ALDEHYDES
KETONES
CARBOXYLIC ACID

TOPIC-WISE STUDY MATERIAL

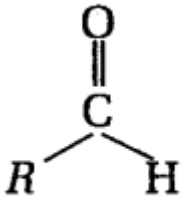
BY

EXAMS ROAD

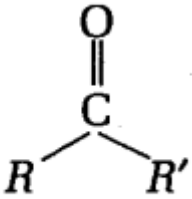
"Bringing Excellence to Students"

Aldehydes and Ketones

The organic compounds containing carbon-oxygen double bond, i.e. $>C=O$ group are called carbonyl compounds. These compounds are widely spread both in plant and animal kingdom and they play an important role in biological processes.



Aldehyde



Ketone

Nomenclature

Aldehydes and ketones are functional isomers.

According to IUPAC nomenclature system, name of aldehyde is obtained by replacing the terminal 'e' of the corresponding alkane by the suffix 'al'.

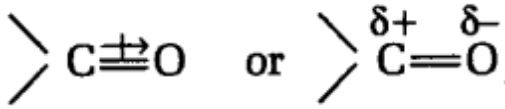
Aldehyde	General name	IUPAC name
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
CH_3CH_2CHO	Propionaldehyde	Propanal

Name of a ketone is obtained by replacing the terminal 'e' of the corresponding alkane by the suffix 'one'.

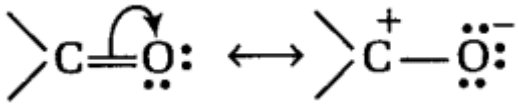
Ketones	General name	IUPAC name
CH_3COCH_3	Acetone	Propanone
$CH_3COCH_2CH_3$	Ethyl methyl ketone	Butanone
$CH_3COCH_2CH_2CH_3$	Methyl *n*-propyl ketone	Pentan-2-one
$CH_3CH_2COCH_2CH_3$	Diethyl ketone	Pentan-3-one

Nature of Carbonyl Group

In carbonyl group, n-electron cloud is displaced towards more electronegative oxygen atom thus, causing polarisation of the bond so that carbon is partially positive and oxygen is partially negative.



In resonance terms, electron delocalisation in the carbonyl group is represented by contributions from two principal resonance forms.



Preparation of Aldehydes and Ketones

There are several methods from which aldehydes as well as ketones can be synthesised. These methods are as follows:

- **By Ozonolysis of Alkenes**

$$CH_2=CH_2 \xrightarrow[(ii)\,Zn+H_2O]{(i)O_3} 2HCHO$$

- **By Hydration of Alkynes**

Acetylene on hydration gives acetaldehyde and other alkynes on hydration give ketones.

$$\text{(a) } \underset{\text{Acetylene}}{CH\equiv CH} + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3CHO$$

$$\text{(b) } R-C\equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} R-\overset{\overset{O}{\|}}{C}-CH_3$$

- **From Grignard Reagent**

HCN when reacts with Grignard reagent and then subjected to hydrolysis, gives aldehydes while RCN gives ketone.

$$R-MgX + H-C\equiv N \xrightarrow{H^+/H_2O} R-CHO + Mg\begin{matrix}X\\OH\end{matrix} + NH_3$$

$$\underset{(R=\text{alkyl group or } C_6H_5)}{RMgX + R'-C\equiv N} \xrightarrow{H^+/H_2O} R-\overset{O}{\overset{\|}{C}}-R' + Mg\begin{matrix}X\\OH\end{matrix} + NH_3$$

Preparation of Aldehydes

The following methods used to synthesise the aldehyde are given as

From Acyl Halides

$$R-\overset{O}{\overset{\|}{C}}-X \xrightarrow[Pd\text{-}BaSO_4]{H_2} RCHO + HX$$

$(R = \text{alkyl group or } C_6H_5)$

This reaction is called Rosemund reduction

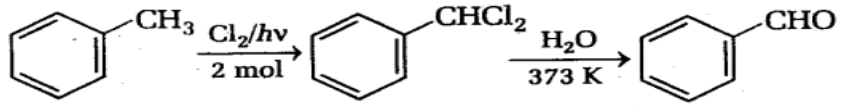
Stephen Reaction
(Reductive Hydrolysis of Alkyl Cyanide)

- $R-CN + SnCl_2 + HCl \longrightarrow \underset{\text{Iminochloride}}{RCH=NH\cdot HCl} \xrightarrow{H_3O^+} RCHO + NH_4Cl + H_2O$
- Nitriles are selectively reduced by diisobutyl aluminium hydride (DIBAL-H) and gives aldehydes.

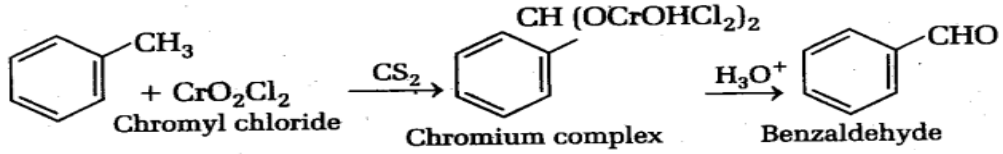
$$CH_3CH=CHCH_2CH_2CN \xrightarrow[(ii)\,H_2O]{(i)\,AlH(i\text{-}Bu)_2} CH_3CH=CHCH_2CH_2CHO$$

$$CH_3(CH_2)_9-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[(ii)\,H_2O]{(i)\,DIBAL\text{-}H} CH_3(CH_2)_9-\overset{O}{\overset{\|}{C}}-H + C_2H_5OH$$

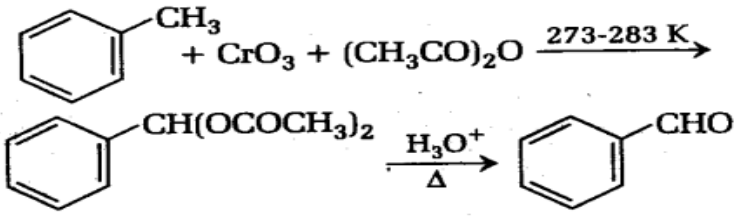
(iii) By Side Chain Chlorination Followed by Hydrolysis



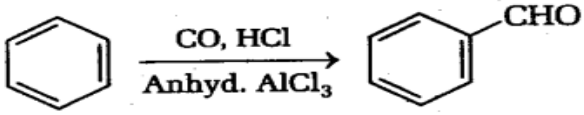
(iv) By Oxidation of Methyl Benzene



(v) Etard Reaction



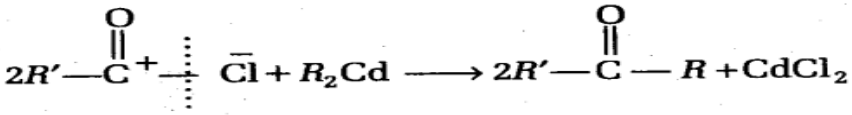
(vi) By Gattermann–Koch Reaction



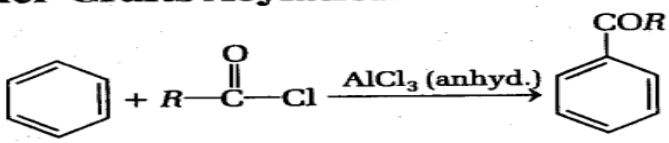
Preparation of Ketones

The following methods are used to synthesise the ketones are given as

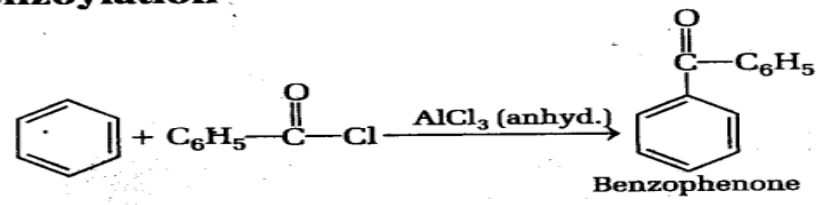
(i) From Acid Chlorides



(ii) By Friedel–Crafts Acylation



(iii) Benzoylation



Physical Properties

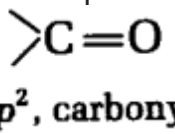
- Aldehydes and ketones are liquid or solid at room temperature. Methanal is a gas at room temperature. Ethanal is a volatile liquid.
- The boiling point of aldehydes and ketones are higher than ethers of comparable molecular masses.
- The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions because they form hydrogen bond with water. However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain.

Chemical Properties

Aldehydes and ketones due to the presence of polar carbonyl group exhibit the following characteristics:

Nucleophilic Addition Reactions

A nucleophile attacks at the electrophilic carbon atom of the polar carbonyl group.

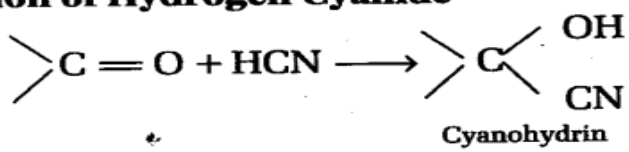


sp^2, carbonyl group

As the number of carbon atoms increases, reactivity decreases due to steric hindrance. Hence, the order of reactivity is

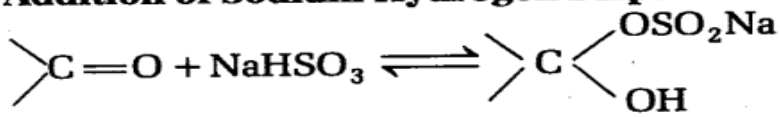
$$HCHO > CH_3CHO > CH_3COCH_3 > C_2H_5COC_2H_5$$

(a) Addition of Hydrogen Cyanide



Cyanohydrin

(b) Addition of Sodium Hydrogen Sulphite

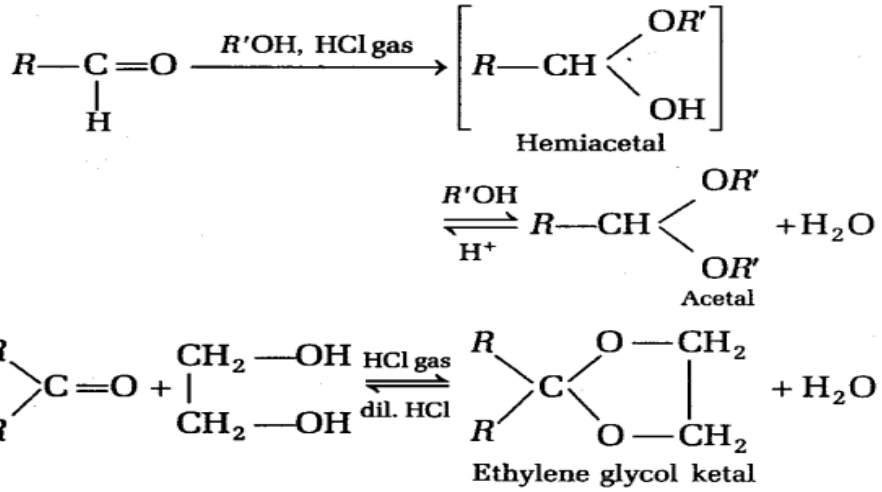


White crystalline solid

This reaction is used for the separation and purification of aldehydes and ketones. The reason for this is that the hydrogen sulphite addition compound formed, is water soluble and can be converted back to the original carbonyl compound by treating with

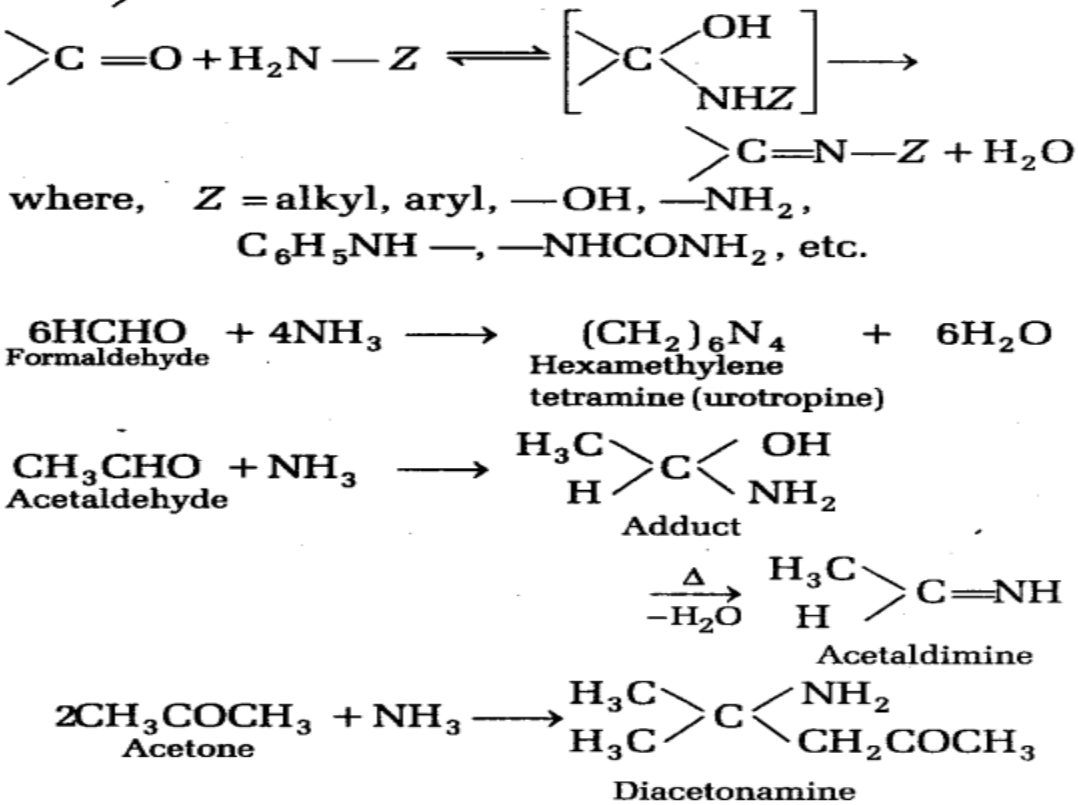
dilute mineral acid or alkali.

(c) Addition of Lower Alcohols



Addition of Ammonia and Its Derivative

This reaction is reversible and catalysed by acid (pH<<4). The equilibrium favours the product formation due to rapid dehydration of the intermediate to form $>C=N-Z$.



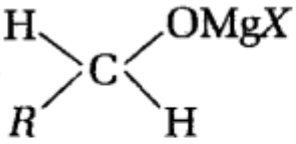
$$>C=O \xrightarrow[HCl]{Zn\text{-}Hg} >CH_2 + H_2O$$

(Clemmensen reduction)

$$>C=O \xrightarrow[-H_2O]{NH_2\cdot NH_2} >C=N\cdot NH_2$$

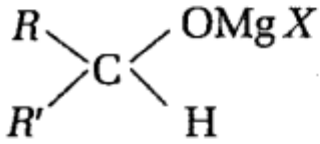
$$\xrightarrow[Heat]{KOH/Ethylene\ glycol} >CH_2 + N_2$$

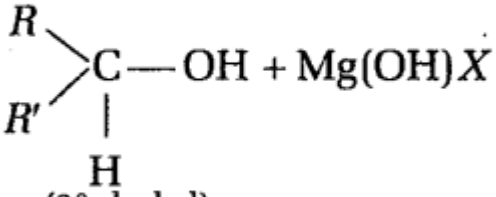
(Wolff-Kishner reduction)

(a) $HCHO + RMgX \longrightarrow$  $\xrightarrow{Hydrolysis}$

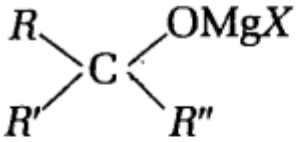
$$R-CH_2-OH + Mg(OH)X$$

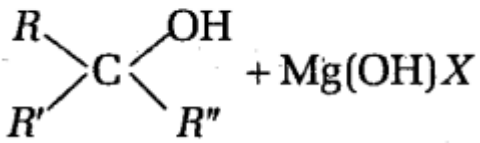
(1° alcohol other than CH_3OH)

(b) $RCHO + R'MgX \longrightarrow$  $\xrightarrow{Hydrolysis}$



(2° alcohol)

(c) $R-COR' + R''MgX \longrightarrow$  $\xrightarrow{Hydrolysis}$



(3° alcohol)

Oxidation

Aldehydes are easily oxidised to carboxylic acids on treatment with strong oxidising agents **(HNO_3, $K_2Cr_2O_7$, $KMnO_4$, etc).** Oxidation of primary alcohols and aldehydes cannot be carried out by alkaline $K_2Cr_2O_7$ because under these conditions, potassium chromate is formed which does not act as an oxidising agent.
Mild oxidising agents, mainly Tollen's reagent and Fehling's reagent also oxidise aldehydes

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow$$

(R = alkyl or C_6H_5 group) Tollen's reagent

$$RCOO^- + 2Ag + 2H_2O + 4NH_3$$

Silver mirror

$$R—CHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + Cu_2O + 3H_2O$$

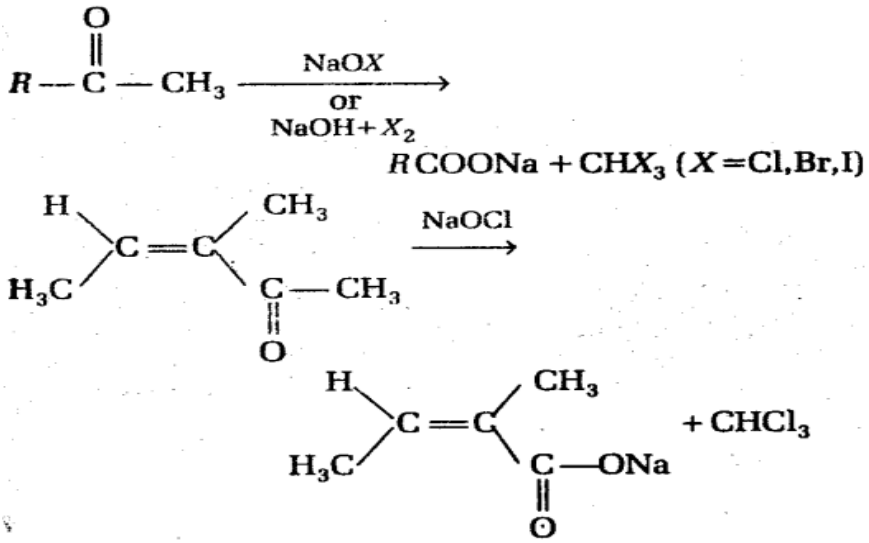
Fehling's solution — Red brown ppt

This reaction is not given by aromatic aldehydes. Ketones are oxidised only in the presence of strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to give a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone, e.g.

$$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3 \xrightarrow{\text{Alkaline } KMnO_4} CH_3COOH + CH_3CH_2COOH$$

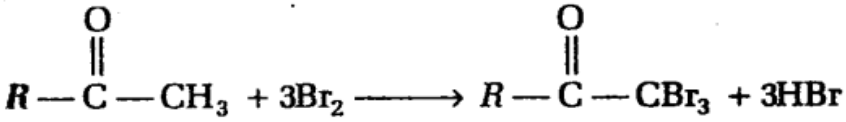
Haloform Reaction

Methyl ketones **($—COCH_3$)** are also oxidised by haloform reaction in which they are treated with halogen in the presence of alkali or hypohalite salt.

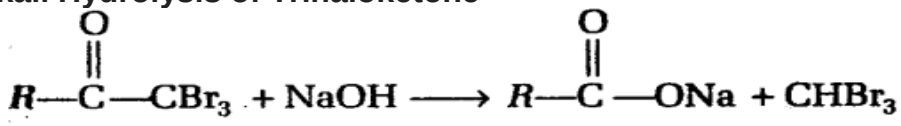


—CH_3 group of **$COCH_3$** is converted into haloform as it contains acidic hydrogen atoms. Acid salt is obtained corresponding to total number of carbon atoms apart from **—CH_3** of ***R*$COCH_3$.**
Mechanism of reaction is as follows:

Halogenation



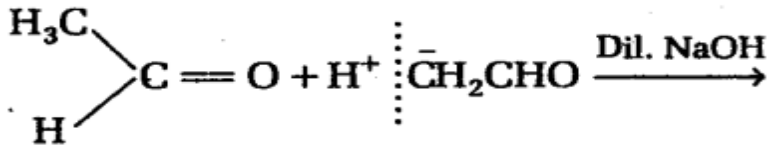
Alkali Hydrolysis of Trihaloketone

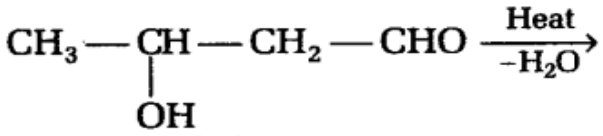


This reaction is used to diagnose the presence of $CH_3—C(=O)—$ group and also to distinguish methyl ketones from others.

Reactions Due to Acidic α-Hydrogen

Aldehydes or ketones having atleast one a-hydrogen atom, undergo a reaction in the presence of dilute alkali , as catalyst to form **β -hydroxy** aldehydes (aldol) or **β -hydroxy** ketones (ketol) respectively, **e.g.** aldol condensation



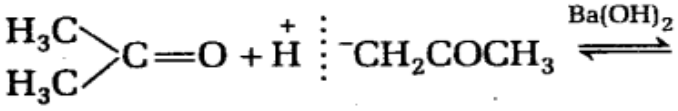


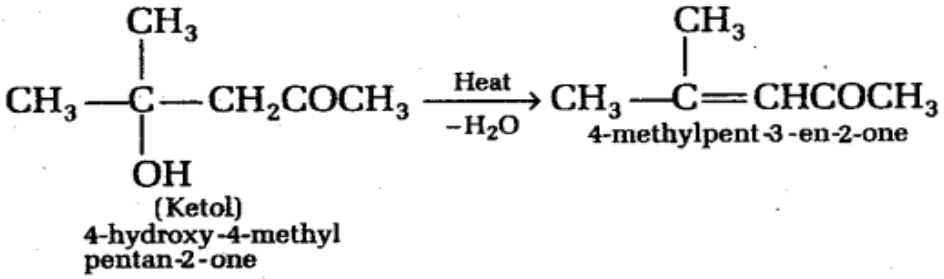
(Aldol) 3-hydroxy butanal

$CH_3—CH=CH—CHO$

Crotonaldehyde (common name)

But-2-enal (IUPAC)

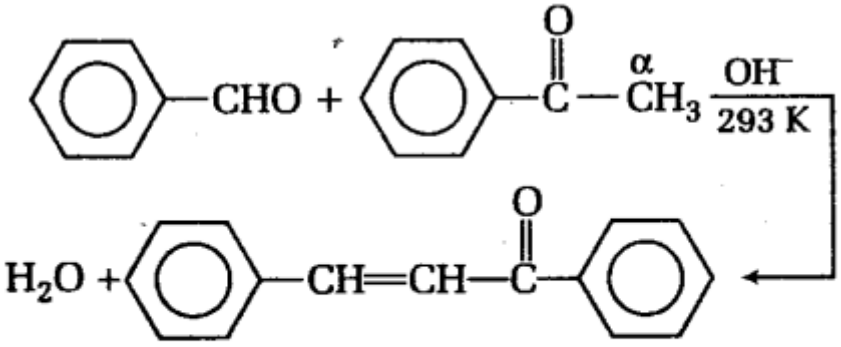




(Ketol)
4-hydroxy-4-methyl
pentan-2-one

4-methylpent-3-en-2-one

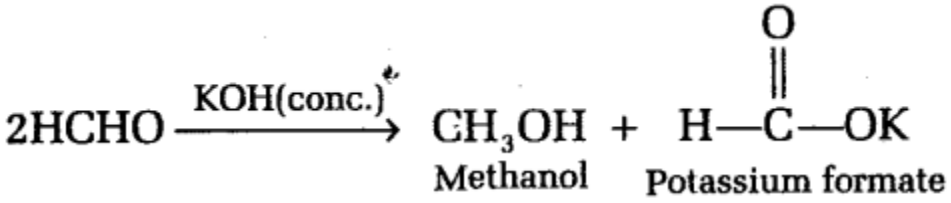
When aldol condensation is carried out between two different aldehydes and/or ketones, it is called cross aldol condensation, **e.g**

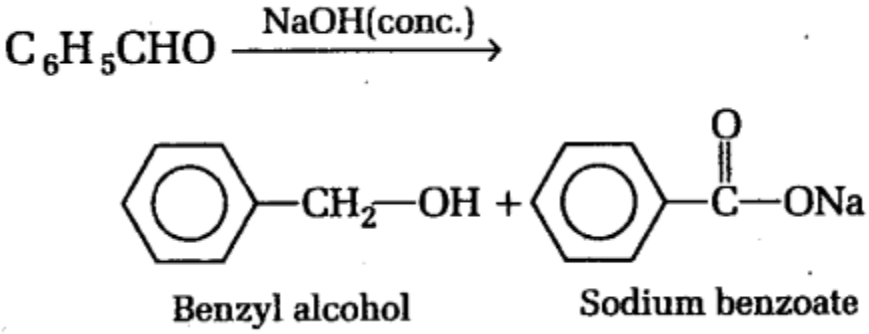


1,3-diphenylprop-2-en-1-one
(Benzalacetophenone)
(major product)

Cannizzaro Reaction

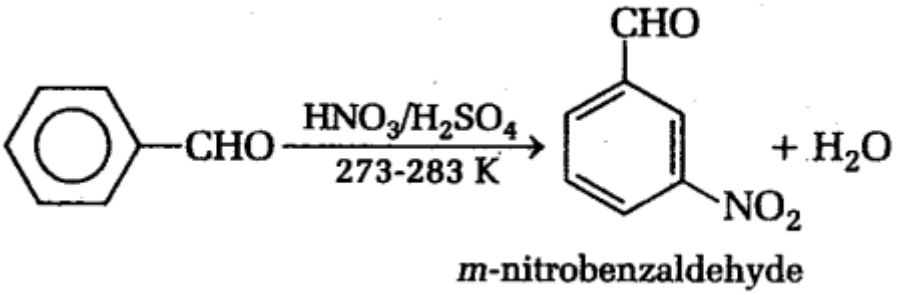
Aldehydes which do not have any a-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali.





Electrophilic Substitution Reaction

Aromatic aldehydes and ketones undergo electrophilic substitution. Carbonyl group' shows **+*R*-effect,** therefore acts as a deactivating and meta directing group.



Uses of Aldehydes and Ketones

- In chemical industry, aldehydes and ketones are used as solvents, starting materials and reagents for the synthesis of other products.
- Formaldehyde, under the name formalin (40% solution) is used to preserve biological specimens.
- Formaldehyde is also used to prepare bakelite, urea-formaldehyde glues and other polymeric products.

Carboxylic Acids

Carbon compounds containing a functional group, **—COOH** are called carboxylic acids. Some higher members of aliphatic carboxylic acids (C_{12}-C_{18}) known as fatty acids, occur in natural fats as esters of glycerol.

Nomenclature

According to IUPAC nomenclature system, name of a carboxylic acid is obtained by replacing the terminal 'e' of the corresponding alkane by the suffix 'oic acid'. Their general formula is C_nH_{2n+1} **COOH.**

Carboxylic acid	General name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$(CH_3)_2CHCOOH$	*Iso*-butyric acid	2-methyl propanoic acid

Nature of the Carboxylic Acids

- Carboxylic acids are acidic in nature but they are weaker acids than mineral acids but stronger acids than phenols (because the carboxylate ion is more stabilised as compared to phenoxide ion).
- The carboxylic acids form salts with alkalies.
- Strength of acid is indicated by pK_a value. Higher the value of K_a or lower value of pK_a, stronger is the acid.
- Aromatic acids are more acidic than aliphatic acids.

Preparation

(i) From Acid Derivatives

All acid derivatives like amides (***R*CONH$_2$**), acid halides (COCl), esters (RCOOR'), acid anhydrides (RCO —O—COR) on hydrolysis give carboxylic acids.

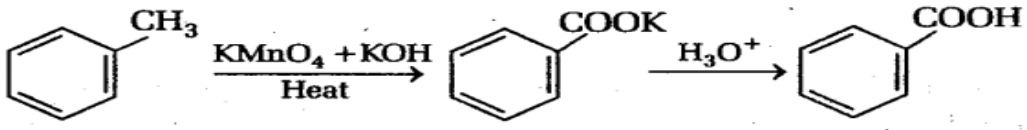
All acid derivatives break form $RC^{+}Q$.

$$RCOZ \xrightarrow[\text{or}\ \text{Dil. NaOH}]{\text{Dil. HCl}} RCOOH$$

$$Z = —NH_2, —X\ (X = Cl, Br, I), OR', RCOO—, \text{etc.}$$

(ii) From Alkyl Benzene

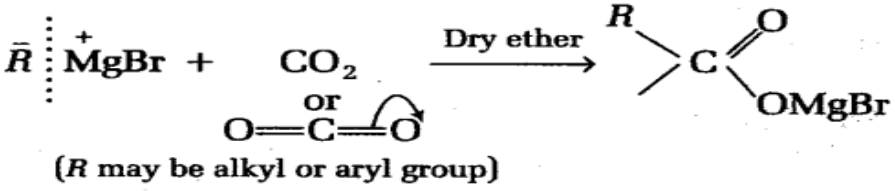
Alkyl benzene when treated with strong oxidising agent like **H_2Cr0_4** (chromic acid), acidic or alkaline **$KMn0_4$** gives benzoic acid.



(iii) From Nitriles

$$R — CN \xrightarrow[\Delta]{\text{Dil. HCl}} R — COOH + NH_3$$

(iv) From Grignard Reagent



(*R* may be alkyl or aryl group)

Chemical Properties

Reactions Showing Acidic Behaviour
Reactions with Metals and Alkalies

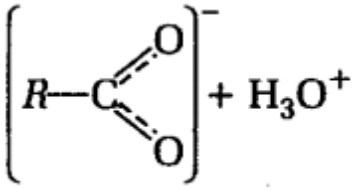
(a) $2RCOOH + 2Na \longrightarrow 2RCOONa + H_2$

(b) $RCOOH + NaOH \longrightarrow RCOONa + H_2O$

(c) $RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2$

Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and

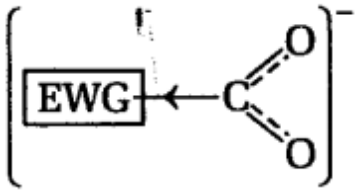
hydronium ion.



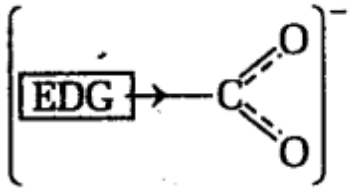
Resonance hybrid

Effect of Substituents on the Acidity of Carboxylic Acids

Electron withdrawing group (EWG) stabilises the carboxylate anion find strengthens the acid.



Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid. Strong acids have higher value of K_a and lower value of pK_a .



Following acids are arranged in decreasing order of acidity

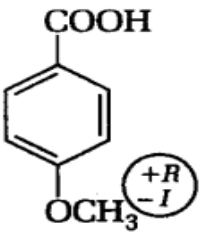
$CF_3COOH > CCl_3COOH > CHCl_2COOH$

$NO_2CH_2COOH > NC — CH_2COOH$

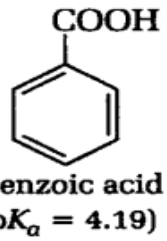
$C_6H_5COOH > C_6H_5CH_2COOH >$

$CH_3COOH > CH_3CH_2COOH$

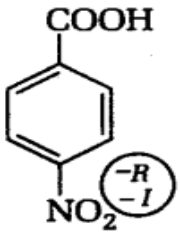
In case of aromatic carboxylic acids, more the –*R*-effect, more is the acidic nature.



4-methoxy benzoic acid (pK_a = 4.46)



Benzoic acid (pK_a = 4.19)

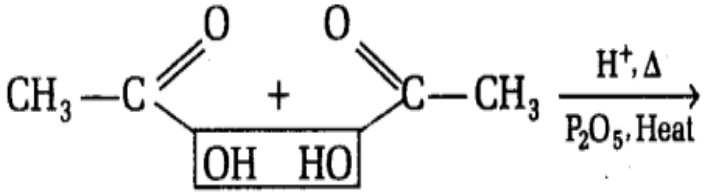


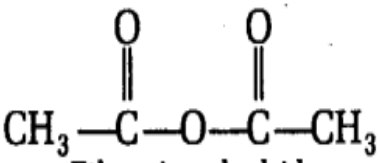
4-nitrobenzoic acid (pK_a = 3.41)

In case of aromatic carboxylic acids, more the –*R* effect, more is the acidic nature.

Reactions Involving Cleavage of C —OH Bond

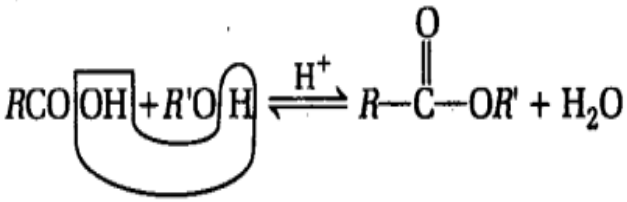
(a) **Formation of Anhydride**





Ethanoic anhydride

(b) **Esterification**



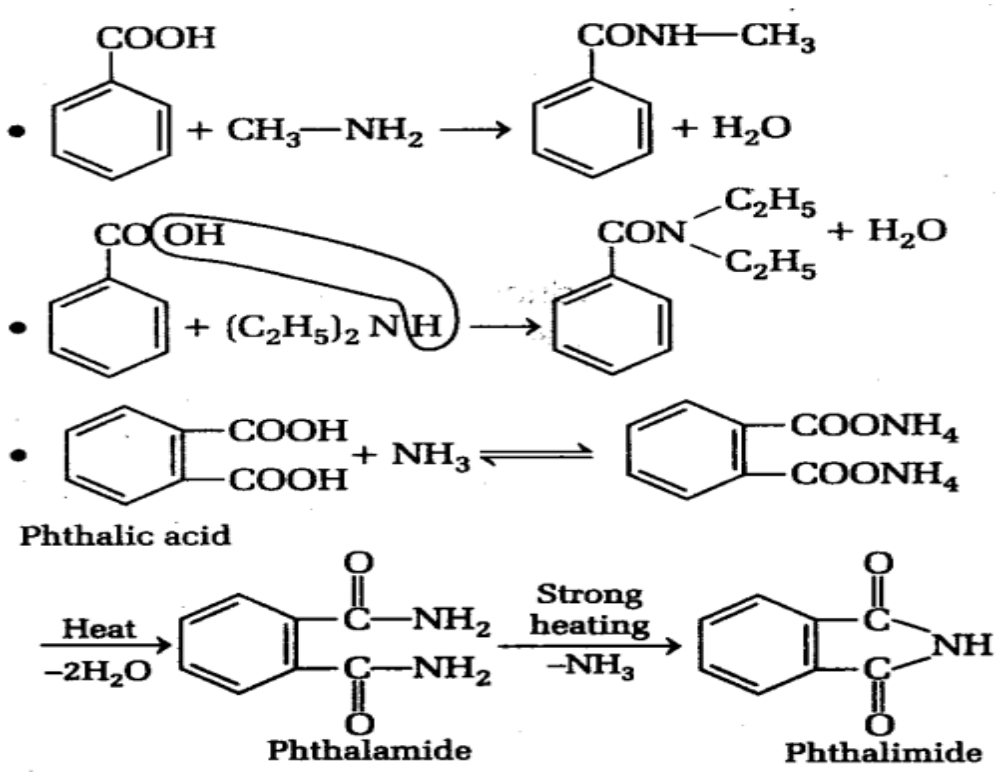
(c) **Reaction with PCl_5, PCl_3 and $SOCl_2$**

- $R\text{COOH} + PCl_5 \longrightarrow R\text{COCl} + PCl_3 + HCl$
- $3R\text{COOH} + PCl_3 \longrightarrow 3R\text{COCl} + H_3PO_3$
- $R\text{COOH} + SOCl_2 \longrightarrow R\text{COCl} + SO_2\uparrow + HCl\uparrow$

(d) **Reactions with NH_3 and its Derivatives**

- $CH_3COOH + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow{\text{Heat}}$

$$CH_3CONH_2 \xrightarrow[P_2O_5]{\text{Heat}} CH_3CN + H_2O$$



Reduction of—COOH Group

Carboxylic acids are reduced to primary alcohols by **$LiAlH_4$** or better with **$B_2H_6.B_2H_6$** does not easily reduce functional groups such as esters, nitro, halo, etc. **$NaBH_4$** does not reduce the carboxyl group.

$$RCOOH \xrightarrow[(ii)\,H_3O^+]{(i)\,LiAlH_4/Ether\ or\ B_2H_6} RCH_2OH + H_2O$$

Decarboxylation

$$RCOONa + NaOH \xrightarrow[Heat]{CaO} RH + Na_2CO_3$$

Methanoic acid and its sodium salt acts as reducing agent due to — CHO group. It reduces Tollen's reagent, Fehling's reagent, **$KMn0_4$**, etc.

Question 1.
A compound does not react with 2,4-dinitrophenyl hydrazine, compound is
(a) acetone
(b) acetaldehyde
(c) CH_3OH
(d) $CH_3CH_2COCH_3$

Question 2.
When ethanal reacts with CH_3MgBr and C_2H_5OH/dry HCl, the product formed are
(a) methyl alcohol and 2-propanol
(b) ethane and hemiacetal
(c) 2-propanol and acetal
(d) propane and methyl acetate

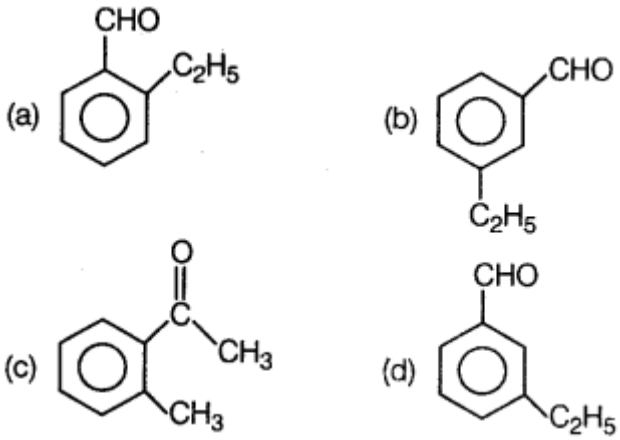
Question 3.
Arrange the following compounds in decreasing order of their boiling points.
CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$
(a) $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$
(b) $CH_3CH_2CH_3 < CH_3CHO < CH_3OCH_3 < CH_3CH_2OH$
(c) $CH_3CH_2CH_3 > CH_3CHO > CH_3OCH_3 > CH_3CH_2OH$
(d) $CH_3CH_2OH > CH_3CHO > CH_3OCH_3 > CH_3CH_2CH_3$

Question 4.
Which of the following compounds on heating with aqueous KOH, produces acetaldehyde?
(a) CH_3COCl
(b) CH_3CH_2Cl
(C) CH_2ClCH_2Cl
(d) CH_3CHCl_2

Question 5.
Which of the following give an explosive RDX on nitration?
(a) Toluene
(b) Benzene
(c) Guanidine
(d) Urotropine

Question 6.
The reagent used for the separation of acetaldehyde from acetophenone is
(a) $NaHS0_3$
(b) $C_6H_5NHNH_2$
(c) NH_2OH
(d) $NaOH\text{-}I_2$

Question 7.
An aromatic compound 'X' with molecular formula $C_9H_{10}O$ gives the following chemical tests
(i) It forms 2,4-DNP derivative.
(ii) It reduces Tollen's reagent.
(iii) It undergoes Cannizzaro reaction.
(iv) On vigorous oxidation, 1,2-benzenedicarboxylic acid is obtained.
Compound X is

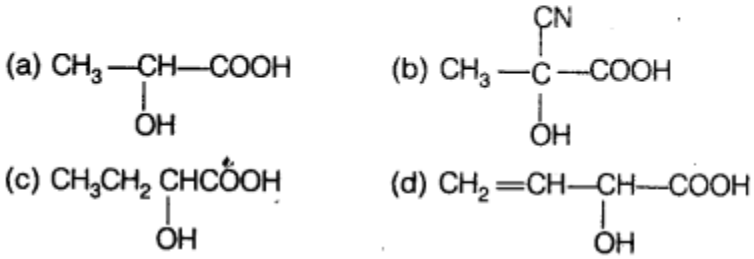


Question 8.
Self condensation of acetaldehyde in the presence of dilute alkalies gives
(a) an acetal
(b) an aldol
(c) mesitylene
(d) propionaldehyde'

Question 9.

$$CH_3CHO + HCHO \xrightarrow[\Delta]{\text{dil. NaOH}} A \xrightarrow[H_3O^+]{HCN} B;$$

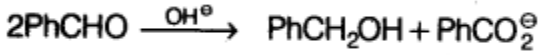
the structure of the compound *B* is



Question 10.
Which of the following compounds will not undergo aldol condensation?
(a) Methanal
(b) 2-methyl pentanal

(c) Cyclohexanone
(d) 1-phenyl propanone

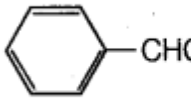
Question 11.
In Cannizaro reaction given below,



the slowest step is
(a) the attack of OH-
(b) the transfer of hydride to the carbonyl group
(c) the abstraction of proton from the carboxylic group
(d) the deprotonation of $PhCH_2OH$

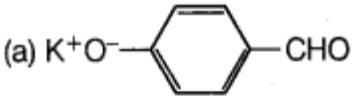
Question 12.
Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid?
(a) Phenol
(b) Benzoic acid
(c) Butanal
(d) Benzaldehyde

Question 13.
Which product is formed when the compound



is treated with concentrated aqueous KOH solution? **[NCERT]**

(a)



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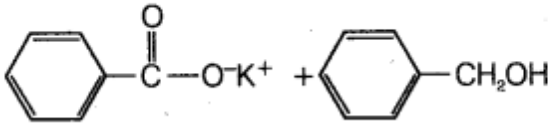

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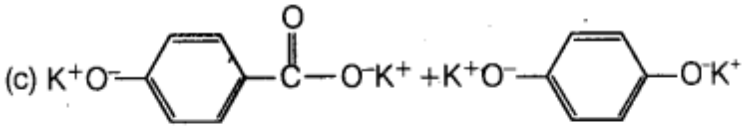
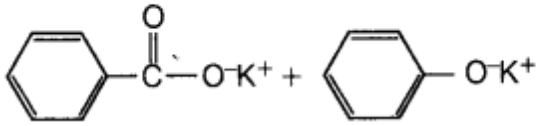
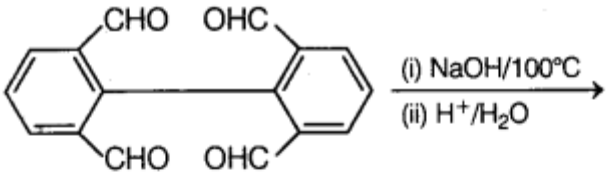


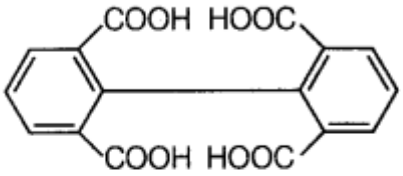
(d)

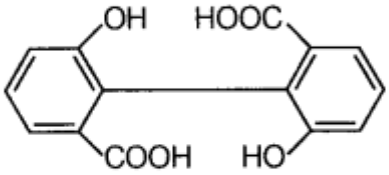


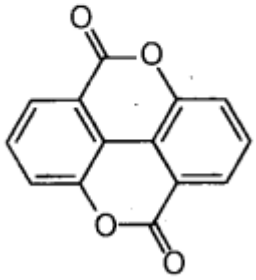
Question 14.

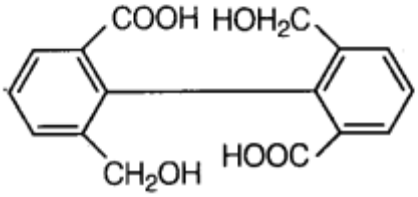


Major product is

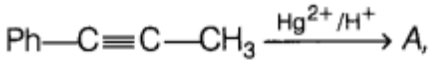
(a) 

(b) 

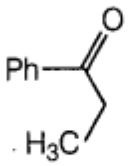
(c) 

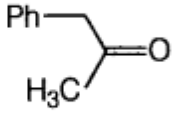
(d) 

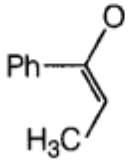
Question 15.

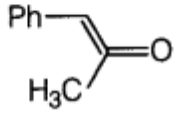


A is

(a) 

(b) 

(c) 

(d) 

Question 16.

The enol form of acetone after treatment with D_2O, gives

(a) $H_3C-\underset{\underset{OD}{|}}{C}=CH_2$ (b) $H_3C-\underset{\underset{O}{||}}{C}-CD_3$

(c) $H_2C=\underset{\underset{OH}{|}}{C}-CH_2D$ (d) $H_2C=\underset{\underset{OH}{|}}{C}-CHD_2$

Question 17.

Compound $Ph-O-\overset{\overset{O}{||}}{C}-Ph$ can be prepared by the reaction of **[NCERT Exemplar]**

(a) phenol and benzoic acid in the presence of NaOH
(b) phenol and benzoyl chloride in the presence of pyridine
(c) phenol and benzoyl chloride in the presence of $ZnCl_2$
(d) phenol and benzaldehyde in the presence of palladium

Question 18.

Ketones react with Mg-Hg over water gives
(a) pinacolone
(b) pinacol
(c) alcohol
(d) None of these

Question 19.

An organic compound X on treatment with acidified $K_2Cr_2O_7$ gives compound Y which reacts with I_2 and sodium carbonate to form triiodomethane. The compound X can be
(a) CH_3OH
(b) CH_3CHO
(C) CH_3COCH_3
(d) $CH_3CH(OH)CH_3$

Question 20.

Which of the following compounds with molecular formula C_5H_{10} yields acetone on ozonolysis?
(a) 2-methyl-2-butene
(b) 3-methyl-1-butene
(c) Cyclopentane
(d) 2-methyl-1 -butene

Question 21.

Which is not true about acetophenone?

(a) On oxidation with alkaline $KMnO_4$ followed by hydrolysis gives benzoic acid
(b) Reacts with I_2/NaOH to form iodoform
(c) Reacts with Tollen's reagent to form silver mirror
(d) Reacts to form 2,4-dinitrophenyl hydrazine

Question 22.
A carbonyl compound reacts with hydrogen cyanide to form cyanohydrin which on hydrolysis forms a racemic mixture of α-hydroxy acid. The carbonyl compound is
(a) acetaldehyde
(b) acetone
(c) diethyl ketone
(d) formaldehyde

Question 23.
A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was
(a) CH_3OH
(b) HCHO
(c) CH_3COCH_3
(d) CH_3COOH

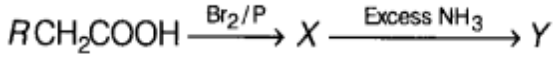
Question 24.
By combining the two calcium salts of carboxylic acids, we are preparing 2-butanone. Find the correct pair from the following
(a) Calcium formate+Calcium propanoate
(b) Calcium acetate+Calcium propanoate
(c) Calcium acetate+Calcium acetate
(d) Calcium formate+Calcium acetate

Question 25.
Which of the following represents the correct order of the acidity in the given compounds?
(a) $CH_3COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$
(b) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$
(c) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$
(d) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$

Question 26.
Consider the acidity of the following carboxylic acids.
I. PhCOOH
II. o-$NO_2C_6H_4COOH$
III. p-$NO_2C_6H_4COOH$
IV. m – $NO_2C_6H_4COOH$
Which of the following order is correct?

(a) I > II > III > IV
(b) II > IV > III > I
(c) II > IV > I > III
(d) II > III > IV > I

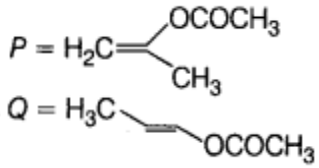
Question 27.
In the following reaction,



The major amounts of X and Y are
(a) $RCHBrCONH_2$;$RCH(NH_2)COOH$
(b) RCHBrCOOH; $RCH(NH_2)COOH$
(c) RCH_2COBr; RCH_2COONH_4
(d) RCHBrCOOH; RCH_2CONH_2

Question 28.
The property which distinguishes formic acid from acetic acid is
(a) Only ammonium salt of formic acid on heating gives amide
(b) When heated with alcohol/H_2SO_4, only acetic acid forms ester
(c) Only acetic acid forms salts with alkali
(d) Only formic acid reduces Fehling's solution

Question 29.
The product of acid hydrolysis of P and Q can be 0 distinguished by



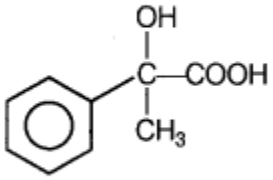
(a) Lucas reagent
(b) 2, 4-DNP
(c) Fehling's solution
(d) $NaHSO_3$

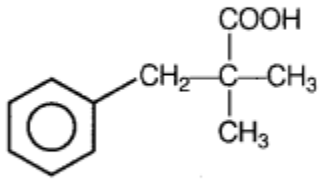
Question 30.

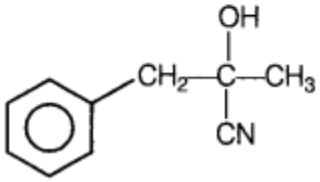
In a set of reactions, acetic acid yielded a product *D*

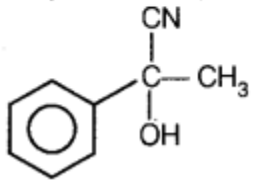
$$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow[\text{Anhyd. } AlCl_3]{\text{Benzene}} B \xrightarrow{HCN} C \xrightarrow{HOH} D$$

The structure of *D* would be

(a) 

(b) 

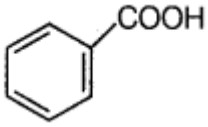
(c) 

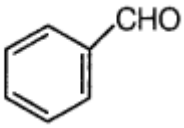
(d) 

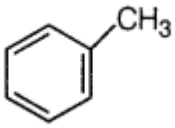
Question 31.

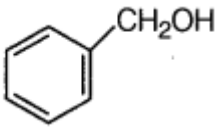
The reactant (*X*) in the reaction,

$$X \xrightarrow[(CH_3CO)_2O]{CH_3COONa} \text{Cinnamic acid, is}$$

(a) 

(b) 

(c) 

(d) 

Question 32.

Hydrolysis of an ester gives a carboxylic acid which on Kolbe's electrolysis yield ethane. The ester is

(a) methyl methanoate
(b) methyl ethanoate
(c) methyl methanoate
(d) None of the above

Question 33.

In the following reaction,

$$CH_3COOH + X \xrightarrow{\text{Conc. } H_2SO_4} Y + CO_2 + N_2$$

X and Y respectively, are

(a) HN_3 and CH_3NH_2

(b) NH_3 andCH_3CONH_2
(c) NH_3 and CH_3NH_2
(d) NH_3 and CH_3CONH_2

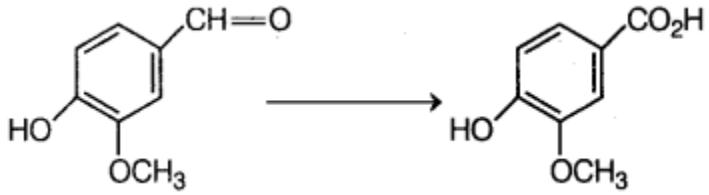
Question 34.
Two moles of acetic acid are heated with P_2O_5. The product formed is
(a) 2 moles of ethanol
(b) 2 moles of methyl cyanide
(c) acetic anhydride
(d) formic anhydride

Question 35.
Vinegar obtained from sugarcane has
(a) CH_3COOH
(b) C_6H_5COOH
(c) HCOOH
(d) CH_3CH_2COOH

Direction (Q.NOs.36-37): In the following questions more than one of the answers given may be correct. Select the correct answers and mark it according to the codes.
Codes
(a) 1,2 and 3 are correct
(b) 1 and 2 are correct
(c) 2 and 4 are correct
(d) 1 and 3 are correct

Question 36.
The acids which do not contain a —COOH group are
1. picric acid
2. lactic acid ,
3. carbolic acid
4. propanoic acid

Question 37.
Following conversion can be carried out by using



1. $KMnO_4$ in alcohol
2. NaClO in a buffer

3. $Ag_2O/NaOH$, HCl
4. $FeCl_3$ in a buffer

Question 38.

Match the Column I with Column II and choose the correct codes given below.

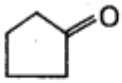
	Column I		Column II
A.	Grignard reagent	1.	$H_2/Pd\text{-}BaSO_4$
B.	Clemmensen reduction	2.	N_2H_4 / KOH / $CH_2(OH)-CH_2(OH)$
C.	Rosenmund reduction	3.	CH_3MgX
D.	Wolff-Kishner reduction	4.	Zn-Hg/conc. HCl
		5.	H_2 / Ni

Codes

	A	B	C	D
(a)	3	4	2	1
(c)	2	1	4	5

	A	B	C	D
(b)	3	4	1	2
(d)	5	3	2	1

Question 39.

Treatment of cyclopentanone,  with methyl lithium gives which of the following species?

(a) Cyclopentanoyl anion
(b) Cyclopentanoyl cation .
(c) Cyclopentanoyl radical
(d) Cyclopentanoyl biradical

Question 40.

An organic compound 'X' having molecular formula $C_5H_{10}O$ yields phenyl hydrazone and gives negative response to the iodoform test and Tollen's test. It produces n-pentane on reduction. 'X' could be

(a) pentanal
(b) 2-pentanone
(c) 3-pentanone
(d) n-amyl alcohol

Direction (Q.Nos.41-44): Each of these questions contains two statements : Assertion and Reason. Each of, these questions also has four alternative choices, only one of

which is the correct answer. You have to select one of the codes (a),(b),(c) and (d) given below.
(a) Assertion is true,Reason is true; Reason is the correct explanation for Assertion
(b) Assertion is true,Reason is true; Reason is not the correct explanation for Assertion
(c) Assertion is true,Reason is false
(d) Assertion is false,Reason is true

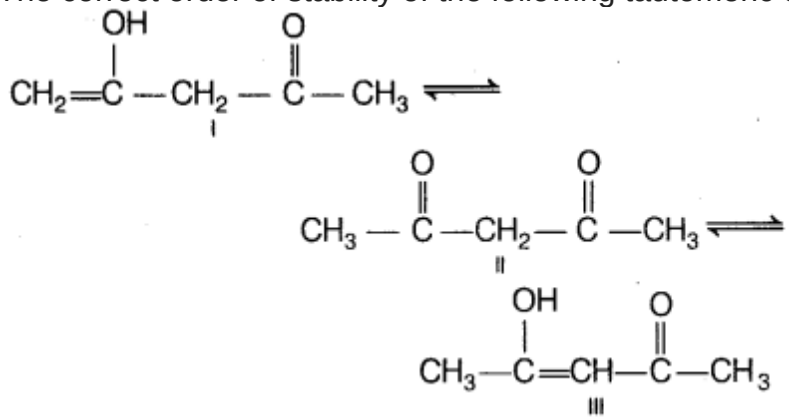
Question 41.
Assertion: Both o-hydroxy benzaldehyde and p-hydroxy benzaldehyde have same molecular weight and show H-bonding.
Reason: Melting point of p-hydroxy benzaldehyde is more.

Question 42.
Assertion: Isobutanal does not give iodoform test.
Reason: It does not have α-hydrogen.

Question 43.
Assertion: Aspirin can cause ulcer in the stomach.
Reason: The ester group in aspirin gets hydrolysed to acid group in the stomach where the p^H is 2.

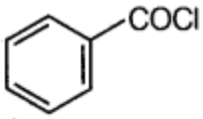
Question 44.
Assertion: The oxidation of ketone by perbenzoic acid gives esters.
Reason: Perbenzoic acid oxidises because of the release of nascent oxygen on dissociation.

Question 45.
The correct order of stability of the following tautomeric compounds,is

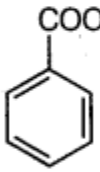


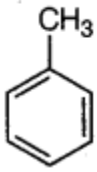
(a) III > II > I
(b) II > I > III
(c) II > III > I
(d) I > II > III

Question 46.
Reaction by which benzaldehyde cannot be prepared is

(a)  + H_2 in the presence of Pd-$BaSO_4$

(b)  + CO + HCl in the presence of anhydrous $AlCl_3$

(c)  + Zn/Hg and conc. HCl

(d)  + CrO_2Cl_2 in CS_2 followed by H_3O^+

Question 47.
CH_3CHO and $C_6H_5CH_2CHO$ can be distinguished chemically by
(a) Benedict's test
(b) Iodoform test
(c) Tollen's reagent test
(d) Fehling's solution test

Question 48.
The correct order of decreasing acidic strength of trichloroacetic acid (A), trifluoroacetic acid (B), acetic acid (C) and formic acid (D) is
(a) B>A>D>C
(b) B>D>C>A
(c) A>B>C>D
(d) A>C>B>D

Question 49.
Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The

product obtained is

(a) $CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

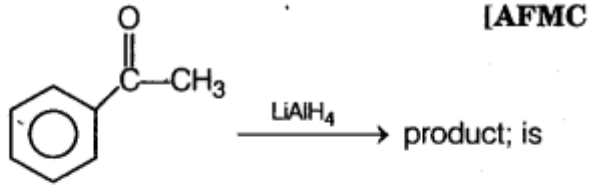
(b) $CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3$

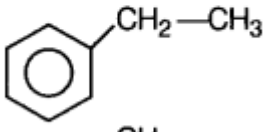
(c) $(CH_3)_2C(OH)(OC_2H_5)$

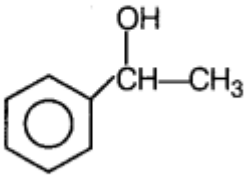
(d) $(CH_3)_2C(OC_2H_5)_2$

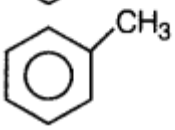
Question 50.

The product formed in the following reaction [AFMC



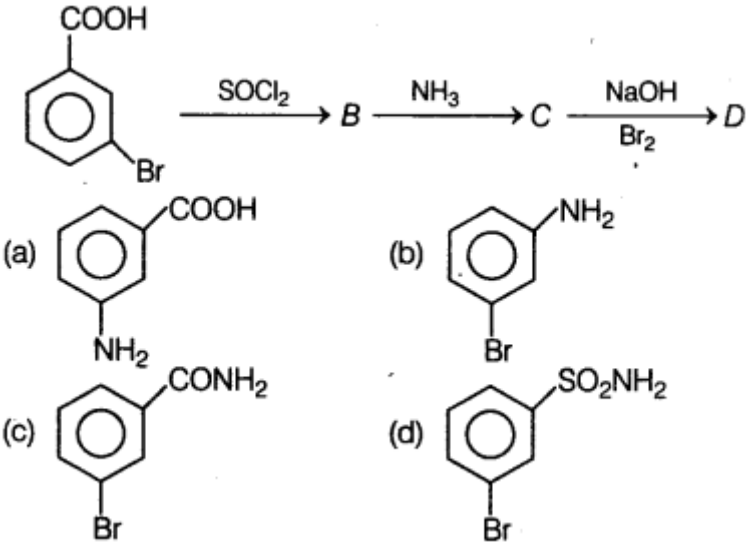
(a) 

(b) 

(c) 

(d) None of these

Question 51.
In a set of reactions, m-bromobenzoic acid gave a product D. Identify the product D



Question 52.
Clemmensen reduction of a ketone is carried out in the presence of which of the following?
(a) Zn-Hg with HCl
(b) $LiAlH_4$
(c) H_2 and Pt as catalyst
(d) Glycol with KOH

Question 53.
The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is
(a) pyridinium chloro chromate
(b) chromic anhydride in glacial acetic acid
(c) acidic dichromate
(d) acidic permanganate

Question 54.

$$CH_3COOH \xrightarrow{LiAlH_4} A + CH_3COOH \xrightarrow{H_3O^+} B + H_2O$$

In the above reactions, *A* and *B* respectively are
[AIIMS 2011]

(a) $CH_3COOC_2H_5$, C_2H_5OH (b) CH_3CHO, C_2H_5OH
(c) C_2H_5OH, CH_3CHO (d) C_2H_5OH, $CH_3COOC_2H_5$

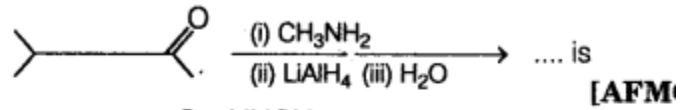
Question 55.
Which of the following reactions will not result in the formation of carbon-carbon bonds?

(a) Reimer-Tiemann reaction
(b) Cannizzaro reaction
(c) Wurtz reaction
(d) Friedel-Crafts acylation

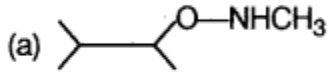
Question 56.
Given, cyclohexanol (I), acetic acid (II) 2,4,6-trinitrophenol (III) and phenol (IV). In these, the order of decreasing acidic character will be
(a) III>II>IV>I
(b) II>III>I>IV
(c) II>III>IV>I
(d) III>IV>II>I

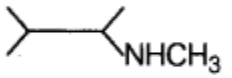
Question 57.
When ethanal is treated with Fehling's solution, it gives a precipitate of
(a) Cu_2O
(b) Cu
(c) Cu_3O
(d) CuO

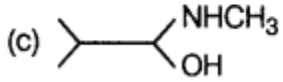
Question 58.
The major organic product formed in the following reaction

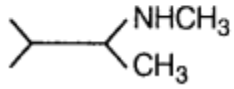


.... is [AFM

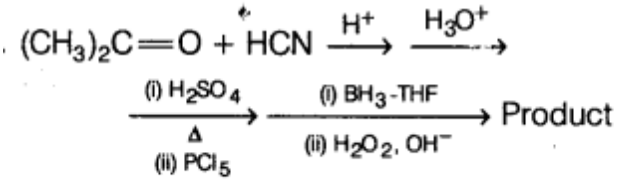
(a) 

(b) 

(c) 

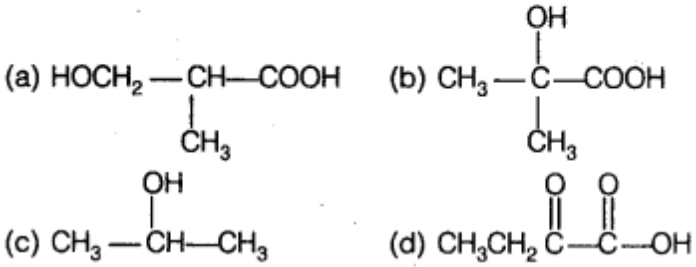
(d) 

Question 59.



$$(CH_3)_2C{=}O + HCN \xrightarrow{H^+} \xrightarrow{H_3O^+} \xrightarrow[\Delta]{\text{(i) } H_2SO_4} \xrightarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } BH_3\text{-THF}} \text{Product}$$

The final predominant product is **[AIIMS 2**



(a) $HOCH_2-CH(CH_3)-COOH$ (b) $CH_3-C(OH)(CH_3)-COOH$

(c) $CH_3-CH(OH)-CH_3$ (d) $CH_3CH_2-C(=O)-C(=O)-OH$

Question 60.

Which of the following aldehydes contains α-C atom but does not have any α-H atom?

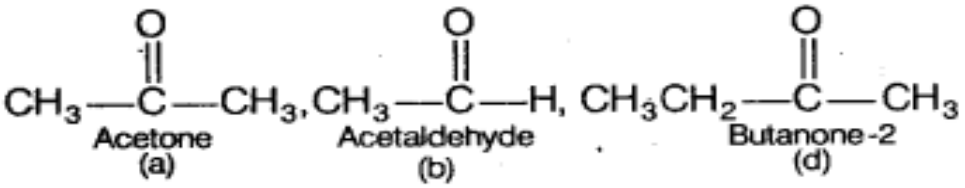
(a) Propionaldehyde
(b) Benzaldehyde
(c) Isobutyraldehyde
(d) Formaldehyde

Answers:

1. (c)	2. (c)	3. (d)	4. (d)	5. (d)	6. (a)	7. (a)	8. (b)	9. (d)	10. (a)
11. (b)	12. (d)	13. (b)	14. (d)	15. (a)	16. (a)	17. (b)	18. (b)	19. (d)	20. (a)
21. (c)	22. (a)	23. (d)	24. (b)	25. (d)	26. (d)	27. (b)	28. (d)	29. (c)	30. (a)
31. (b)	32. (b)	33. (a)	34. (c)	35. (a)	36. (d)	37. (a)	38. (b)	39. (a)	40. (c)
41. (b)	42. (c)	43. (a)	44. (c)	45. (a)	46. (c)	47. (b)	48. (a)	49. (d)	50. (b)
51. (b)	52. (a)	53. (b)	54. (d)	55. (b)	56. (a)	57. (a)	58. (b)	59. (a)	60. (b)

Hints And Solutions:

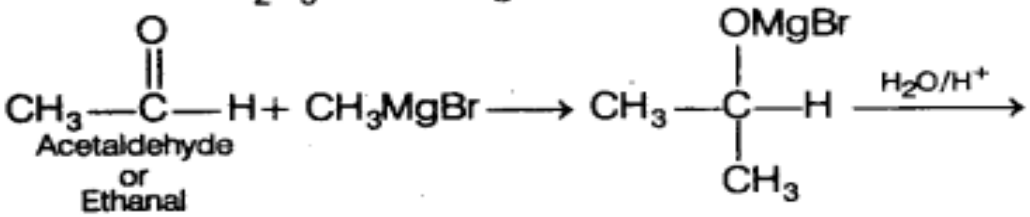
1. Only aldehydes and ketones react with 2, 4-dinitrophenyl hydrazine to give orange coloured precipitate. This reaction is used as test for carbonyl group. Alcohols do not give this reaction.

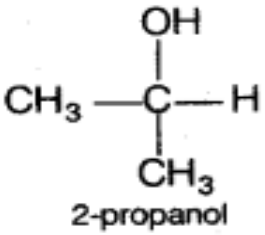


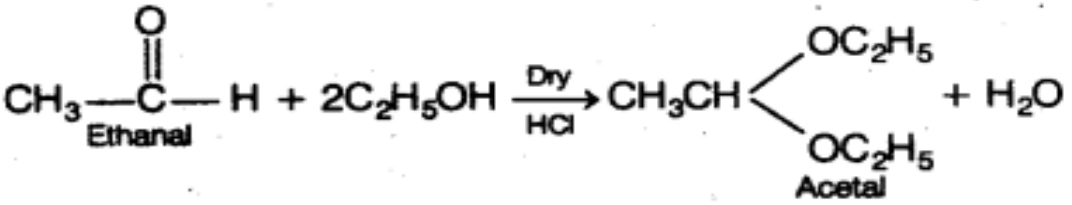
Choices (a), (b) and (d) are carbonyl compounds, so they react with 2, 4-dinitrophenyl hydrazine while CH_3OH [choice (c)] doesn't have carbonyl group.

$\therefore$ CH_3OH doesn't react with 2, 4-dinitrophenyl hydrazine.

2. Grignard reagent ($RMgX$) with aldehyde other than formaldehyde ($HCHO$) gives 2° alcohol. Aldehyde on reaction with C_2H_5OH / HCl gives acetal.







3. Among these only CH_3CH_2OH undergoes H-bonding. So, it will have the highest boiling point. CH_3CHO has higher boiling point than alkane due to appreciable intermolecular attraction (dipole-dipole interaction).

4. (a) $CH_3C(=O)Cl \xrightarrow{KOH\ (aq)} CH_3C(=O)OH + KCl$ (S_N reaction)

(b) $CH_3CH_2Cl \xrightarrow{KOH\ (aq)} CH_3CH_2OH$ (S_N2 reaction)

(c) $ClCH_2CH_2Cl \xrightarrow{KOH\ (aq)} HOCH_2CH_2OH$ (S_N2 reaction)

(d) $CH_3CHClCl \xrightarrow{KOH\ (aq)} CH_3CH(OH)OH$ (unstable)

$\xrightarrow{-H_2O} CH_3CHO$

5. $(CH_2)_6N_4 + 3HNO_3 \xrightarrow{H^+/H_2O}$ RDX $+ 3HCHO + NH_3$

∴ Nitration of urotropine gives powerful explosive, RDX.

6. CH_3CHO gives addition product with $NaHSO_3$ while acetophenone does not.

$CH_3CHO + NaHSO_3 \longrightarrow CH_3CH(OH)SO_3Na$

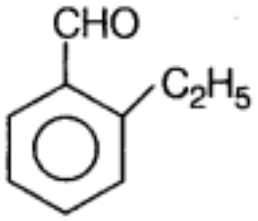
7. (i) *X* forms 2, 4-DNP derivatives, it shows that it is a carbonyl compound ($>C=O$).

(ii) It reduces Tollen's reagent, it shows that it has an aldehyde group.

(iii) It undergoes Cannizzaro reaction that also shows the presence of an aldehyde having no α-hydrogen.

(iv) On vigorous oxidation, it produces 1,2-benzenedicarboxylic acid. It shows that groups are present at 1, 2-position on benzene ring.

Thus, the correct structure of the compound *X* is



8. $CH_3CHO + HCH_2CHO \xrightarrow[NaOH]{Dil.} CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CHO$

Aldol

9. $HCHO + CH_3CHO \xrightarrow{Dil.\ NaOH^-} H-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2CHO \xrightarrow[-H_2O]{\Delta}$

$CH_2=CHCHO \xrightarrow{HCN} CH_2=CH-\underset{OH}{\underset{|}{\overset{CN}{\overset{|}{C}}}}H \xrightarrow{H_3O^+}$

A

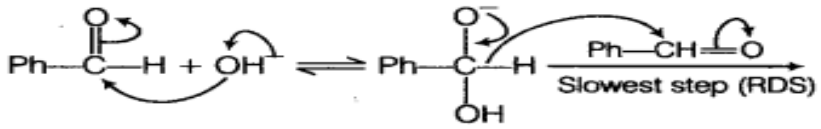
$CH_2=CH-\underset{OH}{\underset{|}{\overset{COOH}{\overset{|}{C}}}}H$

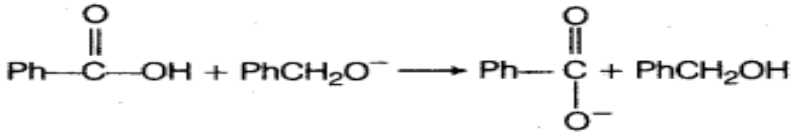
B

10. Aldehydes or ketones having atleast one α-H atom undergo aldol condensation. Among the given, methanal has not α-H atom.

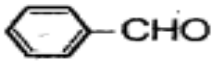
That's why, it does not give aldol condensation.

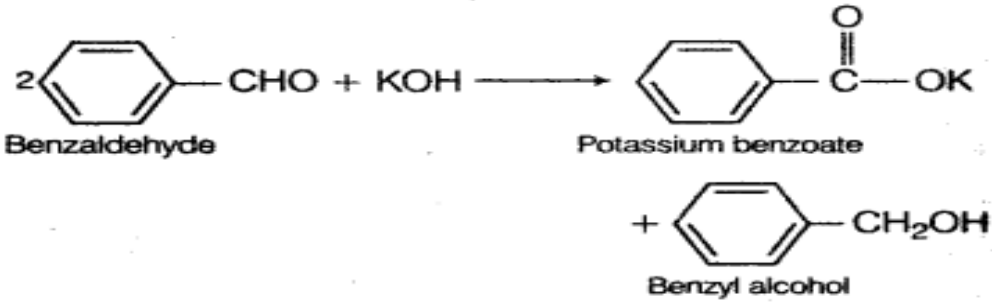
11. In Cannizzaro reaction, the transfer of H^- to another carbonyl group is difficult hence, the slowest slep.



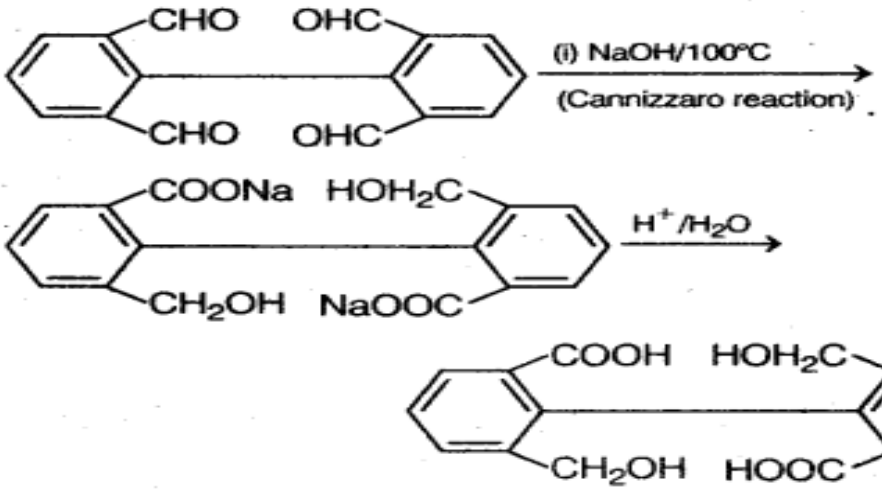


12. 50% NaOH solution reacts with those aldehydes which have no α-hydrogen to yield alcohol and acid (Cannizzaro reaction). Benzaldehyde has no α-hydrogen, so it shows this reaction.

13. Since,  does not contain α-H atom, so it will give Cannizzaro reaction with aqueous KOH solution.

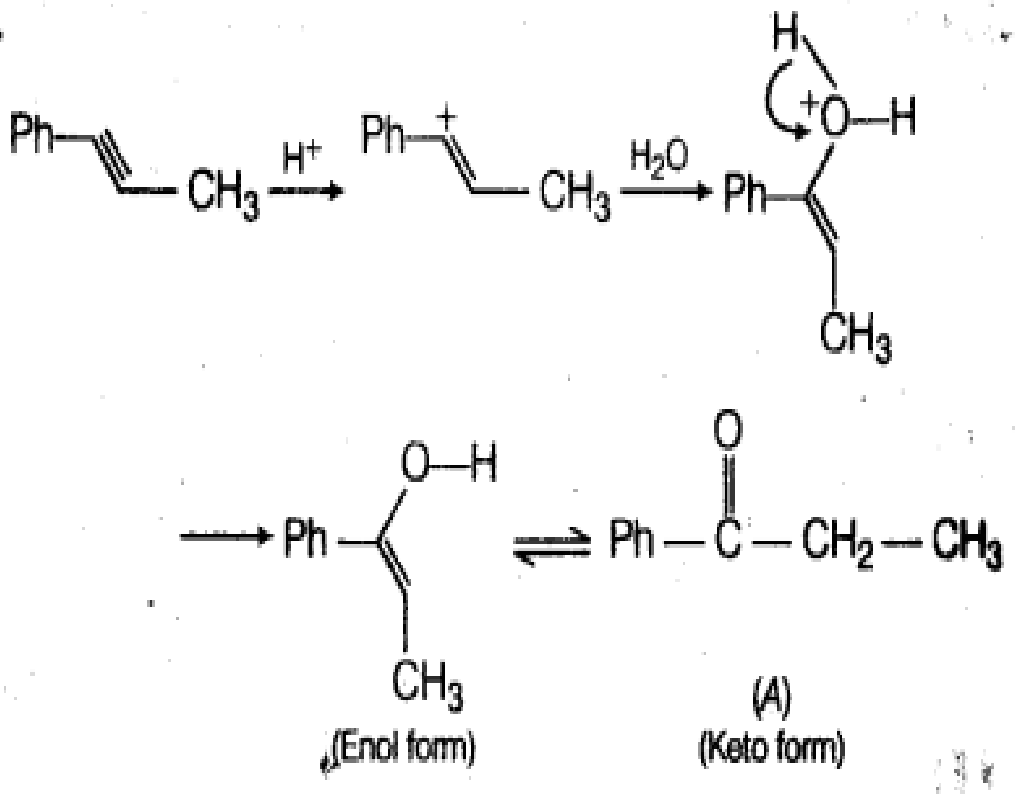


14.



Note Cannizzaro reaction is due to the absence of α-hydrogen.

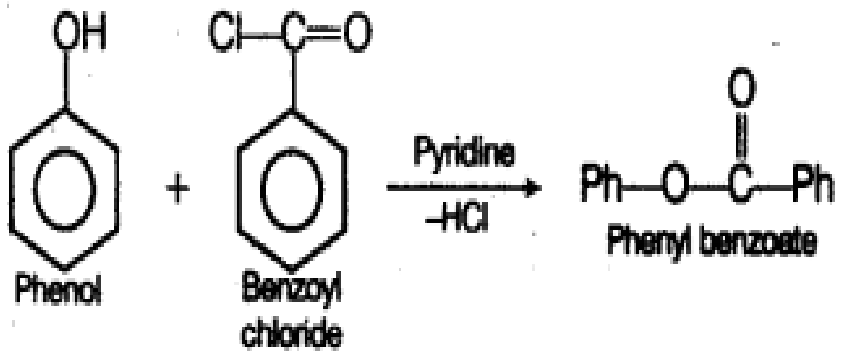
15.

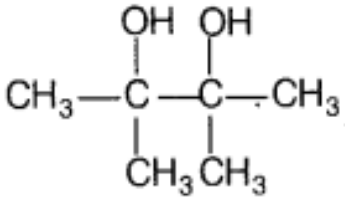


16. $H_3C-\underset{\underset{OH}{|}}{C}=CH_2 + D_2O \longrightarrow H_3C-\underset{\underset{OD}{|}}{C}=CH_2$

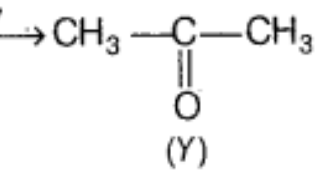
Enol form of acetone

17.



18. $2CH_3COCH_3 \xrightarrow[H_2O]{Mg\text{-}Hg}$ 

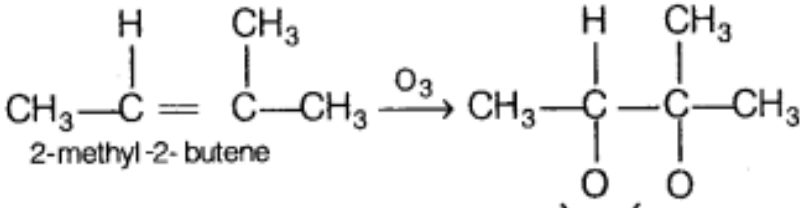
2,3-dimethylbutan-2, 3 -diol (pinacol)

19. $CH_3CHCH_3 \xrightarrow[H^+]{K_2Cr_2O_7}$ 

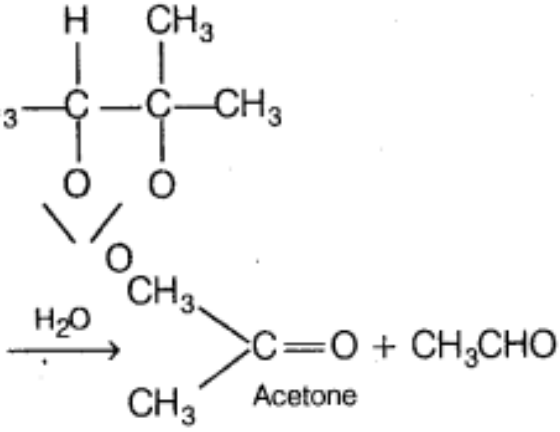
(X) (Y)

The compound Y gives positive iodoform test with I_2 and Na_2CO_3.

20. 2-methyl-2-butene (molecular formula C_5H_{10}) yields acetone on ozonolysis.

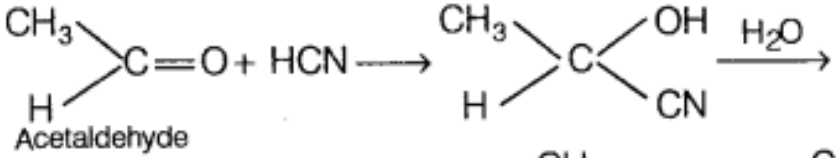


2-methyl -2- butene

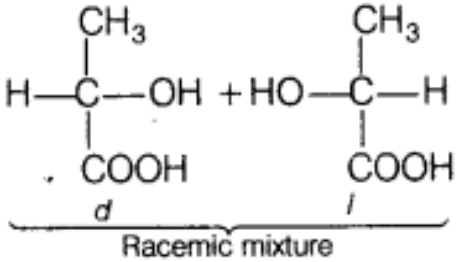


Acetone

21. Acetophenone is a ketone. It does not reacts with Tollen's reagent to give silver mirror.

22. 

Acetaldehyde



Racemic mixture

23. A liquid + $C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4}$ Compound
(Fruity smell)

Fruity smell is the characteristic property of ester, thus reaction can be considered as follows:

$$CH_3COOH + C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} CH_3\overset{\overset{O}{\|}}{C}-OC_2H_5 + H_2O$$

Ethyl acetate
(Fruity smell)

24. Calcium salts of carboxylic acid on heating give carbonyl compound.

(a) $(HCOO)_2Ca + (CH_3CH_2COO)_2Ca \longrightarrow$
Calcium formate — Calcium propanoate

$$2CH_3CH_2\overset{\overset{O}{\|}}{C}-H + 2CaCO_3$$

Propanal

(b) $(CH_3COO)_2Ca + (CH_3CH_2COO)_2Ca \longrightarrow$
Calcium acetate — Calcium propanoate

$$2CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 + 2CaCO_3$$

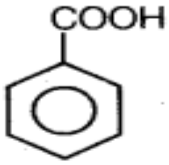
2-butanone

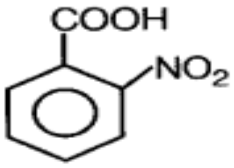
(c) $(CH_3COO)_2Ca + (CH_3COO)_2Ca \longrightarrow 2CH_3-\overset{\overset{O}{\|}}{C}-H + 2CaCO_3$
Calcium acetate — Calcium acetate — Ethanal

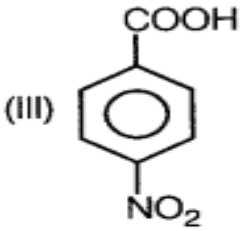
25. The acidity of halogenated acids increases almost proportionately with the increase in electronegativity of the halogen present.

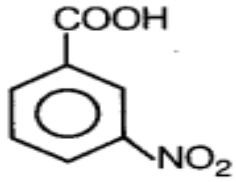
Therefore, the correct order is

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$

26. (I) 

(II) 

(III) 

(IV) 

$-NO_2$ group at any position shows electron withdrawing effect. Thus, acidic strength is increased.

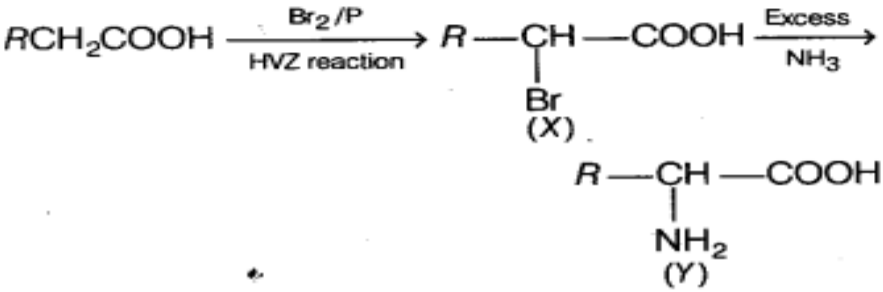
But *o*-nitrobenzoate ion is stabilised by intramolecular H-bonding like forces. Hence, its acidic strength is maximum.

Thus, the order of acidic strength is

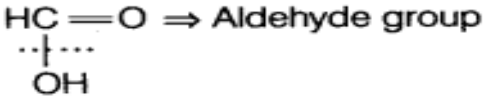
II > III > IV > I.

27. When an acid is heated with Br_2 in the presence of P, α-H atom of the acid is replaced by bromine atom.

This reaction is called Hell-Volhard-Zelinsky reaction. NH_2^- is a better nucleophile than Br^-.



28. Formic acid (HCOOH) also contain a —CHO group, so gives some reducing properties of aldehydes.

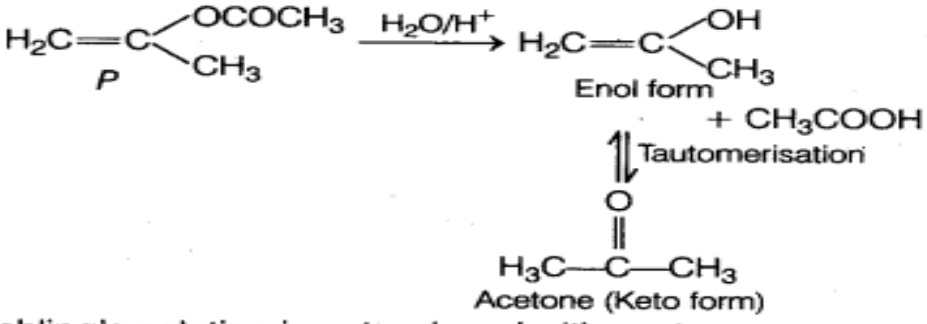


Formic acid is a very strong reducing agent. It reduces Tollen's reagent, Fehling's solution and mercuric chloride.

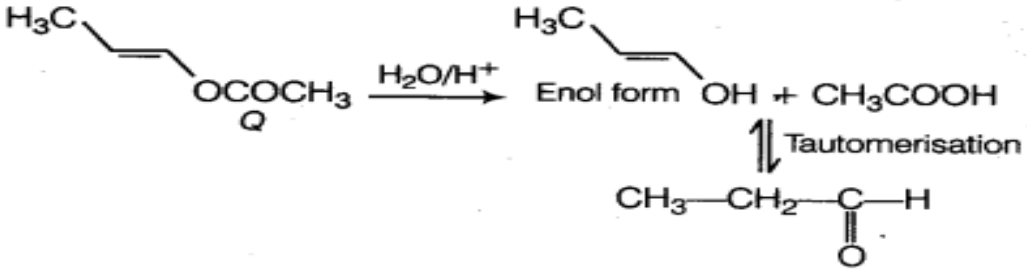
Acetic acid does not give these reactions due to absence of aldehyde group. Formic acid distinguishes from acetic acid by Fehling's solution.

Formic acid gives red precipitate of cuprous oxide with Fehling's solution while acetic acid does not.

29.

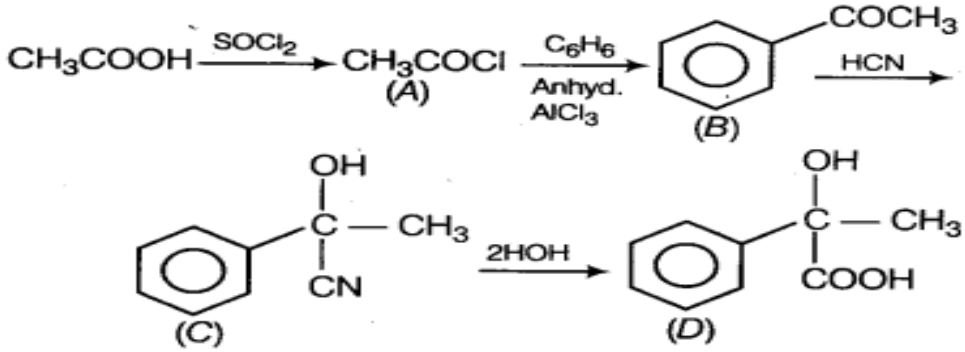


Fehling's solution is not reduced with acetone.

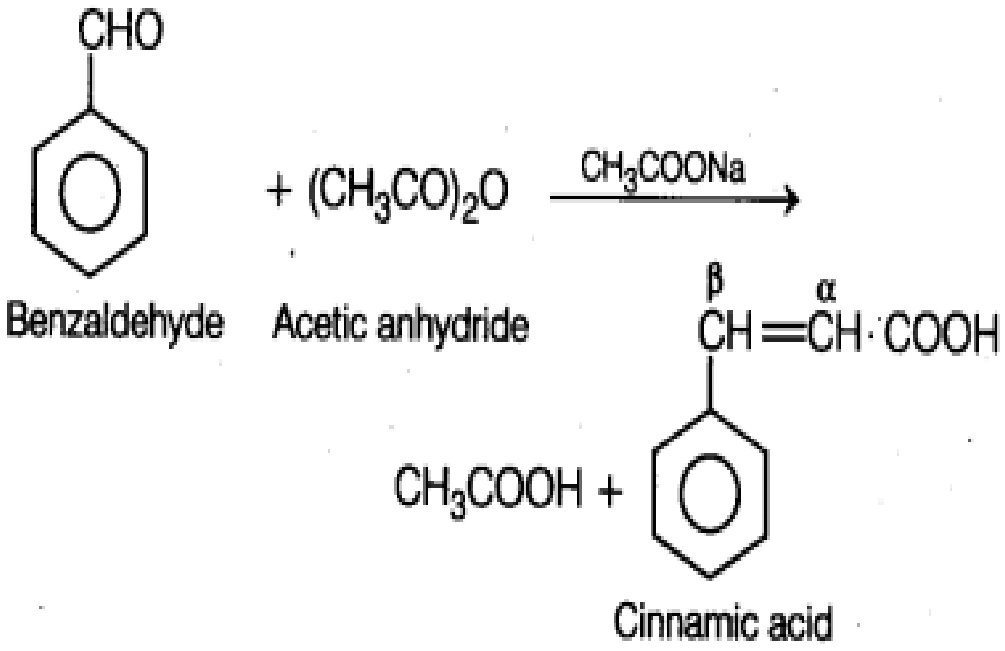


Fehling's solution is reduced with aldehyde, i.e. CH_3CH_2CHO. Hence, the product of acid hydrolysis of *P* (ketone) and *Q* (aldehyde) can be distinguished by Fehling's solution.

30.



31. Perkin reaction is the condensation reaction in which aromatic aldehyde is heated with an anhydride of an aliphatic acid in the presence of sodium salt of the same acid to form α, β -unsaturated acid.



32. $CH_3COOCH_3 \xrightarrow[-CH_3OH]{NaOH} CH_3COONa \xrightarrow[-CO_2, -NaOH, -H_2]{\text{Kolbe's electrolysis}}$

Methyl ethanoate

$CH_3—CH_3$

Ethane

33. $CH_3COOH + \underset{X}{HN_3} \xrightarrow[\text{Schmidt reaction}]{\text{conc. } H_2SO_4}$

$\underset{Y}{CH_3NH_2} + CO_2 + N_2$

34. $2CH_3COOH \xrightarrow[-H_2O]{P_2O_5}$ $(CH_3CO)_2O$

Acetic acid — Acetic anhydride

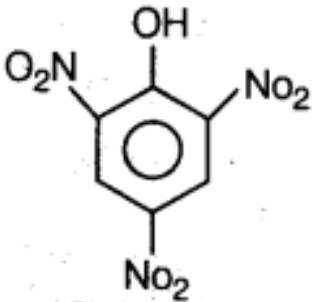
35. Vinegar is 7-10% aqueous solution of CH_3COOH.

$$C_{12}H_{22}O_{11} + HOH \xrightarrow[\text{Yeast}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[\text{Zymase}]{\text{Yeast}} C_2H_5OH + 2CO_2 + H_2O$$

$$C_2H_5OH + O_2 \xrightarrow[\text{Oxidation}]{\text{Acetobacter}} CH_3COOH + H_2O$$

36. 1.

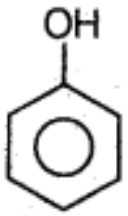


Picric acid

2. $CH_3-\underset{OH}{\underset{|}{CH}}-COOH$

Lactic acid

3.



Carbolic acid
(Phenol)

4. CH_3CH_2COOH

Propanoic acid

37. Only strong oxidising agents oxidises —CHO group into —COOH group.

$FeCl_3$ in a buffer is not a strong oxidising agent, hence it cannot oxidise —CHO group.

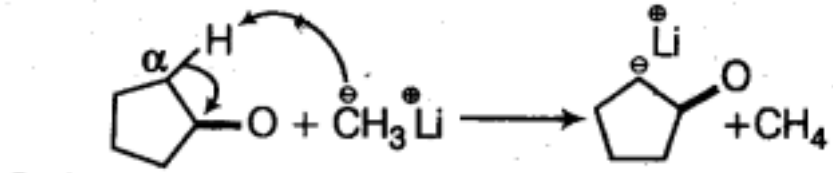
38. Grignard reagent CH_3MgX

Clemmensen reduction $Zn-Hg/conc.\ HCl$

Rosenmund reduction $H_2/Pd\text{-}BaSO_4$

Wolff-Kishner reduction $N_2H_4/KOH/CH_2OH$ (ethylene glycol)

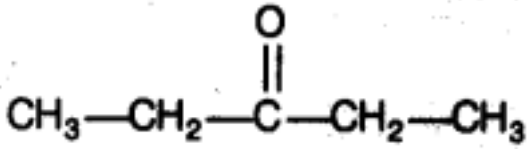
39.



Cyclopentanone Methyl lithium Lithium cyclopentanoyl anion (Intermediate)

Here, CH_3Li abstract is an active proton from cyclopentanone forming methane leaving behind an intermediate lithium cyclopentanoyl anion.

40. Since, the compound *X* yields phenyl hydrazone and gives negative response to the iodoform test and Tollen's test, it must contain a C=O group but is neither a methyl ketone nor an aldehyde. The structure of *X* could be



3-pentanone

having molecular formula $C_5H_{10}O$.

41. *o*-hydroxy benzaldehyde show chelation or intramolecular H-bonding while *p*-hydroxy benzaldehyde shows intermolecular H-bonding.

42. Iodoform test is given by compound which either have $CH_3\underset{\underset{OH}{|}}{CH}-$ group or $H_3C-\overset{\overset{O}{\|}}{C}-$ group. Isobutanal is

$$H_3C-\underset{\underset{CH_3}{|}}{CH}-CHO$$

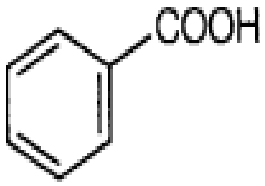
It has one α-H atom. Therefore, it cannot give iodoform test.

43. At low pH, the ester group of aspirin gets hydrolysed to acid, which causes ulcer in the stomach.

44. $$CH_3COCH_3 \xrightarrow{C_6H_5CO_3H} \underset{\text{Ester}}{CH_3COOCH_3} + C_6H_5COOH$$

This reaction is not because of nascent oxygen.

45. Acetyl acetone is liquid and exist mainly as (III) due to intermolecular H-bonding and the correct order is III>II>I.

46. 

+ Zn/Hg and conc. HCl

Given reaction will not yield benzaldehyde.

47. CH_3CHO and $C_6H_5CH_2CHO$ both being aldehydes react with Tollen's reagent, Fehling's solution and Benedict's solution. So, these reagents cannot be used to distinguish them. CH_3CHO reacts with NaOH and I_2 to give yellow crystals of iodoform while $C_6H_5CH_2CHO$ does not react with it.

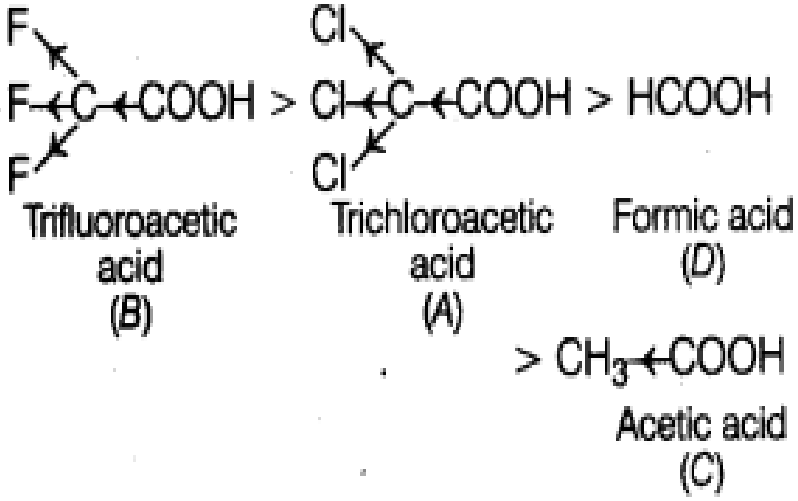
$$CH_3CHO + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$$

$$C_6H_5CH_2CHO + I_2 + NaOH \longrightarrow \text{No reaction}$$

Thus, CH_3CHO and $C_6H_5CH_2CHO$ can be distinguished by iodoform test.

48. If an electron withdrawing group ($-I$ showing group) is present, it makes the removal of proton more easy by stabilising the remaining carboxylate ion and thus, makes the acid more acidic.

The order of acidity of the given compounds is



49. When carbonyl compounds are treated with alcohol, they form hemiacetal (hemiketal and acetal/ketal).

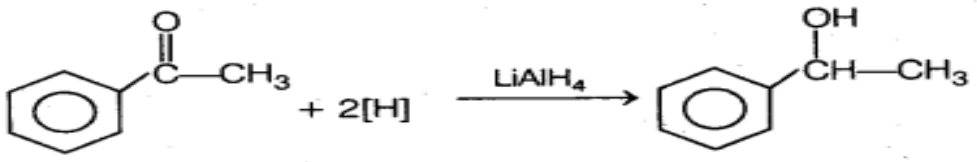
$$(CH_3)_2C{=}O + C_2H_5OH \xrightarrow{HCl} (CH_3)_2C(OH)(OC_2H_5)$$

Acetone (2-propanone) → Hemiketal

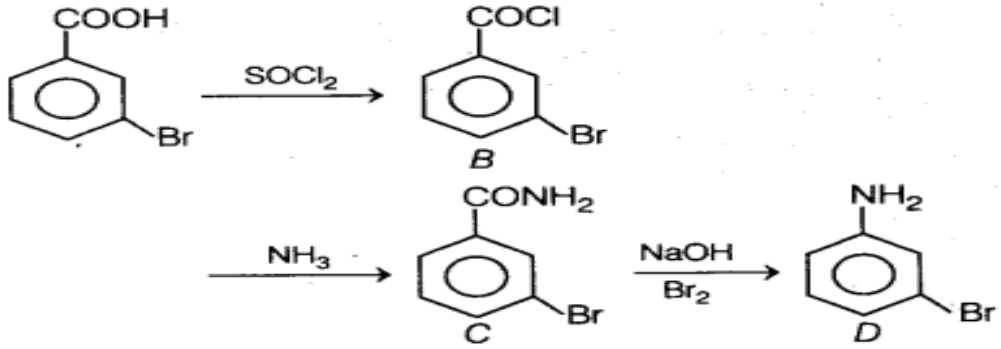
$$\xrightarrow[(Excess)\ HCl]{C_2H_5OH} (CH_3)_2C(OC_2H_5)_2$$

Note Formation of hemiketal is a nucleophilic addition reaction.

50. Ketones on reduction with $LiAlH_4$ gives secondary alcohols.



51.



52. The reducing agent used in Clemmensen reduction is Zn-Hg and HCl.

$$>C{=}O \xrightarrow{Zn\text{-}Hg/HCl} >CH_2$$

53. $CH_3{-}CH(OH){-}CH{=}CH{-}CH_3 \longrightarrow$

Pent-3-en-2-ol

$$CH_3{-}C(=O){-}CH{=}CH{-}CH_3$$

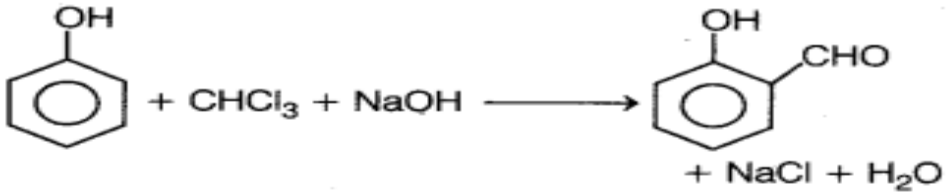
Pent-3-en-2-one

Only suitable reagent is chromic anhydride in glacial acetic acid. Other will also affect (C = C) bond.

54. $CH_3COOH + 4H \xrightarrow{LiAlH_4} \underset{A}{CH_3CH_2OH} + H_2O$

$$\underset{A}{CH_3CH_2OH} + CH_3COOH \xrightarrow{H_3O^+} \underset{B}{CH_3COOC_2H_5} + H_2O$$

55. (a) Reimer-Tiemann reaction,



(Here, a new C— C bond is formed.)

(b) Cannizzaro reaction

$$2HCHO \xrightarrow{\text{Conc. NaOH}} CH_3OH + HCOONa$$

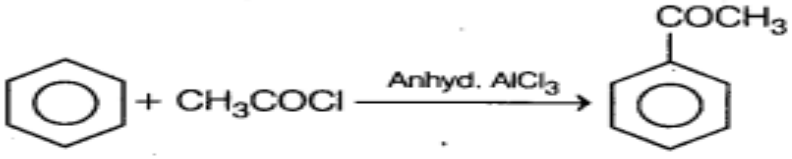
(No new C—C bond is formed in this reaction)

(c) Wurtz reaction

$$2RX + \text{Dry Na} \xrightarrow{\text{Ether}} R—R$$

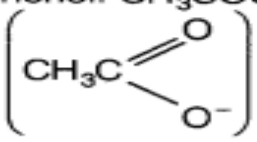
(One new C—C bond is formed)

(d) Friedel-Crafts acylation



(New C — C bond is formed)

Thus, among the given reactions, only Cannizzaro reaction does not involve the formation of a new C—C bond.

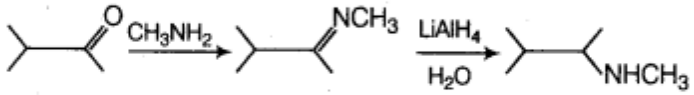
56. Higher the tendency to give a proton, higher is the acidic character, and tendency to lose a proton depends upon the stability of intermediate, i.e. carbanion formed. 2, 4, 6-trinitrophenol after the loss of a proton gives 2,4,6-trinitrophenoxide ion which is stabilised by resonance, $-I$ effect and $-M$ effect, thus is most acidic among the given compounds. Phenol after losing a proton form phenoxide ion which is also stabilised by resonance, $-M$ and $-I$-effects but is less stabilised as compared to 2, 4, 6- trinitrophenoxide ions. Thus, it is less acidic as compared to 2,4,6-trinitrophenol. CH_3COOH after losing a proton gives acetate ion  which is stabilised by only resonance. However, it is more resonace stabilised as compared to a phenoxide ion, thus more acidic as compared to phenol. 2,4,6-trinitrophenol, however, is more acidic than acetic acid due to the presence of three electron withdrawing — NO_2 groups. Cyclohexanol gives an anion that is least stable among the given, thus, it is least acidic. Hence, the correct order of acidic strength is

2, 4, 6-trinitrophenol (III) > acetic acid (II) > phenol (IV) > cyclohexanol (I)

57. Fehling's solution is reduced by aldehydes and a red precipitate of Cu_2O is obtained.

$$\underset{\text{Ethanal}}{CH_3CHO} + \underset{\substack{\text{(From Fehling's}\\ \text{solution)}}}{2CuO} \longrightarrow CH_3COOH + \underset{\text{(Red ppt)}}{Cu_2O\downarrow}$$

58.



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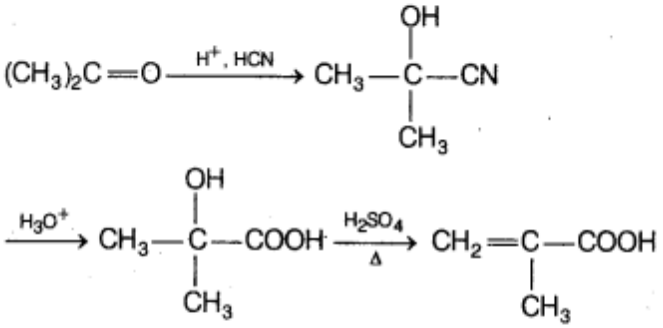
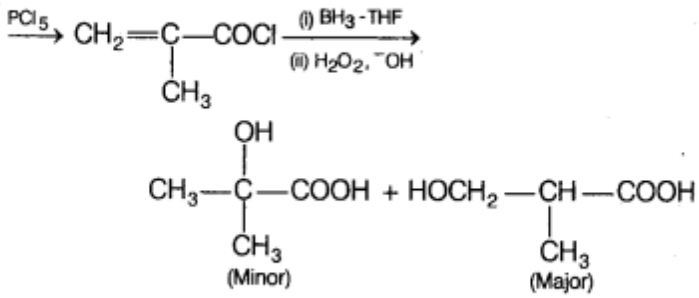
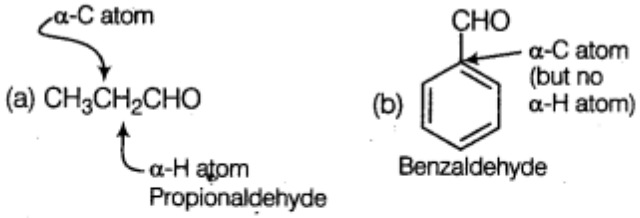
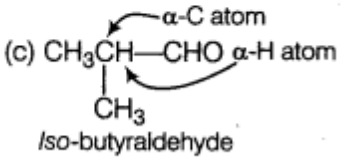




60. The C-atom attached directly to the functional group is called α-C atom and the hydrogen attached to it, is called α-H atom.

The structure of the given compounds are as





(d) HCHO
(No α-C atom)
Formaldehyde

Thus, benzaldehyde is the compound that contains α-C atom but no α-H atom.