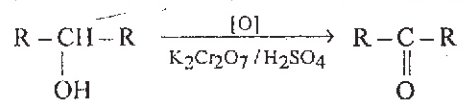
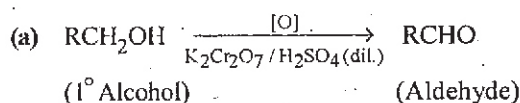


CARBONYL COMPOUNDS

INTRODUCTION

A divalent group in which a double bond (=) is present between carbon and oxygen atoms, is called a "Carbonyl Group" [C=O] and compounds containing [C=O] group are called carbonyl compounds.

GENERAL METHODS OF PREPARATION

1. By Oxidation of Alcohols (by $K_2Cr_2O_7/H_2SO_4$)

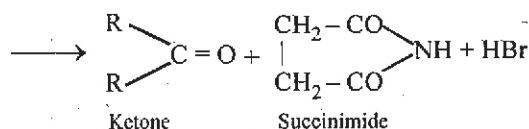
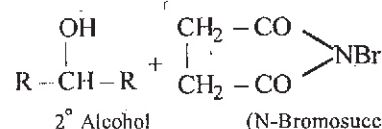
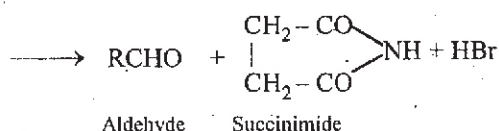
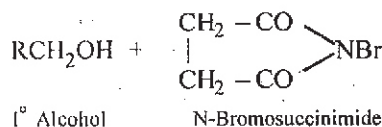
(2° Alcohol) (Ketone)
($K_2Cr_2O_7 / H_2SO_4$) is a strong oxidising agent.

Aldehydes are quite susceptible to further oxidation to acids.



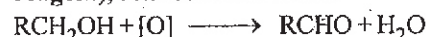
Thus oxidation of primary alcohols is made at the temperature much above the B.P. of aldehyde and thus aldehydes are vapourised out and prevented from being oxidised.

(b) By N-Bromo Succinimide (NBS):



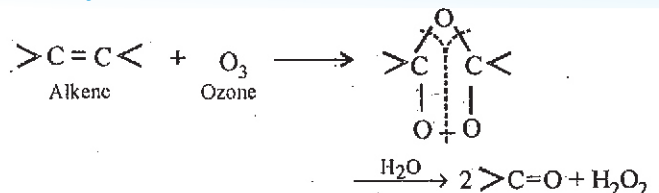
(c) Mild Oxidising Agent:

Only 1° alcohol will get oxidised with CrO_3 / Pyridine (Collin's reagent), controlled oxidation.



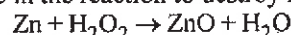
By this reaction, good yield of aldehydes is possible. Ketones can not be prepared by this method.

2. By Ozonolysis of Alkenes:

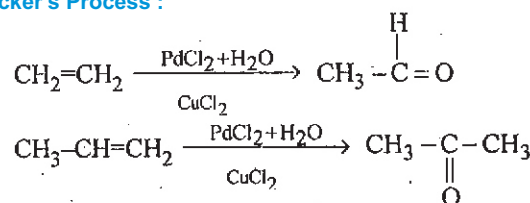


Note:

To prevent further oxidation of carbonyl compound by H_2O_2 , we add zinc in the reaction to destroy H_2O_2

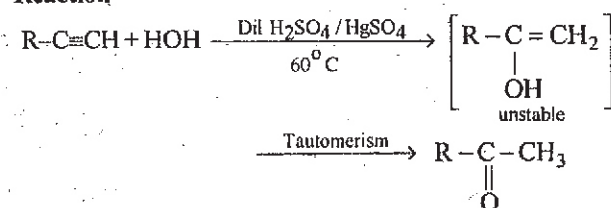


3. By Wacker's Process:

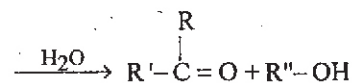
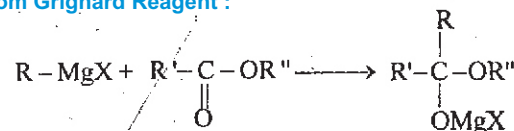


4. By Hydration of Alkynes:

Acetaldehyde is formed by passing acetylene in 40% aqueous solution of H_2SO_4 at 60°C in the presence of 1% $HgSO_4$. The reaction is called "Kucherov Reaction"



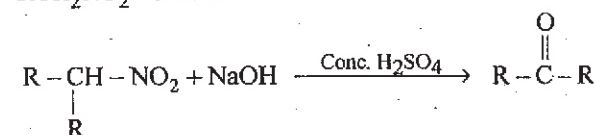
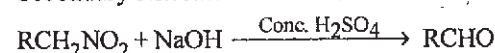
5. From Grignard Reagent:



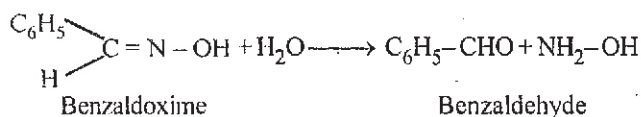
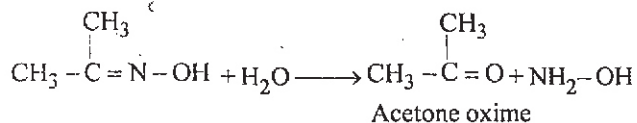
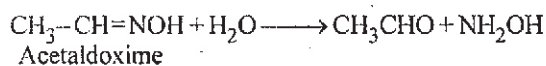
6. Oxidation of Nitroalkane (NEF Reaction):

Primary Nitroalkane $\longrightarrow$ Aldehyde

Secondary Nitroalkane $\longrightarrow$ Ketone

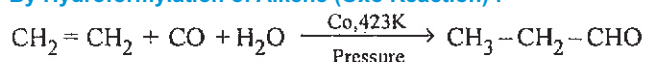


7. By hydrolysis of oximes :

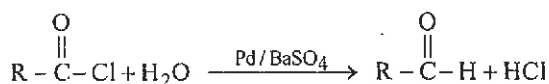


METHODS OF PREPARATION OF ALDEHYDES ONLY

(i) By Hydroformylation of Alkene (Oxo Reaction) :



(ii) Rosenmund's Reaction :

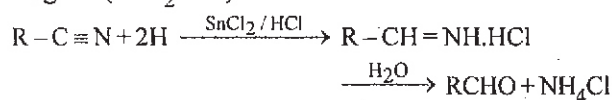


Note :

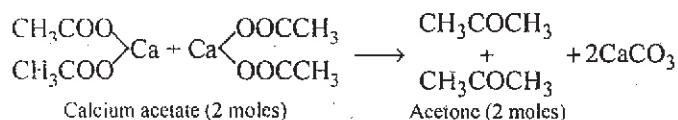
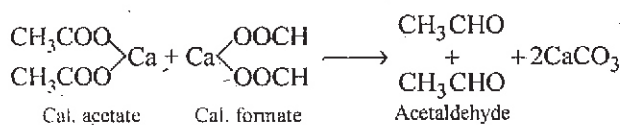
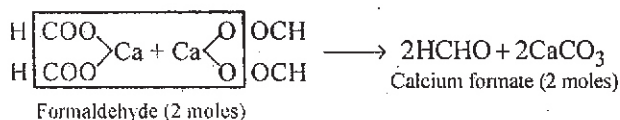
Formaldehyde can not be prepared by this method because, the corresponding acid chloride (HCOCl) is unstable.

(iii) By Reduction of Alkyl Cyanide (Stephen's Reaction) :

Reagent : (SnCl₂/HCl)

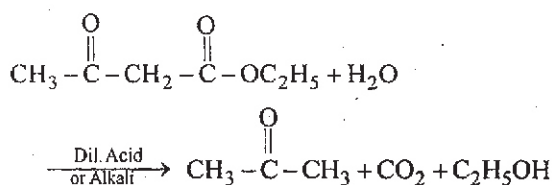


(iv) By Dry Distillation of Calcium Salts of Fatty Acids :

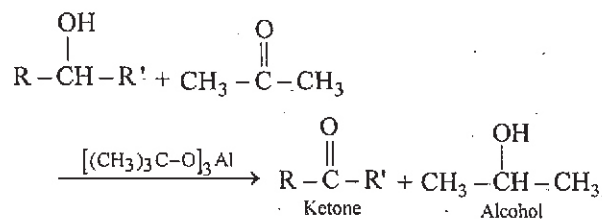


METHODS OF PREPARATION OF KETONES ONLY

(i) By Alkaline Hydrolysis of Acetoacetic Ester of its Alkyl Derivative



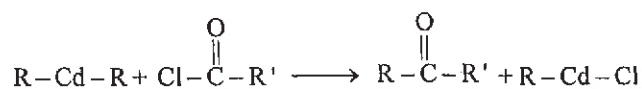
(ii) By Oppenauer Oxidation :



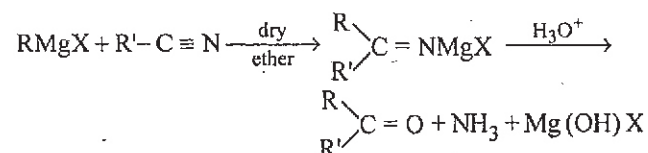
Note :

The reverse of this reaction is called **Meerwein Ponndorf Verley reduction**.

(iii) From Dialkyl Cadmium :



(iv) From Nitriles :



PHYSICAL PROPERTIES

Boiling Point and Melting Point :

Boiling point and Melting point $\propto$ Molecular weight $\propto \frac{1}{\text{Branching}}$

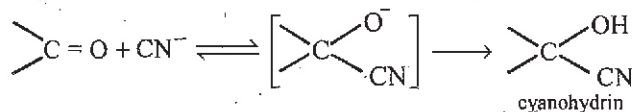
Reactivity :

Reactivity depends on the nature of alkyl group attached to it. Smaller the alkyl group, the more reactive is the compound.
Reactivity $\propto$ Magnitude of +ve charge on carbon atom of the carbonyl group.

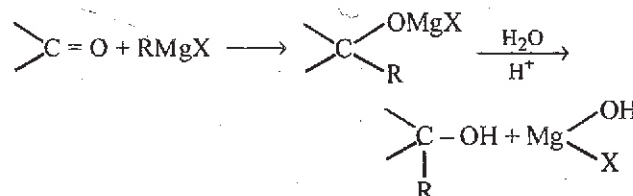
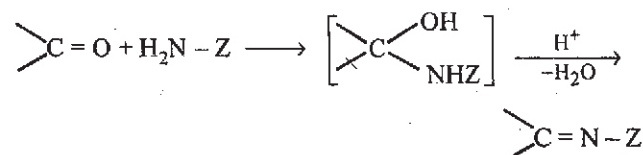
CHEMICAL PROPERTIES

(i) Nucleophilic Addition Reactions :

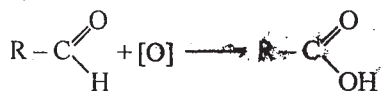
The reaction is catalysed by a base



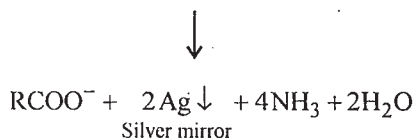
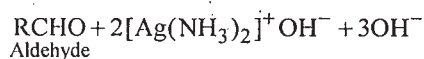
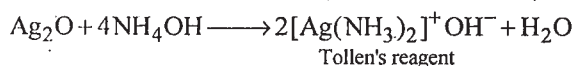
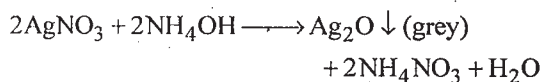
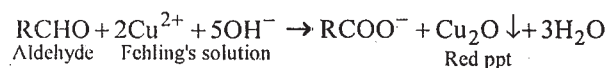
(ii) Addition of Grignard Reagents :

(iii) Addition of NH₃ and its derivatives :

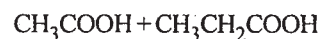
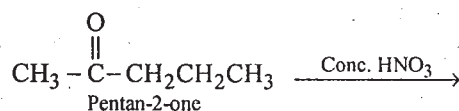
AMMONIA DERIVATIVE USED		PRODUCT OBTAINED	
STRUCTURE	NAME	STRUCTURE	NAME
NH_2OH	Hydroxylamine	$>\text{C}=\text{N}-\text{OH}$	Oxime
NH_2-NH_2	Hydrazine	$>\text{C}=\text{N}-\text{NH}_2$	Hydrazone
$\text{NH}_2-\text{NH}-\text{C}_6\text{H}_5$	Phenylhydrazine	$>\text{C}=\text{N}-\text{NH}-\text{C}_6\text{H}_5$	Phenylhydrazone
$\text{NH}_2\text{CONHNH}_2$	Semicarbazide	$>\text{C}=\text{NNHCONH}_2$	Semicarbazone
$\text{NH}_2-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$	2, 4-Dinitrophenylhydrazine (DNP)	$>\text{C}=\text{N}-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$	2, 4-Dinitrophenylhydrazone

(2) Oxidation Reactions**Oxidation of Aldehydes**

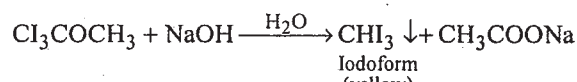
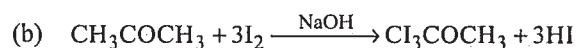
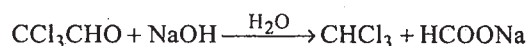
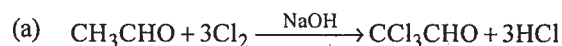
They are easily oxidised to **acids** by strong as well as weak oxidising agents.

(i) by Tollen's reagent**(ii) by Fehling's Solution****Oxidation of Ketones****(i) with strong oxidising agents :**

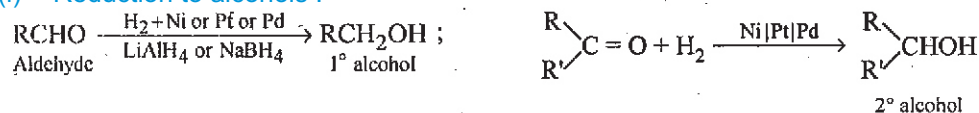
They are not oxidised by weak oxidising agents like Tollen's and Fehling's solution.



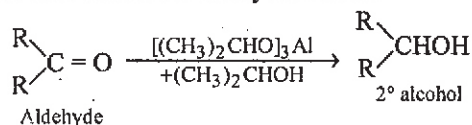
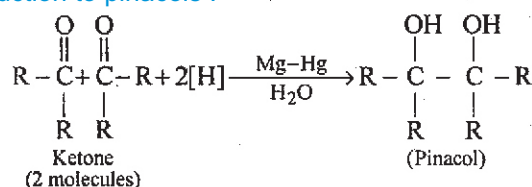
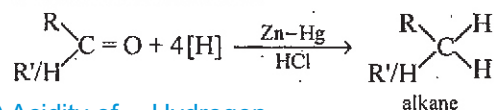
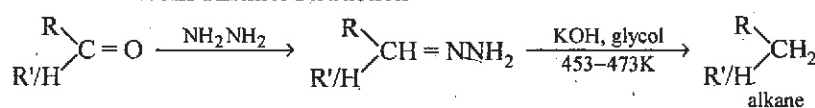
In case of unsymmetrical ketones, the keto group stays preferentially with the smaller alkyl group (**Popoff's rule**).

(ii) by methyl ketones with sodium hypohalite - Haloform reaction -

- This is **Iodoform** test and is used for characterising compounds with CH_3CO group or $\text{CH}_3\text{CH}(\text{OH})$ group.

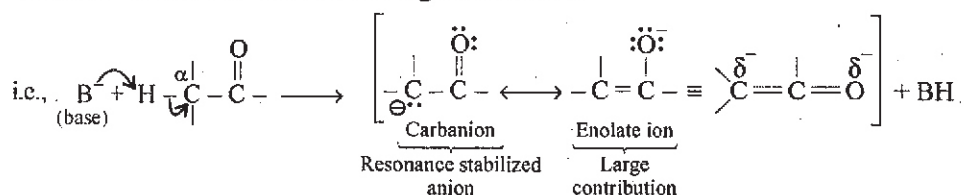
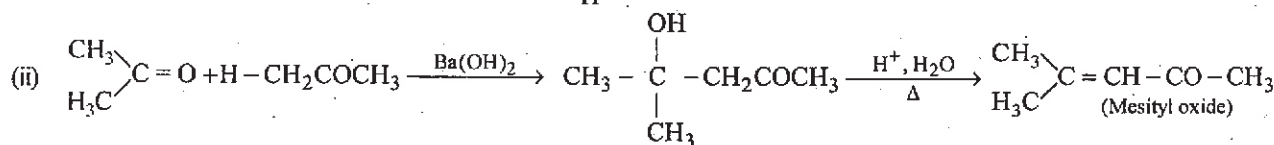
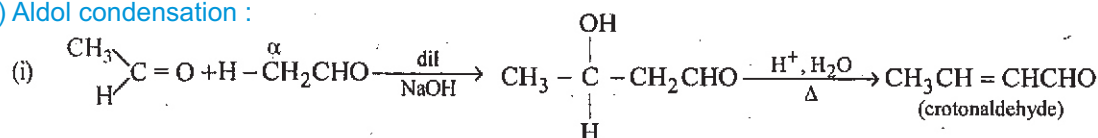
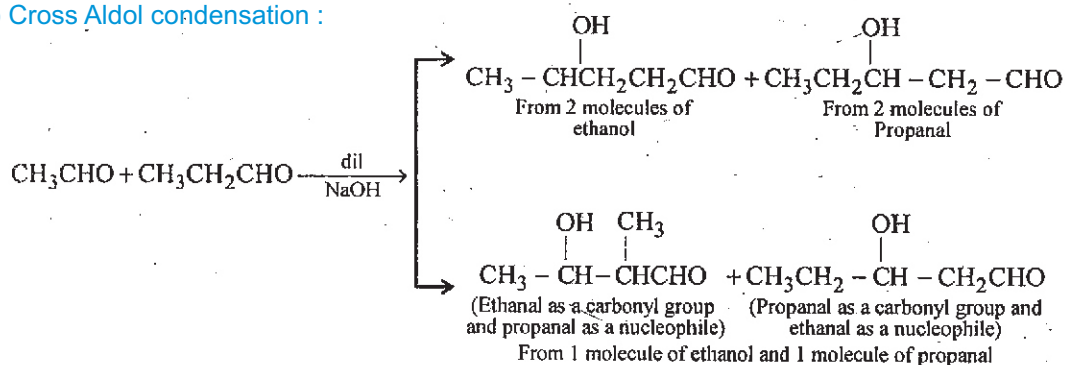
(3) Reduction Reactions**(i) Reduction to alcohols :**

Ketones are also reduced by Aluminium isopropoxide in isopropyl alcohol to corresponding secondary alcohols. This reaction is called **Meerwein-Ponndorf Verley Reduction**

**(ii) Reduction to pinacols :****(iii) Reduction to Hydrocarbons :****Clemmensen Reduction****Wolff-Kishner Reduction****(4) Acidity of α -Hydrogen**

The α -hydrogen of the carbonyl compound is acidic due to 2 reasons :

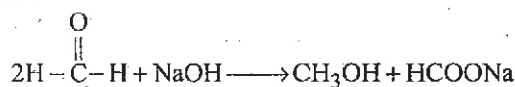
- (i) -I-effect of the carbonyl group which weakens the $\text{C}_\alpha\text{-H}$ bond.
- (ii) Resonance stabilization of the resulting enolate anion.

**Reaction due to Acidity of α -Hydrogen :****(a) Aldol condensation :****(b) Cross Aldol condensation :**

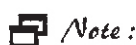
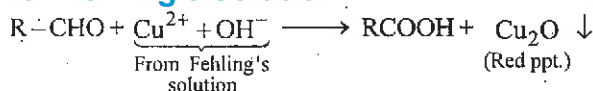
(5) Reactions with Concentrated Alkali Solution

Aldehydes, without α -hydrogen atom, undergo disproportionation, i.e., self oxidation-reduction, when treated with concentrated alkali solution.

Ex.

**REACTIONS OF ALDEHYDE ONLY****(i) Reducing Properties :**

Aldehydes reduce Fehling's solution, Benedict's solution, Tollen's reagent and mercuric chloride solution.

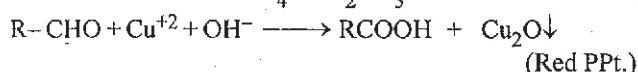
With Fehling's solution :

Note :

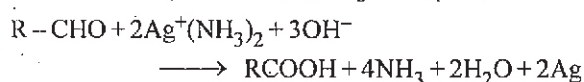
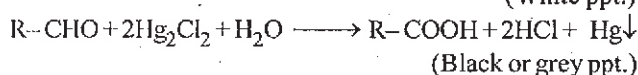
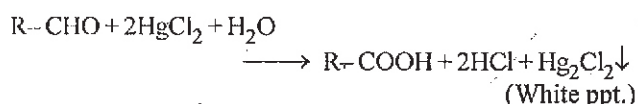
Reacting species of Fehling solution is CuO . In this reaction Cu^{+2} changes to Cu^+ . Benzaldehyde does not reduce Fehling's solutions.

With Benedict's solution :

Benedict solution $\Rightarrow \text{CuSO}_4 + \text{Na}_2\text{CO}_3 + \text{Sodium citrate}$



With Tollens' Reagent : Tollen's reagent is a solution of ammoniacal silver nitrate ($\text{AgNO}_3 + \text{NH}_4\text{OH}$)

**With mercuric chloride solution :****(ii) With Schiff's Reagent :**

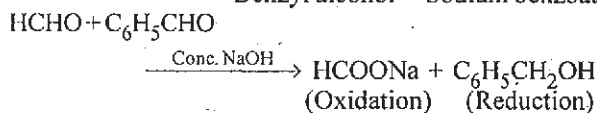
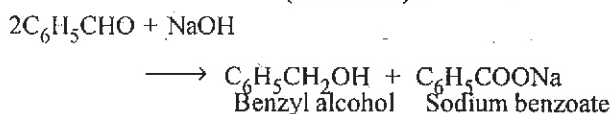
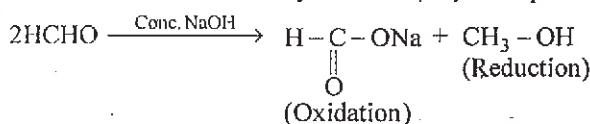
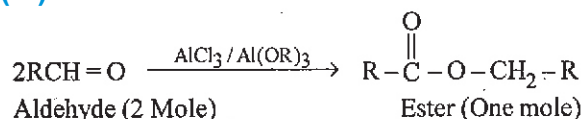
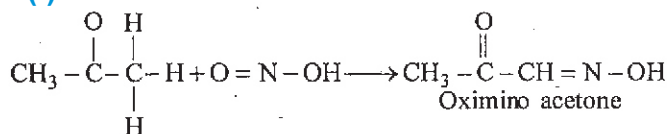
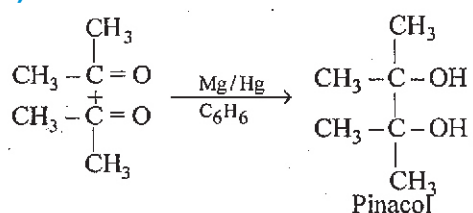
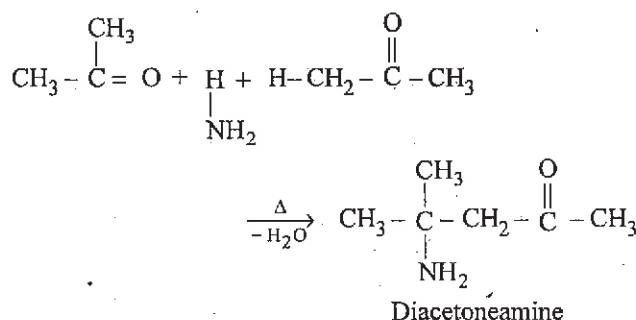
Schiff's reagent is a solution of the magenta dye (rosaniline hydrochloride or fuchsine) decolourised by passing SO_2 .

Cold dilute Schiff's reagent (colour less) + Aldehyde $\longrightarrow$ Pink coloured solution

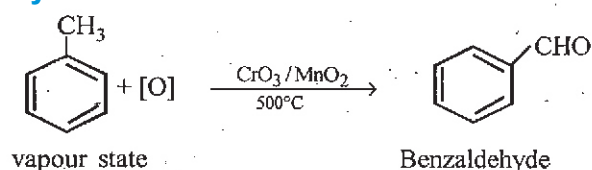
(iii) Cannizzaro's Reaction :

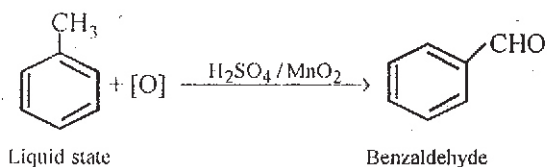
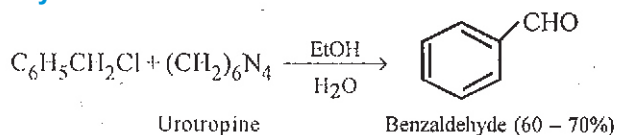
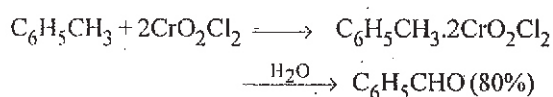
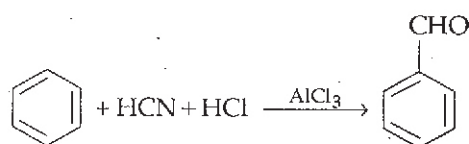
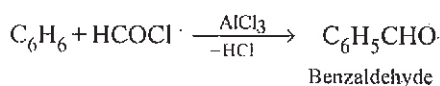
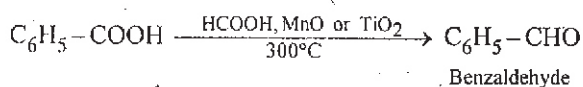
Those aldehydes, which do not contain α -hydrogen atoms give this reaction with conc. alkali like conc. NaOH or KOH .

* In this reaction transfer of hydride ion (H^-) takes place

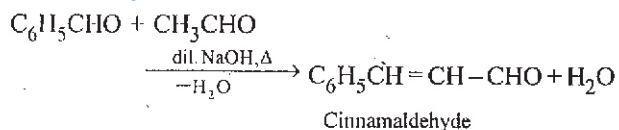
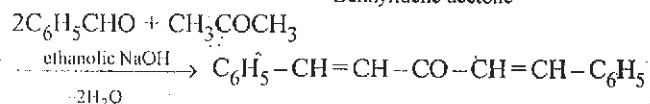
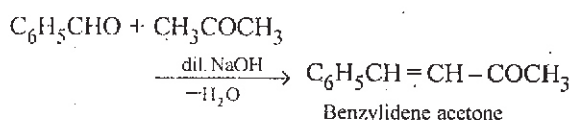
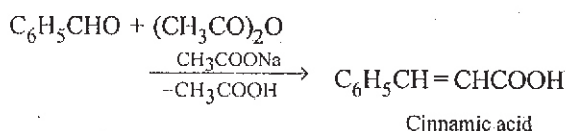
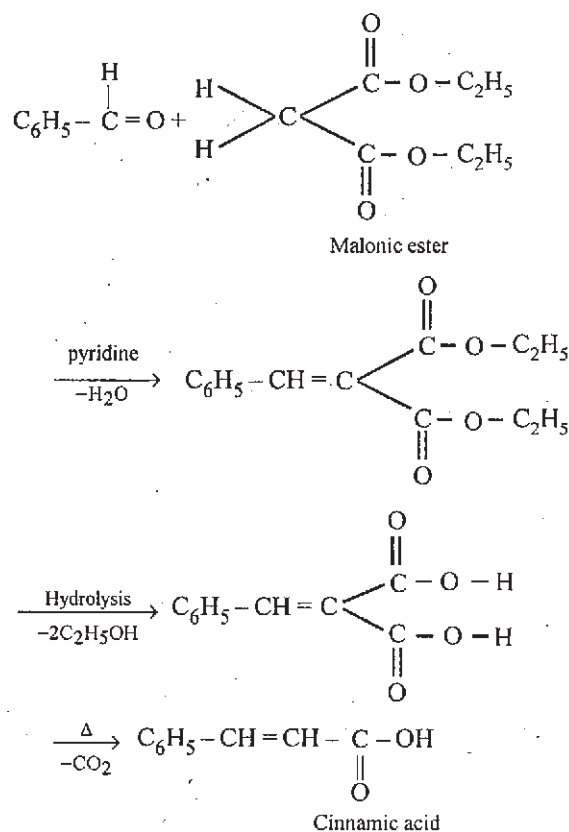
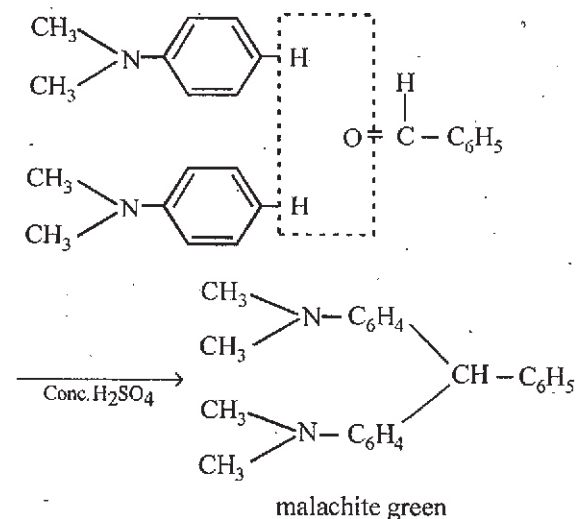
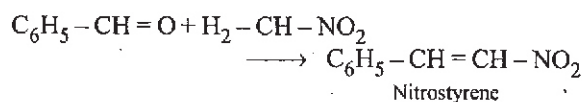
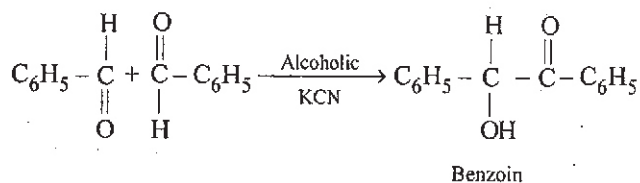
**(iv) Tischenko Reaction :****REACTIONS OF KETONES ONLY****(i) With Nitrous Acid :****(ii) Bimolecular Reduction :****(iii) With Ammonia :****Distinguish between Aldehydes and Ketones**

Test	Aldehydes	Ketones
1. With Tollen's reagent	Give silver mirror	No action
2. With Fehling's solution	Give red ppt of Cu_2O (only aliphatic aldehydes)	No action
3. Reduction with LiAlH_4	1° alcohols are formed	2° alcohols are formed
4. With Schiff's reagent	Restore pink colour	No action
5. Action with alcohols in presence of dry HCl gas	Form acetals easily	Do not form ketals easily

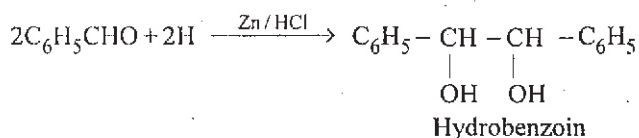
BENZALDEHYDE**1. methods of preparation****(a) By Oxidation of Toluene :**

**(b) By Sommelet's Reaction :****(c) By Etard Reaction****(d) By Gattermann Aldehyde Synthesis :****(e) By Gattermann Koch Reaction :****(f) With Benzoic Acid :****2. PHYSICAL PROPERTIES**

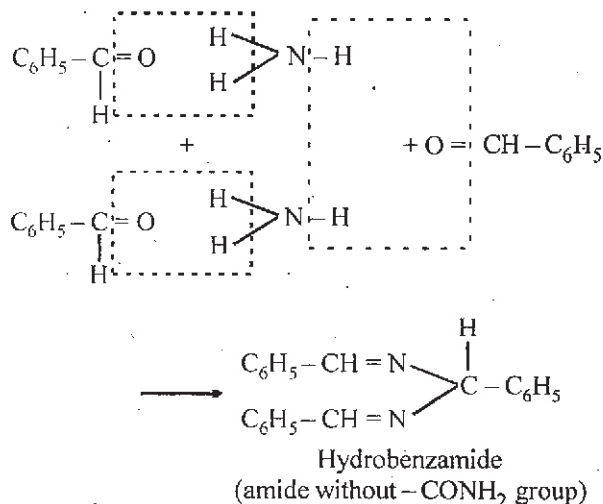
- (i) It is a colourless liquid with a smell of bitter almonds.
- (ii) It is insoluble in water and soluble in organic solvents.
- (iii) Its boiling point is 179°C.
- (iv) It is poisonous in nature.

3. CHEMICAL PROPERTIES**(i) Claisen Condensation :****(a) With acetaldehyde :****(b) With acetone :****(ii) Perkin Reaction :****(iii) Knoevenagel Reaction :****(iv) Reaction with N,N-dimethyl aniline :****(v) Reaction with Nitromethane :****(vi) Benzoin condensation :**

(vii) Bimolecular reduction :

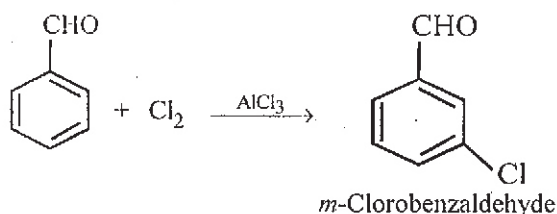


(viii) With ammonia :

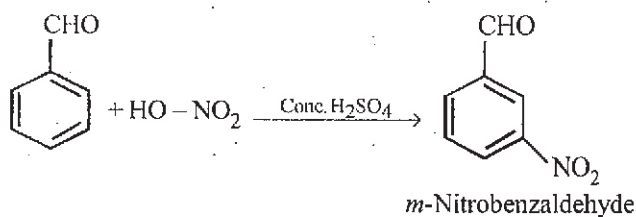


REACTIONS OF BENZENE RING

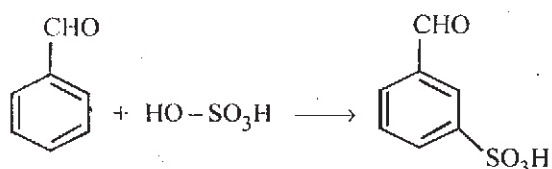
(a) Halogenation :



(b) Nitration :



(c) Sulphonation :



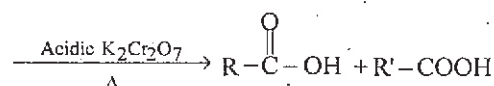
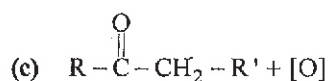
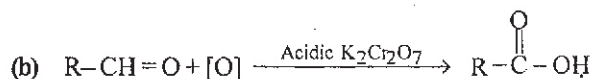
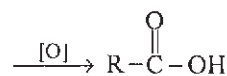
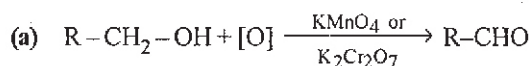
CARBOXYLIC ACIDS

INTRODUCTION

Organic compounds containing carboxyl ($-\text{C}(=\text{O})\text{OH}$) group are known as carboxylic acids and the term 'Carboxylic' was firstly proposed by scientist 'Bayer'.

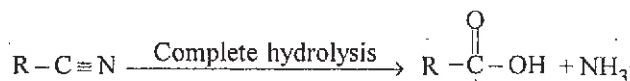
METHODS OF PREPARATION

1. By the Oxidation of Alcohols, Aldehydes and Ketones



2. By Hydrolysis of Cyanides (Nitriles)

Cyanides on complete hydrolysis in presence of dilute HCl forms carboxylic acids.



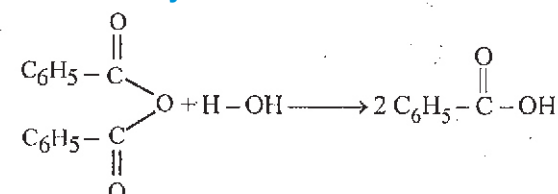
3. By Hydrolysis of Acid Derivatives



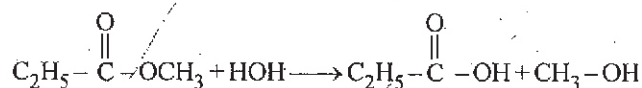
(a) From acyl halides :



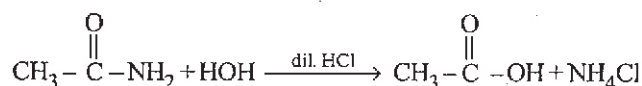
(b) From acid anhydrides :



(c) From carboxylic esters :

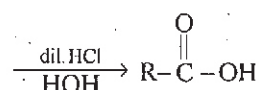
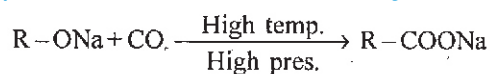


(d) From acid amides :

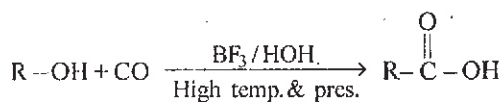


4. By Carboxylation

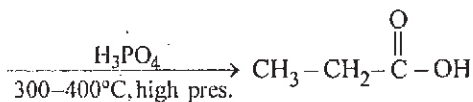
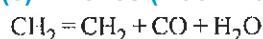
(a) Sodium alkoxide or sodium hydroxide :



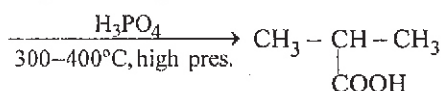
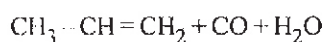
(b) Alcohols :



(c) Alkenes (Koch Reaction) :



Propanoic acid



2-Methylpropanoic acid

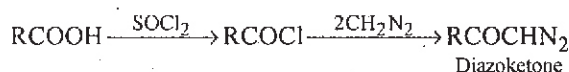
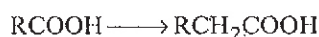


Note :

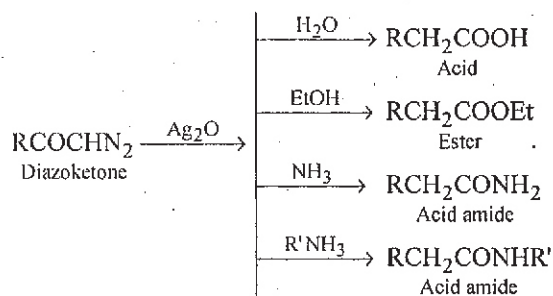
Formic acid and acetic acid can not be prepared by this method.

5. Arndt-Eistert Reaction :

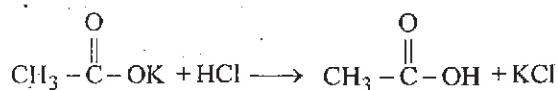
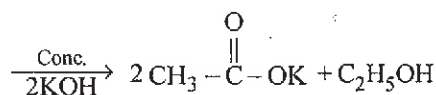
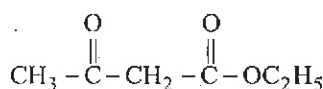
Arndt-Eistert synthesis consists in the conversion of a carboxylic acid into its next higher homologue or its derivative



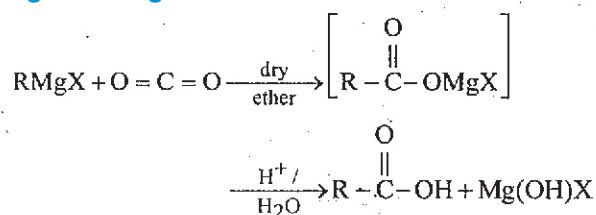
Diazoketone



6. From Acetacetic Ester :



7. Grignard reagent :



PHYSICAL PROPERTIES

1. Solubility :

Upto C_4 , highly soluble in water

$$\text{Solubility} \propto \frac{1}{\text{Molecular weight}}$$

2. Boiling Point (B.P.) :

Boiling point $\propto$ Molecular weight,

Boiling point of acid > Boiling point of alcohol.

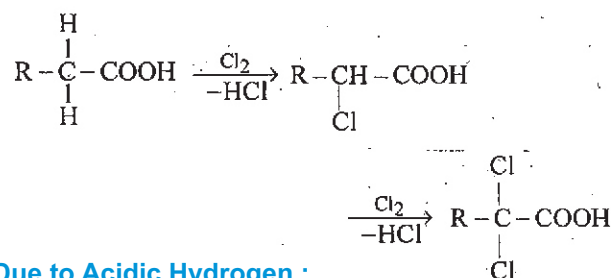
3. Melting Point (M.P.) :

Melting point of carboxylic acid do not vary smoothly from one molecule to another

CHEMICAL PROPERTIES

(1) Reactions due to Alkyl Group :

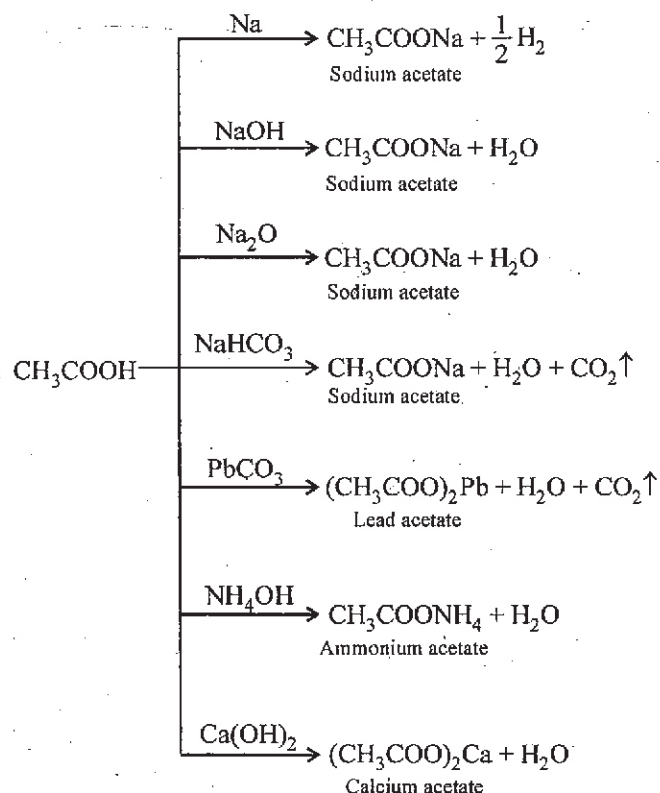
Halogenation : Acids having α -hydrogen atom give this reaction.



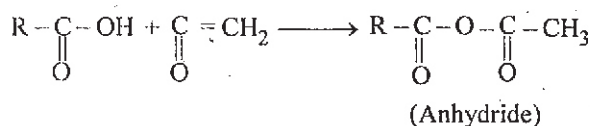
(2) Due to Acidic Hydrogen :

Reaction is known as **Hell-Volhard-Zelinsky (HVZ)** reaction.

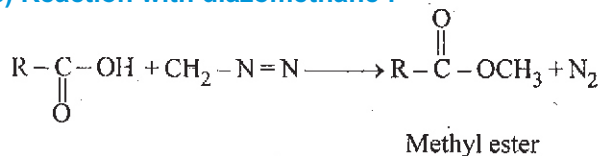
(a) Salt formation : Carboxylic and benzoic acids form salts with metals, metal oxides, hydroxides, carbonates, bicarbonates.



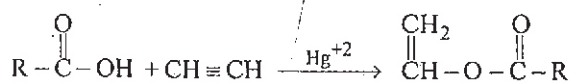
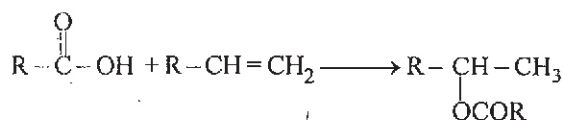
(b) Reaction with ketene :



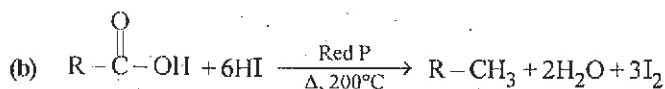
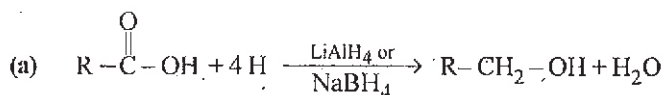
(c) Reaction with diazomethane :



(d) Reaction with alkenes and alkynes :

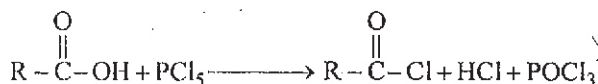
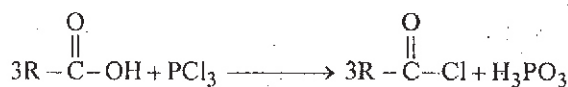


(3) Reactions due to (>C=O) Group

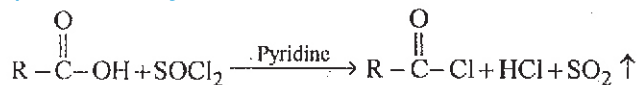


(4) Reactions due to (-OH) Group :

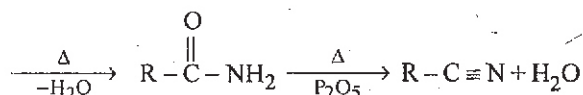
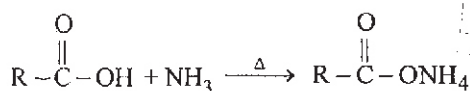
(a) Reaction with phosphorus chloride :



(b) With Thionylchloride :

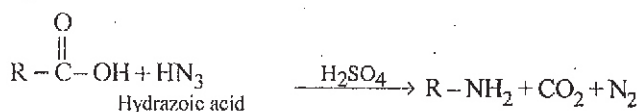


(c) Formation of acidamides and alkanenitrile :



(d) With Hydrazoic acid (Schmidt reaction) :

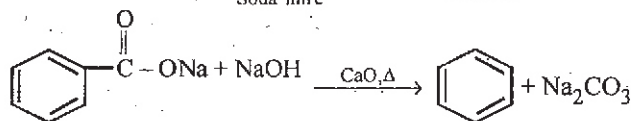
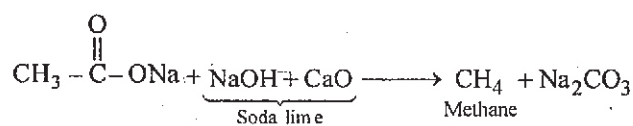
N_3H = Hydrazoic acid



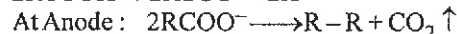
The reaction is a modification of "Curtius reaction".

(5) Reactions due to (-COOH) Group :

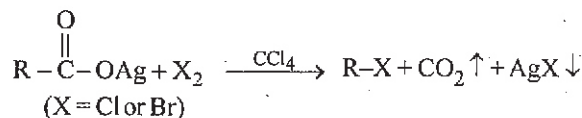
(a) Decarboxylation :



(b) Kolbe's electrolytic synthesis :

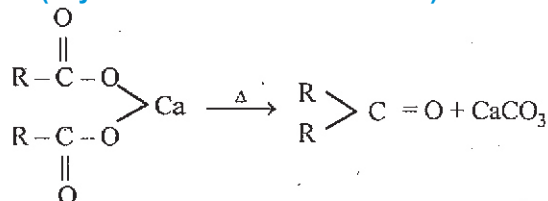


(c) Hunsdiecker reaction :

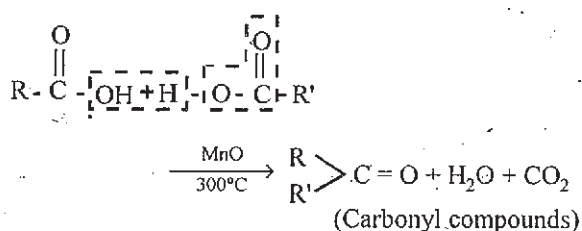


(d) Formation of carbonyl compounds

(Dry Distillation of calcium salt) :



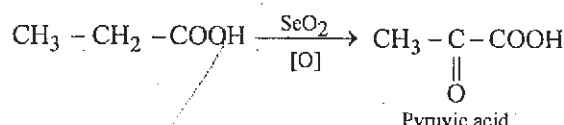
(e) With Manganous oxide :



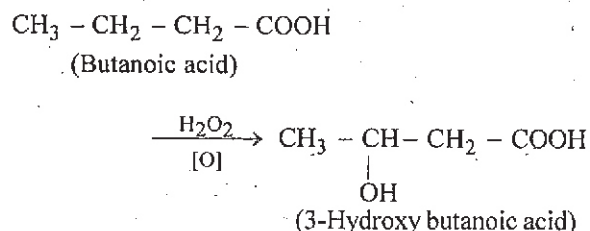
(6) Special Reactions of Alkanoic Acids :

(a) Oxidation :

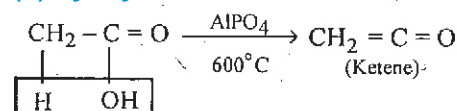
with SeO_2 , α -keto acid is formed



with H_2O_2 , OH group comes at β -C atom.

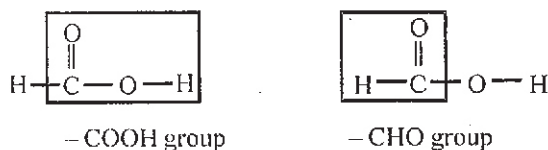


(b) Pyrolysis :

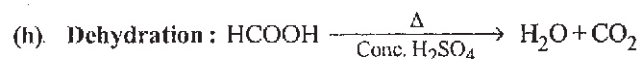


SPECIAL FEATURES OF FORMIC ACID

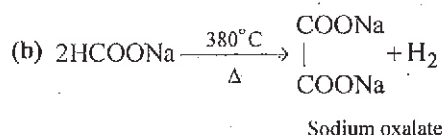
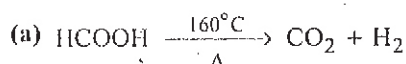
- (a) Formic acid shows acidic character due to presence of $-\text{COOH}$ group as well as shows reducing character due to presence of $-\text{CHO}$ group.



- (b) It reduces Tollen's reagent and forms silver mirror.
 (c) It reduces mercuric chloride and forms black ppt. of mercury.
 (d) It decolourises the pink colour of acidic KMnO_4 .
 (e) It forms brown ppt. of MnO_2 with basic KMnO_4 .
 (f) It converts the orange colour of acidic $\text{K}_2\text{Cr}_2\text{O}_7$ into green colour.
 (g) It reduces Fehling's solution.



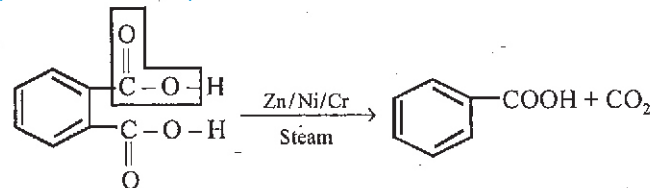
(i) **Effect of heat:**



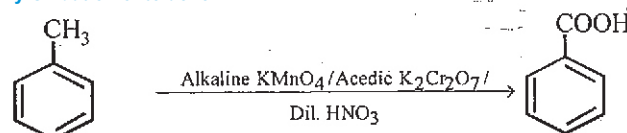
BENZOIC ACID ($\text{C}_6\text{H}_5\text{COOH}$)

PREPARATION:

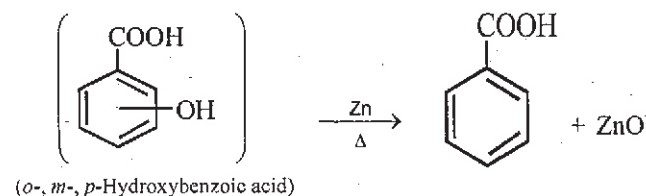
(1) **From Phthalic Acid (Industrial Method):**



(2) **By Oxidation of toluene:**



(3) **From Dehydroxylation of o-, m- or p-Hydroxybenzoic acid:**



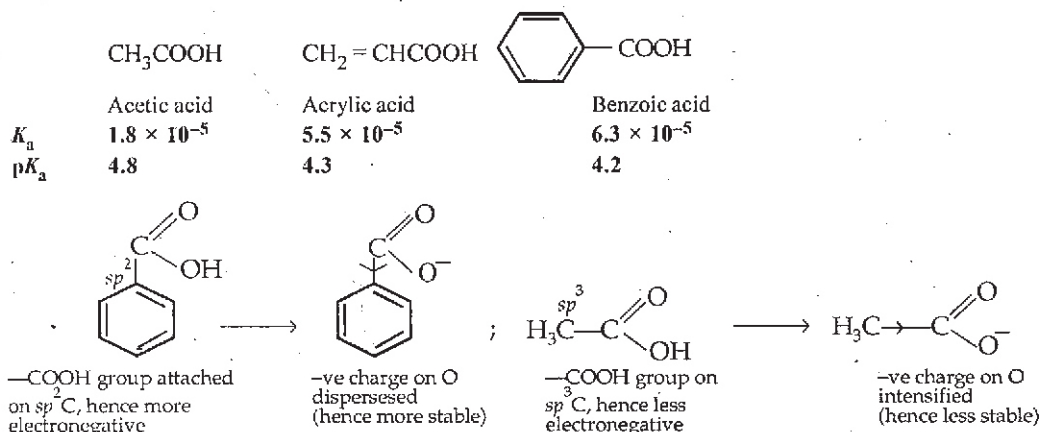
PHYSICAL PROPERTIES

- (i) It is a crystalline solid (M.P. 122°C)
 (ii) Sparingly soluble in cold water but rapidly soluble in hot water, also, soluble in organic solvents like alcohol, ether, etc.

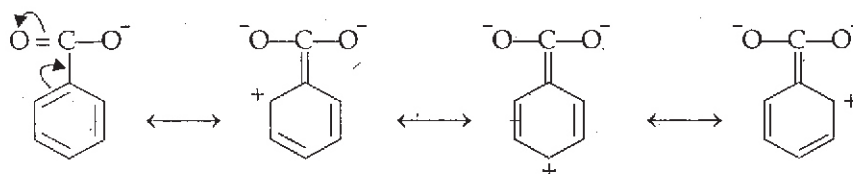
CHEMICAL PROPERTIES

Acidity of Aromatic Acids

Benzoic acid itself is somewhat stronger acid than acetic acid. Its carboxyl group is attached to an sp^2 hybridized carbon and ionizes to a greater extent than one that is attached to an sp^3 hybridized carbon (recall that carbon becomes more electron-withdrawing as its s character increases).

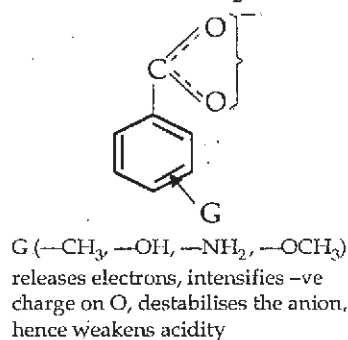
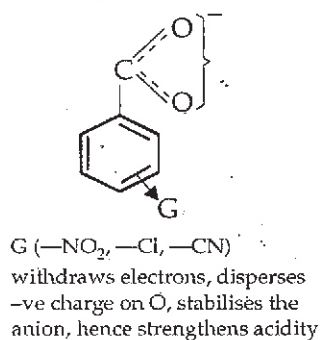


Moreover, benzoate anion is more stable, due to presence of benzene ring, than acetate ion.

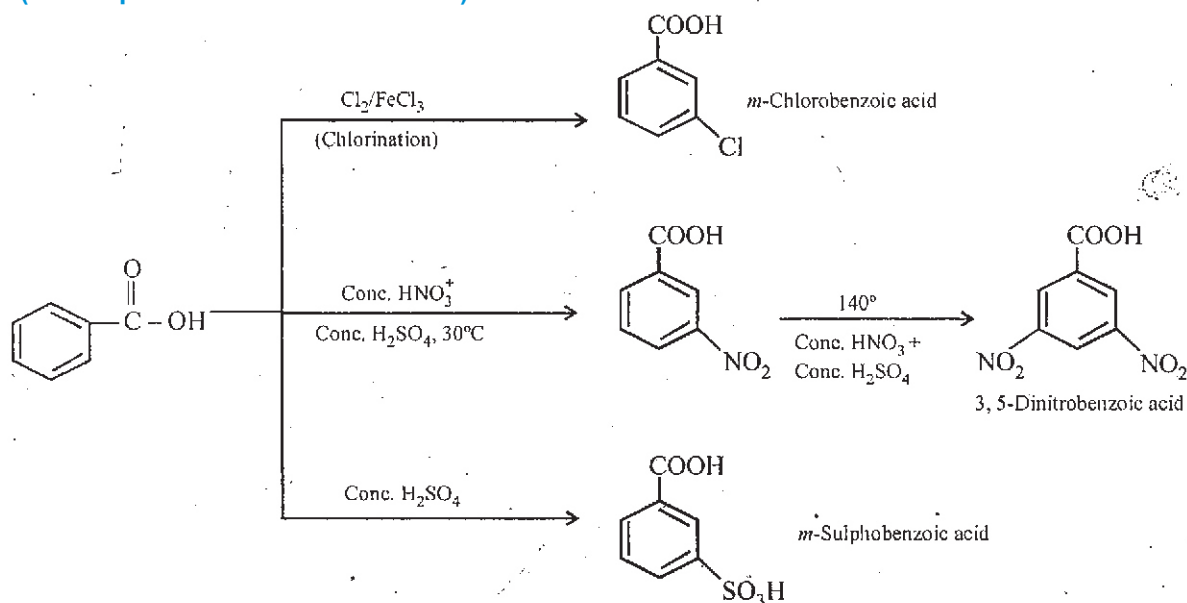


Resonance in benzoate anion due to benzene ring

Like aliphatic acids, acidity of aromatic acids is affected by substituents : electron-releasing groups like $-\text{CH}_3$, $-\text{OH}$ and $-\text{NH}_2$ make benzoic acid weaker, while electron-withdrawing groups like $-\text{Cl}$, $-\text{NO}_2$, $-\text{CN}$, etc. make benzoic acid stronger.



Reactions due to Benzene Ring : (Meta Directing) (Electrophilic substitution reaction)



Note :

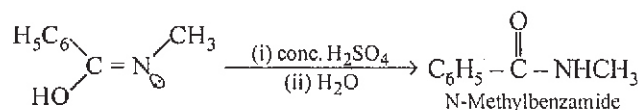
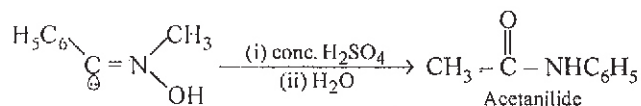
It does not give Friedel Crafts reaction because of presence of deactivating *m*-directing ($-\text{COOH}$) group.

• Test : Benzoic acid + Neutral $\text{FeCl}_3 \longrightarrow$ Red brown ppt.

IMPORTANT POINTS

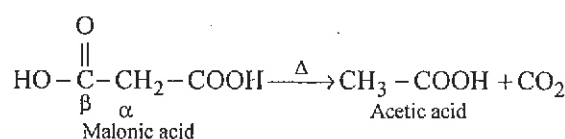
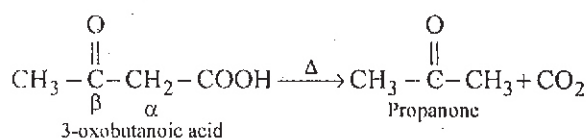
(1) Beckmann Rearrangement :

Oximes on treatment with catalysts such as $\text{conc. H}_2\text{SO}_4$, SOCl_2 , PCl_5 , etc. undergo a rearrangement to form substituted amides. This reaction is called **Beckmann rearrangement**.



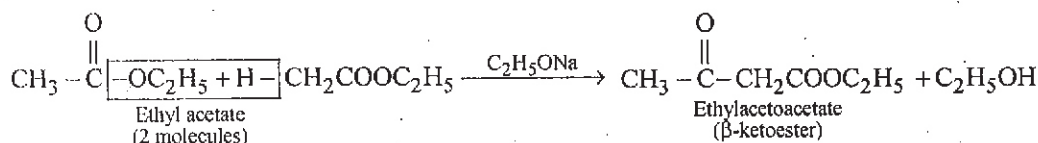
(2) Decarboxylation of β -keto acids :

Carboxylic acids containing an EWG such as $>\text{CO}$, $-\text{COOH}$ or $-\text{NO}_2$ at β -carbon atom wrt the $-\text{COOH}$ group readily undergo decarboxylation on heating. For ex :

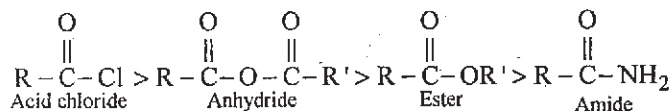


(3) Claisen Condensation :

Esters containing α -H-atoms undergo self-condensation in presence of a strong base such as sodium ethoxide to form β -ketoesters. For ex :

**(4) Comparative reactivity of Acid Derivatives :**

The relative reactivities of different acid derivatives towards nucleophilic acyl substitution reactions follow the order :

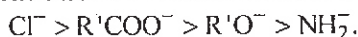


This order can be explained in terms of relative basic strength of the leaving groups (LG). Here, the LG's are :

Cl^- , $\text{R}'\text{COO}^-$, $\text{R}'\text{O}^-$ and NH_2^- . Their relative basic strength decrease in the order : $\text{NH}_2^- > \text{R}'\text{O}^- > \text{R}'\text{COO}^- > \text{Cl}^-$

Since stronger base is a poor LG,

$\therefore$ The ease with which these LG's depart decreases in the reverse order, i.e.,

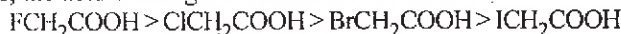


Consequently, relative reactivities of the acid derivatives decrease in the order :

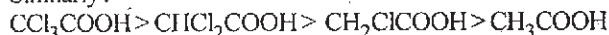


- Electron withdrawing nature of halogen : $\text{F} > \text{Cl} > \text{Br} > \text{I}$

Thus, the acidic strength decreases in the order :

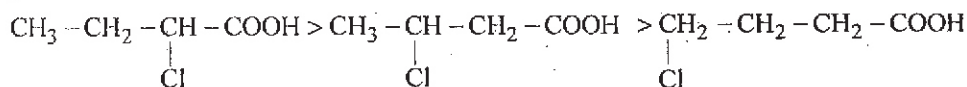


Similarly :

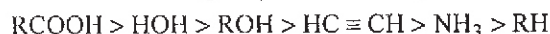


- Inductive effect is stronger at α -position than β -position similarly at β -position it is more stronger than at γ -position.

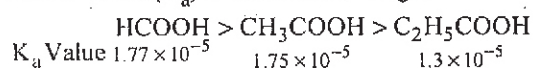
Example :



- Relative acid strength in different compounds



- Greater the value of K_a or lesser the value of pK_a stronger is the acid, i.e., $\text{pK}_a = -\log K_a$
- Acidic nature (K_a) $\propto$ 1/molecular weight.



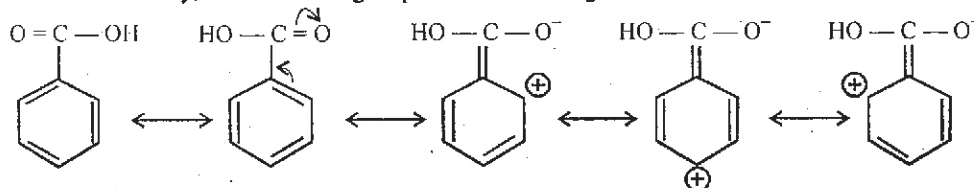
K_a Value 1.77×10^{-5} 1.75×10^{-5} 1.3×10^{-5}

- The formic acid is strongest of all fatty acids.
- Acetic acid is less weak acid than sulphuric acid due to less degree of ionisation.

MISCELLANEOUS SOLVED EXAMPLES

Example 1 : Why electrophilic substitution in benzoic acid takes place to meta position?

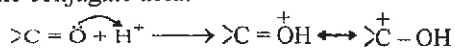
Sol. Carboxyl group ($-\text{COOH}$) is electron withdrawing, i.e., deactivating the benzene ring and thus electron density becomes very less at ortho and para position in comparison to meta position. Electrophiles find it easier to attack at meta position as there is higher electron density, thus $-\text{COOH}$ group is meta directing.



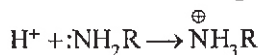
As there is positive charge on ortho and para position, electron density is higher at meta position and hence electrophilic substitution takes place at meta position.

Example 2 : During the preparation of ammonia derivatives from aldehydes or ketones, pH of the reaction is carefully controlled. Why?

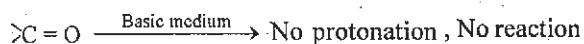
Sol. Formation of ammonia derivatives (oximes, hydrazone, semi-carbazone, etc.) proceeds via the attack of carbonyl carbon with proton to form the conjugate acid.



Therefore, presence of an acid is a must for preparing these derivatives. However, in strongly acidic medium, the proton attacks the unshared pair of electrons on nitrogen to form the species RNH_3^+ which cannot attack the carbonyl carbon.

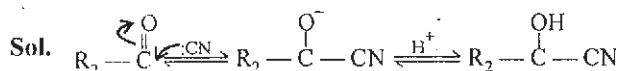


In basic medium, there is no protonation of carbonyl group, and hence no reaction.



Therefore, preparation of ammonia derivatives requires slightly acidic medium ($pH = 3-5$) and its careful control is essential.

Example 3 : Give a mechanism for the addition of HCN to R_2CO .



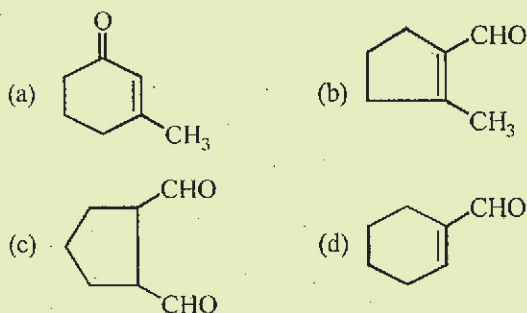
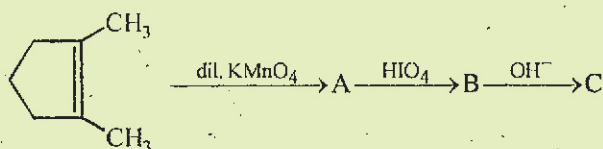
Example 4 :

Why carboxylic acids do not form oximes?

Sol. Due to resonance between lone pairs of electrons on the O-atom of the OH group and $C=O$, the carboxyl carbon is less electrophilic than carbonyl carbon in aldehyde and ketones. Therefore, nucleophilic addition of NH_2OH to the $C=O$ group of carboxylic acids does not occur and hence carboxylic acids do not form oximes.



- Reaction of phenylacetylene with dil. H_2SO_4 and HgSO_4 gives
(a) acetophenone (b) 2-phenylethanol
(c) phenylacetaldehyde (d) phenylacetic acid
- A new C—C bond is formed in :
(a) Cannizzaro's reaction (b) Reimer Tiemann reaction
(c) Friedel Crafts reaction (d) Both (b) and (c)
- A compound X of formula $\text{C}_3\text{H}_8\text{O}$ yields a ketone $\text{C}_3\text{H}_6\text{O}$ on oxidation. To which of the following class of compounds would X belong?
(a) Aldehyde (b) Tertiary alcohol
(c) Secondary alcohol (d) Alkene
- Suggest appropriate structures for the missing final compound. (The number of carbon atom remains the same throughout the reaction)

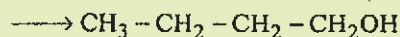
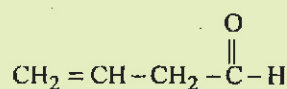


- Identify the product C in the series

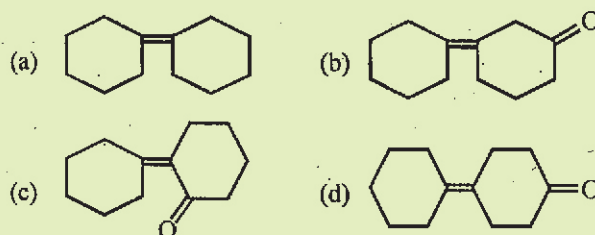
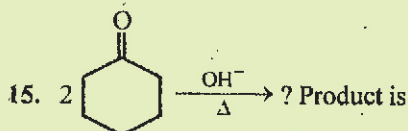


- (a) CH_3COOH (b) $\text{CH}_3\text{CH}_2\text{NHOH}$
 (c) CH_3CONH_2 (d) CH_3CHO
- If formaldehyde and KOH are heated, then we get
(a) methane (b) methyl alcohol
(c) ethyl formate (d) acetylene
 - The reagent (s) which can be used to distinguish acetophenone from benzophenone is (are)
(a) 2,4-dinitrophenylhydrazine
(b) aqueous solution of NaHSO_3
(c) benedict reagent
(d) I_2 and Na_2CO_3
 - $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$ can be oxidized to $(\text{CH}_3)_2\text{C}=\text{CHCOOH}$ by
(a) Chromic acid (b) NaOH
(c) Cu at 300°C (d) KMnO_4
 - Pinacolone is
(a) 2,3-dimethyl-2-butanol
(b) 3,3-dimethyl-2-butanone
(c) 1-phenyl-2-propanone
(d) 1,1-diphenyl-2-ethanol

- Benzaldehyde reacts with ethanoic KCN to give
(a) $\text{C}_6\text{H}_5\text{CHOHCN}$ (b) $\text{C}_6\text{H}_5\text{CHOHCOC}_6\text{H}_5$
(c) $\text{C}_6\text{H}_5\text{CHOHCOOH}$ (d) $\text{C}_6\text{H}_5\text{CHOHCH}_2\text{COC}_6\text{H}_5$
- Which of the following compound will undergo self aldol condensation in the presence of cold dilute alkali ?
(a) $\text{CH}_2=\text{CH}-\text{CHO}$ (b) $\text{CH}=\text{C}-\text{CHO}$
(c) $\text{C}_6\text{H}_5\text{CHO}$ (d) $\text{CH}_3\text{CH}_2\text{CHO}$
- Acetaldehyde reacts with semicarbazide and forms semicarbazone. Its structure is
(a) $\text{CH}_3\text{CH}=\text{NNHCON}=\text{CHCH}_3$
(b) $\text{CH}_3\text{CH}=\text{NNHCONH}_2$
(c) $\text{CH}_3\text{CH}=\text{N}-\text{N}-\text{CONH}_2$
- Phenylmethyl ketone can be converted into ethylbenzene in one step by which of the following reagents?
(a) LiAlH_4 (b) Zn-Hg/HCl
(c) NaBH_4 (d) CH_3MgI
- Appropriate reducing agent for the following conversion is—

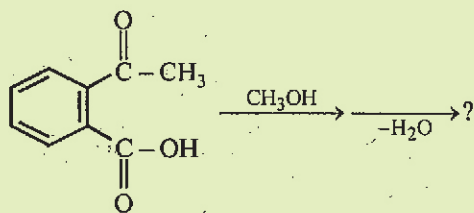


- (a) $\text{LiAlH}_4/\text{H}_2\text{O}$ (b) $\text{NaBH}_4/\text{H}_2\text{O}$
 (c) $\text{Na}+\text{C}_2\text{H}_5\text{OH}$ (d) $\text{B}_2\text{H}_6/\text{H}^+$



- Which of the following is best method for reducing 3-bromopropanal to 1-bromopropane—
(a) Wolf-Kishner reduction
(b) Clemmenson reduction
(c) Either (a) or (b)
(d) Stephen's reduction
- Cannizzaro reaction occurs with
(a) $\text{CH}_3-\text{CH}_2\text{OH}$ (b) $\text{C}_6\text{H}_5\text{CHO}$
(c) CH_3CHO (d) $\text{CH}_3-\text{CO}-\text{CH}_3$
- Which of the following compound will show positive silver mirror test ?
(a) HCOOH (b) $\text{CH}_3(\text{CHOH})_3\text{CHO}$

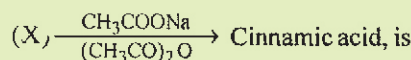
- (c) $\text{CH}_3\text{CO}(\text{CHOH})\text{CH}_3$ (d) Both (a) and (b)
19. In which reaction, $>\text{C}=\text{O}$ can be reduced to $>\text{CH}_2$?
 (a) Wolf-Kishner reaction (b) Reimer-Tiemann reaction
 (c) Wurtz reaction (d) None of these
20. A compound is treated with iodine and an alkali. It gives a yellow ppt. The compound is
 (a) propionaldehyde (b) benzophenone
 (c) methyl acetate (d) acetophenone
21. Which of the following does not show Cannizzaro reaction?
 (a) CH_3CHO (b) HCHO
 (c) $\text{C}_6\text{H}_5\text{CHO}$ (d) $(\text{CH}_3)_3\text{C.CHO}$
22. Which of the following functional groups cannot be reduced to alcohol using NaBH_4 in ethanolic solution?
 (a) $\text{R}-\text{O}-\text{R}$ (b) RCOCl
 (c) $\text{R}-\text{COOH}$ (d) $\text{R}-\text{CHO}$
23. What is the final product of the following reaction?



- (a) (b)
 (c) (d)
24. 2-pentanone and 3-pentanone can be distinguished by :
 (a) Cannizzaro's reaction (b) Aldol condensation
 (c) Iodoform reaction (d) Clemmensen's reduction
25. Which of the following is disproportionation reaction?
 (a) $2\text{HCHO} \xrightarrow{\text{NaOH}} \text{CH}_3\text{OH} + \text{HCOONa}$
 (b) $2\text{CH}_3\text{CHO} \xrightarrow{\text{NaOH}} \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$
 (c) (d) Both (a) & (b)
26. 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
27. Which of the following is an example of aldol condensation?

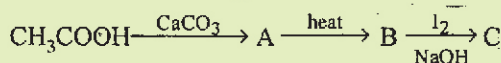
- (a) $2\text{CH}_3\text{COCH}_3 \xrightarrow{\text{dil NaOH}} \text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{CH}_2\text{COCH}_3$
 (b) $2\text{HCHO} \xrightarrow{\text{dil NaOH}} \text{CH}_3\text{OH}$
 (c) $\text{C}_6\text{H}_5\text{CHO} + \text{HCHO} \xrightarrow{\text{dil NaOH}} \text{C}_6\text{H}_5\text{CH}_2\text{OH}$
 (d) None of the above

28. The reactant (X) in the reaction



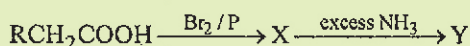
- (a) (b)
 (c) (d)
29. Ketone upon treatment with Grignard Reagent gives
 (a) primary alcohol (b) secondary alcohol
 (c) tertiary alcohol (d) aldehyde
30. Which of the following compounds would be the main product of an aldol condensation of acetaldehyde and acetone?
 (a) $\text{CH}_3\text{CH}=\text{CH}.\text{CHO}$ (b) $\text{CH}_3\text{CH}=\text{CHCOCH}_3$
 (c) $(\text{CH}_3)_2\text{C}=\text{CH}.\text{CHO}$ (d) $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$
31. Among acetic acid, phenol and *n*-hexanol, which of the following compounds will react with NaHCO_3 solution to give sodium salt and carbon dioxide?
 (a) acetic acid (b) *n*-Hexanol
 (c) acetic acid and phenol (d) phenol.
32. Schotten-Baumann reaction is a reaction of phenols with
 (a) benzoyl chloride and sodium hydroxide
 (b) acetyl chloride and sodium hydroxide
 (c) salicylic acid and conc. H_2SO_4
 (d) acetyl chloride and conc H_2SO_4
33. An ester is boiled with KOH . The product is cooled and acidified with concentrated HCl . A white crystalline acid separates. The ester is
 (a) methyl acetate (b) ethyl acetate
 (c) ethyl formate (d) ethyl benzoate
34. In the Friedel Craft's acylation reaction, the effective electrophile is
 (a) $\text{RCOCl}^\oplus$ (b) AlCl_3
 (c) RCOCl (d) $\text{RCO}^\oplus$
35. Which one of the following esters cannot undergo Claisen self-condensation?
 (a) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOC}_2\text{H}_5$
 (b) $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$
 (c) $\text{C}_6\text{H}_5\text{CH}_2\text{COOC}_2\text{H}_5$
 (d) $\text{C}_6\text{H}_{11}\text{CH}_2\text{COOC}_2\text{H}_5$
36. $\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[\text{red P}]{\text{Cl}_2} \text{A} \xrightarrow{\text{alc.KOH}} \text{B}$. What is B?
 (a) $\text{CH}_3\text{CH}_2\text{COCl}$ (b) $\text{CH}_3\text{CH}_2\text{CHO}$
 (c) $\text{CH}_2=\text{CHCOOH}$ (d) $\text{ClCH}_2\text{CH}_2\text{COOH}$
37. When $\text{CH}_2=\text{CH}-\text{COOH}$ is reduced with LiAlH_4 , the compound obtained will be
 (a) $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$ (b) $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{OH}$
 (c) $\text{CH}_3-\text{CH}_2-\text{CHO}$ (d) $\text{CH}_3-\text{CH}_2-\text{COOH}$
38. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is
 (a) $\text{CH}_3\text{COCl} + \text{C}_2\text{H}_5\text{OH} + \text{NaOH}$
 (b) $\text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$

- (c) $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaCl}$
 (d) $\text{CH}_3\text{Cl} + \text{C}_2\text{H}_5\text{COONa}$
39. Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives
 (a) 2-methyl-2-propanol (b) acetamide
 (c) acetone (d) acetyl iodide
40. Acetic anhydride reacts with diethyl ether in the presence of anhydrous AlCl_3 to give :
 (a) $\text{CH}_3\text{CH}_2\text{COOH}$ (b) $\text{CH}_3\text{CH}_2\text{COOC}_2\text{H}_5$
 (c) $\text{CH}_3\text{COOCH}_3$ (d) $\text{CH}_3\text{COOC}_2\text{H}_5$
41. Ethyl acetate on reaction with Grignard's reagent, forms a/an
 (a) alcohol (b) ketone
 (c) ether (d) hydrocarbon
42. Consider the following transformations :



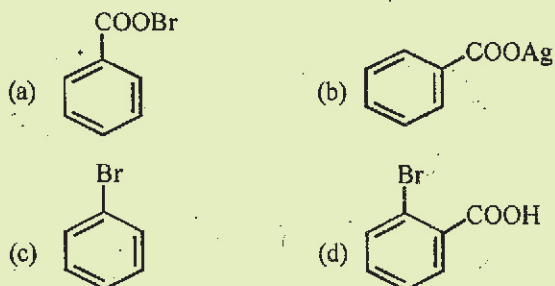
The molecular formula of C is

- (a) $\text{CH}_3 - \underset{\text{I}}{\overset{\text{OH}}{\text{C}}} - \text{CH}_3$ (b) $\text{ICH}_2 - \text{COCH}_3$
 (c) CHI_3 (d) CH_3I
43. In the following reaction



The major compounds X and Y are

- (a) RCHBrCONH_2 ; $\text{RCH}(\text{NH}_2)\text{COOH}$
 (b) RCHBrCOOH ; $\text{RCH}(\text{NH}_2)\text{COOH}$
 (c) RCH_2COBr ; $\text{RCH}_2\text{COONH}_4$
 (d) RCHBrCOOH ; $\text{RCH}_2\text{CONH}_2$
44. Silver benzoate will react with bromine in CCl_4 to form :



45. Reduction of aldehydes and ketones into hydrocarbons using zinc amalgam and conc. HCl is called
 (a) Cope reduction
 (b) Dow reduction
 (c) Wolf-Kishner reduction
 (d) Clemmensen reduction.

46. Which of the following represents the correct order of the acidity in the given compounds?

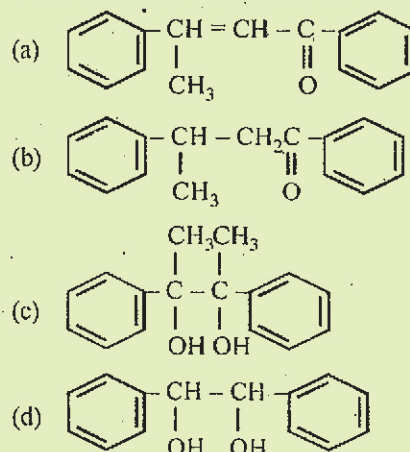
- (a) $\text{FCH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$
 (b) $\text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{CH}_3\text{COOH}$
 (c) $\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{CH}_3\text{COOH}$
 (d) $\text{CH}_3\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH}$

47. Which one of the following on treatment with 50% aqueous sodium hydroxide yields the corresponding alcohol and acid?

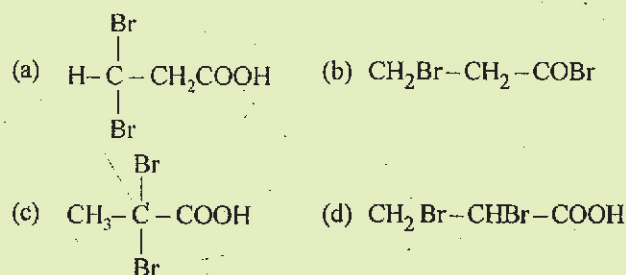
- (a) $\text{C}_6\text{H}_5\text{CHO}$
 (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$
 (c) $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_3$
 (d) $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$

48. The product formed in Aldol condensation is
 (a) a beta-hydroxy aldehyde or a beta-hydroxy ketone
 (b) an alpha-hydroxy aldehyde or ketone
 (c) an alpha, beta unsaturated ester
 (d) a beta-hydroxy acid

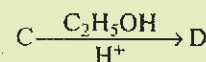
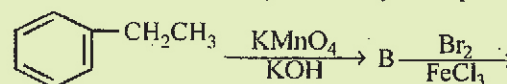
49. Acetophenone when reacted with a base, $\text{C}_2\text{H}_5\text{ONa}$, yields a stable compound which has the structure.



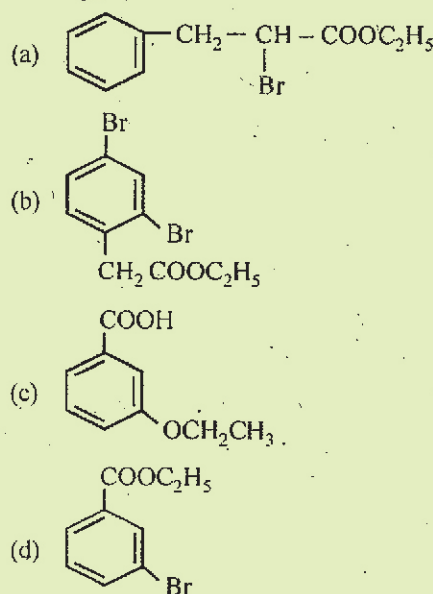
50. Propionic acid with Br_2/P yields a dibromo product. Its structure would be:



51. In a set of reactions, ethylbenzene yield a product D.



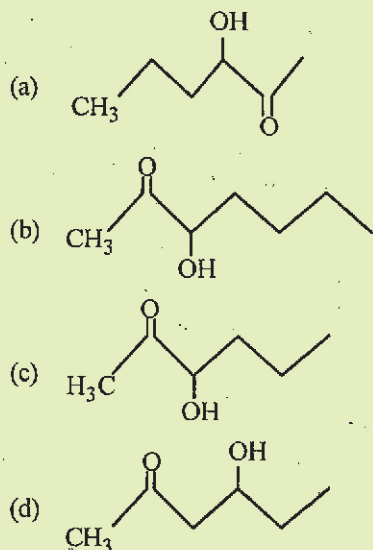
Identify D :



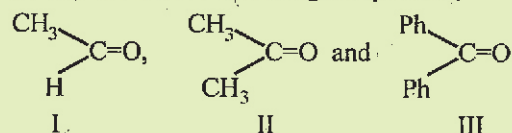
52. Which of the following reactions will not result in the formation of carbon-carbon bonds?
 (a) Reimer-Tiemann reaction (b) Cannizzaro reaction
 (c) Wurtz reaction (d) Friedel-Crafts acylation
53. Following compounds are given:
 (i) $\text{CH}_3\text{CH}_2\text{OH}$ (ii) CH_3COCH_3
 (iii) $\text{CH}_3-\text{CHOH}-\text{CH}_3$ (iv) CH_3OH

Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform?

- (a) (i) and (ii) (b) (i), (iii) and (iv)
 (c) Only (ii) (d) (i), (ii) and (iii)
54. Which one of the following compounds will be most readily dehydrated?



55. Clemmensen reduction of a ketone is carried out in the presence of which of the following?
 (a) Glycol with KOH (b) Zn-Hg with HCl
 (c) LiAlH_4 (d) H_2 and Pt as catalyst
56. The order of reactivity of phenyl magnesium bromide (PhMgBr) with the following compounds



- (a) $\text{III} > \text{II} > \text{I}$ (b) $\text{II} > \text{I} > \text{III}$
 (c) $\text{I} > \text{III} > \text{II}$ (d) $\text{I} > \text{II} > \text{III}$
57. Match the compounds given in List-I with List-II and select the suitable option using the code given below:

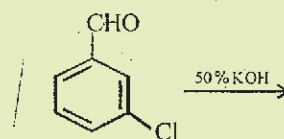
List-I	List-II
(A) Benzaldehyde	(i) Phenolphthalein
(B) Phthalic anhydride	(ii) Benzoin condensation
(C) Phenyl benzoate	(iii) Oil of wintergreen
(D) Methyl salicylate	(iv) Fries rearrangement

Code:

- (a) (A) (B) (C) (D)
 (b) (iv) (i) (iii) (ii)
 (c) (ii) (iii) (iv) (i)
 (d) (ii) (i) (iv) (iii)

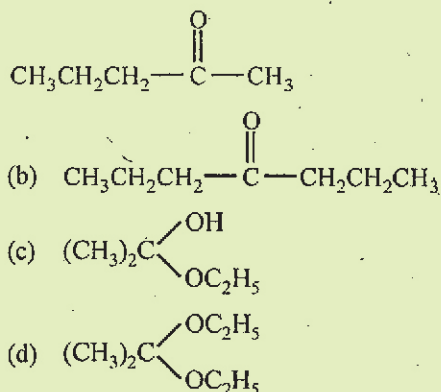
58. An organic compound 'A' on treatment with NH_3 gives 'B' which on heating gives 'C', 'C' when treated with Br_2 in the presence of KOH produces ethylamine. Compound 'A' is:
 (a) CH_3COOH (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
 (c) $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{COOH}$ (d) $\text{CH}_3\text{CH}_2\text{COOH}$

59. Predict the product in the given reaction.



- (a)
- (b)
- (c)
- (d)

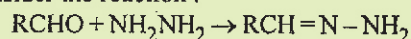
60. Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is: (a)



61. The correct order of decreasing acid strength of trichloroacetic acid (A), trifluoroacetic acid (A), acetic acid (C) and formic acid (D) is:

- (a) $\text{B} > \text{A} > \text{D} > \text{C}$ (b) $\text{B} > \text{D} > \text{C} > \text{A}$
 (c) $\text{A} > \text{B} > \text{C} > \text{D}$ (d) $\text{A} > \text{C} > \text{B} > \text{D}$

62. Consider the reaction:



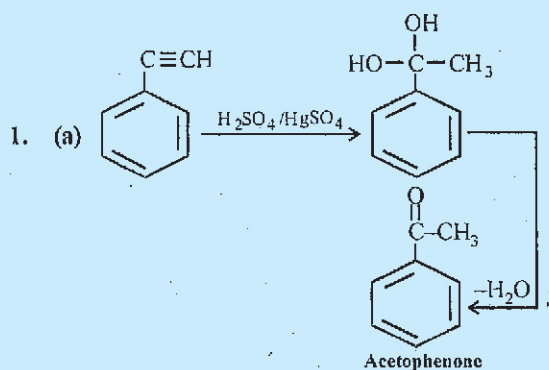
What sort of reaction is it?

- (a) Electrophilic addition-elimination reaction
 (b) Free radical addition-elimination reaction
 (c) Electrophilic substitution-elimination reaction
 (d) Nucleophilic addition-elimination reaction

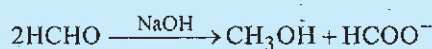
63. Which of the following compounds will give a yellow precipitate with iodine and alkali?

- (i) Acetophenone (ii) Acetamide
 (iii) Methyl acetate (iv) 2-Hydroxypropane
 (a) (i), (ii) and (iii) (b) (i) and (iv)
 (c) (ii) and (iv) (d) (i), (iii) and (iv)

SOLUTION

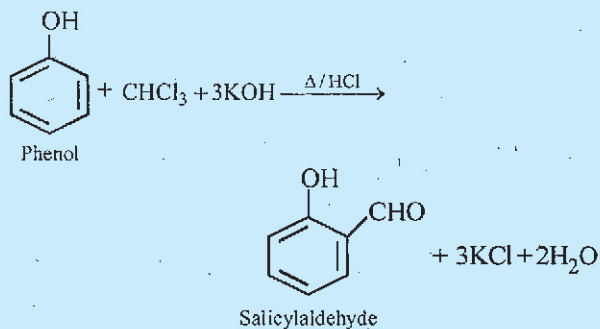


2. (d) (a) Cannizzaro reaction



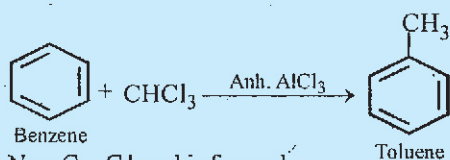
No new C—C bond is formed

(b) Reimer-Tiemann reaction:



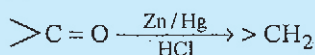
New C—C bond is formed

(c) Friedel-Craft reaction:

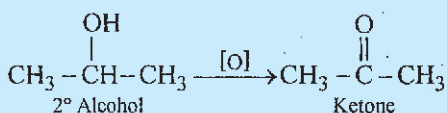


New C—C bond is formed

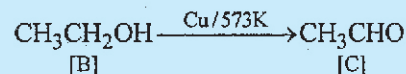
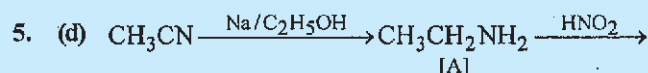
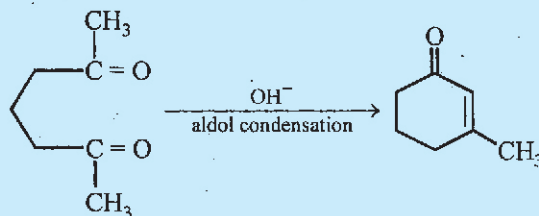
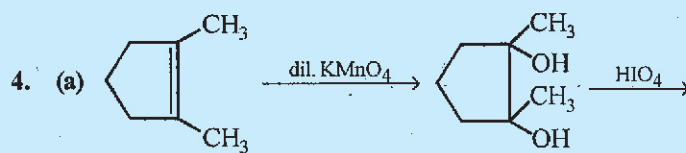
(d) Clemmensen reduction



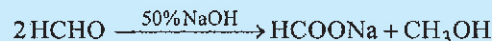
3. (c) $\text{C}_3\text{H}_8\text{O} \xrightarrow{[\text{O}]} \text{C}_3\text{H}_6\text{O}$ (Ketone)
(x)



Ketones are oxidation products of 2° alcohols.

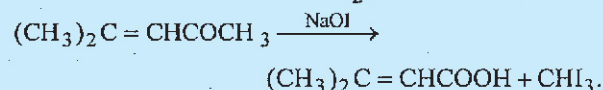


6. (b) Aldehydes containing no α -hydrogen atom on warming with 50% NaOH or KOH undergo disproportionation i.e. self oxidation - reduction known as Cannizzaro's reaction.

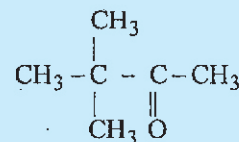


7. (d) I_2 and Na_2CO_3 react with acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$) to give yellow ppt. of CHI_3 but benzophenone ($\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$) does not and hence can be used to distinguish between them.

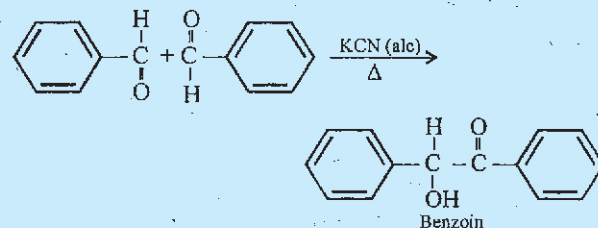
8. (b) Chromic acid and KMnO_4 will cleave the molecule at the site of double bond while Cu at 300°C cannot oxidise $\text{COCH}_3 \longrightarrow \text{COOH}$. The only reagent suitable for this conversion is NaOI or NaOH + I_2 (iodoform test):



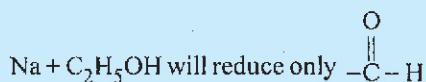
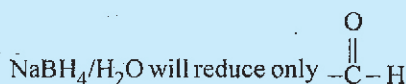
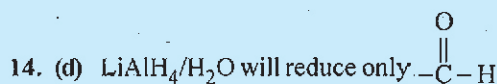
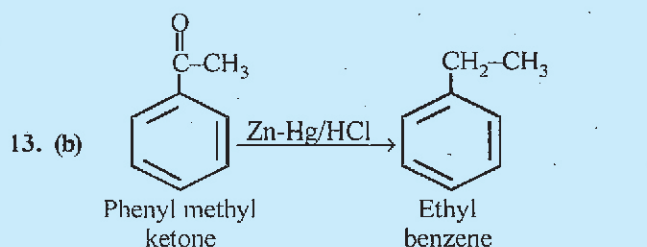
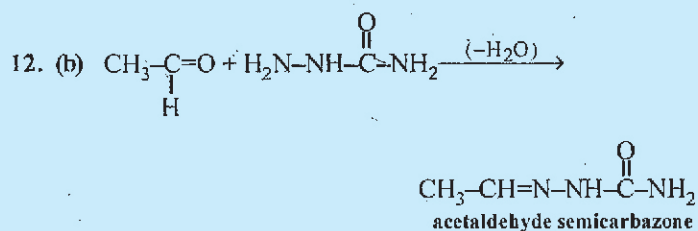
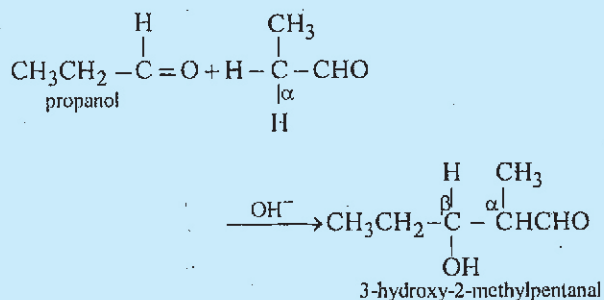
9. (b) Pinacolone is 3,3-dimethyl-2-butanone.



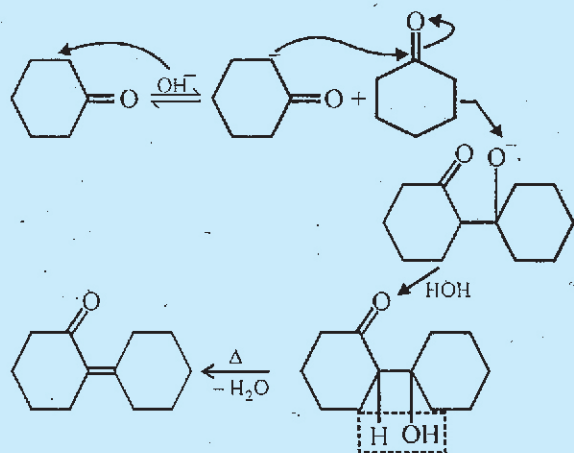
10. (b) When benzaldehyde is refluxed with aqueous alcoholic potassium cyanide, two molecules of benzaldehyde condense together to form benzoin



11. (d) Aldehydes which contain a α -hydrogen on a saturated carbon, i.e., $\text{CH}_3\text{CH}_2\text{CHO}$ undergo aldol condensation.



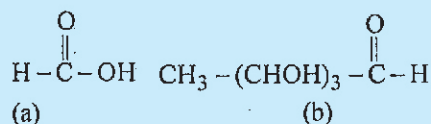
15. (c) In the presence of base, cyclohexanone show aldol condensation.



16. (b) In Wolf-Kishner reduction $\text{NH}_2\text{NH}_2/\text{OH}^-$ is used. Br^- can be replaced by OH^- .

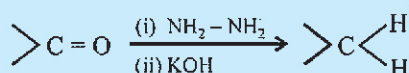
17. (b) Cannizzaro reaction is given by aldehydes and ketones which do not have α -hydrogen atom. Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) does not have α -H atom and hence gives Cannizzaro reaction.

18. (d) Compounds having $-\text{CHO}$ group reduce Tollen's reagent to silver mirror. It is called silver mirror test.

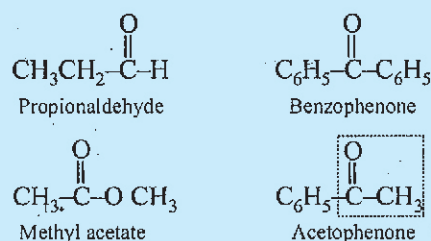


Both (a) and (b) have $-\text{C}(=\text{O})-\text{H}$ group so both of them give positive silver mirror test.

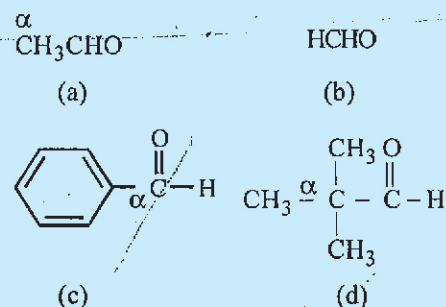
19. (a) Wolf-Kishner reduction



20. (d) This is iodoform test which is given by compounds having $\text{CH}_3\text{CO}-$ group.



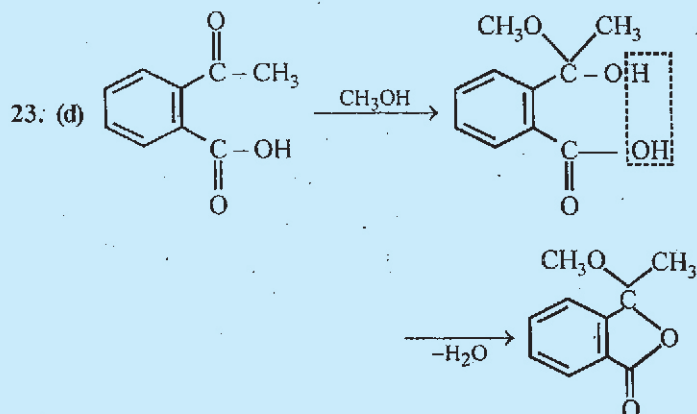
21. (a) Aldehydes having α -hydrogen atom do not show Cannizzaro reaction.



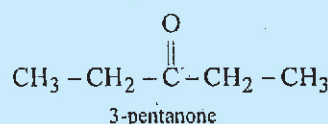
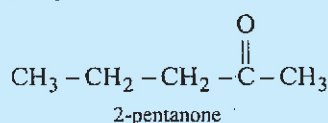
Thus only CH_3CHO has α -hydrogen atom and hence it will not show Cannizzaro reaction.

22. (a) Compounds having $-\text{C}(=\text{O})-$ moiety in their structure are reduced to alcohols using NaBH_4 in ethanolic solution.

Thus $\text{R}-\text{C}(=\text{O})-\text{Cl}$, $\text{R}-\text{C}(=\text{O})-\text{OH}$ and $\text{R}-\text{C}(=\text{O})-\text{H}$ are reduced while, $\text{R}-\text{O}-\text{R}$ (ethers) are inert and can't be reduced by NaBH_4 .

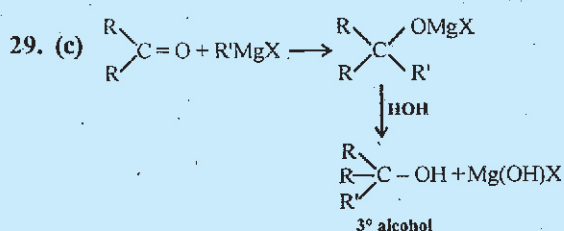
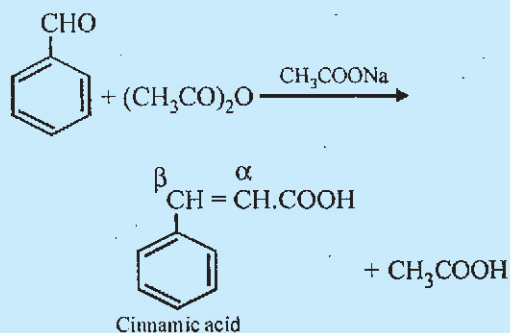


24. (c) Iodoform test is given by compounds which have CH_3CO group.

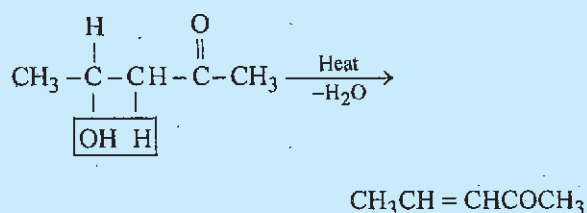
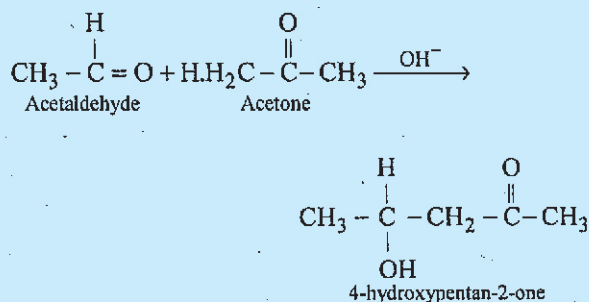


∵ 2-pentanone has CH_3CO group, so it gives iodoform test, while 3-pentanone does not have CH_3CO group, so it does not give iodoform test.

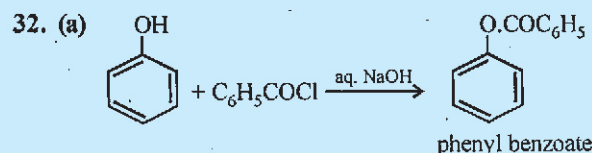
25. (a) In this reaction, one molecule is oxidised and other is reduced simultaneously.
26. (d) We can distinguish between formic acid and acetic acid by their action on Fehling's solution. Formic acid gives a red ppt of cuprous oxide but acetic acid does not give red ppt.
27. (a) Aldol condensation involves an aldehyde or ketone having an α -hydrogen atom. This type of condensation occurs in presence of dilute base (i.e., dil NaOH). Only CH_3COCH_3 will give aldol condensation (Both HCHO and $\text{C}_6\text{H}_5\text{CHO}$ lack α -hydrogen).
28. (b) Benzaldehyde forms cinnamic acid as follows.



30. (b) When aldehyde condensed with ketone, α -hydrogen of the ketone involved in condensation.



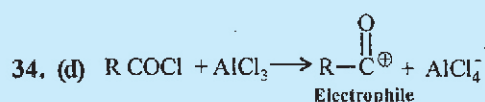
31. (a) among acetic acid, phenol and n-hexanol only CH_3COOH reacts with NaHCO_3 to evolve CO_2 gas.
- $$\text{CH}_3\text{COOH} + \text{NaHCO}_3 \longrightarrow \text{CH}_3\text{COONa} + \text{CO}_2 + \text{H}_2\text{O}$$



The function of NaOH is

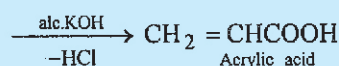
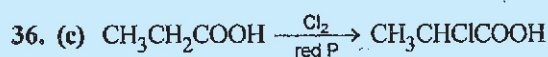
- To convert phenol to more stronger nucleophile PhO^-
- To neutralize the acid formed

33. (d) Methyl acetate and ethyl acetate on hydrolysis give CH_3COOH which is a liquid. Similarly ethyl formate on hydrolysis will give formic acid which is also a liquid. Only ethyl benzoate on hydrolysis will give benzoic acid which is a solid.



35. (b) The ester having α hydrogen atom show Claisen condensation reaction.

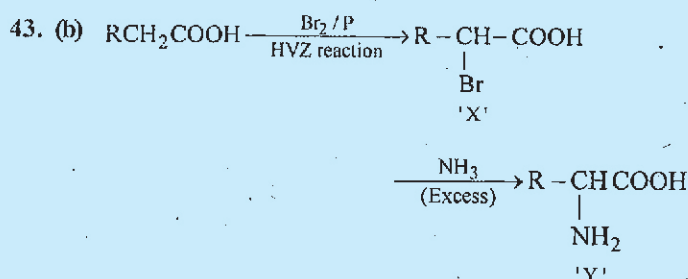
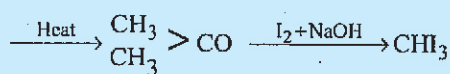
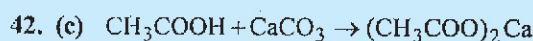
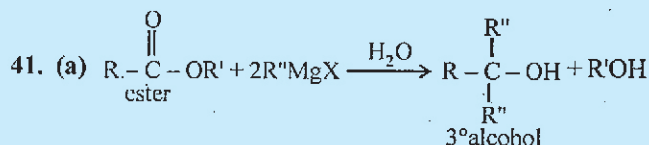
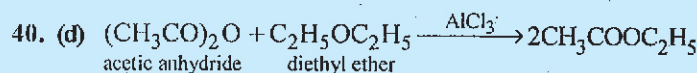
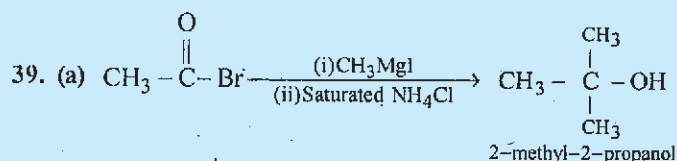
We know that ethyl benzoate ($\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$) does not contain α -hydrogen. Therefore $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$ does not undergo Claisen self condensation.



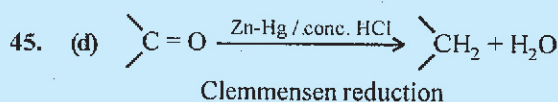
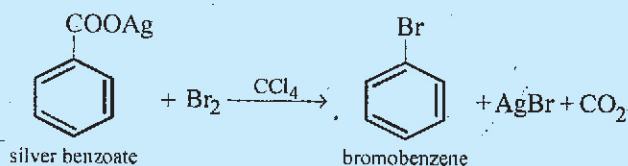
37. (a) LiAlH_4 can reduce COOH group and not the double bond.



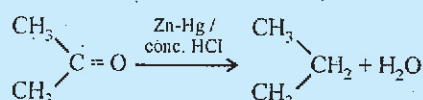
38. (c) There is no reaction hence the resultant mixture contains $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaCl}$.



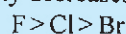
44. (c) This is Hunsdiecker's reaction.



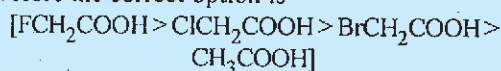
e.g.



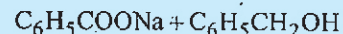
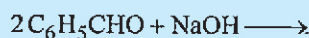
46. (c) Electron withdrawing substituent (like halogen, $-\text{NO}_2$, C_6H_5 etc.) would disperse the negative charge and hence stabilise the carboxylate ion and thus increase acidity of the parent acid. On the other hand, electron-releasing substituents would intensify the negative charge, destabilise the carboxylate ion and thus decrease acidity of the parent acid.
Electronegativity decreases in order



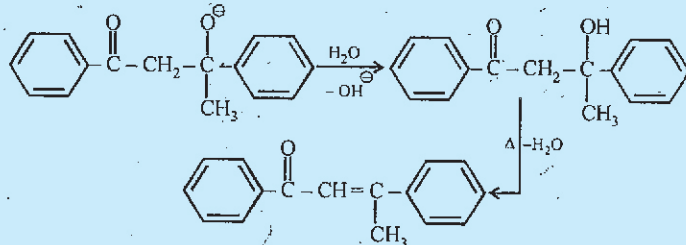
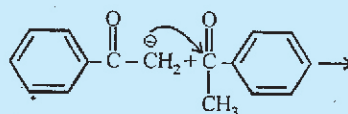
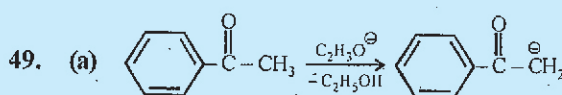
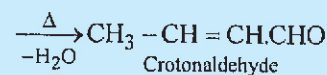
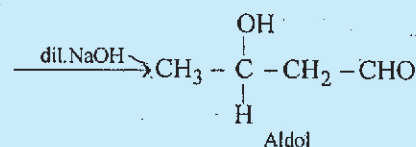
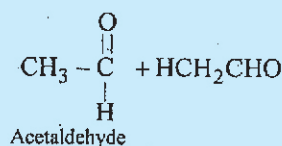
and hence $-I$ effect also decreases in the same order, therefore the correct option is



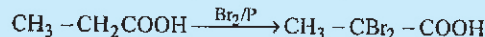
47. (a) Aldehydes containing no α -hydrogen atom on warming with 50% NaOH or KOH undergo disproportionation i.e., self oxidation-reduction known as cannizzaro's reaction.



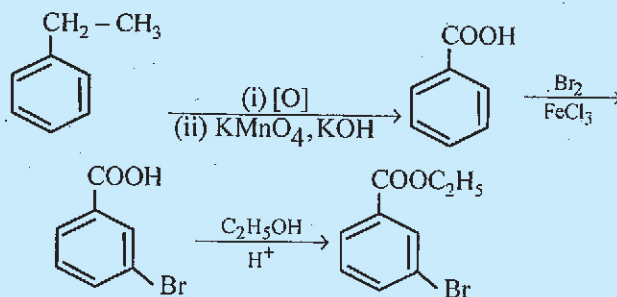
48. (a) Aldehydes and ketones having at least one α -hydrogen atom in presence of dilute alkali give β -hydroxy aldehyde or β -hydroxy ketone

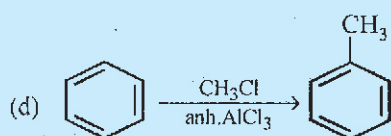
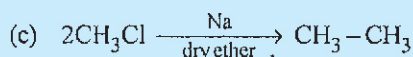
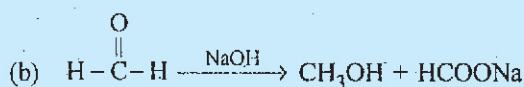
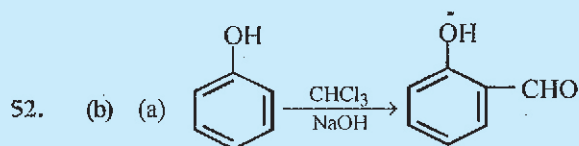


50. (c) This reaction is an example of Hell-Volhard Zelinsky reaction. In this reaction acids containing α -H on treatment with X_2/P give di-halo substituted acid.



51. (d)



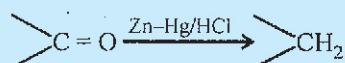


Note that new C-C bond is formed in a, c and d.

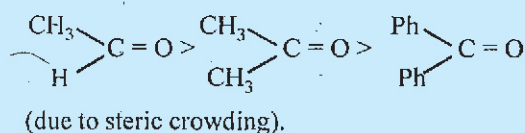
53. (d) Among the given compounds only CH_3OH does not give iodoform reaction.

54. (d) The intermediate is carbocation which is destabilised by C = O group in the first three cases. In (d), α -hydrogen is more acidic which can be removed as water. Moreover, the positive charge on the intermediate carbocation is relatively away from the C = O group.

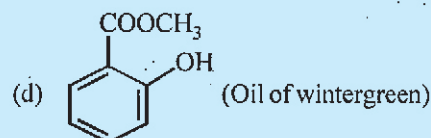
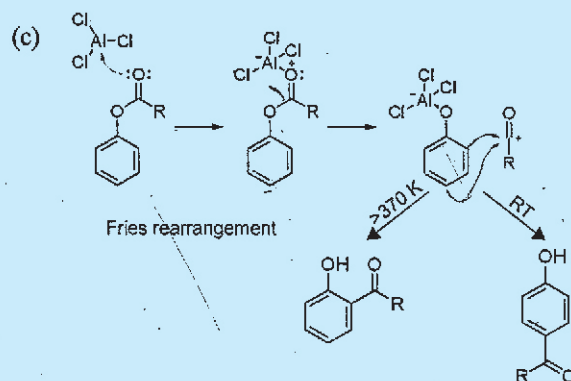
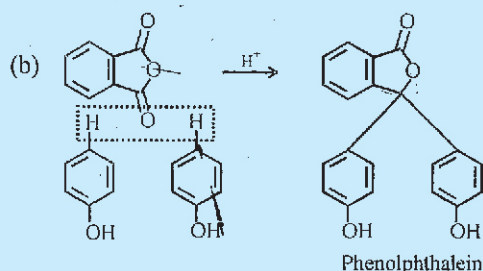
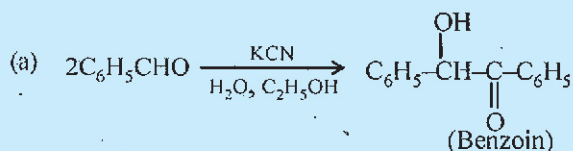
55. (b) Clemmensen reduction is



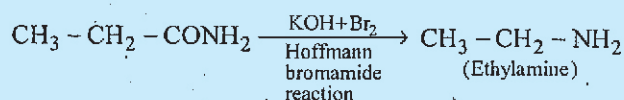
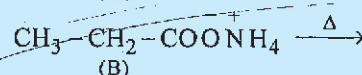
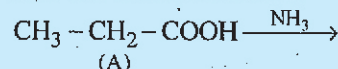
56. (d) The reactivity of the carbonyl group toward the nucleophilic addition reactions depend upon the magnitude of the positive charge on the carbonyl carbon atom (electronic factor) and also on the crowding around the carbonyl carbon atom in the transition state (steric factor). Both these factors predict the following order



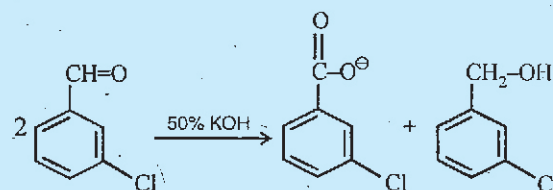
57. (d)



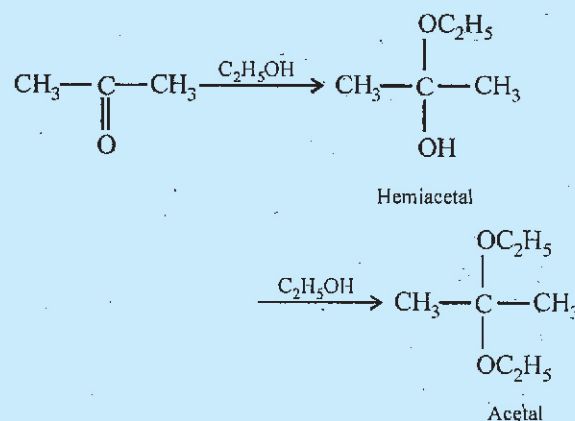
58. (d) Since, C when heated with Br_2 in presence of KOH produces ethylamine, hence it must be propanamide and hence the organic compound (A) will be propanoic acid. The reactions follows.



59. (c) Cannizzaro reaction - when an aldehyde containing α -H undergo reaction in presence of 50% KOH. It disproportionates to form a molecule of carboxylic acid and a molecule of alcohol.



60. (d) Anhydrous alcohols add to the carbonyl group of aldehydes in the presence of anhydrous hydrogen chloride to form acetals via hemiacetals.

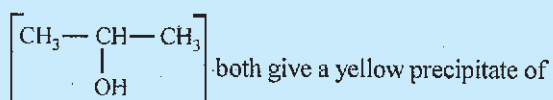
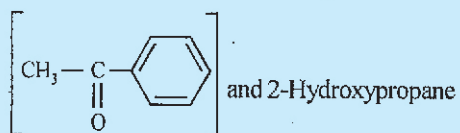


61. (a) $\text{CF}_3\text{COOH} > \text{CCl}_3\text{COOH} > \text{HCOOH} > \text{CH}_3\text{COOH}$ (K_a order)

The halogenated acids are much stronger acids than the parent acid and more over the acidity among the halogenated acid is increased almost proportionately with the increase in electronegativity of the halogen present. Further formic acid having no alkyl group is more acidic than acetic acid.

62. (d) $\text{R}-\text{CH}=\text{O} + \text{H}_2\text{N}-\text{NH}_2 \rightarrow \text{R}-\text{CH}=\text{N}-\text{NH}_2$
Such reactions take place in slightly acidic medium and involve nucleophilic addition of the ammonia derivative.

63. (b) It is iodoform reaction. Acetophenone



CHI_3 (iodoform) with iodine and alkali.