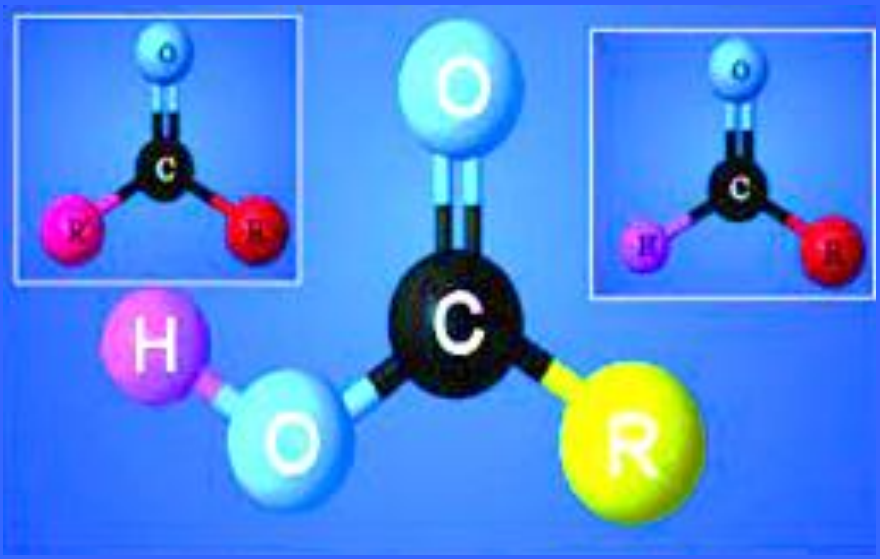
# 12.ALDEHYDES, KETONES AND CARBOXYLIC ACIDS




Chemistry Smart Booklet

Theory + NCERT MCQs + Topic Wise Practice MCQs + NEET PYQs

# ALDEHYDE, KETONES AND CARBOXYLIC ACID

## CARBOXYLIC ACIDS

### STRUCTURE

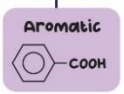
R – C(=O) – OH

### USES

- Rubber, Textiles.
- Food Industry.
- Manufacture of Soap and Detergent.

### CLASSIFICATION

Aliphatic $CH_3COOH$

Aromatic 


### PREPARATIONS

- Oxidation of 1° alcohols

$$RCH_2OH \xrightarrow[(ii)\ H_3O^+]{(i)\text{alk. } KMnO_4} R-COOH$$

- Hydrolysis of Nitriles and Amides

$$R-C\equiv N + 2H_2O \xrightarrow[OH^-]{H^+ \text{ or}} RCOOH + NH_3$$

- Hydrolysis of Esters

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

- From Grignard Reagent

$$CO_2 + RMgBr \xrightarrow[H^+,\ H_2O]{\text{Dry ether}} RCOOH + Mg(OH)Br$$

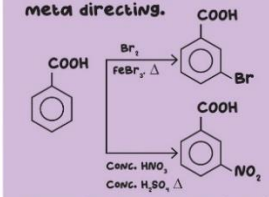
### CHEMICAL PROPERTIES

- Esterification

$$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$$

- Ring Substitution in Aromatic Acids:

COOH group is deactivating and meta directing.



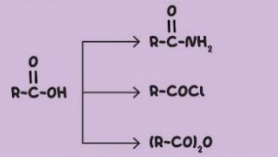

- Reduction of Carboxylic Acid

$$R-C(=O)-OH \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4/\text{ether}} R-CH_2OH$$

- Decarboxylation of Carboxylic Acid

$$R-C(=O)-OH \xrightarrow[CaO]{NaOH \text{ or}} R-H + Na_2CO_3$$

- Reaction involving cleavage of -OH group

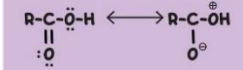



- Hell-Volhard Zelinsky Reaction

$$R-CH_2-OH \xrightarrow[(ii)H_2O]{(i)\ X_2,\ Red\ P} R-CH(X)COOH$$

### PHYSICAL PROPERTIES

- Physical State: Polar substances soluble in organic solvents.
- Acidity: The acidic character is due to the presence of resonance.



- Boiling Points: High boiling point due to intermolecular hydrogen bonding.

### COMPARISON OF MELTING AND BOILING POINT OF AROMATIC AND ALIPHATIC ACID

- Melting Point and Boiling Point of aromatic acid greater than aliphatic acid.

### ACIDIC ORDER

Caboxylic Acid > Phenol > Alcohol

### DISTINCTION TEST FOR CARBOXYLIC ACID

- Brisk effervescence of $CO_2$ gas with $NaHCO_3$
- Gives buff coloured ppt. with $FeCl_3$

## ALDEHYDES AND KETONES

### GENERAL FORMULA

**Aldehyde:** R – C(=O) – H

where R is alkyl and H is Hydrogen.

**Ketones** R – C(=O) – R'

where R and R' can be same or different.

### CLASSIFICATION

Aliphatic | Aromatic

### PREPARATIONS

- Oxidation of alcohol

$$1° \text{ Alcohol} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \text{Aldehyde}$$

$$2° \text{ Alcohol} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \text{Ketone}$$

$$R-CH_2OH \xrightarrow{K_2Cr_2O_7 + H_2SO_4} RCHO + H_2O$$

$$R-\underset{2° \text{ alcohol}}{CH(OH)R'} \xrightarrow{K_2Cr_2O_7 + H_2SO_4} R-CO-R' + H_2O$$

- Ozonolysis of alkenes

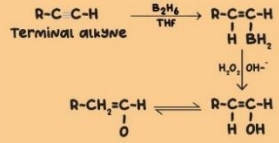
$$CH_3-CH=CH-CH_3 + O_3 \xrightarrow{H_2O,\ Zn} 2CH_3CHO$$

- From Gem-Dihalides:

$$R-\underset{Cl}{\overset{R'}{C}}-Cl \xrightarrow[\text{or } Ba(OH)_2]{\text{aq. KOH}} R-\overset{R'}{C}=O$$

(Aldehyde when R' = H Ketone when R' = alkyl group)

- Hydroboration Oxidation of Alkynes




- Rosenmund Reduction

$$R-\underset{O}{\overset{Cl}{C}} \xrightarrow{H_2,\ Pd\text{-}BaSO_4} R-\overset{O}{\overset{|}{C}}-H$$

### PHYSICAL PROPERTIES

Odour: Lower Aldehyde have an impleasant odour.

Physical State: HCHO is a gas. All other aldehyde and ketone upto $C_{11}$ are volatile liquids.

Solubility: Larger Carbonyl compounds are soluble in water due to the formation of H-bond.

Boiling Point and Melting Point: Boiling Point or Melting Point $\propto$ Molecular weight

$$\propto \frac{1}{\text{Branching}}$$

Due to electron donating alkyl group group ketones have higher boiling point than aldehye.

Reactivity: It depends on the nature of alkyl group. Smaller the group, more reactive will be compound.

### DISTINCTION TEST FOR ALDEHYDE

| TEST | ALDEHYDE | KETONES |
|---|---|---|
| Schiff's reagent | Pink Colour | No colour |
| Fehling's Solution | Red ppt. | No ppt. |
| Tollen's reagent | Silver Mirror | No ppt. |

### CHEMICAL PROPERTIES

Aldehyde > Ketones

Reactivity $\propto \frac{1}{\text{Stearic factor and electronic factror}}$

**Nucleophilic Addition-reaction**

$$>C=O + CN^- \rightleftharpoons >C<_{CN}^{OH}$$

$$>C=O + NaHSO_3 \longrightarrow >C<_{OH}^{SO_3Na}$$

$$>C=O + H_2N-Z \longrightarrow >C=N-Z + H_2O$$

**Clemmensen Reduction:**

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

**Wolff-Kishner reduction**

$$>C=O \xrightarrow[KOH/\text{ethyl glycol}]{(i)\ NH_2-NH_2} >CH_2 + N_2$$

**Aldol Condensation**

$$2CH_3CHO \longrightarrow CH_3CH(OH)CH_2CHO \xrightarrow{\Delta - H_2O} CH_3-CH=CH-CHO$$

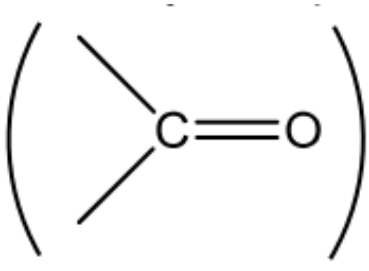
**Cannizaro reaction**

$$2HCHO \xrightarrow{\text{Conc. KOH}} CH_3OH + HCOOK$$

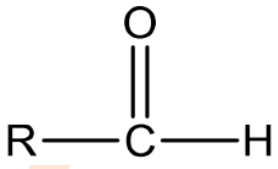
# ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

## Introduction

- Carbonyl compounds are organic compounds containing carbon-oxygen double bond

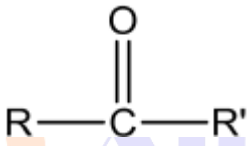


- Aldehydes have carbonyl group bonded to a carbon and hydrogen.



(Where R = H or alkyl or aryl group)

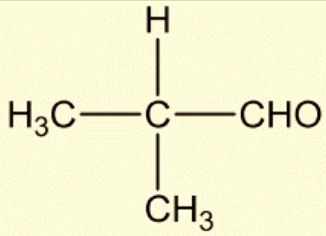
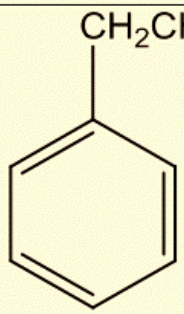
- Ketones have carbonyl group bonded to two carbon atoms.O



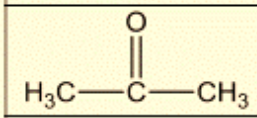
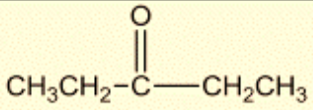
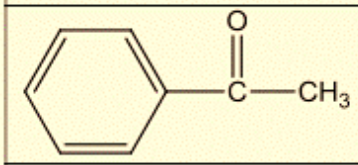
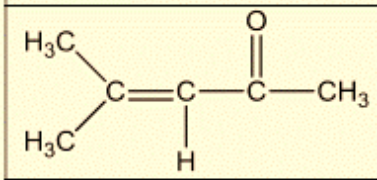
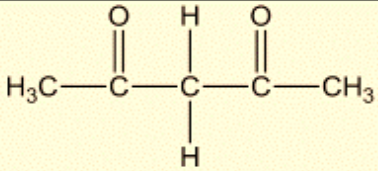
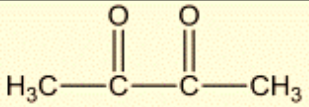
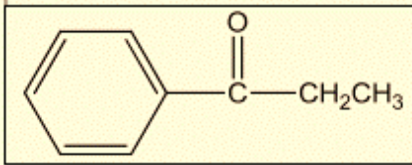
(Where R and R′ may be same or different alkyl or aryl groups)

## Nomenclature of Aldehydes and Ketones

### Aldehydes

| Structure | Common name | IUPAC name |
|---|---|---|
| $CH_3CHO$ | Acetaldehyde | Ethanal |
|  | Isobutyraldehyde | 2-Methylpropanal |
| $H_2C{=}CHCHO$ | Acrolein | Prop-2-enal |
|  | Phenylacetaldehyde | 2-Phenylethanal |
| $CH_3CH{=}CHCHO$ | Crotonaldehyde | But-2-en-al |

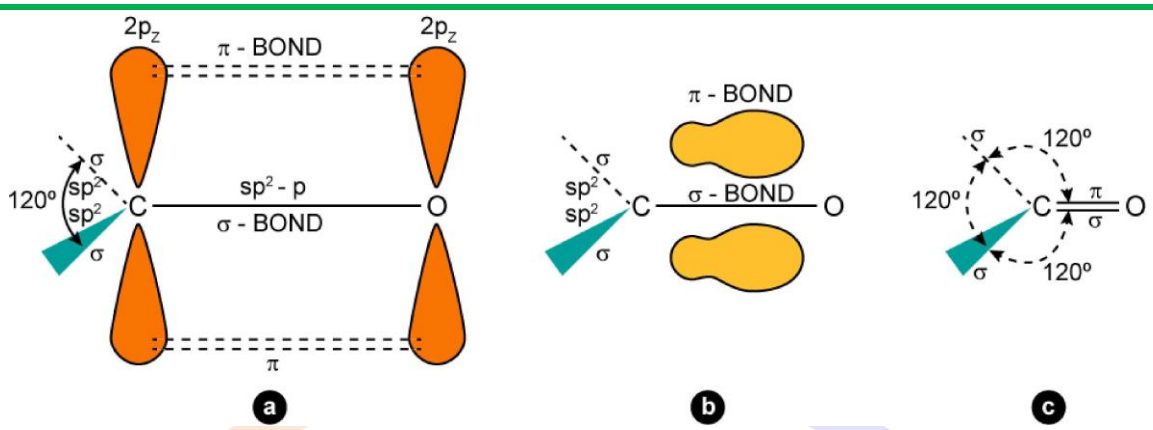
## Ketones

| Structure | Common name | IUPAC name |
|---|---|---|
|  | Dimethyl ketone or Acetone | Propanone |
|  | Diethyl ketone | Pentan-3-one |
|  | Methyl phenyl ketone | 1-Phenylethan-1-one |
|  | Mesityl oxide | 4-Methylpent-3-en-one |
|  | Acetylacetone | Pentane-2,4-dione |
|  | Biacetyl | Butane-2,3-dione |
|  | Ethyl phenyl ketone | 1-Phenylpropan-1-one |

## Structure and Nature of Carbonyl Group

### Structure

- The carbonyl carbon group is $sp^2$ hybridised and forms three sigma bonds.
- The fourth electron in the p-orbital forms a n-bond by overlapping with p-orbital of oxygen.
- The oxygen atom also has two non-bonding electron pairs.
- So the carbonyl carbon with the three atoms linked to it lies in the same plane and the n-cloud liesabove and below the plane.
- The bond angle is 120° with expected trigonal coplanar structure.
-



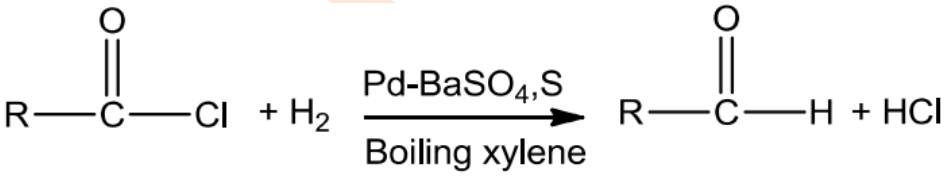

## Nature

- The C-O double bond is polarised since oxygen is electronegative than carbon.
- So the carbonyl carbon is an electrophilic centre and the carbonyl oxygen is a nucleophilic centre.
- The carbonyl compounds have substantial dipole moments and are polar than ethers.
- The high polarity of the carbonyl group can be explained on the basis of resonance involving a neutral
  (A) and a dipolar (B) structures given below.


## Preparation of Aldehydes

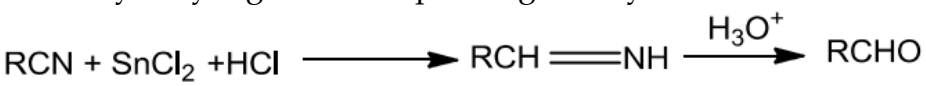
### ➢ Rosenmund Reduction

In this reaction, acyl chloride on hydrogenation in the presence of palladium catalyst and bariumsulphate gives aldehydes.

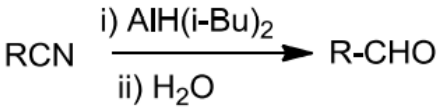



### ➢ Stephen Reaction

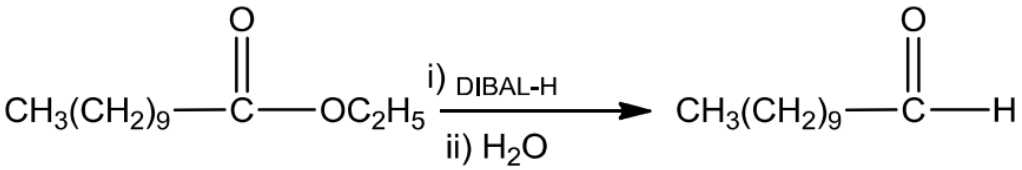
Nitriles on reduction with stannous chloride in the presence of HCI give imine which on hydrolysisgives corresponding aldehyde.




An alternate method to reduce nitriles selectively is by diisobutylaluminium hydride to imines which onhydrolysis yields aldehydes.




Esters can also be reduced to aldehydes with DIBAL-H



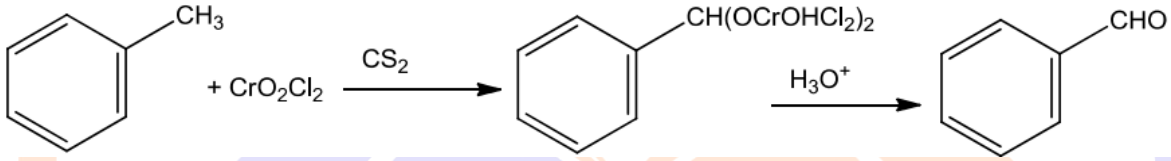

## ➢ From Aromatic Hydrocarbons

Aromatic aldehydes can be prepared using the following methods.

### I) By Oxidation of Methylbenzene

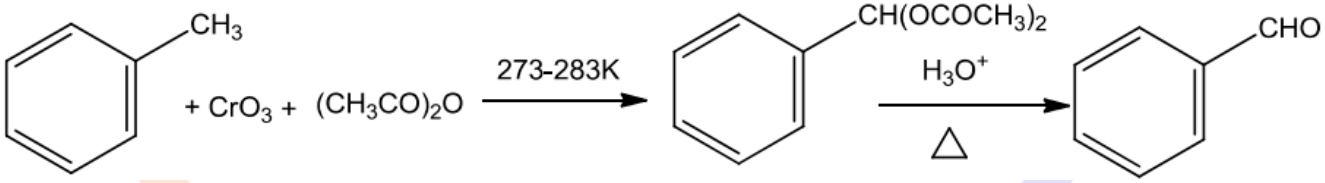
### Etard Reaction ( Use of Chromyl Chloride)

Chromyl chloride oxidises the methyl group to a chromium complex which on further hydrolysisgives corresponding benzaldehyde.



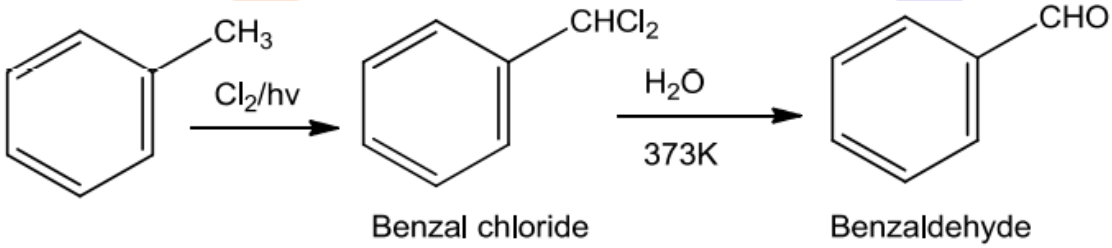

### Use of Chromic oxide($CrO_3$)

Toluene when treated with chromic oxide in acetic anhydride gets converted into benzylidenediacetate which on hydrolysis with aqueous acid gives benzaldehyde.



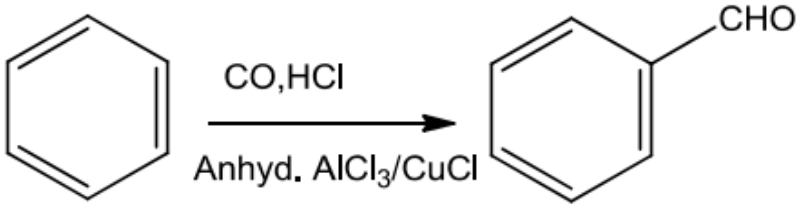

### Side Chain Chlorination

Toluene on side chlorination gives benzal chloride which on hydrolysis gives benzaldehyde.




### Gatterman – Koch Reaction

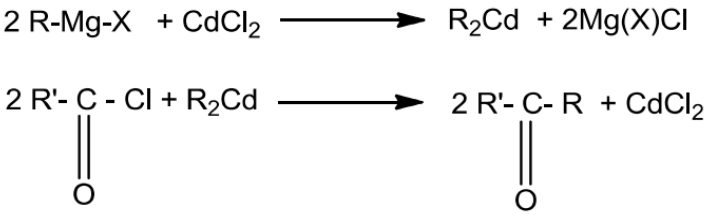
Benzene or toluene on treatment with CO and HCI in the presence of AIC!3 or CuCI gives benzaldehyde or p-tolualdehyde.



## Preparation of Ketones

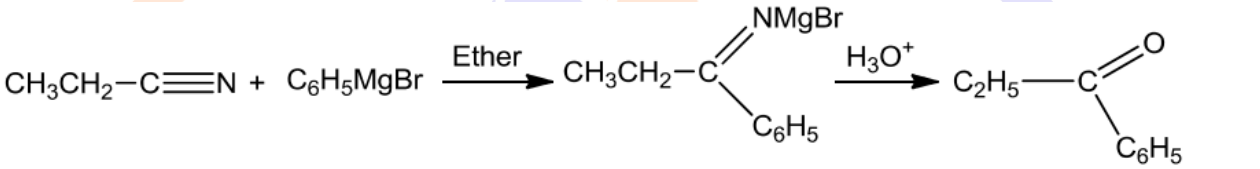
### ➢ From Acid chlorides or Acyl chlorides

Acyl chloride on treatment with dialkylcadmium obtained by reaction of cadium chloride with Grignardreagent gives ketones.




### ➢ From Nitriles

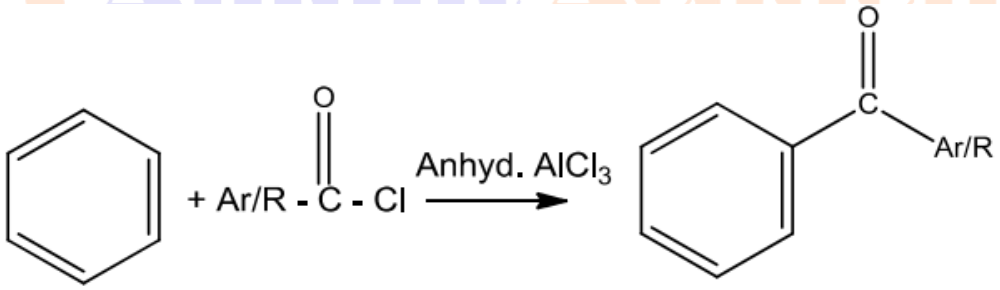
Nitriles on treatment with Grignard reagent followed by hydrolysis yields a ketone




Propiophenone
(1-Phenylpropanone)

### ➢ From Benzenes or Substituted Benzenes

Benzene or substituted benzene on treatment with acid chloride in the presence of anhydrous AICI3gives the corresponding ketone and this reaction is known as Friedel-Crafts acylation reaction.



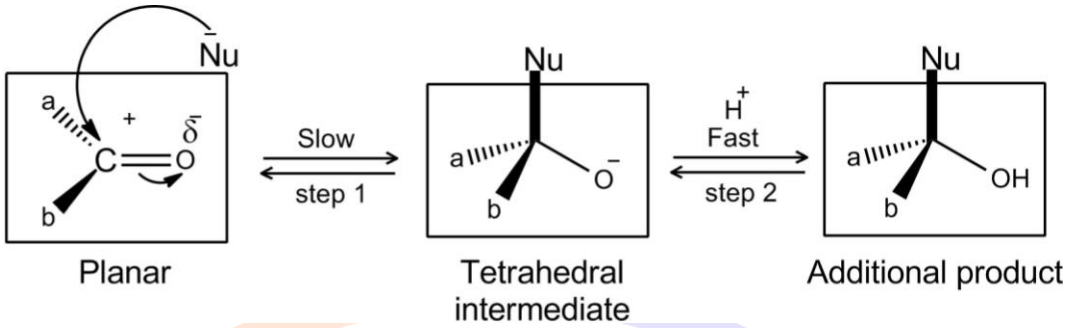

## Chemical Reactions

## Nucleophilic Addition Reactions

Aldehydes and Ketones undergo nucleophilic addition reactions.

### (i) Mechanism for Nucleophilic Addition Reactions

- A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group perpendicularly tothe $sp^3$ hybridised orbitals of carbonyl carbon.
- The hybridisation changes from $sp^2$ to $sp^3$ and a tetrahedral alkoxide intermediate is formed.
- The intermediate grabs a proton from the reaction medium to give an electrically neutral product.
- The net result is addition of Nu- and H' across the C-O double bond.



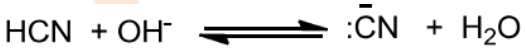

## (ii) Reactivity

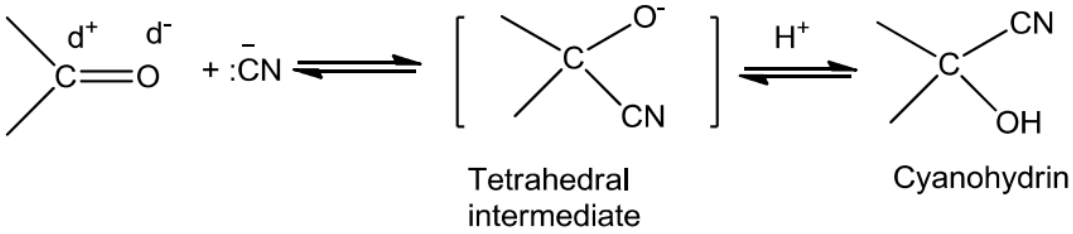
- Aldehydes are more reactive than ketones in nucleophilic reactions because of two reasons:
- Sterically, it is the presence of two relatively large groups in ketones that hinder the approach ofnucleophile to carbonyl carbon than in aldehydes which have only one such substituent.
- Electronically, aldehydes are more reactive than ketones because the two alkyl groups in ketonesdecrease the electrophilicity of the carbonyl carbon more effectively than in aldehydes.

## (iii) Important Examples of Nucleophilic Addition and Nucleophilic Addition- EliminationReactions

## (a) Addition of Hydrogen cyanide (HCN)

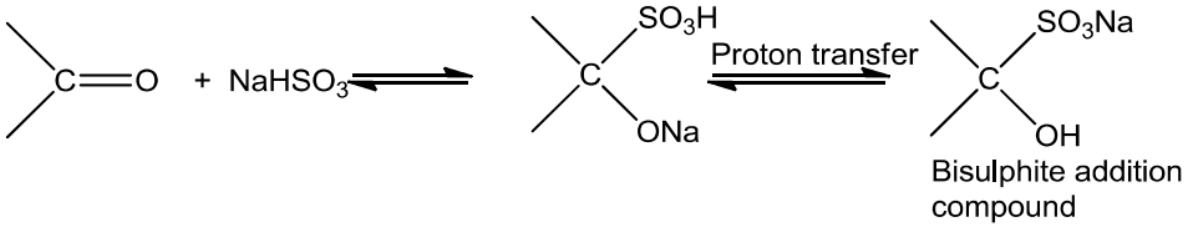
- On addition of HCN to aldehydes and ketones they yield cyanohydrins.
- Since the reaction is very slow with pure HCN, it is catalysed with the help of a base and thecyanide ion (CN-) generated as a strong nucleophile adds to carbonyl compounds to give cyanohydrins.



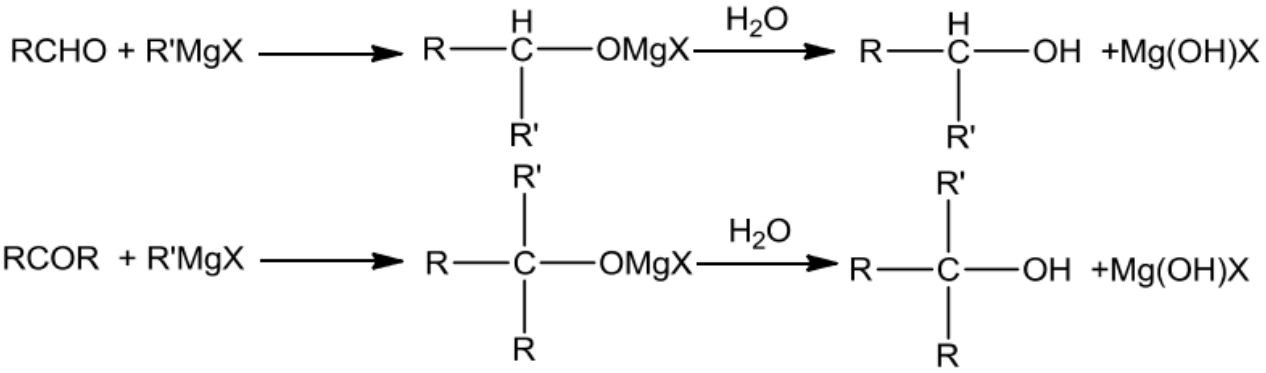

## (b) Addition of Sodium Hydrogensulphite

Sodium hydrogen sulphite when added to aldehydes and ketones yield addition products.



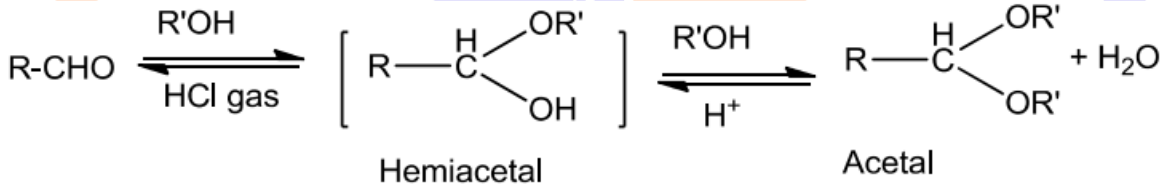

## (c) Addition of Grignard Reagents

Grignard reagents on reacting with aldehydes and ketones yield alcohols.



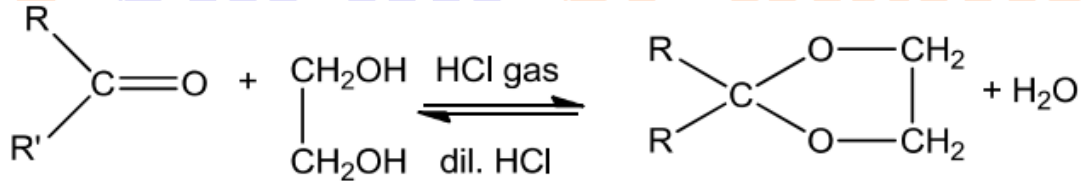

## (d) Addition of Alcohols

- Aldehydes on treatment with one equivalent of monohydric alcohol in the presence of dry HCIgive hemiacetal which on further treatment with one more molecule of alcohol gives acetal.




Hemiacetal Acetal

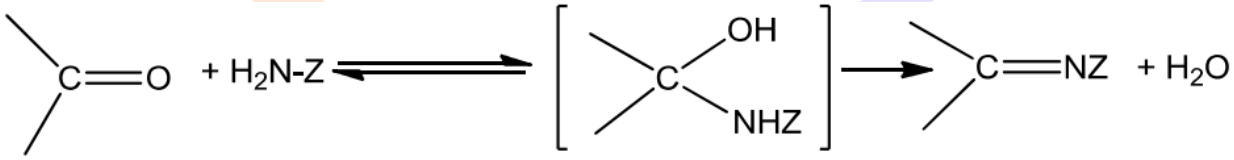
- Ketones also react with ethylene glycols under similar conditions to give ethylene glycol ketals.




Ethylene glycol ketal

## (e) Addition of Ammonia and its Derivatives

Ammonia and its derivative add to the carbonyl group of an aldehydes and ketone

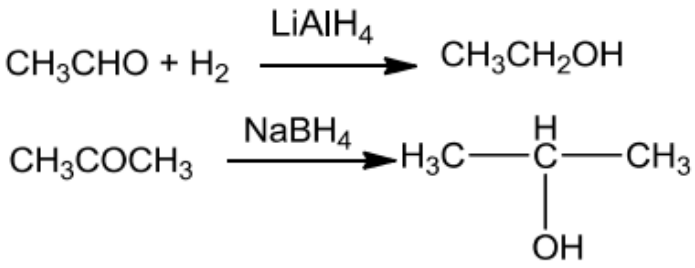



Z = Alkyl, aryl, OH, $NH_2$, $C_6H_5NH$, $NHCONH_2$, etc.

## ➢ Reduction

### (i) Reduction to Alcohols

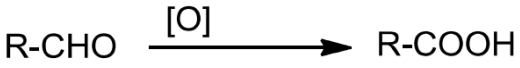
Aldehydes and ketones get reduced to primary and secondary alcohols by NaBH4 or LiAIH4.



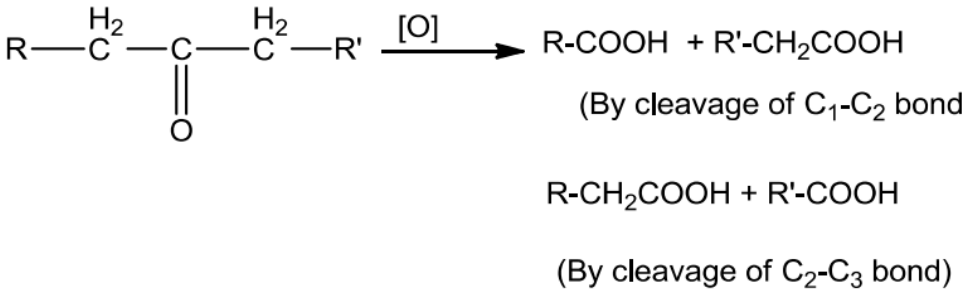
(ii) **Reduction to Hydrocarbons**

Aldehydes and ketones reduce to $-CH_2$ group on treatment with zinc-amalgam and conc. HCI [CIemmenson reduction] or with hydrazine which on heating with sodium or potassiumhydroxide in ethylene glycol[Wolff-Kishner reduction]

- **Oxidation**
- Aldehydes get oxidised to carboxylic acids with common oxidising agents like nitric acid,potassium permanganate, potassium dichromate etc.



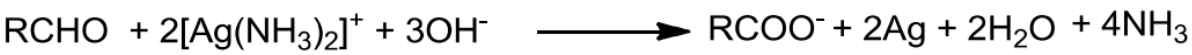
- Ketones undergo oxidation with strong oxidising agents and elevated temperatures. The reaction involves carbon-carbon bond cleavage to give a mixture of carboxylic acids with lessernumber of carbon atoms than the parent ketones.



**Test to distinguish Aldehydes from Ketones**

**Tollens test**

- Aldehydes on warming with freshly prepared ammoniacal silver nitrate solution (Tollensreagent) produce a bright silver mirror due to the formation of silver metal.
- The aldehydes are oxidised to corresponding carboxylate anion in alkaline medium.



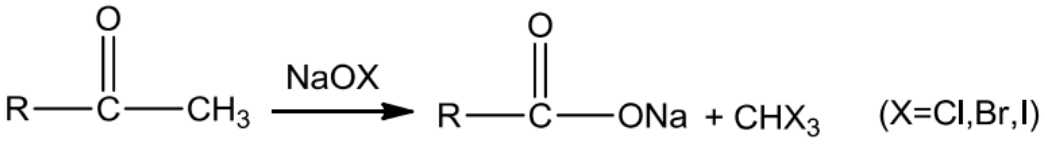
**Fehling's test**

- Fehling reagent comprises of Fehling solution A and Fehling B.Fehling solution A = aqueous copper sulphate
  Fehling solution B = Alkaline sodium potassium tartarate(Rochelle salt)
- On heating Fehling's reagent with an aldehyde, a reddish brown precipitate is obtained.
- Aldehydes are 10xidized to corresponding carboxylate anion while aromatic aldehydes do notrespond to this test.

$$RCHO + 2Cu^{+2} + 5\bar{O}H \longrightarrow RCOO^{-} + Cu_2O + 3H_2O$$

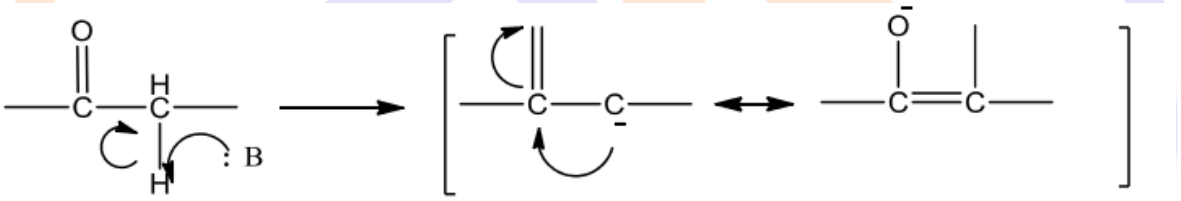
## Haloform reaction

Aldehydes and ketones with at least one methyl group attached to the carbonyl carbon atom on oxidation with sodium hypohalite turn to sodium salts of corresponding acids with one carbon atomless than that of carbonyl compound. In this reaction, the methyl group is converted to haloform.



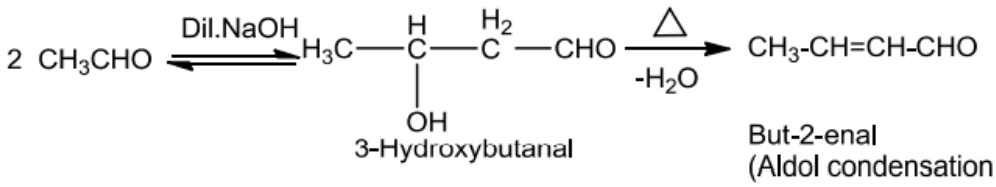

## ➢ Reactions due to a-hydrogen

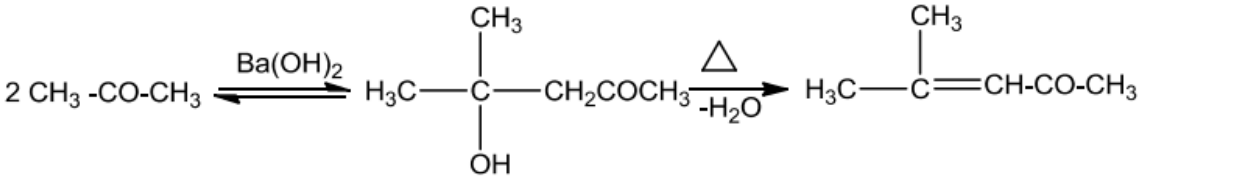
- The a-hydrogen of aldehydes and ketones is acidic in nature hence they undergo a number of reactions.
- The a-hydrogen atoms of carbonyl group is acidic due to the strong electron withdrawing effectof the carbonyl group and resonance stabilisation of the conjugate base.



### (i) Aldol Condensation

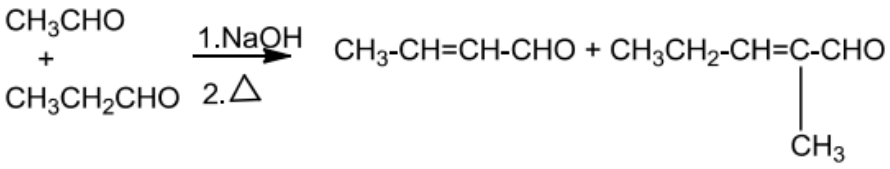
Aldehydes and ketones with at least one a-hydrogen undergo reaction in the presence of dilutealkali as catalyst to form §-hydroxy aldehydes (aldol) or §-hydroxy ketones (ketol) respectively.This is known as Aldol reaction.




### (ii) Cross Aldol Condensation

- In this reaction, two different aldehydes and/or ketones with a-hydrogen atoms reaction inthe presence of dilute alkali as catalyst give a mixture of four products.

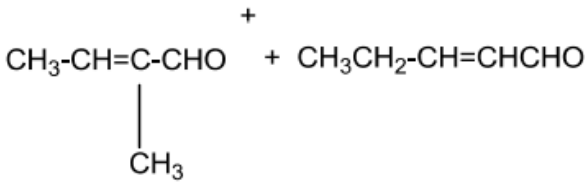



From two molecules of ethanal

2-Methylpent-2-enal from two molecules of propanal

Simple or self aldol products

+

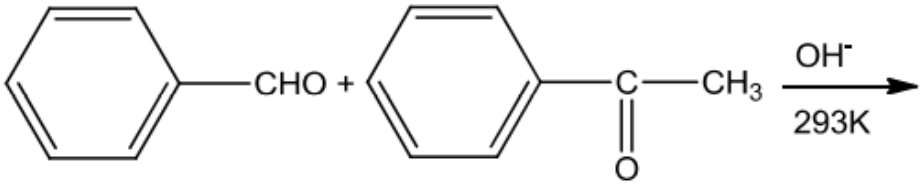


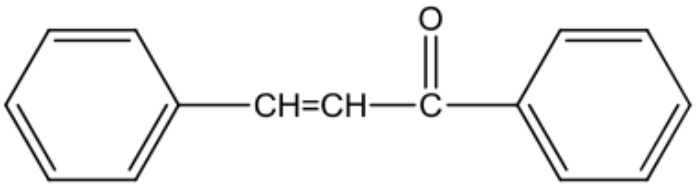

2-Methylbut-2-enal  Pent-2-enal

From one molecule of ethanal and one molecules of propanal

Cross aldol products

Ketones can be taken as one the component in the cross aldol reactions.



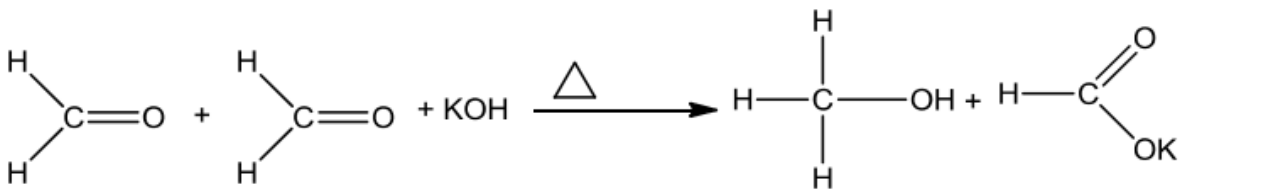




1,3-Diphenylprop-2-en-1-one
(Benzalacetophenone)
(Major product)

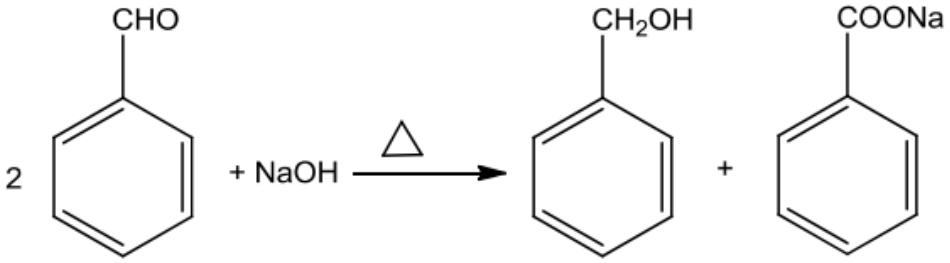
## ➢ Other Reactions

### (i) Cannizzaro reaction

- Aldehydes with no a-hydrogen undergo self oxidation and reduction on heating withconcentrated alkali.
- In this reaction, one molecule of the aldehyde is reduced to alcohol and another is oxidisedto carboxylic acid salt.



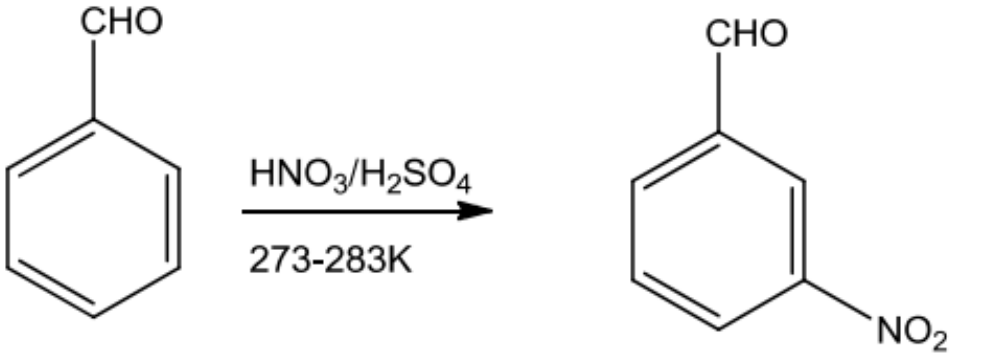

Formaldehyde Methanol Potassium formate




Benzyl alcohol Sodium benzoate

### (ii) Electrophilic Substitution Reaction

Aromatic aldehydes and ketones undergo electrophilic substitution reaction at the ring in whichthe carbonyl group acts as a deactivating and meta-directing group.

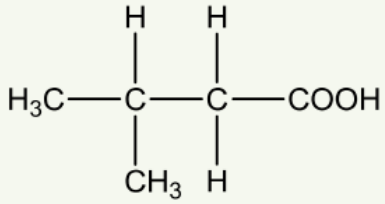
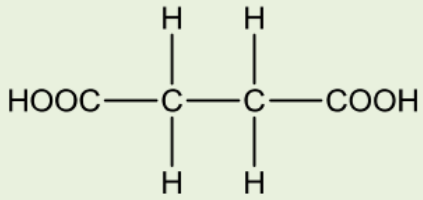
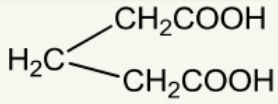



Benzaldehyde m-Nitrobenzaldehyde

## Carboxylic Acids

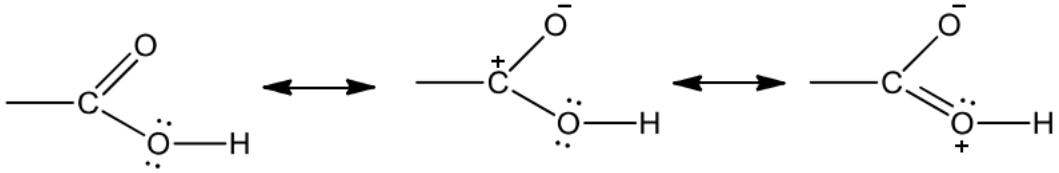
- The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids.
- The derivative compounds of carboxylic acid where carbon is attached to nitrogen and to halogens arecalled amides and acyl halides respectively.

## Nomenclature of Carbonyl Group

| Structure | Common Name | IUPAC Name |
|---|---|---|
| HCOOH | Formic acid | Methanoic acid |
|  | Isovaleric acid | 3-Methylbutanoic acid |
|  | Succinic acid | Butane-1,4-dioic acid |
| $H_3C—CH=CH—COOH$ | Crotonic acid | But-2-enoic acid |
| COOH-COOH | Oxalic acid | Ethane-1,2-dioic acid |
|  | Glutaric acid | Pentan-1,5-dioic acid |

## Structure of Carbonyl Group

The bonds to the carboxyl carbon in carboxylic acids lie in one plane and are separated by about 120°. Due to possible resonance structure given below, the carboxylic carbon is less electrophilic than carbonyl carbon.



## Preparation of Carboxylic Acids

### ➢ From Primary Alcohols and Aldehydes

- Primary alcohols undergo oxidation with the help of oxidising agents like potassium permanganatein neutral, acidic or alkaline media or by potassium dichromate and chromium trioxide in acidic media to give carboxylic acid.

$$RCH_2OH \xrightarrow[ii)\ H_3O^+]{i)\text{Alkaline } KMnO_4} RCOOH$$

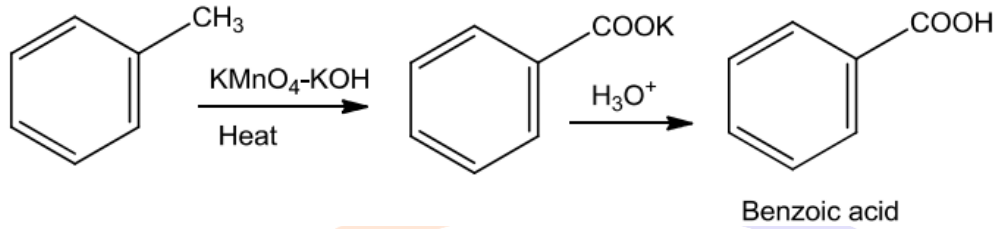
- Carboxylic acids can also be prepared by treating aldehydes with mild oxidising agents.

$$R\text{-}CHO \xrightarrow{[O]} R\text{-}COOH$$

### ➢ From Alkylbenzenes

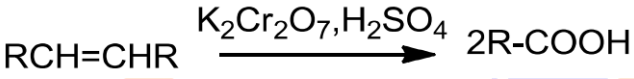
- In this method, alkyl benzenes on vigorous oxidation with chromic acid or acidic or alkalinepotassium permanganate yield aromatic carboxylic acids.

- Primary and secondary alkyl groups are oxidised in this way while tertiary groups remainunaffected.



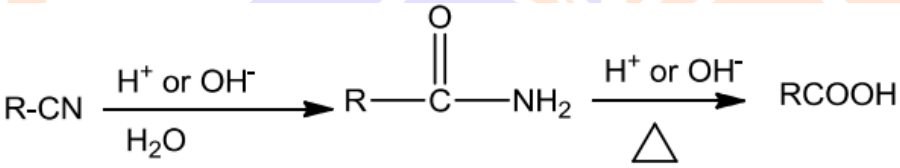

Benzoic acid

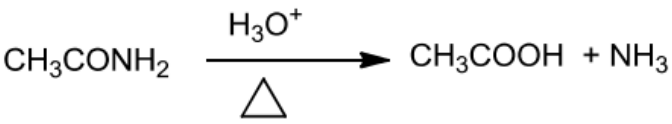
- Substituted alkenes can also be oxidised using the same oxidising agents to yield carboxylic acids.




## ➢ From Nitriles and Amides

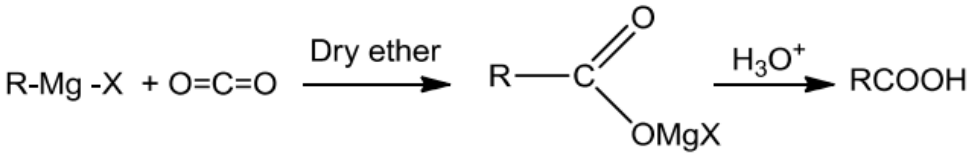
- Nitriles on hydrolysis give amides and then they are converted to acids in the presence of H+ orOH- catalyst.
- Use of mild reaction conditions is done to stop the reaction at the amide stage.



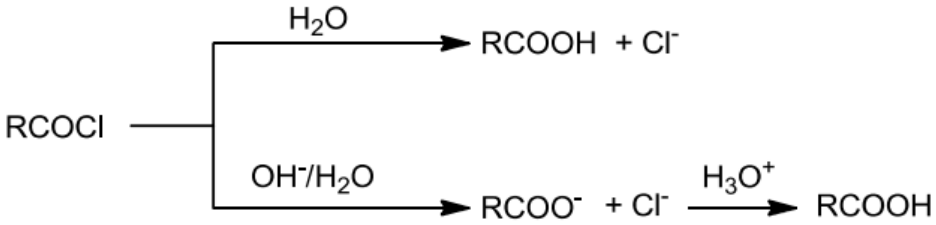

## ➢ From Grignard Reagents

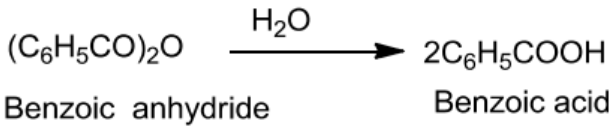
Grignard reagents on treating with carbon dioxide form salts of carboxylic acids which on acidificationwith mineral acid give corresponding carboxylic acids.




## ➢ From Acyl Halides and Anhydrides

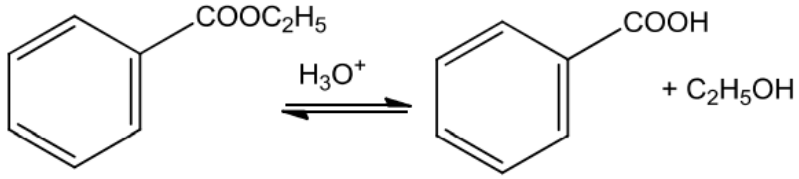
- Acid chlorides on hydrolysis with water give carboxylic acids or readily undergo hydrolysis with aqueous base to give carboxylate ions which on acidification give corresponding carboxylic acids.
- Anhydrides on the other hand undergo hydrolysis with water to give corresponding acids.



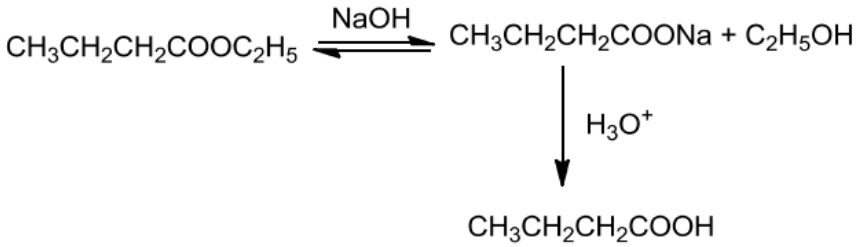




### ➢ From Esters

Esters on hydrolysis with acid give acids directly while basic hydrolysis give carboxylates which onacidification give corresponding acids.




Benzoic acid

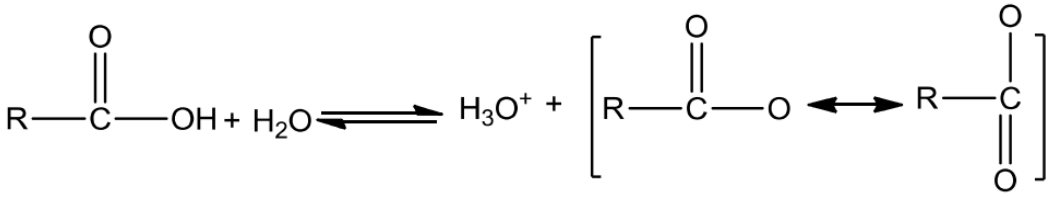



## Chemical Reactions of Carboxylic Acids

### Reactions involving cleavage of O-H bond

### 1. Acidity

- Carboxylic acids react with metals to form salts with the evolution of hydrogen gas.
- They also react with weaker bases such as carbonates and hydrogen carbonates
- This reaction is used to detect the presence of carboxyl group in an organic compound.
- Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions andhydronium ion.




**Acidity of carboxylic acids:** Carboxylic acids are more acidic than phenols. The strength of acid depends on the extent of ionisation, which in turn depends

on the stability of anion formed.

(i) **Effect of electron-donating substituents on the acidity of carboxylic acids:** Electron-donating substituent decreases the stability of carboxylate ion by intensifying the negative charge and hence decreases the acidity of carboxylic acids.

(ii) **Effect of electron-withdrawing substituent on the acidity of carboxylic acids:** The electron-withdrawing group increases the stability of carboxylate ion by delocalising negative charge and hence increases acidity of carboxylic acid.

The effect of the following groups in increasing acidity order is:

Ph < I < Br < CI < F < CN < $NO_2$ < $CF_3$

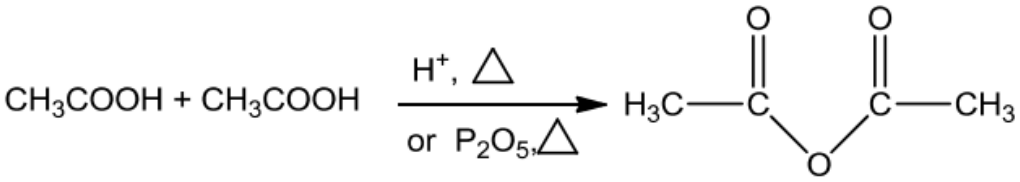
(a) **Effect of the number of electron-withdrawing groups:** As the number of electron-withdrawing groups increases, the −I effect increases, increasing the acid strength.

(b) **Effect of position of electron-withdrawing group:** As the distance between electron-withdrawing group and carboxylic group increases, electron-withdrawing influence decreases.

## ➢ Reactions involving cleavage of C-OH bond

**1. Formation of Anhydride**

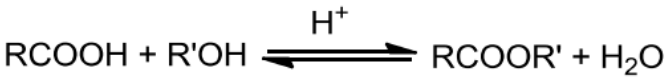
Anhydrides are obtained on treating carboxylic acids with mineral acids such as $H_2SO_4$ or with $P_2O_5$.




Ethanoic anhydride

**2. Esterification**

Esters are formed on treating alcohols or phenols with carboxylic acids in the presence of conc.$H_2SO_4$ or HCI gas as a catalyst.




**3. Reactions with $PCl_5$, $PCl_3$ and $SOCl_2$**

On treating with $PCl_5$, $PCl_3$ or $SOCl_2$, the hydroxyl group of alcohols is replaced by chlorine atom.$SOCl_2$ is preferred since the two products formed are volatile and escape easily making the purification of the products easier.

$RCOOH + PCl_5 \rightarrow RCOCl +$

$POCl_3 + HCl 3RCOOH + PCl_3 \rightarrow$

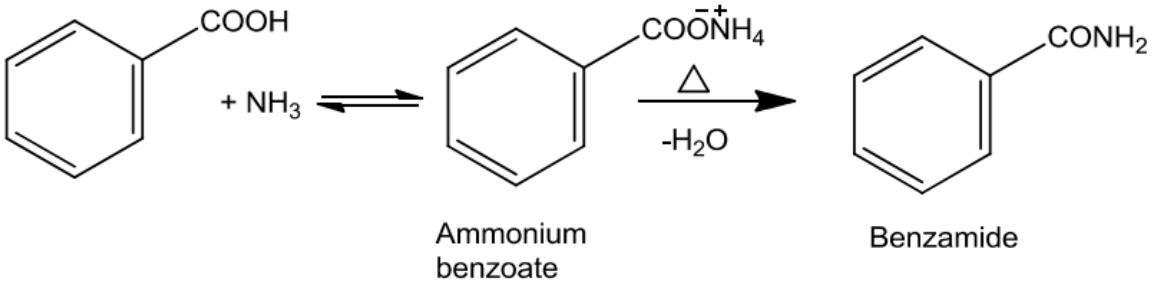
$3RCOCl + H_3PO_3$ RCOOH +

$SOCl_2 \rightarrow RCOCl + SO_2 + HCl$

**4. Reaction with Ammonia**

When carboxylic acids are allowed to react with ammonia, ammonium salt is formed which onfurther heating at high temperature gives amides.

$$CH_3COOH + NH_3 \leftrightharpoons CH_3COO^-NH_4^+ \xrightarrow[-H_2O]{\Delta} CH_3CONH_2$$




Ammonium benzoate

Benzamide

## ➢ Reactions involving -COOH group

**1. Reduction**

On reduction with reducing agents like $LiAlH_4$ or diborane, carboxylic acids are reduced to primary alcohols.

$$RCOOH \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4/ether\ or\ B_2H_6} R\text{-}CH_2OH$$

**2. Decarboxylation**

Sodium salts of carboxylic acids on heating with sodalime lose carbon dioxide to formhydrocarbons. The reaction is known as decarboxylation.

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

**Substitution reactions in the Hydrocarbon**

**1. Halogenation**

Carboxylic acids with a-hydrogen atom undergo halogenation at the a-position on treatment withsmall amount of red phosphorus to give a-halocarboxylic acids. The reaction is known as HeII- Volhard-Zelinsky reaction.

$$R\text{-}CH_2\text{-}COOH \xrightarrow[(ii)\ H_2O]{(i)X_2/Red\ P} R\text{-}\underset{\displaystyle X}{\overset{\displaystyle H}{C}}\text{-}COOH$$

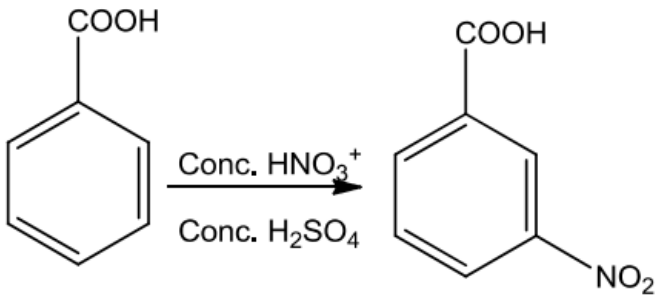
X=Cl,Br

α– Halocarboxylic acid

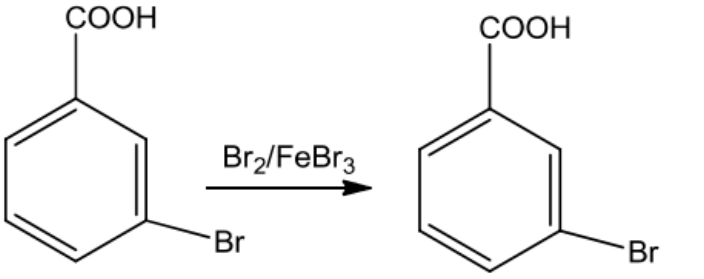
**2. Ring Substitution**

Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl groupacts as a deactivating and meta-directing group.

They however do not undergo Friedel-Crafts reaction because the carboxyl group is deactivatingand the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.



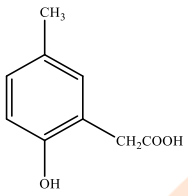

m-nitrobenzoic acid

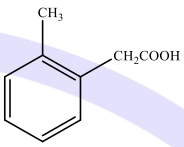


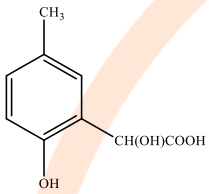

m-Bromobenzoic acid

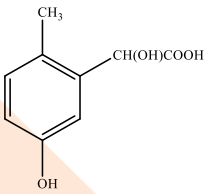
# NCERT LINE BY LINE QUESTIONS

**(1.)** p-cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form the compound B. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of carboxylic acid is

(a.) 


(b.) 


(c.) 


(d.) 

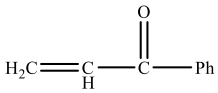
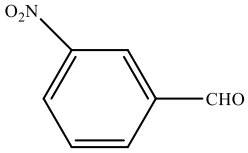
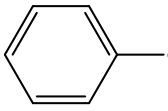

**(2.)** Following reaction is used to prepare alkane from sodium salt of carboxylic acid. The name of reaction is [Page: 383]

$$RCO\overset{-}{O}\overset{+}{N}a \xrightarrow[\text{Heat}]{NaOH\ \&\ CaO} R-H + Na_2CO_3$$

(a.) Decarboxylation (b.) Kolbe electrolysis

(c.) HVZ reaction (d.) None of these

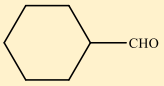
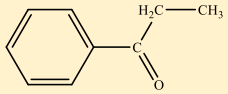
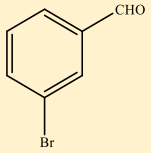
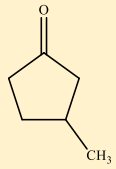
**(3.)** Match the Column I with Column II [Page: 372]

| Column I | Column II |
|---|---|
| (a) $2CH_3CHO \xrightleftharpoons{\text{dil NaOH}}$ | (p) $PhCH_2OH + PhCOONa$ |
| (b) $PhCHO + \text{conc.NaOH} \xrightarrow{\Delta}$ | (q)  |
| (c) $PhCHO + PhCOCH_3 \xrightarrow[293]{OH^-}$ | (r)  |
| (d)  $\xrightarrow[273^{-283}\ K]{HNO_3/H_2SO_4}$ | (s) $CH_3CH{=}CHCHO$ |

Codes

| | A | B | C | D |
|---|---|---|---|---|
| (a.) | r | q | p | s |
| (b.) | p | q | r | s |
| (c.) | s | p | q | r |
| (d.) | p | s | q | r |

**(4.)** Match the structure given in Column I with the name given in Column II [Page: 360]

| **Column I** | **Column II** |
|---|---|
| **(structure)** | **(Name)** |
| (I)  | p) 2-methyl cyclohexanone |
| (II)  | q) 3-bromo benzaldehyde |
| (III)  | r) cyclohexane carbaldehyde |
| (IV)  | s) 1-phenylpropan-1- one |

Codes

I II III IV

(a.) p q r s (b.) r s q p

(c.) s r p q (d.) r s q p

**(5.)** In which of the following solvent, carboxylic acid is/are soluble? [Page: 379]

(a.) benzene (b.) ether

(c.) chloroform (d.) All of these

**(6.)** **Assertion**: Carboxylic acids are reduced to alkanes on reaction with HI in presence of red phosphorus.

**Reason**: Melting point of carboxylic acid shows a regular pattern. [Page: 381]

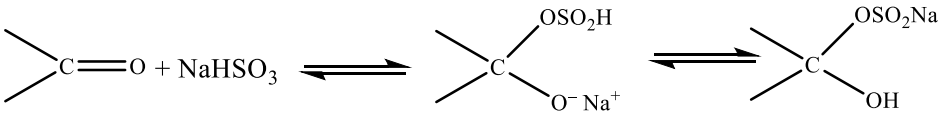
(a.) Both A and R are correct and R is the correct explanation of A.

(b.) Both A and R are correct but R is not correct explanation of A.

(c.) A is correct but R is incorrect.

(d.) Both A and R are false.

**(7.)** Consider the following reaction




Which of the following statement is incorrect for above reaction? [Page: 367]

(a.) Aldehyde and ketone has its sterically hindered to give the required product.

(b.) For aldehydes, the position of equilibrium lies to right hand side.

(c.) For ketones, the position of equilibrium lies to left hand side.

(d.) The product formed is water soluble.

**(8.)** Acyl chloride is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called [Page: 362]

(a.) Stephen reaction
(b.) Rosenmund reduction
(c.) Birch reduction
(d.) Wolff–Kishner reduction

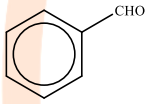
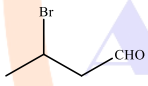
**(9.)** **Assertion**: Strong oxidising agents oxidise toluene and its derivatives to benzoic acid.
**Reason**: Chromyl chloride and chromic oxide stop the oxidation of toluene at aldehyde stage. [Page: 362]

(a.) Both A and R are correct and R is the correct explanation of A.
(b.) Both A and R are correct but R is not correct explanation of A.
(c.) A is correct but R is incorrect.
(d.) Both A and R are false.

**(10.)** **Assertion**: Hydrogen bonding in carboxylic acid is stronger than alcohols.
**Reason**: Highly branched carboxylic acids are more acidic than unbranched acids. [Page: 379]

(a.) Both A and R are correct and R is the correct explanation of A.
(b.) Both A and R are correct but R is not correct explanation of A.
(c.) A is correct but R is incorrect.
(d.) Both A and R are false.

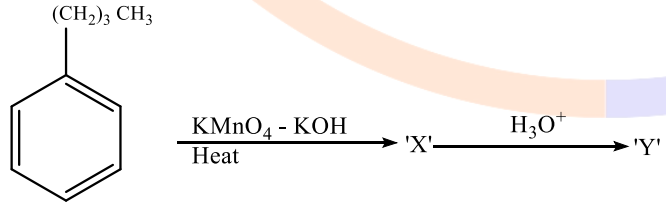
**(11.)** Which of the following is incorrect match? [Page: 360]

(a.)  – Benzaldehyde
(b.) $CH_3CHO$ – Acetaldehyde
(c.)  $\alpha-OXO-\beta-$bromopropane
(d.) HCHO – formaldehyde

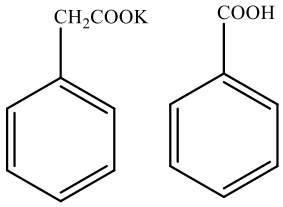
**(12.)** Which of the following statement is correct for Fehling's test? [Page: 369]

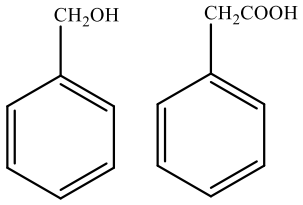
(a.) Fehling's solution is an aqueous copper sulphate solution.
(b.) Aldehydes on heating with Fehling's reagent give green precipitate.
(c.) Ketones does not give positive Fehling's test.
(d.) Aromatic aldehydes also reduces Fehling's solution.

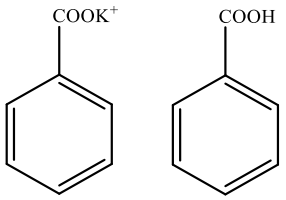
**(13.)** Consider the following reaction [Page: 376]

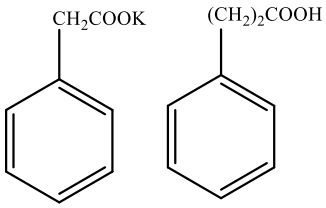



Here, 'X' and 'Y' respectively are:

(a.) 


(b.) 

(c.) 


(d.) 


**(14.)** The carboxylic carbon is less electrophilic than carbonyl carbon because of [Page: 375]

(a.) bond polarity (b.) resonance

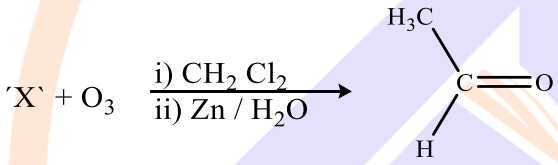
(c.) carbocation formation (d.) carbanion formation

**(15.)** Aldehydes are more reactive towards nucleophilic addition reactions than ketones because of [Page: 366]

(a.) inductive effect (b.) steric effect

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

**(16.)** Consider the following reaction [Page: 361]

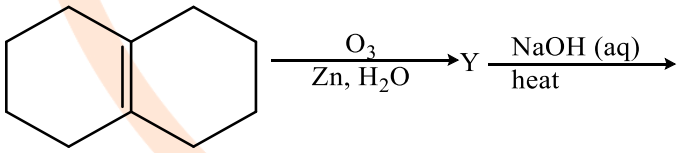



The reactant 'X' is

(a.) But-2-ene (b.) 2,3-dimethybut-2-ene

(c.) But-1-ene (d.) 2-methylpropene

**(17.)** In the reaction given below, the total number of intermolecular aldol condensation products formed 'Y' is




(a.) 1 (b.) 2

(c.) 3 (d.) 4

**(18.)** The product formed by the reaction of an aldehyde with a primary amine **is [NEET-2016, Phase II, Page: 368]**

(a.) Ketone (b.) Carboxylic acid

(c.) Aromatic acid (d.) Schiff base

**(19.)** Which of the following does not act as mild oxidising agent? **[Page: 369]**

(a.) Tollen's reagent (b.) Fehling's reagent

(c.) Benedict's reagent (d.) Alk. $KMnO_4$

**(20.)** A compound A has molecular formula $C_2Cl_3OH$. It reduces Fehling's solution and on oxidation gives a monocarboxylic acid B. A can be obtained by the action of chlorine on ethyl alcohol. A is

(a.) chloroform (b.) monochloroacetic acid

(c.) chloral (d.) methyl chloride

**(21.)** Consider the following reaction: **[Page: 372]**

$2HCHO + Conc.KOH \longrightarrow CH_3OH + HCOO^-K^+$

The name of reaction is

(a.) cross aldol condensation (b.) aldol condensation

(c.) Cannizzaro reaction (d.) Electrophilic reaction

**(22.)** **Assertion**: Carbon–oxygen bond length in formic acid are 1.23 Å and 1.36 Å.
**Reason**: Formic acid gives rise to nucleophilic. **[Page: 375]**

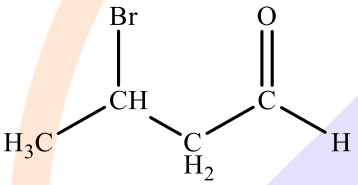
(a.) Both A and R are correct and R is the correct explanation of A.

(b.) Both A and R are correct but R is not correct explanation of A.

(c.) A is correct but R is incorrect.

(d.) Both A and R are false.

**(23.)** The correct common name for the given structure is [Page: 358]



(a.) $\alpha$ – bromobutyraldehyde

(b.) $\beta$ – bromobutyraldehyde

(c.) $\alpha, \beta$ – bromooxobutyraldehyde

(d.) None of these

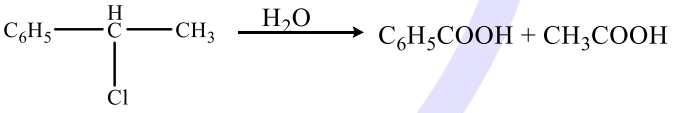
**(24.)** Which of the following reaction is not used to synthesis carboxylic acids? [Page: 377]

(a.) $RCOCl \xrightarrow{H_2O} RCOOH + Cl^-$

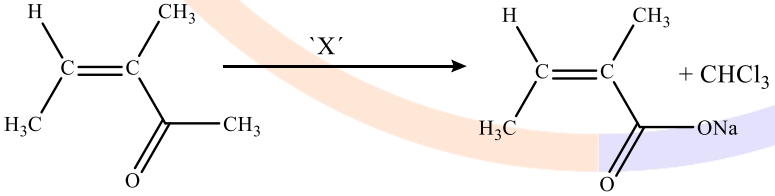
(b.) $RCOCl \xrightarrow{OH/H_2O} RCOO^- + Cl^- \xrightarrow{H_3O^+} RCOOH$

(c.) $(C_6H_5CO)_2O \xrightarrow{H_2O} 2C_6H_5COOH$

(d.)



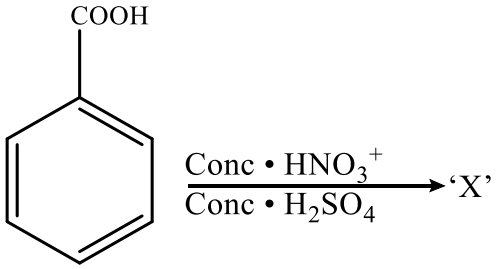
**(25.)** The reagent 'X' in the following reaction is [Page: 370]



(a.) NaOH (b.) NaO

(c.) NaOCl (d.) $Na_2CO_3$

**(26.)** The major product (X) formed in the reaction is [Page: 384]



(a.) m-nitrobenzoic and (b.) p-nitrobenzoic acid
(c.) o-nitrobenzoic acid (d.) None of these

**(27.)** Methanal, ethanal and propanone are miscible with water in all proportions because they [Page: 365]
(a.) form hydrogen bond with water (b.) polar bond
(c.) have high molecular mass (d.) none of these

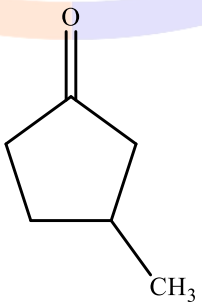
**(28.)** The type of reaction shown by aldehydes and ketones is [Page: 366]
(a.) electrophilic addition reactions (b.) nucleophilic addition reactions
(c.) free radical addition reactions (d.) none of these

**(29.)** **Assertion**: During reaction of carboxylic acids with $NaHCO_3$, the $CO_2$ evolved comes from carboxylic acid and not from $NaHCO_3$.
**Reason**: Carbonic acid is a stronger acid than carboxylic acid. [Page: 379]
(a.) Both A and R are correct and R is the correct explanation of A. (b.) Both A and R are correct but R is not correct explanation of A.
(c.) A is correct but R is incorrect. (d.) Both A and R are false.

**(30.)** Compound **(A)** [molecular formula $C_3H_8O$] is treated with acidified $K_2Cr_2O_7$ to form a product B (molecular formula $C_3H_6O$). B forms a shining silver mirror on warming with ammoniacal silver nitrate. 'B' when treated with an aqueous solution of $H_2NCONHNH_2.HCl$ and sodium acetate gives a product 'C'. The structure 'C' is
(a.) $CH_3CH_2CH = NNHCONH_2$ (b.) $(CH_3)_2 C = NNHCONH_2$
(c.) $(CH_3)_2 C = NCONHNH_2$ (d.) $CH_3CH_2CH = NCONHNH_2$

**(31.)** Consider the following reaction. [Page: 369]
$RCHO + 2Cu^{2+} + 5OH^- \xrightarrow{\Delta} RCOO^- + \text{'X'} + 3H_2O$
'X' in the above reaction is
(a.) CuO (b.) $Cu_2O$
(c.) $CuO_2$ (d.) $Cu_2O_3$

**(32.)** The IUPAC name of the following compound is



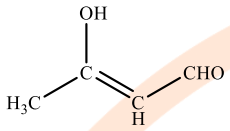

(a.) 3-methyl cyclopentanone (b.) 4-methylcyclopentanone
(c.) 3-oxo-1-methyalcyclopentane (d.) None of these

**(33.)** Which of the following is the incorrect use of carboxylic acid? [Page: 384]

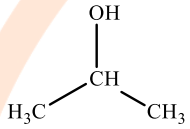
(a.) HCOOH is used in rubber, textile, dyeing and electroplating.
(b.) Ethanoic acid is used as solvent and as vinegar in food industry.
(c.) Sodium benzoate is used in perfumery.
(d.) Ester of benzoic acid is used in perfumery.

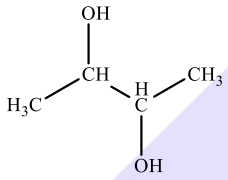
**(34.)** Consider the following reaction [Page: 371]

$$2CH_3-CHO \xrightarrow{dil.\ NaOH} X \xrightarrow[-H_2O]{\Delta} CH_3-CH_2CHCHO$$

(a.) 

(b.) $CH_3CH=CH_2OH$

(c.) 

(d.) 

**(35.)** Consider the following reaction: [Page: 376]

$$"X" \xrightarrow[\Delta]{H_3O^+} C_6H_5COOH + NH_3$$

Here, 'X' is

(a.) $C_6H_5CH_3$
(b.) $C_6H_5(CH_2)_2CH_3$
(c.) $C_6H_5CONH_2$
(d.) $C_6H_5NH_2$

**(36.)** Which of the following is the simplest aromatic aldehyde carrying the aldehyde group? [Page: 359]

(a.) benzene carbaldehyde
(b.) benzaldehyde
(c.) cinnamaldehyde
(d.) Both (a) and (b)

**(37.)** Consider the following reaction [Page: 369]

$$CH_3COCH_3 + 3[O] \xrightarrow{Conc.\ HNO_3} `X' + ´Y´$$

Here, X and Y are

(a.) HCOOH, $CH_3COOH$
(b.) $CH_3COCH_3$, $CH_3CHO$
(c.) HCHO, $CH_3COCH_3$
(d.) $CH_3CHO$, HCHO

**(38.)** Which of the reagent can be used to oxidise primary alcohols to carboxylic acid? [Page: 375]

(a.) $KMnO_4$ in neutral, acid or alkaline media
(b.) $K_2Cr_2O_7$
(c.) $CrO_3$ in acidic media
(d.) All of these

**(39.)** **Assertion**: The carbon-oxygen double bond in carbonyl is polar.
**Reason**: The electronegativity of oxygen is lower than carbon. [Page: 361]

(a.) Both A and R are correct and R is the correct explanation of A.
(b.) Both A and R are correct but R is not correct explanation of A.
(c.) A is correct but R is incorrect.
(d.) Both A and R are false.

**(40.)** Match the structure given in column I with common name given in column II [Page: 374]

| Structure | Common name |
|---|---|
| (I) $HOOC-CH_2-CH(COOH)\ CH_2COOH$ | (p) adipic acid |
| (II) $HOOC-(CH_2)_4\ COOH$ | (q) glutaric acid |
| (III) $HOOC-COOH$ | (r) tricarballylic acid |
| (IV) $HOOC(CH_2)_3\ COOH$ | (s) oxalic acid |

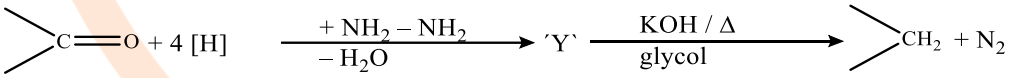
Codes

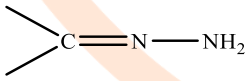
| | I | II | III | IV |
|---|---|---|---|---|
| (a.) | q | p | r | s |
| (b.) | r | p | s | q |
| (c.) | r | q | p | s |
| (d.) | p | q | s | r |

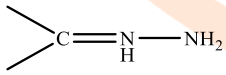
**(41.)** Which of the following order is incorrect? [NCERT Exemplar QR code]

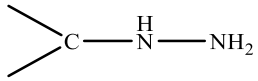
(a.) ethanol < phenol < acetic acid < chloroacetic acid (acidic strength)
(b.) $FCH_2COOH < ClCH_2COOH < C_6H_5CH_2COOH < CH_3COOH$ (acid strength)
(c.) $NO_2CH_2COOH > FCH_2COOH > C_6H_5COOH$ (acid strength)
(d.) $C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2OH$

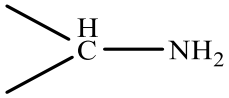
**(42.)** The intermediate 'Y' formed in the following reaction is [Page: 369]




(a.) 


(b.) 

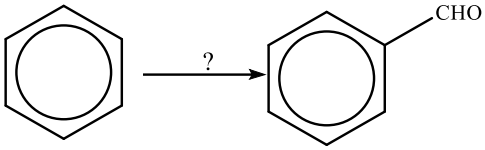

(c.) 


(d.) 


**(43.)** Boiling points of aldehydes are higher than hydrocarbons. It is due to [Page: 365]

(a.) weak molecular association
(b.) high intermolecular hydrogen bonding
(c.) high molecular masses
(d.) None of these

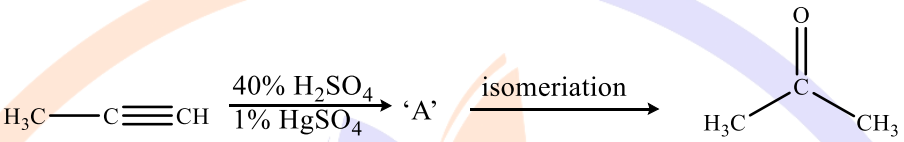
**(44.)** The reagent in following reaction is [Page: 363]




(a.) CO, HCl, Anhyd. $AlCl_3/CuCl$ (b.) $Cl_2/H_2$, $H_2O$, 373 K

(c.) Zn, $AlCl_3$ (d.) Pd, $H_2$

**(45.)** Consider the following reaction: [NCERT Exemplar QR code]




Type of isomerism in the above reaction and structure of 'A' respectively is

(a.) metamerism, prop-1-en-2-ol (b.) tautomerism, prop-1-en-1-ol

(c.) geometrical isomerism, prop-2-en-2-ol (d.) tautomerism, prop-1-en-2-ol

**(46.)** Match the column I with column II [Page: 368]

| **Column I** | **Column II** |
|---|---|
| **(Reaction)** | **(Product)** |
| I. Addition of HCN | p. Imine |
| II. Addition of $NaHSO_3$ | q. Cyanohydrin |
| III. Addition of alcohols | r. Bisulphite addition compounds |
| IV. Addition of ammonia | s. hemiacetal |

Codes

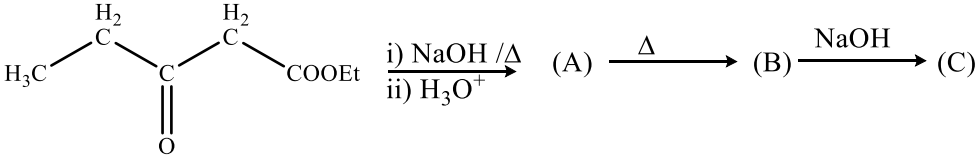
| | I | II | III | IV | | I | II | III | IV |
|---|---|---|---|---|---|---|---|---|---|
| (a.) | r | s | q | p | (b.) | q | r | s | p |
| (c.) | p | q | r | s | (d.) | r | q | p | s |

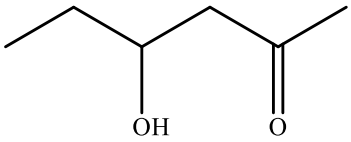
**(47.)** **Assertion**: Fehling's solution can be used to distinguish benzaldehyde from acetaldehyde.
**Reason**: The C—H bond of CHO group in benzaldehyde is stronger than C—H bond of CHO group in acetaldehyde. [Page: 369]

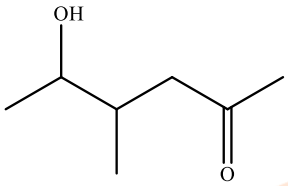
(a.) Both A and R are correct and R is correct explanation of A. (b.) Both A and R are correct but R is not correct explanation of A.

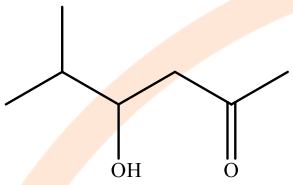
(c.) A is true but R is false. (d.) Both A and R are false.

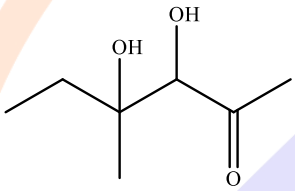
**(48.)** In the given reaction, identify compound C.



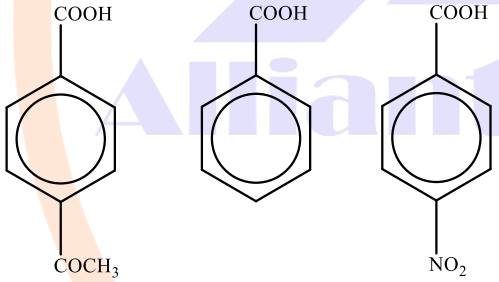
(a.) 


(b.) 


(c.) 


(d.) 


**(49.)** Consider the following compounds [Page: 380]




(I) (II) (III)

The correct order of acidity is

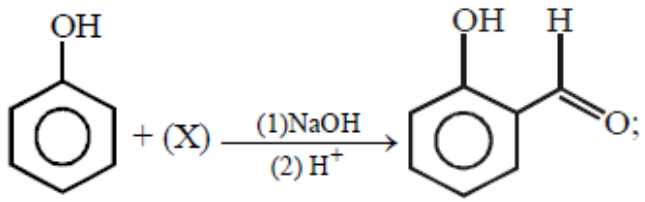
(a.) I > II > III
(b.) III > II > I
(c.) II > III > I
(d.) I > III > II

**(50.)** **Assertion**: Acetaldehyde undergoes aldol condensation with dil. NaOH.
**Reason**: Aldehydes which do not contain α– hydrogen undergo aldol condensation. [Page: 371, 372]

(a.) Both A and R are correct and R is correct explanation of A.
(b.) Both A and R are correct but R is not correct explanation of A.
(c.) A is true but R is false.
(d.) Both A and R are false.

# TOPIC WISE PRACTICE QUESTIONS

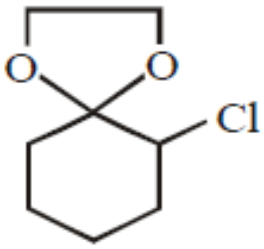
## TOPIC 1: Methods of Preparation of Carbonyl Compounds

1. Calcium acetate, on heating, gives:
   1) acetic anhydride 2) acetone 3) acetaldehyde 4) ethyl alcohol
2. Benzaldehyde can be prepared by the hydrolysis of
   1) benzal chloride 2) benzotrichloride
   3) benzyl chloride 4) benzonitrile
3. 

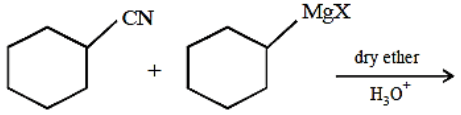
   Reactant X is:
   1) CH3Cl 2) CH2Cl2 3) CHCl3 4) CCl4
4. In the Cannizzaro reaction given below $2C_6H_5CHO \xrightarrow{OH^-} C_6H_5CH_2OH + C_6H_5COO^-$
   1) attack of OH– at the carbonyl group.
   2) transfer of hydride ion to the carbonyl group.
   3) abstraction of proton from the carboxylic acid.
   4)feprotonation of C6H5CH2OH.
5. The end product 3) in the following sequence of reactions is

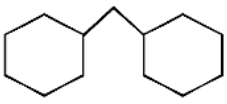
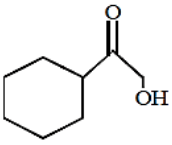
$$HC \equiv CH \xrightarrow[20\%\ H_2SO_4]{1\%\ HgSO_4} A \xrightarrow[H_2O]{CH_3MgX} B \xrightarrow{[O]} (C)$$

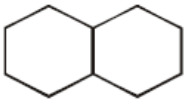
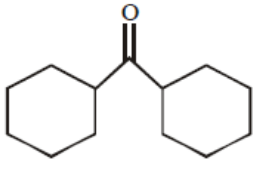
6. Acid catalysed hydrolysis of the cyclic acetal gives



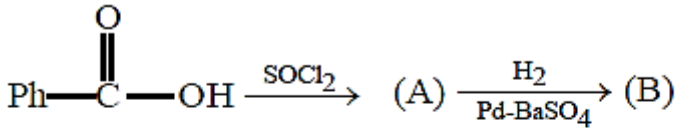

   1) ethanal and 2-chlorocyclohexanol 2) ethanol and 2-chlorocyclohexanol
   3) 1, 2-ethanediol and 2-chlorocyclohexanone 4) 1, 2-ethanediol 2-chlorocyclohexanol
7. Product of the following reaction is



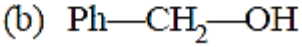
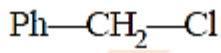
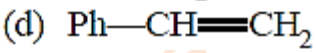

(a) 
(b) 

(c) 
(d) 

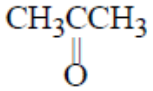
8.

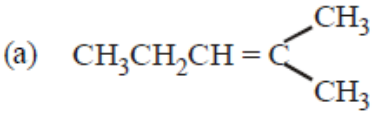
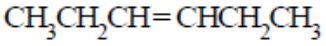
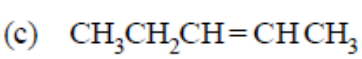
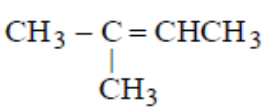


Product (B) is:

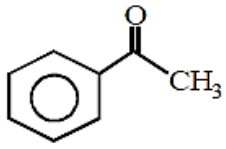
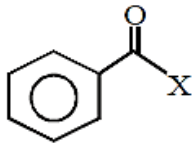
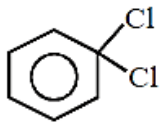
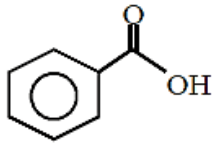
(a) 
(b) 
(c) 
(d) 

9. Which alkene on ozonolysis gives $CH_3CH_2CHO$ and

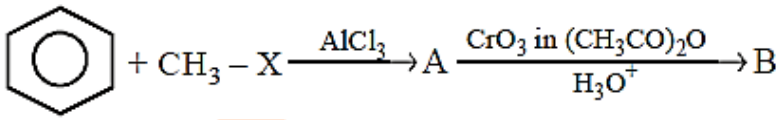


(a) 
(b) 
(c) 
(d) 

10. Benzaldehyde is obtained from Rosenmund's reduction of

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

11. Find out B in the given reactions



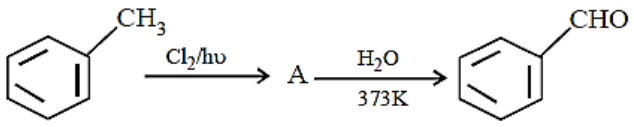
1) acetophenone 2) benzaldehyde 3) cyclohexyl carbaldehyde 4) benzoic acid

12. Which aldehyde cannot be obtained by Rosenmund's reaction?
1) $CH_3CHO$ 2) HCHO 3) $CH_3CH_2CHO$ 4) All of these

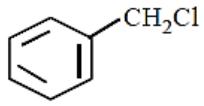
13. The conversion $PhCN \rightarrow PhCOCH_3$ , can be achieved most conveniently by reaction with
1) $CH_3MgBr$ followed by hydrolysis 2) $I_2$ – NaOH, $CH_3I$
3) Dil. $H_2SO_4$ followed by reaction with $CH_2N_2$ 4) $LiAlH_4$ followed by reaction with $CH_3I$

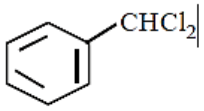
14. Which of the following is used to prepare ketone in good yield from acyl chloride ?
1) R-MgX 2) $R_2Cd$ 3) CO + HCl 4) $CrO_3$

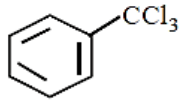
15. In the given reaction

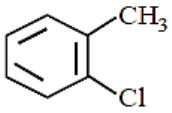



A is

(a) 

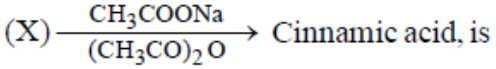

(b) 

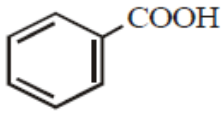

(c) 

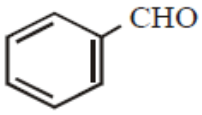

(d) 

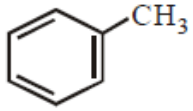

## TOPIC 2: Properties of Carbonyl Compounds

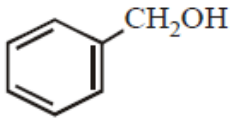
16. The reactant (X) in the reaction



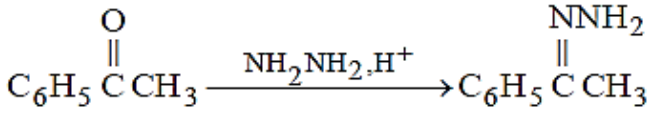

(a) 

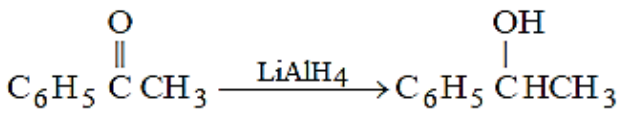

(b) 


(c) 


(d) 


17. Which of the following is an example of nucleophilic addition?

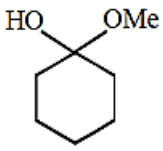
(a) 

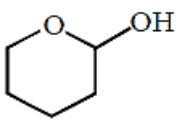

(b) 

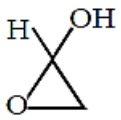

3) Both 1) & 2) 4) None of the two

18. Which of the following acts as a nucleophile in the Cannizzaro reaction involving benzaldehyde?
(i) $OH^-$ (ii) $C_6H_4CHO^-$ (iii) $C_6H_5CH(OH)O^-$ (iv) $H_2O$
1) (i) and (iv) 2) (i) and (ii) 3) (i) and (iii) 4) only (i)

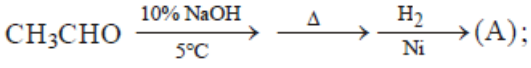
19. Which of following compound is hemiacetal?

(a) 


(b) 


(c) 


(d) all of these

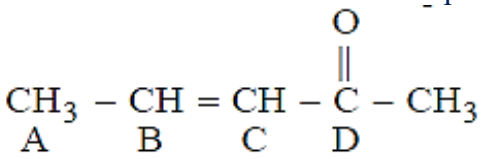
20. 


Product (A) of the reaction is
1) propanol 2) ethanol 3) butanol 4) pentanol

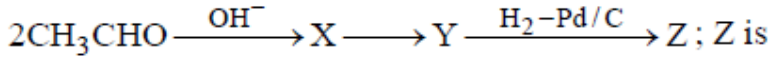
21. The presence of unsaturation in organic compounds can be tested with:

1) Schiff's reagent 2) Tollens' reagent 3) Fehling's reagent 4) Baeyer's reagent

22. Which carbon atoms are most susceptible to nucleophilic attack ?



1) A and B 2) B and C 3) B and D 4) A and D

23. 

(a) $CH_3CH=CHCH_2OH$ (b) $CH_3CH_2CH_2CH_2OH$
(c) $CH_3CH_2CH_2CHO$ (d) $CH_3CH=CHCHO$

24. $CH_3COCH_2Cl \xrightarrow{OH^-, Cl_2}$ Product P is

1) $ClCH_2COCH_2Cl$ 2) $CH_3COCHCl_2$ 3) both a and b 4) $ClCH_2COOH + CH_3Cl$

25. Formalin is an aqueous solution of

1) fluorescein 2) formic acid 3) formaldehyde 4) furfuraldehyde

26. $(CH_3)_2C = CHCOCH_3$ can be oxidized to $(CH_3)_2C = CHCOOH$ by

1) Chromic acid 2) NaOI 3) Cu at 300 °C 4) KMnO4.

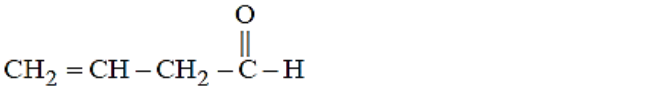
27. Aldehydes and ketones will not form crystalline derivatives with

1) sodium bisulphite 2) phenylhydrazine
3) semicarbazide hydrochloride 4) dihydrogen sodium phosphate.

28. Which of the following compound will undergo self aldol condensation in the presence of cold dilute alkali ?

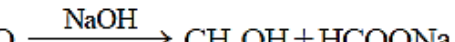
1) $CH_2 = CH\text{-}CHO$ 2) $CH \equiv C - CHO$ 3) $C_6H_5CHO$ 4) $CH_3CH_2CHO$

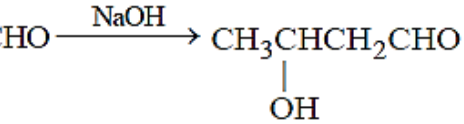
29. Appropriate reducing agent for the following conversion is–

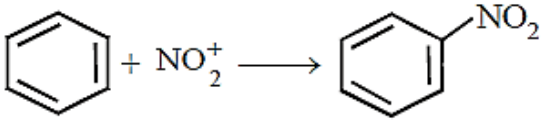


(a) $LiAlH_4/H_2O$ (b) $NaBH_4/H_2O$
(c) $Na + C_2H_5OH$ (d) $B_2H_6/H^+$

30. Which of the following is disproportionation reaction?

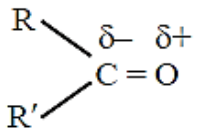
(a) 

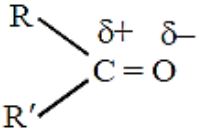
(b) 

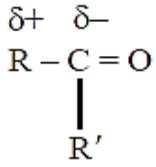
(c) 

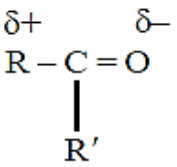
(d) Both (a) & (b)

31. Which of the following is correct for carbonyl compounds?

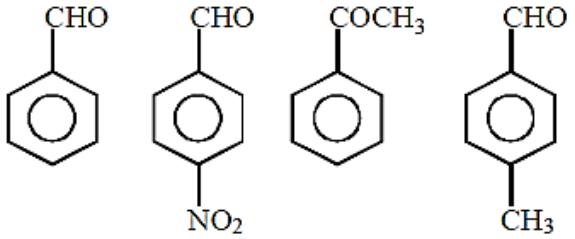
(a) 

(b) 

(c) 

(d) 

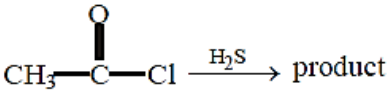
32. Arrange the following carbonyl compounds in decreasing order of their reactivity in nucleophilic addition reaction.

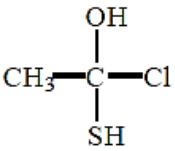


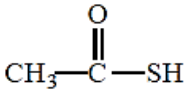
(i) (ii) (iii) (iv)

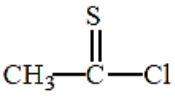
(a) (ii) > (iii) > (i) > (iv) (b) (ii) > (i) > (iv) > (iii)
(c) (iii) > (ii) > (i) > (iv) (d) (iii) > (i) > (iv) > (ii)

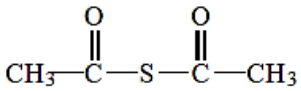
33. Which is the major product of the following reaction?



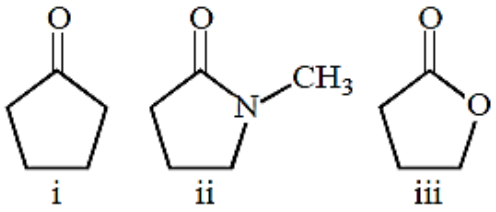
(a) 

(b) 

(c) 

(d) 

34. Arrange the following compounds in order of their reactivity toward $LiAlH_4$.

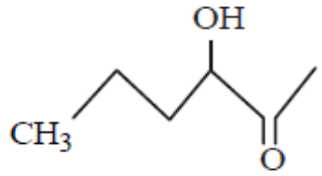


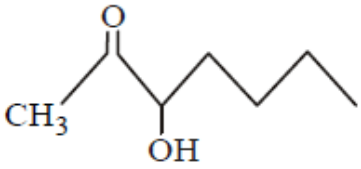
i ii iii

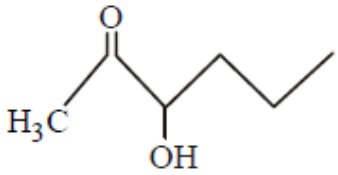
(a) i<ii<iii (b) i<iii<ii (c) ii<i<iii (d) ii<iii<i

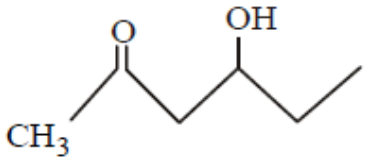
35. An aldehyde group can be present
1) in between carbon chain 2) at any position in carbon atom
3) only at the end of carbon chain 4) at the second carbon atom of the carbon chain

36. Which one of the following compounds will be most readily dehydrated?

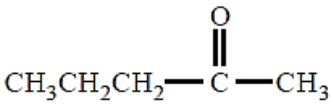
(a) 

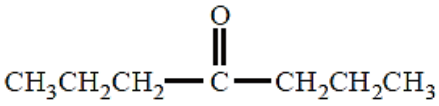
(b) 

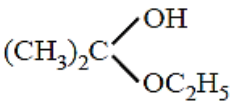
(c) 

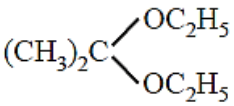
(d) 

37. Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is :

(a) 

(b) 

(c) 

(d) 

38. Consider the reaction :

$RCHO + NH_2NH_2 \rightarrow RCH = N - NH_2$

What sort of reaction is it ?

1) Electrophilic addition – elimination reaction 2) Free radical addition – elimination reaction
3) Electrophilic substitution – elimination reaction 4) Nucleophilic addition – elimination reaction

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

(i) Acetophenone (ii) Acetamide (iii) Methyl acetate (iv) 2-Hydroxypropane

1) (i), (ii) and (iii) 2) (i) and (iv) 3) (ii) and (iv) 4) (i), (iii) and (iv)

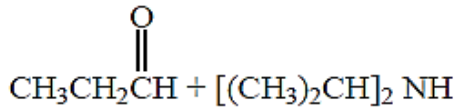
40. The order of stability of the following tautomeric compounds is :

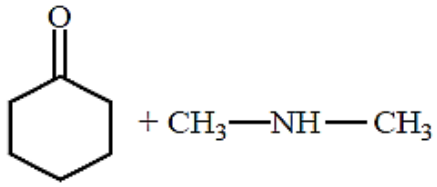
1) III > II > I 2) II > I > III 3) II > III > I 4) I > II > III

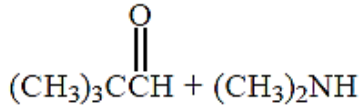
41. Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is

1) a grignard reagent 2) hydrazine in presence of feebly acidic solution
3) hydrocyanic acid 4) sodium hydrogen sulphite

42. Which of the following pairs of reactants is most effective in forming an enamine?

(a) 

(b) 

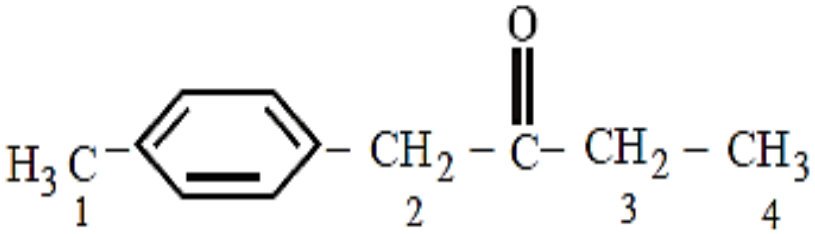
(c) 

4) none of these form an enamine

43. Less reactivity of ketone is due to
1) + I inductive effect decreases positive charge on carbonyl carbon atom
2) steric effect of two bulky alkyl groups
3) *sp*2 hybridised carbon atom of carbonyl carbon atom
4) Both (1) and (2)

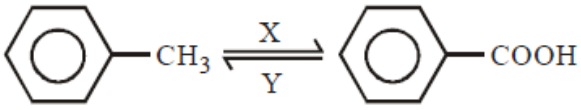
44. Which of the following statement is false?
1) Cannizzaro reaction is given by aldehydes in presence of alkali
2) Aldol condensation is given by aldehydes in presence of alkali
3) Aldol condensation is given by aldehydes and ketones in presence of acids
4) None of the above

45. The most acidic hydrogen for the following compound



1) 2 2) 1 3) 4 4) 3

## TOPIC 3: Preparation and Properties of Carboxylic Acids

46. 

In the above sequence of reaction X and Y are respectively
1) $H_2$/Pt ; $Br_2$ 2) $KMnO_4$; $H_2$/Pt 3) $KMnO_4$ (aq); HI/P 4) $NH_2 - NH_2$/KOH, HI/P

47. Hydrolysis of an ester may be achived under acidic as well as basic conditions. Pick up the correct statement regarding this.
1) Acidic hydrolysis is faster than alkaline hydrolysis.
2) Alkaline hydrolysis is faster than acidic hydrolysis.
3) Both occur at the same rate.
4) In both, the first step is protonation of the —OH part of the —COOH group.

48. When propionic acid is treated with aqueous sodium bicarbonate, $CO_2$ is liberated. The 'C' of $CO_2$ comes from
1) methyl group 2) carboxylic acid group 3) methylene group 4) bicarbonate

49. Formic acid is obtained when
1) calcium acetate is heated with conc. $H_2SO_4$
2) calcium formate is heated with calcium acetate
3) glycerol is heated with oxalic acid at 373 K
4) acetaldehyde is oxidised with $K_2Cr_2O_7$ and $H_2SO_4$.

50. An ester is boiled with KOH. The product is cooled and acidified with concentrated HCl. A white crystalline acid separates. The ester is
1) methyl acetate 2) ethyl acetate 3) ethyl formate 4) ethyl benzoate

51. The cyanohydrin of a compound on hydrolysis gives an optically active a-hydroxy acid. The compound is
1) diethyl ketone 2) formaldehyde 3) acetaldehyde 4) acetone

52. $CH_3CH_2COOH \xrightarrow[\text{red P}]{Cl_2} A \xrightarrow{\text{alc. KOH}} B$. What is $B$?
(a) $CH_3CH_2COCl$ (b) $CH_3CH_2CHO$
(c) $CH_2{=}CHCOOH$ (d) $ClCH_2CH_2COOH$

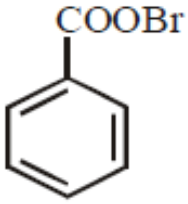
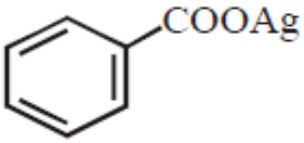
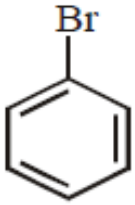
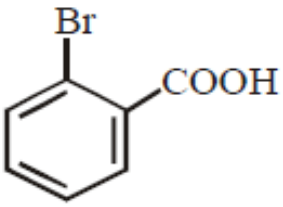
53. Acetic anhydride reacts with diethyl ether in presence of anhydrous $AlCl_3$ to give :
1) $CH_3CH_2COOH$ 2) $CH_3CH_2COOC_2H_5$ 3) $CH_3COOCH_3$ 4) $CH_3COOC_2H_5$

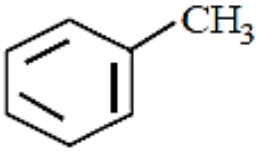
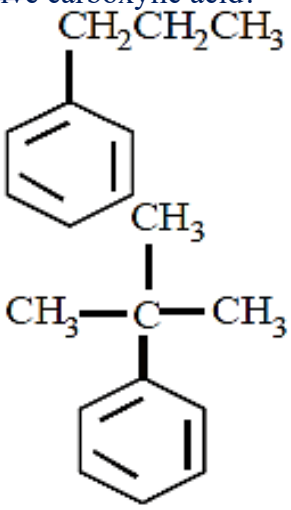
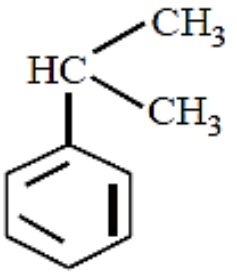
54. $CH_3COOH \xrightarrow{A} CH_3COCl$. What is A?
1) $PCl_5$ 2) $Cl_2$ 3)HCl 4) $COCl_2$

55. The compound not soluble in acetic acid is :
1) $CaCO_3$ 2) CaO 3) $CaC_2O_4$ 4) $Ca(OH)_2$

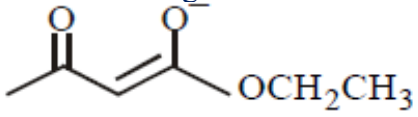
56. In the following reaction
$RCH_2COOH \xrightarrow{Br_2/P} X \xrightarrow{\text{excess } NH_3} Y$
The major compounds X and Y are
1) $RCH(Br)CONH_2$ ; $RCH(NH_2)COOH$ 2) $RCH(Br)COOH$ ; $RCH(NH_2)COOH$
3) $RCH_2COBr$ ; $RCH_2COONH_4$ 4) $RCH(Br)COOH$ ; $RCH_2CONH_2$

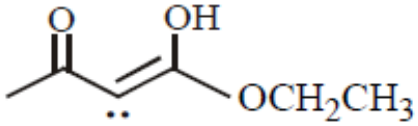
57. At high temperature iodoform reaction is given by –
1) $CH_3COOCH_3$ 2) $CH_3COOC_2H_5$ 3) $C_6H_5COOCH_3$ 4) $CH_3COOC_6H_5$

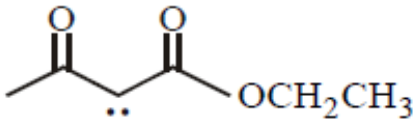
58. Silver benzoate will react with bromine in $CCl_4$ to form :
(a) 
(b) 
(c) 
(d) 

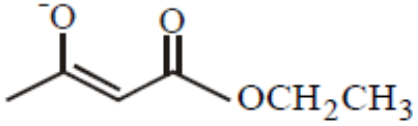
59. Which of the following can not be oxidised to give carboxylic acid?
(a) 
(b) 
(c) 
(d) 

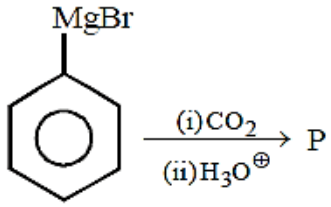
60. Which one of the following is not resonance form of the enolate ion formed from aceto acetic ester ?

(a) 

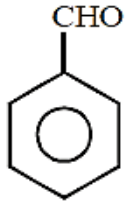
(b) 

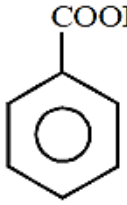
(c) 

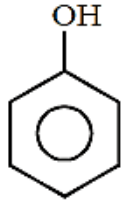
(d) 

61. 

In the above reaction product 'P' is

(a) 

(b) 

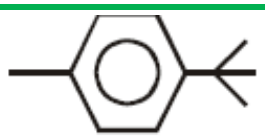
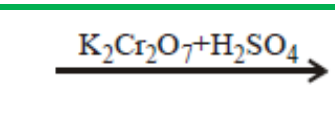
(c) 

(d) $C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5$

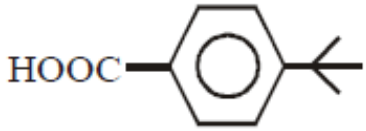
62. Select the acid(s) which cannot be prepared by Grignard reagent.

1) Acetic acid 2) Succinic acid 3) Formic acid 4) All of the above

63.

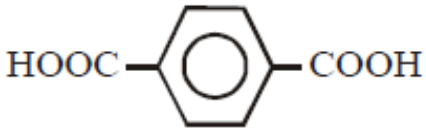




Z. Here Z is

(a) 


(b) $(CH_3)_3CCOOH$

(c) Both (a) and (b)

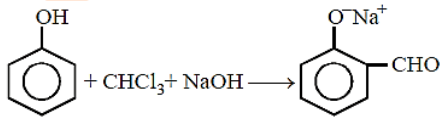
(d) 


64. Carboxylic acids are more acidic than phenol and alcohol because of
1) intermolecular hydrogen bonding 2) formation of dimers
3) highly acidic hydrogen 4) resonance stabilization of their conjugate base

65. Which of the following represents the correct order of the acidity in the given compounds?
1) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$
2) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$
3) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$
4) $CH_3COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$

## NEET PREVIOUS YEARS QUESTIONS

1. In the reaction **[2018]**



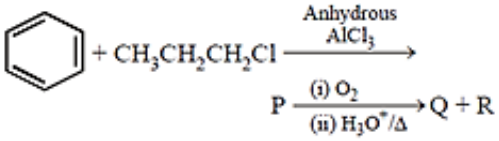

The electrophile involved is

1) Dichloromethyl cation 2) Formyl cation $\left(\overset{\oplus}{C}HO\right)$

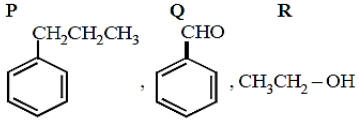
3) Dichlorocarbene $\left(:CCl_2\right)$ 4) Dichloromethyl anion $\left(\overset{\ominus}{C}HCl_2\right)$

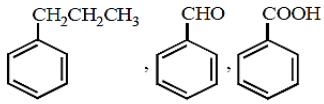
2. Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their **[2018]**
1) Formation of intramolecular H-bonding 2) Formation of carboxylate ion
3) Formation of intermolecular H-bonding
4) More extensive association of carboxylic acid via van der Waals force of attraction

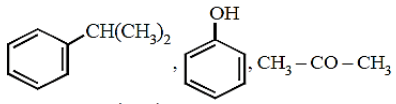
3. Identify the major products P, Q and R in the following sequence of reactions: **[2018]**

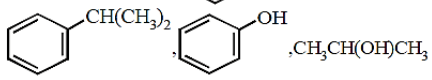


P Q R

(a) 

(b) 

(c) 

(d) 

4. Predict the correct intermediate and product in the following reaction: **[2017]**

$$H_3C-C\equiv CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} \underset{(A)}{\text{Intermediate}} \rightarrow \underset{(B)}{\text{product}}$$

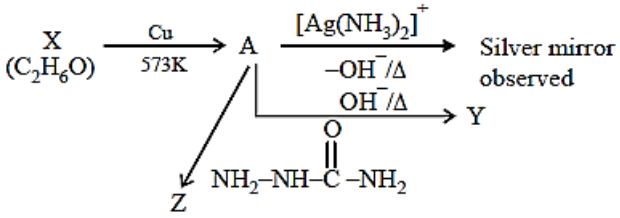
(a) A: $H_3C-\underset{\underset{OH}{|}}{C}=CH$ B: $H_3C-\underset{\underset{SO_4}{|}}{C}=CH_2$

(b) A: $H_3C-\underset{\underset{O}{\|}}{C}=CH_3$ B: $H_3C-C\equiv CH$

(c) A: $H_3C-\underset{\underset{OH}{|}}{C}=CH_2$ B: $H_3C-\underset{\underset{O}{\|}}{C}=CH_3$

(d) A: $H_3C-\underset{\underset{SO_4}{|}}{C}=CH_2$ B: $H_3C-\underset{\underset{O}{\|}}{C}-CH_3$

5. Consider the reactions: **[2017]**




Identify A, X, Y and Z

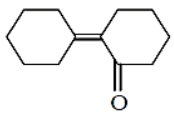
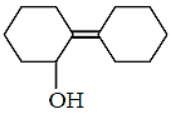
1) A-Methoxymethane, X-Ethanol, Y-Ethanoic acid, Z-Semicarbazide.

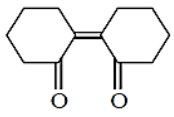
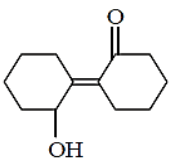
2) A-Ethanal, X-Ethanol, Y-But-2-enal, Z-Semicarbazone

3) A-Ethanol, X-Acetaldehyde, Y-Butanone, Z-Hydrazone

4) A-Methoxymethane, X-Ethanoic acid, Y-Acetate ion, Z-hydrazine.

6. Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating? **[2017]**

(a)  (b) 

(c)  (d) 

7. The correct statement regarding a carbonyl compound with a hydrogen atom on its alphacarbon, is: **[2016]**

1) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol.

2) a carbonyl compound with a hydrgen atom on its alphacarbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration.

3) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation.

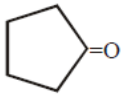
4) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as ketoenol tautomerism.

8. The product formed by the reaction of an aldehyde with a primary amine is **[2016]**

1) Schiff base 2) Ketone 3) Carboxylic acid 4) Aromatic acid

9. 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 :- **[2015]**

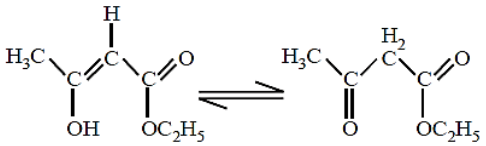
1) 2-pentanone 2) 3-pentanone 3) *n*-amyl alcohol 4) pentanal

10. Treatment of cyclopentanone  with methyl lithium gives which of the following species? **[2015]**

1) Cyclopentanonyl cation 2) Cyclopentanonyl radical

3) Cyclopentanonyl biradical 4) Cyclopentanonyl anion

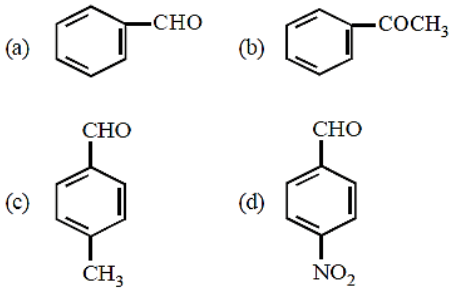
11. The enolic form of ethyl acetoacetate as below has: **[2015]**



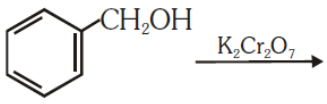
1) 16 sigma bonds and 1 pi – bond 2) 9 sigma bonds and 2 pi - bonds

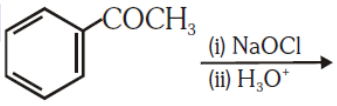
3) 9 sigma bonds and 1 pi – bond 4) 18 sigma bonds and 2 pi - bonds

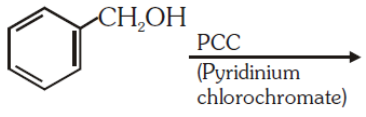
12. Which one is most reactive towards Nucleophilic addition reaction? **[2014]**

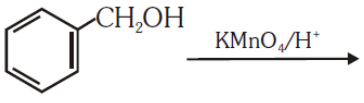


13. The reaction that does not give benzoic acid as the major product is:- **[2019-ODISSA]**

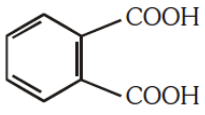
(1) 

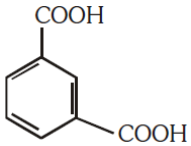
(2) 

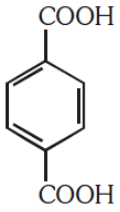
(3) 

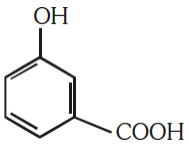
(4) 

14. Which of the following acid will form an (a) Anhydride on heating and (b) Acid imide on strong heating with ammonia? **[2019-ODISSA]**

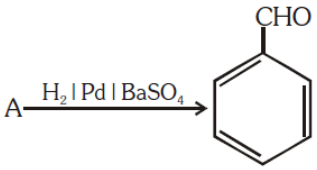
(1) 


(2) 


(3) 


(4) 


15. Identify compound (A) in the following reaction: **[2019-ODISSA]**

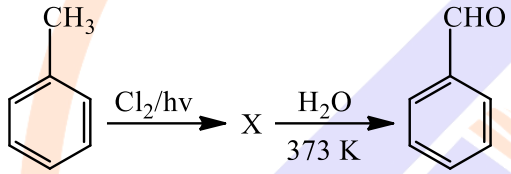


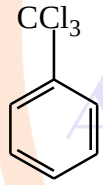

(1) Benzoyl chloride (2) Toluene (3) Acetophenone (4) Benzoic acid

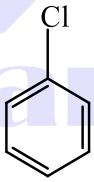
16. Reaction between benzaldehyde and acetophenone in presence of dilute NaOH is known as **[2020]**

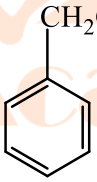
1. Cross Aldol condensation
2. Aldol condensation
3. Cannizzaro's reaction
4. Cross Cannizzaro's reaction

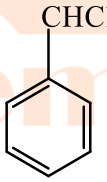
17. Identify compound X in the following sequence reactions. **[2020]**



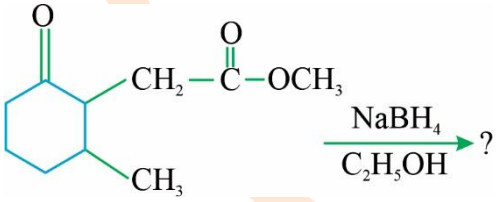

1) 

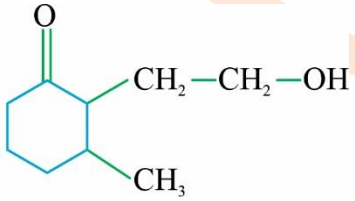

2) 

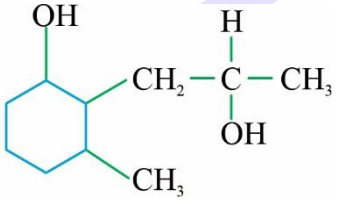

3) 

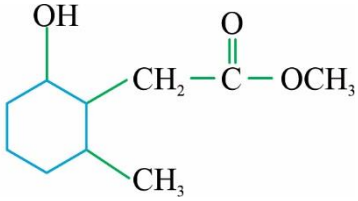

4) 

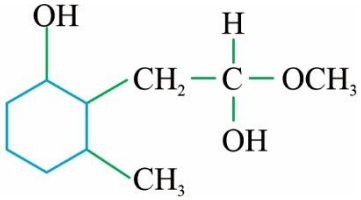

18. The product formed in the following chemical reaction is **[NEET-2021]**




(1) 


(2) 


(3) 


(4) 

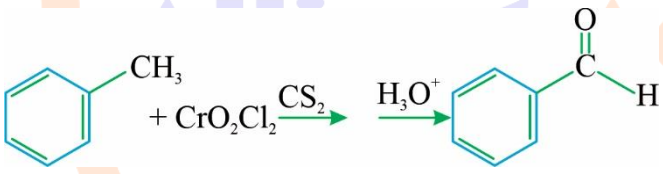

19. Match List – I with Lit – II **[NEET-2021]**

| List - I | | List - II |
|---|---|---|
| (a)  | $\xrightarrow[\text{Anhyd.}AlCl_3/\text{CuCl}]{CO, HCl}$ | (i) Hell-Volhard-Zelinsky reaction |
| (b) $R-\overset{\overset{O}{\|}}{C}-CH_3 + NaOX \longrightarrow$ | | (ii) Gattermann-Koch reaction |
| (c) $R-CH_2-OH + R'COOH$ | $\xrightarrow{\text{Conc. } H_2SO_4}$ | (iii) Haloform reaction |
| (d) $R-CH_2COOH$ | $\xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red P}}$ | (iv) Esterification |

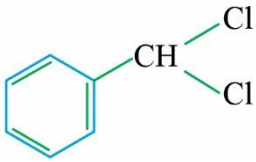
Choose the correct answer from the options given below

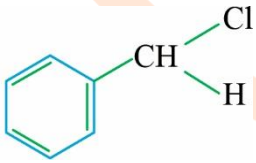
1) a-iii, b- ii, c – i, d – iv
2) a-i, b- iv, c – iii, d – ii
3)a-ii, b- iii, c- iv, d – I
4)a – iv, b- i, c – ii, d – iii

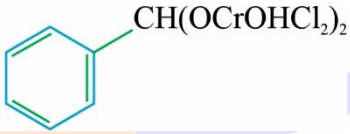
20. The intermediate compound 'X' in the following chemical reaction is: **[NEET-2021]**




(1) 


(2) 


(3) 


(4) 


21. $RMgX + CO_2 \xrightarrow[ether]{dry} Y \xrightarrow{H_3O^+} RCOOH$ What is Y in the above reaction? [NEET-2022]

1) $RCOO^-Mg^+X$ 2) $R_3CO^-\ Mg^+X$ 3) $RCOO^-X^+$ 4) $(RCOO)_2\ Mg$

22. Give below are two statements: **[NEET-2022]**

**Statement I:** The boiling points of aldehydes and ketones are higher than hydrocarbons of comparable molecular masses because of weak molecular association in aldehydes and ketones due to dipole – dipole interactions.

**Statement II:** The boiling points of aldehydes and ketones are lower than the alcohols of similar molecular masses due to the absence of H-bonding.

In the light of the above statements, choose the most appropriate answer from the options given below:

1) Both Statement I and Statement II are correct
2) Both Statement I and Statement II are incorrect
3) Statement I is correct but Statement II is incorrect
4) Statement I is incorrect but Statement II is correct.

23. Match List- I and List – II **[NEET-2022]**

| **List – I (Products formed)** | **List – II (Reaction of carbonyl compound with)** |
|---|---|
| a)Cyanohydrin | i) $NH_2OH$ |
| b) Acetal | ii) $RNH_2$ |
| c)Schiff's base | iii) alcohol |
| d)Oxime | iv) HCN |

Choose the correct answer from the options given below

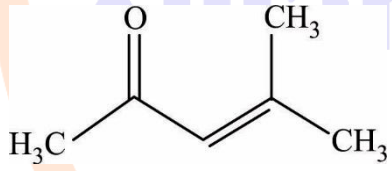
1) (a)-(iii), (b)- (iv), (c)- (ii), (d)- (i)

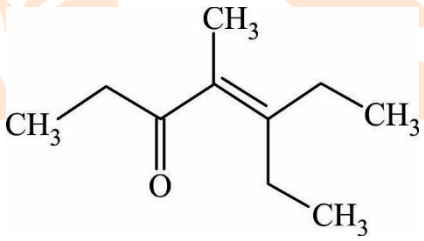
2) (a)-(ii), (b)-(iii), (c)-(iv), (d)-(i)

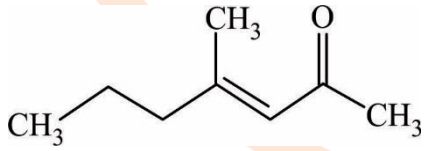
3) (a)-(i), (b)-(iii), (c)-(ii), (d)-(iv)

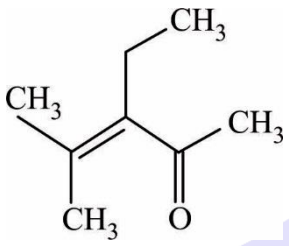
4) (a)-(iv), (b)-(iii), (c)-(ii), (d)-(i)

24. Which one of the following is not formed when acetone reacts with 2- pentanone in the presence of dilute NaOH followed by heating? **[NEET-2022]**

1) 

2) 

3) 

4) 

## NCERT LINE BY LINE QUESTIONS – ANSWERS

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

## TOPIC WISE PRACTICE QUESTIONS - ANSWERS

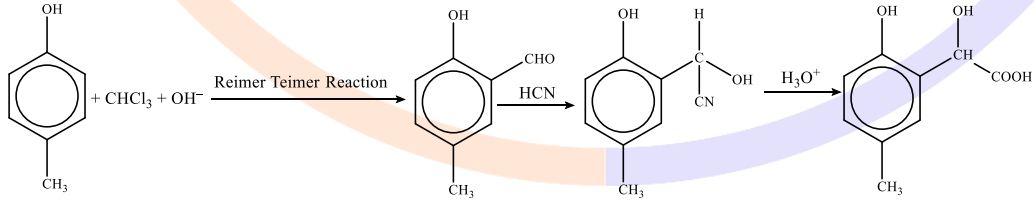
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **1)** 2 | **2)** 1 | **3)** 3 | **4)** 2 | **5)** 3 | **6)** 3 | **7)** 4 | **8)** 1 | **9)** 1 | **10)** 2 |
| **11)** 2 | **12)** 2 | **13)** 1 | **14)** 2 | **15)** 2 | **16)** 2 | **17)** 3 | **18)** 3 | **19)** 4 | **20)** 3 |
| **21)** 4 | **22)** 3 | **23)** 3 | **24)** 2 | **25)** 3 | **26)** 2 | **27)** 4 | **28)** 4 | **29)** 4 | **30)** 1 |
| **31)** 2 | **32)** 2 | **33)** 2 | **34)** 4 | **35)** 3 | **36)** 4 | **37)** 4 | **38)** 4 | **39)** 2 | **40)** 1 |
| **41)** 2 | **42)** 3 | **43)** 4 | **44)** 4 | **45)** 1 | **46)** 3 | **47)** 2 | **48)** 4 | **49)** 3 | **50)** 4 |
| **51)** 3 | **52)** 3 | **53)** 4 | **54)** 1 | **55)** 3 | **56)** 2 | **57)** 2 | **58)** 3 | **59)** 4 | **60)** 2 |
| **61)** 2 | **62)** 3 | **63)** 3 | **64)** 4 | **65)** 3 | **66)** | **67)** | **68)** | **69)** | **70)** |

## NEET PREVIOUS YEARS QUESTIONS-ANSWERS

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **1)** 3 | **2)** 3 | **3)** 3 | **4)** 3 | **5)** 2 | **6)** 1 | **7)** 4 | **8)** 1 | **9)** 2 | **10)** 4 |
| **11)** 4 | **12)** 4 | **13)** 3 | **14)** 1 | **15)** 1 | **16)** 1 | **17)** 4 | **18)** 3 | **19)** 3 | **20)** 4 |
| **21)** 1 | **22)** 1 | **23)** 4 | **24)** 2 | | | | | | |

## NCERT LINE BY LINE QUESTIONS – SOLUTIONS

**(1.)** **(c)** -OH is more activating than $-CH_3$ in o,p directing thus -CHO goes to ortho, w.r.t. -OH.




**(2.)** **(a)** The given reaction is known as decarboxylation. Carboxylic acids lose $CO_2$ to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in ratio of 3:1).

$$RCOO^{-}Na^{+} \xrightarrow[\text{Heat}]{\text{NaOH \&CaO}} R-H + Na_2CO_3$$

**(3.)** **(c)** A → s, B → p, C → q, D → r

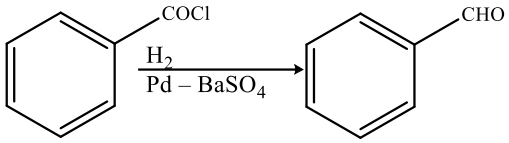
**(4.)** **(b)** I → r, II → s, III → q, IV → p

**(5.)** **(d)** Carboxylic acids are soluble in less polar organic solvents like benzene, ether, alcohol, chloroform etc.

**(6.)** **(c)** A is correct but R is incorrect.

**(7.)** **(a)** Only statement **(a)** is incorrect. Other statements are correct. Corrected statement is "the aldehydes and ketones which are not sterically hindered on reaction with $NaHSO_3$ give bisulphite addition product".

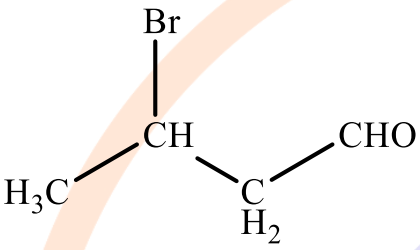
**(8.)** **(b)** Acyl chloride is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called Rosenmund reduction.




**(9.)** **(b)** Both A and R are correct but R is not the correct explanation of A.

**(10.)** **(c)** Highly branched carboxylic acids are less than unbranched acids. The +I effect of alkyl groups in branched acid increases the magnitude of negative group. Thus, –COOH group is shielded from solvent molecules and cannot be stabilized by solvation as effectively as in unbranched carboxylic acids.

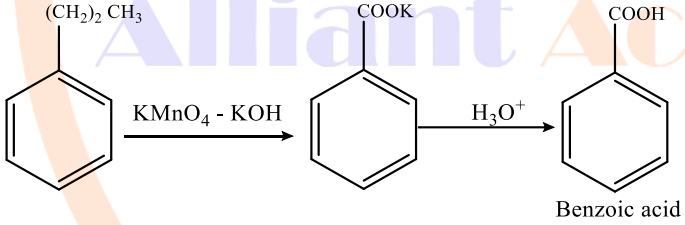
**(11.)** **(c)** The incorrect match is



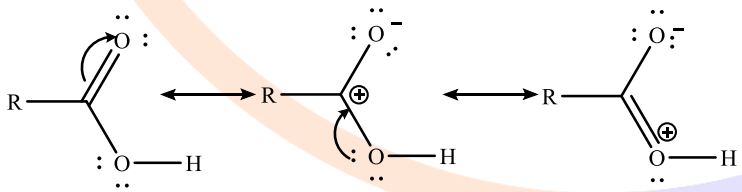

**(c)**.

**(12.)** **(c)** Only statement **(c)** is correct. Other statements are incorrect. Fehling's reagent is a mixture of two solutions, i.e. Fehling's solution A and B. Fehling's solution A is an aqueous copper sulphate and Fehling's solution B is an alkaline sodium potassium tartarate. When an aldehyde is heated with Fehling's reagent, a reddish brown precipitate is obtained.

**(13.)** **(c)** Alkyl benzene on reaction with alk. $KMnO_4$ produces aromatic carboxylic acids. The entire side chain is oxidized to the carboxyl group irrespective of length of side chain.

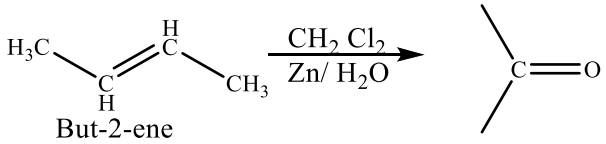


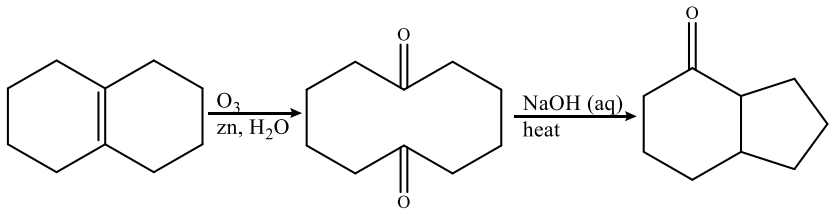

**(14.)** **(b)** The carboxylic carbon is less electrophilic than carbonyl carbon because of resonance. The possible resonance structures are as follows:




**(15.)** **(c)** Aldehydes are more reactive towards nucleophilic addition reactions than ketones because of inductive effect and steric effect. Greater the number of alkyl groups attached to the carbonyl group, greater the electron density on carbonyl carbon. Thus, it lowers the attack of nucleophile and hence, reactivity decreases. Due to steric hindrance, the attack of nucleophile on carbonyl group becomes more difficult.

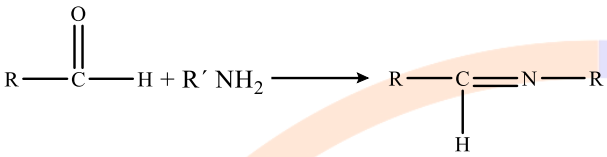
**(16.)** **(a)** But-2-ene on ozonolysis gives two molecules of acetaldehyde






**(17.)** (a)

**(18.)** **(d)** The product formed by the reaction of an aldehyde with 1° amine is Schiff's base.




Schiff's base

**(19.)** **(d)** Alkaline $KMnO_4$ does not act as a mild oxidising agent. It act as a strong oxidising agent whereas Tollen's reagent, Fehling's reagent and Benedict's reagent act as a mild oxidising agent.

**(20.)** **(b)** Molecular formula of A is $C_2Cl_3OH$. As **(a)** reduces Fehling's solution and on oxidation gives a monocarboxylic acid **(b)**, it means **(a)** must be an aldehyde ($CCl_3CHO$). This is further confirmed by the reaction

$$C_2H_5OH + Cl_2 \xrightarrow{[O]} CH_3CHO \xrightarrow{Cl_2} (CCl_3CHO)$$

**(21.)** **(c)** The given reaction is Cannizzaro reaction. Aldehydes which do not have an α-H atom undergo self-oxidation and reduction reaction on treatment with conc. alkali.


**(22.)** **(b)** In carboxylic group, the characteristic nucleophilic additions are not shown because of the resonance in carboxylate ion which resists for addition of HCN and $NaHSO_3$ as well as reactions involving replacement of carboxylic oxygen by reagents.

**(23.)** **(b)** $\beta$ – bromobutyraldehyde is the common name for the given structure. The location of the substituent in the carbon chain is indicated by Greek letters $\alpha$, $\beta$, $\gamma$, , etc.

**(24.)** **(d)** Reaction **(d)** is not possible. The corrected chemical equations is as follows:

$$C_6H_5COOCOCH_3 \xrightarrow{H_2O} C_6H_5COOH + CH_3COOH$$

Benzoic ethanoic anhydride — Benzoic acid — ethanoic acid

**(25.)** **(c)** NaOCl is the reagent 'X' present in the given reaction. It is formed inside from $Cl_2$ and NaOH. The reaction is haloform reaction.

**(26.)** **(a)** Benzoic acid on nitration gives m-nitrobenzoic acid.

**(27.)** **(a)** Methanal, ethanal and propanone are miscible with water in all proportions because they form hydrogen bond with water.

**(28.)** **(b)** Aldehydes and ketones undergo electrophilic addition reactions. The carbonyl group being polar behaves as an electrophile in the presence of nucleophile. Thus, the nucleophile readily attacks the electrophilic carbon atom of carbonyl group and gives nucleophilic addition reactions.

**(29.)** **(d)** During reaction of carboxylic acids with $NaHCO_3$, $CO_2$ evolved comes from $NaHCO_3$. Carboxylic acid is a stronger acid than carbonic acid.

**(30.)** **(d)** As B forms a shining silver mirror on warming with ammoniacal silver nitrate, B must be an aldehyde which can be obtained by the oxidation of alcohols. The complete series of

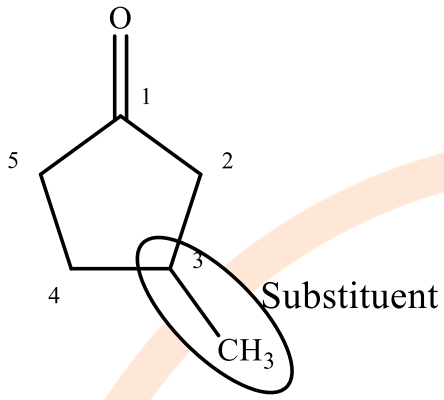
$$CH_3CH_2CH_2OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3CH_2CHO \xrightarrow{H_2NCONHNH_2} CH_3CH_2CH = NCONHNH_2$$

(A) (B) (C)

**(31.)** **(b)** 'X' in the above reaction is $Cu_2O$. Reaction involved is as follows:

$$RCHO + 2Cu^{2+} + 5OH^- \xrightarrow{\Delta} RCOO^- + \text{'X'} + 3H_2O$$

**(32.)** **(a)** The IUPAC name is 3-methylcyclopentanone. The substituents are prefixed in alphabetical order along with numerals indicating their positions in the carbon chain.




**(33.)** **(c)** Incorrect statement is **(c)**. Sodium benzoate is used as a food preservative

**(34.)** **(a)** The 'X' in reaction is $CH_3-CH(OH)=CH_2CHO$ 3-hydroxybutanal. It is an aldol reaction. Complete reaction is an follows:

$$2CH_3-CHO \xrightarrow{\text{dil. NaOH}} CH_3CH(OH)-CH_2CHO \xrightarrow[-H_2O]{\Delta} CH_3CH=CHCHO$$

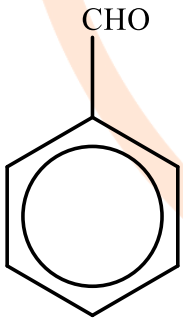
But – 2 – enal

**(35.)** **(c)** Amides on hydrolysis produces acids in the presence of $H^+$ or $OH^-$ as catalyst. Reaction involved is as follows:

$$C_6H_5CONH_2 \xrightarrow[\Delta]{H_3O^+} C_6H_5COOH + NH_3$$

Benzamide Benzoic acid

**(36.)** **(d)** Benzene carbaldehyde and benzaldehyde is the simplest aromatic aldehyde carrying the aldehyde group.




**(37.)** **(a)** The product formed are HCOOH and $CH_3COOH$. In presence of strong oxidising agent like $HNO_3$ ketones are oxidised to carboxylic acids

$$CH_3COCH_3 + 3[O] \xrightarrow{\text{Conc.}HNO_3} HCOOH + CH_3COOH$$

**(38.)** **(d)** Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate ($KMnO_4$) in neutral, acidic or alkaline media or by potassium dichromate ($K_2Cr_2O7$) and chromium trioxide ($CrO_3$) in acidic media.

**(39.)** **(c)** The carbon-oxygen double bond in carbonyls is polarised due to higher electronegativity of oxygen relative to carbon.

**(40.)** **(b)** I → r, II → p, III → s, IV → q

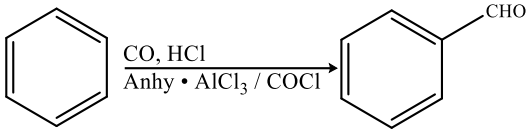
**(41.)** **(b)** $FCH_2COOH > ClCH_2COOH > C_6H_5CH_2COOH > CH_3COOH$ (acid strength) Reason

- More the electron withdrawing nature of substituent, more is the acidic strength.
- Direct attachment of $C_6H_5$ group increases acidity due to resonance and $sp^2$ hybridisation.
- Alcohols are weakly acidic than carboxylic acids.

**(42.)** **(a)** The intermediate 'Y' is $>C=N-NH_2$ . In this reaction, aldehyde or ketone is heated with hydrazine and KOH in high boiling solvent glycol to give hydrocarbon.

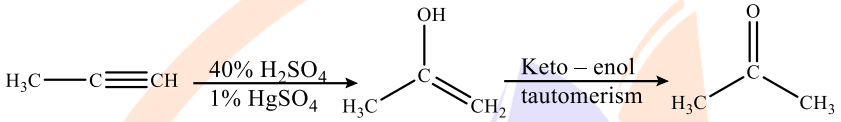
**(43.)** **(a)** Boiling points of aldehydes are higher than hydrocarbons. It is due to weak molecular association.

**(44.)** **(a)** The reagent involved in the given reaction are CO, HCl, Anhyd. $AlCl_3/CuCl$.



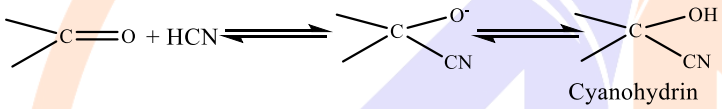

This reaction is called Gattermann–Koch reaction.

**(45.)** **(d)** Chemical reaction can be shown as: [A] is prop-1-en-2-ol, which undergo tautomerism to form acetone




**(46.)** **(b)** I → q, II → r, III → s, IV → p

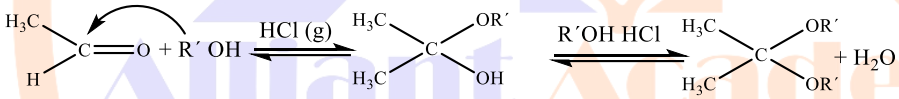
Addition of HCN




Cyanohydrin

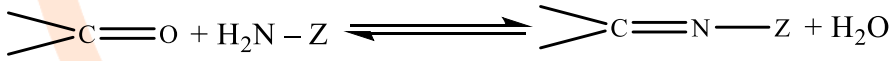
Addition of $NaHSO_3$


Addition of alcohols




Acetal

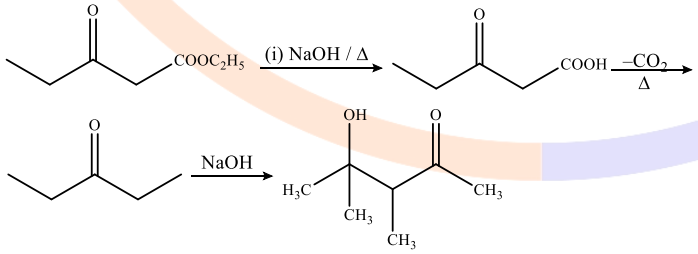
Addition of ammonia




**(47.)** **(a)** Fehling test is positive with acetaldehyde but no reaction occurs with benzaldehyde.

$CH_3CHO + Cu^{2+} + 5OH^- \longrightarrow CH_3COO^- + CH_2O + 3H_2O$

The +R effect of phenyl group increases the electron density on the carbon atom of $>C=O$ group in benzaldehyde.



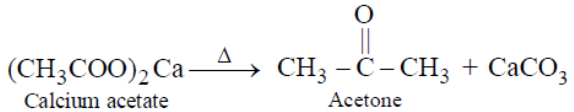

**(48.)** (c)

**(49.)** **(b)** The correct order of acidity is III > II > I. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.

**(50.)** **(c)** Ais correct but R is incorrect. Aldehydes which contain α–hydrogens undergo aldol condensation.

## TOPIC WISE PRACTICE QUESTIONS - SOLUTIONS

1. 2)



2. 1) $C_6H_5CHCl_2 \xrightarrow{H^+/H_2O} C_6H_5CHO + H_2O$
3. 3)
4. 2) Transfer of hydride ion to the carbonyl group is the slowest step of the reaction.
5. 3)

$$HC \equiv CH \xrightarrow[20\%H_2SO_4]{1\%HgSO_4} \underset{[A]}{CH_3CHO} \xrightarrow[H_2O]{CH_3MgX}$$

$$\underset{[B]}{CH_3CH(OH)CH_3} \xrightarrow{[O]} \underset{\text{Acetone [C]}}{CH_3COCH_3}$$

6. 3) Open the ring containing oxygen atoms you will get the products.
7. 4)
8. 1)

(a) $Ph-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[S_N1]{SOCl_2}$

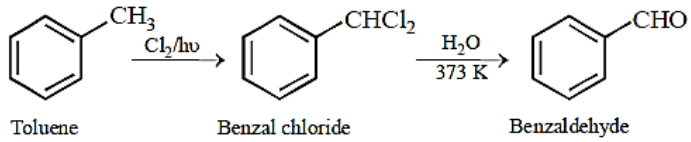
$$Ph-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[\substack{Pd\text{-}BaSO_4\\ \text{Lindlar catalyst}}]{H_2} Ph-\overset{\overset{O}{\|}}{C}-H$$

9. 1)

$$CH_3-CH_2-\underset{H}{C}=\underset{CH_3}{\overset{CH_3}{C}} \xrightarrow{O_3} CH_3-CH_2-\underset{O-O}{\overset{H\ O}{C}}-\overset{CH_3}{\underset{CH_3}{C}}$$

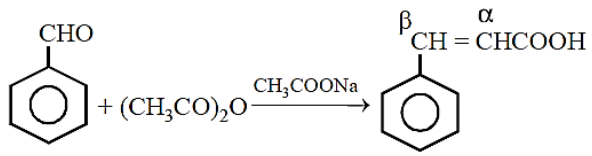
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3-CH_2-CHO \xleftarrow{(-H_2O)}$$

10. 2)
11. 2)
12. 2) Formyl chloride is unstable at room temperature.
13. (1) Alkanenitriles (other than methanenitrile) benzonitrile give ketones with Grignard reagents.
14. 2)
15. 2)




Toluene — Benzal chloride — Benzaldehyde

16. 2) Benzaldehyde forms cinnamic acid as follows.



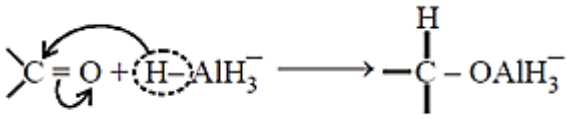

Cinnamic acid

17. 3)

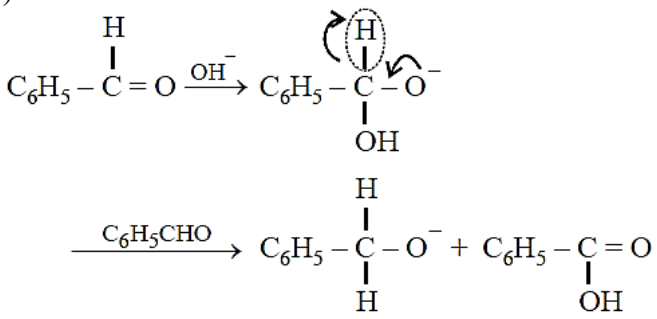
$$>C=O + H_2NNH_2 \xrightarrow{H^+} \underset{NHNH_2}{\overset{}{>C-OH}} \xrightarrow{H^+} >C=NNH_2$$

a)

b) In the reduction of carbonyl group with $LiAlH_4$ or $NaBH_4$, a hydride ion is transferred from the metal to the carbonyl carbon (nuclephilic addition)

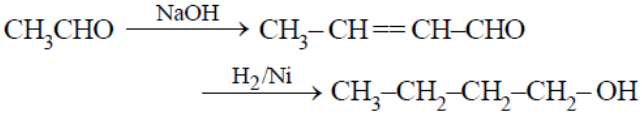


18. 3)



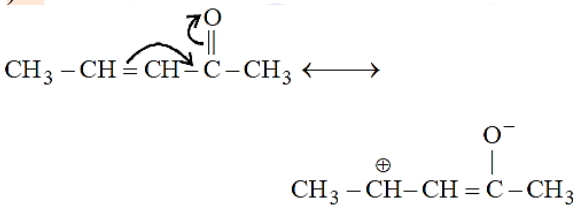
19. 4) Hemiacetal → presence of alcohol and ether on same carbon.

20. 3)

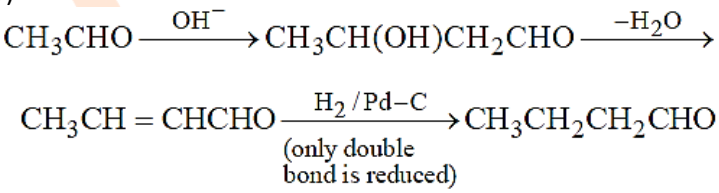


21. 4) Cold dil. alk $KMnO_4$, is Baeyer's reagent.
1) Schiff's reagent is used to test presence of Aldehydes.
2) Tollen's reagent is used to test presence of aldehydes.
3) Fehling's reagent is used to test presence of aldehyde.
4) Baeyer's reagent is cold dil. alk. $KMnO_4$ is used to test presence of unsaturation.

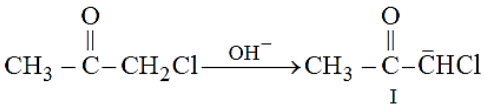
22. 3)

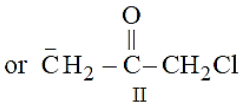


23. 3)

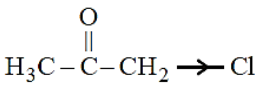


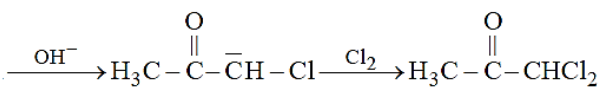
24. 2) The reaction is a part of haloform reaction.





However, – I effect of –Cl makes the H's of $CH_2Cl$ more acidic, hence I is more likely to be formed.





25. (3) Formalin is an aqueous solution (40%) of formaldehyde.

26. (2) Chromic acid and $KMnO_4$ will cleave the molecule at the site of double bond while Cu at 300°C cannot oxidise $COCH_3$ to COOH. The only reagent suitable for this conversion is NaOI or NaOH + $I_2$ (iodoform test):

$$(CH_3)_2C=CHCOCH_3 \xrightarrow{NaOI} (CH_3)_2C=CHCOOH + CHI_3$$

27. 4) Dihydrogen sodium phosphate ($NaH_2PO_4$) does not have a lone pair of electrons on the P atom. As such it cannot act as a nucleophile and hence does not react with aldehydes and ketones.

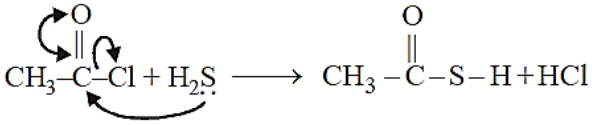
28. (4) Aldehydes which contain a a -hydrogen on a saturated carbon, i.e., $CH_3CH_2CHO$ undergo aldol condensation.

29. (4) $LiAlH_4/H_2O$, $NaBH_4/H_2O$ and $Na/C_2H_5OH$ will reduce only –CHO

30. (1) In this reaction, one molecule is oxidised and other is reduced simultaneously.

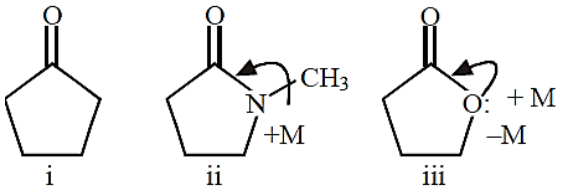
31. (2) O is more electronegative than C.

32. (2) Aldehyde will be more reactive than ketone.



33. 2)

34. 4)




This order is (ii) < (iii) < (i)

35. 3)

36. 4) The intermediate is carbocation which is destabilised by C = O group in the first three cases. In 4), 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.

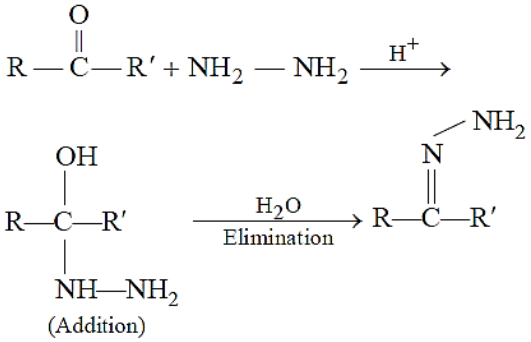
37. 4)

38. 4) $R-CH=O + H_2N-NH_2 \rightarrow R-CH=N-NH_2$ Such reactions take place in slightly acidic medium and involve nucleophilic addition of the ammonia derivative.

39. 2) It is iodoform reaction. Both give a yellow precipitate of $CHI_3$ (iodoform) with iodine and alkali.

40. 1) Enolic form predominates in compounds containing two carbonyl groups separated by a – $CH_2$ group. This is due to following two factors.
(i) Presence of conjugation which increases stability.
(ii) Formation of intramolecular hydrogen bond between enolic hydroxyl group and second carbonyl group which leads to stablisation of the molecule. Hence the correct answer is III > II > I.

41. 2)




While in all other case no elimination take place.

42. 3) 2° amine must be less sterically hindered. In option 2) and 3). 2° amine is being used but due to more reactivity of aldehyde compared to cyclohexanone. Option 3) is correct.

43. (4)

44. (4) Cannizzaro reaction is given by aldehydes having no a-hydrogen atom in the presence of conc. alkali, aldol condensation is given by aldehydes and ketones having at least one a-atom in presence of alkali or in presence of acids

45. (1) Hydrogen atoms attached $C_2$ are most acidic due to presence of electrons withdrawing groups on both sides.

46. 3) $KMnO_4$ converts $-CH_3$ group of toluene into $-COOH$ while HI reduces $-COOH$ group into $-CH_3$ group.

47. 2) Alkaline hydrolysis is irreversible because here $RCOO^-$ is isolated ; moreover the product $RCOO^-$ stabilizes itself due to resonance.

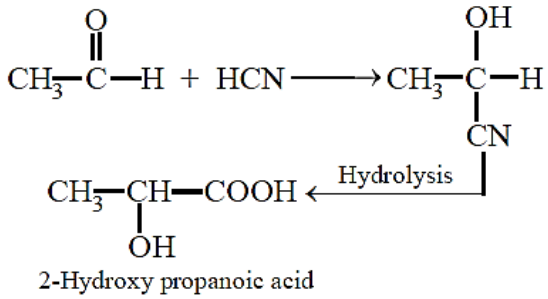
$$C_2H_5COOH + NaH\overset{14}{C}O_3 \rightarrow C_2H_5COONa + H_2O + \overset{14}{C}O_2$$

48. 4)

49. 3)

50. 4)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

51. 3)




2-Hydroxy propanoic acid

(As it has a chiral C-atom thus it is optically active)

52. 3) $CH_3CH_2COOH \xrightarrow[\text{red P}]{Cl_2} CH_3CHClCOOH$

53. 4) $\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} \xrightarrow{AlCl_3} \underset{\text{Ethyl acetate}}{2CH_3COOC_2H_5}$

54. 1) $CH_3COOH \xrightarrow{PCl_5} CH_3COCl + HCl$

$\therefore$ A is $PCl_5$ . It can also be $SOCl_2$

55. 3) $CaC_2O_4$ is the only compound of Ca which is not soluble in acetic acid. This property of Ca is used in inorganic salt analysis.

56. 2) $X = R - \underset{Br}{CH} - COOH; Y = R - \underset{NH_2}{CH}COOH$

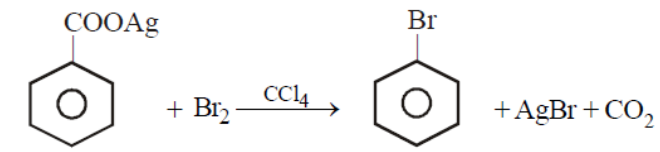
57. 2) At high temperature, esters containing $\beta$-hydrogen atom undergo pyrolysis to give ketene and alcohol.

$$CH_3 - \underset{O}{C} - OC_2H_5 \xrightarrow[\text{Pyrolysis}]{\Delta} CH_2 = \underset{O}{C} + C_2H_5OH$$

$$\underset{O}{C} \xrightarrow{I_2 + NaOH} CHI_3 + HCOONa$$

$$\xrightarrow[-HCl]{alc.KOH} \underset{\text{Acrylic acid}}{CH_2 = CHCOOH}$$

58. 3) This is Hunsdiecker's reaction.

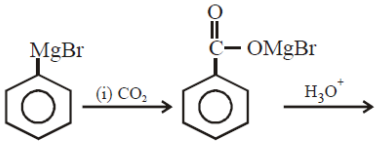


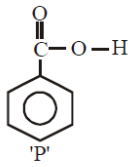

Silver benzoate Bromobenzene

59. (4) Primary and secondary alkyl groups are oxidised to give carboxylic acid, while tertiary alkyl group remains unaffected.

60. (2) The structure 2) differs in the position of H hence not resonating structure.

61. (2) Grignard reagent forms addition product with bubbled carbon dioxide which on hydrolysis with HCl yields benzoic acid.




+ Mg(OH)Br

62. (3) Formic acid cannot be prepared by Grignard reagent.

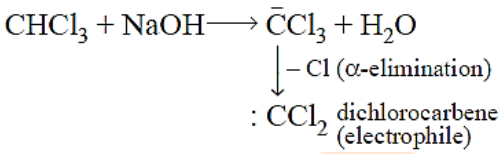
63. (3) An alkyl group attached to benzene ring can be oxidised only when it contains at least one a-hydrogen atom. Thus here $–CH_3$ group is oxidised and $Me_3C–$ group not. However, $Me_3C–$ group may cause oxidation of the benzene ring to –COOH.

64. (4) In carboxylates (conjugate base of carboxylic acids), resonance is more significant because the two resonating structures are similar, while in phenoxide, the resonating structures are not equivalent, alkoxide ions do not show resonance.

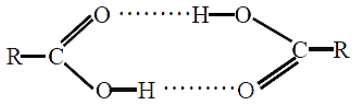
65. (3) Electron withdrawing substituent (like halogen, $—NO_2$, $C_6H_5$ etc.) would disperse the negative charge and hence stabilise the carboxylate ion and thus increases acidity of the parent acid. On the other hand, electron-releasing substituents would intensify the negative charge, destabilise the carboxylate ion and thus decrease acidity of the parent acid. Electronegativity decreases in order
F > Cl > Br
and hence –I effect also decreases in the same order,
therefore the correct option is
[$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$]

## NEET PREVIOUS YEARS QUESTIONS-EXPLANATIONS

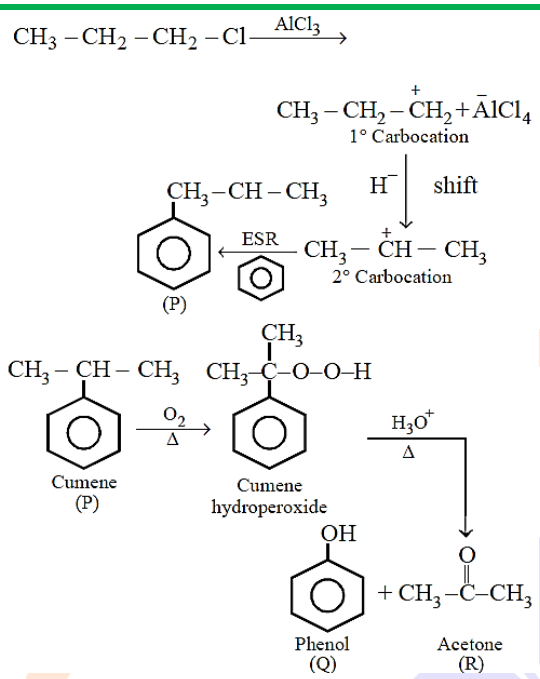
1. 3)



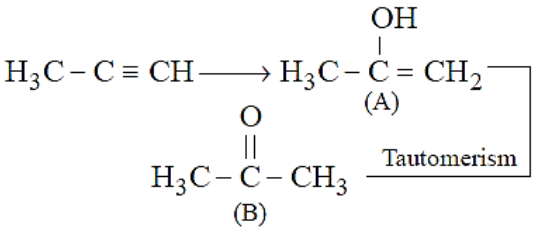

2. 3) Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. This is due to more extensive association through intermolecular H-bonding.



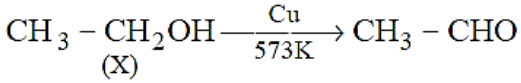

3. 3) Mechanism :

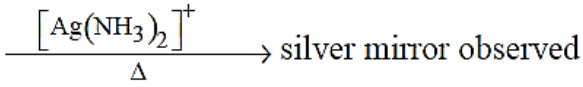


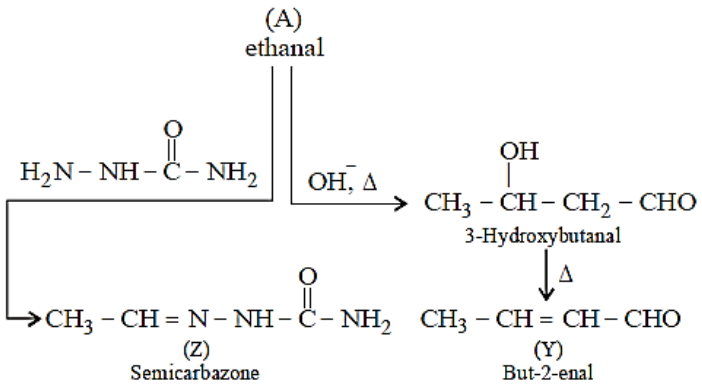

4. 3) Hydration of alkynes give ketones.

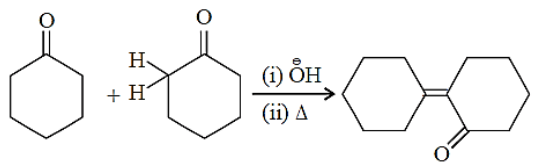



5. 2) Since 'A' gives positive silver mirror test therefore, it must be an aldehyde of a-Hydroxyketone. Also, reaction with $OH^-$ i.e., aldol condensation (by assuming alkali to be dilute) indicates that A is aldehyde as aldol reaction of ketones is reversible and carried out in special apparatus. It indicates that A is an aldehyde



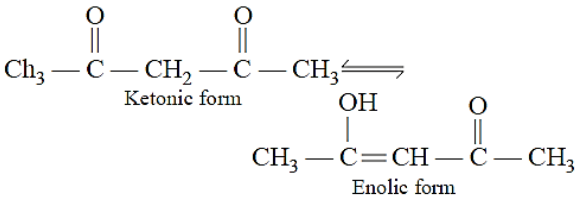



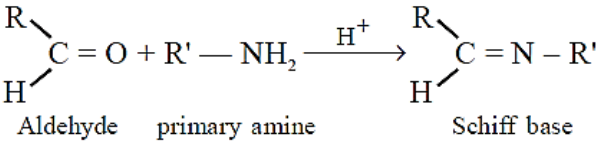




6. 1)

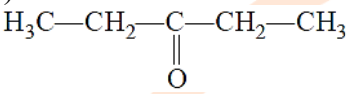
7. 4) Keto-enol tautomerism is possible only in those aldehydes and ketones which have atleast one ahydrogen atom, which can convert the ketonic group to the enolic group. e.g.

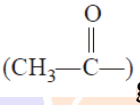


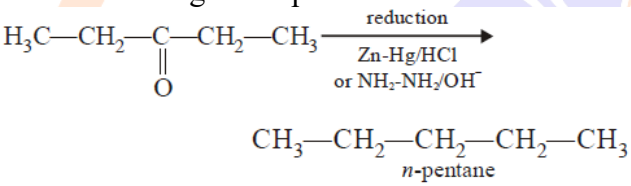

8. 1) Schiff base is formed when 1° amine reacts with aldehydes.



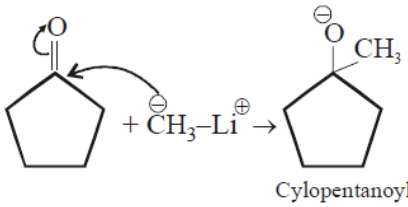

9. 2)



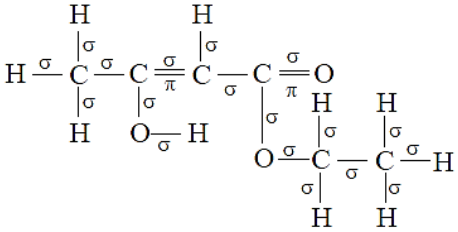
does not give iodoform test due to absence of  group. It also does not give Tollen's test. On reduction it gives n-pentane



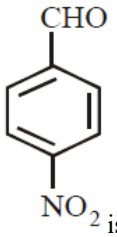

10. 4)




11. 4) Enolic form of ethyl acetoacetate has 18 sigma and 2 pi-bonds as shown below:

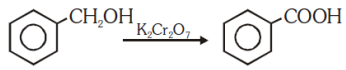


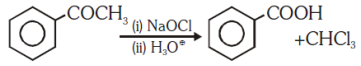
12. (4) Any substituent in the carbonyl compound that increases the positive charge on the carbonyl carbon will increase reactivity towards nucleophilic addition. $-NO_2$ shows – M effect hence

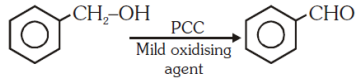


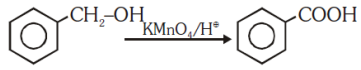
$NO_2$ is most reactive towards nucleophilic addition reaction.

13. 3)

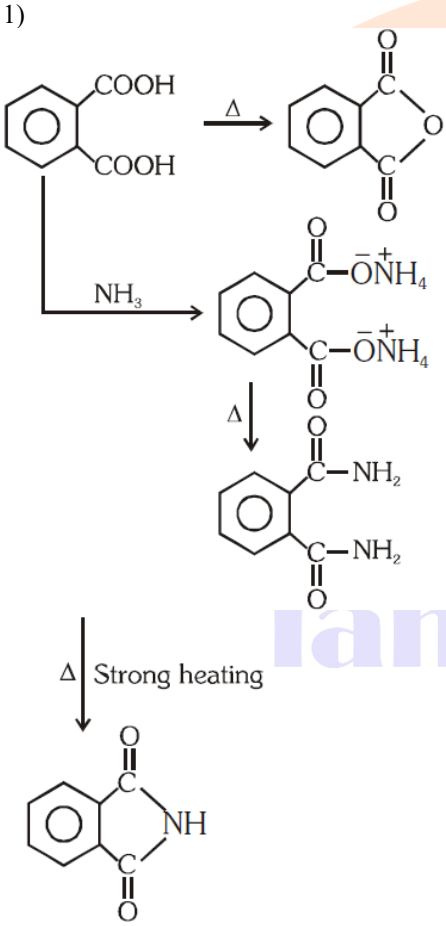
(1) 


(2) 

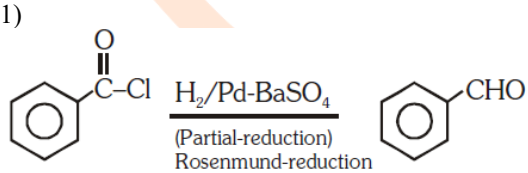

(3) 

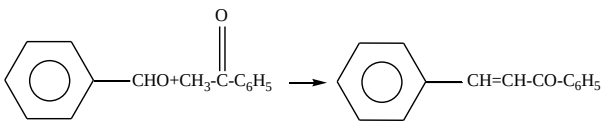

(4) 


14. 1)



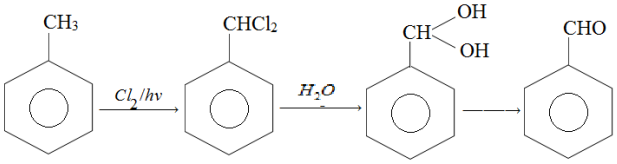

15. 1)



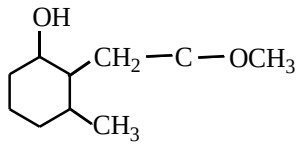

16. 


This is example for cross aldol condensation

17. 4)

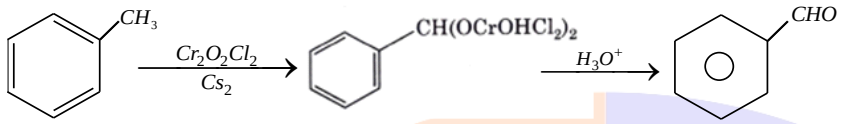



18. 3)




19. 3)a-iv, b-1 c-ii, d-iii

20. 4)




**21.** $R-MgX+\underset{\underset{O}{\|}}{C}\rightarrow R-\underset{\underset{O}{\|}}{\overset{\overset{MgX}{|}}{\overset{O}{\|}}{C}} \xrightarrow{H_3O^+} RCOOH$

**22.** Both Statements are correct

**23.:** (a)-(iv), (b)-(iii), (c)-(ii), (d)-(i)

**24.**