ALDEHYDES, KETONE AND CARBOXYLIC ACID

CHAPTER 12

INTRODUCTION

Both aldehydes & ketones contain carbonyl group as their functional group.

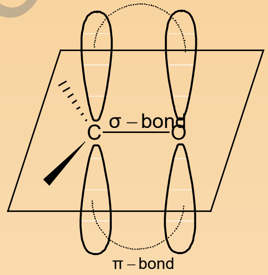
Structure of carbonyl group

Both aldehydes & ketones have carbonyl group as the functional group. The carbonyl carbon is sp^2 hybridized & it uses sp^2 hybrid orbitals to form 3σ bonds, one with oxygen atom & remaining 2 with two other atoms or groups (R or H). All these 3σ bonds lie in same plane at the angle of 120°.

The unhybridized p – orbital of carbonyl carbon form π - bond with oxygen atom by sidewise overlapping with half-filled p – orbital of oxygen atom.

Since carbon & oxygen have different values of electronegativity, the bond between carbon & oxygen is polar. Infect electron density around the oxygen atom is increased which causes the development of partial positive charge (δ+) on carbon & partial negative charge (δ–) on oxygen.

Thus the carbonyl carbon is an electrophilic & carbonyl oxygen is nucleophilic Centre.



Orbital picture of carbonyl group

GENERAL METHODS OF PREPARATION OF ALIPHATIC ALDEHYDES & KETONES

1. From Alcohols

(a) ***By Direct oxidation:*** Aldehydes are prepared by oxidation of 1° alcohols. Refer to Alcohols

(b) **By catalytic dehydrogenation**

When vapours of 1° or 2° alcohols are passed over copper gauze, they get dehydrogenated to form aldehydes or ketones.

$$\underset{\text{n-propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow{Cu/573K} \underset{\text{Propionaldehyde}}{CH_3CH_2CHO} + H_2$$

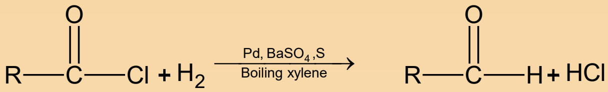
Dehydrogenation reaction is a better method of preparation because there is no risk of further oxidation of aldehyde.

(c) **By using PCC**

PCC stands for pyridinium chlorochromate. It is an equimolar mixture of CrO_3, HCl and pyridine. It is used to oxidize 1° alcohol to aldehyde and 2° alcohol to ketones without affecting double or triple bond.

2. From Acid chlorides

Aldehydes are prepared from acid chlorides by reaction with H_2 in the presence of palladium catalyst supported on $BaSO_4$.



$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow[\text{Boiling xylene}]{Pd,\ BaSO_4,S} R-\overset{O}{\overset{\|}{C}}-H + HCl$$

(Rosamund's reduction)

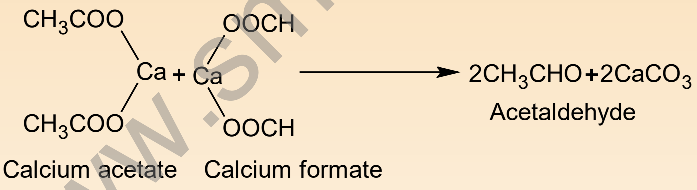
Ketones are obtained by reacting acid chlorides with diallyl cadmium.

$$2RCOCl + CdR'_2 \longrightarrow 2RCOR' + CdCl_2$$

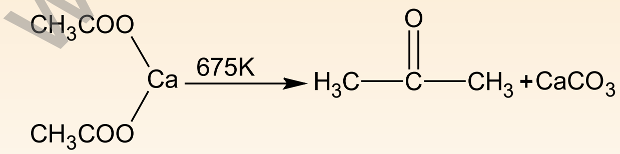
3. From fatty acids

(a) **By heating calcium salt of fatty acid**

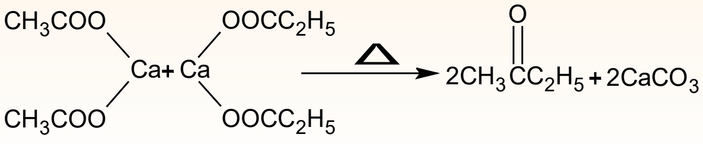
Aldehydes are obtained by heating calcium salt of fatty acids with calcium format.



Ketones are formed by distilling calcium salt of fatty acids alone.



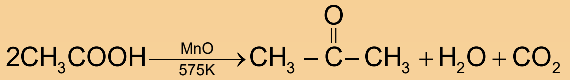
Similarly mixed ketones, can also be obtained by similar reactions:



(b) **By passing vapours of fatty acids over manganese oxide**

In this method, formic acid alone gives formaldehyde. Acetic acid gives acetone & the mixture of two acids gives acetaldehyde.

$$2HCOOH \xrightarrow[575K]{MnO} HCHO + H_2O + CO_2$$



$$2CH_3COOH \xrightarrow[575K]{MnO} CH_3 - \overset{\overset{\displaystyle O}{||}}{C} - CH_3 + H_2O + CO_2$$

$$CH_3COOH + HCOOH \xrightarrow[575K]{MnO} CH_3CHO + H_2O + CO_2$$

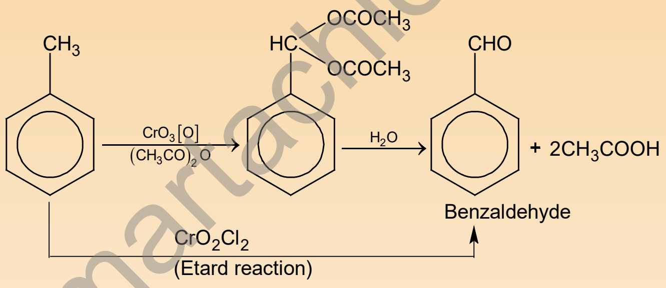
4. **From Alkynes:** (Refer to hydrocarbons)

5. **By reductive ozonolysis of alkenes:** *(*Refer to hydrocarbons)

PREPARATION OF AROMATIC ALDEHYDES & KETONES

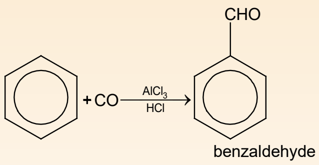
1. **By oxidation of alkyl benzene**

Aromatic aldehydes are obtained by oxidation of side chain in the aromatic ring.



3. **By Gattermann Koch Reaction**

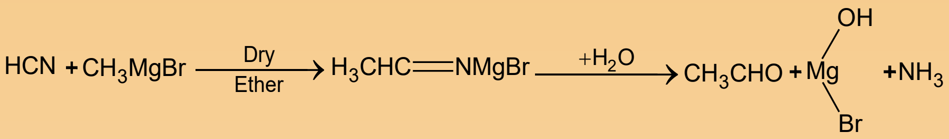
In this method aromatic aldehydes are prepared by formylation of aromatic ring with carbon monoxide.



4. **From Grignard's reaction**

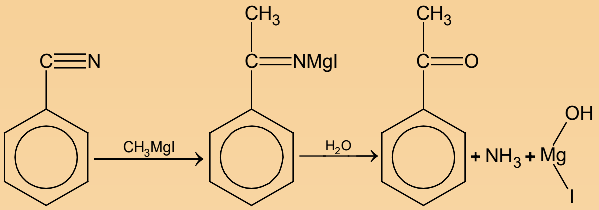
Both aliphatic & aromatic aldehyde can be obtained by this method.

HCN on treatment with Grignard's reagent & subsequently followed by hydrolysis yield an aldehyde.



$$HCN + CH_3MgBr \xrightarrow[\text{Ether}]{\text{Dry}} H_3CHC{=}NMgBr \xrightarrow{+H_2O} CH_3CHO + Mg(OH)Br + NH_3$$

Similarly



PHYSICAL PROPERTIES OF ALDEHYDES & KETONES

(i) **Physical state**

Most of aldehydes (except formaldehyde which is a gas) are liquids at room temperature. The lower ketones are colourless liquids and have pleasant smell.

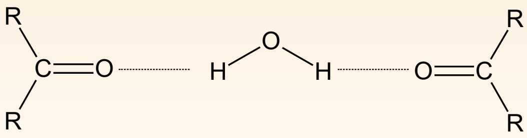
(ii) **Boiling points**

Aldehydes & ketones have relatively high boiling points as compared to hydrocarbons of comparable molecular masses due to polar carbonyl group, which bring stronger intermolecular dipole – dipole interactions between the opposite ends of C = O dipoles.

Ketones are relatively more polar than their corresponding isomeric aldehydes due to the presence of two electron repelling alkyl group around the carbonyl carbon.

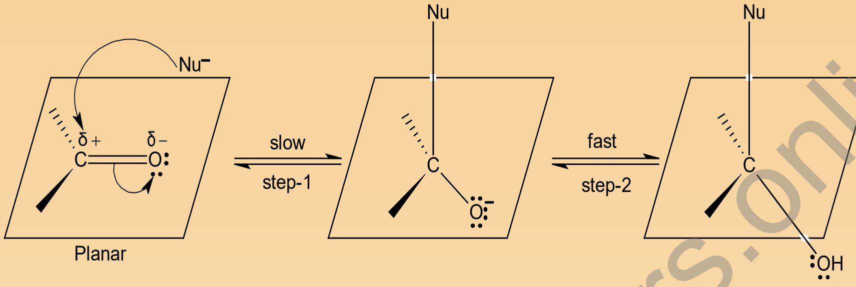
(iii)**Solubility**

The lower members of aldehydes & ketones (up to four carbon atoms) are soluble in water. It is due to their capability of forming hydrogen bonds with water molecules. The solubility of these compounds in water decreases with the increase in the size of alkyl group because of the increase in magnitude of non-polar part in the molecule.



CHEMICAL PROPERTIES

Aldehydes & ketones are highly reactive compounds, they undergo nucleophilic addition reactions. Their reactivity is due to presence of a polar carbonyl group. The positively charged carbon atom of carbonyl group is readily attacked by nucleophilic species for initiation of the reaction. This leads to formation of intermediate anion which further undergoes the attack of H^+ ion or other positively charged species to form the final product. The reaction in general may be represented as:

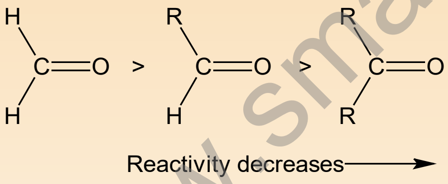


Relative reactivity of aldehydes & ketones

In general ketones are less reactive than aldehydes on a account of following facts:

(i) Electron releasing effect of two alkyl groups, decreases the magnitude of positive charge on ketones.

(ii) Steric effect caused by two alkyl groups also hinders the approach of the nucleophile to the carbonyl carbon.



TYPE OF CHEMICAL REACTIONS IN CARBONYL COMPOUNDS

(i) Addition across C = O bond.

(ii) Replacement of carbonyl oxygen by other groups.

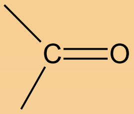
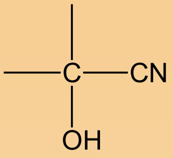
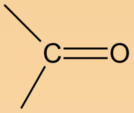
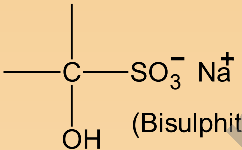
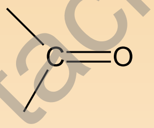
(iii)Oxidation

(iv)Reduction

(v) Reaction with alkalies

(vi)Miscellaneous reactions

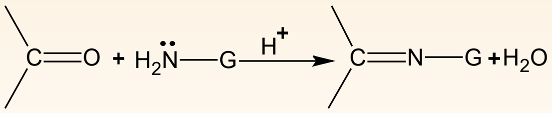
1. Addition across C = O bond

Sr. No.	Addition of	Substrate	Product
1.	Hydrogen cyanide		 (Cyanohydrin)
2.	Sodium bisulfite ($NaHSO_3$)		 (Bisulphite addition product)
3.	Grignard reagent (RMgX) followed by hydrolysis	HCHO	H_3C-CH_2-OH (1^0 alcohol)
		Aldehydes (except formaldehyde)	2° alcohol
		Ketones	3° alcohol
4.	Alcohols (R—OH)		Hemiacetal which finally converts to acetal

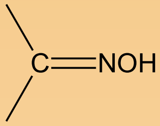
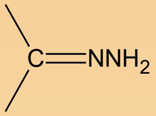
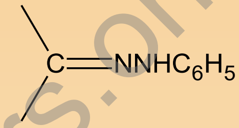
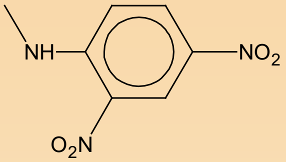
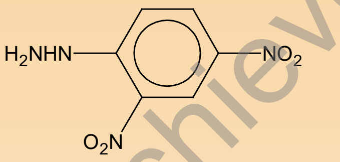
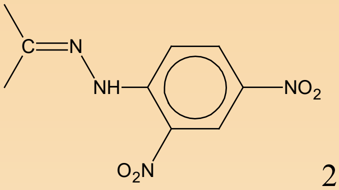
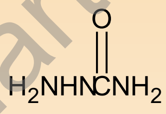
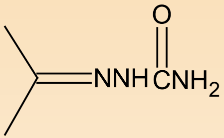
2. Replacement of carbonyl oxygen atom with other groups

(a) Reaction with ammonia derivatives

Aldehydes & ketones react with a number of NH_3 derivatives such as hydroxyl amine, hydrazine, semi carbazide etc., in weak acidic medium. In general, if we represent these derivatives by NH_2 —G, then their reaction with aldehydes & ketones can be represented as follows:

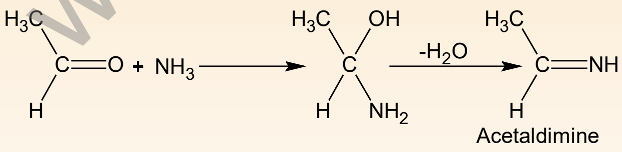


Ammonia derivatives & their products with carbonyl compounds

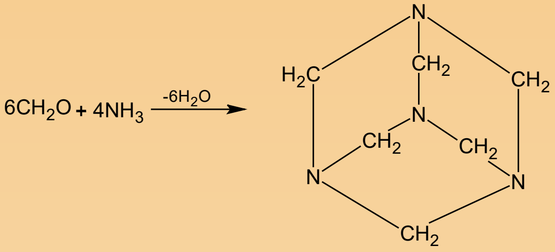
—G	Ammonia Derivative	Product obtained
—OH	NH_2OH Hydroxylamine	 Oxime
—NH_2	NH_2NH_2 Hydrazine	 Hydrazone
—NHC_6H_5	$NH_2NHC_6H_5$ Phenyl hydrazine	 Phenyl Hydrazone
	 2, 4 – dinitrophenyl hydrazine	 2, 4 – dinitrophenyl hydrazone
—$NHCONH_2$	 $H_2NNHCONH_2$ Semicarbazide	 Semicarbazone

(b) **Reaction with ammonia**

Like ammonia derivatives, ammonia also reacts with aldehyde (except formaldehyde) & ketones to form the products, called imines.

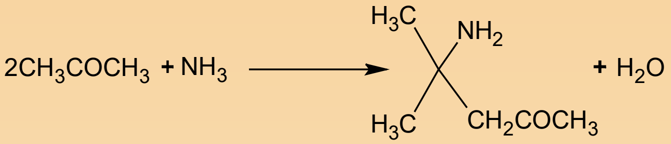


However, formaldehyde reacts with NH_3 to form hexamethylene tetramine, $(CH_2)_6N_4$ also known as urotropine as shown below:



Hexamethylene tetramine

Acetone reacts with NH_3 to form acetocarmine

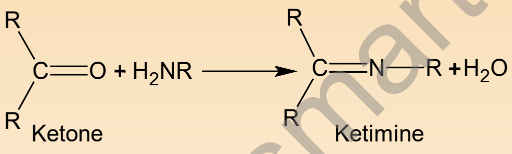


4 - amino - 4 - methyl pentan - 2 - one

(c) Reaction with primary amines

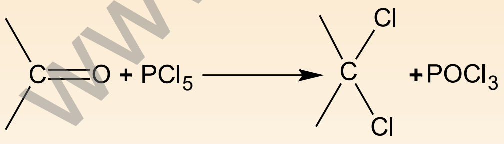
Aldehydes & ketones react with 1^0 amines to form Schiff's bases. These compounds are also called imines.

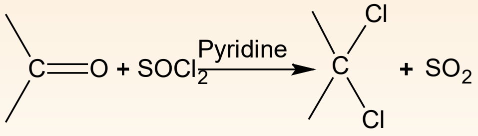
$$\underset{\text{Aldehyde}}{RCHO} + \underset{\text{Amine}}{H_2NR} \longrightarrow \underset{\substack{\text{Aldimine}\\ \text{A Schiff's base}}}{RCH = N - R} + H_2O$$



(d) Reaction with PCl_5 or $SOCl_2$ (thionyl chloride)

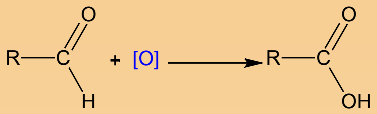
Aldehydes or ketones with PCl_5 or thionyl chloride to form geminal dihalides.





3. Oxidation

Aldehydes are easily oxidised to carboxylic acids containing the same number of carbon atoms, as in parent aldehyde.



The reason for this easy oxidation is the presence of a hydrogen atom on the carbonyl carbon, which can be converted into —OH group without involving the cleavage of any other bond. Hence, aldehydes are oxidised not only by strong oxidizing agent but also by weak oxidizing agents. As a result, aldehydes act as strong reducing agents.

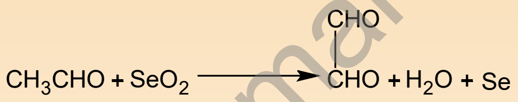
- Aldehydes reduce Tollen's reagent to Ag & appear in the form of silver mirror. This test is called silver mirror test. It is given by all aldehydes & reducing sugars.

  $$RCHO + 2\left[Ag(NH_3)_2\right]^+ + 3OH^- \xrightarrow{\Delta} RCOO^- + \underset{\text{(Silver mirror)}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

- Aldehydes (except benzaldehyde) reduce Fehling's solution (Cu^{+2} reduced to Cu^+) which is an alkaline solution of cupric (Cu^{2+}) ion complexed with tartarated ion.

  $$RCHO + 2Cu^{2+} + 3OH^- \xrightarrow{\Delta} RCOO^- + \underset{\text{red ppt}}{2Cu^+} + 2H_2O$$

- Aldehydes also reduce Benedict's solution (Cu^{2+} complexed with citrate ion) to Cu^+.
- Aldehydes & ketones with a methyl or methylene group adjacent to the carbonyl group are oxidised by SeO_2

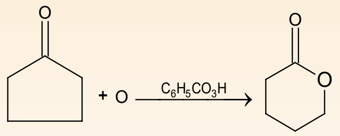


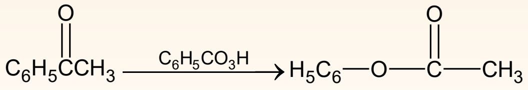
$$CH_3CHO + SeO_2 \longrightarrow \begin{matrix} CHO \\ | \\ CHO \end{matrix} + H_2O + Se$$

$$CH_3COCH_3 + SeO_2 \longrightarrow CH_3COCHO + H_2O + Se$$

- Ketones are also oxidised by Caro's acid (H_2SO_5) or peroxbenzoic acid ($C_6H_5CO_3H$) to esters.

  $$RCOR' + O \xrightarrow{H_2SO_5} RCOOR'$$

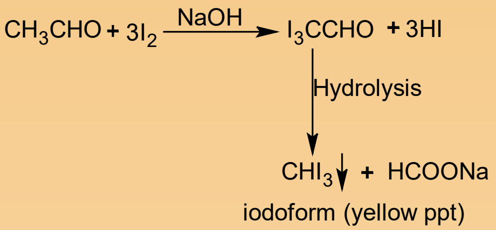




$$C_6H_5\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{C_6H_5CO_3H} H_5C_6—O—\overset{\overset{O}{\|}}{C}—CH_3$$

It is called Bayer villiger oxidation. It is exactly oxygen insertion between carbonyl carbon & the larger of two groups attached to it.

Haloform Reaction



$$CH_3CHO + 3I_2 \xrightarrow{NaOH} I_3CCHO + 3HI \xrightarrow{\text{Hydrolysis}} CHI_3\downarrow + HCOONa$$

iodoform (yellow ppt)

Due to the formation of yellow ppt. of iodoform in this reaction, it is known as iodoform test & used in for characterizing compound containing CH_3CO— or a group like CH_3CH_2OH which can be easily oxidised to CH_3CO— group by halogens.

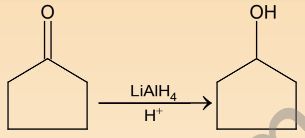
4. Reduction

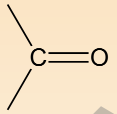
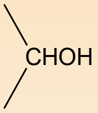
Carbonyl compounds can be reduced to 1° or 2° alcohol, by $LiAlH_4$, $NaBH_4$ or direct reduction with H_2/Ni.

(a) $CH_3CHO \xrightarrow{LiAlH_4} CH_3CH_2OH$

$CH_3CH = CHCHO \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$

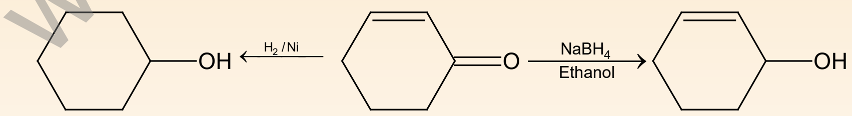
with $LiAlH_4$ —CHO group is reduced to —CH_2OH (1° alcohol) and C = C bond is also reduced when it is in conjugation with carbonyl groups.



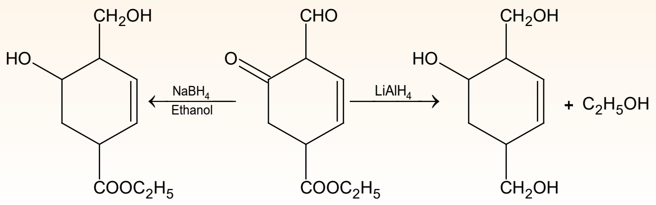
 Group is reduced to  (2° alcohol)

- $LiAlH_4$ also reduces ester & acid chloride to alcohols.

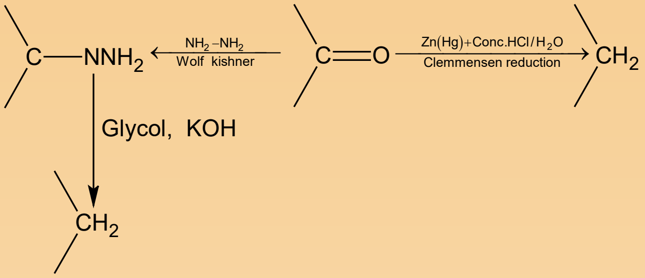
(b) $NaBH_4$ has similar function. But this reagent does not affect (C = C) double bond.



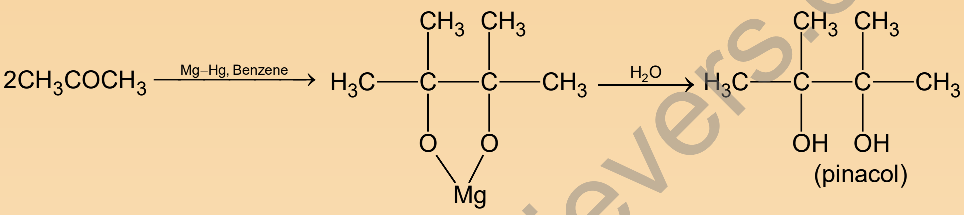
$NaBH_4$ does not reduce ester & acid chloride



(c) Amalgamated zinc, Zn(Hg) & conc. HCl (Clemmensen reduction) & hydrazine (NH_2 –NH_2) followed by reaction with strong base like KOH in alkaline glycol (Wolf Kishner reduction) reduces carbonyl group to alkyl group.



(d) **Reduction to pinacol**

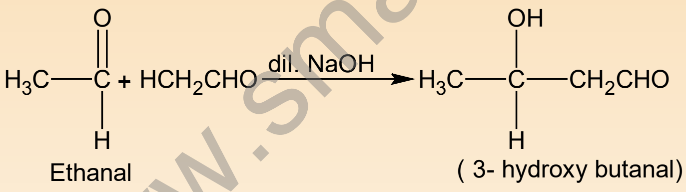


$$2CH_3COCH_3 \xrightarrow{\text{Mg–Hg, Benzene}} H_3C-\underset{\underset{\displaystyle \quad Mg \quad}{O\quad O}}{\overset{CH_3\ \ CH_3}{C-C}}-CH_3 \xrightarrow{H_2O} H_3C-\underset{OH\ \ OH}{\overset{CH_3\ \ CH_3}{C-C}}-CH_3$$

5. Reaction with Alkalis

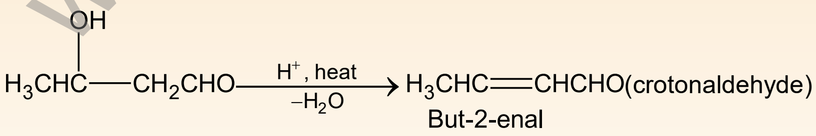
(A) Aldol Condensation

Two molecules of an aldehydes or a ketone having at least one α - hydrogen atom, condense in presence of a dilute alkali to give a β - hydroxy aldehyde or β - hydroxy ketone.



$$H_3C-\underset{H}{\overset{O}{\overset{\|}{C}}} + HCH_2CHO \xrightarrow{\text{dil. NaOH}} H_3C-\underset{H}{\overset{OH}{C}}-CH_2CHO$$

The products of aldol condensation when heated with dilute acids undergo dehydration to form α, β - unsaturated aldehydes or ketones.

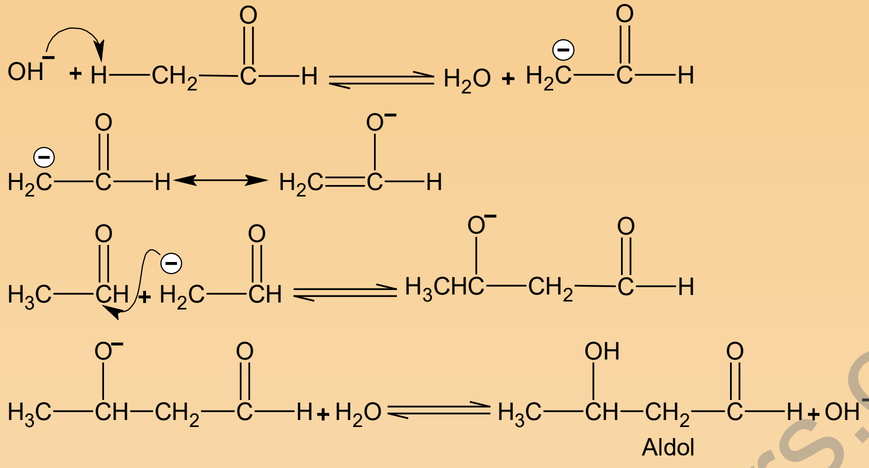


$$H_3C\overset{OH}{\overset{|}{CH}}-CH_2CHO \xrightarrow[-H_2O]{H^+,\text{ heat}} H_3CHC{=}CHCHO\text{(crotonaldehyde)}$$

In general, all aldehydes & ketones which contain α - hydrogen can undergo this reaction. Those which do not contain α - hydrogen like HCHO, C_6H_5CHO etc., do not undergo this reaction.

Mechanism

Mechanism involves formation of carbanions (i) a nucleophile form first molecules which is condensed with second molecule.



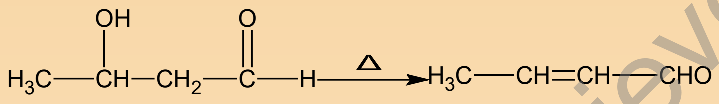
$$OH^- + H-CH_2-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons H_2O + \overset{\ominus}{H_2C}-\overset{O}{\overset{\|}{C}}-H$$

$$\overset{\ominus}{H_2C}-\overset{O}{\overset{\|}{C}}-H \longleftrightarrow H_2C=\overset{O^-}{\overset{|}{C}}-H$$

$$H_3C-\overset{O}{\overset{\|}{C}}H + \overset{\ominus}{H_2C}-\overset{O}{\overset{\|}{C}}H \rightleftharpoons H_3CH\overset{O^-}{\overset{|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$$

$$H_3C-\overset{O^-}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-H + H_2O \rightleftharpoons \underset{\text{Aldol}}{H_3C-\overset{OH}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-H} + OH^-$$

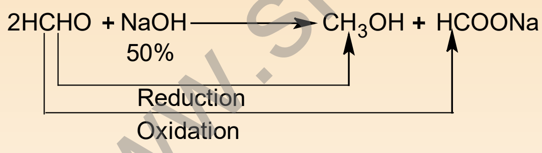
Aldol product on dehydration give α, β - unsaturated ketones.



$$H_3C-\overset{OH}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\Delta} H_3C-CH=CH-CHO$$

(B) **Cannizzaro's reaction**

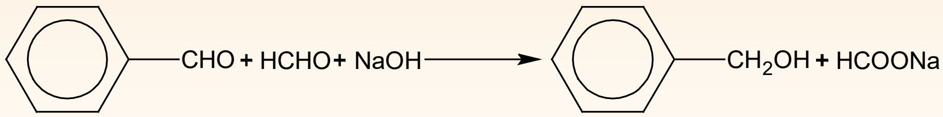
Aldehydes that have no α-hydrogen atom (or acidic hydrogen) undergo Cannizzaro reaction (CR) in which disproportionation reaction takes place one being reduced to alcohol & other being oxidised to salt of the corresponding carboxylic acid. The reaction lakes place with 50% aqueous or ethanolic alkali solution.



$$2HCHO + \underset{50\%}{NaOH} \longrightarrow CH_3OH + HCOONa$$

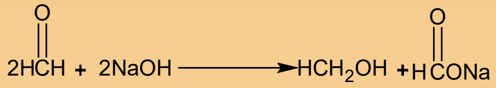
$$2(CH_3)_3CCHO + \underset{50\%}{NaOH} \longrightarrow (CH_3)_3CCH_2OH + (CH_3)_3CCOONa$$

When an aldehyde (showing CR) is treated with HCHO & 50% base, then HCHO undergo oxidation (rather than any other aldehyde). This reaction is called crossed CR.

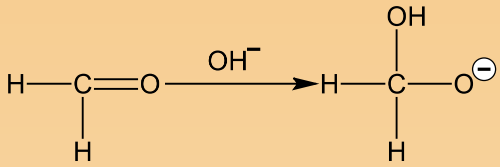


CR involving different aldehydes or same aldehydes is proton (H^+), hydride (H^-) transfer reaction.

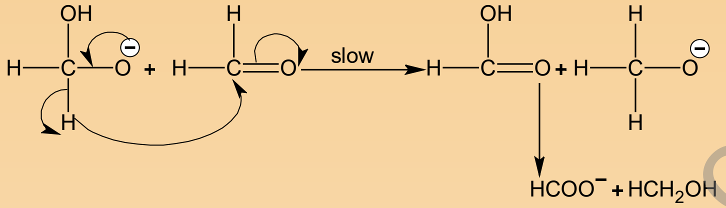
Mechanism



$$2HCHO + 2NaOH \longrightarrow HCH_2OH + HCOONa$$



Step I



Step II

When the reaction is carried out in D_2O instead of in H_2O, it is found that there is no new C – D bond formation. This indicate that the hydrogen must come from aldehyde & not from the solvent.

(C) Perkin reaction

In this reaction aromatic aldehyde is heated with an acid anhydride & its corresponding sodium salt to form condensation products which on hydrolysis gives α, β - unsaturated acids. Acetic anhydride & sodium acetate are commonly used in this reaction.

$$PhCHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} \underset{\text{Cinnamic acid}}{Ph{-}CH{=}CH{-}COOH} + CH_3COOH$$

Carboxylic Acids, Naming Convention, Preparation, and Physical Properties

- Carboxylic acids have a carboxyl functional group (-COOH).
- The carboxyl group consists of a carbonyl group (C=O) and a hydroxyl group (OH) on the same carbon atom.
- They play essential roles in biological processes.
- Naming: Replace 'e' in the corresponding alkane with 'oic acid'.
- Methane (CH4) → Methanoic acid
- Ethane (C2H6) → Ethanoic acid
- Can have additional functional groups.
- Carboxyl group confers acidity due to proton donation.
- High solubility in polar solvents like water.
- Boiling points higher than hydrocarbons and ethers due to hydrogen bonding.
- Various chemical reactions, including esterification, oxidation, and decarboxylation.
- Applications: preservatives, flavoring, pharmaceuticals, and polymers.
- Acidity can be modified by substituents.
- Classified as monocarboxylic (one carboxyl group) or dicarboxylic (two carboxyl groups).

- Resonance stabilization contributes to stability and reactivity.
- Can act as both acids and bases.
- Found in natural and synthetic compounds.

Preparation of Carboxylic Acids

- Hydrolysis of nitriles to amides and carboxylic acids.
- Vigorous oxidation of alkyl benzene to aromatic acid.
- Oxidation of primary alcohol to carboxylic acid.
- Formation of carboxylic acid from Grignard reagent.
- Hydrolysis of acyl halide and anhydride to carboxylic acid.
- Hydrolysis of esters to carboxylic acid.
- Oxidation of aldehydes to carboxylic acids.
- Decarboxylation of β-keto acids to carboxylic acids.
- Microbial fermentation.
- Oxidation of fatty acids.
- Oxidation of alkenes and alkynes.
- Hydrolysis of acid chlorides and anhydrides.
- Oxidative cleavage of alkylbenzenes.
- Oxidation of alcohols followed by decarboxylation.
- Conversion of alkyl halides to carboxylic acids.
- Conversion of aldehydes to carboxylic acids.
- Conversion of cyanides to carboxylic acids.
- Conversion of alkenyl halides to carboxylic acids.
- Conversion of aldehydes to carboxylic acids through aldol condensation.
- Conversion of alcohols to carboxylic acids through oxidation and decarboxylation.
- Conversion of aldehydes to carboxylic acids through Tollens's reagent.
- Conversion of ketones to carboxylic acids through ozonolysis and hydrolysis.
- Conversion of aldehydes to carboxylic acids through the Cannizzaro reaction.
- Conversion of aldehydes to carboxylic acids through the Perkin reaction.
- Conversion of aldehydes to carboxylic acids through the Wittig reaction.
- Conversion of aldehydes to carboxylic acids through the Alder-Rickert reaction.

Physical Properties of Carboxylic Acids

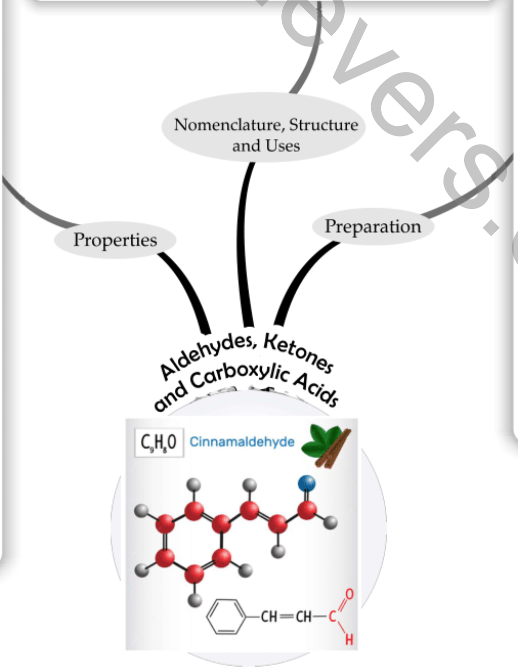
- Higher boiling points due to hydrogen bonding.
- Formation of associated molecules.
- High solubility in water.
- Characteristic sharp or pungent odor.
- Typically colorless liquids or solids.
- Melting points vary with chain length.
- Even carbon atom number leads to higher melting points.
- Soluble in nonpolar solvents, but solubility decreases with longer chains.
- Weak acids that can ionize in water.
- Acidity influenced by substituents and resonance effects.
- Boiling and melting points crucial in various applications.

Chemical Properties

- Carboxylic acids are stronger acids than phenols.
- Heating with mineral acids leads to dehydration.
- Esters can be formed with alcohols or phenols.
- Reaction with phosphorus compounds forms acyl chlorides.
- React with ammonia to form amides.
- Halogenation at the α-position is possible.
- Various other reactions, including decarboxylation, oxidation, reduction, and condensation.
- Participate in nucleophilic substitution reactions.
- Form carboxylate salts through acid-base reactions.
- Undergo decarboxylation under certain conditions.
- Can be oxidized to form CO2 and H2O.
- Can be reduced to alcohols.
- Can undergo condensation reactions.
- Act as ligands in coordination chemistry.
- Acidity influenced by substituents.
- Hell-Volhard-Zelinsky reaction for α-halo carboxylic acids.
- Deactivating and meta-directing effect in electrophilic substitution reactions.
- Do not undergo Friedel-Crafts reactions.
- Various other electrophilic substitution reactions are possible.
- Deactivation explained by electronic effects.
- Importance in organic synthesis and industrial applications.

Aromatic Carboxylic Acids in Electrophilic Substitution Reactions

- Aromatic carboxylic acids have a carboxyl group attached to an aromatic ring.
- Undergo electrophilic substitution reactions.
- Carboxyl group is a deactivating and meta-directing group.
- Deactivating effect due to electron withdrawal.
- Meta-directing effect in electrophilic substitution.
- Do not undergo Friedel-Crafts reactions.
- Can undergo other electrophilic substitution reactions.
- Deactivating and meta-directing effects can be influenced by substituents.
- Applications in various industries.
- Influence of carboxyl group on reactivity is essential in organic synthesis.
- Understanding reactivity is crucial for designing synthetic routes.



Nomenclature, Structure and Uses

Properties

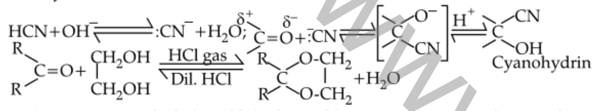
Preparation

Properties

ALDEHYDES AND KETONES:

(i) Physical:
Boiling points are higher than hydrocarbons and ethers of comparable molecular masses and lower than alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.

(ii)Chemical :Nucleophilic addition reactions :
Aldehydes are more reactive than ketones due to steric and electronic reasons.



$HCN + OH^- \rightleftharpoons :CN^- + H_2O$; $\overset{\delta+}{C}=\overset{\delta-}{O} + :CN^- \rightleftharpoons \left[C(O^-)(CN)\right] \xrightleftharpoons{H^+} C(CN)(OH)$ Cyanohydrin

$R_2C=O + \begin{matrix}CH_2OH\\ | \\ CH_2OH\end{matrix} \underset{\text{Dil. HCl}}{\overset{\text{HCl gas}}{\rightleftharpoons}} R_2C\begin{matrix}O\text{-}CH_2\\ | \\ O\text{-}CH_2\end{matrix} + H_2O$

Reduction : (a) To alcohols – aldehydes and ketones reduce to primary and secondary alcohols respectively by $NaBH_4$ or $LiAlH_4$.
(b) To hydrocarbons –

$>C=O \xrightarrow[HCl]{Zn\text{-}Hg} >CH_2 + H_2O$ (Clemmensen Reduction)

$>C=O \xrightarrow[-H_2O]{NH_2NH_2} >C=NNH_2 \xrightarrow[Heat]{KOH/Ethylene\ glycol} >CH_2 + N_2$ (Wolff-Kishner Reduction)

Oxidation: $RCHO \xrightarrow{[O]} R\text{–}COOH$

Tollen's test : $RCHO + 2[Ag(NH_3)]_2^+ + 3OH^- \longrightarrow RCOO^- + 2Ag\downarrow + 2H_2O + 4NH_3$ (Silver mirror)

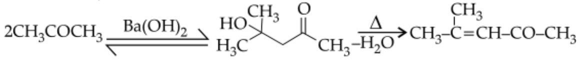
Fehling's test : $RCHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + Cu_2O\downarrow + 3H_2O$ (Red brown ppt)

Haloform reaction:

$R\text{–}\overset{O}{\overset{\|}{C}}\text{–}CH_3 \xrightarrow{NaOX} R\text{–}\overset{O}{\overset{\|}{C}}\text{–}ONa + CHX_3$ (X = Cl, Br, I)

Reactions due to α - hydrogen:

$2CH_3CHO \xrightleftharpoons{dil.NaOH} H_3C\text{—}\overset{OH}{\overset{|}{C}H}\text{—}CH_2\text{—}\overset{O}{\overset{\|}{C}}\text{—}H \xrightarrow[-H_2O]{\Delta} CH_3\text{–}CH=CH\text{–}CHO$

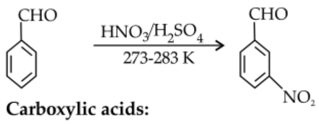


$2CH_3COCH_3 \xrightleftharpoons{Ba(OH)_2} (CH_3)_2C(OH)CH_2COCH_3 \xrightarrow[-H_2O]{\Delta} CH_3\text{–}\overset{CH_3}{\overset{|}{C}}=CH\text{–}CO\text{–}CH_3$

$\begin{matrix}CH_3CHO\\ + \\ CH_3CH_2CHO\end{matrix} \xrightarrow[\Delta]{NaOH} CH_3\text{–}CH=CH\text{–}CHO + CH_3\text{–}CH_2\text{–}CH=\underset{CH_3}{\underset{|}{C}}\text{–}CHO$

Cannizzaro reaction : $2HCHO + conc\ KOH \xrightarrow{\Delta} CH_3OH + HCOOK$

Electrophilic substitution reaction:



Carboxylic acids:

(i) Physical: Higher boiling points than aldehydes, ketones or alcohols. Solubility decreases with increasing number of C atoms.

(ii)Chemical : $2RCOOH + 2Na \longrightarrow 2RCOONa + H_2$

Forms corresponding anhydride on heating with mineral acids

$RCOOH + R'OH \xrightleftharpoons{H^+} RCOOR' + H_2O$

$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^-\ \overset{+}{N}H_4 \xrightarrow[-H_2O]{\Delta} CH_3CONH_2$

$RCOOH \xrightarrow[H_3O^+]{B_2H_6} RCH_2OH$

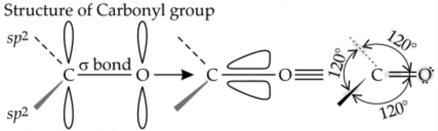
$RCOONa \xrightarrow[NaOH\ \&\ CaO]{Heat} R\text{–}H + Na_2CO_3$

$RCH_2COOH \xrightarrow[H_2O]{X_2/Red\ P} R\text{–}\underset{X}{\underset{|}{C}H}\text{–}COOH$ (HVZ reaction) (X=Cl, Br)

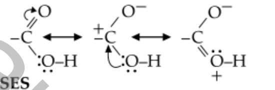
Nomenclature, Structure and Uses

1. **Aldehydes and Ketones**
Common names :
- Replace corresponding carboxylic acids with aldehyde.
- Alkyl phenyl ketones by adding acyl group as prefix to phenone.
- IUPAC names :
- Replacing –e with –al and –one as required.

Structure of Carbonyl group



2. **Carboxylic Acids**
Common names : end with –ic
- IUPAC names : replace –e in the corresponding alkane with –oic acid.
- Structure of Carboxyl Group



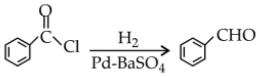
3. **USES**
(a) **Carboxylic acids**
- Methanoic acid in rubber, textile, dyeing, leather industries.
- Ethanoic acid as solvent.
- Higher fatty acids in manufacture of soaps and detergents.

(b) **Aldehydes of ketones**
- As solvents.
- Starting materials and reagents for synthesis of products.

Preparation

ALDEHYDES:

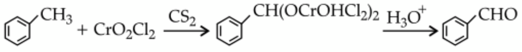
1. From acyl chloride

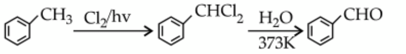


2. From nitriles and esters : Stephen reaction

$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3O^+} R\,CHO$

3. From hydrocarbons : Etard reaction



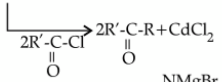


Gattermann – Koch reaction

KETONES:

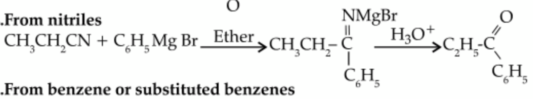
1.From acyl chloride

$2R\text{–}Mg\text{–}X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$



$R_2Cd \xrightarrow{2R'\text{-}\underset{O}{\underset{\|}{C}}\text{-}Cl} 2R'\text{-}\underset{O}{\underset{\|}{C}}\text{-}R + CdCl_2$

2.From nitriles



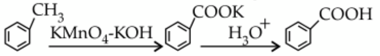
$CH_3CH_2CN + C_6H_5MgBr \xrightarrow{Ether} CH_3CH_2\text{–}\underset{C_6H_5}{\underset{|}{\overset{NMgBr}{\overset{\|}{C}}}} \xrightarrow{H_3O^+} C_2H_5\text{-}\underset{C_6H_5}{\overset{O}{C}}$

3.From benzene or substituted benzenes

Carboxylic Acids:

1.From primary alcohols and aldehydes $RCH_2OH \xrightarrow[H_3O^+]{alk.\ KMnO_4} RCOOH$

2.From alkylbenzenes



3.From nitriles and amides $R\text{–}CN \xrightarrow[H_2O]{H^+ or\ OH^-} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 \xrightarrow[\Delta]{H^+ or\ OH^-} RCOOH$

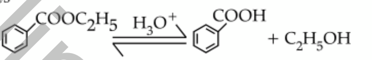
4.From Grignard reagents $R\text{–}Mg\text{–}X + CO_2 \longrightarrow R\text{-}\underset{O^-MgX^+}{\underset{|}{\overset{O}{\overset{\|}{C}}}} \xrightarrow{H_3O^+} RCOOH$

5.From acyl halides and anhydrides

$RCOCl \xrightarrow{OH^-/H_2O} RCOO^- + Cl^- \xrightarrow{H_3O^+} RCOOH$

$C_6H_5COOCOCH_3 \xrightarrow{H_2O} C_6H_5COOH + CH_3COOH$

6.From esters



$CH_3CH_2CH_2COOC_2H_5 \xrightleftharpoons{NaOH} CH_3CH_2CH_2COONa + C_2H_5OH \xrightarrow{H_3O^+} CH_3CH_2CH_2COOH$

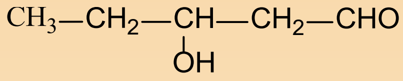
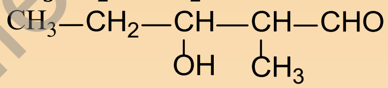
Trace the Mind Map
- First Level
- Second Level
- Third Level

PRACTICE QUESTIONS

1. On heating with aqueous alkali, chloroform yields:
a) HCHO b) HCOOH c) CH_3OH d) CO_2 and H_2O

2. A keto ester (A) with molecular formula $C_6H_{10}O_3$ on treatment with $NaOH + I_2$ does not give iodoform but on boiling with dilute KOH gives a compound (B) with molecular formula $C_4H_5O_3K$ which upon acidification followed by heating undergoes decarboxylation to give acetone. The keto ester (A) is
a) $CH_3COCH_2CH_2COOCH_3$ b) $CH_3COCH_2COOC_2H_5$
c) $CH_3CH_2OCH_2COOCH_3$ d) $CH_3 - COCH(CH_3)COOCH_3$

3. In the reaction, $HCHO + NH_3 \rightarrow X, X$ is
a) *meta*-formaldehyde b) *para*-formaldehyde c) urotropine d) None of these

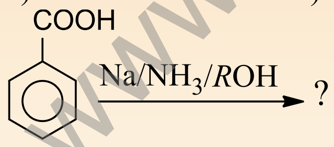
4. $CH_3CH_2 - CHO \xrightarrow[\text{alkali}]{\text{Dil.}}$ product
The product in the above reaction is
a) CH_3CH_2COOH b) $CH_3CH_2 - CH_2OH$
c)

$CH_3-CH_2-\underset{OH}{CH}-CH_2-CHO$
d)

$CH_3-CH_2-\underset{OH}{CH}-\underset{CH_3}{CH}-CHO$

5. One mole of an organic compound requires 0.5 mole of oxygen to produce an acid. The compound may be:
a) Alcohol b) Ether c) Ketone d) Aldehyde

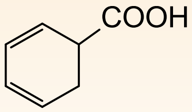
6. Acetic acid reacts with PCl_5 to form
a) $CH_2ClCOOH$ b) $CHCl_2COOH$ c) CH_3COCl d) CH_3COOCl

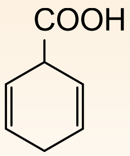
7. CH_3COOH and C_6H_5COOH can be distinguished by:
a) Flame test b) Solubility in water c) Physical state d) All of these

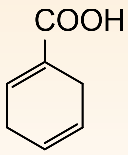
8. Methylene chloride on hydrolysis yields:
a) HCHO b) CH_3CHO c) CH_3COCl d) None of these

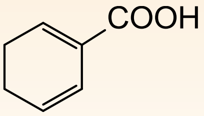
9.


Product is

a)


b)


c)


d)


10. Which of the following compounds does not have a carboxyl group?
a) Methanoic acid b) Ethanoic acid c) Picric acid d) Benzoic acid

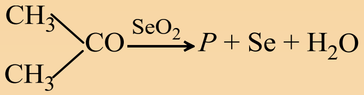
11. 2,4-dichlorophenoxy acetic acid is used as a:
a) Fungicide b) Insecticide c) Herbicide d) Moth repellent

12. Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon?
a) Ethyl acetate b) Acetic acid c) Acetamide d) Butan-2-one

13. 3-pentanol on reaction with aluminum tertiary butoxide in the presence of acetone gives
a) 3-pentanal b) 2-pentanal c) 3-pentanone d) 2-pentanone

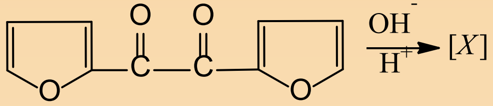
14. The silver salt of a fatty acid on refluxing with an alkyl halide gives an
a) Acid b) Ester c) Ether d) Amine

15. In the reaction, *P* is:

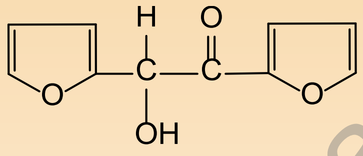


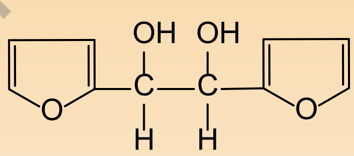
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO \xrightarrow{SeO_2} P + Se + H_2O$$

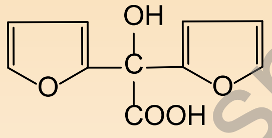
a) CH_3COCHO b) CH_3COOCH_3 c) CH_3COCH_2OH d) None of these

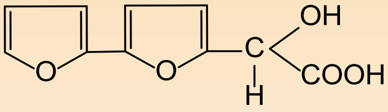
16. 

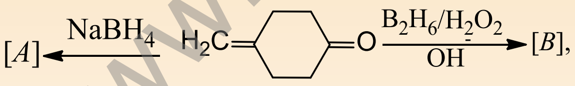
Product is

a) 

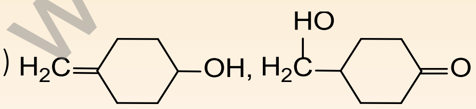
b) 

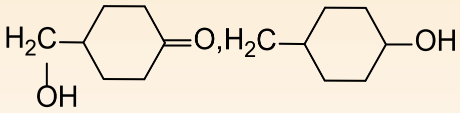
c) 

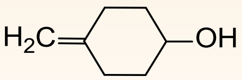
d) 

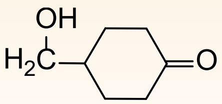
17. 

[*A*] and [*B*] are

a) 

b) 

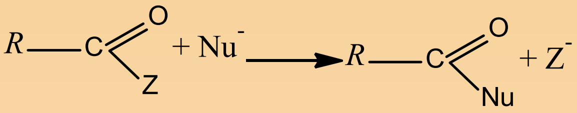
c) both 

d) both 

18. $(CH_3)_2C{=}CHCOCH_3$ can be oxidised to $(CH_3)_2C{=}CHCOOH$ by:
a) Cu at 300°C b) $KMnO_4$ c) Chromic acid d) NaOI

19. The correct order of decreasing boiling points of CH_3CONH_2 (A), CH_3COCl (B), CH_3COOH (C) and $(CH_3CO)_2O$ (D) is:
a) $A > D > C > B$ b) $A > B > C > D$ c) $D > C > B > A$ d) None of these

20. Rate of reaction,



is fastest when *Z* is
a) Cl b) NH_2 c) OC_2H_5 d) $OCOCH_3$

21. Which is useful for separating benzoic acid from a mixture of benzoic acid and methyl benzoate?
a) $NaHCO_3(aq.)$ b) Dil. HCl c) Dil. H_2SO_4 d) Dil. HNO_3

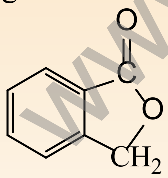
22. The compound *X*, in the reaction is

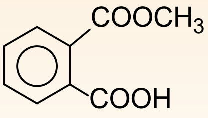
$$X \xrightarrow{CH_3CHO} Y \xrightarrow{\text{Hydrolysis}} Mg(OH)I + CH_3COOH$$

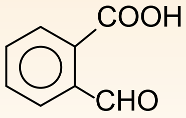
a) CH_3CHO b) CO_2 c) $(CH_3)_2CO$ d) HCHO

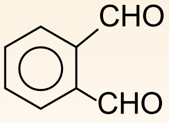
23. Methyl ketones are characterised through:
a) The Tollen's reagent
b) The iodoform test
c) The Schiff's test
d) The Benedict's reagent

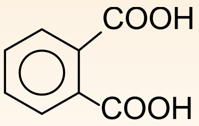
24. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the product



a) 

b) 

c) 

d) 

25. Acetone reacts with Grignard reagent to form

a) 3° alcohol
b) 2° alcohol
c) Ether
d) No reaction

26. Decarboxylation of malonic acid gives

a) CH_4
b) CH_3COOH
c) Both (a) and (b)
d) None of these

27. What is the product in the reaction

$CH_3CONH_2 \xrightarrow{NaOH_2/HCl} X$?

a) CH_3COOH
b) $\overset{+}{CH_3CONH_3}Cl^-$
c) CH_3NH_2
d) CH_3CHO

28. Acetyl nitrate is formed when acetic anhydride reacts with

a) Nitrogen pentoxide
b) Nitric acid
c) Nitrous acid
d) Potassium nitrate

29. Which one is not prepared from tartaric acid?

a) Tartar emetic
b) Fenton's reagent
c) Fehling's solution
d) Rochelle salt

30. The reagent used in Clemmensen's reduction is

a) Conc. H_2SO_4
b) Zn−Hg /conc.HCl
c) aq. KOH
d) alc.KOH

31. The technique of gas chromatography is suitable for compounds which are:

a) Liquids
b) Highly volatile
c) Soluble in water
d) Vaporize without decomposition

32. How many carbon atoms do higher members of aliphatic carboxylic acids, known as fatty acids, contain?

(a) C-C 12-18
(b) C-C 10-15
(c) C-C 5-10
(d) C-C 20-30

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

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

34. Which of the following acids cannot be prepared by Grignard reagent?

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

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

(a) More extensive association of carboxylic acids via van der Waals' force of attraction

(b) Formation of carboxylate ion

(c) Formation of intramolecular hydrogen bonding

(d) Formation of intermolecular hydrogen bonding

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

(a) SOCl2 (with heat) (b) PCl3 (with heat)

(c) P2O5 (with heat) (d) All of these

37.Diborane easily reduces which functional group?

(a) Acid (b) Ester (c) Nitro (d) Halo

38.What is the product formed during the decarboxylation of malonic acid?

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

39.Aromatic carboxylic acids do not undergo the Friedel-Crafts reaction because:

(a) The carboxyl group acts as an activating and meta-directing group

(b) The carboxyl group acts as a deactivating and ortho- and para-directing group

(c) The carboxyl group acts as an activating and ortho-directing group

(d) The carboxyl group acts as a deactivating group, and the catalyst is not compatible

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

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

41. Why are the compounds methanal, ethanal, and propanone miscible with water?

(a) Due to the formation of van der Waals' forces with water

(b) Due to the formation of 'H'-bonding with water

(c) Due to the formation of dipole-dipole bonds with water

(d) Due to the formation of ion-dipole bonds with water

42. In which of the following examples does a carbonyl compound undergo nucleophilic addition followed by an elimination reaction?

(a) Addition of Grignard reagent

(b) Addition of sodium sulphide

(c) Addition of HCN

(d) Addition of NH3

43. What is the acid formed when propyl magnesium bromide is treated with CO_2?

(a) C_3H_7COOH (b) C_2H_5COOH

(c) Both (a) and (b) (d) None of these

44. What does tamarind contain?

(a) + tartaric acid (b) (-) tartaric acid

(c) ± tartaric acid (d) None of the above

45. What is the term for the splitting of an ester by an alcohol?

(a) Acidolysis (b) Alcoholysis (c) Ammonolysis (d) Hydrolysis

46. What is the product formed when hydroxylamine condenses with a carbonyl compound called?

(a) Hydrazide (b) Oxime (c) Hydrazine (d) Hydrazone

47. Which aldehyde undergoes Claisen condensation with another aldehyde to give cinnamaldehyde?

(a) Formaldehyde (b) Acetaldehyde (c) Crotonaldehyde (d) Propanaldehyde

48. When two moles of acetic acid are heated with P_2O_5, what product is formed?

(a) 2 moles of ethyl alcohol (b) Formic anhydride

(c) Acetic anhydride (d) 2 moles of methyl cyanide

49. How can the nitrogen content in proteins be quantitatively estimated?

(a) Carius method (b) Kjeldahl's method

(c) Victor Meyer's method (d) Rast method

50. What is the correct order of reducing power among the following carbonyl compounds?

(a) $HCHO > CH_3COCH_3 > \phi CHO$

(b) $CH_3COCH_3 > \phi CHO > HCHO$

(c) $HCHO > \phi CHO > CH_3COCH_3$

(d) $CH_3COCH_3 > HCHO > \phi CHO$

51. Which carbonyl compound's cyanohydrin forms lactic acid?

(a) HCHO (b) CH3COCH3

(c) CH3CHO (d) CH3CH2CHO

52. What product is obtained when ethyl acetate reacts with a Grignard reagent?

(a) Alcohol (b) Aldehyde (c) Acid (d) Ketone

53. Acetaldehyde reacts with HCN followed by hydrolysis to form a compound that exhibits what type of isomerism?

(a) Optical isomerism (b) Geometrical isomerism

(c) Metamerism (d) Tautomerism

54. Carboxylic acids dissolve in aq. NaOH because they undergo what process?

(a) Protonation (b) Deprotonation

(c) Carboxylation (d) Decarboxylation

55. Which of the following acids cannot be prepared by Grignard reagent?

(a) Acetic acid (b) Succinic acid

(c) Formic acid (d) All of these

56. Compound A, when treated with ethyl magnesium iodide in dry ether, forms an addition compound that, upon hydrolysis, yields compound B. Compound B, upon oxidation, forms 3-pentanone. Therefore, compounds A and B are:

(a) Propanol, 3-pentanol

(b) Pentanol, 3-pentanol

(c) Ethanal, pentanal

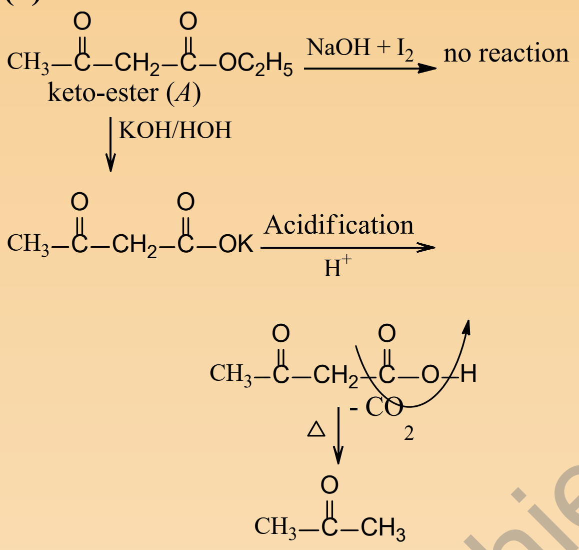
(d) Acetone

HINTS ANS SOLUTIONS

1 **(b)**

$$CHCl_3 \xrightarrow{HOH} CH(OH)_3 \longrightarrow HCOOH$$

2 **(b)**



The keto-ester (A) does not give haloform reaction inspite of the presence of CH_3CO- group in it. The reason is the presence of active methylene group $(ie, -CH_2-)$, which prevents the conversion of CH_3CO- to CX_3CO-

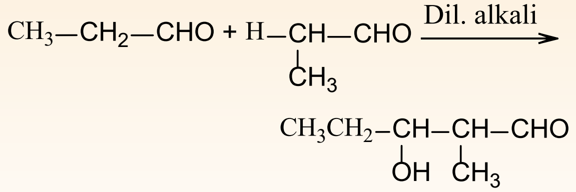
3 **(c)**

Formaldehyde reacts with NH_3 to form urotropine which is used as medicine to cure urinary infections.

$6HCHO \quad + \quad 4NH_3 \rightarrow \quad (CH_2)_6N_4$
Formaldehyde ammonia hexamethylene
tetramine urotropine

4 **(d)**

Aldehydes and ketones having α-hydorgen atom undergo aldol condensation in presence of dilute base



$$CH_3-CH_2-CHO + H-\underset{\displaystyle CH_3}{CH}-CHO \xrightarrow{\text{Dil. alkali}} CH_3CH_2-\underset{\displaystyle OH}{CH}-\underset{\displaystyle CH_3}{CH}-CHO$$

5 **(d)** $CH_3CHO \xrightarrow{[O]} CH_3COOH$

6 **(c)**

Acetic acid reacts with PCl_5 to form acetyl chloride.

$$\underset{\text{acetic acid}}{CH_3COOH} + PCl_5 \longrightarrow \underset{\text{acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$$

7 **(d)**

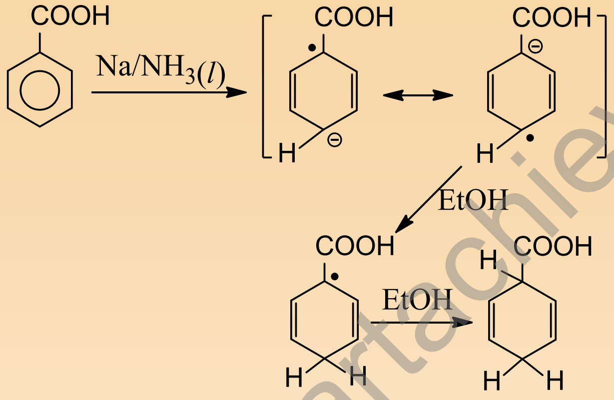
C_6H_5COOH is solid, less soluble in water and burn with smoky flame.

8 **(a)**

$$CH_2Cl_2 \xrightarrow{HOH} HCHO$$

9 **(b)**

When aromatic carboxylic acids are subjected to Birch reduction (*ie,* Na or K in NH_3 and an alcohol), 1, 4-additional of hydrogen takes place and 1, 4-cyclohexadiene carboxylic acids are produced



10 **(c)**

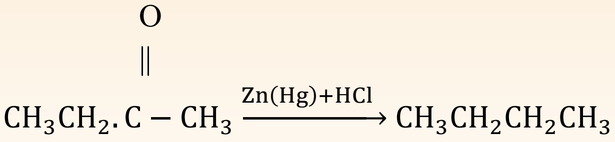
Picric acid is 2,4,6-trinitrophenol.

11 **(c)**

Herbicides are the substances that kills plants or inhibit their growth. Selective herbicides affect only particular plant types, making it possible to attack weeds growing among cultivated plants.

12 **(d)**

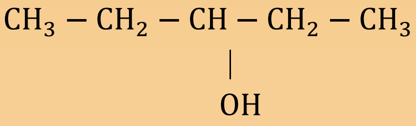
Carbonyl compounds are reduced to corresponding alkanes with (Zn+ conc.HCl). It is called Clemmensen reduction.



$$CH_3CH_2.\overset{\overset{O}{\|}}{C} - CH_3 \xrightarrow{Zn(Hg)+HCl} CH_3CH_2CH_2CH_3$$

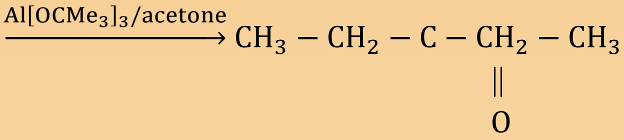
13 **(c)**

Aluminium tertiary butoxide is an oxidising agent used for the oxidation of secondary alcohols into ketones.



$$CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3$$

3-pentanol



$$\xrightarrow{Al[OCMe_3]_3/acetone} CH_3-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-CH_2-CH_3$$

3-pentanone

14 **(b)**

The silver salt of fatty acid on refluxing with an alkyl halide, give an ester.

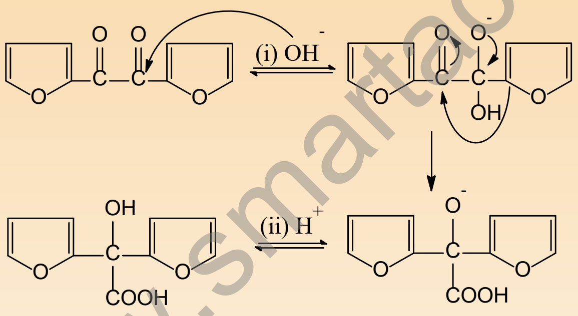
$$RCOOAg + R'Cl \xrightarrow{\Delta} \underset{\text{ester}}{RCOOR'} + AgCl$$

15 **(a)**

$$CH_3COCH_3 \xrightarrow{SeO_2} CH_3CO \cdot CHO + Se + H_2O$$

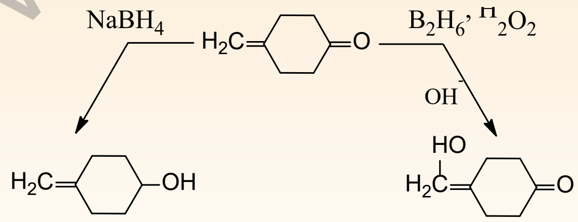
16 **(c)**

1, 2 diketone undergoes rearrangement to α-hydroxy carboxylic acid in presence of base. This reaction is known as benzilic acid rearrangement



17 **(b)**

In the given compound, carbonyl group is reduced to $-OH$ group by $NaBH_4$ and it does not affect double bond. The another is hydroboration-oxidation reaction, in which one water molecule is added to double bond



18 **(d)**

Unsaturated ketones may be converted to unsaturated acids by sodium hypohalite, *i.e.*, NaOCl, NaOI, etc.

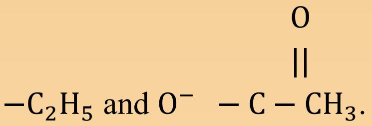
19 **(a)**

The b.p. are $CH_3CONH_2 > (CH_3CO)_2O > CH_3COOH > CH_3COCl$

222°C 139°C 116°C 52°C

20 **(a)**

Cl^- is the best leaving group being the weakest nucleophile out of NH_2^-, Cl^-, O^-



$-C_2H_5$ and $O^- - \overset{\overset{\Large O}{||}}{C} - CH_3$.

21 **(a)**

Former reacts with *aq.* $NaHCO_3$.

22 **(b)**

CO_2 adds to Grignard's reagent to yield acids.

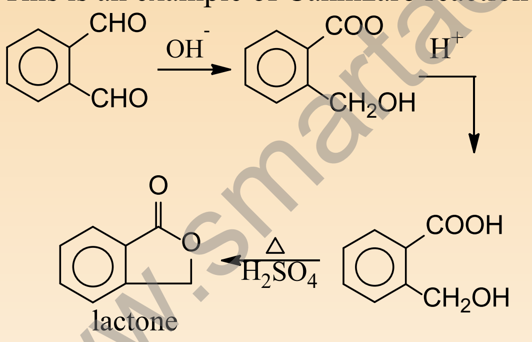
$$CO_2 \xrightarrow{CH_3MgI} CH_3COOMgI \xrightarrow{H.OH} CH_3COOH + Mg(OH)I$$

23 **(b)**

All methyl ketones give iodoform test.

24 **(c)**

This is an example of Cannizaro reaction



25 **(b)**

Grignard reagent $=CH_3MgX$

Clemmensen reduction$=Zn - Hg/Conc\,HCl$

Rosenmund reduction$=H_2/Pd - BaSO_4$

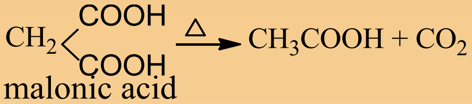
Wolff-Kishner reduction$=N_2H_4/KOH\,/CH_2OH$

|

CH_2OH

26. (b)

Decarboxylation of malonic acid give acetic acid and CO_2



$$CH_2(COOH)_2 \xrightarrow{\Delta} CH_3COOH + CO_2$$

malonic acid

27 **(a)**

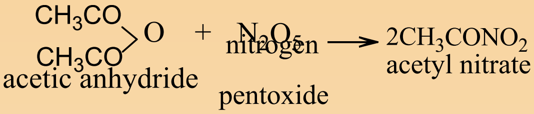
Amides, on treating with HNO_2, give acids.

$$CH_3CONH_2 \xrightarrow[(HNO_2)]{NaNO_2/HCl} CH_3COOH + N_2 + H_2O$$

acetic acid

28 **(a)**

Acetyl nitrate is formed, when acetic anhydride reacts with nitrogen pentoxide.



$$(CH_3CO)_2O + N_2O_5 \longrightarrow 2CH_3CONO_2$$

acetic anhydride nitrogen pentoxide acetyl nitrate

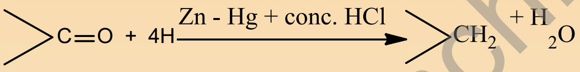
29 **(b)**

Fenton's reagent is $FeSO_4 + H_2O_2$.

30 **(b)**

In Clemmensen's reduction

$Zn - Hg/conc. HCl$ is used



$$>C=O + 4H \xrightarrow{Zn - Hg + conc. HCl} >CH_2 + H_2O$$

This method is used to convert carbonyl compound into alkane.

31 **(d)**

—do—

32. Answer: (a) C-C 12-18

Solution: Fatty acids, which are higher members of aliphatic carboxylic acids, generally contain carbon atoms in the range of 12 to 18.

33. Answer: (c) Isobutyric acid

Solution: The common name of 2-methylpropanoic acid is "Isobutyric acid."

34. Answer: (d) All of these

Solution: Grignard reagents cannot be used to prepare any of the mentioned acids: acetic acid, succinic acid, or formic acid.

36. Answer: (d) All of these

Solution: Ethanoic acid can be converted to ethanoic anhydride using various reagents, including SOCl2 (with heat), PCl3 (with heat), and P2O5 (with heat).

37. Answer: (b) Ester

Solution: Diborane easily reduces ester functional groups.

38. Answer: (a) Acetic acid

Solution: The decarboxylation of malonic acid results in the formation of acetic acid.

39. Answer: (b) The carboxyl group acts as a deactivating and ortho- and para-directing group

Solution: Aromatic carboxylic acids do not undergo the Friedel-Crafts reaction because the carboxyl group acts as a deactivating and ortho- and para-directing group.

40. Answer: (a) Hexanedioic acid

Solution: Hexanedioic acid is commonly used in the rubber, textile, dyeing, leather, and electroplating industries.

41. Answer: (b) Due to the formation of 'H'-bonding with water

Solution: Methanal, ethanal, and propanone are miscible with water due to the formation of hydrogen bonds (H-bonds) with water molecules.

42. Answer: (a) Addition of Grignard reagent

Solution: The Grignard reagent (RMgX) undergoes nucleophilic addition followed by an elimination reaction in a carbonyl compound.

43. Answer: (a) C3H7COOH

Solution: When propyl magnesium bromide reacts with CO2, it forms propanoic acid (C3H7COOH).

44. Answer: (a) + tartaric acid

Solution: Tamarind contains (+) tartaric acid.

45. Answer: (b) Alcoholysis

Solution: The splitting of an ester by an alcohol is known as alcoholysis.

46. Answer: (b) Oxime

Solution: The product formed when hydroxylamine condenses with a carbonyl compound is called an oxime.

47. Answer: (c) Crotonaldehyde

Solution: CHO undergoes Claisen condensation with another aldehyde to give cinnamaldehyde, which is crotonaldehyde.

48. Answer: (c) Acetic anhydride

Solution: Two moles of acetic acid heated with P2O5 yield acetic anhydride.

49. Answer: (b) Kjeldahl's method

Solution: The nitrogen content in proteins can be quantitatively estimated by Kjeldahl's method.

50. Answer: (d) CH3COCH3 > HCHO > ϕCHO

Solution: The correct order of reducing power is CH3COCH3 > HCHO > ϕCHO.

51. Answer: (d) CH3CH2CHO

Solution: Cyanohydrin of ethanal (CH3CHO) forms lactic acid.

52. Answer: (d) Ketone

Solution: Ethyl acetate on reaction with a Grignard reagent gives a ketone.

53. Answer: (d) Tautomerism

Solution: Acetaldehyde reacts with HCN followed by hydrolysis to form a compound that exhibits tautomerism.

54. Answer: (b) Deprotonation

Solution: Carboxylic acids dissolve in aqueous NaOH because they undergo deprotonation.

55. Answer: (d) All of these

Solution: None of the mentioned acids (acetic acid, succinic acid, or formic acid) can be prepared by Grignard reagent.

56. Answer: (c) Ethanal, pentanal

Solution: Compound A is ethanal, and compound B is pentanal.