CHAPTER 8

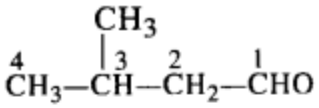
ALDEHYDES,KETONES & CARBOXYLI ACIDS

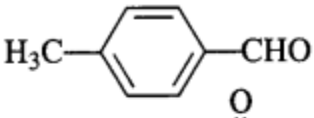
QUESTION AND ANSWERS

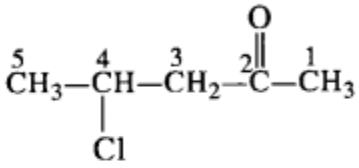
5MARKS

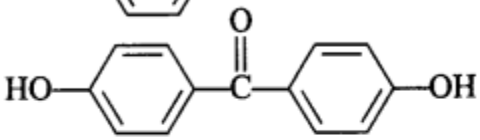
1. Draw the structures of the following compounds.
(i) 3-Methylbutanal
(ii) p-Methylbenzaldehyde
(iii) 4-Chloropentan-2-one
(iv) p, p'-Dihydroxybenzophenone
(v) p-Nitropropiophenone
(vi) 4-Methylpent-3-en-2-one.
(vii) 3-Bromo-4-phenylpentanoic acid
(viii) Hex-2-en-4-ynoic acid

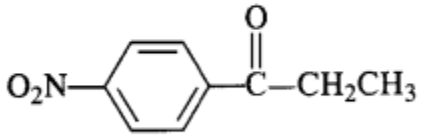
Ans:

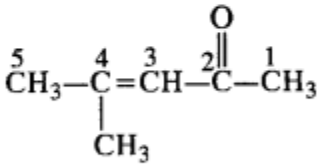
(i) 

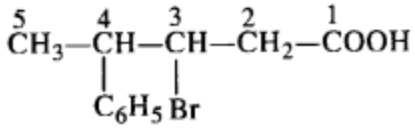
(ii) 

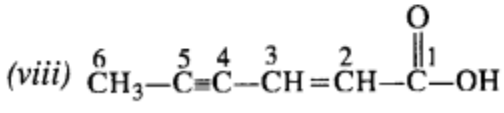
(iii) 

(iv) 

(v) 

(vi) 

(vii) 

(viii) 

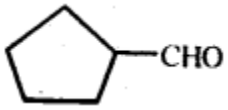
2. Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.

(i) $CH_3CO(CH_2)_4CH_3$

(ii) $CH_3CH_2CH\ BrCH_2CH(CH_3)CHO$

(iii) $CH_3(CH_2)_5CHO$

(iv) Ph—CH=CH—CHO

(v) 

(vi) *Ph*COPh

Ans:

	IUPAC name	Common name
(*i*)	Heptan-2-one	–
(*ii*)	4-Bromo-2-methylhexanal	γ-Bromo-α-methyl caproaldehyde
(*iii*)	Heptanal	–
(*iv*)	3-Phenylpropan-2en -1- al	β-Phenyl acrolein
(*v*)	cyclopentane carbaldehyde	–
(*vi*)	Diphenylmethanone	Benzophenone

3. Draw structures of the following derivatives:

(i) The 2,4-dinitrophenylhydrazone of benzaldehyde

(ii) Cydopropanone oxime

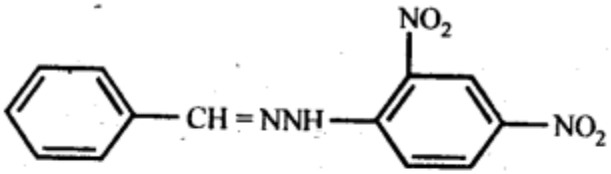
(iii) Acetaldehydedimethylacetal

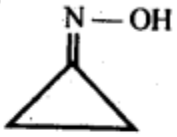
(iv) The semicarbazone of cyclobutanone

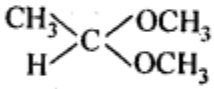
(v) The ethylene ketal of hexan-3-one

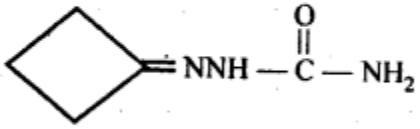
(vi) The methyl hemiacetal of formaldehyde

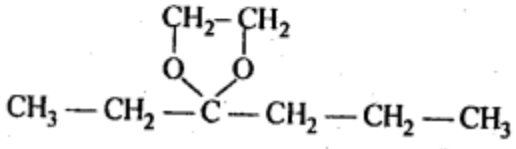
Ans:

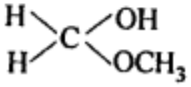
(*i*) 

(*ii*) 

(*iii*) 

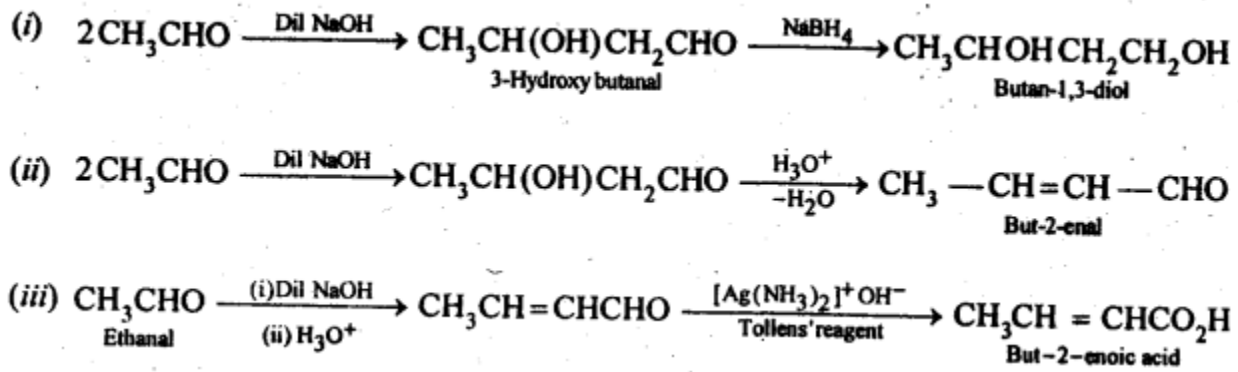
(*iv*) 

(*v*) 

(*vi*) 

4. How will you convert ethanal into the following compounds?
(i) Butane-1,3-diol
(ii) But-2-enal
(iii) But-2-enoic acid

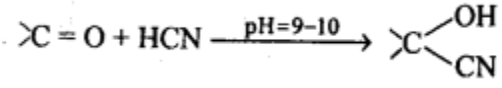
Ans:



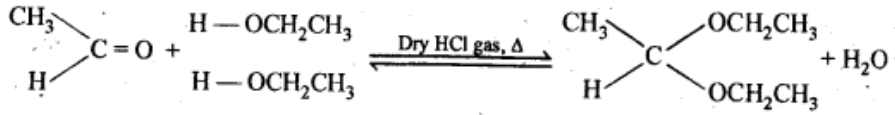
7MARKS

1. What is meant by the following terms? Give an example of the reaction in each case.
(i) Cyanohydrin
(ii) Acetal
(iii) Semicarbazone
(iv) Aldol
(v) Hemiacetal
(vi) Oxime
(vii) Ketal
(viii) Imine
(ix) 2,4-DNP derivative
(x) Schiff's base.

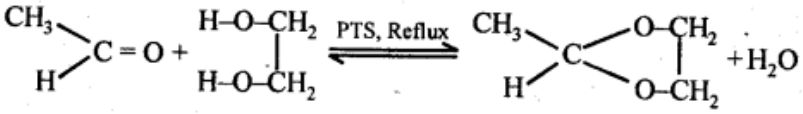
Ans: (i) Cyanohydrin: gem-Hydroxynitriles, i.e., compounds possessing hydroxyl and cyano groups on the same carbon atom are called cyanohydrins. These are produced by addition of HCN to aldehydes or ketones in a weakly basic medium.



(ii) gem – Dialkoxy compounds in which the two alkoxy groups are present on the terminal carbon atom are called acetals. These are produced by the action of an aldehyde with two equivalents of a monohydric alcohol in presence of dry HCl gas.

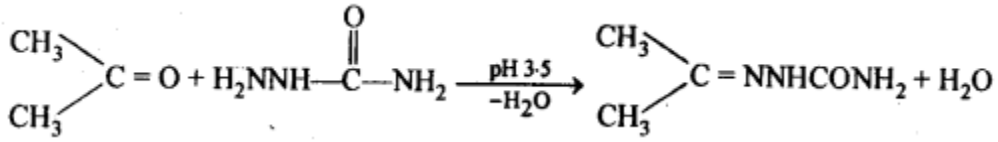


When dihydric alcohol is used cyclic acetal is formed

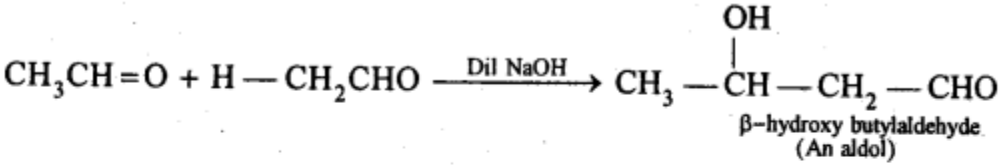


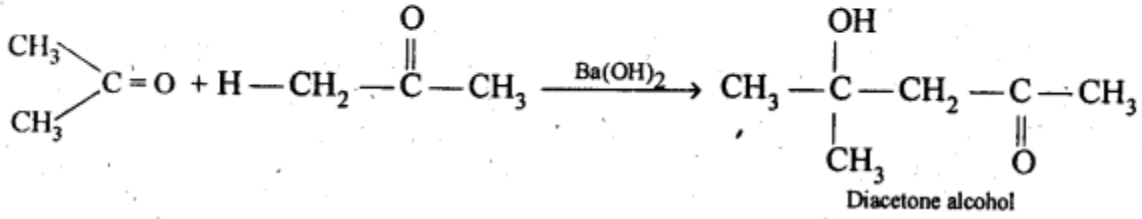
These are easily hydrolysed by dilute mineral acids to regenerate the original aldehydes. Therefore, these are used for the protection of aldehyde group in organic synthesis.

(iii) Semicarbazones are derivatives of aldehydes and ketones and are produced by action of semicarbazide on them in acidic medium.



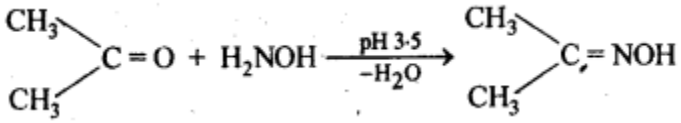
(iv) Aldols are P-hydroxy aldehydes or ketones and are produced by the condensation of two molecules of the same or one molecule each of two different aldehydes or ketones in presence of a dilute aqueous base. For example,



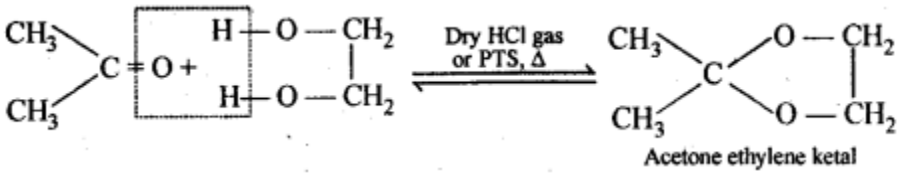


(v) gem – Alkoxyalcohols are called hemiacetals. These are produced by addition of one molecule of a monohydric alcohol to an aldehyde in presence of dry HCl gas.

(vi) Oximes are produced when aldehydes or ketones react with hydroxyl amine in weakly acidic medium.



(vii) Ketals are produced when a ketone is heated with dihydric alcohols like ethylene glycol in presence of dry HCl gas or /3-toluene sulphonic acid (PTS).



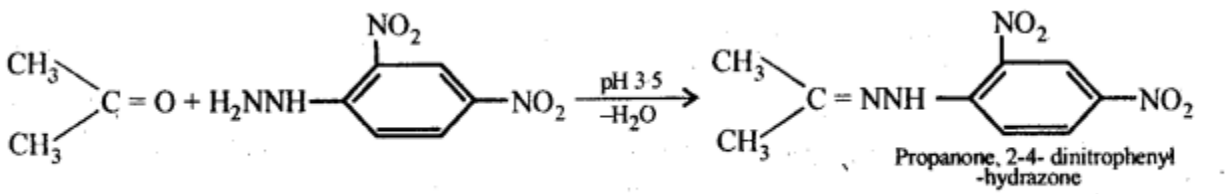
These are easily hydrolysed by dilute mineral acids to regenerate the original ketones. Therefore, ketals are used for protecting keto groups in organic synthesis.

(viii) Compounds containing -C = N – group are called imines. These are produced when aldehydes and ketones react with ammonia derivatives.

$$>C=O + H_2N-Z \longrightarrow >C=N-Z + H_2O$$

Z = alkyl, aryl, $-NH_2$, $-OH$, $-NHC_6H_5$, $-NHNHCONH_2$, etc.

(ix)2, 4-Dinitrophenyl hydrazone (i.e., 2,4-DNP derivatives) are produced when aldehydes or ketones react with 2,4-dinitrophenyl hydrazine in weakly acidic medium.



2, 4-DNP derivatives are used for identification and characterisation of aldehydes and ketones.

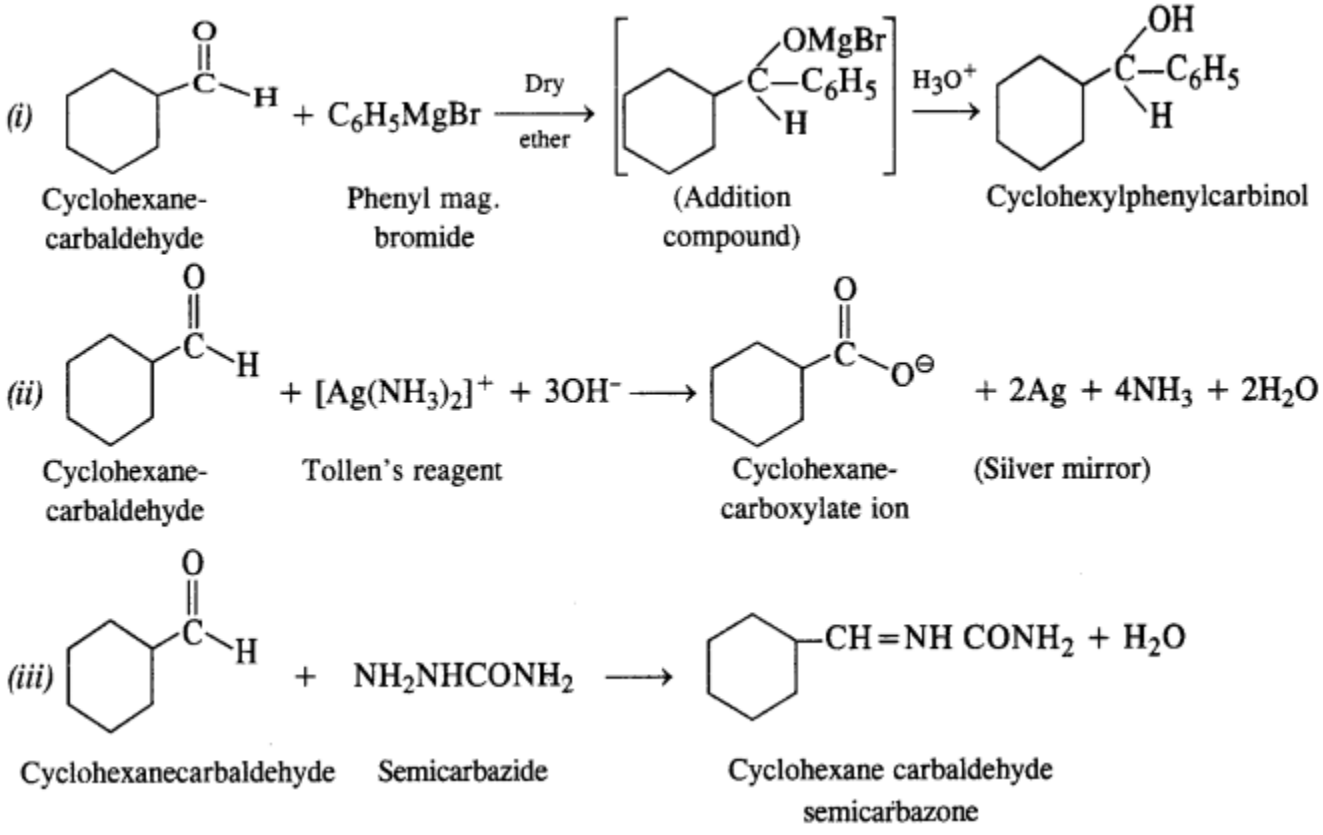
(x) Aldehydes and ketones react with primary aliphatic or aromatic amines to form azomethines or SchifFs bases.

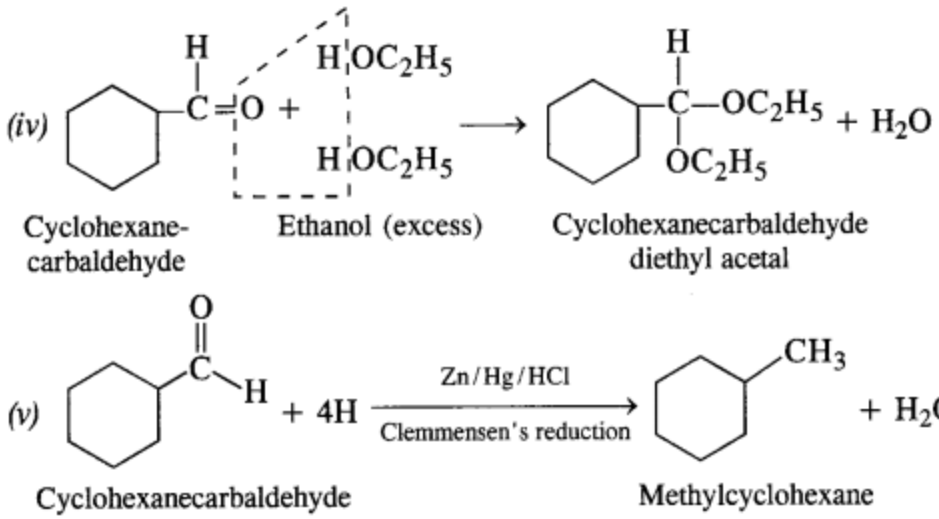
$$R-CH=\boxed{O+H_2}N-R' \xrightarrow[\Delta]{\text{Trace of } H^+} \underset{\text{Schiff's Base}}{R-CH=N-R'} + H_2O$$

e.g., $CH_3CH=O + H_2NCH_2CH_3 \xrightarrow{\text{Trace of } H^+} CH_3CH=NCH_2CH_3 + H_2O$

2. Predict the product when cyclohexanecarbaldehyde reacts with following reagents :
(i) C_6H_5MgBr followed by H_30^+
(ii) Tollen's reagent
(iii) Semicarbazide in the weakly acidic medium
(iv) Excess of ethanol in the presence of acid
(v) Zinc amalgam and Cyclohexanecarbaldehyde Semicarbazide

Ans:





3. Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

(i) Methanal

(ii) 2-Methylpentanal

(iii) Benzaldehyde.

(iv) Benzophenone

(v) Cyclohexanone

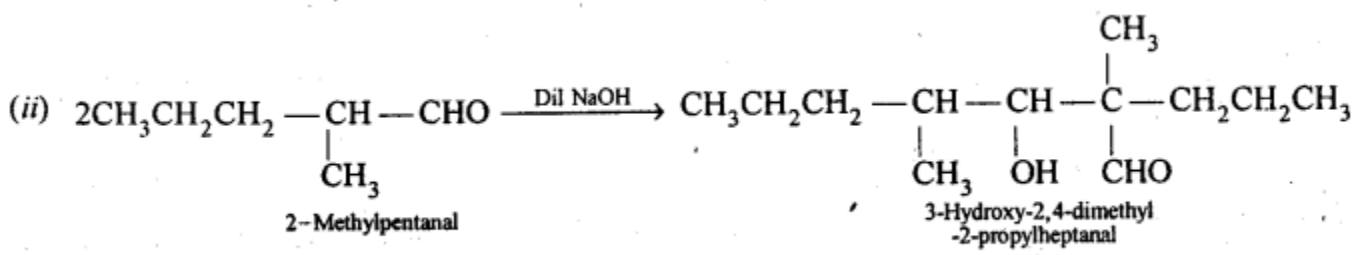
(vi) 1-Phenylpropanone

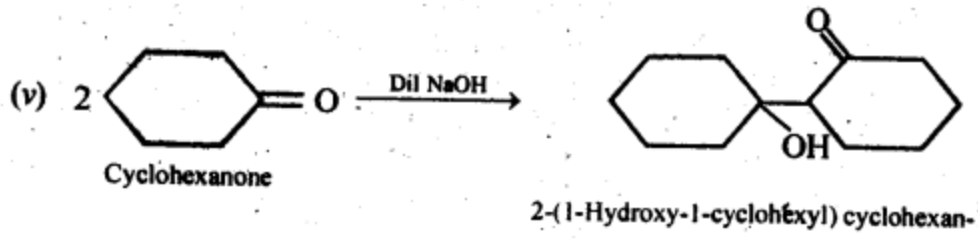
(vii) Phenylacetaldehyde

(viii) Butan-l-ol 1

(ix) 2,2-Dimethylbutanal

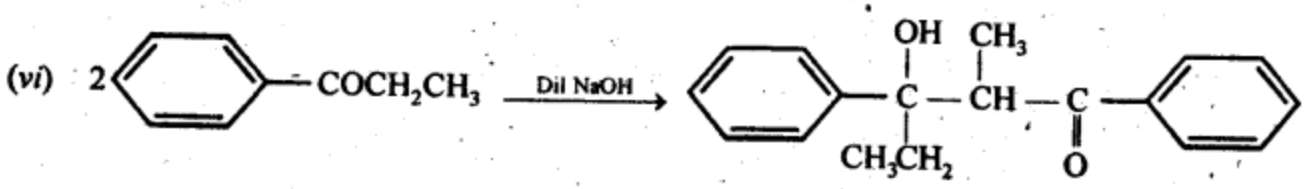
Ans: 2-Methylpertfanal, cyclohexanone, 1-phenylpropanone and phenylacetaldehyde contain one or more a-hydrogen and hence undergo aldol condensation. The reactions and the structures of the expected products are given below:



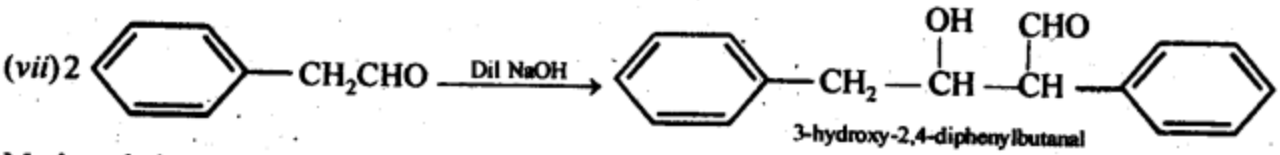
(v) 

Cyclohexanone

2-(1-Hydroxy-1-cyclohexyl) cyclohexan-1-one

(vi) 

3-Hydroxy-2-methyl-1,3-diphenylpentan-1-one

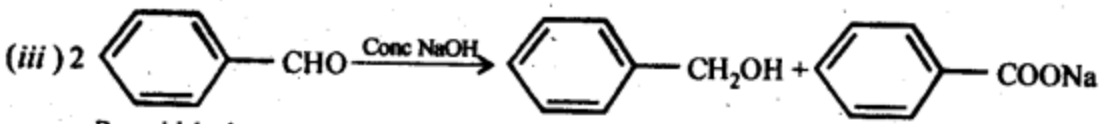
(vii) 

3-hydroxy-2,4-diphenylbutanal

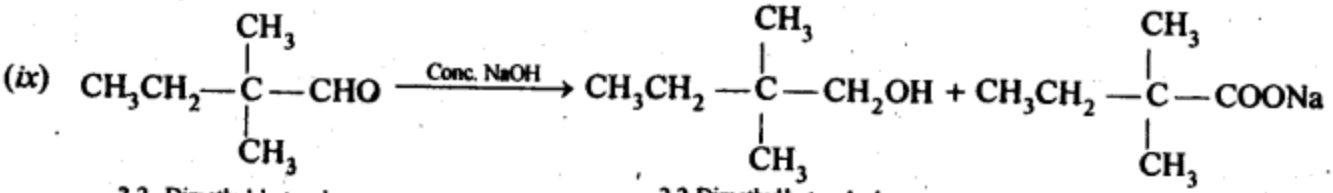
Methanal, benzaldehyde and 2,2-dimethylbutanal do not contain α-hydrogen and hence undergo Cannizzaro reaction. The reactions and the structures of the expected products are given below:

(i) $2HCHO \xrightarrow{\text{Conc NaOH}} CH_3OH + HCOONa$

Methanal — Methanol — Sodium formate

(iii) 

Benzaldehyde — Benzylalcohol — Sodium benzoate

(ix) 

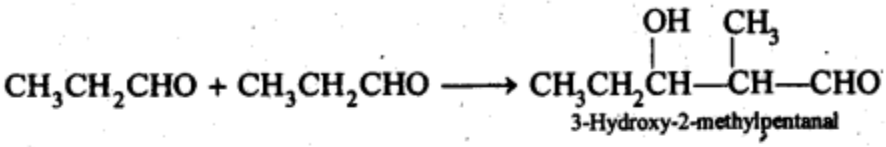
2,2-Dimethyl butanal — 2,2-Dimethylbutan-1-ol

Benzophenone (*iv*) is a ketone having no α-hydrogen while butan-1-ol (*viii*) is an alcohol. Both of these neither undergo aldol condensation nor cannizzaro reaction.

4. Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.

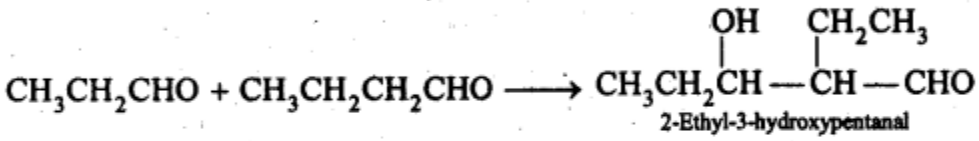
Ans:

(*a*) Propanal acts as both nucleophile as well as electrophile.



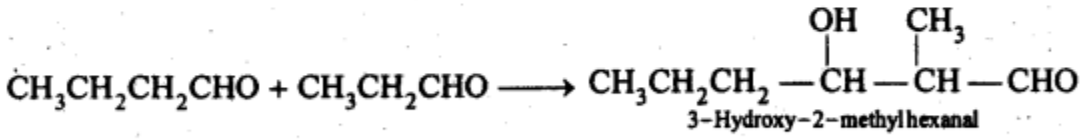
3-Hydroxy-2-methylpentanal

(*b*) Propanal as electrophile and butanal as nucleophile.



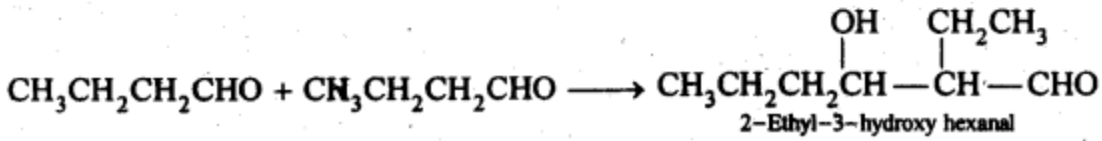
2-Ethyl-3-hydroxypentanal

(*c*) Butanal as electrophile and propanal as nucleophile.



3-Hydroxy-2-methylhexanal

(*d*) Butanal acts as both nucleophile as well as an electrophile.

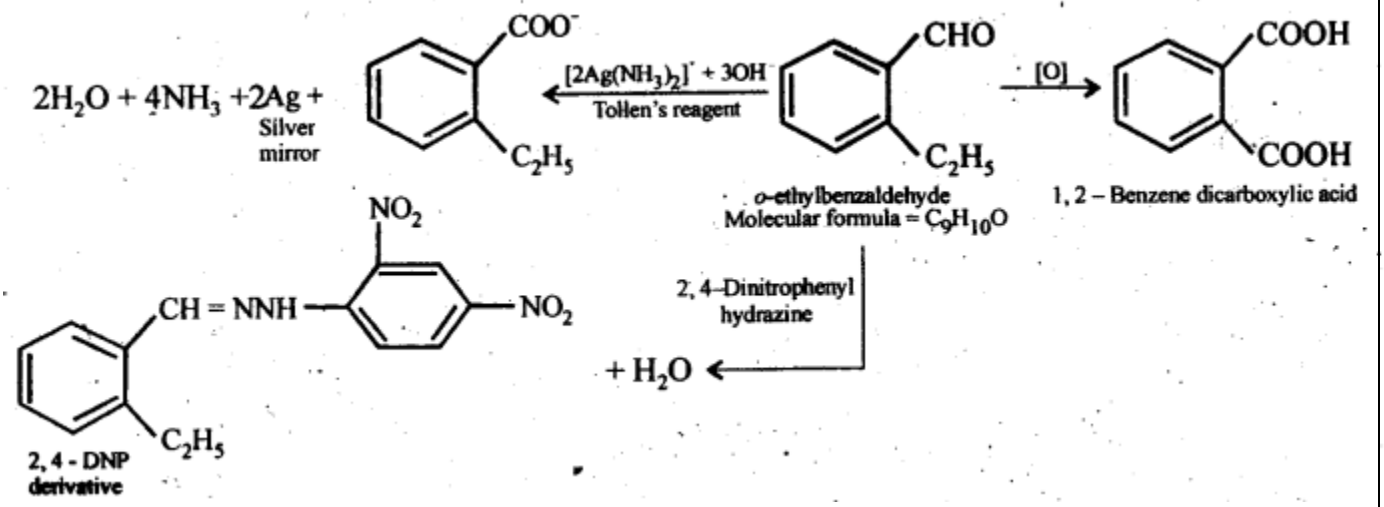


2-Ethyl-3-hydroxy hexanal

5. An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollen's reagent, and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

Ans: Since the given compound with molecular formula $C_9H_{10}O$ forms a 2,4-DNP derivative and reduces Tollen's reagent, it must be an aldehyde. Since it undergoes Cannizzaro reaction, therefore, CHO group is directly attached to die benzene ring. Since on vigorous oxidation, it gives 1, 2-benzene dicarboxylic acid, therefore, it must be an ortho- substituted benzaldehyde.

The only o-substituted aromatic aldehyde having molecular formula $C_9H_{10}O$ is o-ethyl benzaldehyde. Ail the reactions can now be explained on the basis of this structure.



6. An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B} and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (Q on dehydration gives but-l-ene. Write equations for the reactions involved.

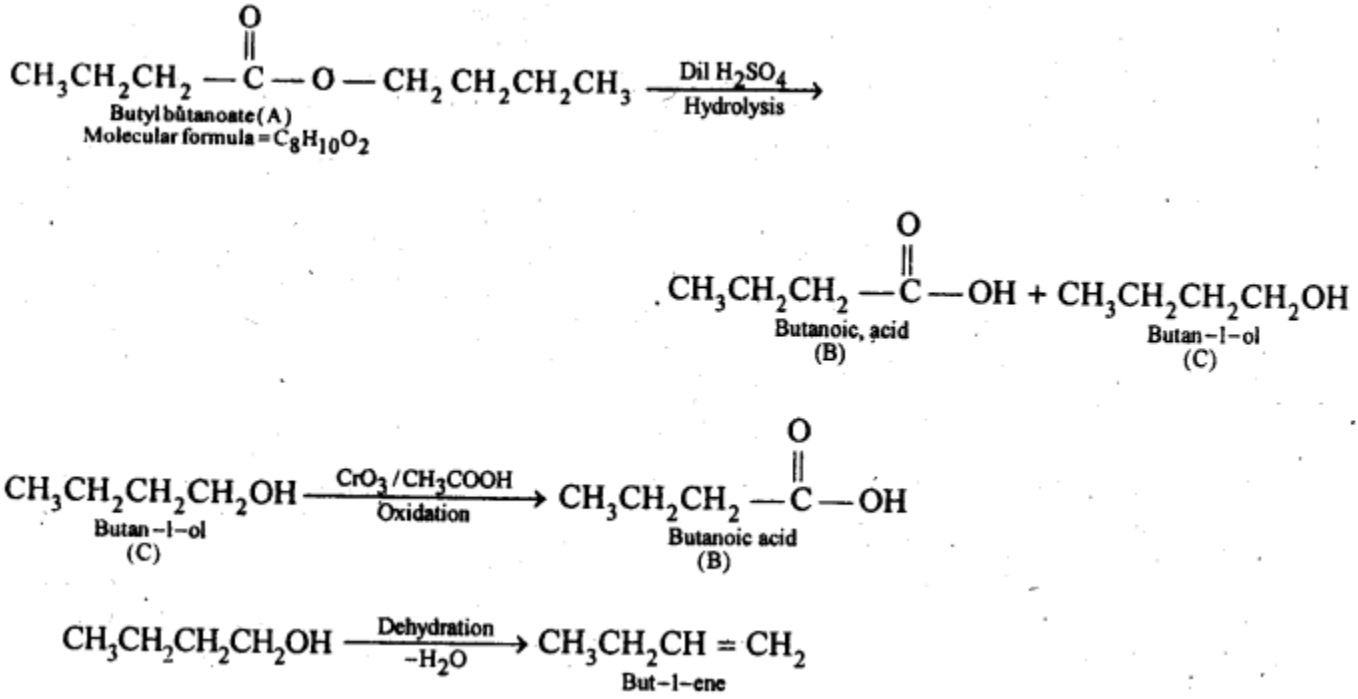
Ans: Since an ester A with molecular formula $C_8H_{16}O_2$ upon hydrolysis gives carboxylic acid B and the alcohol C and oxidation of C with chromic acid produces the acid B, therefore, both the carboxylic acid B and alcohol C must contain the same number of carbon atoms.

Further, since ester A contains eight carbon atoms, therefore, both the carboxylic acid B and the alcohol C must contain four carbon atoms each.

Since the alcohol C on dehydration gives but-l-ene, therefore, C must be a straight chain alcohol, i.e., butan-l-ol.

If C is butan-l-ol, then the acid B must be butanoic acid and the ester A must be butyl butanoate.The chemical equations are as

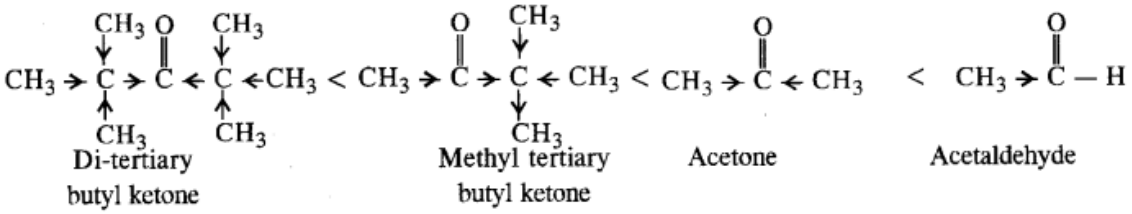
follows:



7. Arrange the following in increasing order of the property indicated :
(i) Acetaldehyde, Acetone, Di tert. butyl ketone, Methyl tert. butyl ketone (reactivity towards HCN). (C.B.S.E. Sample Paper 2011, 2015, C.B.S.E. Delhi 2012)
(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength) (C.B.S.E. Delhi2008)
(iii) Benzoic acid, 4-Nitrobenzoic acid, 3, 5-Dinitrobenzoic acid, 4-Methoxybenzoic acid
Ans: (i) Cyanohydrin derivatives are formed as a result of the reaction in which the nucleophile (CN^- ion) attacks the carbon atom of the carbonyl group. The order of reactivity

- decreases with increase in +I effect of the alkyl group.
- decreases with increase in steric hindrance due to the size as well as number of the alkyl groups. In the light of the above

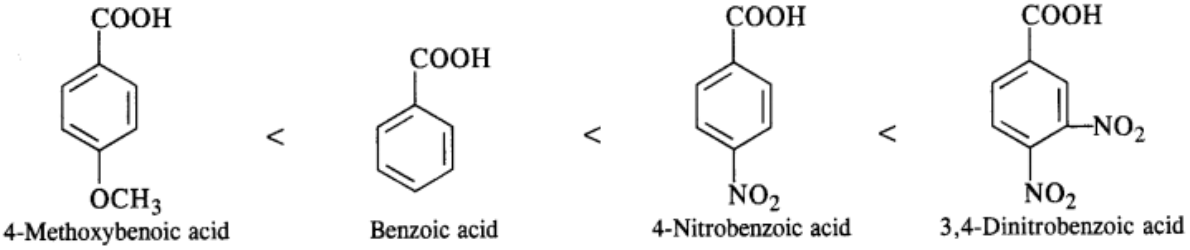
information, the decreasing order of reactivity is :



(ii) We know that alkyl group with +I effect decreases the acidic strength. The +I effect of isopropyl group is more than that of n-propyl group. Similarly, bromine (Br) with -I-effect increases the acidic strength. Closer its position in the carbon atom chain w.r.t., carboxyl (COOH) group, more will be its -I-effect and stronger will be the acid. In the light of this, the increasing order of acidic strength is :

$(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)\ COOH$

(iii) We have learnt that the electron donating group (OCH_3) decreases the acidic strength of the benzoic acid. At the same time, the electron withdrawing group ($N0_2$) increases the same. Keeping this in mind, the increasing order of acidic strength is:



8. Give simple chemical tests to distinguish between the following pairs of compounds.

(i) PropanalandPropanone

(ii) Acetophenone and Benzophenone

(iii) Phenol and Benzoic acid

(iv) Benzoic acid and Ethyl benzoate

(v) Pentan-2-one and Pentan-3-one

(vi) Benzaldehyde and Acetophenone.

(vii) EthanalandPropanal

Ans:

(*i*) Propanal and Propanone can be distinguished by iodoform test.

$$CH_3COCH_3 + 3NaOI \longrightarrow \underset{\text{Iodoform (Yellow ppt.)}}{CH_3I\downarrow} + CH_3COONa + 2NaOH$$

This test is given by aldehydes containing —$COCH_3$ group. Propanal does not have —$COCH_3$ group thus it does not give iodoform test

(*ii*) Acetophenone and Benzophenone can be distinguished by iodoform test.

$$C_6H_5COCH_3 + 3NaOI \longrightarrow C_6H_5COONa + \underset{\text{Iodoform (Yellow ppt.)}}{CH_3I\downarrow} + 2NaOH$$

$$C_6H_5COC_6H_5 \xrightarrow{NaOI} \text{No yellow ppt.}$$

This test is given by aldehydes and ketones containing –$COCH_3$ group

(*iii*) Phenol and Benzoic acid can be distinguished by $FeCl_3$ test

$$3C_6H_5OH + FeCl_3 \longrightarrow \underset{\text{Violet colouration}}{(C_6H_5O)_3Fe} + 3HCl$$

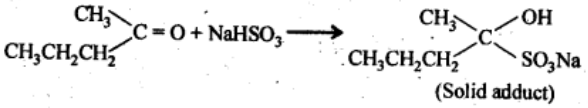
$$3C_6H_5COOH + FeCl_3 \longrightarrow \underset{\text{Buff-colouration ppt.}}{(C_6H_5COO)_3Fe} + 3HCl$$

(*iv*) Benzoic acid and Ethyl benzoate— By $NaHCO_3$ test

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow \underset{\text{Sodiumbenzoate}}{C_6H_5COONa} + H_2O + CO_2\uparrow$$

$$C_6H_5COOC_2H_5 + NaHCO_3 \longrightarrow \text{No } CO_2 \text{ is formed}$$

(*v*) Pentan-2-one and Pentan-3-one can be distinguished by $NaHSO_3$ test



(Solid adduct)

$$CH_3CH_2COCH_2CH_3 + NaHSO_3 \longrightarrow \text{No solid adduct.}$$

Only methyl and cyclic ketones react with $NaHSO_3$ to give solid adduct.

(*vi*) Benzaldehyde and Acetophenone can be distinguished by iodoform test.

$$C_6H_5COCH_3 + 3NaOI \longrightarrow C_6H_5COONa + \underset{\text{(Yellow ppt.)}}{CH_3I\downarrow} + 2NaOH$$

$$C_6H_5CHO + NaOI \longrightarrow \text{No yellow ppt.}$$

(*vii*) Ethanal and propanal can be distinguished by Iodoform test.

$$CH_3CHO + 3NaOI \longrightarrow HCOONa + \underset{\text{(Yellow ppt.)}}{CH_3I\downarrow} + 2NaOH$$

$$CH_3CH_2CHO \xrightarrow{I_2/NaOH} \text{No yellow ppt.}$$

SUMMARY

1. The classes of organic compounds containing carbonyl group (CO) as the functional group are aldehydes, ketones, carboxylic acids and their derivates. These are collectively called carbonyl compounds.

2. Nature of carbonyl group: Oxygen atom in carbonyl group is far more electronegative than carbon atom. As a result, the oxygen atom tends to attract the electron cloud of the π-bond towards itself, i. e., the π-electron cloud of >c = O is unsymmetrical.

Hence carbonyl carbon acquires positive charge and carbonyl oxygen carries negative charge. Thus, the carbonyl group is polar in nature.

3. Methods of preparation of Aldehydes and Ketones:

(a) By controlled oxidation of primary and secondary alcohol, aldehydes and ketones are produced.

(b) By dehydrogenation of alcohols : Primary alcohols on dehydrogenation produce aldehydes while secondary alcohols produce ketones.

4. Preparation of Aldehydes:

(a) Acyl chloride (acid chloride) is hydrogenated using, palladium on barium sulphate which is partially poisoned by the addition of S or quinoline. This reaction is called Rosenmund reduction. This method is used to prepare aldehydes.

(b) N itriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde. This reaction is called Stephen's reduction.