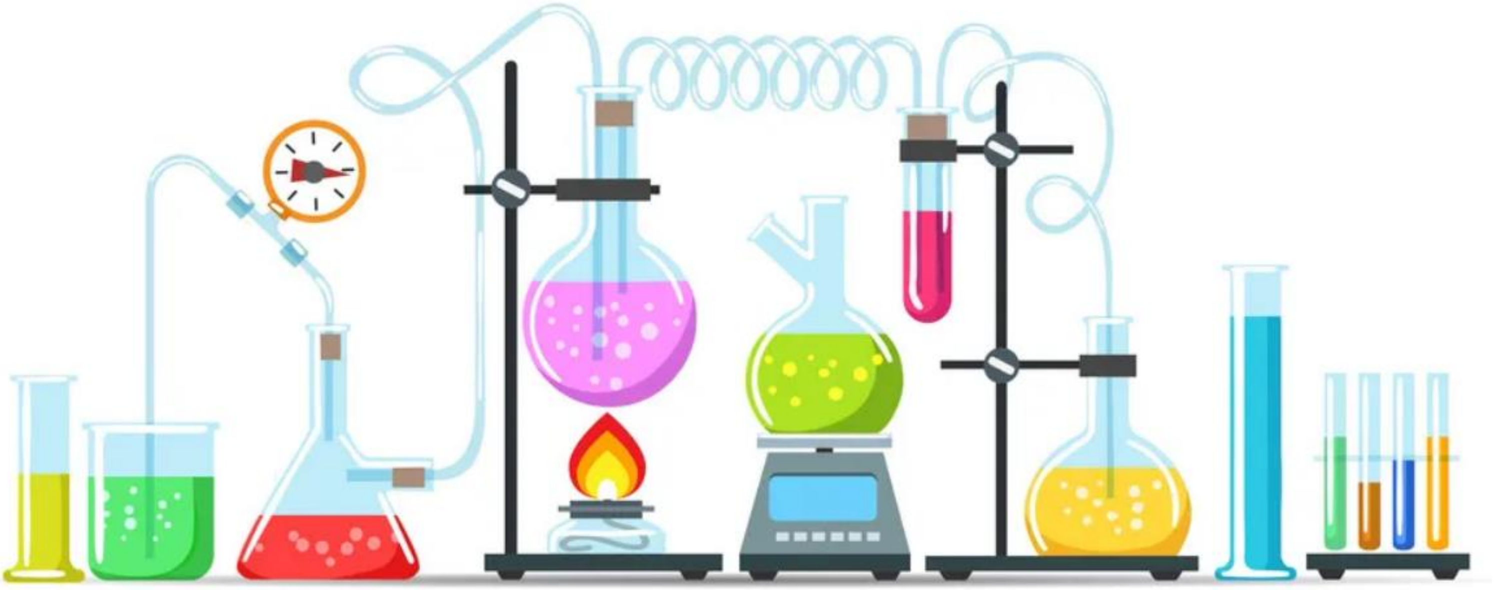
CHEMISTRY

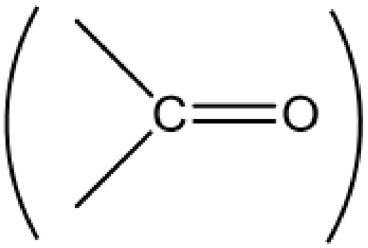
CHAPTER 12: ALDEHYDES, KETONES AND CARBOXYLIC ACIDS



ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Introduction

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



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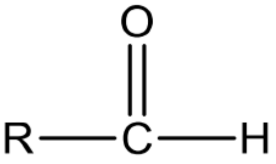
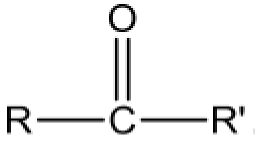
- Aldehydes have carbonyl group bonded to a carbon and hydrogen.



$R-\overset{\overset{O}{\|}}{C}-H$

(Where R = H or alkyl or aryl group)

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

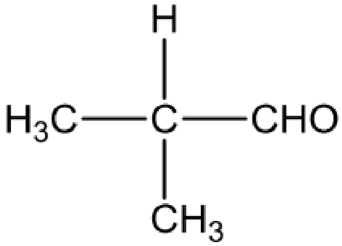
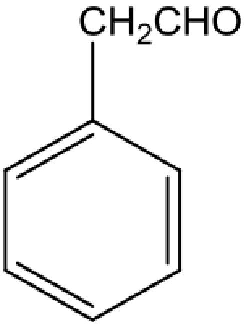


$R-\overset{\overset{O}{\|}}{C}-R'$

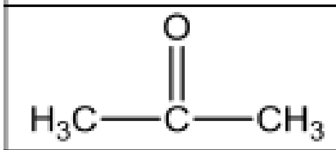
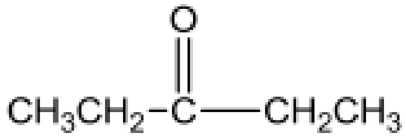
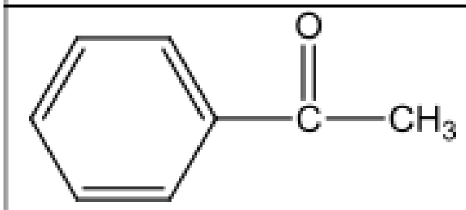
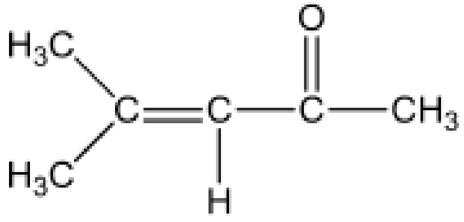
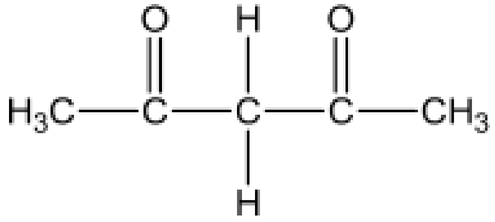
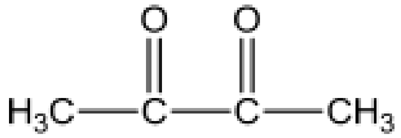
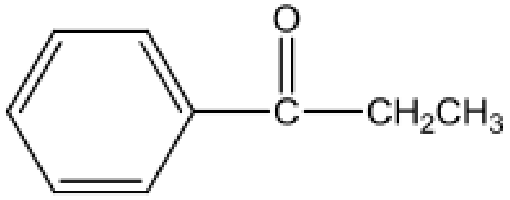
(Where R and R’ may be same or different alkyl or aryl groups)

Nomenclature of Aldehydes and Ketones

Idehydes

Structure	Common name	IUPAC name
CH_3CHO	Acetaldehyde	Ethanal
 $H_3C-\overset{H}{\underset{CH_3}{C}}-CHO$	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
 $H_3C-\overset{O}{\overset{\Vert}{C}}-CH_3$	Dimethyl ketone or Acetone	Propanone
 $CH_3CH_2-\overset{O}{\overset{\Vert}{C}}-CH_2CH_3$	Diethyl ketone	Pentan-3-one
	Methyl phenyl ketone	1-Phenylethan-1-one
	Mesityl oxide	4-Methylpent-3-en-one
 $H_3C-\overset{O}{\overset{\Vert}{C}}-\overset{H}{\overset{\vert}{\underset{\underset{H}{\vert}}{C}}}-\overset{O}{\overset{\Vert}{C}}-CH_3$	Acetylacetone	Pentane-2,4-dione
 $H_3C-\overset{O}{\overset{\Vert}{C}}-\overset{O}{\overset{\Vert}{C}}-CH_3$	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 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.
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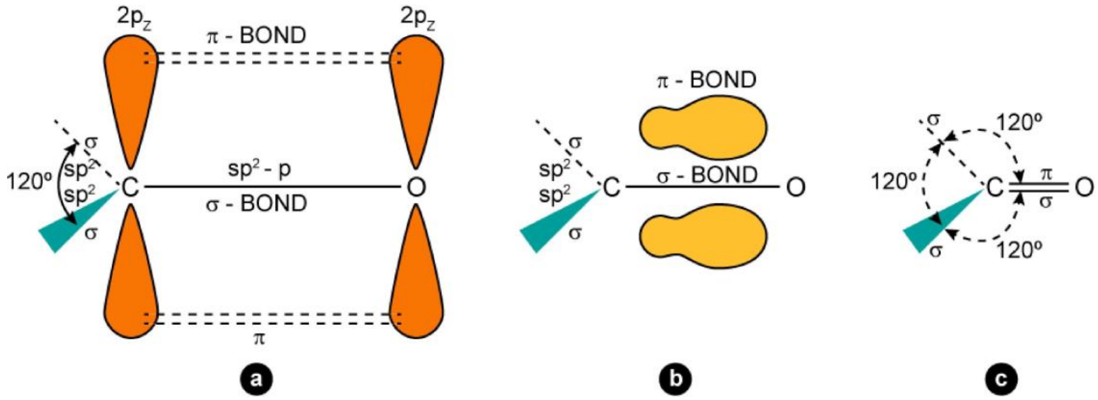
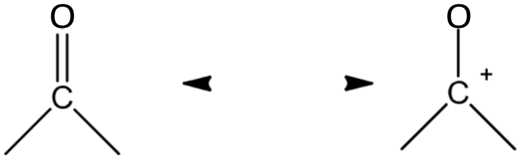
-+



Nature

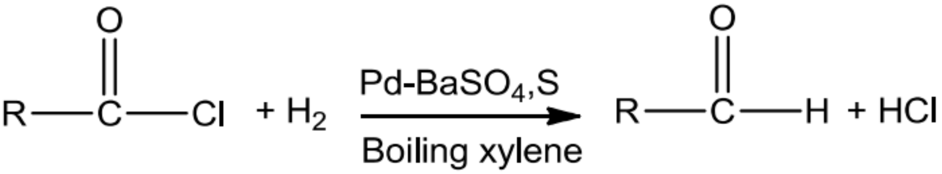
- The C-O double bond is polarised since oxygen is electronegative than carbon.
- So the carbonyl carbon is an electrophilic centre and the carbonyl oxygen is a nucleophilic centre.
- The carbonyl compounds have substantial dipole moments and are polar than ethers.
- The high polarity of the carbonyl 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.



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

- ➢ **Stephen Reaction**

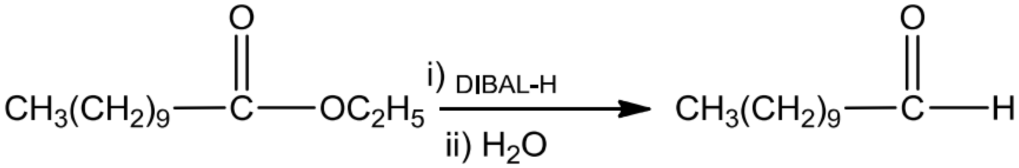
Nitriles on reduction with stannous chloride in the presence of HCl give imine which on hydrolysisgives corresponding aldehyde.

$$RCN + SnCl_2 + HCl \longrightarrow RCH{=}NH \xrightarrow{H_3O^+} RCHO$$

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

$$RCN \xrightarrow[\text{ii) } H_2O]{\text{i) } AlH(i\text{-}Bu)_2} R\text{-}CHO$$

Esters can also be reduced to aldehydes with DIBAL-H



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

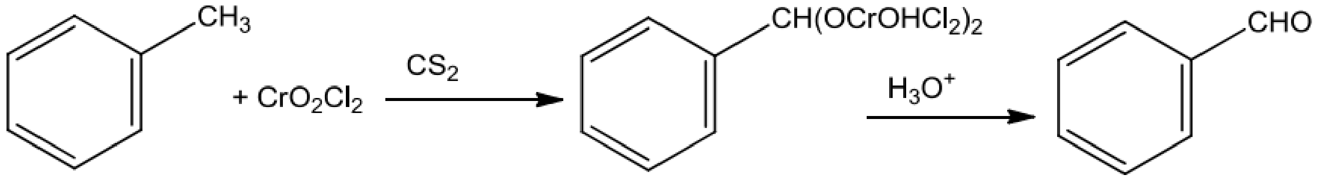
From Aromatic Hydrocarbons

Aromatic aldehydes can be prepared using the following methods.

I) By Oxidation of Methylbenzene

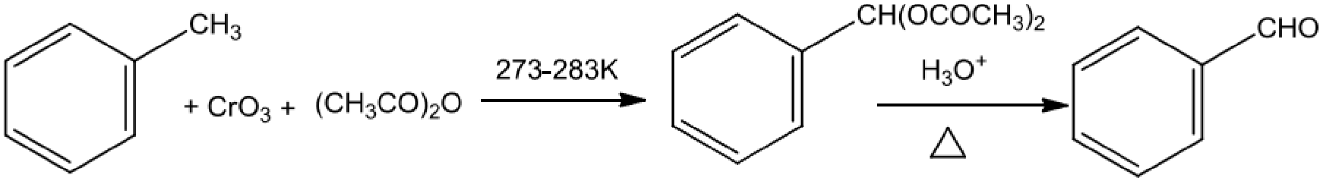
Etard Reaction (Use of Chromyl Chloride)

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



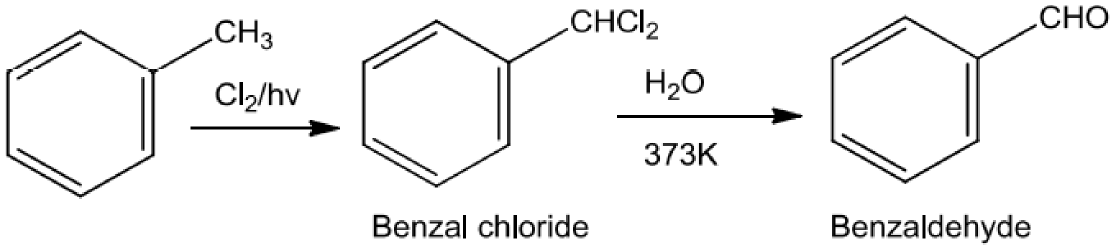
Use of Chromic oxide(CrO_3)

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



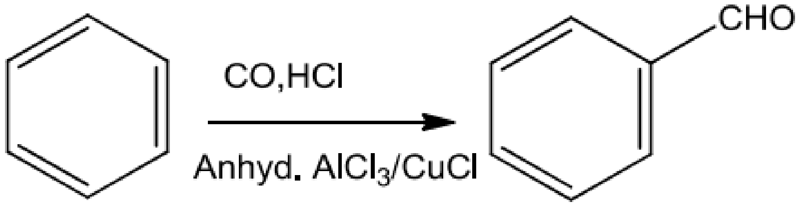
Side Chain Chlorination

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



Gatterman — Koch Reaction

Benzene or toluene on treatment with CO and HCl in the presence of AlCl3 or CuCl givesbenzaldehyde or p-tolualdehyde.

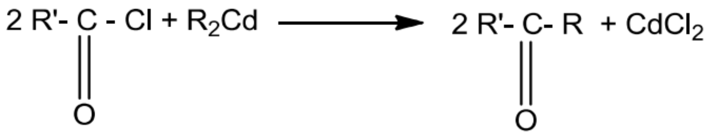


Preparation of Ketones

- ### From Acid chlorides or Acyl chlorides

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

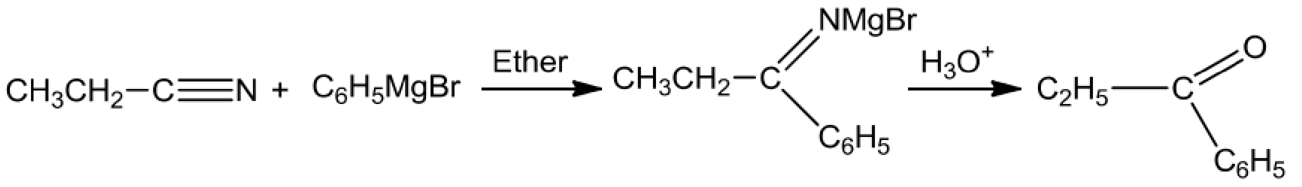
$$2\,R\text{-}Mg\text{-}X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$



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

- ### From Nitriles

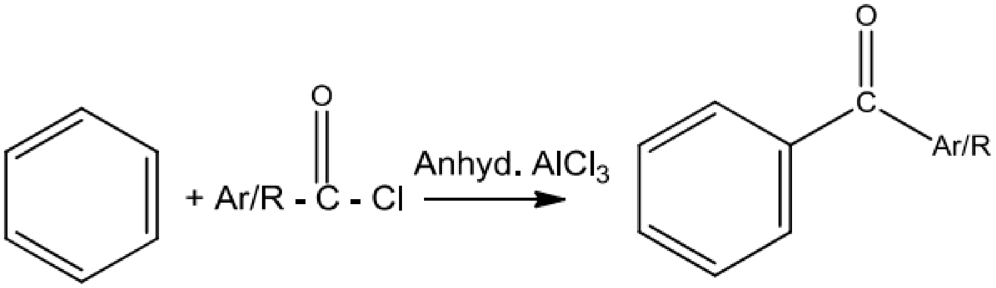
Nitriles on treatment with Grignard reagent followed by hydrolysis yields a ketone



Propiophenone
(1-Phenylpropanone)

- ### From Benzenes or Substituted Benzenes

Benzene or substituted benzene on treatment with acid chloride in the presence of anhydrous AlCl3 gives the corresponding ketone and this reaction is known as Friedel-Crafts acylation reaction.



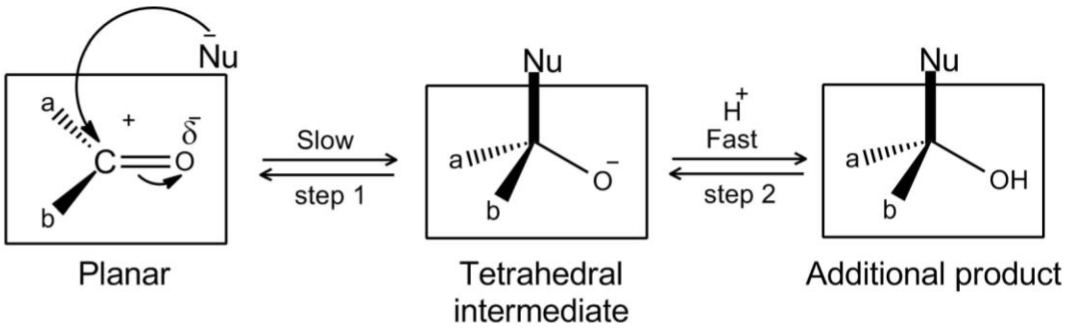
Chemical Reactions

➢ 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 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

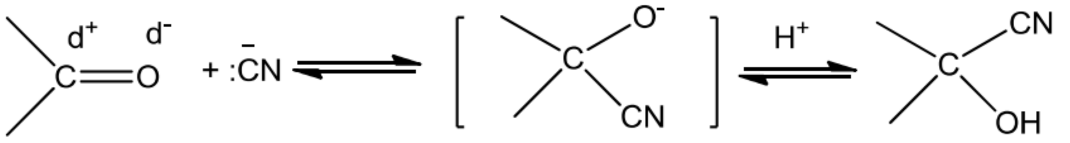
- Aldehydes are more reactive than ketones in nucleophilic reactions because of two reasons:
- Sterically, it is the presence of two relatively large groups in ketones that hinder the approach of nucleophile to carbonyl carbon than in aldehydes which have only one such substituent.
- Electronically,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

$$HCN + OH^- \rightleftharpoons :\bar{C}N + H_2O$$

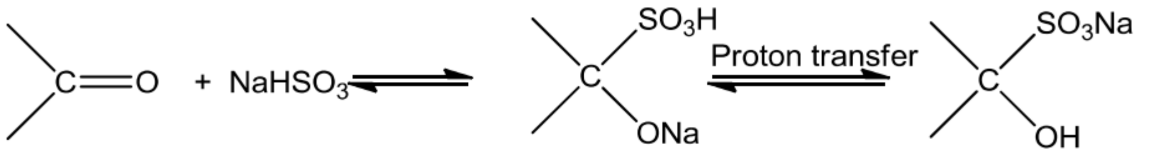


Tetrahedral intermediate

Cyanohydrin

(b) Addition of Sodium Hydrogensulphite

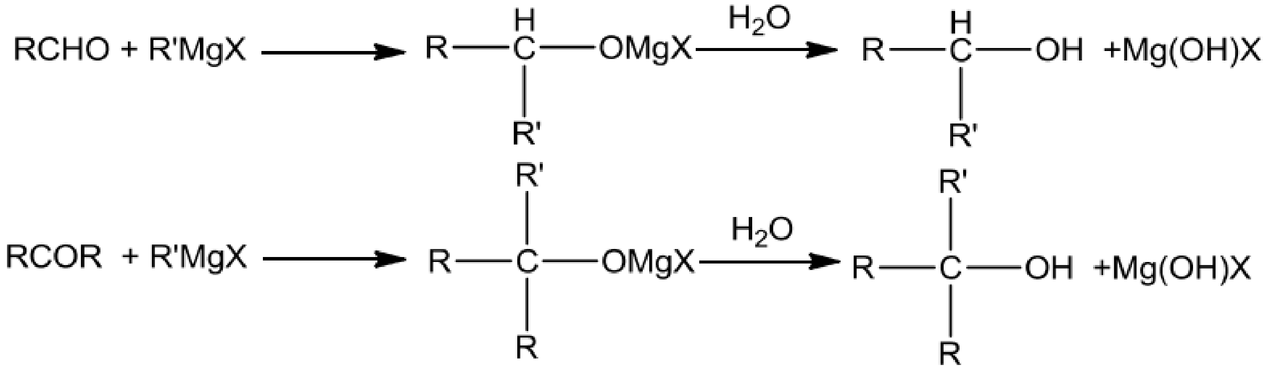
Sodium hydrogen sulphite when added to aldehydes and ketones yield addition products.



Bisulphite addition compound

(c) Addition of Grignard Reagents

Grignard reagents on reacting with aldehydes and ketones yield alcohols.

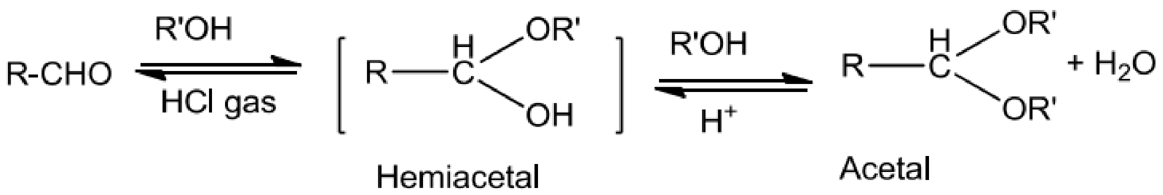


$$RCHO + R'MgX \longrightarrow R-\underset{R'}{\overset{H}{C}}-OMgX \xrightarrow{H_2O} R-\underset{R'}{\overset{H}{C}}-OH + Mg(OH)X$$

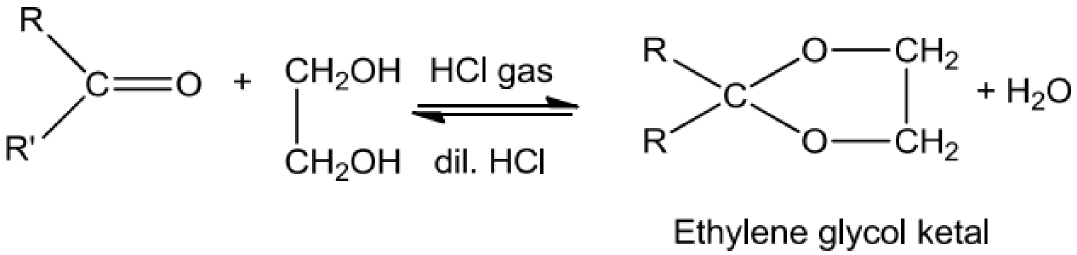
$$RCOR + R'MgX \longrightarrow R-\underset{R}{\overset{R'}{C}}-OMgX \xrightarrow{H_2O} R-\underset{R}{\overset{R'}{C}}-OH + Mg(OH)X$$

(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.

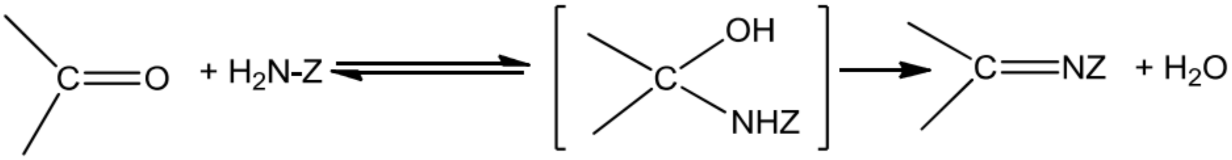


- Ketones also react with ethylene glycols under similar conditions to give ethylene glycol ketals.



(e)Addition of Ammonia and its Derivatives

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



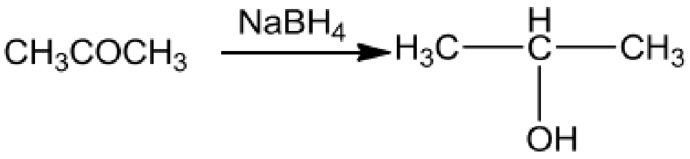
Z = Alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$, etc.

➢ Reduction

(i) Reduction to Alcohols

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

$$CH_3CHO + H_2 \xrightarrow{LiAlH_4} CH_3CH_2OH$$



$$CH_3COCH_3 \xrightarrow{NaBH_4} H_3C-\underset{OH}{\overset{H}{C}}-CH_3$$

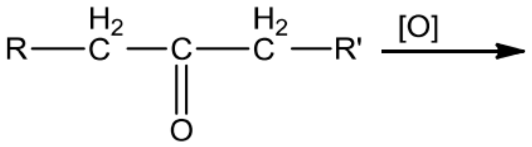
(ii) Reduction to Hydrocarbons

Aldehydes and ketones reduce to —CH_2 group on treatment with zinc-amalgam and conc. HCl [Clemmenson 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.

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

- 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.



$$\text{R}-\overset{H_2}{C}-\underset{\underset{O}{\|}}{C}-\overset{H_2}{C}-\text{R'} \xrightarrow{[O]} \text{R-COOH} + \text{R'-}CH_2\text{COOH}$$

(By cleavage of C_1-C_2 bond

$$\text{R-}CH_2\text{COOH} + \text{R'-COOH}$$

(By cleavage of C_2-C_3 bond)

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.

$$\text{RCHO} + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow \text{RCOO}^- + 2Ag + 2H_2O + 4NH_3$$

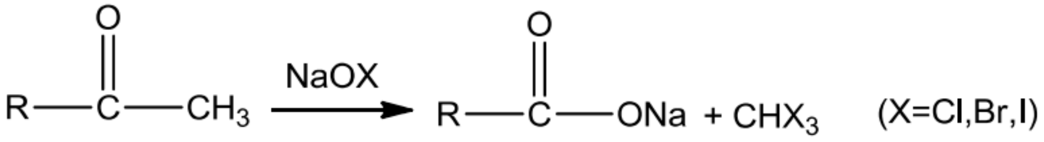
Fehling's test

- 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 notrespond to this test.

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

Haloform reaction

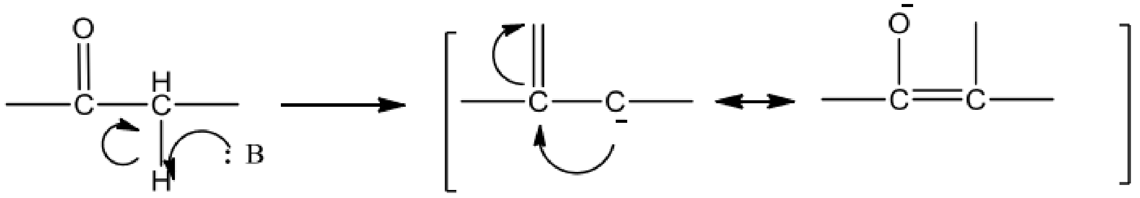
Aldehydes and ketones with at least one methyl group attached to the carbonyl carbon atom on oxidation with sodium hypohalite turn to sodium salts of corresponding acids with one carbon atomless than that of carbonyl compound. In this reaction, the methyl group is converted to haloform.



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

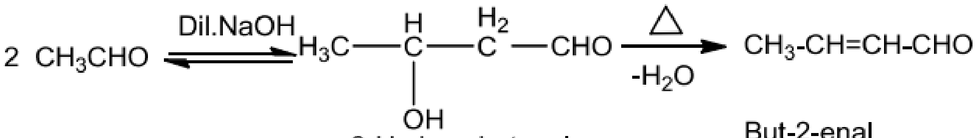
➢ Reactions due to a-hydrogen

- 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 effect of the carbonyl group and resonance stabilisation of the conjugate base.



(i) Aldol Condensation

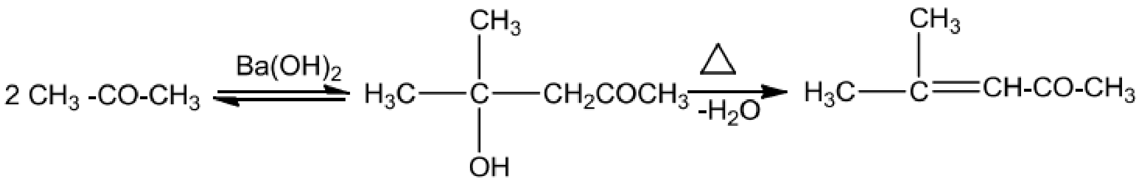
Aldehydes and ketones with at least one a-hydrogen undergo reaction in the presence of dilutealkali as catalyst to form §-hydroxy aldehydes (aldol) or §-hydroxy ketones (ketol) respectively.This is known as Aldol reaction.



$$2\ CH_3CHO \overset{Dil.NaOH}{\rightleftharpoons} H_3C-\underset{OH}{\overset{H}{C}}-\overset{H_2}{C}-CHO \xrightarrow[-H_2O]{\Delta} CH_3\text{-}CH=CH\text{-}CHO$$

3-Hydroxybutanal

But-2-enal
(Aldol condensation product)



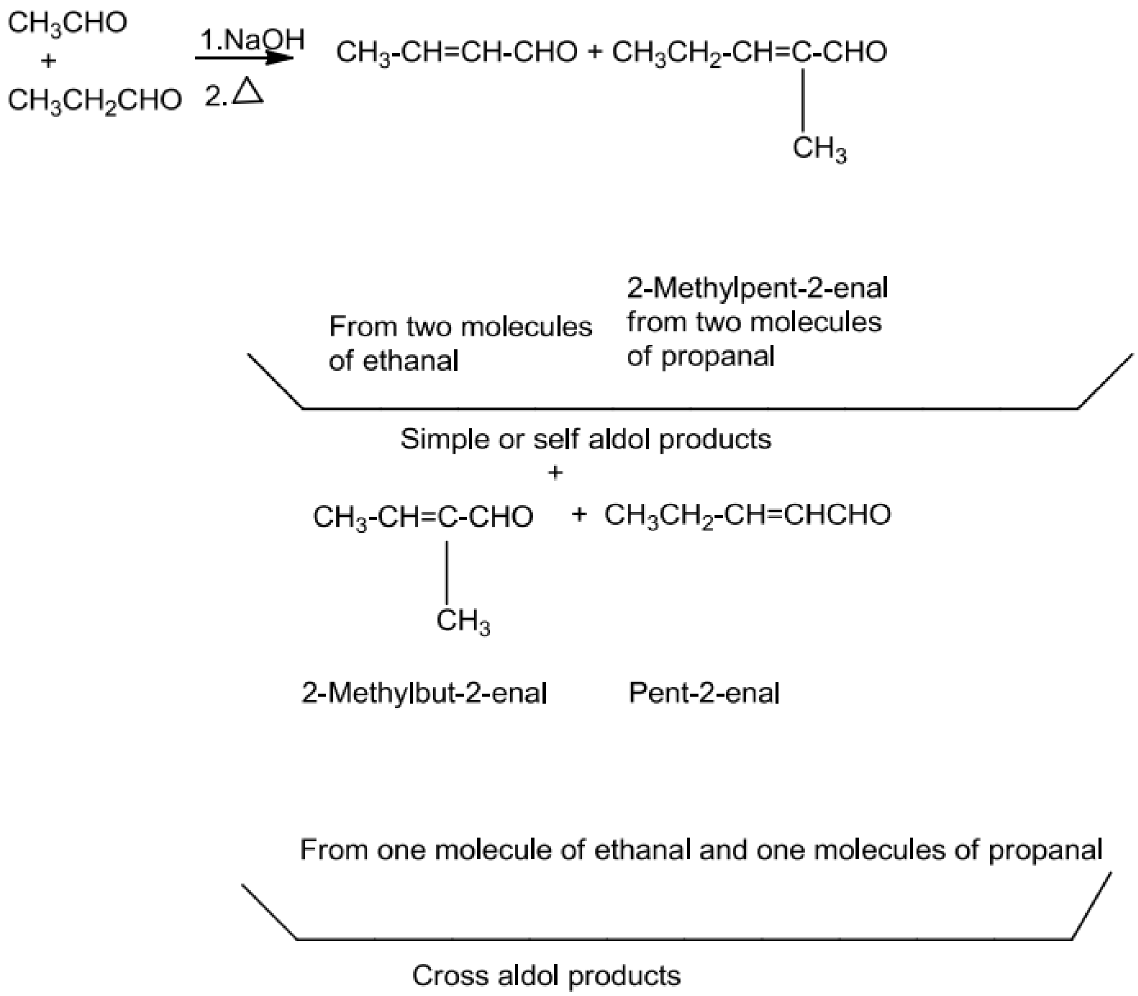
$$2\ CH_3\text{-}CO\text{-}CH_3 \overset{Ba(OH)_2}{\rightleftharpoons} H_3C-\underset{OH}{\overset{CH_3}{C}}-CH_2COCH_3 \xrightarrow[-H_2O]{\Delta} H_3C-\overset{CH_3}{C}=CH\text{-}CO\text{-}CH_3$$

(Ketol)
4-Hydroxy-4-methylpentan-2-one

4-Methylpent-3-en-2-one
(Aldol condensation product)

(ii) Cross Aldol Condensation

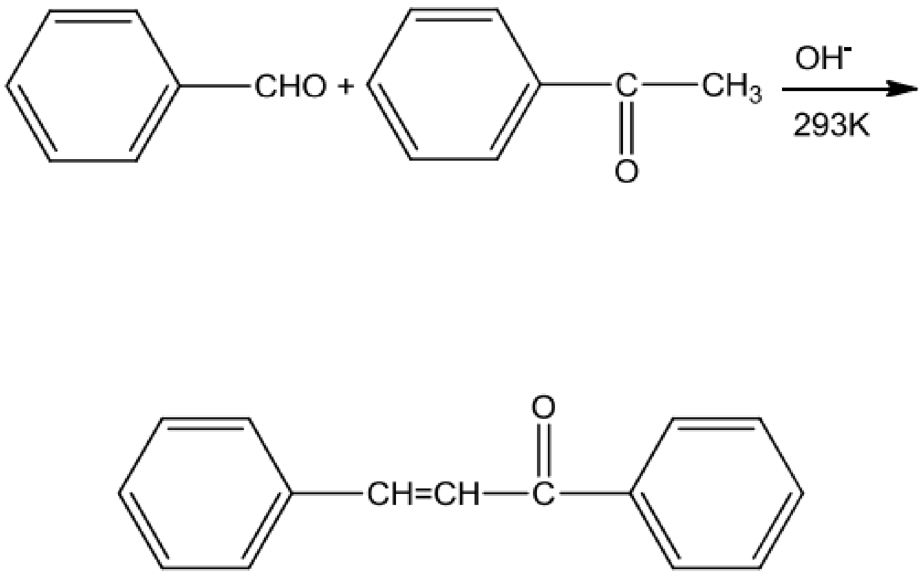
- In this reaction, two different aldehydes and/or ketones with a-hydrogen atoms reaction in the presence of dilute alkali as catalyst give a mixture of four products.



$$CH_3CHO + CH_3CH_2CHO \xrightarrow[2.\Delta]{1.NaOH} CH_3\text{-}CH{=}CH\text{-}CHO + CH_3CH_2\text{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}\text{-}CHO$$

$$+\ CH_3\text{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}\text{-}CHO + CH_3CH_2\text{-}CH{=}CHCHO$$

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

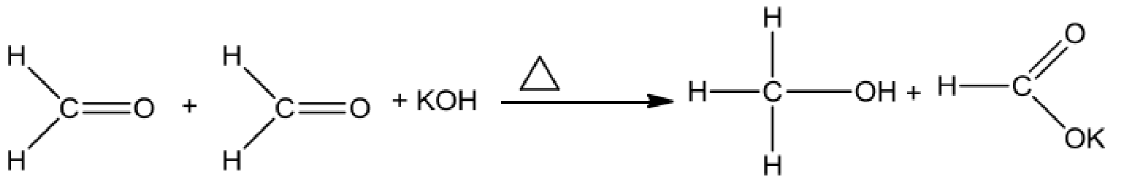


1,3-Diphenylprop-2-en-1-one
(Benzalacetophenone)
(Major product)

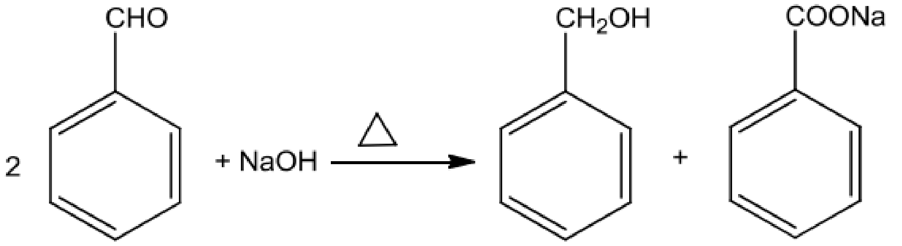
➢ Other Reactions

(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.



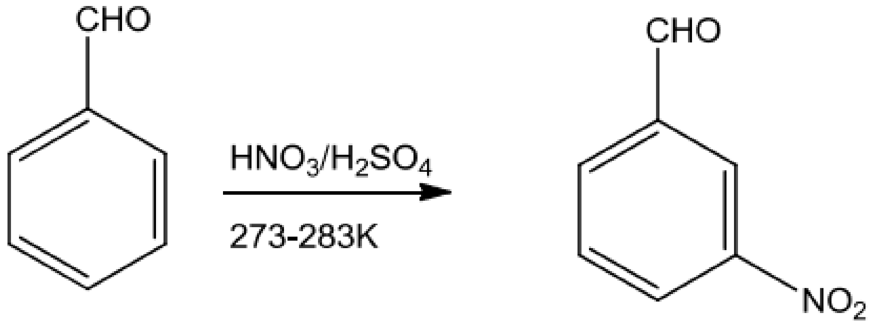
Formaldehyde Methanol Potassium formate



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.



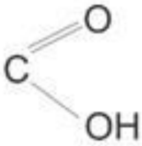
Benzaldehyde

m-Nitrobenzaldehyde

Carboxylic Acids

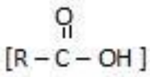
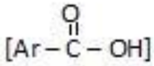
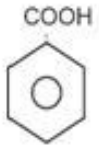
- The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids.

- The derivative compounds of carboxylic acid where carbon is attached to nitrogen and to halogens arecalled amides and acyl halides respectively.

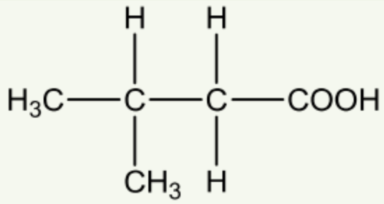
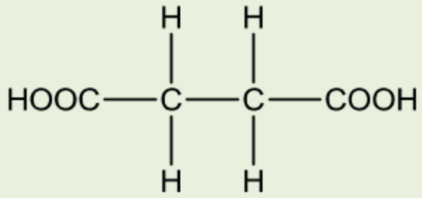
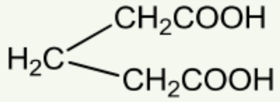
Functional group ⟶ 

[COOH]

General structure :

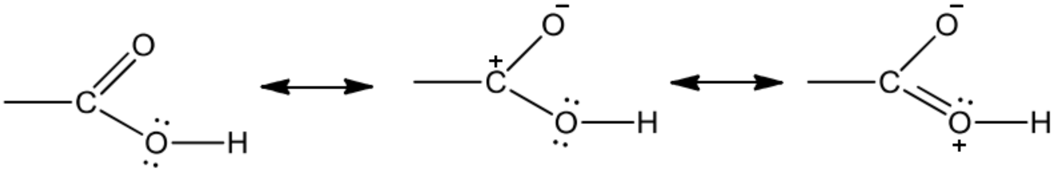
Aliphatic carboxylic acids	R COOH	 $[R-\overset{O}{\overset{\|}{C}}-OH]$
Aromatic carboxylic acid	Ar COOH	 $[Ar-\overset{O}{\overset{\|}{C}}-OH]$
Lower Members	HCOOH	(formic acid) Methanoic acid
	CH_3COOH	Ethanoic acid (acetic acid)
		Benzoic acid
	 $\underset{COOH}{\overset{COOH}{\|}}$	Oxalic acid

Nomenclature of Carbonyl Group

Structure	Common Name	IUPAC Name
HCOOH	Formic acid	Methanoic acid
 $H_3C-CH(CH_3)-CH_2-COOH$	Isovaleric acid	3-Methylbutanoic acid
 $HOOC-CH_2-CH_2-COOH$	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 permanganate in neutral, acidic or alkaline media or by potassium dichromate and chromium trioxide in acidic media to give carboxylic acid.

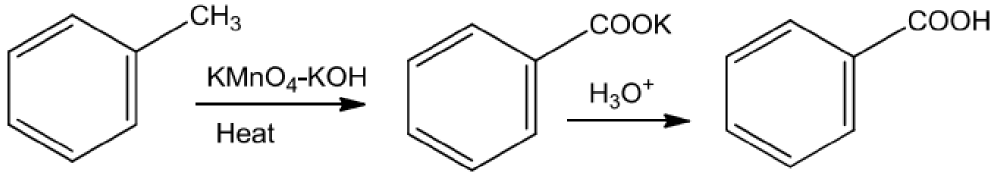
$$RCH_2OH \xrightarrow[\text{ii) } H_3O^+]{\text{i)Alkaline } KMnO_4} RCOOH$$

- 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.



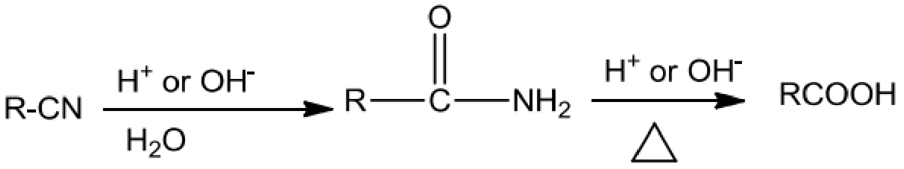
Benzoic acid

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

$$RCH{=}CHR \xrightarrow{K_2Cr_2O_7, H_2SO_4} 2R\text{-}COOH$$

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.

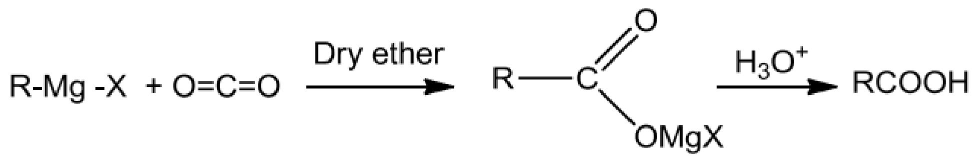


$$R\text{-}CN \xrightarrow[H_2O]{H^+ \text{ or } OH^-} R{-}\overset{\overset{\large O}{\|}}{C}{-}NH_2 \xrightarrow[\Delta]{H^+ \text{ or } OH^-} RCOOH$$

$$CH_3CONH_2 \xrightarrow[\Delta]{H_3O^+} CH_3COOH + NH_3$$

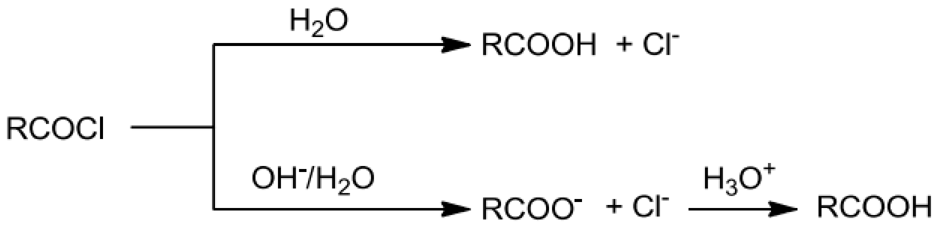
From Grignard Reagents

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

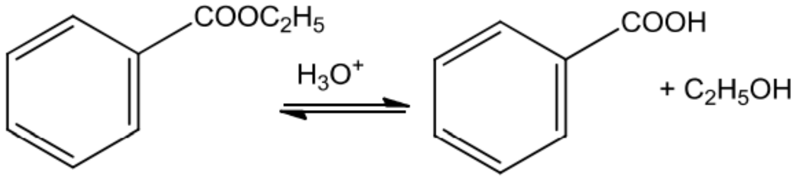
- Acid chlorides on hydrolysis with water give carboxylic acids or readily undergo hydrolysis with aqueous base to give carboxylate ions which on acidification give corresponding carboxylic acids.
- Anhydrides on the other hand undergo hydrolysis with water to give corresponding acids.



$$\underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{2C_6H_5COOH}$$

➢ From Esters

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



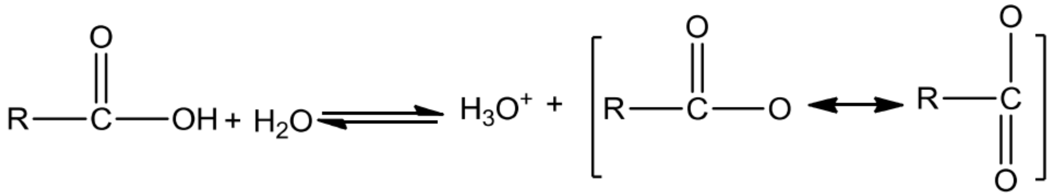
Benzoic acid

$$\begin{tikzcd}
CH_3CH_2CH_2COOC_2H_5 \arrow[r, phantom, "\overset{NaOH}{\rightleftharpoons}"] & CH_3CH_2CH_2COONa + C_2H_5OH \arrow[d, "H_3O^+"] \\
& CH_3CH_2CH_2COOH
\end{tikzcd}$$

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:

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

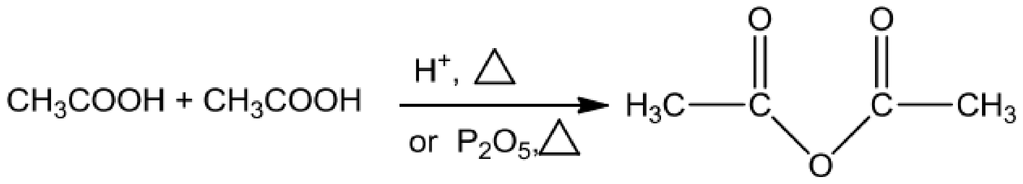
(a) Effect of the number of electron-withdrawing groups: As the number of electron-withdrawing groups increases, the —I effect increases, increasing the acid strength.

(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 H2SO4 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 HCl gas as a catalyst.

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

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.

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

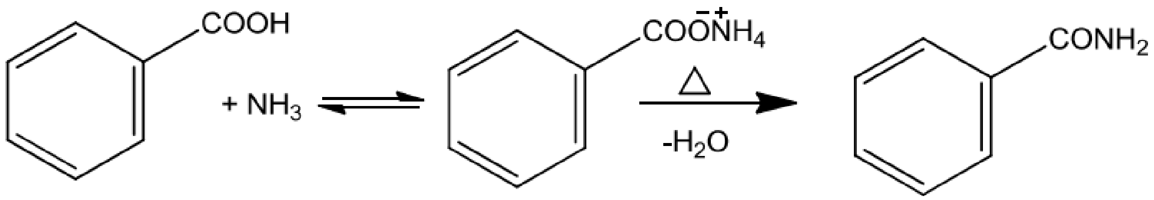
$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$

$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$

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.

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

2. **Decarboxylation**

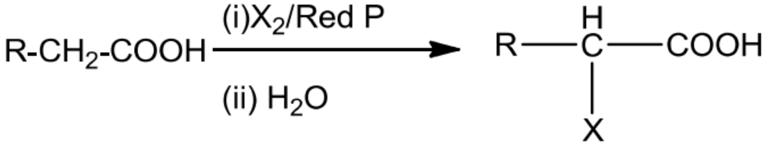
   Sodium salts of carboxylic acids on heating with sodalime lose carbon dioxide to formhydrocarbons. The reaction is known as decarboxylation.

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

Substitution reactions in the Hydrocarbon

1. **Halogenation**

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



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

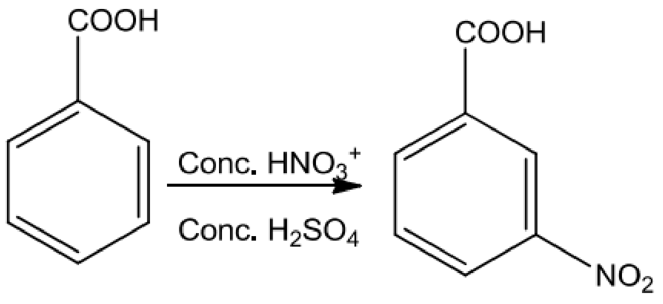
X=Cl,Br

α– Halocarboxylic acid

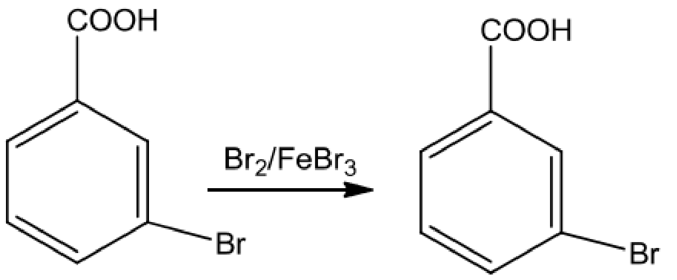
2. **Ring Substitution**

   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 deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.



m-nitrobenzoic acid



m-Bromobenzoic acid

Comparison of acidic strength of alcohol , phenols and carboxylic acid

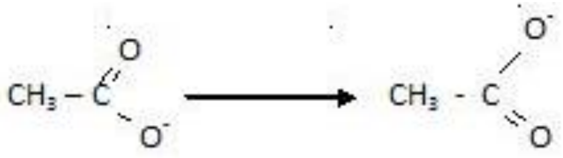
If we compare Alcohol and carboxylic acid, we see that :

In case of alcohols $ROH \longleftrightarrow RO^- + H^+$

Alkokxy gp.

In case of carboxylic acid $CH_3COOH \longleftrightarrow CH_3COO^- + H^+$

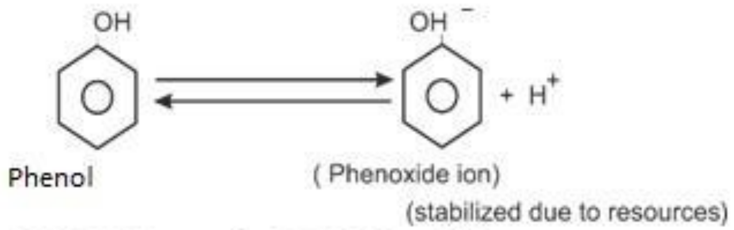
It's seen that more the ion is stablized , more the reaction will be favoured in found direction.Below you can see carboxylic acid is resonance stabilized. So, it is more stable and on the other hand the R group attached to O- in alcohol intensifies its charge. Hence, the stability is lowered in mparison to carboxylic acid.



Therefore, COOH is stronger acid than alcohol.

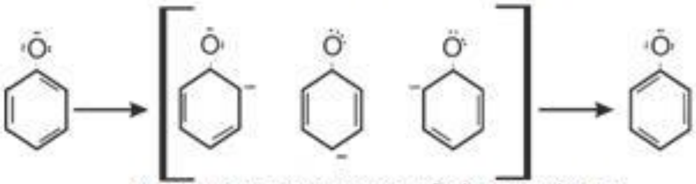
Phenols and carboxylic acid : Acidic character

Similarly, if we look for phenoxide ion and carboxylate ion that is formed by phenol and carboxylic acid after loosing hydrogen ion, we can easily make out that carboxylate ion is more stabilized. In it negative charge resides on electronegative ion (resonating structure) whereas in case of phenoxide ion the negative charge is on carbon.let's see. the structures below :



$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Acetic acid   acetate ion   hydrogen ion



Resonating structures of phenoxide ion

Resonating structures of acetate ion

That is the reason ,carboxylic acid is stronger than phenols .

Reactions to prove acidic character of carboxylic acid

Reaction with metal

$CH_3COOH + Na \qquad CH_3COONa + H_2$

Acetic acid sodium   Sodium acetate hydrogen

- Rxn with alkalis

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

Acetic acid sodium hydroxide sodium acetate water

- Rxn with carbonates and bicarbonates

$CH_3COOH + Na_2CO_3 \longrightarrow CH_3COONa + H_2O + CO_2$

Ethanoic acid sodium carbonate sodium acetate water

$CH_3COOH + Na_2CO_3 \longrightarrow CH_3COONa + H_2O + CO_2$

Ethanoic acid sodium carbonate sodium acetate water

Reaction involving OH group:

In this we react carboxylic acid with compounds like With PCl_5, PCl_3, $SOCl_2$.

$$\underset{\text{ethanoic acid}}{CH_3COOH} + \underset{\text{phosphorous pentahalide}}{PCl_5} \longrightarrow \underset{\text{ethanoyl chloride}}{CH_3COCl} + POCL_3 + \underset{\text{hydrogen chloride}}{HCl}$$

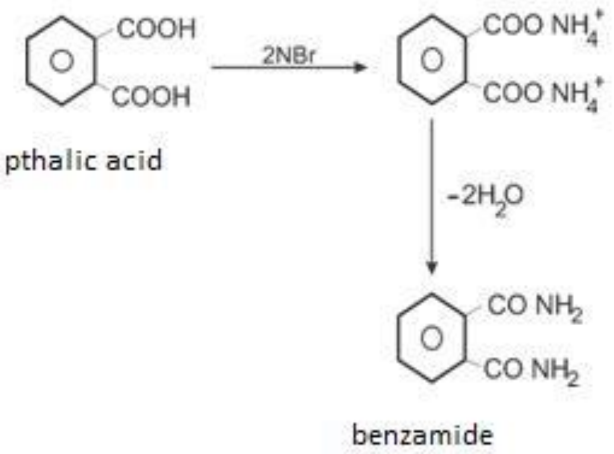
$$\underset{\text{ethanoic acid}}{CH_3COOH} \xrightarrow{PCl_3} \underset{\text{ethanoyl chloride}}{CH_3COCl} + H_3PO_3$$

$$\underset{\text{ethanoic acid}}{CH_3COOH} \xrightarrow{SOCl_2} \underset{\text{ethanoyl chloride}}{CH_3COCl} + SO_2 + HCl$$

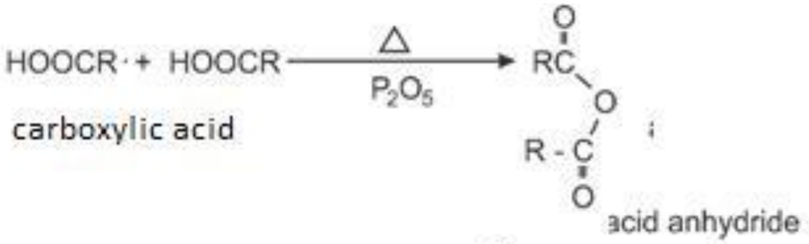
Reaction with alcohol : Esterification

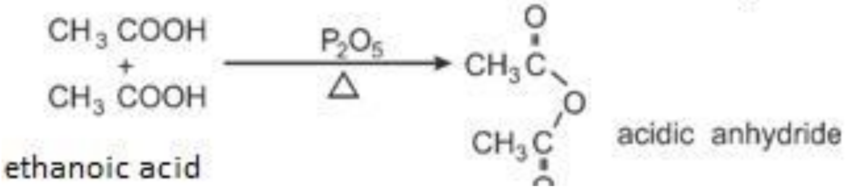
$$\underset{\text{Alcohol}}{ROH} + \underset{\text{carboxylic acid}}{RCOOH} \xrightarrow{H_2SO_4} \underset{\text{(ester)}}{RCOOR} + H_2O$$

Reaction with NH₃



Formation of acid anhydride





3.Reaction involving COOH group

- Decarboxyation --- Removal of CO_2 group

$CH_3COOH + Na \rightarrow CH_3COONa + H_2$

Ethanoic acid sodium sodium acetate

$$CH_3COONa + NaOH \xrightarrow{(Cao)} CH_4 + Na_2CO_3$$

Sodium acetate sodium hydroxide methane sodium carbonate

- Electrolytic decarboxylation

$$CH_3COOH \xrightarrow{e.c} CH_3COO^- + K^+$$

ethanoic acid acetate ion potassium ion

At anode

$2CH_3COO^- - 2e^-$

$CH_3\text{-}CH_3 + CO_2$

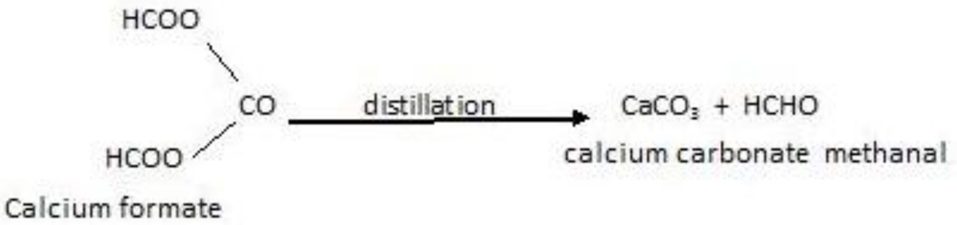
ethane

at cathode

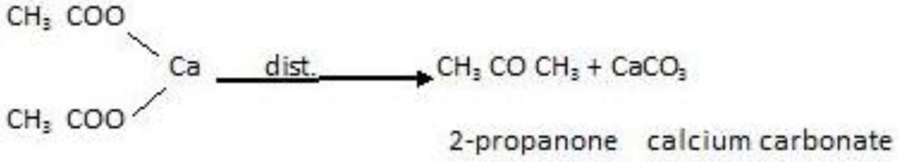
$K^+ + 1e^- \rightarrow K$

potassium ion

Reaction of carboxylic salt of Calcium



Calcium formate



Partial Reduction

The acids on reduction in presence of reducing agents like are Li AlH4 etc forms alcohols that is :

$$RCOOH \xrightarrow[H_2]{Li\ ALH_4} RCOH$$

carboxylic acid alcohol

$$CH_3COOH \xrightarrow[H_2]{LiALH_4} CH_3CH_2OH$$

ethanoic acid ethanol

Complete reduction : When complete reduction is carried out, it forms alkane in presence of red Phosphorous that is :

$$RCOOH + HI \xrightarrow{\text{Red P}} RCH_3 + I_2$$

Carboxylic acid hydrogen iodide alkane iodine

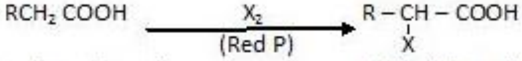
Special name reactions

❖ Borodine Hunsdicker Reaction

$$CH_3COOAg + Br_2 \xrightarrow{CCl_4} CH_3Br + AgBr + CO_2$$

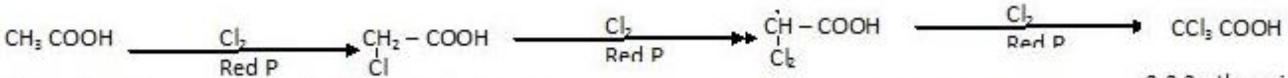
Silveracetate bromine methyl bromide silverbromide

❖ Hellvolhart - Zelincky Reaction



$$RCH_2COOH \xrightarrow[\text{(Red P)}]{X_2} R-\underset{X}{CH}-COOH$$

Carboxylic acid alpha haloacid

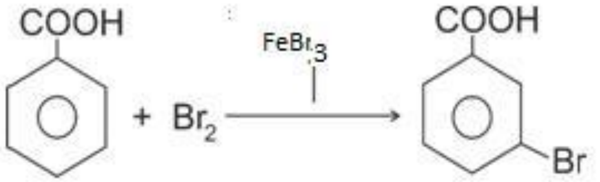


$$CH_3COOH \xrightarrow[\text{Red P}]{Cl_2} \underset{Cl}{CH_2}-COOH \xrightarrow[\text{Red P}]{Cl_2} \underset{Cl_2}{CH}-COOH \xrightarrow[\text{Red P}]{Cl_2} CCl_3COOH$$

Ethanoic acid 2 chloro ethanoic acid 2,2 dichloro ethanoic acid 2,2,2 ethanoic acid

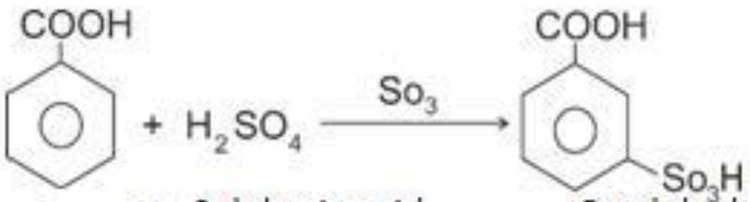
Ring subsitution reactions :

Bromination



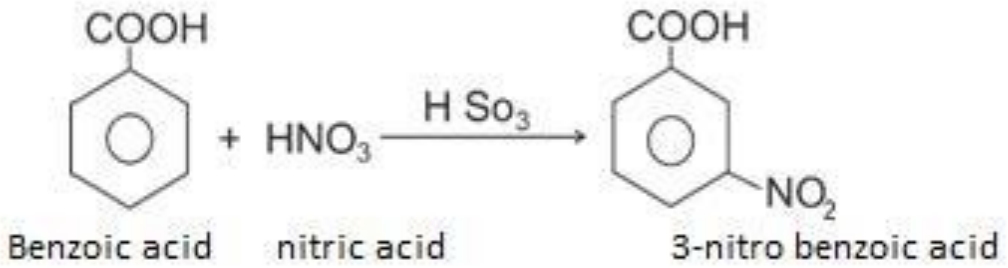
Benzoic acid bromine 3-bromo benzoic acid

Sulphonation



Benzoic acid Sulphuric acid 3-sulpho benzoic acid

Nitration



Uses of carboxylic acid

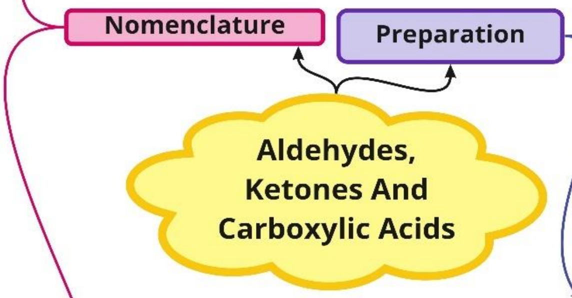
Methanoic acid is used as coagulating agent in rubber industry.

Benzoic acid is used as antiseptic and also in perfumery.

Ethanoic acid is used as solvent and also in cooking as vinegar and much more.

Reaction involving COOH group

Class : 12th Chemistry
Chapter-12 : Aldehydes, Ketones And Carboxylic Acids (Part_1)



Aldehydes, Ketones And Carboxylic Acids

Nomenclature

Preparation

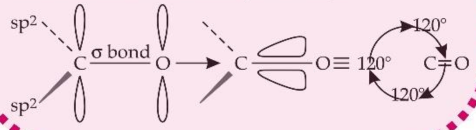
Aldehydes and Ketones

Common names :

- Replace corresponding carboxylic acids with aldehyde
- Alkyl phenyl ketones by adding acyl group as prefix to phenone.

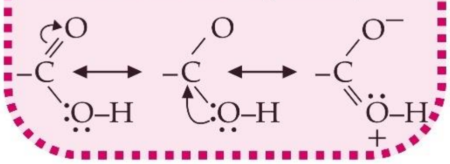
IUPAC names :

- Replacing –e with –al and –one as required.
- Structure of Carbonyl Group



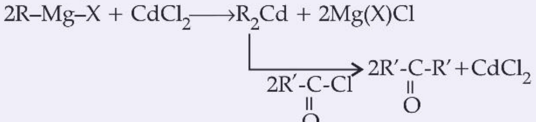
Carboxylic Acids

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



KETONES

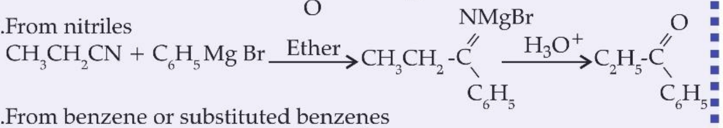
1.From acyl chloride



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

$$R_2Cd \xrightarrow{2R'\text{-}CO\text{-}Cl} 2R'\text{-}CO\text{-}R' + CdCl_2$$

2.From nitriles

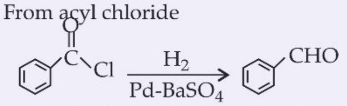


$$CH_3CH_2CN + C_6H_5MgBr \xrightarrow{Ether} CH_3CH_2\text{-}C(=NMgBr)\text{-}C_6H_5 \xrightarrow{H_3O^+} C_2H_5\text{-}C(=O)\text{-}C_6H_5$$

3.From benzene or substituted benzenes

ALDEHYDES

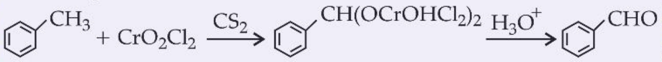
1. From acyl chloride

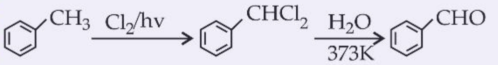


2. From nitriles and esters : Stephen reaction

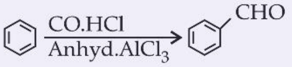
$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3O^+} R\,CHO$$

3. From hydrocarbons : Etard reaction





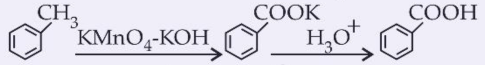
Gratterman – Koch reaction



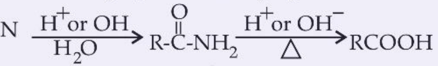
Carboxylic Acids

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

2.From alkylbenzine

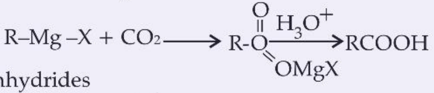


3.From nitriles and amides



$$R\text{–}CN \xrightarrow[H_2O]{H^+ or\ OH} R\text{-}C(=O)\text{-}NH_2 \xrightarrow[\Delta]{H^+ or\ OH^-} RCOOH$$

4.From Grignard reagents



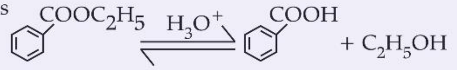
$$R\text{–}Mg\text{–}X + CO_2 \longrightarrow R\text{-}C(=O)\text{-}OMgX \xrightarrow{H_3O^+} RCOOH$$

5.From acyl halides and anhydrides

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

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

6.From esters



$$\begin{tikzcd} CH_3CH_2CH_2COOC_2H_5 \arrow[r, shift left, "NaOH"] & CH_3CH_2CH_2COONa + C_2H_5OH \arrow[l, shift left] \arrow[d, "H_3O^+"] \\ & CH_3CH_2CH_2COOH \end{tikzcd}$$

Class : 12th Chemistry
Chapter-12 : Aldehydes, Ketones And Carboxylic Acids (Part_2)

Aldehydes, Ketones And Carboxylic Acids

Properties

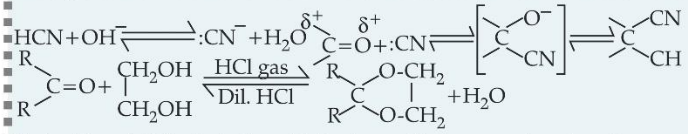
ALDEHYDES AND KETONES:

(i) Physical:

Boiling points are higher than hydrocarbons and ethers of comparable molecular masses.

(ii)Chemical :Nucleophilic addition reactions :

Aldehydes are more reactive than ketones due to steric and electronic reasons.



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

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

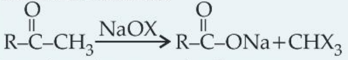
$>C=O \xrightarrow[-H_2O]{NH_2NH_2} >C=NNH_2 \xrightarrow[Heat]{KOH/Ethylene\ glycol} >CH_2 + N_2$ (Wolf-Kishner)

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

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

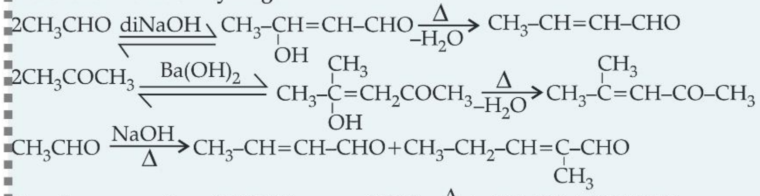
Fehling's test : $RCHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + Cu_2O + 3H_2O$
Red brown ppt

Haloform reaction:



$$R\text{–}\overset{\overset{O}{\|}}{C}\text{–}CH_3 \xrightarrow{NaOX} R\text{–}\overset{\overset{O}{\|}}{C}\text{–}ONa + CHX_3$$

Reactions due to α - hydrogen:



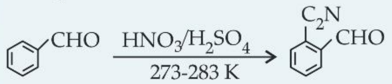
$$2CH_3CHO \underset{}{\overset{diNaOH}{\rightleftharpoons}} CH_3\text{–}\underset{\underset{OH}{|}}{CH}\text{=}CH\text{–}CHO \xrightarrow[-H_2O]{\Delta} CH_3\text{–}CH\text{=}CH\text{–}CHO$$

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

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

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

Electrophilic substitution reaction:



Carboxylic acids:

(i) Physical:

Higher boiling points than aldehydes, ketones or alcohols.
Solubility decreases with increasing number of C atoms

(ii)Chemical :

$2RCOOH + 2Na \longrightarrow 2RCOONa + H_2$

Forms corresponding anhydride on heating with mineral acid

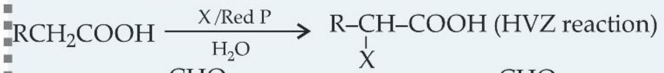
$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$

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

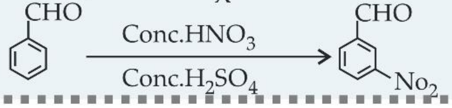
$CH_3COOH + NH_3 \rightleftharpoons CH_3COONH_4 \xrightarrow[-H_2O]{\Delta} CH_3CONH_2$

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

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



$$RCH_2COOH \xrightarrow[H_2O]{X/Red\ P} R\text{–}\underset{\underset{X}{|}}{CH}\text{–}COOH \text{ (HVZ reaction)}$$



Uses

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

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

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 add
(b) Acetic acid
(c) Propionic add
(d) n-butyric acid

Question 3. The acid which does not contain-COOH group is.
(a) Ethanoic acid
(b) Lactic acid
(c) Picric add
(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

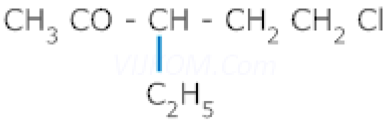
Question 6. Methyl ketones are usually characterised through
(a) Tollen's reagent
(b) Iodoform test
(c) Schiff'stest
(d) Benedict solution test.

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

Question 9.An alkene C_7H_{14} on reductive ozonolysis gives an aldehyde with formula C_3H_6O and and a ketone. The ketone is
(a) 2-butanone
(b) 2-pentanone
(c) 3-pentanone
(d) propanone
Question 10. Acetaldol is a condensation product of
(a) two molecules of ethanal
(b) two molecules of propanone
(c) ethanal and methanal
(d) ethanal and propanone.

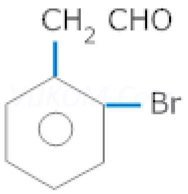
Very Short Questions-

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 C_3H_6O . 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



$CH_3\,CO-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2\,CH_2\,Cl$

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 phenol.

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 $C_5H_{10}O$ 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. Acompound A with molecular formula $C_5H_{12}O$ on oxidation forms compound B with molecular formula $C_5H_{10}O$. 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_5H_{12} . 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.

4. 

$$CH_3COOH \xrightarrow{Cl_2/redP} \underline{(A)} \xrightarrow{alc.NH_3} \underline{(B)}$$

5.

$$C_6H_5CONH_2 \xrightarrow{Br_2/KOH} \textcircled{A} \xrightarrow{NaNO_2/HCl} \textcircled{B} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{} \textcircled{C}$$

6.

$$CH_3Cl \xrightarrow{KCN} \textcircled{A} \xrightarrow{H_2O/H^+} \textcircled{B} \xrightarrow{PCl_5} \textcircled{C}$$

7. $CH_3COOH \xrightarrow{Ca(OH)_2} (A) \xrightarrow{\text{dry distribution}} (B) \xrightarrow{I_2/NaOH} (C)$

8. $CH_3COCH_3 \xrightarrow{LiAlH_4} X \xrightarrow{SOCl_2} Y \xrightarrow{alc.-KOH} Z$

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.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) 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.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

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

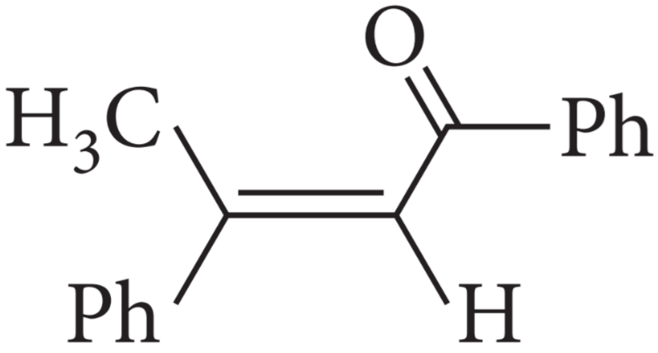
Reason: Increased strength is due to ortho-effect.

Case Study Questions-

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

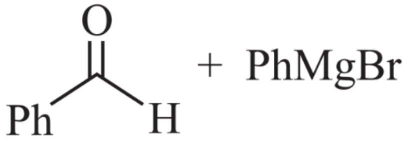
A tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and a compound I, whereas K on reaction with KOH gives only M.

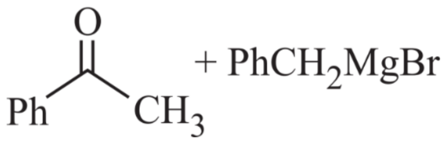
$M =$

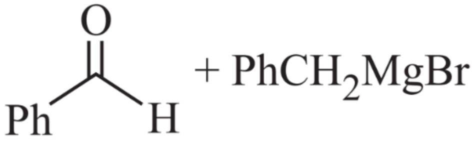


The following questions are multiple choice questions. Choose the most appropriate answer:

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

(a)


(b)


(c)


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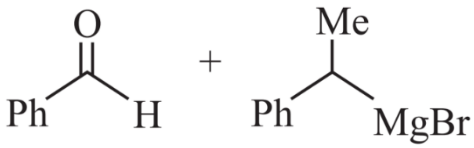
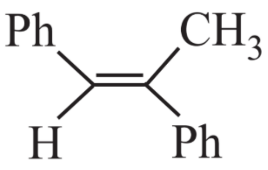
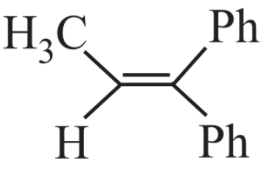


(ii) The structure of compound I is:

(a)


(b)


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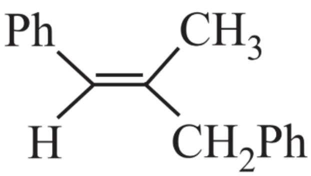
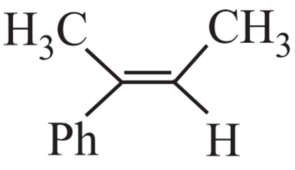


(d)


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

- a) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$
- b) $PhCHO$, $PhCH_2CHO$ and $PhCOO^-K^+$
- c) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$
- 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:

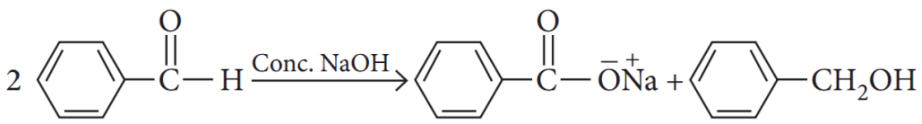
- a) Cinnamic acid.
- b) Crotonic acid.
- c) Maleic acid.
- d) Benzylic acid.

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

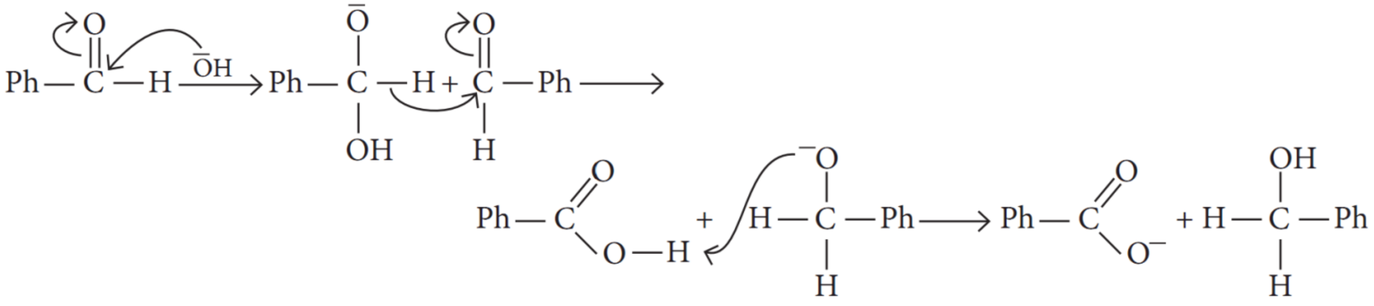
- a) It reacts with alkaline KMn04 followed by acidic hydrolysis and forms benzoic acid.
- b) It reacts with iodine and NaOH to form triiodomethane.
- c) It is prepared by the reaction of benzene with benzoyl chloride in presence of anhydrous aluminium chloride.
- d) It reacts with freshly prepared ammoniacal silver nitrate solution.

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

When an aldehyde with no et-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) C_6H_5CHO
d) $C_6H_5CH_2CHO$

(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 compounds is:

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

(iv) In Cannizzaro reaction given below:

$$2\mathrm{PhCHO} \xrightarrow{\overset{-}{\mathrm{O}}\mathrm{H}} \mathrm{PhCH_2} + \mathrm{OH} + \mathrm{PhCO_2^-}$$

the slowest step is:

a) The attack ^-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-

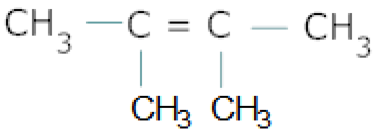
1. Answer: (b) Acetic acid
2. Answer: (a) Formic add
3. Answer: (c) Picric add
4. Answer: (d) alcohol and ester.
5. Answer: (c) Diacetoneamine
6. Answer: (b) Iodoform test
7. Answer: (c) Dimethyl cadmium
8. Answer: (b) α-haloacid
9. Answer: (a) 2-butanone
10. Answer: (a) two molecules of ethanal

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.



$CH_3-\underset{CH_3}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-CH_3$

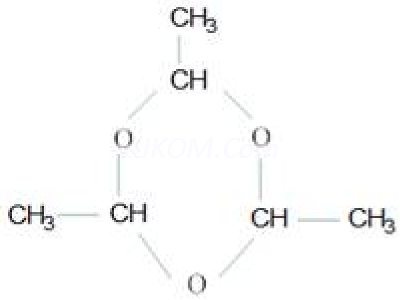
2, 3 - dimethyl but - 2 - ene

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 CH_3CH_2CHO . 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 paraldchyde 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.

$RCONH_2 + Br_2 + KOH \rightarrow RNH_2 + KBr + K_2CO_3 + H_2O$

Ans 9. 5-Chloro -3- ethylpentan -2-one.
Ans 10. 2 –(2-bromophenyl) ethanal

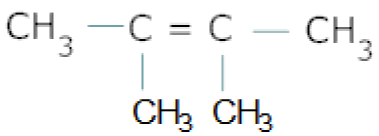
Short Answers-

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 can not. 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. More over the +I effect of alkyl groups reduces the electophilicity 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.



$$CH_3-\underset{CH_3}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-CH_3$$

2, 3 - dimethyl but - 2 - ene

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.

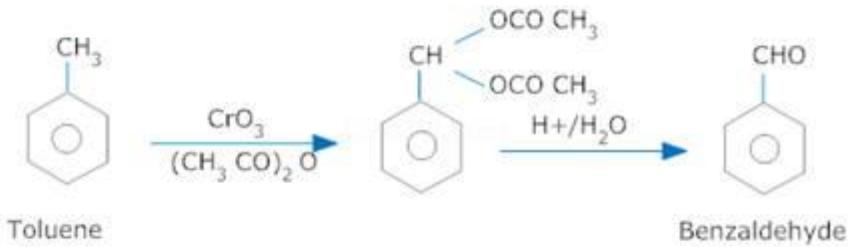
Ans 7. Formaldehyde does not have any $BaSO_4$ – hydrogen and therefore it can not show aldol condensation.

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

C_3H_6O

Therefore fluoroacetic acid is a stronger acid than acetic acid.

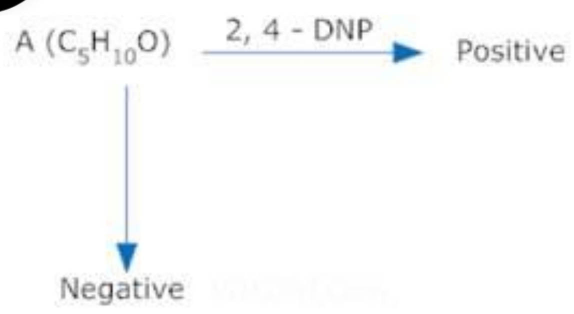
Ans 9.

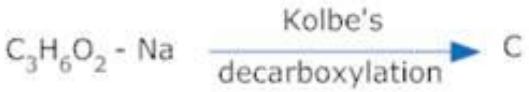


Ans 10.

Long Answers-

Ans 1.





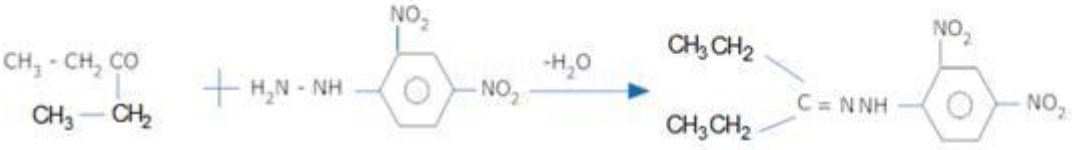
As the compound A gives a positive 2, 4-DNP test but negative Tollen's test, it is a ketone. Since on oxidation, it gives an acid B, of molecular formula $C_3H_6O_2$, it is $CH_3CH_2COCH_2CH_3$ and B is CH_3CH_2COOH. As C is obtained by Kolbes decarboxylation of B, C is $CH_3CH_2\ CH_2\ CH_3$.

Therefore A = Pentan -3 one, $CH_3CH_2CO\ CH_2CH_3$

B = Propanoic acid CH_3CH_2COOH

And C = Butane $CH_3CH_2CH_2CH_3$

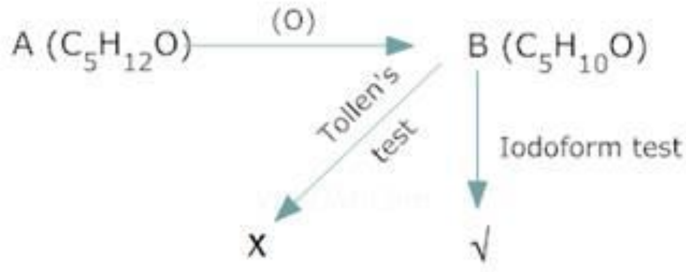
The sequence of reactions is



$$CH_3\ CH_2\ CO\ CH_2\ CH_3 \xrightarrow{alk.kmNo_4} CH_3CH_2COOH + CH_3\ COOH$$

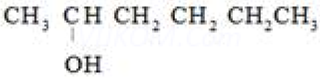
$$CH_3\ CH_2\ COOK \xrightarrow[decarboxylation]{kolbe's} CH_3\ CH_2\ CH_2\ CH_3 + CO_2 + KOH + H_2$$

Ans 2.



Since B gives a negative Tollen's test but positive Iodoform test, it is methyl ketone, i.e,

$CH_3CO\ CH_2CH_2CH_3$. Also it is formed by oxidation of A.

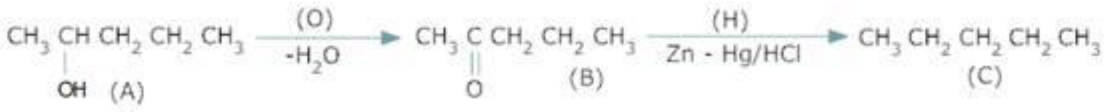
Therefore A is secondary alcohol i.e,  $CH_3\ \underset{OH}{\underset{|}{C}H}\ CH_2\ CH_2\ CH_2CH_3$ on reduction B gives pentane with Zn –Hg/ HCl.

Therefore C is $CH_3CH_2CH_2CH_2CH_3$

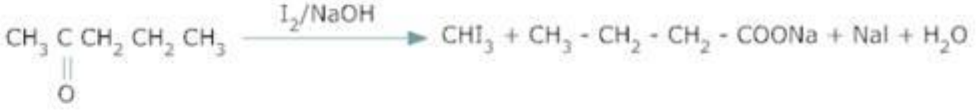
Therefore

A = $CH_3CHOH\ CH_2CH_2CH_3$
B = $CH_3CO\ CH_2CH_2CH_3$
C= $CH_3CH_2CH_2CH_2CH_2CH_3$

Reactions:-

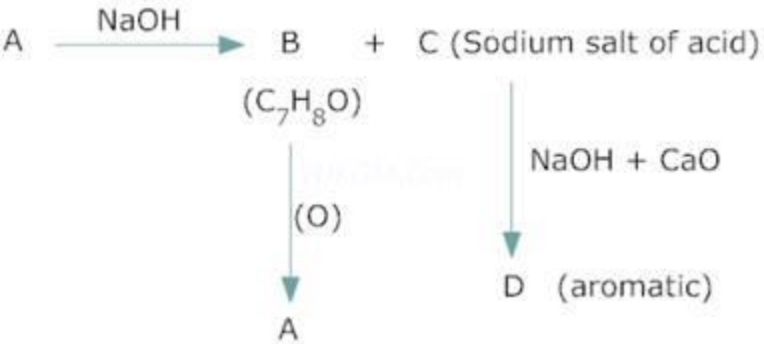


$$\underset{(A)}{CH_3\ \underset{OH}{\underset{|}{C}H}\ CH_2\ CH_2\ CH_3} \xrightarrow[-H_2O]{(O)} \underset{(B)}{CH_3\ \underset{O}{\underset{||}{C}}\ CH_2\ CH_2\ CH_3} \xrightarrow[Zn\text{ - }Hg/HCl]{(H)} \underset{(C)}{CH_3\ CH_2\ CH_2\ CH_2\ CH_3}$$

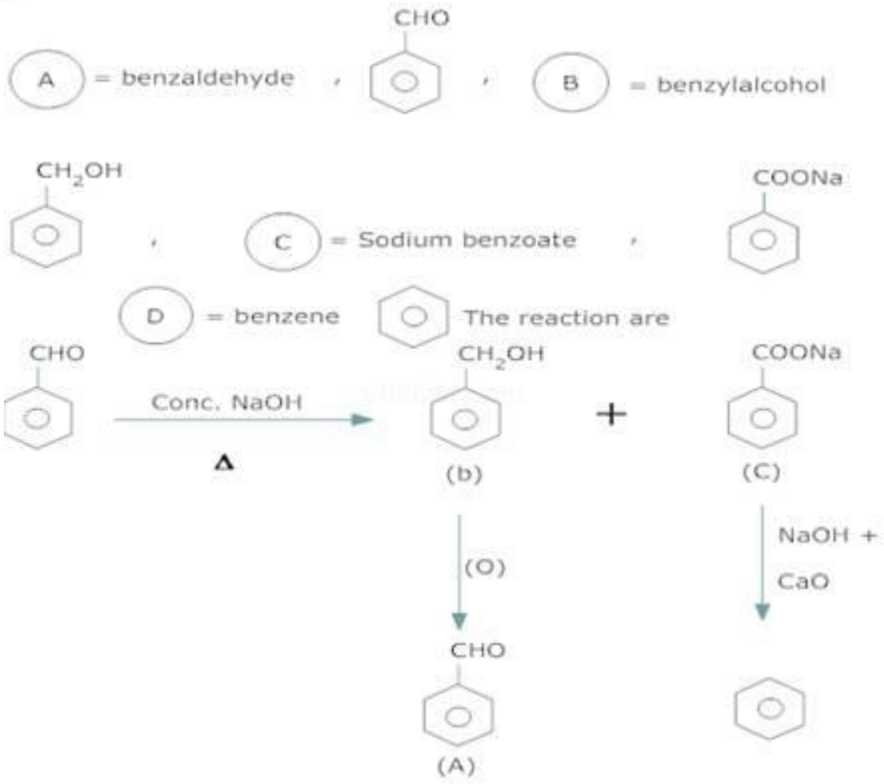


$$CH_3\ \underset{O}{\underset{||}{C}}\ CH_2\ CH_2\ CH_3 \xrightarrow{I_2/NaOH} CHI_3 + CH_3 - CH_2 - CH_2 - COONa + NaI + H_2O$$

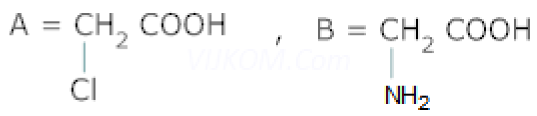
Ans 3.



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:-



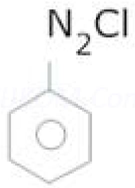
Ans 4.



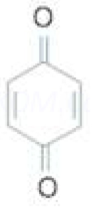
$A = \underset{\underset{Cl}{|}}{CH_2}COOH$, $B = \underset{\underset{NH_2}{|}}{CH_2}COOH$

Ans 5. (A) = $C_6H_5CH_2NH_2$

(B) =



(C) =



Ans 6. (A) = CH_3CN

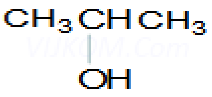
(B) = CH_3COOH

(C) = CH_3COCl

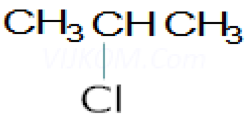
Ans 7. (A) = $(CH_3COO)_2Ca$

(B) = CH_3COCH_3

(C) = CHI_3

Ans 8. X = 

$$\underset{\displaystyle OH}{CH_3\overset{}{C}HCH_3}$$

Y= 

$$\underset{\displaystyle Cl}{CH_3\overset{}{C}HCH_3}$$

Z = $CH_3-CH=CH_2$

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.

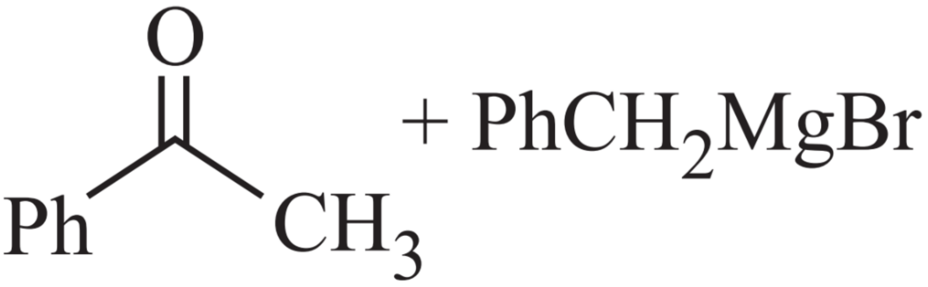
Explanation:

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.

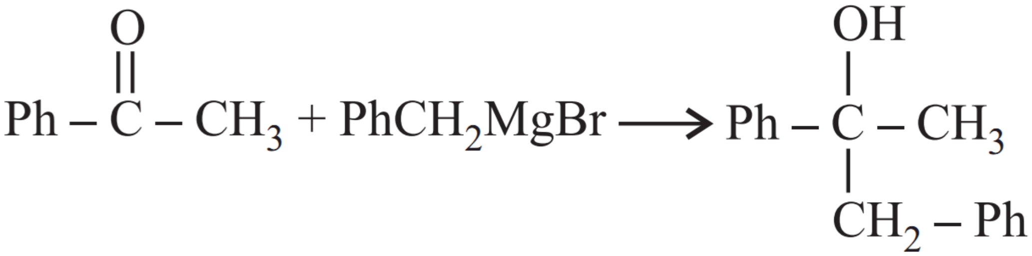
Case Study Answers-

1. Answer :

(i) (b)



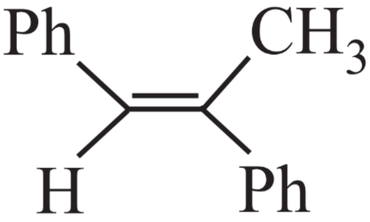
Explanation:



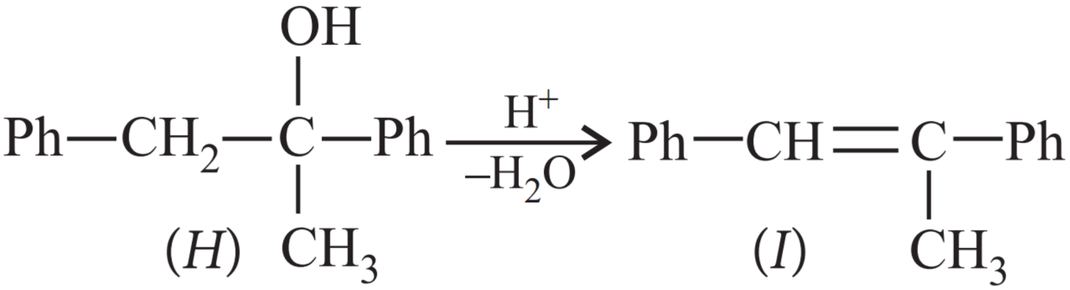
$$\mathrm{Ph-\overset{\overset{\large O}{||}}{C}-CH_3 + PhCH_2MgBr \longrightarrow Ph-\underset{\underset{\large CH_2-Ph}{|}}{\overset{\overset{\large OH}{|}}{C}}-CH_3}$$

(*H*)

(ii) (a)



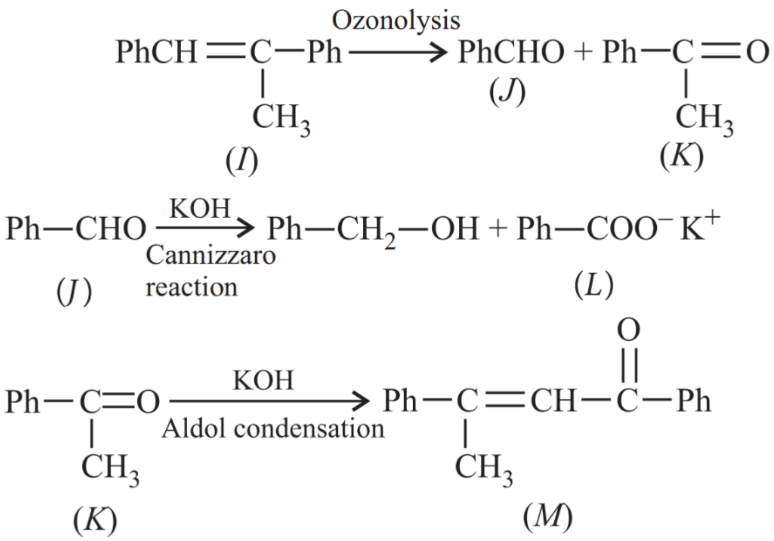
Explanation:



$$\underset{(H)}{\mathrm{Ph-CH_2-\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large OH}{|}}{C}}-Ph}} \xrightarrow[-H_2O]{H^+} \underset{(I)}{\mathrm{Ph-CH=\underset{\underset{\large CH_3}{|}}{C}-Ph}}$$

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

Explanation:



$$\underset{(I)}{\mathrm{PhCH{=}\underset{\underset{\Large CH_3}{|}}{C}{-}Ph}} \xrightarrow{\text{Ozonolysis}} \underset{(J)}{\mathrm{PhCHO}} + \underset{(K)}{\mathrm{Ph{-}\underset{\underset{\Large CH_3}{|}}{C}{=}O}}$$

$$\underset{(J)}{\mathrm{Ph{-}CHO}} \xrightarrow[\text{Cannizzaro reaction}]{\text{KOH}} \mathrm{Ph{-}CH_2{-}OH} + \underset{(L)}{\mathrm{Ph{-}COO^- K^+}}$$

$$\underset{(K)}{\mathrm{Ph{-}\underset{\underset{\Large CH_3}{|}}{C}{=}O}} \xrightarrow[\text{Aldol condensation}]{\text{KOH}} \underset{(M)}{\mathrm{Ph{-}\underset{\underset{\Large CH_3}{|}}{C}{=}CH{-}\overset{\overset{\Large O}{||}}{C}{-}Ph}}$$

(iv) (a) Cinnamic acid.

Explanation:

$$\mathrm{C_6H_5CHO + (CH_2CO)_2O \xrightarrow[\text{-}CH_3COOH]{CH_3COONa}}$$

Benzaldehyde Acetic anhydride

$$\mathrm{C_6H_5 - CH = CH - COOH}$$

Cinnarnlc add

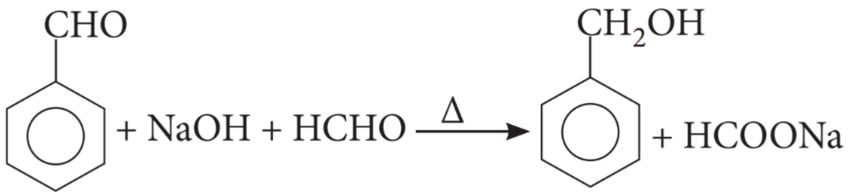
(v) (b) It reacts with iodine and NaOH to form triiodomethane.

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 ∝−∝−hydrogen).

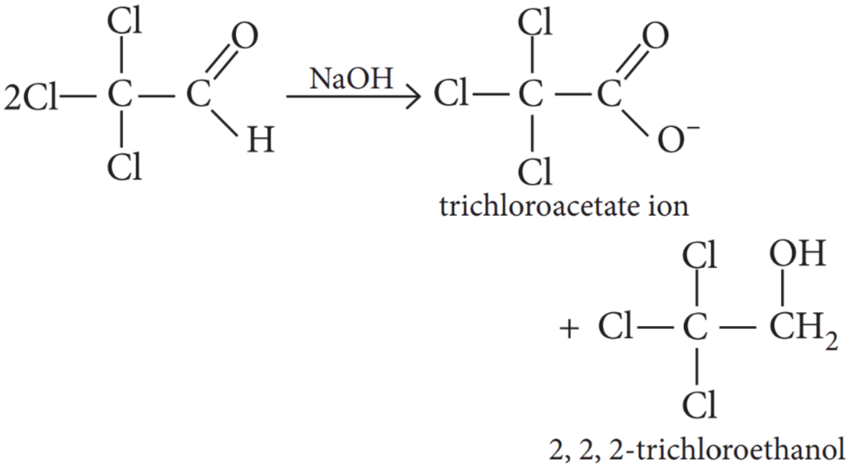


(ii) (c) C_6H_5CHO

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

Explanation:

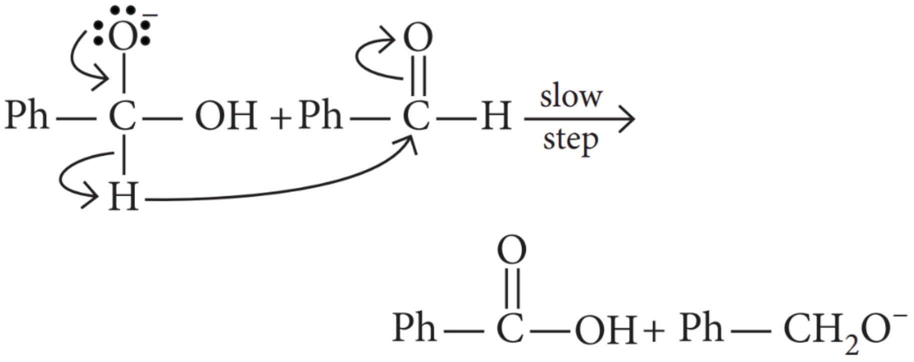
The Cannizzaro product of given reaction yields 2, 2, 2-trichloroethanol.



(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.