CHAPTER / 18

Aldehydes and Ketones

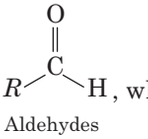
Topics Covered

Nomenclature and General Methods of Preparation of Aldehyde and Ketone
- Nomenclature of Carboxyl Compounds
- Isomerism in Aldehydes and Ketones
- Structure of Carbonyl Group
- General Methods of Preparation of Aldehydes and Ketones
- Special Methods of Preparation for Aromatic Carbonyl Compounds
- Preparation of Aromatic Ketones

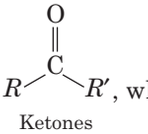
Properties of Aldehydes and Ketones
- Physical Properties
- Chemical Properties
- Uses

TOPIC ~01 Nomenclature and General Methods of Preparation of Aldehyde and Ketone

Aldehydes and ketones are organic compounds containing carbonyl group ($>C=O$) as the functional group. These are collectively called **carbonyl compounds**. The general formulae of aldehydes and ketones are:


, where, R may be or any alkyl or aryl groups.

Aldehydes

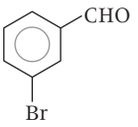
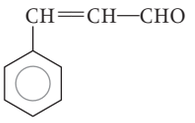
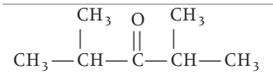

, where, R and R' may be same or different aryl groups.

Ketones

Nomenclature of Carboxyl Compounds

The word 'al' and 'one' replaces the ending 'e' of corresponding alkanes while naming the open chain aliphatic aldehydes and ketones, respectively.

Common and IUPAC names of some aldehydes and ketones

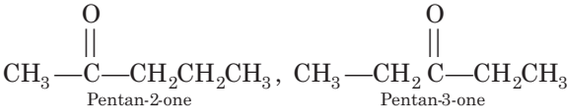
Structural formula	Common name	IUPAC name
Aldehydes HCHO	Formaldehyde	Methanal
$CH_3—CHO$	Acetaldehyde	Ethanal
$CH_3—CH_2—\overset{\alpha}{C}H(CH_3)—CHO$	α-methylbutyraldehyde	2-methylbutanal
	*m*-bromobenzaldehyde	3-bromobenzenecarbaldehyde or 3-bromobenzaldehyde
$CH_3—CH=CH—CHO$	Crotonaldehyde	But-2-enal
	Cinnamaldehyde	3-phenylprop-2-enal
Ketones CH_3COCH_3	Acetone	Propanone
	Diisopropyl ketone	2, 4-dimethylpentan-3-one

Isomerism in Aldehydes and Ketones

Aldehydes and ketones exhibit the following types of isomerism:

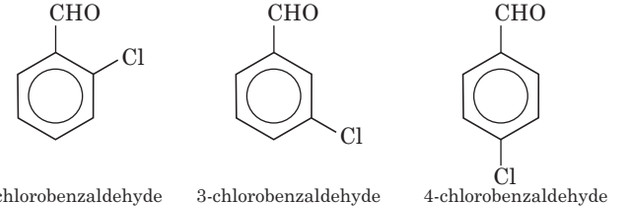
(i) **Position isomerism** Aldehydes do not show this type of isomerism because —CHO group is always present at one end of the chain. However, ketones exhibit position isomerism.

e.g. Pentan-2-one and pentan-3-one are the position isomers of each other.



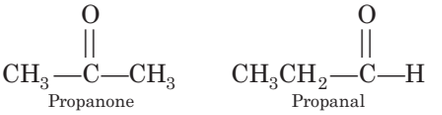
Aromatic substituted aldehydes also show position isomerism.

e.g.

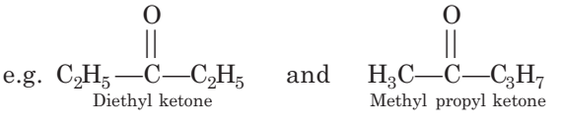


(ii) **Chain isomerism** Both aldehydes and ketones show chain isomerism. For example, butanal ($CH_3CH_2CH_2CHO$) and 2-methyl-propanal ($CH_3—CH(CH_3)—CHO$) are chain isomers of each other.

(iii) **Functional isomerism** Aldehydes and ketones show functional isomerism with one another.
e.g. propanal and propanone are the functional isomers of each other.



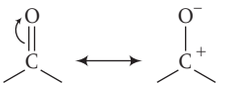
(iv) **Metamerism** Ketones may show metamerism but aldehydes do not.



Higher aldehydes and ketones having an asymmetric carbon can also exhibit optical isomerism in addition to the above mentioned types of isomerism.

Structure of Carbonyl Group

The carbonyl carbon atom is sp^2-hybridised and forms three sigma (σ) bonds. The fourth valence electron of carbon remains in *p*-orbital where it forms a π-bond by overlapping with *p*-orbital of an oxygen. It possesses a trigonal coplanar structure with bond angle 120°. The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon.



Comparison between $>C=O$ Group and $>C=C<$ Bond

Similarities

(i) In $>C=O$ and $>C=C<$ the 'C' atom is sp^2-hybridised.

(ii) Both σ bond and π bond present in $>C=O$ and $>C=C<$ respectively.

(iii) Both have planar structure.

(iv) Both show addition reactions.

Differences

(i) $>C=O$ group is polar while $>C=C<$ bond is non-polar.

(ii) $>C=O$ group undergoes nucleophilic addition reactions while $>C=C$ undergoes electrophilic addition reactions.

(iii) Bond length and bond strength are different in both the cases. Due to small size of oxygen, C = O bond length is shorter (1.23 A°) than C = C bond length (1.34 A°).

(iv) Geometrical isomerism is possible with C = C, whereas no such isomerism in case of $>C=O$ group.

General Methods of Preparation of Aldehydes and Ketones

Some important methods of preparation of aldehydes and ketones are discussed below:

1. From Alcohol

(i) By Oxidation

By oxidation of alcohols with $K_2Cr_2O_7$ / H_2SO_4 or $KMnO_4$ / KOH, aldehydes and ketones can be obtained.

Primary alcohols upon oxidation give aldehydes, whereas secondary alcohols give ketones.

$$\underset{\text{1° alcohol}}{RCH_2OH} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Aldehyde}}{R-CHO} + H_2O$$

$$\underset{\text{2° alcohol}}{\begin{matrix}R\\R\end{matrix}\!\!>\!CHOH} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Ketone}}{\begin{matrix}R\\R\end{matrix}\!\!>\!C=O} + H_2O$$

(ii) By the Catalytic Dehydrogenation

By catalytic dehydrogenation of alcohols with Cu / Ag at 573 K.

(a) Primary alcohol yield corresponding aldehydes

$$\underset{\text{1° alcohol}}{R-CH_2OH} \xrightarrow{Cu/573\ K} \underset{\text{Aldehyde}}{R-CHO} + H_2$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{Cu/573\ K} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2$$

(b) Secondary alcohols yield corresponding ketone

$$\underset{\text{2° alcohol}}{\begin{matrix}R\\R\end{matrix}\!\!>\!CHOH} \xrightarrow{Cu/573\ K} \underset{\text{Ketone}}{\begin{matrix}R\\R\end{matrix}\!\!>\!C=O} + H_2$$

$$\underset{\text{Propan-2 ol}}{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3} \xrightarrow{Cu/573\,K} \underset{\text{Propanone}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3} + H_2$$

2. By the Dry Distillation of Calcium Salts of Fatty Acids

(i) A mixture of calcium formate and calcium salt of any other acid on dry distillation gives aldehydes.

$$\underset{\text{Calcium acetate}}{\begin{matrix}CH_3COO\\CH_3COO\end{matrix}\!\!>\!Ca} + \underset{\text{Calcium formate}}{\begin{matrix}HCOO\\HCOO\end{matrix}\!\!>\!Ca} \xrightarrow{\text{Distillation}} \underset{\text{Acetaldehyde}}{2CaCO_3 + 2CH_3CHO}$$

(ii) Ketones are prepared when calcium salt of carboxylic acid (other than formic acid) is dry distilled.

$$\underset{\text{Calcium acetate}}{\begin{matrix}CH_3COO\\CH_3COO\end{matrix}\!\!>\!Ca} \xrightarrow{\text{Distillation}} CaCO_3 + \underset{\text{Acetone}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3}$$

3. From Carboxylic Acids

By passing vapours of carboxylic acids over manganous oxide at 573 K, aldehydes and ketones are formed. Formic acid gives formaldehyde whereas acids other than HCOOH produce ketones. A mixture of formic acid and other fatty acids produces aldehydes.

$$\underset{\text{Formic acid}}{HCO\boxed{OH + HCOO}H} \xrightarrow{MnO,\ 573\ K} \underset{\text{Formaldehyde}}{\begin{matrix}H\\H\end{matrix}\!\!>\!C=O} + H_2O + CO_2$$

$$\underset{\text{Acetic acid}}{CH_3CO}\underset{\text{Formic acid}}{\boxed{OH + HCOO}}H \xrightarrow{MnO,\ 573\ K} \underset{\text{Acetaldehyde}}{\begin{matrix}H_3C\\H\end{matrix}\!\!>\!C=O} + H_2O + CO_2$$

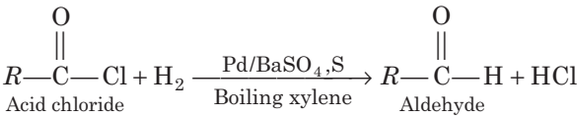
$$\underset{\text{Acetic acid}}{\boxed{\begin{matrix}H_3C\\HO\end{matrix}\!\!>\!C=O + \begin{matrix}H_3C\\HO\end{matrix}\!\!>\!C=O}} \xrightarrow{MnO,\ 573\ K} \underset{\text{Acetone}}{\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>\!C=O} + CO_2 + H_2O$$

4. From Acid Chlorides

Both aldehydes and ketones can be prepared from acid/acyl chloride.

(i) Aldehydes

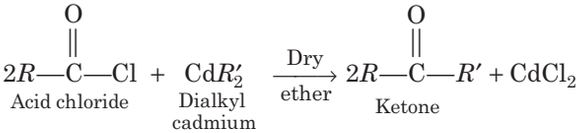
Acid chlorides can be reduced to aldehydes with H_2 in boiling xylene using palladium as catalyst over barium sulphate ($BaSO_4$). To check further reduction, the catalyst is poisoned by adding a little sulphur or quinoline.



This reaction is known as Rosenmund reduction.

(ii) Ketones

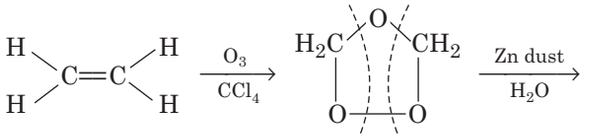
Ketones are obtained when acid chlorides reacts with di-alkyl cadmium in the presence of dry ether.

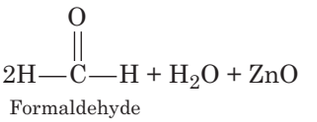


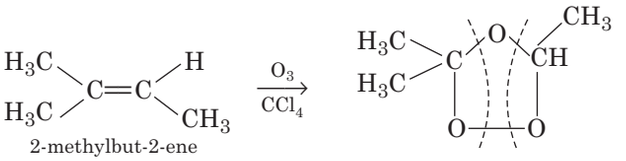
5. From Hydrocarbons

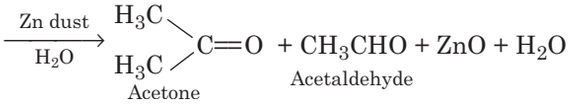
(i) From Alkenes by Ozonolysis

Alkenes form ozonides with ozone which get decomposed with zinc dust and water to form aldehydes and ketones. Zinc dust helps in removing H_2O, else the aldehydes or ketones formed may be oxidised to carboxylic acids.



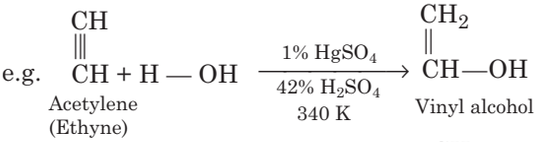


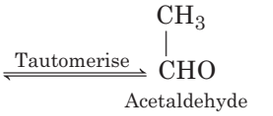


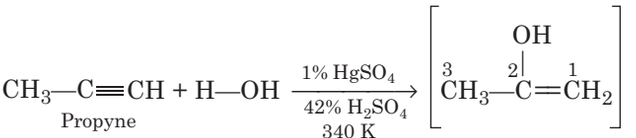


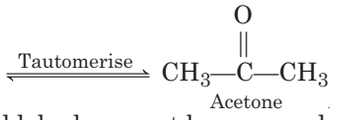
(ii) From Alkynes (Hydration)

Hydration of alkynes in the presence of $HgSO_4$ and H_2SO_4 yields enols which readily tautomerise giving aldehydes or ketones. The addition of water to unsymmetrical alkynes is in accordance with Markownikoff 's rule.









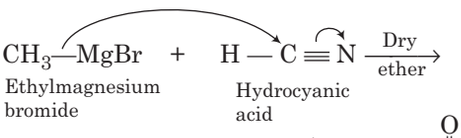
Aldehydes other than acetaldehyde cannot be prepared by this method.

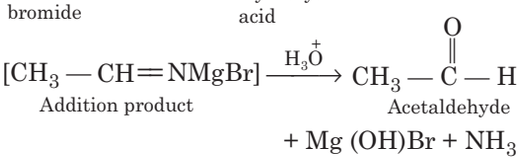
6. From Grignard Reagents

(i) Aldehydes

(a) When Grignard reagents react with hydrocyanic acid and the products are hydrolysed, aldehydes are formed.

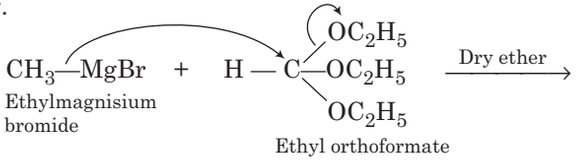
e.g.

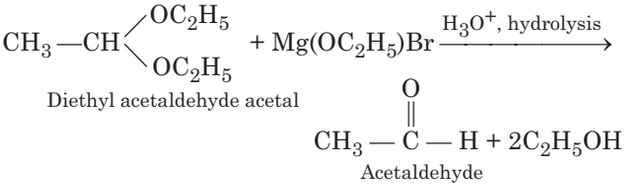




(b) Aldehydes can also be prepared by the action of Grignard reagents on orthoformic esters.

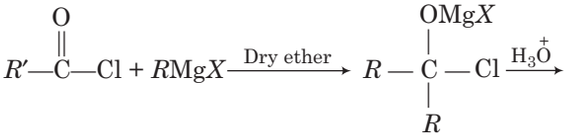
e.g.

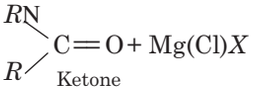


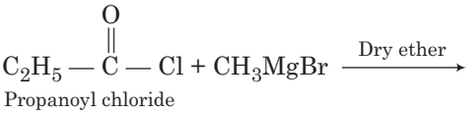


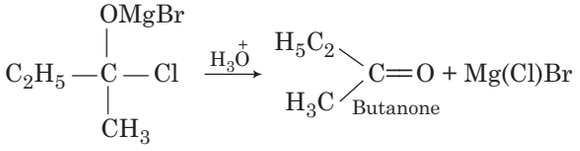
(ii) Ketones

(a) Acid chlorides react with Grignard reagents and the products formed on hydrolysis with dilute mineral acid yield ketones.

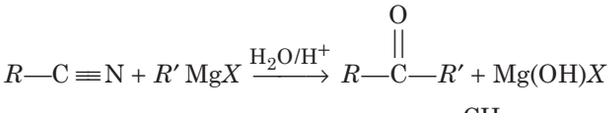


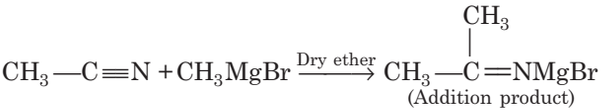


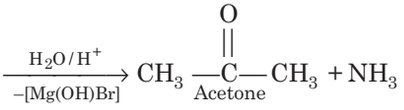




(b) Ketones can be prepared by treating alkane nitrile with Grignard's reagent followed by hydrolysis.







Special Methods of Preparation for Aromatic Carbonyl Compounds

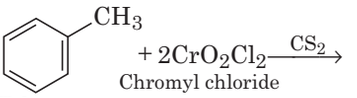
Aromatic aldehydes (benzaldehyde and its derivatives) are prepared from aromatic hydrocarbons by following methods:

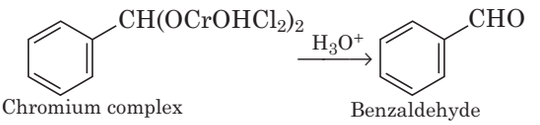
1. By the Oxidation of Toluene

(i) By Etard Reaction

In this process, toluene is oxidised to benzaldehyde with a solution of chromyl chloride (CrO_2Cl_2) in carbon tetrachloride or carbon disulphide.

The brown complex thus precipitated is separated and decomposed with water to give benzaldehyde.



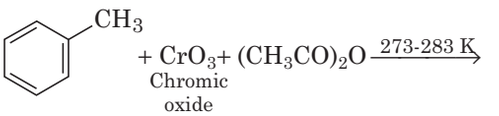


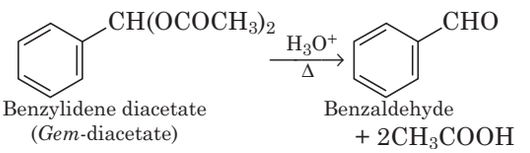
This reaction is called **Etard reaction**.

(ii) Oxidation by Chromic Oxide (CrO_3)

Toluene also reacts with chromic oxide in acetic anhydride to give benzaldehyde.

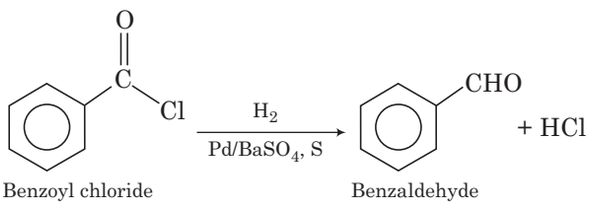
The *gem*-diacetate first formed is isolated which upon hydrolysis with dil. alkali or dil. HCl yield benzaldehyde.





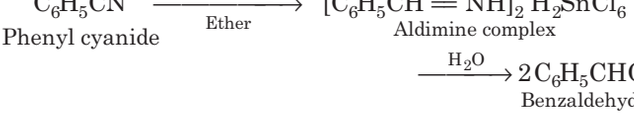
2. From Acid Chlorides (Rosenmund Reduction)

Benzoyl chloride is hydrogenated in the presence of palladium catalyst over barium sulphate to produce the benzaldehyde.

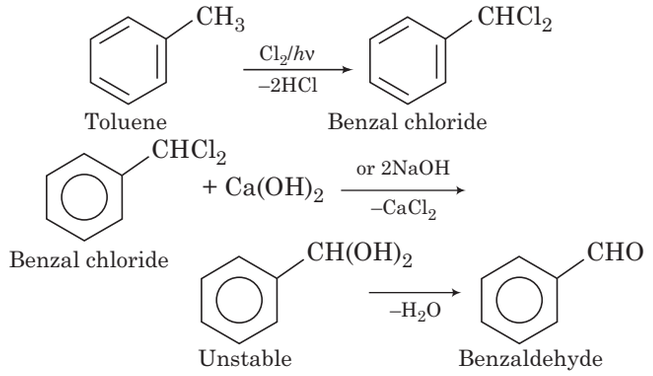


3. From Nitriles (Stephen Reduction)

Benzaldehyde is obtained by partial reduction of phenyl cyanide (benzonitrile) with stannons chloride and passing dry HCl gas in ethereal solution followed by hydrolysis of the aldimine stannic chloride with water.

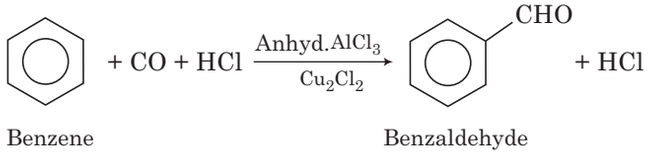


4. By Side Chain Halogenation Followed by Hydrolysis



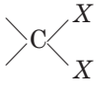
5. By Gattermann-Koch Reaction

A mixture of CO and HCl gas under high pressure is passed into the ether solution of benzene in the presence of anhydrous $AlCl_3$ and Cu_2Cl_2. As a result, benzene is converted into benzaldehyde.

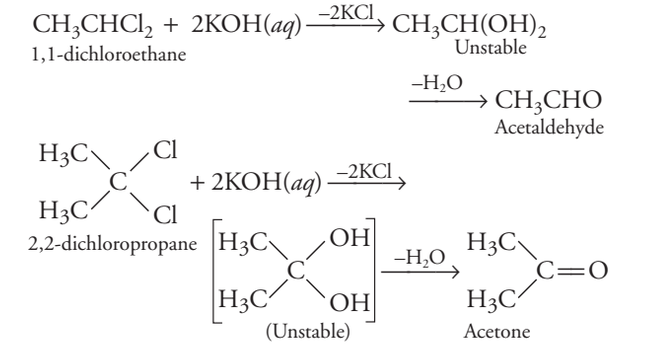


6. From *gem*-Dihalides

A *gem*-dihalide is a compound containing two halogen atoms attached to the same carbon.

i.e.  (X = Cl, Br)

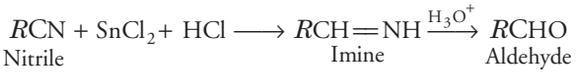
The hydrolysis of *gem*-dihalide yields a carbonyl group with *aq*. KOH.



7. From Nitriles and Esters

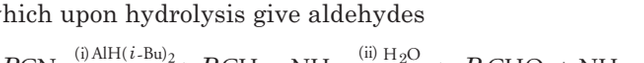
(Stephen Reaction)

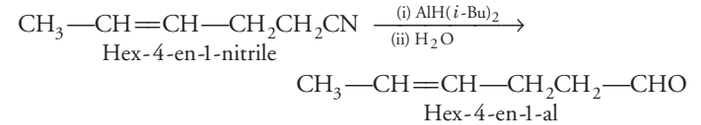
Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.



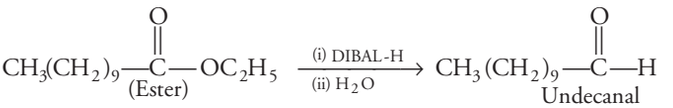
This reaction is called **Stephen reaction**.

Alternatively, diisobutylaluminium hydride, $[(CH_3)_2CHCH_2]_2AlH$ is abbreviated as $AlH(i\text{-}Bu)_2$ or DIBAL-H is used to reduce nitriles (selectively) to imines which upon hydrolysis give aldehydes





Similarly, esters are also reduced to aldehydes with DIBAL-H.



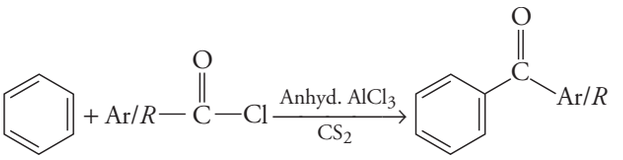
Preparation of Aromatic Ketones

(i) From Nitriles

Nitriles on reaction with Grignard reagent can produce aromatic ketones (discussed in previous section).

(ii) Friedel Crafts Acylation Reaction

When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, a corresponding ketone is obtained.



This reaction is known as **Friedel-Crafts acylation reaction.**

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Exams' Questions

Q.1 What is the product of the following reaction?

$$CH_3—C\equiv CH + H_2O \xrightarrow[60°C]{HgSO_4/\text{dil.}H_2SO_4}$$ **[2018]**

(a) $CH_3—\overset{\overset{O}{\|}}{C}—CH_3$ (b) $CH_3—CH_2—\overset{\overset{O}{\|}}{C}—H$

(c) $CH_3—\overset{\overset{O}{\|}}{C}—H$ (d) $CH_3—CH_2—CH_3$

Ans (*a*) $\underset{\text{Prop-1-yne}}{CH_3—C\equiv CH} + H_2O \xrightarrow[60°C]{HgSO_4/\text{dil.}H_2SO_4}$

$$H_3C—\overset{OH}{\overset{|}{C}}=CH_2 \xrightleftharpoons{\text{Tautomerises}} \underset{\text{Acetone}}{CH_3—\overset{\overset{O}{\|}}{C}—CH_3}$$

Q.2 Write the IUPAC name of the following compounds : $CH_3—\underset{\underset{OCH_3}{|}}{CH}—CHO$ **[2017]**

Ans 2-ethoxy propanal.

Q.3 Write the IUPAC name of

$$CH_3—\underset{\underset{NH_2}{|}}{CH}—CH_2—CO—\underset{\underset{CH_3}{|}}{CH}—Br$$ **[2012]**

Ans IUPAC name is 5-amino-2-bromohexan-3-one.

Q.4 A mixture of calcium acetate and calcium formate on heating gives **[2010]**

(a) $CH_3—\overset{\overset{O}{\|}}{C}—CH_3$ (b) $CH_3—\overset{\overset{O}{\|}}{C}—OH$

(c) $CH_3—\overset{\overset{O}{\|}}{C}—H$ (d) $H—\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{C}}$

Ans (*c*) Mixture of calcium acetate and calcium formate on heating gives acetaldehyde.

$$\underset{\text{Calcium acetate}}{\begin{matrix}CH_3COO\\ \\ CH_3COO\end{matrix}\!\!>\!Ca} + \underset{\text{Calcium formate}}{\begin{matrix}CHOO\\ \\ CHOO\end{matrix}\!\!>\!Ca} \xrightarrow{\text{Distillation}}$$

$$2CH_3CHO + 2CaCO_3$$

Q.5 How is acetaldehyde prepared from acetyl chloride? **[2009]**

Ans It is prepared by Rosenmund reduction as below:

$$\underset{\text{Acetyl chloride}}{CH_3—\overset{\overset{O}{\|}}{C}—Cl} + H_2 \xrightarrow[\text{Boiling xylene}]{\text{Pd-BaSO}_4, \text{ S}} \underset{\text{Acetaldehyde}}{CH_3—\overset{\overset{O}{\|}}{C}—H} + HCl$$

Q.6 Toluene on oxidation using CrO_2Cl_2 gives ..... and the reaction is called ..... . **[2009, 2006]**

Ans benzaldehyde, Etard's reaction.

Q.7 Write the IUPAC name of CH_3COCH_2CHO. **[2008]**

Ans IUPAC name of $\overset{4}{C}H_3\overset{3}{C}O\overset{2}{C}H_2\overset{1}{C}HO$ is 3-oxobutanal.

Q.8 What products are formed when calcium salt of formic acid is distilled? **[2007]**

Ans When calcium formate alone is distilled in a dry test tube, then formaldehyde is obtained.

$$\underset{\text{Calcium formate}}{\begin{matrix}HCOO\\ \\ HCOO\end{matrix}\!\!>\!Ca} \xrightarrow{\text{Heat}} CaCO_3 + \underset{\text{Formaldehyde}}{HCHO}$$

Q.9 Calcium formate on dry distillation gives ..... **[2006]**

Ans formaldehyde

Q.10 Give the IUPAC name of $C_2H_5COCH_3$. **[2006]**

Ans IUPAC name of $C_2H_5COCH_3$ or $CH_3CH_2COCH_3$ is butan-2-one.

Q.11 Write the IUPAC name of the following compound. **[2004]**

$$CH_3—\underset{\underset{Cl}{|}}{CH}—CH_2—CHO$$

Ans The IUPAC name is $\underset{\text{3-chlorobutanal}}{\overset{4}{C}H_3—\overset{3}{\underset{\underset{Cl}{|}}{CH}}—\overset{2}{C}H_2—\overset{1}{C}HO}$

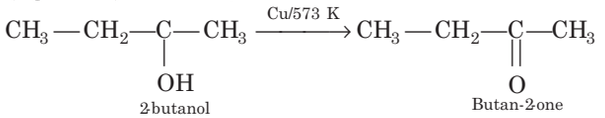
Important Questions

Q.12 Which of the following compounds is oxidised to prepare methyl ethyl ketone? **[Textbook]**

(a) 2-propanol (b) 1-butanol

(c) 2-butanol (d) formaldehyde

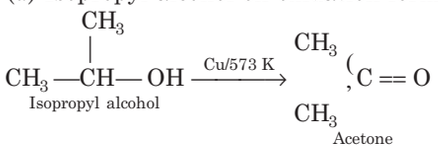
Ans (*c*) When 2-butanol reacts with heavy metal catalysts (Ag or Cu) at 573 K, butan-3-one is formed.



Q.13 Isopropyl alcohol on oxidation forms **[Textbook]**

(a) acetone (b) ether
(c) formalin (d) hydrobenzamide

Ans (*a*) Isopropyl alcohol on oxidation form acetone.



Q.14 Ethyl alcohol on oxidation with $K_2Cr_2O_7$ gives

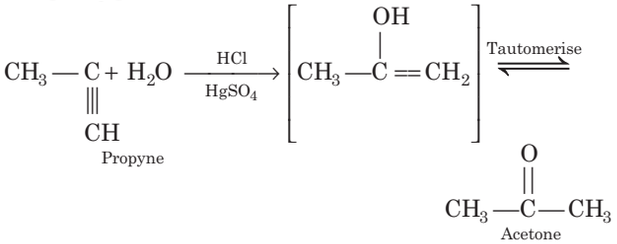
(a) acetic acid (b) acetaldehyde **[Textbook]**
(c) formic acid (d) formaldehyde

Ans (*b*) $CH_3CH_2OH \xrightarrow[[O]]{K_2Cr_2O_7} \underset{\text{Acetaldehyde}}{CH_3CHO}$

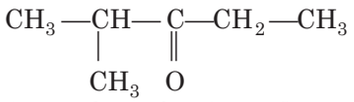
Q.15 Propyne on hydrolysis in presence of HCl and $HgSO_4$ gives **[Textbook]**

(a) acetaldehyde (b) acetone
(c) formaldehyde (d) None of these

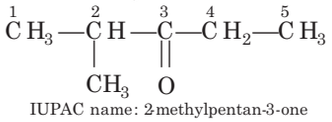
Ans (*b*) Propyne on hydrolysis in the presence of HCl and $HgSO_4$ gives acetone.



Q.16 What is the IUPAC name of **[Textbook]**



Ans



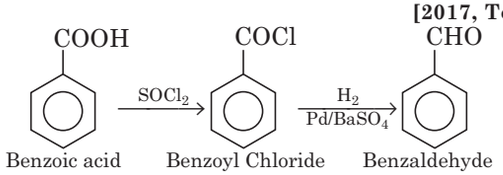
IUPAC name: 2-methylpentan-3-one

2 MARK *Questions*

Exams' Questions

Q.17 How is benzoic acid converted to benzaldehyde? **[2017, Textbook]**

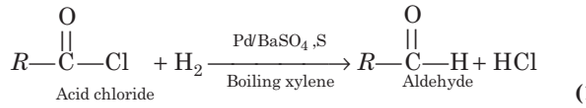
Ans



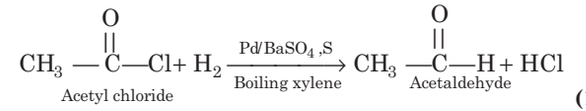
(2)

Q.18 What is Rosenmund's reaction? Explain with equation. **[2011, 2008, 2007, Textbook]**

Ans Acid chlorides can be reduced to aldehydes with H_2 in boiling xylene using palladium as catalyst over barium sulphate ($BaSO_4$). To check further reduction, the catalyst is poisoned by adding a little sulphur or quinoline.



(1)



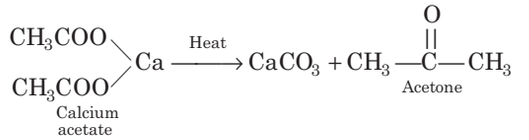
(1)

This reaction is known as Rosenmund reduction.

Formaldehyde cannot be prepared by this method.

Q.19 What happens when calcium acetate is heated? **[2009, Textbook]**

Ans



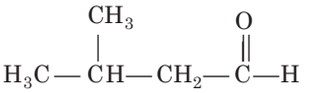
(2)

Important Questions

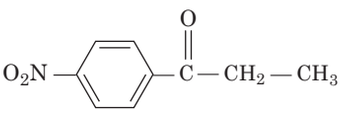
Q.20 Draw the structure of the following compounds.

(i) 3-methylbutanal (ii) *p* -nitropropiophenone

Ans (i) 3-methylbutanal



(ii) *p* -nitropropiophenone



(2)

3 MARK *Questions*

Exams' Questions

Q.21 (i) What is Stephen's reduction reaction? Given equation. **(2006)**

(ii) Give the IUPAC name of $C_2H_5COCH_3$.

Ans (i) Refer to text on page 262. **(1½)**

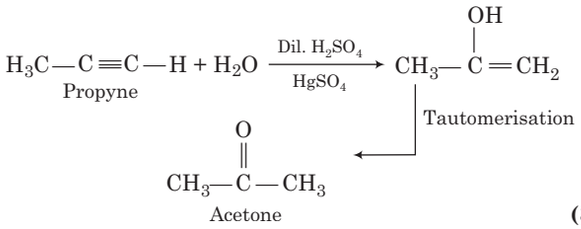
(ii) IUPAC name of $C_2H_5COCH_3$ or $CH_3CH_2COCH_3$ is butanone. **(1½)**

Important Questions

Q.22 Write the structure of the main product

$$H_3C-C\equiv C-H \xrightarrow{Hg^{2+},\ H_2SO_4}$$

Ans



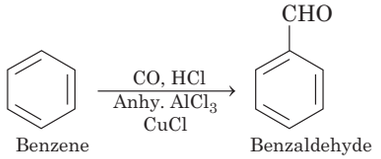
(3)

Q.23 Although both $>C=C<$ and $>C=O$ contain double bond, they differ in their characteristics. Explain. **[Textbook]**

Ans Refer to text on page 260. **(3)**

Q.24 Convert benzene to benzaldehyde. **[Textbook]**

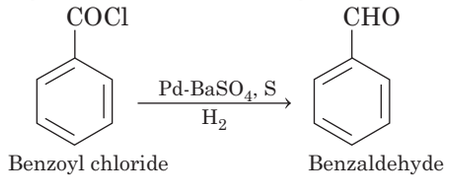
Ans Benzene to benzaldehyde:



(3)

Q.25 Convert benzoyl chloride to benzaldehyde. **[Textbook]**

Ans Benzoyl chloride to benzaldehyde:

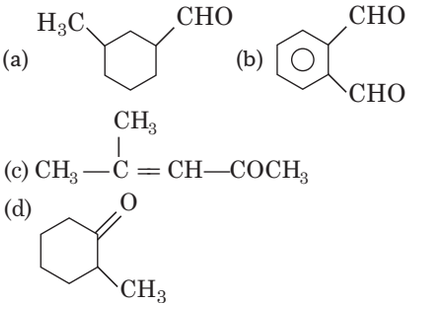


(3)

7 MARK *Questions*

Important Questions

Q.26 (i) Write IUPAC names of the following structures:



(ii) Complete the following reactions:

(a) $CH_3-C\equiv N + CH_3MgBr \xrightarrow{\text{Dry ether}}$

(b) $CH_2=CH_2 \xrightarrow[196\ K]{O_3/CCl_4}$

(c) $(CH_3)CCl_2 + 2KOH \xrightarrow{-2KCl}$

Ans (i) (a) 3-methyl cyclohexane carbaldehyde

(b) Benzene 1, 2-dicarbaldehyde

(c) 4-methyl pent-3-en-2-one

(d) 2-methyl cyclohexanone

(ii) (a) Refer to text on page 262.

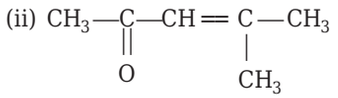
(b) Refer to text on page 261.

(c) Refer to text on page 263. **(7)**

TOPIC TEST 1

1. Write IUPAC names of the following:

(i) $OHCCH_2CH_2CH_2CHO$

(ii) 

2. Write structural formula of the following:

(i) 3-phenylprop-2-enal (ii) 4-chloropentan-2-one

3. Identify *X* in the given reaction:

$$CH_3COCl \xrightarrow[BaSO_4]{H_2/Pd} X$$

(a) Propionaldehyde

(b) Acetone

(c) Acetaldehyde

(d) Acetic acid

4. The reaction of benzene with CH_3COCl in the presence of $AlCl_3$ gives

(a) $C_6H_5COCH_3$ (b) C_6H_5COCl

(c) $C_6H_5CH_3$ (d) C_6H_5Cl

[***Ans.*** **3.** (c), **4.** (a)]

5. How will you bring about the following conversions?

(i) Benzene to acetophenone

(ii) Ethanol to acetone

6. (i) Explain the following reactions:

(a) Gattermann-Koch reaction

(b) Etard reaction

(c) Stephen reaction

(d) Friedel-Crafts acylation reaction

(ii) How does hydration of alkynes to form aldehydes/ketones take place? Explain, by giving examples.

7. Write equations for the ozonolysis reaction of the following:

(i) But-2-ene (ii) Pent-2-ene

TOPIC ~02 Properties of Aldehydes and Ketones

Physical Properties

(i) Boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.

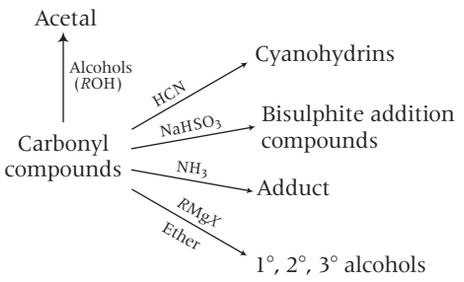
(ii) The lower members of aldehydes and ketones are miscible with water in all proportions, because they form hydrogen bond with water.

(iii) Aldehydes and ketones generally undergo nucleophilic addition reactions.

(iv) Aldehydes are more reactive than ketones toward nucleophiles due to more + *I* and steric effects in ketones.

Chemical Properties

(i) Aldehydes and ketones undergo a number of addition reactions due to the presence of polar carbonyl group (the carbonyl carbon bears partial positive charge, thus, undergoes nucleophilic addition reactions). Common nucleophilic addition reactions are :



(ii) Aldehydes and ketones also react with ammonia derivatives like:

(a) NH_2OH (hydroxylamine) to give oximes.

(b) $NH_2—NH_2$ (hydrazine) to give hydrazones.

(c) $NH_2—NH—$  (phenyl hydrazine)

to give phenyl hydrazones.

(iii) Reaction with 2, 4-DNP can be used to identify the presence of a carbonyl group.

(iv) Clemmensen reduction of aldehydes and ketones (Zn-Hg/conc. HCl) gives alkanes.

(v) **Wolff-Kishner reduction** The carbonyl group of aldehydes and ketones is reduced to $—CH_2$ group on treatment with hydrazine followed by heating with KOH in ethylene glycol.

(vi) Aldehydes give positive Tollen's test, Fehling's test, Benedict's test and Schiff's test.

(vii) Aldehydes can be distinguished from ketones by **Tollen's reagent, Fehling's solution** and **Benedict's solution**.

(viii) **Tollen's reagent** is an ammoniacal silver nitrate ($AgNO_3 + NH_4OH$) solution. It is a mild oxidising agent.

(ix) Aromatic aldehydes do not reduce Fehling's solution.

(x) Iodoform test is given by $CH_3CO—$ or $CH_3CH(OH)—$ group containing compounds.

(xi) Aldol condensation is given by aldehydes and ketones that have α-hydrogen atom in the presence of dilute alkali. It involves carbanion as an intermediate.

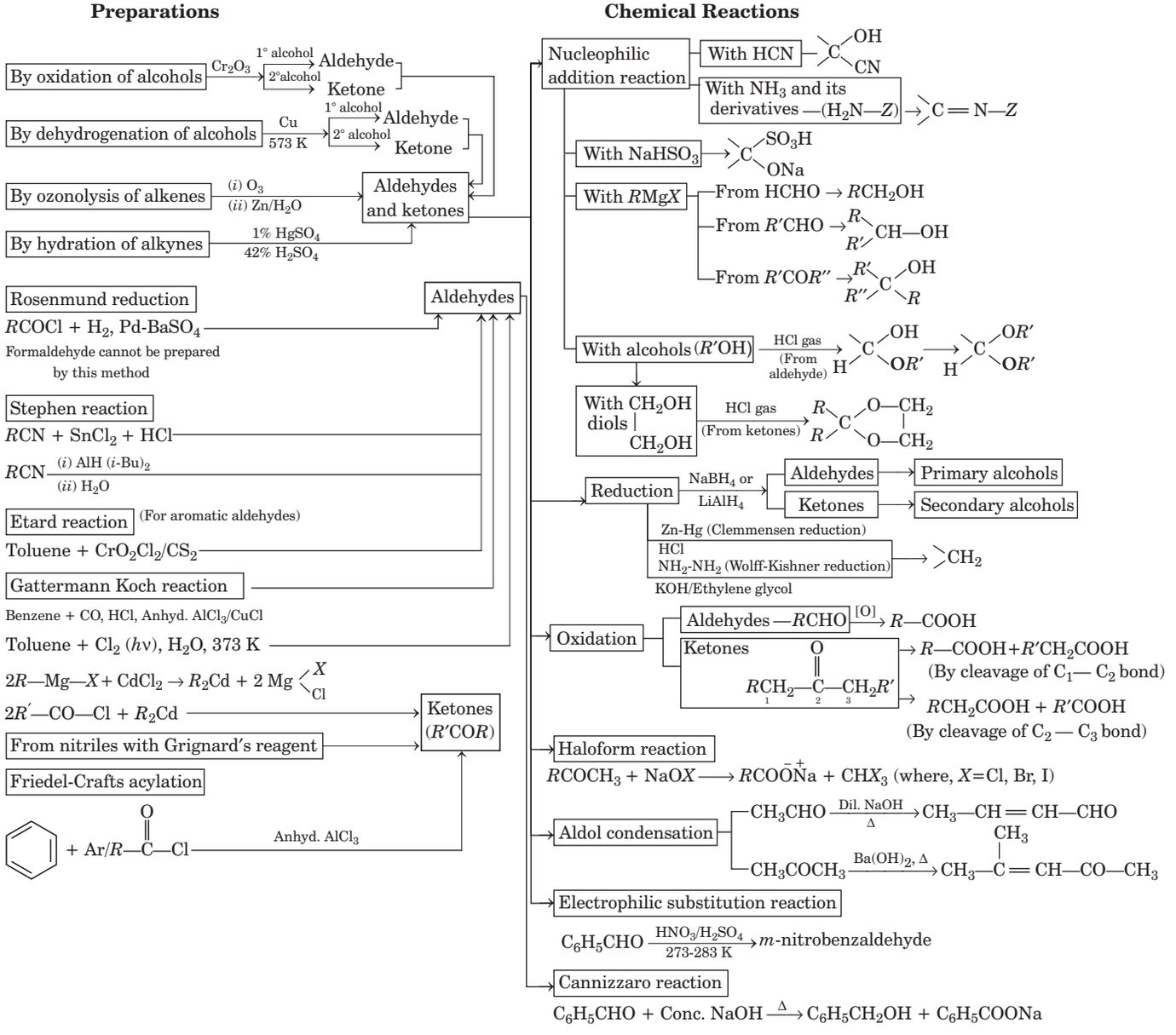
(xii) Cannizzaro reaction is given by those aldehydes which do not have α-hydrogen atom (like C_6H_5CHO, HCHO) in the presence of concentrated alkali.

(xiii) Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta*-directing group.

Uses

Formaldehyde is well known as formalin (40%) solution used to preserve biological specimens and to prepare polymeric products. Benzaldehyde is used in perfumary and in dye industries.

Flow Chart for the Preparations and Chemical Reactions of Aldehydes and Ketones



PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Exams' Questions

Q.1 The compound that reduces Tollen's reagent is

(a) CH_3COCH_3 (b) CH_3CHO **[2019]**

(c) CH_3COOH (d) CH_3CH_2OH

Ans (*b*) The compound which contains —CHO group reduces 'Tollen's reagent'. Thus, (b), i.e. CH_3—CHO is the correct option.

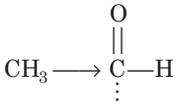
Q.2 Arrange the order of reactivity of the following compounds towards nucleophiles.

$CH_3CHO, (CH_3)_2CO, HCHO$ **[2016]**

Ans The order of reactivity of the given carbonyl compound towards nucleophile is,

$HCHO > CH_3CHO > (CH_3)_2CO$

Reason Electron releasing groups decreases the reactivity of carbonyl compounds by $-I$-effect, while electron withdrawing groups increases the reactivity of carbonyl compound by + I-effect.



(less electron deficient C atom due to $—CH_3$ group)

Q.3 Which one of the following will not react with ammoniacal silver nitrate solution? **[2015, 2012]**

(a) Acetylene (b) Acetone **[2019]**

(c) Acetaldehyde (d) Formic acid

Ans (*b*) Tollen's reagent is an ammoniacal solution of silver nitrate. It reacts with acetylene, acetaldehyde and formic acid. It does not oxidise acetone because ketones do not act as reducing agents. Thus, acetone will not react with Tollen's regent.

Q.4 Methyl-ketone is identified by the reagent. **[2015]**

(a) Tollen's reagent (b) I_2/KOH

(c) Fehling's solution (d) Schiff's reagent

Ans (*b*) Iodoform reaction (I_2/KOH) is shown by all ketones containing CH_3CO^- group. Methyl ketone is also containing CH_3CHO group.

$$2NaOH + I_2 \longrightarrow \underset{\text{Sodium hypoiodite}}{NaI + NaIO} + H_2O$$

$$RCOCH_3 + 3NaIO \longrightarrow RCOCI_3 + 3NaOH$$

$$RCOCI_3 + NaOH \longrightarrow CHI_3\downarrow + RCOONa$$

($R = CH_3, C_2H_5$ etc.)

Q.5 The precipitate formed when an aldehyde reacts with Fehling solution is ..... **[2014]**

Ans cuprous oxide (Cu_2O)

Q.6 When a solution of formaldehyde and KOH is heated, it will give **[2013]**

(a) acetylene and methane

(b) methanol and potassium formate

(c) methanol and methane

(d) methanol and acetylene

Ans (*b*) When a solution of formaldehyde and KOH is heated, it will give methanol and potassium formate.

$$\underset{\text{Formaldehyde}}{2HCHO} + KOH \longrightarrow \underset{\text{Potassium formate}}{HCOOK} + \underset{\text{Methanol}}{CH_3OH}$$

Q.7 Electrophilic substitution reaction in benzaldehyde takes place at **[2012]**

(a) *o*-position (b) *p*-position

(c) *m*-position (d) *o*-and *p*-position

Ans (*c*) *m*-position

Q.8 Calcium acetate on heating gives ..... and ..... . **[2014, 2012 Instant]**

Ans CH_3COCH_3 and $CaCO_3$.

Q.9 Which of the following compounds will not undergo haloform reaction? **[2011 Instant]**

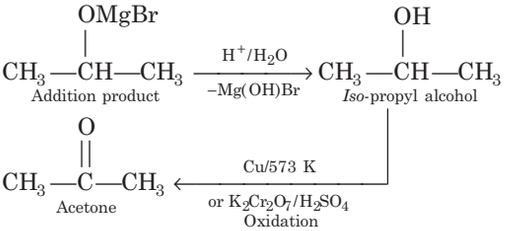
(a) *Iso*-propyl alcohol (b) Acetone

(c) Methyl ethyl ketone (d) Diethyl ketone

Ans (*d*) Diethyl ketone will not undergo haloform reaction. Haloform reaction is shown by acetaldehyde and all ketones containing CH_3CO— group.

Q.10 How acetaldehyde is converted to acetone? **[2011]**

Ans $CH_3CHO \xrightarrow[\text{dry ether}]{CH_3MgBr}$



Q.11 Acetyl chloride cannot be obtained by the reaction of acetic acid with **[2010]**

(a) $SOCl_2$ (b) Cl_2 (c) PCl_3 (d) PCl_5

Ans (*b*) Acetic acid react with thionyl chloride ($SOCl_2$), phosphorus pentachloride (PCl_5) or phosphorus trichloride (PCl_3) to form acetylchloride.

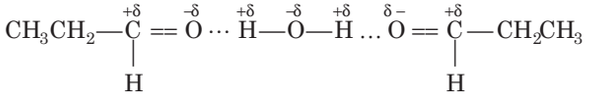
Q.12 Iodoform reaction is not given by **[2009]**

(a) butan-1-ol (b) butan-2-one
(c) ethanol (d) *iso*-propyl alcohol

Ans (*a*) Iodoform reaction is not given by butan-1-ol. Iodoform reaction is used for characterising compounds containing CH_3CO— group or any group such as $CH_3CH(OH)$— which can be easily oxidised to CH_3CO— group by halogens.

Q.13 Which has a higher boiling point propanone or propanol? **[2009]**

Ans Boiling point of propanol is much higher than that of propanone due to intermolecular hydrogen bonding which is present in propanol.



Q.14 Cannizzaro's reaction is given by **[2008]**

(a) acetone (b) acetaldehyde
(c) benzaldehyde (d) acetic acid

Ans (*c*) Cannizzaro's reaction is given by benzaldehyde because it does not contain α-hydrogen atom.

Q.15 What is Tollen's reagent? **[2006, 2000]**

Ans Tollen's reagent is ammoniacal solution of silver nitrate $[Ag(NH_3)_2]OH$.

Important Questions

Q.16 Tollen's reagent is **[Textbook]**

(a) ammoniacal cuprous chloride
(b) ammonical cuprous oxide
(c) ammoniacal silver bromide
(d) ammoniacal silver nitrate

Ans (*d*) Tollen's reagent is a colourless, basic ammoniacal silver nitrate solution.

Q.17 Aldehydes can be distinguished from ketones by using **[Textbook]**

(a) Schiff's reagent (b) conc. H_2SO_4
(c) anhy. $ZnCl_2$ (d) resorcinol

Ans (*a*) Beside Tollen's reagent and Fehling's solution, Schiff's reagent is also used to distinguished aldehyde from ketone.

Q.18 Formaldehyde reacts with NH_3 to give **[Textbook]**

(a) hexamethylenetetramine (b) formaldehuyde ammonia
(c) formalin (d) hydrobenzamide

Ans (*a*) $6HCHO + 4NH_3 \longrightarrow \underset{\text{Hexamethylene tetraamine}}{(CH_2)_6N_4} + 6H_2O$

Q.19 Formaldehyde when treated with conc. KOH gives **[Textbook]**

(a) CH_3CHO (b) C_2H_4
(c) CH_3OH, $HCOO^-K^+$ (d) CH_3OH, CH_3CHO

Ans (*c*) HCHO upon reaction with conc. KOH undergoes Cannizzaro's reaction. Out of two molecules of HCHO, one molecule is oxidised to $HCOO^-K^+$ and other is reduced CH_3OH.

Q.20 Which compound undergoes iodoform reaction? **[Textbook]**

(a) HCHO (b) CH_3CHO (c) CH_3OH (d) CH_3COOH

Ans (*b*) Compounds which contain CH_3CO— group or which produce CH_3CO group on oxidation can undergo iodoform reaction. Hence, only CH_3CHO undergoes iodoform test.

Q.21 Which of the following does not give Cannizzaro's reaction?

(a) Trimethyl acetaldehyde (b) Acetaldehyde
(c) Benzaldehyde (d) Formaldehyde

Ans (*b*) Compounds which do not possess alpha hydrogen undergo Cannizzaro reaction. Acetaldehyde does not give Cannizzaro reaction as it possesses alpha hydrogen atom.

Q.22 The reaction between formaldehyde and caustic soda to produce methyl alcohol is known as **[Textbook]**

(a) Cannizzaro reaction (b) Kolbe's reaction
(c) Rosenmund's reduction (d) Friedel-Craft reaction

Ans (*a*) **Cannizzaro reaction** Aldehydes which do not have α-H atom undergo self oxidation and reduction (disproportionation) on treatement with conc. alkali. In this reaction, one molecule of aldehyde is reduced to alcohol, while another molecule is oxidised to salt of carboxylic acid.

$$\underset{\text{Formaldehyde}}{HCHO} + HCHO \xrightarrow{NaOH} \underset{\text{Methanol}}{HCH_2OH} + \underset{\text{Sodium formate}}{HCOONa}$$

Q.23 Identify '*Z*' in the series **[Textbook]**

$$CH_2 = CH_2 \xrightarrow{HBr} X \xrightarrow{\text{Hydrolysis}} Y \xrightarrow[I_2\text{ (excess)}]{NaOH} Z$$

(a) C_2H_5I (b) C_2H_5OH (c) CHI_3 (d) CH_3CHO

Ans (*c*) $CH_2 = CH_2 \xrightarrow{HBr} \underset{(X)}{CH_3 - CH_2Br} \xrightarrow[HOH]{(X)} \underset{(Y)}{CH_3CH_2OH} \xrightarrow[I_2\text{(excess)}]{NaOH} \underset{(Z)}{CHI_3}$

Q.24 Formaldehyde when treated with conc. KOH gives methanol and potassium formate. The reaction is known is **[Textbook]**

(a) Perkin's reaction (b) Claisen's reaction
(c) Cannizzaro's reaction (d) Knoevenagel's reaction

Ans (*c*) When formaldehyde react with conc. KOH gives methanol and potassium formate is known as Cannizzaro's reaction.

Q.25 At room temperature formaldehyde is **[Textbook]**

(a) gas (b) liquid
(c) solid (d) All of these

Ans (*a*) Formaldehyde is a gas at room temperature. Other aldehydes and ketones up to C_{11} are liquid and higher ones are solids.

Q.26 Which of the following can reduce Tollen's reagent? **[Textbook]**

(a) 2-hydroxyprpoane (b) Acetophenone
(c) Both (a) and (b) (d) None of these

Ans (*d*) Tollen's reagent is a chemical reagent used to determine the presence of aldehyde, aromatic aldehyde and alpha-hydroxy ketone functional groups. Hence, both (a) and (b) cannot reduce Tollen's reagent.

Q.27 In which of the following reactions, both the oxidised and reduced forms of the same compound are obtained? **[Textbook]**

(a) Aldol condensation
(b) Cannizzaro reaction
(c) Reimer Tiemann reaction
(d) Kolbe's synthesis

Ans (*b*) In Cannizzaro reaction, both the oxidised and reduced forms of the same compound are obtained.

Q.28 Hexamethylene tetramine is used as **[Textbook]**

(a) analgesic (b) antipyretic
(c) urinary antiseptic (d) All of these

Ans (*c*) Formaldehyde reacts with NH_3 to form hexamethylene tetramine which is used as a urinary antiseptic under the name urotropine.

Q.29 Which of the following reagents helps to distinguish an aldehyde from a ketone? **[Textbook]**

(a) Phenyl hydrazine
(b) $NaHSO_3$
(c) neutral $FeCl_3$
(d) Ammoniacal $AgNO_3$ solution

Ans (*d*) Ammoniacal $AgNO_3$ solution (Tollen's reagent) is used to distinguish between an aldehyde and a ketone.

Q.30 Which of the following does not show aldol condensation? **[Textbook]**

(a) CH_3CHO (b) CH_3CH_2CHO
(c) $(CH_3)_3C—CHO$ (d) $CH_3(CH_2)_2CHO$

Ans (*c*) Those compounds which have α-hydrogen atom show aldol condensation reaction. $(CH_3)_3C—CHO$ does not contain α-hydrogen atom. So, it does not show aldol condensation reaction.

Q.31 Formalin is an aqueous solution of **[Textbook]**

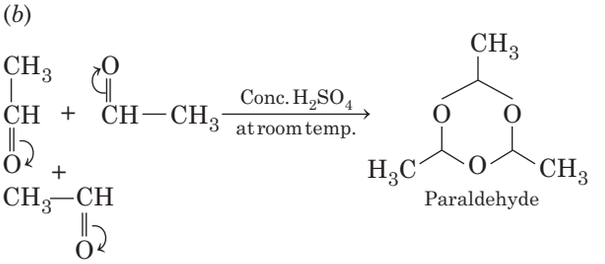
(a) Formic acid (b) Formaldehyde
(c) Fluorescein (d) Furfuraldehyde

Ans (*b*) Formalin is an 40% aqueous solution of formaldehyde.

Q.32 When anhydrous acetaldehyde is brought in contact with a drop of conc.H_2SO_4 at ordinary temperature, the following compound is formed.

(a) Aldol (b) Paraldehyde **[Textbook]**
(c) Metaldehyde (d) acetal

Ans (*b*)



Q.33 In the given reaction '*X*' will be

$$C_6H_5COCl \xrightarrow[Pd-BaSO_4,\ S]{H_2} \text{'}X\text{'}$$

[Textbook]

(a) C_6H_5COOH (b) $C_6H_5CH_2OH$
(c) C_6H_5CHO (d) $C_6H_5CH_3$

Ans (*c*) $\underset{\text{Benzoyl chloride}}{C_6H_5—\overset{\overset{O}{\|}}{C}—Cl} \xrightarrow[Pd\text{-}BaSO_4,S]{H_2} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$

Q.34 Cannizzaro reaction is an example of **[Textbook]**

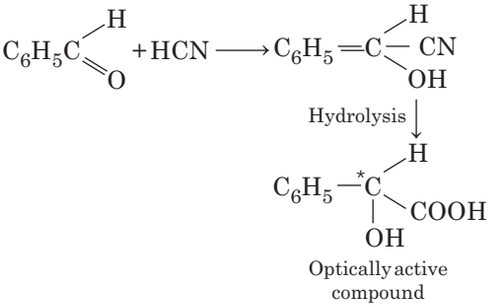
(a) oxidation (b) reduction
(c) disproportionation (d) None of these

Ans (*c*) Cannizzaro reaction is an example of disproportionation or redox reaction in which a compound of intermediate oxidation state converts into two different compounds, one with higher oxidation state and one lower oxidation state.

Q.35 Cyanohydrin of benzaldehyde on hydrolysis will give **[Textbook]**

(a) an optically active hydroxy acid
(b) benzoic acid
(c) benzyl alcohol
(d) acetophenone

Ans (*a*)



Q.36 Which of the following statement is not true about benzaldehyde? **[Textbook]**

(a) Undergoes Cannizzaro reaction
(b) Forms an addition compound with HCN
(c) Undergoes aldol condensation
(d) Reacts with phenylhydrazine

Ans (*c*) Due to absence of α-hydrogen in benzaldehyde does not show aldol condensation.

Q.37 Cannizzaro reaction is given by **[Textbook]**

(a) C_6H_5CHO (b) CH_3CHO
(c) $C_6H_5CH_2CHO$ (d) $C_6H_5COCH_3$

Ans (*a*) Cannizzaro reaction is given by C_6H_5CHO because it does not have α-hydrogen atom and rest of all contain α-hydrogen atom. So, these are not show Cannizzaro's reaction.

Q.38 Aldol condensation will not occur in **[Textbook]**

(a) HCHO (b) CH_3CH_2CHO
(c) CH_3COCH_3 (d) CH_3CHO

Ans (*a*) The carbonyl compounds having at least one α-hydrogen atom undergo condensation reaction in presence of dilute NaOH solution, this reaction is called as **aldol condensation**. As formaldehyde (HCHO) has no α-hydrogen atom attached to carbonyl group. It does not respond to this test.

Q.39 In the Cannizzaro reaction gives below,

$$2ArCHO \xrightarrow{OH^-} ArCH_2OH + AcCOO^-,$$

the slowest step is **[Textbook]**

(a) The attack of OH^- at the carbonyl group
(b) The transfer of hydride ion to the carbonyl group
(c) The abstraction of a proton from the carboxylic acid
(d) The deprotonation of $Ar—CH_2OH$

Ans (*b*) In the slow step of Cannizzaro reaction, the transfer of hydride ion to the carbonyl group takes place when the concentration of the base is low.

Q.40 To what state does ethanol reduce Cu(II)? **[Textbook]**

Ans Ethanol reduce Cu(II) to Cu(I) by forming Cu_2O (red-brown ppt.) in Fehling's test.

Q.41 The Cannizzaro's reaction is given by ..... . **[Textbook]**

Ans HCHO (aldehydes that do not have α-H).

Fill in the Blanks

Q.42 Methanol + Ammonia ⟶ ..... . **[Textbook]**

Ans $(CH_2)_6N_4$

Q.43 Complete the following reactions ..... .

$$(A) \xrightarrow[dil.\,H_2SO_4]{Hg^+} CH_3CHO \xrightarrow{(CH_3CO)_2O} (B)$$

[Textbook]

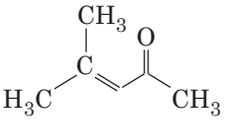
Ans $A = CH \equiv CH$, $B = CH_3CH(OCOCH_3)_2$

2 MARK *Questions*

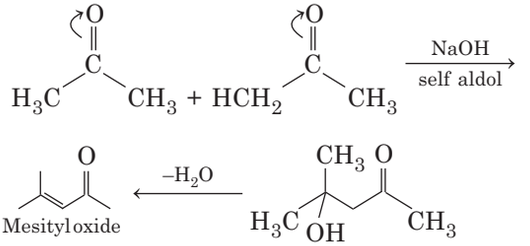
Exams' Questions

Q.44 How is acetone converted to mesityl oxide? **[2015]**

Ans

Mesityl oxide = 

α,β-unsaturated ketone



(2)

Q.45 What happens, when acetaldehyde reacts with iodine in NaOH solution? Give equation. **[2013, 2005]**

Ans When acetaldehyde reacts with iodine in NaOH solution, yellow precipitate of iodoform is obtained.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 3I_2 \xrightarrow{NaOH} CI_3CHO + 3HI$$

$$\underset{\substack{\text{Triiodo}\\\text{acetaldehyde}}}{CI_3CHO} + NaOH \longrightarrow \underset{\substack{\text{Iodoform}\\\text{(Yellow ppt.)}}}{CHI_3\downarrow} + \underset{\text{Sodium formate}}{HCOONa}$$

(2)

Q.46 What is Cannizzaro's reaction? **[2012 Instant, 2005]**

Ans This reaction is shown by only those aldehydes which do not contain α-H atom (e.g. HCHO, C_6H_5CHO). Such aldehyde when heated with concentrated sodium hydroxide solution undergo self oxidation and reduction. Thus, an alcohol and sodium salt of acid result.

e.g.

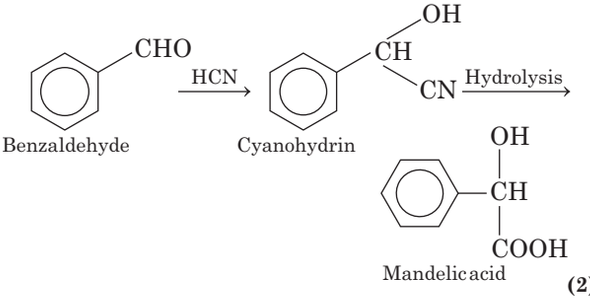
$$\underset{\text{Formaldehyde}}{2HCHO} + NaOH \longrightarrow \underset{\text{Sodium formate}}{HCOONa} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + NaOH \longrightarrow \underset{\text{Sodium benzoate}}{C_6H_5COONa} + \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

(2)

Q.47 What is the action of benzaldehyde with HCN? **[2012]**

Ans



(2)

Q.48 Identify x and y and name the reaction.

$$2C_6H_5CHO + NaOH(conc.) \longrightarrow x + y \quad \textbf{[2011]}$$

Ans $2C_6H_5CHO + \underset{(Conc.)}{NaOH} \longrightarrow \underset{(x)}{C_6H_5CH_2OH} + \underset{(y)}{C_6H_5COONa}$

Then, x is benzyl alcohol and y is sodium benzoate and reaction is known as Cannizzaro reaction. **(2)**

Q.49 What happens when acetone is treated with dilute NaOH? **[2010]**

Ans This reaction is an example of aldol condensation

$$(CH_3)_2C{=}O + CH_3COCH_3 \xrightarrow{\text{Dil. NaOH}} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}-CH_3-COCH_3$$

(2)

Q.50 Arrange HCHO, CH_3CHO and CH_3COCH_3 in the order of increasing reactivity towards HCN with reasons. **[2008]**

Ans Increasing order in reactivity towards HCN is:
$CH_3COCH_3 < CH_3CHO < HCHO$

For reason Refer to the text on page 86. **(2)**

Q.51 What happens when formaldehyde react with NH_3? **(2007, 2003, 2002, 2001)**

Ans Ammonia reacts with formaldehyde to form hexamethylene tetraamine $[(CH_2)_6N_4]$ called urotropine.

$$\underset{\text{Formaldehyde}}{6HCHO} + \underset{\text{Ammonia}}{4NH_3} \longrightarrow \underset{\text{Hexamethylene tetramine}}{(CH_2)_6N_4} + 6H_2O \quad \textbf{(2)}$$

Important Questions

Q.52 What happens when benzaldehyde is treated with Fehling's solution and why? Explain. **[Textbook]**

Ans Aldehydes that lack α-hydrogens, such as C_6H_5CHO cannot form an enolate and thus do not give a positive Fehling's test under usual conditions. **(2)**

Q.53 What happens when acetaldehyde reacts with iodine in dil. NaOH solution? Give equation. **[Textbook]**

Ans When acetaldehyde reacts with iodine in dil. NaOH solution then they are oxidised to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted into iodoform. **(2)**

Q.54 Identify X and Y in the series

$$CH_3CHO \xrightarrow[KMnO_4]{\text{Acidic}} X \xrightarrow{SOCl_2} Y \quad \textbf{[Textbook]}$$

Ans $CH_3CHO \xrightarrow[KMnO_4]{\text{Acidic}} \underset{\text{Acetic acid } (X)}{CH_3COOH} \xrightarrow{SOCl_2} \underset{\text{Acetyl chloride } (Y)}{CH_3COCl}$ **(2)**

Q.55 Name the compound in IUPAC system having molecular formula C_3H_5O, which can reduce Tollen's reagent. What is Tollen's reagent? **[Textbook]**

Ans Aldehydes can be reduced by Tollen's reagent. Ketones need strong oxidising agents to get reduced so, C_3H_6O is an aldehyde.

CH_3CH_2CHO, i.e. propanal is the compound which can reduce Tollen's reagent. **(2)**

Q.56 How will you convert the following?

(*i*) Propanone to propan-2-ol

(*ii*) Ethanal to 2-hydroxy propanoic acid

Ans (i) $\underset{\text{Propanone}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3} \xrightarrow[\text{Reduction}]{LiAlH_4} \underset{\text{Propan-2-ol}}{CH_3-\overset{\displaystyle OH}{\overset{|}{C}}HCH_3}$ **(1)**

(ii) Ethanal to 2-hydroxy propanoic acid

$$\underset{\text{Ethanal}}{H_3C-\overset{\displaystyle H}{\overset{|}{C}}=O} + HCN \longrightarrow \underset{\substack{\text{Acetaldehyde}\\ \text{cyanohydrin}}}{H_3C-\overset{\displaystyle H}{\overset{|}{C}}(OH)CN} \xrightarrow{2H_2O + HCl} \underset{\substack{\text{2-hydroxy}\\ \text{propanoic acid}}}{H_3C-\overset{\displaystyle H}{\overset{|}{C}}(OH)COOH}$$

(1)

Q.57 An organic compound, C_2H_4O gives a red precipitate when warmed with Fehling's solution. It also undergoes aldol condensation in the presence of alkali.

(i) Write the IUPAC name of the compound.

(ii) Write balanced equation for the reaction.

Ans (i) As the compound reduces Fehling solution, it should be an aldehyde.

Aldehyde is C_2H_5O or CH_3CHO.

IUPAC name: Ethanal **(1)**

(ii) $\underset{\text{Ethanal}}{2CH_3CHO} \xrightarrow{NaOH} \underset{\text{3-hydroxybutanal}}{CH_3CH(OH)CH_2CHO}$

(Aldol condensation) **(1)**

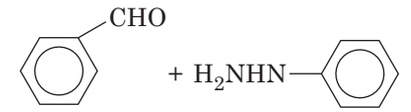
Q.58 Benzaldehyde does not reduce ..... but forms silver mirror with Tollen's reagent. (Fill in the blank)

Ans Fehling's solution **(2)**

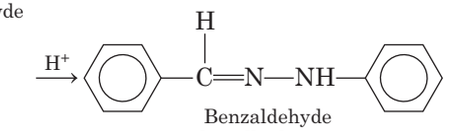
Q.59 Complete the following equation:

$$C_6H_5CHO + C_6H_5NHNH_2 \xrightarrow{H^+}$$

Ans



Benzaldehyde



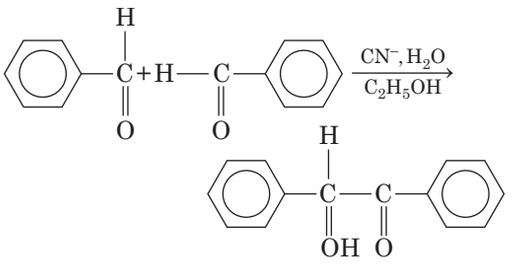
Benzaldehyde phenylhydrazone

(2)

Exams' Questions

Q.60 What is benzoin condensation? Give equation. **[2017]**

Ans When benzaldehyde is heated with aqueous ethanolic NaCN or KCN, it dimerises to form α-hydroxy ketone called benzoin and reaction is called benzoin condensation. It involves self condensation of an aromatic aldehyde in the presence of CN^- as catalyst,



(2)

Q.61 Suggest a chemical list to distinguish between pentan-2-one and pentan-3-one. Give equation. **[2016]**

Ans Pentan-2-one is a methyl ketone, therefore gives the iodoform test with I_2 and NaOH (NaOI).
Pentan-3-one does not give the iodoform test because it is not a methyl ketone.

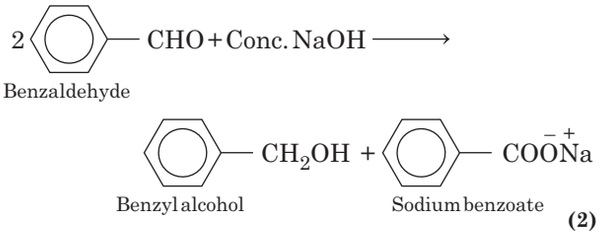
$$\underset{\text{Pentan-3-one}}{CH_3CH_2CH_2COCH_3} + 3NaOI \longrightarrow \underset{\text{(Yellow ppt.)}}{CHI_3\downarrow} + CH_3CH_2CH_2COONa + 2NaOH$$

$$\underset{\text{Pentan-3-one}}{CH_3CH_2COCH_2CH_3} + 3NaOI \longrightarrow$$

No yellow ppt. of CHI_3 **(2)**

Q.62 What is Cannizzaro's reaction? Give equation. **[2016]**

Ans **Cannizzaro reaction** Aldehydes which do not have α-H atoms undergo Cannizzaro reaction on treatment with concentrated alkali. In this reaction, one molecule of aldehyde is reduced to alcohol while another molecule is oxidised to salt of carboxylic acid.



(2)

Q.63 Hos does acetaldehyde react with (i) Tollen's reagent and (ii) Phenyl hydrazine? **[2016]**

Ans (i) **Reaction with Tollen's Reagent** When an aldehyde is warmed with a Tollen's reagent (ammoniacal silver nitrate), a silver mirror formed which appears on the wall of the test tube in which the reaction is carried out.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 2[Ag(NH_3)_2]^+OH^- \xrightarrow{\text{Warm}} CH_3COO^-NH_4^+ + 3NH_3 + H_2O + \underset{\substack{\text{Silver}\\\text{mirror}}}{2Ag\downarrow}$$ **(1)**

(ii) **Reaction with phenyl hydrazine** ($C_6H_5NH\cdot NH_2$)

$$H_3C\underset{H}{\overset{}{)}}C=O + H_2N\cdot NHC_6H_5 \xrightarrow{H^+} H_3C\underset{H}{\overset{}{)}}C=N\cdot NHC_6H_5 + H_2O$$

Acetaldehyde phenyl hydrazone **(1)**

3 MARK *Questions*

Exams' Questions

Q.64 Identify X and Y and name the reaction. **[2011]**

$$2C_6H_5CHO + NaOH(\text{Conc.}) \longrightarrow X + Y$$

Ans $\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + \underset{\text{(Conc.)}}{NaOH} \longrightarrow \underset{\substack{\text{Benzyl alcohol}\\(X)}}{C_6H_5CH_2OH} + \underset{\substack{\text{Sodium benzoate}\\(Y)}}{C_6H_5COONa}$

The reaction is known as aldol condensation. **(3)**

Q.65 What structural features are necessary for an organic compound to exhibit iodoform reaction? Give example. **[2010]**

Ans The compounds which exhibit iodoform reaction should have following structural features :

(i) $CH_3-\overset{\overset{O}{\|}}{C}-$ (acetyl) group in its structure or **(1)**

(ii) should have $CH_3\underset{\underset{OH}{|}}{CH}-$ group in it.

e.g.

$$CH_3COCH_3 + 3NaOI \xrightarrow{I_2/NaOH} CI_3COCH_3 + 3NaOH$$

$$CI_3COCH_3 + NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3\downarrow} + CH_3COONa$$ **(2)**

Q.66 What is Tollen's reagent and how it is prepared? **[2010]**

Ans Tollen's reagent ammoniacal silver nitrate solution. A dilute solution of NH_3 is added to a little $AgNO_3$ till white ppt. is formed.

$$AgNO_3 + 2NH_4OH \longrightarrow [Ag(NH_3)_2]^+NO_3^- + 2H_2O$$ **(3)**

Important Questions

Q.67 Distingusigh between acetaldehyde and acetone. **[Textbook]**

Ans Difference between acetaldehyde and ketone

S.No.	Test	CH_3CHO	CH_3COCH_3
1.	Schiff's reagent	Magneta colour is restored by *R*CHO	No reaction
2.	Tollen's reagent	Reduced by *R*CHO	No reduced
3.	Fehling's solution	Reduced by *R*CHO (except C_6H_5CHO)	Not reduced, α-hydroxy ketones reduce Tollen's reagent and Fehling's solution $(—\overset{\alpha}{C}H(OH)—CO—)$
4.	Iodoform test (Haloform test)	Only CH_3CHO gives this test	$R—\overset{O}{\overset{\|\|}{C}}—CH_3$ (all ketones containing acetyl group CH_3CO) gives this test.

(3)

Q.68 Distinguish between formaldehyde and acetaldehyde. **[Textbook]**

Ans **Difference between formaldehyde and acetaldehyde**

S. No.	Reaction/Test	HCHO	CH_3CHO
1.	Cannizzaro reaction	Yes (With no α-H)	No
2.	Aldol condensation	No	Yes (With at least one α-H)
3.	Haloform reaction	No	Yes
4.	With conc. NaOH solution	Cannizzaro reaction	resinous product
5.	With NH_3	Urotropine	$CH_3CH=NH$ (aldimine) that undergoes trimer formation $CH_3CH(NH—CH(CH_3))_2NH$

(3)

Q.69 Distinguish between ethyl alcohol and acetone. **[Textbook]**

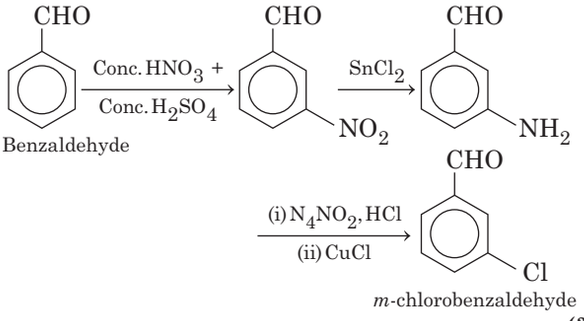
Ans Benzaldehyde and acetaldehyde

S. No.	Reaction/Test	C_6H_5CHO	CH_3CHO
1.	Fehling solution	Not reduced	Reduced (giving red ppt.)
2.	Cannizzaro reaction	Yes (with no α—H)	No
3.	Aldol condensation	No	Yes
4.	Iodoform test	No	Yellow ppt.

(3)

Q.70 Convert benzaldehyde to *m*-chlorobenzaldehyde. **[Textbook]**

Ans **Benzaldehyde to *m*-chlorobenzaldehyde**



(3)

Q.71 Give the structure and IUPAC name of the product obtained when propanal reacts with NaOH.

Ans $CH_3CH_2CHO + CH_3—\underset{\text{Propanal}}{CH_2}—CHO \xrightarrow{NaOH}$

$CH_3—CH_2—CH(OH)—CH(CH_3)—CHO$

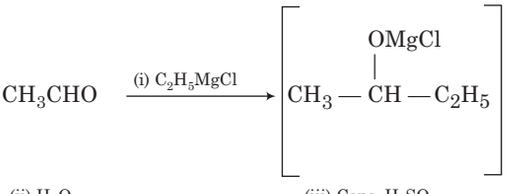
3-hydroxy-2-methyl pentanal

(3)

Q.72 Identify *A*, *B* and *C* in the following sequence of the reaction.

$CH_3CHO \xrightarrow[(ii)\ H_2O]{(i)\ C_2H_5MgCl} A \xrightarrow{(iii)\ Conc.\ H_2SO_4} B \xrightarrow{HBr/Peroxide} C$

Ans



$\xrightarrow{(ii)\ H_2O} CH_3—CH(OH)—C_2H_5 \xrightarrow{(iii)\ Conc.\ H_2SO_4}$ (*A*)

$CH_3CH=CHCH_3 \xrightarrow{HBr/peroxide} H_3C—CH(H)—CH(Br)—CH_3$

But-2-ene (*B*)

7 MARK *Questions*

Exams' Questions

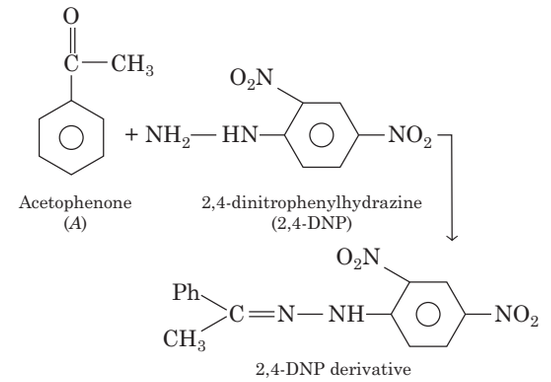
Q.73 An organic compound (*A*) with molecular formula C_8H_8O forms an orange red precipitate with 2, 4 dinitrophenyl hydrazine and gives yellow precipitate on heating with iodine in presence of sodium hydroxide. It neither reduces Tollen's reagent nor Fehling solution and it also does not decolourise bromine water or Baeyer's reagent.

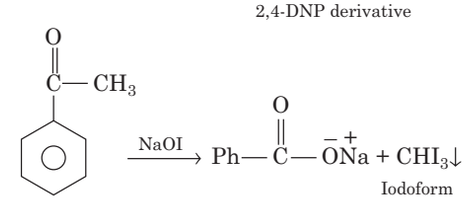
On drastic oxidation with chromic acid, it gives a carboxylic acid (*B*) having molecular formula $C_7H_6O_2$. Identify the compound (*A*) and (*B*) and explain in detail the reactions involved. **[2018]**

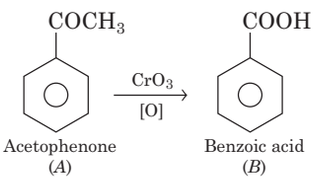
Ans The given organic compound (*A*) with molecular formula C_8H_8O forms an orange red ppt. with 2, 4-DNP and does not reduce Tollen's reagent and Fehling solution. So, it must be a ketone. It also gives yellow precipitate on heating with iodine in presence of sodium hydroxide. So, it must have $—COCH_3$ group.

On drastic oxidation, compound (*A*) gives a carboxylic acid with molecular formula $C_7H_6O_2$. That clearly indicates that organic compound (*A*) is acetophenone. **(3)**

Following reactions are involved:







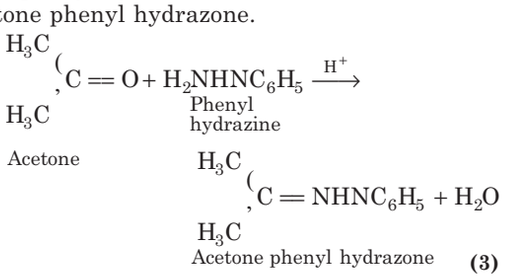
(4)

Q.74 How does acetone react with

(i) phenyl hydrazine? (ii) $NaHSO_3$ and

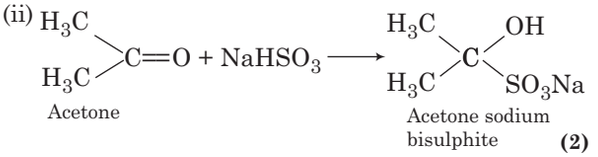
(iii) I_2/*aq*. KOH **[2017]**

Ans (i) With phenyl hydrazine, acetone forms acetone phenyl hydrazone.



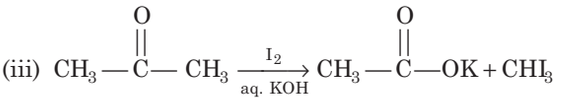
(3)

(ii)



(2)

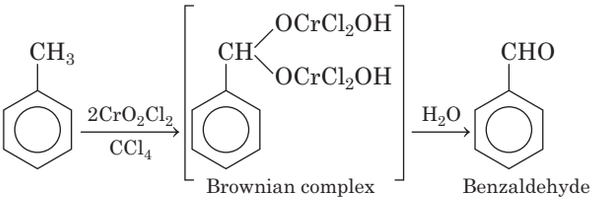
(iii)



Acetone reacts with I_2/aq KOH to form yellow precipitate of iodoform. **(2)**

Q.75 How is benzaldehyde prepared by Etard's reaction? How does it react with (i) conc. HaOH and (ii) phenyl hydrazine? **[2010]**

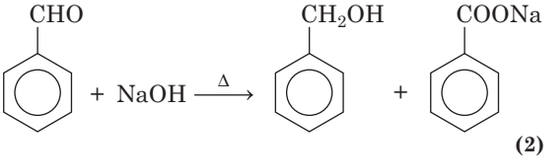
Ans **Preparation of Benzaldehyde** Toluene when treated with chromyl chloride in CCl_4 or CS_2 a brown complex is precipitated as intermediate when can be isolated and decomposed to form benzaldehyde.



(3)

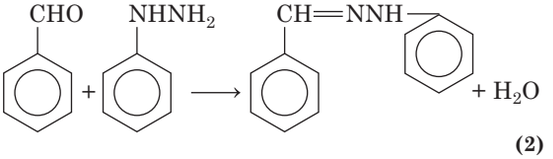
Reaction

(i) **With Conc.NaOH** Benzaldehyde when treated with conc. NaOH yield a mixture of alcohol and sodium salt of benzoic acid.



(2)

(ii) **With phenyl hydrazine** Produce phenyl hydrozone.



(2)

Important Questions

Q.76 How can you bring out the following conversions?

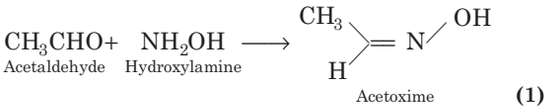
(i) Acetaldehyde to acetoxime **[Textbooks]**

(ii) Methanal to ethanal

(iii) Ethanal to 2-hydroxybutanoic acid

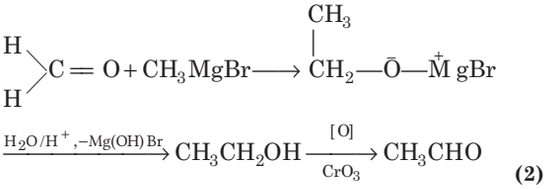
(iv) Acetylene to acetone (4 steps)

Ans (i) Acetaldehyde to acetoxime



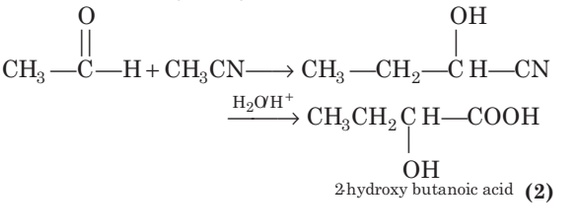
(1)

(ii) Methanal to ethanal



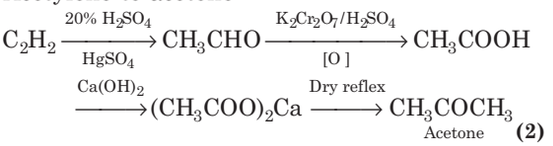
(2)

(iii) Ethanal to 2-hydroxybutanoic acid.



(2)

(iv) Acetylene to acetone



(2)

Q.77 Discuss the reaction used to distinguish between aldehydes and ketones? **[Textbooks]**

Ans **Distinguish between aldehydes and ketone**

The two compounds shows lot of distinct effects when mixed with certain reagents. This process is the basis for many chemical tests that help or spot the type of chemical under study.

Thus, in distinguishing the two, these tests often show varied results.

(i) For the Schiff's test, aldehydes show a pink colour while ketones don't have any colour at all.

(ii) In Fehling's test, aldehyde shows an occurrence of a reddish precipitate while in ketones there's none.

(iii) For Tollen's test, a black precipitate is formed while in ketones there's again none.

(iv) With the sodium hydroxide test, aldehydes show a brownish resinous material (except for formaldehyde) while ketones don't have any reaction to such.

(v) For the reagent sodium nitroprusside plus some drops of sodium hydroxide, aldehydes emit a deep reddish colour while ketones exhibit a reddish colour later transforms to orange. **(7)**

TOPIC TEST 2

1. Which of the following reagents will not be able to distinguish between pentanol and pentan-2-one?

(a) Br_2 in CCl_4 (b) Fehling's solution

(c) Tollen's reagent (d) I_2 in NaOH

2. By which of the following reactions is benzyl alcohol obtained from benzaldehyde?

(a) Aldol condensation (b) Etard reaction

(c) Rosenmund reduction (d) Cannizzaro reaction

[***Ans.*** **1.** (a), **2.** (d)]

3. Methyl ketones are characterised by ..... .

[***Ans.*** iodoform reaction]

4. Why are the boiling points of aldehydes and ketones higher than hydrocarbons and ethers of comparable molecular masses?

5. Rearrange the following compounds in decreasing order boiling points:

CH_3CH_2OH, CH_3CHO, $CH_3CH_2CH_3$

6. Describe the following reactions:

(i) Clemmensen's reduction

(ii) Wolff-Kishner reduction

7. Give chemical tests to distinguish between:

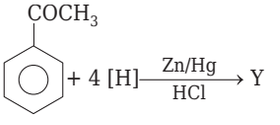
(i) Acetophenone and benzophenone

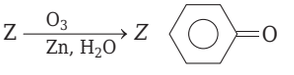
(ii) Ethanal and propanal

(iii) Propanone and propanal

8. Identify *X, Y* ad *Z* in the following reactions:

(i) $HCHO + NaOH(dil.) \longrightarrow X$

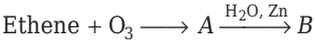
(ii) 

(iii) 

9. (i) Write short notes on Cannizzaro reaction?

(ii) Show how propanal is obtained from ethanol?

(iii) Complete the reaction given below:



Chapter Test

1 MARK *Questions*

1 The formation of cyanohydrin from a ketone is a/an example of **[Textbook]**
(a) electrophilic addition
(b) nucleophilic addition
(c) nucleophilic substitution
(d) electrophilic substitution

2 When acetaldehyde is heated with Fehling's solution, it gives a precipitate of **[Textbook]**
(a) Cu
(b) CuO
(c) Cu_2O
(d) Cu + CuO + Cu_2O

3 In Etard reaction, which of the following is used to oxidise toluene to benzaldehyde? **[Textbook]**
(a) H_2O_2 (b) $KMnO_4$
(c) Chromyl chloride (d) Cl_2

4 The reagent with which both acetaldehyde and acetone react easily is **[Textbook]**
(a) Fehling solution (b) Grignard reagent
(c) Schiff's reagent (d) Tollen's reagent

5 Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution.
(a) Butan-1-ol (b) Butan-2-ol
(c) Both (a) and (b) (d) None of these

[***Ans.*** **1.** (b), **2.** (c), **3.** (c), **4.** (b), **5.** (b)]

6 The precipitate formed when an aldehyde reacts with Fehling's solution is ..... . [***Ans.*** Cu_2O]

7 Formaldehyde reacts with ammonia to give ..... .
[***Ans.*** $(CH_2)_6N_4$ (Hexamethylene tetraamine)]

8 Clemmensen's reduction convert carbonyl group to methane group. Explain it.

9 Write the structure of the compound 4-oxopentanol.

2 MARK *Questions*

10 Why do aldehyde and ketones have high dipole moments?

11 Oximes are more acidic than hydroxylamine. Why?

12 Give reason in one or two sentence hydrazones of aldehydes and ketones are not prepared in acidic medium.

13 What is haloform reaction?

14 How all you differentiate between ethyl alcohol and acetone?

3 MARK *Questions*

15 Arrange the following compounds in increasing order of their boiling points with plaurible explanation. **[Textbook]**

CH_3CH_2OH, CH_3OCH_3, CH_3CHO, CH_3CH_3

16 Write the chemical reaction to effect the following transformation.
(i) Butan-1-ol to butanoic acid
(ii) Butanal to butanoic acid
(iii) But-2-ene to ethanal

17 Give simple chemical test to distinguish between the following pairs of compound.
(i) Ethanal and propanal
(ii) Propanal and propanone

18 What products will be formed on reaction of propanal with 2-methyl propanal in the presence of NaOH? Write the name of the reaction also.

7 MARK *Questions*

19 An organic compound $A(C_3H_5O)$ is resistant to oxidation but forms compound $B(C_3H_8O)$ on reduction. B reacts with HBr to form the compound C, C with Mg forms Grignard reagent D which reacts with A to form a product which on hydrolysis gives E. Identify A to E. Write the equations involved.

20 Explain with equation how aldehydes and ketones can be prepared from calcium salts of organic acids. What happens, when acetaldehyde reacts with the following substances? **[Textbook]**
(i) NH_2OH (ii) Phenyl hydrazine
(iii) Hydrogen in presence of nickel catalyst.