ALDEHYDES AND KETONES

STANISLAO CANNIZZARO

Stanislao Cannizzaro (1826 - 1910) was an Italian chemist.

In 1861, he made his first contribution to chemical research, when he prepared cyanamide by the action of ammonia on cyanogen chloride in ethereal solution. In the same year he was appointed professor of physical chemistry at the National College of Alessandria, where he discovered that aromatic aldehydes are decomposed by an alcoholic solution of potassium hydroxide into a mixture of the corresponding acid and alcohol, e.g. benzaldehyde into benzoic acid and benzyl alcohol, the Cannizzaro reaction.

In 1858, he insisted on the distinction, previously hypothesised by Avogadro, between molecular and atomic weights, and showed how the atomic weights of elements contained in volatile compounds can be deduced from the molecular weights of those compounds, and how the atomic weights of elements of whose compounds the vapour densities are unknown can be ascertained from a knowledge of their specific heats. For this achievement, of fundamental importance for the atomic theory in chemistry, he was awarded the Copley Medal by the Royal Society in 1891.

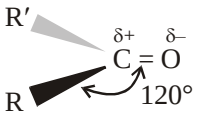
INTRODUCTION

Aldehydes are the compounds which have general formula RCHO, ketones are compounds having general formula RR'CO. The groups R and R' may be aliphatic or aromatic, similar or different alkyl/aryl groups.

An aldehyde A ketone

Both aldehydes and ketones contain the corbonyl group, >C=O, and are often referred to collectively as carbonyl compounds.

1.1 STRUCTURE OF CARBONYL GROUP



Carbonyl carbon is joined to three other atoms by bonds; since these bonds utilize sp^2 orbitals, they lie in a plane, and are 120° apart. The remaining p-orbitals of carbon overlaps a p-orbital of oxygen to form a bond; carbon and oxygen are thus joined by a double bond. The part of

the molecule immediately surrounding carbonyl carbon lie in a plane.

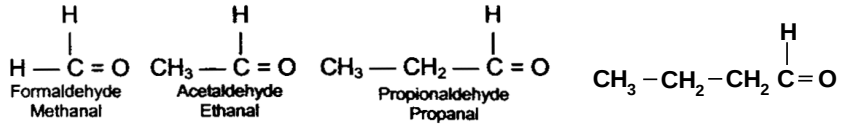
The electrons of a carbonyl double bond hold together atoms of quite different electronegativity and hence the electrons are not equally shared; in particular the polar □-cloud is pulled strongly toward the more electronegative atom, oxygen.

1.2NOMENCLATURE

The common name of aldehydes are derived from the names of the corresponding carboxylic acids by replacing -ic acid by -aldehyde.

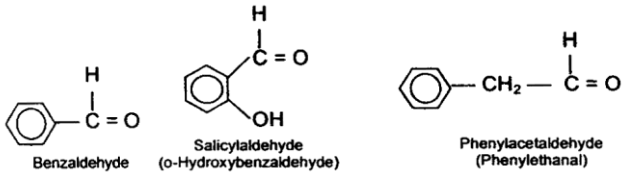
The IUPAC names of aldehydes follow the usual pattern. The longest chain containing the -CHO group is considered the parent structure and named by replacing -e of the corresponding alkane by -al. The position of the substituent is indicated by a number, the carbonyl carbon always being considered C-1.

Common name

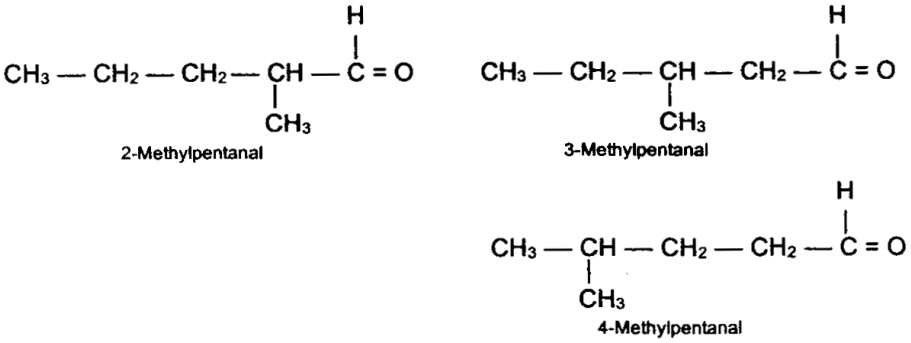


IUPAC name

Common name



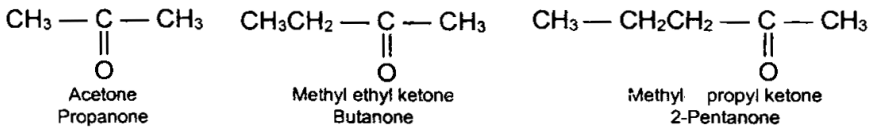
IUPAC Name



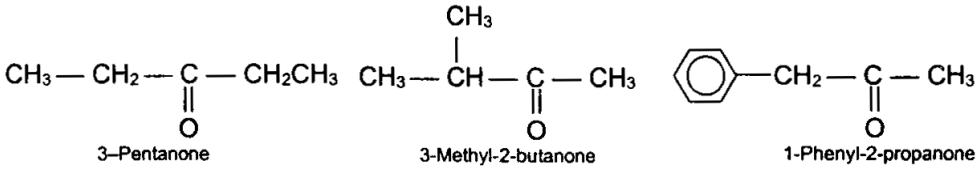
The simple aliphatic ketone has the common name acetone. For most other aliphatic ketones we name the two groups that are attached to carbonyl carbon and follow these names by the word ketone. A ketone in which the carbonyl group is attached to a benzene ring is named as phenone, as illustrated below. According to IUPAC system, the longest chain carrying the carbonyl group is considered as the parent structure, and is named by replacing -e of the corresponding alkane with -one. The positions of various groups are indicated by numbers.

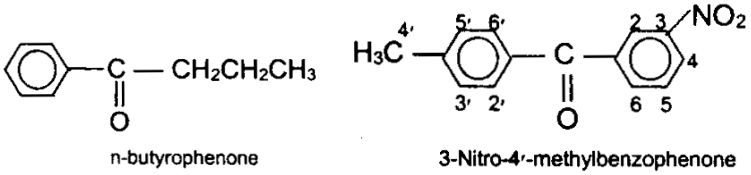
Common name:

IUPAC Name:



IUPAC Name:





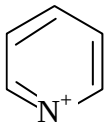
1.3 METHODS OF PREPARATION OF ALDEHYDES

☐ Oxidation of primary alcohols

The oxidation of an alcohol involves the loss of one or more □-hydrogen atoms from the carbon containing– OH group. The kind of product formed depends upon now many of these □-H atoms the alcohol contains.

$$\underset{1^\circ \text{ alcohol}}{RCH_2OH} \xrightarrow[\text{Aq. } KMnO_4]{\text{Aq. } K_2Cr_2O_7 \text{ or}} \underset{\text{Aldehyde}}{R-\overset{H}{\overset{|}{C}}=O}$$

$$RCH_2OH \xrightarrow[CH_2Cl_2]{\text{P.C.C.}}$$



$H \quad CrO_3\bar{C}l$

(Pyridinium chloro-chromate) (P.C.C.)

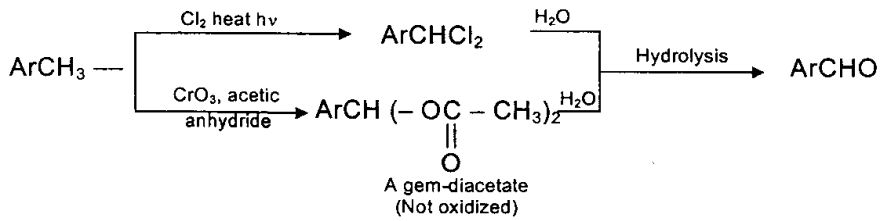
Example:

$$CH_3CH_2CH_2OH \xrightarrow[\text{warm}]{K_2Cr_2O_7/H_2SO_4} CH_3CH_2CHO$$

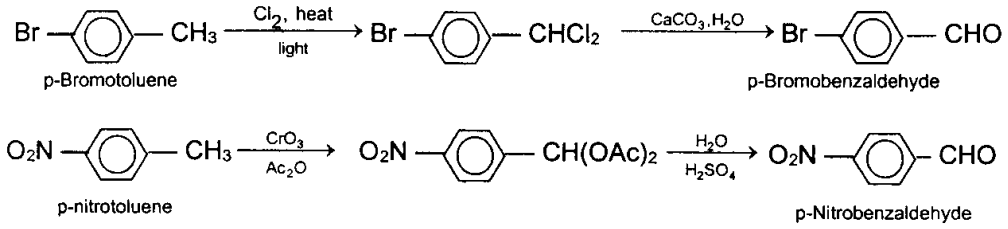
☐ Oxidation of Methyl Benzenes (For Aromatic Aldehydes Only)

Methyl benzene on treatment with either Cl_2 in presence of uv light or CrO_3 in acetic anhydride gives Ar-$CHCl_2$ or Ar – $CH(OOCH_3)_2$.

Both these compounds on decomposition with water gives benzaldehyde.



Example



☐ Reduction of Acid Chlorides

Acid chlorides can be reduced to aldehydes, only by the use of bulky hydride reducing agent, tri-t-butoxy lithium aluminium hydride. If $LiAlH_4$ is used as a reducing agent, the product isolated is an alcohol and not an aldehyde.

$$R–COCl \text{ or } Ar–COCl \xrightarrow{LiAlH(OBu-t)_3} R–CHO \text{ or } Ar–CHO$$

Acid chlorides can also be reduced to aldehydes by H_2 gas in the presence of Pd supported on $BaSO_4$ in xylene, poisoned with quinoline or sulphur. This reaction is called **Rosenmund's reduction**, which is applicable for the preparation of aliphatic as well as aromatic aldehydes.

$$R–COCl \text{ or } Ar–COCl \xrightarrow[\text{Poisoned with quinoline or S}]{H_2/Pd-BaSO_4} R–CHO \text{ or } Ar–CHO + HCl$$

☐ Distillation of Carboxylic Acid-salts

By heating a mixture of the calcium salts of formic acid and any one of its homologues.

When calcium salt of formic acid is dry distilled, formaldehyde is obtained. If a mixture of calcium salt of formic acid and any of its higher homologous is used, then aldehydes other than formaldehyde are obtained while when only calcium salt of monocarboxylic acid (other than formic acid) is dry distilled, the product obtained is a ketone.

$$(RCO_2)_2Ca + (HCO_2)_2\,Ca \square 2RCHO + 2CaCO_3$$

☐ Stephen's Method

An alkyl or aryl cyanide dissolved in ether is reduced with stannous chloride and HCl to give aliphatic or aromatic aldehydes. The reaction proceeds by the formation of aldimine hydrochloride (present as stannichloride), which are not stable and hydrolyse to give aldehydes).

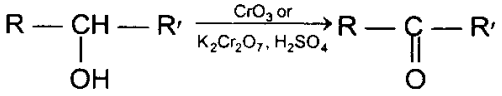
$$R-C\equiv N \xrightarrow[2.\ H_2O]{1.\ SnCl_2+HCl} RCHO$$

H_2O Hydrolyses RCH = NH to RCHO and NH_3.

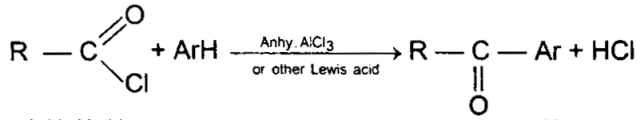
1.4 Preparation of Ketones

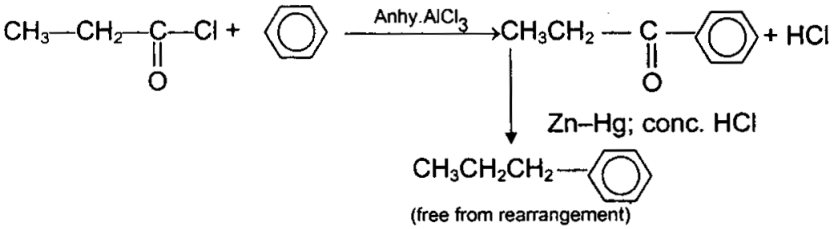
☐ Oxidation of Secondary alcohols

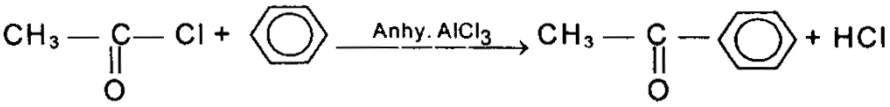
Secondary alcohols can also be oxidized by aluminium t–butoxide, $[(CH_3)_3CO]_3Al$ in acetone. The reaction is called **oppenauer oxidation**. In presence of p–benzoquinone solvent 1° alcohol can also be oxidized to aldehyde on distillation.

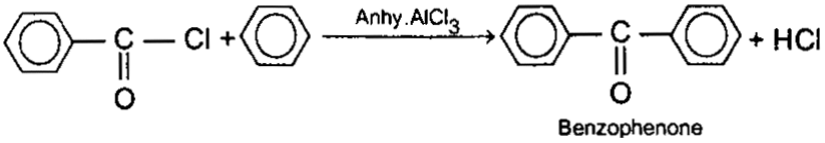


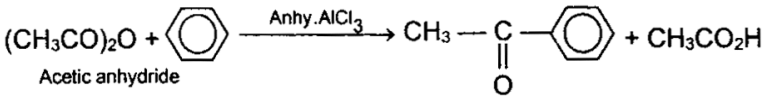
☐ Friedel - Crafts Acylation

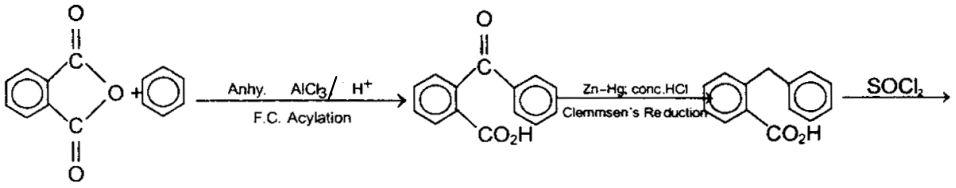


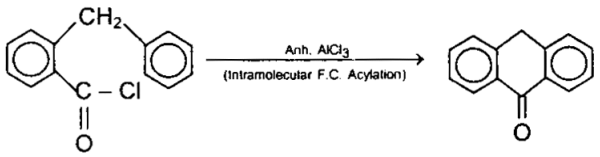


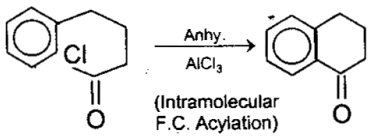




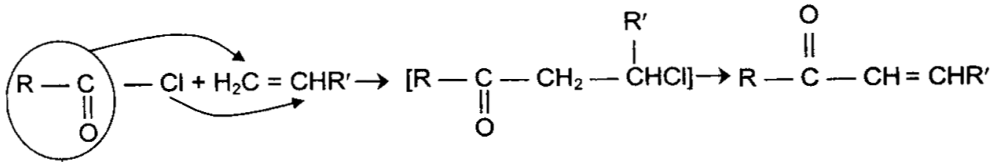








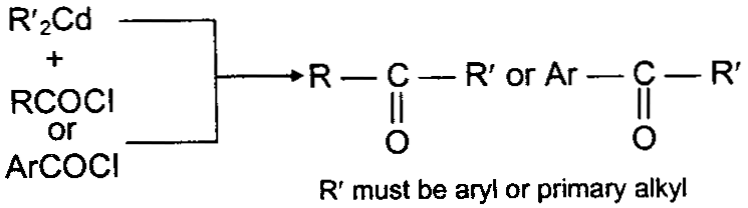
- **Acylation of Alkenes**



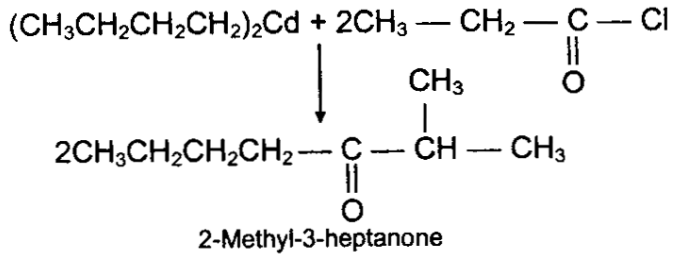
This is Markovnikov addition initiated by an acylium cation.

- **From Organometallics Compounds**

(a) Reaction of acid chlorides with organocadmium compounds.



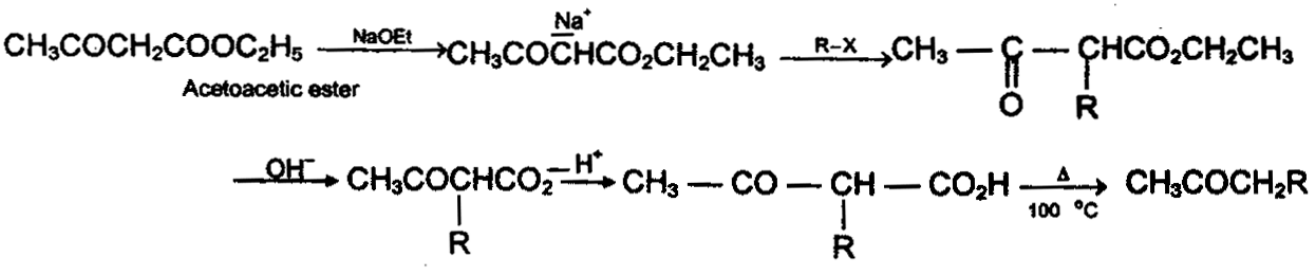
R′ must be aryl or primary alkyl



2-Methyl-3-heptanone

- **Acetoacetic ester synthesis of ketones**

This synthesis is used for preparing ketones only and is based on the fact that active methylene group (which is sandwiched between two strongly electron-withdrawing groups) have more acidic hydrogen than other □-hydrogens.



1.5 Physical Properties of Aldehydes and Ketones:

The polar carbonyl group makes aldehydes and ketones as polar compounds and hence they have higher boiling points than non-polar compounds of comparable molecular weight. By themselves they are not capable of intermolecular hydrogen bonding since they contain hydrogen bonded only to carbon; as a result they have lower boiling points than comparable alcohols or carboxylic acids.

The lower aldehydes and ketones are appreciably soluble in water, presumably because of hydrogen bonding between solute and solvent molecules; borderline solubility is reached at about 5 carbons. Aldehydes and ketones are soluble in the usual organic solvents. Formaldehyde is a gas (b.p -21°) and is handled either as an aqueous solution (Formalin), or as one of its solid polymer: paraformaldehyde $(CH_2O)_n$, or trioxane, $(CH_2O)_3$.

Acetaldehyde (b.p. 20°) is often generated from its higher-boiling trimer by heating the trimer with acid.

1.6 Chemical Reactions of Aldehydes and Ketones

☐ Oxidation

Aldehydes are easily oxidized to carboxylic acids but ketones are not. Aldehydes are oxidized not only by the same reagents, which oxidizes primary and secondary alcohols (like acidified $KMnO_4$, $K_2Cr_2O_7$) but also by mild oxidizing agents like Tollen's reagent, Fehling's solution and Benedict's solution. Aldehydes are very easily oxidized and thus are very powerful reducing agents.

Tollen's reagent contains diamminesilver (I) ion, which is obtained through ammoniacal $AgNO_3$ solution. Tollen's reagent oxidizes aldehydes to acid salt and they reduces to free silver in the form of silver mirror.

$$\underset{\text{Colourless Solution}}{RCHO + 2Ag(NH_3)_2^+ + 3OH^-} \rightarrow RCO_2^- + \underset{\text{Silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

Tollen's reagent is useful in differentiating aldehydes from ketones because ketones do not react with them. Tollen's reagent is a mild and selective oxidizing agent, attacking only aldehydic group, keeping other groups untouched. Unsaturated aldehydes can be converted to unsaturated acid salt using Tollen's reagent.

$$\underset{\alpha,\beta-\text{unsaturated uldehyde}}{R-\overset{\beta}{C}H=\overset{\alpha}{C}H-CH=O} \xrightarrow[\text{reagent}]{\text{Tollen's}} \underset{\alpha,\beta-\text{unsaturated acid salt}}{R-\overset{\beta}{C}H=\overset{\alpha}{C}H-CO_2^-} + Ag\downarrow$$

Aldehydes are easily oxidized, thus they also reduce Fehling's solution (an alkaline solution containing a complex of copper tartarate) to red cuprous oxide. Aldehydes also reduce Benedict's solution (an alkaline solution containing a complex of copper citrate) to red precipitate of cuprous oxide.

$$R-CHO + 2CuO \rightarrow RCOO^- + \underset{(Red)}{Cu_2O}\downarrow$$ (Fehling's and Benedict's test)

Ketones are not easily oxidized, thus they do not reduce Fehling's solution or Tollen's reagent. But □-hydroxy ketones (compounds containing the unit $-CH(OH)-\overset{\overset{O}{\|}}{C}-R)$ readily reduce. The compounds which respond to the test with Fehling's solution and ammoniacal silver nitrate are given below in the tabulated manner.

Name of the compounds	**Fehling's test**	**Tollen's test**
Glucose, Fructose	□	□
□-hydroxy ketone	□	□
□-hydroxy aldehyde	□	□
Glyoxal (OHC.CHO)	□	□
Benzaldehyde and other aromatic aldehydes	□	□
Formic acid	□	□
Glyoxylic acid ($OHC.CO_2H$)	□	□
Sucinaldehyde ($OHCCH_2CH_2CHO$)	□	□
Pyruvaldehyde (CH_2COCHO)	□	□

Aldehydes restore the magenta colour the Schiff's reagent (rosaniline hydrochloride is dissolved in H_2S and SO_2 is passed till the magenta colour is decolourised). Ketones do not restore the colour of Schiff's reagent except acetone, which restores the colour very slowly.

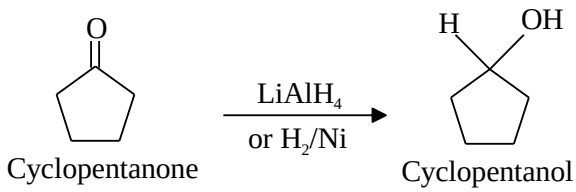
Oxidation of ketones requires breaking of carbon-carbon bonds, which requires vigorous conditions. Cleaveage involves the double bond of the enol form and wherever the structure permits, occurs on both sides of carbonyl group. Thus, in general, ketones on oxidation give a mixture of carboxylic acids.

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3 \xrightarrow[\Delta]{\text{Acidified } KMnO_4} CH_3CO_2H + CH_3CH_2CH_2CO_2H$$

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3 \xrightarrow[\Delta]{\text{Acidified } KMnO_4} CH_3CH_2CO_2H + CH_3CH_2CO_2H$$

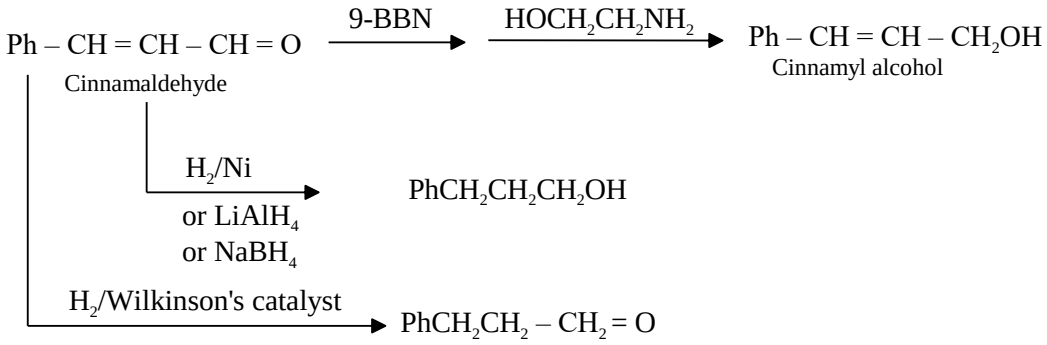
□ Reduction

Aldehydes can be reduced to primary alcohols and ketones to secondary alcohols, either by catalytic hydrogenation or by $LiAlH_4$.



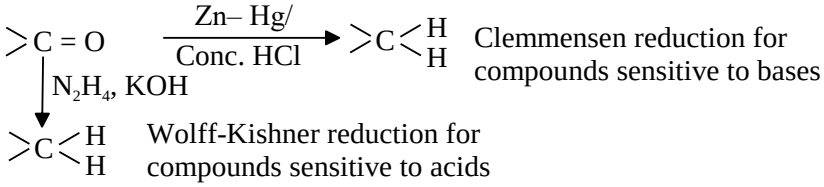
$$CH_3CH=CH-CH=O \xrightarrow[\text{or } NaBH_4]{H_2Ni} CH_3CH_2CH_2CH_2OH$$

Crotonaldehyde — n–butanol

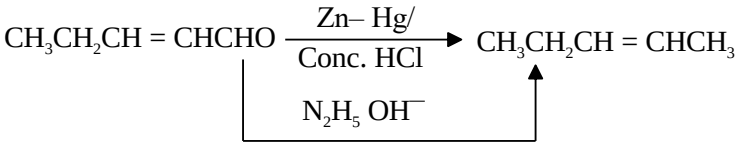


To reduce a carbonyl group that is conjugated with a carbon-carbon bond without reducing the carbon-carbon double bond requires a regioselective reducing agent. One such reagent is 9-BBN, 9-Borabicyclo [3.3.1] nonane. This reduction can also be achieved by $LiAlH_4$ but not by $NaBH_4$, which reduces carbon-carbon double bond as well as the carbonyl group. While carbon-carbon double bond can be selectively reduced without affecting carbonyl group by hydrogenation in presence of Wilkinson's catalyst. $LIAlH_4$ reduces the carbon-carbon double bond, which is in conjugation with carbonyl group only when the □-carbon bears an aryl group.

Aldehydes and ketones can be reduced to hydrocarbons by the action of (a) amalgamated zinc and concentrated hydrochloric acid **(Clemmensen reduction)** or (b) hydrazine (N_2H_4) and a strong base like KOH or potassium tertiary butoxide **(Wolff-Kishner reduction)**.



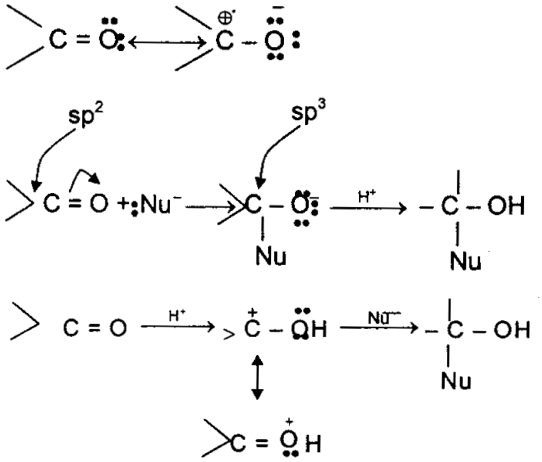
For example,



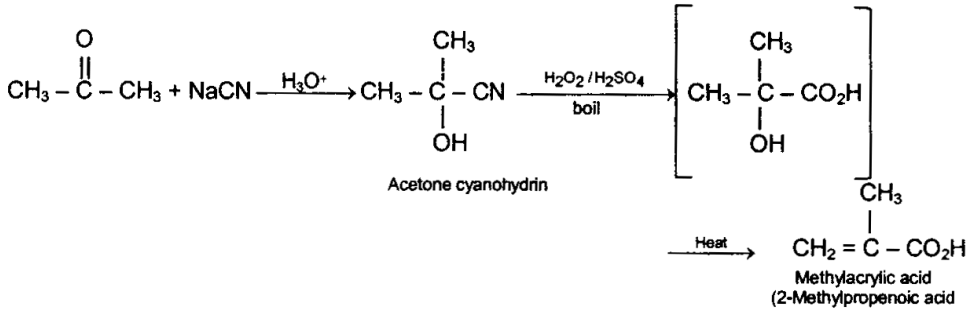
Raney nickel desulfurization is also used for reducing carbonyl compounds to hydrocarbons. Raney nickel has absorbed hydrogen.

☐ Nucleophilic Addition Reactions of Carbonyl Compounds

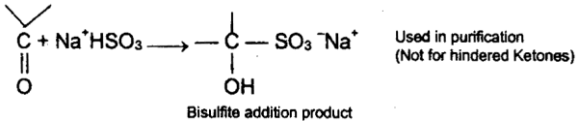
Due to the difference in electronegativity between carbon and oxygen, the □-electrons shift towards oxygen creating partial positive charge or carbon and making it electrophilic. So this electrophilic carbon can be attacked by different nucleophiles.



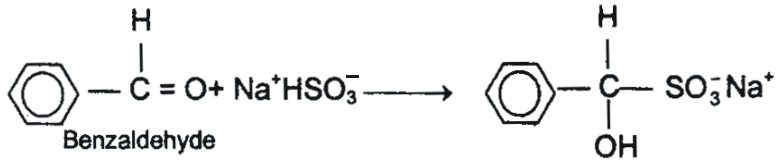
(a) Addition of cyanide

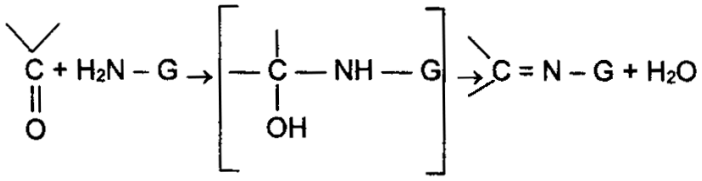


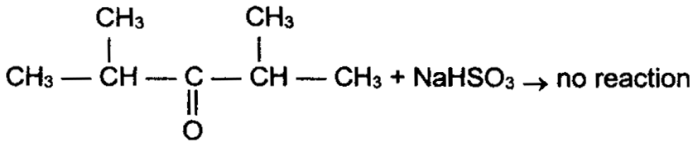
(b) Addition of sodium bisulphile



Example:



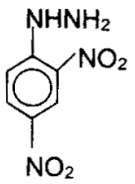
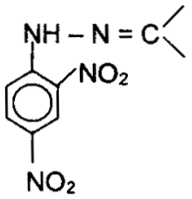




(c) Addition of derivative of ammonia.

The addition of ammonia derivatives to aldehydes and ketones is *catalysed* by acids. In acidic medium, the oxygen of the carbonyl group gets protonated which, in turn, by resonance increases the positive charge on the carbonyl carbon. As a result, weak nucleophiles like ammonia derivatives readily attack the carbonyl group.

In case, the medium is *too acidic*, the ammonia derivatives being basic in nature will form their respective ammonium salts. Due to the absence of a lone pair of electrons on the nitrogen atom, these ammonium salts will no longer be nucleophilic and hence the reaction will not occur. However, if the medium is *only very slightly acidic or basic*, the protonation of the carbonyl group will not occur. This, in turn, will not increase the electron-deficiency (or +ve charge) on the carbonyl atom of the carbonyl group and hence weak nucleophiles like ammonia derivatives will not be able to react. In other words, the reaction does not occur. Therefore, to carry out such reactions, an optimum value of pH is needed. *Usually a pH of around 4.6 is employed.*

$H_2N - G$		PRODUCT	
H_2NOH	Hydroxylamine	$> C = N - OH$	Oxime
$H_2N - NH_2$	Hydrazine	$> C = N - NH_2$	Hydrazone
$H_2N - NH - C_6H_5$	Phenylhydrazine	$> C = N - NHC_6H_5$	Phenylhydrazone
$H_2N - NH - C - NH_2$ $\parallel$ O	Semicarbazide	$> C = N - NHCONH_2$	Semicarbazone
	2, 4-Dinitrophenyl hydrazine		2, 4 dinitrophenylhydrazone (bright orange or yellow precipitate used for identifying aldehydes and ketones

The rate of such reaction is maximum at some particular pH. These reactions are catalysed by the presence of slightly acidic conditions. In slightly acidic conditions, dehydration step is the RDS, whose rate is increased by the protonation of OH, leading to overall increase in rate of the reaction. But, when the acidity increases for the rate of addition step decreases because concentration of $NH_2 - Z$ reduces due to its conversion to conjugate acid, $NH_3^+ - Z$ (which can not function as a nucleophile because of absence of lone pair). Thus, at low pH or more acidity, the addition step becomes the RDS.

For example,

$$CH_3 - CHO = O + H_2N - OH \xrightarrow{H^+} \underset{\text{Acetaldoxime}}{CH_3CH = N - OH} + H_2O$$

(Capable of showing geometrical isomerism)

$$Ph - CH = O + H_2N - NHPh \rightarrow Ph - CH = N - NHPh + H_2O$$

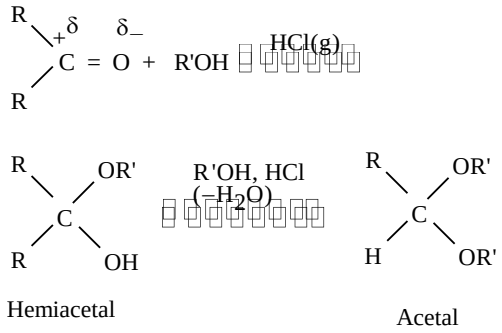
Benzaldehyde phenyl hydrazone

(Capable of showing geometrical isomerism)

Acetone semicarbazone

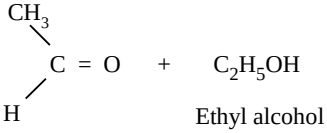
(d) Addition of alcohols – Acetal and ketal formation.

Aldehydes react with alcohol in presence of dry HCl gas to form *gem* – dialkoxy compound known as **acetals.** A hemiacetal (hemi = half) is first formed by the addition of one molecule of an alcohol to the carbonyl group. It being unstabnle immediately reacts with another molecule of alcohol to form stable **acetal.**



Hemiacetal

Acetal

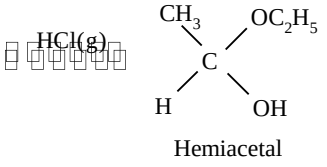


Acetaldehyde

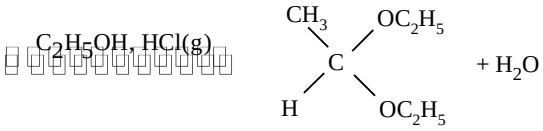
$+ \quad C_2H_5OH$

Ethyl alcohol

e.g.,



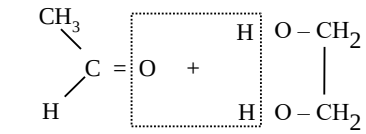
Hemiacetal



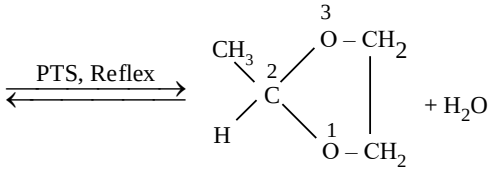
Acetal

Dry HCl gas absorbs the water produced in these reaction and shifts the equilibrium in the forward direction.

If instead of two molecules of monohydric alcohol, one molecule of a dihydric alcohol such as ethylene glycol is used, a cyclic acetal is formed. In actual practice, a mixture of an aldehyde is refluxed with excess of ethylene glycol in presence of *p*-toluenesulphonic acid (PTS).

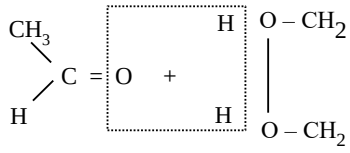


Acetaldehyde Ethylene glycol

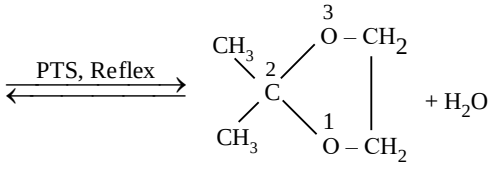


2-Methyl-1, 3-dioxolane
(A cyclic acetal)

Ketones, however, do not react with monohydric alcohols but do so with dihydric alcohols to give cyclic ketals.

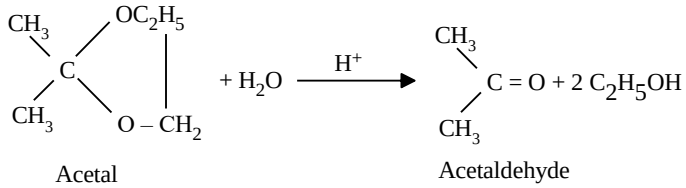


Acetone Ethylene glycol



2, 2-Dimethyl-1, 3-dioxolane
(A cyclic ketal)

The above reactions being reversible, the acetals and ketals formed are decomposed by dilute acids to regenerate the aldehydes and ketones.



Acetal Acetaldehyde

ILLUSTRATIONS

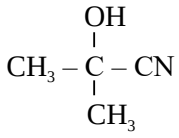
***Illustration* 1**

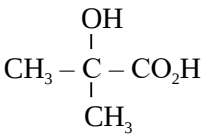
Write structures for (A) through (D) in the given reaction sequence.

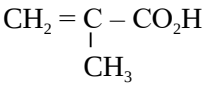
$$Me_2C=O+HCN \rightarrow (A) \xrightarrow{H_3O^+} (B) \xrightarrow[\Delta]{H_2SO_4} (C) \xrightarrow[2.\ H_2O_2/OH^-]{1.\ B_2H_6/THF} (D).$$

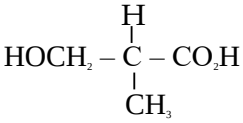
Product (D) is optically active.

Solution

(a): 

(b): 

(c): 

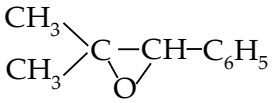
(d): 

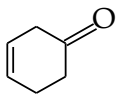
(D) is optically active due to the absence of symmetry elements.

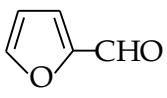
Illustration 2

Give structures for the product formed by treatment of the following compounds with benzyl magnesium chloride followed by hydrolysis in aqueous acid.

(a) CH_3CHO

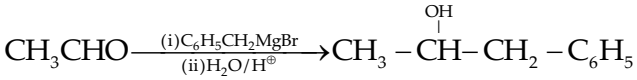
(b) 

(c) 

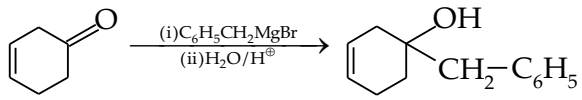
(d) 

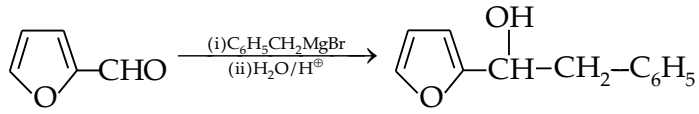
(e) $CH_3-CH_2-O-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

Solution

(a) 

(b) 

(c) 

(d) 

(e)

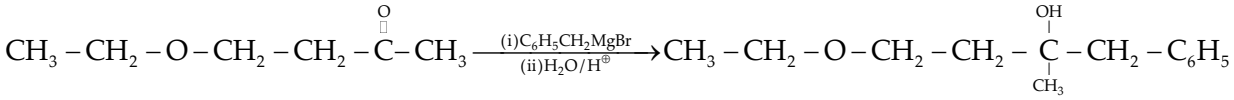
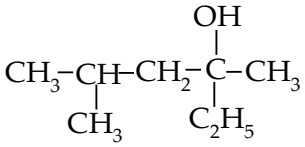
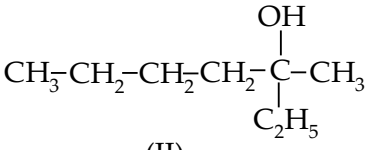


Illustration 3

Show how to synthesise the following isomeric alcohols by treatment of ethyl methyl ketone with a Grignard reagent.



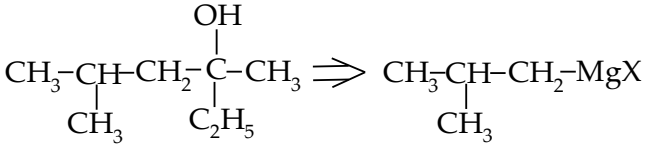
(I)



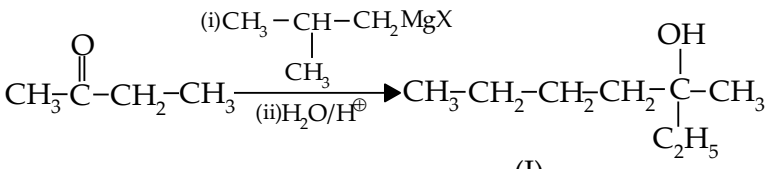
(II)

Solution

Compound (I) can be synthesized by the following Grignard reagent

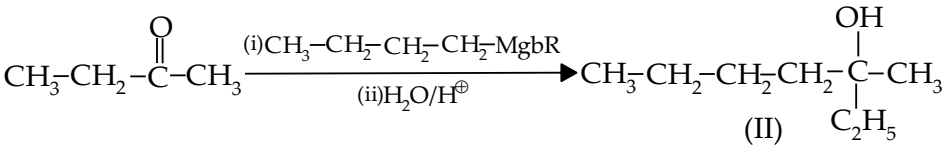


Synthesis of I:



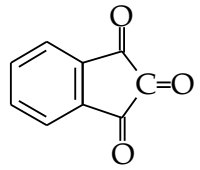
(I)

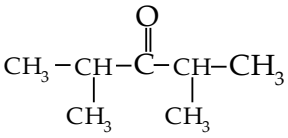
Synthesis of compound II:

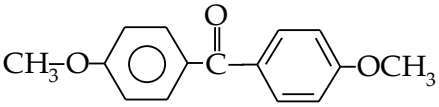


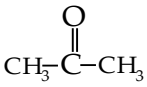
PRACTICE EXERCISE

1. Which of the following ketones forms most stable hydrate?

(a) 

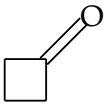
(b) 

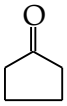
(c) 

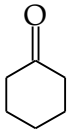
(d) 

2. Which of the following ketones has the largest equilibrium constant for addition of water?

(a) 

(b) 

(c) 

(d) 

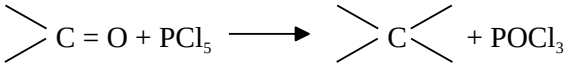
Answers

1. (a) In this compound C = O group is bonded with two electron withdrawing groups (i.e., C = O)

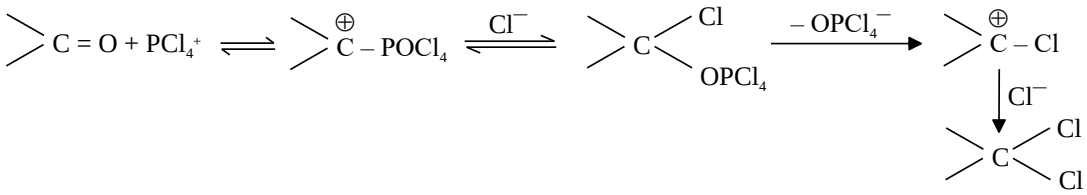
2. (a) Small ring ketone forms stable hydrate.

☐ Reaction with PCl_5

Phosphorus pentachloride reacts with simple carbonyl compounds to given 1,1-dichlorides (gem dichloride).



The possible mechanism of the reaction is



The reaction is initiated by the attack of PCl_4 (solid PCl_5 is PCl_4^+ PCl_6^-) and the chloride ion are obtained from PCl_6^-.

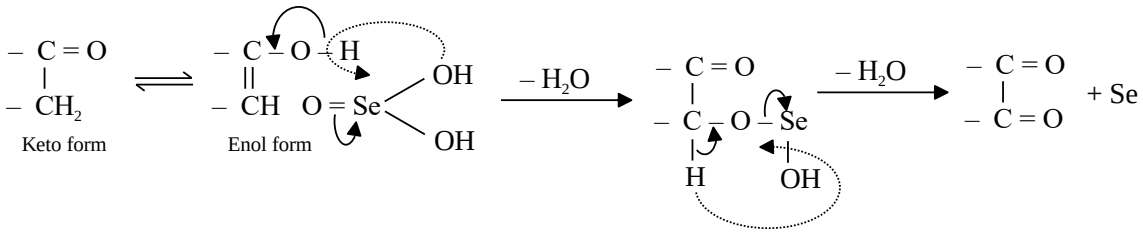
☐ Reaction with SeO_2:

Aldehydes and ketones with a methyl of methylene group adjacent to the carbonyl group are oxidized by selenium dioxide in acetic acid at room temperature to dicarbonyl compounds. For example, acetaldehyde forms glyoxal and acetone forms methyl glyoxal.

$$CH_3CHO + SeO_2 \xrightarrow[\text{acid}]{\text{Acetic}} OHC - CHO + Se + H_2O$$

$$CH_3COCH_3 + SeO_2 \xrightarrow[\text{acid}]{\text{Acetic}} CH_3COCHO + Se + H_2O$$

The actual reagent of the reaction is selenous acid (H_2SeO_3) and the probable mechanism is

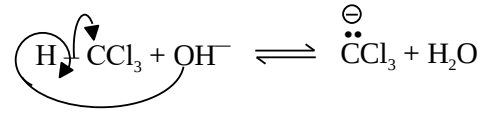


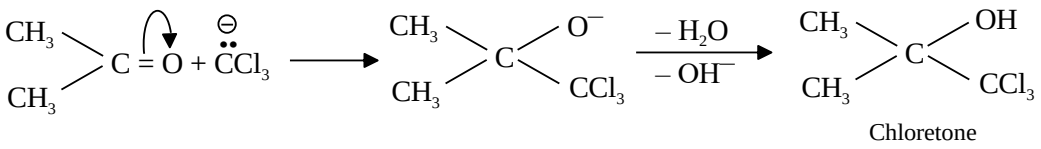
☐ Reaction with Chloroform:

Ketones condense with chloroform in the presence of potassium hydroxide to give chloretone, which is used as a hypnotic drug.

$$CH_3COCH_3 + CH_3 + CHCl_3 \xrightarrow{KOH} \underset{\text{Chloretone}}{(CH_3)_2C(OH)CCl_3}$$

The reaction proceeds as





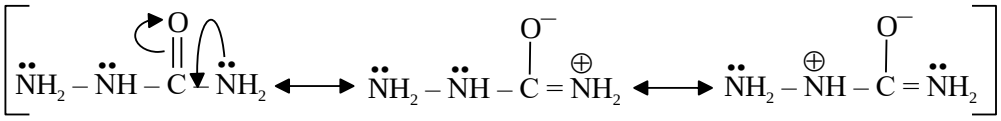
ILLUSTRATIONS

Illustration 4

There are two NH_2 groups in semicarbazide that might react with a ketone or an aldehyde. Explain why the reaction occurs with one of the terminal NH_2

Solution

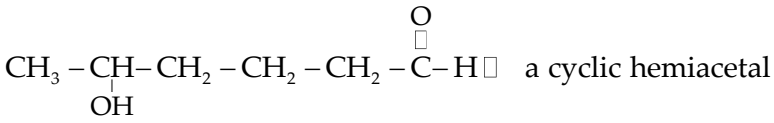
The NH_2 group close to the carbonyl group is deactivated due to resonance stabilization, as compared to the other end NH_2 group.



The electron pair availability is more on the terminal nitrogen, thus making it more nucleophilic and semicarbazone is formed through its attack.

Illustration 5

5-Hydroxyhexanal forms a six member hemiacetal, with predominates at equilibrium in aqueous solution.



(a) Give mechanism for the reaction

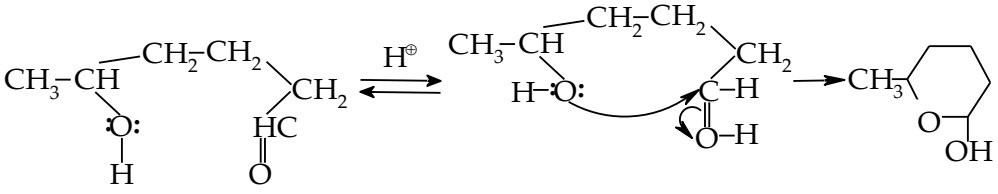
(b) How many streoisomers are possible for 5-hydroxyhexanal?

(c) How many stereoisomers are possible for this cyclic hemiacetal?

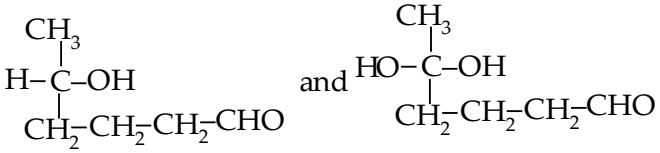
(d) Draw chain conformation of cyclic hemiacetals

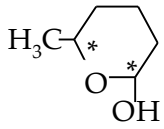
Solution

(a)

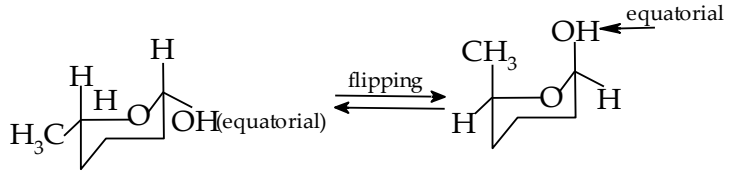


(b) 5-Hydroxyhexanal has one chiral carbon hence two stereo-isomers (optical isomers or enantiomers) are possible.



(c) 

Cyclic hemiacetal has two chiral carbons hence four stereoisomers are possible

(d) 

PRACTICE EXERCISE

3. Prepare

(i) Lactic acid, $CH_3CH(OH)CO_2H$ from acetaldehyde and

(ii) Mandelic acid, $PhCH(OH)CO_2H$ from benzaldehyde.

Answers

3. (i) Treatment with HCN followed by hydrolysis

(ii) Treatment with HCN followed by hydrolysis

1.7 Aldol Condensation

Aldehyde having □□hydrogen(s) undergo self-condensation on warming with dilute or mild base to give □-hydroxy aldehydes, called aldols (aldehyde + alcohol). This reaction is known as aldol condensation. A typical example is the reaction of acetaldehyde with base under mild condition.

$$CH_3CHO + CH_3CHO \xrightarrow{\ominus OH} \underset{\text{Acetaldol}}{CH_3CH(OH)CH_2CHO}$$

Various basic reagents such as dilute sodium hydroxide, aqueous alkali carbonate, alkali metal alkoxides, etc., may be used. The reaction is not favourable for ketones.

Aldol condensation has broad scope. It can occur between

(*i*) two identical or different aldehydes,

(*ii*) two identical or different ketones and

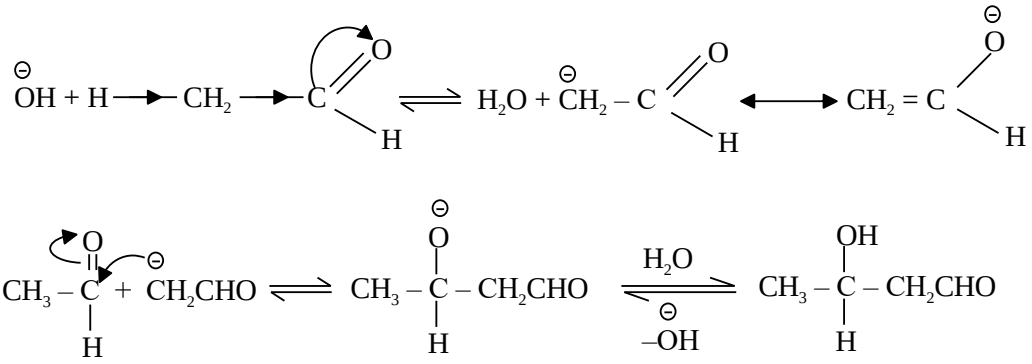
(*iii*) an aldehyde and a ketone.

When the condensation is between two different carbonyl compounds, it is called crossed aldol condensation.

□ Mechanism

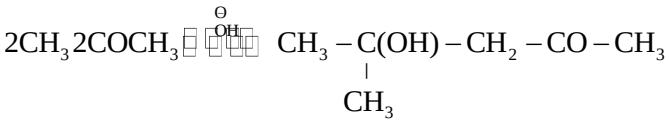
The first step involves the formation of a resonance-stabilized enolate anion by the removal of an □-hydrogen from the aldehyde by the base. In the second step the enolate anion attacks the carbonyl carbon of the second molecule of the aldehyde to form an

alkoxide ion. The later then takes up a proton from the solvent to yield aldol in the third step.



Thus, the overall reaction is an addition of enolate anion to the carbonyl double bond.

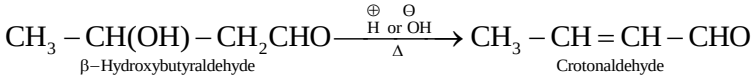
The reaction between two ketones is not very successful. The equilibrium is not favourable and lies to the left.

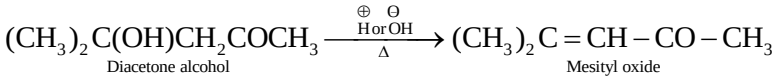


This is because the carbonyl carbon of ketone is less positive (due to +I effect) and more sterically hindered relative to aldehydes. This reduces the nucleophillic attack on the carbonyl carbon. However, it is possible to prepare diacetone alcohol in reasonable good yield by boiling acetone with solid $Ba(OH)_2$ in a specially devised apparatus.

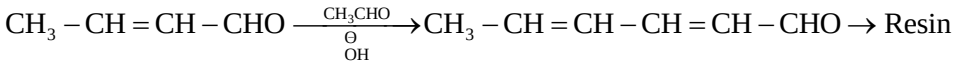
☐ Salient Features of Aldol Condensation

(*a*) Aldols are easily dehydrated to □□□□-unsaturated compounds on heating along or with acid or base.





(*b*) When aldol condensation is carried out in the presence of strong alkali, repeated condensation and dehydration results in the formation of resins.



(*c*) The condensation is between two different carbonyl compounds, it is called **crossed aldol condensation.**

(*i*) **Crossed aldol condensation between two different aldehydes.** When both the aldehydes have □-hydrogen(s) both can form carbanions and also can act as carbanion acceptors. Hence a mixture of four products are formed which has little synthetic use.

If one of the aldehydes has no α-hydrogen then it can act only as a carbanion acceptor. In such case two products are formed, *e.g.*

(*a*) $R_3C-CHO + CH_3CHO \xrightarrow{\overset{\ominus}{O}H} \underset{\text{Crossed product}}{R_3C-CH(OH)-CH_2-CHO}$

(*b*) $CH_3CHO + CH_3CHO \xrightarrow{\overset{\ominus}{O}H} \underset{\text{Simple product (normal)}}{CH_3CH(OH)CH_2CHO}$

However, a good yield of the crossed product is obtained by slowly adding the aldehyde having α-hydrogen to a mixture of the aldehyde having no α-hydrogen and the catalyst, *e.g.*

$$C_6H_5CHO + \overset{\ominus}{O}H \xrightarrow[\text{Slow addition}]{CH_3CHO} C_6H_5CH(OH)CH_2CHO \xrightarrow{-H_2O} \underset{\text{Cinnamaldehyde}}{C_6H_5.CH=CH-CHO}$$

Formaldehyde having no α-hydrogen is a reactive carbanion acceptor due to the absence of steric hindrance and +I effect. Hence, when acetaldehyde is treated with excess of formaldehyde in the presence of $Ca(OH)_2$, crossed aldol condensation continues (three times) until trihydroxymethyl acetaldehyde, $(HOCH_2)_3CCHO$ is formed. The latter having no α-hydrogen undergoes crossed Cannizzaro reaction to form pentaerythritol.

$$CH_3CHO + \overset{\ominus}{O}H \rightleftharpoons \overset{\ominus}{C}H_2CHO + H_2O$$

$$H-\underset{H}{\overset{O}{\overset{\curvearrowleft}{\underset{\curvearrowright}{C}}}}+CH_2CHO \rightleftharpoons H_2C(\overset{\ominus}{O})-CH_2CHO \xrightarrow{H_2O} H_2C(OH)-CH_2CHO \xrightarrow[\text{(Twice)}]{\overset{\ominus}{O}H\ (1)\ CH_2O\ (2)\ H_2O\ (3)} HOH_2C-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CHO$$

$$HOH_2C-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CHO + CH_2O \xrightarrow[\text{Crossed Cannizzaro Reaction}]{\overset{\ominus}{O}H} \underset{\text{Pentaerylhritol}}{HOH_2C-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2OH} + HCO\overset{\ominus}{O}$$

(*ii*) **Crossed aldol condensation between two different ketones.** Due to poor reactivity of carbonyl carbons (+I effect and crowding) of ketones, a poor yield is obtained and so it is rarely attempted.

(*iii*) **Crossed aldol condensation between an aldehyde and a ketone.**

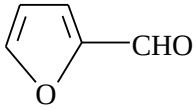
(*a*) When an aldehyde and a ketone both having α-hydrogens are condensed, two products are obtained. This is because ketones are poor carbanion acceptors and so cannot undergo self-condensation. Aldehydes being more reactive than ketones act as carbanion acceptors and the ketones provide the carbanions.

$$CH_3CHO + CH_3COCH_3 \xrightarrow{\overset{\ominus}{O}H} \underset{4-\text{Hydroxypentan}-2-\text{one (crossed product)}}{CH_3-CH(OH)-CH_2-COCH_3}$$

$$CH_3CHO + CH_3CHO \xrightarrow{\overset{\ominus}{OH}} \underset{\text{Acetaldol (normal product)}}{CH_3 - CH(OH) - CH_2 - CHO}$$

Usually, the crossed product is the predominant product. The formation of acetaldol can be minimized by slowly adding the aldehyde to the mixture of ketone and the catalyst base.

1.8 CANNIZZARO REACTION

In the presence of a strong base, aldehydes without α-hydrogens, *i.e.*, nonaldolizable aldehydes undergo self-oxidation-reduction *i.e.*, disproportionation reaction. This is known as Cannizzaro reaction. Thus, aromatic aldehydes (ArCHO), formaldehyde (HCHO), trialkyl acetaldehydes (R_3CCHO), heterocyclic aldehydes,  etc., undergo Cannizzaro reaction, *e.g.*

$$2C_6H_5CHO + NaOH \xrightarrow{\Delta} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sodium benzoate}}{C_6H_5COONa}$$

$$2HCHO + NaOH \xrightarrow{\Delta} \underset{\text{Methyl alcohol}}{CH_3OH} + \underset{\text{Sodium formate}}{HCOONa}$$

The reaction best proceeds with aromatic aldehydes. Although the reaction is characteristic of aldehydes without α-hydrogen, a few aldehydes with α-hydrogen are known which undergo Cannizzaro reaction (exception).

$$\underset{\text{Dimethyl acetaldehyde}}{2(CH_3)_2CHCHO} \xrightarrow{200°C} \underset{\text{2-Methylpropanol-1}}{(CH_3)_2CHCH_2OH} + \underset{\text{Sodium-2-methyl propanoate}}{(CH_3)_2CHCOONa}$$

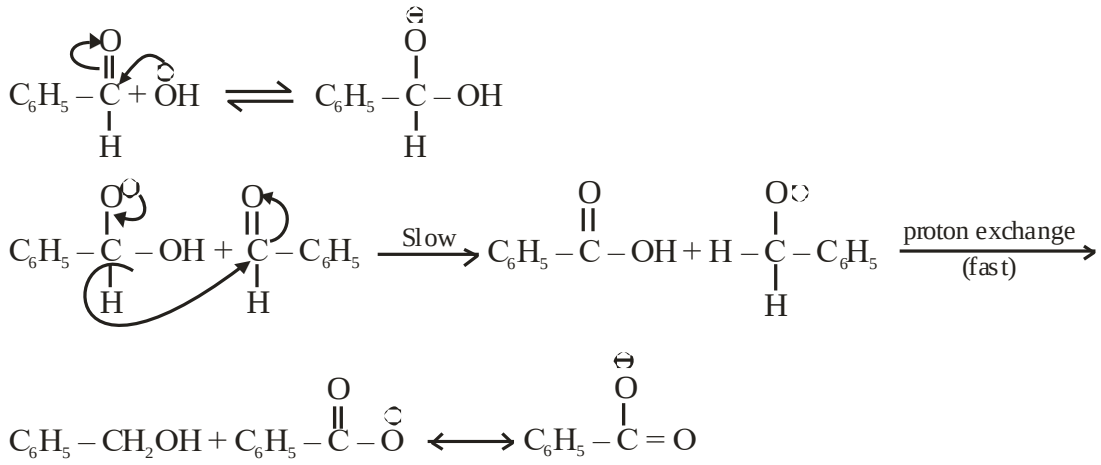
The reaction can also occur between two different aldehydes having no α-hydrogen when it is called crossed Cannizzaro reaction.

$$C_6H_5CHO + HCHO \xrightarrow[\Delta]{NaOH} C_6H_5CH_2OH + HCOONa$$

When formaldehyde undergo crossed Cannizzaro reaction with other aldehydes without α-hydrogens, it is seen that formaldehyde is oxidized and the other is reduced. This is because the nucleophilic attack occurs more readily on formaldehyde than on other aldehydes.

Mechanism

Rapid addition of $\overset{\ominus}{OH}$ to one molecule of aldehyde results in the formation of a hydroxyl alkoxide ion which like aluminium-isopropoxide acts as a hydride-ion donor to the second molecule of aldehyde. In the final step of the reaction the acid and the alkoxide ion exchange proton for reasons of stability.



Evidence in Support of the Mechanism

(*i*) The reaction follows third-order law (second in aldehyde and first order in base), *i.e.*, rate $\propto [\text{Ald}]^2[\bar{\text{O}}\text{H}]$. This suggests the reaction between the first-formed anion (from base and aldehyde) and another molecule of aldehyde in the rate-determining step.

(*ii*) That the hydride ion is directly transferred from one molecule of the aldehyde to the other, and does not become free in solution has been proved by the observation that the recovered alcohol does not contain deuterium when the reaction is performed in the presence of D_2O.

It is seen that the reaction depends on the nucleophilic attack on the carbonyl carbon. Hence, factors which reduce the positive charge of the carbonyl carbon retard the reaction. In extreme cases the reaction may not occur. *e.g,* *p*-dimethylaminobenzaldehyde does not undergo Cannizzaro reaction.

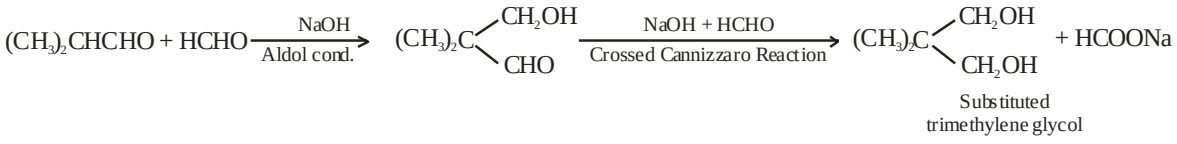
Similarly, sterically hindered aldehydes do not undergo the reaction.

Applications

1. **Crossed Cannizzaro reaction.** One of the most important applications is the crossed Cannizzaro reaction between formaldehyde and other aldehydes having □-hydrogens.

During the reaction, the □-hydrogens are replaced by hydroxymethyl groups $-CH_2OH$ through aldol condensation and then the product, □-hydroxyaldehyde undergoes crossed Cannizzaro reaction with formaldehyde.

Thus, aldehydes containing one, two or three □-hydrogens react as given below.

(i) 

(ii) $CH_3CH_2CHO \xrightarrow[\text{Aldol cond.}]{2HCHO + NaOH} CH_3-C(CH_2OH)_2-CHO \xrightarrow[\text{Crossed Cannizzaro Reaction}]{HCHO + NaOH} CH_3-C(CH_2OH)_3$

1,1,1 - Trihydroxymethyl ethane

(iii) $CH_3CHO \xrightarrow[\text{Aldol cond.}]{3HCHO + Ca(OH)_2} HOH_2C-C(CH_2OH)_2-CHO \xrightarrow[\text{Crossed Cannizzaro Reaction}]{HCHO + NaOH} HOH_2C-C(CH_2OH)_3$

Tetramethylol methale (Pentaerythritol)

2. **Intramolecular cannizzaro reaction.** Dialdehyde and □-keto aldehydes undergo intramolecular Cannizzaro reaction giving various valuable products.

(i) $C_6H_5-CO-CO-H \xrightarrow{OH^-} C_6H_5-C(O^-)(OH)-CO-H \longrightarrow C_6H_5-C(O^-)H-CO-OH \xrightarrow[\text{proton transfer}]{\text{Intermolecular}} C_6H_5-C(OH)H-CO_2Na$

Phenyl glycol

Sod. salt of mandelic acid

(ii) $H-CO-CO-H \xrightarrow[2.\ H^{\oplus}]{1.\ NaOH} H-C(OH)H-COOH$

Glycol

Glycolic acid

1.9 PERKIN REACTION

In Perkin reaction, condensation has been effected between aromatic aldehydes and aliphatic acid anhydrides in the presence of sodium or potassium salt of the acid corresponding to the anhydride, to yield □□□□-unsaturated atomatic acids.

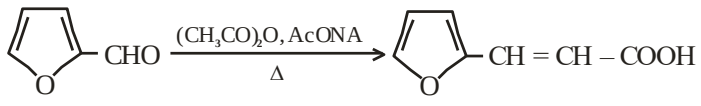
The acid anhydride should have at least two □-hydrogens.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow[170-180^\circ C]{AcONa} C_6H_5-CH=CH-COOH + CH_3COOH$$

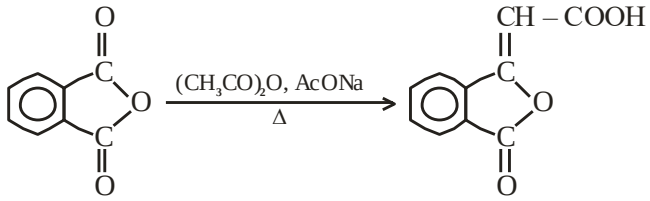
Besides simple aromatic aldehydes, heterocyclic aldehydes and even phathalic anhydride (as the carbonyl component) give reaction.

(*a*) $C_6H_5-CH=CH-CHO \xrightarrow[\Delta]{(CH_3CO)_2O,\ AcONa} C_6H_5-CH=CH-CH=CH-COOH$

5–Phenyl–pen2,4–dienoic acid

(*b*) 

3-(α-Furyl)-acrylic acid

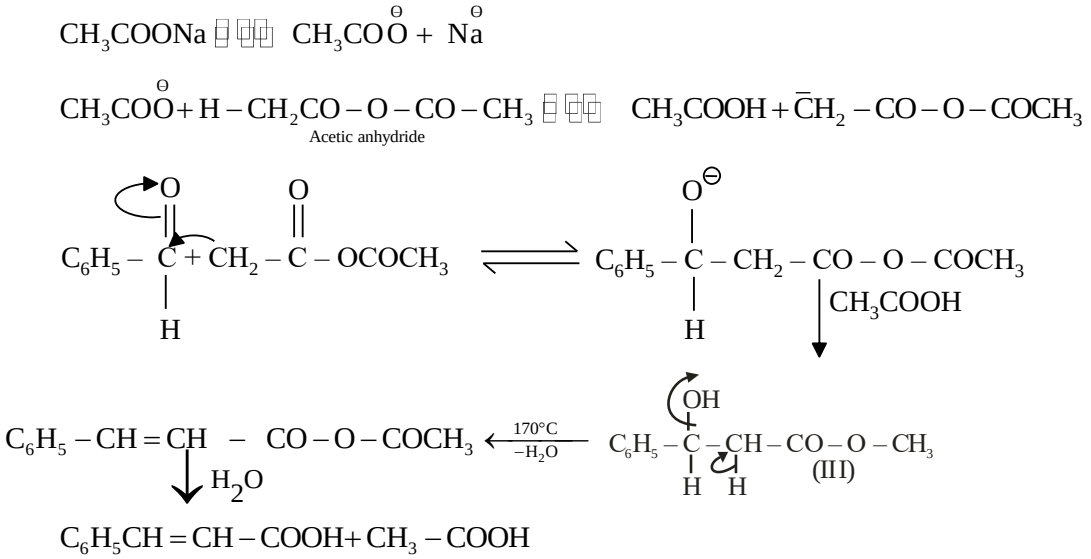
(*c*) 

Phthalyacetic acid

Mechanism

It is suggested that the acetate ion abstracts a proton from the □-carbon of the anhydride producing a carbanion which then attacks the carbonyl group of the aldehyde. The product then abstracts a proton from the acid to form aldol-type compound. The later then undergoes dehydration in the presence of hot acetic anhydride.

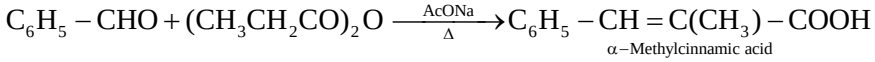
On pouring the hot mixture in water, the mixed anhydride is hydrolysed to □□□-unsaturated acid.



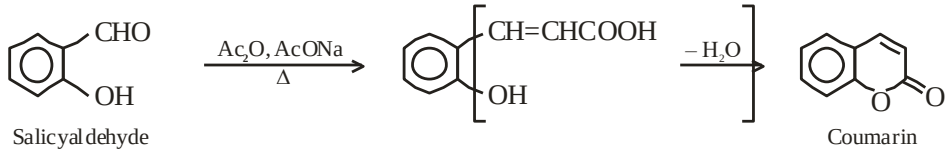
APPLICATIONS

Perkin reaction has many useful synthetic applications.

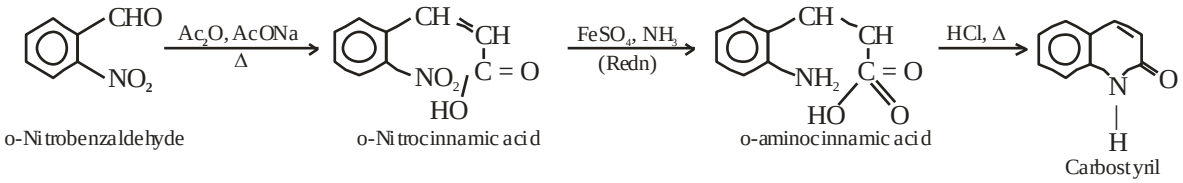
1. Preparation of □-substituted unsaturated acids



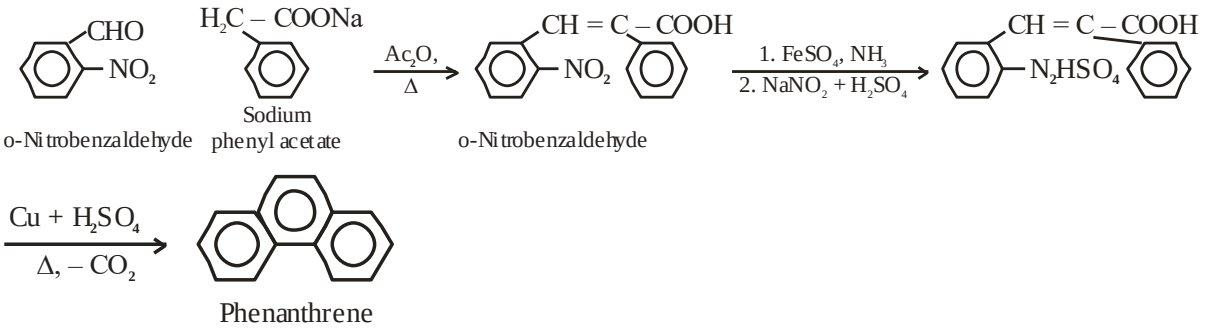
2. Synthesis of coumarin



3. Synthesis of Carbostyril (nitrogen analogue of coumarin)



4. Synthesis of phenanthrene



1.10 CLAISEN CONDENSATION

Esters having □-hydrogen on treatment with a strong base, *e.g.*, C_2H_5ONa, undergo self-condensation to produce □-ketoesters.

$$2CH_3COOC_2H_5 \xrightarrow[2.\ H^{\oplus}]{1.\ C_2H_5ONa} \underset{\text{Ethyl acetoacetate}}{CH_3COCH_2COOC_2H_5}$$

$$2R'CH_2COOC_2H_5 \xrightarrow[2.\ H^{\oplus}]{1.\ C_2H_5ONa} R'CH_2COCH(R')COOC_2H_5$$

This reaction is called Claisen condensation.

Mixed or crossed claisen condensation also occurs between two different esters or between an ester and a ketone.

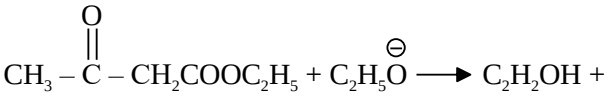
□ Mechanism

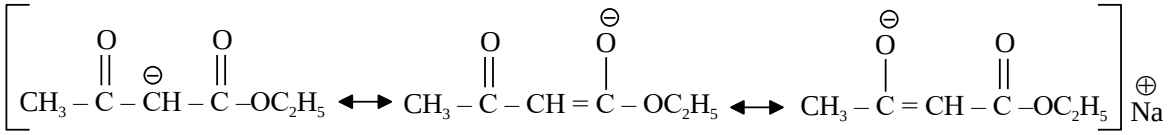
The ethoxide ion abstracts a proton from the □-carbon of the ester to produce the anion (of the ester) which is a powerful nucleophile (1st step). The nucleophilic attack of the anion on the carbonyl carbon of a second molecule of ester produces an oxonium ion (2nd step), which eliminates an ethoxide ion to give the □-ketoester (3rd step). The □-ketoester having an active methylene group is acidic and reacts with sodium ethoxide to form enolate salt (4th step). Subsequent acidification with acitic acid (1 : 1) regenerates the □-ketoester.

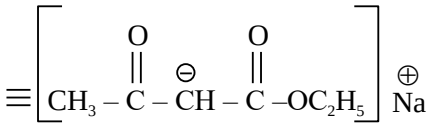
$$C_2H_5\overset{\ominus}{O} + H - CH_2COOC_2H_5 \rightleftharpoons C_2H_5OH + :\overset{\ominus}{C}H_2COOC_2H_5 \quad \ldots (i)$$

$$CH_3 - \underset{\displaystyle OC_2H_5}{\overset{\displaystyle O}{\overset{\|}{C}}} + CH_2COOHC_2H_5 \rightleftharpoons CH_3 - \underset{\displaystyle OC_2H_5}{\overset{\displaystyle \overset{\ominus}{O}}{\overset{|}{C}}} - CH_2COOC_2H_5 \quad \ldots (ii)$$

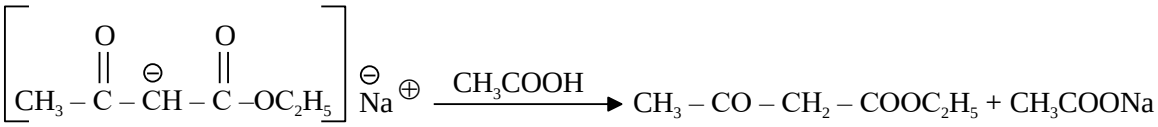
$$CH_3 - \underset{\displaystyle OC_2H_5}{\overset{\displaystyle \overset{\ominus}{O}}{\overset{|}{C}}} - CH_2COOC_2H_5 \rightleftharpoons CH_3 - \overset{\displaystyle O}{\overset{\|}{C}} - CH_2COOC_2H_5 + C_2H_5\overset{\ominus}{O} \quad \ldots (iii)$$







… (iv)



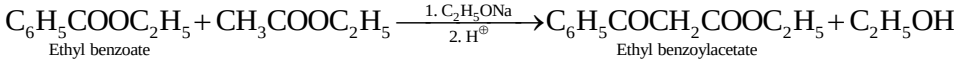
Applications

Crossed Claisen condensations between two different esters (both having □-hydrogens) have little synthetic value, for a mixture of four products are obtained. However, if one of the ester has no □-hydrogen it acts as a carbanion acceptor and the self-condensation of the other ester is minimized. Commonly used ester with no □-hydrogen are ethylbenzoate, ethyl formate, ethyloxalate, ethyl carbonate, etc. These esters are good carbanion acceptors.

Ketones are generally more acidic than esters and the rate of their base-catalyzed condensation (aldol) is very slow. Hence, ketones serve as nucleophiles in mixed Claisen condensation to give a large variety of products.

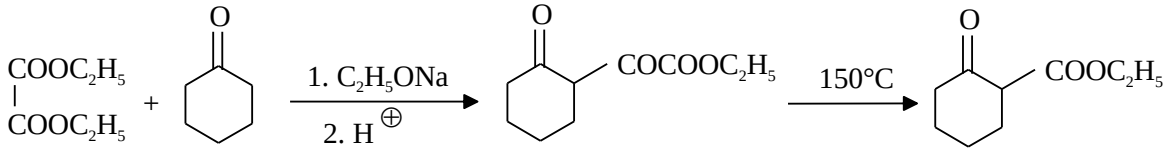
Some of the examples of crossed Claisen condensation and their applications are given below.

1. Condensation with ethyl benzoate



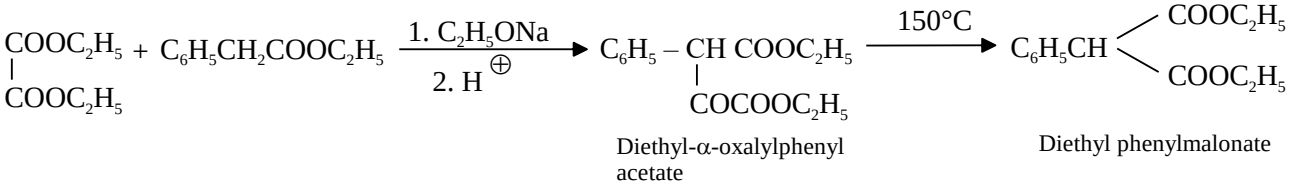
2. Condensation with diethyl oxalate. Ketones and ester condense with diethyl oxalate to give oxalyl derivatives which have ynthetic utility since they lose carbon monoxide on heating to give malonic ester derivates which may be used for the preparation of aryl-substituted dibasic acid derivatives and □-keto acids.

(a)



2-(Ethyl oxalyl)-cyclohexanone 2-Carbethoxy cyclohexanone

(b)

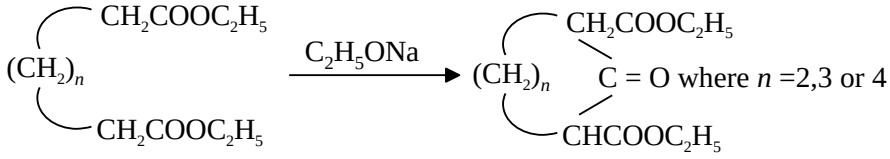


Diethyl-α-oxalylphenyl acetate

Diethyl phenylmalonate

1.11 DIECKMANN REACTION

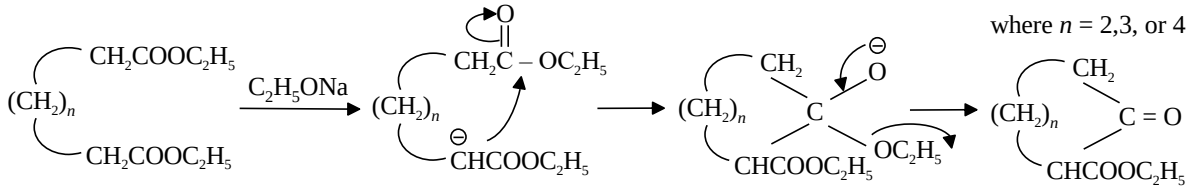
Intramolecular Claisen condensation in dibasic acid esters is called Dieckmann reaction. The resulting products are invariably cyclic □-ketone derivatives. The condensing bases may be sodium, sodium ethoxide, sodium hydride potassium *t*-butoxide, etc.



□ Mechanism

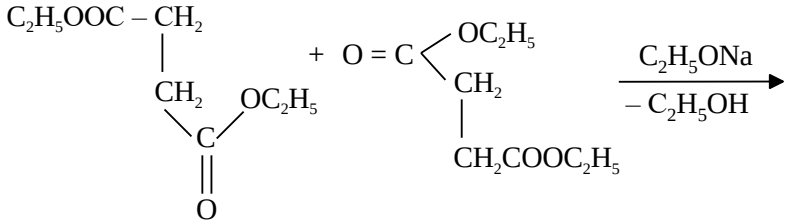
The mechanism of the reaction is similar to that of Claisen condensation

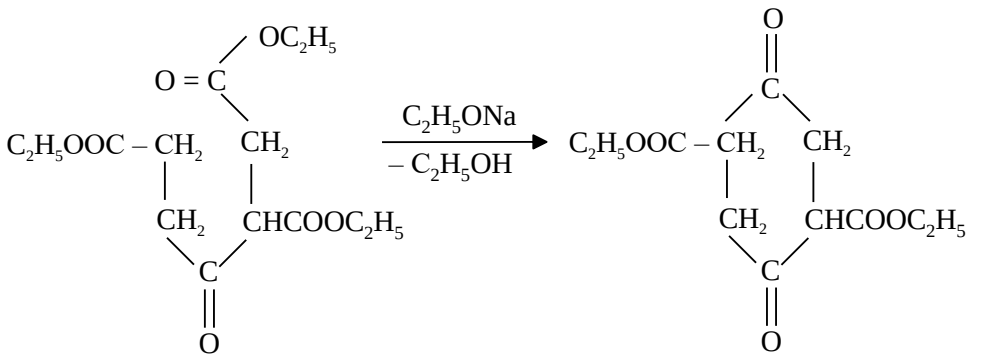
The base abstracts a proton from one of the □-carbons. The resulting carbanion then attacks the carbonyl carbon of the other ester group. Subsequent expulsion of the alkoxide ion gives the cyclic ketone derivative.



The compound on hydrolysis and decarboxylation gives cyclic ketone.

Ester of acids lower than adipic acid undergo more of intermolecular condensation with subsequent cyclisation. Thus, ethyl succinate gives cyclohexandione derivative. This may be due to reasons of stability of six-membered rings.





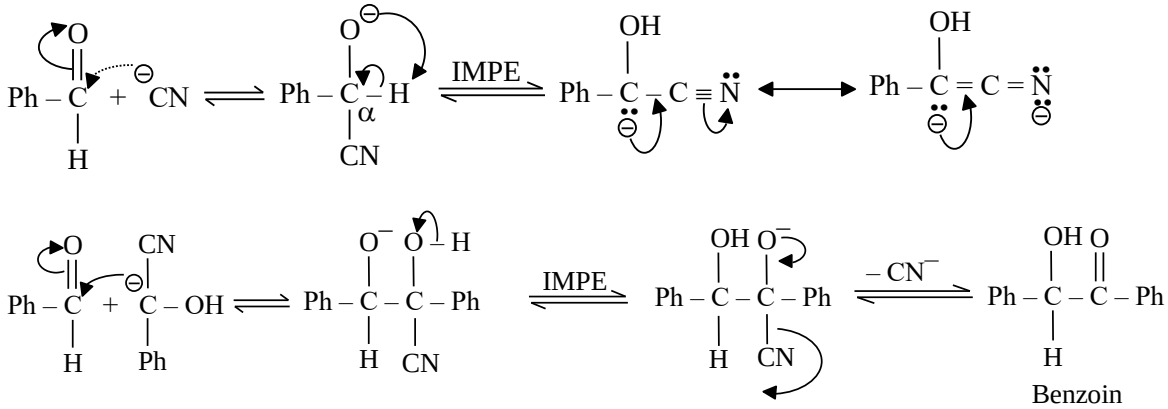
Cyclohexan-2, 5-dione-1, 4-dicarboxylic ester

1.12 BENZOIN CONDENSATION

$$2PhCHO \xrightarrow[KCN]{\text{Alcoholic}} \underset{\text{Benzoin}}{PhCH(OH)COPh}$$

When aromatic aldehydes is treated with alcoholic KCN, the product is not a cyanohydrin but □-hydroxy aromatic ketone called benzoin. The product of aromatic aldehydes with KCN is different than aliphatic aldehydes because after the attack of CN^-, the intermediate (I) in aromatic aldehyde has sufficient acidity (due to – I effect of Ph) so that intramolecular proton exchange takes place to form a carbanion, which is resonance stabilized. This carbanion then attacks another molecule of aromatic aldehyde, which undergoes intramolecular proton exchange and then ejection of CN^- to give final product *i.e.* benzoin. The rate-limiting step of the reaction is attack of carbanion on second molecule of aromatic aldehyde.

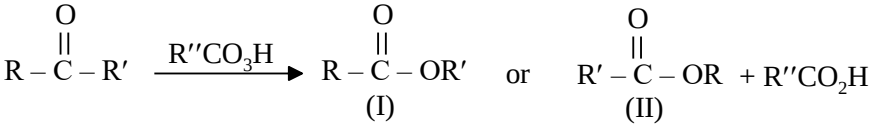
□ Mechanism



IMPE = Intra molecular proton exchange

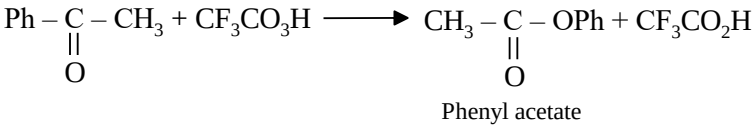
1.13 BAEYER-VILLIGER OXIDATION:

The reaction of oxidation of ketones to ester by peroxy acids (CF_3COOOH) or BF_3/H_2O_2 or H_2O_2/Base is called Baeyer – Villiger oxidation.



Product (I) is formed when migratory aptitude of R□ is greater than that of R and if it is greater for R, then product (II) is produced.

For example, acetophenone on treatment with peroxy trifluoro acetic acid gives phenyl acetate and not methyl benzoate. This reflects phenyl group has a greater migrating tendency than methyl group.

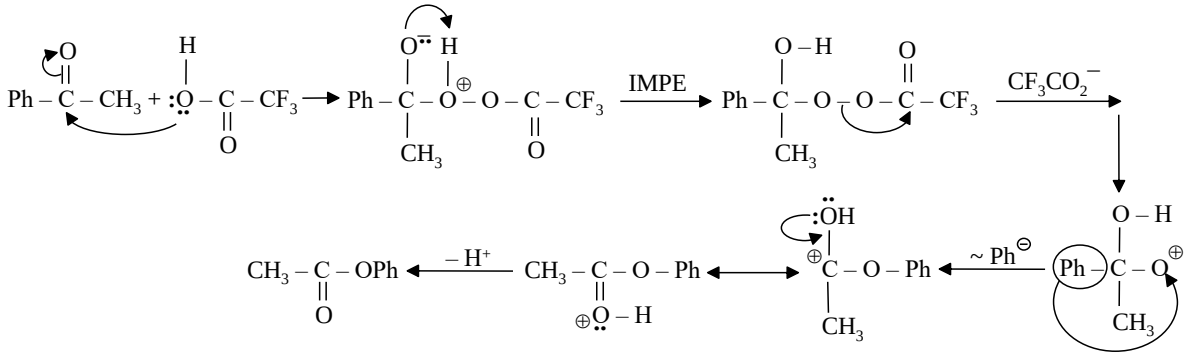


Phenyl acetate

The overall reaction is an insertion of oxygen atom between the carbonyl group and the group that has greater migrating tendency.

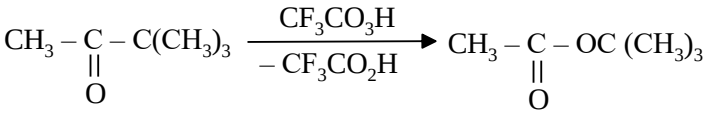
□ Mechanism

The proposed mechanism involves transfer of acidic hydrogen from peroxy acid to carbonyl oxygen and attack of $CF_3CO_3^-$ on carbonyl carbon of acetophenone. As O–O linkage is weak, it cleaves to release $CF_3CO_2^-$ (which is a good leaving group) and oxygen becomes electron deficient. On electron deficient oxygen, phenyl group migrates from the adjacent carbon to give a carbocation, which then loses $H^+$to give phenyl acetate



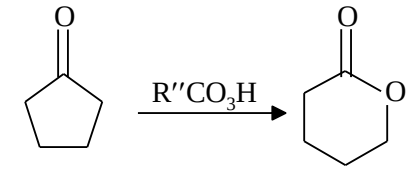
Thus the reaction establishes the migratory aptitude of various alkyl groups and H as H□ > 3°R□ > 2°R□ > 1°R□ > CH_3□ and that of aryl groups as p-anisyl > p-tolyl > phenyl > p-chloro phenyl > p-nitro phnyl. In case of alkyl aryl ketones, it is the aryl group which migrates (exception in case of $(CH_3)_3C$ group).

For example,



t-butyl acetate

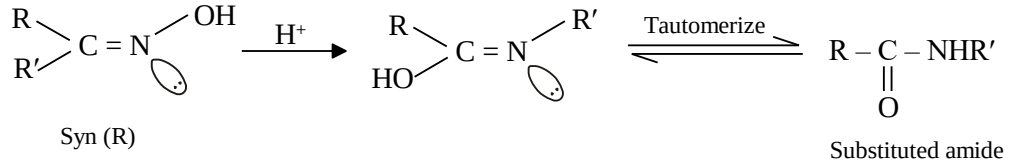
Cyclic ketones get converted to lactones with ring expansion on treatment with peroxy acids.



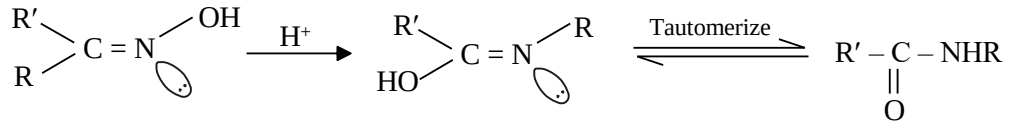
Cyclopentanone δ-lactone

1.14 Beckmann Rearrangement

When oximes (especially ketoximes) are treated with acidic catalyst like H^+, PCl_5, $SOCl_2$, SO_3, P_2O_5 etc., They are transformed into substituted amides. The structure of the substituted amide depends on the structure of ketoxime as the migration of the groups does not depend on their migratory aptitude but on the group that is at trans position to the hydroxyl group.



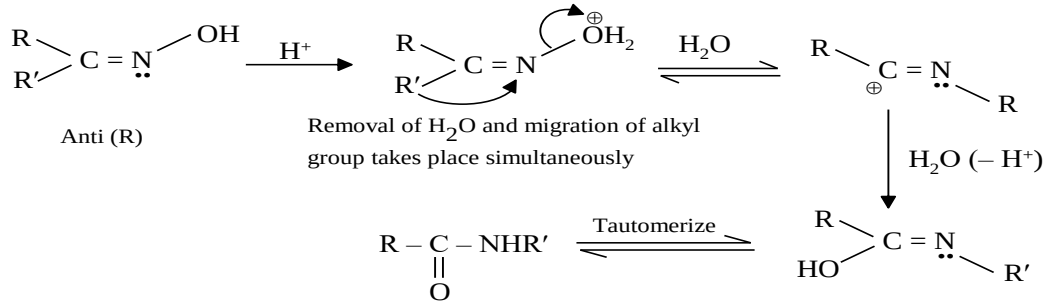
Syn (R) Substituted amide



Anti (R) Substituted amide

☐ Mechanism

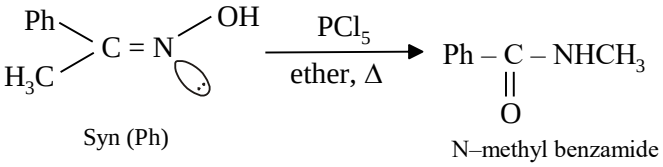
The given reaction adopts following mechanism, in which group that migrates is anti to the –OH group.



Anti (R)

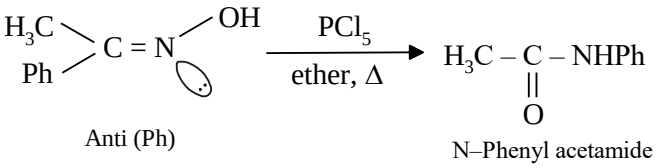
Removal of H_2O and migration of alkyl group takes place simultaneously

For example,



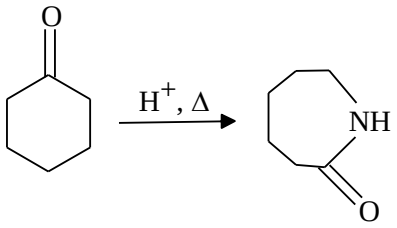
Syn (Ph)

N–methyl benzamide



Anti (Ph)

N–Phenyl acetamide

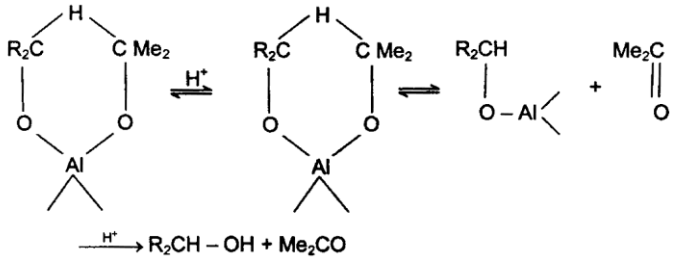


Cyclohexanone oxime

Caprolactam

1.15 Meerwein - Ponndorf - Verley Reduction

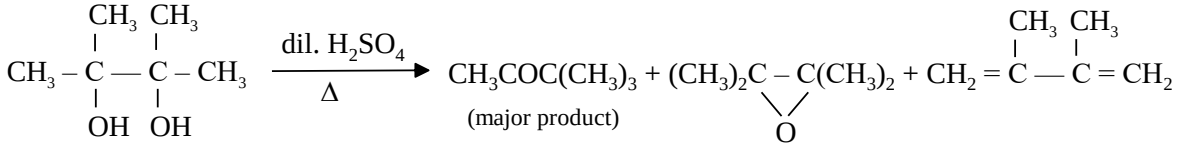
The carbonyl compound is heated with aluminium isopropoxide in isopropanol solution, the isopropoxide is oxidised to acetone, which is removed by slow distillation.



The reducing agent is specific for the carbonyl group, and so may be used for reducing aldehydes and ketones containing some other functional group that is reducible e.g., a double bond or a nitro group.

1.16 Pinacol – Pinacolone Rearrangement

Pinacol (a vicinal diol) on treatment with hot and dilute sulphuric acid undergoes dehydration with rearrangement to give aldehydes or ketones as the major product depending upon the structure of diol. With pinacol, a major product is pinacolone.



Pinacol

(major product)

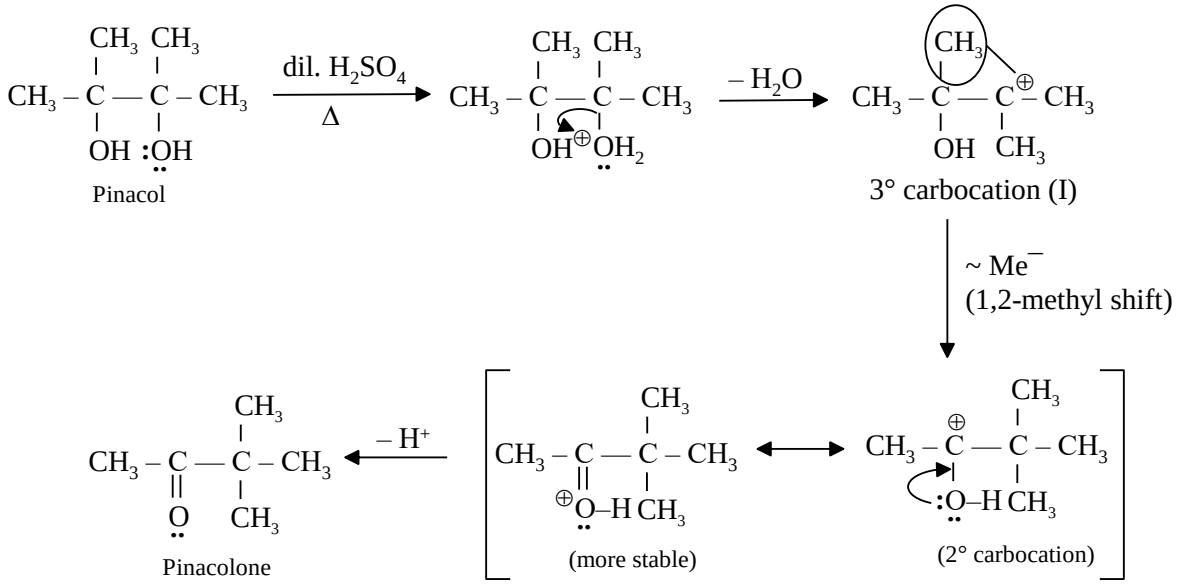
For a symmetrical 1, 2 –diol, any of the –OH group can be protonated but for an unsymmetrical 1,2-diol, that –OH group is protonated whose loss as H_2O can form a sable carbocation. Although the initially formed carbocation is 3° (or some other type of carbocation), it rearranges by alkyl or aryl shift to give a secondary carbocation. This secondary carbocation formed as a result of rearrangement is more stable than the initially formed carbocation because of lone pair delocalization, it gives a resonating form in which octet of every atom is complete, except hydrogen, which has a duplet only. The group that migrates is the one that has a higher migratory aptitude. The rearranged carbocation then loses a proton to the base to give final product.

(*i*) Aryl > hydrogen > alkyl

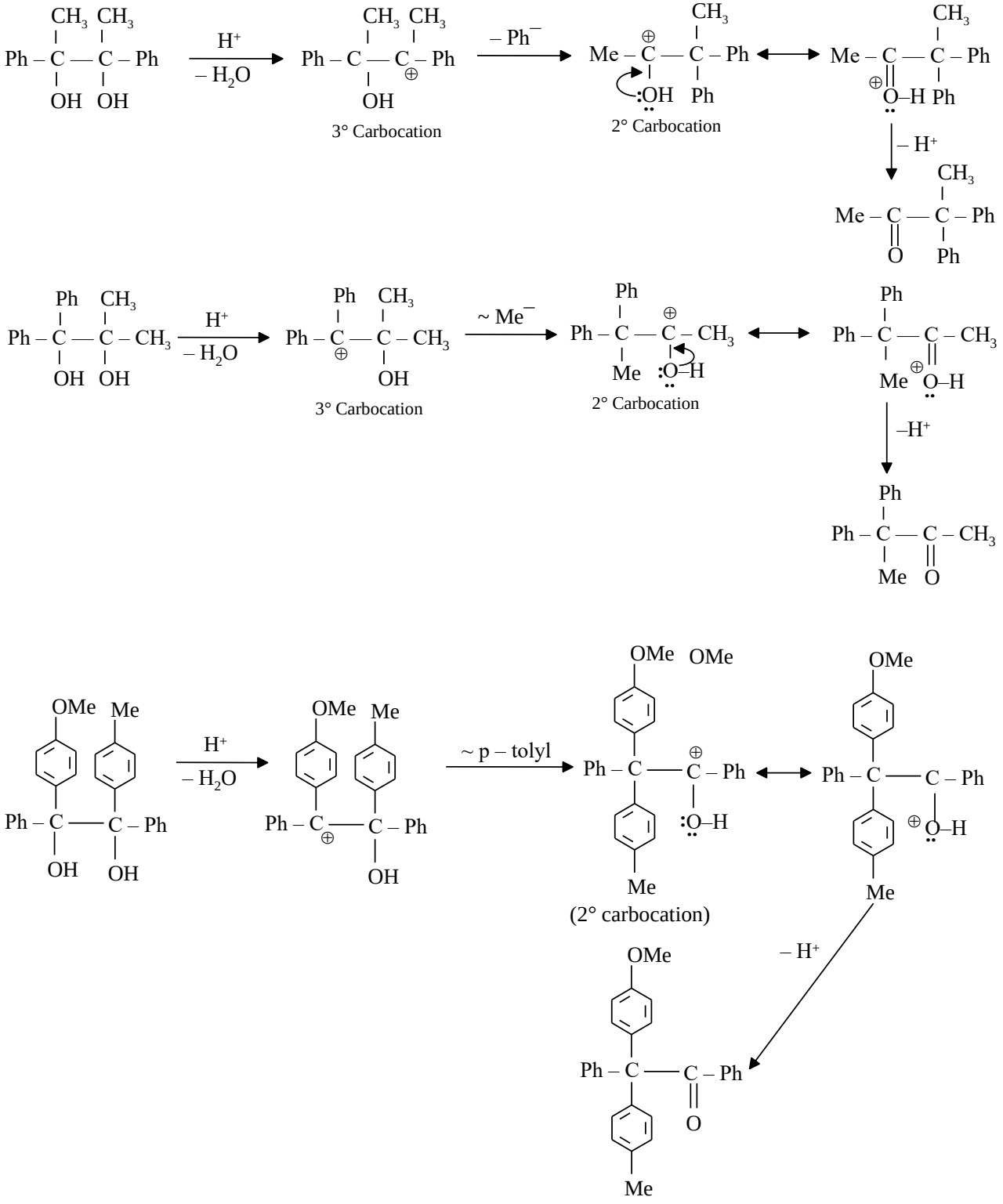
(*ii*) p-anisyl > p-tolyl > m – tolyl > m – anisyl > phenyl > p-chlorophenyl > o – anisyl > o – tolyl

(*iii*) Me_3C(3° alkyl) > Me_2CH (2° alkyl) > $MeCH_2$ (2° alkyl) > Me

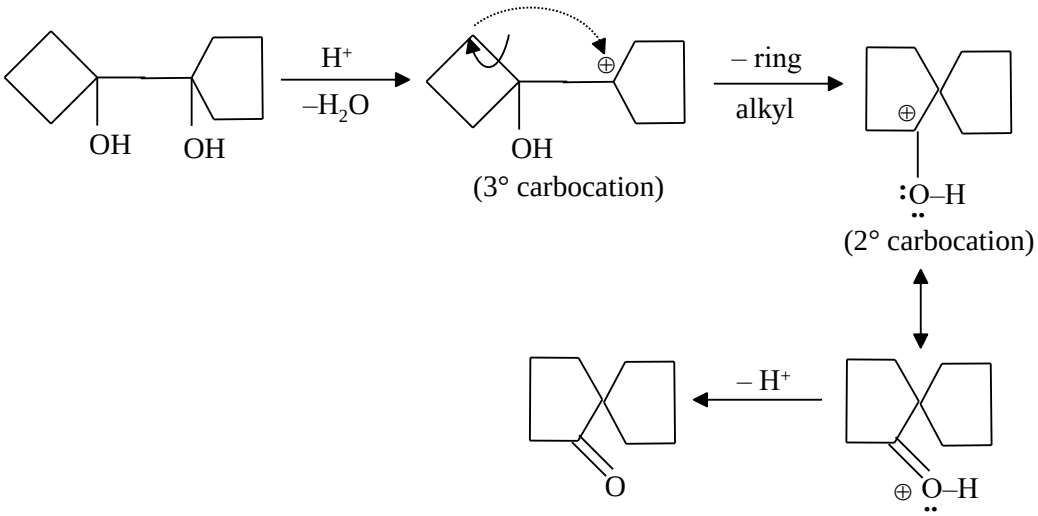
For Example



The conjugated alkene product would be obtained when intermediate (I) loses another OH as H_2O to give a dication, which then loses 2 protons from □-positions. The epoxide product would be obtained when in intermediate (I), OH attacks C□ through its lone pair to form a three – membered ring, which finally loses H^+. But diene is a minor product as the dication formed is not stable due to the presence of positive charges on adjacent carbanions. Epoxide is also not the stable product as it gets cleaved in acidic medium to give back (I).

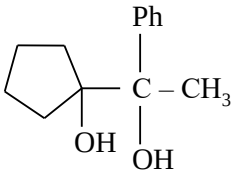


Bicyclic 1,2-diols also undergo pinacol-pinacolone type mechanism with the ring expansion/ring contraction depending on the ring sizes.

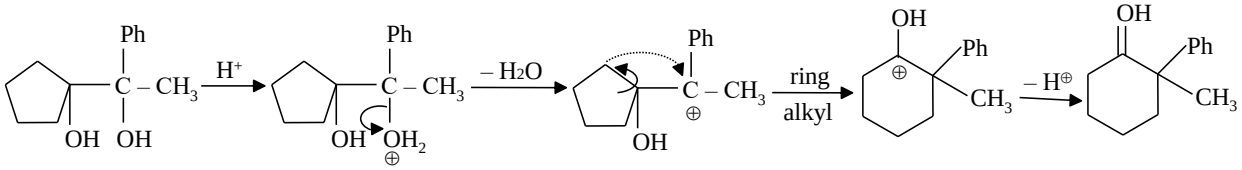


ILLUSTRATIONS

Illustration 6

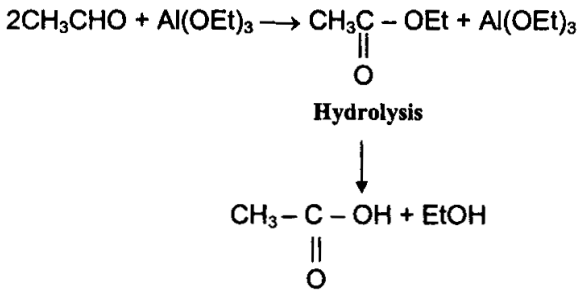
Given the product of the rearrangement of the cyclopentyl glycol,  and show how it is formed.

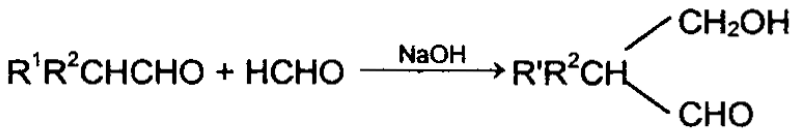
Solution



1.17 TISCHENKO REACTION

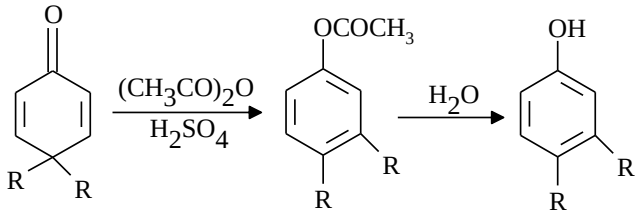
All aldehydes can be made to undergo the Cannizzaro reaction by treatment with aluminium ethoxide. Under these conditions the acids and alcohols are combined as the ester, and the reaction is then known as the Tischenko reaction; eg, acetaldehyde gives ethyl acetate, and propionaldehyde gives propyl propionate.





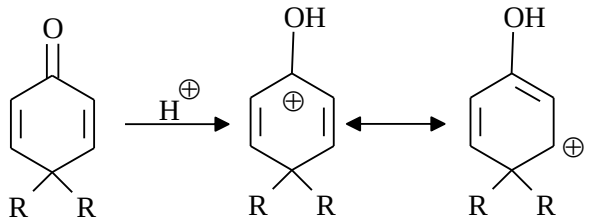
1.18 Dienone–Phenol Rearrangement

When 4, 4–dialkyl cyclohexadienone is treated with acid, it is converted to phenol with migration of one of the alkyl groups to the adjacent carbon. This is known as dienone–phenol rearrangement. The dienone is dissolved in acetic anhydride and treated with catalytic amount of sulphuric acid. The product on hydrolysis gives the phenol.

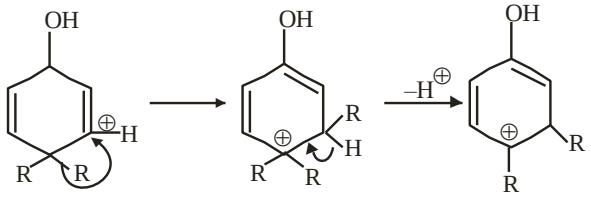


Mechanism

On protonation of the oxygen, a carbocation is generated which is stabilized by delocalization of the positive charge.



In one of the canonical structures, the positive charge is on a carbon adjacent to a highly substituted carbon. Hence, a carbocation rearrangement occurs. Subsequent loss of a proton gives the 3, 4–disubstituted phenol.



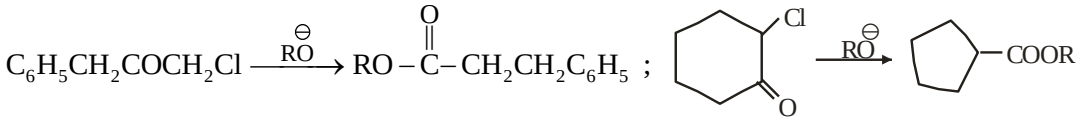
The ease of dienone-phenol rearrangement is due to the creation of a stable aromatic system.

When one of the alkyl group forms a part of the cyclic system, either the alkyl group or the ring methylene group may migrate.

1.19 Favorskii Rearrangement

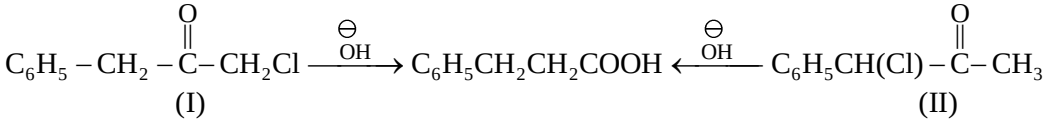
The transformation of α-haloketones to esters with rearranged carbon skeleton by the treatment with alkoxide ions is called Favorskii rearrangement. Alkali hydroxides or amines in place of metal alkoxides give acids or amides respectively.

Cyclic α–haloketones give esters with ring contraction.



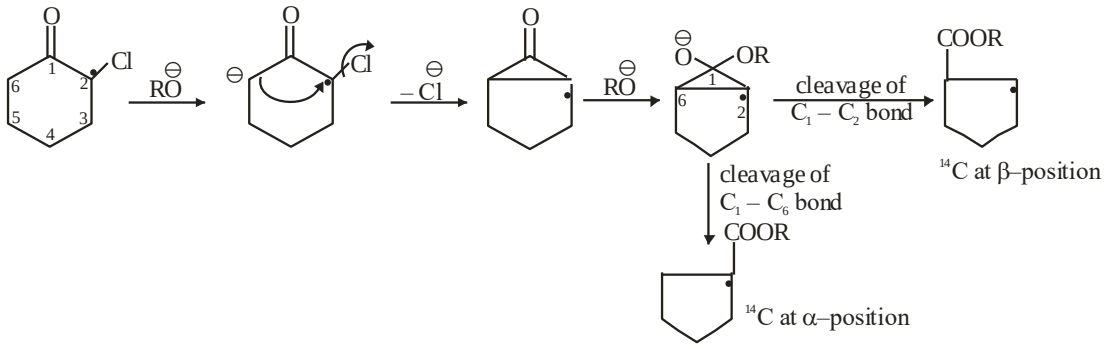
☐ Mechanism

The mechanism of the rearrangement has been the subject of much investigation. It was observed that both the isomeric ketones. (I) and (II) gave β-phenylproplonic acid on treatment with hydroxide ions.

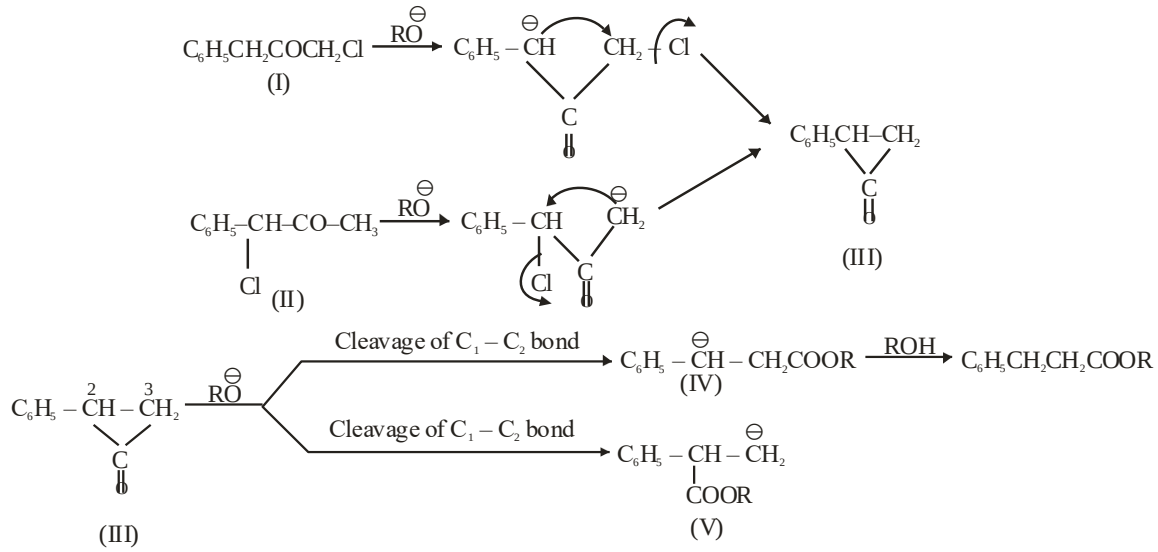


This observation indicates that the chlorine is not being directly replaced by the incoming group from the other side of the carbonyl group, as otherwise (II) would give $C_6H_5CH(CH_3)COOH$ which is not obtained. Further, it was observed that a cyclic ketone (2-chlorocyclohexanone) with labeled carbon bearing the chlorine atom, on treatment with alkoxide ion gave a product in which equal amounts of ^{14}C were present at the α-carbon and at the β-carbon. The suggests a symmetrical cyclopropanone intermediate which opens up with equal ease on either side of the carbonyl group.

On the basis of the above observations, the following mechanism has been suggested. The base abstracts an α-hydrogen to produce a carbanion. Intramolecular nucleophilic attack on the carbon bearing the chlorine displaces the chlorine atom with the formation of a transient symmetrical cyclopropanone ring. Subsequent attack of the alkoxide ion on the carbonyl carbon opens the ring with equal ease on either side of the carbonyl carbon so that the product contains 50% of ^{14}C at the α-position and 50% at the β-position.



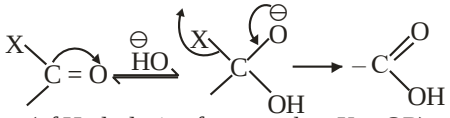
In case of unsymmetrical ketones, the unsymmetrical cyclopropanone ring which is formed, opens up to give the most stable carbanion. Thus, the two isomeric ketones (I) and (II) give the same cyclic intermediate (III) which may open on either side of the carbonyl group to give two carbanions (IV) and (V).



Although the cyclopropanone intermediate has not been isolated. It has been trapped to give an adduct with furan.

1.20 Benzilic Acid Rearrangement

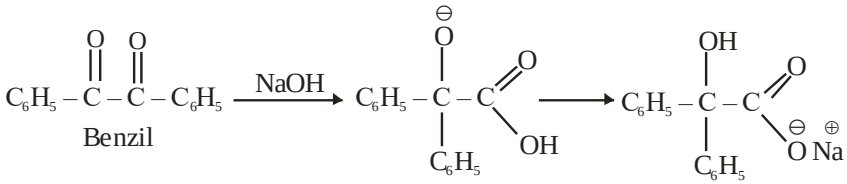
The addition of a strong base to a carbonyl group results in the formation of an anion. The reversal of the anionic charge may cause expulsion of the attached group, X, e.g.,



(cf.Hydrolysis of esters when X = OR)

However, in a 1,2-diketone the group X may migrate to the adjacent electron- deficient carbonyl carbon forming α-hydroxy acids.

Thus, benzil on treatment with a strong base forms benzilic acid (salt), whence the name benzilic acid rearrangement.



Sodium salt of benzilic acid

Barium and thallous hydroxides are more effective than sodium or potassium hydroxdides. Alkoxide ions (Methoxide, t-butoxide, etc.) in place of hydroxide ion give the corresponding esters.

$$C_6H_5 - CO - CO - C_6H_5 \xrightarrow{CH_3ONa} (C_6H_5)_2C(OH)COOCH_3$$

Benzilic acid methyl ester

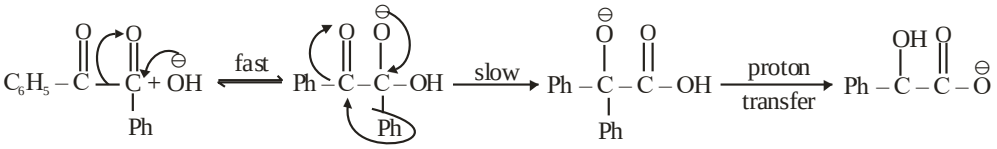
Phenoxide ions are too weak a nucleophile to attack. Besides aromatic 1, 2-diketone, alilphatic and heterocyclic diketones as also o-quinones undergo this rearrangement.

☐ Mechanism

It has been seen that the rate of reaction is proportional to the concentrations of benzyl and the hydroxide ion, i.e., rate $\propto [C_6H_5COCOC_6H_5][O\bar{H}]$

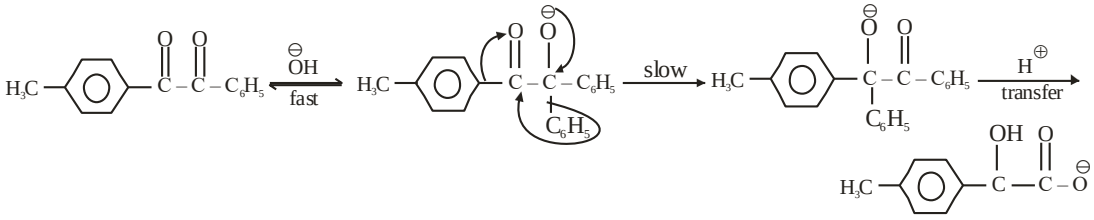
It has also been found that when the reaction is carried out in the presence of H_2O^{18}, benzyl exchanges ^{18}O faster that it rearranges.

On the basis of the above observations, it has been suggested that a fast reversible nucleophilic attack occurs at the carbonyl carbon in the first step. The second step is the rate-determining step in which the migration occurs. Finally, a rapid proton transfer completes the process.



The rearrangement is analogous to intramolecular Cannizzaro reaction of glyoxal.

The carbonyl group which is attached to the less electron releasing of the two aryl groups is relatively more positively charged and hence, is attacked $\bar{O}H$. Consequently, the less electron-donating aryl group

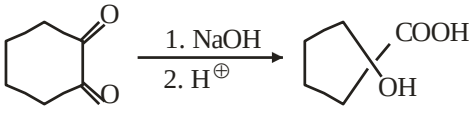


(p-Tolyl group is more electron-releasing than phenyl group)

☐ Applications

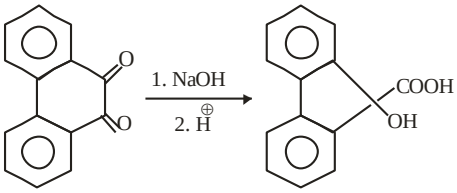
The reaction is a general one end can take place with aromatic, heterocyclic, allicyclic, and aliphatic 1, 2-diketones as also 1, 2-quinones.

(i)



Cyclohexane -1, 2-dione — Cyclopentanol -1-carboxylic acid

(ii)



Phenanthraquinone — 9-Hydroxyfluorene-9-carboxylic acid

1.21 KNOEVENAGEL REACTION

Condensations of aldehydes and ketones with compounds having active methylene group in the presence of basic catalyst to form α, β-unsaturated compounds is called Knoevenagel reaction. The basic catalysts may be ammonia or its derivatives. Thus, primary, secondary or tertiary amines, e.g., aniline, di-or tri-alkyl amines, pyridine, piperidine, etc., are used

$$C_6H_5CHO + \underset{\text{Malonic ester}}{H_2C(COOR)_2} \xrightarrow[\text{Piperidine}]{\text{Pyridine}} C_6H_5CH=C(COOR)_2 \xrightarrow[2.\,\Delta,-CO_2]{1.\,H_2O} \underset{\text{Cinnamic acid}}{C_6H_5-CH=CH-COOH}$$

☐ Mechanism

The initial stage of the reaction is base-catalysed aldol condensation with subsequent dehydration.

In the first step the base removes a proton from the active methylene group to generate a carbanion. The carbanion then attacks the carbonyl carbon of the substrate to form an alkoxide ion which abstracts the proton from the protonated catalyst to form a hydroxyl compound. Subsequent dehydration gives the α, β-saturated compound which is hydrolysed and decarboxylated to obtain α, β-unsaturated acid. The reaction with a malonic ester is as shown:

$$R_3\ddot{N} + H_2C(COOR)_2 \rightleftharpoons R_3\overset{\oplus}{N}H + \overset{\ominus}{H}C(COOR)_2$$

$$R'-CH=C(COOR)_2 \xrightarrow[2.\,\Delta-CO_2]{1.\,H_2O} R'-CH=CHCOOH$$

☐ Application

Various α, β-unsaturated acids such as crotonic, cinnamic, fumaric and β-piperonyl acrylic acids can be prepared.

(a) $$CH_3CHO + H_2C(COOR)_2 \xrightarrow{Pip} CH_3-CH=C(COOR)_2 \xrightarrow[2.\,\Delta,-CO_2]{1.\,H_2O} \underset{\text{Crotonic acid}}{CH_3-CH=CH-COOH}$$

(b) $$C_6H_5CHO + H_2C(COOR)_2 \xrightarrow{Pip} C_6H_5-CH=C(COOR)_2 \xrightarrow[2.\,\Delta,-CO_2]{1.\,H_2O} \underset{\text{Cinnamic acid}}{C_6H_5-CH=CH-COOH}$$

1.22 REFORMATSKY REACTION

Reformatsky reaction involves the preparation of β-hydroxyesters by the treatement of a reactive organic halide e.g., α-haloester in the presence of zinc metal and subsequent hydrolysis.

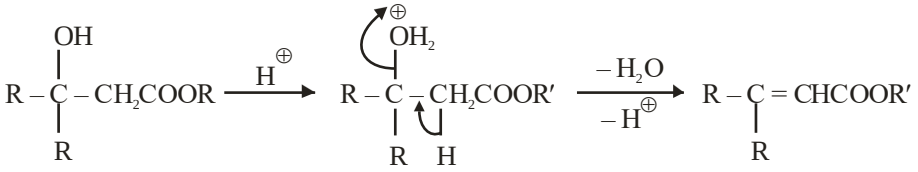
$$R-\underset{R'}{\overset{|}{C}}=O + BrCH_2COOEt \xrightarrow[2.\,H_3O^{\oplus}]{1.\,Zn+Et_2O} R-\underset{R'}{\overset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2COOEt$$

In practice, a mixture of the carbonyl compound, α-bromoester and zinc in dry ether is cautiously heated under reflux when zinc dissolves. Zinc may be activated by adding traces of iodine, mercuric bromide or copper powder. The mixture is then treated with ice-cold dilute sulphuric acid and ether layer separated. Ether is distilled off when β-hydroxyester is obtained.

Generally used solvents for this reaction are ether, benzene, toluene. THF etc. In place of zinc, activated indium, tin or zinc-copper couple have been used.

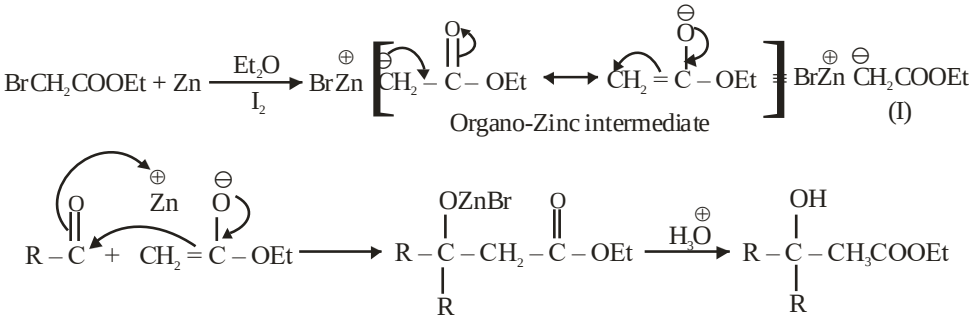
The aldehyde or ketone may be aliphatic, aromatic, or heterocyclic and may contain various functional groups which remain unaffected (difference from Grignard Reagent).

Acid catalyzed dehydration of the β-hydroxyester gives α, β-unsaturated ester.



☐ Mechanism

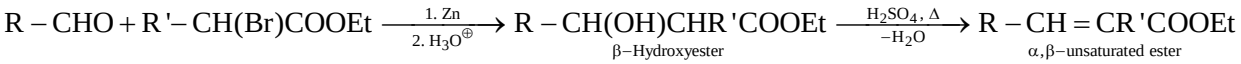
At first zinc and the α-bromoester react to form an organo-zinc intermediate (i). The zinc salt of the enol ester then adds to the carbonyl group of the aldehyde or ketone subsequent hydrolysis gives β-hydroxyester.



☐ Applications

The reaction has many valuable applications:

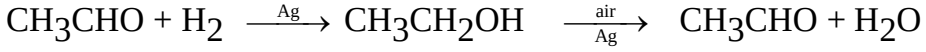
Preparation of β-hydroxyesters and unsaturated esters



1.23 ACETALDEHYDE, ETHANAL $CH_3-CH=O$

Acetaldehyde (ethanal) is prepared industrially:

(i) By the dehydrogenation or air oxidation of ethanol in the presence of silver catalyst at 300°C.



(ii) By passing a mixture of ethylene and oxygen, under pressure, into an aqueous solution of Pd and cupric chlorides at 50°C

CH_2= CH_2 + $PdCl_2$ + H_2O □ CH3CHO + Pd + 2HC1

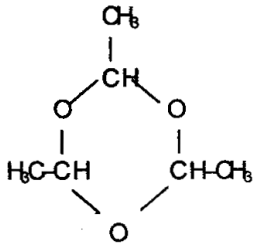
$2CuCl_2$ + Pd □ 2CuCI + $PdCI_2$

2CuCl + 2HCl + ½O_2 □ $2CuCI_2$ + H_2O

Acetaldehyde is a colourless, pungent smelling liquid, b.p, 21 °C.

□ Polymers of Acetaldehyde

When acetaldehyde is treated with a few drops of conc H_2SO_4, a vigorous reaction takes place and the trimer paraldehyde, $(CH_3CHO)_3$ is formed. It's structure is believed to be (I)



□ Polymers of Formaldehyde

(i) In dilute aqueous solution, formaldehyde is almost 100% hydrated to form nvathylene glycol this is believed to be the reason for the stability of dilute formaldehyde solutions.

$CH_2O + H_2O$ □□□ $CH_2(OH)_2$

(ii) When formaldehyde solution is evaporated to dryness, white crystalline solid, m.p.-121-123°C, is obtained this is known as paraformaldehyde, $(CH_2O)n.H_2O$, and it appears to be a mixture of polymers, n having values between 6 and 50. Paraformaldehyde reforms formaldehyde when heated.

(iii) When formaldehyde gas is allowed to stand at room temperature formaldehyde gas slowly polymerises to a white solid, trioxymethylene $(CH_2O)_3$, mp 61-62°C. Trioxan is prepared by distilling formaldehyde solution (60%) containing a little sulphuric acid. This trimer is soluble in water and does not show any reducing properties.

1.24 BENZALDEHYDE

Benzaldehyde (and aromatic aldehydes in general) resemble aliphatic aldehydes in the following reactions:

(i) It gives the Schiffs reaction.

(ii) It is readily oxidized, i.e. it is a strong reducing agent : eg. it reduces ammoniacal silver nitrate to silver, itself being oxidised to benzoic acid. Benzaldehyde oxidizes to benzoic acid when exposed to air.

Benzaldehyde differs from aliphatic aldehydes in following ways:

(i) It does not reduce Fehling's solution.

(ii) It does not readily polymerise eg. it does not resinify with NaOH, but undergoes cannizzaro reaction.

Benzaldehyde may be prepared by any of the following methods, which are general for its homologues as well.

1. By hydrolysis of benzilidene chloride with aqueous acid (this is also a commercial method).

$C_6H_5CHCl_2 + H_2O \square C_6H_5CHO + 2HCI$

2. Benzaldehyde may be conveniently prepared in the laboratory by oxidising toluene with CrO_3 in acetic anhydride.

As the benzaldehyde is formed, it is converted into benzilidene acetate, thereby preventing further oxidation of the benzaldehyde. Hydrolysis of the acetate with dilute sulphuric acid or hydrochloric acid gives benzaldehyde.

$$C_6H_5CH_3 \xrightarrow[(CH_3CO)_2O]{CrO_3} C_6H_5\,CH(OCOCH_3)_2 \xrightarrow{H^+} C_6H_5CHO + 2CH_3CO_2H$$

A better yield of benzaldehyde may be obtained by oxidising benzyl alcohol with CrO_3 in acetic anhydride.

An interesting oxidising agent is chromyl chloride (Etard's reaction). In this method toluene is treated with chromyl chloride in CCI_4 solution and the complex, which is precipitated is decomposed with water.

$$C_6H_5CH_3 + 2CrO_2CL_2 \square C_6H_5\,CH(OCrCI_2OH)_2 \xrightarrow{H_2O} C_6H_5\,CHO$$

1.25 Gatterman-Koch Aldehyde Synthesis

Benzaldehyde may be synthesized by bubbling a mixture of carbon-monoxide and hydrogen chloride through a solution of either nitrobenzene or solution containing benzene and a catalyst of $AlCl_3$ (An.) and small amount of cuprous chloride.

$$C_6H_6 + CO + HCl \xrightarrow{AlCl_3} C_6H_5CHO + HCI$$

The mechanism of this reaction is uncertain, but it appears likely that the formyl cation is the

active species.

$$CO + HCI + AICl_3 \square [\overset{\oplus}{C}H = O \longleftrightarrow H\text{-}C \square O^+] + AICl_4^-$$

It also appears likely that the cuprous chloride forms a complex with the CO, thereby increasing its local concentration.

1.26 Analysis of Aldehydes And Ketones

Aldehydes and ketones are characterized through the addition to the carbonyl group of nucleophilic reagents, especially derivatives of ammonia. All aldehyde or ketone will, for example react with 2,4-dinitrophenylhydrazine to form an insoluble yellow or red solid.

Aldehydes are characterized, and in particular are differentiated from ketones through their ease of oxidation: aldehydes give a positive test with Tollen's reagent; ketones do not.

Aldehydes are also, of course, oxidized by many other oxidizing agents : by cold, dilute, neutral $KMnO_4$ and by CrO_3 in H_2SO_4.

A highly sensitive test for aldehydes is the Schiff's test.

Aldehydes and ketones are generally identified through the melting points of derivatives like 2,4-dinitrophenylhydrazones, oximes, and semicarbazones.

Methyl Ketones are characterized through the iodoform test. Aldehydes can be oxidised by Fehling's solution.

Fehling's solution, an alkaline solution of cupric ion complexed with tartarate ion (or Benedict's solution, in which complexing is with citrate ion); the deep-blue colour of the solution is discharged, and red cuprous oxide precipitates.

Fehling's solution is made by mixing, Fehling A solution, which contains copper sulphate, + Fehling B solution, which contains sodium hydroxide and Rochelle salt (Sodium Potassium Tartarate). During the oxidation of aldehydes to acids, the cupric ions are reduced to cuprous ions which are precipitated as red cuprous oxide.

$$RCHO + 2Cu^{2+} + 3\bar{O}H \rightarrow RCO_2^- + 2Cu^+ + 2H_2O$$

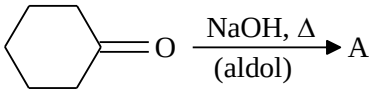
$$2Cu^+ + 2\bar{O}H \rightarrow \underset{\text{Cuprous oxide (red)}}{Cu_2O\downarrow} + H_2O$$

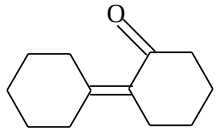
*****

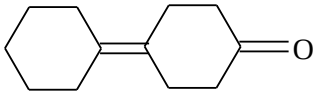
MISCELLANEOUS PROBLEMS

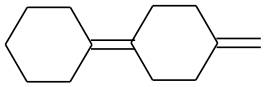
OBJECTIVE TYPE

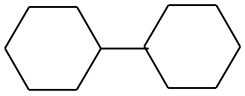
Example 1



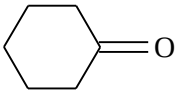
(a) 

(b) 

(c) 

(d) 

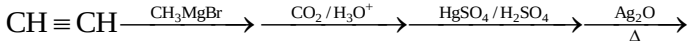
Solution

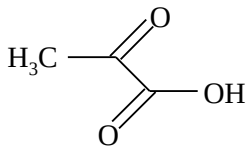


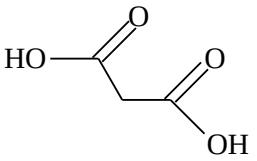
H at □ – C takes part which is condensed to carbonyl group of second molecule; heating causes □, □ elimination. **Ans (a)**

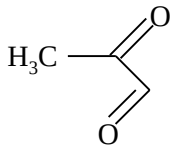
Example 2

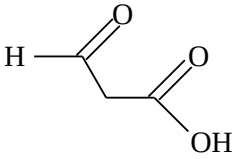
End product of the following sequence of reaction is



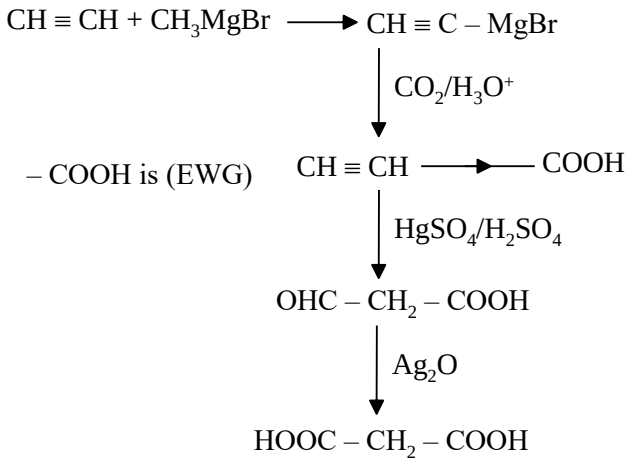
(a) 

(b) 

(c) 

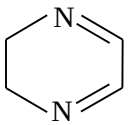
(d) 

Solution



Ans (b)

Example 3

A + B forms  A and B are

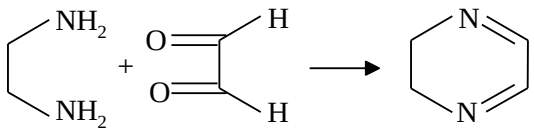
(a) $H_2N - CH_2CH_2 - NH_2$, CH_3CHO

(b) CH_3CHO, $NH_2 - NH_2$

(c) $H_2N - CH_2CH_2 - NH_2$, $CHO - CHO$

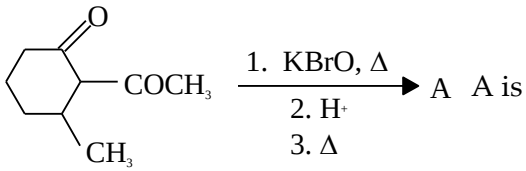
(d) $HCHO$, CH_3NH_2

Solution

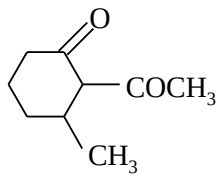


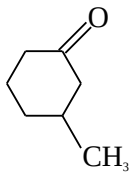
Ans (c)

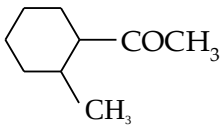
Example 4

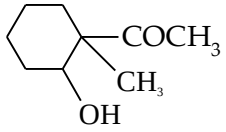


A is

(a) 

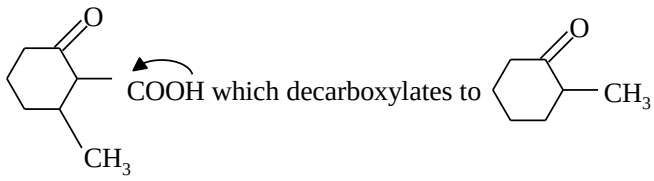
(b) 

(c) 

(d) 

Solution

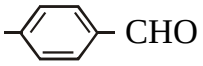
Intermediate is

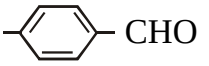


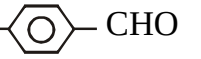
(when □-keto acid is heated, CO_2 is lost). **Ans (b)**

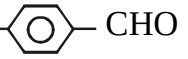
Example 5

In which of the following substrate, rate of Benzoin condensation will be maximum?

(a) O_2N  CHO

(b) H_3C  CHO

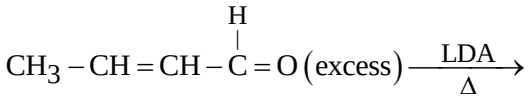
(c) HO  CHO

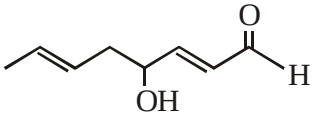
(d) H_2N  CHO

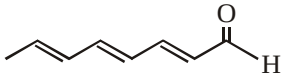
Solution

Benzoin condensation is due to stability of intermediate when negative charge on C is extensively delocalised in benzene ring, Nitro and C □ N group. In all other cases, such dispersal is not extensively possible. On the other hand, NO_2 – is also creating positive charge centre on carbonyl carbon, making it more susceptible to nucleophilic attack of CN^-. **Ans (a)**

Example 6



(a) 

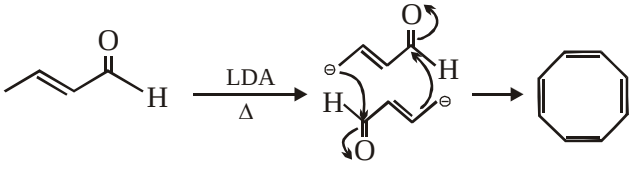
(b) 

(c) 

(d) 

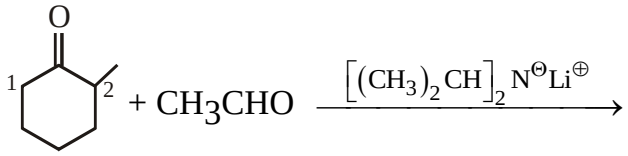
Solution

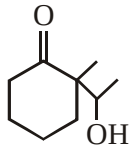
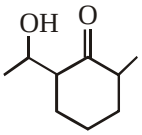
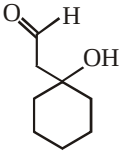
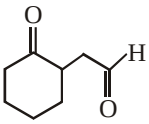
In the absence of □ – H on saturated carbon, □ – H become acidic. This acidic g – H would be abstracted by LDA to give carbanion, which condense with another molecule to give cyclooctatetraene. The high temperature reaction condition helps in the dehydration of aldol product.



Ans (c)

Example 7



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

Solution

LDA is a sterically hindered and strong base. It will abstract H^+ from position (1) rather than position (2). Carbanion formed will attack on CH_3CHO to give intermolecular aldol reaction.

Ans (b)

Example 8

The order of reactivity of the following compounds with PhMgBr is

(I) PhCOPh (II) CH_3CHO (III) CH_3COCH_3

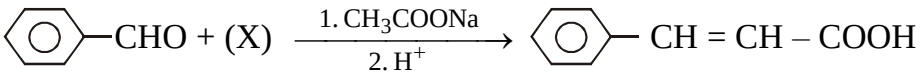
(a) I > II > III (b) III > I > II (c) II > I > III (d) II > III > I

Solution

Reactivity of carbonyl compounds with PhMgBr is based on electrophilicity of carbonyl group and steric crowding around it. Based on electrophilicity and crowding, CH_3CHO is the most reactive. The least reactive would be PhCOPh due to excessive steric crowding.

Ans (d)

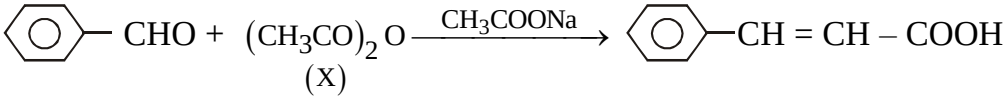
Example 9



Identify the compound (X)

(a) CH_3COOH (b) $(CH_3CO)_2O$ (c) $BrCH_2COOH$ (d) CHO–COOH

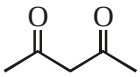
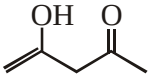
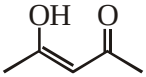
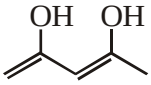
Solution



Since, the given reaction is a Perkin reaction, it requires reaction between an aromatic aldehyde and acid anhydride in the presence of corresponding acid carboxylate. As the acid carboxylate is sodium acetate, so the acid anhydride would be acetic anhydride. **Ans (b)**

Example 10

Which structure is the most stable?

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

Solution

The compound given in (a) is not stable because 1, 3-dicarbonyl compound with a-hydrogen atom exists in enol form. Compounds in (b) and (c) are the mono enol forms of compound in (a), of which enol is (c) is more stable because of conjugation of C = C double bond with carbonyl group. Conjugation exists in (d) also, which is the dienol of compound in (a). Compound in (c) is more stable than the compound in (d), as it involves greater delocalization of □-electron density. Thus, resonance energy of compound in (c) is more than that of compound in (d). Hence, compound in (c) is the most stable. **Ans (c)**

Example 11

Which one of the following compound contains deuterium after reaction with NaOD in D_2O?

(a) $C_6H_5-\underset{\underset{O}{\|}}{C}-H$ (b) $C_6H_5-CH_2-\underset{\underset{O}{\|}}{C}-H$

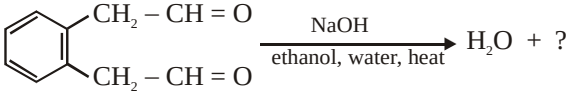
(c) $C_6H_5-\underset{\underset{O}{\|}}{C}-C(CH_3)_3$ (d) $(CH_3)_3C-\underset{\underset{O}{\|}}{C}-C(CH_3)_3$

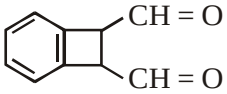
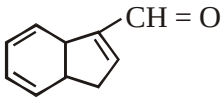
Solution

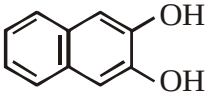
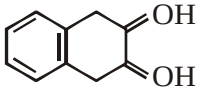
Reaction of the carbonyl compound (with an a-hydrogen atom) with NaOD in D_2O would replace a-hydrogen with deuterium. Carbonyl compound with a-hydrogen atom is $C_6H_5-CH_2-\underset{\underset{O}{\|}}{C}-H$ and this compound on reaction with NaOD in D_2O gives $C_6H_5-CD_2-\underset{\underset{O}{\|}}{C}-H$. **Ans (b)**

Example 12

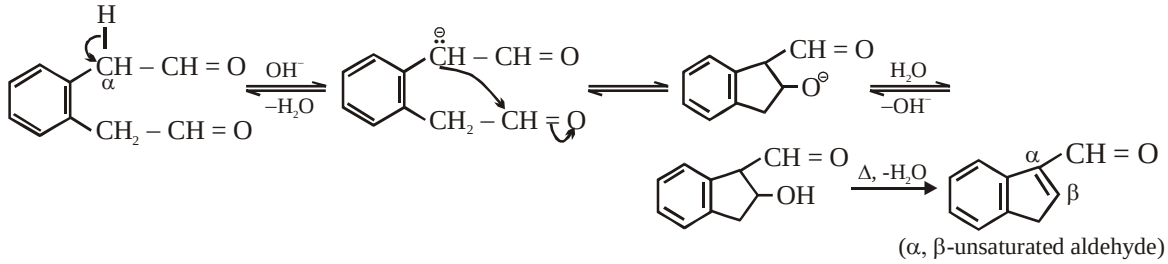
What is the principal product of the following reaction?



(a)  (b) 

(c)  (d) 

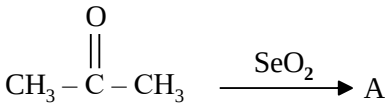
Solution



(α, β-unsaturated aldehyde)

Ans (c)

Example 13



A will be

(a) reduce Tollens reagent (b) give iodoform test

(c) form dioxime (d) give Cannizzaro reaction

Solution

SeO_2 oxides $-CH_2-$ □ w.r.t keto group. **Ans (a, b, c and d)**

Example 14

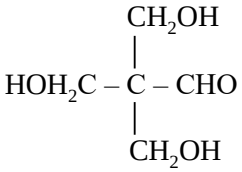
$3HCHO + CH_3CHO \xrightarrow{NaOH} A.A$ found can

(a) reduce Tollen's reagent (b) give Cannizzaro reaction

(c) react with Na (d) give green colour with $Cr_2O_7^{2-}/H^+$

Solution

A is by aldol condensation



Ans (a, b, c and d)

SUBJECTIVE TYPE

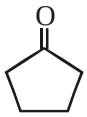
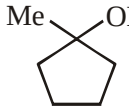
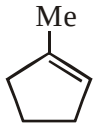
Example 1

Synthesize the following compounds, starting with cyclopentane (C_5H_{10}), alcohols of three or fewer carbones, H_2CO and Inorganic reagents. (a) Cyclopentane carbaldehyde (b) 1, 5-pentanedial and (c) 5-oxohexanal.

Solution

(a) $C_5H_{10} \xrightarrow{Cl_2 / hv} C_5H_9Cl \xrightarrow{Mg / Dry\ ether} C_5H_9MgCl \xrightarrow[H_3O^+]{H_2CO} C_5H_9 - CH_2OH \xrightarrow{CrO_3 / Py} C_5H_9 - CHO$

(b) $C_5H_9Cl \xrightarrow[EtOH]{KOH}$  $\xrightarrow{O_3 / Zn} OHC(CH_2)_3CHO$

(c) $C_5H_9Cl \xrightarrow[2.\ HCO_3^-]{1.\ DMSO}$  $\xrightarrow[2.\ H_3O^+]{1.\ CH_3MgI}$  $\xrightarrow{H_2SO_4 / \Delta}$  $\xrightarrow{O_3 / Zn} OHC(CH_2)_3COCH_3$

Example 2

Write structures for (A) and (B) in the following reactions.

(A) $\xleftarrow[0°C]{LBAH} CH_3CH(CH_3)COCl \xrightarrow{LiAlH_4}$

(B) where LBAH is lithium tri-t-butoxyaluminium hydride. Also account for the different products.

Solution

(A) : $CH_3CH(CH_3)CHO$ (B) : $CH_3CH(CH_3)CH_2OH$

LBAH is a less reactive reducing agent than $LiAlH_4$ because of its bulky alkoxide groups, which reduces its ability to donate hydride ion.

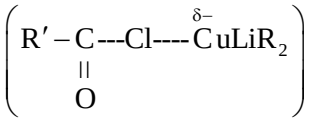
Example 3

The reaction of R'COCl with R_2CuLi gives a ketone, but with RMgX gives a 3° alcohol, $R_2R'COH$. Explain why the later reaction does not give a ketone.

Solution

With RMgX, initially a ketone is formed.

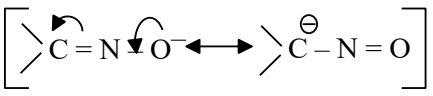
$$R'COCl + RMgX \rightarrow R'COR + MgX(Cl)$$

But since the ketone is more reactive than R□COCl, it reacts further with RMgX to form 3°alcohol. R_2CuLi reacts with the less reactive R□COCl but not with the more reactive R□COR. This is because they do not react by typical nucleophilic addition of R^- to >C=O instead Cu complexes with the Cl of R□COCl as  producing an acylium like ion with greater □+ on the carbon. This strongly electrophilic carbon can form a bond with even less nucleophilic R^- of R_2CuLi.

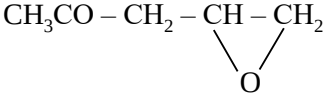
Example 4

Compare the acidity of hydroxylamine and oximes and explain the difference.

Solution

Loss of a proton from $H_2N - OH$ gives a conjugate base, $H_2N–O^-$, in which the negative charge is localized on oxygen. Loss of H^+ from oxime, >C = N – H gives conjugate base  . The conjugate base of oxime is stabilized by lone pair-p□ delocalization. Thus, > =N–O^- is a weaker base than $H_2N–O^-$ and consequently, oximes becomes more acidic than hydroxylamine.

Example 5

Select the best way for reducing the >C=O group in each of the following: (a) $BrCH_2CH_2CHO$ (b) $(CH_3)_2C(OH)CH_2CH_2COCH_3$ (c) $PhCH(OH)CH_2COCH_2CH_3$ (d) 

Solution

(a) Clemmensen reduction is used for reducing it. Strong base causes dehydrohalogenations. $HSCH_2CH_2SH$ can displace Br^-. (b) and (c) require Wolff-Kishner reduction or desulfurization. In (b), the 3° alcohol is dehydrated in acid. In (c), the 2° alcohol is easily dehydrated because the C = C formed is conjugated with the benzene ring. (d) None. All methods lead to opening of the epoxide ring.

Example 6

How can we convert $PhCH = CHCOCH_3$ to

(a) $PhCH = CHCOOH$ (b) $PhCH = CHCH(OH)CH_3$

(c) $PhCH_2CH_2COCH_3$ (d) $PhCH = CHCH_2CH_3$

(e) $Ph(CH_2)_3CH_3$?

Solution

(a) Cl_2 in NaOH (haloform reaction)

(b) $[Me_2CHO^-]_3Al^{3+}$ in Me_2CHOH (Meerwein-Ponndorf reduction) or $LiAlH_4$

(c) To reduce only C = C or □□□□-unsaturated carbonyls use dissolving metal conditions (Birch reduction), Li in liq. NH_3, ether.

(d) H_2NNH_2, OH^- (Wolff-Kishner reduction)

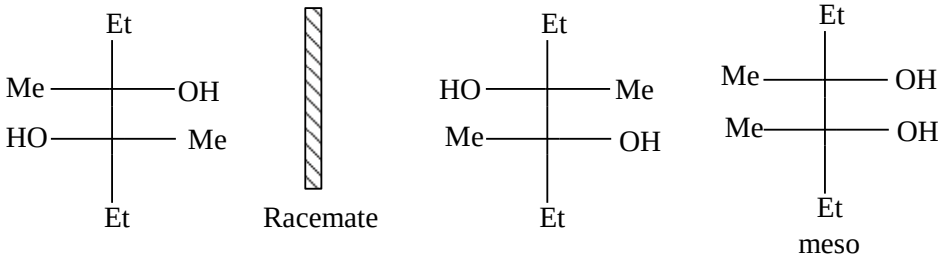
(e) Reduce the compound in (d) with H_2/Pt or reduce the compound in (c) by Clemmensen or wolff-Kishner method.

Example 7

Two isomers are formed from the reaction of butanone with Mg/Hg. Write their structures.

Solution

Two chiral carbons are formed in this reaction leading to a racemate and a meso structures.



Example 8

Compounds X, $C_9H_{10}O$, is inert to Br_2 in CCl_4. Vigorous oxidation with hot alkaline permanganate yields benzoic acid. X gives a precipitate with semicarbazide hydrochloride and with 2, 4 – dinitro phenylhydrazine (DNPH). Write all possible structure for X.

Solution

The oxidation to benzoic acid reveals that there is one side chain with the three remaining C's. The formula reveals five degrees of unsaturation, for for the ring and one in the side chain. The extra degree of unsaturation must be due to a C = O (positive test with DNPH) and not due to C = C (negative test with Br_2). Some possible structure are therefore,

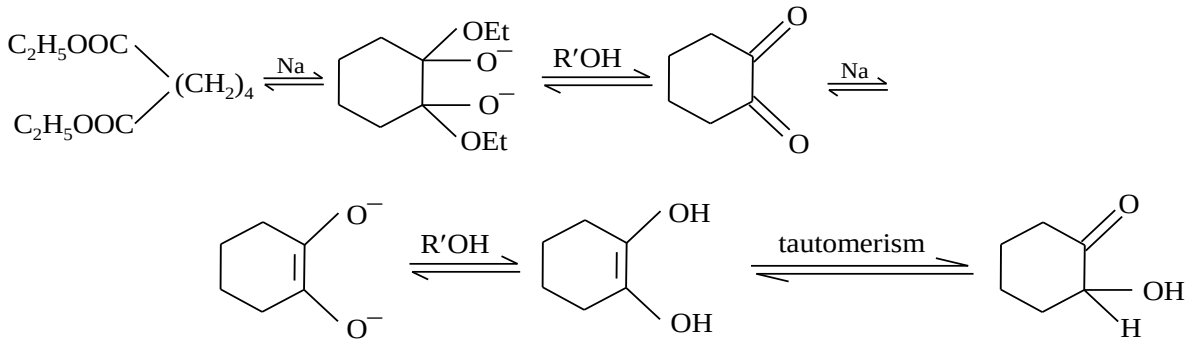
(a) $PhCOCH_2CH_3$ (b) $PhCH_2COCH_3$

(c) $PhCH_2CH_2CHO$ (d) $PhCH(CH_3)CHO$

Example 9

$H_5C_2OOC - (CH_2)_4 - COOC_2H_5$ □□□□ Na, xviene A □□□□ R'OH B. Predict A and B with proper mechanism.

Solution

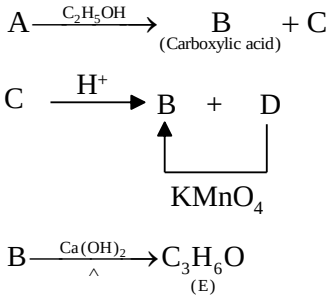


Example 10

An organic compound A on treatment with ethyl alcohol gives a carboxylic acid B and compound C. Hydrolysis of C under acidic conditions gives B and D. Oxidation of D with $KMnO_4$ also gives B. The compound B on heating with $Ca(OH)_2$ give E (molecular formula C_3H_6O). E does not give Tollen's test and does not reduce Fehling's solution but forms a 2, 4-dinitrophenylhydrazone. Identify A, B, C, D and E.

Solution

The given reactions are as follows.



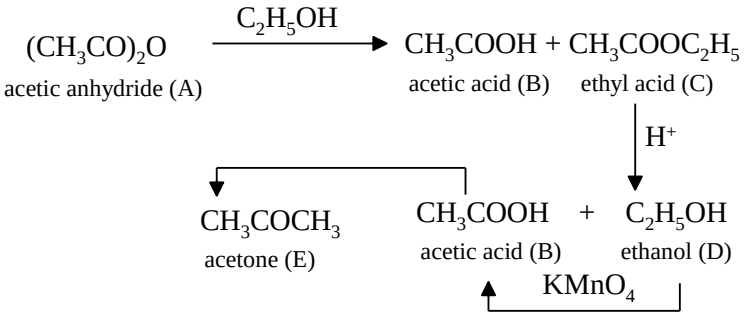
The compounds E must be ketonic compound as it does not give Tollens test and does not reduce Fehling's solution but forms a 2, 4-dinitrophenyl hydrazone. Therefore, its structure would be CH_3COCH_3 (acetone).

Since E is obtained by heating B with $Ca(OH)_2$, the compound B must be CH_3COOH (acetic acid).

Since B is obtained by oxidation of D with $KMnO_4$, the compound D must be an alcohol with molecular formula CH_3CH_2OH (ethanol).

Since B and D are obtained by acid hydrolysis of C, the compound C must be an ester $CH_3COOC_2H_5$ (ethyl acetate).

Since the compounds B (acetic acid) and C (ethyl acetate) are obtained by treating A with ethanol, the compound A must be anhydride $(CH_3CO)_2O$ (acetic anhydride). The give reactions are



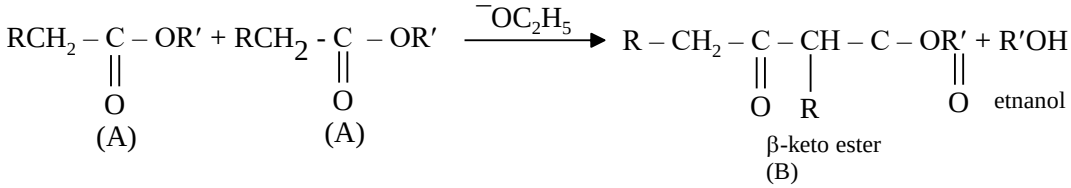
Example 11

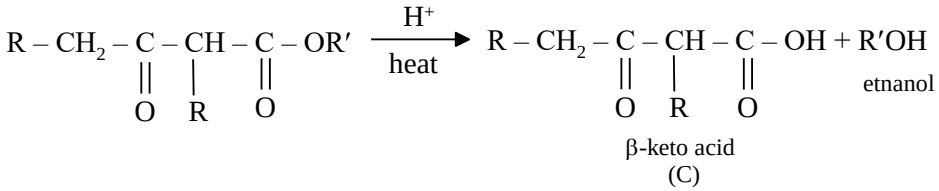
Two moles of an ester *A* are condensed in the presence of sodium ethoxide to give a □-keto ester, *B* and ethanol. On heating in an acidic solution, *B* gives ethanol and a □-keto acid , *C* on decarboxylation *C* gives 3-pentanone. Identify *A*, *B* and *C* with proper reasoning.

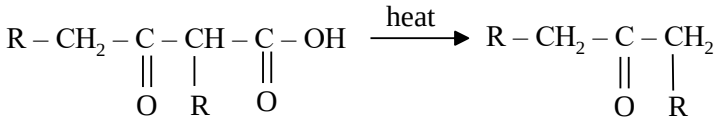
Solution

The reaction of 2 mol of an ester given □-keto ester and alcohol in presence of sodium ethoxide is known as Claisen condensation.

Let the given reactions be depicted as shown in the following.





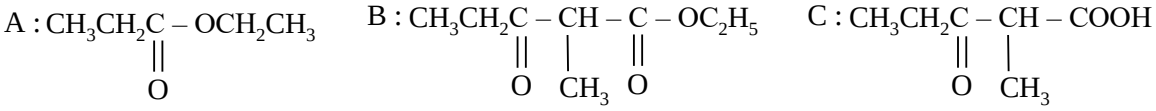


From these reactions, it is obvious that

$R' \equiv CH_2CH_3$

$R' \equiv -CH_3$

Hence, the compounds A, B and C are



Example 12

An organic compound A(C_6H_{10}) on reduction first gives B(C_6H_{12}) and finally C(C_6H_{14}). Compound A on ozonolysis followed by hydrolysis gives two aldehydes D (C_2H_4O) and E($C_2H_2O_2$). Oxidation of B with acidified $KMnO_4$ gives the acid F($C_4H_8O_2$). Determine the structure of the compounds A to F with reasoning.

Solution

Since ozonolysis of A gives two aldehydes, the compound A contains the carbon-carbon double bond. In fact, the molecule of A contains two double bonds as it is successively ozonolyzed products will remain same as in the compound A. Hence, it may be concluded that the ozonolysis products include two molecules of D(CH_3CHO) and one molecule of E (OHC – CHO).

From this, we derive the structure of A as shown in the following

$$\underset{(D)}{CH_3CHO} + \underset{(E)}{OHC-CHO} + \underset{(D)}{OHCCH_3} \xleftarrow{O_3} \underset{2,4-\text{hexadiene a(A)}}{CH_3CH=CH-CH=CHCH_3}$$

The structures of B and C are as follows

$$CH_3CH=CHCH=CHCH_3 \xrightarrow{H_2} \underset{2-\text{hexadiene (B)}}{CH_3CH_2CH_2CH=CHCH_3} \xrightarrow{H_2} \underset{\text{hexane (C)}}{CH_3CH_2CH_2CH_2CH_2CH_3}$$

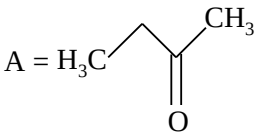
The structure of F is as follows.

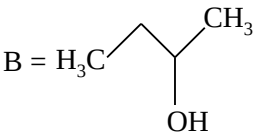
$$CH_3CH_2CH_2CH=CHCH_3 \xrightarrow{KMnO_4} CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}-OH + CH_3\overset{\overset{O}{\|}}{C}-OH$$

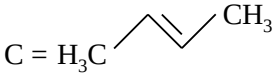
Example 13

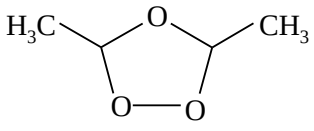
A ketone (A) which undergoes haloform reaction gives compound B on reduction. B on heating with sulphuric acid gives compound C, which forms mono ozonide D. D on hydrolysis in presence of Zn dust gives only acetaldehyde. Identify A, B and C. Write down the reactions involved.

Solution

A = 

B = 

C = 

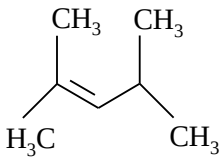
D = 

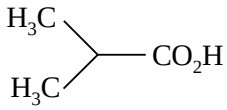
Example 14

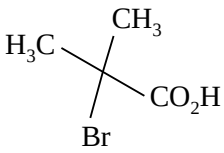
An alkene A on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidized to an acid B. When B is treated with Br_2 in the presence of P, it yields a compound C

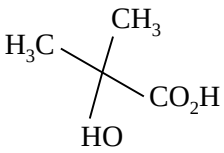
which on hydrolysis gives a hydroxyl acid D. The acid can also be obtained from acetone by reaction with HCN followed by hydrolysis. Identify the compounds A to D.

Solution

A = 

B = 

C = 

D = 

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Exercise - I

OBJECTIVE TYPE (ONLY ONE CHOICE CORRECT)

Multiple choice questions with ONE correct option.

1. $\begin{matrix}CHO\\|\\CHO\end{matrix} \xrightarrow{OH^-} X$; the product X is

   (a) $CH_3OH + CH_3OH$ (b) $CH_2OH - COO^-$

   (c) $CH_3OH + HCOOH$ (d) $^-OOC - COO^-$

2. In the Cannizzaro's reaction given below $2Ph - CHO \xrightarrow{OH^-} PH - CH_2OH + PhCOO^-$ the slowest step is

   (a) The attack of OH^- at the carbonyl group

   (b) The transfer of hydride to the carbonyl group

   (c) The abstraction of proton from the carboxylic acid

   (d) The deprotonation of $Ph - CH_2OH$

3. Condensation of acetone and chloroform in presence of alkali gives

   (a) Chloropicrin (b) Chloretone (c) Chloral (d) Chloroacetone

4. Which one of the following aldehydes will not form an aldol when treated with dil. NaOH.

   (a) CH_3CHO (b) CH_3CH_2CHO (c) $(CH_3)_3CCHO$ (d) $C_6H_5CH_2CHO$

5. Acetaldehyde cannot exhibit

   (a) Iodoform test (b) Benedict's test (c) Tollen's test (d) Lucas test

6. Aldehydes behave as

   (a) Oxidizing agent (b) Reducing agent

   (c) Dehydrating agent (d) Oxidizing as well as reducing agent

7. $\begin{matrix}R\\R\end{matrix}\!\!>C = O \xrightarrow{HCN} (A) \xrightarrow{NH_3} (B) \xrightarrow{Hydrolysis} (C)$. Compound (C) in above reaction is

   (a) □-hydroxy acid (b) □-amino acid

   (c) □-amino alkanol (d) □-amino □-hydroxy acid

8. Compound 'A' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product 'B' (molecular formula C_3H_6O). 'B' forms a shining silver mirror on warming with ammoniacal silver nitrate 'B' when treated with an

aqueous solution of $H_2NCONHNH_2$. HCl and sodium acetate gives a product 'C'. Identify the structure of 'C'.

(a) $CH_2CH_2CH = NNHCONH_2$ (b) $CH_3 - \underset{\underset{CH_3}{|}}{C} = NNHCONH_2$

(c) $CH_3 - \underset{\underset{CH_3}{|}}{C} = NCONHNH_2$ (d) $CH_3CH_2CH = NCONHNH_2$

9. Compound (A), $C_9H_{10}O$ is inert to Br_2 in CCl_4. Vigorous oxidation with hot alkaline $KMnO_4$ yields benzoic acid. (A) gives yellow precipitate with 2, 4-dinitro phenyl hydrazine as well as with NaOI. The possible structure of compound (A) would be
   (a) $PhCOCH_2CH_3$ (b) $PhCH_2COCH_3$
   (c) $PhCH_2CH_2CHO$ (d) $PhCH(CH_3)CHO$
10. An organic liquid has an empirical formula C_4H_8O. The liquid gives a pale yellow precipitate on warming with iodine in alkaline potassium hydroxide solution. The structural formula of the organic liquid could be
   (a) CH_3COCH_3 (b) $CH_2 = CHCH(OH)CH_3$
   (c) $CH_3CH_2CH_2CHO$ (d) $CH_3CH_2OCH = CH_2$
11. A substance $C_6H_{12}O$ does not react with Fehling's solution but gives positive reactions for a carbonyl group. It also gives positive iodoform reaction. Which of the following structure will best correspond to the above statements?
   (a) $CH_3CH_2CH(CH_3)COCH_3$ (b) $CH_3CH_2COCH_2CH_2CH_3$
   (c) $CH_3CH_2COCH(CH_3)_2$ (d) $CH_3CH_2CH(CH_3)CH_2CHO$
12. The compound which gives a yellow solid on adding to an alcoholic solution of 2, 4-dinitrophenylhydrazione but does not reduce Fehling's solution and ammoniacal silver nitrate solution is
   (a) CH_3COCH_3 (b) $CH_3CH(OH)CH_3$ (c) CH_3CHO (d) CH_3COOH
13. In the reaction,
   $CH_3 - CH = CH - CHO \xrightarrow[\text{agent}]{\text{Oxidising}} CH_3CH = CH - COOH,$ the oxidizing agent can be
   (a) alkaline $KMnO_4$ (b)acidified $K_2Cr_2O_7$
   (c) Benedict's solution (d)All of these
14. Which statement is incorrect in the case of acetaldehyde and acetone?
   (a) Both react with hydroxylamine
   (b) Both react with $NaHSO_3$
   (c) Both react with hydrazine
   (d) Both reduce ammoniacal silver nitrate
15. A neutral compound (A), molecular formula $C_4H_8O_2$ reduced Fehling's solution, liberates hydrogen when treated with sodium metal and give a positive iodoform test.

The structure of (A) is

(a) $CH_3CH(OH)CH_2CHO$ (b) $CH_2CH_2CH_2CHO$

(c) CH_2COCH_2CHO (d) $CH_3COCH_2CH_2OH$

Multiple choice questions with MORE THAN ONE correct option.

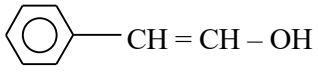
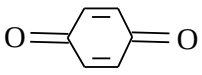
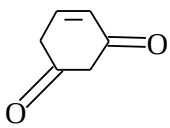
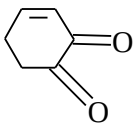
1. Which of the following statements about benzaldehyde is / are true?
   (a) Reduces Tollens' reagent
   (b) Undergoes aldol condensation
   (c) Undergoes Cannizzaro reaction
   (d) Does not form an addition compound with sodium hydrogen sulphite.

2. The Cannizaro reaction is given by
   (a) Trimethyl acetaldehyde (b) Acetaldehyde
   (c) Benzaldehyde (d) Formaldehyde

3. Which of the following reagents are used for detecting the presence of carbonyl group?
   (a) NH_2OH (b) NH_2NH_2
   (c) $H_2NCONHNH_2$. HCl (d) $C_6H_5NHNH_2$. HCl

4. Which of the following are examples of aldol condensation?
   (a) $2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CHOHCH_2CHO$
   (b) $2CH_3COCH_3 \xrightarrow{\text{dil.NaOH}} CH_3COH(CH_3)CH_2COCH_3$
   (c) $2HCHO \xrightarrow{\text{dil. NaOH}} CH_3OH + HCOOH$
   (d) $C_6H_5CHO + HCHO \xrightarrow{\text{dil. NaOH}} C_6H_5CH_2OH$

5. Use Wolf-Kishner reduction conditions, the conversion which may be brought about are
   (a) Benzophenone into diphenylmethane (b) Benzaldehyde into benzyl alcohol
   (c) Cyclohexanone into cyclohexane (d) Cyclohexanone into cyclohexanol

6. Tautomerism is exhibited by
   (a) 
   (b) 
   (c) 
   (d) 

7. A new carbon-carbon bond formation is possible in
   (a) Cannizzaro reaction (b)Friedel-Crafts reaction
   (c) Clemmensen reduction (d)Reimer-Tiemann reaction

8. Which of the following do not react with Fehling's solution ?
   (a) Benzaldehyde (b) Acetaldehyde (c) Glucose (d) Acetophenone

9. Which of the following statements are correct about the C = O bond ?
   (a) It is made up of one □-bond and one □-bond
   (b) It uses the sp^2-hybrid orbital of carbon for its formation
   (c) It is planar is nature
   (d) It undergoes addition reactions

10. $CH_3-CHO \xrightarrow{\bar{O}H} CH_3CH(OH)CH_2CHO$. In the aldol condensation of acetaldehyde represented above, which of the following intermediate species are obtained ?

(a) $CH_2=\underset{|}{\overset{O^-}{C}}-H$ (b) $:\bar{C}H_2-\overset{O}{\overset{||}{C}}-H$

(c) $CH_3-\underset{|}{\overset{\bar{O}}{C}}-CH_2-CHO$ (d) $CH_3-\underset{|}{\overset{O^-}{C}}-O-CH=CH_2$

H H

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Exercise – II

ASSERTION & REASON , COMPREHENSION & MATCHING TYPE

Assertion and Reason

Following questions consist of an Assertion (A) and the Reason ®. Use the following key to choose the appropriate answer

(a) If both (A) and (R) are correct and ® is the correct explanation of (A).

(b) If both (A) and (R) are correct but (R) is not the correct explanation of 'A'.

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

(d) If (A) is incorrect but (R) is correct.

1. A : Carbonyl compounds take part in nucleophilic addition reactions.
   R : These reactions are initiated by nucelophilic attack at the electron deficient carbon atoms.

2. A : Primary alcohols can be easily oxidized to aldehydes.
   R : Aldehydes are prone to further oxidation to carboxylic acids.

3. A : The addition ammonia derivatives on carbonyl compounds is carried in weakly acidic medium.

R : In weakly acidic medium attacking nucleophile is also protonated.

4. A : Fehling's reagent is a test for all aliphatic aldehydes.
   R : Aliphatic aldehydes can be easily oxidized even with mild oxidizing agents.
5. A : 2-Methylpropanal undergoes Cannizzaro's reaction.
   R : It has an α-hydrogen atom.

Passage Based Questions

Passage – I

Due to electronegativity difference between carbon and oxygen atoms, the C = O group undergoes nucleophilic addition reactions which are governed by electrophilicity of the carbonyl carbon and the steric hindrance in the transition state. Further, since the □-hydrogens of aldehydes and ketones are weakly acidic, they readily form enolate ions on treatment with strong bases. These enolate ions, in turn, can participate in nucleophilic addition reaction leading to the formation of aldols which subsequently undergo acid-catalysed dehydration to form □□□-unsaturated carbonyl compounds. Crossed aldol condensation between two different aldehydes is not of any synthetic utility unless one of the aldehydes does not contain □-hydrogen/s. If one of the aldehydes used in benzaldehyde, the initially formed aldol undergoes dehydration in *situ*, to form □□□-unsaturated carbonyl compounds.

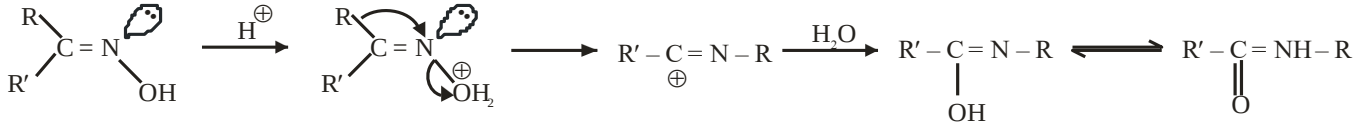
Aldehydes which do not contain □-hydrogen/s can add a hydroxide ion to form an anion which acts as a hydride donor to another molecule of the same aldehyde giving a mixture of an alcohol and the corresponding carboxylate ion. Such self oxidation-reduction or disproportionation reactions between two different aldehydes, one of which is always formaldehyde, leads to oxidation of formaldehyde and reduction of the other aldehyde.

1. The correct order of increasing reactivity towards nucleophilic addition reaction is
   (a) benzaldehyde < *p*-tolualdehyde < acetophenone < *p*-nitrobenzaldehyde
   (b) acetophenone < *p*-tolualdehyde < benzaldehyde < *p*-nitrobenzaldehyde
   (c) benzaldehyde < acetophenone < *p*-nitrobenzaldehyde < *p*-tolualdehyde
   (d) *p*-nitrobenzaldehyde < *p*-tolualdehyde < acetophenone < benzaldehyde
2. The lease reactive compound towards nucleophilic addition reactions is
   (a) Propanone (b) 3-Pentanone
   (c) 2-Pentanone (d) 2,4 Dimenthylpentan-3-one
3. The crossed aldol product formed when propanol acts as the electrophile and butanal as nucleophilie is
   (a) 3-Hydroxy-2-methylpentanal (b) 3-Hydroxy-2-methyhexanal
   (c) 2-Ethyl-3-hydroxypentanal (d) 2-Ethyl-3-hydroxyhexanal

4. Which of the following reagents converts C_6H_5COCHO to $C_6H_5CHOHCOOH$?
   (a) Aq. NaOH (b) Acidic Na_2SO_3 (c) Na_2CrO_4/H_2SO_4 (d) $NaNO_2/HCl$
5. Aldol condensation between which of the following two compounds followed by dehydration gives methyl vinyl ketone?
   (a) Formaldehyde and acetone (b) Formaldehyde and acetaldehyde
   (c) Two molecules of acetaldehyde (d) Two molecules of acetone.

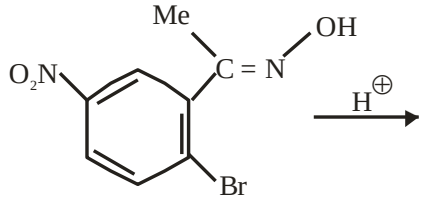
Passage – II

Aldehydes and Ketones reacts with NH_2OH to form Aldoximes and Ketoximes respectively. Configuration of these can be determined by Beckmann rearrangement as that group migrates which is anti w.r.t. –OH

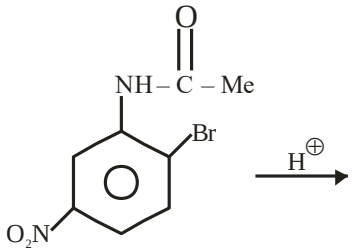


It is interesting to note that the migration of group is completely Retentive and no loss of optical activity is seen.

1.



(a)



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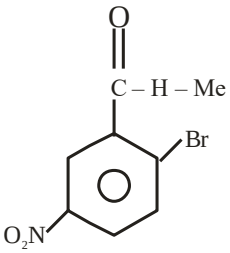
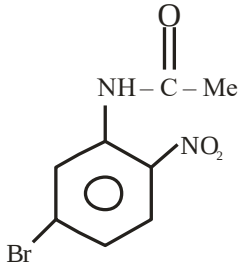
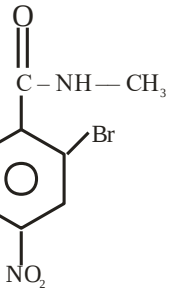


(c)



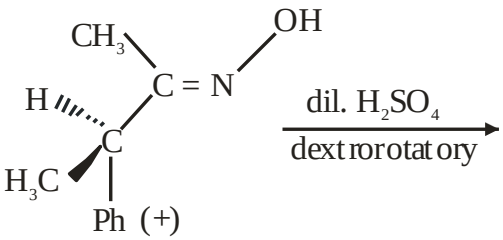
(d)



2. $CH_3CHO + NH_2OH \xrightarrow{\Delta} P \xrightarrow{H^{\oplus}} Q \xrightarrow{Br_2KOH} R(CH_3NH_2)$ (as only product) Following is correct

(a) Oxime P is syn form of geometrical isomer (b)Oxime P is anti form

(c) Q is more basic than R (d)Q is $H-\underset{\underset{O}{\|}}{C}-NH-CH_3$

3. 

Following is true about product

(a) It is also (+) dextrorotatory

(b) Both (+) (–) forms are obtained in equal amount

(c) It is having 'S' configuration for chiral carbon

(d) It is having R configuration for chiral carbon

Matching Type Questions

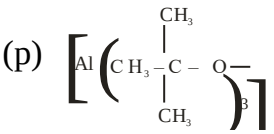
1. Match the column

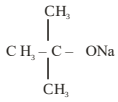
Reaction	**Reagent**
(a) Perkin reaction	(p) $CHCl_3/KOH$
(b) ClasienSchmidt reaction	(q) CH_3COOK/CH_3COOH
(c) Cannizzaro reaction	(r) dil. KOH
(d) RiemerTiemann reaction	(s) conc. KOH

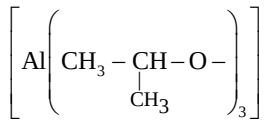
(a) (a-s), (b-r), (c-p), (d-q) (b)(a-q), (b-r), (c-s), (d-p)

(c) (a-s), (b-p), (c-r), (d-q) (d)(a-p), (b-r), (c-s), (d-q)

2. Match the column

Reaction	**Reagent**
(a) Meervein pondroff reaction	(p) 
(b) Oppeneur reaction	(q) $[Al(EtO)_3]$

(c) Tischenko reaction (r) 

(d) Hoffmann reaction (s) 

(a) (a-s), (b-r), (c-p), (d-q) (b)(a-q), (b-r), (c-s), (d-p)

(c) (a-s), (b-p), (c-q), (d-r) (d)(a-p), (b-r), (c-s), (d-q)

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Exercise - III

SUBJECTIVE TYPE

1. The organic compounds (A and B) containing c = 62.1%, H = 10.3%, O = 27.6% with KCN and H_2SO_4 gave compounds which on hydrolysis gave two isomeric monobasic and (C) and (D) of molecular weight 104. Identify (A) and (B). Also report the III isomer if any to (A) and (B).
2. An organic compound (A) contains C = 60.12%, H = 13.13% and has a vapour density 30. On oxidation, it gives (B) C_3H_6O which on further oxidation by NaOH +I_2 produces a salt of the acid (C) $C_2H_4O_2$. When (B) is treated with hydroxyl amine, a compound of molecular formula C_3H_7NO (D) is formed. What are (A) to (D) ?
3. An organic compound C_2Cl_3HO reduces Tollens reagent and on oxidation gave monocarboxylic acid (B) $C_2Cl_3HO_2$. (B) on distillation with sodalime gave a sweet smelling liquid (C) containing 89.12% Cl. What are (A), (B) and (C) ?
4. A ketone (A) gives iodoform on reaction with I_2 + NaOH. (A) on reduction gives (B) which on heating with H_2SO_4 gives (C). (C) on ozonolysis gives acetaldehyde and acetone. Identify (A), (B) and (C).
5. An organic compound $C_5H_8O_2$ is reduced to n-pentane by Zn/Hg + HCl. It forms dioximes and also gives iodoform test. It reduces Tollens reagent.What is compound ?
6. An organic compound (A) containing C = 69.77%, H = 11.63% and rest oxygen has molecular weight 86. It does not reduce Fehling solution but forms bisulphite addition and shows iodoform test. What is (A) ? Give all possible isomes.
7. A hydrocarbon (A) is treated with excess of HCl, a dihalogen derivative (B) is formed. Compound (B) on treatedm with aq.KOH gives (C). (C) can also be obtained by heating Ca salt of 2-methyl propanoic acid with Ca acetate.What are (A), (B) and(C) ?

8. A neutral compound (A) $C_4H_8O_2$ reduces Tollens reagent, liberates H_2 when treated with sodium metal and slowly gives the iodoform test. What is (A) ?

9. An organic compound (A) $C_6H_{12}O$ reacts with NH_2OH but does not reduce Fehling solution. On reduction it gives an alcohol (X) of which (C) reduces Tollens reagent but does not give yellow precipitate with I_2 and NaOH. (D) gives iodoform test but does not reduce Tollens reagent. What are (A), (B), (C) and (D)?

10. An organic compound (A) (C_3H_6O) is quite resistant to oxidation. On reduction (A) forms another compound (B) of molecular formula C_3H_8O. (B) is highly reactive towards HBr to give (C). Grignard reagent of (C) reacts with (A) to give (D) $C_6H_{14}O$. What are (A), (B), (C) and (D).

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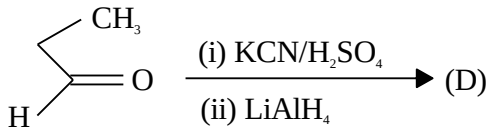
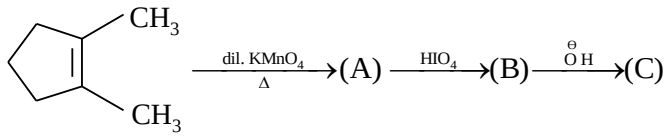
Exercise - IV

NEET PROBLEMS

1. Iodoform is obtained by the reaction of acetone with hypiodite but not with iodide. Why.
2. An organic compounds 'A' on treatment with ethyl alcohol gives a carboxylic acid 'B' and compound 'C'. Hydrolysis of 'C' under acidic conditions gives 'B' and 'D'. Oxidation of 'D' with $KMnO_4$ also gives 'B'. 'B on heating with $Ca(OH)_2$ gives 'E' (C_3H_6O). E does not give Tollen's test and does not reduce Fehling's solution but form a 2,4-dinitrophenyl hydrazone. Identify (A), (B), (C), (D) and (E).
3. Complete the following reaction with appropriate structure.

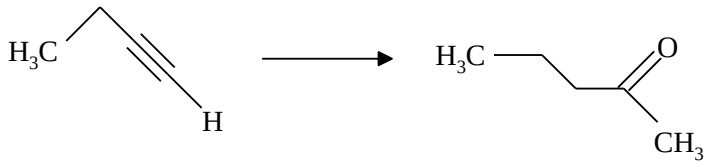


4. Suggest appropriate structures for the missing compounds. (The number of carbon atoms remains the same throughout the reactions).



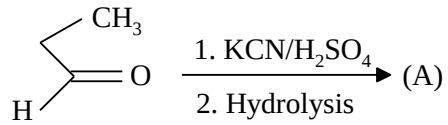
5. (a) Compound 'A' (C_8H_8O) on treatment with $NH_2OH.HCl$ gives 'B' and 'C'. 'B' and 'C' rearrange to give 'D' and 'E', respectively, on treatment with acid. 'B', 'C', 'D' and 'E' are all isomers of molecular formula (C_8H_9NO). When 'D' is boiled with alcoholic KOH an oil 'F' (C_6H_7N) separates out. 'F' reacts rapidly with CH_3COCl to give back 'D'. On the hand E' on boiling with alkali followed by acidification gives a white solid 'G' ($C_7H_6O_2$). Identify 'A' to 'G'.

   (b) Carry out the following transformation is not more than three steps.

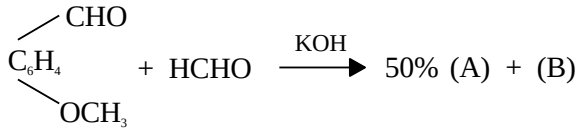


6. An organic compound (A), $C_6H_{10}O$, on reaction with CH_3MgBr followed by acid treatment gives compound (B). The compound (B) on ozonolysis gives compound (C), which is presence of a base give 1-acetyl cyclopentene (D). The compound (B) on reaction with HBr gives compound (E). Write the structures of (A), (B), (C) and (E). Show how (D) is formed from (C).

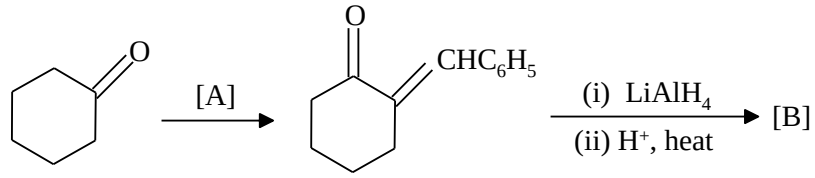
7. An organic compound (A) reacts with H_2 to give (B) and (C) successively. On ozonolysis of (A), two aldehydes (D) C_2H_4O and (E) $C_2H_2O_2$ and formed. On ozonolysis of (B) only propanal is formed. What are (A) to (E)?
8. An unknown compound of carbon, hydrogen and oxygen contains 69.77%C and 11.63%H, and has a molecular weight of 86. It does not reduce Fehling solution but forms a bisulphate addition compound and gives a positive iodoform test. What are the possible structures?
9. Predict the major product in the following reaction.



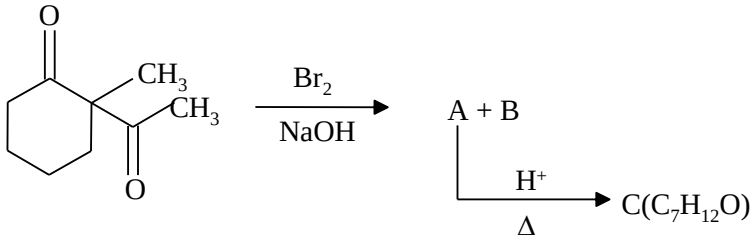
10. Complete the following:

(i) 

(ii) $C_6H_5-CHO+CH_3-COOC_2H_5 \xrightarrow[C_2H_5OH \text{ and heat}]{NaOC_2H_5 \text{ in absolute}} (A)$

(iii) 

11. Identify (A), (B) and (C), and give their structures.



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ANSWERS

Exercise - I

Only One Option is correct

1.	(b)	2.	(b)	3.	(b)	4.	(c)	5.	(d)
6.	(b)	7.	(b)	8.	(a)	9.	(b)	10.	(b)
11.	(a)	12.	(a)	13.	(c)	14.	(d)	15.	(a)

More Than One Choice Correct

1.	(a, c)	2.	(a,c, d)	3.	(a, b, c, d)	4.	(a, b)	5.	(a, c)
6.	(a, c, d)	7.	(b, d)	8.	(a, b)	9.	(a, b, c,)	10.	(a, b, c, d)

Exercise - II

Assertion and Reason

1.	(a)	2.	(d)	3.	(c)	4.	(a)	5.	(d)

Passage I

1.	(b)	2.	(d)	3.	(c)	4.	(a)	5.	(b)

Passage II

1.	(a)	2.	(b)	3.	(b, d)

Matching Type Questions

1.	(b)	2.	(c)

Exercise - III

Subjective Type

1. (a) CH_3CH_2CHO; (b) CH_3COCH_3, (c) $CH_3CH_2CH(OH)COOH$ (d) $(CH_3)_2C(OH)COOH$

   III isomer $CH_2 = CHCH_2OH$

2. (a) $(CH_3)_2CHOH$; (b) CH_3COCH_3 (c) CH_3COOH; (d) $CH_3C(=NOH)CH_3$

3. (a) CCl_3CHO; (b) CH_3COOH; (c) $CHCl_3$

4. (a) $CH_3COCH(CH_3)_2$; (b) $CH_3CHOHCH(CH_3)_2$; (c) $CH_3CH = C(CH_3)_2$

5. $CH_3COCH_2CH_2CHO$

6. $CH_3COCH_2CH_2CH_3$ and $CH_3COCH(CH_3)_2$

7. (a) $(CH_3)_2CHC \square CH$, (b) $(CH_3)_2CHCCl_2CH_3$, (c) $(CH_3)_2CHCOCH_3$

8. $CH_3CHOHCH_2CHO$ or $CH_3CHOHCOCH_3$

9. (a) $CH_3CH_2COCH(CH_3)_2$, (X) $CH_3CH_2CHOHCH(CH_3)_2$ (b) $CH_3CH_2CH = C(CH_3)_2$; (c) CH_3CH_2CHO ; (d) CH_3COCH_3

10. (a) CH_3COCH_3; (b) $(CH_3)_2CHOH$; (c) $(CH_3)_2CHBr$; (d) $(CH_3)_2\underset{\underset{OH}{|}}{C}CH(CH_3)_2$

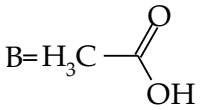
Exercise - IV

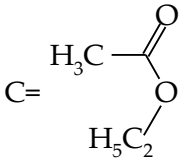
NEET Level Problem

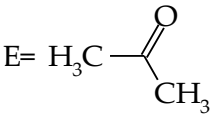
1. The formation of CHI_3 takes place as follows:

$$CH_3COCH_3 \xrightarrow{OH} CH_3COCI_3 \xrightarrow{OH} CH_3COO^-CHI_3$$

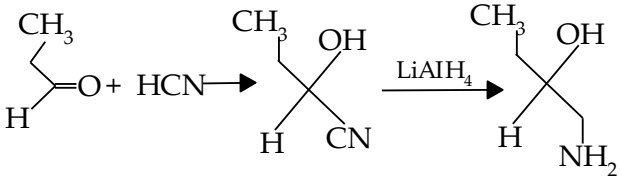
The active species is OI^-, I^- cannot bring about this reaction. OI^- is an oxidant and an iodination agent.

2. A= B= 

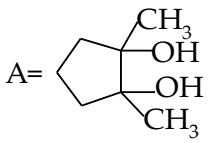
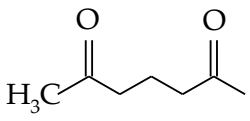
C=  D = H_5C_2—OH

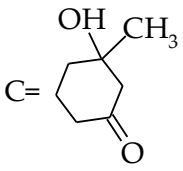
E= 

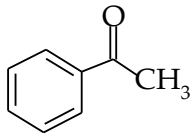
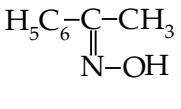
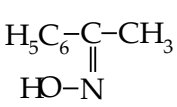
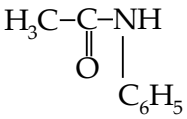
3. $KCN + H_2SO_4 \longrightarrow KHSO_4 + HCN$

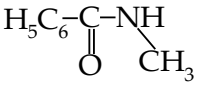
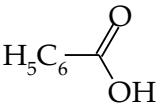


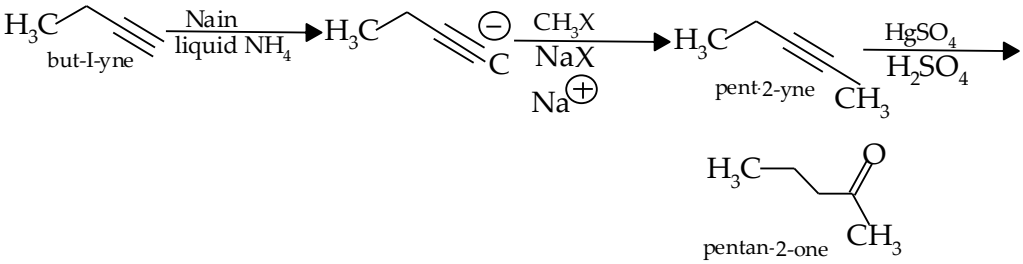
1-aminobutan-2-ol

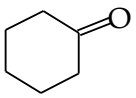
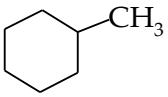
4. A=  B= 

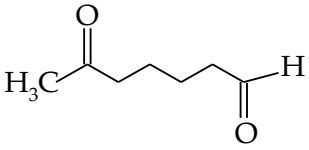
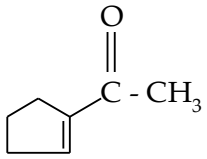
C=  Aldol

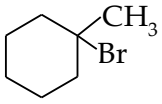
5. a) A=  B=  C=  D= 

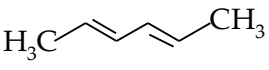
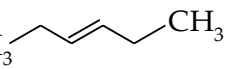
E=  F= G= 

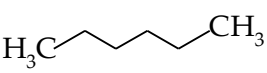
b) 

6. A=  B= 

C=  D= 

E= 

7. A=  B = 

C =  D = CH_3—CHO

E = 

8. i) For empirical formula

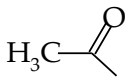
Element	%	Relative no. of atoms	Simplest ratio
C	69.77	5.76	5
H	11.63	11.63	10
O	19.20	1.2	1

∴ Empirical formula of compound is $C_5H_{10}O$.
and Empirical formula wt. = 86
Also Molecular wt. = 86

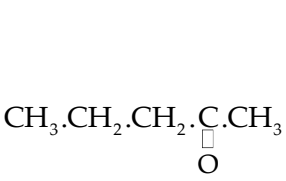
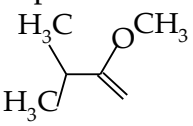
ii) Compound forms bisulphite addition compound and thus, has carbonyl gp. i.e., aldehyde or ketone.

iii) It does not reduce Fehling solution and thus, it is not aldehyde but is ketone.

iv) It gives positive iodoform test and thus, it has

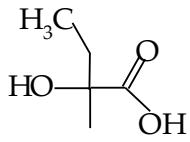


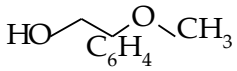
v) Above facts reveals that compound is

 or 

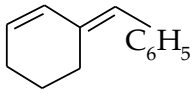
Pentan-w-one 3-methylbutan-2-one

9.



10. i) A=  B= HCOOK

ii) $C_6H_5CH=CH=CHOOC_2H_5$

iii) A= C_6H_5CHO, base B= 

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