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Chapter 9

Alcohols, Phenols and Ethers

CHAPTER'S SUMMARY

Alcohols and phenols are the hydroxy derivatives of aliphatic and aromatic hydrocarbons, respectively, and the hydroxyl functional group (OH) is responsible for most of their chemistry. In ethers, two alkyl or aryl, or one alkyl and one aryl groups are linked together through oxygen atom.

The geometry of alcohols and ethers is similar to that of water.

ALCOHOLS

Alcohols are classified as monohydric, dihydric, trihydric or polyhydric alcohols, depending on the number of hydroxyl groups present in their molecules.

The monohydric alcohols may be primary, secondary or tertiary alcohols, depending on whether the hydroxyl group is attached to a primary, secondary or tertiary alkyl group, respectively.

Nomenclature

The simple alcohols are generally known by their common names, as alkyl alcohols, the substituents in the alkyl group being indicated by the Greek letters. The other alcohols are generally named according to the IUPAC system, as alkanols, following the general rules of this system. In IUPAC system, if a functional group is used as a suffix, it becomes a part of the parent name and gets the highest priority in numbering the chain.

Preparation of Alcohols

Although many methods are available for the preparation of alcohols, only the more important preparations of representative nature are mentioned here. Alcohols are generally prepared by the:

1. Hydration of alkenes.

2. Hydrolysis of alkyl halides by means of water or an aqueous alkali.

3. Reaction of a Grignard reagent with a carbonyl compound. Formaldehyde gives a primary alcohol, other aldehydes give secondary alcohols and ketones give tertiary alcohols.

4. Reduction of aldehydes and ketones either catalytically or by chemical reducing agents.

Physical Properties of Alcohols

The physical properties of alcohols are generally governed by the hydroxyl group but are influenced by the alkyl group. Lower alcohols behave more like water and are miscible with it, whereas the higher alcohols more resemble the corresponding hydrocarbons, the alcohols with four and five carbon atoms being at the borderline. In general, the physical properties of alcohols change gradually with molecular weight in consistence with the generalizations explained earlier in the case of hydrocarbons.

Reactions of Alcohols

Some of the more important reactions of alcohols are as under.

1. **Reaction with metals.** Alcohols react readily with alkali metals to form metal alkoxides which are extremely useful reagents for organic syntheses.

2. **Esterification.** Alcohols react with carboxylic acids in the presence of conc. H_2SO_4 to form esters.

3. **Reaction with inorganic acids.** Alcohols also react with oxygen-containing inorganic acids, such as H_2SO_4 and H_3PO_4, to form esters. Dimethyl sulfate, obtained by the reaction of methanol with conc. H_2SO_4 is a very useful methylating agent. Esters of H_3PO_4 are very important in biochemical reactions.

4. **Oxidation of alcohols.** Alcohols can be oxidized by various oxidizing agents. Different types of alcohols give different oxidation products.

5. **Dehydration of alcohols.** Alcohols on heating at 180°C with strong acids such as H_2SO_4, undergo intramolecular dehydration to form alkenes. Intermolecular dehydration of alcohols result in the formation of ethers.

6. **Conversion to alkyl halides.** On treatment with a variety of reagents such as hydrogen halides, phosphorus trihalides or thionyl chloride, alcohols are converted to alkyl halides, a synthetically very important class of organic compounds.

Distinction between Pri., Sec. and Tert. Alcohols

Distinction between pri., sec. and tert. alcohols can be made on the basis of their behaviour either toward a solution of chromic oxide in aq. H_2SO_4 or toward the Lucas test.

POLYHYDRIC ALCOHOLS

The most common of the polyhydric alcohols are glycol (a dihydric alcohol) and glycerol (a trihydric alcohol).

Glycol

Glycol is prepared on commercial scale by the acid-catalysed hydrolysis of ethylene oxide which is obtained by the air oxidation of ethylene.

It is a colourless viscous liquid, miscible with water in all proportions. A 50% solution of glycol in water is an excellent antifreeze for automotives.

The chemical reactions of glycol are essentially those of the hydroxyl group, but one hydroxyl group reacts completely before the other starts. Glycols undergo oxidative cleavage to form carbonyl fragments.

Glycerol

Glycerol is obtained on commercial scale as a by-product in the soap industry where soap is made by the alkaline hydrolysis of oils and fats which are glycerol esters of long chain carboxylic acids. It is also synthesized commercially from propene.

Glycerol is a viscous hygroscopic liquid and is used as a moistening agent. It is also used for making explosives, e.g., glyceryl trinitrate is used as dynamite.

Glycerol contains two primary and one secondary alcoholic groups, and undergoes many of the reactions expected of these types of alcohols. Glycerol also undergoes oxidative cleavage.

THIOLS

Sulfur analogs of alcohols are called **thiols** which are named by adding the suffix *-thiol* to the name of the corresponding alkane.

Thiols can be prepared either by the reaction of an alkyl halide with thiourea, followed by hydrolysis or by the reaction of Grignard reagents with sulfur.

The most conspicuous property of thiols is their foul odour. Thiols resemble alcohols in many of their reactions. However, oxidation of thiols yields disulfides which are reduced back to thiols.

PHENOLS

Phenols are the hydroxy derivatives of aromatic hydrocarbons. The word phenol is also used as a name of the parent member of the family, i.e., hydroxybenzene.

Nomenclature

Phenol is used as a parent name in most of its derivatives. Many of the phenol derivatives are known by their common names. The hydroxy derivatives of polycyclic aromatic hydrocarbons are named in a similar way.

Preparations

Phenol and its homologs are extracted from wood, coal and petroleum distillates. Synthetically, phenol itself is prepared on commercial scale from benzene mainly by three routes:

1. By the sulfonation of benzene, followed by the fusion of the sodium salt of benzenesulfonic acid with sodium hydroxide.

2. By the chlorination of benzene, followed by the hydrolysis of chlorobenzene with 10% aq. NaOH at 360°C under high pressure.

3. By the air-oxidation of cumene which is obtained by the alkylation of benzene with propylene.

4. Phenols in general can be prepared by the hydrolysis of aryl diazonium salts formed by the reaction of primary aromatic amines with HNO_2.

5. Phenol derivatives are prepared from phenol through electrophilic aromatic substitution reactions.

Physical Properties of Phenols

Simple monohydric phenols are either liquid or low-melting crystalline solid with distinctive odour. Phenols are generally colourless; the colour of some phenols is due to the presence of their oxidation products as impurities.

Phenols form stronger H-bond than the corresponding cyclic alcohols, resulting in their higher b.pts. and greater solubility in water. Symmetrical phenols have higher b.pts. than the unsymmetrical phenols, particularly those having an electronegative substituent ortho to the hydroxyl group, e.g., in *o*-nitrophenol, which can be attributed to chelation.

Phenol containing 5% of water is known as carbolic acid, and is used as disinfectant and germicide.

Acidity of Phenols

Phenols are much more acidic than alcohols, though considerably weaker acids than carboxylic acids. The acidity of phenols is increased by the electron-withdrawing substituents on the aromatic ring, while it is decreased by the electron-donating substituents. 2,4,6-Trinitrophenol (commonly known as picric acid) is nearly as strongly acidic as mineral acids.

Reactions of Phenols

Phenols generally give two types of reactions: (i) the reactions due to the hydroxyl group, mostly involving the cleavage of the O—H bond; (ii) the reactions due to the aromatic ring, most of the reactions falling in this category.

1. Salt formation. Most phenols form their sodium salts on treatment with aq. NaOH.

2. Ether formation. Phenols form alkyl aryl ethers on treatment with alkyl halides in the presence of aq. NaOH. The reaction is known as Williamson ether synthesis.

3. Ester formation. Phenols react with acid chlorides or acid anhydrides in the presence of an acid or a base to form esters.

4. Electrophilic substitution. The most striking feature of a phenol is the very high reactivity of its ring toward electrophilic substitution, due to the presence of the strongly activating hydroxyl group. Thus, phenols undergo most of the electrophilic substitution reactions, such as nitration, halogenation, Friedel-Crafts reaction, sulfonation and nitrosation. Special care should be taken to prevent polysubstitution and oxidation. Under basic conditions, phenoxide ion can react with even weaker electrophiles, such as aryldiazonium ion, carbon dioxide and dichlorocarbene.

5. Diazo coupling. Phenols react with an aryldiazonium ion, $Ar\overset{+}{N}_2$ in a basic solution, to give the corresponding arylazophenols.

6. Carbonation. Salicylic acid is prepared by the reaction of sod. phenoxide with CO_2 at 125°C under pressure, followed by acidification. At 250°C, the para isomer, a thermodynamic product, is formed.

7. Formylation. Salicylaldehyde is formed by the treatment of phenol with chloroform in the presence of an aq. alkali.

8. Formation of phenol-formaldehyde resin. On heating with formaldehyde in the presence of a dilute acid or an alkali, phenol forms a polymer known as Bakelite.

9. Oxidation. Phenols are easily oxidized by various oxidizing agents, the nature of the product depending on the oxidizing agent used. The most important reaction is the oxidation of 1,2- or 1,4- dihydroxybenzene to quinones which can easily be reduced back to the dihydroxybenzenes.

Chemical Tests for Phenols

Phenol reacts readily with bromine water to form a precipitate of 2,4,6-tribromophenol. It also gives violet coloration with neutral $FeCl_3$ solution in water or alcohol. Other phenols may give different colours.

ETHERS

Organic molecules involving C—O—C linkages are known as **ethers**. They may be aliphatic, aromatic or mixed.

Nomenclature

Ethers may be commonly named either as dialkyl (or diaryl or alkyl aryl) ethers or as alkoxy derivatives of hydrocarbons. In the IUPAC system, they are named by using the prefix *oxa-* for the ether linkage in the chain.

Preparations of Ethers

Ethers may be prepared:

1. By the intermolecular dehydration of alcohols on heating with conc. H_2SO_4 at 140°C.

2. By the Williamson ether synthesis involving the reaction of an alkoxide or a phenoxide with a primary alkyl halide.

3. By the treatment of alkenes with mercuric acetate in the presence of an alcohol, followed by reduction with sodium borohydride.

Physical Properties of Ethers

The lower members of the ether family are either gases or volatile liquids, and their vapours are highly inflammable. The melting and boiling points of ethers are comparable with those of the corresponding hydrocarbons. Ethers have solubilities in water that are comparable with those of the alcohols of similar molecular weights. Ethers are generally less dense than water. They are readily soluble in organic solvents, and are also themselves used as solvent.

Reactions of Ethers

Generally the ethers are relatively inert to most reagents. Their reactions mostly involve the cleavage of the ether linkage.

1. **Cleavage of the ether linkage.** On prolonged heating with dil. H_2SO_4, ethers undergo hydrolysis to original alcohols; tertiary alkyl ethers yield alkenes. Treatment of ethers with hot conc. HI or HBr yields alkyl halides.

2. **Autoxidation.** Ethers on exposure to atmospheric oxygen form hydroperoxides and peroxides at α carbon atom.

3. **Halogenation.** Ethers on treatment with Cl_2 or Br_2 undergo halogenation replacing α-hydrogen.

CYCLIC ETHERS

Cyclic ethers have their oxygen atom as a part of a ring. Their chemistry is essentially the same as that of the open-chain ethers. Cyclic ethers having more than one ether linkage in their rings are called *polyethers*. Cyclic polyethers containing 4 or more ether linkages in a ring of 12 or more atoms are called **crown ethers**. Epoxides (three-membered cyclic ethers) and crown ethers have unusual properties and therefore deserve special attention.

Epoxides

Epoxides are named as alkene oxides, epoxyalkanes or oxiranes.

Ethylene oxide is prepared on industrial scale by the air oxidation of ethylene in the presence of a catalyst at an elevated temperature. In the laboratory, epoxides are prepared either by the treatment of alkenes with peracids or by the base-promoted intramolecular S_N2 displacement reaction of β-halo alcohols.

Epoxides undergo carbon-oxygen bond cleavage under acidic as well as alkaline conditions to form 1,2-diols. They react with a Grignard reagent to yield primary alcohols containing two more carbon atoms than the alkyl halides from which the Grignard reagent was prepared.

Crown Ethers

Crown ethers are named as *x*-crown-*y*, where *x* is the total number of atoms in the ring and *y* is the number of oxygen atoms. They form much more stable complexes with metal ions than do the simple ethers. They are called crown ethers because cations can be crowned and uncrowned with them.

The metal ion complexing property of the crown ethers increases the solubility of salts, such as KF, in nonpolar solvents, such as benzene. The fluoride ion in this solution is relatively free from the influence of the potassium ion, and is better able to express its anionic reactivity. Thus, alkyl halides react with potassium fluoride in benzene containing 18-crown-6, providing a method for the preparation of an otherwise difficultly accessible alkyl fluoride.

Crown ethers have high specificity for cations. For example, 18-crown-6 shows high affinity for K^+, 15-crown-5 for Na^+ and 12-crown-4 for Li^+.

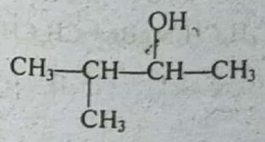
18-Crown-6 may be prepared by treating a mixture of triethylene glycol and its dichloride with aq. KOH.

Some naturally occurring polyethers can be used as antibiotics.

ANSWERS TO EXERCISES

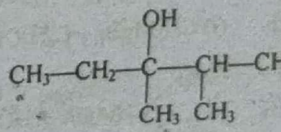
1. (a) 2,3,5-Trimethyl-3-hexanol
   (b) 2-Ethyl-3-methyl-1-pentanol
   (c) 3-Buten-1-ol
   (d) 1-(2-Propenyl)-3-buten-1-ol (or Diallylmethanol)
   (e) 1,1-Di-(2-propenyl)-3-buten-1-ol (or Triallylmethanol)
   (f) 1,3-Diphenyl-2-propanol (or Dibenzylmethanol)
   (g) 3-Pentanethiol

2. (a)



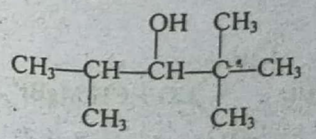
$CH_3{-}\underset{CH_3}{\underset{|}{CH}}{-}\overset{OH}{\overset{|}{CH}}{-}CH_3$

(b)



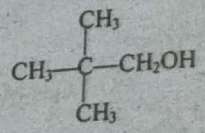
$CH_3{-}CH_2{-}\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}\underset{CH_3}{\underset{|}{CH}}{-}CH_3$

(c)



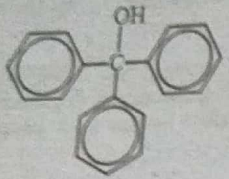
$CH_3{-}\underset{CH_3}{\underset{|}{CH}}{-}\overset{OH}{\overset{|}{CH}}{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}CH_3$

(d)

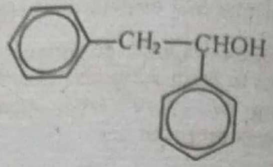


$CH_3{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}CH_2OH$

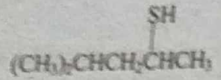
(e)



(f)

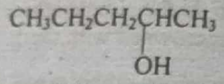


(g)



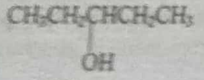
$(CH_3)_2CHCH_2\overset{SH}{C}HCH_3$

3. $CH_3CH_2CH_2CH_2CH_2OH$,
1-Pentanol
(Primary)



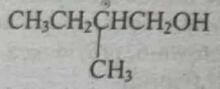
$CH_3CH_2CH_2\underset{OH}{C}HCH_3$

2-Pentanol
(Secondary)



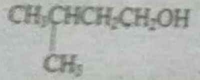
$CH_3CH_2\underset{OH}{C}HCH_2CH_3$

3-Pentanol
(Secondary)



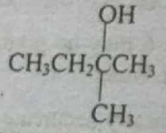
$CH_3CH_2\underset{CH_3}{C}HCH_2OH$

2-Methyl-1-butanol
(Primary)



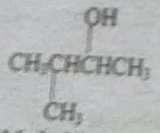
$CH_3\underset{CH_3}{C}HCH_2CH_2OH$

3-Methyl-1-butanol
(Primary)



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

2-Methyl-2-butanol
(Tertiary)



$CH_3\underset{CH_3}{C}H\overset{OH}{C}HCH_3$

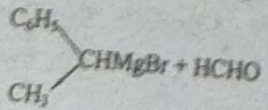
3-Methyl-2-butanol
(Secondary)

$(CH_3)_3CCH_2OH$
2,2-Dimethyl-1-propanol
(Primary)

4. (a) (i) $C_6H_5MgBr + CH_3CH_2CHO$ (ii) $CH_3CH_2MgBr + C_6H_5CHO$

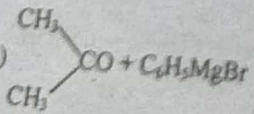
(b) (i) $CH_3MgBr + C_6H_5CH_2CHO$ (ii) $C_6H_5CH_2MgBr + CH_3CHO$

(c)



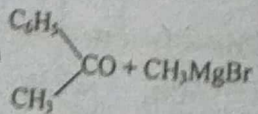
$(C_6H_5)(CH_3)CHMgBr + HCHO$

(d) (i)



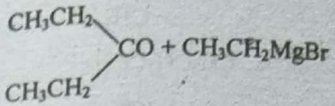
$(CH_3)(CH_3)CO + C_6H_5MgBr$

(ii)



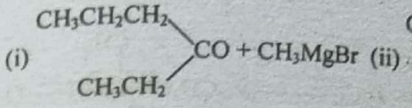
$(C_6H_5)(CH_3)CO + CH_3MgBr$

(e)



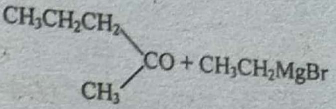
$(CH_3CH_2)(CH_3CH_2)CO + CH_3CH_2MgBr$

(f) (i)



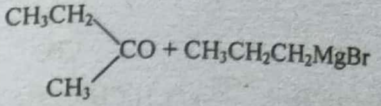
$(CH_3CH_2CH_2)(CH_3CH_2)CO + CH_3MgBr$

(ii)



$(CH_3CH_2CH_2)(CH_3)CO + CH_3CH_2MgBr$

(iii)



$(CH_3CH_2)(CH_3)CO + CH_3CH_2CH_2MgBr$

5. (a) 3-Methyl-3-pentanol < 3-Hexanol < 1-Hexanol

(b) Glycol has two hydroxyl groups in its molecule, and can form hydrogen bonds through both hydroxyl groups to form a larger association of the molecules which will require larger energy (higher temperature) to break for volatilization. On the other hand, isopropyl alcohol has only one hydroxyl group to form hydrogen bond. Its association will therefore break relatively easily and would require less energy (lower temperature).

6. (a) $CH_3CH_2CH_2OH \xrightarrow[130°C]{H_2SO_4} CH_3CH_2CH_2OCH_2CH_2CH_3$

(b) $CH_3CH_2CH_2ONa + (CH_3)_3CCl \rightarrow \underset{\text{(Major)}}{(CH_3)_2C{=}CH_2} + (CH_3)_3COCH_2CH_2CH_3$

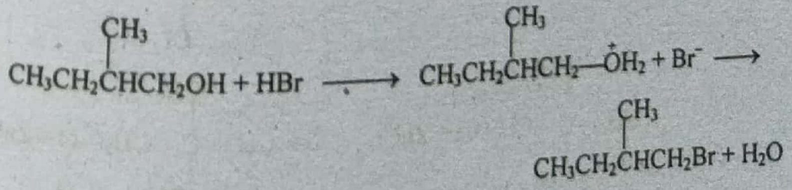
(c) $(CH_3)_3CONa + CH_3CH_2CH_2Br \rightarrow \underset{\text{(Major)}}{CH_3CH{=}CH_2} + (CH_3)_3COCH_2CH_2CH_3$

(d) $CH_3CH_2CH_2OH \xrightarrow[50°C]{K_2Cr_2O_7 + H_2SO_4} CH_3CH_2CHO \longrightarrow CH_3CH_2COOH$

(e) $CH_3CH_2CH_2OSO_2C_6H_5 \xrightarrow[\text{Acetone}]{\text{NaI}} CH_3CH_2CH_2I$

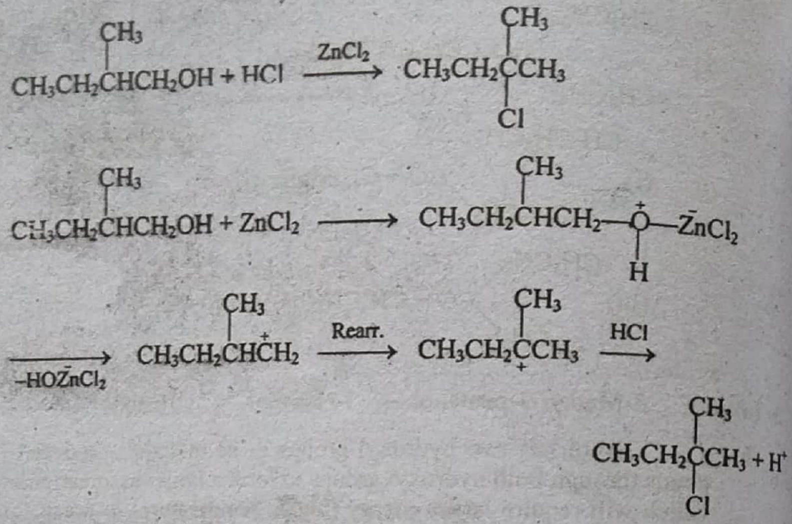
(f) $CH_3CH_2CH_2OH \xrightarrow[H_2SO_4]{HBr} CH_3CH_2CH_2Br$

7. (a)



$$CH_3CH_2\overset{CH_3}{C}HCH_2OH + HBr \longrightarrow CH_3CH_2\overset{CH_3}{C}HCH_2{-}\overset{+}{O}H_2 + Br^- \longrightarrow CH_3CH_2\overset{CH_3}{C}HCH_2Br + H_2O$$

(b)



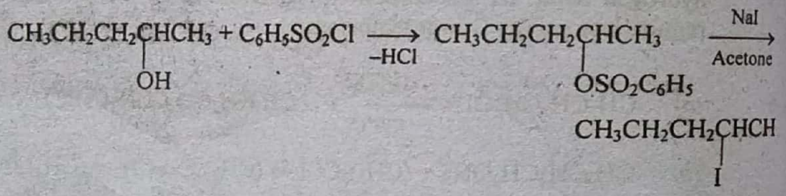
$$CH_3CH_2\overset{CH_3}{C}HCH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2\underset{Cl}{\overset{CH_3}{C}}CH_3$$

$$CH_3CH_2\overset{CH_3}{C}HCH_2OH + ZnCl_2 \longrightarrow CH_3CH_2\overset{CH_3}{C}HCH_2-\underset{H}{\overset{+}{O}}-\bar{Z}nCl_2$$

$$\xrightarrow[-HO\bar{Z}nCl_2]{} CH_3CH_2\overset{CH_3}{C}H\overset{+}{C}H_2 \xrightarrow{Rearr.} CH_3CH_2\underset{+}{\overset{CH_3}{C}}CH_3 \xrightarrow{HCl} CH_3CH_2\underset{Cl}{\overset{CH_3}{C}}CH_3 + H^+$$

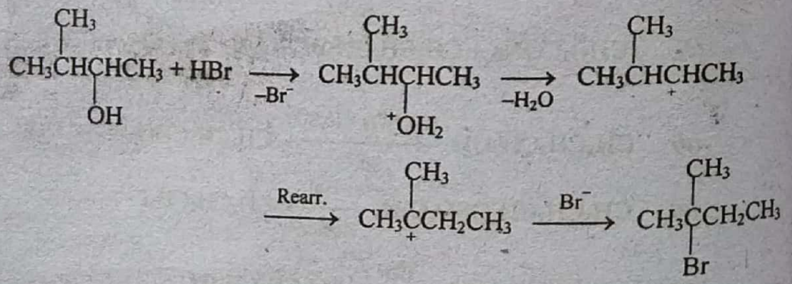
$$HO\bar{Z}nCl_2 + H^+ \longrightarrow H_2O + ZnCl_2$$

(c)



$$CH_3CH_2CH_2\underset{OH}{C}HCH_3 + C_6H_5SO_2Cl \xrightarrow[-HCl]{} CH_3CH_2CH_2\underset{OSO_2C_6H_5}{C}HCH_3 \xrightarrow[Acetone]{NaI} CH_3CH_2CH_2\underset{I}{C}HCH$$

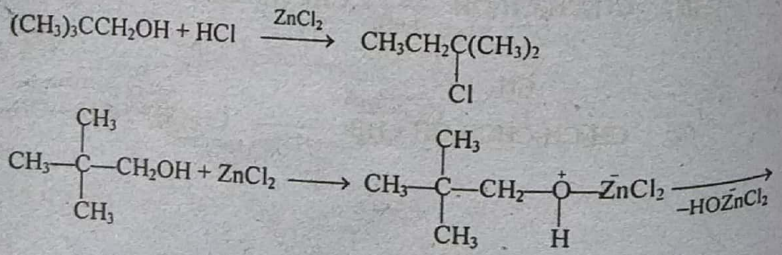
(d)



$$CH_3\overset{CH_3}{C}H\underset{OH}{C}HCH_3 + HBr \xrightarrow[-Br^-]{} CH_3\overset{CH_3}{C}H\underset{^+OH_2}{C}HCH_3 \xrightarrow[-H_2O]{} CH_3\overset{CH_3}{C}H\underset{+}{C}HCH_3$$

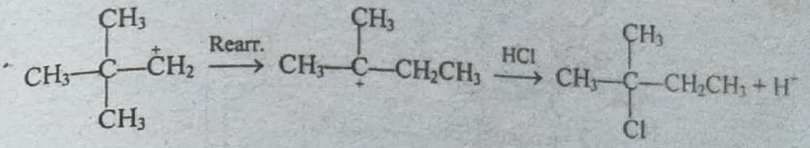
$$\xrightarrow{Rearr.} CH_3\underset{+}{\overset{CH_3}{C}}CH_2CH_3 \xrightarrow{Br^-} CH_3\underset{Br}{\overset{CH_3}{C}}CH_2CH_3$$

(e)



$$(CH_3)_3CCH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2\underset{Cl}{C}(CH_3)_2$$

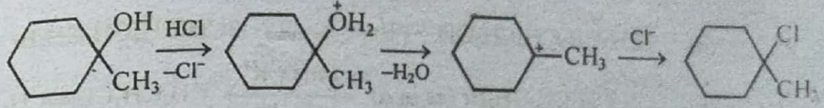
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2OH + ZnCl_2 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{H}{\overset{+}{O}}-\bar{Z}nCl_2 \xrightarrow[-HO\bar{Z}nCl_2]{}$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{+}{C}H_2 \xrightarrow{Rearr.} CH_3-\underset{+}{\overset{CH_3}{C}}-CH_2CH_3 \xrightarrow{HCl} CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_2CH_3 + H^+$$

$$HO\bar{Z}nCl_2 + H^+ \longrightarrow H_2O + ZnCl_2$$

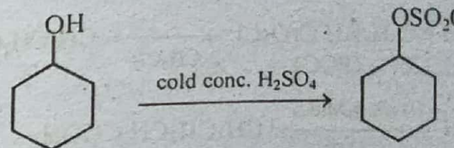
(f)



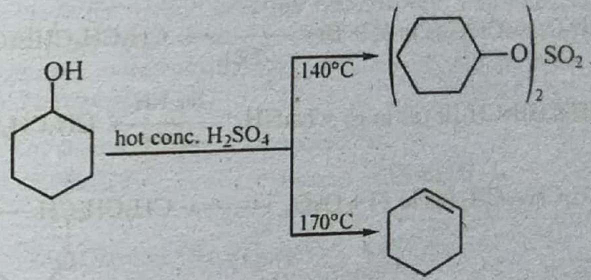
(g) $(CH_3)_3CCH_2Br \xrightarrow[Ether]{Mg} (CH_3)_3CCH_2MgBr \xrightarrow{S} (CH_3)_3CCH_2SMgBr \xrightarrow{HCl}$

$(CH_3)_3CCH_2SH + ClMgBr$

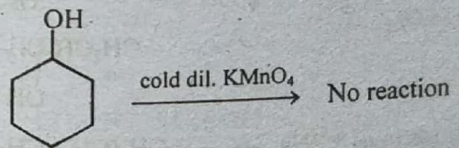
8. (a)



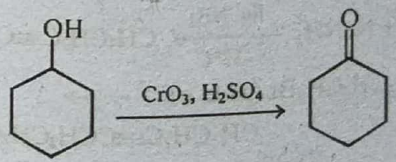
(b)



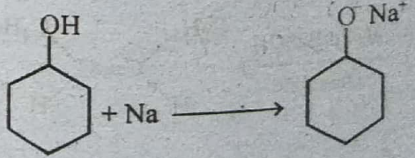
(c)

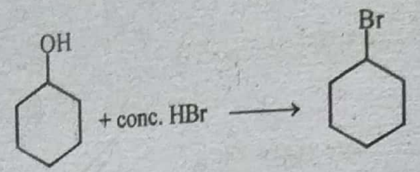


(d)



(e)



(f) 

9. (a) $3CH_3CH_2CH_2CH_2OH + PBr_3 \longrightarrow 3CH_3CH_2CH_2CH_2Br + H_3PO_3$

(b) $CH_3CH_2CH_2CH_2Br$ (as in *a*) $\xrightarrow[t\text{-BuOH}]{t\text{-BuO}^- K^+} CH_3CH_2CH{=}CH_2$

(c) $CH_3CH_2CH_2CH_2OH + H_2SO_4 \longrightarrow CH_3CH_2CH_2CH_2OSO_2OH + H_2O$

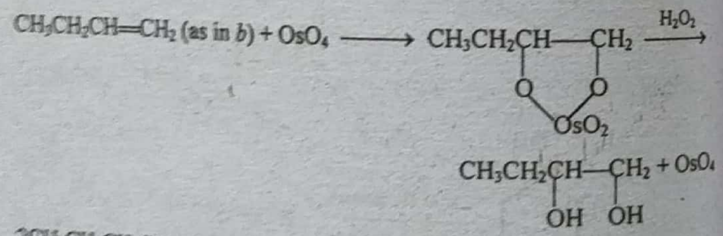
(d) $2CH_3CH_2CH_2CH_2OH + 2K \longrightarrow CH_3CH_2CH_2CH_2O^- K^+ + H_2$

(e) $CH_3CH_2CH_2CH_2OH + C_5H_5\overset{+}{N}H\ \bar{C}rO_3Cl \xrightarrow[CH_2Cl_2]{} CH_3CH_2CH_2CHO$
(PCC)

(f) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{(ii) } H^+]{\text{(i) alk. } KMnO_4} CH_3CH_2CH_2COOH$

(g) $CH_3CH_2CH{=}CH_2$ (as in *b*) $+ Br_2 \xrightarrow[CCl_4]{} CH_3CH_2CHBrCH_2Br$

(h) $CH_3CH_2CHBrCH_2Br$ (as in g) $+ NaNH_2 \xrightarrow[-33°C]{\text{liq. } NH_3} CH_3CH_2C{\equiv}CH$

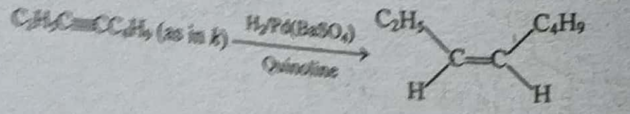
(i) 

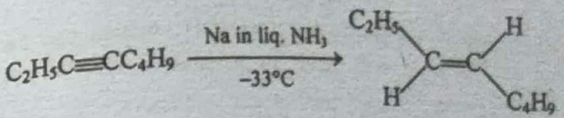
(j) $2CH_3CH_2CH_2CH_2Br$ (as in *a*) $+ 2Na \longrightarrow CH_3(CH_2)_6CH_3 + 2NaBr$

(k) $CH_3CH_2C{\equiv}CH$ (as in *h*) $+ NaNH_2 \xrightarrow[-33°C]{\text{liq. } NH_3} CH_3CH_2C{\equiv}C^- Na^+$

$CH_3CH_2C{\equiv}C^- + CH_3CH_2CH_2CH_2Br$ (as in *a*) $\longrightarrow$

$CH_3CH_2C{\equiv}CCH_2CH_2CH_2CH_3 + Br^-$

(l) 

(m) 

10. (a) $CH_3CHOHCH_2OH + HIO_4 \longrightarrow CH_3CHO + HCHO + HIO_3$

(b) $CH_3CHOHCHO + HIO_4 \longrightarrow CH_3CHO + HCOOH + HIO_3$

(c) $CH_2OHCHOHCH_2OCH_3 + HIO_4 \longrightarrow HCHO + OHCCH_2OCH_3 + HIO_3$

(d) $CH_2OHCH(OCH_3)CH_2OH + HIO_4 \longrightarrow$ No reaction

(e) $CH_2OH(CHOH)_3CH_2OH + 4HIO_4 \longrightarrow 2HCHO + 3HCOOH + 4HIO_3$

(f) $CH_2OH(CHOH)_3CHO + 4HIO_4 \longrightarrow HCHO + 4HCOOH + 4HIO_3$

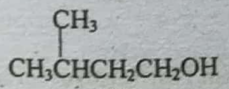
(g) 

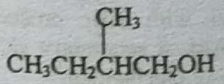
11.(a) Tertiary butyl alcohol reacts with Lucas reagent ($ZnCl_2$ + conc. HCl) and forms insoluble *t*-butyl chloride immediately, which appears as cloudiness in the test tube. Isopropyl alcohol (a secondary alcohol) forms cloudiness in about five minutes time, whereas ethanol (a primary alcohol) does not react with the reagent at room temperature.

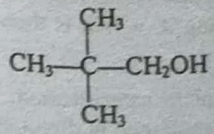
(b) The isomeric pentyl alcohols are:

Primary

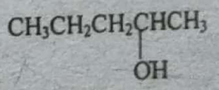
$CH_3CH_2CH_2CH_2CH_2OH$
(1)

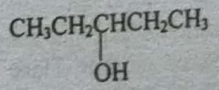

$CH_3\overset{CH_3}{CH}CH_2CH_2OH$
(2)

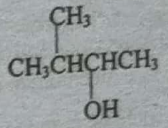

$CH_3CH_2\overset{CH_3}{CH}CH_2OH$
(3)


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH$
(4)

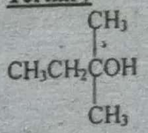
Secondary


$CH_3CH_2CH_2\underset{OH}{CH}CH_3$
(5)


$CH_3CH_2\underset{OH}{CH}CH_2CH_3$
(6)


$CH_3\overset{CH_3}{CH}\underset{OH}{CH}CH_3$
(7)

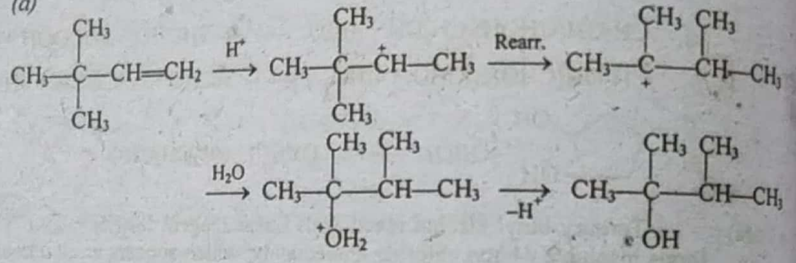
Tertiary


$CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}OH$
(8)

(a) Only alkyl methyl carbinols ($RCHOHCH_3$) which can be oxidized to a methyl ketone ($RCOCH_3$), will give a positive iodoform test. Such pentyl alcohols are 5 and 7.

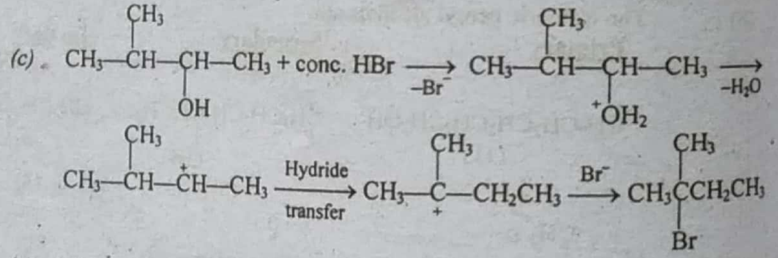
(b) Tertiary pentyl alcohol (8) will give a positive test with the Lucas reagent immediately. The secondary pentyl alcohols (5, 6 and 7) will give a positive test with the Lucas reagent after five minutes, whereas the primary pentyl alcohols (1, 2, 3 and 4) will not give a positive test with the Lucas reagent at room temperature.

12. *(a)*



(b) $(CH_3)_2CHCH_2OH + HBr \xrightarrow{H_2SO_4} (CH_3)_2CHCH_2\overset{+}{O}H_2 + Br^- \xrightarrow{S_N2} (CH_3)_2CHCH_2Br + H_2O$

(c)



13. *(a)* The reaction of a primary alcohol with HBr involves an S_N2 attack of Br^- on the protonated alcohol. Since protonated methyl alcohol offers less steric hindrance than the other primary alcohols, it reacts faster.

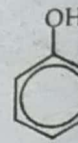
(b) The reaction of a tertiary alcohol with HBr proceeds through the protonated alcohol involving S_N1 mechanism. A secondary alcohol is neither a good substrate for S_N1 mechanism nor for S_N2 mechanism.

(c) When ethyl alcohol is made to react with NaBr, the leaving group is OH^- which is not a good leaving group. On the other hand, HBr first converts —OH to a good leaving group (H_2O) by protonating it, which is then easily displaced by S_N2 attack of Br^-.

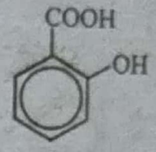
(d) Steric hindrance is an important factor in esterification. Since secondary and tertiary alcohols offer significant steric hindrance in direct esterification, it is restricted to primary alcohols.

14. *(a)* 2-Hydroxy-4-methylbenzoic acid
(b) 2-Hydroxy-3-methylbenzaldehyde
(c) 4-Methoxy-2-methylphenol
(d) 5-Carboxy-2-hydroxybenzenesulfonic acid
(e) 5-Acetyl-2-aminophenol
(f) 4-Hydroxyacetanilide

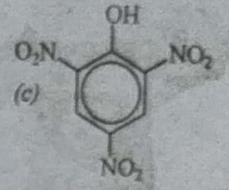
15. *(a)*



(b)

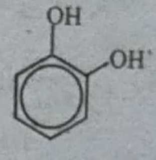


(c)



(d)

(e)



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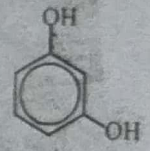
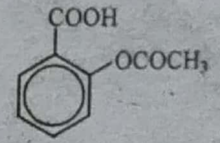
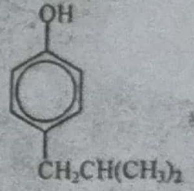


(g)

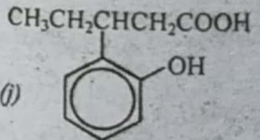
(h)



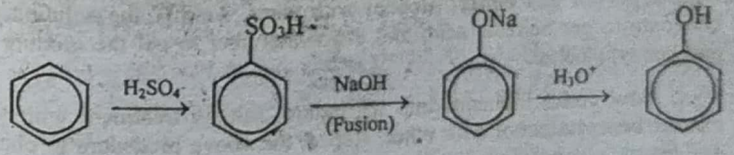
(i)



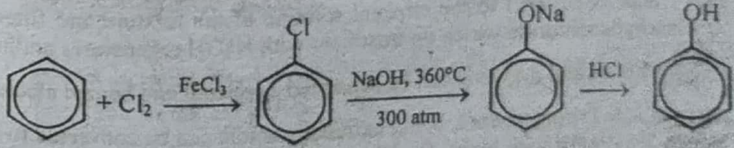
(j)



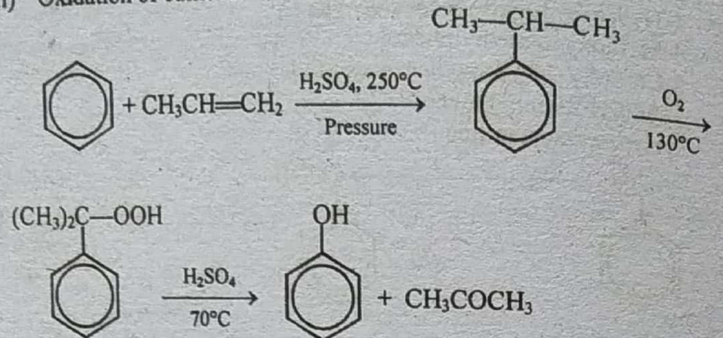
16. (i) Fusion of sodium benzenesulfonate with alkali.



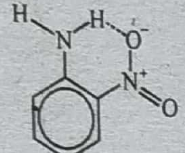
(ii) Hydrolysis of chlorobenzene.



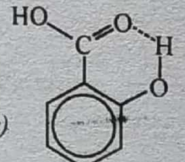
(iii) Oxidation of cumene.



17. (b)



(c)



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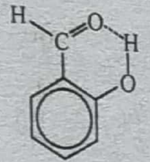

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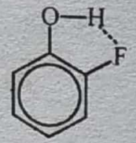


18. For discussion see inductive and resonance effects and hydrogen bonding:

(a) Benzoic acid > phenol > benzyl alcohol

(b) *p*-Chlorophenol > phenol > *p*-methylphenol

(c) *p*-Nitrophenol > *m*-nitrophenol > phenol

19. (a) Convert benzoic acid into its sodium salt by treatment with $NaHCO_3$ and extract phenol and benzyl alcohol with ether. Acidify the solution of sodium benzoate to get benzoic acid, and evaporate ether to get the mixture of phenol and benzyl alcohol.

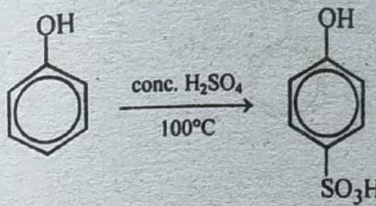
Now convert phenol into its sodium salt by treatment with NaOH and extract benzyl alcohol with ether. Repeat the above procedure to obtain phenol and benzyl alcohol. Extract phenol from its acidified solution with ether.

(b) Add conc. HCl to the ethereal solution of the mixture and filter to obtain aniline hydrochloride which on treatment with NaOH regenerates aniline.

Phenol and *p*-xylene can be separated as phenol and benzyl alcohol in *(a)*.

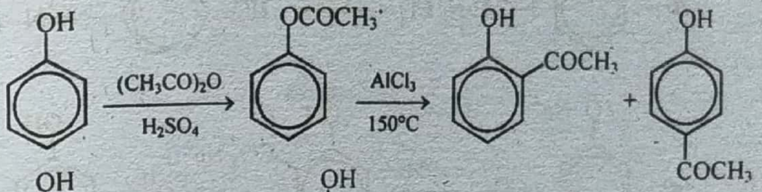
(c) 2,4,6-Trinitrophenol, being extremely acidic can be converted to its sodium salt by treatment with $NaHCO_3$. The mixture can therefore be separated as in *(a)*.

20. (a)



(b) No reaction

(c)



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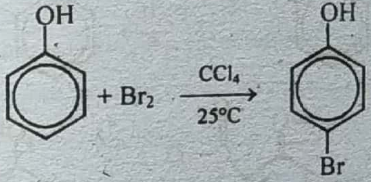

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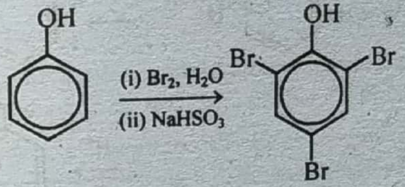
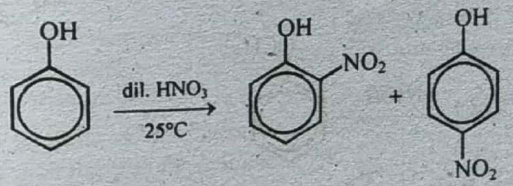
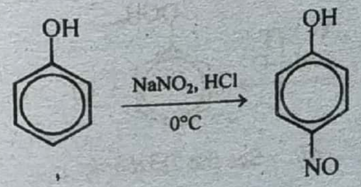


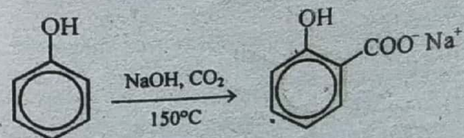
(f)

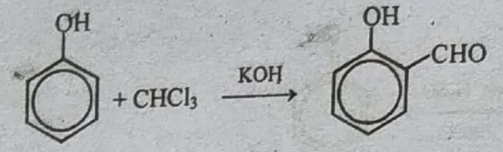


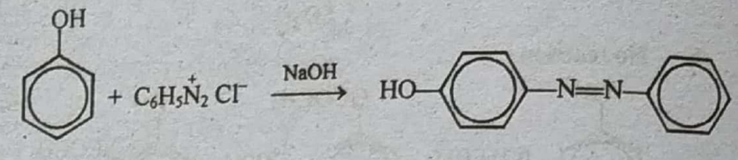
(g)

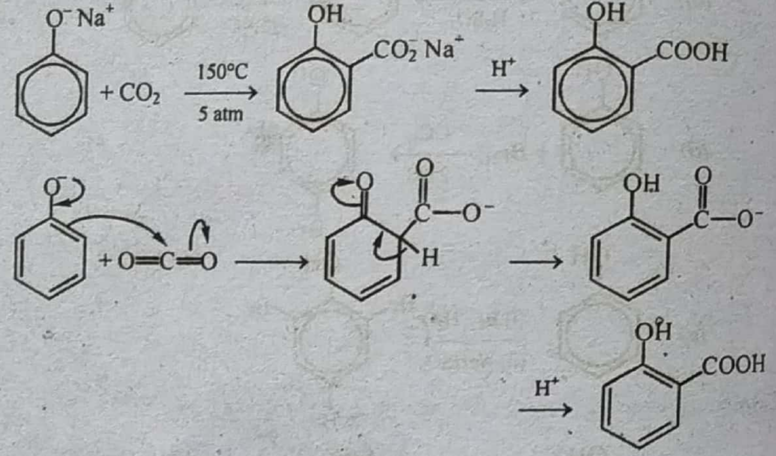


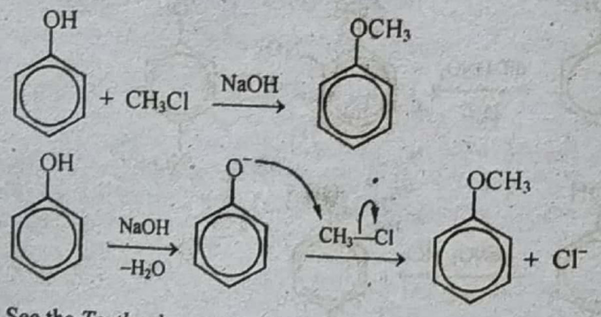
(h)



(i) 

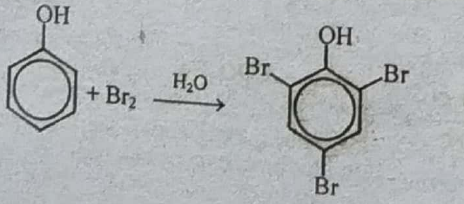
(j) 

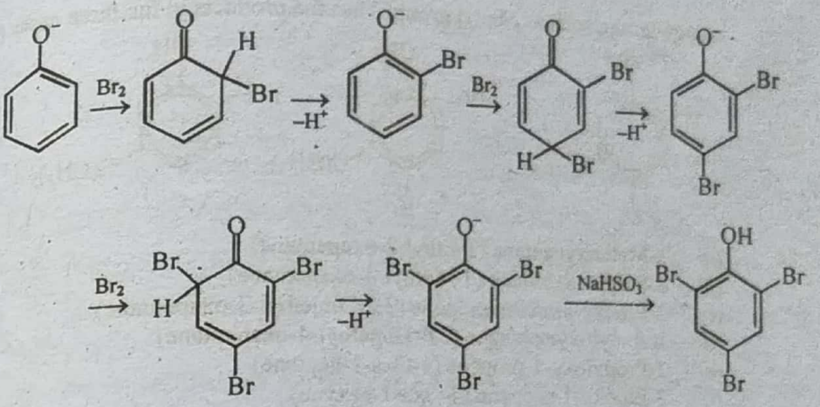
21. (a) 

(b) 

(c) See the *Textbook*.

(d) See the *Textbook*.

(e) 



22. (a) **Antipyretic.** An agent used to reduce temperature (fever).

(b) **Analgesic.** An agent used to alleviate pain.

(c) **Chelation.** Intramolecular hydrogen bonding.

(d) **Formylation.** Introduction of the formyl group (CHO) into an activated aromatic ring such as phenol, by treatment with $CHCl_3$ in aq. alkali.

(e) **Carbonation.** Introduction of the carboxylic group (COOH) into an activated aromatic ring, e.g., phenol, by treatment with CO_2

(f) **Diazo coupling.** Coupling of an aryldiazonium ion, ArN_2^+, with an activated aromatic ring to form an arylazo compound.

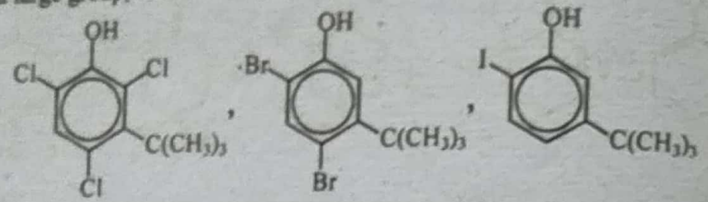
(g) **Steam-distillation.** Distillation of a compound by carrying it along with steam. The compounds which can mix with boiling water but are not dissolved, can be steam-distilled.

(h) **Bakelite.** It is a phenol-formaldehyde resin formed by the base-catalyzed reaction of phenol with formaldehyde.

23. (a) Intramolecular H-bonding in *o*-nitrophenol prevents intermolecular association, lowering the boiling point, and reduces H-bonding with water, decreasing water-solubility. *p*-Nitrophenol involves intermolecular H-bonding, raising its b.pt. and forms H-bond with H_2O, increasing its solubility.

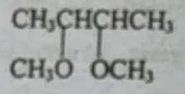
(b) Two large *t*-butyl groups at ortho positions to the OH group of phenol do not permit the proton to come off the OH group, and hence reduce its acidity.

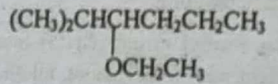
(c) Phenol is very reactive toward halogenation and the halogens enter all the positions ortho and para to the hydroxyl group unless any of these positions is already occupied or is sterically hindered. Chlorine, being smaller in size, does not face much steric hindrance, and can enter any of the ortho/para positions. Bromine is larger in size than chlorine and cannot enter a position in between the two meta groups. Iodine is still larger in size and cannot enter a position ortho to a large group, such as *t*-butyl group. Thus the products in the three cases are:

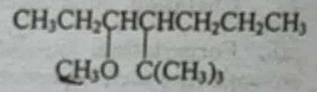


24.
(*a*) 3-Methoxypentane (3-Ethyl-2-oxapentane)
(*b*) 2-Propyloxybutane (3-Methyl-4-oxaheptane)
(*c*) 2-Ethoxy-2-methylpropane (2,2-Dimethyl-3-oxapentane)
(*d*) Isobutyloxyisobutane (2,6-Dimethyl-4-oxaheptane)
(*e*) 3-Propyloxy-1-propene (4-Oxa-1-heptene)
(*f*) 3-Ethoxy-1-propyne (4-Oxa-1-hexyne)

25.
(*a*) $(CH_3)_3COCH(CH_3)_2$

(*b*) 
$CH_3\underset{CH_3O}{CH}\underset{OCH_3}{CH}CH_3$

(*c*) 
$(CH_3)_2CH\underset{OCH_2CH_3}{CH}CH_2CH_2CH_3$

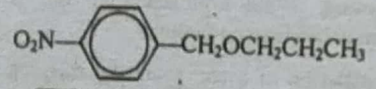
(*d*) 
$CH_3CH_2\underset{CH_3O}{CH}\underset{C(CH_3)_3}{CH}CH_2CH_2CH_3$

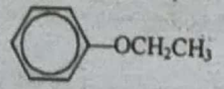
(*e*) $(CH_3)_2CHCH_2OCH_2CH(CH_3)_2$

(*f*) $CH_2{=}CHOR$

(*g*) $C_6H_5CH_2OCH_2C_6H_5$

(*h*) $C_6H_5CH_2CH_2OCH_2CH_2C_6H_5$

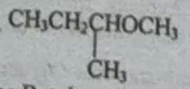
(*i*) 

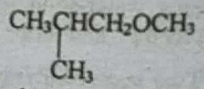
(*j*) 

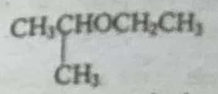
26.

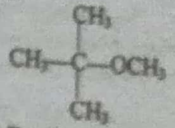
$CH_3CH_2CH_2CH_2OCH_3$
n-Butyl methyl ether
1-Methoxybutane
2-Oxahexane

$CH_3CH_2CH_2OCH_2CH_3$
Ethyl *n*-propyl ether
1-Ethoxypropane
3-Oxahexane


$CH_3CH_2\underset{CH_3}{CH}OCH_3$
sec-Butyl methyl ether
2-Methoxybutane
3-Methyl-2-oxapentane


$CH_3\underset{CH_3}{CH}CH_2OCH_3$
Isobutyl methyl ether
Methoxyisobutane
4-Methyl-2-oxapentane


$CH_3\underset{CH_3}{CH}OCH_2CH_3$
Ethyl isopropyl ether
2-Ethoxypropane
2-Methyl-3-oxapentane


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OCH_3$
t-Butyl methyl ether
2-Methoxy-2-methylpropane
2,2-Dimethyl-3-oxabutane

27. (a) (i) $CH_3O^- Na^+ + (CH_3)_2CHCl \longrightarrow CH_3OCH(CH_3)_2 + NaCl$

(ii) $(CH_3)_2CHO^- Na^+ + CH_3Cl \longrightarrow (CH_3)_2CHOCH_3 + NaCl$

(ii) is a better method because the substrate in this case is a primary alkyl halide.

(b) (*a*) is the effective reaction for the preparation of methyl neopentyl ether because in this case methyl benzenesulfonate is the substrate. Neopentyl benzenesulfonate is not a good substrate for the S_N2 attack by an alkoxide ion.

28.
$$CH_3CH_2OH + CH_3CH_2CH_2OH \xrightarrow[\Delta]{H_2SO_4} CH_3CH_2OCH_2CH_3 + CH_3CH_2OCH_2CH_2CH_3 + CH_3CH_2CH_2OCH_2CH_2CH_3$$

$$CH_3CH_2OH + (CH_3)_3COH \xrightarrow[\Delta]{H_2SO_4} CH_3CH_2OC(CH_3)_3$$

t-Butyl alcohol under these conditions is readily converted to the *t*-butyl carbocation which reacts with ethyl alcohol to give the mixed ether.

29. The Williamson ether synthesis involves an S_N2 displacement on a primary alkyl substrate by an alkoxide ion. Since methyl sulfate has a better leaving group than a methyl halide for S_N2 reaction, it is a better O-methylating agent. Methyl tosylate is another substrate better than methyl halides for this reaction.

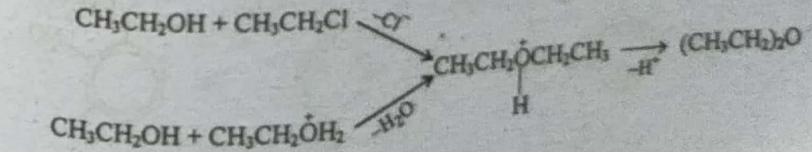
30. HI adds to C_2H_4 to form ethyl iodide.

$$CH_2{=}CH_2 + HI \longrightarrow CH_3-\overset{+}{C}H_2 + I^- \longrightarrow CH_3CH_2I$$

HI also reacts with CH_3CH_2OH to form CH_3CH_2I.

$$CH_3CH_2OH + HI \longrightarrow CH_3CH_2\overset{+}{O}H_2 + I^- \longrightarrow CH_3CH_2I + H_2O$$

I^- is a better nucleophile than CH_3CH_2OH. On the other hand, ethyl chloride (formed by the addition of HCl to $CH_2{=}CH_2$) and the protonated ethyl alcohol are better attacked by CH_3CH_2OH, rather than Cl^- which is a poorer nucleophile.



31. The boiling point of *n*-butyl alcohol is higher than diethyl ether, due to the intermolecular association in the former case. The solubility of both in water is about the same because both can form H-bond with water.

32. *(a)* (i) Alcoholic solution of methyl iodide gives precipitate of silver iodide with silver nitrate. Ether does not give this test.

(ii) Dimethyl ether dissolves in cold conc. H_2SO_4 (as $CH_3\underset{H}{\overset{+}{O}}CH_3\ HSO_4^-$), whereas methyl iodide does not.

(b) *n*-Butyl alcohol turns orange colour of $K_2Cr_2O_7 + H_2SO_4$ into greenish blue. Di-*n*-butyl ether does not give this test.

(c) (i) Treatment of methyl *n*-propyl ether with HI liberates methyl iodide which is collected in an alc. solution of silver nitrate where it forms precipitate of silver iodide.

(ii) 1-Pentene decolorizes bromine water, whereas methyl *n*-propyl ether does not.

(d) (i) Anisole gives Zeisel test as in *c* (i).

(ii) Anisole dissolves in cold conc. H_2SO_4, whereas toluene does not.

33. *(a)* $C_2H_5OH + H_2SO_4 \xrightarrow[140°C]{} C_2H_5OC_2H_5$

(b) $(CH_3)_3CO^-K^+ + C_2H_5I \longrightarrow (CH_3)_3COC_2H_5$

(c) $C_2H_5O^-K^+ + (CH_3)_3CI \longrightarrow (CH_3)_2C{=}CH_2 + C_2H_5OH$

(d) $(CH_3CH_2CH_2CH_2)_2O + \text{aq. NaOH} \xrightarrow[\text{boiling}]{} \text{No reaction}$

(e) $CH_3CH_2CH_2OCH_2CH_3 + \underset{\text{(excess)}}{HI} \xrightarrow[\Delta]{} CH_3CH_2CH_2I + CH_3CH_2I$

(f) $(CH_3CH_2)_2CHOCH_3 + \underset{\text{(excess)}}{HBr} \xrightarrow[\Delta]{} (CH_3CH_2)_2CHBr + CH_3Br$

(g) $(CH_3CH_2)_2O + Na \longrightarrow \text{No reaction}$

(h) $(CH_3CH_2)_2O + \text{cold conc. } H_2SO_4 \longrightarrow CH_3CH_2\underset{H}{\overset{+}{O}}CH_2CH_3\ HSO_4^-$

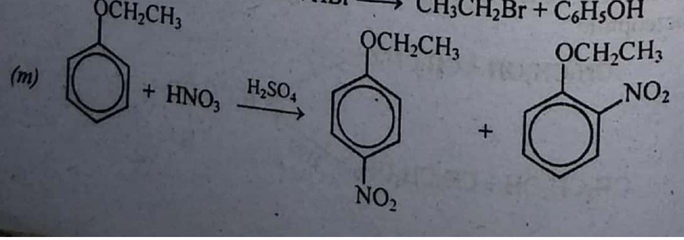
(i) $(CH_3CH_2)_2O + \text{hot conc. } H_2SO_4 \longrightarrow 2C_2H_5OSO_3H$

(j) $(CH_3)_3COCH_2CH_3 + \text{cold conc. HBr} \longrightarrow (CH_3)_3CBr + CH_3CH_2OH$

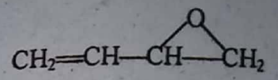
(k) $CH_3CH_2CH_2CH_2OCH_2CH_3 + \text{hot conc. HBr} \longrightarrow CH_3CH_2CH_2CH_2Br + CH_3CH_2Br$

(l) $C_6H_5OCH_2CH_3 + \text{hot conc. HBr} \longrightarrow CH_3CH_2Br + C_6H_5OH$

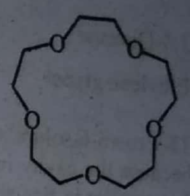
(m)



34. (a) (i)



(ii)



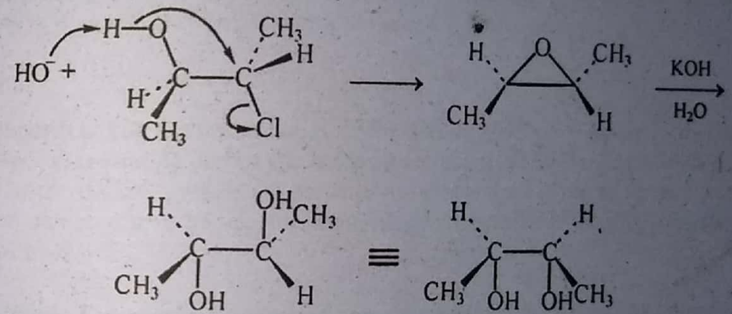
(b) (i) 2-Methyl-2-propyloxirane (ii) (2*R*,3*R*)-Dimethyloxirane

35. $(CH_3)_2CHCH_2OH \xrightarrow{PBr_3} (CH_3)_2CHCH_2Br \xrightarrow[\text{Ether}]{Mg} (CH_3)_2CHCH_2MgBr$

$(CH_3)_2CHCH_2CH_2CH_2OMgBr \xrightarrow{H_2O} (CH_3)_2CHCH_2CH_2CH_2OH \xrightarrow{PBr_3}$

$(CH_3)_2CHCH_2CH_2CH_2Br$

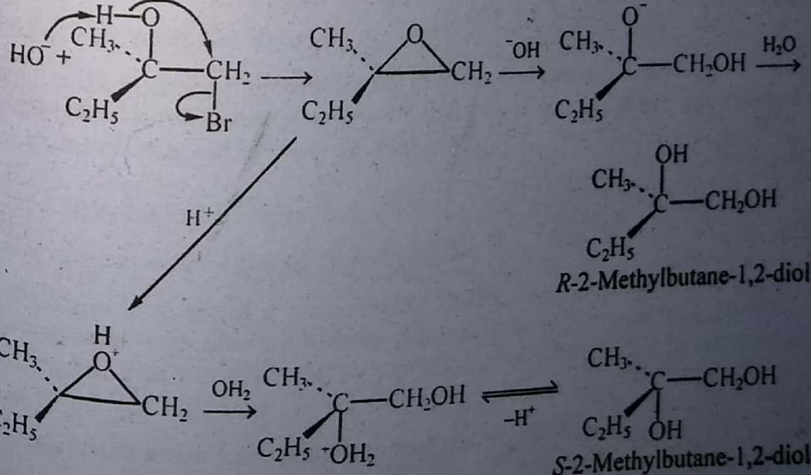
36.



Optically inactive

(meso)

37.



R-2-Methylbutane-1,2-diol

S-2-Methylbutane-1,2-diol

The two products are enantiomers.

38.(a) 1,4-Dioxane

(b) Ethylene glycol

39. 18-Crown-6 solubilizes potassium salts much more effectively than sodium salts, because the cavity inside the crown ether is just the right size for K^+ to fit in. Na^+ is smaller in size and is not coordinated so tightly.

Chapter 10

Aldehydes and Ketones

CHAPTER'S SUMMARY

Structurally aldehydes are generally represented by RCHO, and ketones by RCOR′, where R and R′ may be alkyl or aryl groups.

Nomenclature

Aldehydes. The common names of the simple aldehydes are derived from the names of the corresponding carboxylic acids by replacing the suffix *-ic* (or *-oic*) *acid* by *-aldehyde*. In the IUPAC system the name of an aliphatic aldehyde is derived from the name of the parent alkane having the same number of carbon atoms by replacing the ending *-e* with *-al*.

Ketones. The simple ketones are commonly named by listing the names of the two alkyl (or aryl) groups, in alphabetical order, followed by the word *ketone*. In the IUPAC system, the names of the ketones are derived from the names of the corresponding alkanes by replacing the ending *-e* with *-one*.

Preparation of Aldehydes and Ketones

Some of the methods of preparation are of general nature and can be used for the preparation of both aldehydes and ketones, while some are of specific nature and are used for the preparation of either aldehydes or ketones only.

Methods for Aldehydes and Ketones

Aldehydes and ketones may be prepared by the:

1. Oxidative cleavage of a carbon-carbon double bond either on ozonolysis or through hydroxylation with alkaline $KMnO_4$. Acetaldehyde is prepared industrially by the Wacker process which involves the air oxidation of ethylene in the presence of a catalyst.

2. Oxidation of primary and secondary alcohols, respectively.

3. Dry distillation of calcium or barium salts of carboxylic acids. This method yields a variety of carbonyl compounds, depending on the nature of the carboxylic acids used.

Methods for Aldehydes

1. An aldehyde can be prepared by the hydroformylation of a terminal alkene on treatment with carbon monoxide and hydrogen in the presence of a cobalt catalyst.

2. An aromatic aldehyde can be prepared by the reaction of an aromatic hydrocarbon with CO and HCl in the presence of a Lewis acid (Gatterman-Koch reaction).

3. An aromatic aldehyde can also be prepared either by the oxidation of an alkylbenzene with alkaline $KMnO_4$ in the presence of acetic anhydride, or by the halogenation of methylbenzene in the presence of light, both followed by hydrolysis.

4. A phenolic aldehyde can be prepared by the treatment of a phenol with $CHCl_3$ in aq. alkali (Reimer-Tiemann reaction).

5. Aldehydes can be prepared by the catalytic hydrogenolysis of acid chlorides by passing a stream of hydrogen gas through a solution of the acid chloride in boiling xylene in the presence of palladium deposited on $BaSO_4$, and a catalyst poison such as quinoline (Rosenmund reduction). The most useful reducing agent for this purpose is $LiAlH(t\text{-}BuO)_3$.

6. Aldehydes can also be prepared by the treatment of nitriles with $SnCl_2$ and HCl in anhydrous ether (Stephen reaction).

Methods for Ketones

1. Ketones may be prepared by the hydration of alkynes in the presence of $HgSO_4$ and H_2SO_4.

2. Ketones may be prepared by the reaction of Grignard reagents with either nitriles or acid halides, followed by hydrolysis.

3. Aromatic Ketones may be prepared by the Friedel-Crafts acylation of aromatic compounds by acid halides or anhydrides in the presence of a Lewis acid.

4. Ketones may be prepared by the reaction of a carboxylic acid with two equivalents of alkyl- or aryllithium.

5. Ketones may also be prepared by the treatment of acid chlorides with lithium organocuprates.

Physical Properties of Aldehydes and Ketones

Most of the aldehydes and ketones are volatile liquids with characteristic odours. Formaldehyde is a gas, and is usually handled as a 40% solution in water under the name of **formalin**.

The boiling points of the straight-chain aldehydes and methyl *n*-alkyl ketones increase smoothly with the increasing molecular weights, and are generally higher than those of the *n*-alkanes but lower than those of the alcohols having the comparable molecular weights.

Aldehydes and ketones, particularly of low molecular weights, show appreciable solubility in water. However, they are quite soluble in the usual organic solvents.

Structure and Reactivity of the Carbonyl Group

The carbonyl group is highly polar with a partial positive charge on the carbon atom and a partial negative charge on the oxygen atom. The carbonyl double bond is therefore very strong and stable. Thus, many of the addition reactions of the carbonyl group do not take place, while the others are reversible.

On the other hand, the polarity of the carbonyl group makes it susceptible to the attack by a nucleophilic reagent at the electron-deficient carbonyl carbon. This means that the nucleophilic addition to the carbonyl double bond may be rapid, but reversible; the equilibrium constant depends on the structure of the carbonyl compound.

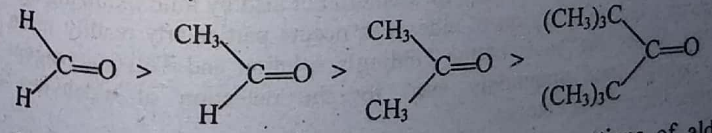
Furthermore, the carbonyl group makes the α-hydrogen acidic, which is responsible for the reactions at the α-carbon atom of aldehydes and ketones.

The hydrogen atom directly attached to the carbonyl carbon in aldehydes makes them to be oxidized quite easily.

Reactions of Aldehydes and Ketones

Aldehydes and ketones undergo a very large variety of reactions. They may be addition reactions to the carbonyl group or the reactions at the α-carbon atom. Since aldehydes and ketones are in an intermediate oxidation state, they can be oxidized as well as reduced. Some of the more important reactions of aldehydes and ketones are mentioned below:

1. Nucleophilic addition reactions. The nucleophilic addition reactions of aldehydes and ketones are catalysed by acids and bases; the products are stabilized by the electron-withdrawing substituents at the α position. The inductive and steric effects of the alkyl groups make ketones less reactive than aldehydes toward nucleophilic addition. The general order of reactivity is:



Some of the representative nucleophilic addition reactions of aldehydes and ketones are as under:

(i) Aldehydes and ketones add a molecule of water to form *gem*-diols.

(ii) With alcohols, aldehydes form hemiacetals, while ketones form hemiketals. Hemiacetals react with another molecule of alcohol to form acetals (*gem*-diethers). Ketals are not formed from hemiketals. However, cyclic ketals can be formed by the treatment of a ketone with a 1,2-diol. Acetals and ketals are commonly used to protect the carbonyl group during a synthetic scheme.

(iii) Aldehydes and ketones react with ammonia and its derivatives, such as primary amine, hydroxylamine, hydrazine, phenylhydrazine and semicarbazide to form the corresponding addition products which undergo dehydration to form stable imine derivatives. Since the imine derivatives are solid with sharp melting points, and are insoluble in water, they can be used for the characterization of carbonyl compounds.

(iv) Aldehydes and unhindered ketones add a molecule of HCN to form cyanohydrins which on hydrolysis yield α-hydroxycarboxylic acids.

(v) Aldehydes and unhindered ketones react with conc. aq. sodium bisulfite to give solid sodium salts of α-hydroxysulfonic acids which can be decomposed back to the carbonyl compounds on treatment with strong acids or bases. Thus, this reaction is frequently used for the separation, purification and identification of carbonyl compounds.

(vi) Aldehydes and ketones react with Grignard reagents to give the products which on hydrolysis yield a wide variety of alcohols.

(vii) Aldehydes and unhindered ketones react with α-bromoesters in the presence of zinc metal in benzene to form β-hydroxyesters which on dehydration yield α,β-unsaturated esters.

2. Aldol condensation. An aldehyde or a ketone containing an α-hydrogen reacts with another molecule of either the same or different aldehyde or ketone in the presence of an acid or a base to form a β-hydroxy aldehyde or ketone, commonly called **aldol**, which can undergo dehydration to produce an α,β-unsaturated aldehyde or ketone. This reaction is important for preparing a larger molecule from two smaller molecules, involving a carbon-carbon bond formation.

3. Halogenation. Aldehydes and ketones undergo halogenation readily at α position in the presence of an acid or a base. In the case of methyl ketones, this reaction forms the basis of the iodoform test.

4. Oxidation. Aldehydes and ketones behave differently toward oxidation.

(i) *Oxidation of aldehydes.* Aldehydes are easily oxidized to carboxylic acids not only by strong oxidizing agents such as $KMnO_4$, but also by mild oxidizing agents, such as moist silver oxide. Oxidation of aldehydes occurs particularly readily in an alkaline solution; this forms the basis of the Fehling's solution and Tollen's reagent tests of aldehydes, which are commonly used for the detection of aldehydes and for distinguishing them from ketones.

(ii) *Oxidation of ketones.* Ketones generally are resistant to oxidation. However, on prolonged heating with strong oxidizing agents such as $KMnO_4$, $Na_2Cr_2O_7$ or HNO_3, ketones undergo oxidative cleavage to yield a mixture of carboxylic acids.

(iii) *Baeyer-Villiger oxidation.* Both aldehydes and ketones can be oxidized by peracids. Aldehydes yield acids, whereas ketones give esters; cyclic ketones form lactones.

(iv) *Oxidation of methylene group.* A methylene group adjacent to a carbonyl group is oxidized to a second carbonyl group on treatment with SeO_2 in acetic acid.

5. Reduction. Aldehydes and ketones can be reduced by a large variety of reducing agents. Some reducing agents reduce the carbonyl compounds to alcohols, e.g., molecular hydrogen in the presence of a suitable catalyst like Ni, Pt or Pd, or complex metal hydrides like $LiAlH_4$ or $NaBH_4$, while some other reduce them directly to hydrocarbons, e.g., zinc amalgam in conc. HCl (Clemmensen reduction) or hydrazine in a suitable base (Wolff-Kishner reduction).

6. Cannizzaro's reaction. Aldehydes without an α-hydrogen atom on treatment with a cold conc. aq. NaOH undergo self-oxidation and reduction such that one molecule is oxidized to the corresponding acid, while another is reduced to the primary alcohol.

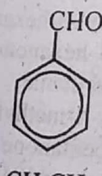
7. Benzoin condensation. In the presence of a catalytic amount of sodium cyanide in boiling aq. ethanol, aromatic aldehydes (without α-hydrogen) undergo a condensation reaction resulting in the formation of benzoin, an α-hydroxy ketone.

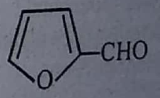
8. Wittig reaction. Aldehydes and ketones react with phosphorus ylides, prepared from triphenylphosphine and alkyl halides, to yield alkenes and triphenylphosphine oxide.

9. Polymerization. Aldehydes on heating undergo addition polymerization to form both linear and cyclic polymers.

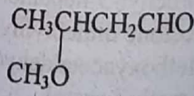
ANSWERS TO EXERCISES

1. (a) CH_3CHO (b) $C_6H_5CH_2CHO$

(c) 

(d) 

(e) $CH_3CH{=}CHCHO$ (f) $C_6H_5CH{=}CHCHO$

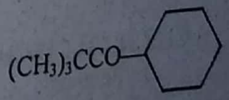
(g) 

$CH_3\underset{\substack{|\\ CH_3O}}{C}HCH_2CHO$

(h) CH $COCH_2CH_2CH_2CHO$

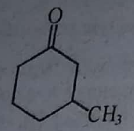
(i) CH_3COCH_3 (j) $C_6H_5COCH_3$

(k) $C_6H_5COC_6H_5$ (l) $C_6H_5CH_2COC_6H_5$

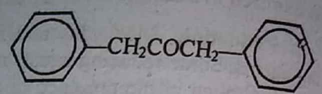
(m) $(CH_3)_3CCH_2COCH_2CH(CH_3)_2$ (n) 

(o) $(CH_3)_2CHCH_2COCH_2CH(CH_3)_2$ (p) $(CH_3)_2CHCOCH_3$

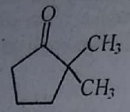
(q)



(r)



(s)



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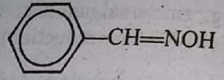

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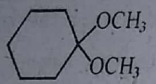

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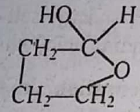

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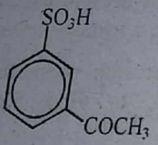

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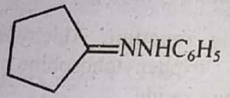

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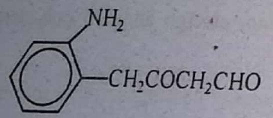
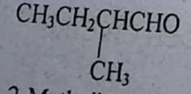


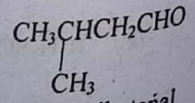
(z) Cl_3CCHO

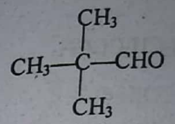
2\.
- (a) 2-Methylpropanal (or Isobutanal)
- (b) 3,3-Dimethyl-2-butanone
- (c) Pentanal
- (d) 3-Heptanone
- (e) 3-Methylbutanal
- (f) 5,5-Dimethyl-3-hexanone
- (g) 4-Methylhexanal
- (h) 2-Methyl-3-hexanone
- (i) 4-Methyl-3-pentenal
- (j) 3-Methoxybutanal
- (k) 1-Penten-3-one
- (l) 5-Hydroxy-4-methyl-1-phenyl-2-pentanone
- (m) 1-Cyclopropylpropanone
- (n) Cyclopentyl methyl ketone
- (o) 2-Ethylcyclohexanone
- (p) 5-Phenyl-3-heptanone
- (q) Cyclopropyl methyl ketoxime
- (r) Acetone dimethylhydrazone
- (s) Acetaldehyde methyl hemiacetal
- (t) Methoxyacetaldehyde dimethyl acetal
- (u) 2,6-Dimethyl-4-octanone

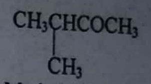
3\. $C_5H_{10}O$,

$CH_3CH_2CH_2CH_2CHO$
Pentanal


$CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCHO$
2-Methylbutanal


$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CHO$
3-Methylbutanal


$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CHO$
2,2-Dimethylpropanal

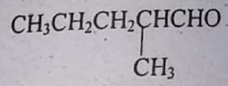

$CH_3\underset{CH_3}{\underset{|}{C}}HCOCH_3$
3-Methyl-2-butanone

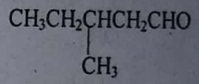
$CH_3CH_2CH_2COCH_3$
2-Pentanone

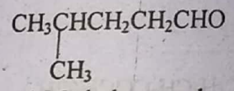
$CH_3CH_2COCH_2CH_3$
3-Pentanone

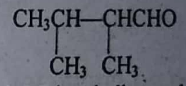
$C_6H_{12}O$,

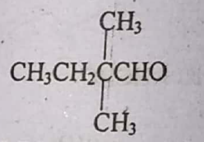
$CH_3CH_2CH_2CH_2CH_2CHO$
Hexanal

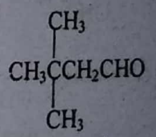

$CH_3CH_2CH_2\underset{CH_3}{\underset{|}{C}}HCHO$
2-Methylpentanal


$CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCH_2CHO$
3-Methylpentanal


$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH_2CHO$
4-Methylpentanal

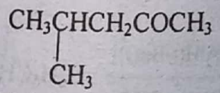

$CH_3\underset{CH_3}{\underset{|}{C}}H-\underset{CH_3}{\underset{|}{C}}HCHO$
2,3-Dimethylbutanal

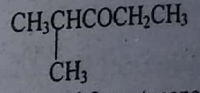

$CH_3CH_2\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}CHO$
2,2-Dimethylbutanal

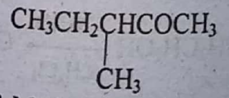

$CH_3\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}CH_2CHO$
3,3-Dimethylbutanal

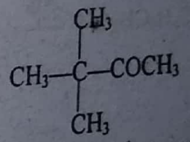
$CH_3CH_2CH_2CH_2COCH_3$
2-Hexanone

$CH_3CH_2CH_2COCH_2CH_3$
3-Hexanone


$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2COCH_3$
4-Methyl-2-pentanone

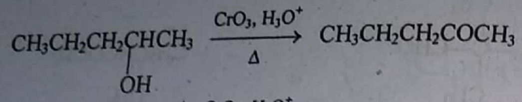

$CH_3\underset{CH_3}{\underset{|}{C}}HCOCH_2CH_3$
4-Methyl-3-pentanone

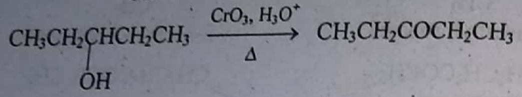

$CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCOCH_3$
3-Methyl-2-pentanone

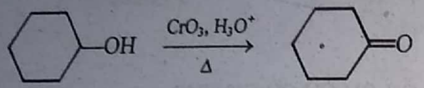

$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-COCH_3$
3,3-Dimethyl-2-butanone

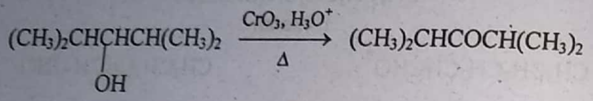
4\.
(a) $CH_3CH_2CH_2CH_2CH_2OH + PCC \xrightarrow{CH_2Cl_2} CH_3CH_2CH_2CH_2CHO$

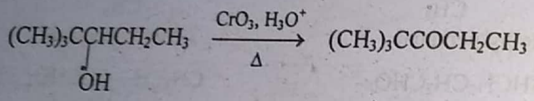
(b) $(CH_3)_2CHCH_2OH + PCC \xrightarrow{CH_2Cl_2} (CH_3)_2CHCHO$

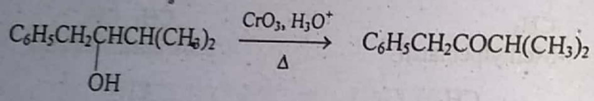
(c) 
$$CH_3CH_2CH_2\underset{OH}{C}HCH_3 \xrightarrow[\Delta]{CrO_3,\ H_3O^+} CH_3CH_2CH_2COCH_3$$

(d) 
$$CH_3CH_2\underset{OH}{C}HCH_2CH_3 \xrightarrow[\Delta]{CrO_3,\ H_3O^+} CH_3CH_2COCH_2CH_3$$

(e) 

(f) 
$$(CH_3)_2CH\underset{OH}{C}HCH(CH_3)_2 \xrightarrow[\Delta]{CrO_3,\ H_3O^+} (CH_3)_2CHCOCH(CH_3)_2$$

(g) 
$$(CH_3)_3C\underset{OH}{C}HCH_2CH_3 \xrightarrow[\Delta]{CrO_3,\ H_3O^+} (CH_3)_3CCOCH_2CH_3$$

(h) 
$$C_6H_5CH_2\underset{OH}{C}HCH(CH_3)_2 \xrightarrow[\Delta]{CrO_3,\ H_3O^+} C_6H_5CH_2COCH(CH_3)_2$$

5. (a) (a) $C_6H_5CH{=}CH_2 \xrightarrow[(ii)\ Zn + H_3O^+]{(i)\ O_3} C_6H_5CHO + HCHO$

(b) $C_6H_5C{\equiv}CH \xrightarrow[Quinoline]{Pd/BaSO_4} C_6H_5CH{=}CH_2 \xrightarrow[(ii)\ Zn + H_3O^+]{(i)\ O_3} C_6H_5CHO$

(c) $C_6H_5CH_2OH + PCC \xrightarrow{CH_2Cl_2} C_6H_5CHO$

(d) $C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow[Ether,\ -78°C]{LiAlH(t\text{-}BuO)_3} C_6H_5CHO$

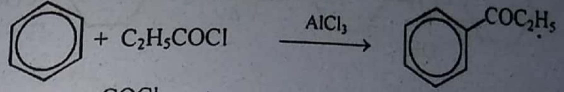
(b) (i) $C_6H_5CH_2OH \xrightarrow{HBr} C_6H_5CH_2Br \xrightarrow[Ether]{Mg} C_6H_5CH_2MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ HCHO}$

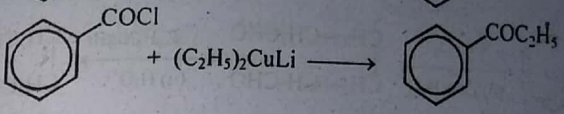
$C_6H_5CH_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} C_6H_5CH_2CHO$

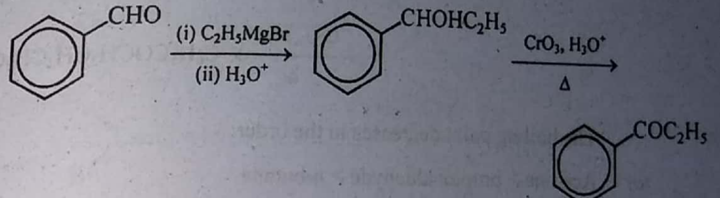
(ii) $C_6H_5CH_2OH \xrightarrow{HBr} C_6H_5CH_2Br \xrightarrow{CN^-} C_6H_5CH_2CN \xrightarrow{H_3O^+}$

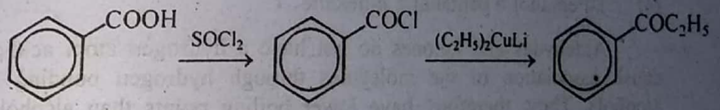
$C_6H_5CH_2COOH \xrightarrow{SOCl_2} C_6H_5CH_2COCl \xrightarrow[Ether,\ -78°C]{LiAlH(t\text{-}BuO)_3} C_6H_5CH_2CHO$

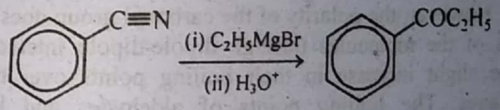
Trimethylacetaldehyde can be prepared from *t*-butyl alcohol by the method (i) but not by the method (ii) because the step 2 would involve an S_N2 attack by CN^- on a tertiary alkyl halide which would undergo elimination, rather than substitution.

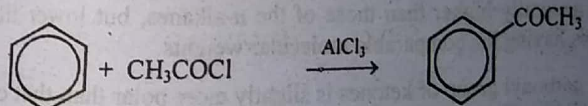
6. (a) (a) 

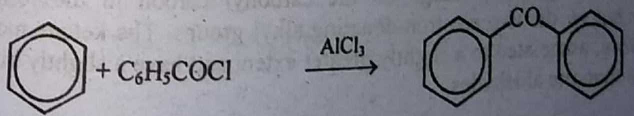
(b) 

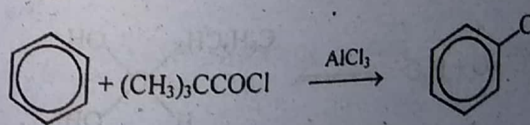
(c) 

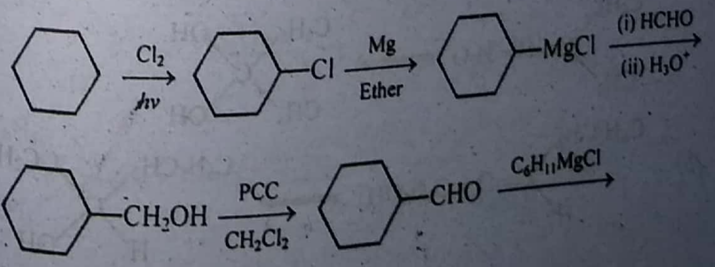
(d) 

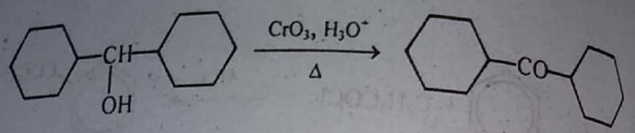
(e) 

(b) (a) 

(b) 

(c) 

(d) 



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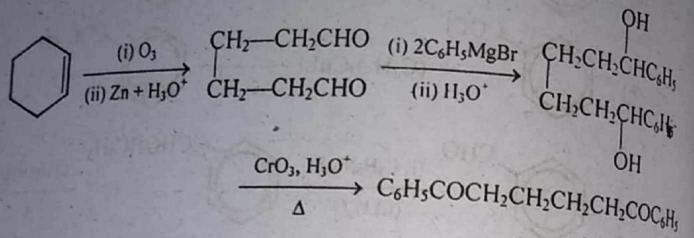


7. The boiling point decreases in the order:

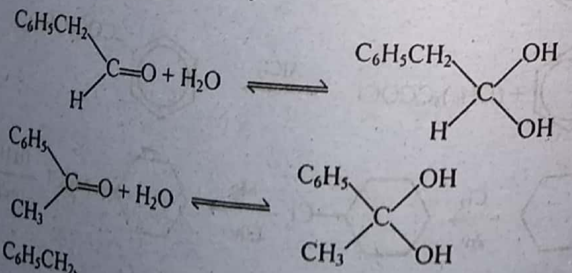
(a) Acetone > propionaldehyde > *n*-butane

(b) 1-Pentanol > pentanal > *n*-hexane

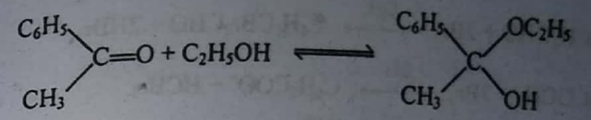
Aldehydes and ketones do not have a hydrogen atom acidic enough to cause association of the molecules through hydrogen bonding like that in alcohols. They, therefore, have lower boiling points than alcohols of similar molecular weights. However, the polarity of the carbonyl group does cause some sort of association of the molecules through dipole-dipole interaction that is responsible for the slight increase in their boiling points over those of the corresponding alkanes. The boiling points of aldehydes and ketones are, therefore, generally higher than those of the *n*-alkanes, but lower than those of the alcohols having the comparable molecular weights.

The carbonyl group of ketones is slightly more polar than that of aldehydes because the positive charge on the carbonyl carbon in the former case is stabilized by the two electron-donating alkyl groups. The ketone molecules are, therefore, associated to a slightly greater extent and have a slightly higher boiling points than the aldehydes.

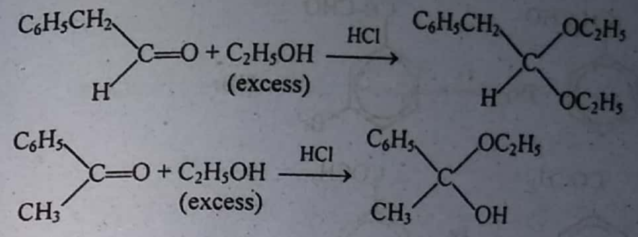
8. (a)



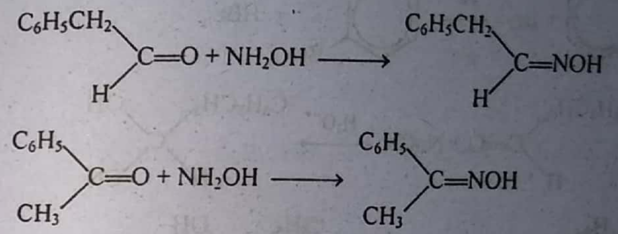
(b)



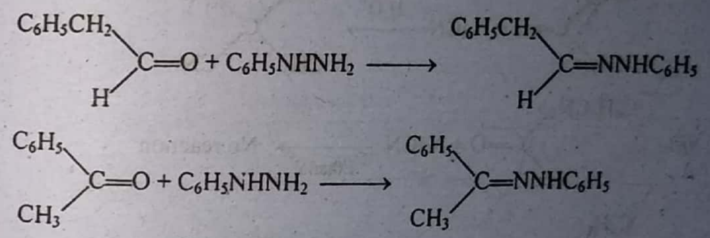
(c)



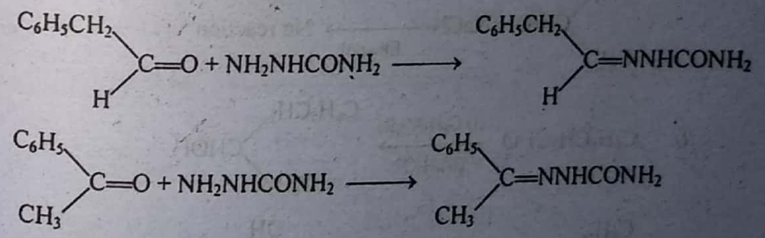
(d)



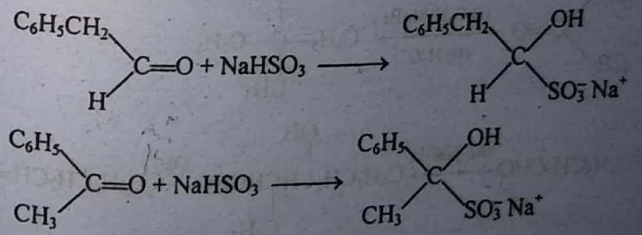
(e)



(f)



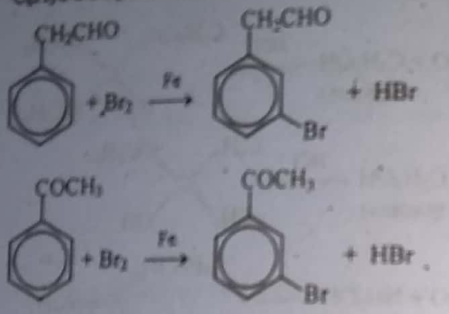
(g)



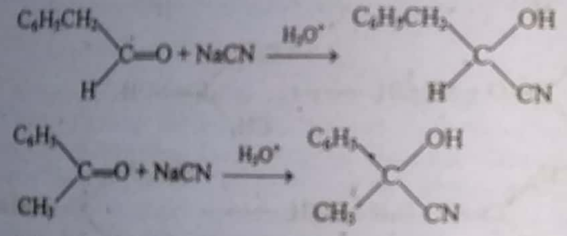
(h) $C_6H_5CH_2CHO + 2Br_2 \xrightarrow{OH^-} C_6H_5CBr_2CHO + 2HBr$

$C_6H_5COCH_3 + 3Br_2 \xrightarrow{OH^-} C_6H_5COO^- + HCBr_3$

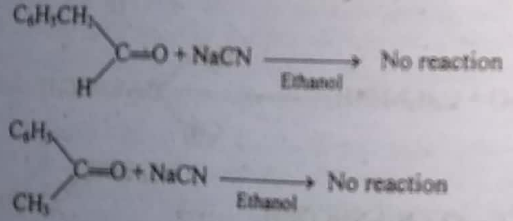
(i)



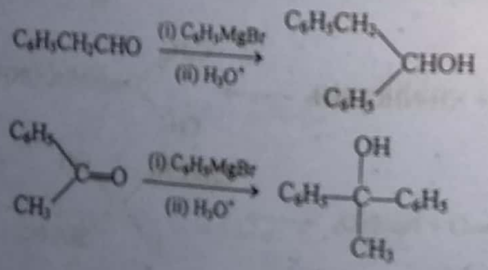
(j)



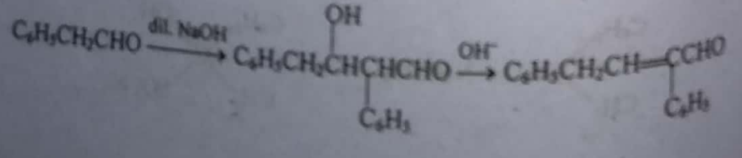
(k)



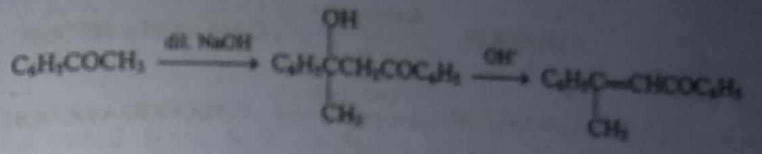
(l)



(m)

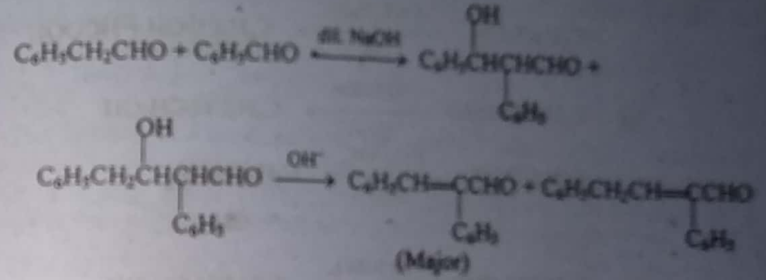


$$C_6H_5CH_2CHO \xrightarrow{\text{dil. NaOH}} C_6H_5CH_2\overset{\overset{OH}{|}}{C}H\underset{\underset{C_6H_5}{|}}{C}HCHO \xrightarrow{OH^-} C_6H_5CH_2CH{=}\underset{\underset{C_6H_5}{|}}{C}CHO$$



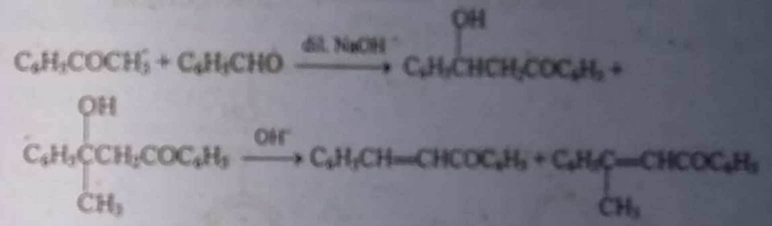
$$C_6H_5COCH_3 \xrightarrow{\text{dil. NaOH}} C_6H_5\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2COC_6H_5 \xrightarrow{OH^-} C_6H_5\underset{\underset{CH_3}{|}}{C}{=}CHCOC_6H_5$$

(n)



$$C_6H_5CH_2CHO + C_6H_5CHO \xrightarrow{\text{dil. NaOH}} C_6H_5\overset{\overset{OH}{|}}{C}H\underset{\underset{C_6H_5}{|}}{C}HCHO +$$

$$C_6H_5CH_2\overset{\overset{OH}{|}}{C}H\underset{\underset{C_6H_5}{|}}{C}HCHO \xrightarrow{OH^-} \underset{\text{(Major)}}{C_6H_5CH{=}\underset{\underset{C_6H_5}{|}}{C}CHO} + C_6H_5CH_2CH{=}\underset{\underset{C_6H_5}{|}}{C}CHO$$



$$C_6H_5COCH_3 + C_6H_5CHO \xrightarrow{\text{dil. NaOH}} C_6H_5\overset{\overset{OH}{|}}{C}HCH_2COC_6H_5 +$$

$$C_6H_5\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2COC_6H_5 \xrightarrow{OH^-} C_6H_5CH{=}CHCOC_6H_5 + C_6H_5\underset{\underset{CH_3}{|}}{C}{=}CHCOC_6H_5$$

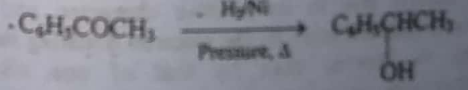
(o) $C_6H_5CH_2CHO \xrightarrow{\text{Fehling's solution}} C_6H_5CH_2COOH$

$C_6H_5COCH_3 \xrightarrow{\text{Fehling's solution}}$ No reaction

(p) $C_6H_5CH_2CHO \xrightarrow{\text{Tollen's reagent}} C_6H_5CH_2COOH$

$C_6H_5COCH_3 \xrightarrow{\text{Tollen's reagent}}$ No reaction

(q) $C_6H_5CH_2CHO \xrightarrow[\text{Pressure, }\Delta]{H_2/Ni} C_6H_5CH_2CH_2OH$



$$C_6H_5COCH_3 \xrightarrow[\text{Pressure, }\Delta]{H_2/Ni} C_6H_5\underset{\underset{OH}{|}}{C}HCH_3$$

(r) $C_6H_5CH_2CHO \xrightarrow{\text{Cold. dil. }KMnO_4} C_6H_5CH_2COOH$

$C_6H_5COCH_3 \xrightarrow{\text{Cold. dil. }KMnO_4}$ No reaction

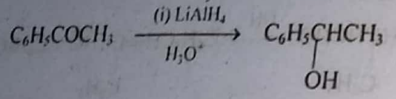
(s) $C_6H_5CH_2CHO \xrightarrow[\Delta]{KMnO_4,\ H_3O^+} C_6H_5COOH + HCOOH$

$$C_6H_5COCH_3 \xrightarrow[\Delta]{KMnO_4,\ H_3O^+} C_6H_5COOH + HCOOH$$

(t) $C_6H_5CH_2CHO \xrightarrow[\Delta]{CrO_3,\ H_2SO_4} C_6H_5COOH + HCOOH$

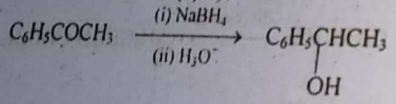
$$C_6H_5COCH_3 \xrightarrow[\Delta]{CrO_3,\ H_2SO_4} C_6H_5COOH + HCOOH$$

(u) $C_6H_5CH_2CHO \xrightarrow[2H_3O^+]{(i)\ LiAlH_4} C_6H_5CH_2CH_2OH$



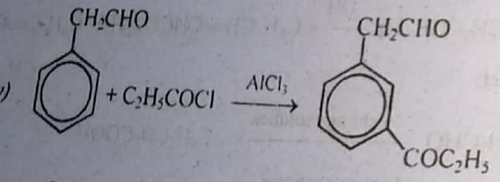
$$C_6H_5COCH_3 \xrightarrow[H_3O^+]{(i)\ LiAlH_4} C_6H_5\underset{OH}{\underset{|}{C}}HCH_3$$

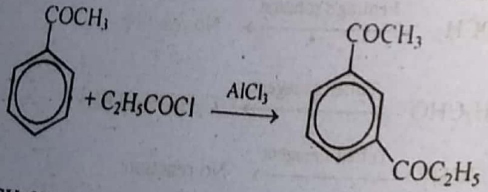
(v) $C_6H_5CH_2CHO \xrightarrow[(ii)\ H_3O^+]{(i)\ NaBH_4,} C_6H_5CH_2CH_2OH$



$$C_6H_5COCH_3 \xrightarrow[(ii)\ H_3O^+]{(i)\ NaBH_4} C_6H_5\underset{OH}{\underset{|}{C}}HCH_3$$

(w)





9. (a) $CH_3CH_2CHO > CH_3COCH_3$

Propionaldehyde is more reactive than acetone because the nucleophile attacks the carbonyl carbon due to its positive character, and the positive character of this carbon is reduced more by the electron-donating inductive effect of two alkyl groups in acetone than by that of one alkyl group in propionaldehyde. Furthermore, two alkyl groups cause greater steric hindrance to the nucleophilic attack than one alkyl group.

(b) $CH_3COCH_3 > (CH_3)_3CCHO$

The bulky *t*-butyl group hinders the attack of a nucleophile to the carbonyl carbon.

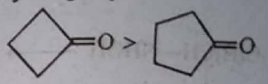
(c) $CH_3CH_2CH_2CH_2CHO > (CH_3)_3CCHO$

Due to the same reason as in (b)

(d) $CH_3COCH_3 > CH_3COOCH_3$

The carbonyl carbon is not as positive in the ester as in the ketone, due to the contribution of $-\overset{O^-}{\overset{|}{C}}=\overset{+}{\ddot{O}}R$. Furthermore, the addition of a nucleophile to the carbonyl carbon of the ester will require the loss of stabilization of the carboxylate group.

(e)



The addition of a nucleophile to the carbonyl carbon of cyclobutanone is accompanied by the relief of angle strain from 30° (120 – 90) to 19.5° (109.5 – 90). On the other hand, in the case of cyclopentanone, the addition of a nucleophile does not provide much additional relief from the angle strain.

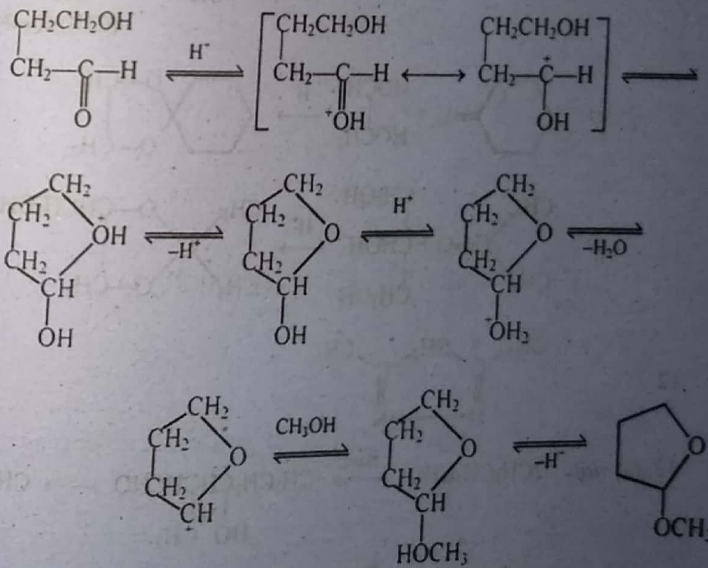
(f) $CH_3COCl > CH_3COCH_3$

The inductive effect of chlorine in acetyl chloride makes the carbonyl carbon more positive.

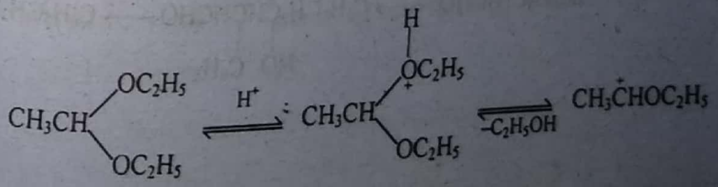
(g) $CH_3COCCl_3 > CH_3COCH_3$

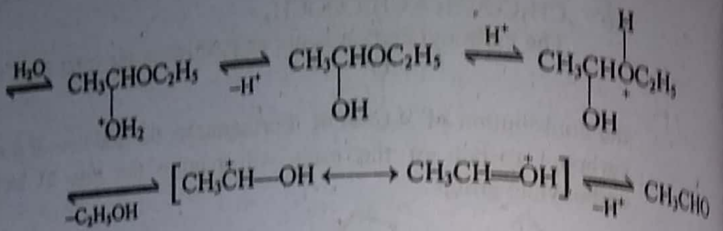
Due to the same reason as in (f).

(a)



(b)

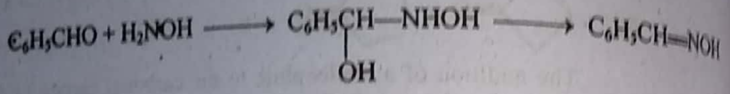




$$\overset{H_2O}{\longleftarrow} \underset{{}^{+}OH_2}{CH_3CHOC_2H_5} \underset{-H^+}{\rightleftharpoons} \underset{OH}{CH_3CHOC_2H_5} \overset{H^+}{\rightleftharpoons} \underset{OH}{CH_3CH\overset{H}{\overset{+}{O}}C_2H_5}$$

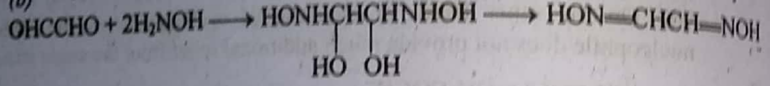
$$\xrightarrow[-C_2H_5OH]{} [CH_3\overset{+}{C}H{-}OH \longleftrightarrow CH_3CH{=}\overset{+}{O}H] \underset{-H^+}{\rightleftharpoons} CH_3CHO$$

11. (a)



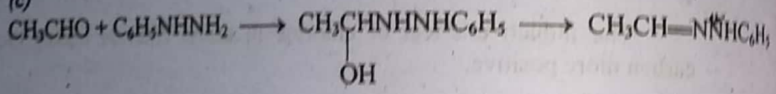
$$C_6H_5CHO + H_2NOH \longrightarrow C_6H_5\underset{OH}{CH}{-}NHOH \longrightarrow C_6H_5CH{=}NOH$$

(b)



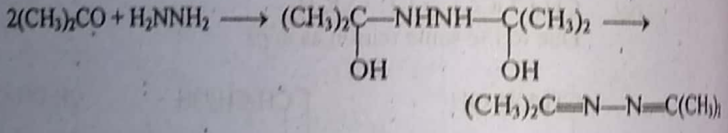
$$OHCCHO + 2H_2NOH \longrightarrow HONH\underset{HO}{CH}\underset{OH}{CH}NHOH \longrightarrow HON{=}CHCH{=}NOH$$

(c)



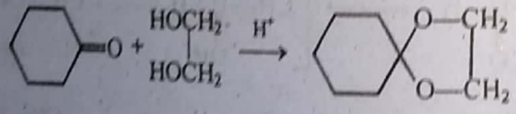
$$CH_3CHO + C_6H_5NHNH_2 \longrightarrow CH_3\underset{OH}{CH}NHNHC_6H_5 \longrightarrow CH_3CH{=}NNHC_6H_5$$

(d)

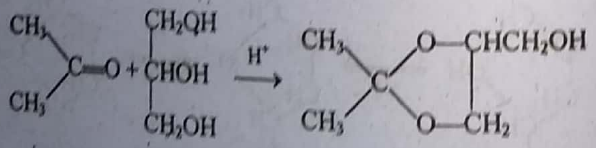


$$2(CH_3)_2CO + H_2NNH_2 \longrightarrow (CH_3)_2\underset{OH}{C}{-}NHNH{-}\underset{OH}{C}(CH_3)_2 \longrightarrow (CH_3)_2C{=}N{-}N{=}C(CH_3)_2$$

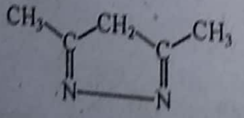
(e)



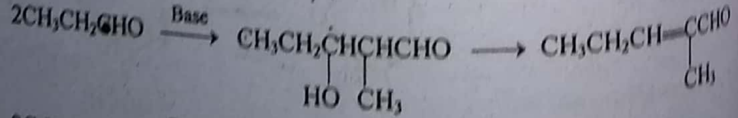
(f)



12.

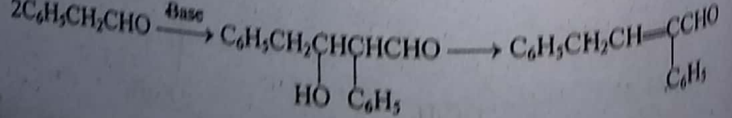


13. (a) (a)



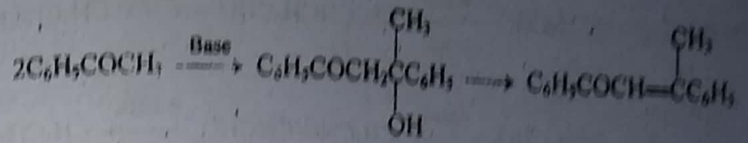
$$2CH_3CH_2CHO \xrightarrow{Base} CH_3CH_2\underset{HO}{CH}\underset{CH_3}{CH}CHO \longrightarrow CH_3CH_2CH{=}\underset{CH_3}{C}CHO$$

(b)



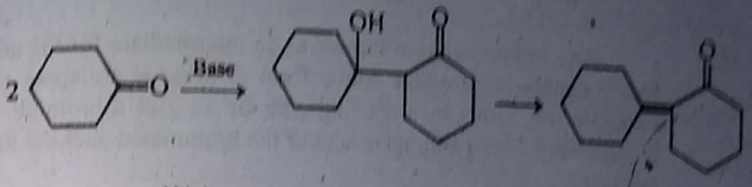
$$2C_6H_5CH_2CHO \xrightarrow{Base} C_6H_5CH_2\underset{HO}{CH}\underset{C_6H_5}{CH}CHO \longrightarrow C_6H_5CH_2CH{=}\underset{C_6H_5}{C}CHO$$

(c)



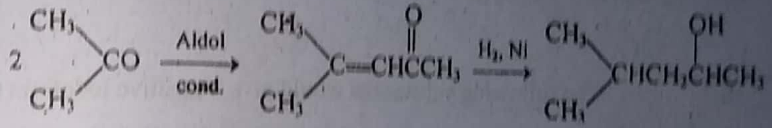
$$2C_6H_5COCH_3 \xrightarrow{Base} C_6H_5COCH_2\underset{OH}{\overset{CH_3}{C}}C_6H_5 \longrightarrow C_6H_5COCH{=}\overset{CH_3}{C}C_6H_5$$

(d)

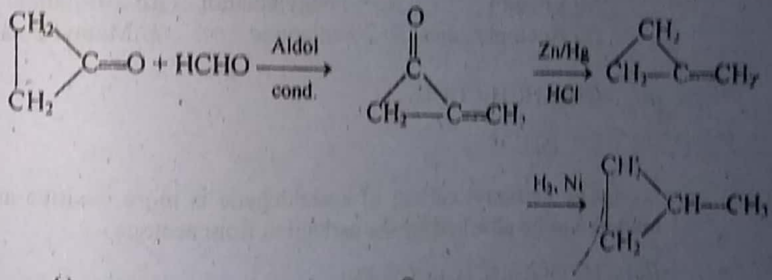


(b) (a) $2CH_3CHO \xrightarrow[\text{cond.}]{\text{Aldol}} CH_3CH{=}CHCHO \xrightarrow{H_2,\ Ni} CH_3CH_2CH_2CH_2OH$

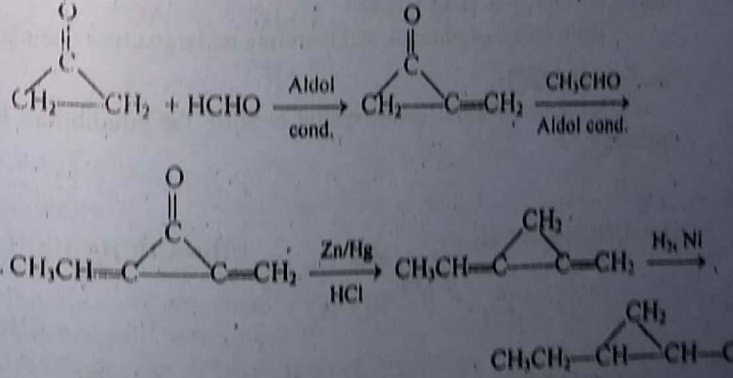
(b)



(c)



(d)

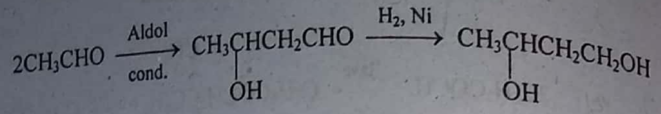


14. (a) (a) $CH_3CH{=}CHCHO$ and $CH_2{=}CHCHO$

(b) $CH_3CH{=}CHCHO$ and $CH_3CH{=}CHCOCH_3$

(c) $CH_3CH_2CH{=}CCHO$ and $(CH_3)_3CCH{=}CCHO$

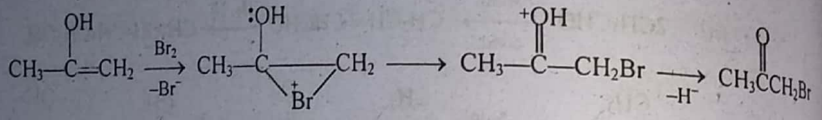
(b) (a)



$$2CH_3CHO \xrightarrow[\text{cond.}]{\text{Aldol}} CH_3\underset{\substack{|\\ OH}}{C}HCH_2CHO \xrightarrow{H_2,\ Ni} CH_3\underset{\substack{|\\ OH}}{C}HCH_2CH_2OH$$

(b) $2CH_3CHO \xrightarrow[\text{cond.}]{\text{Aldol}} CH_3CH{=}CHCHO \xrightarrow{NaBH_4} CH_3CH{=}CHCH_2OH$

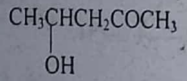
15. Any bromonium ion formed as an intermediate for the addition of bromine to the double bond of the enolic form of acetone collapses to the more stable oxonium ion, rather than reacting with Br^- to give dibromide. The oxonium ion being a very strong conjugate acid of the brominated acetone loses H^+ to give the product.



16. The following substances would give a positive iodoform test:

(a) Ethanol
(b) 1-Phenylethanol
(d) 2-Butanol
(g) Acetone
(h) Acetophenone
(i) 2-Pentanone
(k) Methyl 2-naphthyl ketone.

17. *(a)*



$$CH_3\underset{\substack{|\\ OH}}{C}HCH_2COCH_3$$

The carbonyl carbon of acetaldehyde is more positive and less sterically hindered to be attacked by the carbanion from acetone.

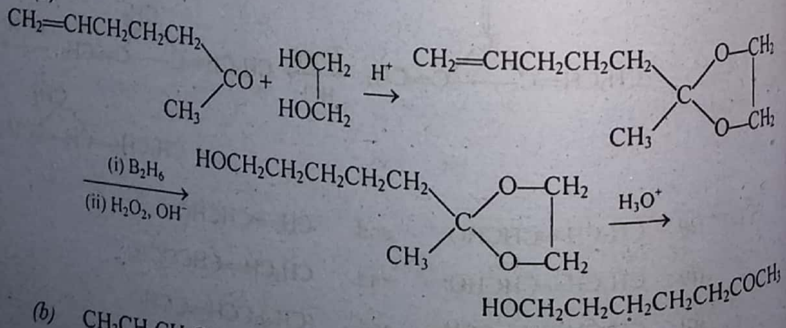
(b) $HCOO^- + (CH_3)_3CCH_2OH$

Both lack α-hydrogen, and therefore undergo cross-Cannizzaro's reaction.

(c) CH_3COCH_3

Reverse of aldol condensation because the equilibrium lies in favour of acetone.

18. *(a)*



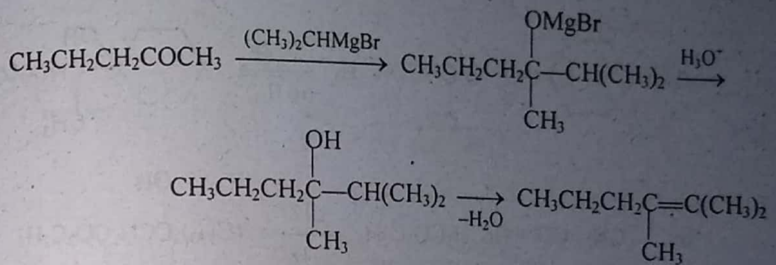
(b) $CH_3CH_2CH_2CH_2CH_2CH_2C{\equiv}CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3(CH_2)_5COCH_3$

$\xrightarrow{LiAlH_4} CH_3(CH_2)_5CHOHCH_3$

(c) $CH_3CH_2CH_2CHO \xrightarrow[\text{(ii) }H_3O^+]{\text{(i) }CH_3CH_2CH_2MgBr} CH_3CH_2CH_2CHOHCH_2CH_2CH_3$

$\xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3CH_2CH_2COCH_2CH_2CH_3 \xrightarrow{Br_2,\ OH^-} CH_3CH_2CH_2COCHBrCH_2CH_3$

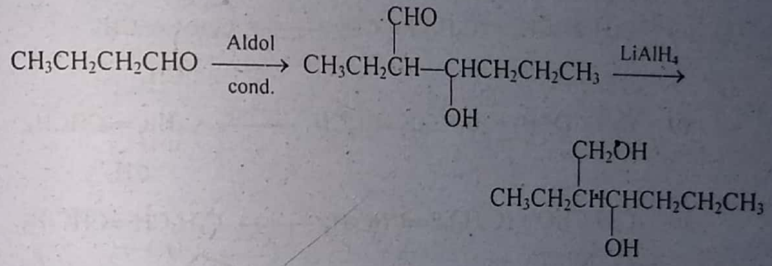
(d)



$$CH_3CH_2CH_2COCH_3 \xrightarrow{(CH_3)_2CHMgBr} CH_3CH_2CH_2\overset{\substack{OMgBr\\|}}{\underset{\substack{|\\ CH_3}}{C}}—CH(CH_3)_2 \xrightarrow{H_3O^+}$$

$$CH_3CH_2CH_2\overset{\substack{OH\\|}}{\underset{\substack{|\\ CH_3}}{C}}—CH(CH_3)_2 \xrightarrow[-H_2O]{} CH_3CH_2CH_2\underset{\substack{|\\ CH_3}}{C}{=}C(CH_3)_2$$

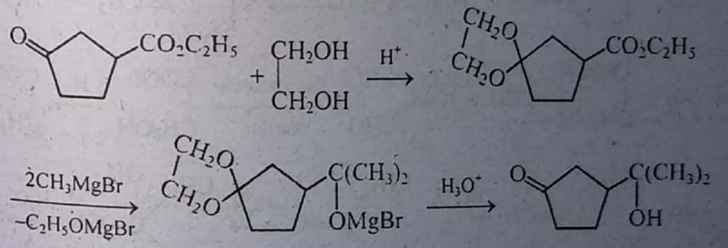
(e)



$$CH_3CH_2CH_2CHO \xrightarrow[\text{cond.}]{\text{Aldol}} CH_3CH_2\overset{\substack{CHO\\|}}{C}H—\underset{\substack{|\\ OH}}{C}HCH_2CH_2CH_3 \xrightarrow{LiAlH_4}$$

$$CH_3CH_2\overset{\substack{CH_2OH\\|}}{C}H\underset{\substack{|\\ OH}}{C}HCH_2CH_2CH_3$$

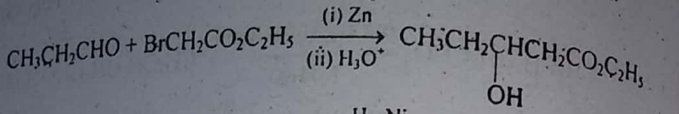
(f)



19. *(a)* Hexanal will give positive Tollen's reagent test.
(b) 2-Hexanone will give positive iodoform test.
(c) 2-Hexanone will form 2,4-dinitrophenylhydrazone.
(d) 2-Cycloheptenone will decolorize bromine water.
(e) $CH_3COCH_2COCH_3$ will undergo bromination instantaneously due to its high enolic content.
(f) $[(CH_3)_3C]_2CO$ is too sterically congested to react readily with 2,4-dinitrophenylhydrazine.
(g) $(CH_3)_2C(OH)CH_2COCH_3$ will be cleaved to acetone with a dilute base.
(h) $CH_3CH_2CH(OCH_3)_2$ will give positive Tollen's reagent test after treatment with an acid.

(i) $C_6H_5COCH_2COC_6H_5$ will give a positive test for its enolic form.

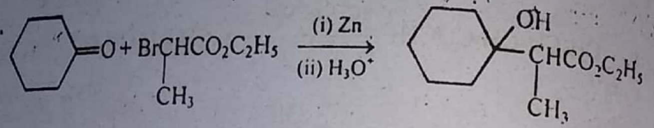
20.(a) (a)



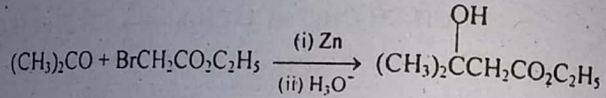
$CH_3CH_2CHO + BrCH_2CO_2C_2H_5 \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Zn}} CH_3CH_2\underset{OH}{C}HCH_2CO_2C_2H_5$

$\xrightarrow[\Delta]{H_3O^+} CH_3CH_2CH{=}CHCO_2C_2H_5 \xrightarrow{H_2,\ Ni} CH_3CH_2CH_2CH_2CO_2C_2H_5$

(b)

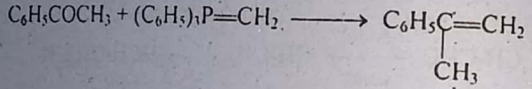


(c)



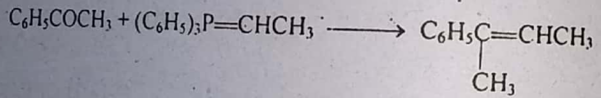
$(CH_3)_2CO + BrCH_2CO_2C_2H_5 \xrightarrow[\text{(ii) } H_3O^-]{\text{(i) Zn}} (CH_3)_2\overset{OH}{C}CH_2CO_2C_2H_5$

(b) (a)



$C_6H_5COCH_3 + (C_6H_5)_3P{=}CH_2 \longrightarrow C_6H_5\underset{CH_3}{C}{=}CH_2$

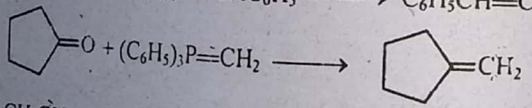
(b)



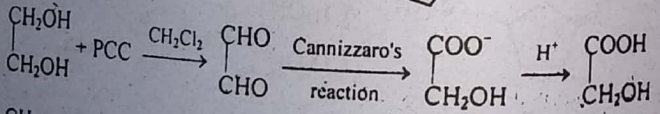
$C_6H_5COCH_3 + (C_6H_5)_3P{=}CHCH_3 \longrightarrow C_6H_5\underset{CH_3}{C}{=}CHCH_3$

(c) $C_6H_5CHO + (C_6H_5)_3P{=}CHC_6H_5 \longrightarrow C_6H_5CH{=}CHC_6H_5$

(d)

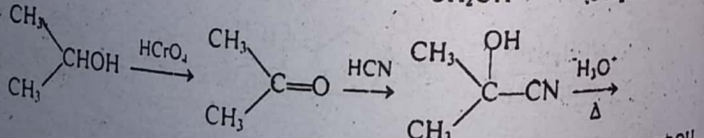


21.(a) (a)



$\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} + PCC \xrightarrow{CH_2Cl_2} \begin{matrix}CHO\\|\\CHO\end{matrix} \xrightarrow[\text{reaction}]{\text{Cannizzaro's}} \begin{matrix}COO^-\\|\\CH_2OH\end{matrix} \xrightarrow{H^+} \begin{matrix}COOH\\|\\CH_2OH\end{matrix}$

(b)



$(CH_3)_2C(OH)COOH$

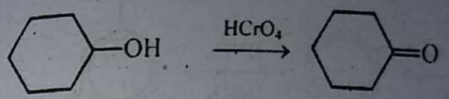
(b) (a) $CH{\equiv}CH + NaNH_2 \xrightarrow[\text{liq. } NH_3]{} CH{\equiv}C^-\ Na^+ \xrightarrow{CH_3Br} CH_3C{\equiv}CH$

$CH_3C{\equiv}CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3COCH_3 \xrightarrow[NaOH]{HCHO} CH_3COCH_2CH_2OH$

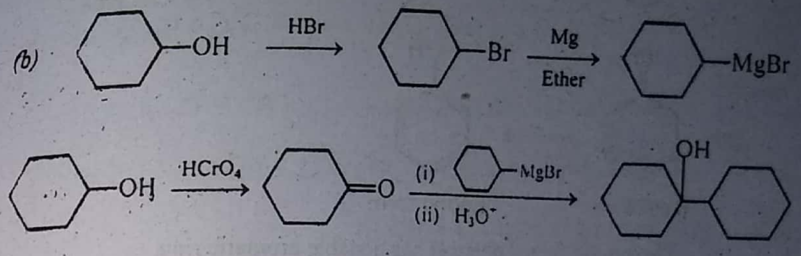
$\xrightarrow[-H_2O]{OH^-} CH_3COCH{=}CH_2$

(b) $CH{\equiv}CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3CHO \xrightarrow[\text{cond.}]{\text{Aldol}} CH_3CH{=}CHCHO$

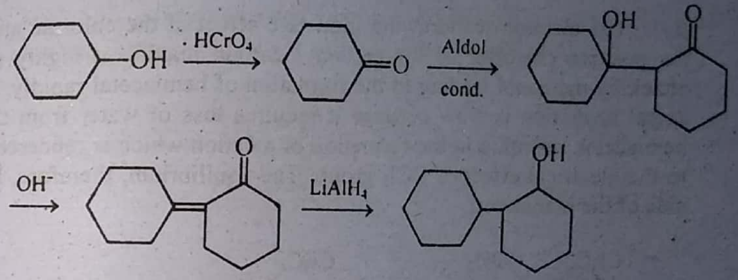
(c) (a)



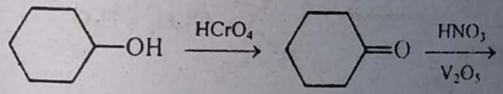
(b)



(c)

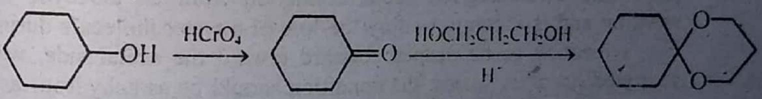


(d)

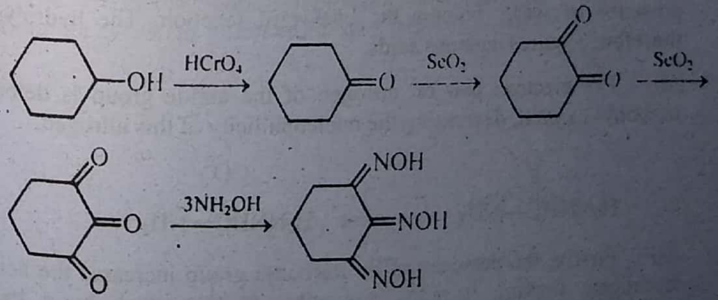


$HOOC(CH_2)_4COOH$

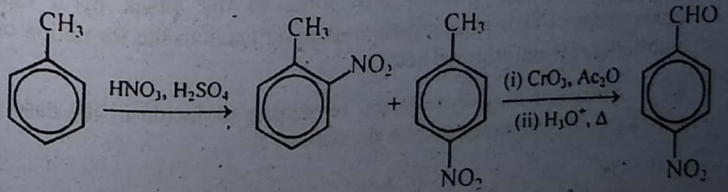
(e)



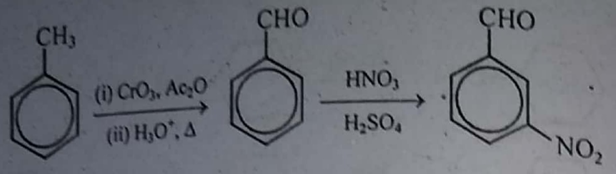
(f)



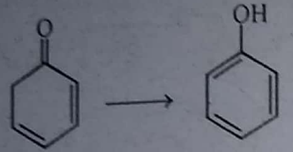
(d) (a)



(b)



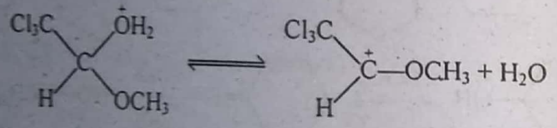
22. (a)



Keto form Enolic form

The enolic form (phenol) has a stable aromatic ring.

(b) The electron-withdrawing inductive affect of the chlorine atoms enhances the positive character of the carbonyl carbon making it highly susceptible to attack by methanol leading to the formation of hemiacetal rapidly. However, the acetal formation is slow because it requires loss of water from the protonated hemiacetal, resulting in the formation of a cation which is rendered unstable due to the electrical effect of CCl_3 group. The equilibrium, therefore, lies far on the side of the hemiacetal.



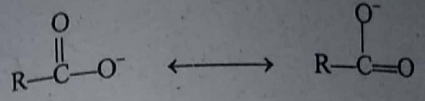
(c) The acid-catalysed acetal formation from an aldehyde is a reversible reaction and is accompanied by the loss of a water molecule during the process. For a reaction to be pushed forward toward the acetal side, water should be removed. In other words, the condition should be as anhydrous as possible. The presence of water favours the backward reaction. The hydrolysis of acetals therefore requires aqueous acids.

(d) The electron pair on nitrogen of the amide group is delocalized to the carbonyl oxygen, decreasing the nucleophilicity of this nitrogen.

$$H_2NNH\overset{O}{\overset{\|}{C}}—\ddot{N}H_2 \longleftrightarrow H_2NNH\overset{O^-}{\overset{|}{C}}{=}\overset{+}{N}H_2$$

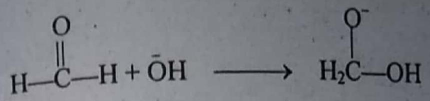
(e) Firstly, the presence of the carbonyl group increases the acidity of the α-hydrogen, making it more susceptible to the attack by a base. Secondly, elimination of HBr from a β-bromoketone leads to the formation of a resonance stabilized α,β-unsaturated ketone.

(f) After donating hydride the remaining molecule in the case of A is more stabilized by resonance than in the case of B.



$$R—\overset{O}{\overset{\|}{C}}—O^- \longleftrightarrow R—\overset{O^-}{\overset{|}{C}}{=}O$$

23.



$$H—\overset{O}{\overset{\|}{C}}—H + \bar{O}H \longrightarrow H_2\overset{O^-}{\overset{|}{C}}—OH$$

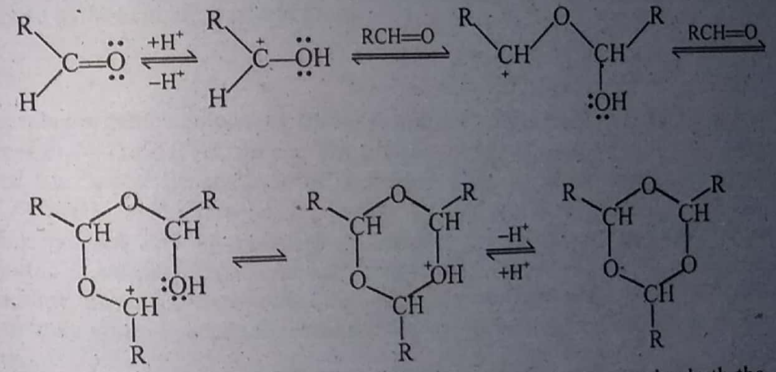
$$HOCH_2—O^- + CH_2{=}O \longrightarrow HOCH_2—O—CH_2—O^- \xrightarrow{nCH_2=O}$$

$$HOCH_2—O—CH_2—O—(CH_2—O)_{n-1}—CH_2—O^- \xrightarrow{H_2O}$$

$$HOCH_2—O—CH_2—O—(CH_2—O)_{n-1}—CH_2OH$$

No; Trioxymethylene formation would necessarily require OH^- to come off as a a leaving group which is not likely to occur in basic solution.

24.



The intermediate carbocation in the case of an aldehyde contains both the electrophilic as well as nucleophilic sites required for cyclization.

Chapter 11

Carboxylic Acids and Their Derivatives

CHAPTER'S SUMMARY

Carboxylic acids are the organic compounds containing carboxy group (—COOH) in their molecules, and may be represented by the general formula RCOOH, where R may be hydrogen, alkyl or aryl group.

Nomenclature

Like other organic compounds, carboxylic acids are known either by the common (trivial) names or by the IUPAC names. The common names are generally derived from the origin of the carboxylic acids. Some carboxylic acids are conveniently named as derivatives of acetic acid. The IUPAC names are derived from the names of the corresponding hydrocarbons by replacing the ending *-e* of the name of the hydrocarbon with *-oic acid*. The aromatic carboxylic acids are named either as derivatives of benzoic acid or by adding the suffix *-carboxylic acid* to the name of the aromatic hydrocarbon to which the carboxy group is attached, without dropping the ending *-e* of the name of the hydrocarbon.

Preparation of Carboxylic Acids

Most of the straight-chain carboxylic acids of even number carbon atoms ranging from six to eighteen are obtained from the naturally occurring oils and fats by hydrolysis. Other carboxylic acids can be prepared by synthetic methods involving oxidation of various compounds as follows:

1. By the oxidative cleavage of unsaturated hydrocarbons on treatment with alkaline $KMnO_4$ or acidic $K_2Cr_2O_7$.

2. By the oxidation of aliphatic side-chain present on the aromatic ring on treatment with alkaline $KMnO_4$ or acidic $K_2Cr_2O_7$.

3. By the oxidation of primary alcohols on treatment with alkaline $KMnO_4$ or acidic $K_2Cr_2O_7$.

4. By the base-catalysed halogenation of a methyl ketone, followed by hydrolysis.

5. By passing carbon dioxide into the ethereal solution of a Grignard reagent, followed by hydrolysis.

6. By the hydrolysis of nitriles on treatment with hot water in the presence of an acid or a base.

Physical Properties of Carboxylic Acids

The lower-molecular-weight monocarboxylic aliphatic acids are volatile liquid; decanoic and higher acids are solid, some with very high melting point.

Carboxylic acids are polar substances and can form hydrogen bonds, stronger than alcohols, with each other and with water, and mostly exist in a cyclic dimeric form. They have melting and boiling points notably higher than those of the alcohols of comparable molecular weights.

The first four members of the series are completely miscible with water; the five-carbon acid is partly soluble, followed by a gradual decrease in solubility as the chain-length increases. All aromatic carboxylic acids, including benzoic acid, are insoluble in water. Carboxylic acids are generally soluble in organic solvents.

Acidity of Carboxylic Acids

Although carboxylic acids are very weak acids as compared to the mineral acids, they are much stronger than the other acidic organic compounds we have studied so far, including phenols. The relative acidity of different types of compounds are: $RCOOH > ArOH > HOH > ROH > HC \equiv CH > RH$. However, the acid strength of carboxylic acids is influenced by many factors as explained in the *Textbook*.

Reactions of Carboxylic Acids

The reactions of carboxylic acids are essentially those of the hydroxy part of the carboxy group, of course under the influence of the carbonyl group. The reactions due to the other part of the molecule depend on the nature of that part:

1. Salt formation. In aqueous solutions carboxylic acids are readily converted to their salts on treatment with either moderately active metals such as Ca, Mg, Zn, Al, etc. or Arrhenius bases such as ammonia, NaOH, etc. Since treatment of carboxylic acids with $NaHCO_3$ results in the formation of salts accompanied by the evolution of CO_2, it is used for the identification of the carboxy group, and as a test to distinguish between a carboxylic acid and a phenol. Since the salts of some of the insoluble carboxylic acids are soluble in water, they may be used for the isolation and identification of the carboxylic acids; the salts are readily converted back to the carboxylic acids on treatment with aq. mineral acids.

2. Nucleophilic acyl substitution. Carboxylic acids undergo nucleophilic substitution at the carbonyl carbon on treatment with various reagents such as thionyl chloride, another molecule of the carboxylic acid, an alcohol or ammonia (or an amine), resulting in the replacement of OH of the carboxy group by Cl, OCOR, OR and NH_2, to form the derivatives of carboxylic acids, such as acid chlorides, acid anhydrides, esters and amides, respectively. These derivatives are readily converted back to the parent carboxylic acids on simple hydrolysis. They can also be mutually interconverted.

3. Reduction of carboxylic acids. On treatment with $LiAlH_4$, carboxylic acids are smoothly reduced to primary alcohols.

4. Decarboxylation. Carboxylic acids undergo decarboxylation (loss of CO_2) either on simple heating or by heating their sodium salts in the presence of soda lime.

Carboxylic acids also undergo decarboxylative halogenation to form alkyl halides either by treating their silver salts with halogens, usually bromine, or by treating them with lead tetraacetate and LiCl.

Aromatic carboxylic acids are decarboxylated by heating their salts with an alkali in the presence of copper and quinoline.

5. α-Halogenation. Aliphatic carboxylic acids react with bromine (or chlorine) in the presence of small amounts of phosphorus to form α-halocarboxylic acids which are important intermediates for the synthesis of a variety of α-substituted carboxylic acids.

FUNCTIONAL DERIVATIVES OF CARBOXYLIC ACIDS

The most important feature of the functional derivatives of carboxylic acids, and the acids themselves, is the presence of the carbonyl group which plays a dominant role in their chemistry in two ways: (i) it provides a site for nucleophilic attack and (ii) it increases the acidity of the α-hydrogen. Unlike aldehydes and ketones which involve nucleophilic addition to the carbonyl double bond, the acid derivatives involve nucleophilic substitution at the acyl carbon atom. The order of reactivity of the carboxylic acid derivatives is: acid chlorides > acid anhydrides > esters > amides, i.e., in the order of the nucleofugality of their leaving groups.

Acid Chlorides

The names of the acid chlorides are derived from the names of the parent carboxylic acids by replacing the ending *-ic* by *-yl*, and *acid* by *chloride*.

Acid chlorides of up to thirteen carbon atoms are liquid with their boiling points lower than those of the parent carboxylic acids, but close to the unassociated liquid compounds such as alkyl chlorides, aldehydes and ketones, having about the same molecular weight. Acid chlorides are generally soluble in common organic solvents.

Preparation of acid chlorides. Since acid chlorides are the most reactive derivatives of carboxylic acids, they are usually prepared so that they can be used for the preparation of other derivatives of carboxylic acids.

Acid chlorides are usually prepared by treating the carboxylic acids with acid chlorides of inorganic acids, e.g., PCl_3, PCl_5 and $SOCl_2$.

Reactions of acid chlorides. Acid chlorides are rapidly hydrolysed to their parent carboxylic acids on treatment with water.

The preparation of acid chlorides as well as their conversion to the other derivatives of carboxylic acids is rapid and essentially irreversible. It is therefore more convenient to prepare carboxylic acid derivatives through acid chlorides, rather than from the acids directly.

1. *Conversion to acid anhydrides.* Acid chlorides are converted to acid anhydrides on treatment either with carboxylic acids in the presence of pyridine or with sodium salts of carboxylic acids.

2. *Conversion to esters.* Acid chlorides are converted to esters on treatment with alcohols in the presence of a base, such as pyridine.

3. *Conversion to amides.* Acid chlorides are converted to amides on treatment with ammonia.

4. *Friedel-Crafts acylation.* Acid chlorides react with aromatic hydrocarbons in the presence of a Lewis acid to yield aromatic ketones.

5. *Reactions with organometallic compounds.* Acid chlorides react with various organometallic reagents, such as Grignard reagents or organocuprates, to produce ketones.

6. *Reduction.* Acid chlorides are reduced to aldehydes on treatment with $LiAlH(t\text{-}BuO)_3$.

7. *Conversion to acyl peroxides.* Acid chlorides are converted to diacyl peroxides on treatment with a cold aq. solution of Na_2O_2. Acyl peroxides are useful radical-initiators.

Acid Anhydrides

Acid anhydrides are obtained after the elimination of a water molecule from two carboxy groups of either two different molecules or the same molecule. They are named by replacing the word *acid* of the parent carboxylic acid(s) by *anhydride*.

The lower anhydrides are liquid with boiling points close to the unassociated liquid organic compounds of comparable molecular weights. Anhydrides above nonanoic anhydride are solid. Anhydrides are generally soluble in common organic solvents.

Preparation of acid anhydrides. The anhydride of formic acid is unknown. The simplest anhydride is that of acetic acid. Acetic anhydride is a very important industrial chemical. It is generally prepared by adding acetic acid to acetylene in the presence of $MgSO_4$, followed by pyrolysis. Another method involves the addition of acetic acid to ketene, $CH_2{=}C{=}O$, which is produced by the pyrolysis of acetone.

A general method for the preparation of acid anhydrides involves the elimination of a water molecule from two molecules of carboxylic acids in the presence of a dehydrating agent, such as P_2O_5 or conc. H_2SO_4 or even acetic anhydride. They are also generally prepared from acid chlorides as mentioned above.

Five- or six-membered cyclic anhydride is obtained simply on heating a suitable dicarboxylic acid.

Reactions of acid anhydrides. Acid anhydrides generally undergo the same reactions as acid chlorides, but a little more slowly.

1. *Hydrolysis of acid anhydrides.* Acid anhydrides undergo acid- or base-catalysed hydrolysis to parent carboxylic acids.

2. *Conversion to esters.* Acid anhydrides react with alcohols to form esters.

3. *Conversion to amides.* Acid anhydrides react with ammonia to form amides.

4. *Friedel-Crafts acylation.* Acid anhydrides are usually used in place of acid chlorides for the acylation of aromatic hydrocarbons to form aromatic ketones.

Esters

Esters are obtained from the reaction of a carboxylic acid with an alcohol accompanied by the elimination of a water molecule, and are named by writing the name of the alkyl group of the alcohol followed by the name of the acid with the ending *-ic acid* replaced by *–ate*.

Generally, esters are liquid, with their boiling points close to those of aldehydes and ketones of comparable molecular weights, or they are low-melting solid, and are lighter than water. Esters generally are insoluble in water but soluble in common organic solvents.

Preparation of esters. Esters are generally prepared from carboxylic acids or their derivatives by their reaction with alcohols (or phenols).

1. Esters are usually prepared by refluxing a mixture of a carboxylic acid and an alcohol in the presence of a little mineral acid. The reaction is reversible.

2. Methyl esters can be prepared by the reaction of carboxylic acids with diazomethane in ether.

3. Esters can also be prepared by the reaction of either acid chlorides or acid anhydrides with alcohols, as mentioned above.

Reactions of esters. Some of the common reactions of esters are as follows:

1. *Hydrolysis.* Esters are hydrolysed slowly to a carboxylic acid and an alcohol on heating with water. Hydrolysis can be catalysed either by a mineral acid or by NaOH (saponification).

2. *Transesterification.* An ester can be transformed into another by its treatment either with an alcohol in the presence of a strong acid or with an alkoxide.

3. *Conversion to amides.* Esters react slowly with ammonia to yield amides.

4. *Reaction with Grignard reagents.* Esters react with Grignard reagents to form tertiary alcohols with two identical alkyl groups.

5. *Reduction.* Esters can be reduced either catalytically or by the use of a chemical reducing agent such as $LiAlH_4$, to yield a primary alcohol corresponding to the

acid portion of the ester, in addition to the original alcohol.

Amides

The amides are named by replacing *-oic* (or *-ic*) *acid* of the name of the parent carboxylic acid by *-amide*. Formamide is a liquid, while all other amides are solid with sharp melting points. They form strong intermolecular hydrogen bonds the possibility of which gradually decreases by replacing amino hydrogens by methyl groups. Lower amides (up to five carbons) are soluble in water.

Preparation of amides. Amides can be prepared from acid chlorides, acid anhydrides or esters, as described earlier. On industrial scale, amides are usually made by heating the dry ammonium salts of carboxylic acids, which are prepared by the reaction of carboxylic acids with aq. ammonia.

Reactions of amides. Some of the common reactions of amides are:

1. *Hydrolysis.* Amides are hydrolysed to carboxylic acids and ammonia on heating with aq. acid or alkali.

2. *Dehydration.* Amides can be converted to the corresponding nitriles on treatment with an efficient dehydrating agent, such as P_2O_5, $POCl_3$, $SOCl_2$ or acetic anhydride.

3. *Hofmann degradation.* On treatment with bromine (or chlorine) in NaOH, amides give amines with one carbon less than the starting material.

ACTIVE METHYLENE COMPOUNDS

The methylene hydrogen of malonic and acetoacetic esters is highly acidic and can be easily removed to create a resonance-stabilized carbanion which is very useful for the formation of a new carbon-carbon bond. The ease with which the substituted malonic and acetoacetic acids undergo decarboxylation provides a useful tool for the synthesis of substituted acetic acids (from malonic ester) and substituted acetones (from acetoacetic ester).

Malonic Ester

The malonic ester syntheses generally involve the following steps: (i) the methylene hydrogen of malonic ester is removed by a base to create a carbanion; (ii) the carbanion reacts with an alkyl halide to yield an alkylmalonic ester; (iii) the substituted malonic ester is hydrolysed to substituted malonic acid which on heating undergoes decarboxylation to yield a monocarboxylic acid.

Thus, by choosing appropriate reagents we can synthesize substituted acetic acids, dicarboxylic acids and cycloalkanecarboxylic acids, in a variety of forms.

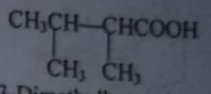
Acetoacetic Ester

Acetoacetic ester syntheses essentially involve the same steps as the malonic ester syntheses, to lead to the formation of methyl ketones, diketones and carboxylic acids, in a variety of forms, by choosing appropriate reagents.

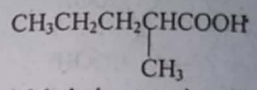
ANSWERS TO EXERCISES

1\. $CH_3CH_2CH_2CH_2CH_2COOH$

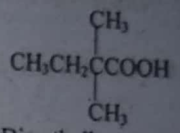
Hexanoic acid
(*n*-Butylacetic acid)


$\mathrm{CH_3\underset{\underset{CH_3}{|}}{C}H\!-\!\underset{\underset{CH_3}{|}}{C}HCOOH}$

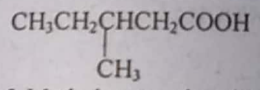
2,3-Dimethylbutanoic acid
(Isopropylmethylacetic acid)


$\mathrm{CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{C}HCOOH}$

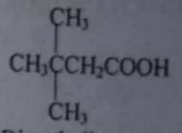
2-Methylpentanoic acid
(Methyl-*n*-propylacetic acid)


$\mathrm{CH_3CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}COOH}$

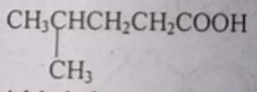
2,2-Dimethylbutanoic acid
(Ethyldimethylacetic acid)


$\mathrm{CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH_2COOH}$

3-Methylpentanoic acid
(*sec*-Butylacetic acid)


$\mathrm{CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2COOH}$

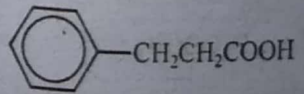
3,3-Dimethylbutanoic acid
(*t*-Butylacetic acid)


$\mathrm{CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2COOH}$

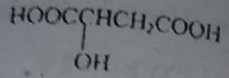
4-Methylpentanoic acid
(Isobutylacetic acid)

2\.
(*a*) 4-Methylpentanoic acid
(*b*) 2,4-Hexadienoic acid
(*c*) 3-Methyl-3-pentenoic acid
(*d*) 4-Methoxybutanoic acid
(*e*) 4-Phenylbutanoic acid
(*f*) 4-Carboxybenzenesulfonic acid
(*g*) 4-Methylbenzenecarboxylic acid
(*h*) Diallylethanoic acid
(*i*) Heptanedioic acid
(*j*) 2-Butynedioic acid

3\.
(*a*) Sodium butyrate
(*b*) γ-Phenylbutyryl chloride
(*c*) Magnesium oxalate
(*d*) 1,1-Dicarbomethoxycyclohexane
(*e*) Acetic anhydride
(*f*) Acetyl peroxide
(*g*) Acrylic anhydride
(*h*) Divinyl oxalate
(*i*) Methyl acrylate
(*j*) Vinyl acetate
(*k*) N,N-Dimethylacetoacetamide
(*l*) Diethyl acetylmalonate
(*m*) Butanoic anhydride
(*n*) Ethyl acetoacetate
(*o*) Carbomethoxycyclohexane
(*p*) Cyclohexyl acetate

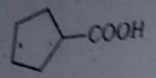
4\.
(*a*)

(*b*) $CH_3CH_2CH{=}CHCH_2COOH$

(c) $HOOCCH_2CH_2CH_2CH_2COOH$ (d)

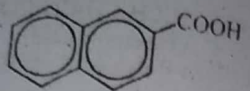


$$\begin{array}{l}HOOC\underset{\displaystyle \overset{|}{OH}}{C}HCH_2COOH\end{array}$$

(e)

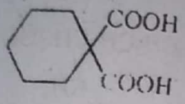


(f)



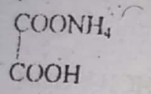
(g) $(CH_3)_2CHCH_2COOH$ (h) $CH_2{=}CHCOOH$

(i) $HOOCCH_2CH_2CH_2CH_2COOH$ (j)



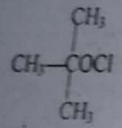
(k) CH_3CN (l) $NCCH_2CN$

(a) $(CH_3CH_2COO)_2Mg$ (b)



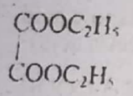
$$\begin{array}{l}COONH_4\\ |\\ COOH\end{array}$$

(c)



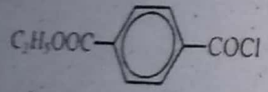
$$\begin{array}{c}CH_3\\ |\\ CH_3-C-COCl\\ |\\ CH_3\end{array}$$

(d)



$$\begin{array}{l}COOC_2H_5\\ |\\ COOC_2H_5\end{array}$$

(e)



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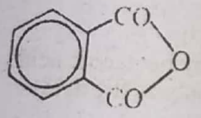

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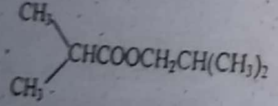

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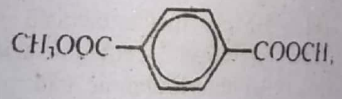
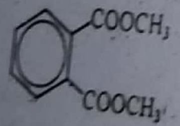
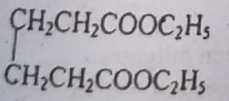


(i)

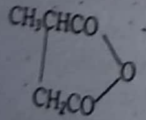


(j)

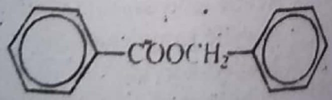


$$\begin{array}{l}CH_2CH_2COOC_2H_5\\ |\\ CH_2CH_2COOC_2H_5\end{array}$$

(k)



(l)



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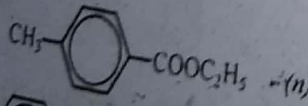
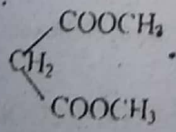
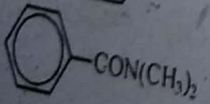


(n)

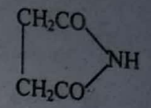


(o)

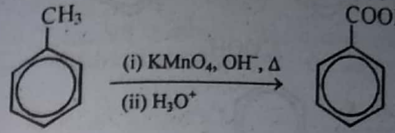


(p) $CH_3CH_2CH_2CH_2CH_2CONHC_2H_5$

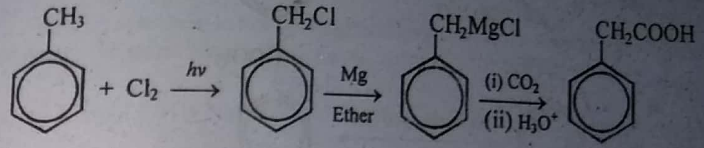
(q) $HCON(CH_3)_2$ (r)



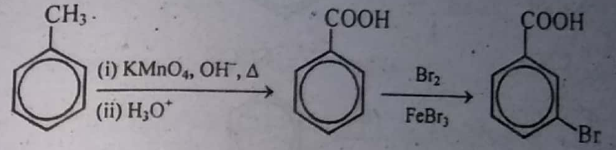
(a)



(b)



(c)



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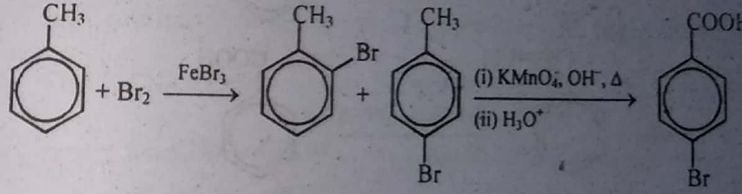
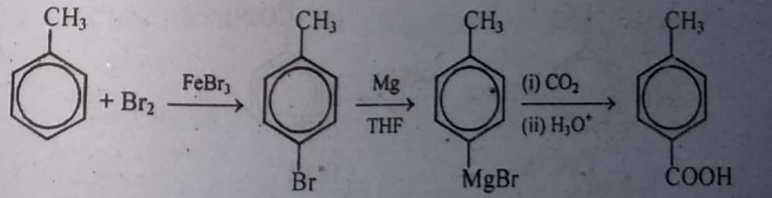


(e)



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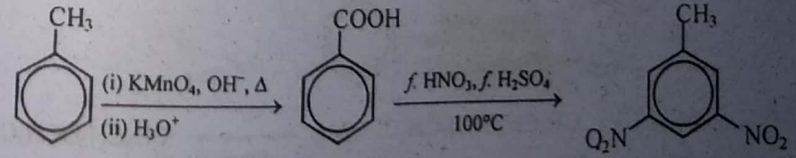
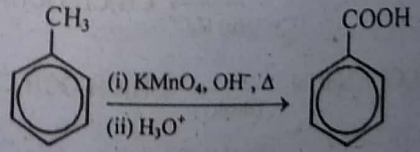
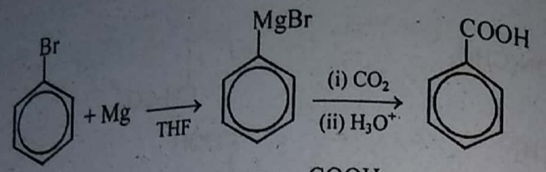


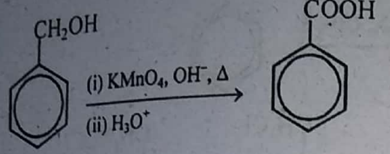
7. (a)



(b)



(c)



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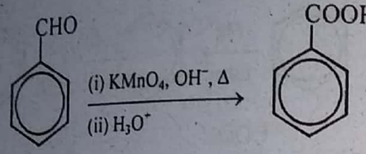

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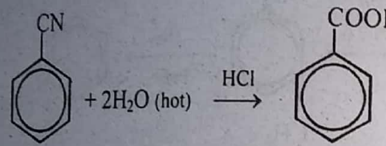

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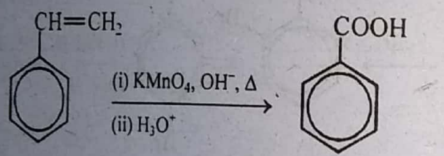
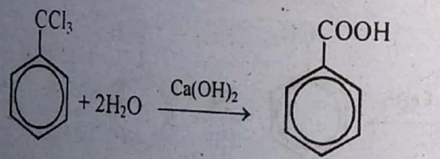
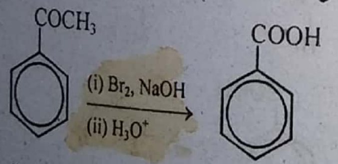


(g)



(h)



8. (a) (i) $CH_3CH_2OCH_2CH_2Cl + Mg \xrightarrow[\text{Ether}]{} CH_3CH_2OCH_2CH_2MgCl \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CO_2} CH_3CH_2OCH_2CH_2COOH$

(ii) $CH_3CH_2OCH_2CH_2Cl + NaCN \xrightarrow[\text{DMSO}]{} CH_3CH_2OCH_2CH_2CN \xrightarrow[\text{HCl}]{2H_2O\text{ (hot)}} CH_3CH_2OCH_2CH_2COOH$

This conversion can be affected by [illegible] methods.

(b) $CH_3COCH_2CH_2CH_2Br + NaCN \xrightarrow[\text{DMSO}]{} CH_3COCH_2CH_2CH_2CN \xrightarrow[\text{HCl}]{2H_2O\text{ (hot)}} CH_3COCH_2CH_2CH_2COOH$

Grignard synthesis cannot be applied due to the presence of a carbonyl group which can also react with the initially formed Grignard reagent.

(c) $(CH_3)_3CCH_2Br + Mg \xrightarrow[\text{Ether}]{} (CH_3)_3CCH_2MgBr \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CO_2} (CH_3)_3CCH_2COOH$

Nitrile synthesis is not applicable because Br cannot be easily displaced by CN due to the steric hindrance to the S_N2 attack.

(d) $ClCH_2COOH + NaOH \longrightarrow ClCH_2COONa \xrightarrow{CN^-} NCCH_2COONa \xrightarrow{H_3O^+} HOOCCH_2COOH$

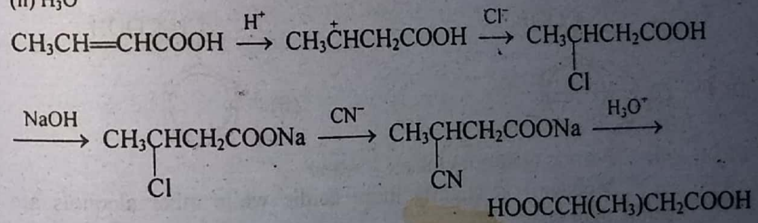
Grignard synthesis is not applied due to the presence of the carboxy group.

(e) $BrCH_2CH_2Br + NaCN \xrightarrow[\text{DMSO}]{} NCCH_2CH_2CN \xrightarrow{H_3O^+} HOOCCH_2CH_2COOH$

Mg would lead to the loss of the *vic*-bromines as $MgBr_2$ to give alkene.

(f) $CH_3CH_2CH_2OH + HCl \longrightarrow CH_3CH_2CH_2Cl \xrightarrow[\text{Ether}]{Mg} CH_3CH_2CH_2MgCl$

$\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CO_2} CH_3CH_2CH_2COOH \xrightarrow{Br_2/P} CH_3CH_2CHBrCOOH \xrightarrow{\text{alc. KOH}}$

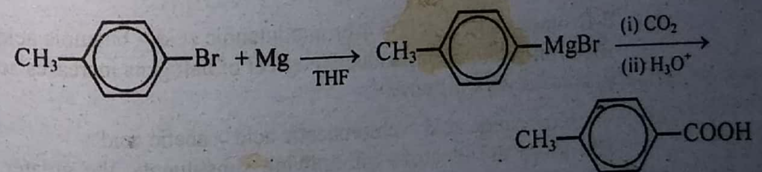


$CH_3CH{=}CHCOOH \xrightarrow{H^+} CH_3\overset{+}{C}HCH_2COOH \xrightarrow{Cl^-} CH_3\underset{Cl}{C}HCH_2COOH$

$\xrightarrow{NaOH} CH_3\underset{Cl}{C}HCH_2COONa \xrightarrow{CN^-} CH_3\underset{CN}{C}HCH_2COONa \xrightarrow{H_3O^+}$

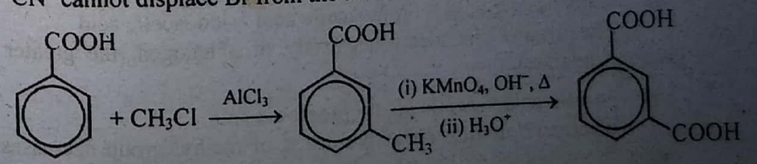
$HOOCCH(CH_3)CH_2COOH$

(g)



CN⁻ cannot displace Br from the aromatic ring.

(h)



9. (a) $(CH_3CH_2)_3CBr + Mg \xrightarrow[Ether]{} (CH_3CH_2)_3CMgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ CO_2} (CH_3CH_2)_3CCOOH$

(b) $HOCH_2CH_2CH_2CH_2CH_2Br + NaCN \xrightarrow[DMSO]{} HOCH_2CH_2CH_2CH_2CH_2CN$

$\xrightarrow{H_3O^+} HOCH_2CH_2CH_2CH_2CH_2COOH$

(c) $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow[(ii)\ H_2O_2/NaOH]{(i)\ B_2H_6/THF} CH_3CH_2CH_2CH_2CH_2OH$

$\xrightarrow[(ii)\ H_3O^+]{(i)\ KMnO_4,\ OH^-,\ \Delta} CH_3CH_2CH_2CH_2COOH$

(d) $(CH_3)_3CCH_3 + Br_2 \xrightarrow[127°C]{h\nu} (CH_3)_3CCH_2Br \xrightarrow[Ether]{Mg} (CH_3)_3CCH_2MgBr$

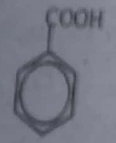
$\xrightarrow[(ii)\ H_3O^+]{(i)\ CO_2} (CH_3)_3CCH_2COOH \xrightarrow{Br_2/P} (CH_3)_3CCHBrCOOH$

(e) $CH_3CH_2CH_2CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2CH_2CH_2OH$

$\xrightarrow[180°C]{conc.\ H_2SO_4} CH_3CH_2CH_2CH_2CH{=}CH_2 \xrightarrow{KMnO_4} CH_3CH_2CH_2CH_2COOH$

(f) $CH_3CH_2CH_2CH_2CH_2COOH \xrightarrow[(ii)\ Br_2]{(i)\ Ag^+} CH_3CH_2CH_2CH_2CH_2Br$

10. (i)



(ii)

11. (a) Formic acid > methanol > water

Methanol is slightly more acidic while other alcohols are slightly less acidic than water.

(b) 2-Bromobutanoic acid > 4-bromobutanoic acid > butanoic acid

Electron-withdrawing inductive effect of halogens increases acidity but this effect decreases with distance.

(c) Trichloroacetic acid > chloroacetic acid > acetic acid

The more the electron-withdrawing substituents, the greater the acidity-increasing effect.

(d) Chloroacetic acid > bromoacetic acid > iodoacetic acid

The greater the electronegativity of a halogen, the greater the acidity-increasing effect.

(e) Formic acid > acetic acid > propionic acid.

Electron-donating inductive effect of methyl group decreases acidity; the effect decreases with distance.

(f) Acetic acid > propionic acid > trimethylacetic acid.

The more the electron-donating substituents, the greater the acidity-decreasing effect.

(g) Oxalic acid > malonic acid > succinic acid.

The same reason as in (b).

(h) Oxalic acid > formic acid > acetic acid

See above.

(i) $CH{\equiv}CCOOH > CH_2{=}CHCOOH > CH_3CH_2COOH$

Increasing *s* character of the orbital of an atom increases the electronegativity of the atom, and hence increases its acid-strengthening effect.

(j) Benzoic acid > phenylacetic acid > *p*-toluic acid.

See the *Textbook*.

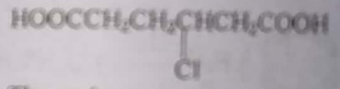
(k) *p*-Nitrobenzoic acid > benzoic acid > *p*-toluic acid

Nitro group is an electron-withdrawing group, while methyl group is electron-donating; hence they have opposite effect.

(l) *o*-Nitrobenzoic acid > *p*-nitrobenzoic acid > *m*-nitrobenzoic acid.

The nitro group has same –M effect at ortho and para positions but smaller –I effect at para position. It has only –I effect at meta position.

12.



$HOOCCH_2CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2COOH$

The carboxy group nearer to the chlorine atom is more acidic due to the greater electron-withdrawing influence of Cl on this carboxy group.

13. The dissociation equilibrium for acetic acid can be written as:

$$CH_3COOH \overset{K}{\rightleftharpoons} CH_3COO^- + H^+$$

Thus, $$K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]_{eq}} = 1.8 \times 10^{-5}$$

where, $[CH_3COOH]_{eq}$ is the concentration of acetic acid at equilibrium.

If we assume that only a small fraction of CH_3COOH dissociates so that $[CH_3COOH]_{eq} \approx [CH_3COOH]_{initial}$ and $[H^+] = [CH_3COO^-]$, the equilibrium equation becomes:

$$\frac{[CH_3COO^-]^2}{[CH_3COOH]_{initial}} = 1.8 \times 10^{-5}$$

or $$[CH_3COO^-] = \sqrt{(1.8 \times 10^{-5})[CH_3COOH]_{initial}}$$

Now for (a), $[CH_3COOH]_{initial} = 1.0\ M$

Thus, $$\frac{[CH_3COO^-]}{[CH_3COOH]_{eq}} = \frac{\sqrt{(1.8 \times 10^{-5}) \times (1)}}{1} = 0.00424 \text{ or } 0.424\%$$

For (b), $[CH_3COOH]_{total} = 0.01$ M

Thus, $$\frac{[CH_3COO^-]}{[CH_3COOH]_{eq}} = \frac{\sqrt{(1.8 \times 10^{-5}) \times (0.01)}}{0.01} = 0.0424 \text{ or } 4.24\%$$

Note that the percent dissociation increases as the concentration decreases.

For more accurate calculations,

$$[CH_3COOH]_{total} = [CH_3COOH]_{eq.} + [CH_3COO^-]$$

The equilibrium equation thus becomes:

$$\frac{[CH_3COO^-]^2}{[CH_3COOH]_{total} - [CH_3COO^-]} = 1.8 \times 10^{-5}$$

or $[CH_3COO^-]^2 + (1.8 \times 10^{-5})[CH_3COO^-] - (1.8 \times 10^{-5})[CH_3COOH]_{total} = 0$

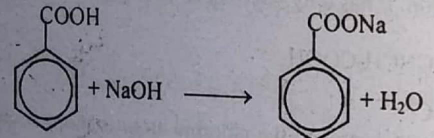
This can be solved according to the quadratic equation, $ax^2 + bx + c = 0$

where,

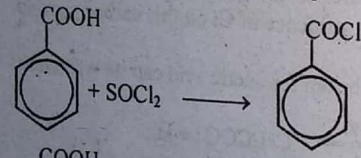
$x = [CH_3COO^-]$, $a = 1$, $b = 1.8 \times 10^{-5}$ and $c = -(1.8 \times 10^{-5})[CH_3COOH]_{total}$

The solution will be: $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

14. (a)



(b)



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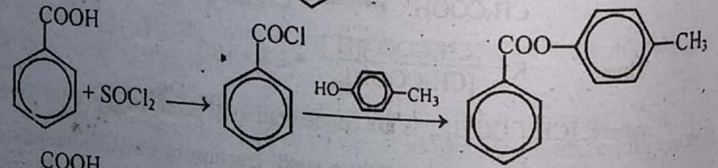

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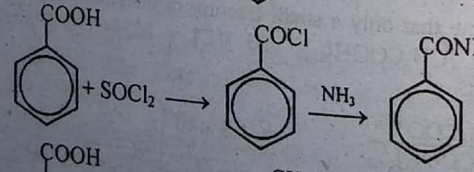

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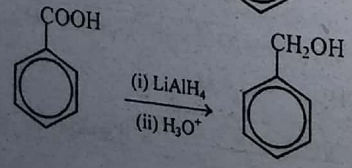
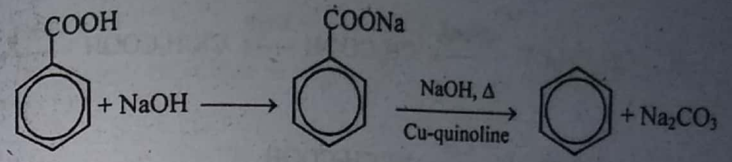


(f)



15.(a) $(CH_3)_3CCOOH \xrightarrow{SOCl_2} (CH_3)_3CCOCl \xrightarrow{NH_3} (CH_3)_3CCONH_2 \xrightarrow{P_2O_5} (CH_3)_3CCN$

(b) $(CH_3)_2C{=}CH_2$

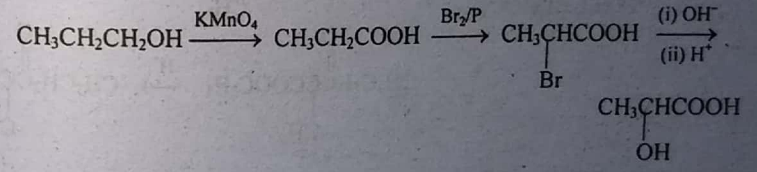
16. (a) $CH_3CH_2CH_2OH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } KMnO_4,\ OH^-,\ \Delta} CH_3CH_2COOH \xrightarrow{KOH} CH_3CH_2COOK$

(b) $(CH_3)_2CHCH_2OH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } KMnO_4,\ OH^-,\ \Delta} (CH_3)_2CHCOOH \xrightarrow{SOCl_2} (CH_3)_2CHCOCl \xrightarrow{C_2H_5OH} (CH_3)_2CHCOOC_2H_5$

(c) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } KMnO_4,\ OH^-,\ \Delta} CH_3CH_2CH_2COOH \xrightarrow[\Delta]{P_2O_5} (CH_3CH_2CH_2CO)_2O$

(d) $CH_3CH_2OH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } KMnO_4,\ OH^-,\ \Delta} CH_3COOH \xrightarrow{Br_2/P} BrCH_2COOH$

(e)



$CH_3CH_2CH_2OH \xrightarrow{KMnO_4} CH_3CH_2COOH \xrightarrow{Br_2/P} \underset{\displaystyle Br}{CH_3CHCOOH} \xrightarrow[\text{(ii) } H^+]{\text{(i) } OH^-} \underset{\displaystyle OH}{CH_3CHCOOH}$

(f) $CH_3CH_2OH \xrightarrow{KMnO_4} CH_3COOH \xrightarrow{SOCl_2} CH_3COCl \xrightarrow{NH_3} CH_3CONH_2$

(g) $CH_3CH_2OH \xrightarrow{KMnO_4} CH_3COOH \xrightarrow{Cl_2/P} ClCH_2COOH \xrightarrow{NaOH}$

$ClCH_2COONa \xrightarrow{CN^-} NCCH_2COONa \xrightarrow[\text{(ii) } H_2O]{\text{(i) } C_2H_5OH/HCl} CH_2(COOC_2H_5)_2$

(h) $CH_2(COOC_2H_5)_2$ (from g) $\xrightarrow[C_2H_5OH]{C_2H_5ONa} {}^-CH(COOC_2H_5)_2 \xrightarrow{CH_3Cl} CH_3CH(COOC_2H_5)_2$

$\xrightarrow[\text{(ii) } H^+]{\text{(i) } OH^-} CH_3CH(COOH)_2$

(i) $CH_3CH_2OH \xrightarrow{KMnO_4} CH_3COOH \xrightarrow{Cl_2/P} ClCH_2COOH \xrightarrow{SOCl_2} ClCH_2COCl$

(j) $ClCH_2COOH \xrightarrow{CN^-} NCCH_2COOH$
(from i)

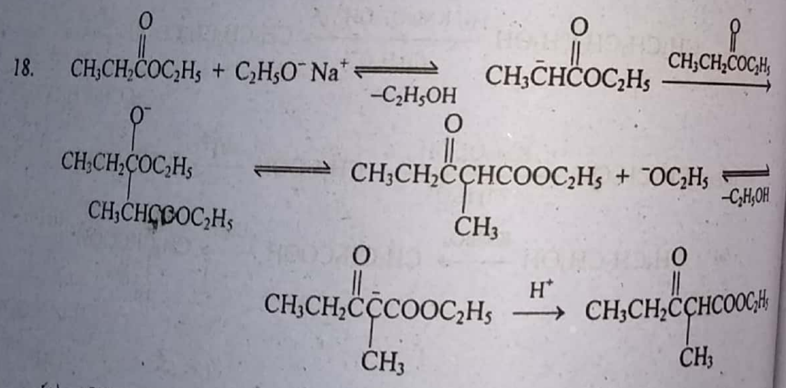
(k) $ClCH_2COOH \xrightarrow{CH_3CH_2ONa} CH_3CH_2OCH_2COOH$

(l) $CH_3COCl \xrightarrow{C_2H_5OH} CH_3COOC_2H_5 \xrightarrow[(ii)\ CH_3COCl]{(i)\ C_2H_5ONa} CH_3COCH_2COOC_2H_5$
(from f)

17. $CH_3CONH_2 > CH_3COOH > HCOOCH_3$

Amides generally have quite high boiling points as a consequence of the association due to strong intermolecular hydrogen bonding. Carboxylic acids also form hydrogen bonds but they generally exist in a cyclic dimeric form. The esters are not capable of forming hydrogen bonds.

18.



$$CH_3CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 + C_2H_5O^- Na^+ \underset{-C_2H_5OH}{\rightleftharpoons} CH_3\bar{C}H\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow{CH_3CH_2\overset{O}{\overset{\|}{C}}OC_2H_5}$$

$$\begin{array}{c} O^- \\ | \\ CH_3CH_2COC_2H_5 \\ | \\ CH_3CHCOOC_2H_5 \end{array} \rightleftharpoons CH_3CH_2\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{|}{C}}HCOOC_2H_5 + {}^-OC_2H_5 \underset{-C_2H_5OH}{\rightleftharpoons}$$

$$CH_3CH_2\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{|}{\bar{C}}}COOC_2H_5 \xrightarrow{H^+} CH_3CH_2\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{|}{C}}HCOOC_2H_5$$

19. (a) $CH_3COCH_2COOC_2H_5 + CH_3COCH(CH_3)COOC_2H_5 +$
$CH_3CH_2COCH(CH_3)COOC_2H_5 + CH_3CH_2COCH_2COOC_2H_5$

(b) $CH_3COCH_2COCH_3 + CH_3COCH_2COOC_2H_5$

(c) $(CH_3)_3CCOCH_2COOC_2H_5 + CH_3COCH_2COOC_2H_5$

(d) $HCOCH_2COOC_2H_5 + CH_3COCH_2COOC_2H_5$

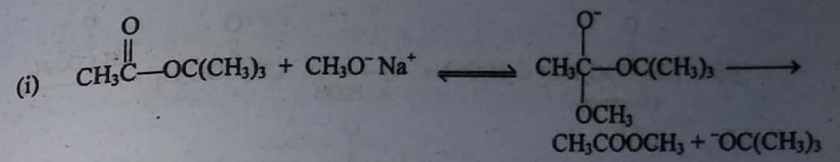
(e) $C_2H_5OOCCOCH(CH_3)COOC_2H_5 + CH_3CH_2COCH(CH_3)COOC_2H_5$

20. (a), (c) and (d) Benzoic acid evolves CO_2 with aq. $NaHCO_3$.

(b) Benzoyl chloride gives precipitates of AgCl with $AgNO_3$.

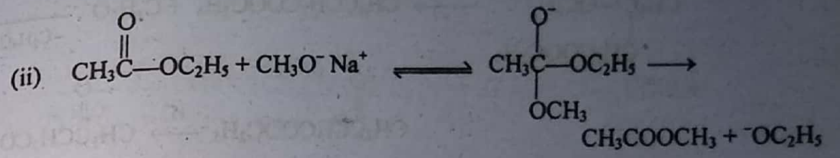
(e) Cinnamic acid decolorizes acidified $KMnO_4$ or bromine water.

21. (i)



$$CH_3\overset{O}{\overset{\|}{C}}-OC(CH_3)_3 + CH_3O^- Na^+ \rightleftharpoons CH_3\underset{OCH_3}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-OC(CH_3)_3 \longrightarrow CH_3COOCH_3 + {}^-OC(CH_3)_3$$

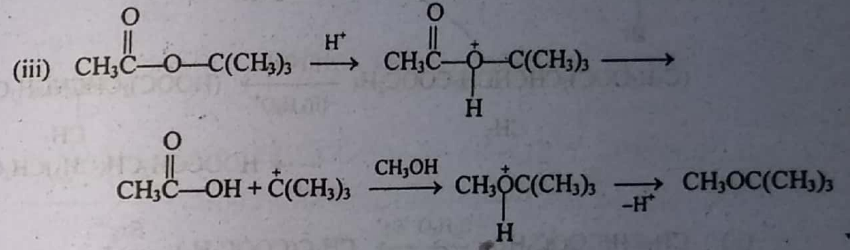
(ii)



$$CH_3\overset{O}{\overset{\|}{C}}-OC_2H_5 + CH_3O^- Na^+ \rightleftharpoons CH_3\underset{OCH_3}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-OC_2H_5 \longrightarrow CH_3COOCH_3 + {}^-OC_2H_5$$

Reaction (i) is slower due to steric hindrance by the large t-butyl group.

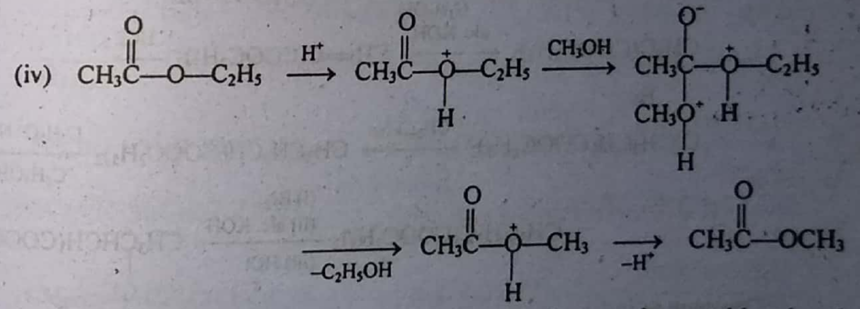
(iii)



$$CH_3\overset{O}{\overset{\|}{C}}-O-C(CH_3)_3 \xrightarrow{H^+} CH_3\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{\overset{+}{O}}}-C(CH_3)_3 \longrightarrow$$

$$CH_3\overset{O}{\overset{\|}{C}}-OH + \overset{+}{C}(CH_3)_3 \xrightarrow{CH_3OH} CH_3\underset{H}{\underset{|}{\overset{+}{O}}}C(CH_3)_3 \xrightarrow[-H^+]{} CH_3OC(CH_3)_3$$

(iv)



$$CH_3\overset{O}{\overset{\|}{C}}-O-C_2H_5 \xrightarrow{H^+} CH_3\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{\overset{+}{O}}}-C_2H_5 \xrightarrow{CH_3OH} CH_3\underset{\underset{H}{|}}{\underset{CH_3\overset{+}{O}}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}}-\underset{H}{\underset{|}{\overset{+}{O}}}-C_2H_5$$

$$\xrightarrow[-C_2H_5OH]{} CH_3\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_3 \xrightarrow[-H^+]{} CH_3\overset{O}{\overset{\|}{C}}-OCH_3$$

The protonated t-butyl acetate rapidly dissociates to form stable t-butyl carbocation which combines with methanol to form ether.

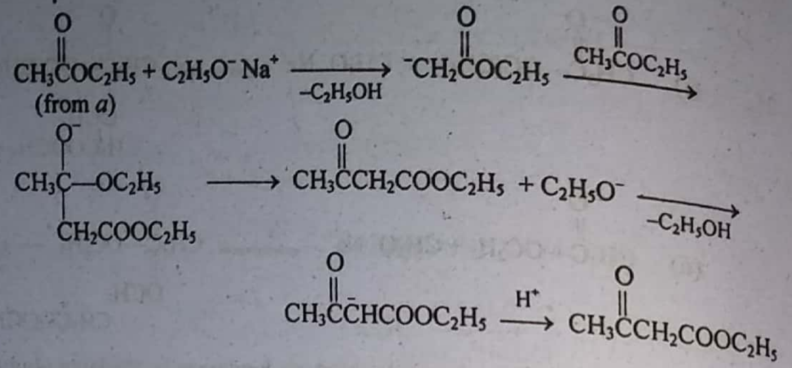
22. (a) $CH_3CH_2OH \xrightarrow[(ii)\ H_3O^+]{(i)\ KMnO_4,\ OH^-,\ \Delta} CH_3COOH \xrightarrow[H^+,\ \Delta]{C_2H_5OH} CH_3COOC_2H_5$

(b) $CH_3COOH \xrightarrow{Br_2/P} BrCH_2COOH \xrightarrow[H^+,\ \Delta]{C_2H_5OH} BrCH_2COOC_2H_5$
(from a)

(c) $CH_3COOH \xrightarrow{Cl_2/PBr_3} ClCH_2COOH \xrightarrow{NaOH} ClCH_2COONa \xrightarrow{CN^-}$
(from a)

$NCCH_2COONa \xrightarrow[(ii)\ H_2O]{(i)\ 2C_2H_5OH/HCl} CH_2(COOC_2H_5)_2$

(d)

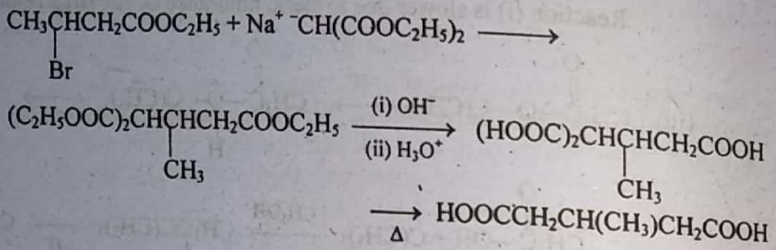


$$\underset{\text{(from }a\text{)}}{CH_3\overset{\overset{O}{\|}}{C}OC_2H_5} + C_2H_5O^-\,Na^+ \xrightarrow[-C_2H_5OH]{} {}^-CH_2\overset{\overset{O}{\|}}{C}OC_2H_5 \xrightarrow{CH_3\overset{\overset{O}{\|}}{C}OC_2H_5}$$

$$CH_3\underset{\underset{CH_2COOC_2H_5}{|}}{\overset{\overset{O^-}{|}}{C}}{-}OC_2H_5 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}CH_2COOC_2H_5 + C_2H_5O^- \xrightarrow[-C_2H_5OH]{}$$

$$CH_3\overset{\overset{O}{\|}}{C}\bar{C}HCOOC_2H_5 \xrightarrow{H^+} CH_3\overset{\overset{O}{\|}}{C}CH_2COOC_2H_5$$

23. (a) (i)

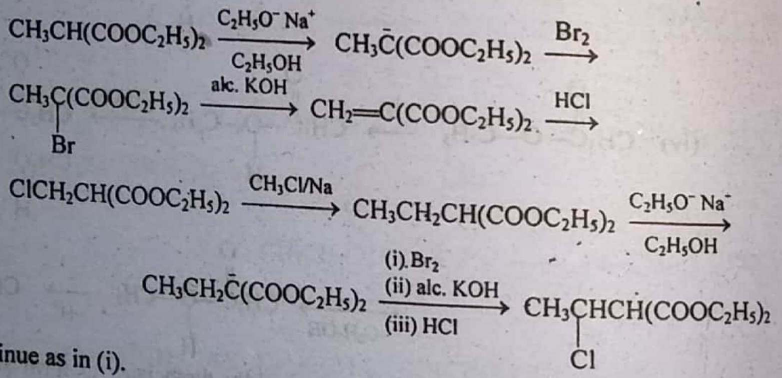


$$CH_3\underset{\underset{Br}{|}}{C}HCH_2COOC_2H_5 + Na^+\,{}^-CH(COOC_2H_5)_2 \longrightarrow$$

$$(C_2H_5OOC)_2CH\underset{\underset{CH_3}{|}}{C}HCH_2COOC_2H_5 \xrightarrow[\text{(ii) }H_3O^+]{\text{(i) }OH^-} (HOOC)_2CH\underset{\underset{CH_3}{|}}{C}HCH_2COOH$$

$$\xrightarrow[\Delta]{} HOOCCH_2CH(CH_3)CH_2COOH$$

(ii)



$$CH_3CH(COOC_2H_5)_2 \xrightarrow[C_2H_5OH]{C_2H_5O^-\,Na^+} CH_3\bar{C}(COOC_2H_5)_2 \xrightarrow{Br_2}$$

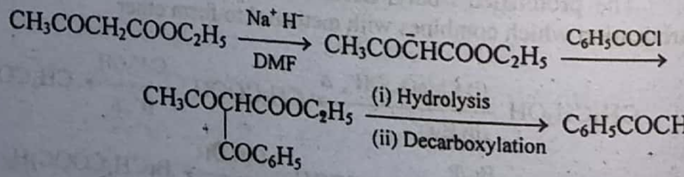
$$CH_3\underset{\underset{Br}{|}}{C}(COOC_2H_5)_2 \xrightarrow{\text{alc. KOH}} CH_2{=}C(COOC_2H_5)_2 \xrightarrow{HCl}$$

$$ClCH_2CH(COOC_2H_5)_2 \xrightarrow{CH_3Cl/Na} CH_3CH_2CH(COOC_2H_5)_2 \xrightarrow[C_2H_5OH]{C_2H_5O^-\,Na^-}$$

$$CH_3CH_2\bar{C}(COOC_2H_5)_2 \xrightarrow[\text{(iii) HCl}]{\substack{\text{(i) }Br_2\\ \text{(ii) alc. KOH}}} CH_3\underset{\underset{Cl}{|}}{C}HCH(COOC_2H_5)_2$$

Continue as in (i).

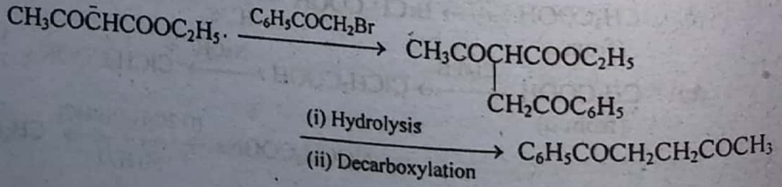
(b) (i)



$$CH_3COCH_2COOC_2H_5 \xrightarrow[DMF]{Na^+\,H^-} CH_3CO\bar{C}HCOOC_2H_5 \xrightarrow{C_6H_5COCl}$$

$$CH_3CO\underset{\underset{COC_6H_5}{|}}{C}HCOOC_2H_5 \xrightarrow[\text{(ii) Decarboxylation}]{\text{(i) Hydrolysis}} C_6H_5COCH_2COCH_3$$

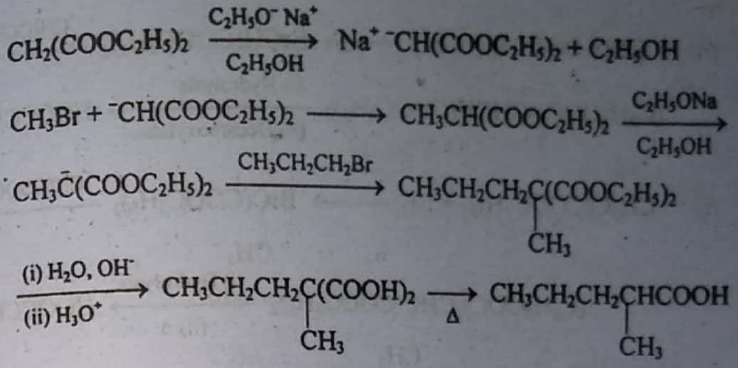
(ii)



$$CH_3CO\bar{C}HCOOC_2H_5 \xrightarrow{C_6H_5COCH_2Br} CH_3CO\underset{\underset{CH_2COC_6H_5}{|}}{C}HCOOC_2H_5$$

$$\xrightarrow[\text{(ii) Decarboxylation}]{\text{(i) Hydrolysis}} C_6H_5COCH_2CH_2COCH_3$$

24. (a)



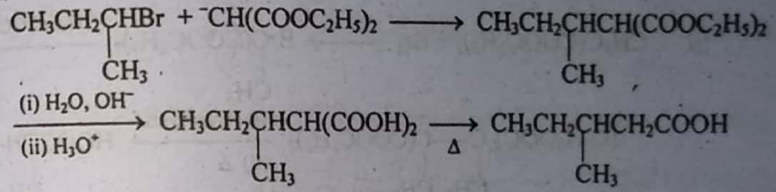
$$CH_2(COOC_2H_5)_2 \xrightarrow[C_2H_5OH]{C_2H_5O^-\,Na^+} Na^+\,{}^-CH(COOC_2H_5)_2 + C_2H_5OH$$

$$CH_3Br + {}^-CH(COOC_2H_5)_2 \longrightarrow CH_3CH(COOC_2H_5)_2 \xrightarrow[C_2H_5OH]{C_2H_5ONa}$$

$$CH_3\bar{C}(COOC_2H_5)_2 \xrightarrow{CH_3CH_2CH_2Br} CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{C}(COOC_2H_5)_2$$

$$\xrightarrow[\text{(ii) }H_3O^+]{\text{(i) }H_2O,\ OH^-} CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{C}(COOH)_2 \xrightarrow[\Delta]{} CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{C}HCOOH$$

(b)



$$CH_3CH_2\underset{\underset{CH_3}{|}}{C}HBr + {}^-CH(COOC_2H_5)_2 \longrightarrow CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH(COOC_2H_5)_2$$

$$\xrightarrow[\text{(ii) }H_3O^+]{\text{(i) }H_2O,\ OH^-} CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH(COOH)_2 \xrightarrow[\Delta]{} CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH_2COOH$$

(c) $(CH_3)_2CHCH_2Br + {}^-CH(COOC_2H_5)_2 \longrightarrow (CH_3)_2CHCH_2CH(COOC_2H_5)_2$

$\xrightarrow[\text{(ii) }H_3O^+]{\text{(i) }H_2O,\ OH^-} (CH_3)_2CHCH_2CH(COOH)_2 \xrightarrow[\Delta]{} (CH_3)_2CHCH_2CH_2COOH$

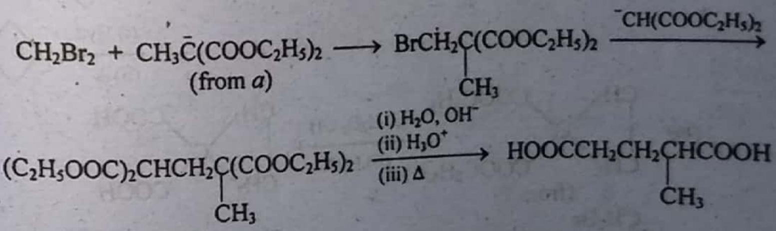
(d) $CH_2{=}CHCH_2Br + {}^-CH(COOC_2H_5)_2 \longrightarrow CH_2{=}CHCH_2CH(COOC_2H_5)_2$

$\xrightarrow[\text{(ii) }H_3O^+]{\text{(i) }H_2O,\ OH^-} CH_2{=}CHCH_2CH(COOH)_2 \xrightarrow[\Delta]{} CH_2{=}CHCH_2CH_2COOH$

(e) $CH_2Br_2 + {}^-CH(COOC_2H_5)_2 \longrightarrow BrCH_2CH(COOC_2H_5)_2 \xrightarrow{{}^-CH(COOC_2H_5)_2}$

$(C_2H_5OOC)_2CHCH_2CH(COOC_2H_5)_2 \xrightarrow[\text{(ii) Decarboxylation}]{\text{(i) Hydrolysis}} HOOCCH_2CH_2CH_2COOH$

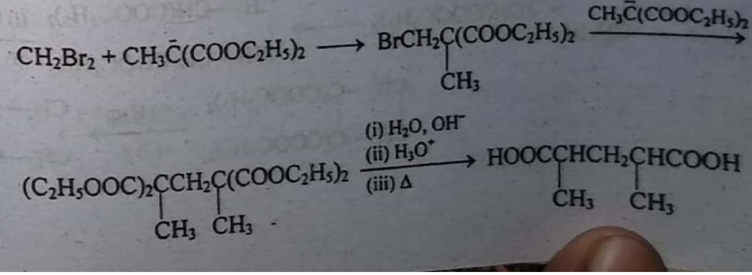
(f)



$$CH_2Br_2 + \underset{\text{(from }a\text{)}}{CH_3\bar{C}(COOC_2H_5)_2} \longrightarrow BrCH_2\underset{\underset{CH_3}{|}}{C}(COOC_2H_5)_2 \xrightarrow{{}^-CH(COOC_2H_5)_2}$$

$$(C_2H_5OOC)_2CHCH_2\underset{\underset{CH_3}{|}}{C}(COOC_2H_5)_2 \xrightarrow[\text{(iii) }\Delta]{\substack{\text{(i) }H_2O,\ OH^-\\ \text{(ii) }H_3O^+}} HOOCCH_2CH_2\underset{\underset{CH_3}{|}}{C}HCOOH$$

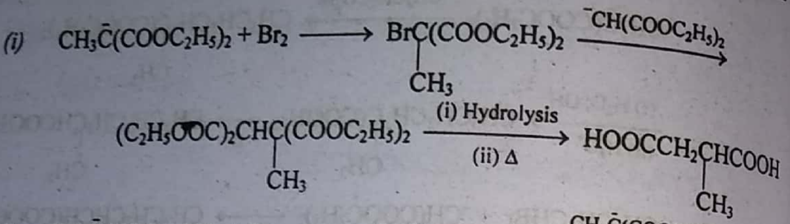
(g)



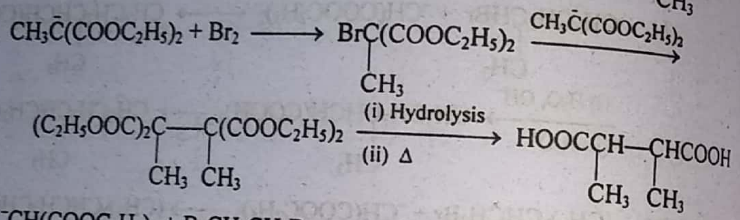
$$CH_2Br_2 + CH_3\bar{C}(COOC_2H_5)_2 \longrightarrow BrCH_2\underset{\underset{CH_3}{|}}{C}(COOC_2H_5)_2 \xrightarrow{CH_3\bar{C}(COOC_2H_5)_2}$$

$$(C_2H_5OOC)_2\underset{\underset{CH_3}{|}}{C}CH_2\underset{\underset{CH_3}{|}}{C}(COOC_2H_5)_2 \xrightarrow[\text{(iii) }\Delta]{\substack{\text{(i) }H_2O,\ OH^-\\ \text{(ii) }H_3O^+}} HOOC\underset{\underset{CH_3}{|}}{C}HCH_2\underset{\underset{CH_3}{|}}{C}HCOOH$$

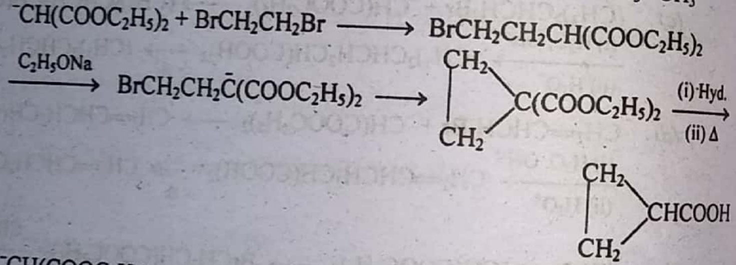
(h) $^-CH(COOC_2H_5)_2 + Br_2 \longrightarrow BrCH(COOC_2H_5)_2 \xrightarrow{^-CH(COOC_2H_5)_2} (C_2H_5OOC)_2CHCH(COOC_2H_5)_2 \xrightarrow[\text{(ii) Decarboxylation}]{\text{(i) Hydrolysis}} HOOCCH_2CH_2COOH$

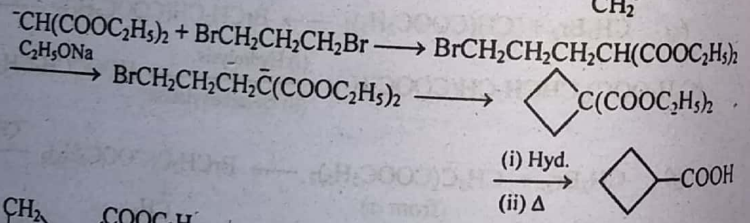
(i)


$CH_3\bar{C}(COOC_2H_5)_2 + Br_2 \longrightarrow Br\underset{CH_3}{C}(COOC_2H_5)_2 \xrightarrow{^-CH(COOC_2H_5)_2} (C_2H_5OOC)_2CH\underset{CH_3}{C}(COOC_2H_5)_2 \xrightarrow[\text{(ii) }\Delta]{\text{(i) Hydrolysis}} HOOCCH_2\underset{CH_3}{C}HCOOH$

(j)


$CH_3\bar{C}(COOC_2H_5)_2 + Br_2 \longrightarrow Br\underset{CH_3}{C}(COOC_2H_5)_2 \xrightarrow{CH_3\bar{C}(COOC_2H_5)_2} (C_2H_5OOC)_2\underset{CH_3}{C}—\underset{CH_3}{C}(COOC_2H_5)_2 \xrightarrow[\text{(ii) }\Delta]{\text{(i) Hydrolysis}} HOOC\underset{CH_3}{C}H—\underset{CH_3}{C}HCOOH$

(k)


(l)


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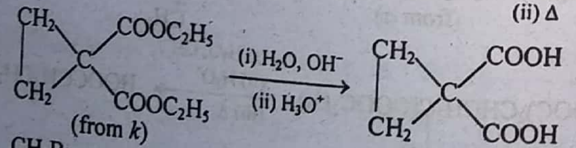
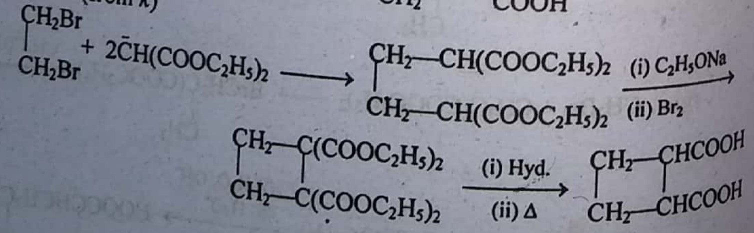
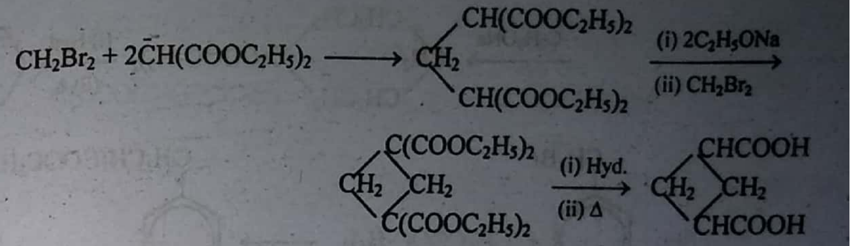


(from k)

(n)


(o)


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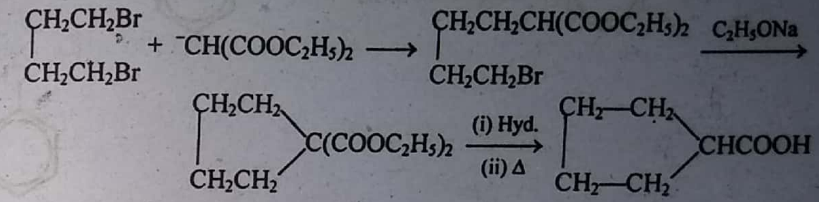
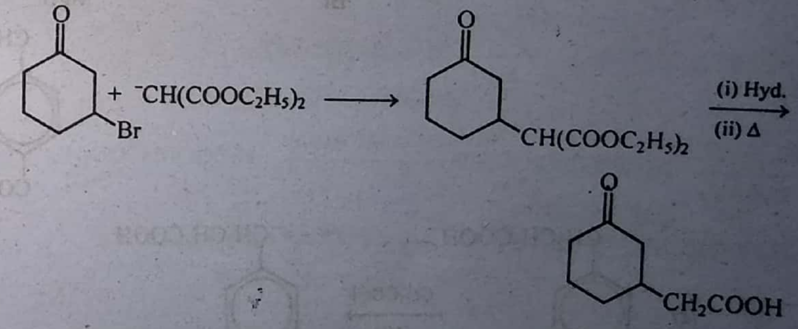


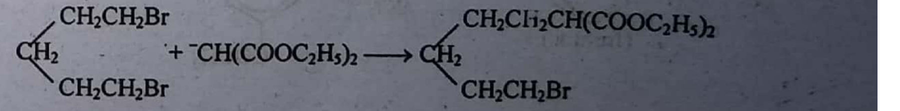
(q) $CH_3CH_2CH_2Br + ^-CH(COOC_2H_5)_2 \longrightarrow CH_3CH_2CH_2CH(COOC_2H_5)_2 \xrightarrow[\text{(ii) }\Delta]{\text{(i) Hyd.}} CH_3CH_2CH_2CH_2COOH$

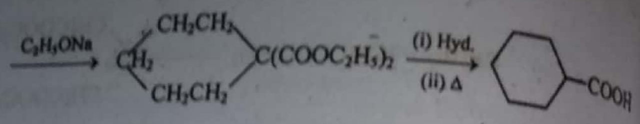
(r) $(CH_3)_2CHCH_2Br + ^-CH(COOC_2H_5)_2 \longrightarrow (CH_3)_2CHCH_2CH(COOC_2H_5)_2 \xrightarrow[\text{(ii) }\Delta]{\text{(i) Hyd.}} (CH_3)_2CHCH_2CH_2COOH \xrightarrow[\text{(ii) }H_3O^+]{\text{(i) }LiAlH_4} (CH_3)_2CHCH_2CH_2CH_2OH$

(s) $CH_3CH_2Br + ^-CH(COOC_2H_5)_2 \longrightarrow CH_3CH_2CH(COOC_2H_5)_2 \xrightarrow{\text{Hyd.}} CH_3CH_2CH(COOH)_2 \xrightarrow[\text{(ii) }H_3O^+]{\text{(i) }LiAlH_4} CH_3CH_2CH(CH_2OH)_2$

(t) $HOOCCH_2CH_2COOH \xrightarrow[\text{(ii) }H_3O^+]{\text{(i) }LiAlH_4} HOCH_2CH_2CH_2CH_2OH$
(from *h*)

(u)


(v)




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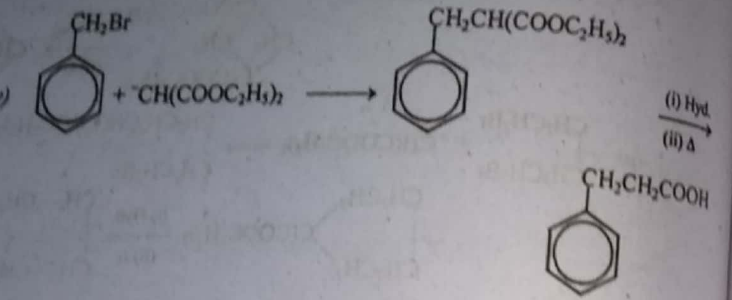
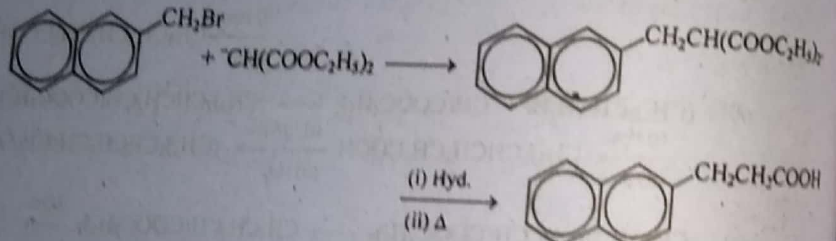
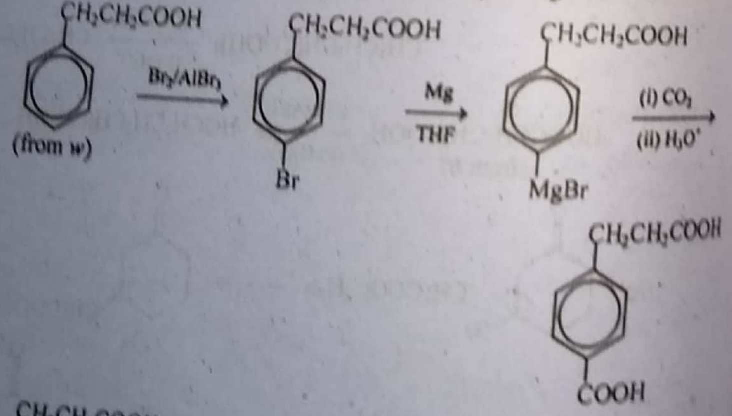


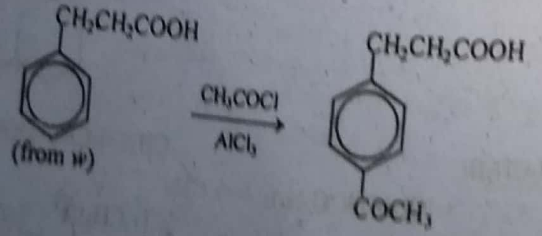
(x)



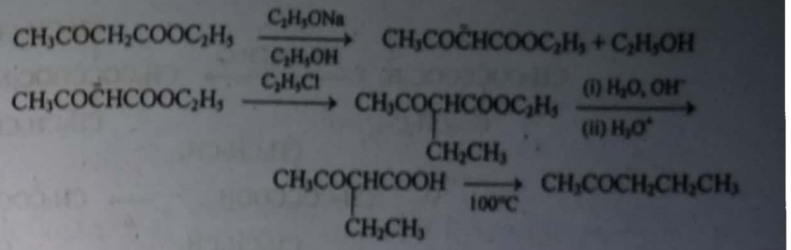
(y)



(z)



25. (a)

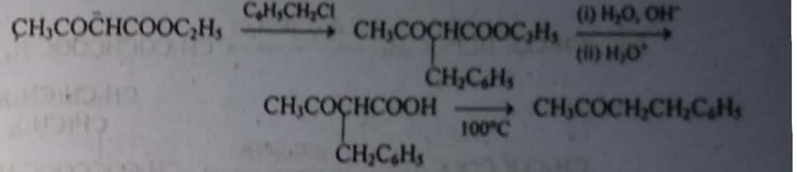


$$CH_3COCH_2COOC_2H_5 \xrightarrow[C_2H_5OH]{C_2H_5ONa} CH_3CO\overset{-}{C}HCOOC_2H_5 + C_2H_5OH$$

$$CH_3CO\overset{-}{C}HCOOC_2H_5 \xrightarrow{C_2H_5Cl} CH_3CO\underset{\substack{|\\ CH_2CH_3}}{C}HCOOC_2H_5 \xrightarrow[(ii)\ H_3O^+]{(i)\ H_2O,\ OH^-}$$

$$CH_3CO\underset{\substack{|\\ CH_2CH_3}}{C}HCOOH \xrightarrow[100^\circ C]{} CH_3COCH_2CH_2CH_3$$

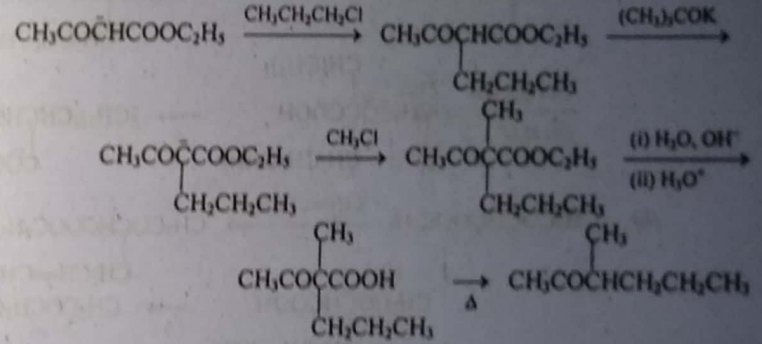
(b)



$$CH_3CO\overset{-}{C}HCOOC_2H_5 \xrightarrow{C_6H_5CH_2Cl} CH_3CO\underset{\substack{|\\ CH_2C_6H_5}}{C}HCOOC_2H_5 \xrightarrow[(ii)\ H_3O^+]{(i)\ H_2O,\ OH^-}$$

$$CH_3CO\underset{\substack{|\\ CH_2C_6H_5}}{C}HCOOH \xrightarrow[100^\circ C]{} CH_3COCH_2CH_2C_6H_5$$

(c)

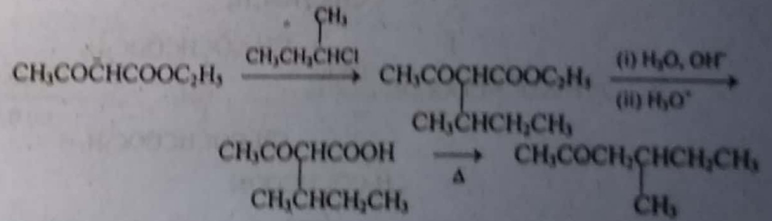


$$CH_3CO\overset{-}{C}HCOOC_2H_5 \xrightarrow{CH_3CH_2CH_2Cl} CH_3CO\underset{\substack{|\\ CH_2CH_2CH_3}}{C}HCOOC_2H_5 \xrightarrow{(CH_3)_3COK}$$

$$CH_3CO\underset{\substack{|\\ CH_2CH_2CH_3}}{\overset{-}{C}}COOC_2H_5 \xrightarrow{CH_3Cl} CH_3CO\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_2CH_2CH_3}}{C}}COOC_2H_5 \xrightarrow[(ii)\ H_3O^+]{(i)\ H_2O,\ OH^-}$$

$$CH_3CO\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_2CH_2CH_3}}{C}}COOH \xrightarrow[\Delta]{} CH_3CO\overset{\substack{CH_3\\ |}}{C}HCH_2CH_2CH_3$$

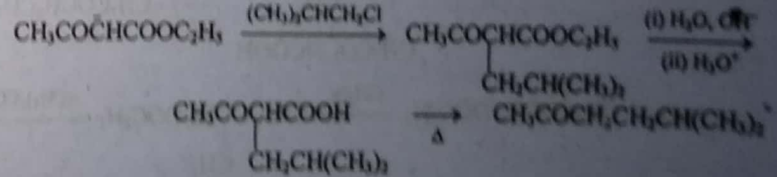
(d)



$$CH_3CO\overset{-}{C}HCOOC_2H_5 \xrightarrow{CH_3CH_2\overset{\substack{CH_3\\ |}}{C}HCl} CH_3CO\underset{\substack{|\\ CH_3CHCH_2CH_3}}{C}HCOOC_2H_5 \xrightarrow[(ii)\ H_3O^+]{(i)\ H_2O,\ OH^-}$$

$$CH_3CO\underset{\substack{|\\ CH_3CHCH_2CH_3}}{C}HCOOH \xrightarrow[\Delta]{} CH_3COCH_2\underset{\substack{|\\ CH_3}}{C}HCH_2CH_3$$

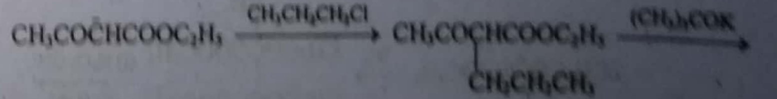
(e)



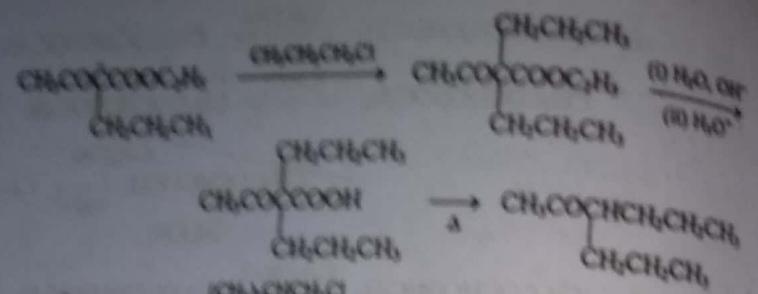
$$CH_3CO\overset{-}{C}HCOOC_2H_5 \xrightarrow{(CH_3)_2CHCH_2Cl} CH_3CO\underset{\substack{|\\ CH_2CH(CH_3)_2}}{C}HCOOC_2H_5 \xrightarrow[(ii)\ H_3O^+]{(i)\ H_2O,\ OH^-}$$

$$CH_3CO\underset{\substack{|\\ CH_2CH(CH_3)_2}}{C}HCOOH \xrightarrow[\Delta]{} CH_3COCH_2CH_2CH(CH_3)_2$$

(f)



$$CH_3CO\overset{-}{C}HCOOC_2H_5 \xrightarrow{CH_3CH_2CH_2Cl} CH_3CO\underset{\substack{|\\ CH_2CH_2CH_3}}{C}HCOOC_2H_5 \xrightarrow{(CH_3)_3COK}$$



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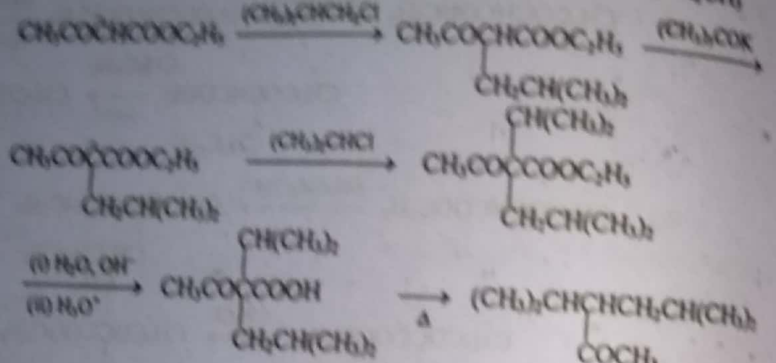
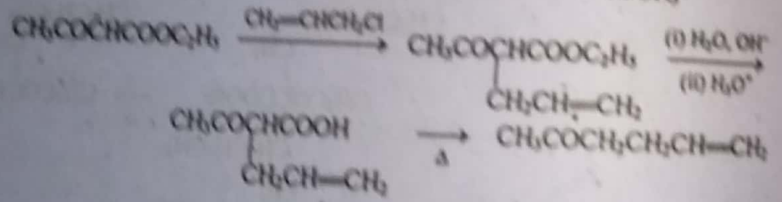
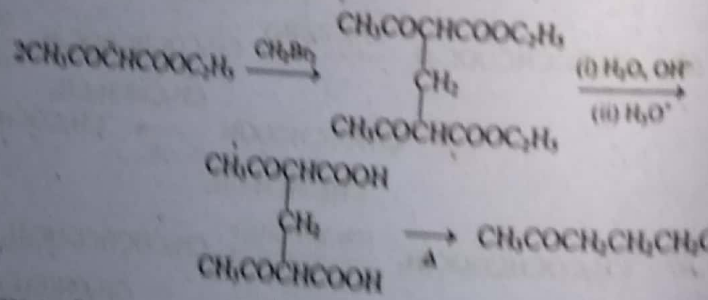


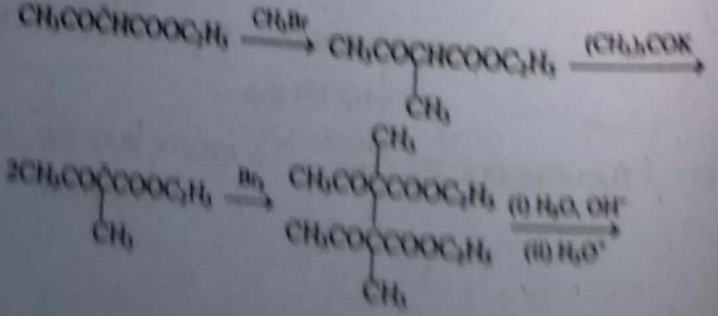
(h)

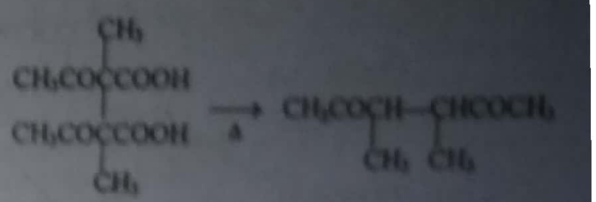


(i)



(j)





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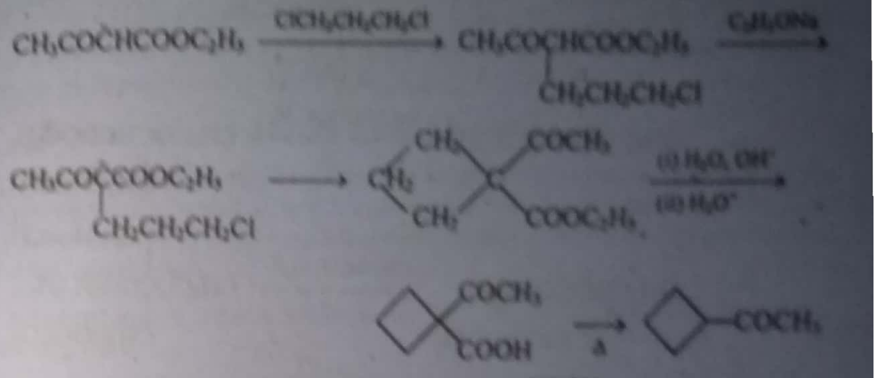
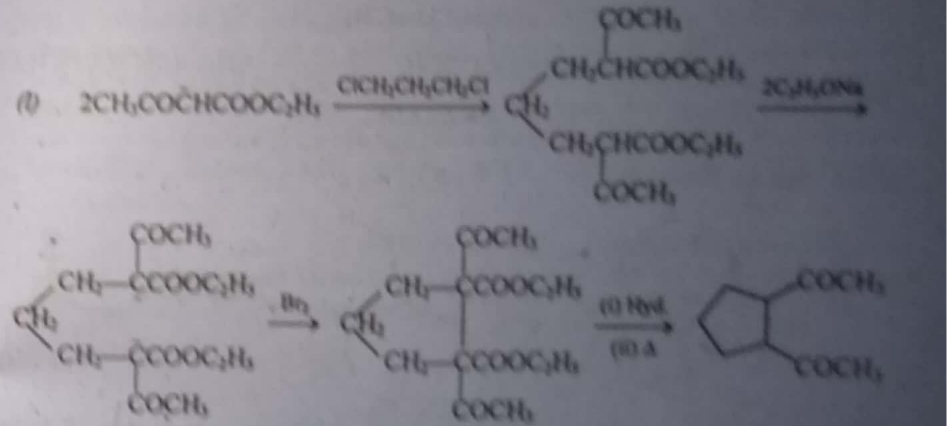
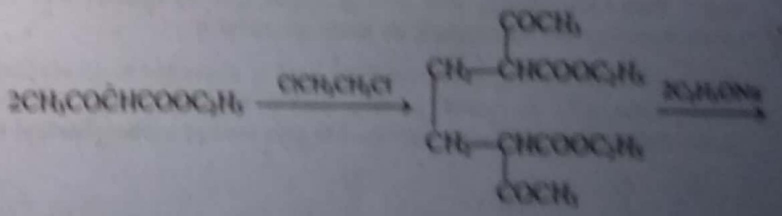
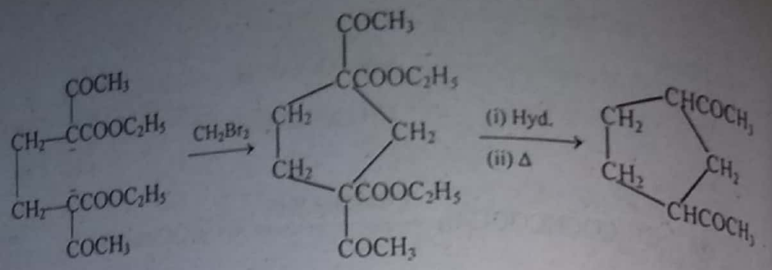


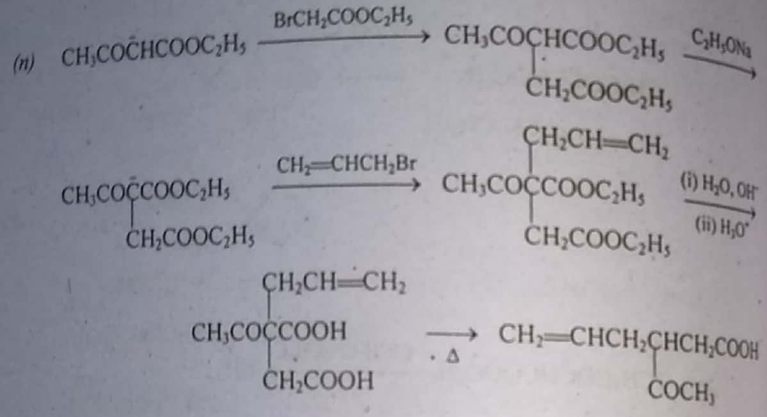
(l)



(m)







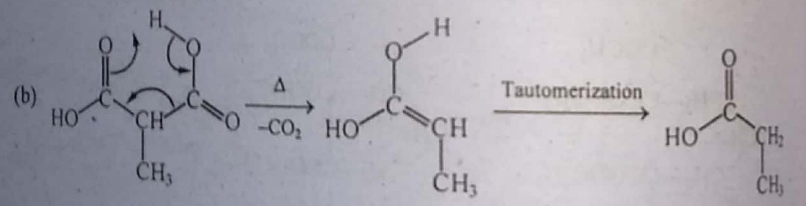
(n) $$CH_3CO\bar{C}HCOOC_2H_5 \xrightarrow{BrCH_2COOC_2H_5} CH_3CO\underset{CH_2COOC_2H_5}{CH}COOC_2H_5 \xrightarrow{C_2H_5ONa}$$

$$CH_3CO\underset{CH_2COOC_2H_5}{\bar{C}}COOC_2H_5 \xrightarrow{CH_2=CHCH_2Br} CH_3CO\overset{CH_2CH=CH_2}{\underset{CH_2COOC_2H_5}{C}}COOC_2H_5 \xrightarrow[(ii)\ H_3O^+]{(i)\ H_2O,\ OH^-}$$

$$CH_3CO\overset{CH_2CH=CH_2}{\underset{CH_2COOH}{C}}COOH \xrightarrow[\Delta]{} CH_2=CHCH_2\underset{COCH_3}{CH}CH_2COOH$$

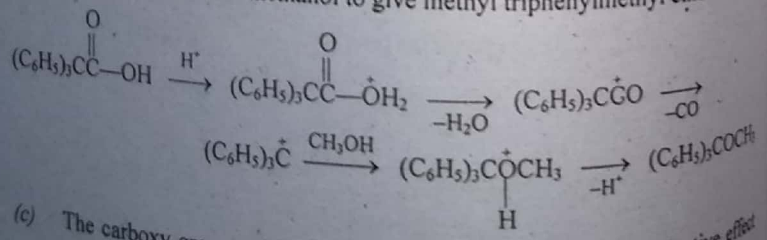
26.(a) See the *Textbook*.

(b)



27. (a) Free chloroacetic acid will protonate CN^- to convert it to HCN (a very toxic species) and thus reduce its nucleophilicity.

(b) In conc. H_2SO_4, triphenylacetic acid is converted to an acylium ion which then loses CO to yield a very stable triphenylmethyl carbocation. This carbocation combines with methanol to give methyl triphenylmethyl ether.



$$(C_6H_5)_3C\overset{O}{\overset{\|}{C}}-OH \xrightarrow{H^+} (C_6H_5)_3C\overset{O}{\overset{\|}{C}}-\overset{+}{O}H_2 \xrightarrow[-H_2O]{} (C_6H_5)_3C\overset{+}{C}O \xrightarrow[-CO]{}$$

$$(C_6H_5)_3\overset{+}{C} \xrightarrow{CH_3OH} (C_6H_5)_3C\underset{H}{\overset{+}{O}}CH_3 \xrightarrow[-H^+]{} (C_6H_5)_3COCH_3$$

(c) The carboxy group (COOH) has an electron-withdrawing inductive effect and thus increases the acid strength of another carboxy group (K_1) in the same molecule. On the other hand, the carboxylate ion (COO^-) has an electron-donating inductive effect and thus decreases the acid strength of another carboxy group (K_2) in the same molecule. Since the inductive effect decreases with distance, beyond certain distance the two carboxy groups do not influence the strength of each other, and show almost the same strength.

(d) $C_2H_5O^-$, instead of abstracting proton from $CH_3COOC_2H_5$ and converting it into a carbanion ($^-CH_2COOC_2H_5$), reacts with CH_3I in an S_N2 manner, which is faster, to yield ethyl methyl ether ($C_2H_5OCH_3$).

(e) The attack on the acyl carbon is sterically hindered.

(f) Malonic ester has only two active hydrogens which can be removed by the base to produce carbanion in turn for alkylation. The dimethylated malonic ester has no more active hydrogen, and therefore cannot be converted to a carbanion for further methylation.

(g) Bromobenzene cannot undergo an S_N2 attack by the carbanion from acetoacetic ester.

(h) Alkylation of acetoacetic ester involves an S_N2 attack of the carbanion from acetoacetic ester on an alkyl halide. Since a primary alkyl halide is a good substrate for an S_N2 reaction, it generally gives best yields as an alkylating agent. On the other hand, a tertiary alkyl halide is a very poor substrate for an S_N2 reaction; it practically gives no alkylation product, rather it undergoes elimination reaction, e.g., tertiary butyl bromide yields isobutylene, $(CH_3)_2C=CH_2$.

(i) The free halo acid will protonate the base ethoxide ion to convert it into alcohol, and thus will render it unable to abstract the active hydrogen from acetoacetic ester to produce carbanion.

Chapter 12

Organic Nitrogen Compounds

CHAPTER'S SUMMARY

AMINES

There is a very large number of organic compounds in which nitrogen forms a part of their functional groups. The most important of such compounds are amines which are considered as the derivatives of ammonia in which one are more hydrogens have been replaced by alkyl or aryl groups. The amines are classified as primary, secondary or tertiary if one, two or three hydrogens of ammonia, respectively, are replaced by alkyl (or aryl) groups.

Nomenclature

Like all other organic compounds, amines are known by either common or IUPAC names. The common names are derived by using the suffix *-amine* preceded by the name(s) of the alkyl group(s) in alphabetical order, writing as one word. In IUPAC names, the ending *-e* of the name of the parent hydrocarbon containing the —NH_2 group is replaced by *-amine*. The remaining alkyl groups (in secondary and tertiary amines) are named as substituents by using the prefix *N*-.

Preparation of Amines

There are a number of methods available for the preparation of amines. Some of them are of general nature and can be used for all the classes of amines, while the others are applicable only to a specific class of amines.

1. Alkylation of ammonia. Primary amines are formed if primary alkyl halides are treated with aq. or alc. solution of ammonia, followed by treatment with a base. However, the primary amine may be further alkylated to yield secondary and tertiary amines, and even quaternary salts.

2. Gabriel synthesis. A pure primary amine may be prepared by the treatment of potassium phthalimide with an alkyl halide, followed by hydrolysis.

3. Reductive amination. Condensation of ammonia (or a primary or secondary amine) with an aldehyde or a ketone, followed by reduction, yields the corresponding amine.

4. Acylation-reduction. Acylation of ammonia, a primary or a secondary amine with an acid chloride or acid anhydride, followed by the reduction of the initially formed amide or substituted amide, yields the corresponding amine.

5. Hofmann degradation of amides. A primary amine, free of secondary and tertiary amines and with one less carbon atom, may be prepared by the reaction of an amide with a solution of bromine (or chlorine) in sodium hydroxide.

6. Reduction of nitriles. A primary amine with one more carbon atom may be prepared by the reduction of a nitrile, either catalytically or with $LiAlH_4$ in ether.

7. Reduction of nitro compounds. A primary amine may be prepared by the reduction of a nitro group by a variety of reducing agents. This method is particularly useful for the preparation of aromatic amines which lead to a host of aromatic compounds.

Physical Properties of Amines

Amines are polar substances, mostly liquid with fishy odour. The boiling points of primary amines are in between those of hydrocarbons and alcohols of comparable molecular weights, indicating that although primary amines are associated by hydrogen bonding but this association is weaker than that in alcohols. Tertiary amines are unable to form intermolecular hydrogen bonds, and thus have boiling points close to those of hydrocarbons. However, all types of amines can form hydrogen bonds with water, making them soluble in water; the solubility decreases with increasing carbon chain.

Basicity of Amines

Because of the presence of a nonbonding electron pair on nitrogen, an amine can accept a proton, and thus can act as a base. The aliphatic amines are somewhat stronger bases than ammonia, whereas the aromatic amines are considerably weaker bases than ammonia. The relative basicity of aliphatic pri., sec. and tert. amines is a consequence of the compromise between the electron-donating inductive effect of the alkyl groups and the steric hindrance to solvation of their ammonium ions. The basicity of the aromatic amines is influenced by the electronic effects of the ring substituents.

Reactions of Amines

The chemical behaviour of amines is based on the tendency of nitrogen to share its electron pair, as is evident from the following reactions:

1. Salt formation. Amines can react with aq. acids to form non-volatile salts from which amines can be regenerated on treatment with aq. NaOH. The salts are useful for the isolation and characterization of amines, and in the formulation of drugs.

2. Alkylation. Like ammonia, an amine can react with an alkyl halide to give another amine of the next higher class. A tertiary amine yields a quaternary ammonium salt. This reaction can be used to distinguish between pri., sec. and tert. amines through exhaustive methylation, and for structure determination through Hofmann degradation.

3. Acylation. Primary and secondary (not tertiary) amines can react with acid halides or anhydrides to form substituted amides. In the case of acid halides an extra equivalent of the amine (or another base) is required to neutralize HCl formed as a co-product.

4. Sulfonation. Primary and secondary (not tertiary) amines react with an alkyl or arylsulfonyl chloride to form sulfonamides which can be used to distinguish between and separate pri., sec. and tert. amines (Hinsberg test).

5. Reactions with nitrous acid. All classes of amines react with nitrous acid to yield different products, depending on whether the amine is primary, secondary or tertiary, and whether it is aliphatic or aromatic. The most important is the reaction of primary aromatic amines with nitrous acid to yield arenediazonium salts which have numerous synthetic applications.

The utility of the arenediazonium salts in syntheses largely lies in the fact that it undergoes aromatic nucleophilic substitution under mild conditions. It yields phenol on treatment with water; aryl halide with halide ion, aryl nitrile with cyanide ion; benzene with hydrogen; diaryl with an aromatic compound in the presence of NaOH; and arylhydrazines on reduction. It also undergoes aromatic electrophilic substitution to yield azo dyes.

6. Oxidation. Amines are easily oxidized by H_2O_2, RCO_3H, and even by air to yield amine oxides. Amine oxides from pri. and sec. amines rearrange to hydroxylamines. Suitable tertiary amine oxides may undergo Cope elimination. Aromatic amines may also involve oxidation of the ring.

7. Formation of isonitriles. In the presence of alc. KOH, primary amines (aliphatic or aromatic) react with $CHCl_3$ to yield isonitriles, also known as carbylamines, which have a very foul odour. This reaction can be used as a characteristic test for primary amines (carbylamine test).

HETEROCYCLIC COMPOUNDS

Heterocyclic compounds are those cyclic compounds in which one or more ring atoms are other than carbon. The most important of these are pyrrole and pyridine.

Pyrrole

Pyrrole is a five-membered nitrogen heterocycle, and is a part of the structure of many naturally occurring compounds.

Synthesis of pyrrole. Pyrrole may be isolated from bone oil where it occurs naturally. It may also be synthesized: (i) by passing a mixture of acetylene and ammonia through a red hot tube, (ii) by the pyrolysis of diammonium mucate and (iii) by the distillation of succinimide with zinc dust. On commercial scale, pyrrole is prepared by passing a mixture of furan, ammonia and steam over alumina at 400°C.

Pyrrole derivatives may be synthesized: (i) by heating a 1,4-dicarbonyl compound with ammonia or a primary amine (Paal-Knorr synthesis), (ii) by the condensation of an α-amino ketone and a β-keto ester (Knorr pyrrole synthesis) and (iii) by the condensation of chloroacetone, a β-keto ester and ammonia or a primary amine (Hantzsch synthesis).

Reactions of pyrrole. Pyrrole is an extremely weak base. In fact, it is acidic enough to form potassium salt when fused with solid potassium hydroxide. Potassiopyrrole can be used for the preparation of 1-derivatives of pyrrole. Pyrrole can be reduced to pyrrolidine on catalytic hydrogenation.

Pyrrole is an aromatic compound, and therefore can undergo electrophilic aromatic substitution reactions similar to those given by aniline, preferentially at position 2.

In the presence of conc. acids, pyrrole undergoes polymerization.

Pyridine

Pyridine is a six-membered nitrogen heterocycle. It is also found in bone oil.

Synthesis of pyridine. Pyridine may be synthesized: (i) by passing a mixture of acetylene and hydrogen cyanide through a red hot tube and (ii) by heating the hydrochloride of pentamethylenediamine, followed by dehydrogenation.

Derivatives of pyridine may be synthesized by the condensation of two molecules of a β-keto ester with one molecule of an aldehyde and one molecule of ammonia.

Reactions of pyridine. Pyridine is a much stronger base than pyrrole, although much weaker than aliphatic amines. In one set of reactions, pyridine acts as a base or a nucleophile through nitrogen. In another set of reactions, it undergoes substitution, both electrophilic and nucleophilic, at its ring, due to the aromatic character of the ring.

Toward electrophilic substitution, pyridine resembles nitrobenzene in its behaviour and is substituted preferentially at position 3. The nucleophilic substitution occurs at position 2, and if this position is occupied, then at position 4.

Pyridine also undergoes reduction to yield piperidine, and oxidation to yield pyridine N-oxide.

AMINO ACIDS

Amino acids are the bifunctional compounds containing an amino group usually at α-position to a carboxy group, and form the structural units of proteins. They are crystalline solid with very high melting points, typical of salts. They are fairly soluble in water and polar organic solvents. They are amphoteric in nature and have characteristic isoelectric points.

Synthesis of Amino Acids

Naturally occurring amino acids can be obtained by the hydrolysis of proteins, followed by separation. However, they can also be synthesized by a number of methods, where they are usually obtained as a racemic mixture that must be resolved if a pure enantiomer is required. They can be obtained by: (i) the treatment of an α-keto acid with an excess of ammonia, followed by catalytic reduction, (ii) the treatment of α-halo acid with a large excess of ammonia, (iii) a combined Gabriel-malonic ester synthesis and (iv) the treatment of an aldehyde with ammonia and HCN, followed by hydrolysis (Strecker synthesis).

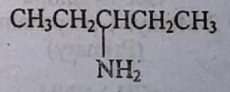
Reactions of Amino Acids

The reactions of amino acids in general are those of the amino and the carboxy groups. For example, the carboxy group can be esterified under acidic conditions, whereas the amino group can be acylated under basic conditions. However, amino acids also give some specific reactions. For example, when an aqueous solution of an α-amino acid is treated with an alcoholic solution of ninhydrin, a purple-coloured dye is produced. This reaction is used for the detection and estimation of α-amino acids.

ANSWERS TO EXERCISES

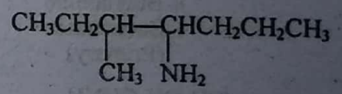
1.
- *(a)* *n*-Butylamine (1-Butanamine)
- *(b)* Diethylamine (N-Ethylethanamine)
- *(c)* Triethylamine (N,N-Diethylethanamine)
- *(d)* Benzylamine (Phenylmethanamine)
- *(e)* Isopentylamine (3-Methyl-1-butanamine)
- *(f)* 2-Methylbutylamine (2-Methyl-1-butanamine)
- *(g)* 1-Ethylbutylamine (3-Hexanamine)
- *(h)* Allylethylmethylamine (N-Ethyl-N-methyl-2-propenamine)
- *(i)* Benzylammonium chloride (Phenylmethanamine hydrochloride)
- *(j)* 4-Bromophenyltrimethylammonium chloride
- *(k)* Tetramethylammonium chloride
- *(l)* Benzenediazonium chloride
- *(m)* γ-Aminovaleric acid (4-Aminopentanoic acid)
- *(n)* Dimethyl-*n*-propylamine oxide
- *(o)* 1-Methylpyrrole
- *(p)* 4-Methylpyridine N-oxide

2. *(a)*



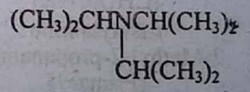
$CH_3CH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_2CH_3$

(b)



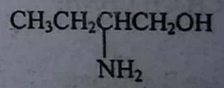
$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H-\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_2CH_2CH_3$

(c)



$(CH_3)_2CH\underset{\displaystyle CH(CH_3)_2}{\underset{|}{N}}CH(CH_3)_2$

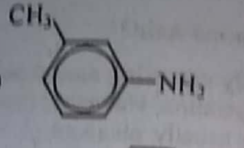
(d)



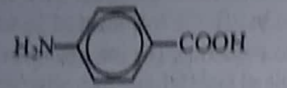
$CH_3CH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_2OH$

(e) $C_6H_5CH_2CH_2NH_2$

(f)



(g)



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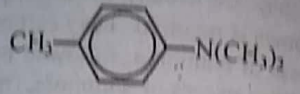
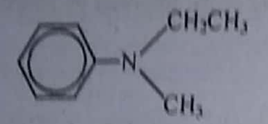
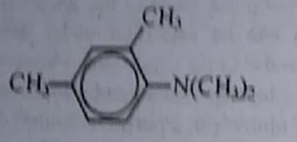


(i)



(j)

(k)

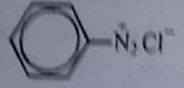


(l) $(CH_3CH_2)_2\overset{+}{N}H_2\ Cl^-$

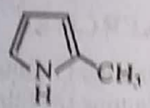
(m) $CH_3CH_2\overset{+}{N}(CH_3)_3\ OH^-$

(n) $(C_6H_5CH_2)_3\overset{+}{N}H\ ^-OCOCH_3$

(o)



(p)



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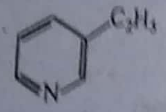

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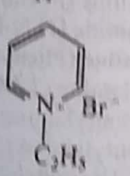
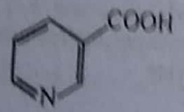
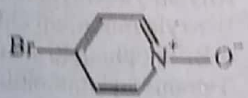


(s)



(t)



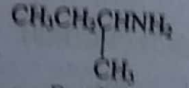
(u) $(CH_3CH_2)_3\overset{+}{N}{-}O^-$

(v) $H_2NCH_2CH_2COOH$

(a) $C_4H_{11}N$,

$CH_3CH_2CH_2CH_2NH_2$
n-Butylamine
1-Butanamine
(Primary)

$(CH_3)_2CHCH_2NH_2$
Isobutylamine
2-Methyl-1-propanamine
(Primary)



$CH_3CH_2\underset{CH_3}{\underset{|}{C}}HNH_2$

sec-Butylamine
2-Butanamine
(Primary)

$(CH_3)_3CNH_2$
t-Butylamine
2-Methyl-2-propanamine
(Primary)

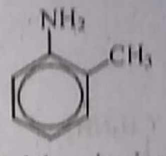
$CH_3CH_2CH_2NHCH_3$
Methyl-*n*-propylamine
N-Methyl-1-propanamine
(Secondary)

$(CH_3CH_2)_2NH$
Diethylamine
N-Ethylethanamine
(Secondary)

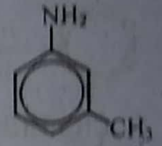
$(CH_3)_2CHNHCH_3$
Isopropylmethylamine
N,1-Dimethylethanamine
(Secondary)

$CH_3CH_2N(CH_3)_2$
Ethyldimethylamine
N,N-Dimethylethanamine
(Tertiary)

(b) C_7H_9N,



2-Methylphenylamine
2-Methylbenzenamine
o-Methylaniline
o-Toluidine
(Primary)



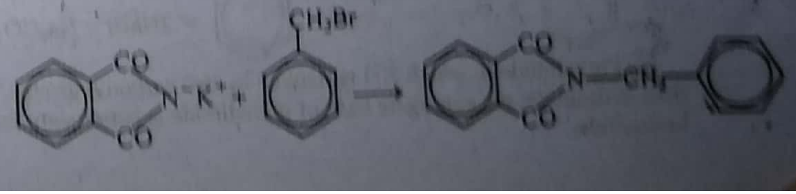
3-Methylphenylamine
3-Methylbenzenamine
m-Methylaniline
m-Toluidine
(Primary)

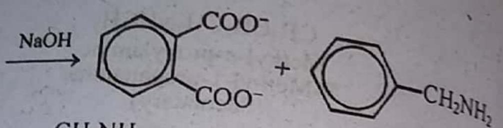
4-Methylphenylamine
4-Methylbenzenamine
p-Methylaniline
p-Toluidine
(Primary)

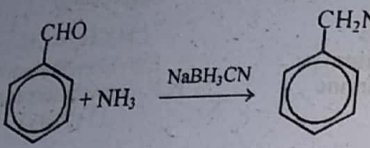
Benzylamine
Phenylmethanamine
(Primary)

Methylphenylamine
N-Methylbenzenamine
N-Methylaniline
(Secondary)

4. (a) (i)





(ii)


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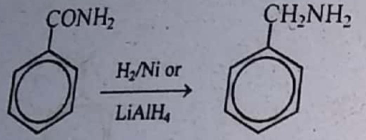

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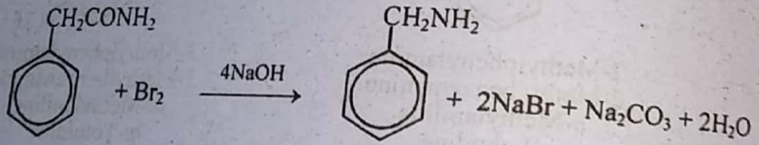
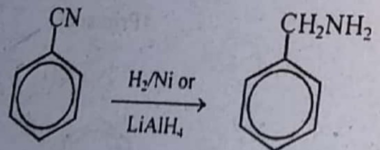
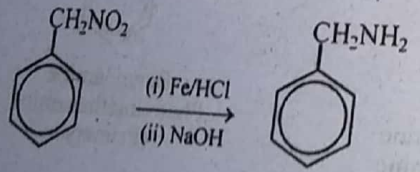
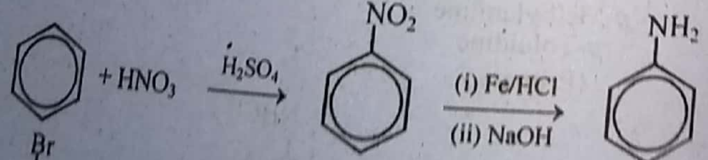
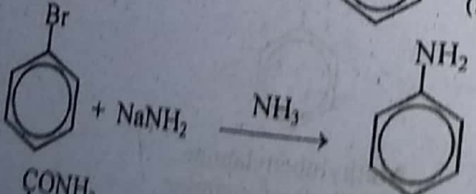


(v)


(vi)


(b) (i)


(ii)


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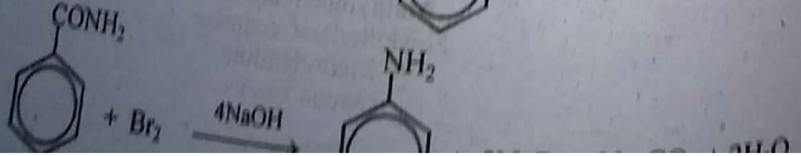
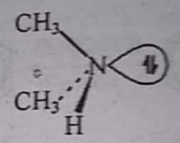
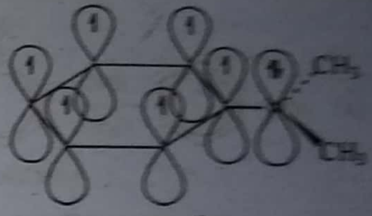
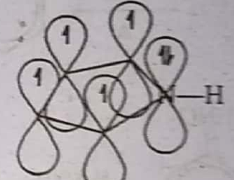


6. (a)


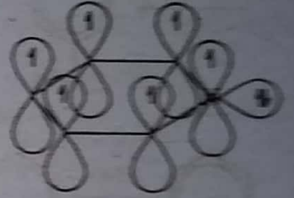
N is sp^3

(b)


N is sp^2

(c)


N is sp^2

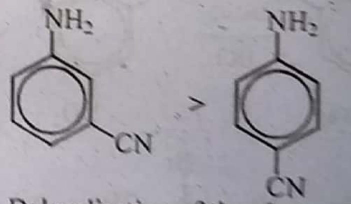
(d)


N is sp^2

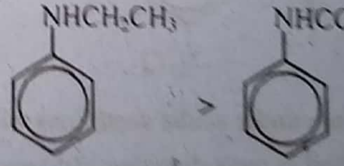
7. (a) $(CH_3)_3N > (CCl_3)_3N$
Electron-withdrawing inductive effect of Cl decreases the electron density on N.

(b) $C_6H_5CH_2NH_2 > CH_3C_6H_4NH_2$
The electron pair of nitrogen is delocalized over to the ring in a methylaniline.

(c) Cyclohexylamine > aniline
The same reason as in *(b)*

(d)


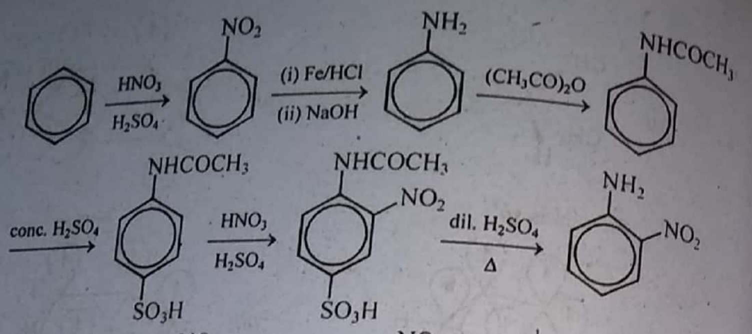
Delocalization of the electron pair of nitrogen extends up to the CN group in para position.

(e)


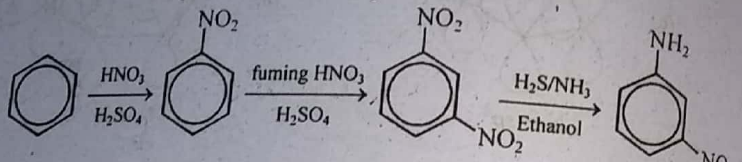
The electron pair of N is also delocalized to the carbonyl oxygen.

(f)

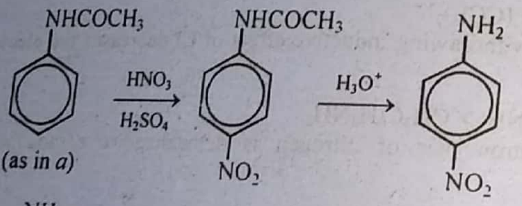

8. (a) (a)



(b)

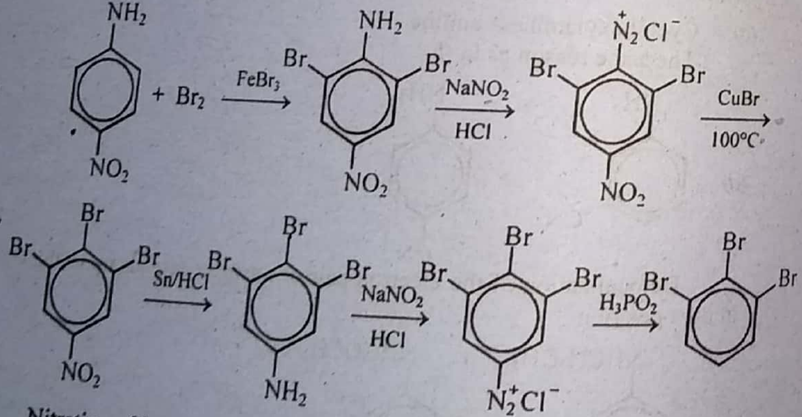


(c)



(as in a)

(b)

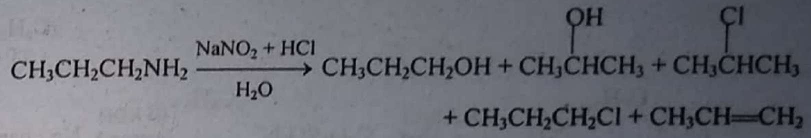


9. Nitration of benzene ring takes place under acidic conditions where —NH_2 group is protonated to —$\overset{+}{N}H_3$ group which is meta-directing and hence yields to the larger proportion of meta nitration.

10. (a) The carboxylic acid is separated as a sodium salt on treatment with $NaHCO_3$. The amine is then separated by converting it to the ammonium chloride on treatment with HCl. Thus, we are left behind with the hydrocarbon.

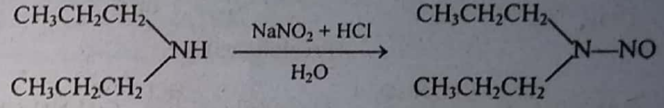
(b) Aniline is first separated as anilinium chloride on treatment with HCl. Benzoic acid is then separated as a sodium salt on treatment with $NaHCO_3$, followed by the separation of p-cresol as its sodium salt on treatment with NaOH. We are then left with toluene.

11.(a) (i)

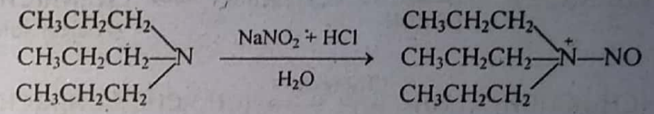


$$CH_3CH_2CH_2NH_2 \xrightarrow[H_2O]{NaNO_2 + HCl} CH_3CH_2CH_2OH + CH_3\overset{OH}{C}HCH_3 + CH_3\overset{Cl}{C}HCH_3 + CH_3CH_2CH_2Cl + CH_3CH{=}CH_2$$

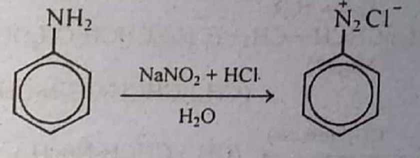
(ii)



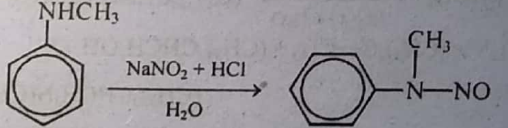
(iii)



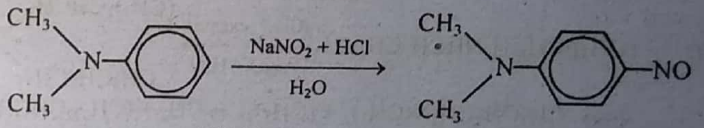
(iv)



(v)

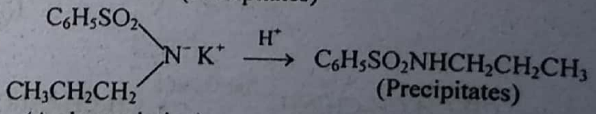


(vi)



(b) (i) $CH_3CH_2CH_2NH_2 \xrightarrow{C_6H_5SO_2Cl} C_6H_5SO_2NHCH_2CH_2CH_3 \xrightarrow{KOH}$

(Precipitates)



(A clear solution)

(ii) $(CH_3CH_2CH_2)_2NH \xrightarrow{C_6H_5SO_2Cl} C_6H_5SO_2N(CH_2CH_2CH_3)_2 \xrightarrow[(ii)\ H^+]{(i)\ KOH}$

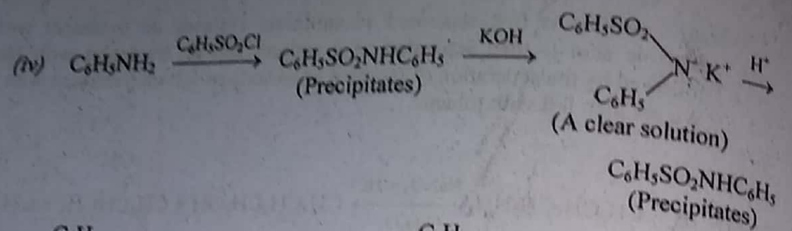
(Precipitates)

No change

(iii) $(CH_3CH_2CH_2)_3N \xrightarrow[(ii)\ KOH]{(i)\ C_6H_5SO_2Cl}$ No reaction $\xrightarrow{HCl} (CH_3CH_2CH_2)_3\overset{+}{N}H\ Cl^-$

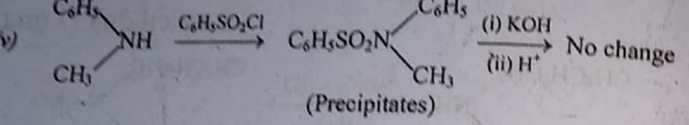
A clear solution

(iv)



$C_6H_5NH_2 \xrightarrow{C_6H_5SO_2Cl} \underset{\text{(Precipitates)}}{C_6H_5SO_2NHC_6H_5} \xrightarrow{KOH} \underset{\text{(A clear solution)}}{(C_6H_5SO_2)(C_6H_5)\overset{-}{N}K^+} \xrightarrow{H^+} \underset{\text{(Precipitates)}}{C_6H_5SO_2NHC_6H_5}$

(v)



$(C_6H_5)(CH_3)NH \xrightarrow{C_6H_5SO_2Cl} \underset{\text{(Precipitates)}}{C_6H_5SO_2N(C_6H_5)(CH_3)} \xrightarrow[\text{(ii) } H^+]{\text{(i) KOH}} \text{No change}$

(vi) $C_6H_5N(CH_3)_2 \xrightarrow[\text{(ii) KOH}]{\text{(i) } C_6H_5SO_2Cl} \text{No reaction} \xrightarrow{HCl} \underset{\text{(A clear solution)}}{C_6H_5\overset{+}{N}H(CH_3)_2\ Cl^-}$

12. (a) $(CH_3)_2CHCH_2CH_2NH_2 \xrightarrow[Ag_2O + H_2O]{CH_3I \text{ (excess)}} (CH_3)_2CHCH_2CH_2\overset{+}{N}(CH_3)_3\ OH^-$

$\xrightarrow[130°C]{} (CH_3)_3N + \underset{\text{(Major)}}{(CH_3)_2CHCH{=}CH_2} + (CH_3)_2CHCH_2CH_2OH +$

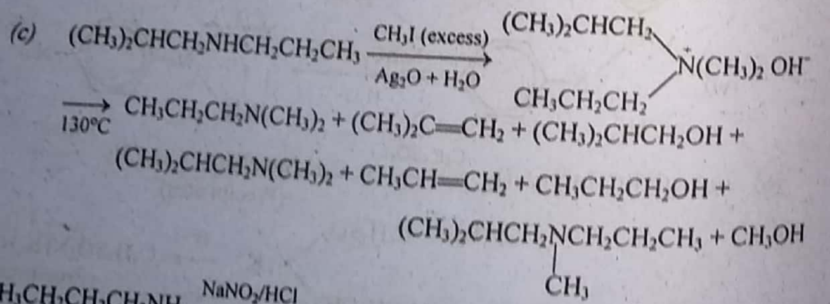
$(CH_3)_2CHCH_2CH_2N(CH_3)_2 + CH_3OH$

(b) $(CH_3)_2CHCH_2NHCH_3 \xrightarrow[Ag_2O + H_2O]{CH_3I \text{ (excess)}} (CH_3)_2CHCH_2\overset{+}{N}(CH_3)_3\ OH^-$

$\xrightarrow[130°C]{} (CH_3)_3N + (CH_3)_2C{=}CH_2 + (CH_3)_2CHCH_2OH +$

$(CH_3)_2CHCH_2N(CH_3)_2 + CH_3OH$

(c)



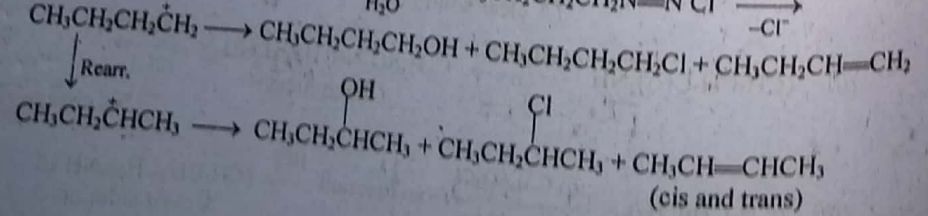
$(CH_3)_2CHCH_2NHCH_2CH_2CH_3 \xrightarrow[Ag_2O + H_2O]{CH_3I \text{ (excess)}} ((CH_3)_2CHCH_2)(CH_3CH_2CH_2)\overset{+}{N}(CH_3)_2\ OH^-$

$\xrightarrow[130°C]{} CH_3CH_2CH_2N(CH_3)_2 + (CH_3)_2C{=}CH_2 + (CH_3)_2CHCH_2OH +$

$(CH_3)_2CHCH_2N(CH_3)_2 + CH_3CH{=}CH_2 + CH_3CH_2CH_2OH +$

$(CH_3)_2CHCH_2N(CH_3)CH_2CH_2CH_3 + CH_3OH$

13. $CH_3CH_2CH_2CH_2NH_2 \xrightarrow[H_2O]{NaNO_2/HCl} CH_3CH_2CH_2CH_2\overset{+}{N}{\equiv}N\ Cl^- \xrightarrow[-Cl^-]{-N_2}$

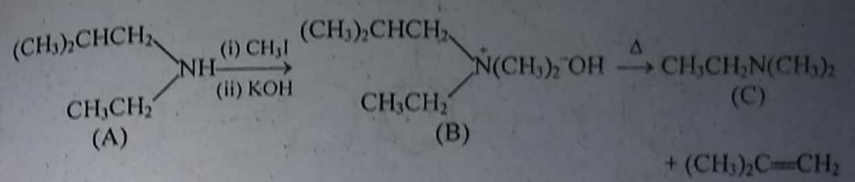


$CH_3CH_2CH_2\overset{+}{C}H_2 \longrightarrow CH_3CH_2CH_2CH_2OH + CH_3CH_2CH_2CH_2Cl + CH_3CH_2CH{=}CH_2$

$\downarrow \text{Rearr.}$

$CH_3CH_2\overset{+}{C}HCH_3 \longrightarrow CH_3CH_2CH(OH)CH_3 + CH_3CH_2CH(Cl)CH_3 + \underset{\text{(cis and trans)}}{CH_3CH{=}CHCH_3}$

14.



$\underset{(A)}{((CH_3)_2CHCH_2)(CH_3CH_2)NH} \xrightarrow[\text{(ii) KOH}]{\text{(i) } CH_3I} \underset{(B)}{((CH_3)_2CHCH_2)(CH_3CH_2)\overset{+}{N}(CH_3)_2\ {}^-OH} \xrightarrow{\Delta} \underset{(C)}{CH_3CH_2N(CH_3)_2} + (CH_3)_2C{=}CH_2$

15. (a) On treatment with nitrous acid ($NaNO_2$ + HCl), $(CH_3)_3CNH_2$ will evolve nitrogen which will be detected as bubbles.

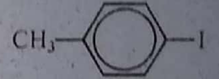
(b) With nitrous acid, cyclohexylamine will evolve bubbles of N_2, whereas aniline will give a highly coloured azo compound when the treatment with nitrous acid is followed by the addition of β-naphthol.

(c) Treatment of toluidine with nitrous acid followed by the addition of β-naphthol gives a highly coloured azo compound, whereas N-methylaniline with nitrous acid gives a precipitate of the acid-insoluble nitrosamine.

(d) On heating with NaOH, benzamide evolves ammonia.

16. (a)

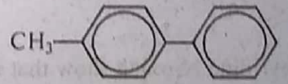
(b)



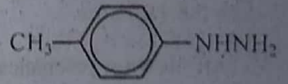
(c)

(d)

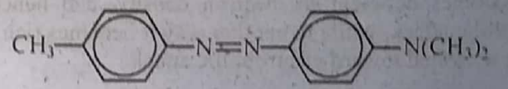
(e)



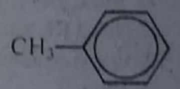
(f)



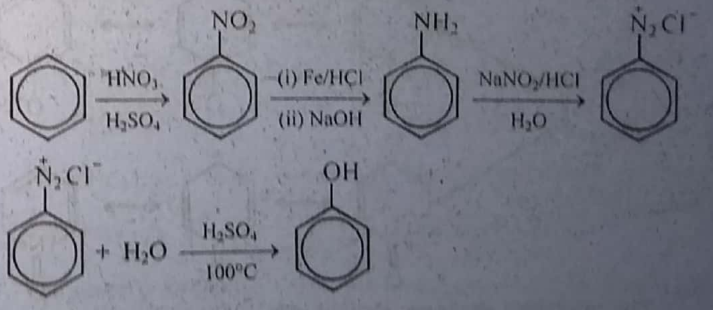
(g)



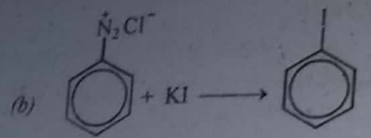
(h)



17. (a)

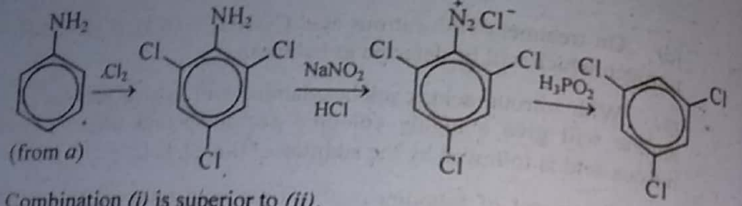


(b)



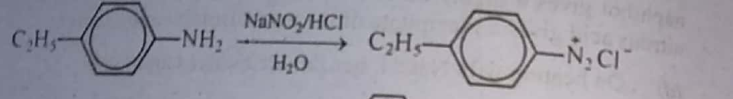
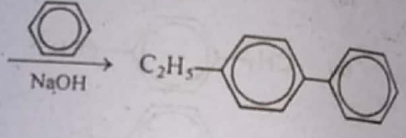
(from *a*)

(c)

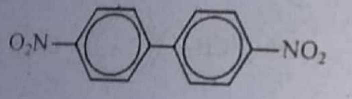


(from *a*)

18.(a) Combination *(i)* is superior to *(ii)*.

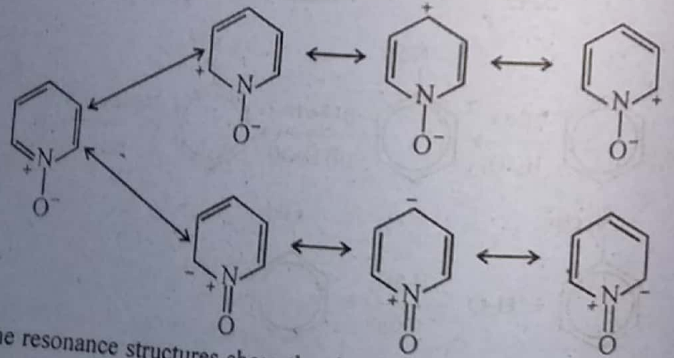



(b)



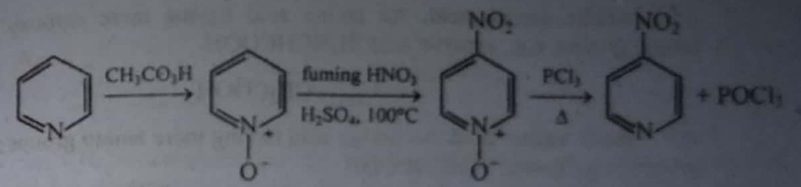
19. See the *Textbook*.

20.(a) The following resonance forms of pyridine N-oxide show that in one way the pyridine ring becomes deficient in electron density, and hence becomes activated for nucleophilic attack, while in another way it becomes rich in electron density, and hence is activated toward electrophilic attack.

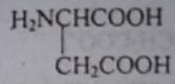


The resonance structures show that it is the positions 2, 4 and 6 which are either electron-rich or electron-deficient. The electrophilic or nucleophilic attack would therefore occur at these positions. However, since the position 4 is least hindered sterically as well as electrostatically, substitution predominantly occurs at this position.

(b)

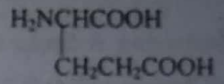


21. **Acidic amino acids**



$$\begin{array}{l} H_2NCHCOOH \\ \quad | \\ \quad CH_2COOH \end{array}$$

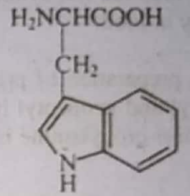
Aspartic acid



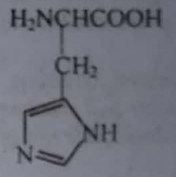
$$\begin{array}{l} H_2NCHCOOH \\ \quad | \\ \quad CH_2CH_2COOH \end{array}$$

Glutamic acid

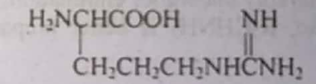
Basic amino acids



Tryptophan

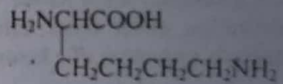


Histidine



$$\begin{array}{l} H_2NCHCOOH \qquad\qquad NH \\ \quad | \qquad\qquad\qquad\qquad \| \\ \quad CH_2CH_2CH_2NHCNH_2 \end{array}$$

Ariginine



$$\begin{array}{l} H_2NCHCOOH \\ \quad | \\ \quad CH_2CH_2CH_2CH_2NH_2 \end{array}$$

Lysine

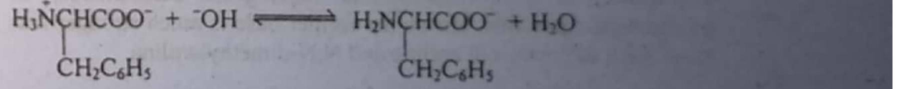
22. (*a*) pH 2, $H_3\overset{+}{N}CH_2COOH$

(*b*) pH 6, $H_3\overset{+}{N}CH_2COO^-$

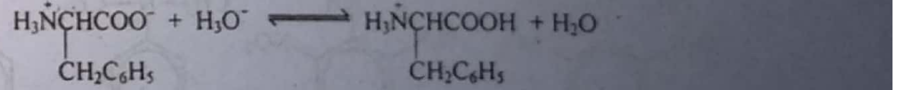
(*c*) pH 10, $H_2NCH_2COO^-$

23.(a) At isoelectric pH.

(b)



$$\begin{array}{l} H_3\overset{+}{N}CHCOO^- + {}^-OH \rightleftharpoons H_2NCHCOO^- + H_2O \\ \qquad | \qquad\qquad\qquad\qquad\qquad\quad | \\ \quad CH_2C_6H_5 \qquad\qquad\qquad\quad CH_2C_6H_5 \end{array}$$

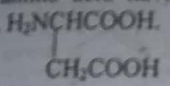


$$\begin{array}{l} H_3\overset{+}{N}CHCOO^- + H_3O^- \rightleftharpoons H_3\overset{+}{N}CHCOOH + H_2O \\ \qquad | \qquad\qquad\qquad\qquad\qquad\quad | \\ \quad CH_2C_6H_5 \qquad\qquad\qquad\quad CH_2C_6H_5 \end{array}$$

24. (*a*) **Amphoteric substances.** The substances that show both acidic and basic properties, e.g., amino acids.

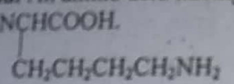
(*b*) **Peptide bond.** A bond formed by the intermolecular elimination of a water molecule from an amino group of one molecule and a carboxy group of another, e.g., $-\boxed{CO—NH}-$.

(c) **Acidic amino acid.** An amino acid having more carboxy groups than amino groups, e.g., aspartic acid, H₂NCHCOOH.



$H_2N\underset{CH_2COOH}{\underset{|}{C}}HCOOH$

(d) **Basic amino acid.** An amino acid having more amino groups than carboxy groups, e.g., lysine, H₂NCHCOOH.



$H_2N\underset{CH_2CH_2CH_2CH_2NH_2}{\underset{|}{C}}HCOOH$

(e) **Zwitterion.** A dipolar ion, e.g., glycine, $H_3\overset{+}{N}CH_2COO^-$.

(f) **Isoelectric point.** It is the pH at which an amino acid exists only as a dipolar ion with zero net charge, e.g., the isoelectric point of glycine is 6.

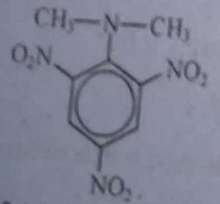
(g) **Essential amino acids.** The amino acids which are not synthesized in the body, and it is essential to supply them to the body in food.

25. (a) The Gabriel synthesis is used only for the preparation of primary amines and proceeds by S_N2 mechanism for which *t*-butyl and neopentyl halides, being sterically hindered, are not good substrates, and di-*n*-propylamine is a secondary amine.

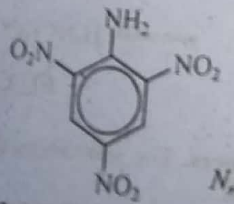
(b) For the preparation of R_2CHNH_2 by the alkylation of ammonia we have to use a secondary alkyl halide which preferably undergoes elimination, rather than substitution under these conditions. So, R_2CHNH_2 is better prepared by the reductive amination of a ketone.

(c) In triphenylamine the electron-pair of nitrogen is delocalized to three benzene rings, and *p*-nitroaniline involves an extended delocalization of the electron-pair, making these amines much weaker bases than aniline.

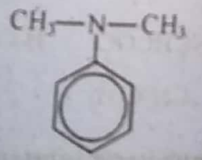
(d) In 2,4,6-trinitro-N,N-dimethylaniline, $(CH_3)_2N$— group is not coplanar with the benzene ring due to steric hindrance between the two methyl groups and the two nitro groups in the ortho positions. The electron-pair of nitrogen is therefore not delocalized to the ring. There is no such steric hindrance to coplanarity in 2,4,6-trinitroaniline, making the delocalization of its nitrogen electron-pair possible. Hence the former base is much stronger than latter. There is no such difference in aniline and N,N-dimethylaniline.



2,4,6-Trinitro-N,N-dimethylaniline



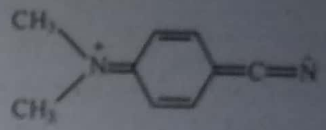
2,4,6-Trinitroaniline



N,N-Dimethylaniline

Aniline

(e) Due to the extended separation of charges.



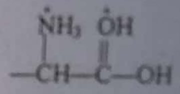
(f) In N,N,2,6-tetramethylaniline, the dimethylamino group does not activate the ring for electrophilic substitution as it does in N,N-dimethylaniline, because of the steric inhibition to coplanarity by the two methyl groups at ortho positions.

(g) The same reason as in (f).

(h) The aromatic carboxylic acid is a weaker acid and needs a stronger base for ionization. Similarly, the aromatic amine is a weaker base and needs a stronger acid for protonation.

(i) Glutamic acid is an acidic amino acid.

(j) Acid-catalysed esterification of a carboxylic acid starts with the protonation of the carboxy group. The protonation of the carboxy group of an amino acid is difficult because of the electrostatic repulsion from the $-\overset{+}{N}H_3$ group.



$$-\overset{\overset{+}{N}H_3}{\overset{|}{C}H}-\overset{\overset{+}{O}H}{\overset{\|}{C}}-OH$$

Chapter 13

Carbohydrates

CHAPTER'S SUMMARY

The term carbohydrate is generally used for naturally occurring optically active polyhydroxy aldehydes and ketones. They are extremely widespread in plants comprising up to 80% of their dry weight. The most familiar carbohydrates are glucose, sucrose, starch and cellulose. The carbohydrates may be classified as monosaccharides, disaccharides and polysaccharides.

MONOSACCHARIDES

The monosaccharides are named such that the name indicates whether it is an aldehyde or a ketone. The number of carbon atoms is also indicated in the name which mostly ends in *-ose*, e.g., aldopentose, ketohexose, etc.

The monosaccharides are generally represented by Fischer projections which are drawn as vertical carbon chains with the carbonyl group closest to the top from where the numbering starts. These are then designated as D or L, depending on whether the configuration of the chiral carbon atom closest to the bottom of the vertical chain is similar to that of D- or L-glyceraldehyde, respectively. The naturally occurring monosaccharides generally belong to the D series.

Reactions of Monosaccharides

The reactions of monosaccharides are essentially those of glucose, the most abundant organic compound in nature. All the reactions of D-(+)-glucose can be explained if we consider the open-chain structure of glucose in equilibrium with its cyclic structure. However, since the concentration of the open-chain form of glucose at equilibrium is too low (0.5%), it does not show certain reversible reactions which are usually given by aldehydes.

1. Methylation. The anomeric hydroxyl group of a monosaccharide can be methylated on treatment with methanol in the presence of HCl to form a glycoside. On the other hand, the other hydroxyl groups can be methylated on treatment with excess of dimethyl sulfate in 30% NaOH to form polymethyl derivatives. Methylation of the anomeric hydroxyl group is reversible and thus can be used for its protection.

2. Acetylation. All the hydroxyl groups of a monosaccharide may be acetylated indiscriminately by treatment with acetic anhydride in the presence of sodium acetate or pyridine.

3. Reaction with aldehydes and ketones. The cis 1,2- and 1,3- hydroxyl groups of a monosaccharide condense with aldehydes and ketones to form acetals and ketals, respectively. This reaction is also used for the protection of two cis hydroxyl groups.

4. Oxidation. Monosaccharides can be oxidized by different oxidizing agents to give rise to different (usually specific) products which can be used for their identification.

Fehling's and Tollen's reagents are mild oxidizing agents in basic media and oxidize aldoses to aldonic acids ($\text{—CHO} \longrightarrow \text{—COOH}$). These reagents also oxidize ketoses (α-hydroxy ketones) but not ketones. These reagents are used clinically to detect sugar in blood or urine.

Bromine water is also a mild oxidizing agent but the medium in this case is acidic. It oxidizes only aldoses to aldonic acid, but not ketoses.

Dilute nitric acid is a stronger oxidizing agent than bromine water, and oxidizes not only —CHO group but also $\text{—CH}_2\text{OH}$ group to yield aldaric acid. This reaction is useful for determining the relative configuration of aldoses.

Aqueous periodic acid causes cleavage of the carbon-carbon bonds in compounds containing two or more adjacent hydroxyl or/and carbonyl groups, producing various types of carbonyl compounds, depending on the structure of the starting compound. This reaction gives useful information about the structure of a monosaccharide.

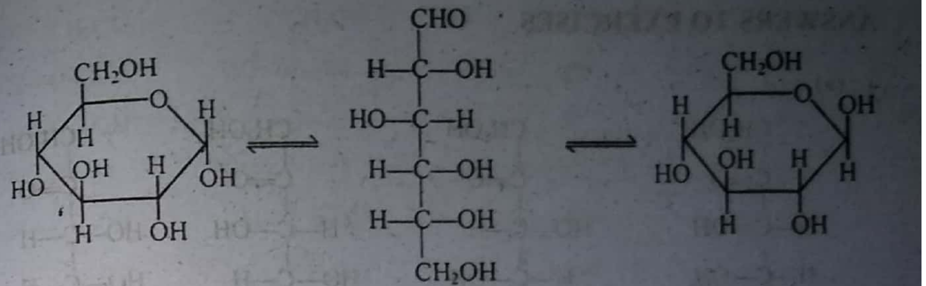
5. Reduction. Monosaccharides may be reduced either by $NaBH_4$ or by catalytic hydrogenation to produce alditols.

6. Reaction with phenylhydrazine. Monosaccharides react with phenylhydrazine in acetic acid to produce initially a .phenylhydrazone and then an osazone. This reaction is particularly useful for the purification and identification of monosaccharides.

7. Interconversion of monosaccharides. Through various synthetic schemes, one monosaccharide can be converted into another with either the same or different number of carbon atoms, and also with either the same or different functional group. These interconversions can be used not only for the synthesis of new monosaccharides but also to correlate their configurations.

Structure of Glucose

On the basis of various experimental observations it was established that glucose ($C_6H_{12}O_6$) is an aldohexose, belongs to D series and exists in two anomeric forms, α-D-glucose and β-D-glucose which are interconvertible through an open-chain structure. In solution, the ring structure is in equilibrium with the open-chain structure whose concentration is less than 0.5%.

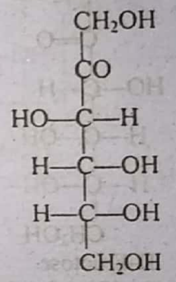


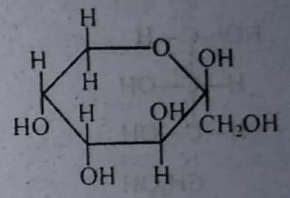
α-D-Glucose β-D-Glucose

In accordance with the ring structure, β-D-glucose is named as β-D-(+)-glucopyranose.

Structure of Fructose

Fructose ($C_6H_{12}O_6$) was established to be a ketohexose. Its open-chain and ring structures are shown below:





β-D-(−)-Fructopyranose

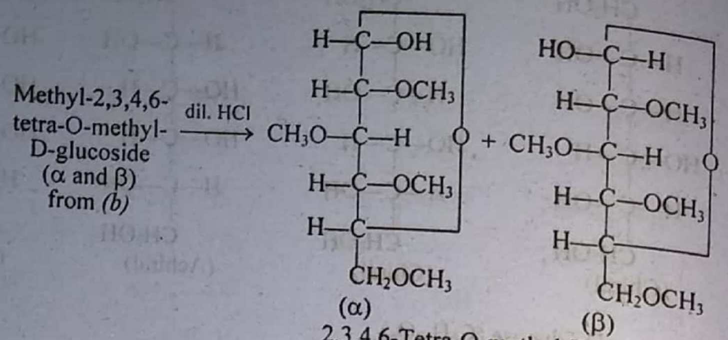
DISACCHARIDES

Disaccharides ($C_{12}H_{22}O_{11}$) contain two monosaccharide units, that may be the same or different, joined by a glycosidic linkage involving a hydroxyl group of one monosaccharide and the anomeric carbon of the other. Most of their reactions are essentially those given by the monosaccharides. The most important disaccharides are maltose, lactose and sucrose.

POLYSACCHARIDES

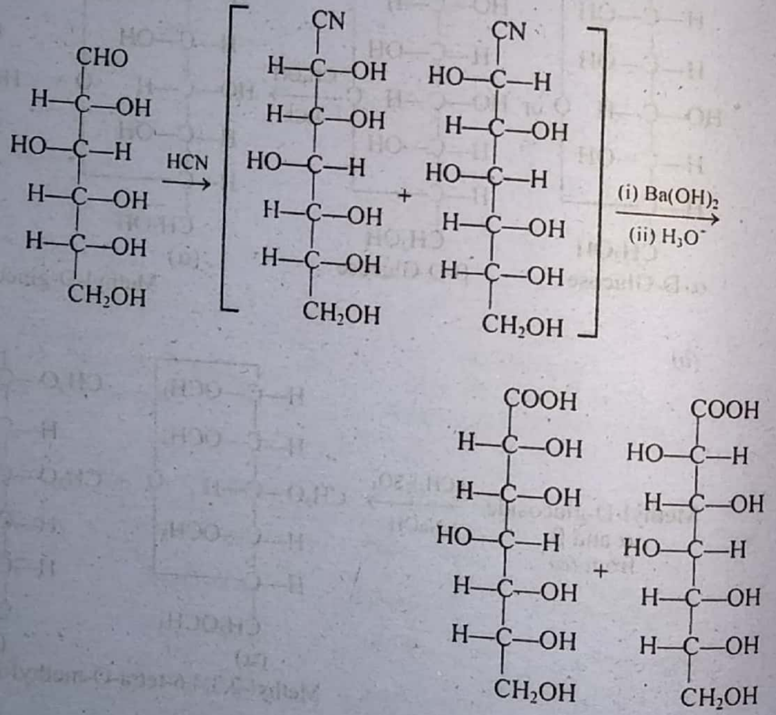
Polysaccharides, $(C_6H_{10}O_5)_n$, contain many monosaccharide units held together by glycosidic linkages. The number of monosaccharide units in majority of natural polysaccharides is 80–100, but in some cases the number may be much more, e.g., cellulose has about 3000 glucose units per molecule. Polysaccharides may have a linear, a branched or a cyclic structure. The most important polysaccharides are starch, glycogen and cellulose, all of which are polymers of D-glucose.

(c)

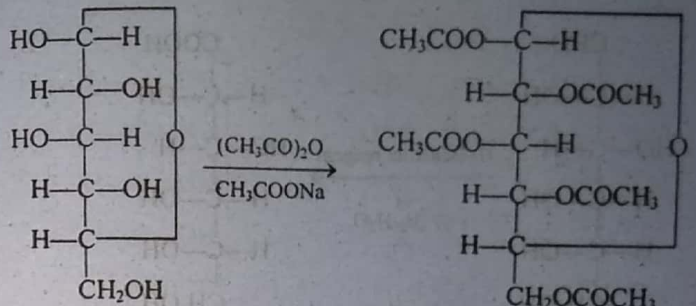


2,3,4,6-Tetra-O-methyl-D-glucose

(d)

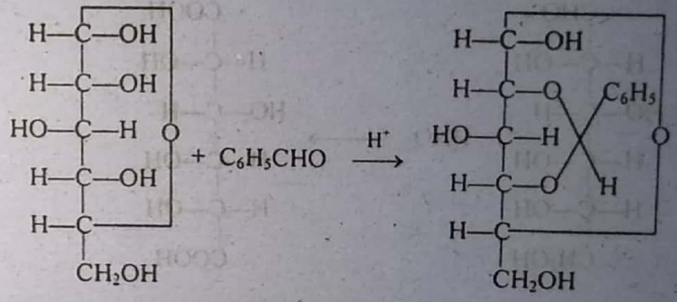


(e)

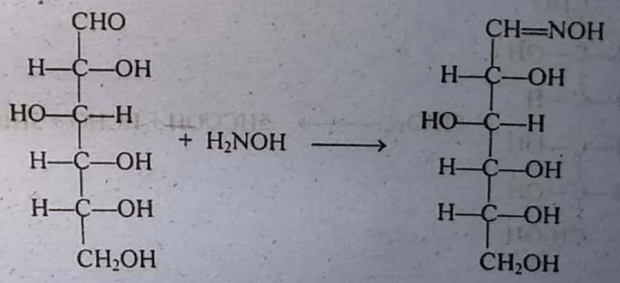


β-D-Glucose β-D-Glucose pentaacetate

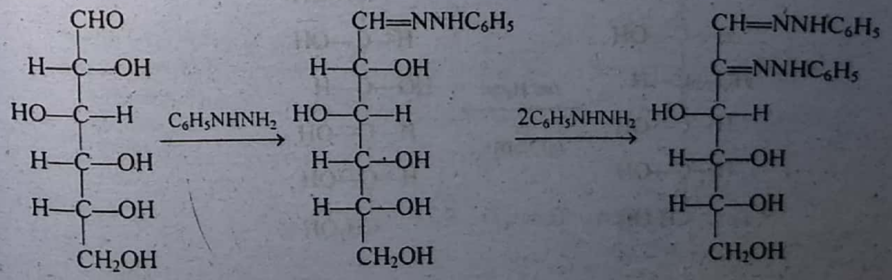
(f)



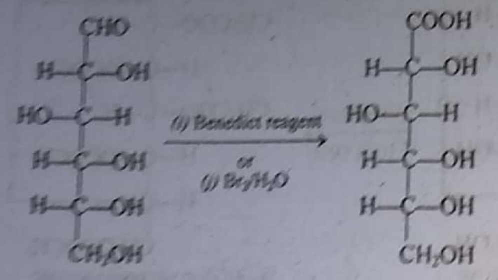
(g)



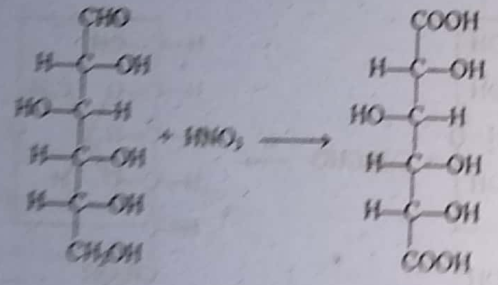
(h)



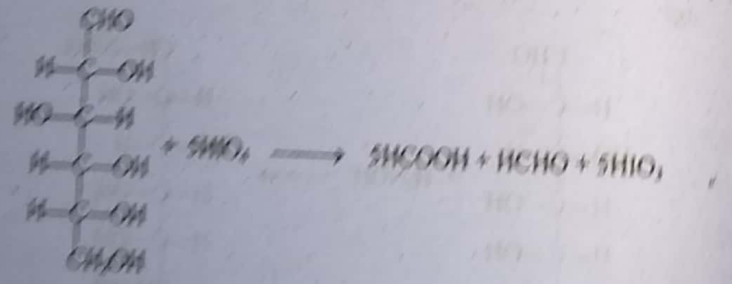
(i, j)



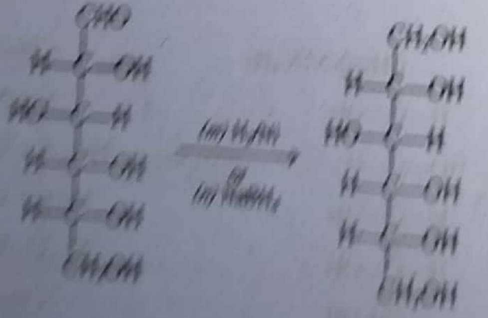
(k)



(l)

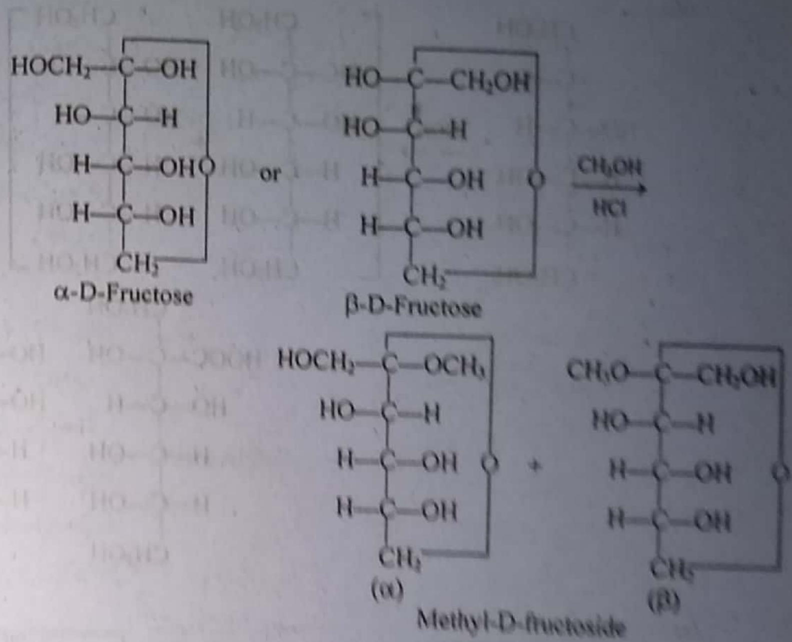


(m, n)

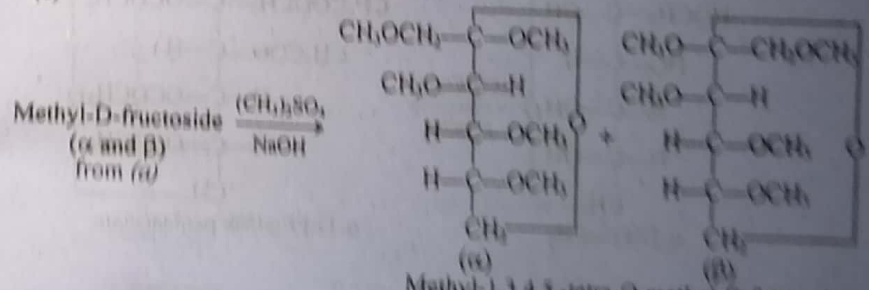


(ii) D-Fructose ($C_6H_{12}O_6$)

(a)

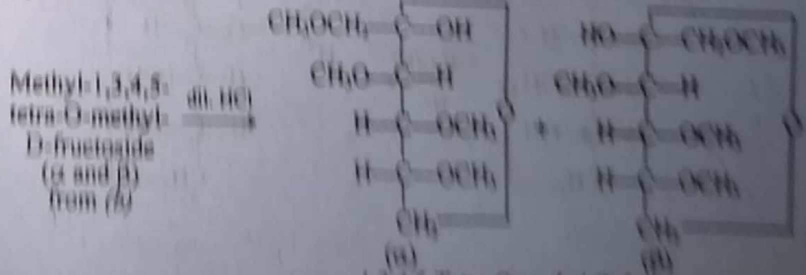


(b)



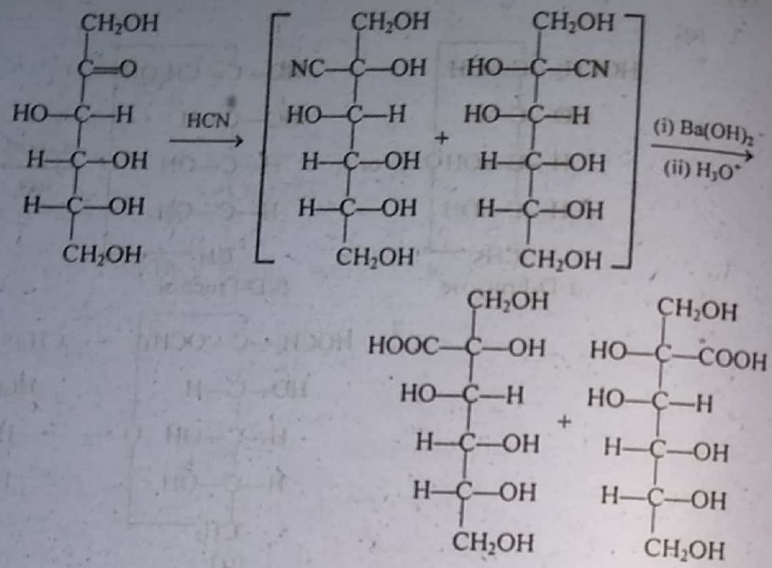
Methyl-1,3,4,5-tetra-O-methyl-D-fructoside

(c)

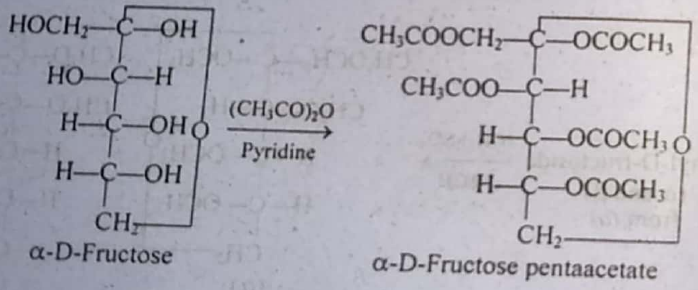


1,3,4,5-Tetra-O-methyl-D-fructose

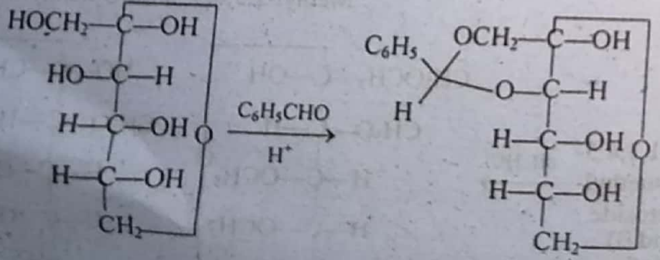
(d)


HCN
(i) Ba(OH)$_2$
(ii) H$_3$O$^+$

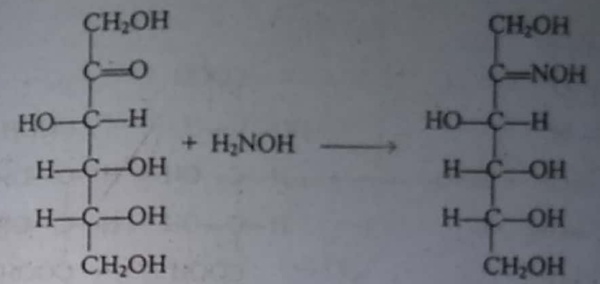
(e)


(CH$_3$CO)$_2$O
Pyridine
α-D-Fructose
α-D-Fructose pentaacetate

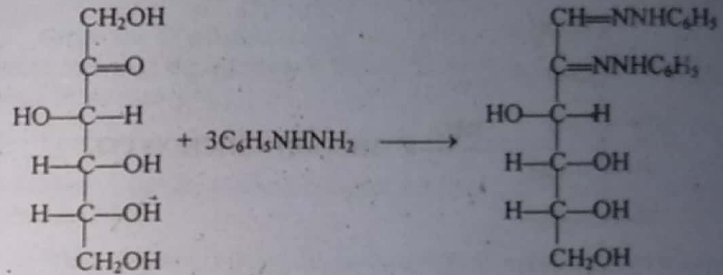
(f)


C$_6$H$_5$CHO
H$^+$

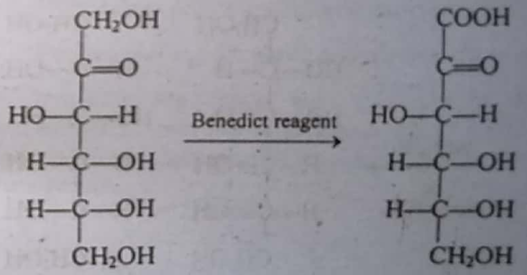
(g)


+ H$_2$NOH

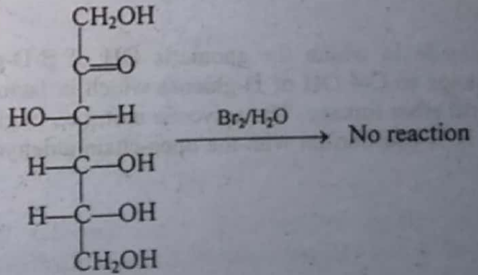
(h)


+ 3C$_6$H$_5$NHNH$_2$

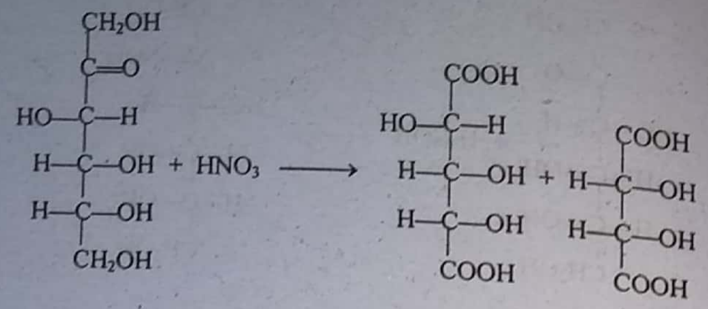
(i)


Benedict reagent

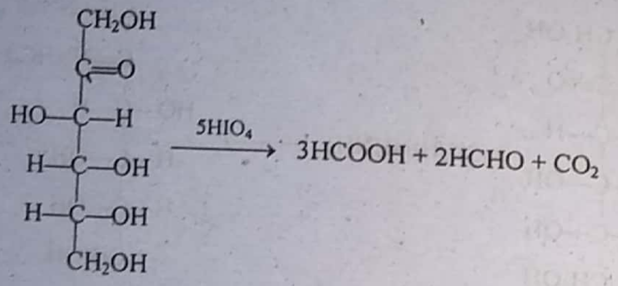
(j)


Br$_2$/H$_2$O
No reaction

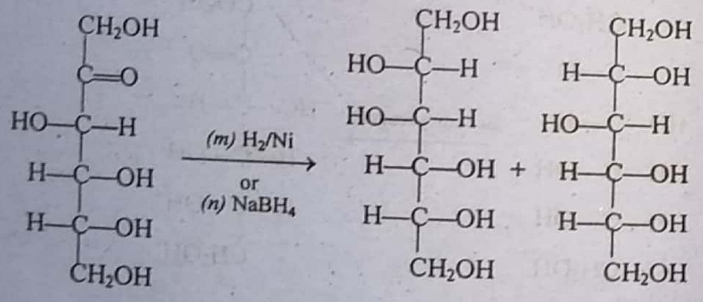
(k)



(l)

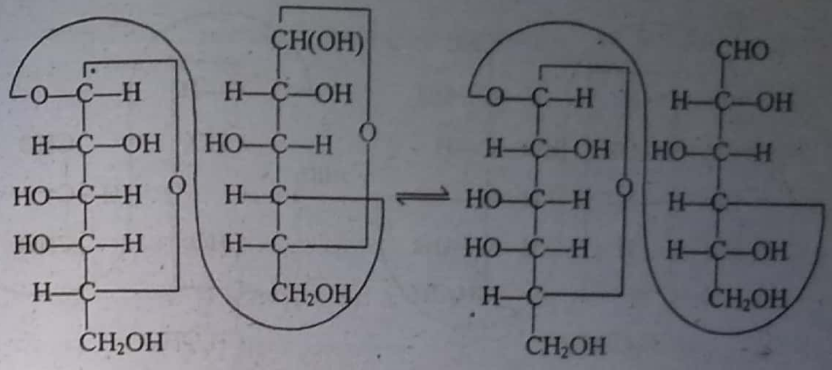


(m, n)



(iii) Lactose ($C_{12}H_{22}O_{11}$)

Lactose is a glycoside in which the anomeric OH of β-D-galactose is bonded by an acetal linkage to C-4 OH of D-glucose which in lactose is called aglycone and has a typical ether linkage. The aglycone unit, i.e., D-glucose has a free anomeric OH, and is in equilibrium with the open-chain aldehydic form, as shown below:



Since the D-glucose unit of lactose has a free anomeric OH which is in equilibrium with the open-chain aldehydic form, lactose behaves like D-glucose toward these reagents.

(a) Lactose reacts with methanolic HCl to form methyl lactoside.

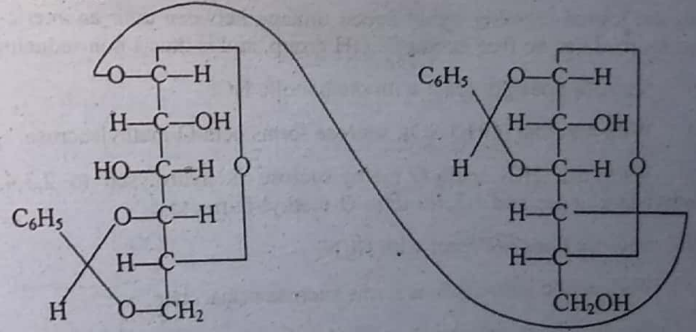
(b) Methyl lactoside reacts with alkaline $(CH_3)_2SO_4$ to form methyl hepta-O-methyllactoside.

(c) With dil. HCl, methyl hepta-O-methyllactoside is hydrolysed to 2,3,4,6-tetra-O-methyl-β-D-galactose and 2,3,6-tri-O-methyl-α(or β)-D-glucose.

(d) HCN reacts with the aldehydic group of the D-glucose unit.

(e) Lactose reacts with acetic anhydride to form lactose octaacetate.

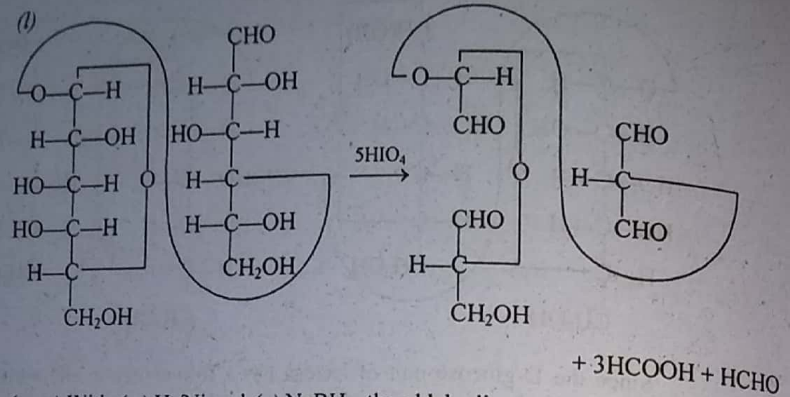
(f) Benzaldehyde reacts with β-lactose to form cyclic acetal in each monosaccharide unit, one in galactose unit as 4,6-O-benzylidene and the other in glucose unit as 1,3-O-benzylidene; α-lactose forms only one cyclic acetal in the galactose unit.



(g-j) Glucose unit of lactose reacts with: (g) hydroxylamine, (h) phenylhydrazine, (i) Benedict reagent and (j) Br_2/H_2O just like free glucose.

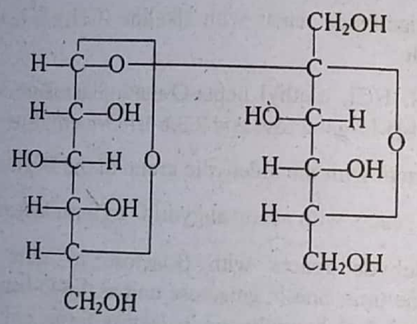
(k) With HNO_3, lactose is hydrolysed to galactose and glucose which are oxidized to aldaric acids.

(l)



(m, n) With *(m)* H_2/Ni and *(n)* $NaBH_4$, the aldehydic group of the glucose unit of lactose is reduced to CH_2OH, just like that of free glucose.

(iv) Sucrose ($C_{12}H_{22}O_{11}$)



Sucrose is a disaccharide in which one D-glucose unit and one D-fructose unit are joined together by an acetal linkage between their anomeric carbons so that sucrose has no free anomeric OH group, and is thus a non-reducing sugar.

(a) Sucrose does not react with methanolic HCl

(b) With alkaline $(CH_3)_2SO_4$, sucrose forms octa-O-methylsucrose.

(c) With dil. HCl, octa-O-methylsucrose is hydrolysed to 2,3,4,6-tetra-O-methyl-D-glucose and 1,3,4,6-tetra-O-methyl-D-fructose.

(d) Sucrose does not react with HCN.

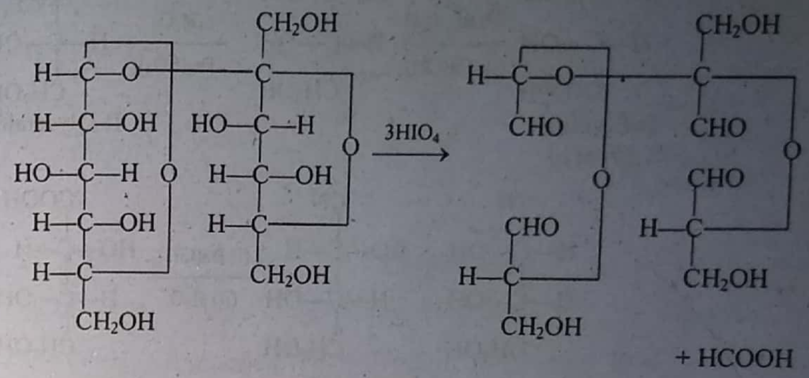
(e) With acetic anhydride, it forms sucrose octaacetate.

(f) Benzaldehyde reacts with sucrose to form a cyclic acetal in the glucose unit as a 2,4-O-benzylidene derivative.

(g-j) Sucrose does not react with: *(g)* hydroxylamine, *(h)* phenylhydrazine, *(i)* Benedict reagent and *(j)* Br_2/H_2O.

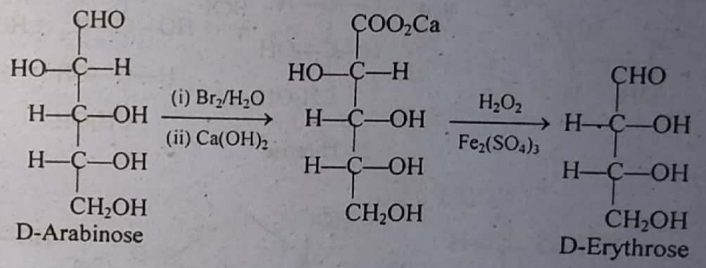
(k) With HNO_3, sucrose is hydrolysed to glucose and fructose which are oxidized as described before.

(l)

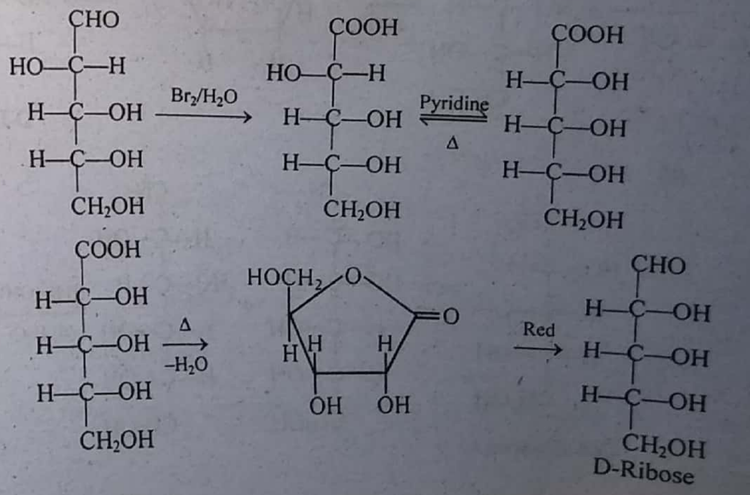


(m, n) Sucrose does not react with: *(m)* H_2/Ni and *(n)* $NaBH_4$.

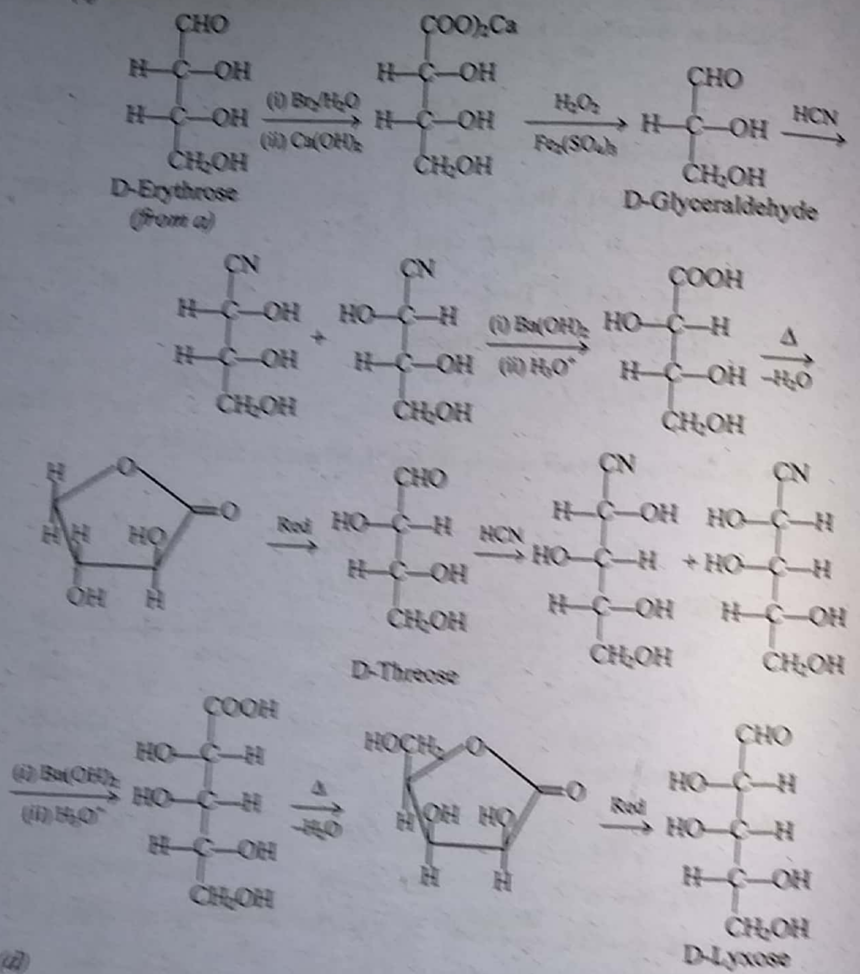
4. *(a)*



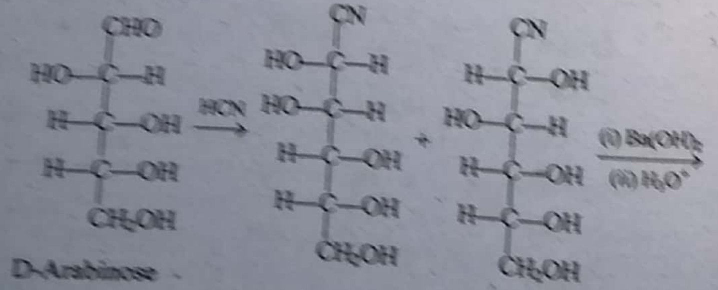
(b)

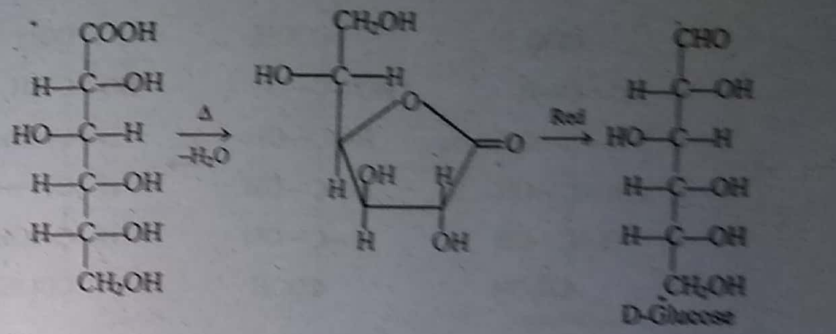


(c)

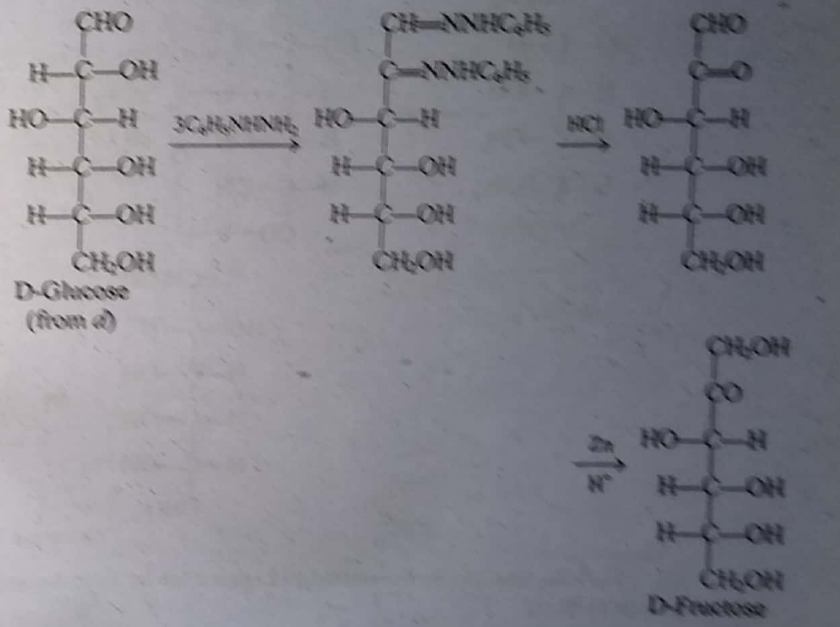


(d)

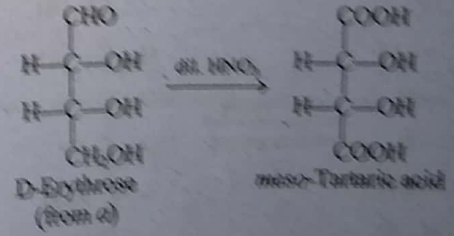




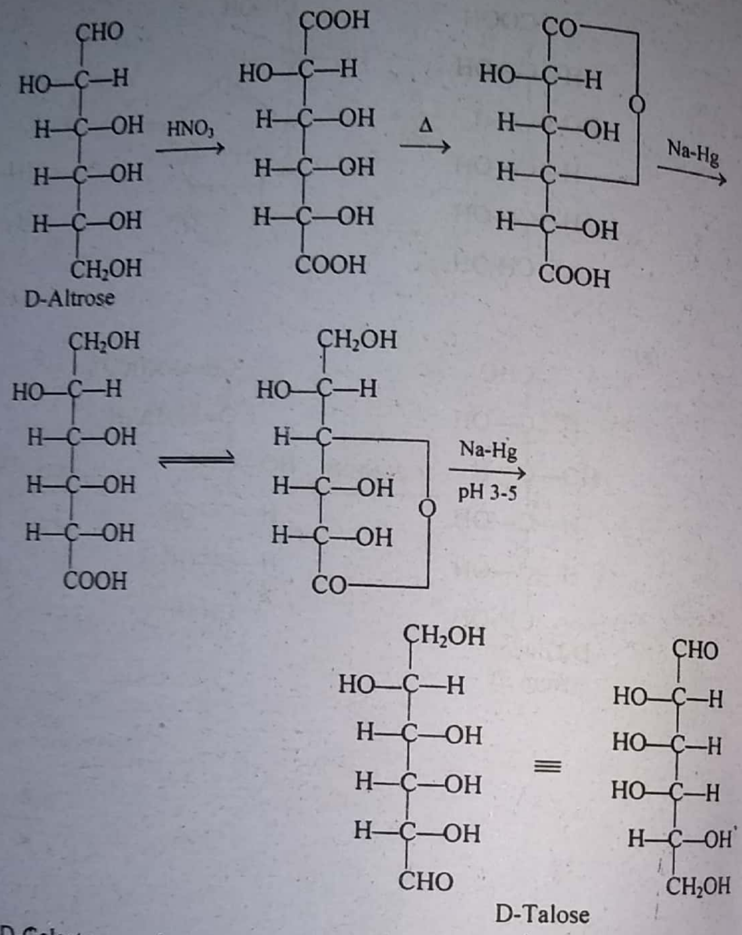
(e)



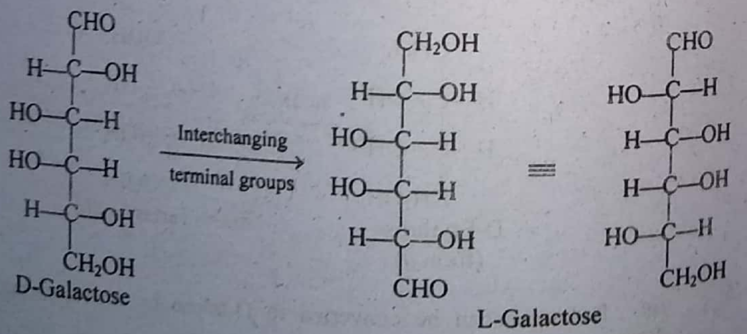
(f)



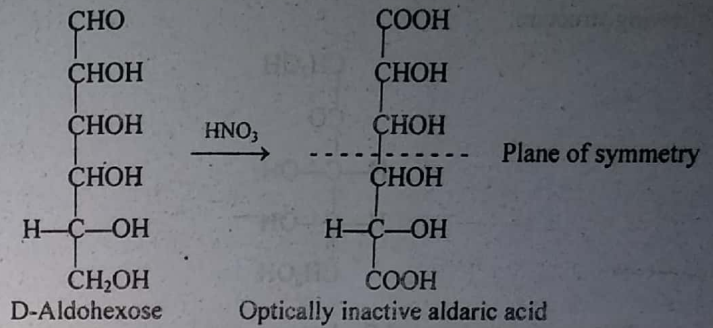
5. (a) D-Altrose can be converted to D-talose by interchanging the terminal groups.



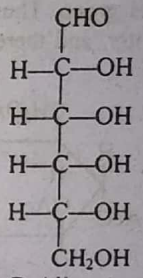
(b) D-Galactose can be converted to L-galactose by interchanging the terminal groups as in *(a)*:



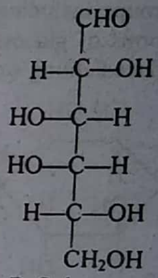
6. (a)



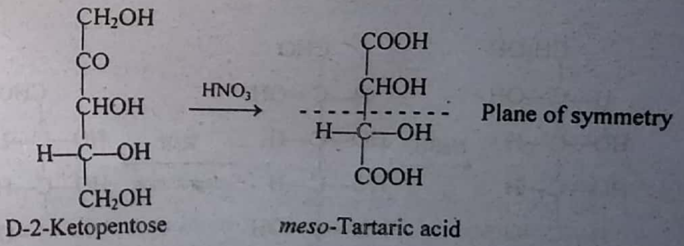
There are only two D-aldohexoses which on oxidation by nitric acid can give aldaric acids which shall have a plane of symmetry and thus be optically inactive. These are:


D-Allose

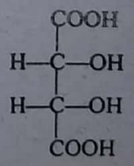
and


D-Galactose

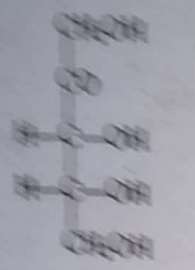
(b)



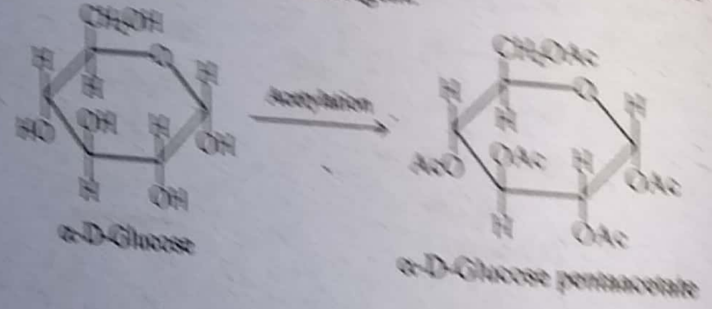
For tartaric acid to be meso OH groups of both the chiral carbon atoms must be on the same side of the molecule, i.e., the structure of *meso*-tartaric acid is:



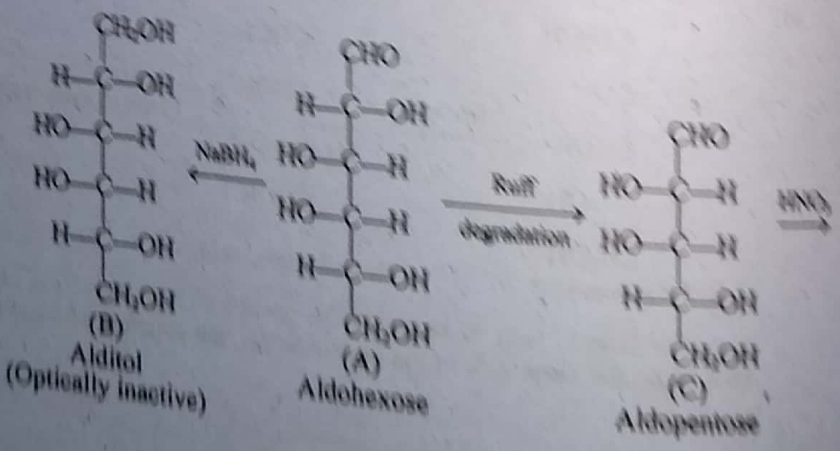
Thus, meso-tartaric acid is produced from the D-2-ketopentose having the following structure:

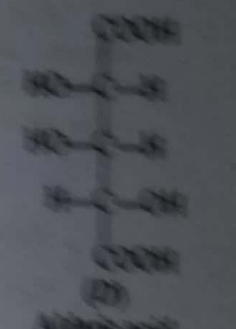


7. The cyclic structure of D-glucose exists in two anomeric forms both of which are in equilibrium with the open-chain structure which has a free aldehydic group due to which glucose reduces Fehling's or Tollen's reagent. When D-glucose is acetylated, both anomeric forms are completely acetylated at their hydroxyl groups including the anomeric OH group. Thus, both the acetylated anomeric forms of glucose exist independently, and there is no free aldehydic group to reduce Fehling's or Tollen's reagent.



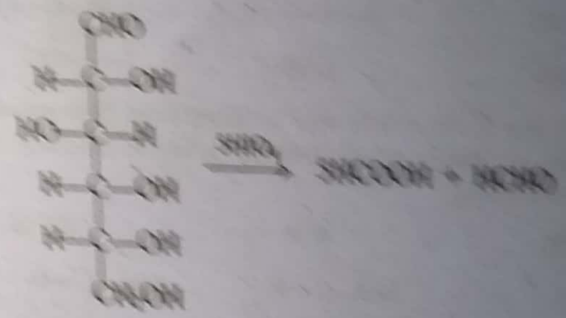
8.



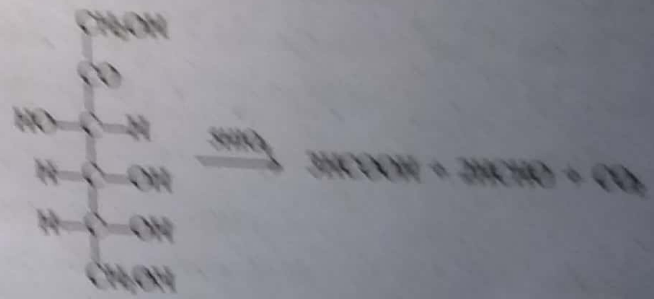


(D)
Aldaric acid
(Optically active)

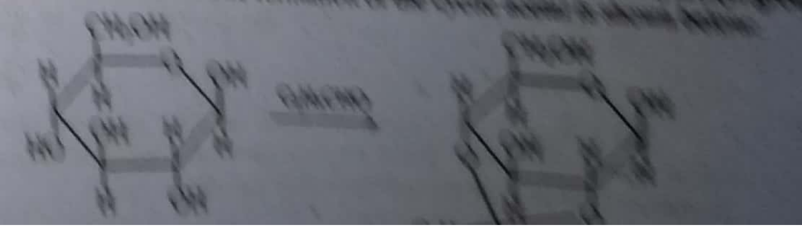
9. (i)



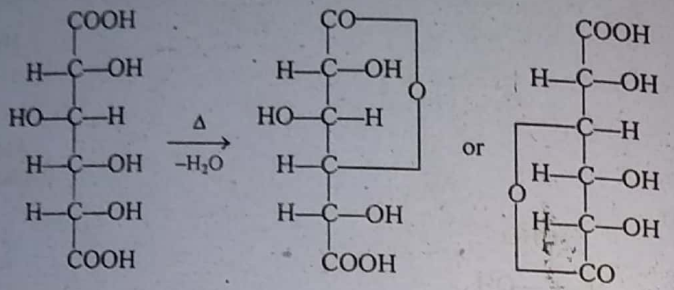
(ii)



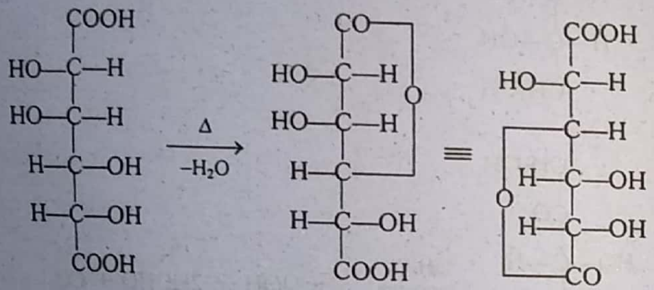
10. An aldehyde usually forms a six-membered cyclic acetal with a cis 1,3-diol. If we look at the cyclic structure of D-glucose, we find that only the hydroxyl groups at positions 2 and 4 meet this requirement. The hydroxyl group at position 1 is anomeric. The formation of the cyclic acetal is shown below.



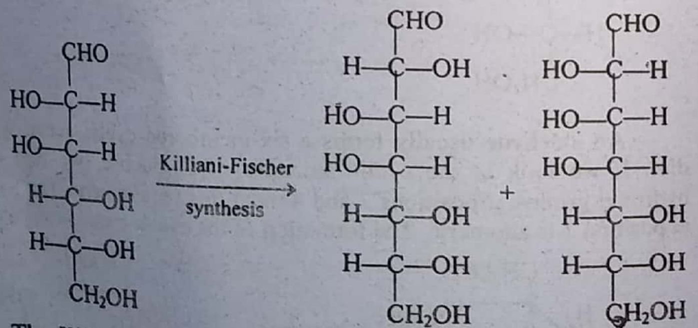
11. The aldaric acid obtained from D-glucose gives rise to two different γ-lactones, depending on whether the carboxy group at position 1 or 6 is involved in the lactone formation. In one lactone the α- and β-OH groups are trans, while in the other they are cis, as shown below:



On the other hand, the aldaric acid obtained from D-mannose gives rise to the same γ-lactone no matter which carboxy group is involved in the lactone formation, as shown below:



12.



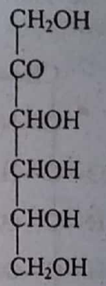
The Killiani-Fischer synthesis on D-mannose produces two aldoheptoses which are diastereomers. Since diastereomers are formed at different rates, one product is formed in larger quantities than the other.

13.(a) 1. Elemental analysis and molecular weight determination shows that the molecular formula of fructose is $C_6H_{12}O_6$.

2. On acetylation, fructose forms a pentaacetate derivative, indicating the presence of five hydroxyl groups in the molecule. The stability of fructose rules out the possibility of the presence of —$CH(OH)_2$ group. Thus, each —OH group is on a separate carbon atom.

3. On treatment with hydroxylamine, fructose gives an oxime, indicating the presence of a carbonyl group in the molecule.

4. Reaction of fructose with HCN followed by hydrolysis produces an acid which on reduction with red phosphorus and hydriodic acid gives 2-methylhexanoic acid, indicating that the carbonyl group is in the form of a ketonic group which is adjacent to one of the terminal carbon atoms. Thus, fructose is a 2-ketohexose, and has the following constitution which is a pentahydroxy-2-hexanone.



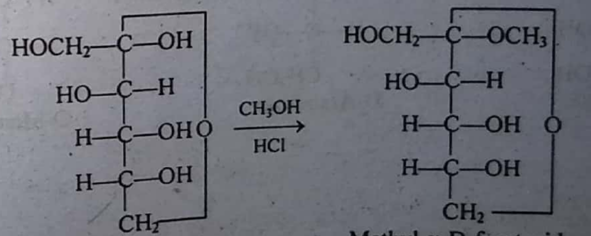
$$\begin{array}{c} CH_2OH \\ | \\ CO \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

(b) 1. D-Fructose exists in two isomeric forms which undergo mutarotation.

2. D-Fructose pentaacetate does not form an oxime with hydroxylamine, indicating the absence of the ketonic group in this derivative.

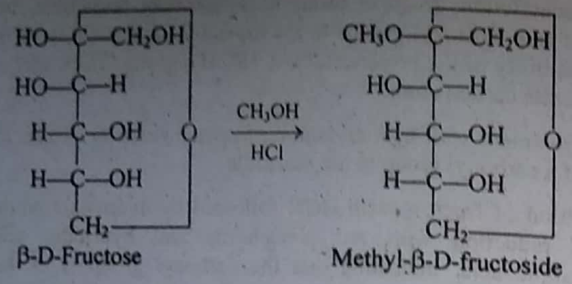
3. Reaction of D-fructose with methanol in the presence of HCl produces two isomeric ketals, methyl D-fructosides, each containing only one —CH_3 group. The fructosides do not undergo mutarotation.

These observations can be explained if D-fructose is considered to have a cyclic structure that results from an intramolecular addition of a hydroxyl group to the carbonyl group, forming a hemiacetal. The formation of the cyclic hemiacetal involves the creation of a new chiral centre at C-2, giving rise to two cyclic isomers of D-fructose, which lead to two methyl D-fructosides, as shown below:



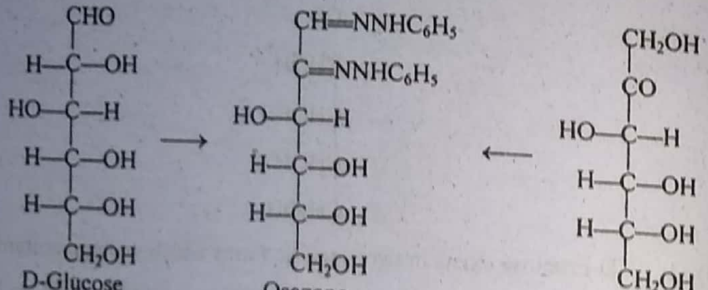
α-D-Fructose

Methyl α-D-fructoside



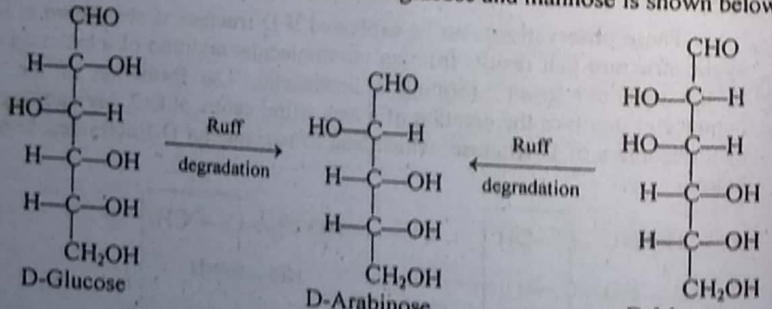
β-D-Fructose Methyl-β-D-fructoside

14\. Natural fructose and natural glucose both belong to the D family and both have the same configuration at C-3, C-4, C-5 and C-6. This is established from the fact that with phenylhydrazine both form the same osazone which involves C-1 and C-2 only, as shown below:



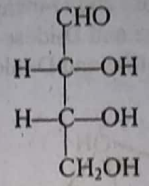
D-Glucose Osazone D-Fructose

15\. There are four pairs of D-aldohexoses each member of which on Ruff degradation leads to the same aldopentose. These are: (1) allose and altrose, (2) glucose and mannose, (3) gulose and idose, and (4) galactose and talose. The formation of the same aldopentose from glucose and mannose is shown below:

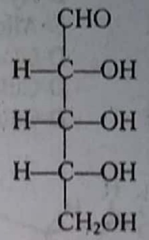


D-Glucose D-Arabinose D-Mannose

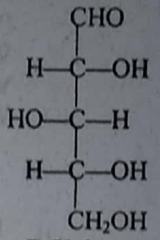
16\. The following D-aldoses will give *meso*-aldaric acids on oxidation by nitric acid.



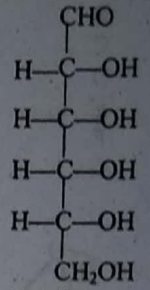
D-Erythrose



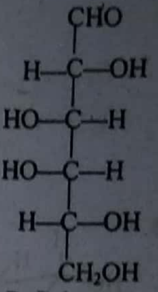
D-Ribose



D-Xylose

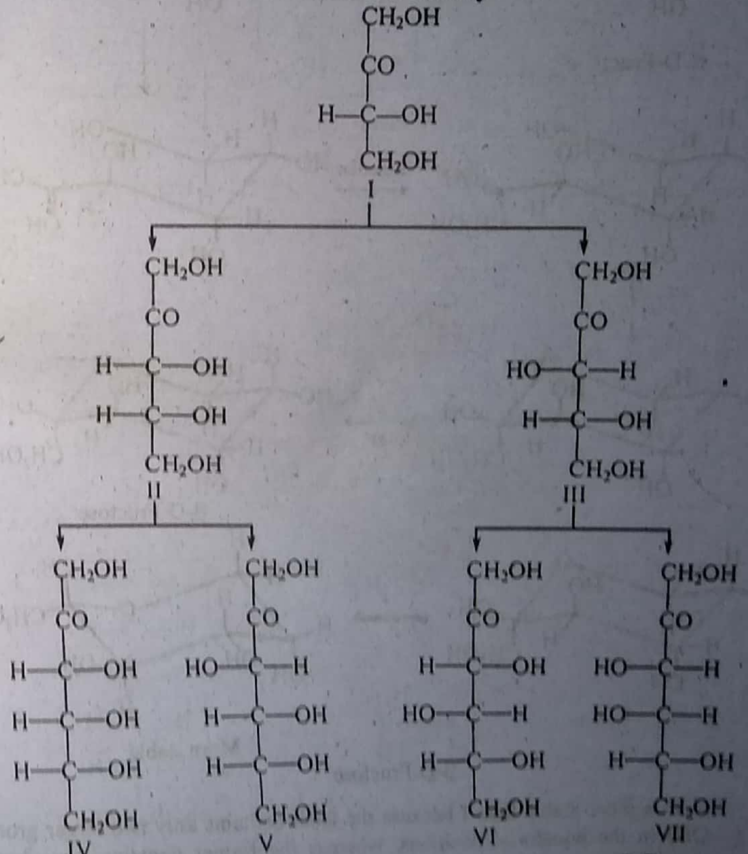


D-Allose



D-Galactose

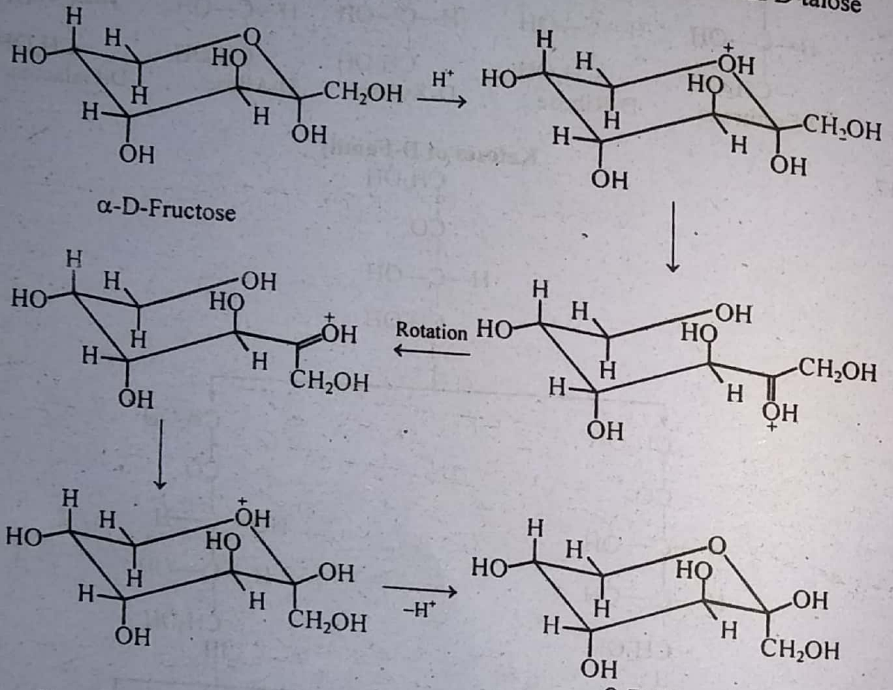
17\. **Ketoses of D-Family**



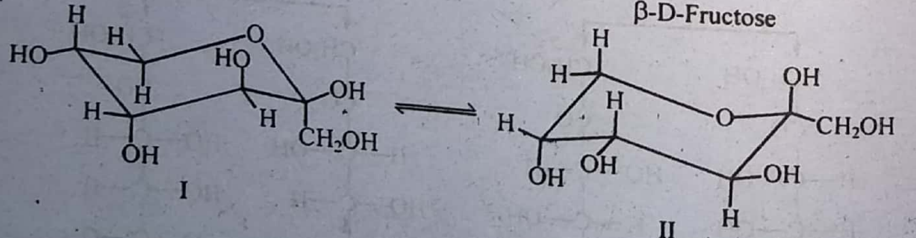
D-Psicose D-Fructose D-Sorbose D-Tagatose

Group giving identical osazone	Ketose	Aldoses
A	I	D-Erythrose and D-threose
B	II	D-Ribose and D-arabinose
C	III	D-Xylose and D-lyxose
D	IV	D-Allose and D-altrose
E	V	D-Glucose and D-mannose
F	VI	D-Gulose and D-idose
G	VII	D-Galactose and D-talose

18.

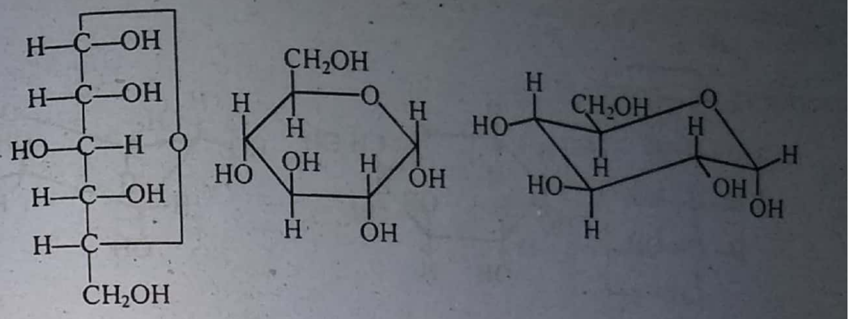


19.

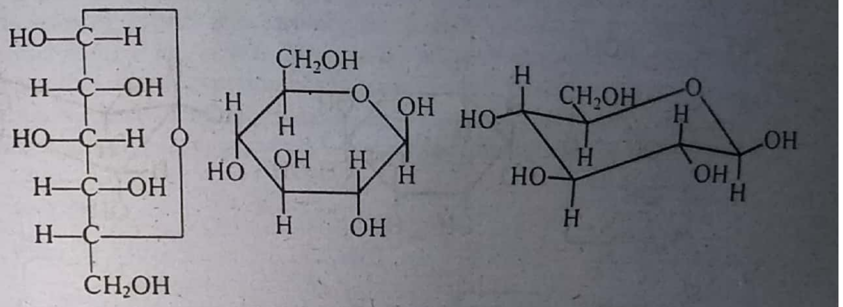


II is more stable than I because the latter contains only two larger groups (—OH) in the equatorial positions, whereas the former contains three larger groups, including —CH$_2$OH group, in the equatorial positions.

20. (a)



(b)



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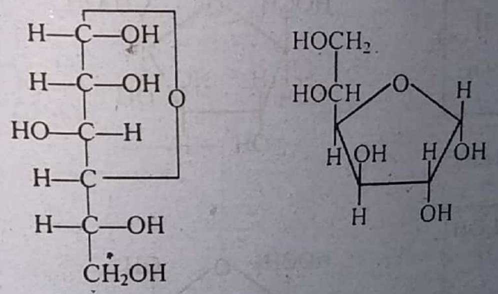

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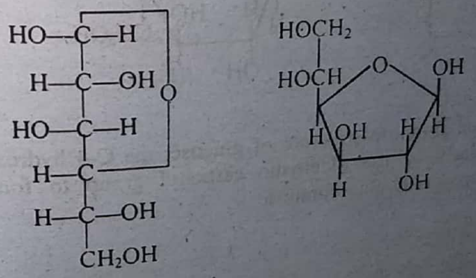

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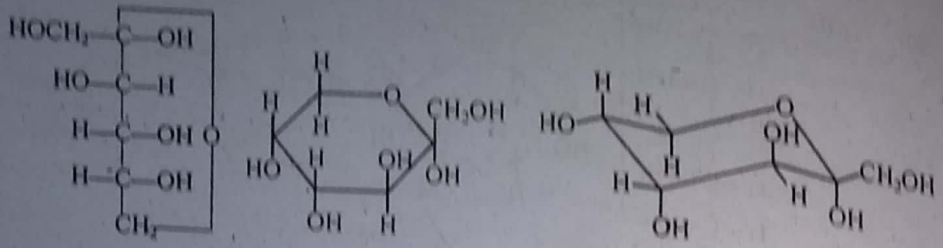

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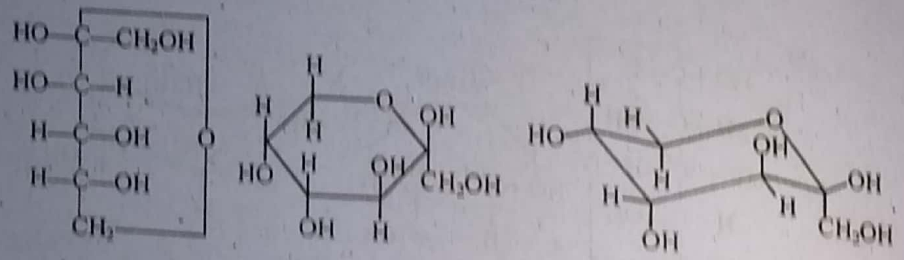

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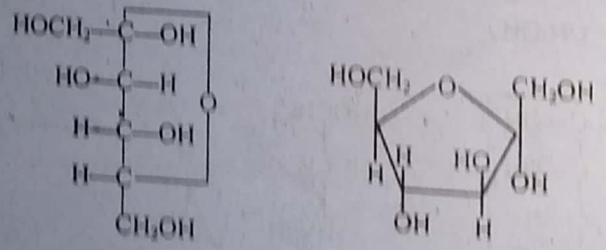
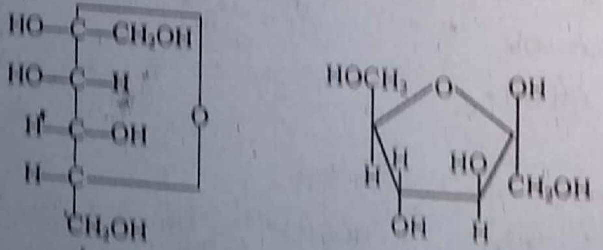
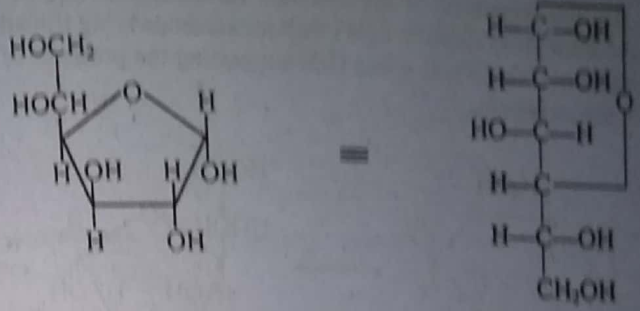


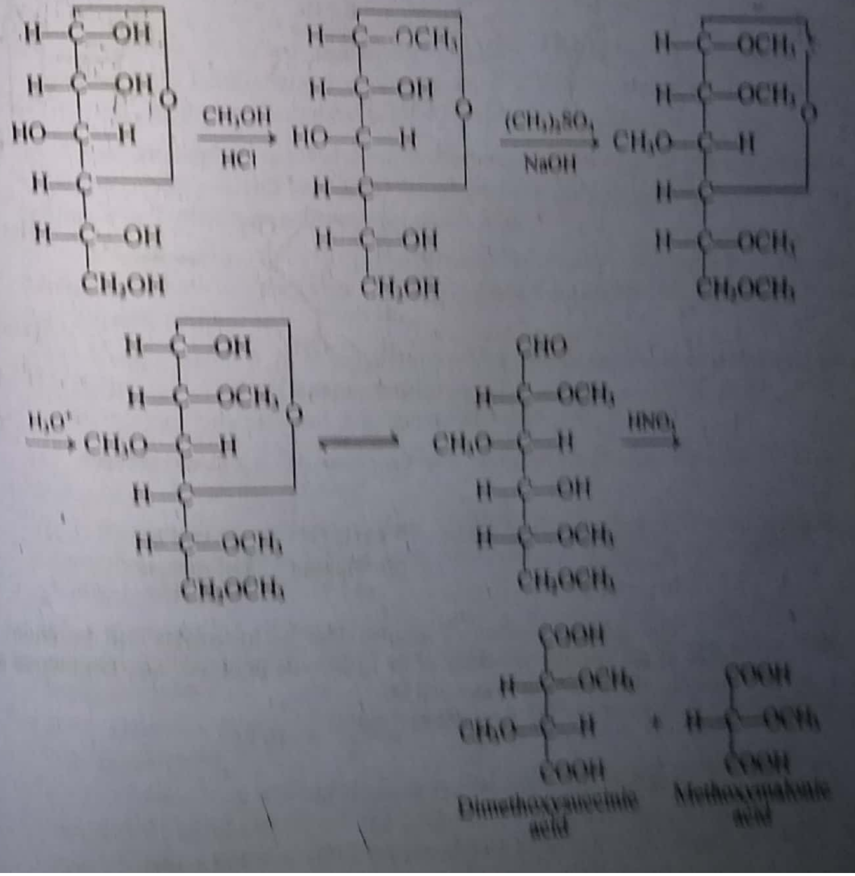
(h)



21. In the assumed furanose structure of glucose, the C-4 hydroxyl group is added intramolecularly to the aldehydic carbonyl group to form a cyclic hemiacetal, as shown in α-D-glucofuranose.

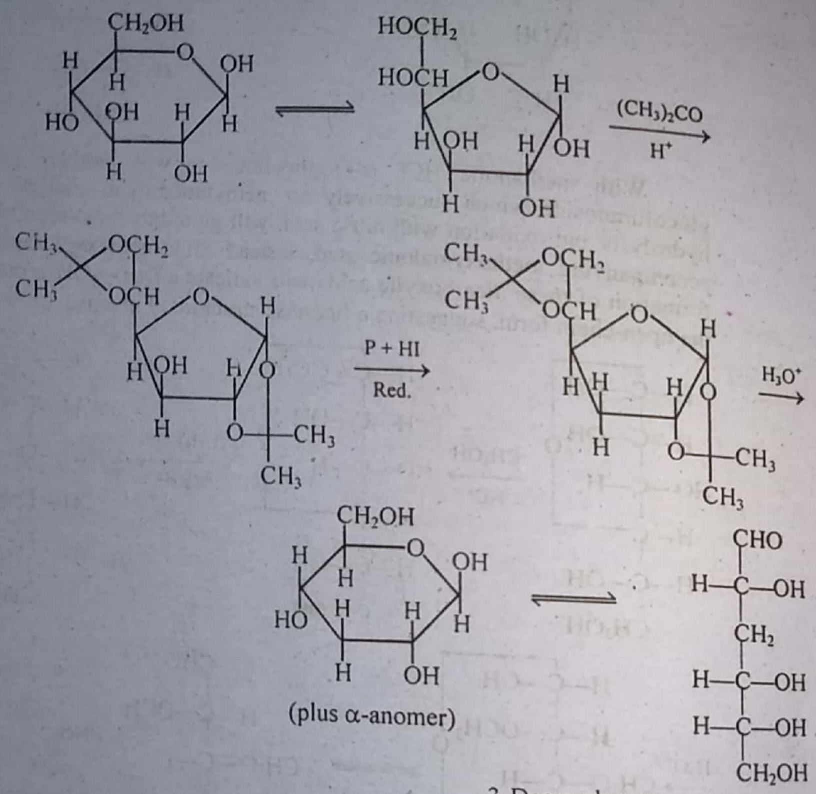


With methanolic HCl, α-D-glucofuranose will produce methyl α-D-glucofuranoside which successively on methylation with alkaline $(CH_3)_2SO_4$, hydrolysis and oxidation with nitric acid, will give dimethoxysuccinic acid with accompanying methoxymalonic acid, instead of trimethoxyglutaric acid. The formation of these dicarboxylic acids will indicate a free —OH group on C-4 in the open-chain form, suggesting a furanose structure of glucose.



Similar treatment of the assumed furanose structure of fructose will also produce dimethoxysuccinic acid (without accompanying trimethoxyglutaric acid) coming from C-2, C-3, C-4 and C-5, suggesting the presence of a five-membered ring in the molecule.

22.



3-Deoxyglucose

23.(a)

$$\underset{\substack{\text{Sucrose}\\ [\alpha], +66.5^\circ}}{C_{12}H_{22}O_{11}} \xrightarrow{H_3O^+} \underset{\substack{\text{D-Glucose}\\ +52.7^\circ}}{C_6H_{12}O_6} + \underset{\substack{\text{D-Fructose}\\ -92.4^\circ}}{C_6H_{12}O_6}$$

The specific rotation of sucrose after its hydrolysis will be equal to the mean of the specific rotations of its hydrolysis products, i.e., D-glucose and D-fructose, which will be thus equal to:

$$\frac{52.7+(-92.4)}{2} = \frac{-39.7}{2} = -19.85^\circ$$

(b) Let the percentage of α-D-mannose be $= x$
and the percentage of β-D-mannose be $= 100 - x$
Then $x \times 29.3 + (100 - x) \times (-17.0) = 100 \times 14.2$

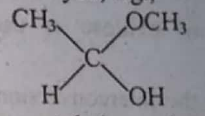
$$\begin{aligned} \text{or} \quad 29.3x - 1700 + 17.0x &= 1420 \\ 29.3x + 17.0x &= 1420 + 1700 \\ 46.3x &= 3120 \\ x &= \frac{3120}{46.3} = 67.38 \end{aligned}$$

So, α-D-mannose $= 67.38\%$
and β-D-mannose $= 100 - 67.38 = 32.62\%$

24. (a) **Aldopentose.** A five-carbon monosaccharide containing an aldehydic group, e.g., arabinose.

(b) **Ketohexose.** A six-carbon monosaccharide containing a keto group, e.g., fructose.

(c) **Hemiacetal.** It is an α-hydroxy ether formed by the addition of an alcohol to the carbonyl group of an aldehyde, e.g.,



(d) **Glycoside.** It is an acetal (or a ketal) formed by the reaction of a hemiacetal (or a hemiketal) of a monosaccharide with an alcohol in the presence of HCl, e.g., methyl-α-D-glucoside or methyl-α-D-fructoside.

(e) **Aldonic acid.** It is a polyhydroxycarboxylic acid obtained by the selective oxidation of the —CHO group of an aldose by a mild oxidizing agent, such as Fehling's or Tollen's reagent, e.g., gluconic acid.

(f) **Aldaric acid.** It is a polyhydroxydicarboxylic acid obtained by the oxidation of both —CHO and —CH_2OH groups of an aldose with nitric acid, e.g., glucaric acid.

(g) **Uronic acid.** It is a polyhydroxyaldehydocarboxylic acid in which the —CH_2OH group of an aldose has been oxidized to —COOH group, while —CHO group remains intact, e.g., glucuronic acid.

(h) **Alditol.** It is a polyhydroxy alcohol obtained by the reduction of aldehydic group of an aldose, e.g., glucitol.

(i) **Pyranose.** A monosaccharide with a six-membered cyclic structure containing five carbon atoms and one oxygen atom in the ring, e.g., glucopyranose.

(j) **Furanose.** A monosaccharide with a five-membered cyclic structure containing four carbon atoms and one oxygen atom in the ring, e.g., fructofuranose.

(k) **Osazone.** It is a 1,2-diphenylhydrazone derivative of a monosaccharide, e.g., glucosazone.

(l) **Osone.** It is a dicarbonyl compound obtained by the hydrolysis of an osazone with HCl, resulting in the removal of both phenylhydrazino groups.

(m) **Epimer.** A stereoisomer obtained by the inversion of configuration at one chiral carbon of a molecule having more than one chiral carbon atom, e.g., D-glucose and D-mannose are epimers.

(n) **Anomer.** Two epimers of a monosaccharide that differ in configuration at the hemiacetal carbon, e.g., α-D-glucose and β-D-glucose are anomers.

(o) **Glycone.** A glycoside contains a glycosidic linkage (ether linkage) usually between a carbohydrate and a non-carbohydrate molecules. The carbohydrate portion of a glycoside is called glycone.

(p) **Aglycone.** The non-carbohydrate portion of a glycoside is called aglycone. In disaccharides, the carbohydrate molecule that provides anomeric carbon for the glycosidic linkage is called glycone and the molecule that provides carbon other than anomeric carbon is called aglycone.

(q) **Dextrose.** The term dextrose is used for D-glucose because it is dextrorotatory.

(r) **Levulose.** The term levulose is used for D-fructose because it is levorotatory.

(s) **Mutarotation.** It is the interconversion of the anomers of a sugar in aq. solution to give an equilibrium mixture, e.g., the sp. rotation shown by D-glucose with a value in between the values of the sp. rotations of α- and β-D-glucose is the result of mutarotation.

(t) **Oligosaccharide.** It is a carbohydrate that on hydrolysis yields monosaccharide units numbering between 2 to 10.

(u) **Reducing sugar.** A sugar that contains a hemiacetal or a hemiketal group and therefore can reduce mild oxidizing agents such as Fehling's or Tollen's reagent, is known as a reducing sugar, e.g., glucose, lactose, etc.

(v) **Non-reducing sugar.** A sugar that cannot reduce the above-mentioned oxidizing agents, is called non-reducing sugar, e.g., sucrose.

(w) **Invert sugar.** The mixture of glucose and fructose obtained after the hydrolysis of sucrose is called invert sugar, because the sp. rotation is inverted after hydrolysis.

(x) **Animal starch.** Glycogen is called animal starch because it is obtained from liver and muscles of animals, and structurally it resembles starch.

25. *(a)* D-Glucose is oxidized by bromine water and thus decolorises it, whereas D-fructose does not react with bromine water.

(b) On oxidation with HNO_3, D-glucose gives an aldaric acid which is optically active, whereas the aldaric acid obtained from D-galactose is not optically active.

(c) Interchange of the end groups of D-glucose would yield a different product, whereas the interchange of the end groups of D-mannose would yield a product which is not different from the starting compound.

(d) D-Glucose forms an osazone with phenylhydrazine, whereas D-glucitol does not react with this reagent.

(e) α-D-Glucose reduces Fehling's or Tollen's reagent, whereas methyl α-D-glucoside does not.

(f) Maltose reduces Fehling's or Tollen's reagent, whereas sucrose does not.

26. **Reducing carbohydrates**

Glucose, fructose, maltose and lactose.

Non-reducing carbohydrates

Sucrose and methyl glucoside.

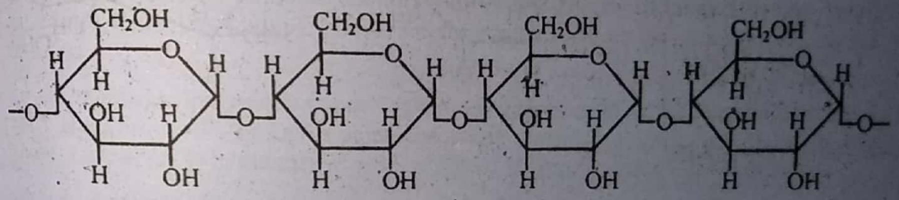
In sucrose, D-glucose and D-fructose are linked by an acetal-ketal linkage involving the anomeric carbons of both the monosaccharide units. In this way sucrose does not contain a free aldehydic or ketonic group, and is thus non-reducing.

Similarly, methyl glucoside does not contain an open-chain structure to have a free aldehydic group. It is therefore also non-reducing.

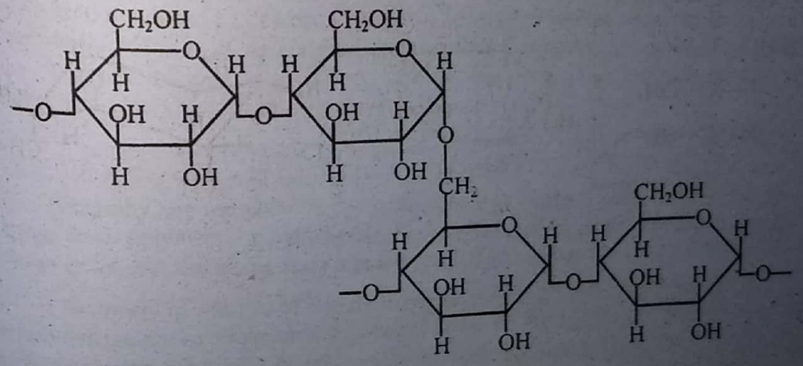
27. **Structure of starch**

Starch from any source contains two structurally different polysaccharides, i.e., amylose and amylopectin, both entirely consisting of glucose units.

Amylose consists of about 1000 D-glucopyranose units which are connected to each other linearly by α-glycosidic linkage, involving C-1 of one D-glucose unit and C-4 of the next one, as in maltose.

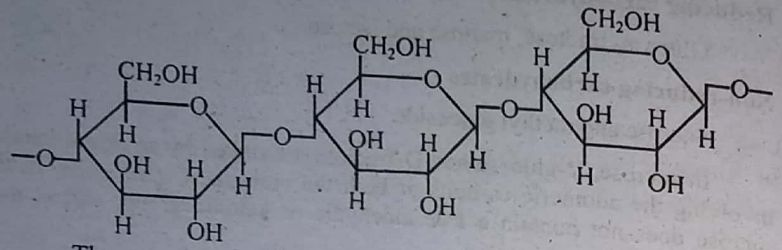


Amylopectin consists of thousands of D-glucose units in amylose-like chains which are branched by 1,6-linkages at intervals of 20–25 glucose units.



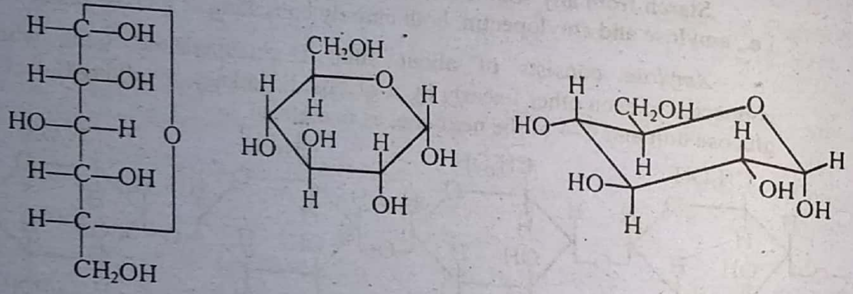
Structure of cellulose

Cellulose consists of 10,000–15,000 D-glucose units linked linearly through β-glycosidic bonds between the anomeric carbon of one unit and C-4 of the next.

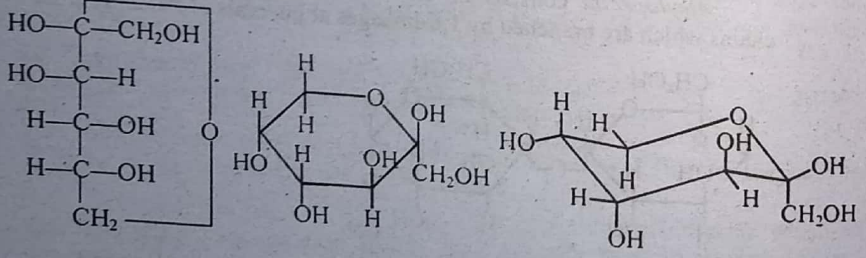


28. The source of invert sugar is sucrose which on hydrolysis yields an equimolar mixture of D-(+)-glucose and D-(–)-fructose, known as invert sugar. In nature, invert sugar is present in honey where sucrose is hydrolysed by an enzyme 'invertase' which is supplied by bees.

α-D-(+)-Glucopyranose



β-D-(–)-Fructopyranose



Chapter 14

Synthetic Polymers

CHAPTER'S SUMMARY

Polymers are the macromolecules made up of many repeating sub-units, calle *monomers*, which are joined together in a regular way in a process known a *polymerization*. There are two general types of polymerizations: (i) additio polymerization and (ii) condensation polymerization.

Addition Polymerization

Addition polymerization involves a series of reactions each of which consumes a reactive species and produces another similar but larger species. It occurs between molecules containing multiple bonds, and the reactive species can be a cation, a radical or an anion.

Cationic polymerization. Cationic polymerization is initiated by strong acids such as sulfuric acid, or Lewis acids containing a small amount of water. The growing chain is a cation, as in the case of acid-catalysed polymerization of isobutylene.

Radical polymerization. Polymerization of a large number of compounds having carbon-carbon double bonds has been carried out in the presence of a *radical initiator*, such as a peroxide. A peroxide is cleaved homolytically to provide a radical that could add to a molecule of alkene giving rise to another radical which then starts a chain of step-wise addition of radicals to alkene molecules until the reaction is terminated either by combination or by disproportionation. A typical example is the radical polymerization of ethylene to give polyethylene.

$$nCH_2{=}CH_2 \longrightarrow -(CH_2{-}CH_2)_n-$$

Polyethylene (or polyethene) is flexible and can be molded to any shape after heating. Such polymers are called *plastics*. Radical polymerization results not only in a linear polymer but can also give rise to a cross-linked polymer.

A variety of plastics of widely different characteristics and uses can be made by the polymerization of substituted ethylenes. Some of the important ethylenic monomers which are commonly used in polymerization are: propylene ($CH_2{=}CHCH_3$) used for polypropylene, vinyl chloride ($CH_2{=}CHCl$) for poly(vinyl chloride), commonly known as PVC, tetrafluoroethylene ($F_2C{=}CF_2$) for polytetrafluoroethylene which is marketed as Teflon, styrene ($CH_2{=}CHC_6H_5$) for polystyrene, acrylonitrile ($CH_2{=}CHCN$) for polyacrylonitrile (Orlon or Acrilon) and methyl methacrylate, $CH_2{=}C(CH_3)COOCH_3$, for poly(methyl methacrylate) which is marketed under the names of Lucite, Plexiglas and Perspex, as a glass substitute. In general, these polymers are used to make wool substitutes (carpets, blankets, etc.), cloths, leather substitutes, rain-coats, shower curtains, pipes, furniture, utensils, automobile tires, packaging materials, garden hoses, sheets and a variety of molded articles.

Anionic polymerization. Anionic polymerization of alkenes takes place only in the presence of an extremely powerful base, such as $NaNH_2$ in liq. NH_3 or $n\text{-}C_4H_9Li$, and the reaction continues until all the monomer is consumed. The resulting polymer has a much longer chain and is more rigid than the polymer formed by radical polymerization.

Coordination polymerization. Polymerization of ethylene can also be brought about by a catalyst known as Ziegler-Natta catalyst ($C_2H_5TiCl_4$) which coordinates with the π bond of ethylene to start the reaction. Polyethylene formed in this way is essentially a linear molecule, and is much stronger than the polymer formed by the radical polymerization.

Another advantage of the Ziegler-Natta catalyst is that it permits stereochemical control of the polymerization reaction. For example, the polymerization of propylene can be brought about so as to have isotactic, syndiotactic or atactic arrangement of the methyl groups on the zigzag backbone of the polypropylene molecule by the proper choice of experimental conditions.

Diene polymers. Butadiene and other conjugated dienes can also undergo radical polymerization. The diene polymers can be linear as well as cross-linked to give a complex mixture of 1,2- and 1,4-addition products.

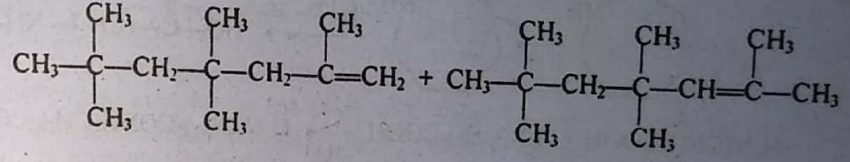
Natural rubber is a polymer of isoprene (2-methyl-1,3-butadiene). Polyisoprene can also be made artificially by the radical polymerization of isoprene. Polychloroprene made by the radical polymerization of chloroprene (2-chlorobutadiene) is another synthetic rubber called *neoprene* which is commonly used for electrical insulations, conveyer belts, hoses and weather balloons. Styrene-butadiene rubber (SBR), a copolymer of styrene and butadiene, is produced in largest quantity and is mostly used in tires.

Condensation Polymerization

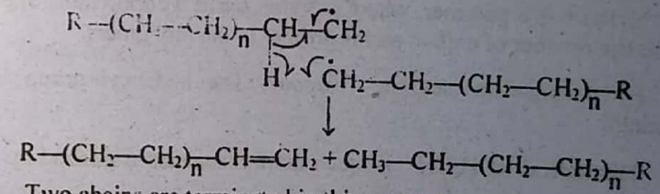
Condensation polymerization involves a series of reactions in which monomeric sub-units are joined together through intermolecular elimination of small molecules such as water or an alcohol. For example, a dicarboxylic acid reacts with a diol to form an ester with the elimination of water, but each moiety of the simple ester still contains a functional group on each end of the molecule to continue the reaction. The most important condensation polymers are polyesters, polyamides, polyurethanes and phenol-formaldehyde resins.

Poly(ethylene terephthalate) obtained by the condensation of dimethyl terephthalate and ethylene glycol, is one of the most important polyester which can be melt-spun into fibers to produce *Dacron* or *Terylene*. Condensation of a dicarboxylic acid, e.g., adipic acid, and a diamine, e.g., 1,6-hexanediamine, yields a polyamide, known as *Nylon 6,6*, with properties similar to those of silk which is a naturally occurring polyamide. Polyurethanes are made by allowing a diisocyanate to react with a diol in the presence of a calculated amount of water. A light-weight spongy material called *polyurethane foam* is obtained which is used for building-insulations and paddings and in pillows. A highly cross-linked space-network polymer, phenol-formaldehyde resin, is obtained when phenol is heated with formaldehyde in the presence of a dilute acid or an alkali. The polymer thus formed is known as *Bakelite*, and is used for making electric shoes, plugs, etc.

ANSWERS TO EXERCISES

1. 

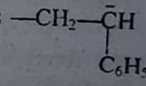
2. Isobutylene on cationic dimerization yields two isomeric diisobutylenes both of which on catalytic hydrogenation yield isooctane.

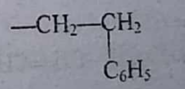
3. 

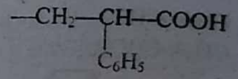
Two chains are terminated in this process.

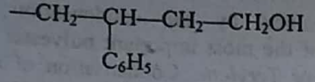
4. The corresponding monomer, vinyl alcohol (an enol), readily tautomerizes to its keto form, acetaldehyde, which has no carbon-carbon double bond that is required for polymerization.

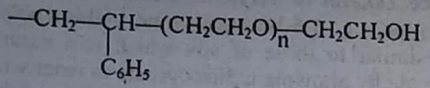
$$\underset{0.1\%}{CH_2{=}CHOH} \rightleftharpoons \underset{99.9\%}{CH_3CHO}$$

5. The structure of the living polystyrene is  $-CH_2-\underset{C_6H_5}{\underset{|}{\bar{C}H}}$ and the products are:

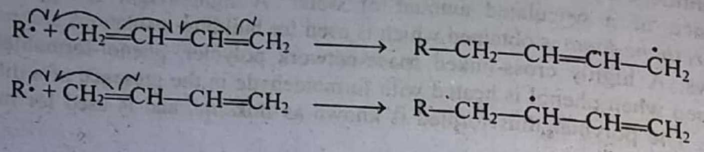
(a)  $-CH_2-\underset{C_6H_5}{\underset{|}{CH_2}}$

(b)  $-CH_2-\underset{C_6H_5}{\underset{|}{CH}}-COOH$

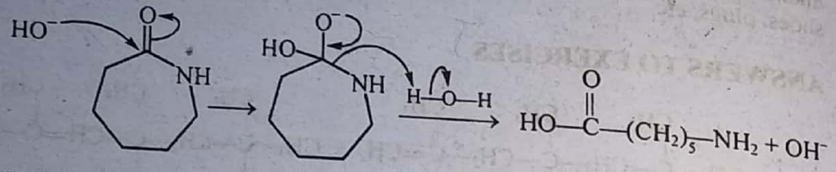
(c) 
$-CH_2-\underset{C_6H_5}{CH}-CH_2-CH_2OH$

(d) 
$-CH_2-\underset{C_6H_5}{CH}-(CH_2CH_2O)_n-CH_2CH_2OH$

6.


$R^{\cdot} + CH_2=CH-CH=CH_2 \longrightarrow R-CH_2-CH=CH-\dot{C}H_2$
$R^{\cdot} + CH_2=CH-CH=CH_2 \longrightarrow R-CH_2-\dot{C}H-CH=CH_2$

7.



$$H_2N(CH_2)_5COOH + H_2N(CH_2)_5COOH \xrightarrow[-H_2O]{} H_2N(CH_2)_5CONH(CH_2)_5COOH \xrightarrow{H_2N(CH_2)_5COOH} \text{etc.}$$

It is the condensation type of polymerization.

8. Nylon 6 is a polymer, whereas Nylon 6,6 is a copolymer. The numbers '6' signify the number of carbon atoms present in the monomers.

9. For mechanism, see the *Textbook*. The hydroxyl group is ortho/para directing.

10. (a) The radical $RCH_2\underset{C_6H_5}{\dot{C}H}$ is much more resonance stabilized by the attached phenyl group than the radical $R\underset{C_6H_5}{C}H\dot{C}H_2$.

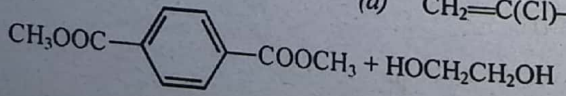
(b) Ethylene would involve the formation of a less favourable primary carbocation as an intermediate.

(c) The polymer obtained from isobutylene has no chiral carbon in the molecule.

(d) *p*-Cresol forms a linear phenol-formaldehyde polymer because its para position is not available for cross-linking.

11. (a) $CH_2=CHCl$ (b) $CF_2=CF_2$

(c) $CH_2=CHCN$ (d) $CH_2=C(Cl)-CH=CH_2$

(e) 
$CH_3OOC-C_6H_4-COOCH_3 + HOCH_2CH_2OH$

(f) $H_2NCH_2CH_2CH_2CH_2CH_2COOH$

12. (a) **Monomer** is the sub-unit from which a polymer is formed. **Polymer** is the substance formed when many sub-units are joined together in a regular way.

(b) **Thermoplastic** is a substance consisting of linear molecules, which on heating becomes soft and can be molded; on cooling it becomes hard again. Heating and cooling do no affect its properties. **Thermosetting plastic** has a three-dimensional network and can be heat-treated only once before setting; further heating will decompose it.

(c) **Polymer** is a substance formed when many molecules of the same monomer are joined together in a regular way. **Copolymer** is a substance formed by the polymerization between two or more kinds of monomeric sub-units.

(d) **Addition polymerization** is the process that involves a series of reactions each of which consumes a reactive species and produces another similar but larger species. It occurs between molecules containing multiple bonds. **Condensation polymerization** is the process that involves a series of reactions in which monomeric sub-units are joined together through intermolecular elimination of small molecules, such as water or an alcohol.

(e) **Linear polymer** is a substance that is formed when the monomeric sub-units are attached to each other in an end-to-end way. **Cross-linked polymer** is a substance that is formed when the polymeric chains are also interconnected through cross-links to yield a complex space-network.

(f) **Isotactic** polypropylene has all the methyl groups on the same side of the zigzag carbon chain. **Syndiotactic** polypropylene has the methyl groups alternating regularly on opposite sides of the chain. **Atactic** polypropylene has the methyl groups in a random orientation.

13. (a) **Elastomer** is a synthetic polymer that possesses elasticity like rubber, e.g., styrene-butadiene rubber.

(b) **Radical initiator** is a substance that initiates a radical reaction, e.g., a peroxide.

(c) **Plasticizer** is a substance that when added to an otherwise hard polymer, during its formulation, makes the polymer soft, e.g., *bis*-2-ethylhexyl phthalate.

(d) **Living polymer** is the reactive species obtained when the polymerization reaction stops because the whole of the monomer has been consumed. If more monomer is added, the polymer continues to grow, e.g., anionic polyethylene.

(e) **Latex** is a liquid suspension obtained from the rubber tree, a tropical plant.

(f) **Vulcanization** is a process in which the natural rubber is heated with sulfur to make the gummy rubber material harder and stronger. Sulfur forms cross-links between different polymer chains.

Answers to the Objective Questions

Chapter 1. The Nature of Covalent Bond

A

01. Where there is a probability of finding an electron
02. Molecular orbital
03. Hybrid orbital
04. Hybrid orbital
05. Principal quantum number
06. Azimuthal quantum number
07. Magnetic quantum number
08. Four
09. Eighteen
10. The two electrons in the same atomic orbital must have the same values for all the four quantum numbers.
11. Bonding orbitals
12. Hybrid orbital
13. H_2O
14. NH_3
15. CCl_4
16. BF_3
17. (i) Tetrahedral (ii) Unhybridized (iii) Tetrahedral (iv) Trigonal (v) Tetrahedral (vi) Digonal
18. One sigma and one pi bonds
19. Hybrid orbital
20. $^{-}CH_3$
21. F
22. C—N
23. N—Cl
24. Sigma bonds
25. Sigma bonds
26. Temperature
27. H_2O
28. *p*-Xylene
29. $CH_2{=}C{=}CH_2$
30. $CH_2{=}CH{-}CH{=}CH_2$

B

01. is not
02. the same
03. not possible
04. spherical
05. are
06. overlapping
07. not equal
08. an atomic
09. higher
10. greater
11. weaker
12. increases
13. decreases
14. the same
15. different from
16. the same
17. increases
18. different
19. higher
20. different
21. lower
22. higher
23. larger
24. higher
25. bond dissociation energy

C

01. covalent
02. nucleus
03. electrons
04. nucleus
05. probability
06. degenerate
07. degenerate
08. spin
09. Bohr radius
10. zero
11. vacant
12. antibonding
13. nonbonding
14. diatomic
15. Fluorine

D

01. True
02. False
03. True
04. False
05. True
06. False
07. True
08. True
09. False
10. True
11. True
12. False
13. False
14. True
15. False
16. False
17. False
18. False
19. False
20. False

Chapter 2. Basic Concepts in Organic Chemistry

A
01. 1.39 Å
02. Inductive effect
03. Both of these
04. All of these
05. Tautomerism
06. Acetylacetone

B
01. localized
02. electrons
03. less
04. experiments
05. dimethylamine
06. 1.46 Å
07. lower
08. is not

C
01. three
02. resonance hybrid
03. different
04. hyperconjugation
05. less

D
01. True
02. False
03. False
04. False
05. False
06. True
07. True
08. True

Chapter 3. Spectroscopy

A
01. Both of these
02. $\sigma \to \sigma^*$
03. Acetone
04. Both of these
05. Triple bond
06. $1900\text{–}1600\ cm^{-1}$
07. $CH_2{=}CH{-}CH{=}CH{-}CH_3$
08. Ethanol
09. Chloroform

B
01. different from
02. inversely
03. directly
04. directly
05. more
06. will
07. less
08. less
09. more

C
01. wave-like
02. infrared
03. visible
04. ultraviolet
05. conjugation
06. Beer-Lambert
07. stretching
08. infrared
09. solid
10. triple
11. 3000
12. dipole moment

D
01. True
02. False
03. False
04. False
05. True
06. True
07. False
08. False

Chapter 4. Saturated Hydrocarbons

A
01. Saturated hydrocarbons
02. Both of these
03. Isopropyl group
04. Black

05. Primary alkyl halides
06. Three
07. Grignard method
08. van der Waals forces
09. Two
10. Isopentane
11. Heterocyclic componds
12. All of these
13. One
14. 1-Methylpentane
15. Cracking

B
01. also contains
02. combustion
03. higher
04. lower
05. hydrocarbons
06. hydrocarbons
07. more
08. less
09. smaller
10. possible
11. the same

C
01. molecular formula
02. Methane
03. catalytic
04. separation
05. paraffins
06. pyrolysis
07. cycloalkanes
08. cycloalkanes
09. cycloaddition
10. planar
11. Methane

D
01. False
02. False
03. False
04. False
05. True
06. True
07. True
08. True
09. True
10. False
11. True
12. True

Chapter 5. Unsaturated Hydrocarbons

A
01. Double bond
02. Cumulated
03. Butylene
04. Hofmann reaction
05. Neopentyl chloride
06. Both of these
07. Hydroxylation
08. Hydrocarbons
09. One sigma and two pi bonds

B
01. anti
02. cis
03. Saytzeff
04. evolution
05. two
06. cis
07. difficult
08. less
09. slower

C
01. cumulated
02. elimination
03. pyrolytic
04. Wittig
05. electrophilic
06. surface
07. reverse
08. Ozone
09. oxyacetylene
10. calcium carbide
11. cis
12. terminal

D
01. True
02. True
03. False
04. True
05. True
06. False
07. False
08. False
09. True
10. True
11. True
12. True
13. False
14. True
15. False
16. True

Chapter 6. Stereoisomerism

A

01. Infinite
02. Racemization
03. Three
04. 2-Butene
05. Person
06. Fork
07. $CH_3CH{=}C{=}C(CH_3)_2$
08. Both hands
09. It has a plane of symmetry

B

01. are
02. cannot
03. configurational
04. are
05. more
06. cannot
07. chair
08. optical rotation
09. can also

C

01. connectivity
02. two-dimensional
03. chair
04. cyclohexane
05. monochromatic
06. polarimeter
07. chirality
08. similar
09. configuration

D

01. False
02. False
03. True
04. True
05. False
06. False
07. False
08. False
09. True
10. True
11. True
12. False

Chapter 7. Alkyl Halides

A

01. Alkyl fluoride
02. Neopentane
03. Ozonolysis
04. Racemization
05. Inversion of configuration
06. Pseudo-first-order
07. None of these
08. Alkylmagnesium fluoride
09. Formamide
10. Tetrahydrofuran
11. $(CH_3CH_2)_3N$

B

01. have
02. slowest
03. poorest
04. two-step
05. more
06. more
07. higher

C

01. ozone layer
02. monohaloalkanes
03. free-radical
04. iodide
05. alcoholic
06. substrates
07. carbocation
08. inversion
09. seldom
10. nucleophile
11. polarity
12. antiperiplanar
13. Grignard reagent
14. catalysed
15. retarded

D

01. True
02. True
03. False
04. True
05. True
06. False
07. False
08. True
09. True
10. True
11. True
12. False

Chapter 8. Aromatic Hydrocarbons

A

01. $CH_3{-}C{\equiv}C{-}C{\equiv}C{-}CH_3$
02. Six
03. None of these
04. Cyclic polyene
05. Both of these
06. *pri*-Alkylbenzene
07. Aryl chloride
08. Both of these
09. *tert*-Butylbenzene
10. Anthracene
11. The position 1 is more reactive than the position 2.

B

01. higher
02. four
03. nonplanar
04. shows
05. almost the same
06. slower
07. more
08. are not
09. more
10. less
11. more
12. towards
13. the rates of their formation

C

01. aromatic
02. aromatic
03. benzene
04. ring
05. not
06. three
07. resonance energy
08. annulenes
09. even
10. 4n + 2
11. nonaromatic
12. acidic
13. planar
14. isomer
15. dipolar
16. arenes
17. smoky
18. acylation
19. resistant
20. coal tar
21. 900–700

D

01. True
02. False
03. False
04. True
05. True
06. True
07. True
08. True
09. False
10. True
11. True
12. False

Chapter 9. Alcohols, Phenols and Ethers

A

01. $NaBH_4$
02. *tert*-Butyl alcohol
03. Both of these
04. Both of these
05. Glycerol
06. Oxidation of cumene
07. *o*-Nitrophenol
08. None of these
09. Hydroquinone
10. *o*-Cresol
11. Wood spirit

B

01. more
02. less
03. weaker
04. weaker
05. in the laboratory
06. stronger
07. stronger
08. higher

C

01. derivatives
02. sp^3
03. hydroxy
04. ethylene oxide
05. *t*-Butyl alcohol
06. base
07. methylating
08. Nitroglycerin
09. alcohols

10. thiols
11. ethanethiol
12. hydroxybenzene
13. phenols
14. oxidation
15. phenol
16. inert
17. Crown ethers
18. 18-crown-6
19. ethanol

D

01. True
02. True
03. True
04. True
05. False
06. True
07. False
08. False
09. False
10. True

Chapter 10. Aldehydes and Ketones

A

01. None of these
02. Acetone
03. Four
04. None of these
05. Formaldehyde
06. Diethyl ketone
07. Both of these
08. Aldol condensation

B

01. more
02. endothermic
03. more
04. the same as
05. can
06. do not undergo

C

01. formaldehyde
02. acetylene
03. formaldehyde
04. formalin
05. protect
06. carbonyl

D

01. True
02. True
03. True
04. False
05. True
06. True
07. False
08. False

Chapter 11. Carboxylic Acids and Their Derivatives

A

01. $NaHCO_3$
02. Acid chlorides
03. Adipic acid
04. Amides

B

01. without
02. the same
03. stronger
04. two
05. an irreversible
06. lower

C

01. aliphatic
02. higher
03. dry ice
04. complimentary
05. cyclic
06. addition, substitution
07. Lactones
08. saponification
09. liquid

D

01. True
02. True
03. False
04. True
05. False
06. True
07. False
08. False

Chapter 12. Organic Nitrogen Compounds

A

01. $(CH_3)_2NH$
02. Reductive amination
03. Gabriel synthesis
04. Both of these
05. Sulfonation
06. None of these

B

01. less
02. weaker
03. does not react
04. does not react
05. possible
06. aromatic
07. more
08. opposite to
09. less
10. does not undergo
11. are not

C

01. primary
02. aromatic
03. tertiary
04. stronger, weaker
05. an amine
06. acetylated
07. primary
08. Amino acids
09. proteins

D

01. False
02. False
03. False
04. False
05. False
06. True
07. False
08. True
09. False

Chapter 13. Carbohydrates

A

01. Sucrose
02. Ketone
03. Mannose
04. Maltose
05. Sucrose

B

01. fructose
02. cannot
03. dissimilar
04. does not reduce
05. the same as

C

01. polyhydroxy
02. D
03. D-(+)-Glucose
04. two
05. invert sugar
06. Glycogen

D

01. True
02. False
03. True
04. True
05. False
06. True

Chapter 14. Synthetic Polymers

A

01. SBR
02. Dacron
03. Terylene
04. Acrilon

B

01. does not undergo
02. longer
03. thermoplastic
04. is

C

01. multiple
02. copolymer
03. linear
04. coordination

D

01. False
02. True
03. False
04. False