CSIR-JRF (NET), GATE

DRDO, BARC, IISC…...

LONG COURSE For CSIR-NET (JRF)-June-2017

CHEMISTRY BY H. GAUR

ORGANIC CHEMISTRY

NAMED REACTIONS

SHEET-1

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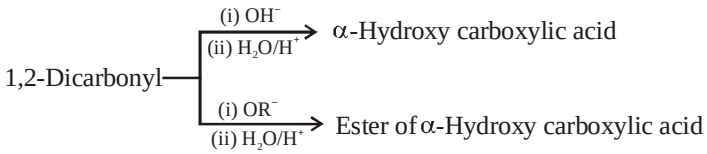
BENZIL-BENZILIC ACID REARRANGEMENT:

* Exist in 1,2-Dicarbonyls

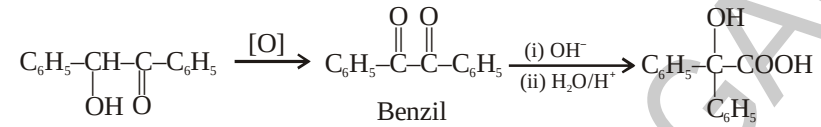
* Condition:



*** Driving force:** Formation of carboxylate ion

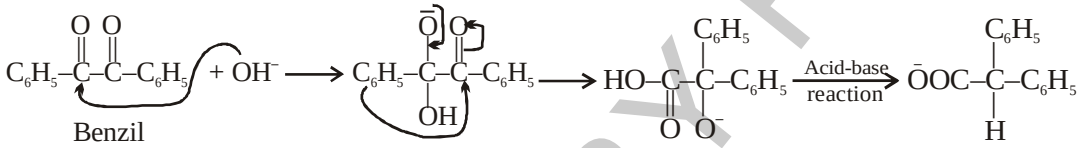
* **Attack of OH^- or OR^-:** On the more electron defficient carbonyl group (>=O)

* >=O group on this, attack of OH^- or OR^- occur convert into –COOH or –COOR group while another carbonyl, convert into alcoholic group (-OH).



Benzoin (α- Hydroxy Ketone) | Benzil (1,2-Diketone) | Benzil acid (α-Hydroxy carboxylic acid)

*** Mechanism:**



Benzil

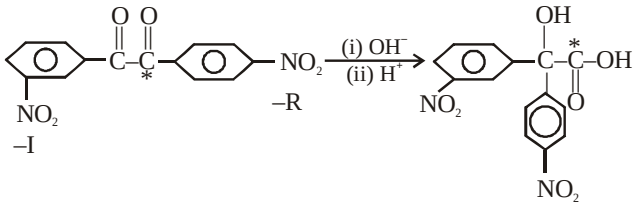
Carboxylate ion

Acidification H_2O/H^+

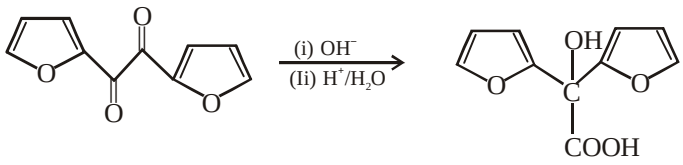
Benzilic acid

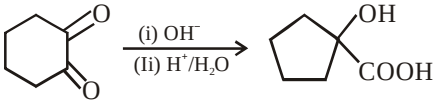
*** Examples:**

(1) $CH_3–\underset{*}{C}(=O)–\underset{*}{C}(=O)–H \xrightarrow[(ii)\ H^+]{(i)\ OH^-} CH_3–\underset{OH}{\underset{|}{CH}}–\underset{O}{\underset{||}{\overset{*}{C}}}–OH$

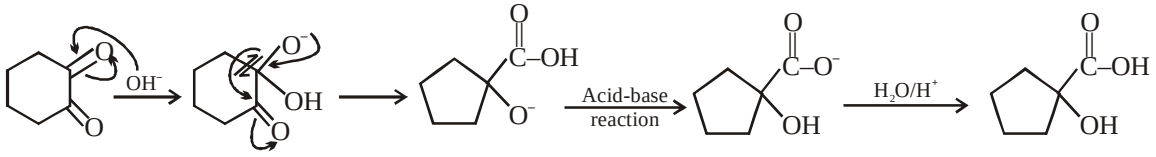
(2) 

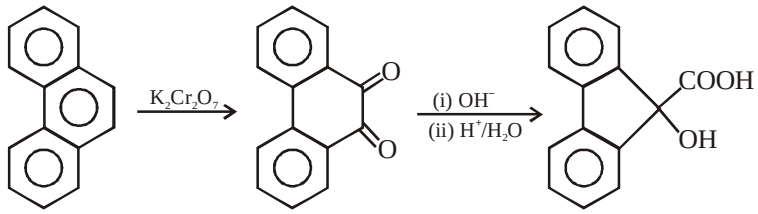
(3) $CH_3–\underset{O}{\underset{||}{C}}–\underset{O}{\underset{||}{C}}–CH_3 \xrightarrow[(ii)\ H^+/H_2O]{(i)\ OH^-} CH_3–\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}–COOH$

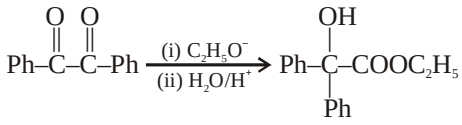
(4) 

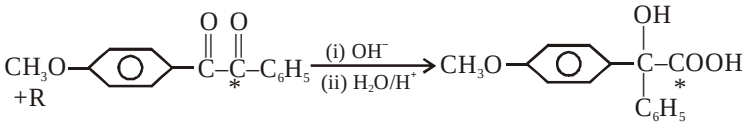
(5) 

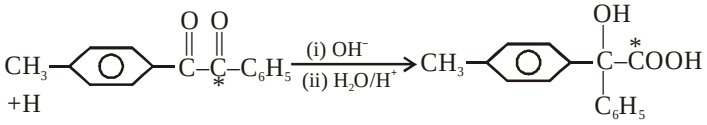
This reaction takes place through the following mechanism.

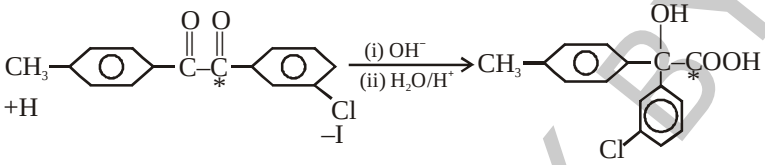


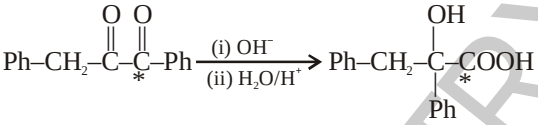
(6) 

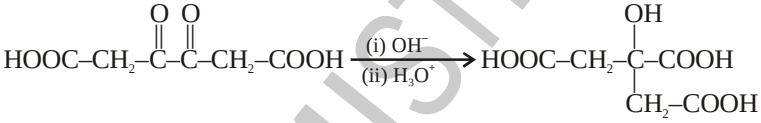
(7) 

(8) 

(9) 

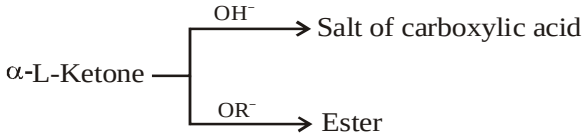
(10) 

(11) 

(12) 

SEMIBENZIL-BENZILIC ACID REARRANGEMENT:

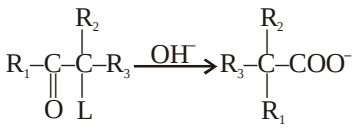
* Exist in $\alpha - L -$ Ketone
* Condition:



*** Driving force:** Formation of carboxlate ion.

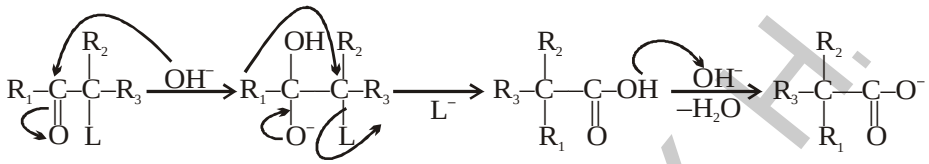
* Attack of OH^- or OR^- $\Rightarrow$ Always on the >=O group

* >=O group convert into $-COO^-$ or –COOR group



α-L-Ketone Carboxylate ion (As a salt of carboxylic acid)

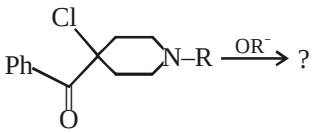
***Mechanism:**



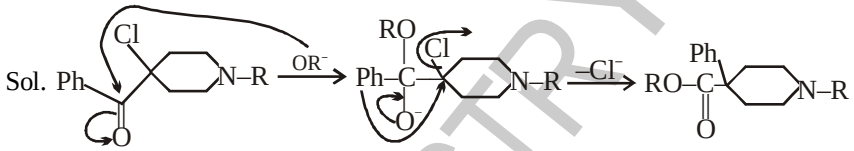
α-L-Ketone

Questions:

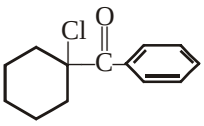
Q.1



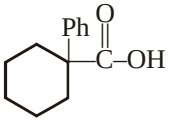
Sol.



Q.2



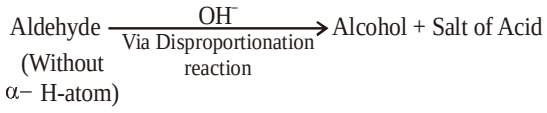
Ans.



CANNIZARO REACTION:

* Exist in aldehydes which does not have α – H-atoms (Aromatic or Aliphatic)

*** Condition:**

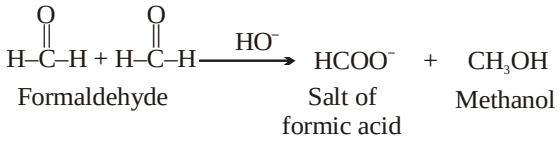


(Without α – H- atom)

***** Disproportionation reaction takes place (one molecule is reduced while another is oxidised)

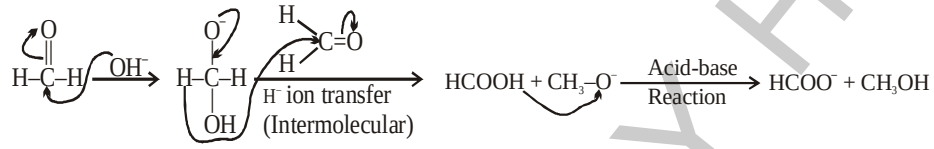
***** Hydride ion (H^-) transfer occur

***** Aldehyde molecule, on this attack of OH^- occur convert into salt of acid while another aldehyde molecule convert into alcohol



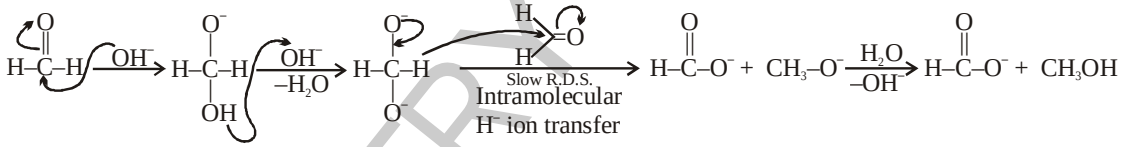
*** Mechanism:**

(A) At Low concentration of base:



Rate $\alpha\ [HCHO]^2[OH^-] \Rightarrow$ Third order kinetics

*** At high Concentration of Base:**

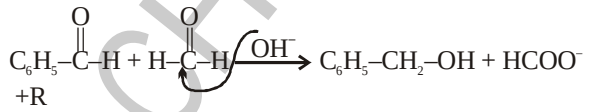


Rate $\alpha\ [OH^-]^2[HCHO]^2$: Forth order kinetics

* When in cannizaro reaction involve in two different types aldehyde molecules (without $\alpha - H$) called c**ross cannizaro reation**.

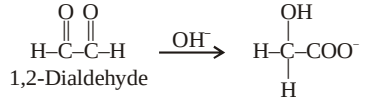
* When both aldehyde present within same molecule then cannizaro reaction is called **internal cannizaro reaction** or **intramolecular cannizaro reaction**. (If both aldehydic group within molecule are different then this reaction also called **internal cross cannizaro** or **intramolecular cross cannizaro reaction)**

*** Cross Cannizaro Reaction:**



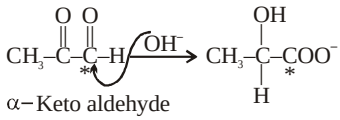
(OH^- attack on the more electron defficient carbonyl)

*** Internal cannizaro reaction:**



Mechanism operate as a benzil-benzilic acid rearrangement.

*** Internal Cross Cannizaro Reaction:**

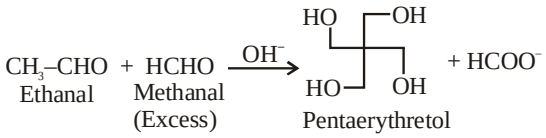


α−Keto aldehyde

(OH^- attack on the more electron defficient carbonyl)

* Mechanism operate as a benzil-benzilic acid rearrangement.

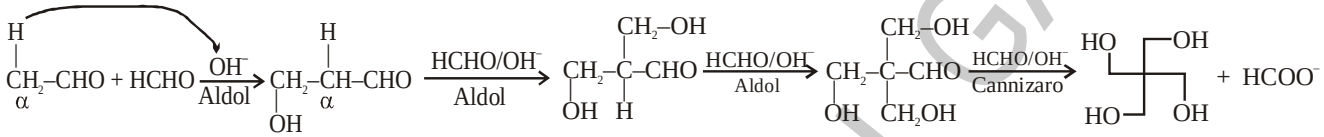
*** Aldol As Well As Cannizaro Reaction:**



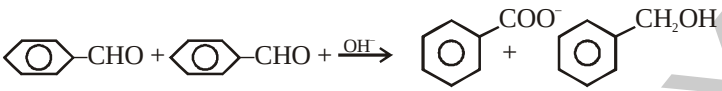
Ethanal Methanal (Excess) Pentaerythretol

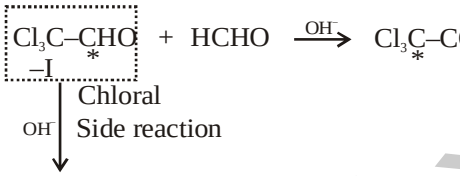
Via three time aldol & one time cannizaro

*** Mechanism:** Always first aldol after then cannizaro.

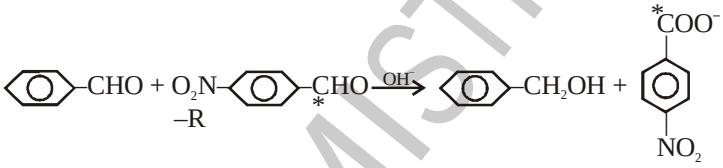


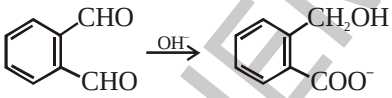
Example of Cannizaro Reaction:

(1) 

(2) 

(Via halo form reaction)

(3) 

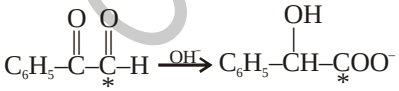
(4) 

(5) 

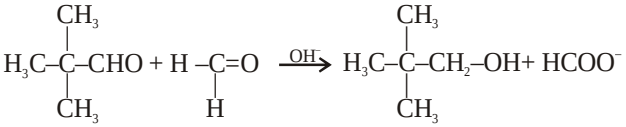
Not involve

Salt due to basic medium

(6) $Me_3C–CHO + Me_3C–CHO \xrightarrow{OH^-} Me_3C–CH_2–OH + Me_3C–COO^-$

(7) 

Phenyl Glyoxal Mendilate ion

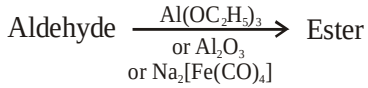
(8) 

Trimthyl Acetaldehyde Neo-Pentyl alcohol

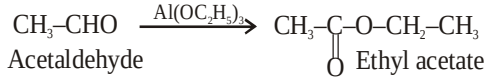
TISCHENKO REACTION:

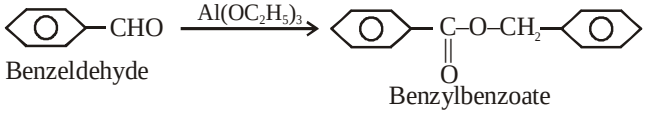
* Exist in all aldehydes

* Condition:



* It s extention of cannizaro reaction so during this reaction firstly formed alcohol & acid which react to each other & formed product as a ester.

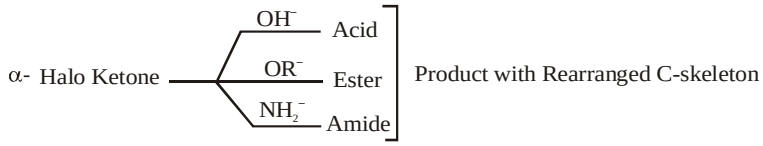




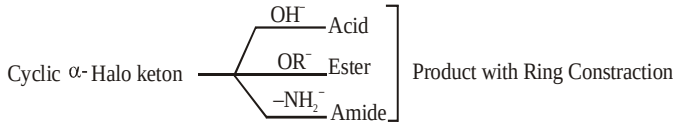
THE FAVORSKII REARRANGEMENT:

* Exist in α - halo ketones

* Condition:

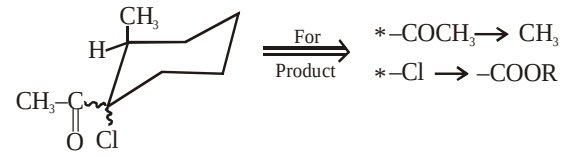


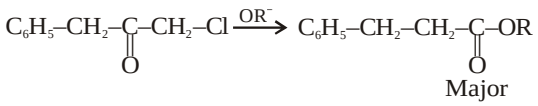
But for cyclic α – halo ketone



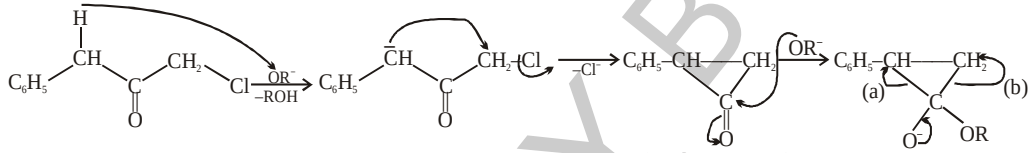
* Gem-dihalo ketones & 1,3-dihaloketones always give α,β -unsaturated ester or acid as a cis alkene.

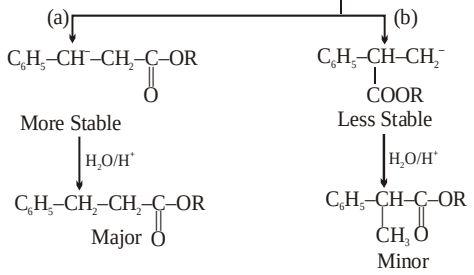
* α,β -Epoxy ketones alwas give β – Hydroxy ester/acid.



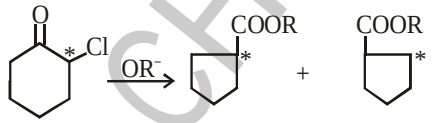


Mechanism:

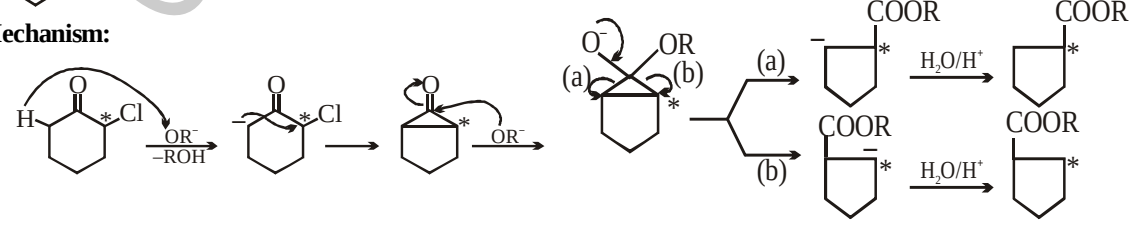




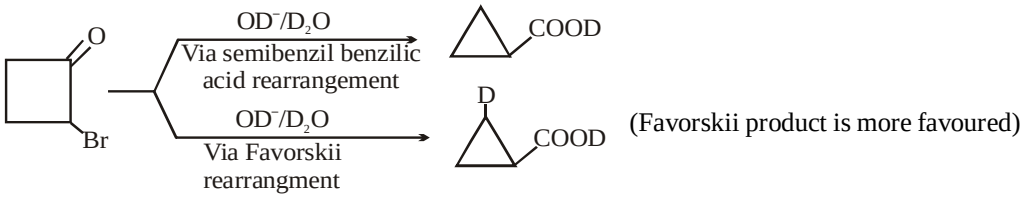
* Similarly



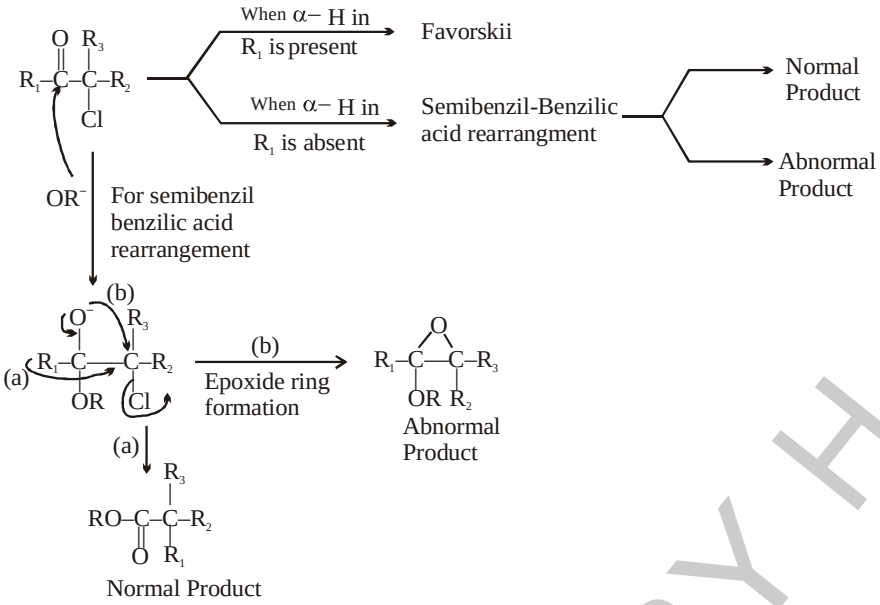
Mechanism:



FAVORSKII AS WELL AS SEMIBENZIL-BENZILIC ACID REARRANGEMENT:



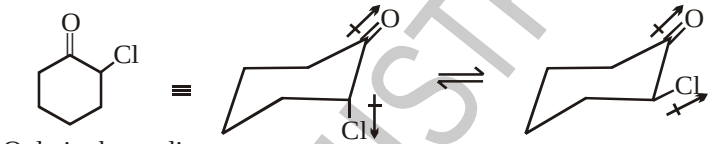
(Favorskii product is more favoured)



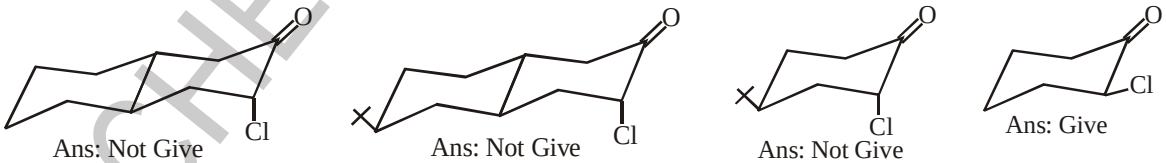
SETEROCHEMISTRY OF THE FAVORSKII REARRANGEMENT:

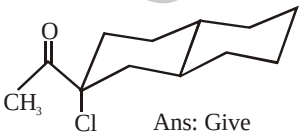
* **For favorskii in cyclic ketones:** The presence of equitorial halogen at α – position is must.

* If halogen present at axial position then favorskii does not take place.

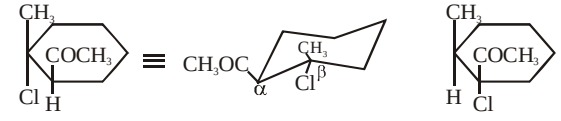


Q.1 Which one of the following compounds give the Favorskii rearrangement.



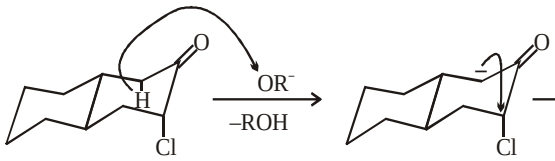


(B'coz of this compound Does not cyclic)

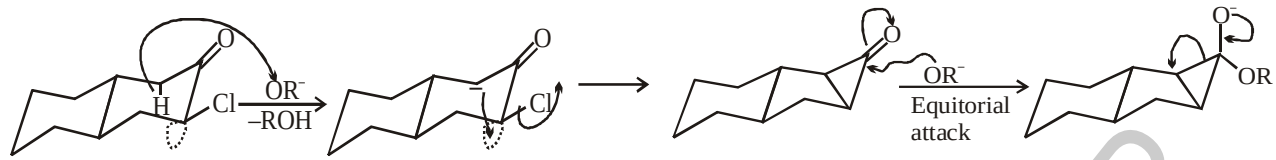


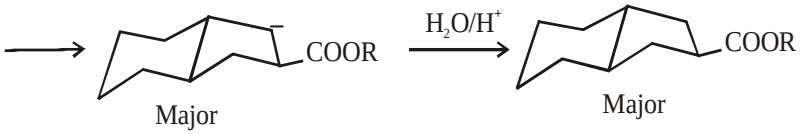
(B'coz of Cl does not at α-position)

Mechanism with stereochemistry:

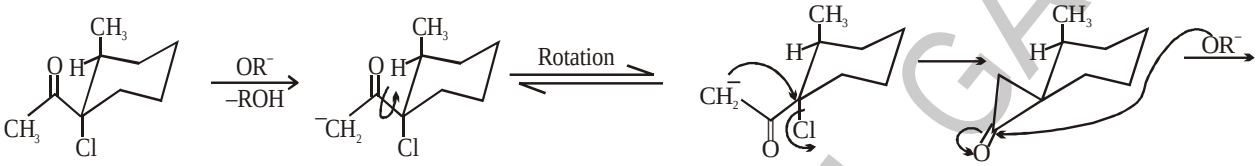
* 

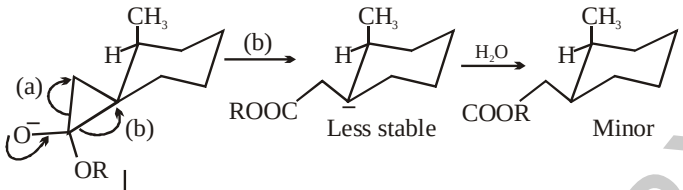
No Reaction (B'coz of does not possible back side attack)

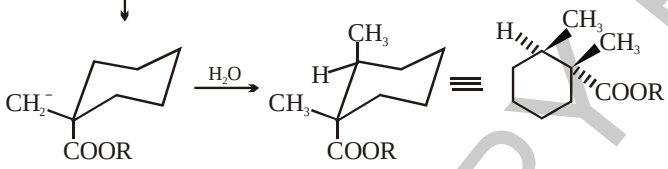
* 

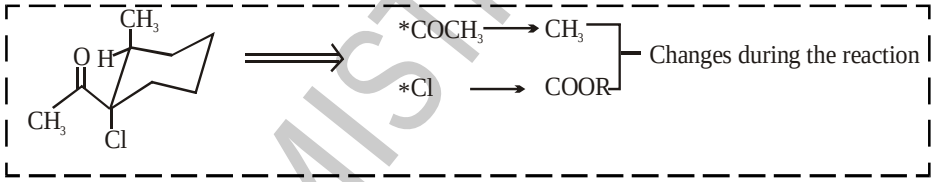


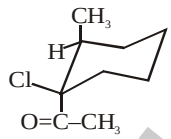
Major Major

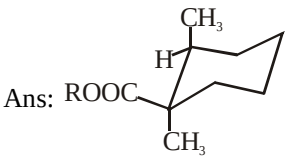
* 



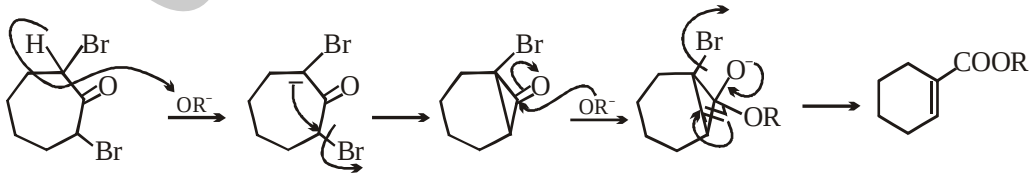


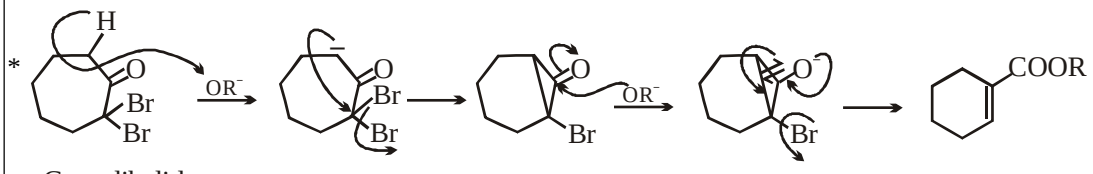


Q. 

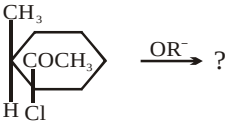
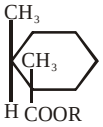
Ans: 

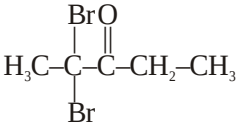
*** FAVORSKII REARRANGEMENT IN GEM & 1,3-DIHALIDE:**



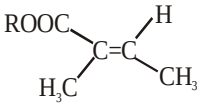


Gem-dihalide

Q.  Ans: 

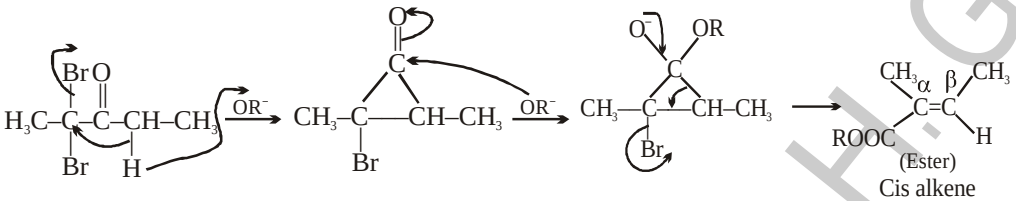
Q. 

Gem-Dihalide

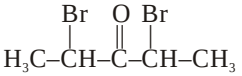
Ans: 

Cis-alkene
(Always cis)

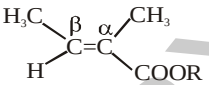
* Duing this reaction always cis product obtain, reaction takes place as follows.



(Ester)
Cis alkene

Q. 

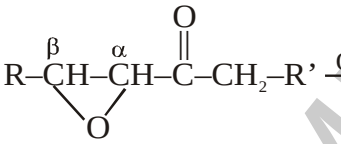
1,3-dihalide

Ans: 

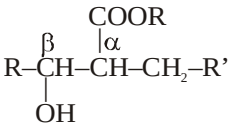
(Ester)
Cis alkene
(Always cis)

Gem-dihaloketone (α,α – dihalo)
and
1,3-Dihalo ketone (α,α'– dihalo)
$\Longrightarrow$ Always give α,β -unsaturated acids or ester

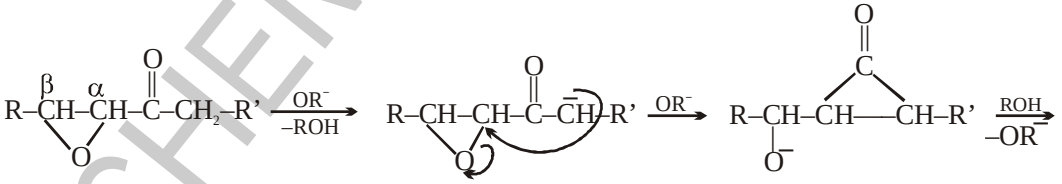
* During the reaction always **cis product** is obtained

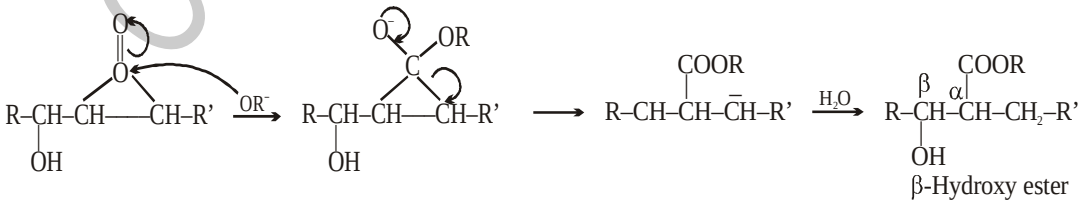
Q. 

α,β–Epoxy ketone

Ans: 

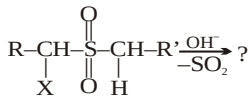
β-Hydroxy ester/acid

Sol. 



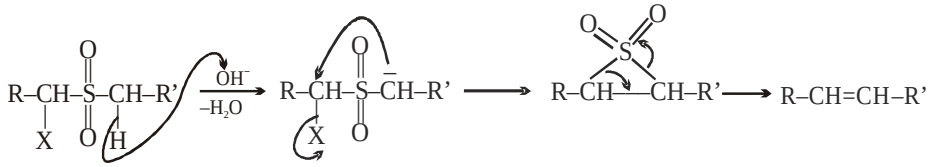
β-Hydroxy ester

* α,β – Epoxy ketone always give β **-Hydroxy ester** or β **-Hydroxy acid**

Q.  ?

Ans: R–CH=CH–R'

α- Halo Sulphone

Sol. 

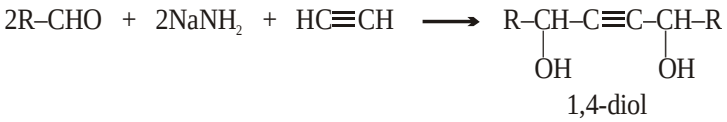
α- Halo Sulphone

* This rearrangement is called **ramberg backlund rearrangement**.

FAVORISKII REACTION:

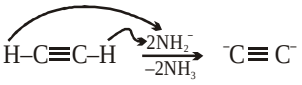
* Exist in carbonyl compounds.

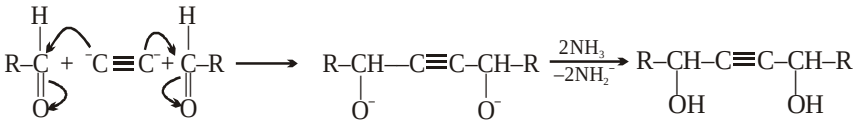
* The conversion of carbonyl compounds into 1,4-diol, usin acetylene & $NaNH_2$ is called **Favorskii reaction**.



1,4-diol

Mechanism:



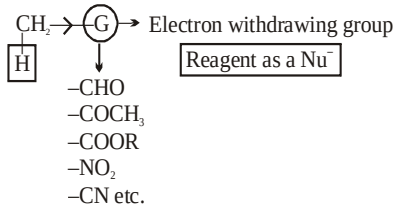


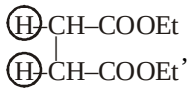
* If electron with drawin group is present in alkyl group (R) then Rate of reaction is increase.

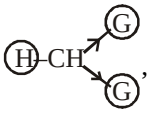
CONDENSATION REACTIONS:

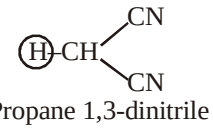
Substrate + Reagent $\xrightarrow{Basic}$ Product

*** Reagent For Condensation Reaction:**

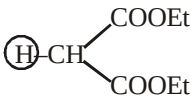




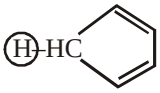


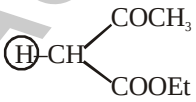


Propane 1,3-dinitrile

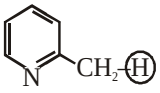


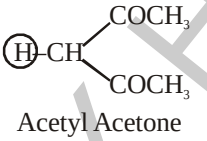
Malonic ester



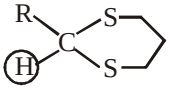


Malonic ester
AAE or B-keto ester





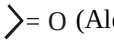
Acetyl Acetone

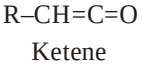


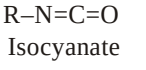
RMgX, RLi, R_2CuLi, R_2Cd

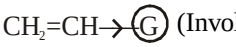
SUBSTRATE FOR CONDENSATION REACTION:

[I] Substrate for Nucleophilic Attack in Nucleophilic Addition Reaction:

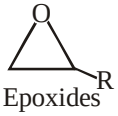

(Aldehydes & Ketones)


Ketene

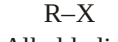

Isocyanate


(Involve in michael addition)

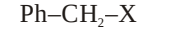

Benzyne

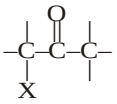

Epoxides

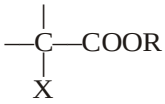
(II) Substracte for Nucleophilic Attack in Nucleophilic Substitution Reaction:

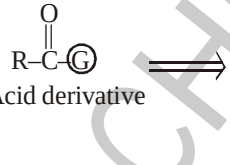

Alkyl halide


Allylic halides

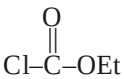

Benzylic halides

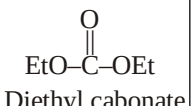

α-Halo ketones

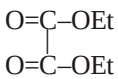

α-Halo ester

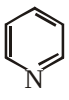


Acid derivative

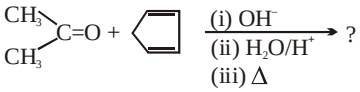


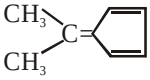

Diethyl cabonate



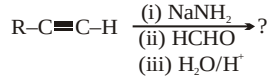

(But very less reactive)
Pyridine

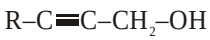
IMPORTANT QUESTIONS:

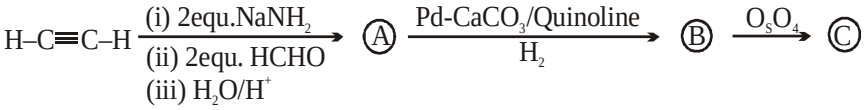
Q.1 

Ans. 

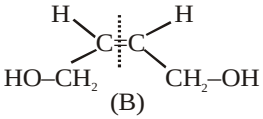
* It is application of **Knoevenagel reaction**.

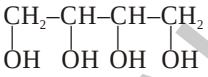
Q.2 

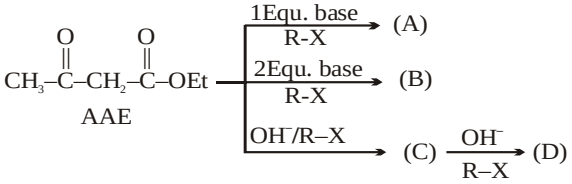
Ans. 

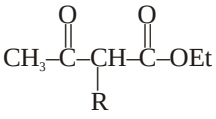
Q.3 

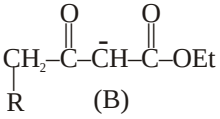
Ans: 
(A)


(B)
Meso, Optically inactive, cis


(C)

Q.4 

Ans: 
(A) & (C)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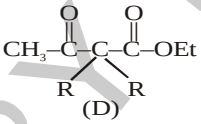
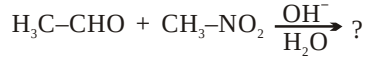
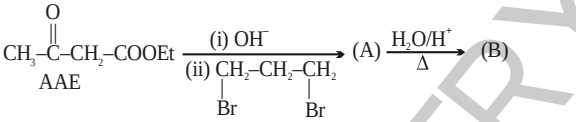
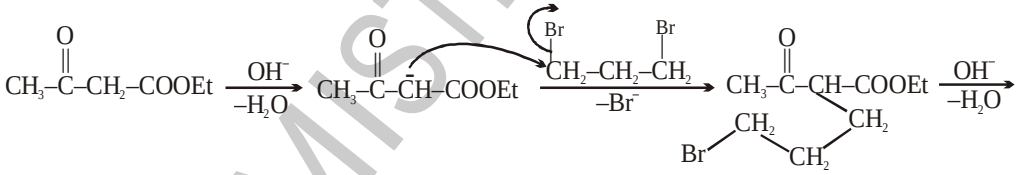
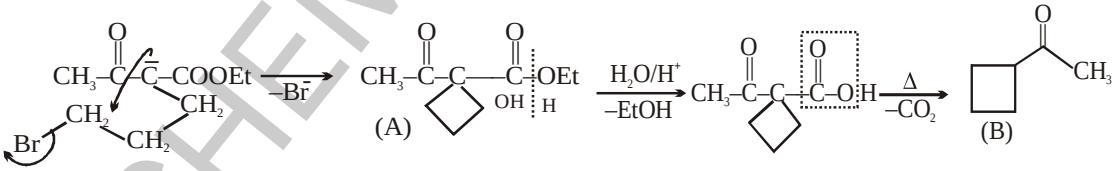

(D)

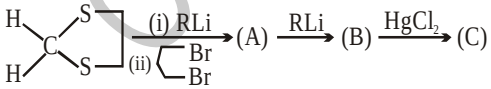
Q.5 

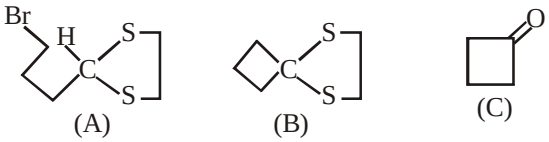
Ans: 

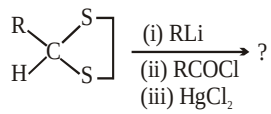
Q.6 

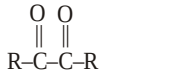
Ans. 



Q.7 

Ans: 
(A) (B) (C)

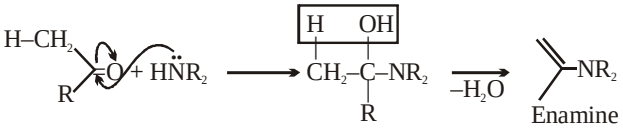
Q.8 

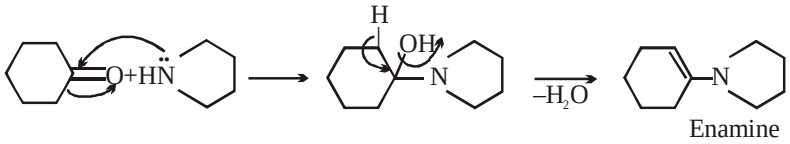
Ans: 
Substrate for Benzil-Benzilic acid Rearrangement

STARK ENAMINE CONDENSATION:

* Enamine = Ene + Amine

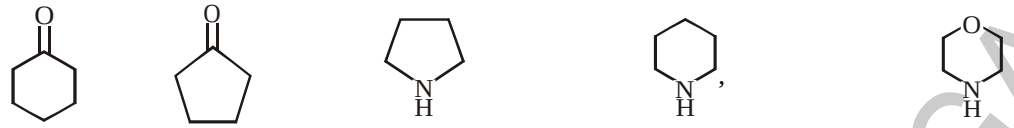
* **Preparation of Enamine:**



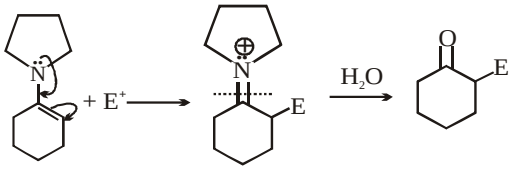


* Enamine has two nucleophilic site; N & α – C – atom of carbonyl but use only C–nucleophilic site

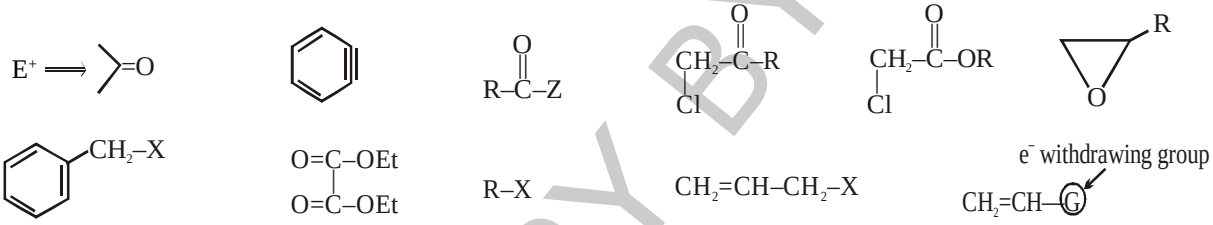
* Here following types of carbonys and 2^0 - Amineas are used:

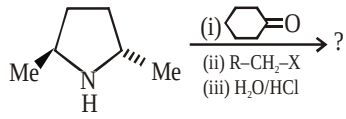


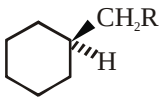
* The reaction of Enamine with electrophile (E^+) is called **stark Enamine reaction**. (or **stark Enamine condensation**)



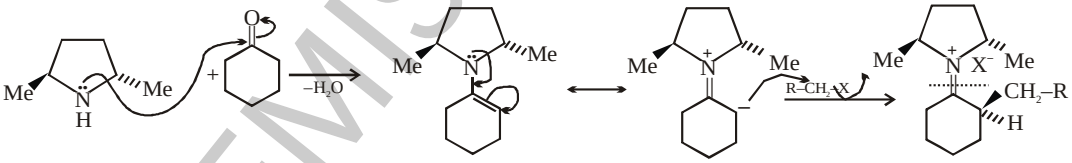
* In this reaction as a Electrophile, the following reagents can be used.

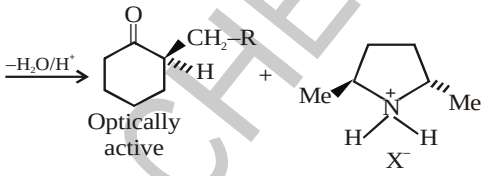


Q.1 

Ans: 

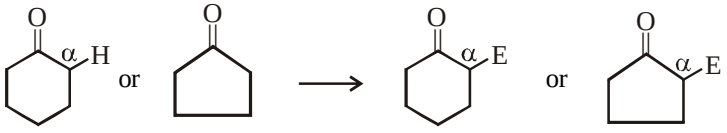
Optically active

Sol. 



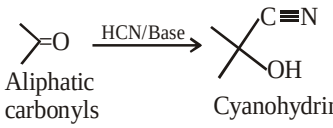
* This reaction is the example of enantioselective reaction.

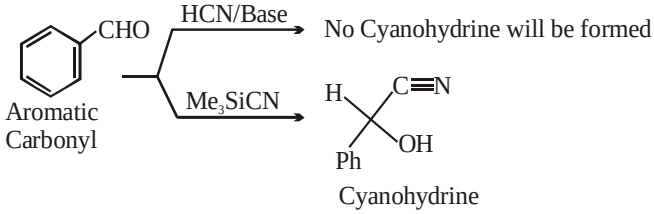
* The important use of this reaction is as following reaction.



BENZOIN CONDENSATION REACTION:

* Exist in Aromatic carbonyls, $\alpha,\beta-$ unsaturated carbonyls & Heterocyclic aromatic carbonyls (Mostly only in aldehydes)



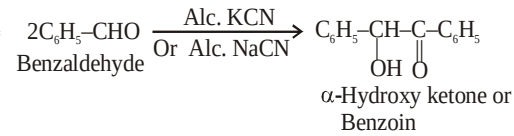


* Thus aromatic carbonyls does not give cyanohydrine with HCN, while formed cyanohydrine with Me_3SiCN.

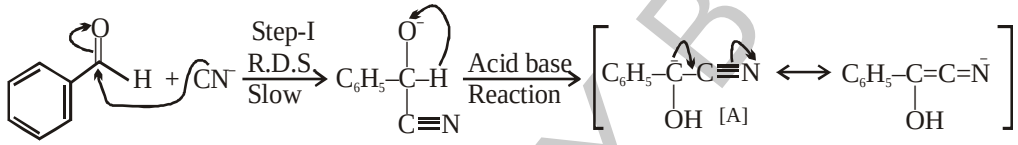
* In R.D.S., CN^- attack on this carbonyl which is convert into more nucleophilic carbanion (C^-) after the attack of CN^- ion. This

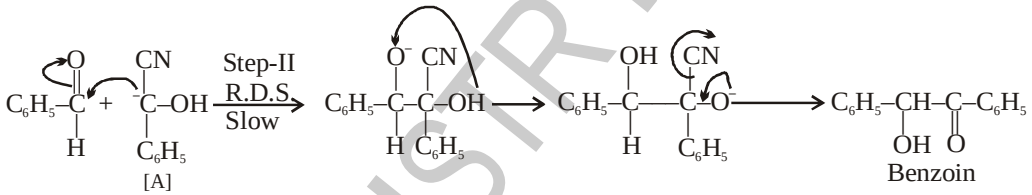
carbonyl is maintain at the end of reaction. while another carbonyl convert into $-\underset{|}{C}H-OH$ group.

* Rate $\alpha\ [C_6H_5CHO]^2[CN^-] \Rightarrow$ Follow third order kinetics



Mechanism:





* Rate $\alpha\ [C_6H_5CHO]^2[CN^-] \Rightarrow$ Follow third order kinetics

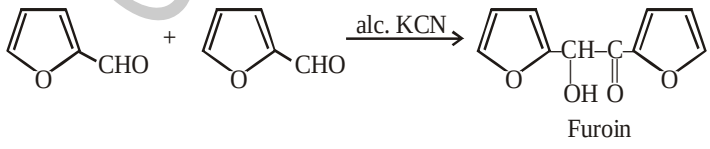
* KCN is used in the Benzoin condensation B'coz of

(i) It is a good nucleophile

(ii) It is a good leaving group

(iii) It also increase the acidity of H-atom, attach on the carbonyl carbon

Examples of Benzoin Condensation Reaction:



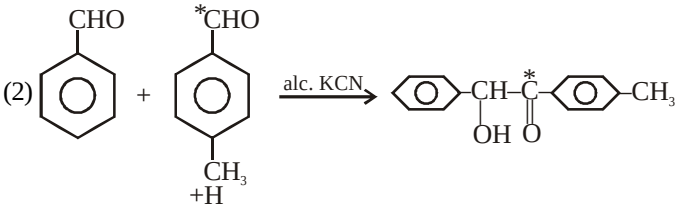
Important Points:

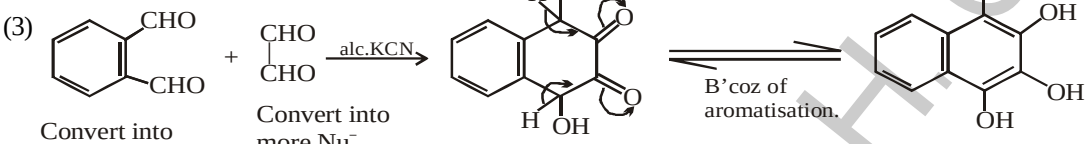
* Electron withdrawing group is present at o- or p-position of –CHO, then decrease the reaction rate due to decreasing nucleophilicity of carbanion [A]. B'coz of in this condition step-II is hardly proceed.

* If electron donating group is present at o- or p-position of –CHO, then also rection rate decrease B'coz of in this condition reactivity of aldehyde is decrease w.r.t. CN^- attack in the step-I.

* Thus, electron withdrawing as well as electron donating both types of group at o- or p- position decrease the reaction rate.

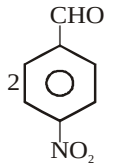
* Generally, CN^- attack on the that carbonyl which convert into more nucleophilic carbanion (have more electron charge density) after the attack.

(2) 

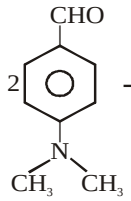
(3) 

Convert into less Nu^- Carbanion

Convert into more Nu^- Carbanion So Cn^- attack on this

(4) 

alc.KCN → No. Reaction

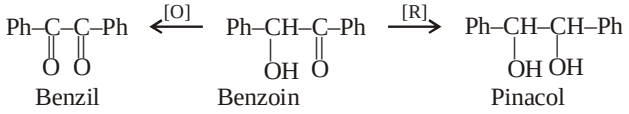
(5) 

alc.KCN → No. Reaction

* In ex.-4, step-II does not proceed b'coz of NO_2 has strong electron withdrawing effect, so nucleophilicity of carbanion is highly decrease

* In ex.-5, step-I does not occur due to strong electron donating effect of $-N(CH_3)_2$

ACYLOIN CONDENSATION REACTION:



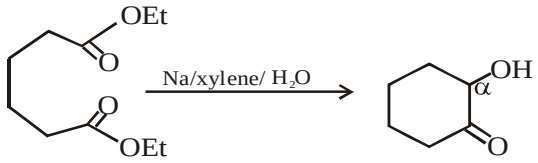
Benzil — Benzoin — Pinacol

Involve in Benizil-Benzilic acid rearrangement

Involve in Pinacol Pinacolone rearrangement

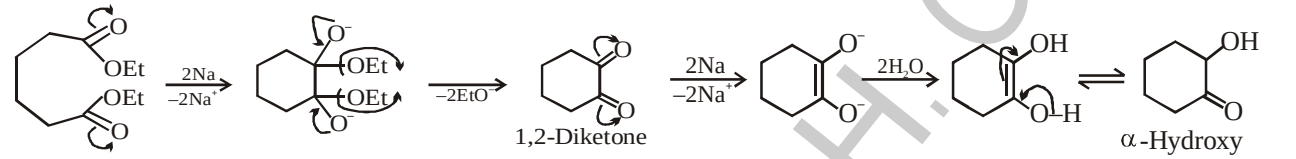
* Exist in Dibasic acid ester.
* Condition:

Dibasic acid ester $\xrightarrow[\text{In xylene}]{\text{Akali Metal}}$ α-Hydroxy Cyclic Ketone



Dibasic acid ester — α– Hydroxy Cyclic Ketone

Mechanism:

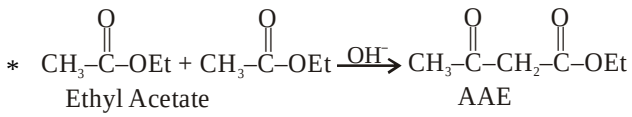


Dibasic acid ester — 1,2-Diketone — α-Hydroxy Cyclic Ketone

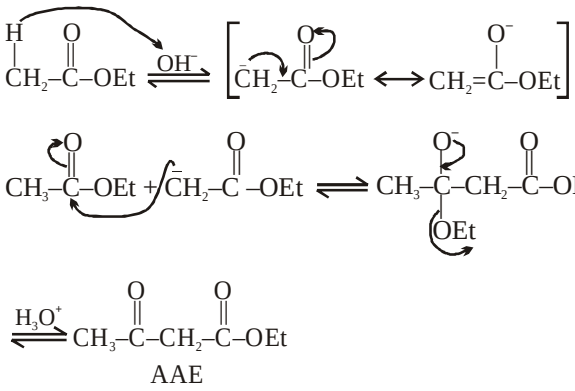
CLAISEN ESTER CONDENSATION REACTION:

* Takes palace in between to ester molecules.

* Presence of stronge base like $C_2H_5O^-$, NH_2^- or OH^-



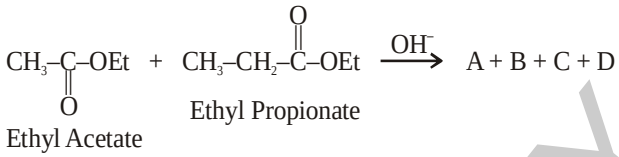
Mechanism:



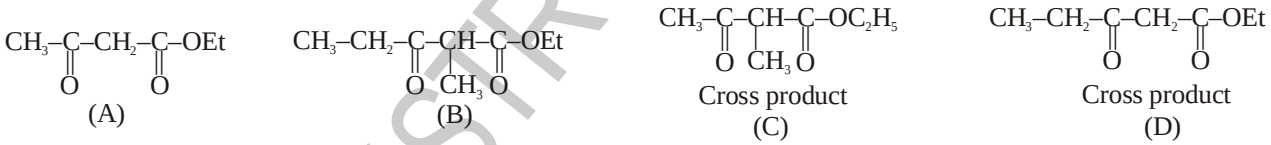
* In order to shift the equilibrium in the forword direction, ester should have atleast $2\alpha - H -$ atom.

CROSS CLAISEN ESTER CONDENSATION REACTION:

* If the reaction takes place in between two different ester molecules called **Cross Claisen Ester Condensation Reaction.**

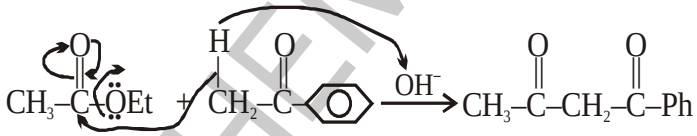


Here products are;



CLAISEN CONDENSATION REACTION:

* If the reaction takes place in between ester & Ketone, the reaction is known as **claisen condensation reaction.**

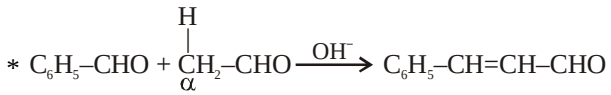


* L.P. of electron is easily transfer compaire to π – bond, so enolisation of ester does not occur, while the enolisation of ketone is takes place.

CLAISEN REACTION OR CLAISEN-SCHMIDT REACTION:

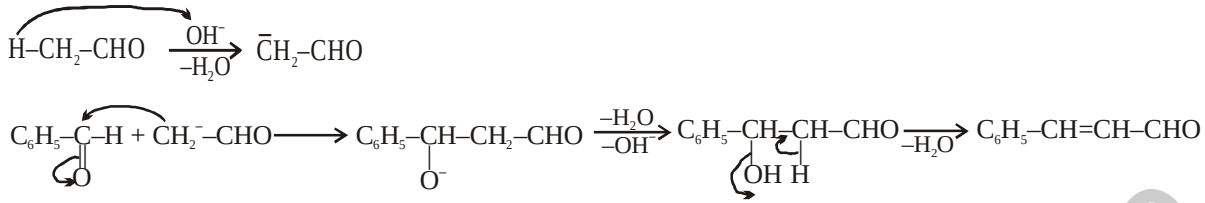
* It is example of cross aldol condensation reaction.

Aromatic Carbonyl Compound (Aldehyde or Ketone) + α–H-Containing Carbonyl Compound (Aldehyde of Ketone) $\xrightarrow{\text{Dil. } OH^-}$ α,β– Unsaturated Compound



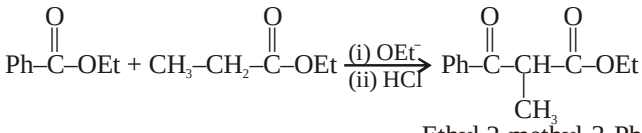
Cinamaldehyde

Mechanism:



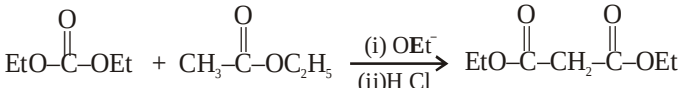
EXAMPLE OF CLAISEN ESTER CONDENSATION / CLAISEN CONDENSATION/CLAISEN-SCHMIDT REACTION:

(1)



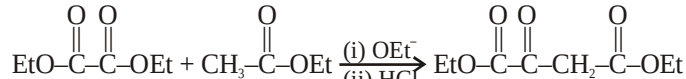
Ethyl 2-methyl-3-Phenyl
-3-Oxopropanoate

(2)



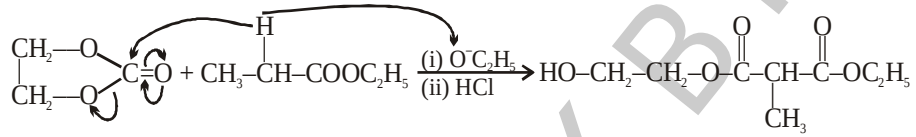
Diethyl Malonate

(3)



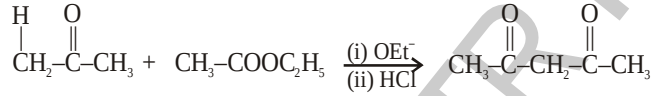
Diethyloxaloacetate

(4)



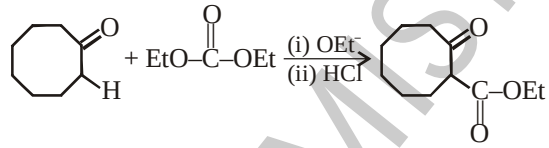
(2-Hydroxyethyl)ethyl- 2-methyl propanedioate

(5)

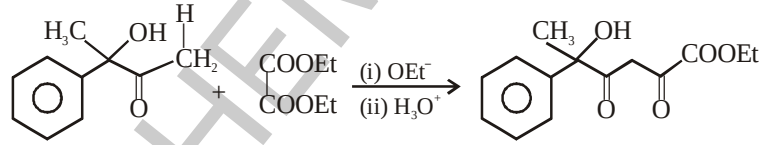


Acetylacetone

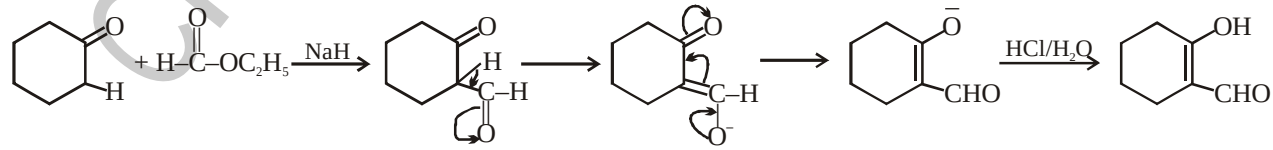
(6)



(7)

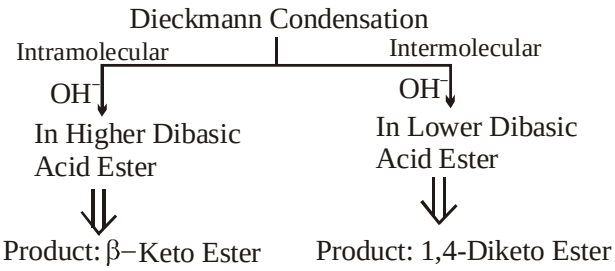


(8)



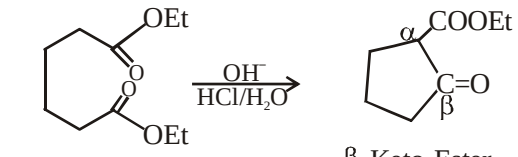
DIECKMANN CONDENSATION REACTION:

* Exist in dibasic acid ester.



Intramolecular Dieckmann Condensation reaction:

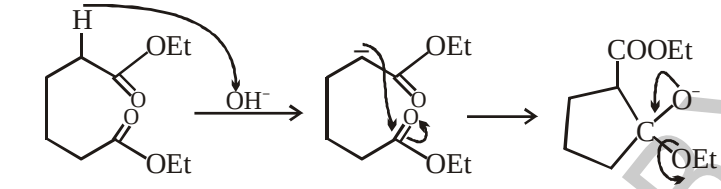
* Exist in higher Dibasic Acid Esters.



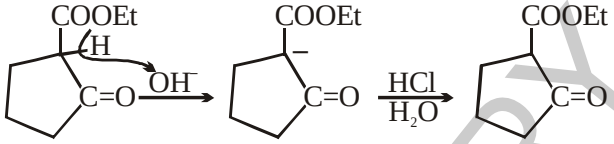
Dibasic Acid Ester — β-Keto-Ester

Mechanism:

* (Similar to Claisen Condensation)

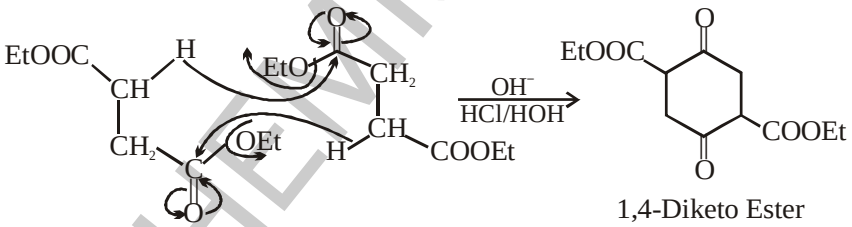


Dibasic Acid Ester



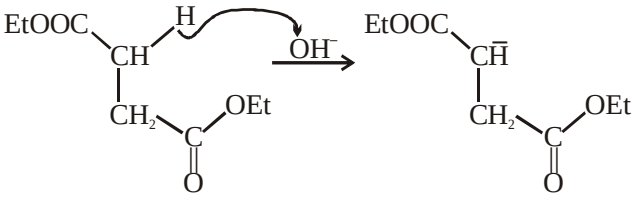
Intermolecular Dieckmann Condensation Reaction:

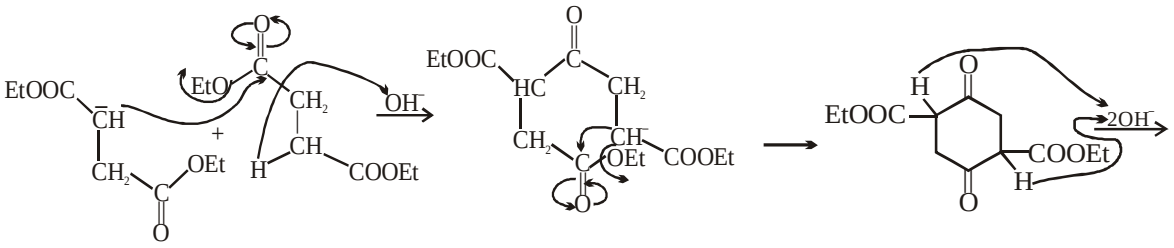
* Exist in diester of succinic acid

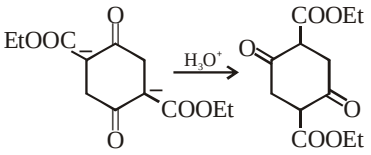


Diester of Succinic Acid — 1,4-Diketo Ester

Mechanism:



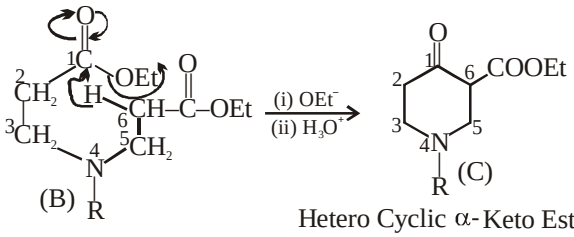




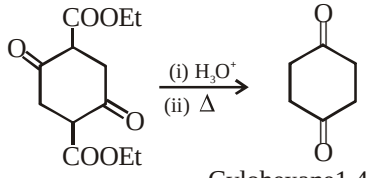
Q.1 $R-NH_2 + CH_2=CH-COOEt \longrightarrow (A) \xrightarrow{CH_2=CH-COOEt} (B) \xrightarrow[(ii)\ HCl/H_2O]{(i)\ C_2H_5ONa/C_2H_5OH} (C)$

Sol. $R-\ddot{N}H-H + CH_2=CH-COOEt \xrightarrow{\text{Michael addition}} R-\ddot{N}H-CH_2-CH_2-COOEt \xrightarrow[\text{Michael addition}]{CH_2=CH-COOEt}$

(A)

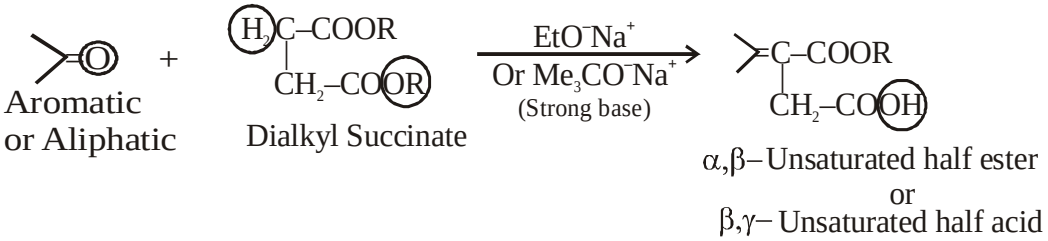


Hetero Cyclic α-Keto Ester

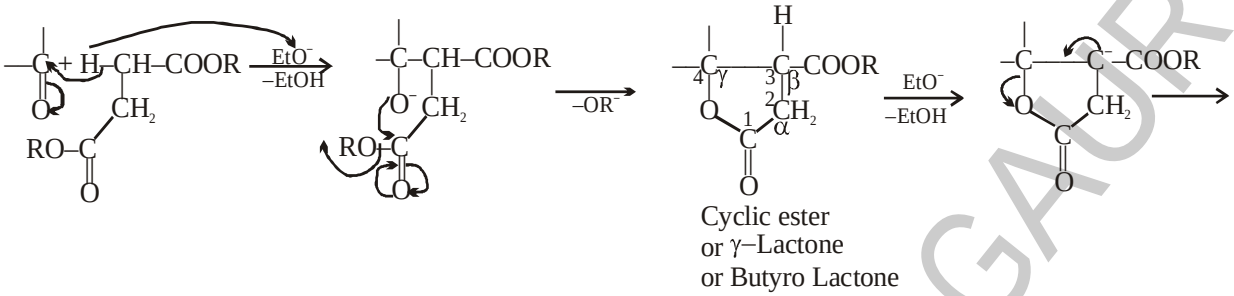
Q.2 

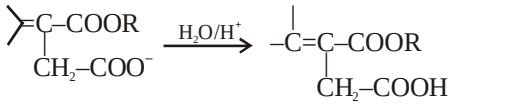
Cylohexane1,4-dione

STOBBE CONDENSATION REACTION:

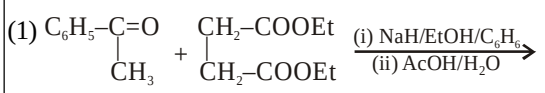


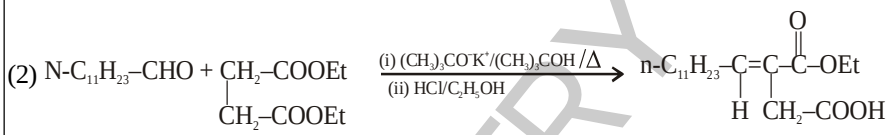
Mechanism:





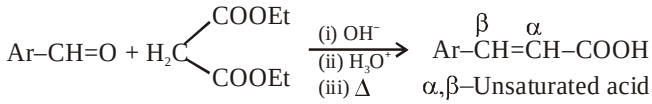
Example of Stobbe Condensation reaction:

(1) 

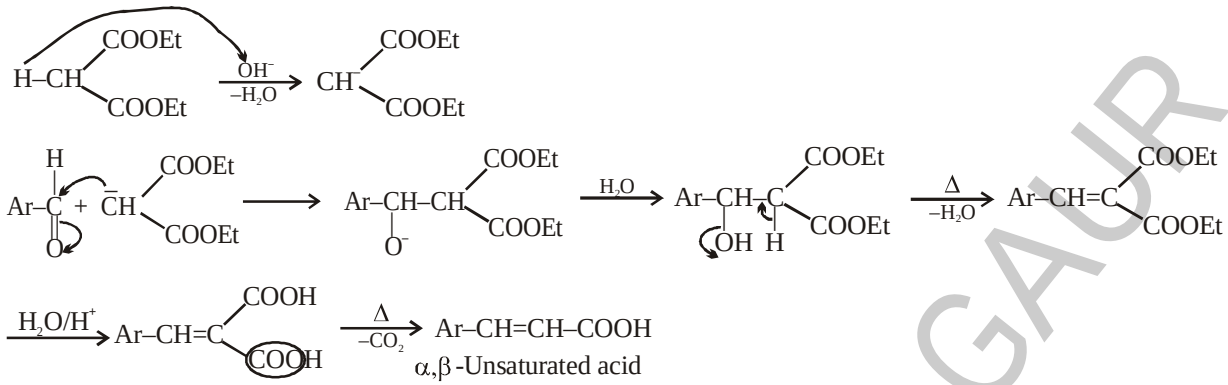
(2) 

KNOEVENAGEL REACTION:

* When the aromatic aldehydes are treated with active methylene compound in the presence of base followed by Hydrolysis, α,β – unsaturated compound will be form.



Mechanism:



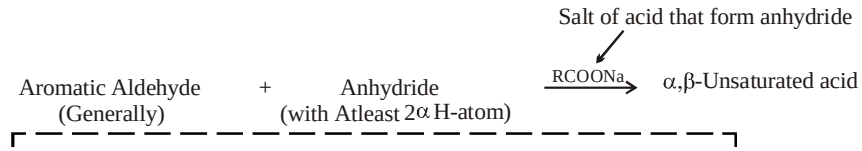
Example of Knowledge Reaction:

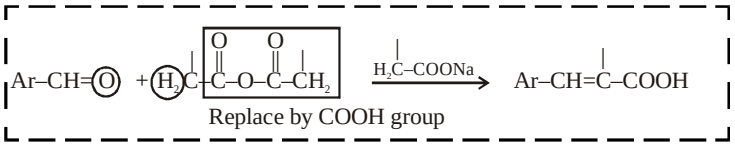
(i) Ph–CHO + H_2C(COOEt)(COOEt) $\xrightarrow[(ii)\ H_3O^+]{(i)\ OH^-}_{(iii)\ \Delta}$ Ph–CH=CH–COOH (Cinnamic acid)

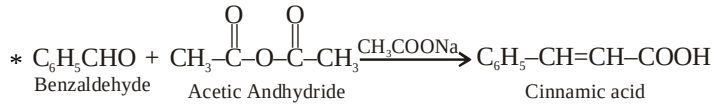
(ii) Ph–CHO + H_2C($COCH_3$)(COOEt) $\xrightarrow[(ii)\ H_3O^+]{(i)\ OH^-}_{(iii)\ \Delta}$ Ph–CH=CH–C(=O)–CH_3

α,β -Unsaturated Ketone
(Substrate for Michael addition)

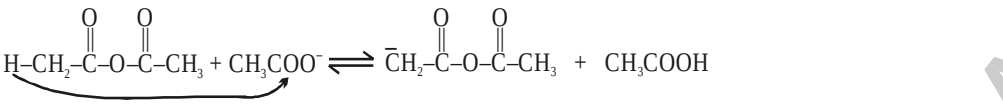
PARKIN REACTION:

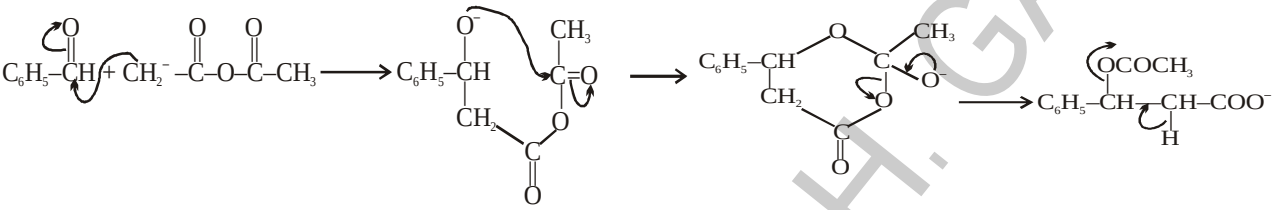


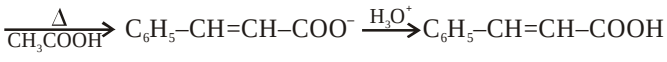




Mechanism:



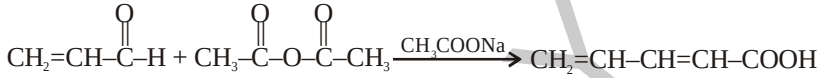


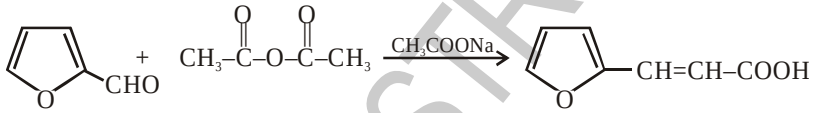


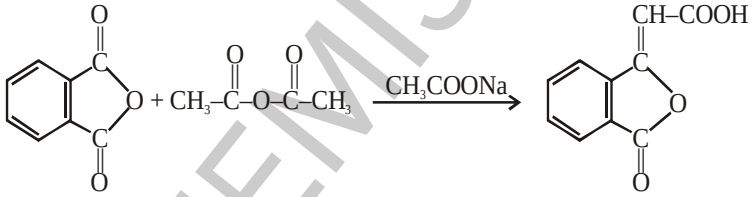
Cinnamic Acid

* Anhydride should posses atleast 2α H-atoms. It's characterisic of anhydride for this reaction.

EXAMPLE OF PERKIN REACTION (PERKIN CONDENSATION):

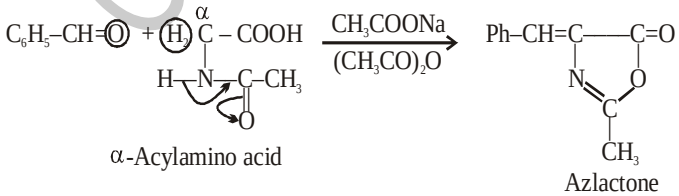
(1) 

(2) 

(3) 

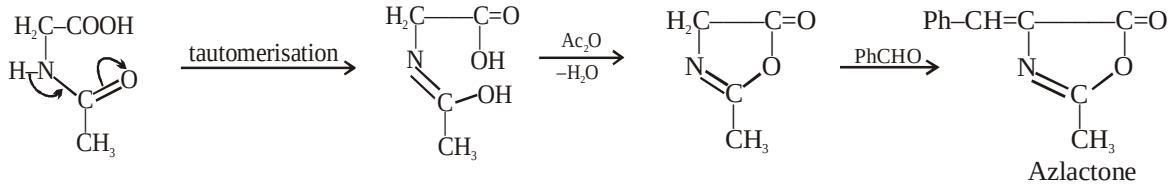
(4) 

(5) α – Acylamino acids can be used in place of acid anhydride in he Perkin reaction.



This reaction specially known as **Erlenmeyer Azlactone synthesis.**

Mechanism:



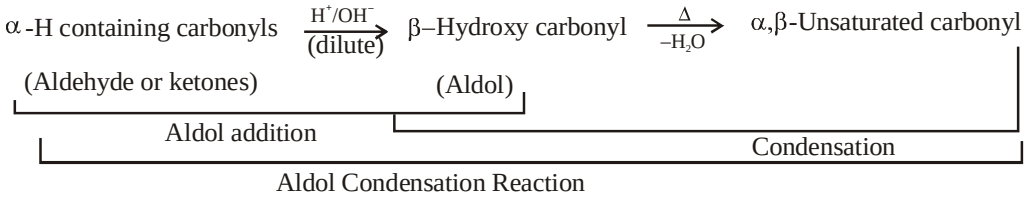
Azlactone

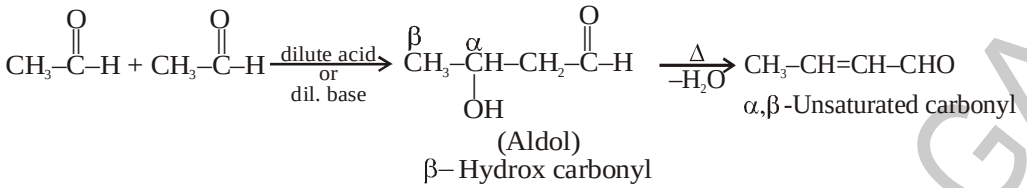
ALDOL CONDENSATION REACTION:

* The carbonyl compounds having α – H-atom undergoes self condensation reaction in the presence of dilute acid or base & formed a β – Hydroxy carbonyl compound (Aldol). This reaction is known as **Aldol addition reaction.**

* Which on heating loss one H_2O molecule & give α,β – unsaturated carbonyl compounds this is called **condensation reaction.**

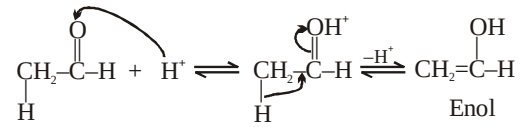
* The aldol addition followed by dehydration of aldol is known as **Aldol condensation reaction.**

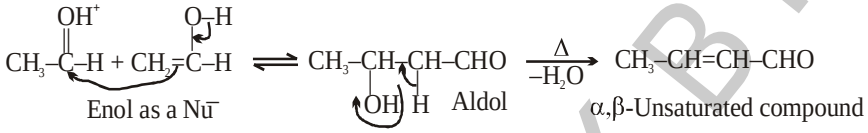




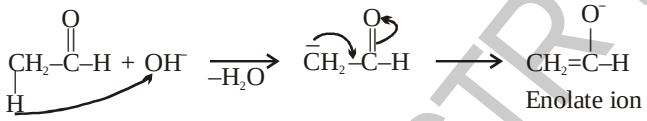
Mechanism:

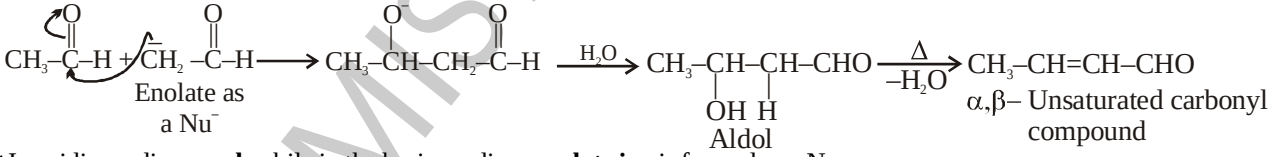
(I) In Acidic Medium :



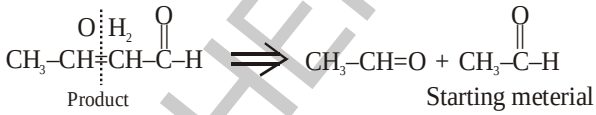


(II) In Basic Medium:





* In acidic medium **enol**, while in the basic medium **enolate ion** is formed as a Nu^-.



*

Type of Aldol Condensation Reactions

- **Simple**
  - B/w Same Carbonyls
    - Structurally possible product always one.
- **Cross**
  - B/w different Carbonyls
    - * B/w two diff. Aldehydes
    - * B/w two diff. Ketones
    - * B/w Aldehydes & Ketones

* Between two different aldehydes

When both have α−H-atom ⇓ 4-Product formed

When one have α− H-atom ⇓ 2-Product formed

*** Between Aldehyde & Ketone:** Enolate form by the ketone

*** Between two different ketones:** Unfavourable Because of Enolate is a bulky Nu^- as well as ketones are less reactive towards the Nucleophilic addition reaction.

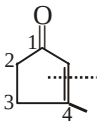
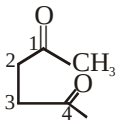
* When this reaction is carried out in Ketone yield is very poor due to

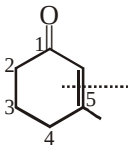
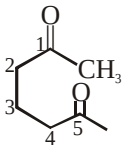
(i) Enol is a bulky Nucleophile, so increases steric repulsion.

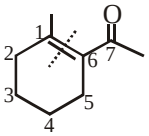
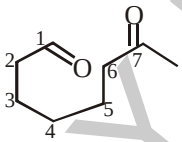
(ii) Ketones are less reactive towards the the Nucleophilic addition reaction.

Q.1 Identify the initial material of the given product.

(1) $CH_2=CH-CHO \Rightarrow HCHO + CH_3CHO$

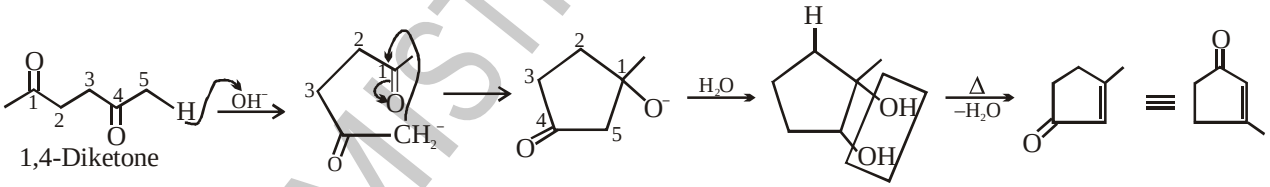
(2)  ⇒  1,4-Diketone

(3)  ⇒  1,5-Diketone

(4)  ⇒  1,7-Diketone

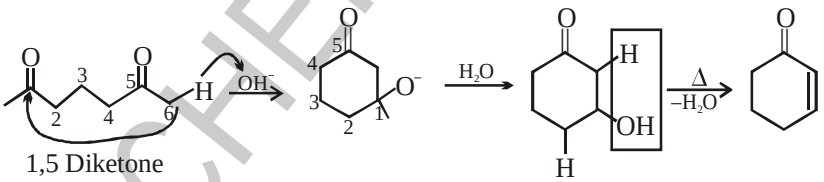
Intramolecular Aldol Condensation Reaction:

(I) In 1,4-Diketones:



1,4-Diketone

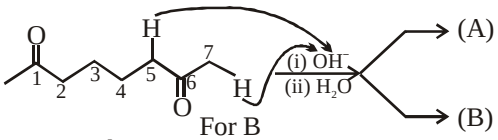
(II) In 1,5-Diketone:



1,5 Diketone

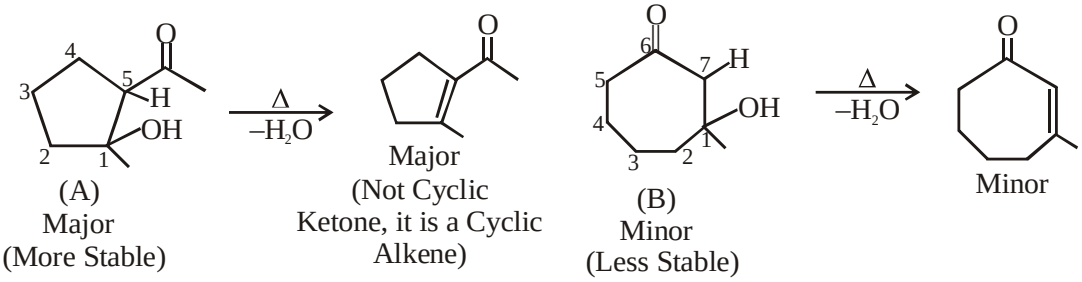
It is reagent for Michael Addition

(III) In 1,6-Diketone:

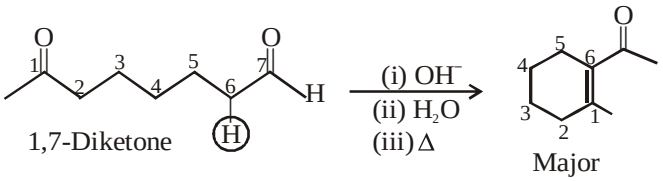


For B

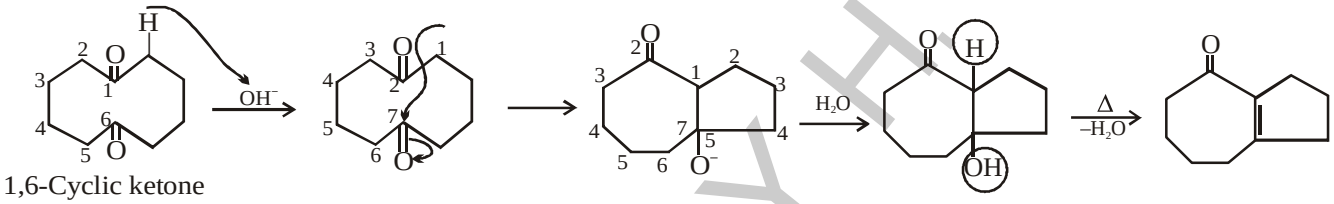
1,6-Diketone



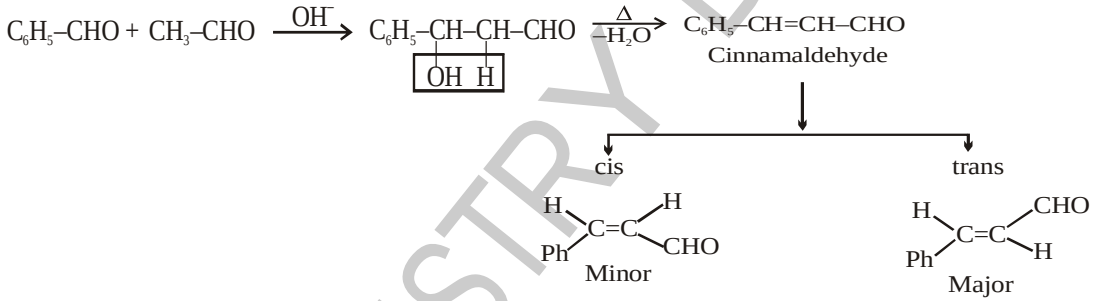
(IV) In 1,7-Diketone:



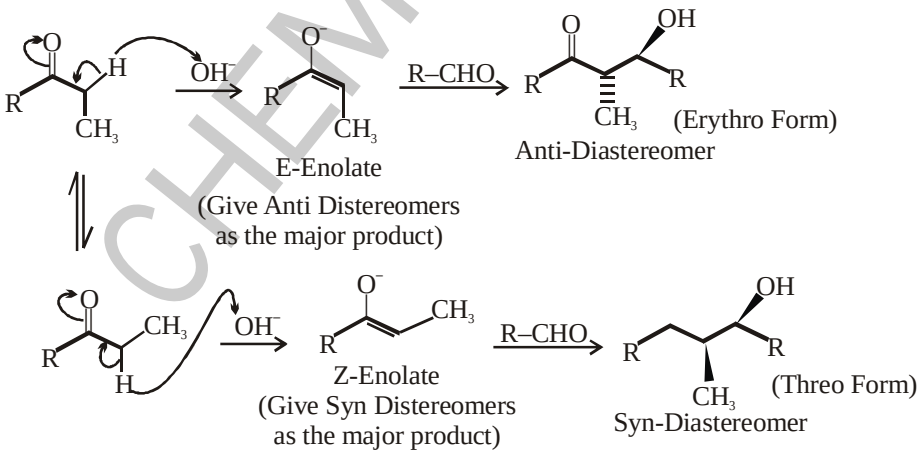
(V) In Cyclic Diketone:

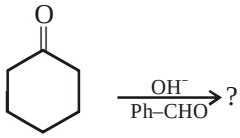


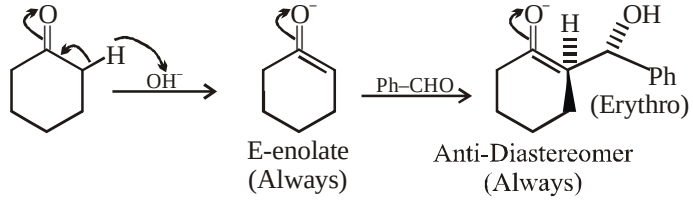
Stereochemistry of Aldol Condensation:



Diastereoselectivity of the Aldol Condensation:

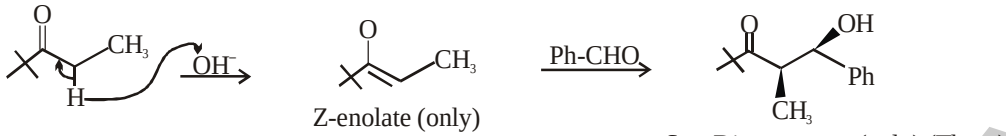


Q.1 

Sol. 

E-enolate (Always)

Anti-Diastereomer (Always)

* 

Z-enolate (only)

Bulky group, so increase Hindrance in E-enolate so that E-enolate is not form

Syn-Diastereomer (only) (Threo)

DIRECT ALDOL CONDENSATION REACTION:

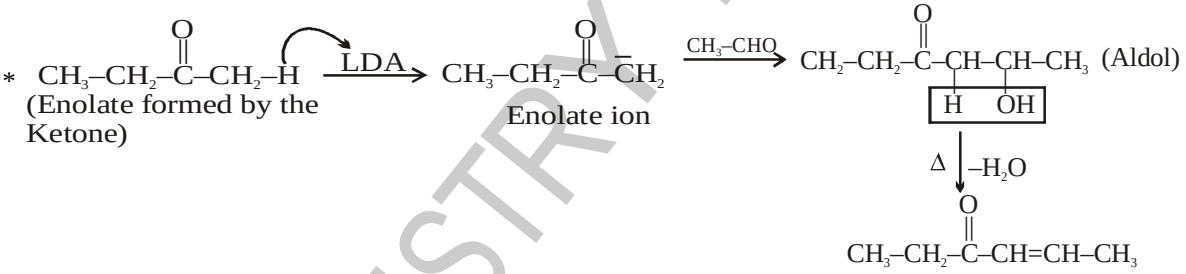
* When cross aldol condensation is carrid out by the help fo LDA then this reaction known as **directed aldol condensation reaction.**

LDA

* It is strong base but it is not a Nu^- (Weak Nu^-)

* Abstract more acidic $\alpha - H$ -atom.

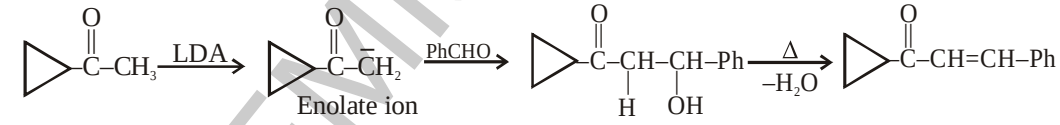
* But if acidity is same then, abstract less sterically Hindard $\alpha - H$ -atom. because it is a bulky base.

* 

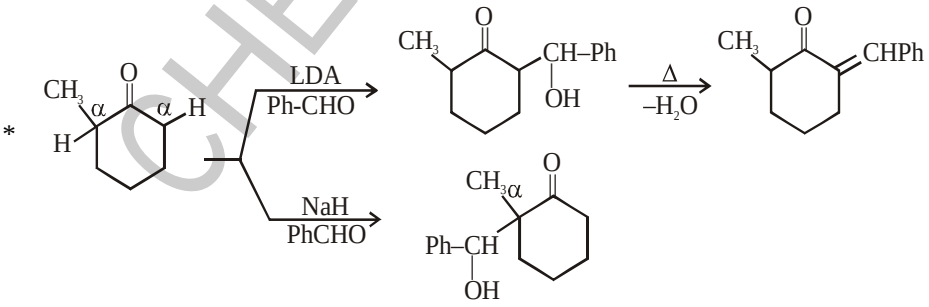
(Enolate formed by the Ketone)

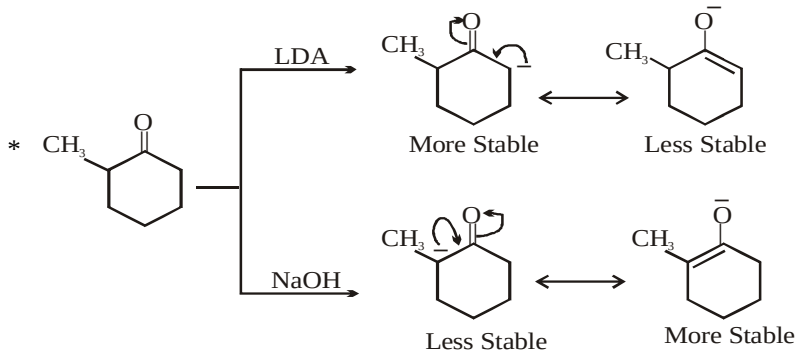
Enolate ion

(Aldol)

* 

Enolate ion

* 

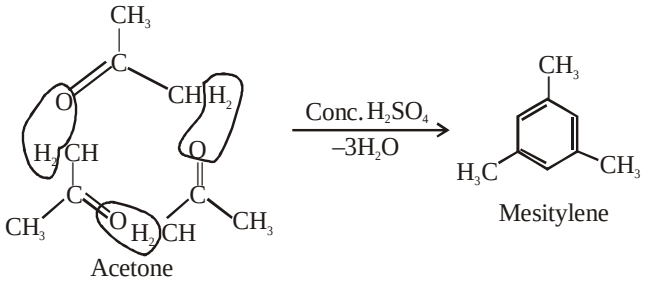


* NaH is not used for reducing agent (Bad Reducing agent.)

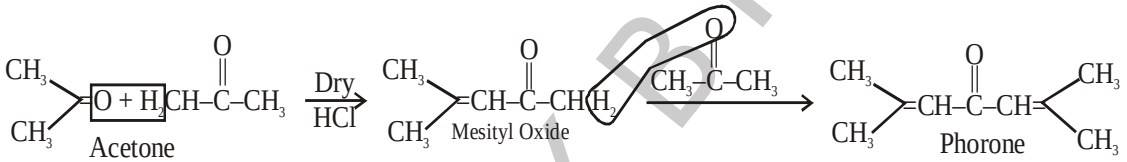
Example of Aldol Condensation Reaction:

(1) $CH_3–CHO + CH_3–\overset{O}{\overset{\|}{C}}–CH_3 \xrightarrow[(ii)\ \Delta]{(i)\ OH^-} CH_3–CH=CH–\overset{O}{\overset{\|}{C}}–CH_3$

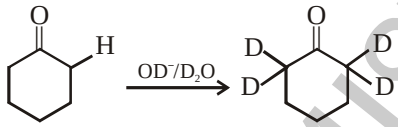
(2)



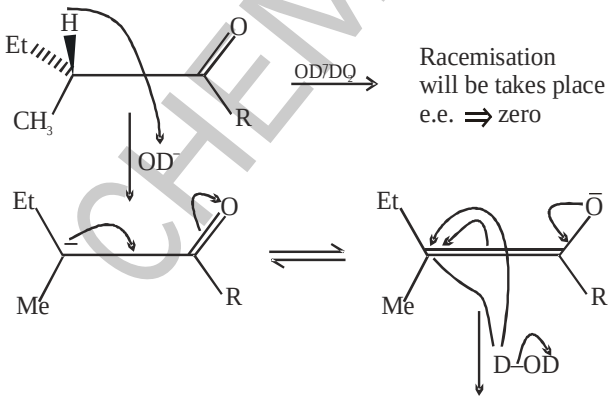
(3)



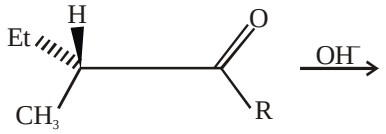
(4)

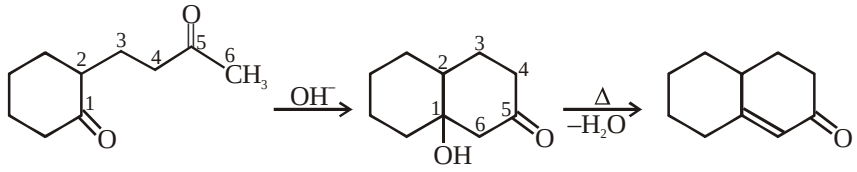


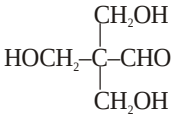
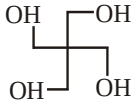
(5)



* Racemisation will be take place
* Enantiomeric Axis (e.e.) - Zero
* Rate of Duterium exchange & rate of Racemisation will be same

(6)  $\xrightarrow{OH^-}$ Racemic mixture
e.e. $\Rightarrow$ Zero

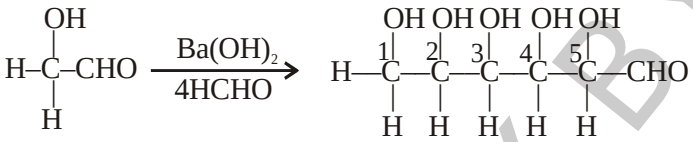
(7) 

(8) $CH_3–CHO + HCHO \xrightarrow[(Excess)]{OH^-}$  (Via 3 times aldol) $\xrightarrow[\text{Cross Cannizaro}]{HCHO}$  Pentaerythretol $+ HCOO^-$ Salt of formic acid

(9) $2CH_3–CHO \xrightarrow[Conc.]{OH^-} CH_3–CH=CH–CHO \xrightarrow{nCH_3CHO} CH_3(–CH=CH)_{n+1}–CHO$
Rasin

(10) $HCHO + HCHO \xrightarrow[\text{(Conc.) Cannizaro reaction}]{OH^-} CH_3OH + CHOO^-$

$Ba(OH)_2$ Soln. (Baryta) — Aldol condensation exceptional case

 Formose