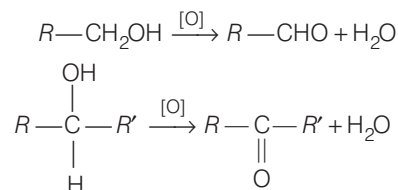


Aldehydes, Ketones and Carboxylic Acids

- The C=O group is known as the carbonyl group and the compounds containing C=O group are known as **carbonyl compounds**. In aldehydes, the carbonyl group is bonded with a carbon and a hydrogen, while in ketones, it is bonded with two carbon atoms. Aldehydes are named by adding suffix 'al' and ketones by adding suffix 'one'.

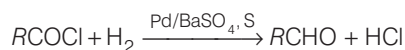
- Preparation of aldehydes and ketones** are obtained by the oxidation of 1° and 2° alcohols respectively by using PCC (Pyridine Chloro Chromate) or K₂Cr₂O₇ / H₂SO₄ as reagents.



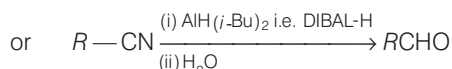
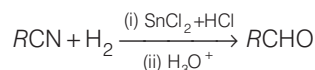
These are also obtained by dehydrogenation of alcohols, ozonolysis of alkenes, hydration of alkynes.

3. Preparation of Aldehydes

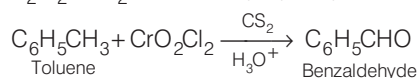
- Aldehydes are obtained by the reduction of carbonyl chloride with Pd / BaSO₄, S. (Rosenmund reduction).



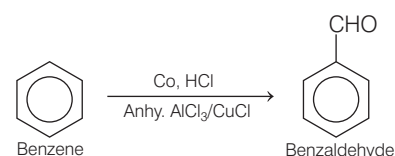
or by the reduction of —CN with SnCl₂ + HCl (Stephen reduction) followed by hydrolysis.



- Etard reaction** is also used to synthesise benzaldehyde from toluene by treating it with CrO₂Cl₂ / CS₂ followed by hydrolysis.

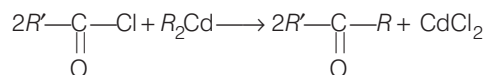


• Gattermann-Koch reaction

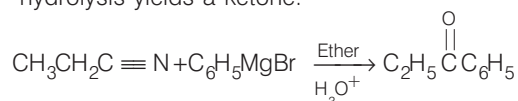


4. Preparation of Ketones

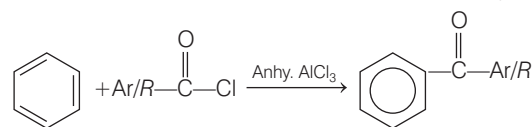
- Treatment of acyl chlorides with dialkyl cadmium give ketones.



- Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.



- Treatment of benzene or substituted benzene with acid chloride in presence of anhyd. AlCl₃ gives ketone. This reaction is called Friedel Craft's acylation.

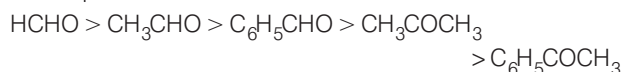


5. Physical Properties

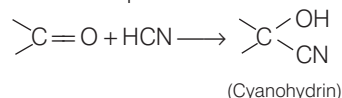
- Boiling points of aldehydes and ketones** are higher than hydrocarbons and ethers of comparable molecular masses.
- The solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain.

6. Chemical Properties

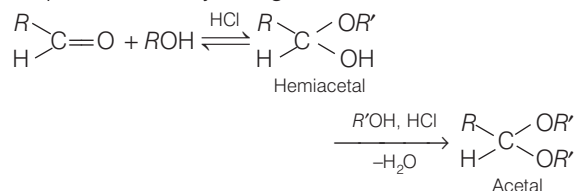
The order of reactivity of aldehydes and ketones for nucleophilic addition reactions are



- Carbonyl compound form **cyanohydrin** when treated with HCN in the presence of a base.

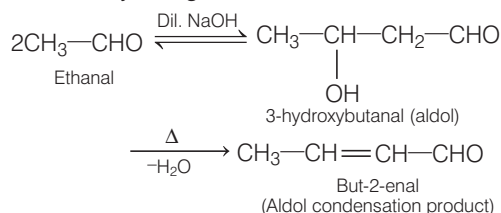


- Aldehydes form **hemiacetal** and **acetal** when treated with one or two equivalents of alcohol respectively in the presence of dry HCl gas.



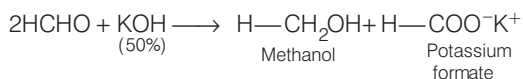
Ketones in this reaction form ketals.

- Carbonyl compounds form **2,4-DNP derivatives** (orange or yellow or red ppt.) with 2,4-DNP (2,4-dinitrophenyl hydrazine), Brady's reagent.
- Aldehydes reduce Tollen's reagent (ammoniacal silver nitrate) into silver mirror, Fehling's solution into red ppt. of Cu_2O and Benedict's solution into red ppt. These reactions are not given by ketones.
- $>C=O$ group is reduced to CH_2 group by using Zn-Hg/conc. HCl (Clemmensen reduction) or by using $NH_2-NH_2 + KOH$ (Wolff-Kishner reduction).
- Aldehydes and ketones containing α -H atoms undergo **aldol condensation** in the presence of dilute alkali as catalyst, e.g.



β -hydroxy aldehydes or ketones are collectively called **aldols** and the reaction is called **aldol condensation**.

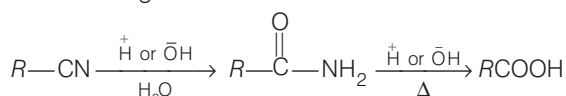
- When aldehydes having lack of α -H atoms are treated with 50% alkali, it disproportionates to give reduction product, alcohol and oxidised product, salt of acid. This reaction is called **Cannizzaro reaction**.



- Carbon compounds containing a carboxyl functional group ($-COOH$) are known as **carboxylic acids**. Their names are derived by replacing the terminal 'e' from the name of corresponding straight chain alkane with suffix 'oic acid'.

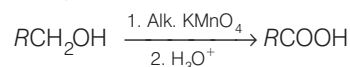
8. Preparation of Carboxylic Acids

- Nitriles are first hydrolysed to amides and then to acids in the presence of H^+ or $\bar{OH}$ as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.

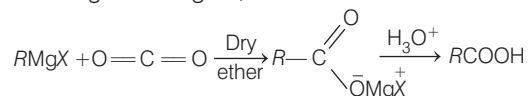


- Aromatic acids are obtained by vigorous oxidation of alkyl benzene with chromic acid or acidic or alkaline $KMnO_4$.

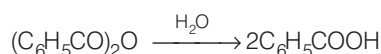
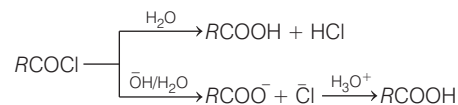
- From primary alcohols,



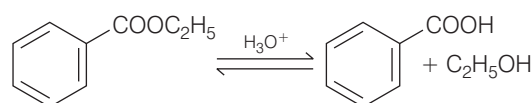
- From Grignard reagent,



- From acyl halide and anhydrides,



- From esters,

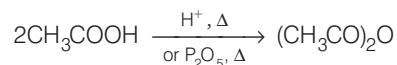


9. Physical Properties

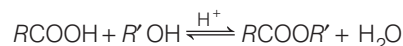
- Carboxylic acids have higher boiling points as compared to hydrocarbons, aldehydes and ketones, because they have high extent of hydrogen bonding with water due to which they exist as associated molecules.
- Melting point of an acid containing even number of carbon atoms is higher than the adjacent members containing odd number of carbon atoms.

10. Chemical Properties

- Carboxylic acids are stronger acids than phenols because carboxylate ion is much more resonance stabilised than phenoxide ion. Electron withdrawing groups (EWG) increase the stability of the carboxylate ion by dispersing the negative charge, while electron donating group decreases the stability of the carboxylate ion by intensifying the negative charge.
- Carboxylic acids on heating with mineral acids such as H_2SO_4 or P_2O_5 give anhydride.



- Carboxylic acids are esterified with alcohols or phenols in presence of a mineral acids such conc. H_2SO_4 or HCl gas.

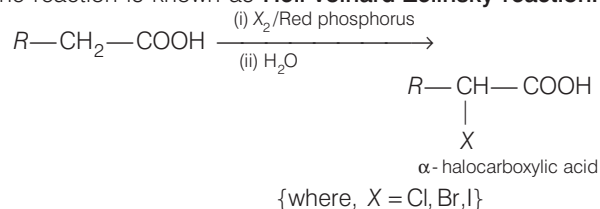


- Carboxylic acids react with PCl_3 , PCl_5 and $SOCl_2$ to give acyl chloride.
- Carboxylic acid react with ammonia to form amides.



- Carboxylic acids having an α -hydrogen are halogenated at the α -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α -halocarboxylic acids.

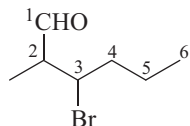
The reaction is known as **Hell-Volhard-Zelinsky reaction**.



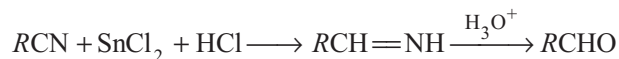
11. Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and *meta*-directing group. However, they do not undergo Friedel-Crafts reaction because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.

Practice Questions

- Carbonyl compounds are the constituents of
(a) fabrics (b) flavouring
(c) plastics and drugs (d) All of these
- The name of simplest aromatic aldehyde carrying the aldehyde group on a benzene ring is/are
(a) carbaldehyde
(b) benzene carbaldehyde
(c) benzaldehyde
(d) Both (b) and (c)
- Write IUPAC name of the following :



- 2-bromo-2-ethyl hexanal
 - 3-bromo-2-methyl hexanal
 - 2-methyl-3-bromo hexanal
 - 3-bromo-2-formyl hexane
- The bond angle and structure of carbonyl compounds respectively are
(a) 120° and trigonal planar
(b) 109°28' and tetrahedral
(c) 120° and tetrahedral
(d) 109°28' and trigonal planar
 - The most suitable reagent for the conversion of $R-CH_2-OH \longrightarrow R-CHO$ is
(a) $KMnO_4$
(b) $K_2Cr_2O_7$
(c) H_2SO_4
(d) PCC (pyridinium chlorochromate)
 - Alcohol vapours are passed over which of the following catalysts to give aldehydes and ketones?
(a) S or Pd (b) Ag or Cu
(c) F or Cl (d) Li or K
 - The reaction,



is known as

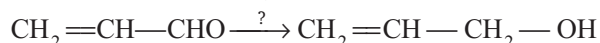
- Etard reaction
 - Haloform reaction
 - Gattermann-Koch reaction
 - Stephen reaction
- The major product of following reaction is

$$R-C \equiv N \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlH (iBu)_2} ?$$
 - $RCHO$
 - $RCONH_2$
 - $RCOOH$
 - RCH_2NH_2
 - Which of the following substrates give the same product on the reduction with DIBAL-H?
 - $CH_3-(CH_2)_9-CN$ and $CH_3(CH_2)_9-COOH$
 - $CH_3-(CH_2)_9-CN$ and $CH_3(CH_2)_9-COOC_2H_5$
 - $CH_3-(CH_2)_9-COOH$ and $CH_3(CH_2)_9-CHO$
 - $CH_3(CH_2)_9-COOH$ and $CH_3(CH_2)_9-COOC_2H_5$
 - Reaction by which benzaldehyde cannot be prepared is
 - + CrO_2Cl_2 in CS_2 followed by H_3O^+
 - + $CO + HCl$ in the presence of anhyd. $AlCl_3$
 - + H_2 in the presence of $Pd-BaSO_4$
 - + Zn/Hg and conc. HCl
 - The compounds methanal, ethanal and propanone are miscible with water because they form
 - van der Waals' forces with water
 - 'H'-bonding with water
 - dipole-dipole bond with water
 - ion-dipole bond with water

12. Identify the example in which nucleophilic addition followed by elimination reaction occur respectively in the carbonyl compound.

(a) Addition of Grignard reagent
(b) Addition of sodium sulphide
(c) Addition of HCN
(d) Addition of NH_3

13. Consider the reaction given below.



Which of the following is the suitable reagent for the conversion of following reaction?

(a) NaBH_4 (b) Ni / H_2
(c) $\text{Zn} / \text{Hg} / \text{HCl}$ (d) Red P + HI

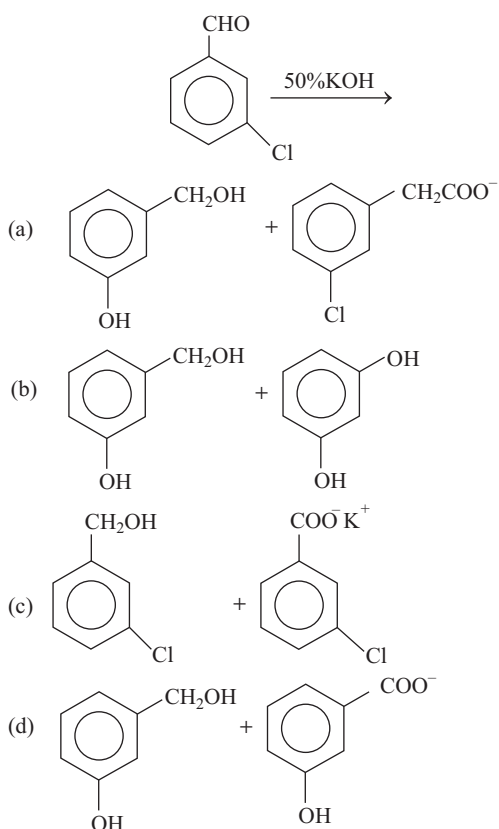
14. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained due to the formation of

(a) CuO (b) Cu_2O
(c) CuSO_4 (d) $\text{Cu}^{2+} + \text{OH}^-$

15. Which of the following compounds produces an orange-red precipitate with 2, 4-DNP reagent?

(a) Acetamide (b) Dimethyl ether
(c) Butanone (d) Propylbutanoate

16. Predict the products in the given reaction.



17. Some higher members of aliphatic carboxylic acids known as fatty acids occur in natural fats as esters of glycerol. How many C-atoms do they contain?

(a) $\text{C}_{12}-\text{C}_{18}$ (b) $\text{C}_{10}-\text{C}_{15}$
(c) C_5-C_{10} (d) $\text{C}_{20}-\text{C}_{30}$

18. What is the common name of 2-methylpropanoic acid?

(a) Adipic acid
(b) Crotonic acid
(c) Isobutyric acid
(d) Acrylic acid

19. Select the acid(s) which cannot be prepared by Grignard reagent?

(a) Acetic acid (b) Succinic acid
(c) Formic acid (d) All of these

20. Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to

(a) more extensive association of carboxylic acid via van der Waals' force of attraction
(b) formation of carboxylate ion
(c) formation of intramolecular H-bonding
(d) formation of intermolecular H-bonding

21. Which of the following reagents is/are used for the conversion of ethanoic acid to ethanoic anhydride?

(a) SOCl_2, Δ (b) PCl_3, Δ
(c) $\text{P}_2\text{O}_5, \Delta$ (d) All of these

22. Diborane easily reduce the functional group such as

(a) acid (b) ester
(c) nitro (d) halo

23. Name the product formed during the decarboxylation of malonic acid.

(a) Acetic acid (b) Ethanone
(c) Propanone (d) Formic acid

24. Aromatic carboxylic acids do not undergo Friedel-Crafts reaction because

(a) carboxyl group acts as an activating and *meta*-directing group
(b) carboxyl group act as a deactivating and *ortho* and *para* directing group
(c) carboxyl group act as an activating and *ortho*-directing group
(d) carboxyl group acts as deactivating and the catalyst

25. Which of the following acid is used in rubber, textile, dyeing, leather and electroplating industries?

(a) Hexanedioic acid
(b) Ethanoic acid
(c) Methanoic acid
(d) Sodium benzoate

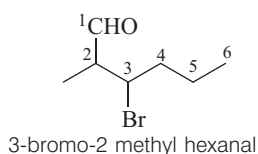
ANSWERS

1. (d)	2. (d)	3. (b)	4. (a)	5. (d)	6. (b)	7. (d)	8. (a)	9. (b)	10. (d)
11. (b)	12. (d)	13. (a)	14. (b)	15. (c)	16. (c)	17. (a)	18. (c)	19. (a)	20. (d)
21. (c)	22. (a)	23. (a)	24. (b)	25. (c)					

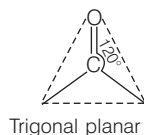
Hints & Solutions

1. (d) Carbonyl compounds are of almost importance to organic chemistry. They are the constituents of fabrics, flavourings, plastics and drugs.

3. (b) The priority order of functional group is $\text{—CHO} > \text{Br}$.
Therefore, IUPAC name of the given compound is as follows :



4. (a) The bond angles are approximately 120° as expected of a trigonal planar structure in the carbonyl compounds.



5. (d) The most suitable reagent for the conversion of alcohol ($R\text{CH}_2\text{—OH}$) to aldehyde ($R\text{—CHO}$) is PCC :



Pyridinium chlorochromate is a mild oxidising agent which causes the conversion of alcohol to aldehyde and not carboxylic acid.

Whereas, $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 are strong oxidising agents which causes conversion of alcohol directly to acid and H_2SO_4 is a dehydrating agent.

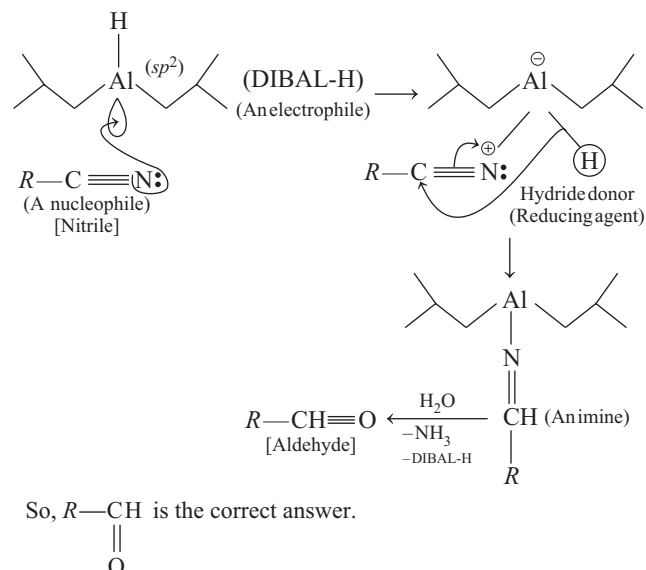
Thus, they cannot be used for the conversion.

6. (b) Alcohol vapours are passed over heavy metal catalysts (Ag or Cu) to give aldehydes and ketones. Primary and secondary alcohols give aldehydes and ketones respectively.

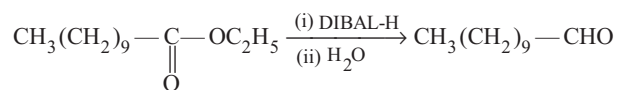
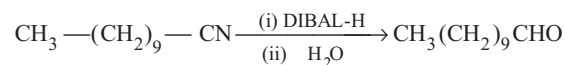
7. (d) $\text{RCN} + \text{SnCl}_2 + \text{HCl} \rightarrow \text{RCH}=\text{NH} \xrightarrow{\text{H}_3\text{O}^+} \text{RCHO}$

This reaction is called Stephen reaction, where nitriles are reduced to corresponding imine with stannous chloride in the presence of HCl, which on hydrolysis gives corresponding aldehyde.

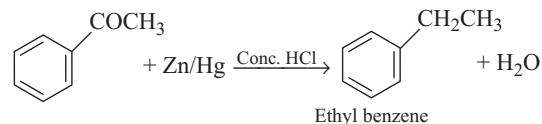
8. (a) The mechanism of the reaction is as follows :



9. (b) Nitrile are selectively reduced by DIBAL-H to imines followed by hydrolysis to aldehyde. Esters are also reduced to aldehydes with DIBAL-H.

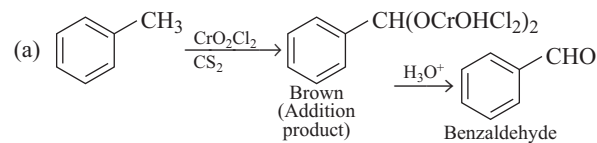


10. (d) Reaction (d) will not give benzaldehyde.

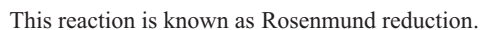


This reaction is known as Clemmensen reduction.

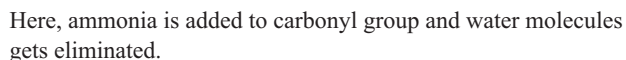
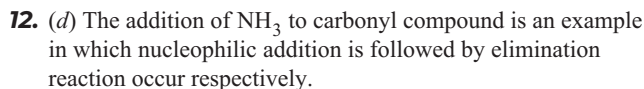
Rest of the reactions will give benzaldehyde.



This reaction is known as Etard reaction.

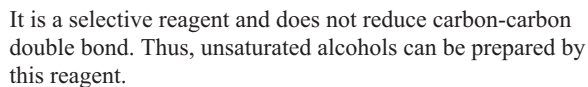


- 11. (b)** The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions because they form hydrogen bonding with water.

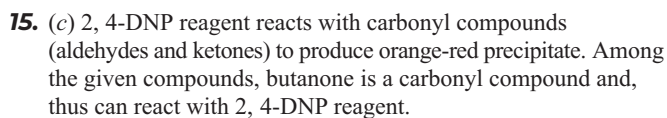


Another example in which the nucleophilic addition is followed by elimination is the addition of alcohols.

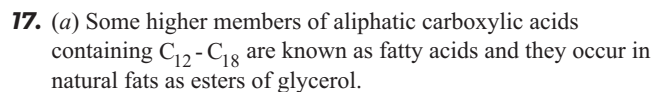
- 13.** (a) The suitable reagent for the given conversion is NaBH_4 .



- 14. (b)** On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained due to the formation of Cu_2O . Aldehydes are oxidised to corresponding carboxylate anion. The reaction involved is as follows :



16. (c) When *m*-chlorobenzaldehyde is treated with 50% alkali, it undergoes oxidation to give an acid salt as well as reduction to give an alcohol. This reaction is called Cannizzaro's reaction and the products formed as shown below :

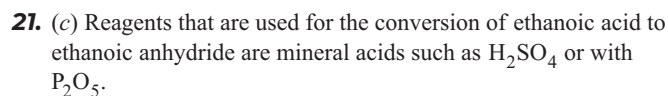
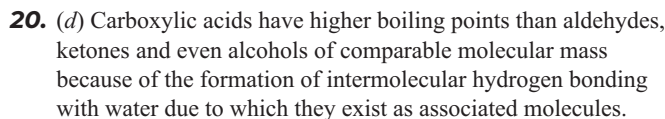


Therefore, the correct option is (a).

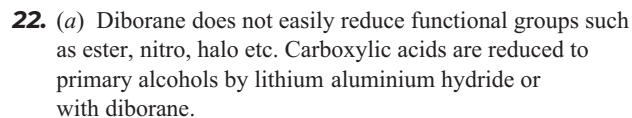
- 18.** (c) The structure of compound 2-methyl propanoic acid is shown below :



- 19** (a) The major product of the given reaction is benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$). On vigorous oxidation of alkyl benzene with acidic or alkaline KMnO_4 , aromatic acids are obtained. During oxidation of alkyl benzene, the aromatic nucleus remains intact and the entire chain is oxidised to $-\text{COOH}$ group irrespective of the length of carbon chain.



Reaction is as follows :



- 23. (a)** The decarboxylation of malonic acid is shown below :

