzene remains unreacted when the whole of H_2 has been consumed if they are used in equimolar quantities.

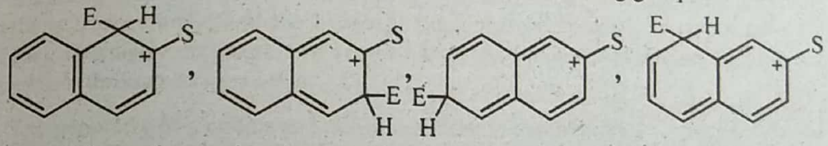
(k) Aromatic compounds, being highly stable, generally react with bromine to give substitution products, rather than addition products. However, in phenanthrene, the 9,10-bond has the double bond character almost comparable, showing the same reactivity, to an olefinic double bond. Bromine therefore adds across the 9,10-bond of phenanthrene almost as easily as across a pure olefinic double bond, to give 9,10-dibromo-9,10-dihydrophenanthrene, $C_{14}H_{10}Br_2$.

(l) In the case of naphthalene having an activating group at 1-position, the intermediate arenium ions obtained as a result of the attack by an electrophile at only four of the available vacant positions have a resonance contributing structure that contains + charge at the carbon atom bonded to the activating group so that the + charge can be stabilized by the activating group.



Out of these, the arenium ions resulting from the attack at positions 2 and 4 are the most stable because only these intermediates have an aromatic ring. This is why that an ortho/para-directing group (activating) at the 1-position of naphthalene directs substitution to the 2- and 4-positions.

In the case of naphthalene having an activating group at 2-position, the following intermediate arenium ions have a resonance contributing structure that contains + charge at the carbon atom bonded to the activating group.



Out of these, the arenium ion resulting from the attack at only position 1 has an aromatic ring, and is therefore the most stable. The activating group at 2-position of naphthalene therefore directs substitution almost exclusively to the 1-position.