

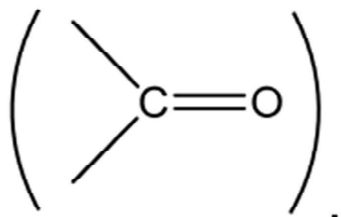
CHEMISTRY



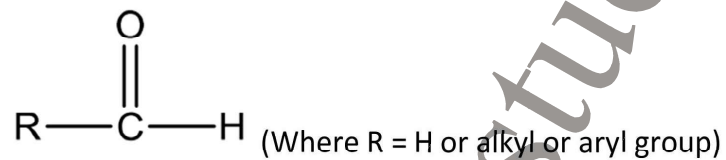
ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Introduction

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



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



- Ketones have carbonyl group bonded to two carbon atoms.

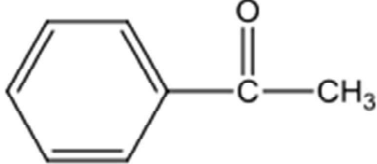
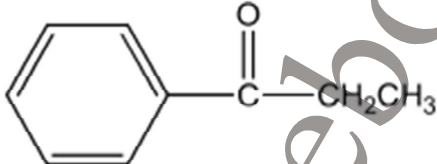


Nomenclature of Aldehydes and Ketones

Aldehydes

Structure	Common name	IUPAC name
CH_3CHO	Acetaldehyde	Ethanal
$\begin{array}{c} \text{H} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CHO} \\ \\ \text{CH}_3 \end{array}$	Isobutyraldehyde	2-Methylpropanal
$\text{H}_2\text{C}=\text{CHCHO}$	Acrolein	Prop-2-enal
$\begin{array}{c} \text{CH}_2\text{CHO} \\ \\ \text{C}_6\text{H}_5 \end{array}$	Phenylacetaldehyde	2-Phenylethanal
$\text{CH}_3\text{CH}=\text{CHCHO}$	Crotonaldehyde	But-2-enal

Ketones

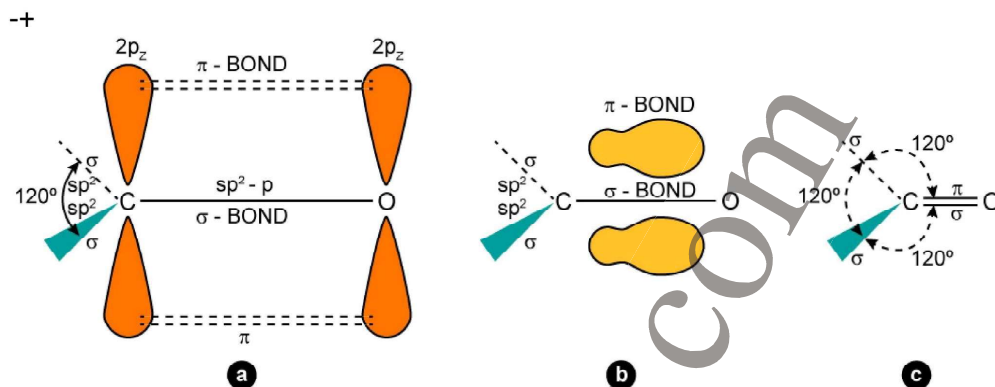
Structure	Common name	IUPAC name
$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	Dimethyl ketone or Acetone	Propanone
$\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_3$	Diethyl ketone	Pentan-3-one
	Methyl phenyl ketone	1-Phenylethan-1-one
$\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C}=\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3 \\ \diagup \quad \\ \text{H}_3\text{C} \quad \text{H} \end{array}$	Mesityl oxide	4-Methylpent-3-en-one
$\begin{array}{c} \text{O} \quad \text{H} \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{H} \end{array}$	Acetylacetone	Pentane-2,4-dione
$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	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 π -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 π -cloud lies above and below the plane.

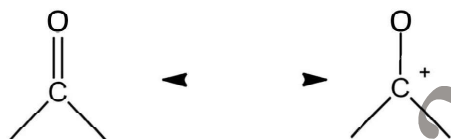
- The bond angle is 120° with expected trigonal coplanar structure.
-



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 neutral

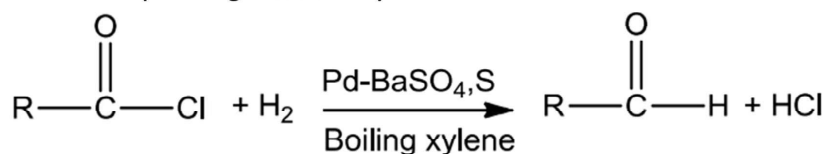
(A) and a dipolar (B) structures given below.



Preparation of Aldehydes

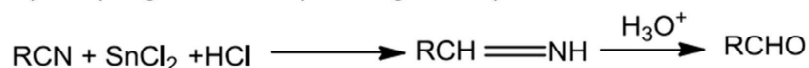
➤ Rosenmund Reduction

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

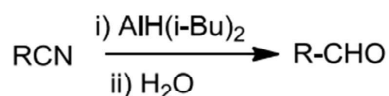


➤ Stephen Reaction

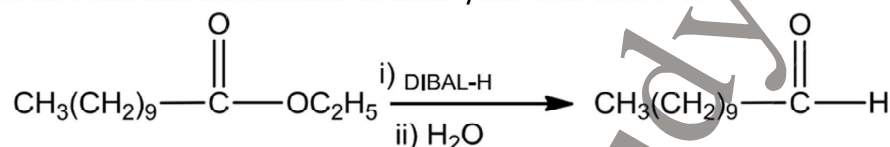
Nitriles on reduction with stannous chloride in the presence of HCl give imine which on hydrolysis gives corresponding aldehyde.



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



Esters can also be reduced to aldehydes with DIBAL-H



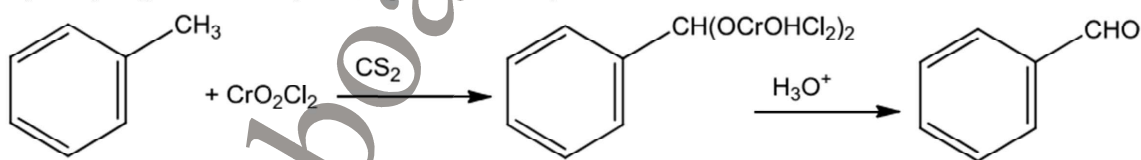
➤ From Aromatic Hydrocarbons

Aromatic aldehydes can be prepared using the following methods.

I) By Oxidation of Methylbenzene

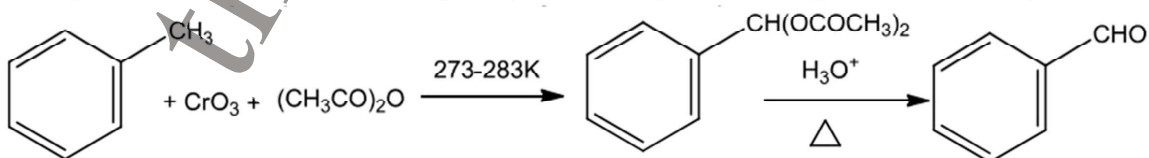
Etard Reaction (Use of Chromyl Chloride)

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



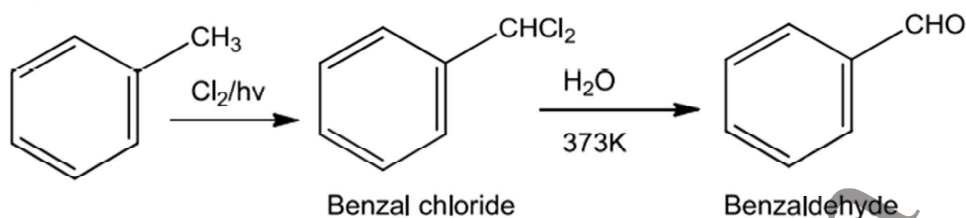
Use of Chromic oxide(CrO_3)

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



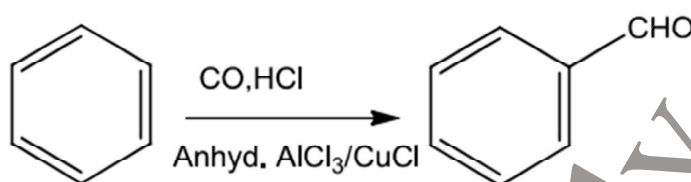
Side Chain Chlorination

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



Gatterman — Koch Reaction

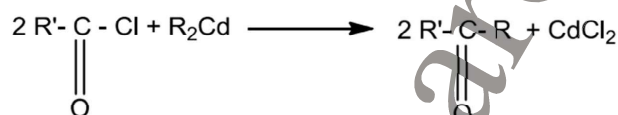
Benzene or toluene on treatment with CO and HCl in the presence of AlCl_3 or CuCl gives benzaldehyde or p-tolualdehyde.



Preparation of Ketones

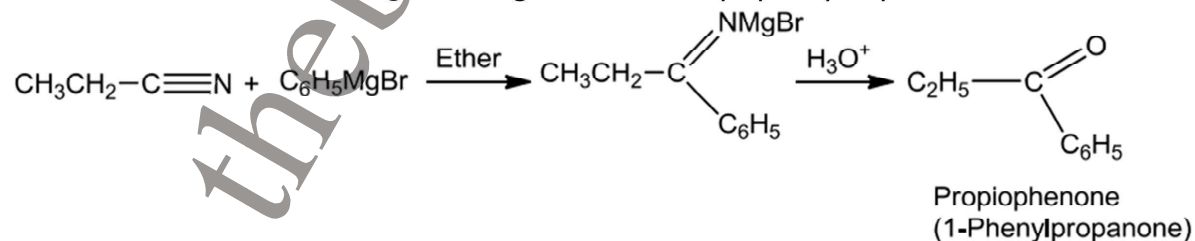
➤ From Acid chlorides or Acyl chlorides

Acyl chloride on treatment with dialkylcadmium obtained by reaction of cadmium chloride with Grignard reagent gives ketones.



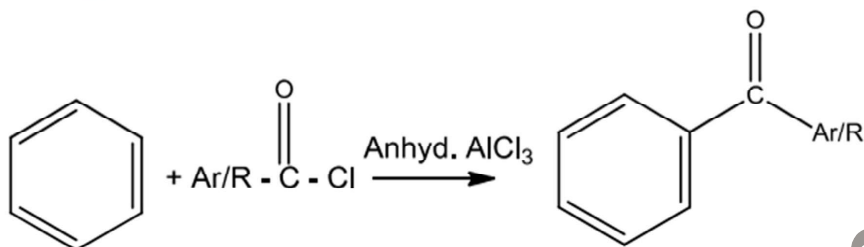
➤ From Nitriles

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



➤ From Benzenes or Substituted Benzenes

Benzene or substituted benzene on treatment with acid chloride in the presence of anhydrous AlCl_3 gives the corresponding ketone and this reaction is known as Friedel-Crafts acylation reaction.



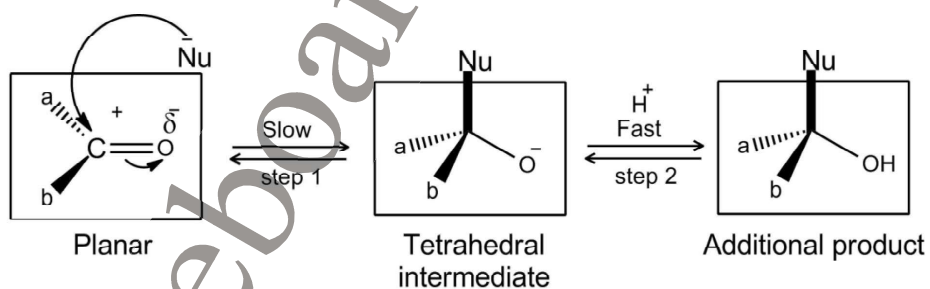
Chemical Reactions

➤ 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 to the sp^2 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.



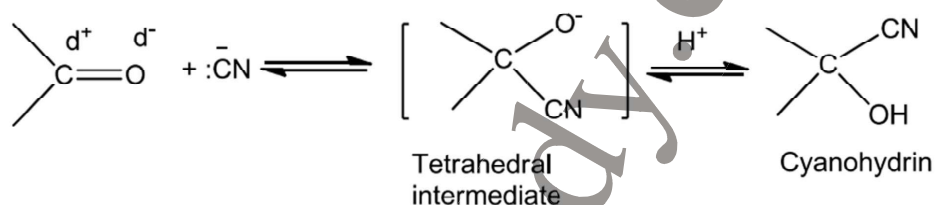
(ii) Reactivity

- 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 of nucleophile 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 ketones decrease the electrophilicity of the carbonyl carbon more effectively than in aldehydes.

(iii) Important Examples of Nucleophilic Addition and Nucleophilic Addition-Elimination Reactions

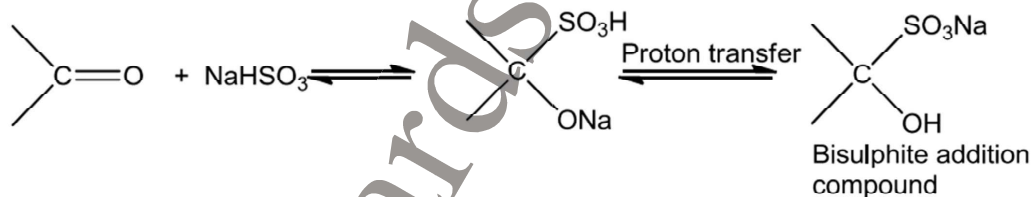
(a) Addition of Hydrogen cyanide (HCN)

- 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 the cyanide ion (CN^-) generated as a strong nucleophile adds to carbonyl compounds to give cyanohydrins.



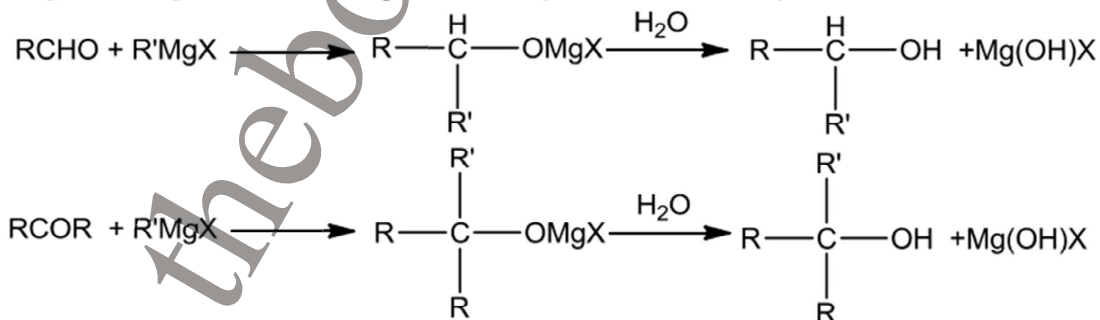
(b) Addition of Sodium Hydrogensulphite

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



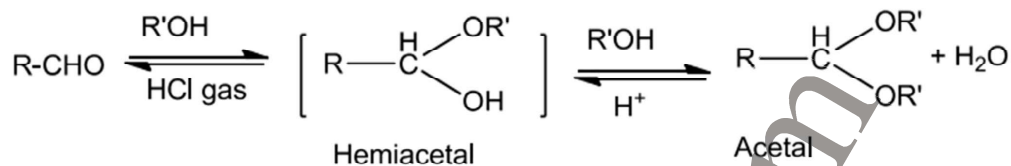
(c) Addition of Grignard Reagents

Grignard reagents on reacting with aldehydes and ketones yield alcohols.

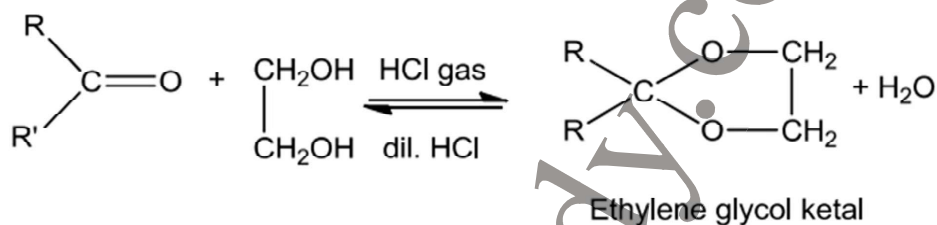


(d) Addition of Alcohols

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

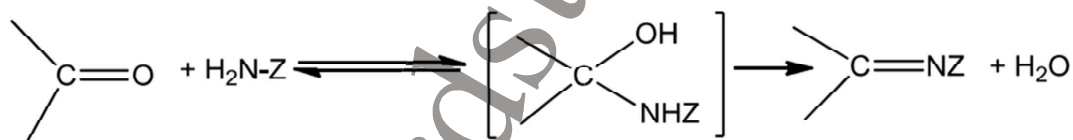


- Ketones also react with ethylene glycols under similar conditions to give ethylene glycol ketals.



(e) Addition of Ammonia and its Derivatives

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

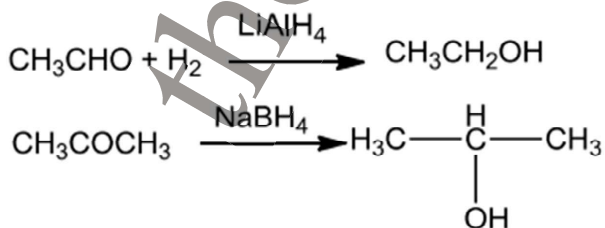


Z = Alkyl, aryl, OH, NH₂, C₆H₅NH, NHCONH₂, etc.

➤ Reduction

(i) Reduction to Alcohols

Aldehydes and ketones get reduced to primary and secondary alcohols by NaBH₄ or LiAlH₄.



(ii) Reduction to Hydrocarbons

Aldehydes and ketones reduce to —CH₂ group on treatment with zinc-amalgam and conc. HCl [Clemmenson reduction] or with hydrazine which on heating with

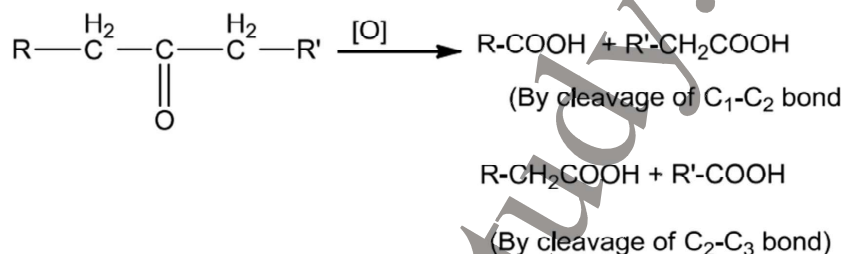
sodium or potassium hydroxide in ethylene glycol [Wolff-Kishner reduction]

- **Oxidation**

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



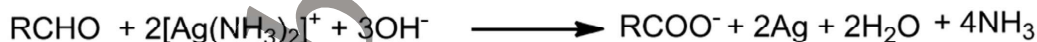
- Ketones undergo oxidation with strong oxidising agents and elevated temperatures. The reaction involves carbon-carbon bond cleavage to give a mixture of carboxylic acids with less number of carbon atoms than the parent ketones.



Test to distinguish Aldehydes from Ketones

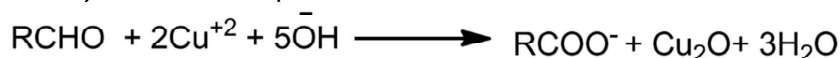
Tollens test

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



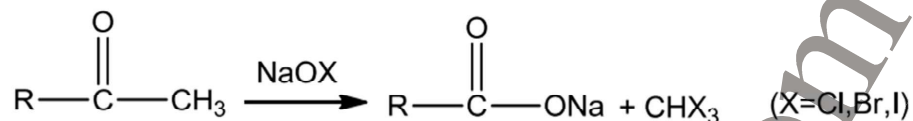
Fehling's test

- 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 oxidised to corresponding carboxylate anion while aromatic aldehydes do not respond to this test.



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 atom less than that of carbonyl compound. In this reaction, the methyl group is converted to haloform.



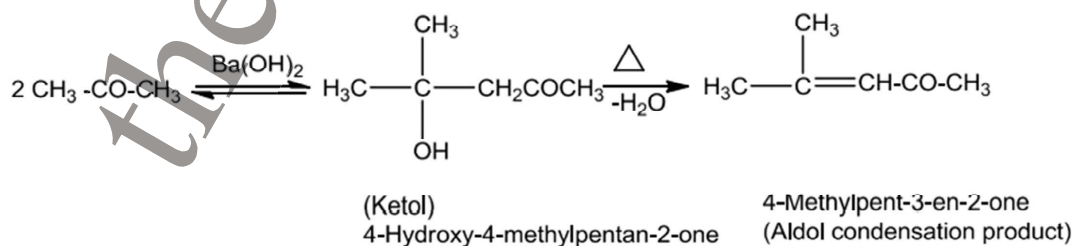
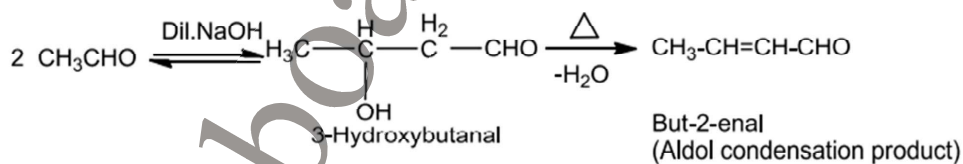
➤ Reactions due to α -hydrogen

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



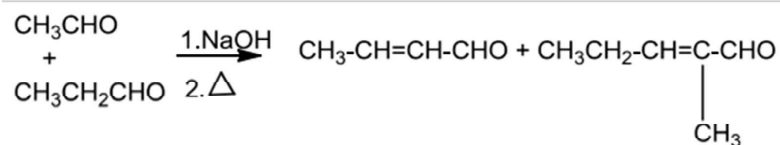
(i) Aldol Condensation

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



(ii) Cross Aldol Condensation

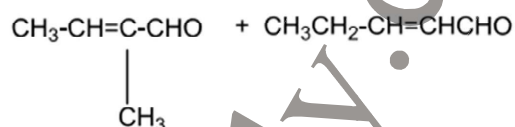
- In this reaction, two different aldehydes and/or ketones with α -hydrogen atoms reaction in the presence of dilute alkali as catalyst give a mixture of four products.



From two molecules
of ethanal

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

Simple or self aldol products



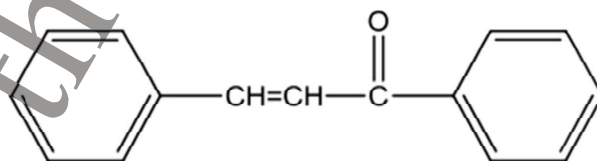
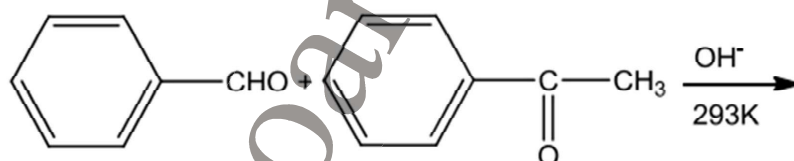
2-Methylbut-2-enal

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.

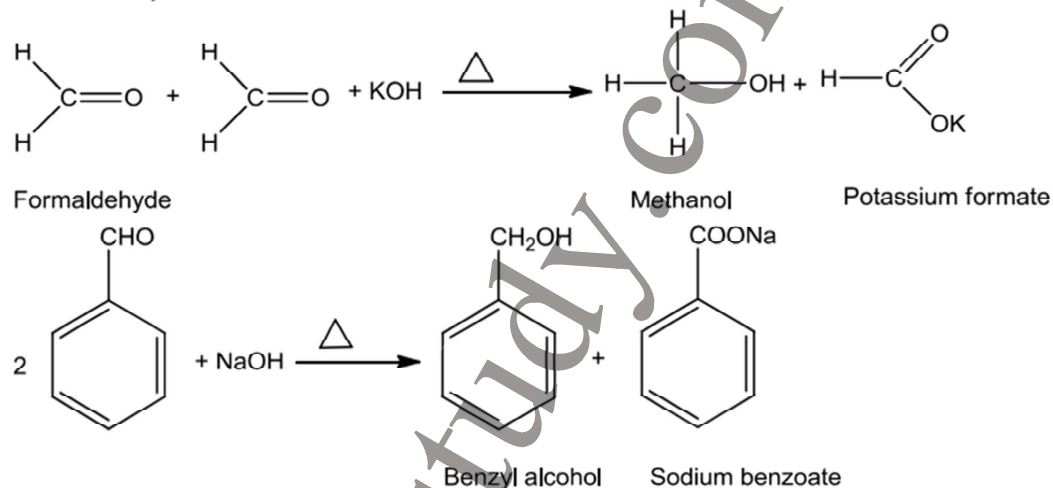


1,3-Diphenylprop-2-en-1-one
(Benzalacetophenone)
(Major product)

➤ Other Reactions

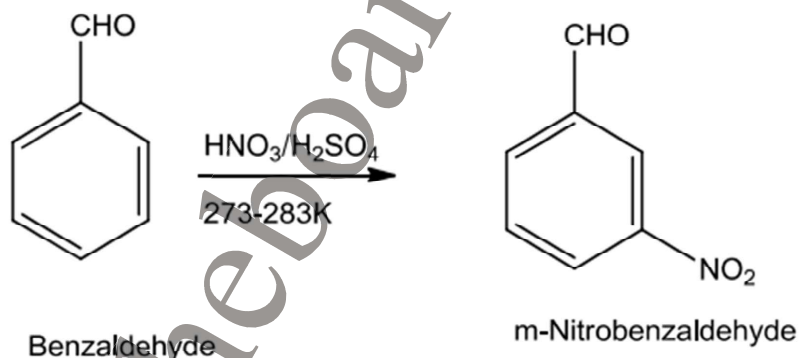
(i) Cannizzaro reaction

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



(ii) Electrophilic Substitution Reaction

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



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

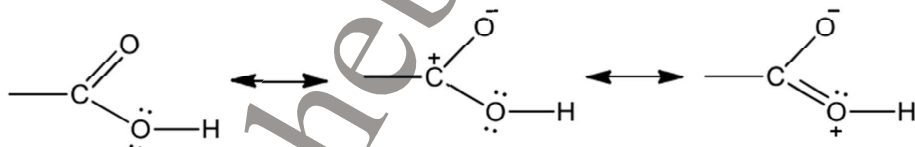
halogens are called amides and acyl halides respectively.

Nomenclature of Carbonyl Group

Structure	Common Name	IUPAC Name
HCOOH	Formic acid	Methanoic acid
$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{COOH} \\ \quad \\ \text{CH}_3 \quad \text{H} \end{array} $	Isovaleric acid	3-Methylbutanoic acid
$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{HOOC}-\text{C}-\text{C}-\text{COOH} \\ \quad \\ \text{H} \quad \text{H} \end{array} $	Succinic acid	Butane-1,4-dioic acid
$\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{COOH}$	Crotonic acid	But-2-enoic acid
$\text{COOH}-\text{COOH}$	Oxalic acid	Ethane-1,2-dioic acid
$ \begin{array}{c} \text{CH}_2\text{COOH} \\ \\ \text{H}_2\text{C} \\ \\ \text{CH}_2\text{COOH} \end{array} $	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.

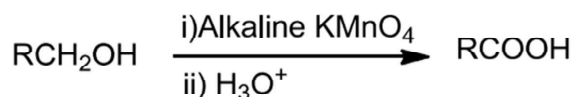


Preparation of Carboxylic Acids

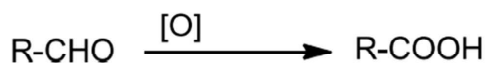
➤ From Primary Alcohols and Aldehydes

- Primary alcohols undergo oxidation with the help of oxidising agents like potassium permanganate in neutral, acidic or alkaline media or by potassium dichromate and

chromium trioxide in acidic media to give carboxylic acid.

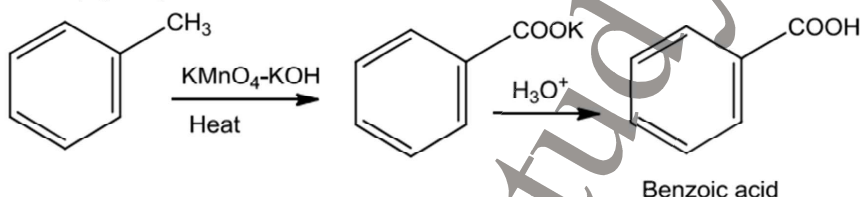


- Carboxylic acids can also be prepared by treating aldehydes with mild oxidising agents.

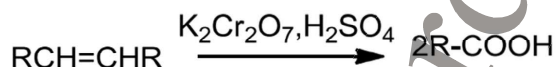


➤ From Alkylbenzenes

- In this method, alkyl benzenes on vigorous oxidation with chromic acid or acidic or alkaline potassium permanganate yield aromatic carboxylic acids.
- Primary and secondary alkyl groups are oxidised in this way while tertiary groups remain unaffected.

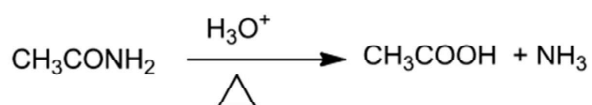
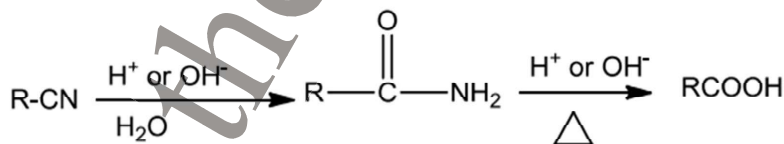


- Substituted alkenes can also be oxidised using the same oxidising agents to yield carboxylic acids.



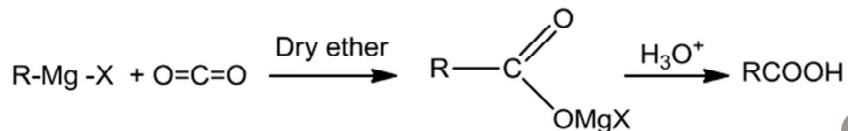
➤ From Nitriles and Amides

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



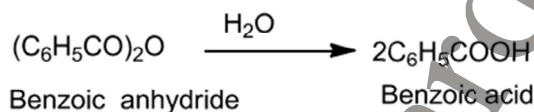
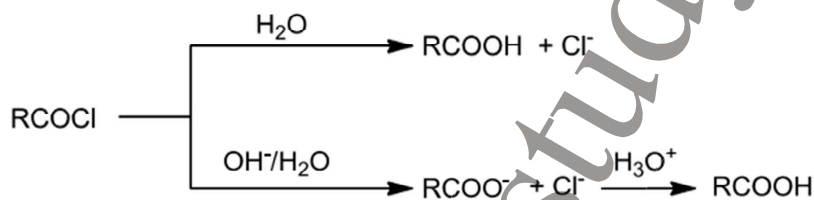
➤ From Grignard Reagents

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



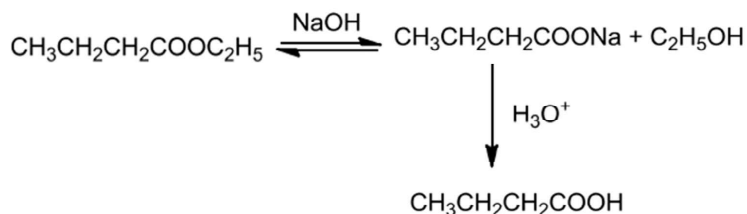
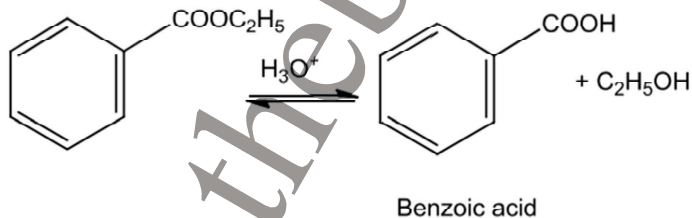
➤ From Acyl Halides and Anhydrides

- 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 on acidification give corresponding acids.

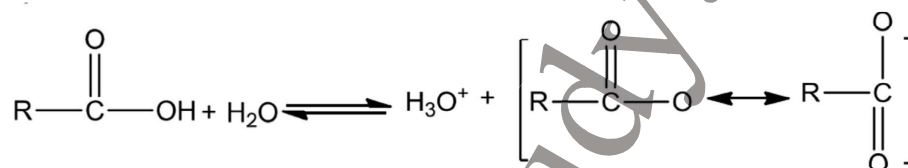


Chemical Reactions of Carboxylic Acids

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 and hydronium ion.

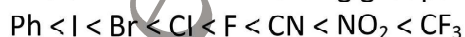


Acidity of carboxylic acids: Carboxylic acids are more acidic than phenols.

The strength of acid depends on the extent of ionisation, which in turn depends on the stability of anion formed.

- 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.
- 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:



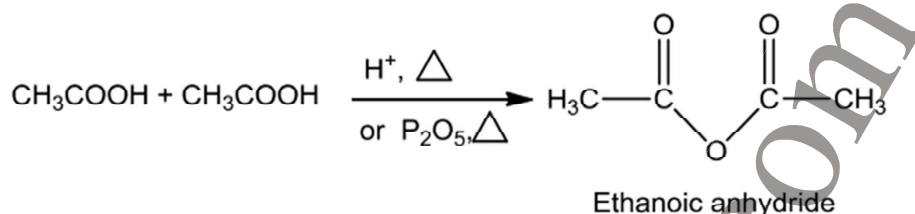
(a) Effect of the number of electron-withdrawing groups: As the number of electron-withdrawing groups increases, the $-\text{I}$ effect increases, increasing the acid strength.

(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

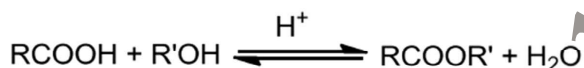
1. Formation of Anhydride

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



2. Esterification

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



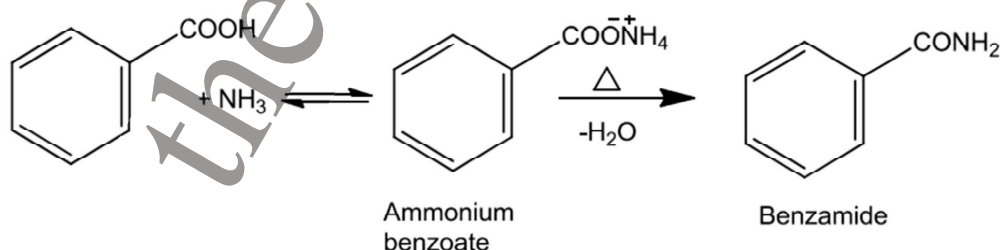
3. Reactions with PCl_5 , PCl_3 and SOCl_2

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.



4. Reaction with Ammonia

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

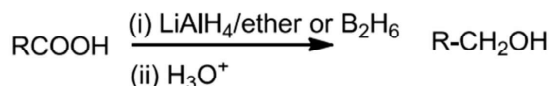


➤ Reactions involving -COOH group

1. Reduction

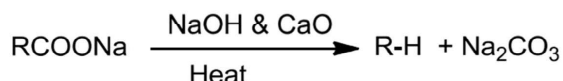
On reduction with reducing agents like LiAlH_4 or diborane, carboxylic acids are reduced

to primary alcohols.



2. Decarboxylation

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



Substitution reactions in the Hydrocarbon

1. Halogenation

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



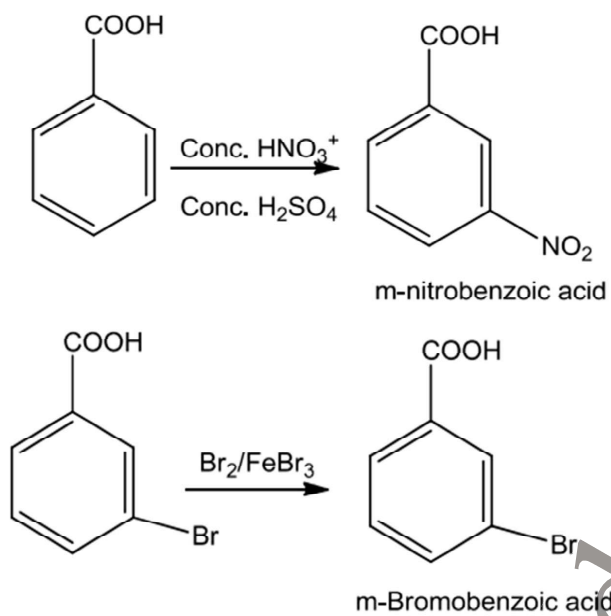
$\text{X}=\text{Cl, Br}$

α - Halocarboxylic acid

2. Ring Substitution

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

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



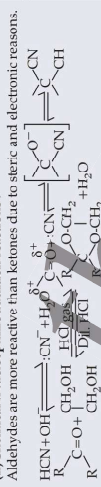
MIND MAP : LEARNING MADE SIMPLE

CHAPTER - 12

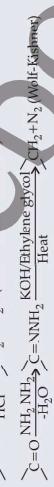
ALDEHYDES AND KETONES:

(i) **Physical:** Boiling points are higher than hydrocarbons and ethers of comparable molecular masses.

(ii) **Chemical:** Nucleophilic addition reactions:



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

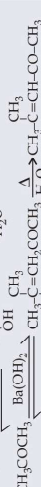


Oxidation: $\text{RCHO} \xrightarrow[\text{Heat}]{\text{O}_2} \text{RCOOH}$

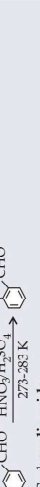
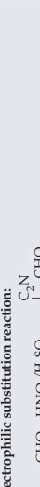
Tollens' test: $\text{RCHO} + 2[\text{Ag}(\text{NH}_3)_2]^+ + 3\text{OH}^- \rightarrow \text{RCOO}^- + 2\text{Ag} + 2\text{H}_2\text{O} + 4\text{NH}_3$

Fehling's test: $\text{RCHO} + 2\text{Cu}^{2+} + 5\text{OH}^- \rightarrow \text{RCOO}^- + \text{Cu}_2\text{O} + 3\text{H}_2\text{O}$

Haloform reaction:

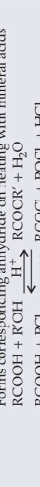


Reactions due to α -hydrogen:



Cannizzaro reaction: $2\text{HCHO} + \text{conc KOH} \xrightarrow{\Delta} \text{CH}_3\text{OH} + \text{HCOOK}$

Electrophilic substitution reaction:

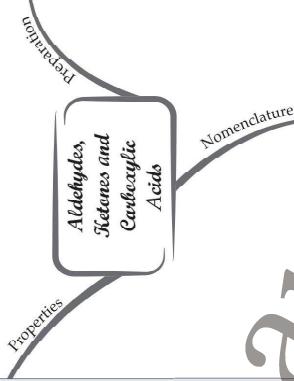
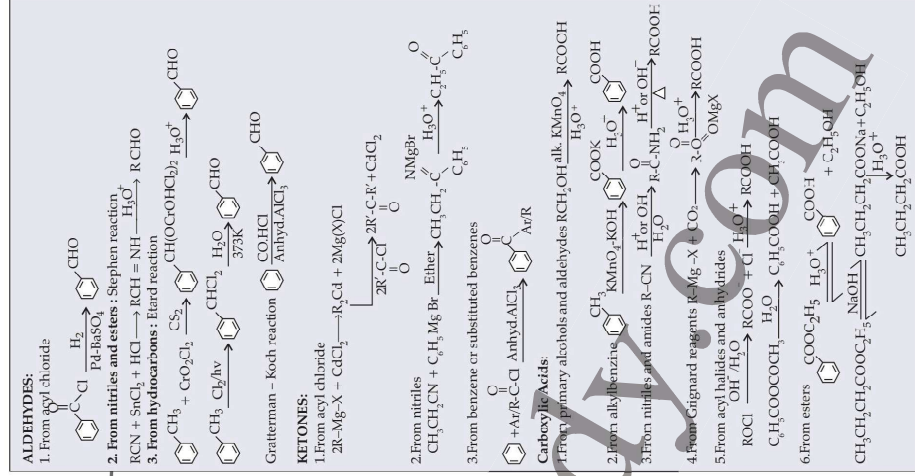
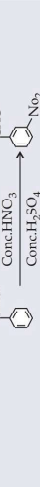


Carboxylic acids:

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

(ii) **Chemical:** $2\text{RCOOH} + 2\text{Na} \rightarrow 2\text{RCOONa} + \text{H}_2$

Forms corresponding anhydride on heating with mineral acids



1. Aldehydes and Ketones

Common names:

- Replace corresponding carboxylic acids with aldehyde.
- Alkyl phenyl ketones by adding acyl group as prefix to phenone.
- IUPAC names:
 - Replacing -e with -al and -one as required.
 - Structure of Carbonyl Group: sp^2 hybridization, trigonal planar geometry, bond angles 120° .

2. Carboxylic Acids

- Common names: end with -ic.
- IUPAC names: replace -e in the corresponding alkane with -oic acid.
- Structure of Carboxyl Group: sp^2 hybridization, trigonal planar geometry, bond angles 120° .

3. USES

(a) Carboxylic acids:

- Methanoic acid in rubber, textile, dyeing, leather industries.
- Ethanoic acid as solvent.
- Higher fatty acids in manufacture of soaps and detergents.

(b) Aldehydes of ketones:

- As solvents.
- Starting materials and reagents for synthesis of products.

Important Questions

Multiple Choice questions-

Question 1. Which of the following cannot reduce Fehling's solution?

- (a) Formic acid
- (b) Acetic acid
- (c) Formaldehyde
- (d) Acetaldehyde

Question 2. Which of the following acids does not form anhydride?

- (a) Formic acid
- (b) Acetic acid
- (c) Propionic acid
- (d) n-butyric acid

Question 3. The acid which does not contain-COOH group is

- (a) Ethanoic acid
- (b) Lactic acid
- (c) Picric acid
- (d) Palmitic acid

Question 4. Trans-esterification is a reaction between

- (a) two ester molecules
- (b) alcohol and carboxylic acid
- (c) alcohol and ether
- (d) alcohol and ester.

Question 5. Acetone on heating with ammonia produces

- (a) Acetaldehyde
- (b) Diacetone alcohol
- (c) Diacetoneamine
- (d) Hydrobenzamide

Question 6. Methyl ketones are usually characterised through

- (a) Tollen's reagent
- (b) Iodoform test
- (c) Schiff's test
- (d) Benedict solution test.

Question 7. Which of the following reagents can be used to prepare ketone from acid chloride?

- (a) Grignard's reagent
- (b) LiAlH_4
- (c) Dimethyl cadmium
- (d) Cadmium chloride

Question 8. HVZ reaction is used to prepare

- (a) β -haloacid
- (b) α -haloacid
- (c) α, β -unsaturated add
- (d) None of these

Question 9. An alkene C_7H_{14} on reductive ozonolysis gives an aldehyde with formula $\text{C}_3\text{H}_6\text{O}$ and a ketone. The ketone is

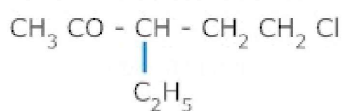
- (a) 2-butanone
- (b) 2-pentanone
- (c) 3-pentanone
- (d) propanone

Question 10. Acetaldehyde is a condensation product of

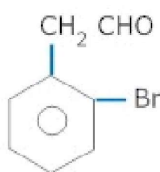
- (a) two molecules of ethanal
- (b) two molecules of propanone
- (c) ethanal and methanal
- (d) ethanal and propanone.

Very Short Questions-

1. Give one use of Formalin.
2. What is the chemical name of Tollen's reagent and Fehling's solution.
3. Write the structure of alkenes that on ozonolysis will give ketone only.
4. What is the function of BaSO_4 in Rosenmund reaction?
5. Name the isomers with molecular formula $\text{C}_3\text{H}_6\text{O}$. Which one will have high boiling point?
6. Write a chemical test to distinguish between aldehyde and ketone.
7. What happens when acetaldehyde is kept with a trace of sulphuric acid? Write the structure of product.
8. What is the Hofmann bromamide reaction? Illustrate with one example.
9. Give IUPAC name of following



10. Give IUPAC name of following



Short Questions-

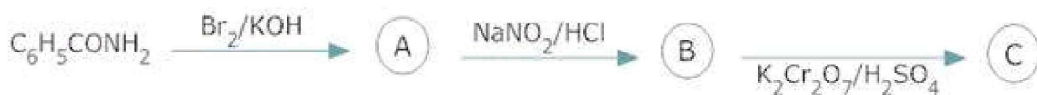
1. Ethanoic acid has molar mass of 120 in vapour state.
2. Carboxylic acids do not give characteristic reactions of Carboxylic acid is stronger acid than phen
3. Ethanol is more soluble in water than ethyl chloride
4. Aldehydes are more reactive than Ketones towards nucleophilic additions.
5. Carboxylic acids has higher boiling points than alcohols of same no. of carbon atoms.
6. carbonyl group.
7. Formaldehyde does not undergo aldol condensation.
8. Floro acetic acid is a stronger acid than acetic acid.
9. Toluene to benzaldehyde
10. Acetaldehyde to Acetamide

Long Questions-

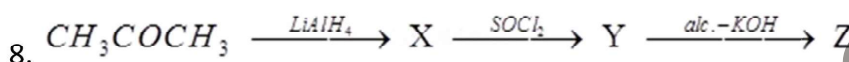
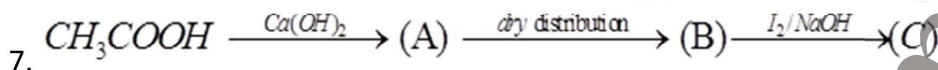
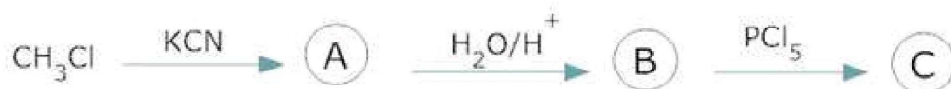
1. A compound 'A' with formula $C_3H_{10}O$ gives a positive 2, 4 -DNP test but a negative Tollen's test It can be oxidizing to carboxylic acid 'B' of molecular formula $C_3H_6O_2$, when treated with alk. $KMnO_4$ under vigorous conditions. The salt of 'B' gives a hydrocarbon 'C' on Kolbes' electrolytic decarboxylation. Identify A, B, C & write chemical equations.
2. A compound A with molecular formula $C_3H_{12}O$ on oxidation forms compound B with molecular formula $C_3H_{10}O$. The compound B gives iodoform test but does not reduce ammoniacal silver nitrate. The compound B on reduction with Zn - Hg/ HCl gives compound C with molecular formula C_3H_8 . Identify A, B, C & give the chemical reactions involved.
3. An organic compound A, which has a characteristic odour, on treatment with NaOH forms two compound B and C. Compound B has molecular formula C_7H_8O which on oxidation gives back A. Compound C is the sodium salt of an acid. C, when heated with soda lime yields an aromatic hydrocarbon D. deduce the structures of A to D.



5.



6.



Assertion and Reason Questions-

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- Assertion and reason both are correct statements and reason is correct explanation for assertion.
- Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- Assertion is correct statement but reason is wrong statement.
- Assertion is wrong statement but reason is correct statement.

Assertion: Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

Reason: Aromatic aldehydes are almost as reactive as formaldehyde.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- Assertion and reason both are correct statements and reason is correct explanation for assertion.
- Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- Assertion is correct statement but reason is wrong statement.
- Assertion is wrong statement but reason is correct statement.

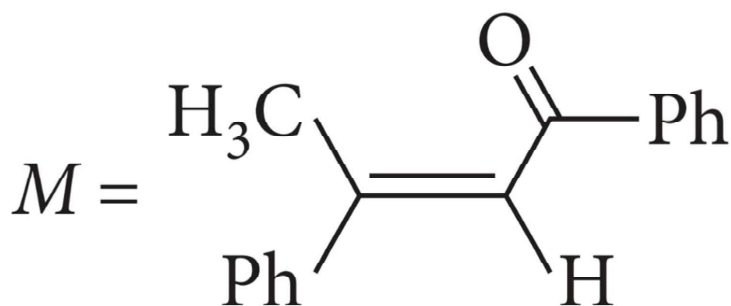
Assertion: O-Substituted benzoic acids are generally stronger acids than benzoic acids.

Reason: Increased strength is due to ortho-effect.

Case Study Questions-

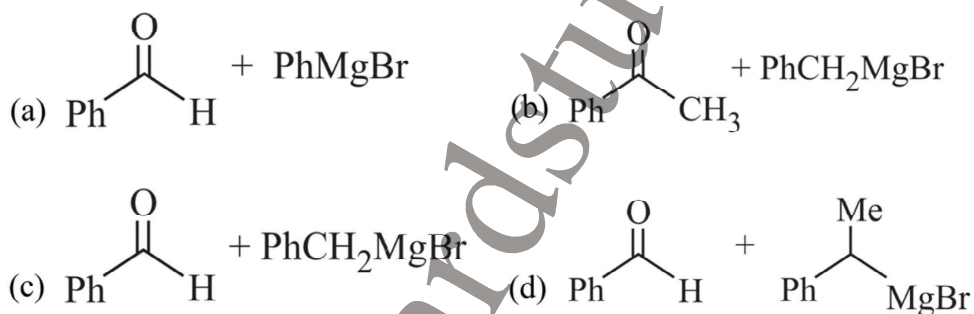
1. Read the passage given below and answer the following questions:

A tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and a compound I, whereas K on reaction with KOH gives only M.

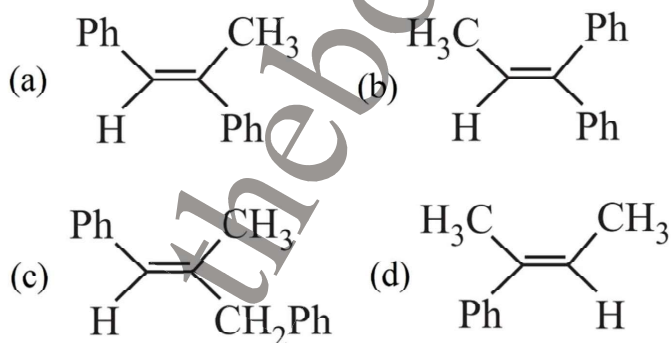


The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Compound H is formed by the reaction of:



(ii) The structure of compound I is:



(iii) The structures of compound J, K and I, respectively, are:

- a) PhCOCH_3 , $\text{PhCH}_2\text{COCH}_3$ and $\text{PhCH}_2\text{COO}^-\text{K}^+$
 b) PhCHO , PhCH_2CHO and PhCOO^-K^+
 c) PhCOCH_3 , PhCH_2CHO and $\text{CH}_3\text{COO}^-\text{K}^+$

d) PhCHO , PhCOCH_3 and PhCOO^-K^+

(iv) When (J) is treated with acetic anhydride, in the presence of corresponding salt of an acid, the product obtained is:

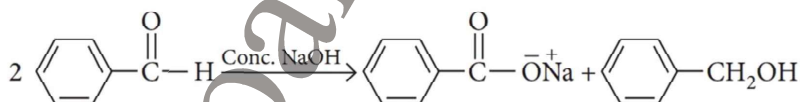
- a) Cinnamic acid.
- b) Crotonic acid.
- c) Maleic acid.
- d) Benzylic acid.

(v) Which of the following statements is correct for compound (K)?

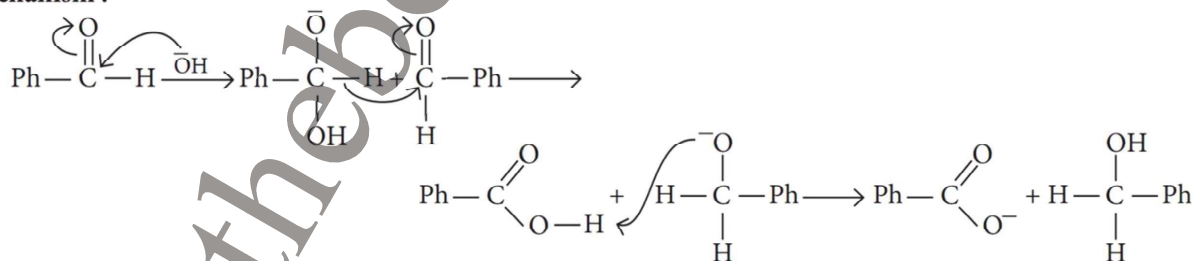
- a) It reacts with alkaline KMnO_4 followed by acidic hydrolysis and forms benzoic acid.
- b) It reacts with iodine and NaOH to form triiodomethane.
- c) It is prepared by the reaction of benzene with benzoyl chloride in presence of anhydrous aluminium chloride.
- d) It reacts with freshly prepared ammoniacal silver nitrate solution.

2. Read the passage given below and answer the following questions:

When an aldehyde with no α -hydrogen reacts with concentrated aqueous NaOH , half the aldehyde is converted to carboxylic acid salt and other half is converted to an alcohol. In other words, half of the reactant is oxidized and other half is reduced. This reaction is known as Cannizzaro reaction.



Mechanism :



The following questions are multiple choice questions. Choose the most appropriate answer:

(i) A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives:

- a) Benzyl alcohol and sodium formate.
- b) Sodium benzoate and methyl alcohol.

- c) Sodium benzoate and sodium formate.
- d) Benzyl alcohol and methyl alcohol.

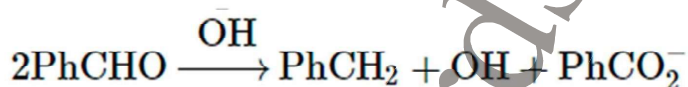
(ii) Which of the following compounds will undergo Cannizzaro reaction?

- a) CH_3CHO
- b) CH_3COCH_3
- c) $\text{C}_6\text{H}_5\text{CHO}$
- d) $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$

(iii) Trichloroacetaldehyde is subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compound is:

- a) 2, 2, 2-trichloroethanol.
- b) Trichloromethanol.
- c) 2, 2, 2-trichloropropanol.
- d) Chloroform.

(iv) In Cannizzaro reaction given below:



the slowest step is:

- a) The attack of OH^- at the carboxyl group.
- b) The transfer of hydride to the carbonyl group.
- c) The abstraction of proton from the carboxylic group.
- d) The deprotonation of PhCH_2OH .

(v) Which of the following reaction will not result in the formation of carbon-carbon bonds?

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

MCQ Answers-

1. Answer: (b) Acetic acid
2. Answer: (a) Formic acid

3. Answer: (c) Picric acid
4. Answer: (d) alcohol and ester.
5. Answer: (c) Diacetoneamine
6. Answer: (b) Iodoform test
7. Answer: (c) Dimethyl cadmium
8. Answer: (b) α -haloacid
9. Answer: (a) 2-butanone
10. Answer: (a) two molecules of ethanal

Very Short Answers-

Ans 1. Formalin is used as a disinfectant, preservative for biological specimens and in leather industry.

Ans 2. Tollen's reagent = Ammoniacal Silver Nitrate
Fehlings solution = Sodium Potassium Tartarate.

Ans 3.

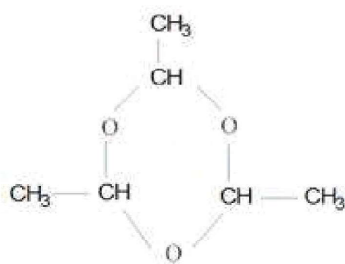


Ans 4. BaSO_4 acts as a catalytic poison which prevents further reduction of aldehyde to alcohol.

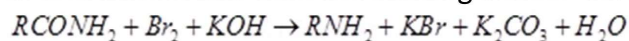
Ans 5. The two isomers are CH_3COCH_3 and $\text{CH}_3\text{CH}_2\text{CHO}$. Acetone boils at higher temperature due to presence of two electron donating alkyl groups.

Ans 6. Aldehydes and ketones can be distinguished by Tollen's test. Aldehydes give a silver mirror on reacting with Tollen's reagent whereas ketones will not react.

Ans 7. A trimer of acetaldehyde, called paraldehyde is formed.



Ans 8. Hoffman bromamide reaction is a reaction in which amides are converted to amines of one carbon less than the starting amide. It is a very important step – down reaction.



Ans 9. 5-Chloro -3- ethylpentan -2-one.

Ans 10. 2 -(2-bromophenyl) ethanal

Short Answers-

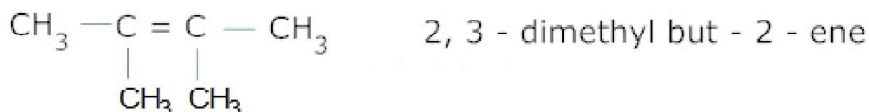
Ans 1. Carboxylic acid on dissociation form carboxylate ion which is stabilized by two equivalent resonance structure in which negative charge is at the more electronegative oxygen atom, whereas the conjugate base of phenol, phenoxide ion, has non – equivalent resonance structures in which negative charge is at the less electronegative carbon atom. Therefore resonance is not as important as it is in carboxylate ion. Moreover the negative charge is delocalized over two more electronegative oxygen atoms in carboxylate ion whereas it is less effectively delocalized over one oxygen atom and one carbon atom in phenoxide ion. Therefore the carboxylate ion is more stabilized than phenoxide ion and carboxylic acids are stronger acids than phenol.

Ans 2. Ethanol can form intermolecular Hydrogen bonding with water molecules, ethyl chloride cannot. Therefore ethanol is soluble in water and ethyl chloride is not.

Ans 3. Aldehydes are more reactive than Ketones due to steric and electronic reasons. In Ketones due to presence of two relatively large alkyl groups, the approach of nucleophile is more hindered than in aldehydes having only one such substitute. Moreover the +I effect of alkyl groups reduces the electrophilicity of carbonyl group more in Ketone than in aldehydes.

Ans 4. Carboxylic acids have more extensive association of molecules through intermolecular hydrogen bonding than alcohols. Moreover their boiling points are higher than alcohols of same carbon atoms.

Ans 5. Ethanoic acid exists as dimer in vapour state in which two molecules remain together by hydrogen bonding. This increases the effective molecular mass to 120.



Ans 6. In carboxylic acids due to presence of resonance, the C=O group is not a pure carbonyl group & therefore they do not show characteristic reactions of carbonyl group.

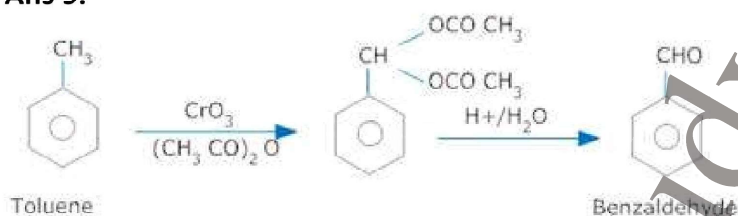
Ans 7. Formaldehyde does not have any BaSO_4 -hydrogen and therefore it can not show aldol condensation.

Ans 8. In fluoroacetic acid, Fluorine being electron withdrawing group stabilizes the conjugate base through delocalization of the negative charge

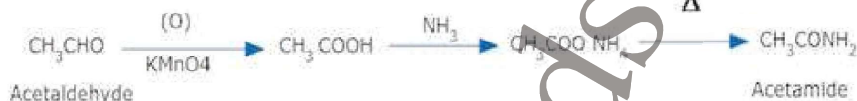


Therefore fluoroacetic acid is a stronger acid than acetic acid.

Ans 9.

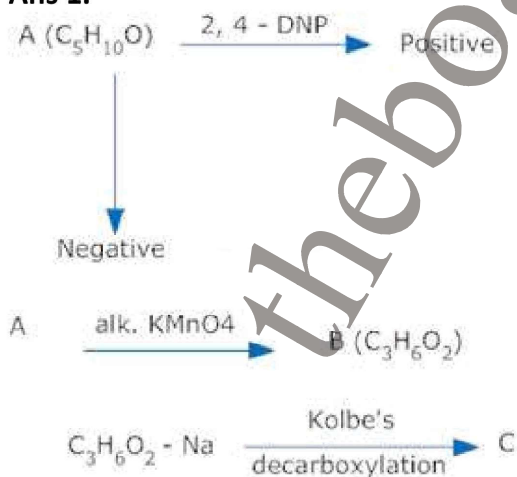


Ans 10.



Long Answers-

Ans 1.



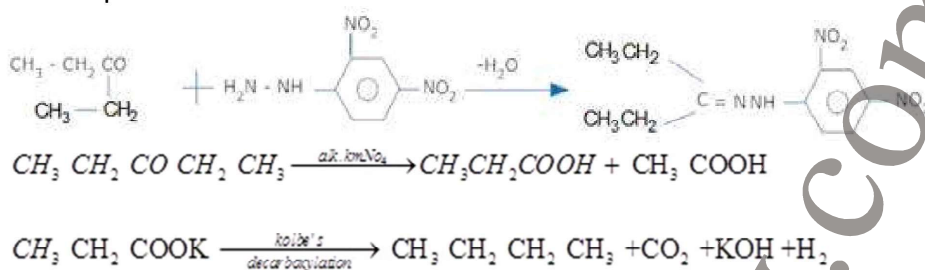
As the compound A gives a positive 2, 4-DNP test but negative Tollen's test, it is a ketone. Since on oxidation, it gives an acid B, of molecular formula $\text{C}_3\text{H}_6\text{O}_2$, it is $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$ and B is $\text{CH}_3\text{CH}_2\text{COOH}$. As C is obtained by Kolbe's decarboxylation of B, C is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$.

Therefore A = Pentan -3 one, $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$

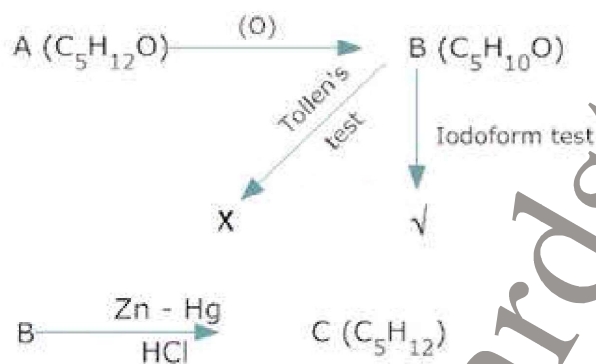
B = Propanoic acid $\text{CH}_3\text{CH}_2\text{COOH}$

And C = Butane $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

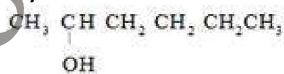
The sequence of reactions is



Ans 2.



Since B gives a negative Tollen's test but positive Iodoform test, it is methyl ketone, i.e., $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$. Also it is formed by oxidation of A.



Therefore A is secondary alcohol i.e.,

on reduction B gives pentane with Zn -HCl.

Therefore C is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

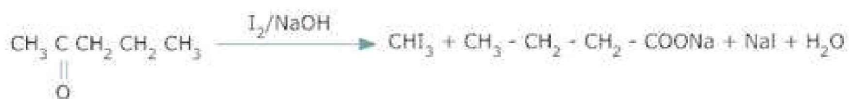
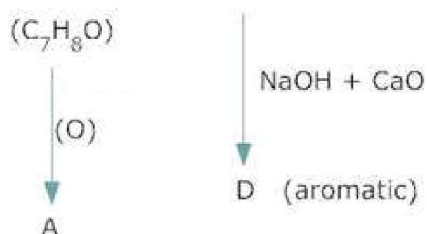
Therefore

A = $\text{CH}_3\text{CHOHCH}_2\text{CH}_2\text{CH}_3$

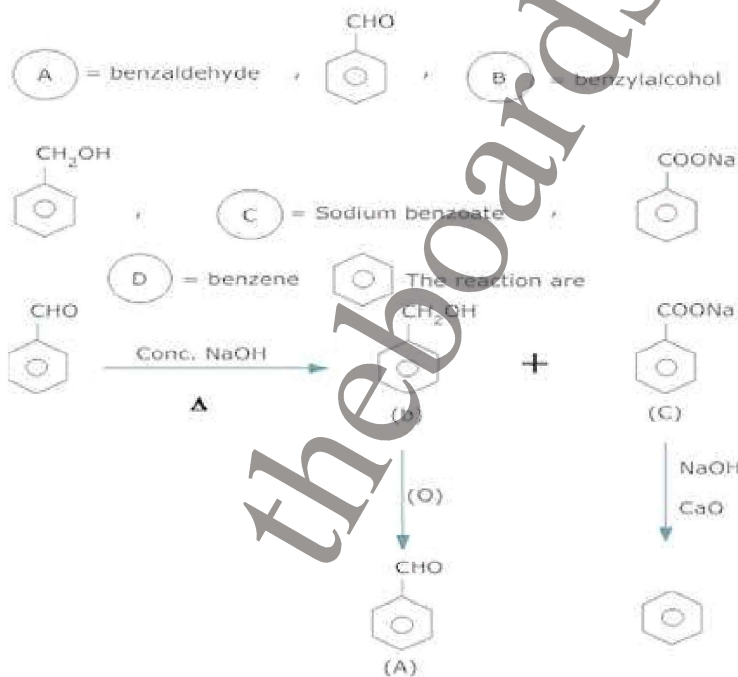
B = $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$

C = $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

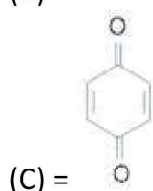
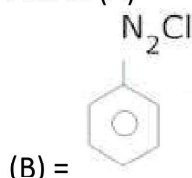
Reactions:-


$$A \xrightarrow{\text{NaOH}} B + C \text{ (Sodium salt of acid)}$$


The molecular formula of (B) and characteristic odour of (A) suggests that (A) is an aromatic aldehyde, C_6H_5CHO and (B) is alcohol, $C_6H_5CH_2OH$. As (C) is a sodium salt of an acid & gives hydrocarbon (D) on heating with soda lime, (C) is sodium benzoate and (D) is benzene. Therefore:-


$$A = \begin{array}{c} \text{CH}_2\text{COOH} \\ | \\ \text{Cl} \end{array} \quad , \quad B = \begin{array}{c} \text{CH}_2\text{COOH} \\ | \\ \text{NH}_2 \end{array}$$

Ans 5. (A) = $C_6H_5CH_2NH_2$



Ans 6. (A) = CH_3CN

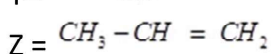
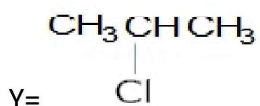
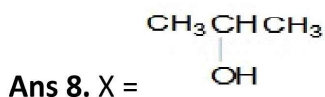
(B) = CH_3COOH

(C) = CH_3COCl

Ans 7. (A) = $(CH_3COO)_2Ca$

(B) = CH_3COCH_3

(C) = CHI_3



Assertion and Reason Answers-

1. (c) Assertion is correct statement but reason is wrong statement.

Explanation:

Aromatic aldehydes and formaldehyde do not contain α -hydrogen and thus undergo Cannizzaro reaction. Formaldehyde is more reactive than aromatic aldehydes.

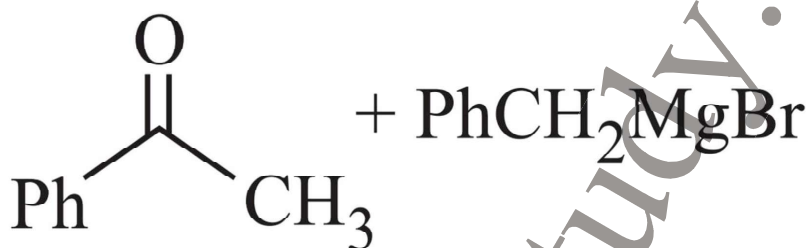
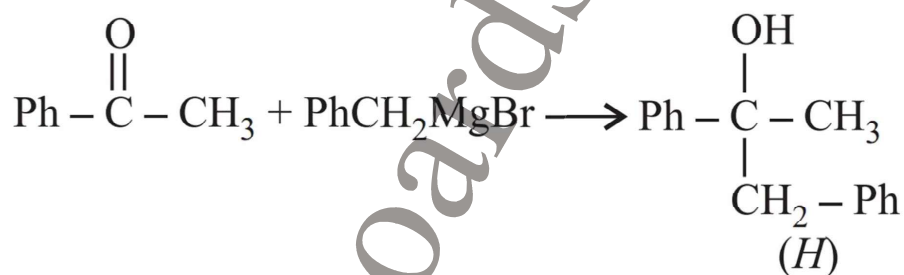
2. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Explanation:

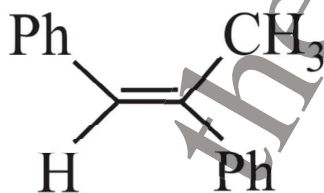
O-Substituted benzoic acids are generally stronger acids than benzoic acid. This is regardless of the nature(+I or -I) of the substituent. This is called ortho-effect and is probably due to a combination of steric and electronic factors.

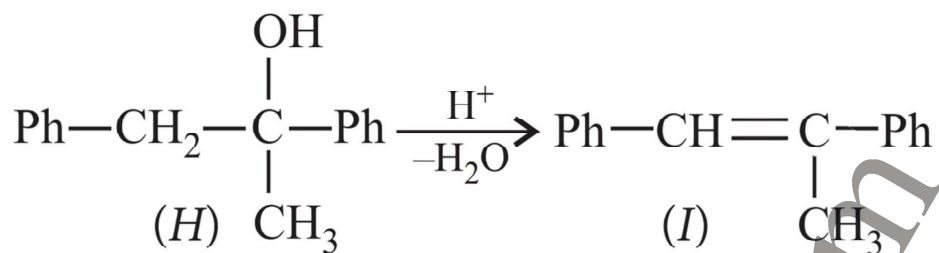
Case Study Answers-**1. Answer :**

(i) (b)

**Explanation:**

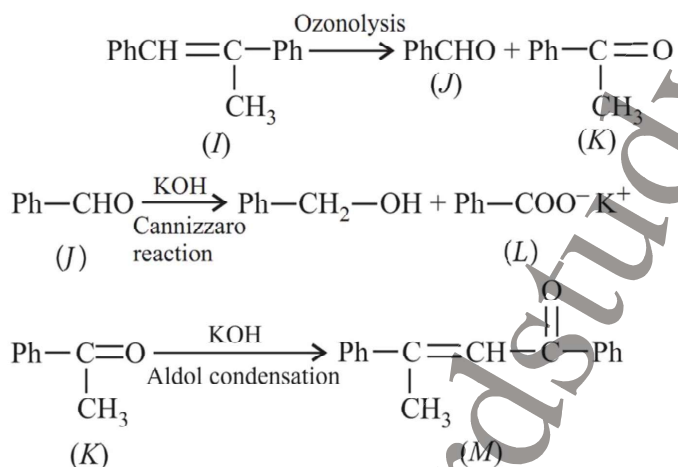
(ii) (a)

**Explanation:**



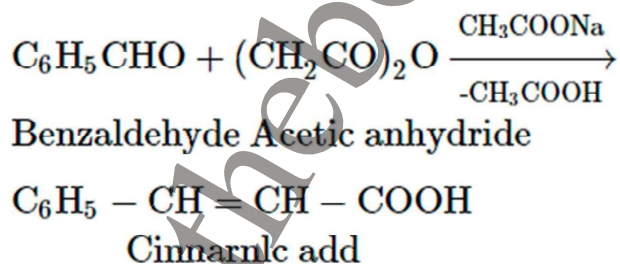
(iii) (d) PhCHO , PhCOCH_3 and PhCOO^-K^+

Explanation:



(iv) (a) Cinnamic acid.

Explanation:



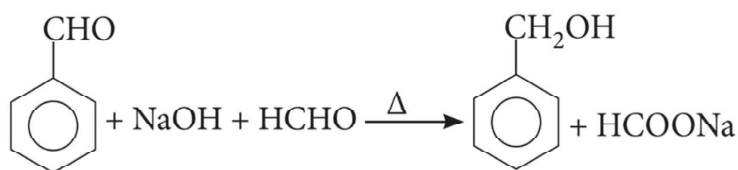
(v) (b) It reacts with iodine and NaOH to form triiodomethane.

2. Answer :

(i) (a) Benzyl alcohol and sodium formate.

Explanation:

It is an example of cross Cannizzaro reaction where aromatic aldehyde gets reduced to alcohol and aliphatic aldehyde gets oxidised to its sodium salt (both aldehydes must not contain any α - α -hydrogen).

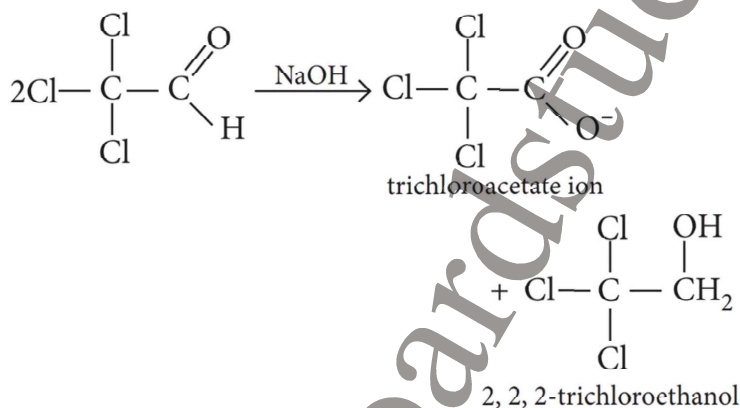


(ii) (c) $\text{C}_6\text{H}_5\text{CHO}$

(iii) (a) 2, 2, 2-trichloroethanol.

Explanation:

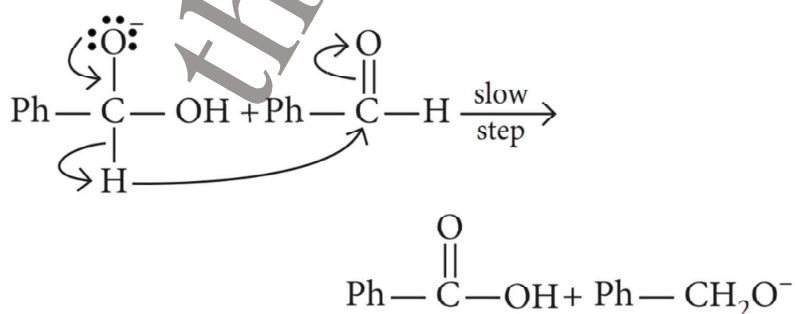
The Cannizzaro product of given reaction yields 2, 2, 2-trichloroethanol.



(iv) (b) The transfer of hydride to the carbonyl group.

Explanation:

Hydride transfer is the slowest step.



(v) (a) Cannizzaro reaction.

Explanation:

C-C bond is not formed in Cannizzaro reaction while other reactions result in the formation of C-C bond.

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