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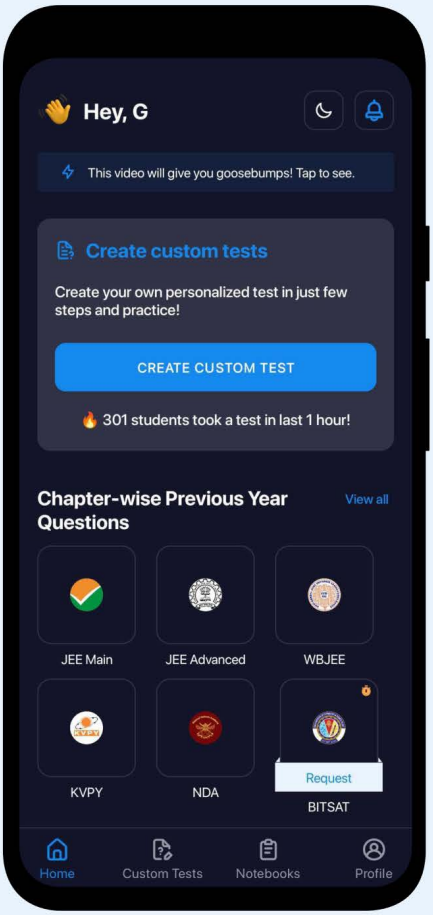

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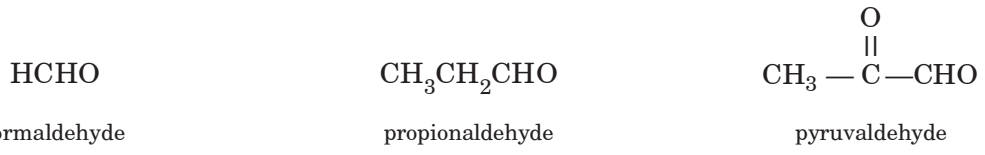
ALDEHYDES AND KETONES

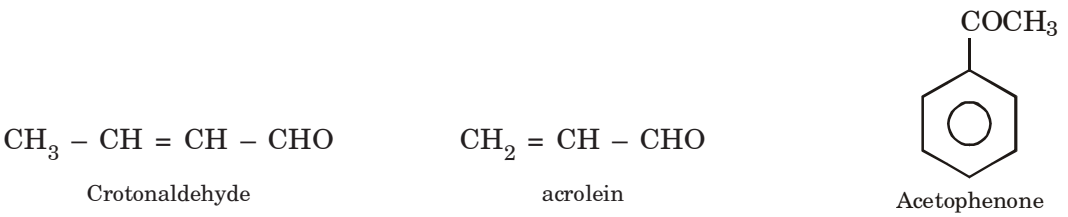
ALDEHYDES AND KETONES

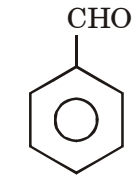
- Aldehydes and ketones are first oxidation products of alcohols and carry carbonyl group (> C = O) in their molecules.
- In aldehyes >CO group must also carry one H atom linked to C while in ketones no H atom should be linked to C atom of CO group. Thus functional group of aldehydes is — CHO while that for ketones is $\overset{|}{—CO}$.
- In aliphatic aldehydes, — CHO group is linked to alkyl (Group R — CHO) while in aromatic aldehyde, — CHO group is linked to aryl group (Ar — CHO).
- In aliphatic ketones, the CO group is linked to alkyl groups (RCOR) while in aromatic ketones, the CO group is linked to aryl groups (ArCOAr).
- In simple ketones, the alkyl or aryl groups linked to CO group are same but in mixed ketones, the alkyl or aryl groups linked to CO group are different.
- Aldehydes and ketones are functional isomers of each other and can be represented by the formula $C_nH_{2n}O$.

Nomenclature

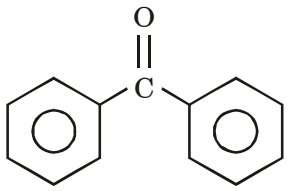
- Common names of aldehyde is derived from the corresponding carboxylic acids by replacing the suffix ic acid with aldehyde.
- Common name of ketones is written by using the names of the alkyl groups followed by the word ketone.
- IUPAC name of aldehydes is alkanals while that for ketones is alkanones.
- Aldehydes are isomeric with ketones, unsaturated ethers and unsaturated alcohols, cyclic ethers as well as cyclic alcohols.



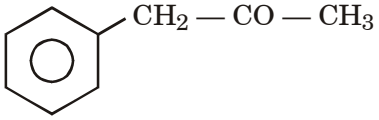




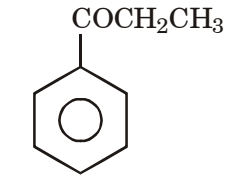
Benzaldehyde



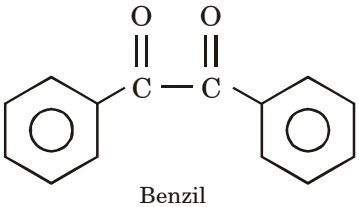
Benzophenone



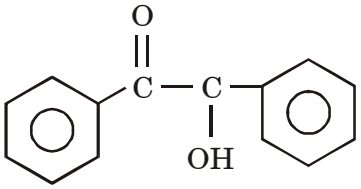
Benzyl Methyl ketone



Propiophenone



Benzil



Benzion

Preparation of Aldehydes & Ketones

1. From Alcohols

(a) By Controlled oxidation using

$K_2Cr_2O_7/H_2SO_4$ or $KMnO_4$ / H_2SO_4

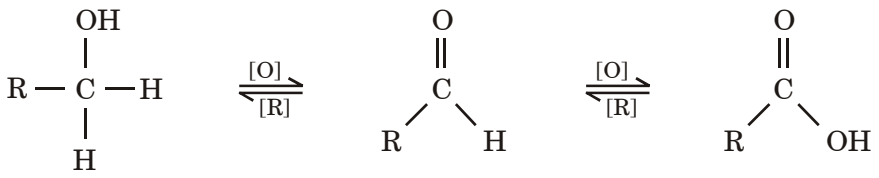
(i) aldehydes from 1 alcohols

$$RCH_2OH \xrightarrow{[O]} RCHO \xrightarrow{[O]} RCOOH$$

(ii) ketones from 2 alcohols

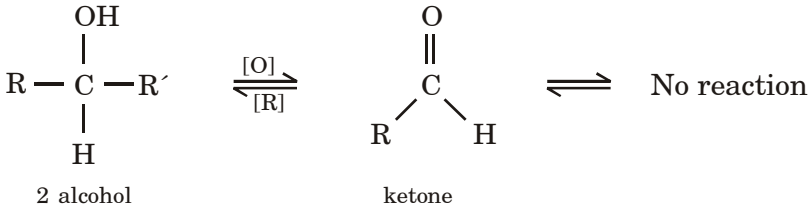
$$R_2CHOH \xrightarrow{[O]} R_2CO + H_2O$$

- **Primary alcohols** can be oxidised to aldehydes (or further to carboxylic acids).
- In aqueous media, the carboxylic acid is usually the major product.
- PCC or PDC, which are used in dichloromethane, allow the oxidation to be stopped at the aldehyde.



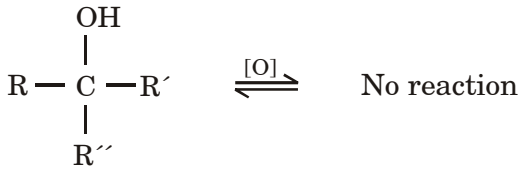
1 alcohol aldehyde

- **Secondary alcohols** can be oxidised to ketones, no further;



2 alcohol ketone

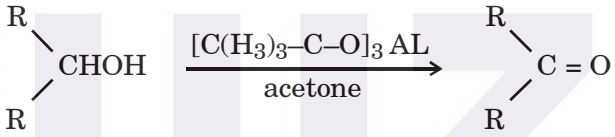
- **Tertiary alcohols** cannot be oxidised



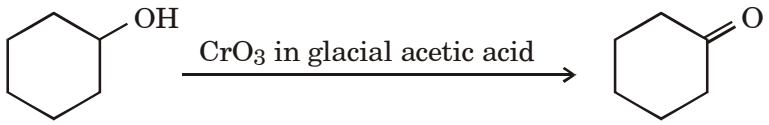
3 alcohol

Oppenauer Oxidation :

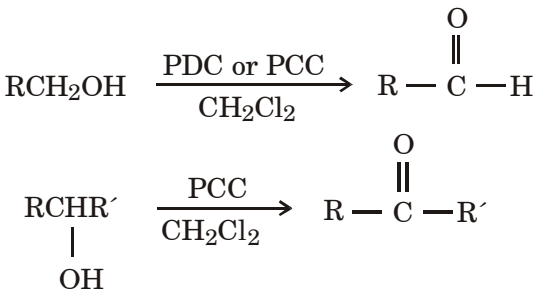
Using a specific oxidising agent like Aluminium tertiary Butoxide $\{[(CH_3)_3C — O]_3Al\}$ in presence of Acetone, secondary alcohols can be oxidised to ketones.



(b) Cr oxidation of alcohols.



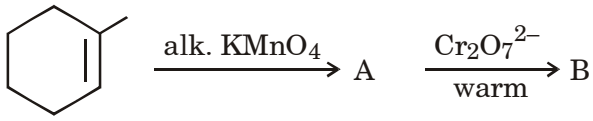
Pyridinium dichromate (PDC) or Pyridinium Chlorochromate (PCC) in anhydrous media such as CH_2Cl_2 oxidises primary alcohols to aldehydes and secondary alcohols to ketones.



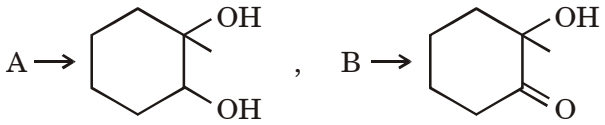
Example 1

Identity A and B in the following

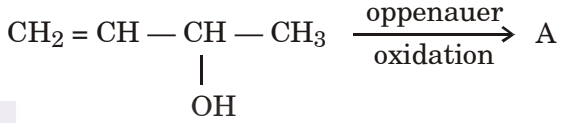
(1)



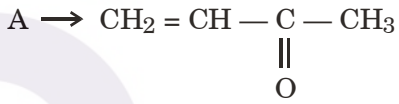
Solution :



(2)



Solution :



(3) Suggest suitable reagents for the following conversions :

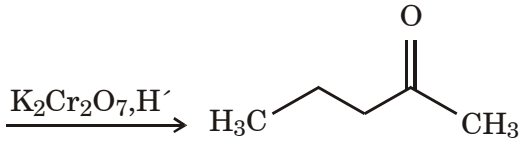
(a) $CH_3CH_2CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH_2CH_2CHO$

(b)

Solution :

(a) $\xrightarrow[\triangle]{Cu \text{ or } CuO} CH_3CH_2CH_2CH_2CHO$

(b)



(4) In acylium ion, the structure R — C ≡ O^+ is more stable than R — C^+ = O. Explain.

Solution :

Both C and O are non metals and try to complete their octet. In R — C ≡ O^+ each has complete octet whereas in R — C^+ = O, carbon atom has incomplete octet.

2. From Acid Chlorides (RCOCl) :

(a) For aldehydes

By reduction with H_2 in the presence of $Pd/BaSO_4$ in Xylene.

$$RCOCl + H_2 \xrightarrow[Xylene]{Pd/BaSO_4} RCHO + HCl$$

- This reaction is called Rosenmund's Reaction.
- $BaSO_4$ poisons the catalyst and reduce its efficiency. Thus, it checks the further reduction of aldehydes to alcohols.
- If $LiAlH_4$ is used as a reducing agent, the produced is an alcohol.

$$R — COCl \quad or \quad Ar — COCl \xrightarrow{LiAlH_4} RCH_2OH \quad or \quad ArCH_2OH$$

Note : Formaldehyde cannot be prepared by this method because formyl chloride is highly unstable and non-existing.

(b) For ketones : Acid chlorides on reaction with lithium organocuprates, R_2 CuLi or Ar_2CuLi yield ketones. Here, the R part of organocopper compound acts as nucleophile and displaces Cl of acid chloride to undergo nucleophilic substitution.

$$R'X \quad or \quad ArX \xrightarrow[-LiX]{2Li} R'Li \quad or \quad ArLi \xrightarrow[-LiX]{CuX} R'_2\,CuLi \quad or \quad Ar_2CuLi$$

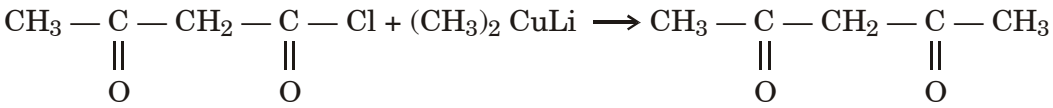
$$R'_2\,CuLi + 2RCOCl \longrightarrow 2RCOR + CuCl + Li$$

- Grignard reagent can also react with acid Chlorides, but the product is tertiary alcohols because the Ketone produced reacts with additional RMgX. This shows that organo copper reagents are less reactive than grignard reagents towards the carbonyl group of ketones and the reaction stops at the ketone formation stage.

  This low reactivity shows that the organo copper compounds donot react with the functional groups with which organomagnesium and organo lithium reagents react.

  Thus, the presence of some functional groups (like $-NO_2$, $-CN$, $-CO^-$, $-CO_2R$ etc.) does not interfere with the synthesis of ketone.

Example :

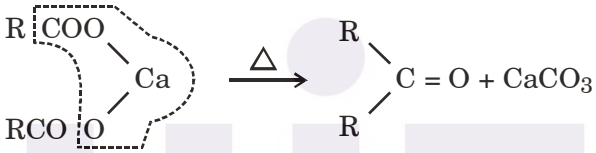


3. FROM CALCIUM SALT OF CARBOXYLIC ACID (PYROLYSIS)

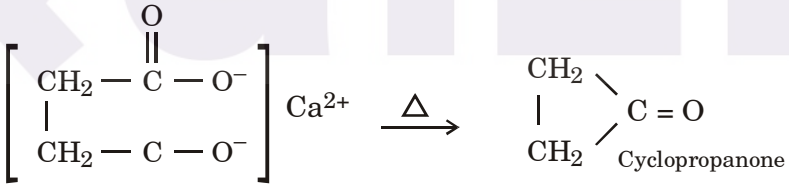
Formal dehyde is formed when calcium salt of formic acid is dry distilled.

$$(HCO_2)_2\ Ca \xrightarrow{\text{dry distillation}} HCHO + CaCO_3$$

Ketones are formed when calcium salt of monobasic acid (other than formic acid) is heated.



Illustration



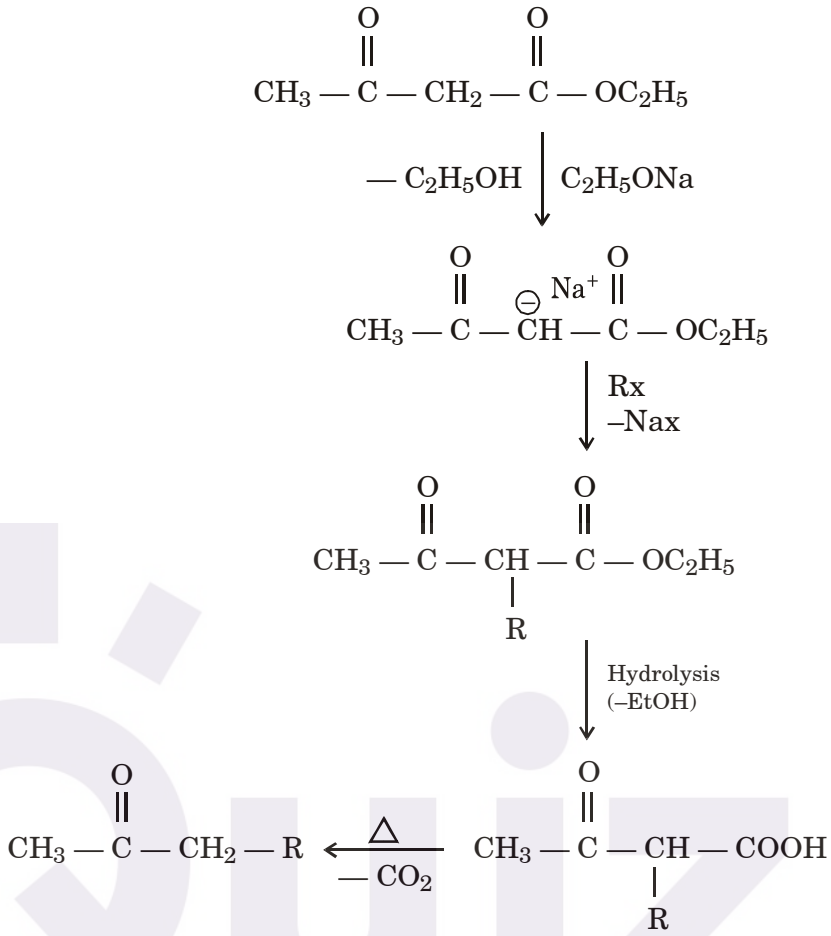
- Instead of using calcium salt of an acid vapours of an acid or mixture of acids can be passed over heated MnO at 300 C.

$$CH_3COOH + HCOOH \xrightarrow[300\ C]{MnO} CH_3CHO + CO_2 + H_2O$$

$$2CH_3COOH \xrightarrow[300\ C]{MnO} CH_3COCH_3 + CO_2 + H_2O$$

$$CH_3COOH + CH_3CH_2\ COOH \xrightarrow[300\ C]{MnO} CH_3COCH_2CH_3 + CO_2 + H_2O$$

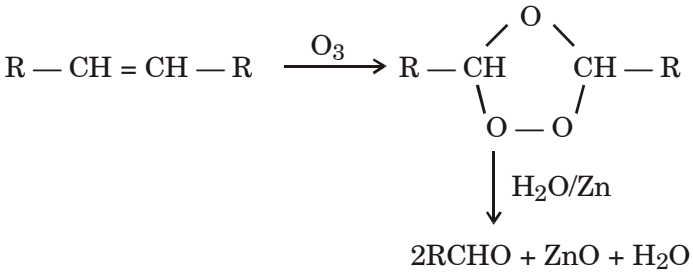
- **From** acetoacetic ester



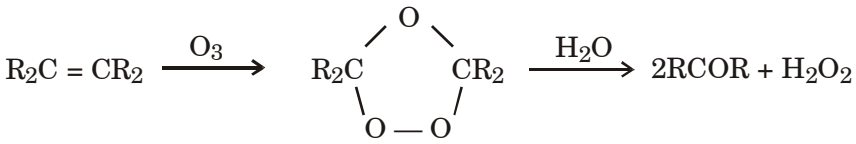
4. From alkenes

(i) **By reductive ozonolysis**

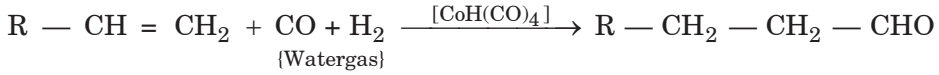
Aldehydes can be prepared by the ozonolysis of alkenes of the type R — CH = CH — R in presence of Zn (Reductive Ozonolysis)



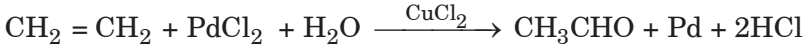
Ketones can also be prepared by the ozonolysis of alkenes of the type $R_2 C = CR_2$

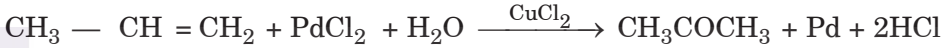


(ii) **Oxo process :** It involves the conversion of alkenes to aldehydes with one C atom more than parent alkene.



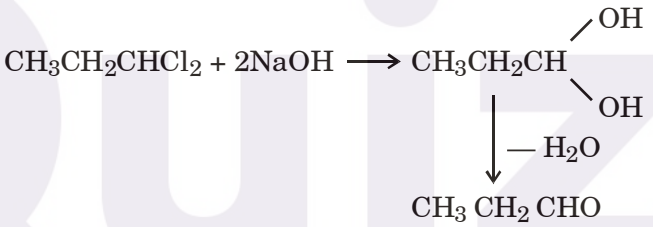
(iii) **Wacker's Process**





5. From geminal dihalides :

By alkaline hydrolysis, the geminal halides gets converted into aldehydes and ketones.



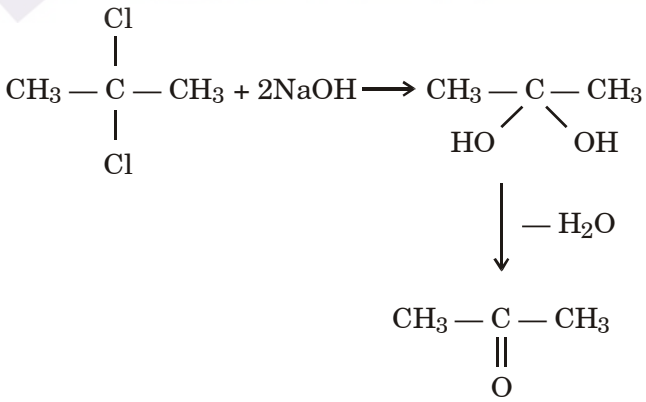
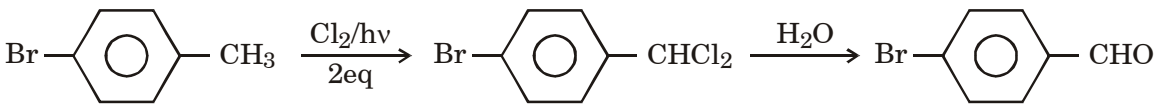


Illustration :



P-bromo benzaldehyde

6. From Alkynes

(1) Hydration :

Hydration of alkynes gives ketones (except CH ≡CH that gives CH_3CHO)

$$CH \equiv CH \xrightarrow[HgSO_4]{H_2O/H^+} CH_3CHO$$

$$CH_3 - C \equiv CH \xrightarrow[HgSO_4]{H_2O/H^+} CH_3COCH_3$$

(2) Hydroboration – oxidation

Hydroboration of a non-terminal alkyne followed by oxidation of the intermediate yields a ketone but terminal alkyne yields aldehyde.

$$CH_3C \equiv CCH_3 \xrightarrow{BH_3.THF} \left[CH_3CH = \underset{|}{C} - CH_3\right]_3 B$$

$$\downarrow H_2O_2/OH^-$$

$$CH_3CH_2\underset{\|}{C}CH_3 \xleftarrow{\text{tautomerises}} CH_3CH = \underset{|}{C} - CH_3$$
$$O \qquad\qquad\qquad OH$$

$$CH_3C \equiv CCH_3 \xrightarrow{BH_3THF} \left[CH_3CH = \underset{|}{C} - \right]_3 B$$
$$H$$

$$\downarrow H_2O_2 / OH^-$$

$$CH_3CH_2CHO \xleftarrow{\text{tautomerises}} CH_3CH = CHOH$$

Example 2

$B \xleftarrow{HgSO_4/H_2SO_4} CH_3CH_2C \equiv CH \xrightarrow[H_2O_2, OH^-]{BD_3.THF} A$ identity A & B.

Solution :

$$A \longrightarrow CH_3 - CH_2 - \underset{|}{CH} - CHO \qquad B \longrightarrow CH_3CH_2COCH_3$$
$$D$$

Example 3

$$\mathbf{B \xleftarrow{HgSO_4 / H_2SO_4} CH_3CH_2CH_2C \equiv C - CH_3 \xrightarrow[H_2O_2, OH^-]{BH_3 .THF} A}$$

Solution :

$A \longrightarrow CH_3CH_2CH_2CH_2COCH_3$, $B \longrightarrow CH_3CH_2CH_2CH_2COCH_2CH_3$

---

7. From Nitriles

(i) Stephen's Reduction (only for aldehydes)

$$R - C \equiv N \xrightarrow{SnCl_2/HCl} \underset{\text{Aldiminie hydrochloride}}{R - CH = NH.HCl} \xrightarrow{H_2O} RCHO + NH_4Cl$$

The formation of aldimine hydrochloride is unstable and hydrolyse to give aldehydes.

(ii) Treatment with Grignard Reagent (for ketones)

$$R' - C \equiv N \xrightarrow{RMgX} \left[R - \underset{R'}{\underset{|}{C}} = N - MgBr \right] \xrightarrow{2H_2O} R' - \overset{O}{\overset{\|}{C}} - R + NH_3 + Mg(OH)Br$$

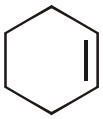
(iii) Using di-isobutyl aluminium hydride (DIBAL – H) to imines and then to by aldehydes

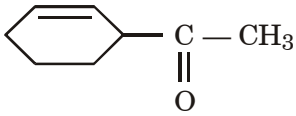
$$RCN \xrightarrow[2.\ H_2O]{1.\ AlH\ (iso - Bu)_2} R - CHO$$

Example 4

(1) $H - C \equiv N \xrightarrow[(ii)\ H_2O]{(i)\ \text{C}_6\text{H}_5\text{MgBr}} \text{C}_6\text{H}_5\text{CHO}$

(2) $CH_3CN \xrightarrow[(ii)\ H_2O]{(i)\ \text{C}_6\text{H}_5\text{MgBr}} \text{C}_6\text{H}_5\overset{O}{\overset{\|}{C}} - CH_3$

(3)  + NBS $\longrightarrow$ A $\xrightarrow[\text{ether}]{Mg}$ B $\xrightarrow[(ii)\ H_2O/H^+]{(i)\ CH_3CN}$ C

Ans. A $\longrightarrow$  Br , B $\longrightarrow$  MgBr , C $\longrightarrow$ 

(4) Convert $CH_3CH_2CH_3$ to $(CH_3)_2CH-\overset{\overset{O}{\|}}{C}-CH(CH_3)_2$

Ans.

$$CH_3CH_2CH_3 \xrightarrow{Br_2,\Delta} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{Mg/ether} CH_3-\underset{\underset{MgBr}{|}}{CH}-CH_3$$

$$CH_3-\underset{\underset{CN}{|}}{CH}-CH_3 \xrightarrow{H_3O^+} (CH_3)_2CH-\overset{\overset{O}{\|}}{C}-CH-(CH_3)_2$$

8. From Dialkyl cadmium :

(Only for Ketones)

$$R'-Cd-R' + 2R-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow 2R-\overset{\overset{O}{\|}}{C}-R' + CdCl_2$$

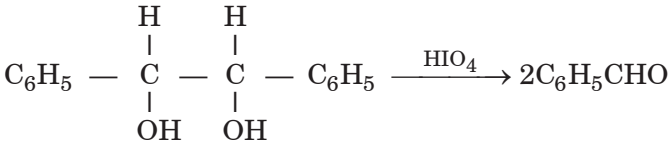
9. From Lithium Dialkyl cuprates

(Only for ketones)

$$R_2-CuLi + 2R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{\text{ether}} 2R-\overset{\overset{O}{\|}}{C}-R'$$

10. Cleavage of Diols

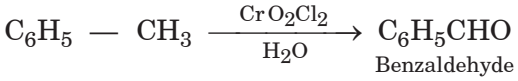
By oxidative clearage of 1, 2 diols (glycols) by periodic acid (HIO_4) or by lead tetra acetate, both aldehyde and ketones may be produced.



Preparation of aromatic aldehydes and ketones

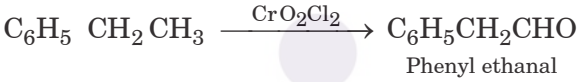
1. Oxidation of toluene

(a) Using chromyl chloride CrO_2Cl_2

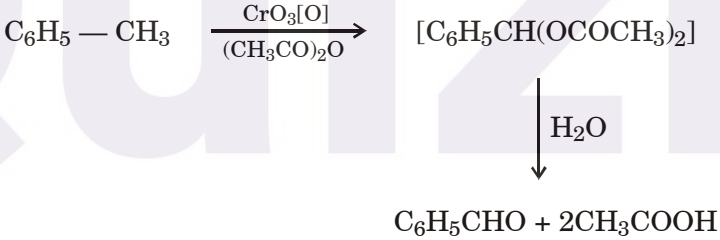


This is called **Etard's Reaction**

Note : if side chain is bigger than — CH_3 group, then terminal C is changed to — CHO group. For example,

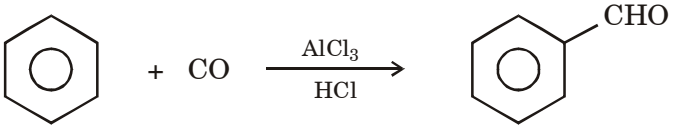


(b) Oxidation using CrO_3 in acetic anhydride

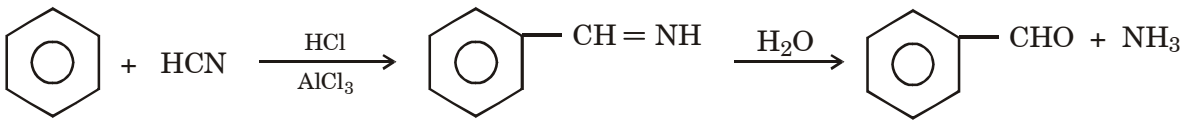


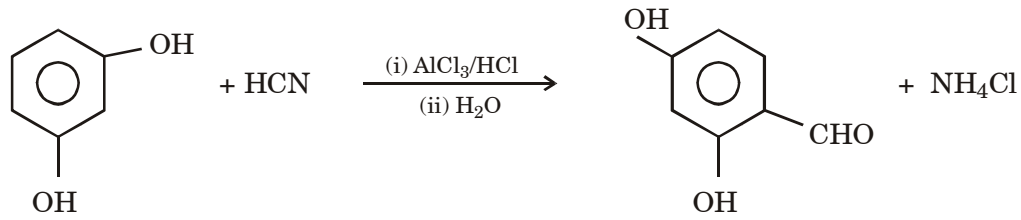
2. Gattermann Koch Reaction :

This involves formylation of aromatic ring with CO.



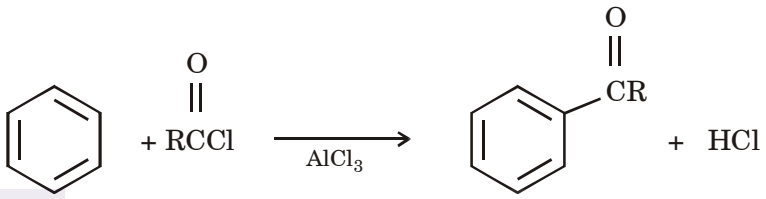
3. Gattermann Aldehyde Synthesis





This process involves the treatment of benzene or other aromatic compounds having activating groups like, — OH, — OR etc.

4. Friedel-Crafts Acylation of Benzene

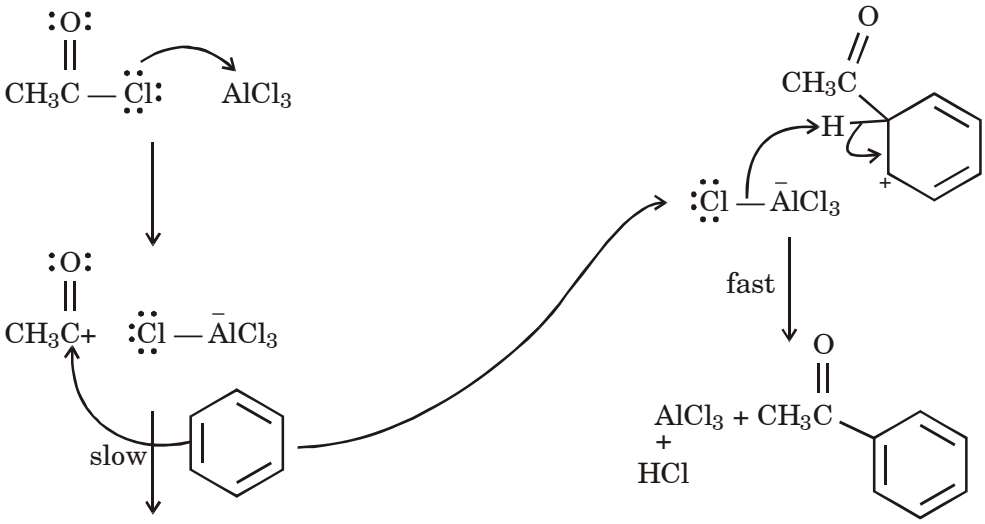


- Electrophilic species : the acyl cation or acylium ion (i.e. RCO^+) formed by the "removal" of the halide by the Lewis acid catalyst.
- The acylium ion is stabilised by resonance as shown below. This extra stability prevents the problems associated with the rearrangement of simple carbocations :

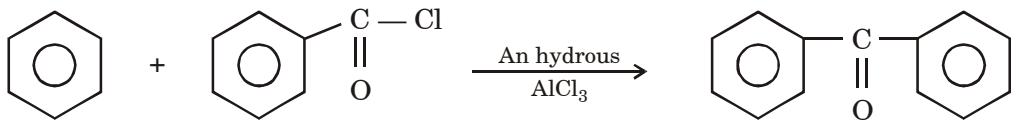
- The reduction of acylation products can be used to give the equivalent of alkylation but avoids the problems of rearrangement
- Friendel-Crafts reactions are limited to arenes as or more reactive than mono-halobenzenes.

Mechanism

The acyl halide reacts with the Lewis acid to form a more electrophilic C, an acylium ion

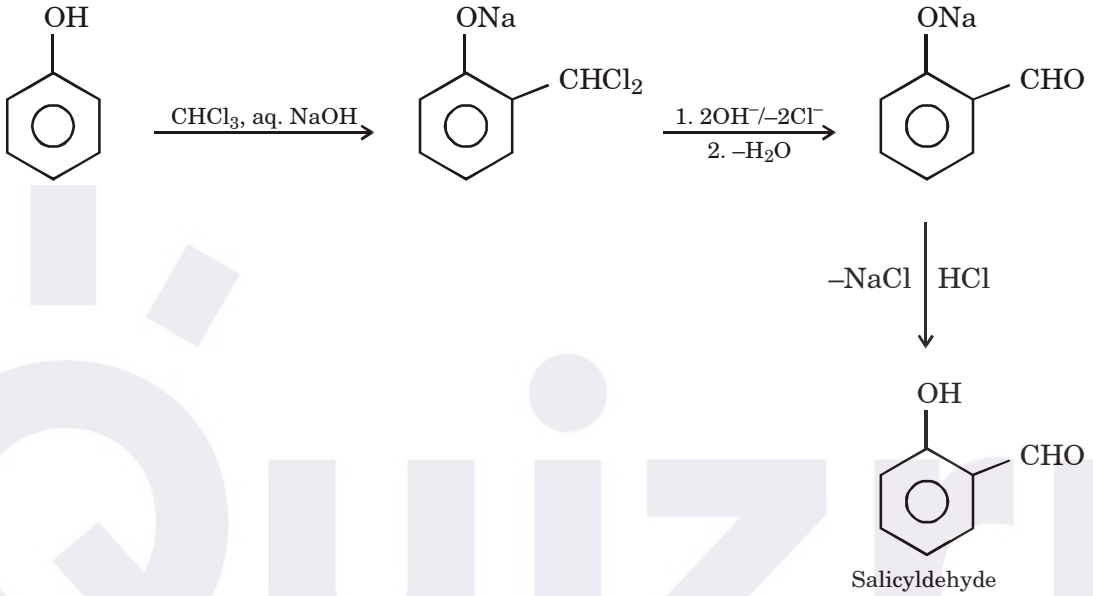


For example :



5. Reimer – Tiemann Reaction

When phenol is treated with chloroform and aqueous NaOH/KOH, an aldehyde group is introduced in the aromatic ring, generally at the ortho position.



PROPERTIES OF ALDEHYDES AND KETONES

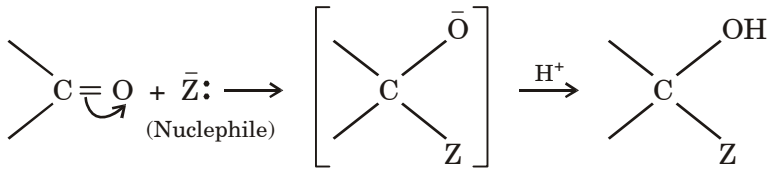
Physical Properties

- Formaldehyde is gas but other aldehydes are liquids at room temperature.
- Lower ketones are colourless liquids while higher ketones are colourless solids.
- Boiling points of ald/ketones are relatively higher than hydrocarbons but lower than alcohols of comparable molecular mass.
- Boiling points of ketones are more than the corresponding isomeric aldehydes.
- Lower aldehydes / Ketones (up to 4 carbons) are soluble in water but higher aldehydes / ketones are almost immiscible with water.

Chemical Properties

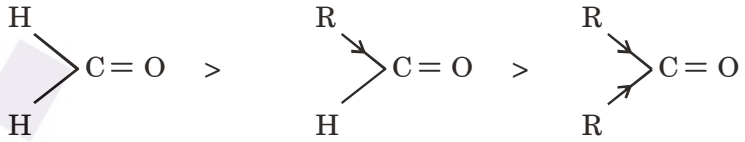
- Aldehydes and ketones owe their highly reactive nature to the polar carbonyl group $\left(>\overset{\delta+}{C}=\overset{\delta-}{O}\right)$ in their molecules.

- The electron deficient carbon atom of CO group readily undergo the nucleophilic attack for initiation of reaction.
- The general mode of reaction being :



(Intermediate)

- Crowding at the carbonyl carbon and presence of electron releasing group hinder's the nucleophilic attack on the carbonyl carbon and decreases the reactivity of the compound. For example, crowding as well as electron releasing effect increases from formaldehyde to other aldehydes to ketones. Hence, reactivity decreases as follows.

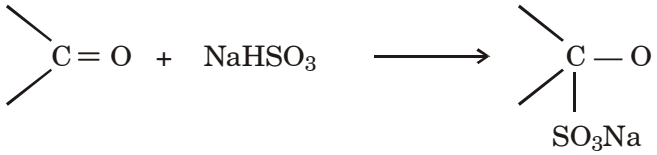


- The presence of electron withdrawing groups at the carbonyl carbon increases the reactivity.
- The attachment of benzene ring to CO group decreases the reactivity because C = O bond comes in conjugation with aromatic ring and resonance stabilisation of molecule occurs.
- CO group withdraws electron density from the ring. Hence it becomes less susceptible to the electrophilic substituion.
- Ring substitution in benzaldehyde occurs at m-position.

REACTIONS

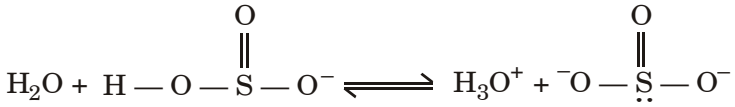
I. ADDITION REACTIONS

1. Addition of $NaHSO_3$



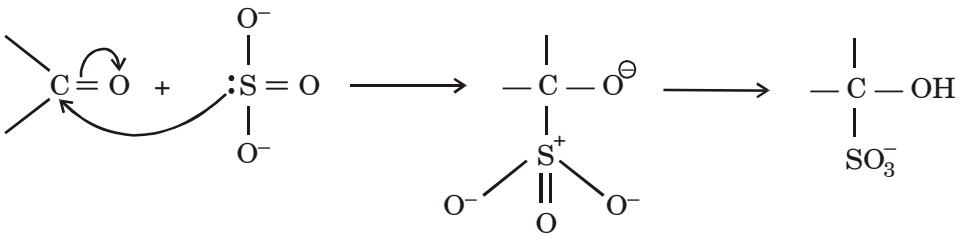
(Sodium bisulphite)

Mechanism :

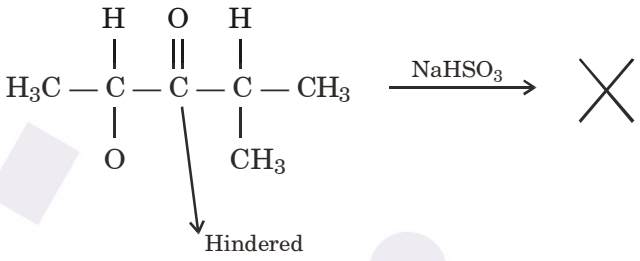


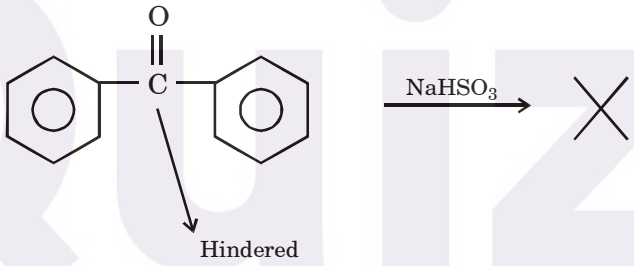
- Here SO_3^{2-} is a stronger base than SO_3^{2-} because of more electron density.

Hence, SO_3^{2-} will be the attacking species

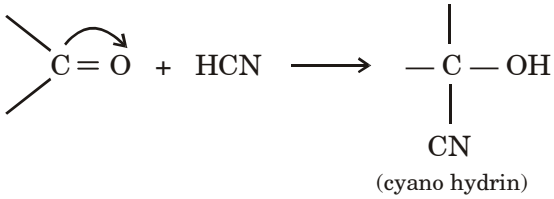


Note : Hindered ketone does not give the reaction.

(a) 

(b) 

2. Addition of HCN

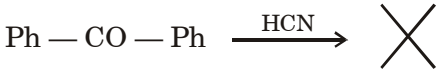


Mechanism :

$$HCN \rightleftharpoons H^+ + CN^-$$

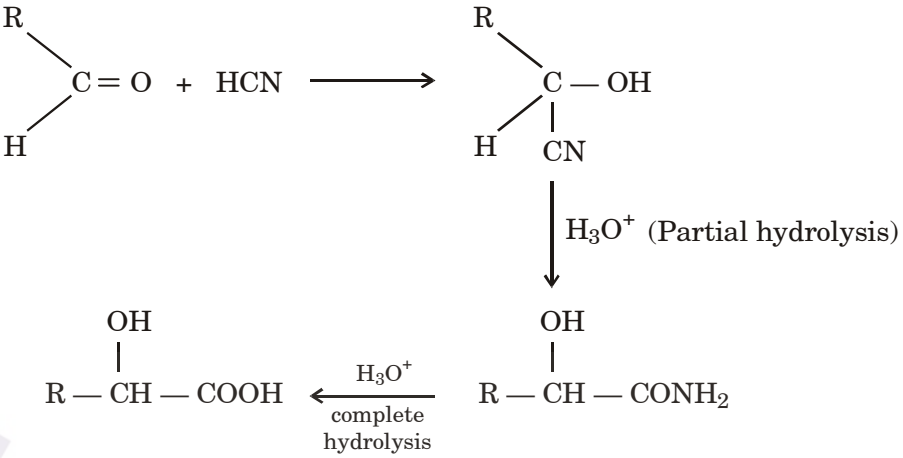
Note :

(1) As done in the case of $NaHSO_3$, here also hindered ketone does not give the reaction.

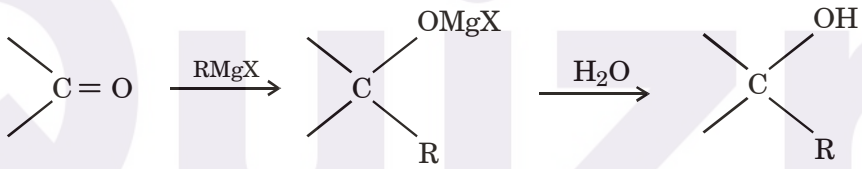


(2) $-C \equiv N-$ → (Reduce, H_2/Li or $LiAlH_4$) CH_2N_2; (Hydrolysis) $-COOH$

Illustration :

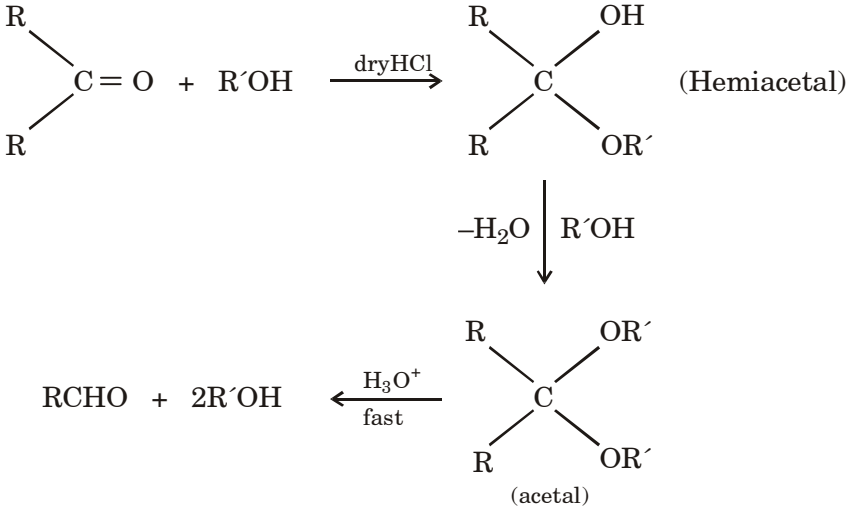


3. Addition of Griguard's reagent (RMgX)

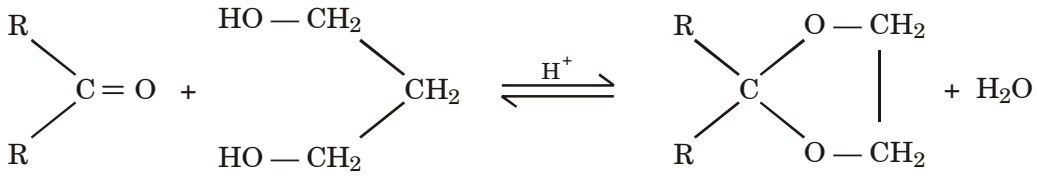


- Aldehydes form 2 alcohol (except HCHO which gives RCH_2OH) (1 alcohol) while ketones form 3 alcohol.

4. Addition of Alcohols



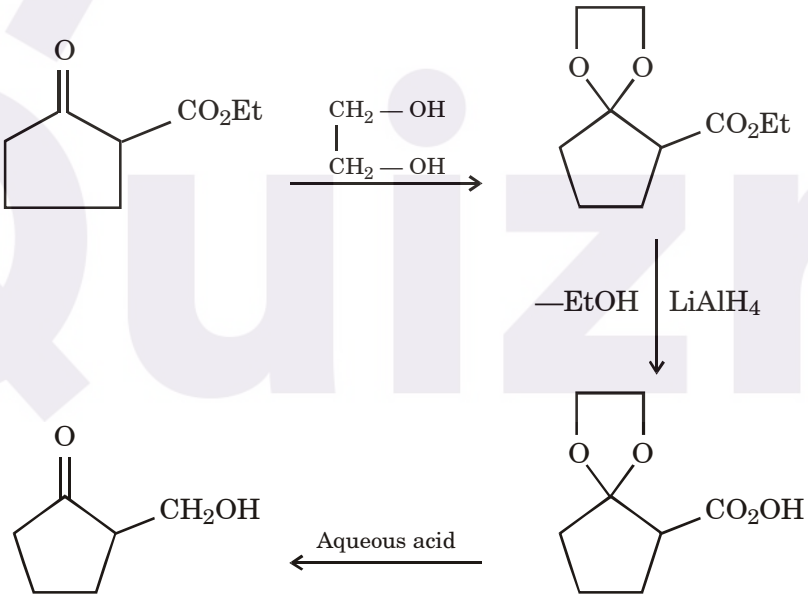
- Hemiacetal is very reactive and easily forms acetal
- The above reaction is not so favourable with ketones but can be favourable if 1, 2 or 1, 3-diols are used. With diols, cyclic ketals are formed.



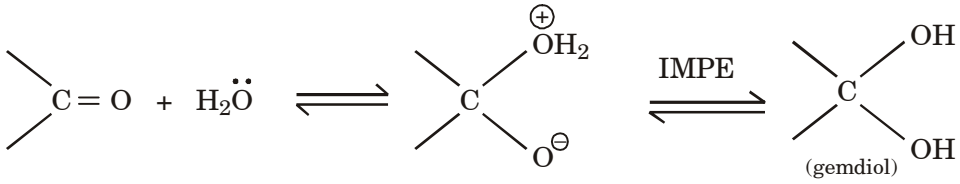
Note : ketals are formed only by unhindered ketones.

- Acetals or ketals are stable in neutral or basic conditions but in acidic medium, they undergo acid catalysed cleavage similar to that of ethers to regenerate carbonyl compounds. Thus this reaction can be used to protect carbonyl groups.

For example

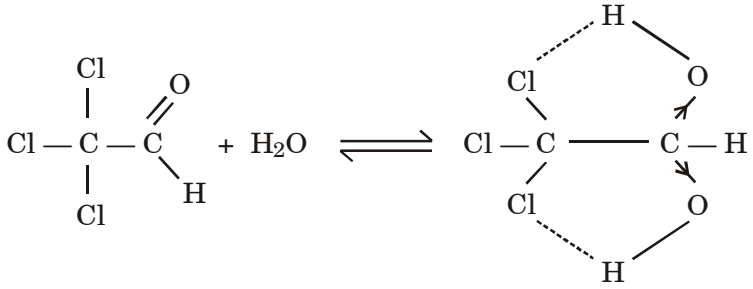


5. Addition of water

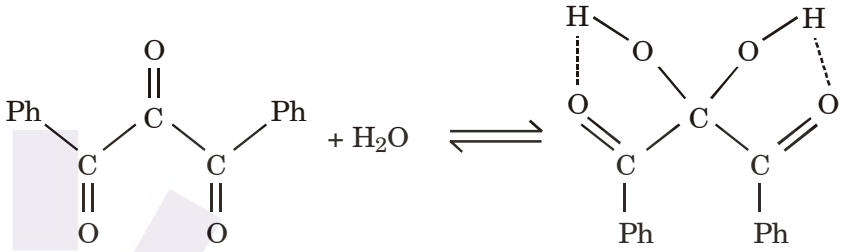


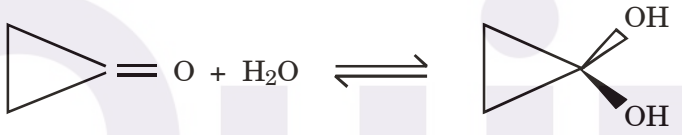
The rate of hydration decreases due to the presence of electron donating substituents while electron withdrawing substituents increase the rate.

Some examples of stable hydrated

(a) 

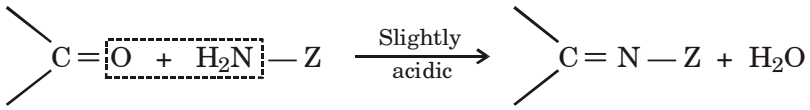
This is stable due to the intramolecular H-bonding.

(b) 

(c) 

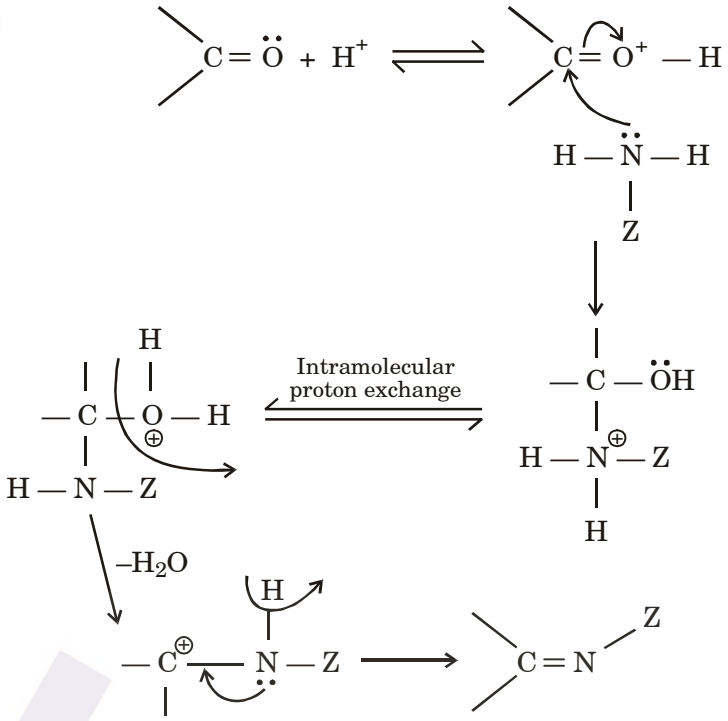
The diving force of this reaction is the relief in angle strain on going from carbonyl compound (C – C – C bond angle = 60°, compared with normal sp^2 bond angle of 120) to hydrate (C – C – C bond angle = 60 , compared with normal sp^3 bond angle of 109.5 .)

6. Addition of ammonia derivatives



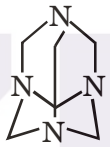
(pH controlled reaction)

Mechanism :



- pH should be controlled carefully. Medium should be neither too acidic nor too basic.
- HCHO reacts with NH_3 differently forming UROTROPINE (hexamethylene tetraamine)

$$6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 4H_2O$$



- The reaction of ammonia with aldehydes and ketones forms imines, but the products are unstable and cannot usually be isolated. If a secondary amine is used, an enamine is formed. An enamine has an amino group bonded to one of the carbons of a carbon-carbon double bond and can be said to form when enolic form of a carbonyl compound reacts.

The table give below uses the following abbreviations (A, B, C)

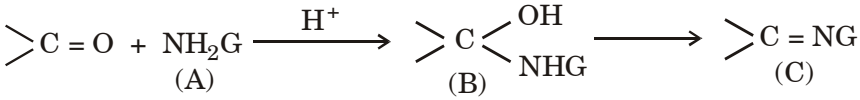
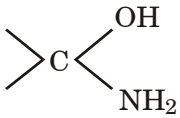
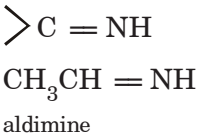
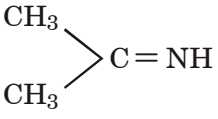


Table : Reactions of NH_2G with carbonyl compounds

G	A	B	C
—H	NH_3		 aldimine
			 ketimine

— OH	NH_2OH hydroxylamine	$>C<^{OH}_{NHOH}$	$C=NOH$ oxime
— R	RNH_2 (aliphatic)	$>C<^{OH}_{NHR}$	$>C=NR$ (Schiff base) azomethine
— NH_2	NH_2NH_2 hydrazine	$>C<^{OH}_{NHNH_2}$	$>C=N\ NH_2$ hydrazone
— NHC_6H_5	$NH_2NHC_6H_5$ phenyl hydrazine	$>C<^{OH}_{NHNHC_6H_5}$	$>C=NNHC_6H_5$ phenylhydrazone
— $NHC_6H_3(CO_2)_2$	$NH_2NHC_6H_3(NO_2)_2$ 2, 4-dinitro phenyl hydrazine (2 : 4 DNP)	$>C<^{OH}_{NHNHC_6H_3(NO_2)_2}$	$>C=NNHC_6H_3(NO_2)_2$ 2, 4-dinitro phenylhydrazone
— $NHCONH_2$	$NH_2NHCONH_2$ semicarbazide	$>C<^{OH}_{NHNHCONH_2}$	$>C=NNHCONH_2$ semicarbazone

In aqueous acidic solution, an enamine is hydrolysed back to the carbonyl compound and secondary amine.

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CH_2 \xrightarrow{(CH_3)_2NH} CH_3-\overset{\overset{N(CH_3)_2}{|}}{C}=CH_2$$

$$CH_3-\overset{\overset{N(CH_3)_2}{|}}{C}=CH_2 \xrightarrow{H_3O^+} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + (CH_3)_2NH$$

Example 5

$$CH_3MgBr + CH_2=CH-\overset{\overset{O}{\|}}{C}-H \xrightarrow{H_3O^+} X.\ X \text{ is}$$

(a) $CH_2=CH-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-H$

(b) $CH_2-CH=CH-CH_3$ (with CH_3 branch on the second carbon)

(c) $CH_3-CH_2-CH_2-CHO$

(d) None is correct

Solution :

$CH_2=CH-\overset{\overset{O}{\|}}{C}-H$ is conjugate system

(I)

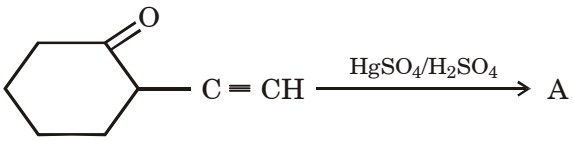
hence (I) + $CH_3-Mg-Br \xrightarrow{H_3O^+}$ $CH_3-CH_2-CH=\overset{\overset{OH}{|}}{C}-H$

$\rightleftharpoons$ tautomerises

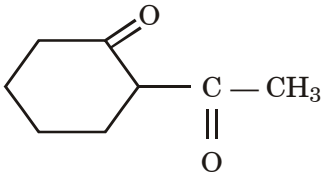
$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H$

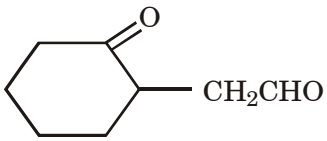
Hence, (C) is correct.

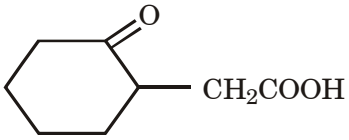
Example 6

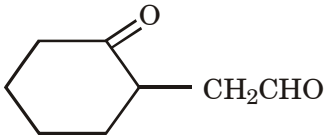


A is

(a) 

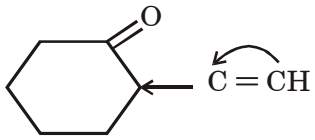
(b) 

(c) 

(d) 

Solution :

C = O is (EWG) hence π electron transfer is towards ring.



Hence, (B) is correct.

Example 7

End product of the following sequence of reactions is

$$CH \equiv CH \xrightarrow{CH_3MgBr} \xrightarrow{CO_2/H_2O^+} \xrightarrow{HgSO_4\,/\,H_2SO_4} \xrightarrow[\Delta]{Ag_2\,O}$$

(a) $CH_3 - \overset{\overset{O}{\|}}{C} - COOH$ **(b)** $CH_2(COOH)_2$

(c) $CH_3 - \overset{\overset{O}{\|}}{C} - CHO$ **(d)** $H - \overset{\overset{O}{\|}}{C} - CH_3COOH$

Solution :

$$CH \equiv CH + CH_3MgBr \longrightarrow CH \equiv C - MgBr$$

$$\downarrow O_2/H_3O^+$$

$$CH \equiv C \longrightarrow COOH \quad (-COOH \text{ is (EWG)})$$

$$\downarrow HgSO_4/H_2SO_4$$

$$OHC - CH_2 - COOH$$

$$\downarrow Ag/O$$

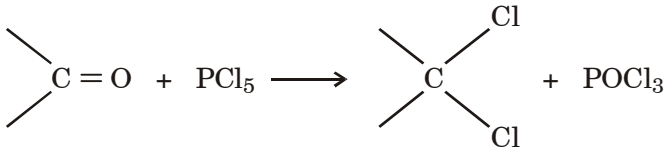
$$HOOC - CH_2 - COOH$$

$$\downarrow \Delta$$

$$CH_3COOH$$

Hence, (B) is correct.

II. Reaction with PCl_5 or $SOCl_2$ / pyridine



Dichloroalkane

- The products are geminal dihalides.

III. Reaction with SeO_2

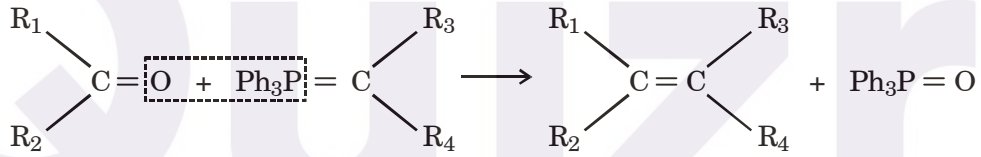
$$CH_3CHO + SeO_2 \xrightarrow[\text{acid}]{\text{Acetic}} OHC - Se + H_2O$$

$$CH_3COCH_2CH_3 + SeO_2 \xrightarrow[\text{acid}]{\text{Acetic}} CH_3CO\overset{\overset{O}{\|}}{C}CH_3 + Se + H_2O$$

The reaction is only given by methylene group adjacent to the carbonyl group.

IV. Witting Reaction

It is a reaction used for converting carbonyl compounds to alkenes



phosphorus ylide

V. Oxidation

- Aldehydes are easily oxidised to carboxylic acids with same number of C atoms.

$$RCHO \xrightarrow{[O]} RCOOH$$

- Not only strong oxidizing agents ($KMnO_4$, $K_2Cr_2O_7$) but even mild oxidants like Ag^+, Cu^{2+} etc., can oxidise aldehydes. Thus aldehydes are very powerful reducing agents.

(a) **Tollen's reagent :** This is also called silver mirror test. It is reduced by aldehyde to Ag.

$$RCHO + 2[Ag(NH_3)_2]OH \longrightarrow RCOONH_4 + 2Ag(\downarrow) + 3NH_3 + H_2O$$

Tollen's reagent {colour less solution} — (silver mirror)

Note : ketones do not react with them, hence it is used in differentiating aldehydes from ketones.

(b) **Fehling's solution :** Aldehydes (except benzaldehyde) reduce fehling's solution (Cu^{2+} reduced to Cu^{+}) ion complexed with tartarate ion.

$$RCHO + 2Cu^{2+} + 3OH^{-} \xrightarrow{\Delta} RCOO^{-} + \underset{\text{Red ppt.}}{2Cu^{+}(\downarrow)} + 2H_2O$$

(c) Adehydes also reduce Benedict's solution (Cu^{2+} complexed with citrate ion) to Cu^{+}

(d) **Oxidation of Ketones**

In general, oxidation of ketones give a mixture of carboxylic acid.

- During oxidative cleavage of mixed ketones, the lower alkyl group is retained by carbonyl group. This is known as Popoff's Rule.

$$\underset{\text{2 - pentanone}}{CH_3CH_2CH_2 - \overset{O}{\overset{\|}{C}} - CH_3} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{propionic acid}}{CH_3CH_2COOH} + \underset{\text{acetic acid}}{CH_3COOH}$$

(e) **Oxidation with sodium hypohalite**

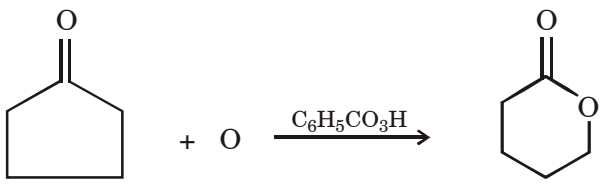
- The reaction is given by aldehydes or ketones having $\mathbf{CH_3 - \overset{O}{\overset{\|}{C}} -}$ group
- Hypohalite is a selective oxidizing agent as it does not attack carbon carbon double bonds.
- This is also called haloform reaction

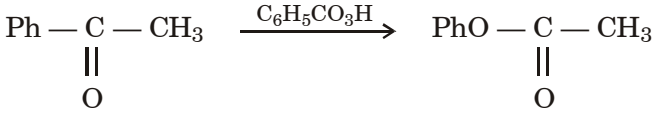
$$R - \overset{O}{\overset{\|}{C}} - CH_3 + 3NaOI \longrightarrow R - \overset{O}{\overset{\|}{C}} - O^{-}\ Na^{+} + \underset{\text{(yellow ppt.)}}{CHI_3\ (\downarrow)} + 2NaOH$$

(f) **Baeyer – Villiger Oxidation**

ketones are oxidised by caro's acid (H_2SO_5) or peroxy benzoic acid ($C_6H_5CO_3H$) to esters.

$$RCOR' + O \xrightarrow{H_2SO_5} RCOOR'$$





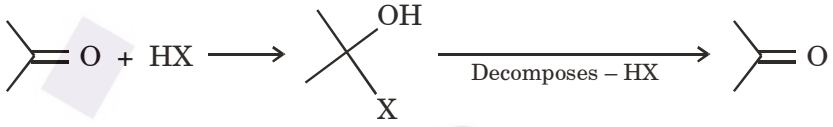
- The insertion of oxygen atom takes place between the carbonyl group and the group having greater migrating tendency.

Example 8

Halogen acids HX easily add to > C = C < bond but they do not add on > C = O bond. Why ?

Solution :

The high degree of polarity in HX as well as in > C = O bond shows the easy addition of HX on > C = O bond but as soon as addition products are formed, the product loses HX to show the backward reaction.

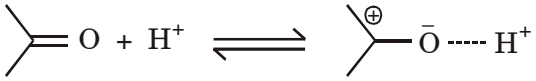


Example 9

Presence of acids and bases activates carbonyl compounds for reaction. Explain.

Solution :

Presence of acid intensifies the partial positive charge on carbonyl carbon and hence activates the group.

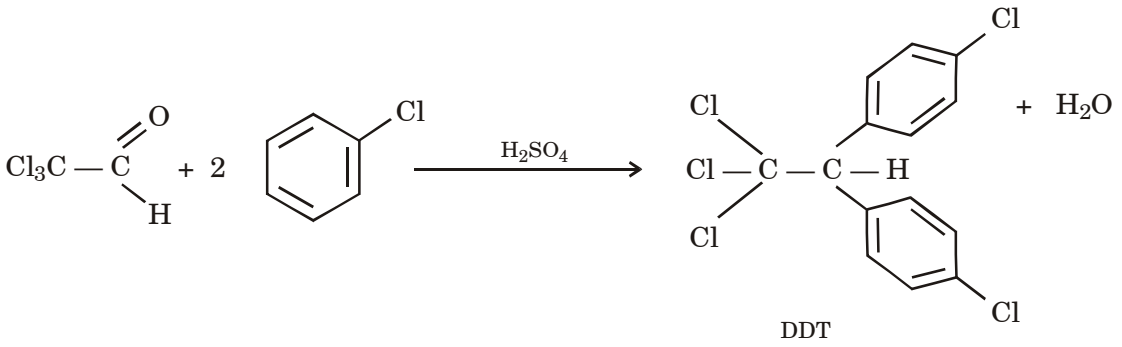


Presence of base activates a-methylene component of the carbonyl compounds by converting them in carbanions.

Formation of DDT

Chloral (trichloro acetaldehyde) on reaction with chlorobenzene in presence of H_2SO_4 gives dichloro diphenyl trichloroethane (DDT). The product is used as an insecticide for killing insects and mosquito.

It is used in household under the name DDT

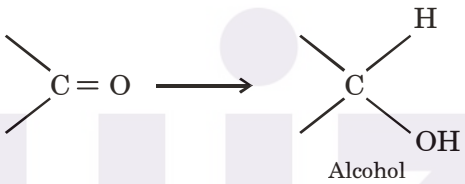


DDT

VI. REDUCTION

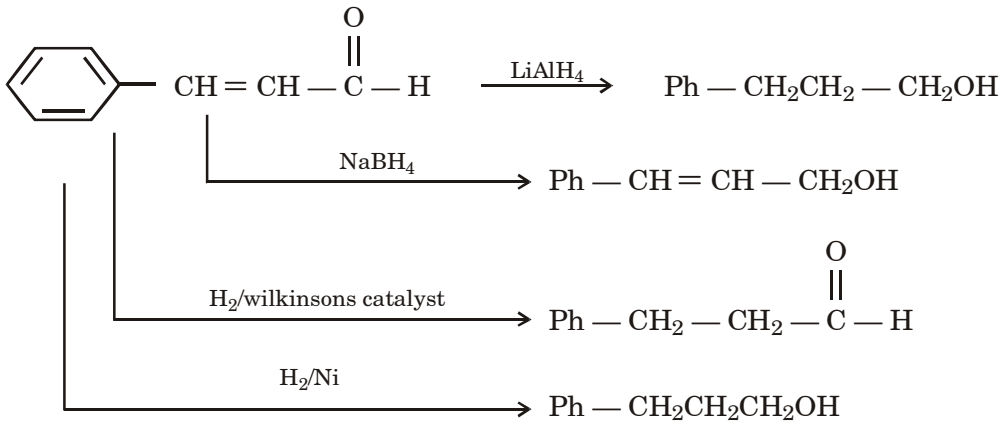
(a) Mild Reduction

- This is carried out by reducing agents like H_2/Pt, H_2/Pd, $LiAlH_4$, $NaBH_4$ etc. and converts CO to CHOH

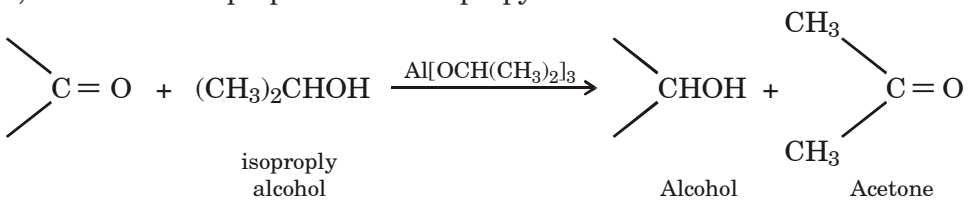


Alcohol

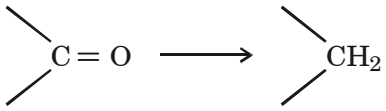
- Aldehydes give 1 alcohol and ketones give 2 alcohols.
- $NaBH_4$ and $LiAlH_4$ reduce C = O bond without reducing C = C bonds in the compound.
- However, $LiAlH_4$ reduced the carbon-carbon double bond, which is in conjugation with carbonyl group only when the β-carbon bears an aryl group.



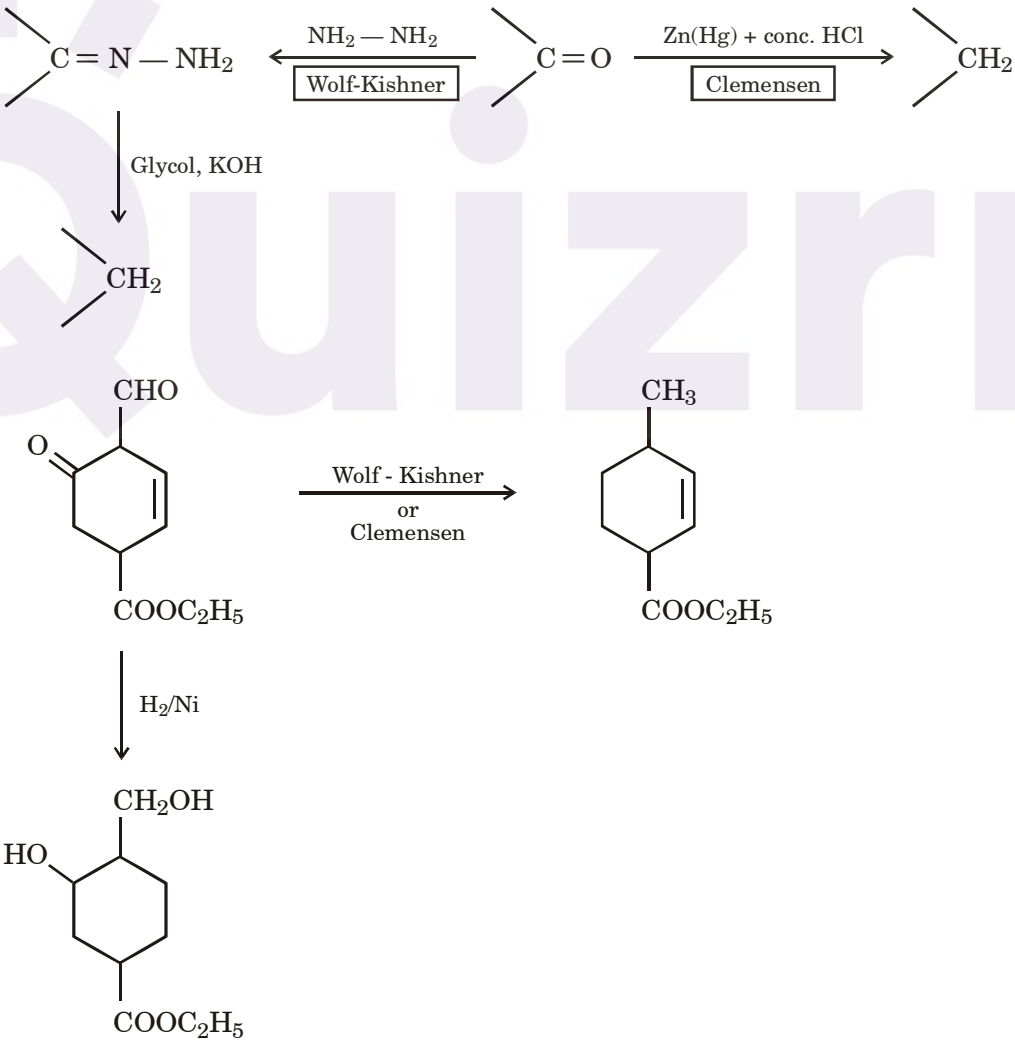
(b) MPV reduction : This is Meervein – Ponndroff – Verley reduction and it involves reduction of C = O group to CHOH without affecting the other reducible group in the molecule. The reagent used are, aluminium isopropoxide and isopropyl alcohol.



(c) Strong reduction :

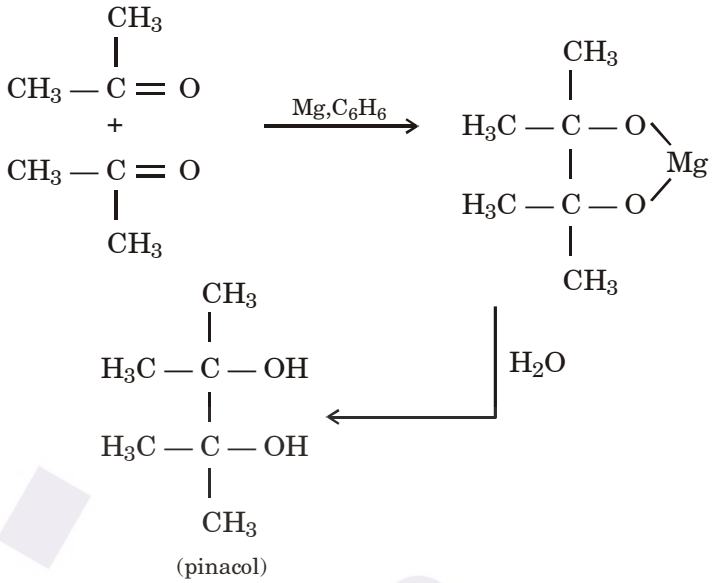


- Various reducing agents employed are Zn – Hg/HCl (Clemmensen's reduction); NH_2 — NH_2 / KOH (wolf – Kishner reduction); Na/alcohol; HI/red P.



Note : $NaBH_4$ also does not reduce esters or acid chlorides but $LiAlH_4$ reduces them to alcohols.

(d) Reduction to pinacol



(pinacol)

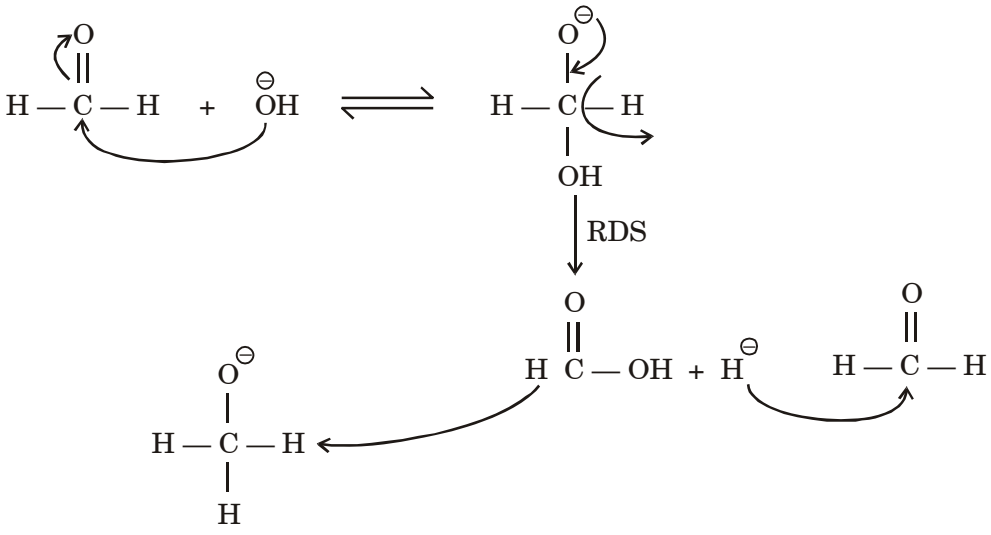
VII. CANNIZARO'S REACTION

2 moles of aldehydes containing no α-hydrogen $\xrightarrow[\text{medium}\ (OH^-)]{\text{Conc. basic}}$ Undergo disproportionation to produce one mole of alcohol and one mole of carboxylic acid

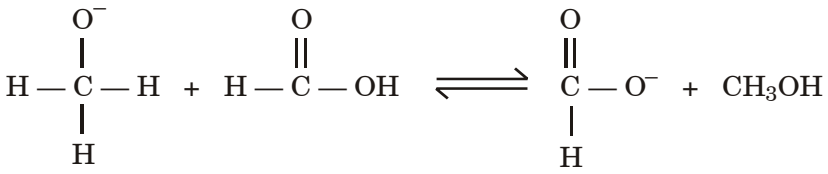
(1) $2HCHO + NaOH \longrightarrow CH_3OH + HCOONa$

(2) $2PhCHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$

Mechanism :

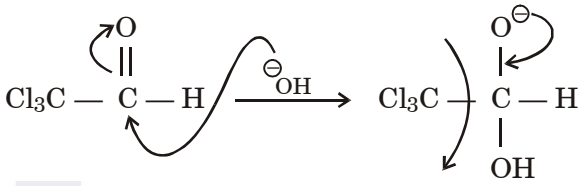


{This is a strong base, hence it abstracts proton from acid}

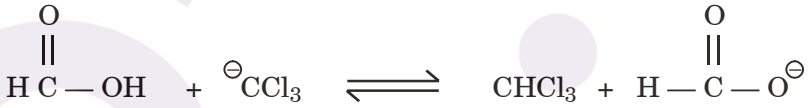


Rocking Illustration :

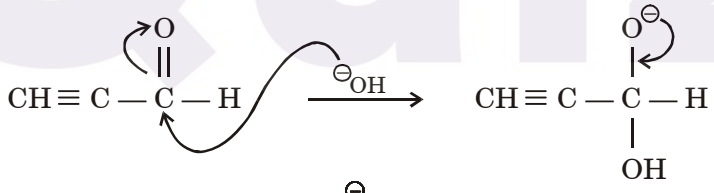
1. $CCl_3\ CHO \xrightarrow{\bar{O}H} ?$



{Here $\bar{C}Cl_3$ is more stable than H^-, hence H^- is not removed, thus cannizaro reaction does not occur}



2. $CH \equiv C - CHO \xrightarrow{\ominus OH} ?$



{in this case also, $CH \equiv \overset{\ominus}{C}$ is more stable than $H^{\ominus}$}

Hence, products are HC ≡ CH and H $COO^{\ominus}$

Cross Cannizaro's Reaction

$$HCHO + PhCHO + \underset{\text{(conc.)}}{NaOH} \longrightarrow PhCH_2OH + HCOONa$$

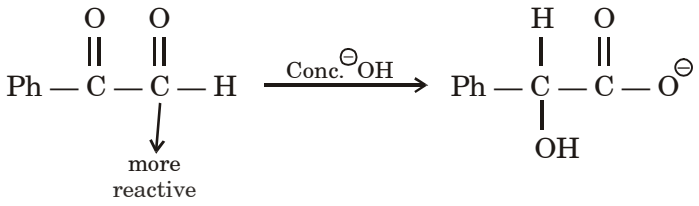
This reaction yields benzyl alcohol and not benzoic acid because carbonyl carbon of formaldehyde is more electrophilic than that of benzaldehyde.

So, ^{-}OH finally attacks at formaldehyde (steric affects can also be said to have a major role in this attack).

Note : the presence of electron withdrawing substituent increases the rate of cannizaro reaction while electron releasing substituent decreases the rate.

Intramolecular Cannizzaro

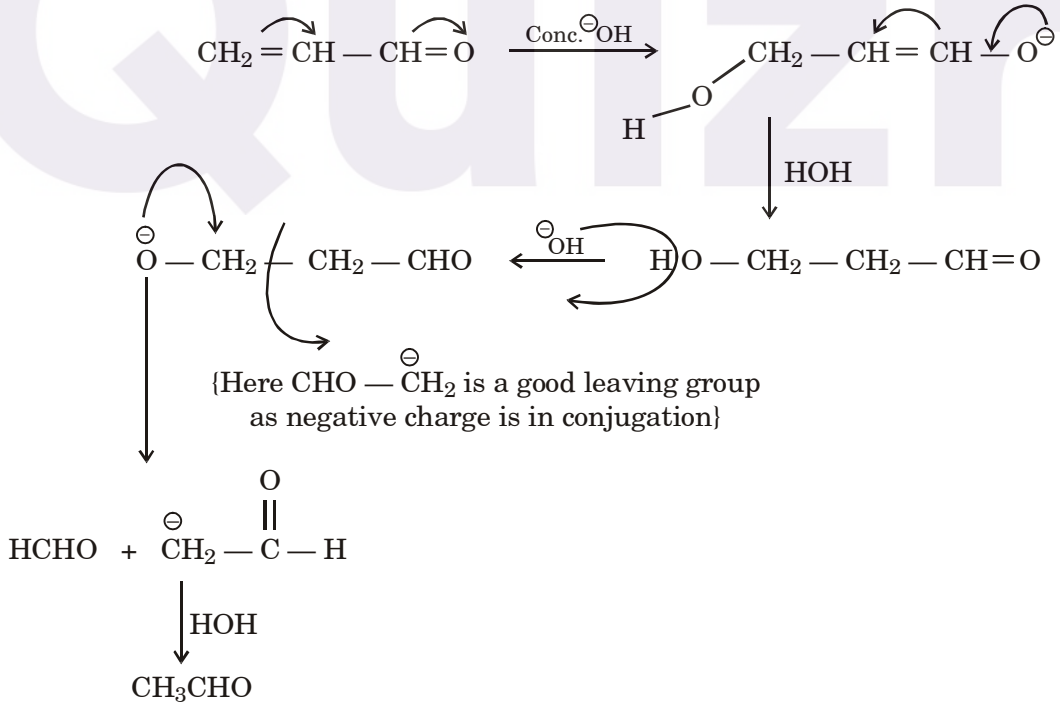
Glyoxal on reaction with conc. NaOH gives 2-hydroxy ethanoate by intramolecular cannizaro reaction. The product is a α-hydroxy acid.



Rocking Illustration

$CH_2 = CH - CH = O \xrightarrow[^{-}OH]{conc.}$?

Solution :



Example 10

$2CD_2 = C + OH \xrightarrow{\text{Cannizzaro}}$ X and Y (Y is alcohol, D is deuterium)

X and Y will have structure :

(A) $D-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O}$, $D-\overset{\overset{D}{|}}{\underset{\underset{D}{|}}{C}}-OH$

(B) $D-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O}$, $D-\overset{\overset{D}{|}}{\underset{\underset{H}{|}}{C}}-OH$

(C) $D-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O}$, $D-\overset{\overset{D}{|}}{\underset{\underset{H}{|}}{C}}-OH$

(D) None is correct

Solution :

$$D-\underset{\underset{D}{|}}{C}=O + \bar{O}H \longrightarrow \overset{\ominus}{O}-\underset{\underset{OH}{|}}{\overset{\overset{D}{|}}{C}}-D + \underset{D}{\overset{D}{>}}C=O \longrightarrow O=C\underset{D}{\overset{D}{<}} + D-\overset{\overset{D}{|}}{\underset{\underset{D}{|}}{C}}-\overset{\ominus}{O}$$

Proton transfer

$$O=C\underset{O^-}{\overset{D}{<}} + D-\overset{\overset{D}{|}}{\underset{\underset{D}{|}}{C}}-OH$$

Hence, (A) is correct.

VIII. CONDENSATION REACTIONS :

(1) Aldol Condensation : This is shown by aldehyde / ketones having atleast one α – H atom. Here, α – C of one of the molecules joins with the carbonyl carbon of the other.

(a)

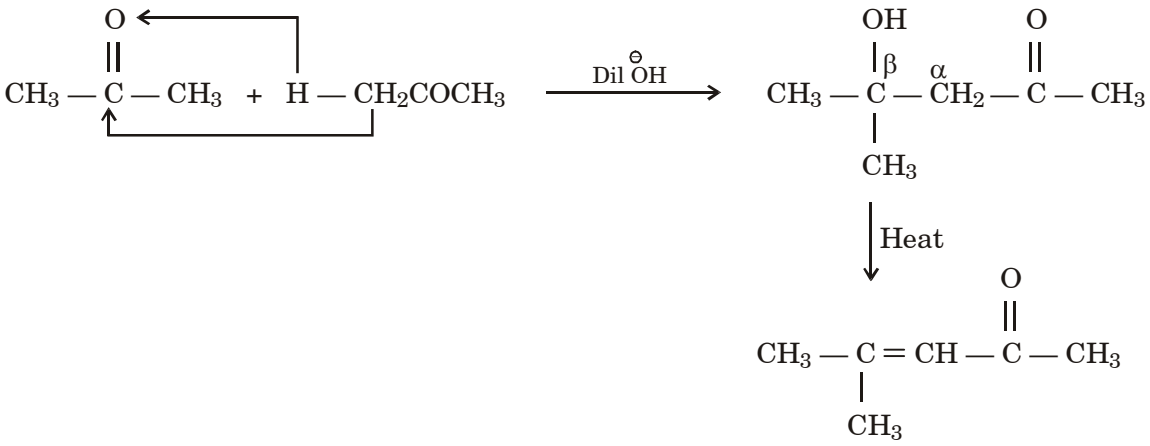
$$CH_3-\overset{\overset{O}{\|}}{C}-H + H-CH_2CHO \xrightarrow{\text{Dil NaOH}} CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{\overset{\beta}{C}}}-\overset{\alpha}{C}H_2CHO$$

Acetal

$$\xrightarrow[\text{Heat}]{-H_2O} CH_3-CH=CH-CHO$$

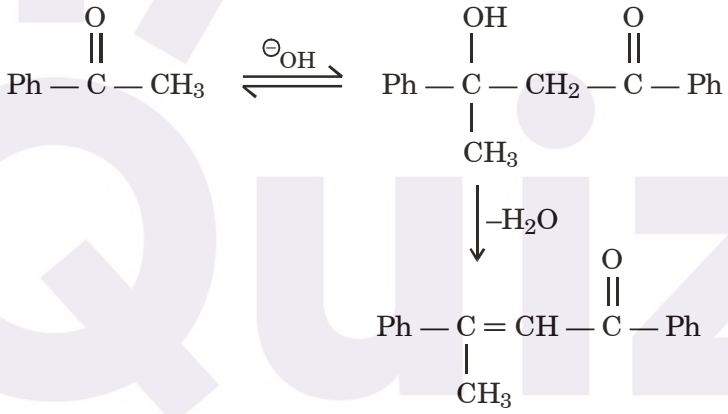
(Croton aldehyde)

(b)

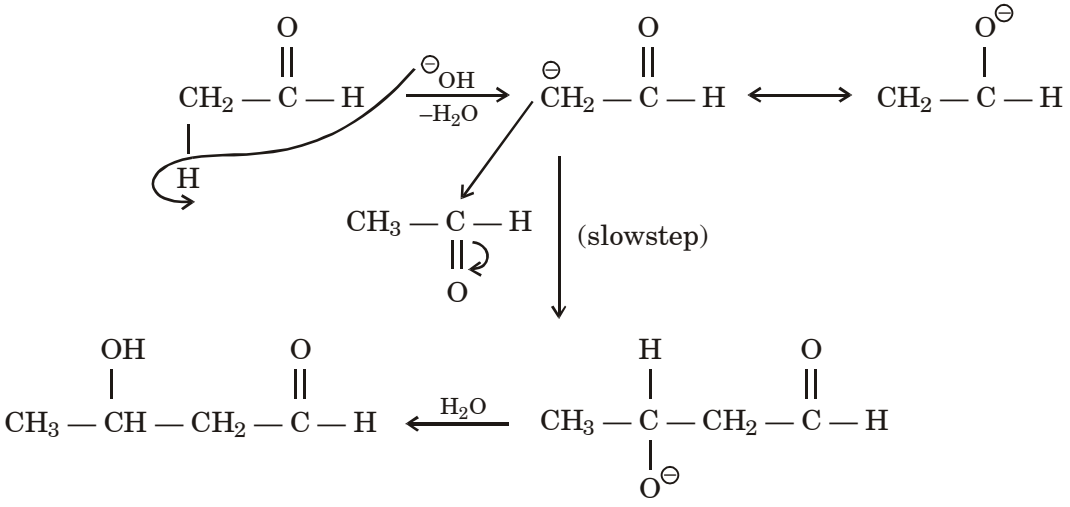


- The aldol reaction is more favourable for aldehydes than for ketones because of more acidic α-Hydrogen atoms and more electrophilic carbon.
- The dehydration product is α, β – unsaturated carbonyl compound due to the conjugated structure formed.

(c)

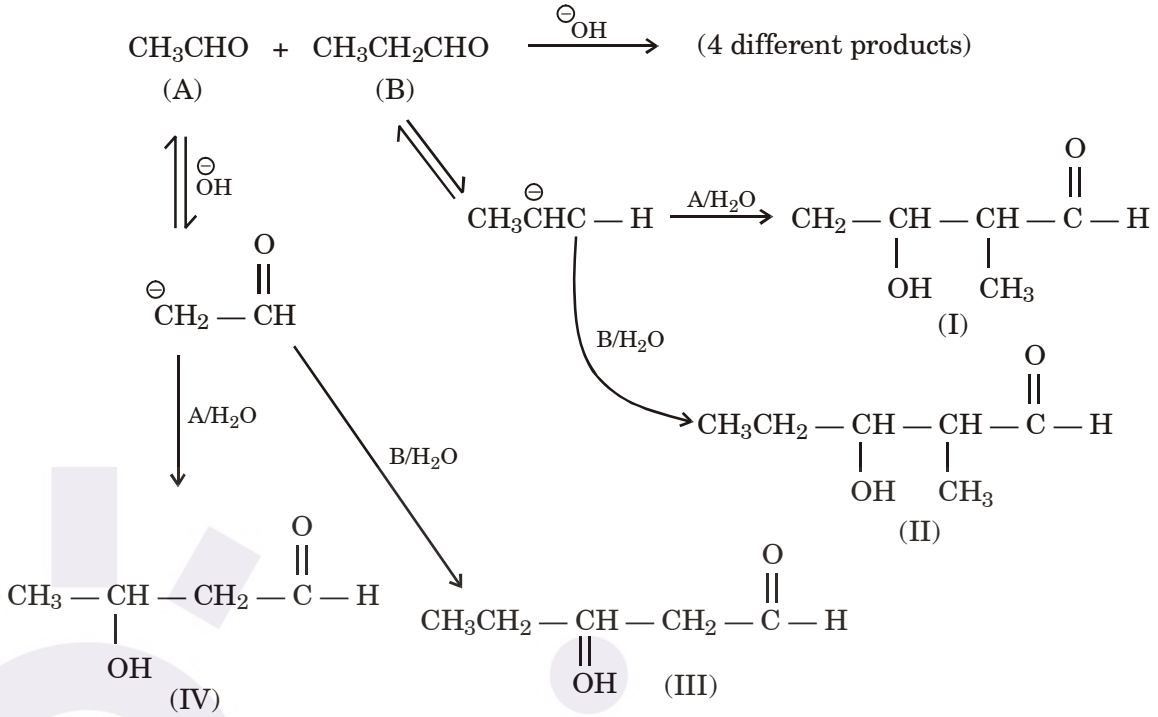


Mechanism :



CROSS ALDOL

When two different carbonyl compounds are used, it is called cross-aldol condensation.



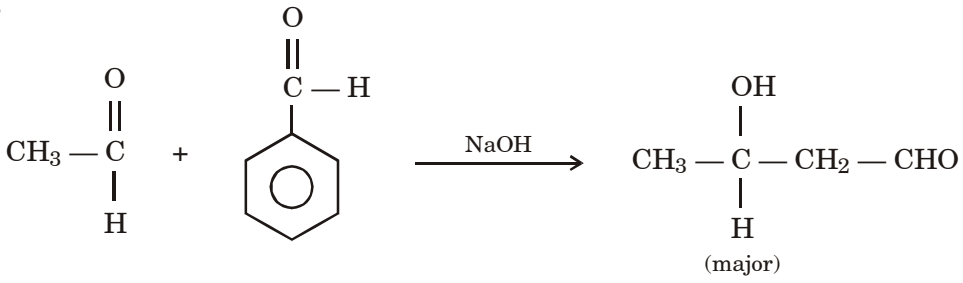
All the four products are β-hydroxy carbonyl compounds.

When one of the carbonyl compound does not have any α-hydrogen, it cannot form carbanion and number of possible products reduces to two.

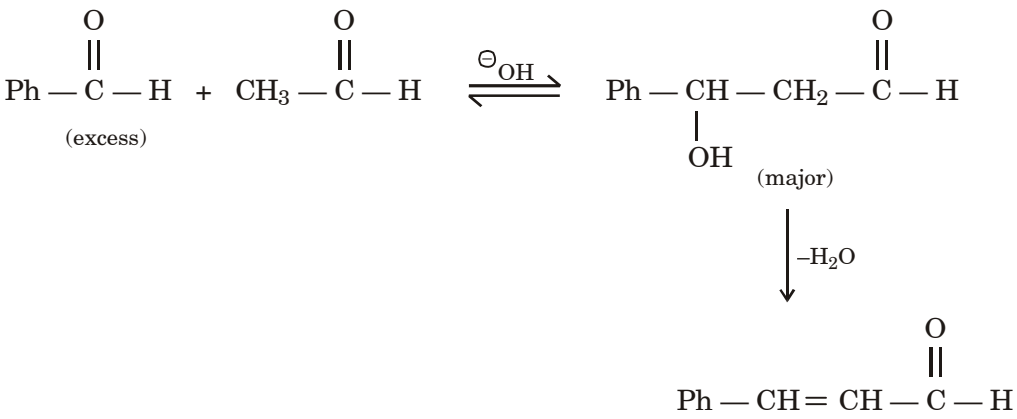
Note : Cannizzaro products $\xleftarrow[\text{O}]{\text{Conc. } {}^{-}\text{OH}}$ HCHO or $C_6H_5CHO \xrightarrow{\text{dil. } OH^-}$ no reaction

In the case of $CH_3CHO + CH_3CH_2CHO$, since $\overset{\ominus}{C}H_2CHO$ is more stable than $CH_3\overset{\ominus}{C}HCHO$, hence major product will be of $\overset{\ominus}{C}H_2CHO$

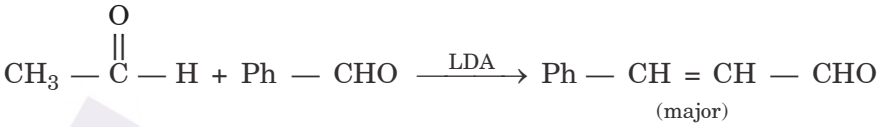
similarly,



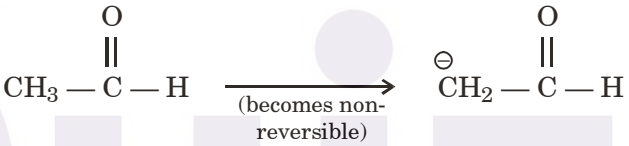
But if $Ph - \overset{O}{\overset{\|}{C}}H$ is in excess then,



another way to obtain a single aldol product is to convert one carbonyl compound completely into carbanion using a strong base like LDA (Lithium diisopropyl amide). Thus, this carbanion attacks the other carbonyl compound.

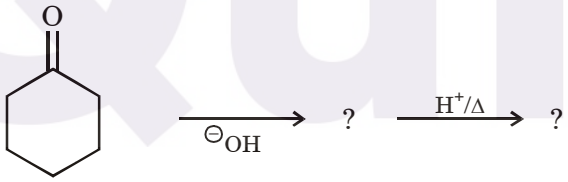


because here all the substrate is converted into carbanions.

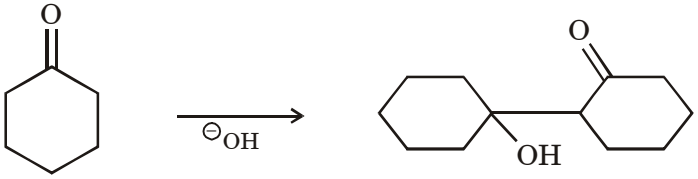


Illustration

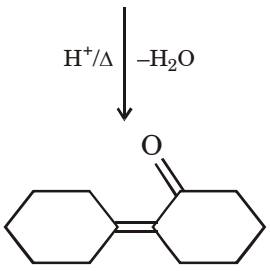
(1)



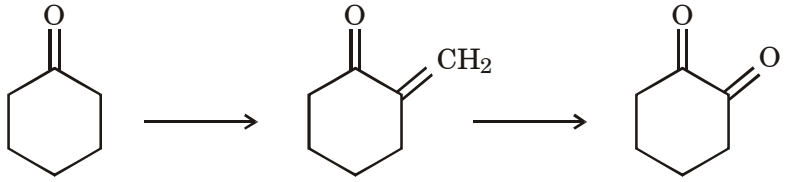
Solution :



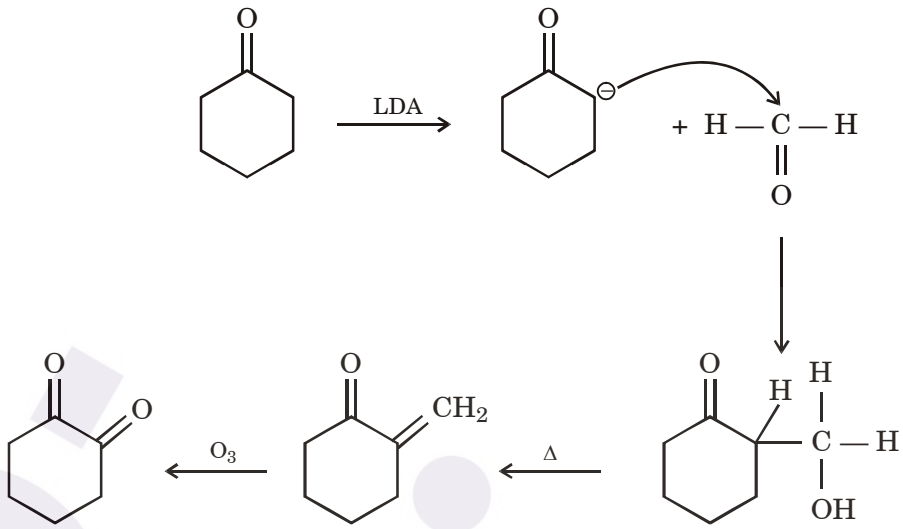
{since α-hydrogen is present, hence aldol condensation occurs}



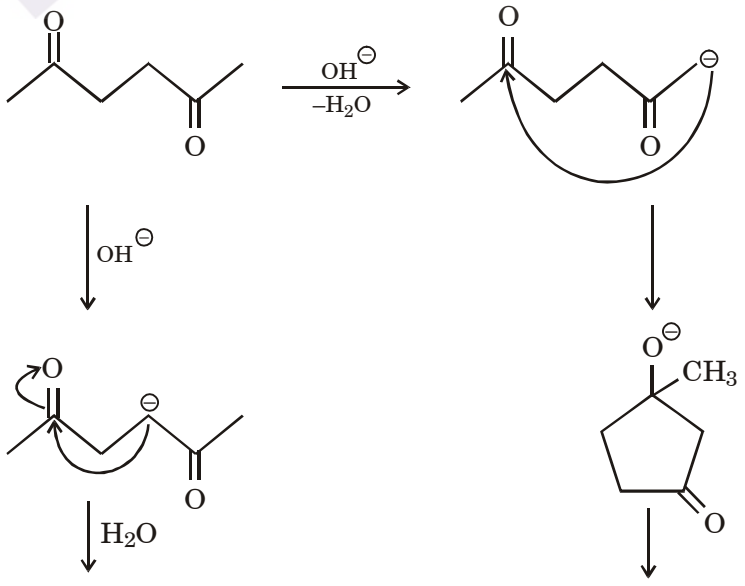
(2) Convert

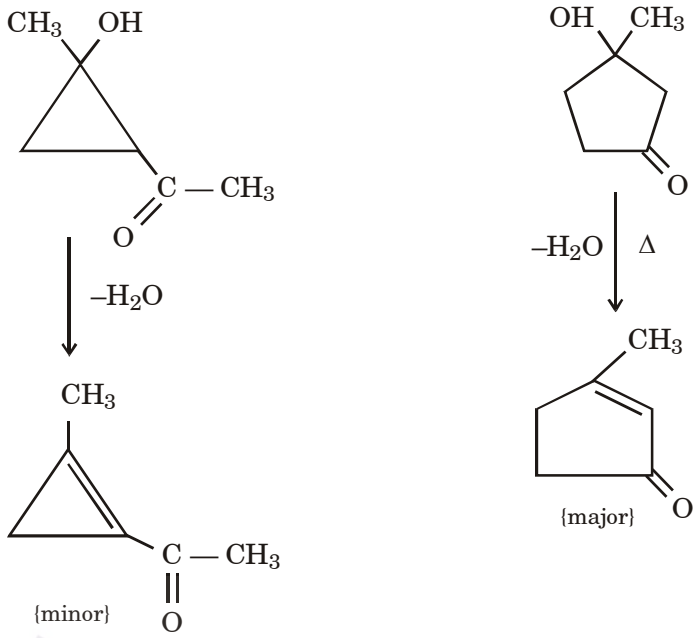


Solution :



Intramolecular aldol condensation : When a compound has two carbonyl groups, it can undergo intramolecular aldol condensation in presence of dilute base (if α–H atoms are present in the compound). An intramolecular reaction is readily favoured if the reaction leads to the formation of a 5 or 6-membered ring.

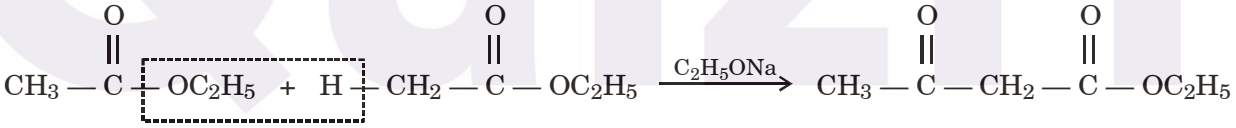




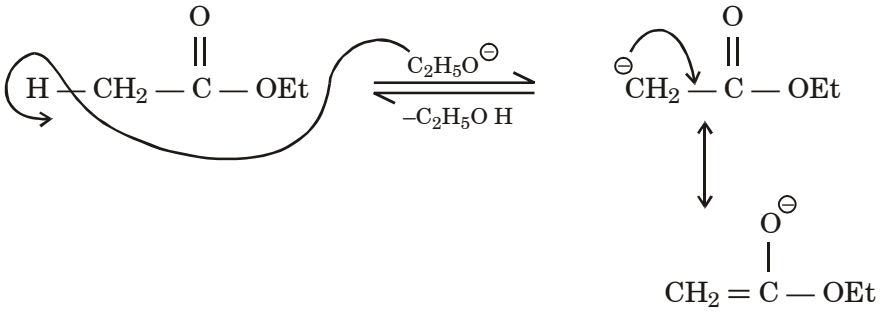
{Hence, in intra-molecular aldolization, the major product is decided according to the stability of ring formed}

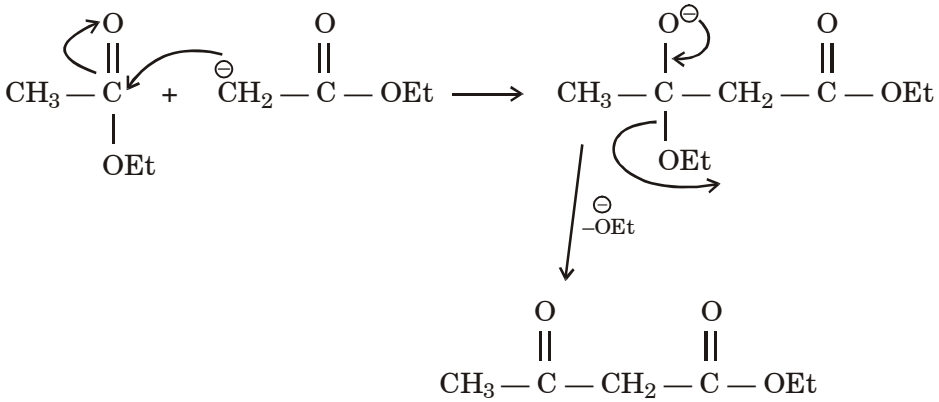
(2) Claisen Condensation

2 moles of ester containing atleast 2 α-hydrogen $\xrightarrow{C_2H_5ONa}$ β– keto ester

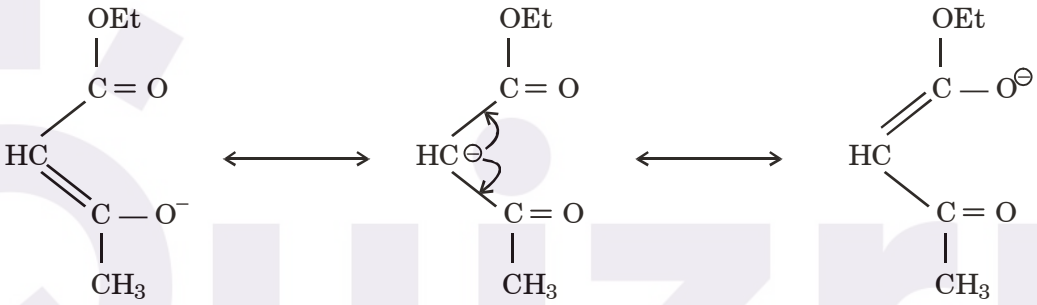


Mechanism :



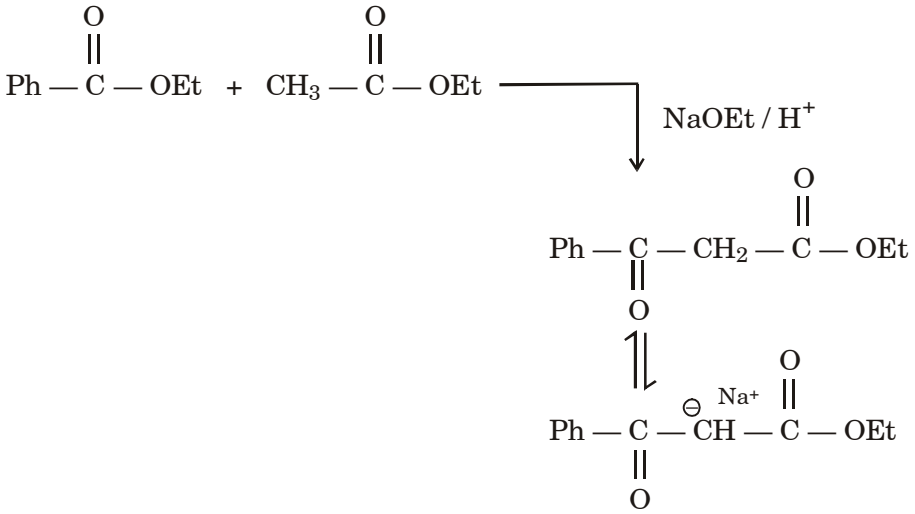


Although it is expected to be β-ketoester as formed above, but the final product is the sodium salt of β-ketoester. This is because acetoacetic ester (having α-hydrogen between two carbonyl groups) is much stronger acid than ethyl alcohol. So, the ester reacts with ethoxide ion to form ethyl alcohol and the anion of sodium ester. The salt is stabilized by resonance.



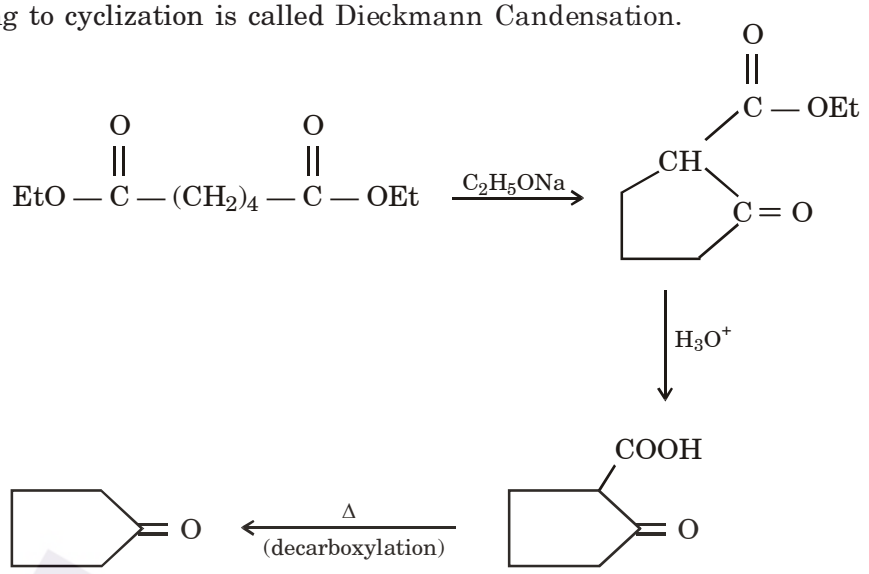
Mixed Claisen Condensation :

Just like mixed aldol, a mixed claisen condensation also takes place when two different ester are present. Here also, only one product will be formed when one of the ester has no α-hydrogen and is taken in excess while the other ester is added slowly to the reaction mixture.



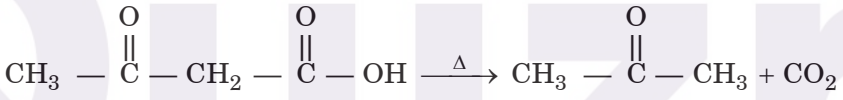
(3) Dieckmann Condensation :

Intramolecular Claisen condensation of esters with α-hydrogen atoms in the presence of sodium ethoxide leading to cyclization is called Dieckmann Candensation.

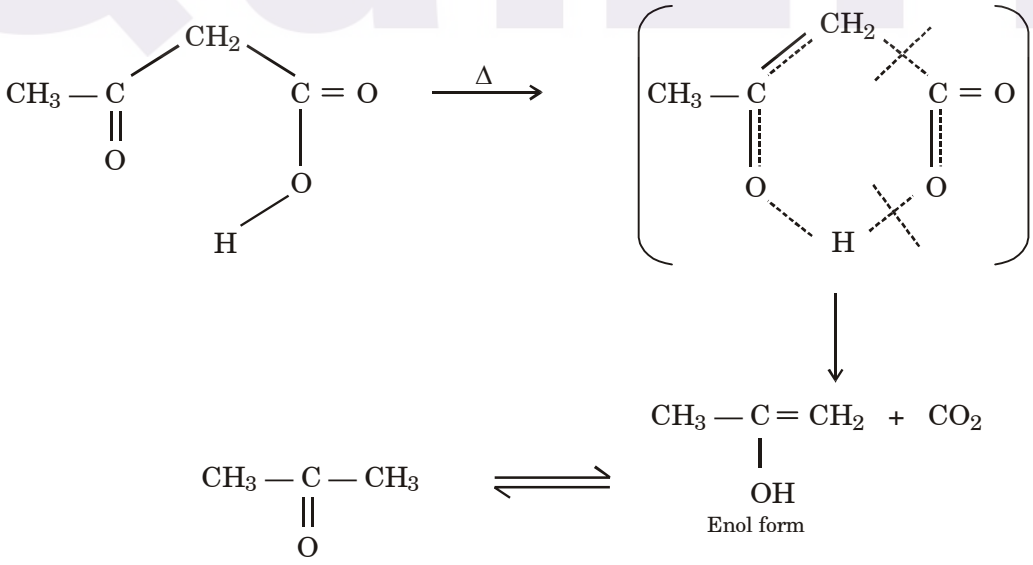


(4) Decarboxylation of β-keto Carboxylic acid

β-keto acids on slightest warming alone or in presence of base undergoes ready removal of CO_2.



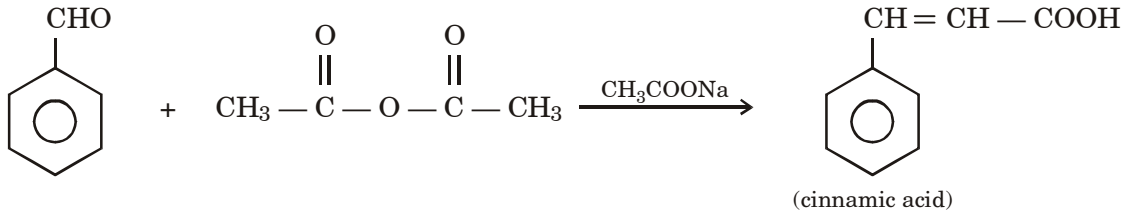
Mechanism :



(5) Perkin Condensation :

aromatic aldehydes + alkanoic anhydride $\xrightarrow{\text{alkonoate}}$ α,β unsaturated Carboxylic acid

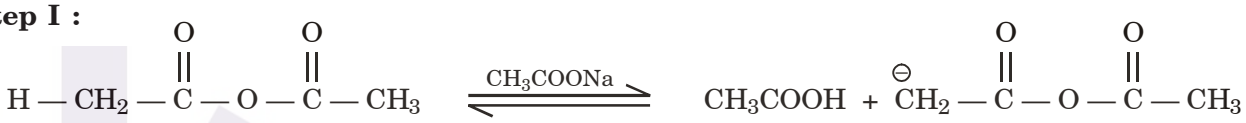
This is also similar to aldol condensation.



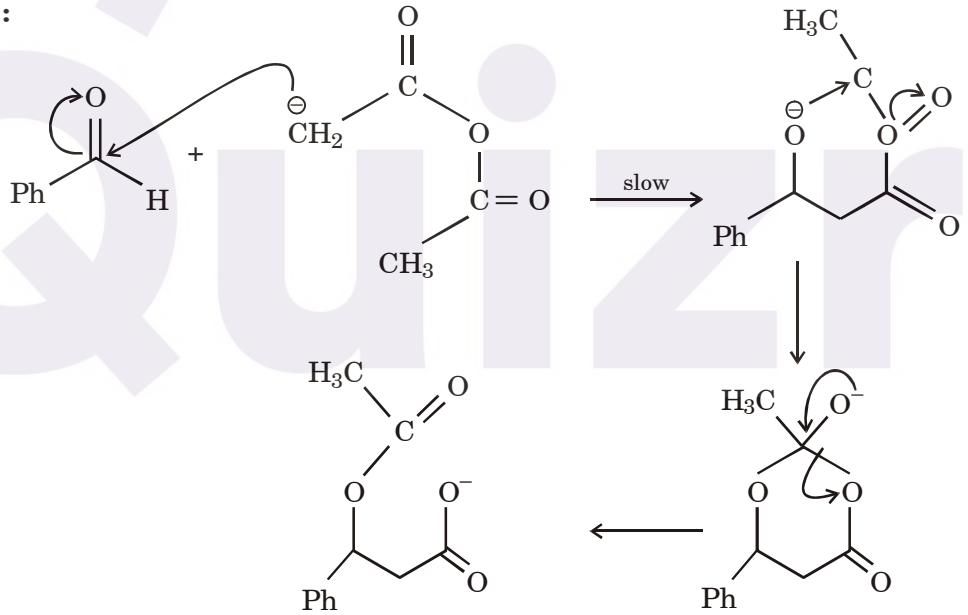
(cinnamic acid)

Mechanism :

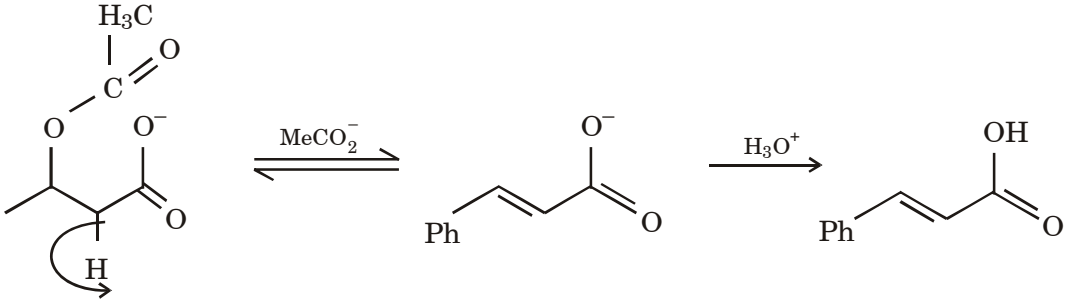
Step I :



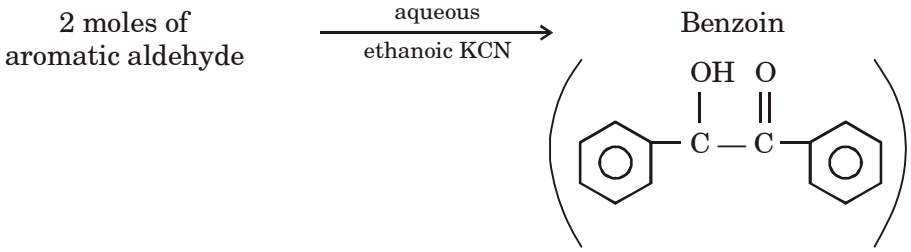
Step II :



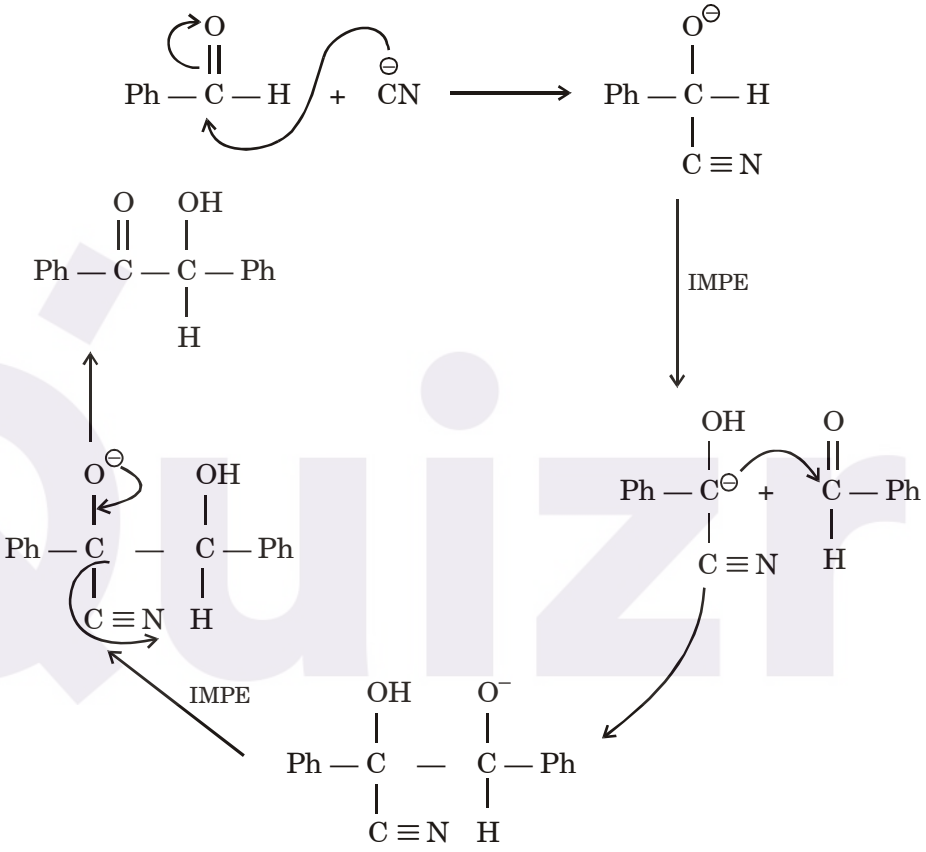
Step III :

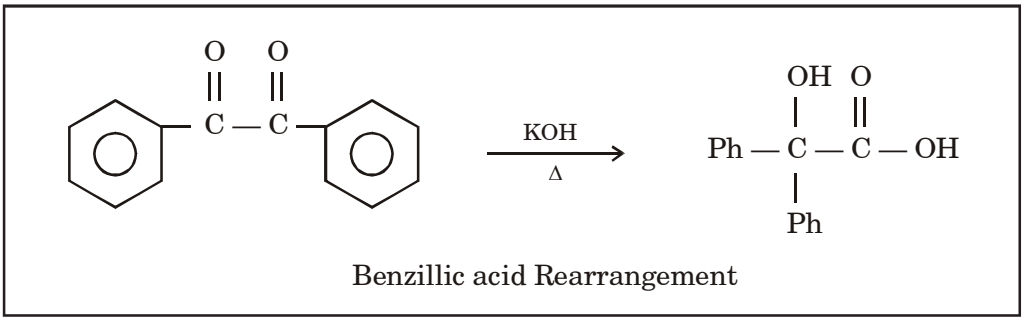


(6) Benzoin Condensation

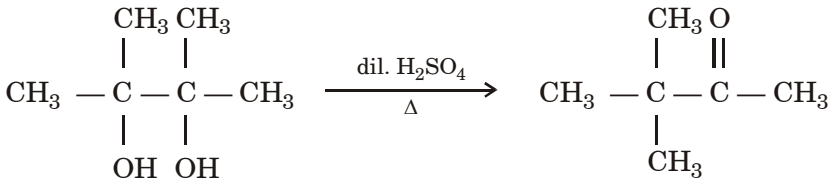


Mechanism :



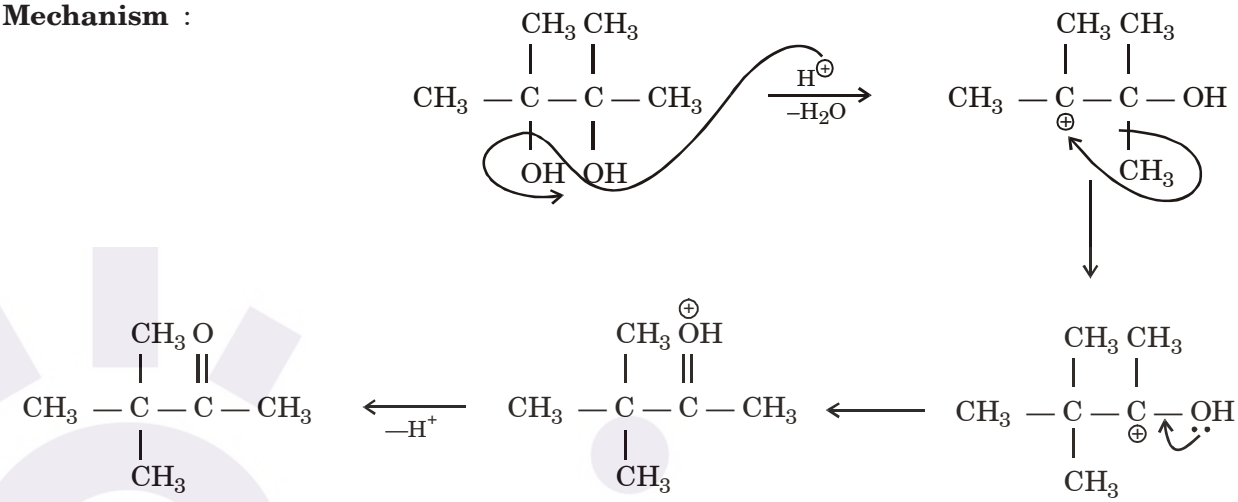


IX. PINACOL – PINACOLONE REARRANGEMENT



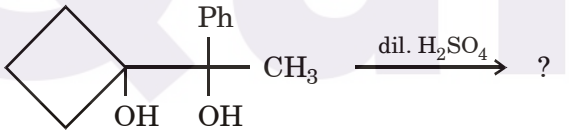
(pinacol) (pinacolone)

Mechanism :

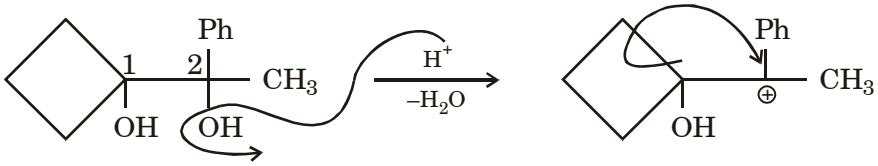


Here, migration of group will take place according to the migration aptitude.

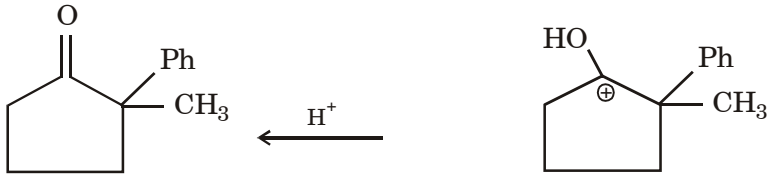
Illustration



Solution :



{Here H^+ will abstract the $\ddot{O}H$, which gives more stable carbocation}



{5-mem ring}

X. Tischenko Reaction :

This reaction is only given by aldehydes, where 2 molecules of aldehydes undergo condensation type reaction to give an ester when treated with aluminium ethoxide or iso propoxide.

$$RCHO \xrightarrow{(C_2H_5O)_3Al} R-\overset{\overset{O}{\|}}{C}-O-CH_2R$$

$$2C_6H_5CHO \xrightarrow{(C_2H_5O)_3Al} C_6H_5-\overset{\overset{O}{\|}}{C}-O-CH_2C_6H_5$$

benzyl benzoate

XI. Halogenation

(a) $CH_3CHO + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$

$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3 + 3Cl_2 \longrightarrow Cl_3C-\overset{\overset{O}{\|}}{C}-CH_3 + 3HCl$$

(b) ketones can be halogenated in presence of dilute solution of bases or an acid catalyst.

$$CH_3COCH_3 + Br \xrightarrow[\text{acid}]{\text{base or}} CH_3COCH_2Br + HBr$$

Mechanism :

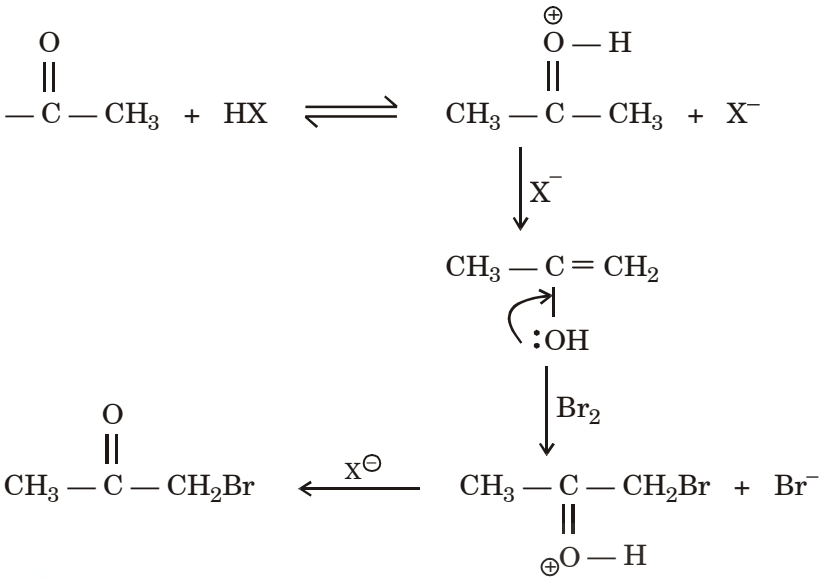
(1) In presence of base

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + B^- \underset{}{\overset{\text{RDS}}{\rightleftharpoons}} \overset{\ominus}{C}H_2-\overset{\overset{O}{\|}}{C}-CH_3 + B-H$$

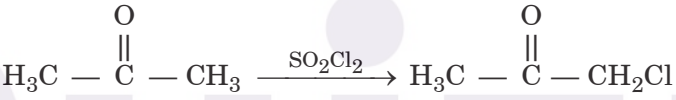
$$\overset{\text{fast}}{\downarrow} Br_2$$

$$CH_2-\overset{\overset{O}{\|}}{C}-CH_2Br + Br^{\ominus}$$

(2) In presence of acid



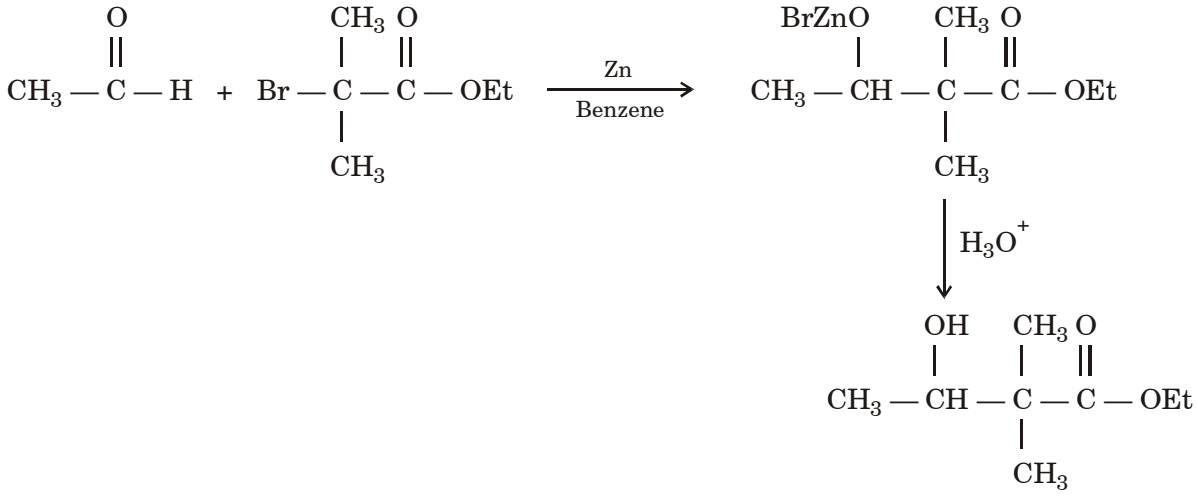
Note : The above substitution can also be carried out using SO_2Cl_2

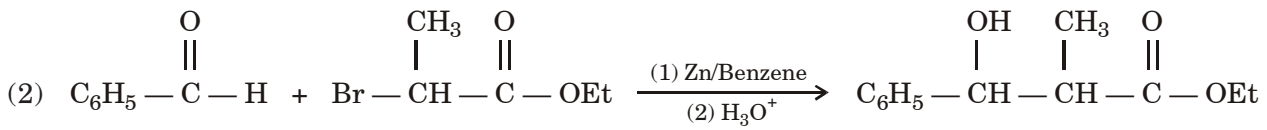


XII. Reformatsky Reaction

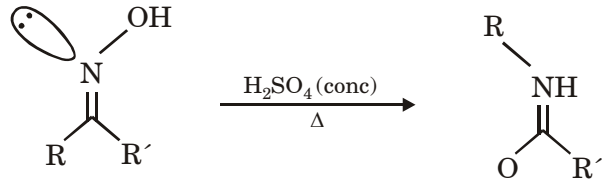
It is an addition reaction in which an organozinc reagent is used, instead of Grignard reagent, to attack the carbonyl group of an aldehyde or ketone. Because the organozinc reagent is less reactive than a grignard reagent, a second nucleophilic addition to the ester group does not occur. The organozinc reagent is prepared by treating an α-bromoester with zinc.

(1)



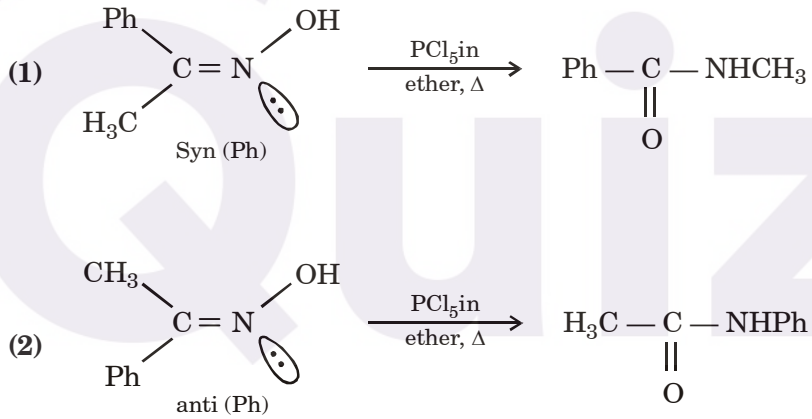


XIII. Beckmann Rearrangement

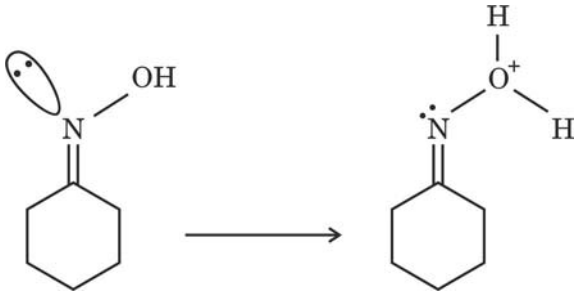


An acid-induced rearrangement of oximes to give amides. When oximes are treated with acidic catalyst like H^+, PCl_5, $SOCl_2$, SO_3, P_2O_5 etc., they are transformed into substituted amides. This reaction is related to the Hofmann and Schmidt Reactions and the Curtius Rearrangement, in that an electropositive nitrogen is formed that initiates an alkyl migration.

Example

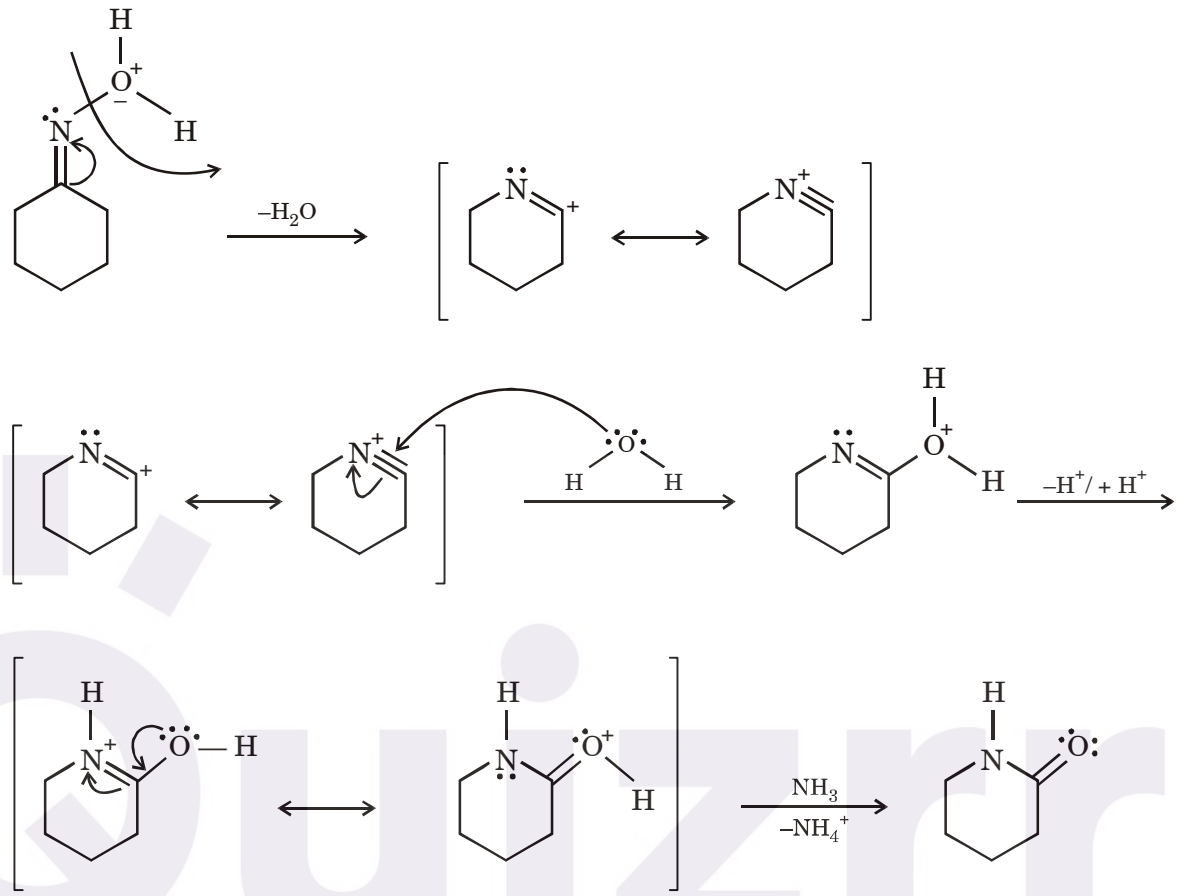


Mechanism :



Oximes generally have a high barrier to inversion, and accordingly this reaction is envisioned to proceed by protonation of the oxime hydroxyl, followed by migration of the alkyl substituent

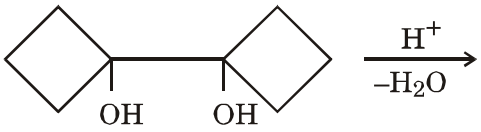
"trans" to nitrogen. The N–O bond is simultaneously cleaved with the expulsion of water, so that formation of a free nitrene is avoided.



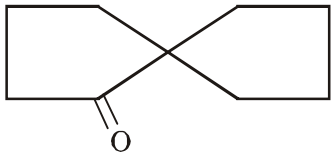
The migrating group is always anti to — OH.

SOLVED EXAMPLES

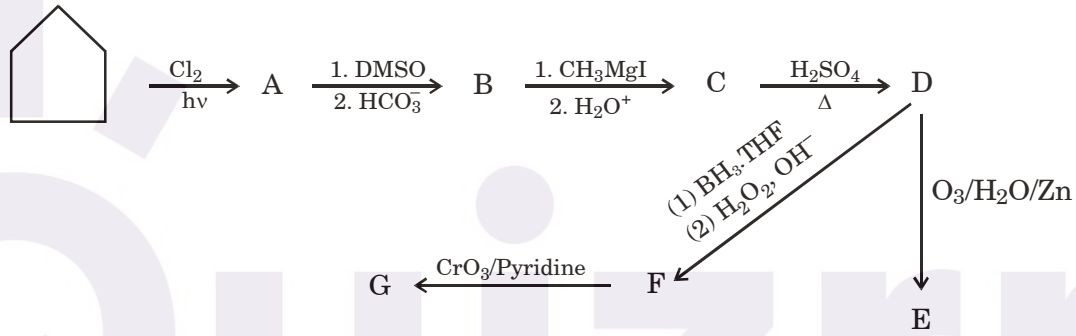
Example 1



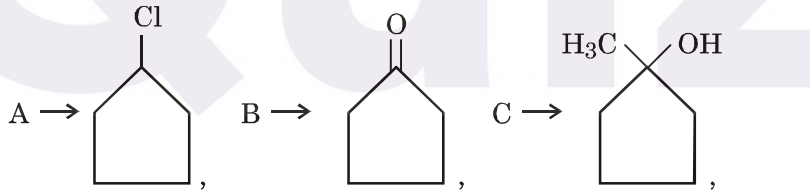
Solution :

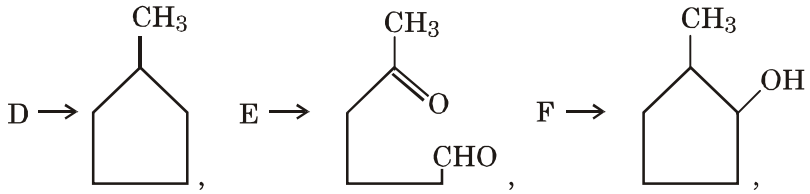


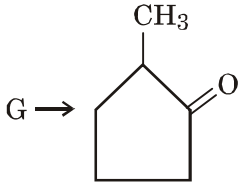
Example 2



Solution :

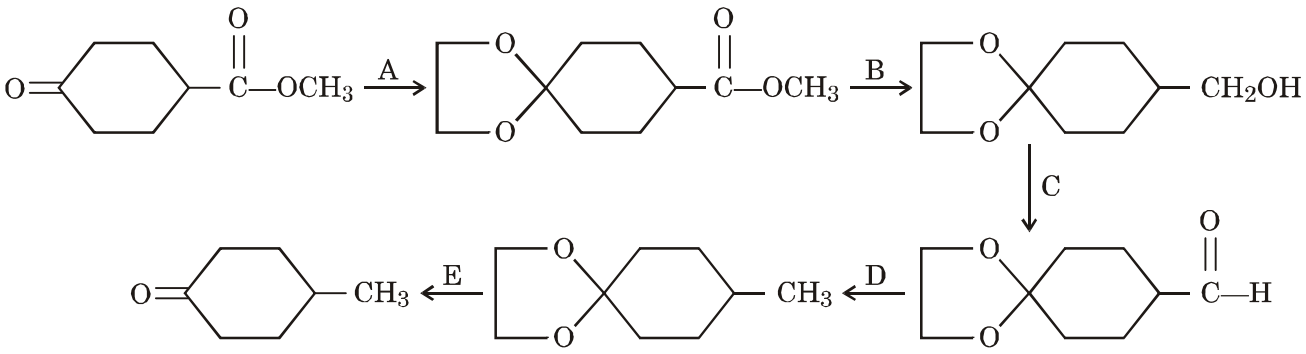






Example 3

Suggest reagent required at each step :



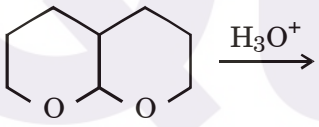
Solution :

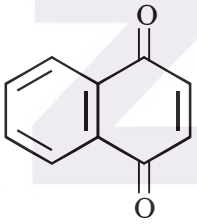
(A) $\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$ to protect keto grp from being reduced in step (B).

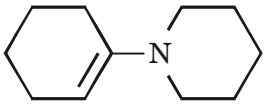
(b) $LiAlH_4$/ether, H_3O^+, (C) PCC, (D) NH_2NH_2/glycol – KOH, (wolf – Kisher), (E) H_3O^+

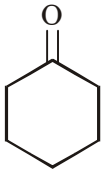
Example 4

What are the final products of the following reactions :

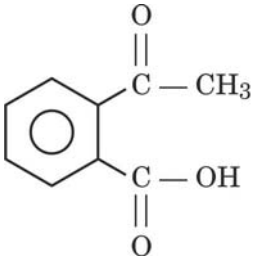
(a)  $\xrightarrow{H_3O^+}$

(b)  $+ CH_3CH_2SH \longrightarrow$

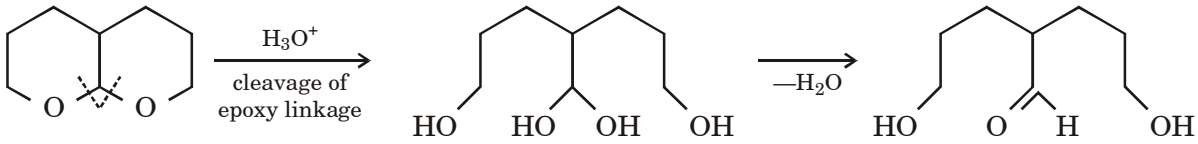
(c)  $\xrightarrow{H_3O^+}$

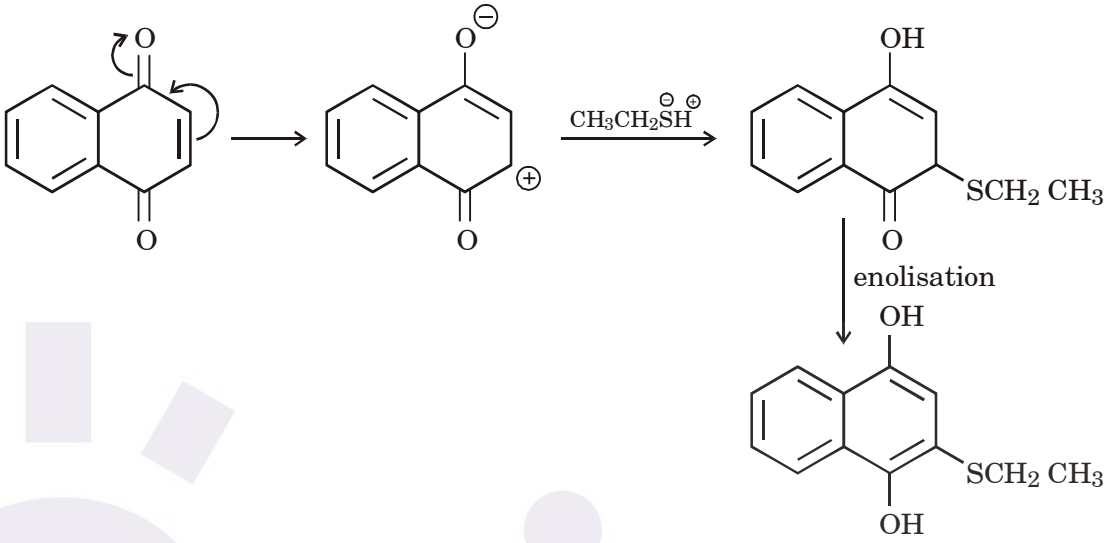
(d)  $+ CH_2N_2 \longrightarrow$

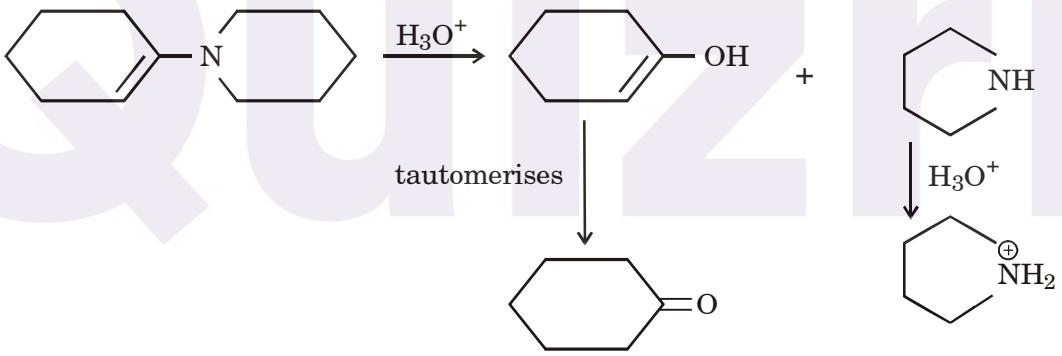
(e) $CH_3 - \overset{O}{\overset{\|}{C}} - CH_2 - CH_2 - \overset{O}{\overset{\|}{C}} - OCH_2CH_3 \xrightarrow[(2)\ H_3O^+]{(1)\ CH_3MgBr}$

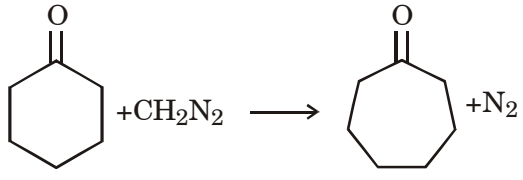
(f)  $\xrightarrow[CH_3OH]{H^+}$

Solution :

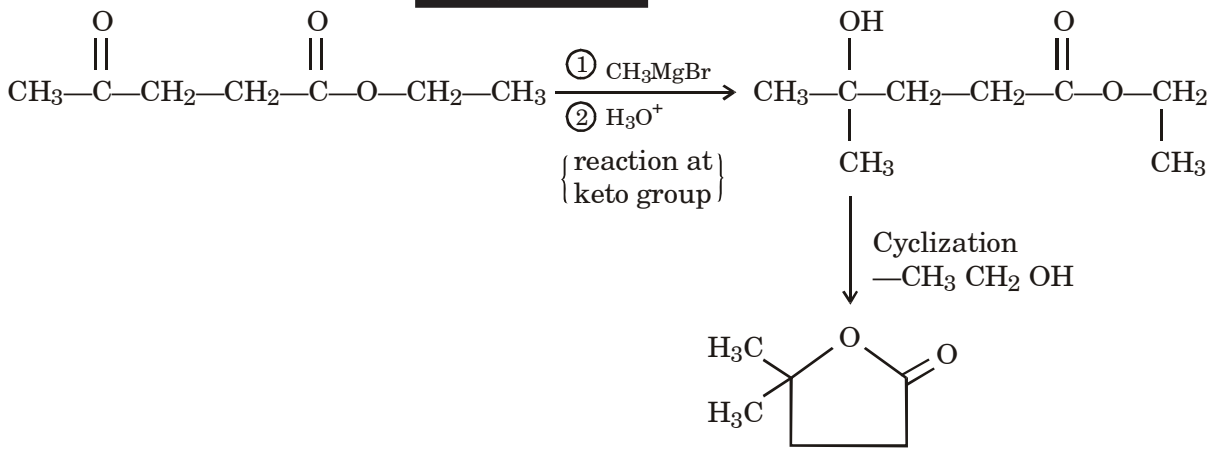
(a) 

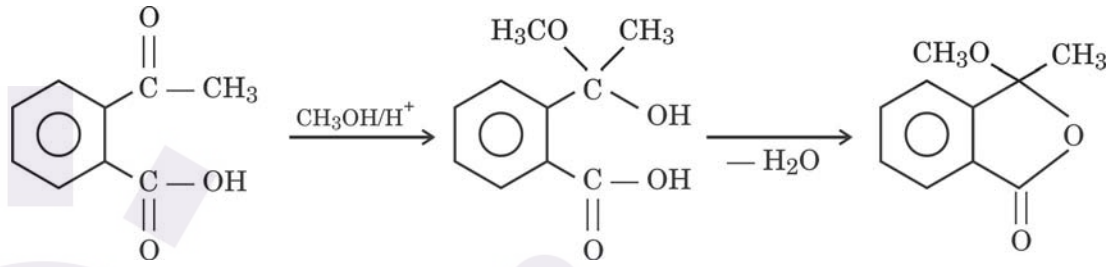
(b) 

(c) 

(d) 

cycloheptanone

(e) 

(f) 

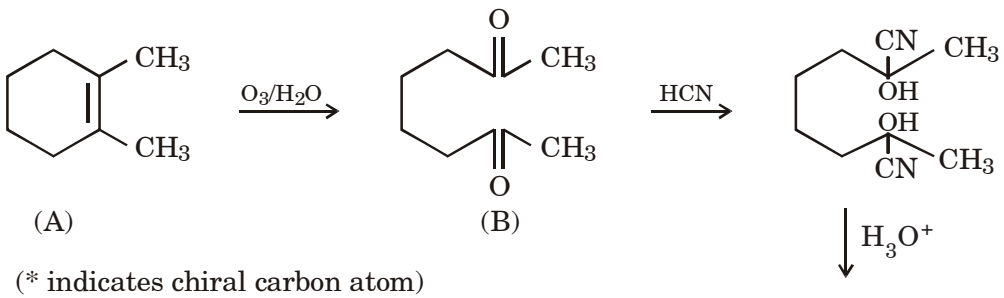
Example 5

A (C_8H_{14}) by ozonolysis forms B ($C_8H_{14}O_2$). B on reaction with HCN followed by acidic hydrolysis forms a dibasic acid (C) with two chiral carbon atoms. HI reduces [C] to another optically active dibasic acid (D). Identity A, B, C and D and explain reactions if [A] has one six-membered rings.

Solution :

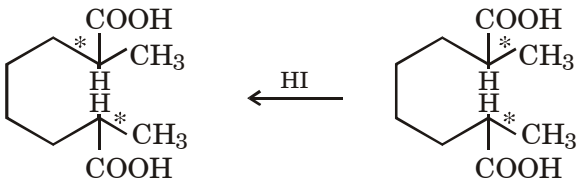
Degree of unsaturation in A (C_8H_{14}) = $\frac{16 - 14 + 2}{2} = 2$

Ozonolysis product B($C_8H_{14}O_2$) has also eight carbon atoms that indicates A is cyclic compound (one saturation) with a double bond in it (another saturation). Thus, A is symmetrical cyclohexene (given six membered ring).



(A) (B)

(* indicates chiral carbon atom)



(C)

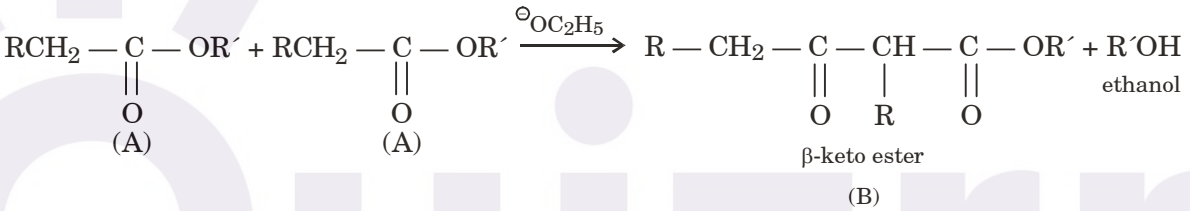
Example 6

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

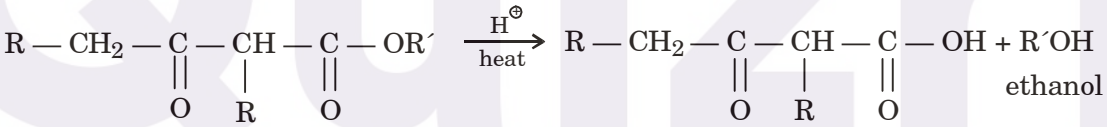
Solution :

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

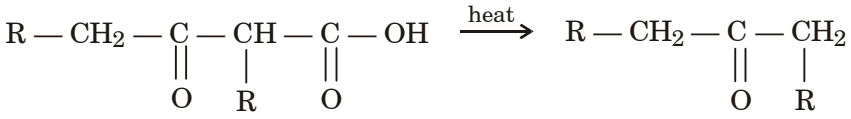
Let the given reactions may be depicted as shown in the following.



(A) (A) β-keto ester (B)



β-keto ester (C)



From these reactions, it is obvious that

$R' \equiv -CH_2CH_3$

$R \equiv -CH_3$

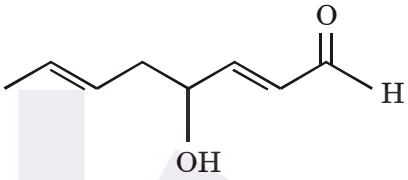
Hence, the compounds A, B and C are

A: $CH_3CH_2\overset{\overset{O}{\|}}{C}-OCH_2CH_3$ B: $CH_3CH_2\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OC_2H_5$ C: $CH_3CH_2\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-COOH$

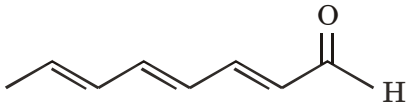
Example 7

$$CH_3-CH=CH-\overset{\overset{H}{|}}{C}=O \text{ (excess)} \xrightarrow[\Delta]{\text{LDA}}$$

(a)

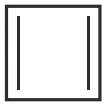


(b)



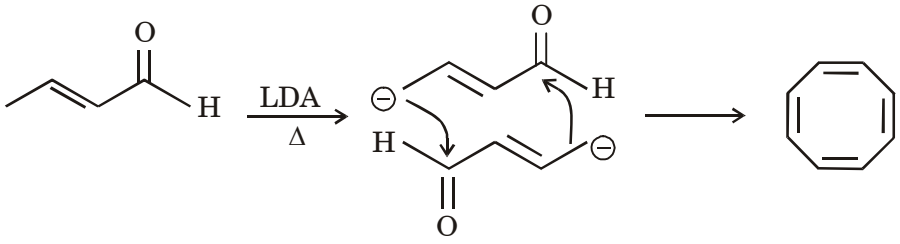
(c)

(d)

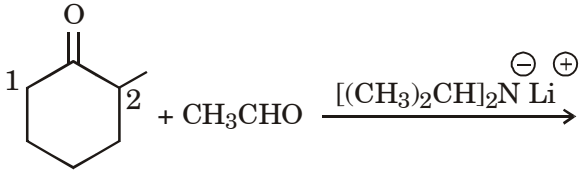


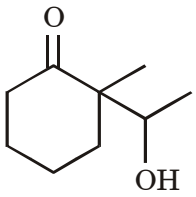
Solution :

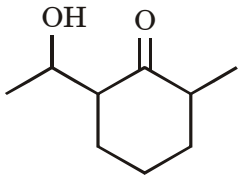
In the absence of α–H on saturated carbon, γ–H becomes acidic. This acidic γ–H would be abstracted by LDA to give carbanion, which condense with another molecule to give cyclooctatetraene. The high temperature reaction condition helps in the dehydration of aldol product.

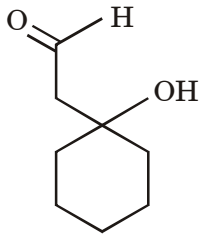


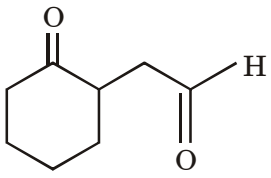
Example 8



(a) 

(b) 

(c) 

(d) 

Solution :

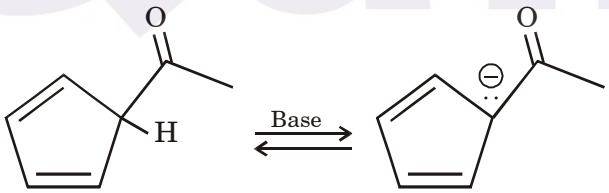
LDA is a sterically hindered and strong base. It will abstract H^+ from position (1) rather than position (2). Carbanion formed will attack on CH_3CHO to give intermolecular aldol reaction.

$\therefore$ (b)

Example 9

Which of the following ketones is more acidic ? Give a reason.

Solution :



This ketone is more acidic because the resulting enolate ion obeys Huckel's rule of aromaticity and is thus more stable.

Example 10

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

Solution :

We are given that

$$A \xrightarrow{\text{reduction}} B$$

$$B \xrightarrow{H_2SO_4} C$$

C forms mono-ozonide, D

$$D \xrightarrow{H_2O/Zn} CH_3CHO$$

The compound A gives a haloform reaction; it must contain CH_3CO group. The compound C contains a double bond as it forms mono-ozonide D. Since, the compound D on hydrolysis gives only CH_3CHO, the structure of C would be

$CH_3CH = CHCH_3$ 2-butene
(C)

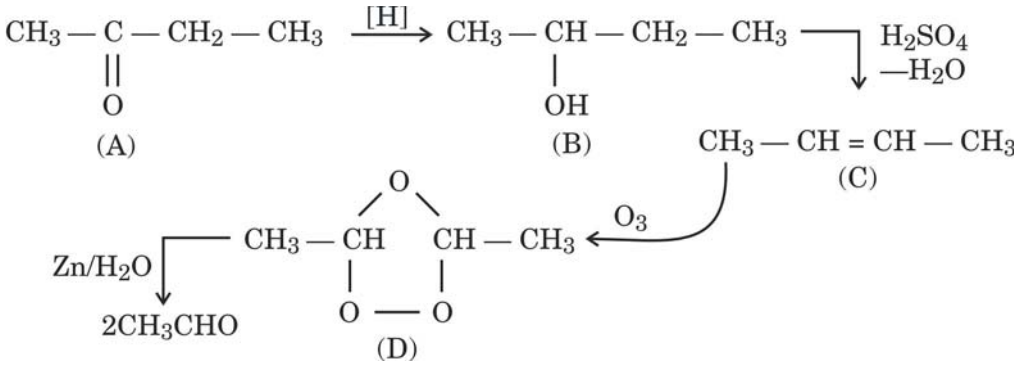
The compound C is obtained by dehydration of B, thus the latter should be

$CH_3 - CH(OH) - CH_2 - CH_3$ 2-butanol
(B)

Finally, B is obtained by the reduction of A. Hence, the compound A should be

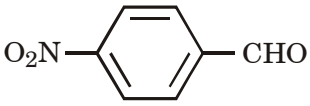
$CH_3 - C(=O) - CH_2 - CH_3$ 2-butanone
(A)

The equations involved are as follows :

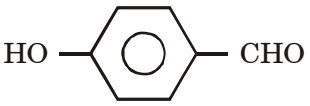


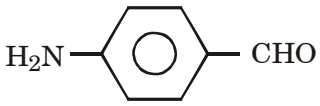
Example 11

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

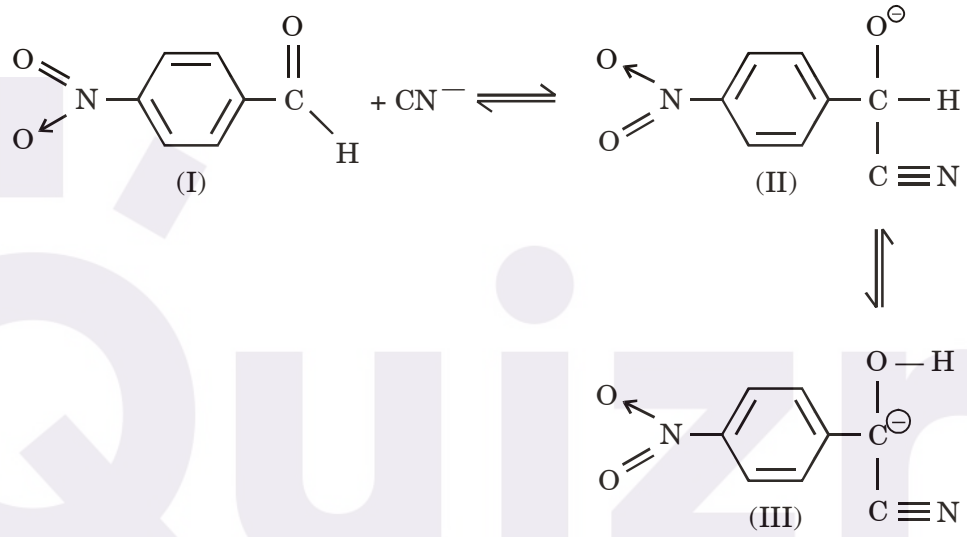
(a) 

(b) 

(c) 

(d) 

Solution :



Benzoin condensation is due to stability of intermediate (III) 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^-.

∴ (a)

Example 12

An ester (A) is condensed in the presence of sodium methoxide to give a β-keto ester (B) and Methanol. On mild hydrolysis with cold conc. HCl, (B) gives methanol and 3-oxo-acid (C). (C) underwent readily decarboxylation to give cyclopentanone.

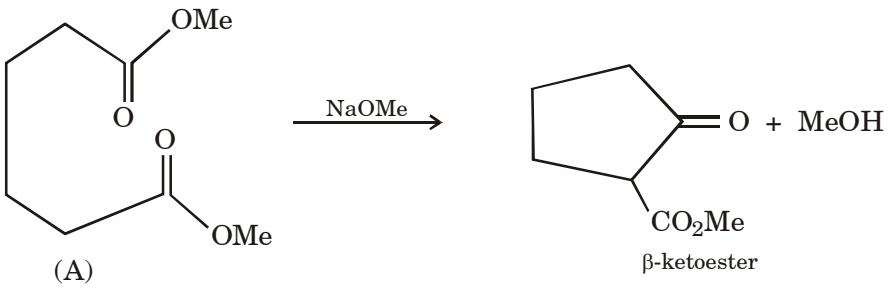
(a) Identify (A), (B) and (C)

(b) Name the reaction involved in conversion of (A) to (B)

(c) Give the mechanism of decarboxylation

Solution :

(a)



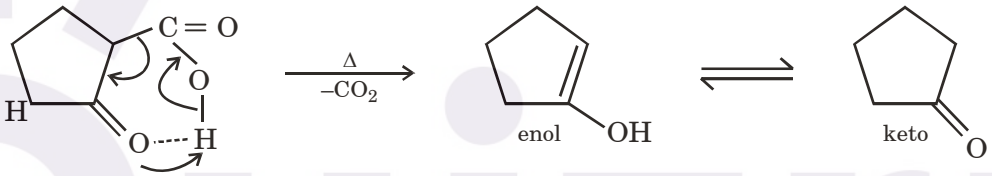
(A) β-ketoester (B)

(B) $\xrightarrow[\text{hydrolysis}]{\text{mild}}$ 3-oxo-acid or β-keto acid + MeOH

(C) $\xrightarrow[-CO_2]{\Delta}$ + CO_2

(b) Diekmann condensation (intramolecular Claisen ester condensation)

(c) Mechanism of decarboxylation



$\xrightarrow[-CO_2]{\Delta}$

Example 13

A organic compound (A), $C_{10}H_{16}O$, reacts with hydroxylamine to yield a compound of formula $C_{10}H_{17}ON$ (B), and with Tollen's reagent to give a silver mirror and a compound of formula $C_{10}H_{16}O_2$(C). Upon vigorous oxidation it gives acetone, oxalic acid and γ-ketovaleric acid ($CH_3COCH_2CH_2COOH$). What are (A), (B) and (C) ?

Explain these reactions.

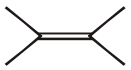
Solution :

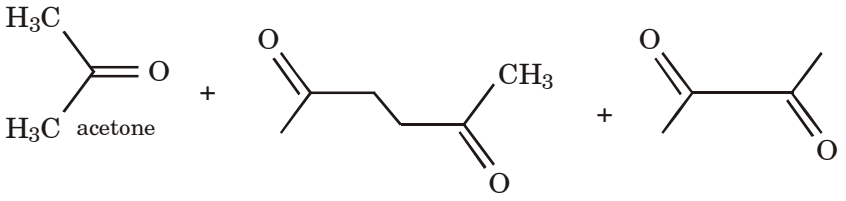
(i) (A) reacts with hydroxylamine to form (B), $C_{10}H_{17}ON$; hence it contains a carbonyl group.

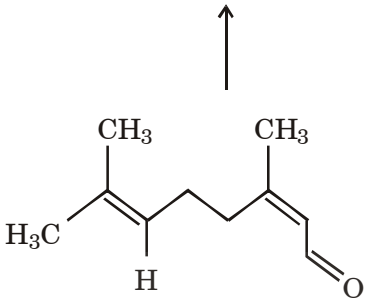
(ii) Since (A) reacts with Tollen's reagent to give (C), $C_{10}H_{16}O_2$, hence the $> C = O$ function is an aldehydic group i.e., (A), $C_9H_{15}CHO$

$$\underset{\text{(A)}}{C_9H_{15}CHO} + H_2NOH \xrightarrow{-H_2O} \underset{\text{(B)}}{C_9H_{15}CH = NOH}$$

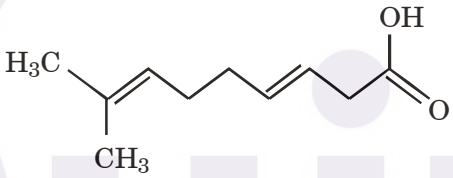
$$\underset{\text{(A)}}{C_9H_{15}CHO} \xrightarrow[-2Ag]{Ag_2O} \underset{\text{(C)}}{C_9H_{15}COOH}$$

(iii) Since (A) on oxidation gives three products hence it contains  double bonds.





(A)



(C)

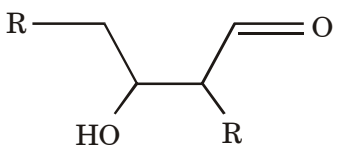
Example 14

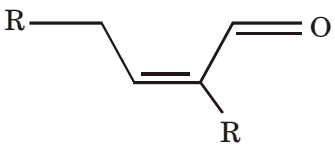
Write the products of the following reaction sequence :

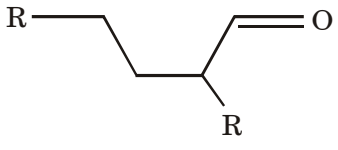
$$2RCH_2CHO \xrightarrow[H_2O]{OH^-} (A) \xrightarrow[-H_2O]{HA} (B) \xrightarrow[Pd,C]{H_2} (C)$$

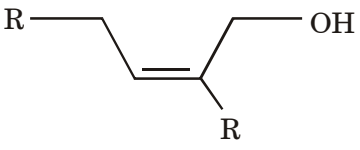
$$(B) \xrightarrow{LiAlH_4} D$$

Solution :

A = 

B = 

C = 

D = 

Example 15

Pure HCN fails to react with aldehydes and ketones. Explain.

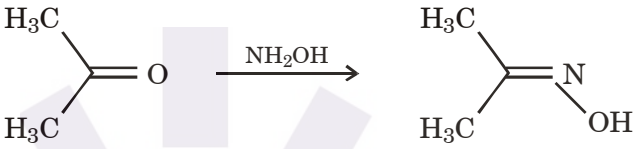
Solution :

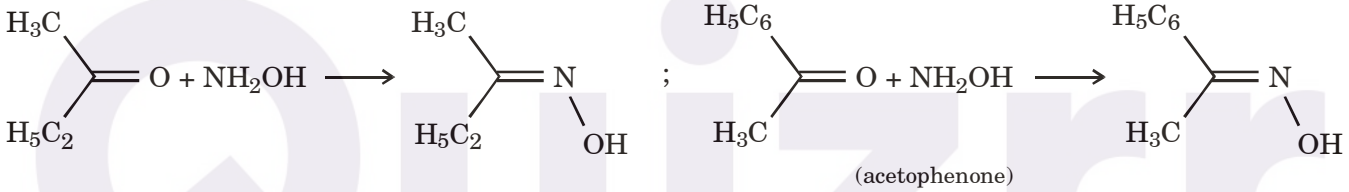
HCN is weak acid and have low degree of dissociation but in presence of a base (even H_2O), the dissociation increases appreciably to provide appreciable CN to attack > C = O bond.

Example 16

Acetone when treated with hydroxylamine forms only one oxime whereas ethyl methyl ketones (or acetophenone) forms two isomeric oximes under the same conditions. Give their structures.

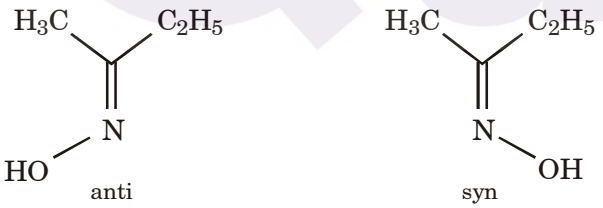
Solution :





(acetophenone)

Oximes of aldehydes and unsymmetrical ketones show geometrical isomerism i.e.



Whereas oximes of symmetrical ketones do not show geometrical isomerism.