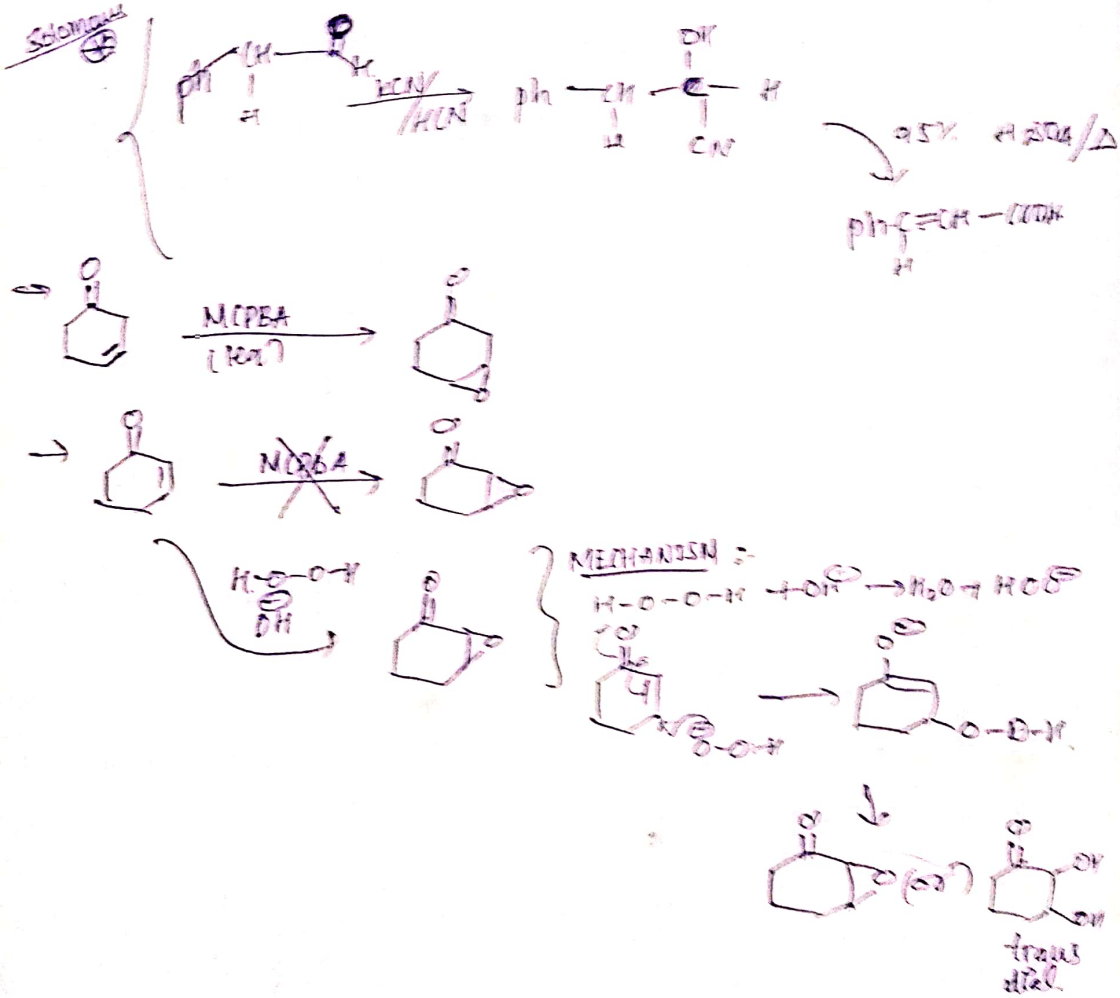
Carbonyl Compounds



Carbonyl Compounds

(i) from alkane

$CH_4 \xrightarrow{Mo_2O_3,\ 450°C,\ 100\ atm} CH_3OH$

$RCH_3 \xrightarrow{MnO_2,\ \Delta} RCHO$

$R{-}CH_3 \xrightarrow{?} RCOOH$

(ii) Alkenes

(a) Ozonolysis

(b) OXO process

(c) Wacker's process

reagent :- O_2, H_2O

catalyst :- $PdCl_2$ and $CuCl_2$.

(iii) Lumax-Johnson ($CrO_3/AcOH + OsO_4$)

(iii) from alkynes

(a) Ozonolysis

(b) Hydro boration-oxd.

(c) Oxy-mercuration demercuration.

(iv) from Benzene

(a) Friedel-crafts rxn.

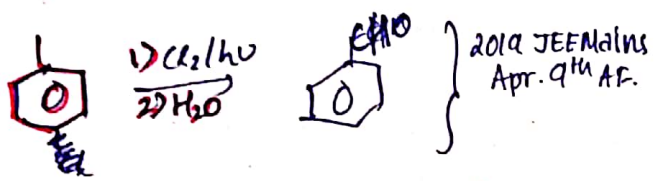
(b) Gatterman koch

(c) Gatterman rxn

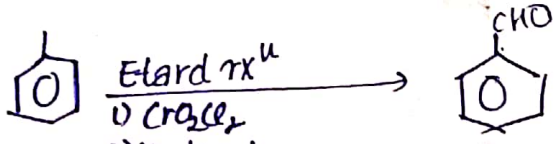
(d) Vilsmeir-Haack rxn

(v) from toulene

(a)

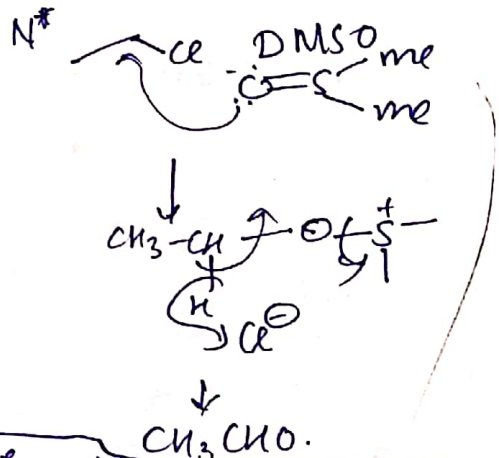


(b)



c) By using CrO_3 and Ac_2O/Δ and hydrolysis.

(vi) from alkyl halides



(vii) from alcohols

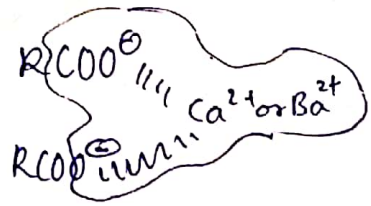
reuse all oxdising and reducing reagent.

Including oppaneur oxd. and MPV red.

(viii) from carboxylic acids

Dry distillation

$R{-}C(=O){-}OH \xrightarrow[Ba(OH)_2/BaO]{Ca(OH)_2/CaO}$



$-CaCO_3 \downarrow \Delta$

$R{-}C(=O){-}R$

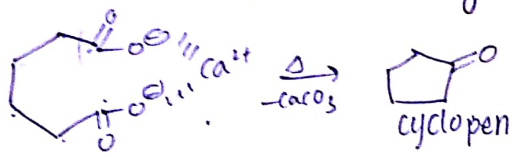
Ex:

e.

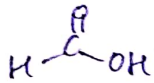
Q equimolar mix. of HCOOH and CH_3COOH gives majorly CH_3CHO.

minorly HCHO and .

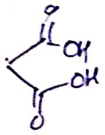
§ Calcium salt of adepate on strong heating gives ——.



⇒ Heating of dicarboxylic acids (Along with H_2SO_4 or without it.)

*  $\xrightarrow{\Delta}$ $H_2O + CO$
*  $\xrightarrow{\Delta}$ $H_2O + CO + CO_2$

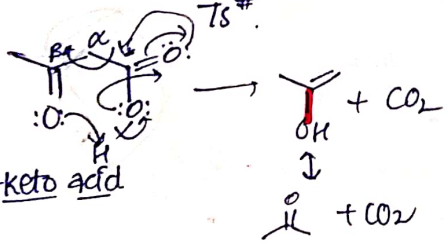
} for BITSAT / EAMCET

*  $\xrightarrow{\Delta}$ $H_2O + CO + CH_3COOH + CO_2$

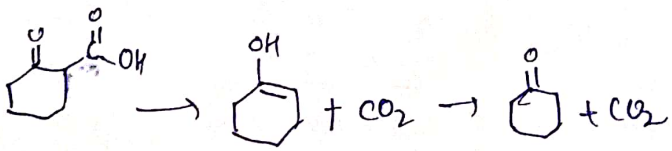
[∵ Mc Lafferty]

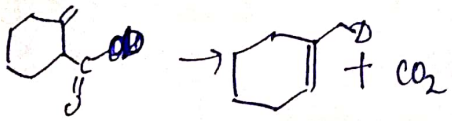
Condition :- Acids which contains carbonyl group at 'β-position' are (or) C=C at β-position (or) similar groups i.e. ,  , etc, on heating decarboxylation takes place.

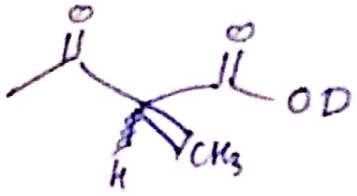
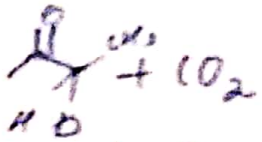
Mechanism :- (i) concerted
(ii) proceeds through cyclic 6 membered ring



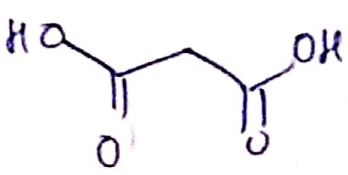
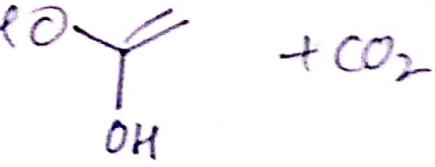
Examples :-

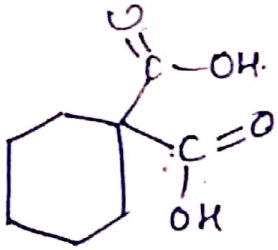
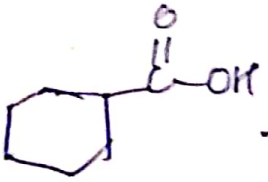
(i) 

(ii) 

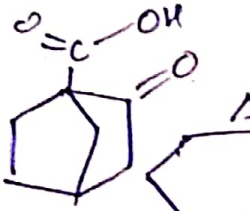
Q  

Optically inactive
(Due to racemisation)

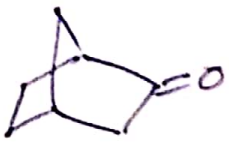
Q  

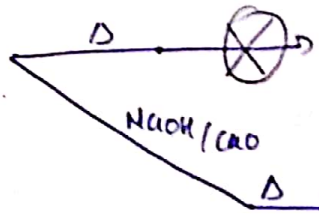
Q   $CH_3COOH + CO_2$

$+ CO_2$

Q 

 no rxn (Due to Bredtg rule)

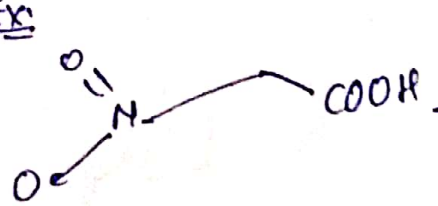
NaOH/CaO 

Q $N \equiv C - CH_2 - \overset{O}{\overset{\|}{C}} - OH$  $HN=C=CH_2$ (X Norm)

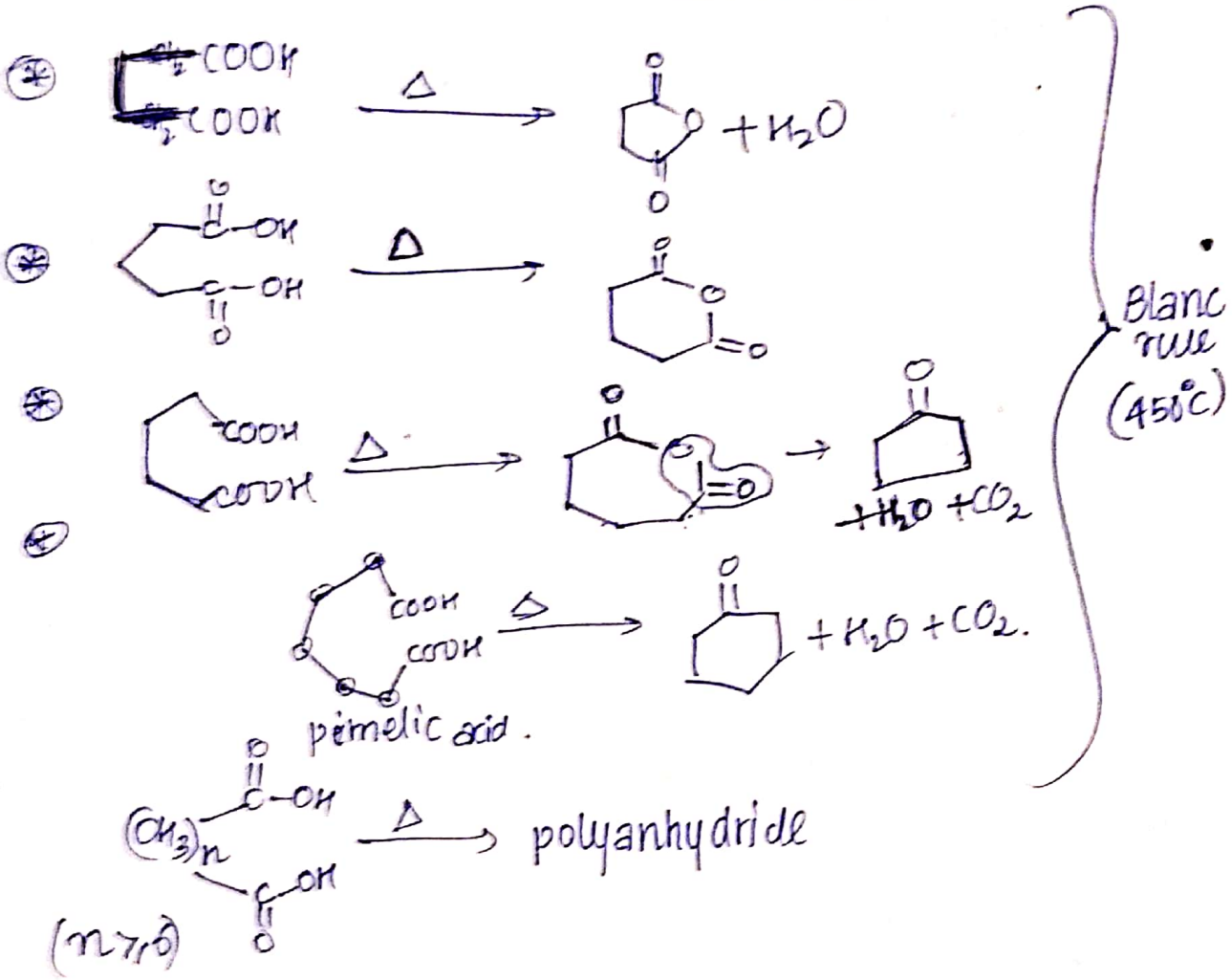
because 6 TS with 2 consecutive double bonds is not formed.

NaOH/CaO

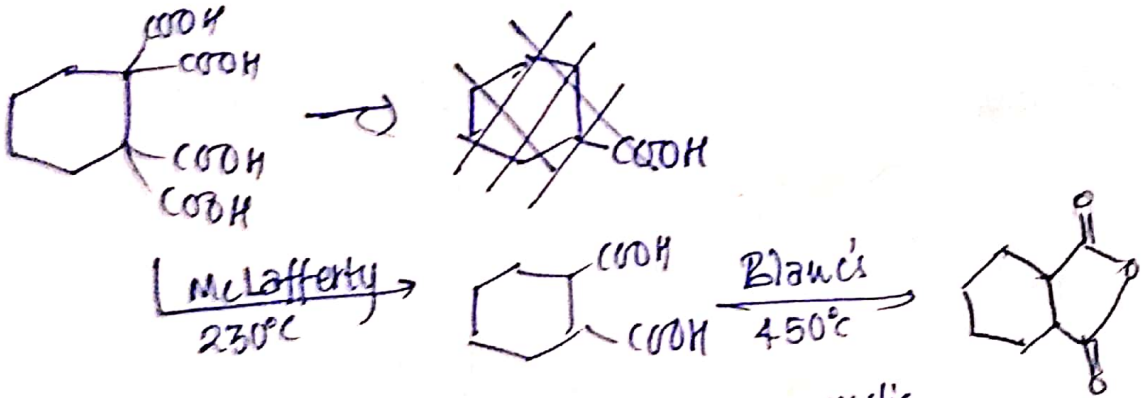
 $N \equiv C - CH_2 - H$

Ex:   $NO_2 - CH_3$

NaOH/CaO $NO_2 - CH_3$



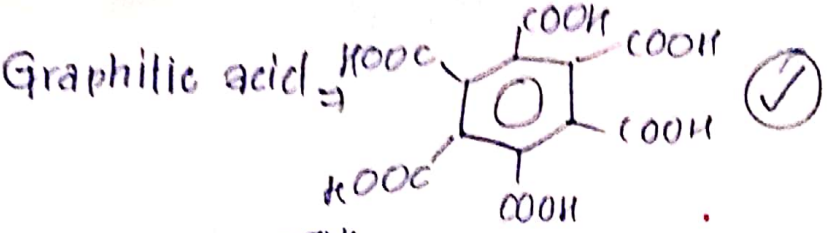
Q1 

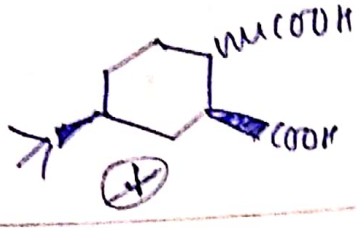
Q2 

Q3 How many of following compounds result cyclic anhydride on heating

tartaric acid ✓ Graphitic acid ✓

Graphilic acid ⇒





(ix) from ROSENMUND REDUCTION

$RCOCl \xrightarrow[Ba(OH)_2 \; BaCO_3]{H_2/Pd} RCHO$

except formaldehyde.

because H-C(=O)-Cl doesn't exist at experimental conditions

⇓

CO + HCl.

(X) from R−C≡N:

(A) Sn + HCl (B) $SnCl_2$ + HCl.

$-NO_2 \rightarrow -NH_2$

$-C\equiv N \rightarrow -CH_2-NH_2$

$-C\equiv N \rightarrow -CH=NH$

Imine

Stephen rxn (reduction)

$R-C\equiv N \xrightarrow{SnCl_2+HCl} R-CH=NH \xrightarrow{Hydrolysis} RCHO.$

$R-C\equiv N \xrightarrow[excess]{RMgX} R-\underset{R}{\overset{|}{C}}=N-MgX \xrightarrow{Hydrolysis} R-\overset{O}{\overset{||}{C}}-R$

(XI) BITSAT Nef carbonyl synthesis

$R-CH_2-N(=O)=O \xrightarrow{dil.\ NaOH} R-CH=N(-O-H)\rightarrow O \xrightarrow{dil.\ NaOH} RCHO$

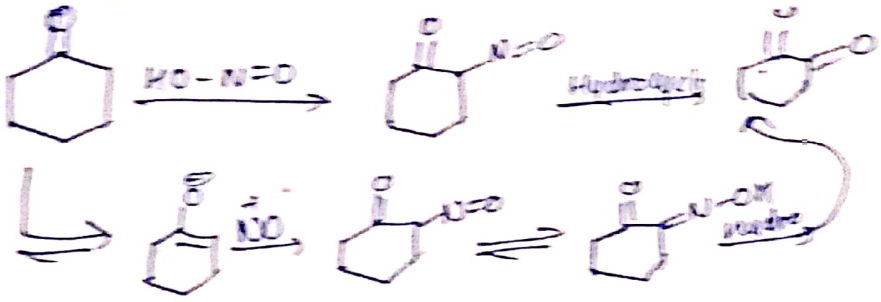
Nitro

Aci-Nitro

$R-\underset{R}{\overset{|}{CH}}-N(=O)=O \xrightarrow{dil.\ NaOH}$ Ketone

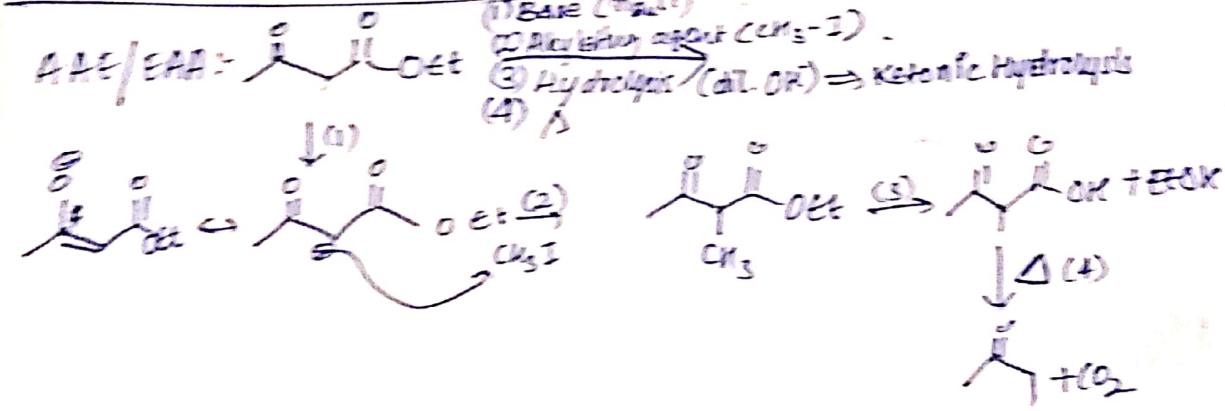
$(R)_3C-N(=O)=O \xrightarrow{dil.\ NaOH}$ INERT

(XII)

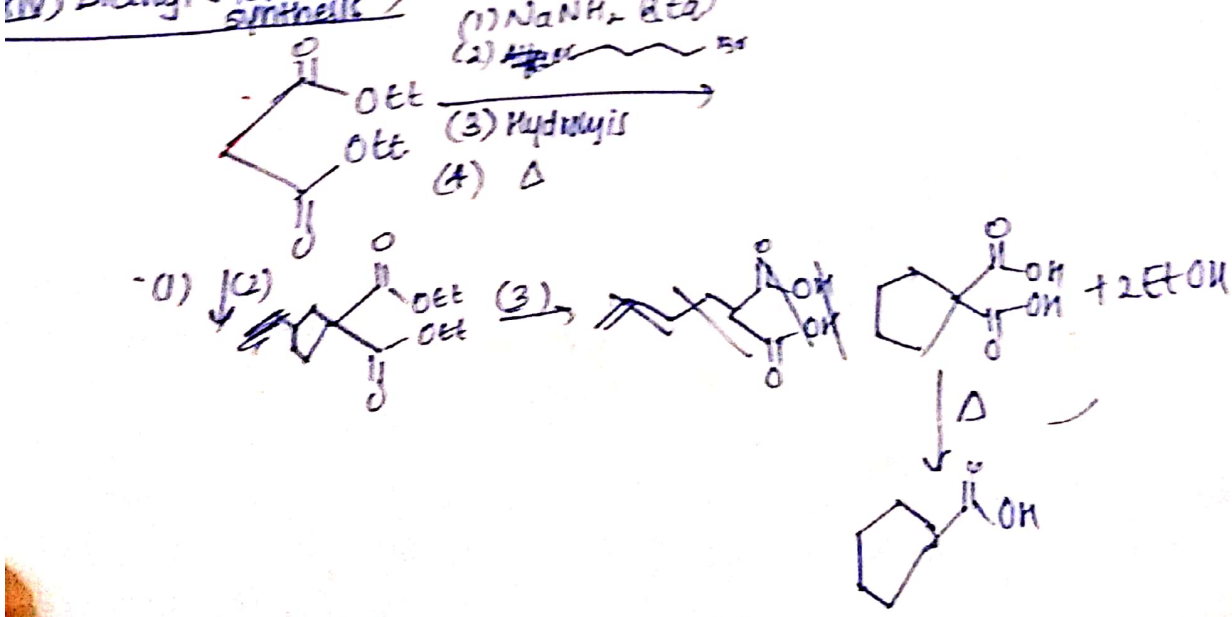


Aceto-Acetic-Ester

(XIII) Synthesis

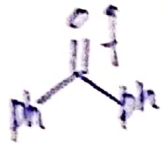


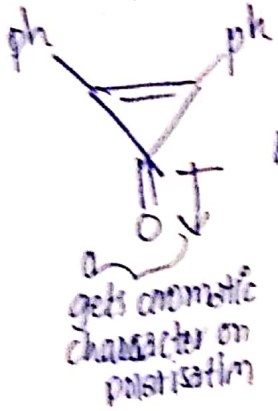
(XIV) Diethyl Glutaconate synthesis



operties of carbonyl compounds

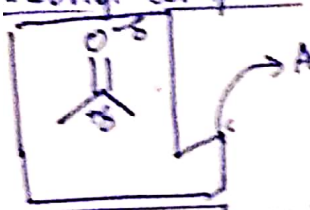
(i) μ: 3 > 2 > 1
(ii) BP: 3 > 2 > 1



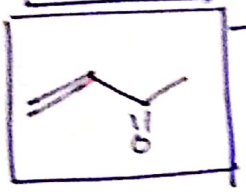


μ : 2 > 1

arbonyl comp^nd



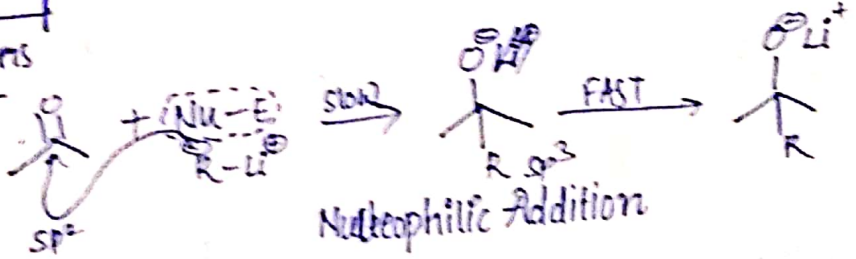
→ Ambiphile (Both as nucleophile and electrophile)



→ It is an ambient ⊖phile, not simple ⊖philes.

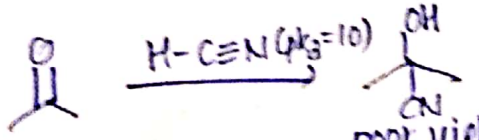
Type of rx^ns

Type①



Nucleophilic Addition

Type②

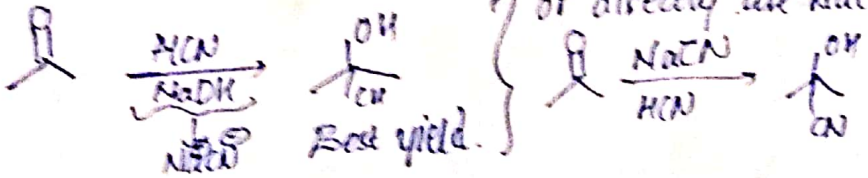


poor yield

$H-C\equiv N \rightleftharpoons H^{\oplus} + C\equiv N^{\ominus}$

K_a is low ⇒ $CN^{\ominus}$ ions conc. is low ⇒ low yield.

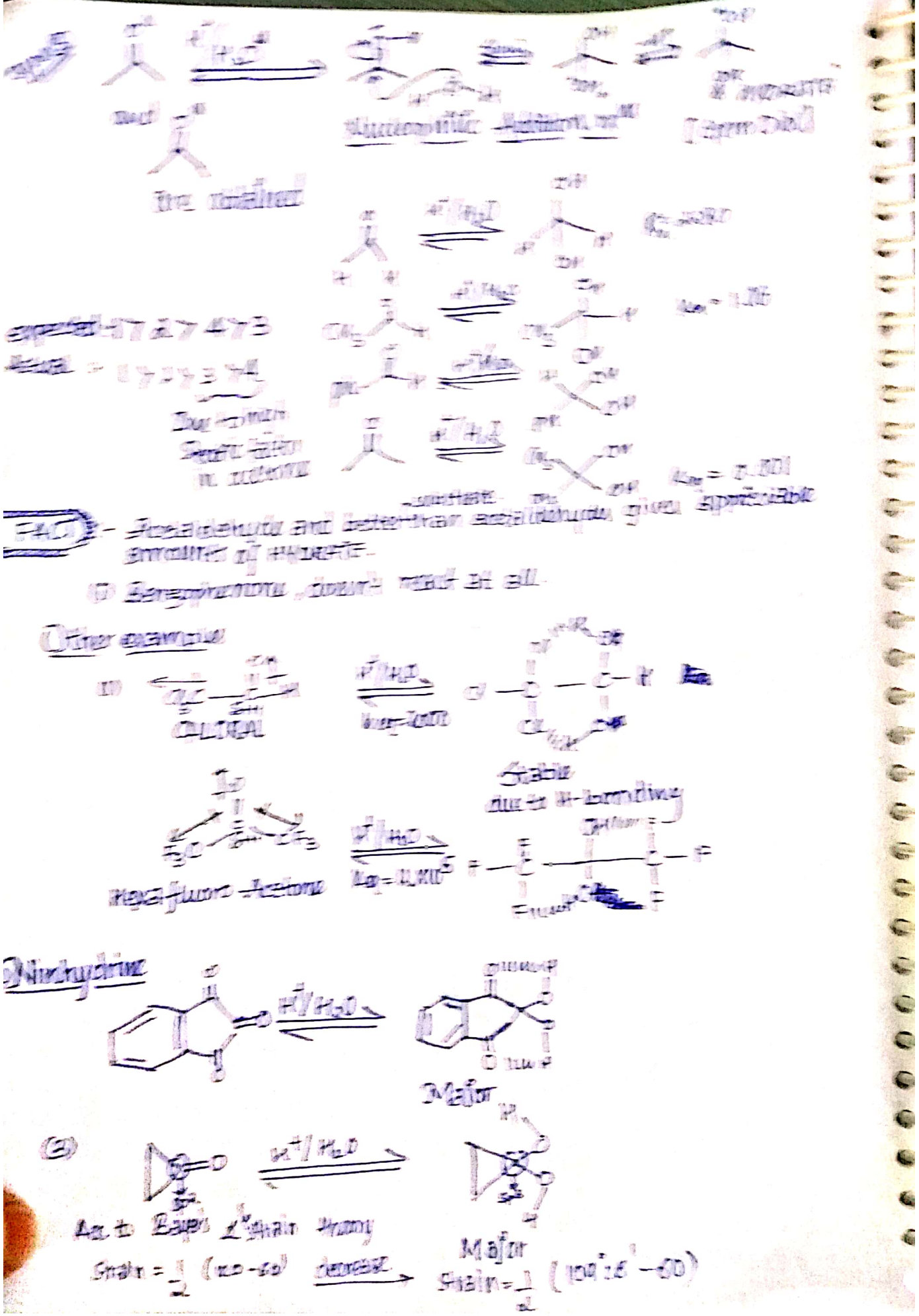
To get best yield, conduct rx^n in presence of alkaline medium



Nucleophilic Addition

Note → Benzophenone doesn't give this rx^n.

$PhCOPh \xrightarrow{HCN}$ no rx^n.

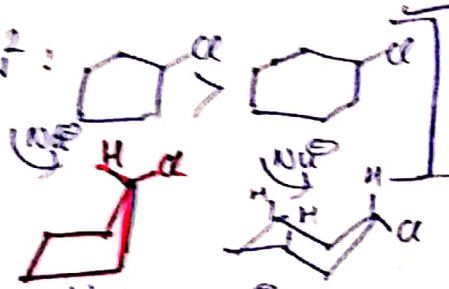


Rate of Hydrate formation :-

(i) 

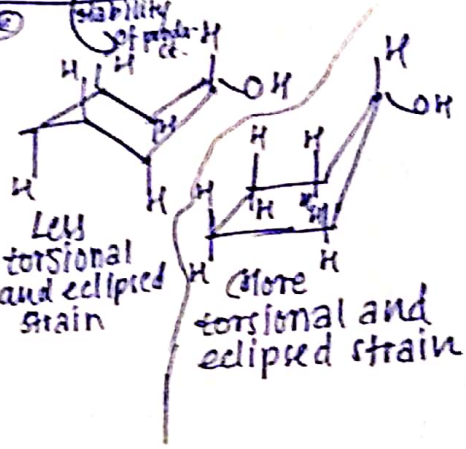
∴ Overall order of reactivity towards $Nu^{\ominus}$ Addition

S_N2 :



Approaching $Nu^{\ominus}$ doesn't have any steric.

$Nu^{\ominus}$ faces High repulsion from axial carbon



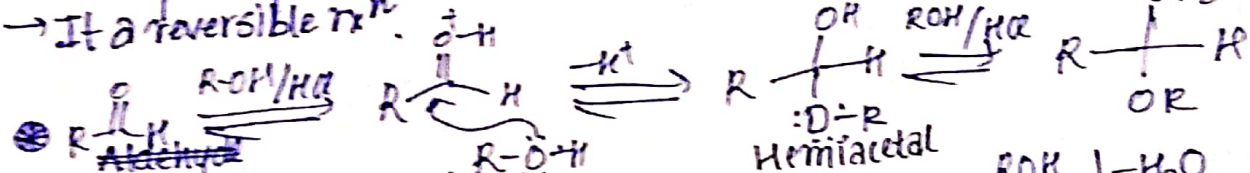
Less torsional and eclipsed strain

More torsional and eclipsed strain

Addition of Alcohols

→ Catalysed by $H^{\oplus}$ (dry HCl)

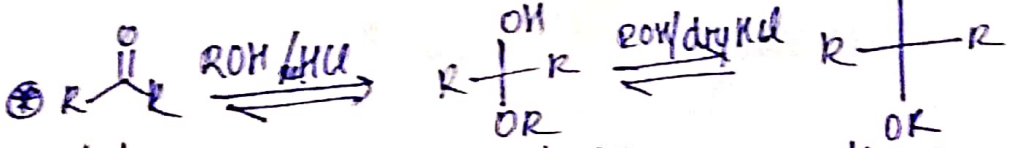
→ It a reversible rxn.



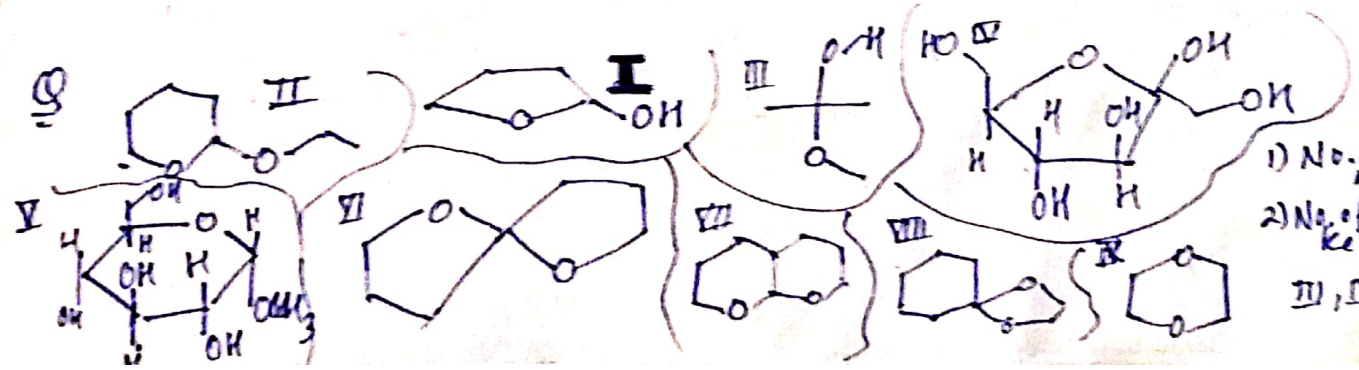
→ Forward rxn is favoured by dry HCl.

→ Backward rxn is favoured by dilute HCl

Reactant	Hemiacetal	Acetal
Aldehyde	Hemiacetal	Acetal
Ketone	Hemiketal	Ketal



Ketone Hemiketal Ketal



1) No. of ② XI, VIII

2) No. of Hemi-ketals ③

III, IV,

Note :- Now-a-days ketals are also considered as acetals and any hemiketals are considered as hemiacetals, however vice versa is not true.

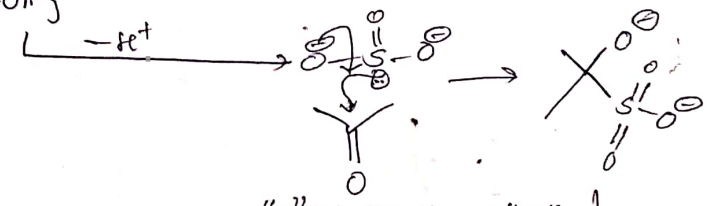
No. of Acetals in previous question :- ⑤ II, IV, VII, VIII, V

No. of hemiacetals in previous question :- ③ I, III, VI

Addition of $NaHSO_3$

Na Hydrogen sulphite

eg. Na $\ominus$ –S(=O)–OH } Ambident Nu$^\ominus$.



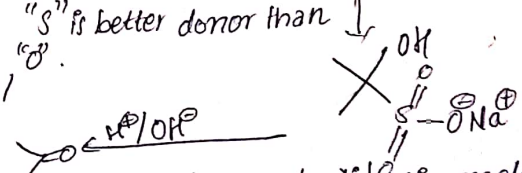
→ Reversible rxn.

→ Soluble in H_2O

→ White solid

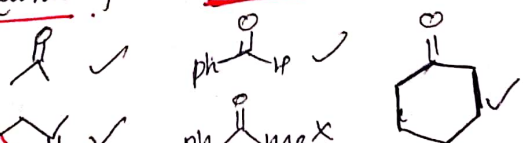
→ Advantage - used to purify carbonyl compound. Also separate carbonyl from other functional groups.

"S" is better donor than "O".



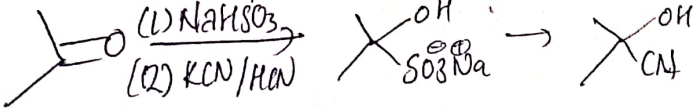
→ Nucleophile is bulkier therefore all aldehydes, and aliphatic methyl ketones, cyclic ketones from C_3–C_7 reacts with $NaHSO_3$.

Ex :-



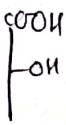
compounds giving add. prod. with $NaHSO_3$:- All aldehydes, aliphatic methyl ketones, cyclic ketones from C_3–C_7.

Another advantage :- product is readily converted to cyanohydrin upon rxn with KCN/HCN or HCN/OH$^-$.

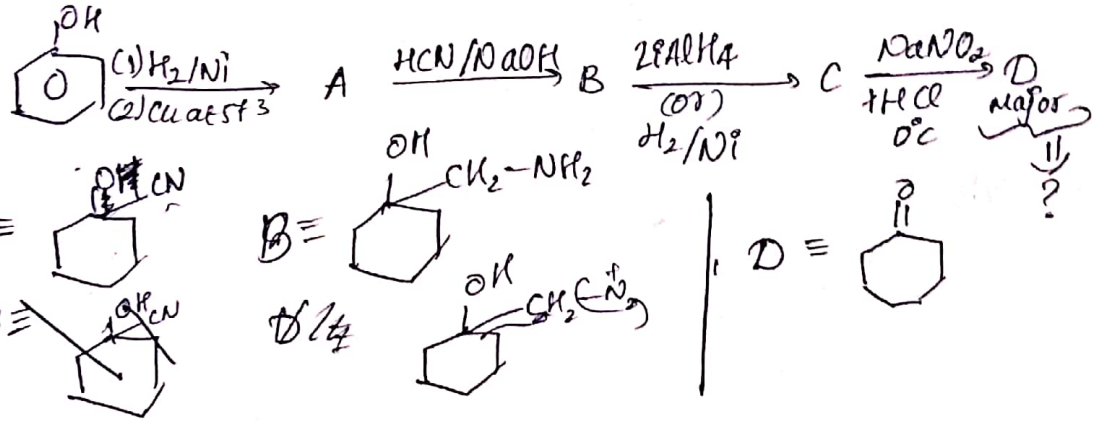


Important Questions

Q1 Carbonyl compd. $\xrightarrow[OH^-]{H-C\equiv N}$ A $\xrightarrow[\Delta]{\text{Hydrolysis}}$ B ~~lactic acid~~.

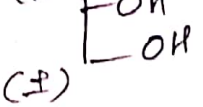


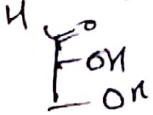
Q2



Q3

~~Acidic~~

(±) Glyceraldehyde $\xrightarrow{KCN/HCN}$  $\xrightarrow{Hydrolysis}$ x. no. of acids



$x + y = 6$

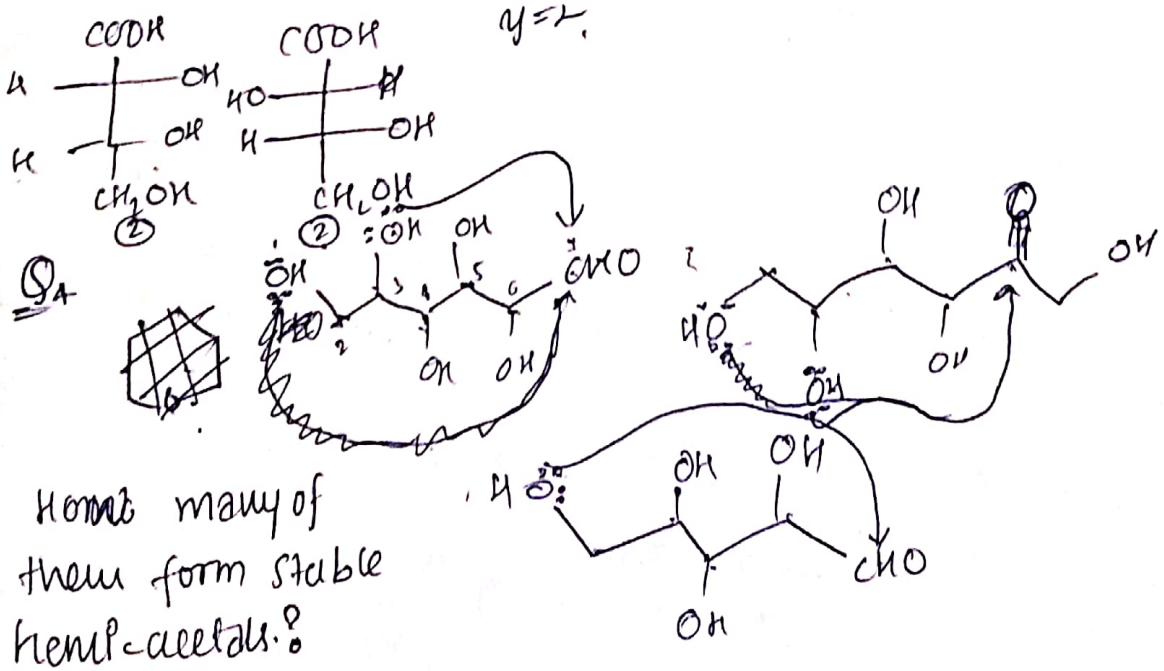
$x = 4$

$y = 2$

↓ F. Distillation

y no. of fractions

Q4

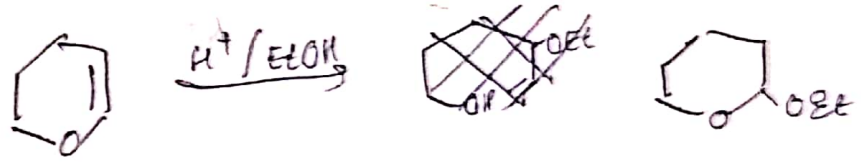


How many of them form stable hemi-acetals?

Ans:- 3

Soln:- FACT:- optically active Polyhydroxy carbonyl compds are known as carbohydrates. In nature, in aqueous soln, they exist as a cyclic 5-membered or 6-membered rings.

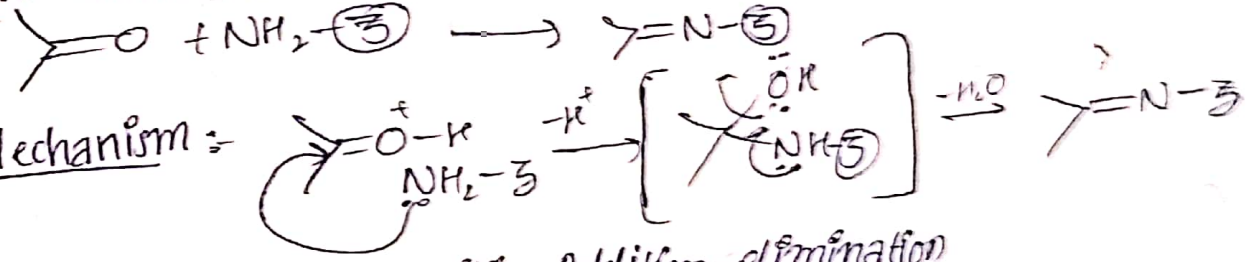
Q Product of following rxn is?



Rxn with NH_3 or NH_2-③

(i) rxn is catalysed by slightly acidic medium. (pH = 4.8 – 5.2)

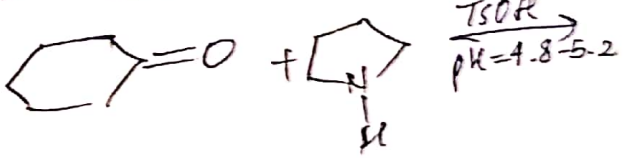
rxn with NH_2-③



Mechanism :-

Nucleophilic Addition-elimination

(ii) rxn with 2°-amine

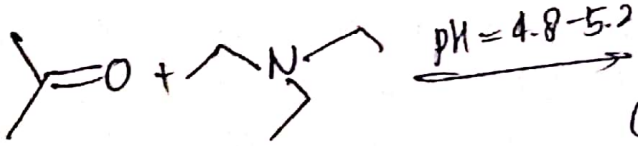


Mechanism :-

This is Stork's enamine synthesis.

NOTE :- Carbonyl compd should possess atleast one α-Hydrogen to react with 2°-amine, to form enamine. under suitable condition

(iii) rxn with 3°-amine



INERT (No rxn is observed)

In case (i)

(i) If -Z is '-H' ⟹ product is imine (>C=NH)

(ii) ~~If -Z is~~

NOTE → $NaBH_4$ reduces imine to corresponding amine.

(ii) If -Z is '-R' ⟹ product is N-alkyl imine (>C=N-R)

(iii) If -Z is '-Ar' ⟹ >C=N-Ar (N-Aryl imine).

NOTE :-

Schiff's reagent :- Generally carbonyl compⁿd. (best aromatic aldehyde) reacts with, generally primary amine (best aromatic 1° amine) to gives N-alkyl or N-aryl imine known as Schiff's base, ~~which is p~~ (pink in color) which when passed through SO_2 gas becomes colourless solⁿ, commonly known as Schiff's reagent or pararosaniline or rosaniline hydrochloride solⁿ.

Use :- To detect aldehydes only.

Observation :- becomes coloured (generally Magenta)

Exception :- Acetone shows schiff's test.

Mechanism:-

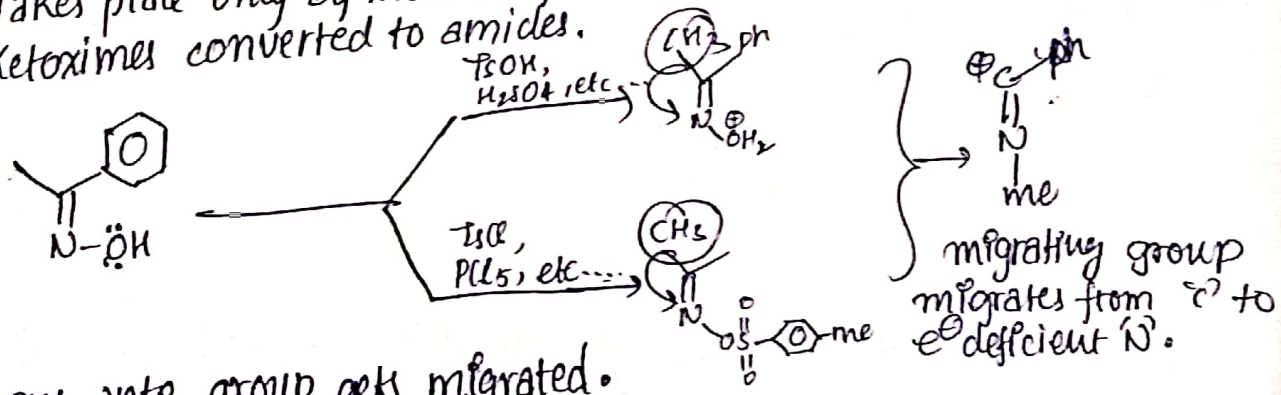
(viii) if $\exists \equiv -OH \Rightarrow$ Hydroxylamine $\Rightarrow$ oxime

NOTE:- (i) ~~symmetrical~~ symmetrical aldoximes and ketoximes doesn't exhibit Geometrical isomerism.

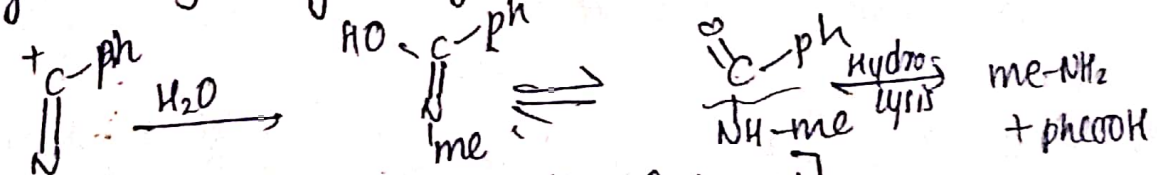
Q i. Simple aldehyde and its Homologous aldehyde treated with Hydroxylamine under suitable conditions results 3rr. no. of oximes.

Beckman's rearrangement

(i) 100% stereospecific.
(ii) Takes place only by means of acid catalyst.
(iii) Ketoximes converted to amides.

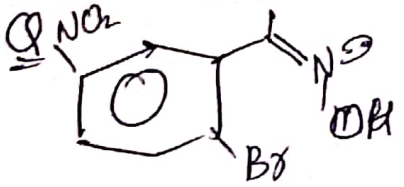


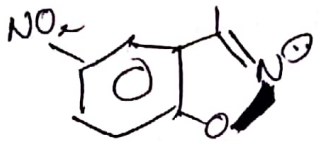
* Always ante group gets migrated.



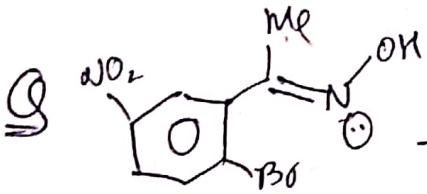
[external water is faster than internal]

In basic medium -OH becomes $-\overset{\ominus}{O}$, i.e., resonance enhances and rxn. doesn't happen, i.e., rearrangement doesn't take place.



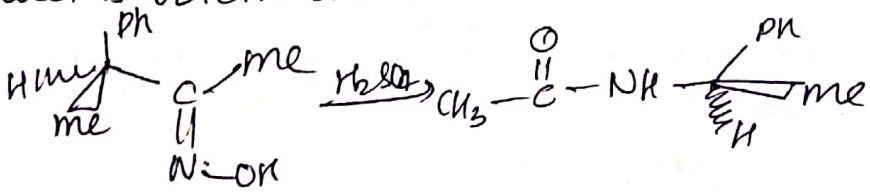


∵ SNAr (Add–Elim.)



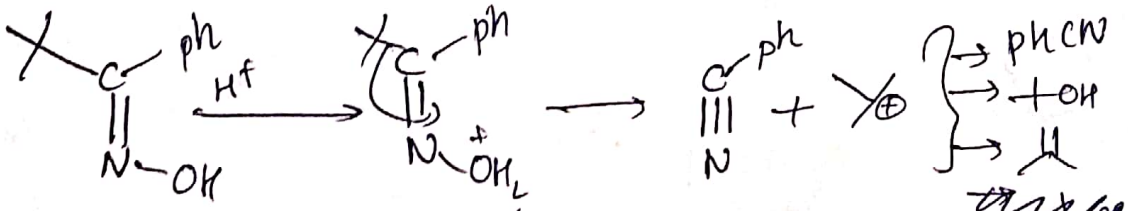
No cyclization takes place
(Nucleophile is not in suitable orientation)

NOTE :- It is intramolecular rearrangement.
∴ product is obtained with 100% retention.



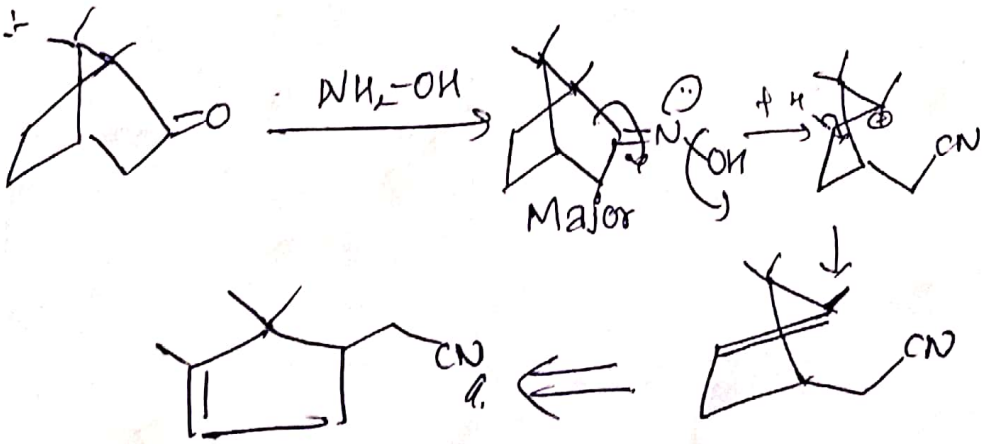
Abnormal Beckmann Rearrangement

If ante group is ~~H~~, instead of group migration,

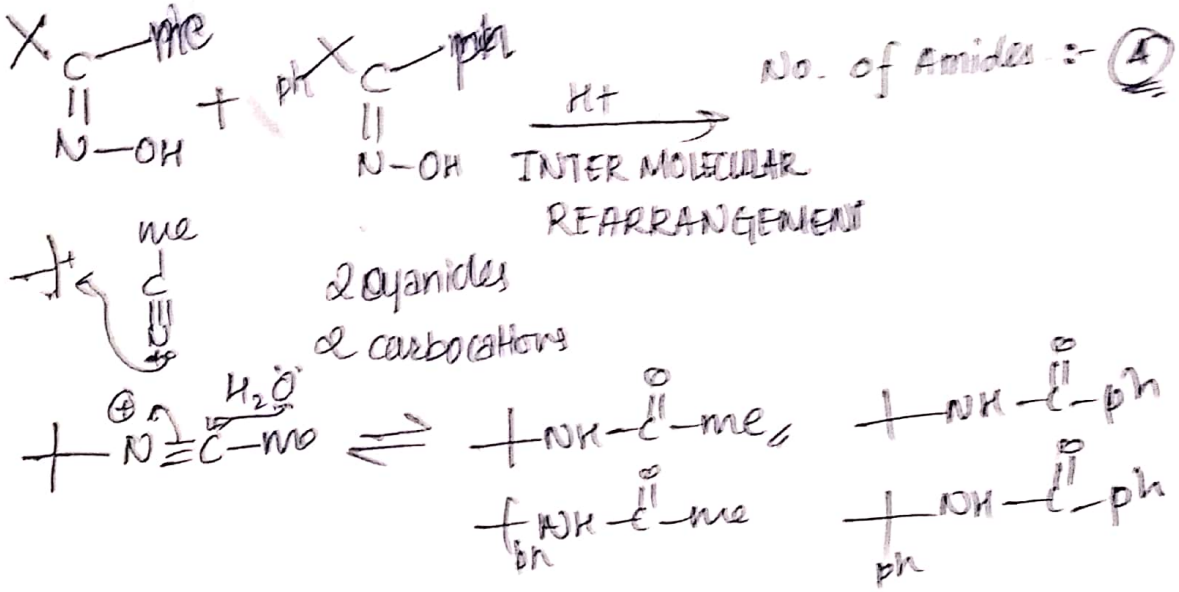


Group · bond gets collapsed.

Best example :-

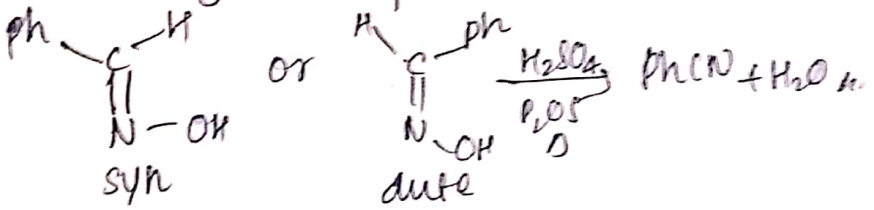


Q

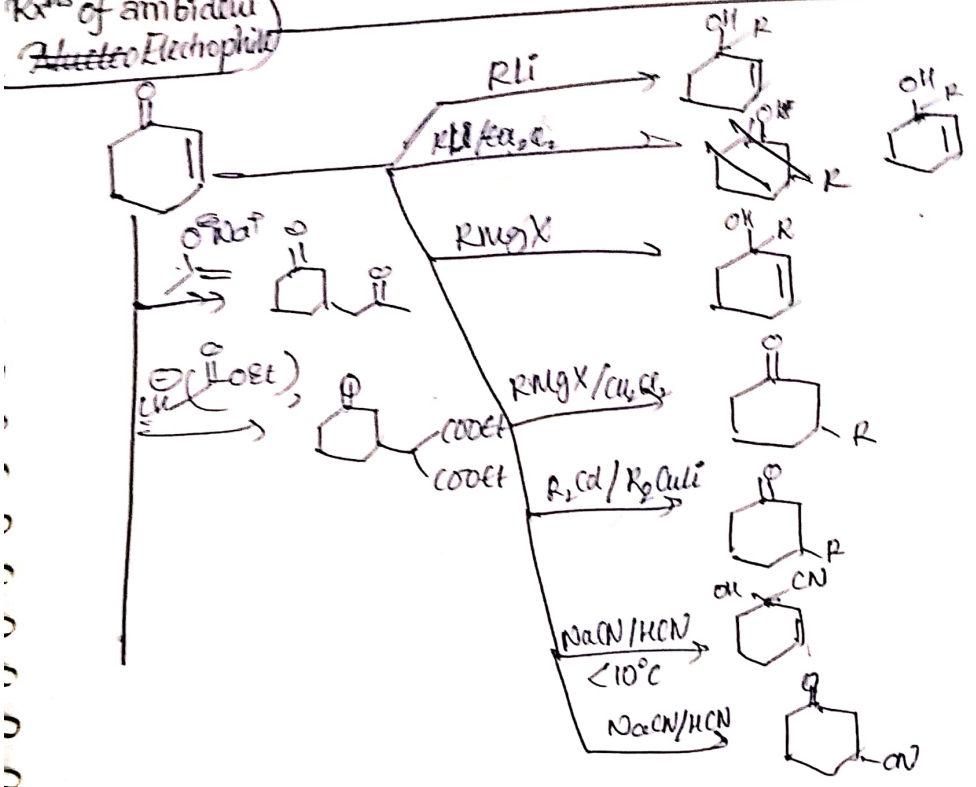


No. of Amides :- (4)

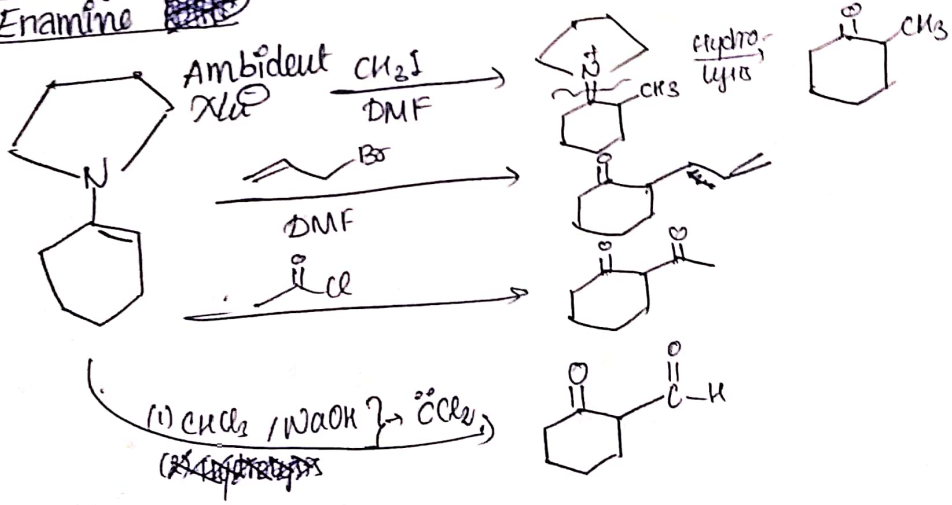
NOTE :- Aldoximes doesn't give Beckmann's Rearraugement, because irrespective of their configuration C-H bond becomes more polar, gets dehydrated.

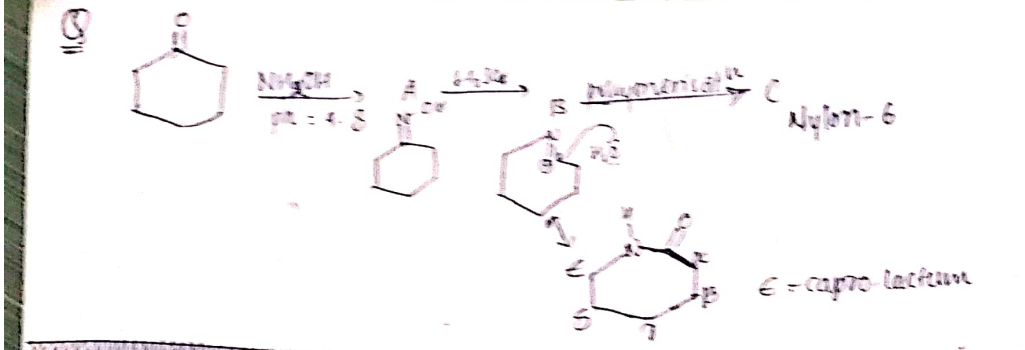


Rxns of ambident ~~Nucleo~~ Electrophile



Properties of Enamine





Detection of carbonyl comp^{n}

(i) → Using 2,4-DNP (Brady's reagent) (Borche's reagent)

All carbonyl compⁿ give either yellow color or orange color or red color solid.

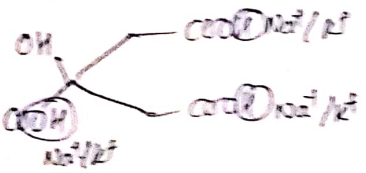
(ii) → Schiff's test

+ve for all aldehyde and acetone give this test.

colorless sol^{n} ⟷ Magenta colored.

(iii) → Benedict's test

⊕ Mixture of aqueous $CuSO_4$ and Na^+K^+ citrate.

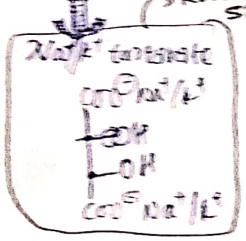


(iv) → Fehling's test

Fehling's sol^{n} : mix of Fehling's A + Fehling's B

Fehling's A → $CuSO_4$

Fehling's B → Rochelle salt → Na^+K^+ tartarate



Function :-

(i) Both Benedict's and Fehling's tests function the same.

(ii) All aliphatic aldehydes (–CHO) oxidized to corresponding $-COO^-Na^+/K^+$

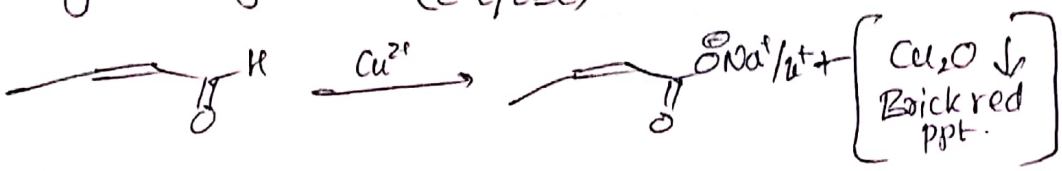
$-CHO \xrightarrow{Cu^{2+}} -COO^-Na^+$ Cu_2O ↓ Brick red ppt.

Observation :- Brick red ppt. (Cu_2O) is generated.

NOTE :- Benzaldehyde doesn't give this test.

(iv) Ph-CH_2-CHO ⇒ Aliphatic aldehyde ⇒ +ve test results.

⇒ During Fehling's test, unsaturat^n doesn't get spoiled. (C=C/C≡C)

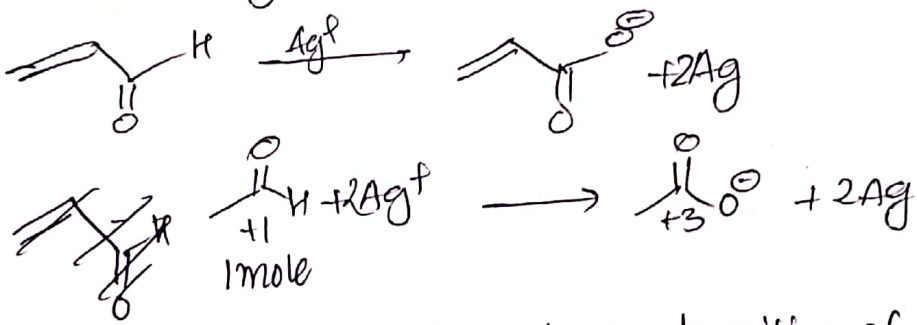


(v) Tollen's test

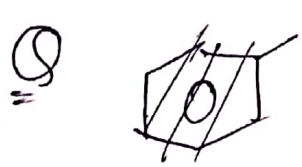
⇒ Tollen's reagent ⇒ Ammonical silver Nitrate sol^n

$[Ag(NH_3)_2]^{+1}$ (or) moist Ag_2O (or) Ag^{+1}

Function : All aldehydes gets oxidised to carboxylic acid salts without affecting unsaturat^n.



Observat^n :- If Formation of silver mirror due to deposition of Ag (s) thus we say it gives +ve test.



(A)

$CH_3-C\equiv C-H$ (B)

(i) 'A' and 'B' are distinguished by Tollen's reagent. ~~False~~ True

A → silver mirror

$CH_3\equiv C^{\ominus}Ag^{\oplus}$ ← B

white ppt.

(ii) 'A' and 'B' are distinguished by Fehling's sol^n. True

A $\xrightarrow{Cu^{2+}}$ Cu_2O ↓ Brick red ppt.

B $\xrightarrow{Cu^{2+}}$ Inert

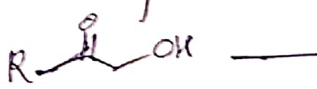
(vi) Common reports for above ~~two~~ three reagents.

(a) HCOOH $\xrightarrow{(O)}$ CO_2 and Cu_2O ppt (or) Ag mirror

(b) For all ketones show (-ve) test.

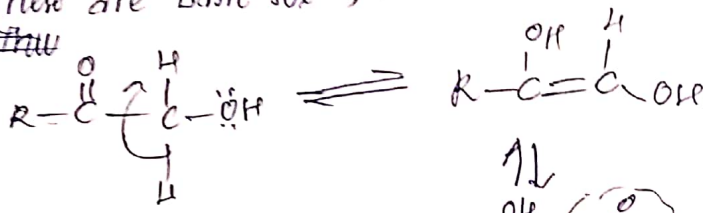
(c) ~~Few~~ Aldehyde

(c) Few α-hydroxy ketones :-



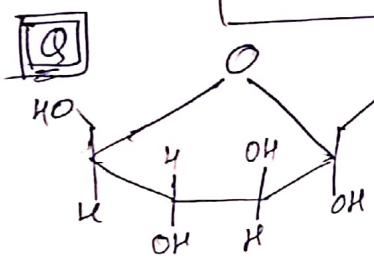
→ +ve test

Explanation :- These are basic soln, which favour tautomerism

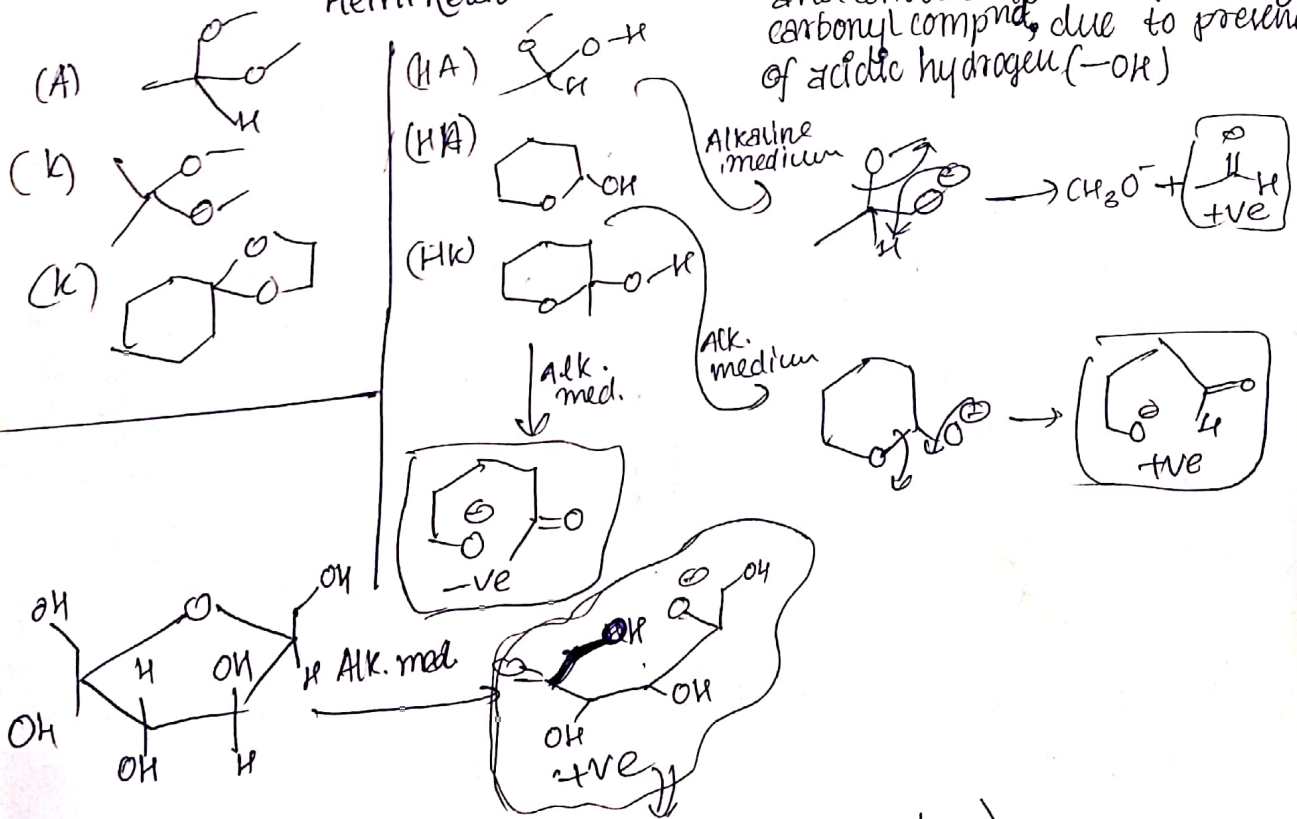


Ans ⇒ +ve test

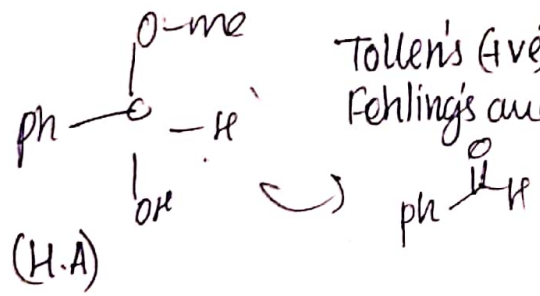
Explanation :- Acetals and ketals are stable in basic soln, whereas hemiacetals and hemiketals are unstable in basic soln, they get destroyed and converted to corresponding carbonyl compnd, due to presence of acidic hydrogen (–OH)



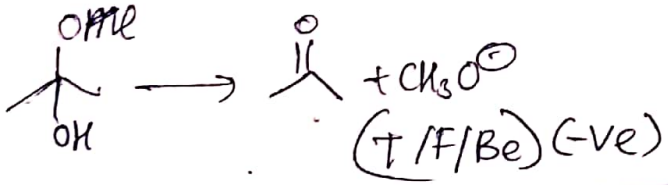
Hemi Ketal



(Because of α-hydroketone's tautomerism to aldehyde)

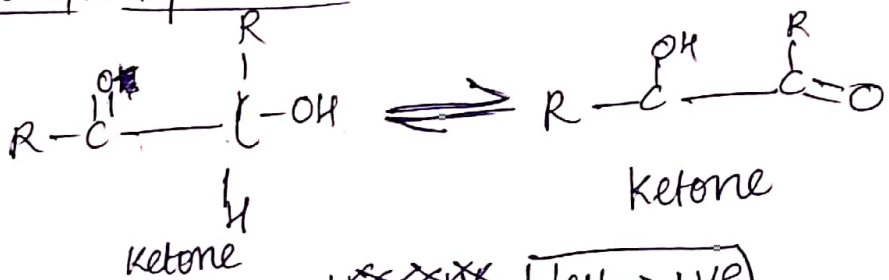
Q 

Tollen's (+ve)
Fehling's and Benedict's (-ve)
(H.A)

Q 

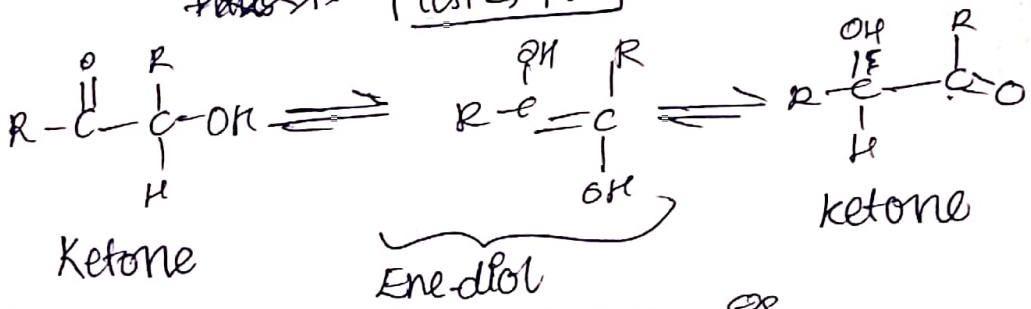
(T/F/Be) (-ve)

(α) Few hydroxy Ketones.

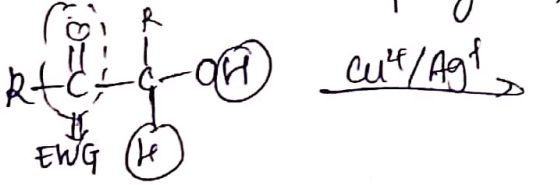


test ⇒ +ve

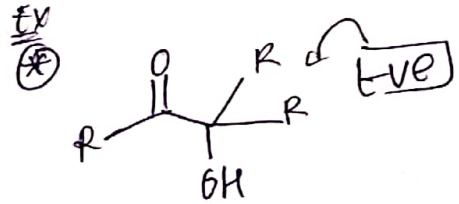
Explanation :-

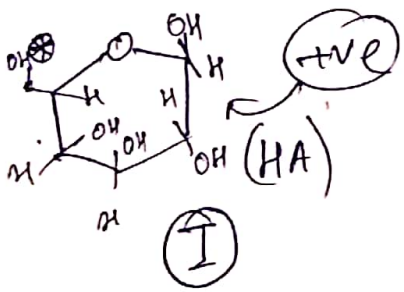


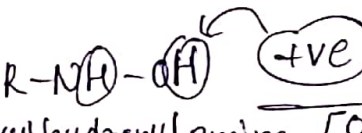
Due to active Hydrogens, they simply lose the e⊖s.



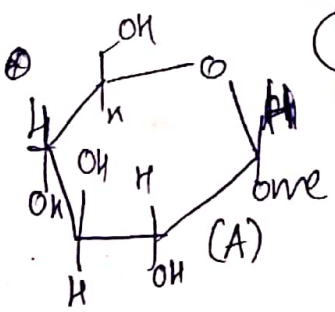
Ex

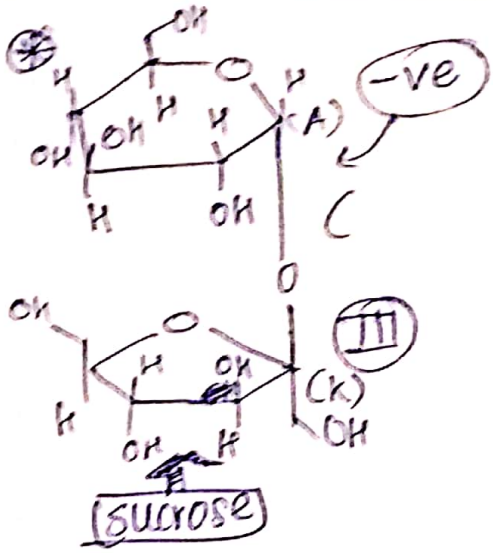


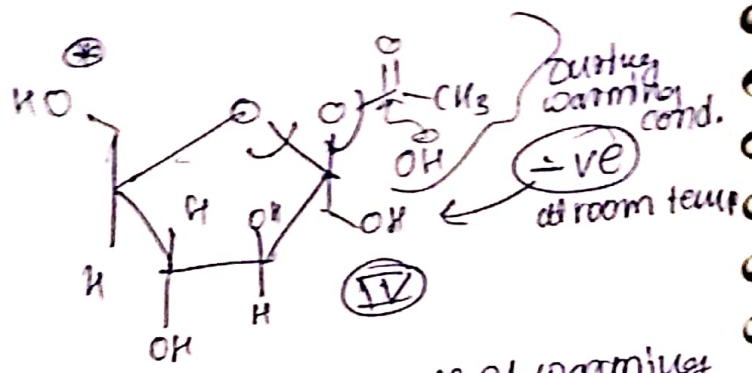




(Due to active sites)



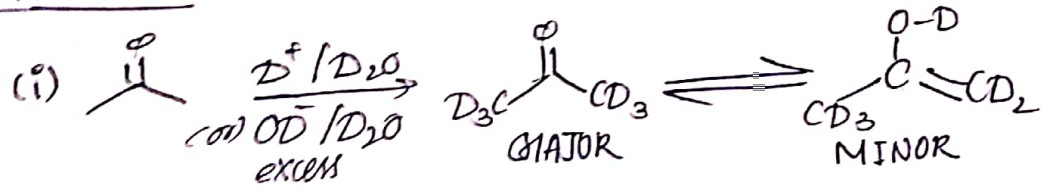




⇒ -ve at room temp, +ve at warming condition.

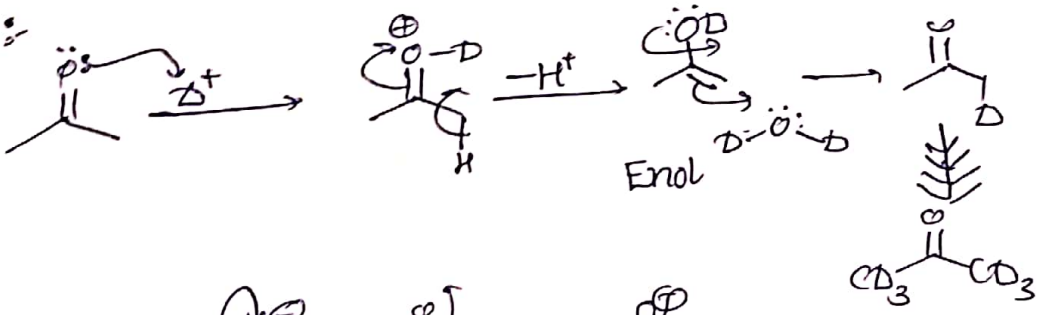
Rxns of carbonyl compds due to α-Hydrogen

Tautomerism

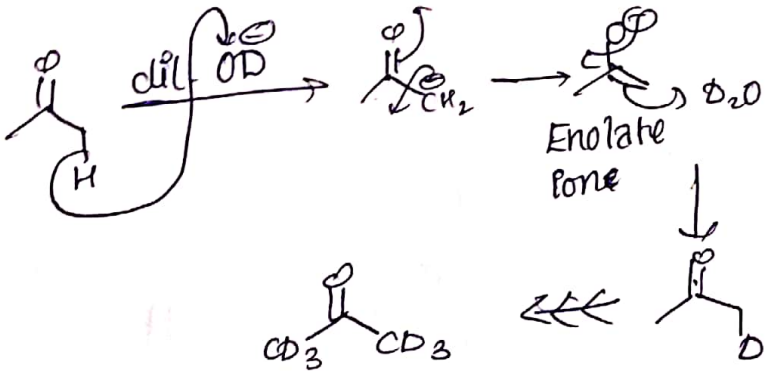
(i) 

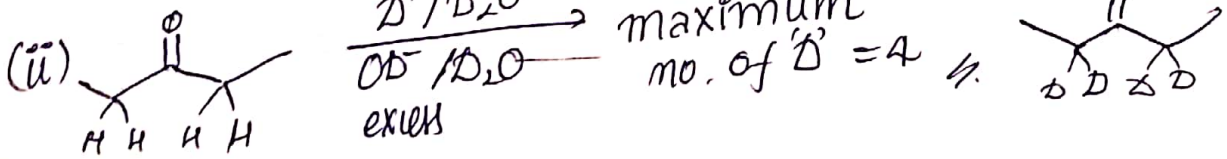
MECHANISM :-

In Acidic medium

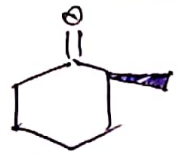


In basic medium



(ii) 

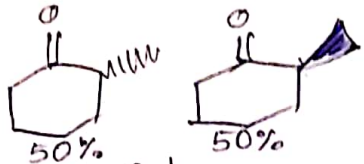
(iii)



optically pure

dil. NaOH

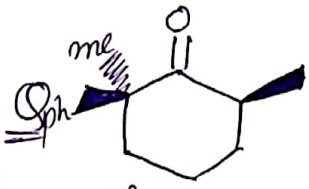
After long time product is?



50% 50%

Ans:- Racemised mixture (±)

Due to formation of enolate ions.



optically pure

dil. NaOH

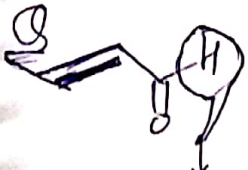
After long time product is? at room temp

'x' no. of products $\xrightarrow{\text{fractional distillation}}$ 'y' = 2x fractions

= 2

Diastereomeric pairs.

x + y = 4.



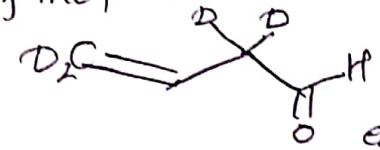
doesn't get replaced (no participation in resonance)

$\xrightarrow[\text{(Room temp) long time}]{OD^-/D_2O \text{ (excess)}}$

maximum no. of D's = 4

and

one of the product



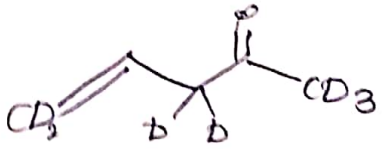
explain

$\xrightarrow[\text{excess}]{OD^-/D_2O}$

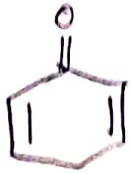
maximum no. of D's = 7

And

one of the product is

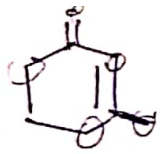


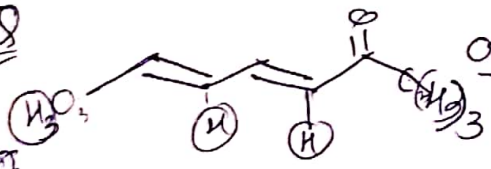
explain



$\xrightarrow{D^+/D_2O}$ maximum no. of D's = 4.

Why not '5' or '7'?

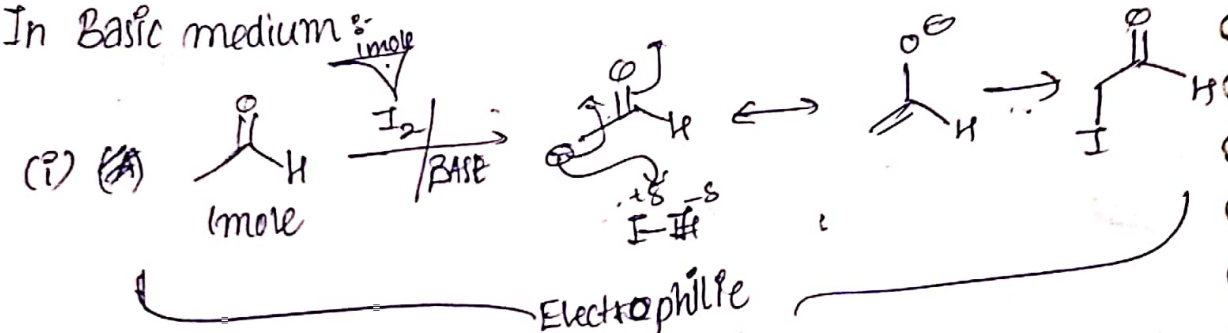
Q  OD^-/D_2O → Max. no. of D's = 8

Q  OD^-/D_2O → max. no. of D's = 8

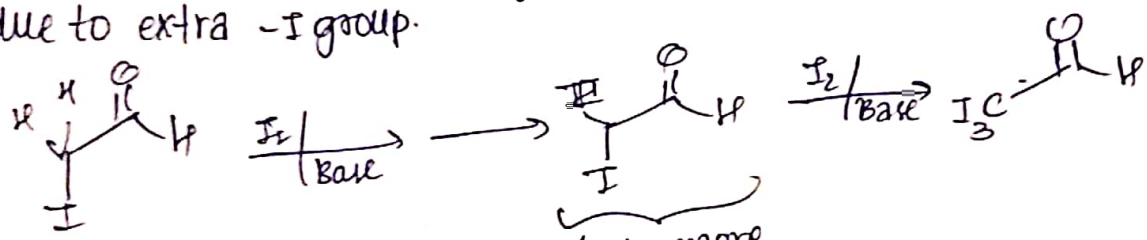
Q

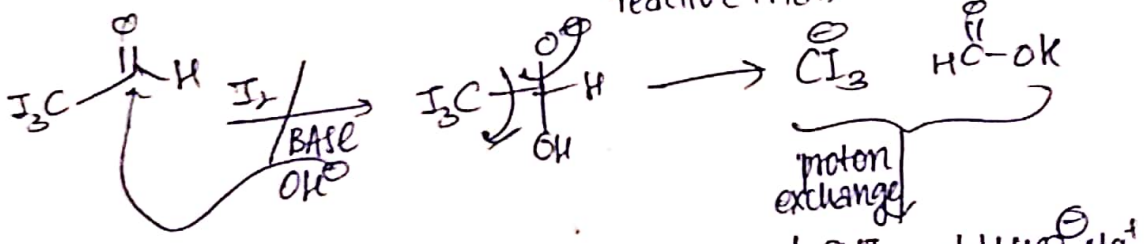
2 Halogenation

Case (I) In Basic medium :-

(i) 

product is possessing more acidic hydrogen due to extra -I group.

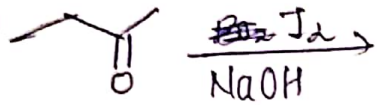


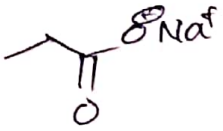


∴ products are :- $\frac{1}{3}$ mole iodoform

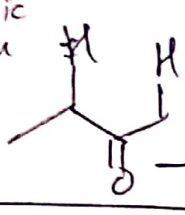
$+\frac{2}{3}$ mole of

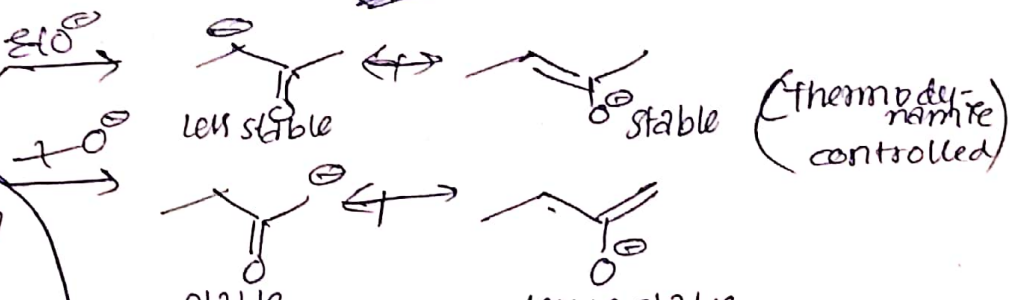
$+\frac{1}{3}$ mole of $HCOO^\ominus Na^\oplus$

(ii) 

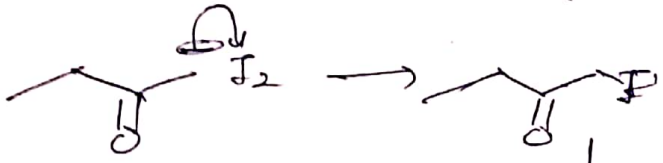
$CHI_3\downarrow$ + 

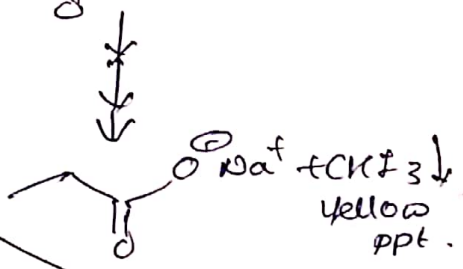
yellow ppt.

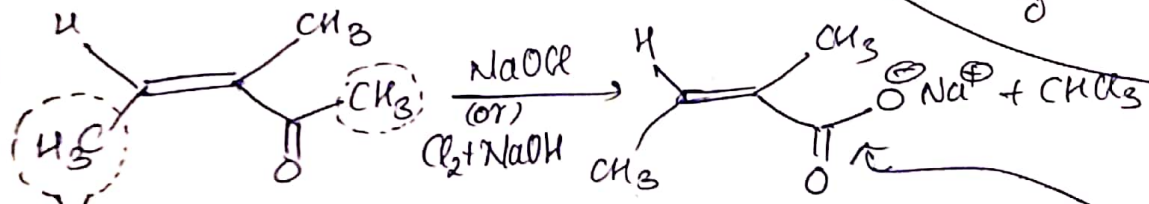
In basic medium 



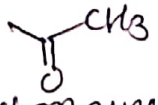
⊖ Which side -I goes in basic medium?
** Always towards $-CH_3$ side



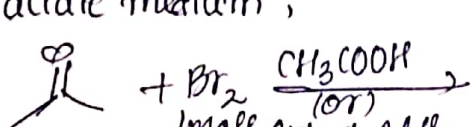


(iii) 

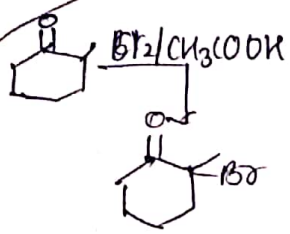
most acidic

(i) But  only gets halogenated
(ii) No effect on unsaturation
(iii) The product is

case(2) In acidic medium,

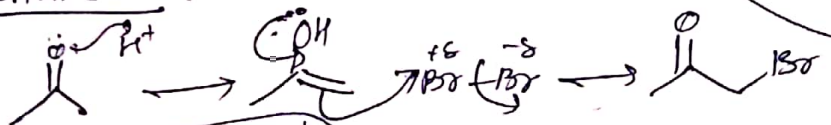


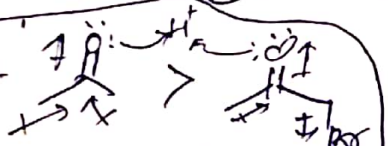
1mole 1mole



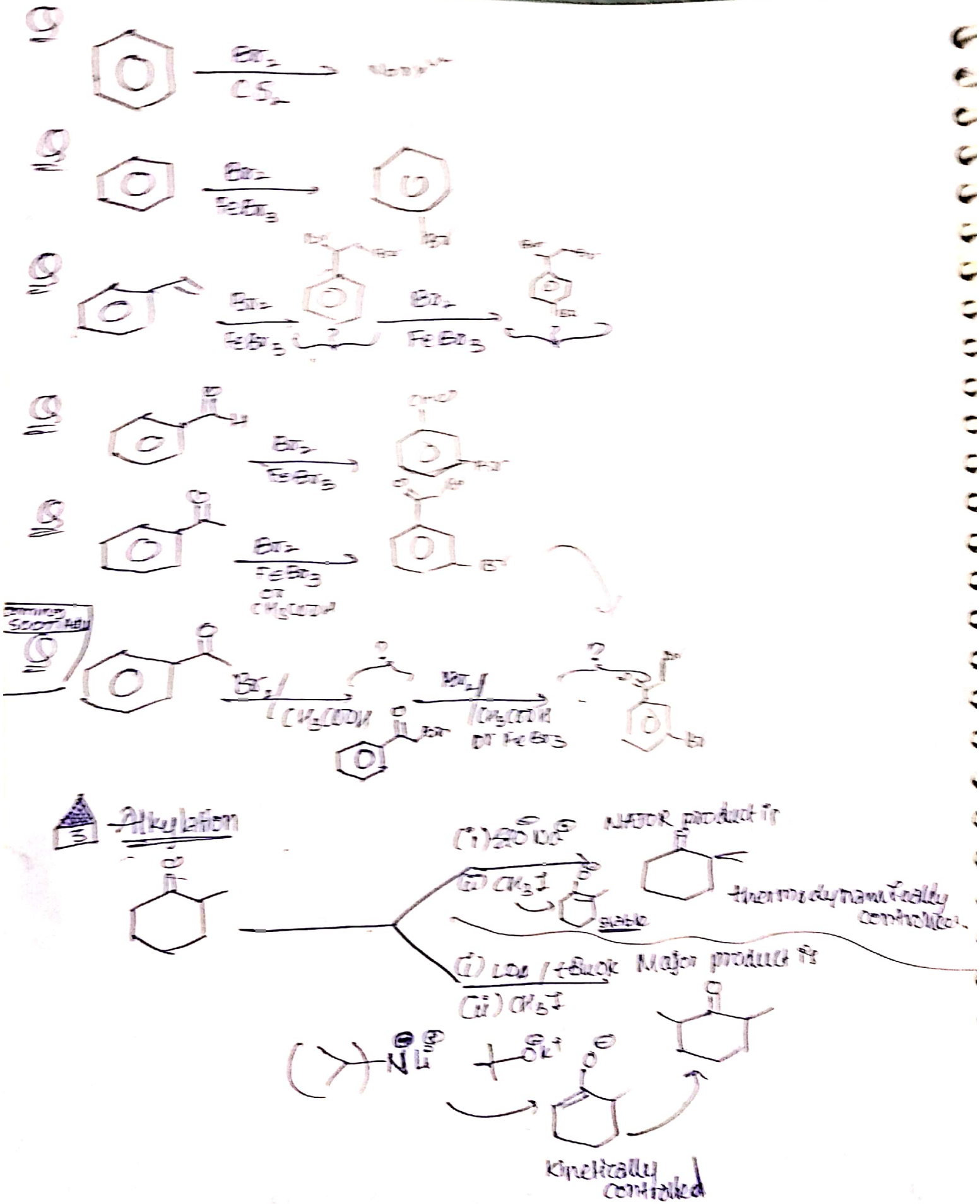
Major

MECHANISM :-

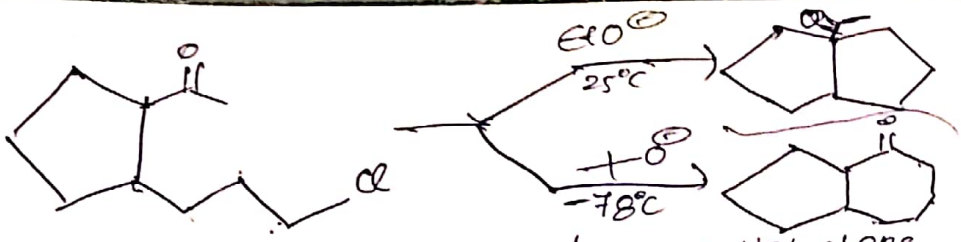


DONOR :- 

Due to less donating ability new reactant molecule reacts rather than formed product molecule.

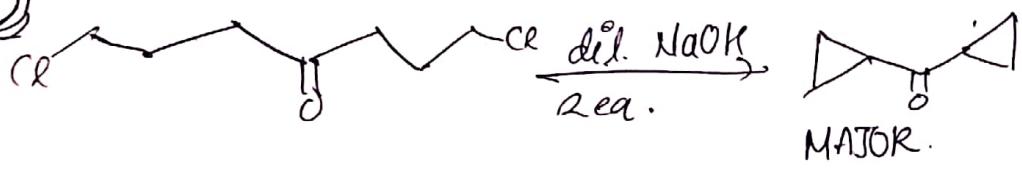


Q Forming room Advanced



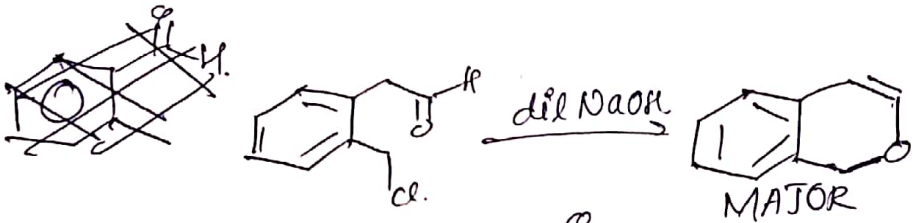
propose major products and sequential steps-

Q



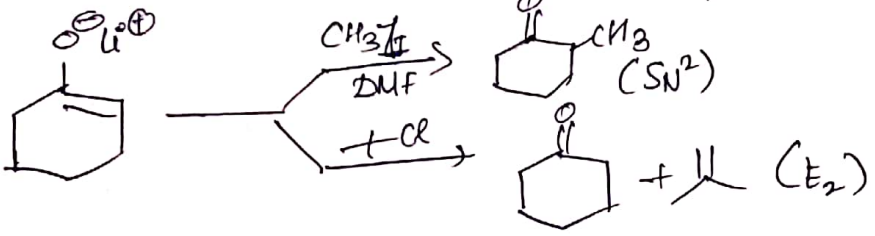
MAJOR.

Q



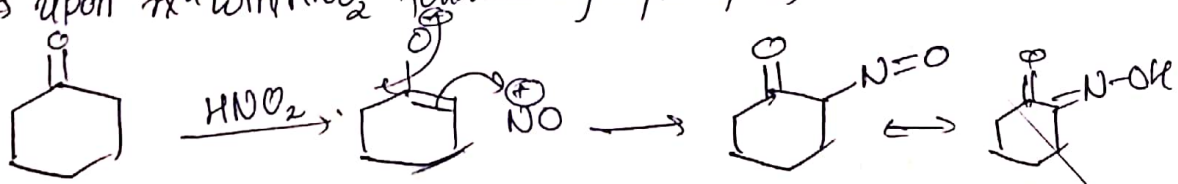
MAJOR

Q



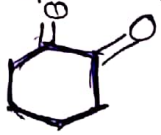
4 carbonyl to di-carbonyl

⇒ upon rxn with HNO_2 followed by hydrolysis, gives



dicarbonyl compound by nitrososation.

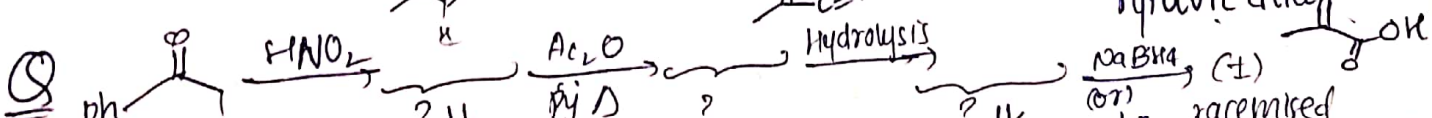
Hydrolysis



Q

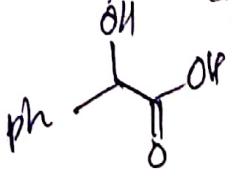
Pyruvic acid

Q



racemised product ___?

Mandelic acid



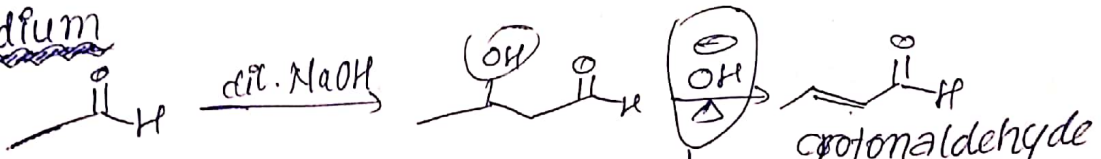
5 Aldol rxn and Aldol condensation

⇒ β-hydroxy aldehydes is known as aldol.
⇒ β-hydroxy ketones are known as ketol.
⇒ Now-a-days, ketol are also considered as aldol but vice versa not true.
⇒ Rxn is catalysed (or) takes place either by means of dilute acid or by means of dilute base.

dil. H_3O^+	dil. OH^-
↳ dil HCl, dil H_2SO_4 etc.	↳ dil KOH, dil. NaOH, dil $Ba(OH)_2$, dil Na_2CO_3

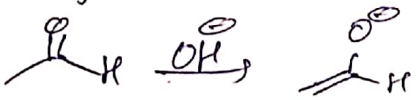
case(A)

Basic medium

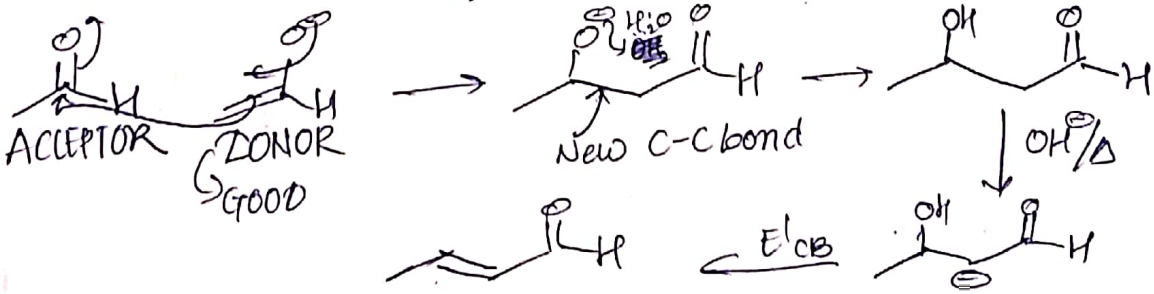


MECHANISM

(i) - formation of enolate ion. (ambident Nu$^{\ominus}$)



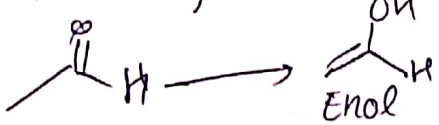
(ii)



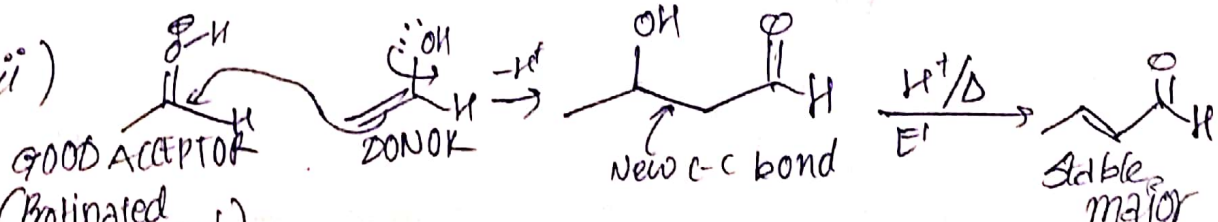
NUTE:-

case (B) In acidic medium,

(i) formation of enol (DONOR)

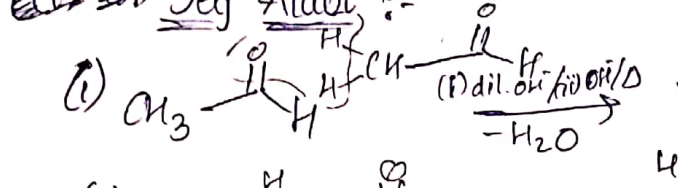


(ii)

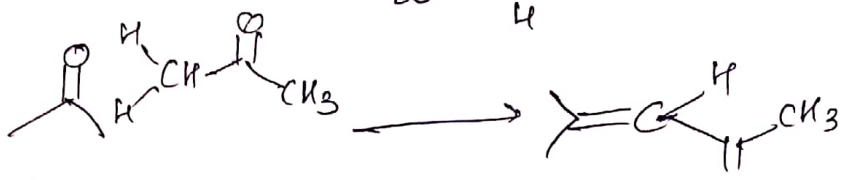


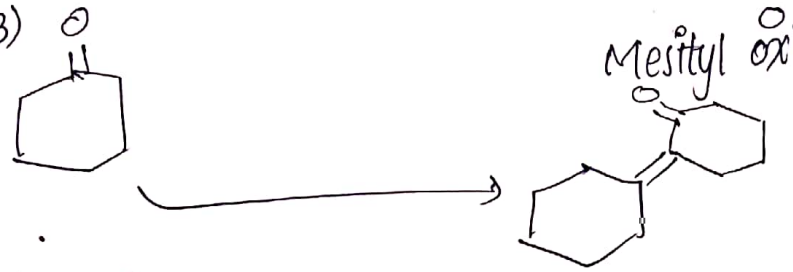
Aldol rxns are of 3 types:-

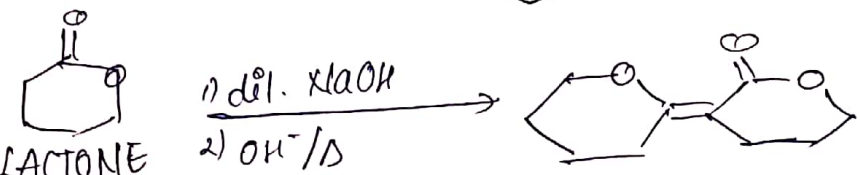
(i) Self Aldol :-

(1) 

crotonaldehyde

(2) 

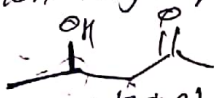
(3) 

(4) 

(ii) crossed Aldol

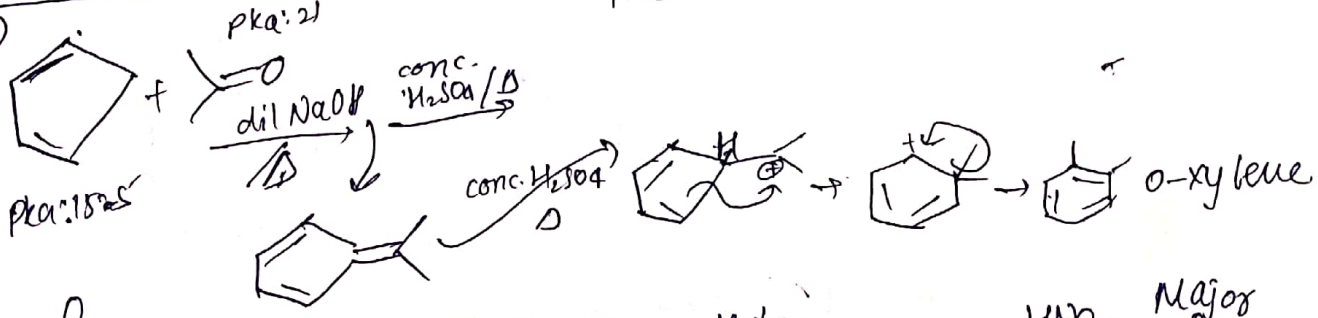
(1) 

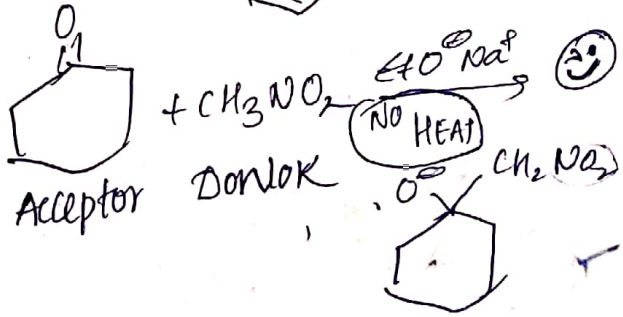
(a) No. of ketols :- 3 (including stereo).
(b) No. of aldols :- 6 (including ketols)
(c) If eqs are leq. and leq, then major product is:

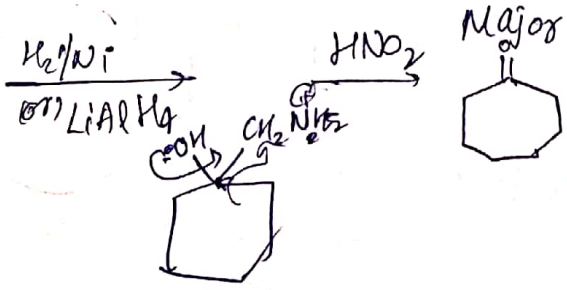


Because acceptor should be stearically free.

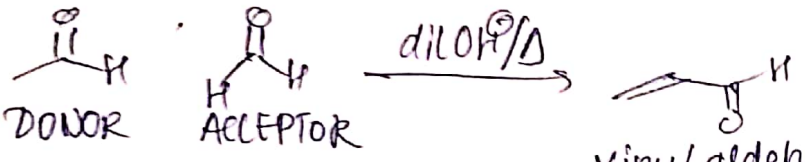
If both are carbonyls best acceptor is imp. if both are diff. most acidic one is donor.

(2) 

(3) 



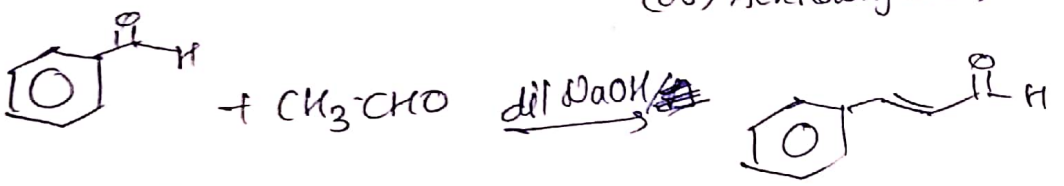
(4)



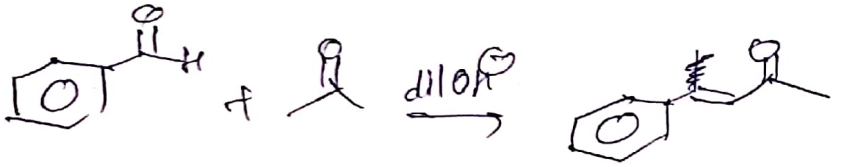
DONOR ACCEPTOR

Vinyl aldehyde
(or) Acraldehyde (or) Acrolein.

(5)



(6)



In (5) and (6) type, heat may be there or may not be there dehydration is most common due to more conjugation.

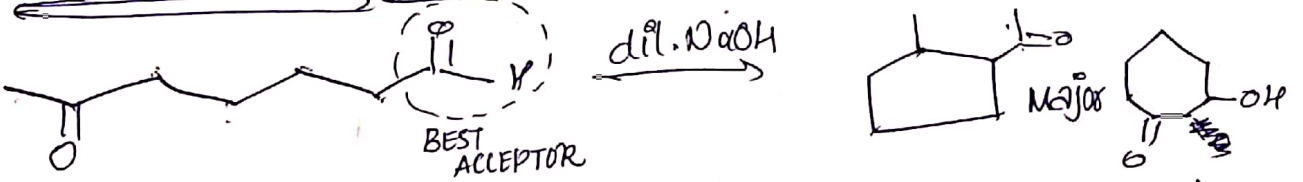
NOTE:- Schmidth
Claisen-~~Smith~~ rxn

If acceptor is benzaldehyde in aldol rxn those rxns are called claisen-schmidth rxn.

Ex:- (5) and (6)

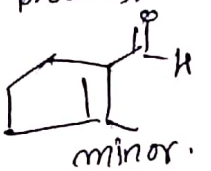
(iii) Intramolecular Aldol.

(A)

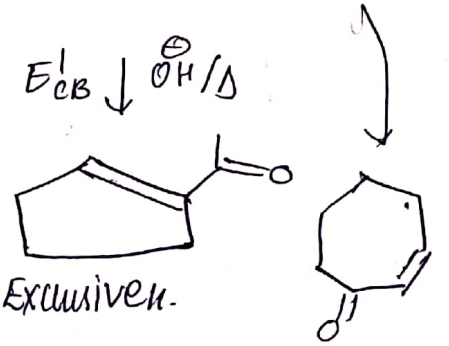


NOTE :- smeubered > 6 > 7
ease of formation of ring in intramolecular aldol.

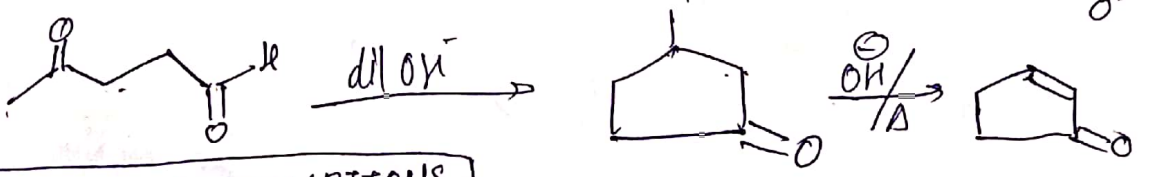
Other minor products.



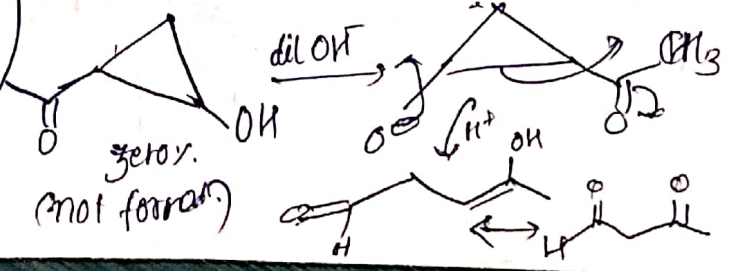
minor.



(B)

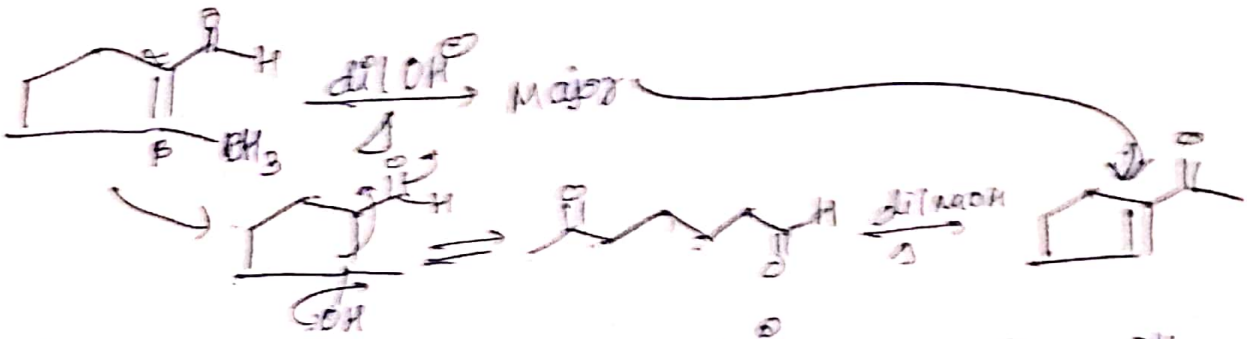


NOTE :- OTHER RING FORMATIONS ARE NOT ~~FORM~~ OBSERVED (i.e, only 5,6,7)

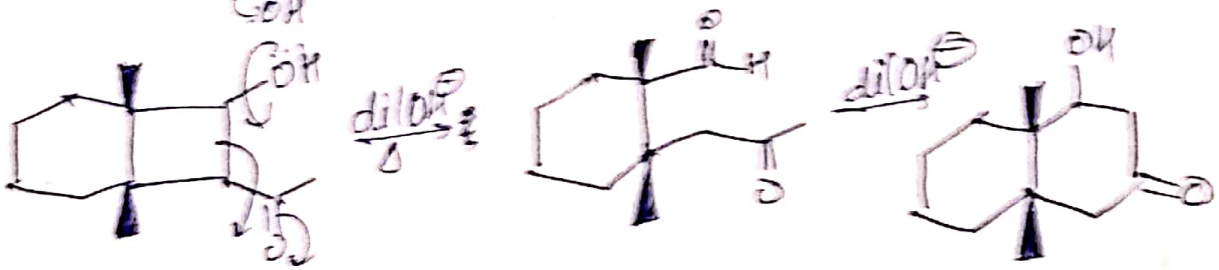


⟹ In Aldol rxn, always products maintain equilibrium with reacts.

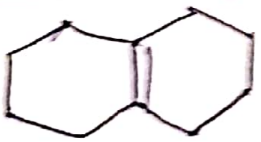
Q1



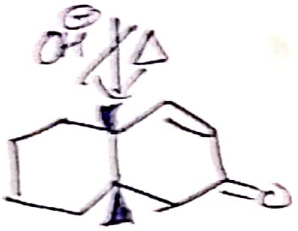
Q2



(c)

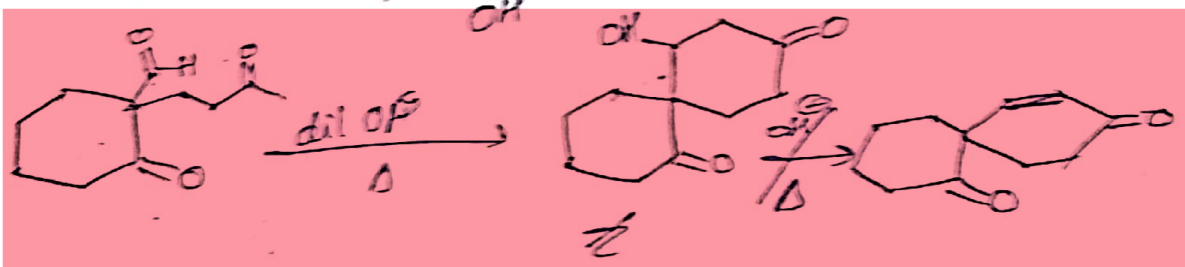


How many aldol condensation products are formed? Ans ①

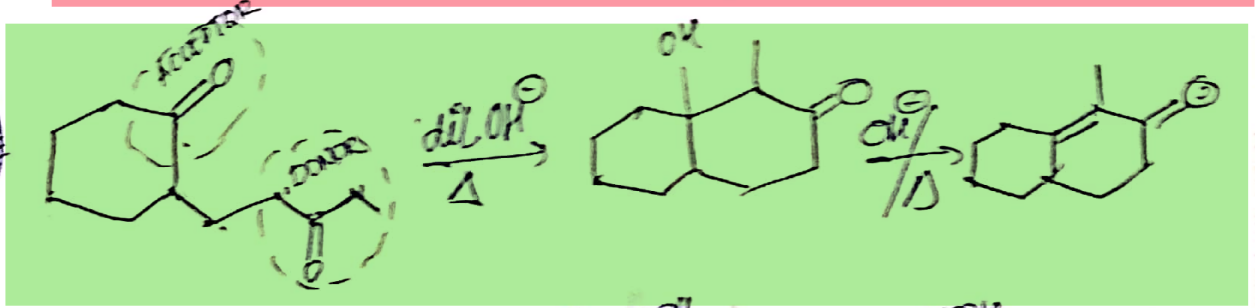


(b)

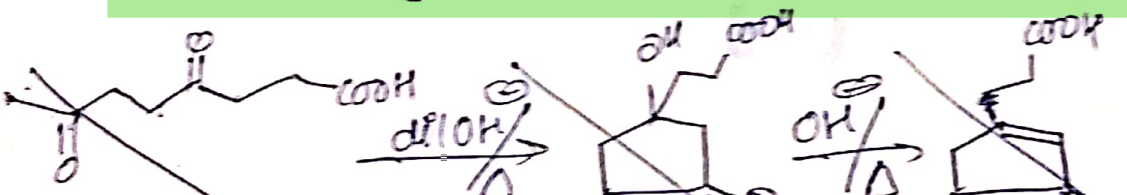
(d) Comp. Sec. Advanced



(e) Advanced Q

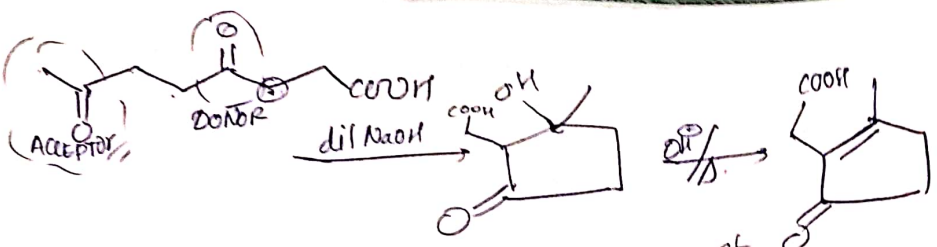


(f)

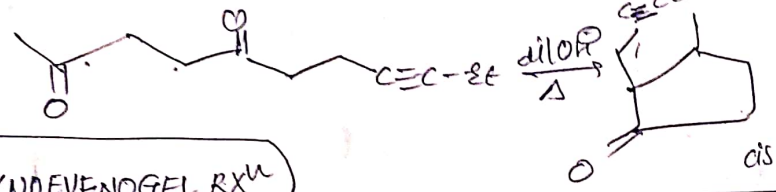


(g)

(f)



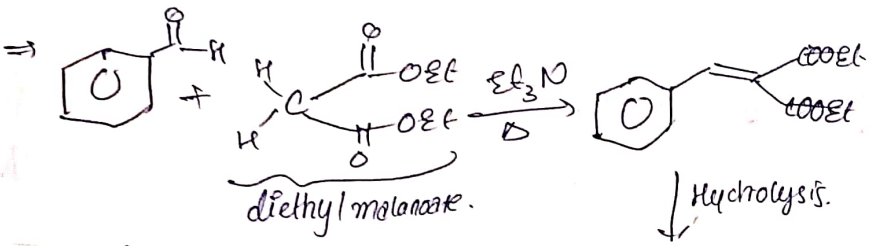
(g)

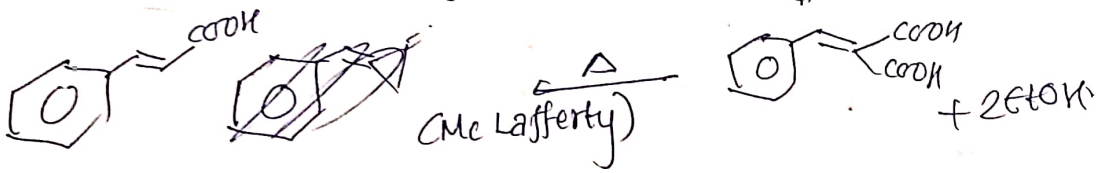


cis jasmine.

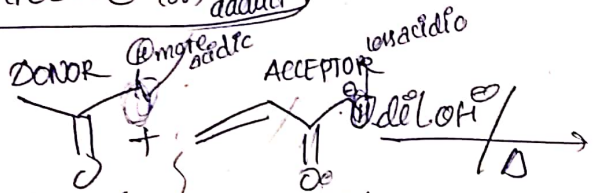
KNOEVENAGEL RXN

⇒ Aromatic aldehyde rcts with active methylene.





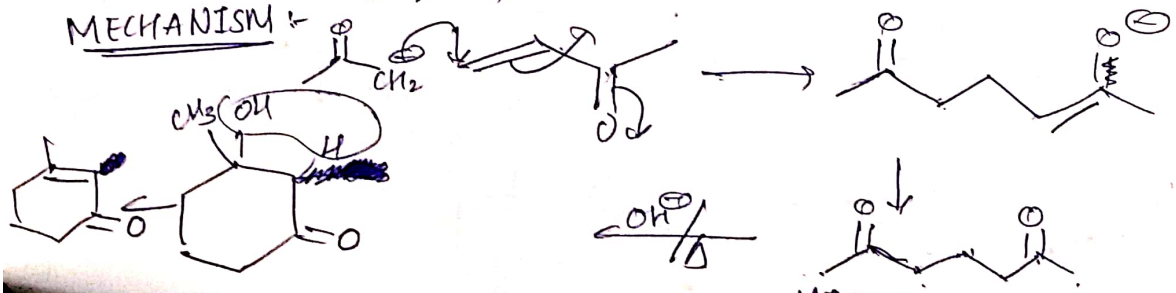
Michael Rxn (or) Michal adduct.



carbonyl compd. with α-Hydrogen

conjugated carbonyl (methyl vinyl ketone) [MVK]

MECHANISM :-

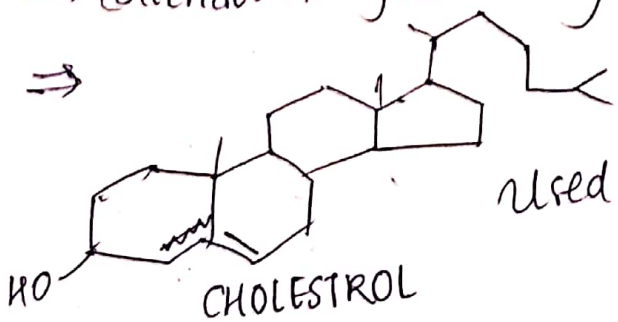


MICHAEL ADDUCT

Robinson's Annulation

→ Michael rxn followed by aldol.

⇒



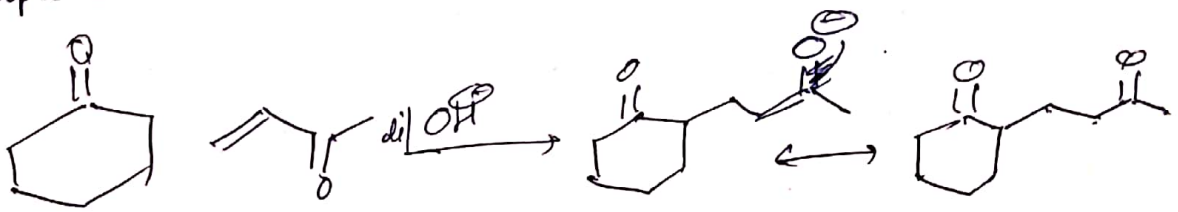
HO

CHOLESTROL

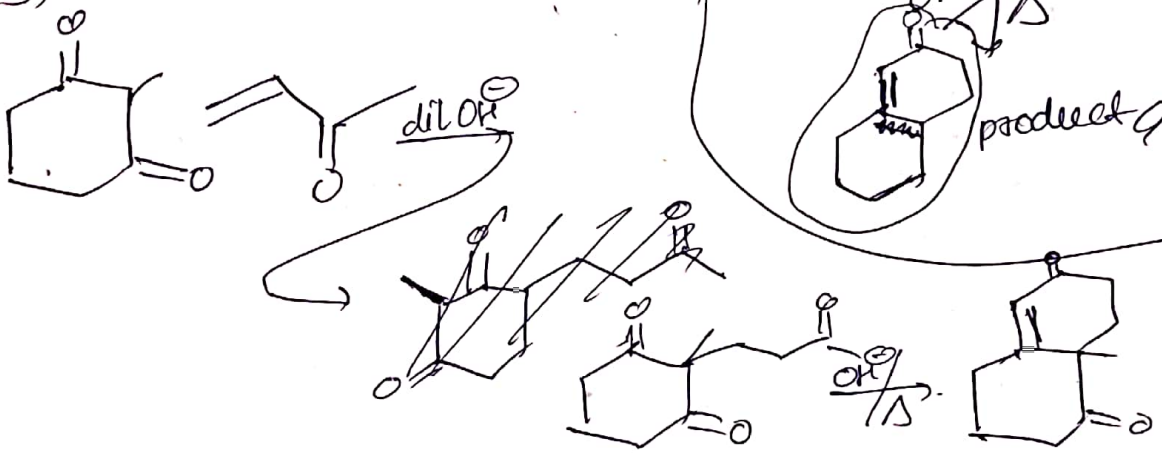
Used to make steroides.

Example ① :- In Michael adduct rxn.

(2)



(3)

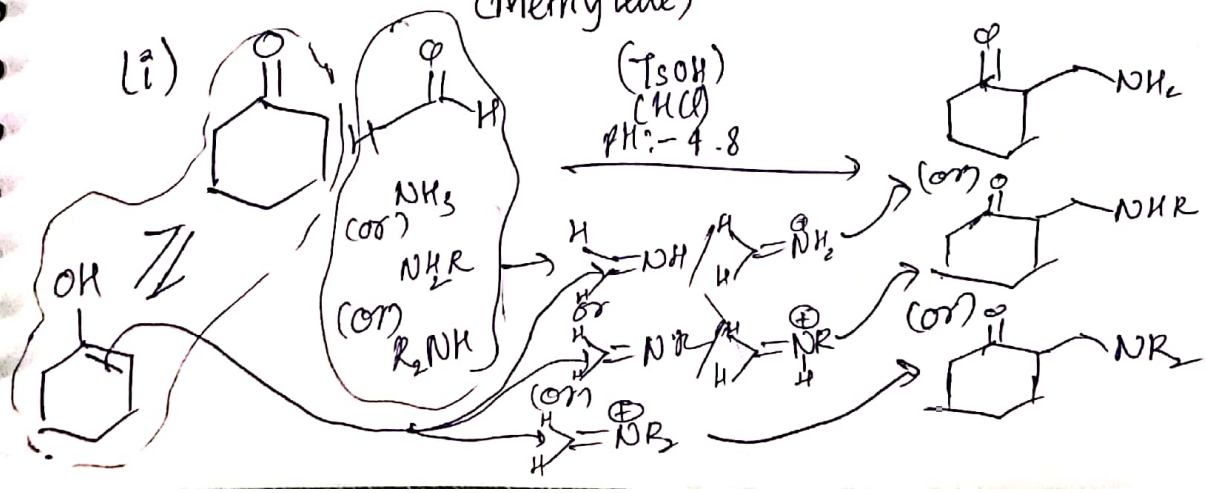


Mannich Rxn

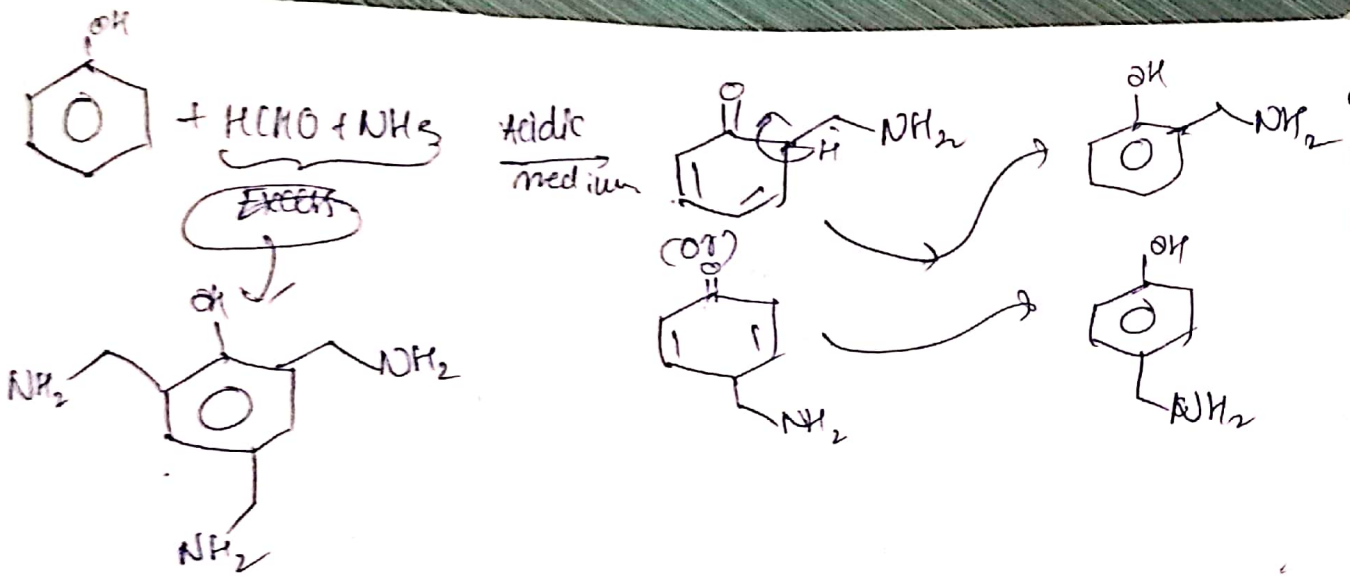
⇒ Amino-methylation at active site. (Hint)

(Methylene)

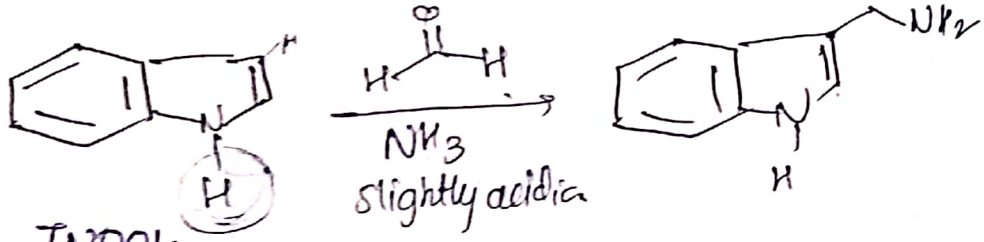
(i)



(2)

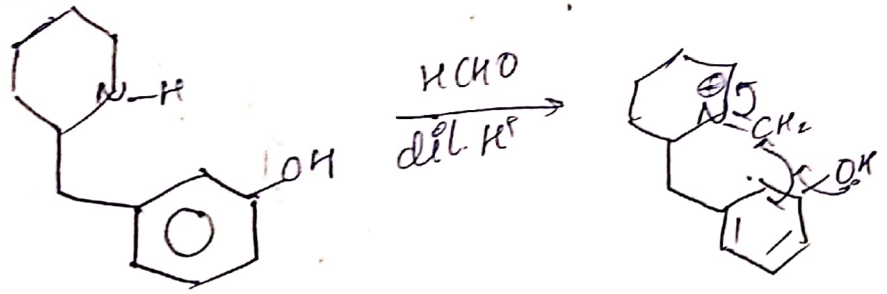


(3)

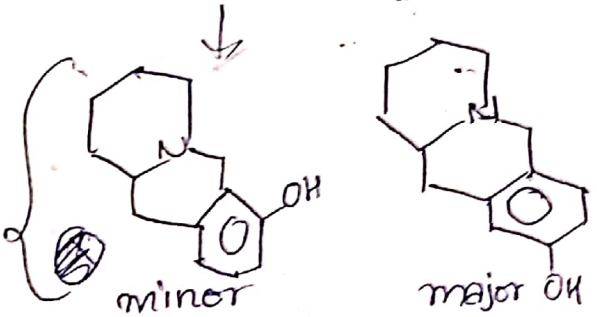


INDOL

(4)



Due to high steric reasons, disubstituted benzene never become 1,2,3, trisubstituted.

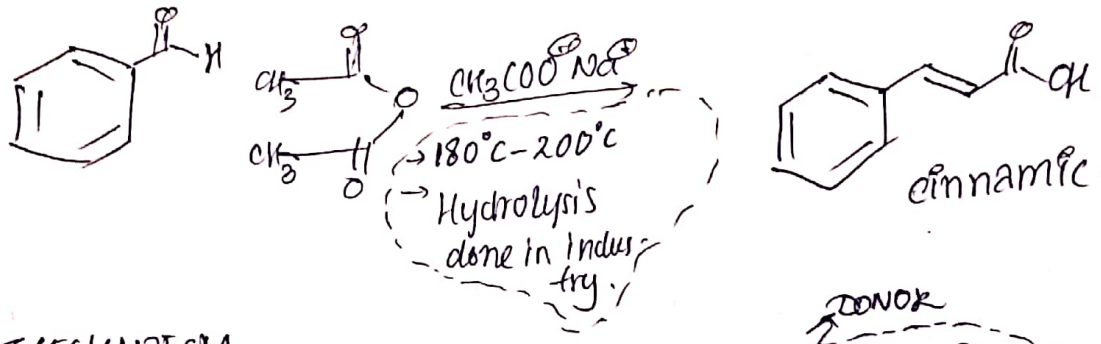


Imp for Adv.

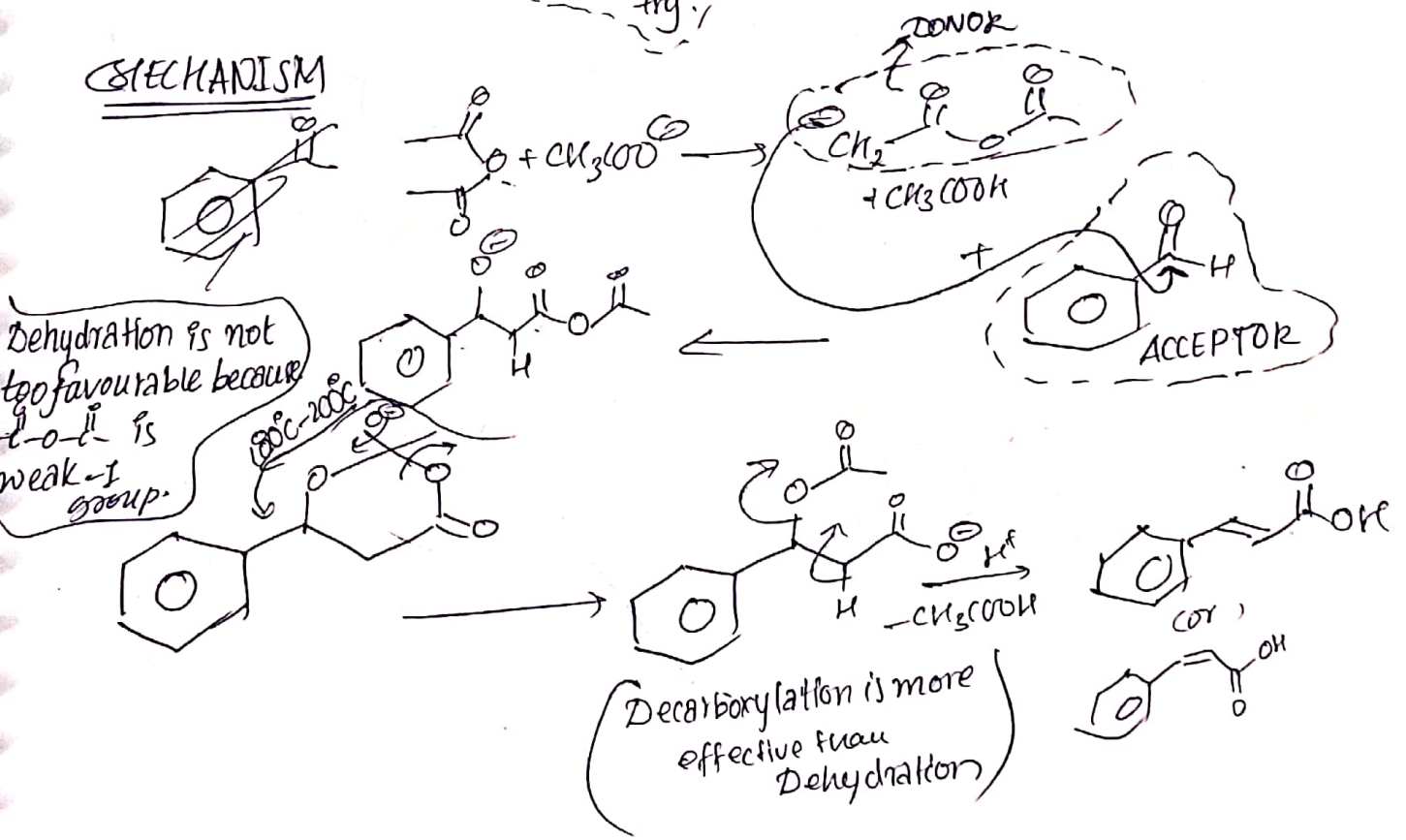
⊛ Perkin Reaction

→ Reactant should be aromatic aldehyde.

→ Aromatic aldehydes reacts with aliphatic acid anhydride (with minimum two α-hydrogens with anhydride) in presence of salt of its corresponding ~~acid~~. aliphatic acid of anhydride to give α,β-unsaturated carboxylic acid.

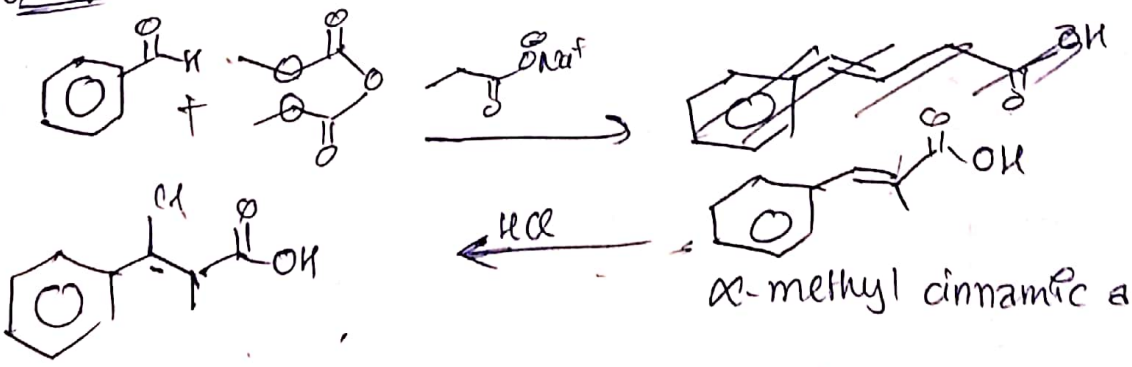


MECHANISM

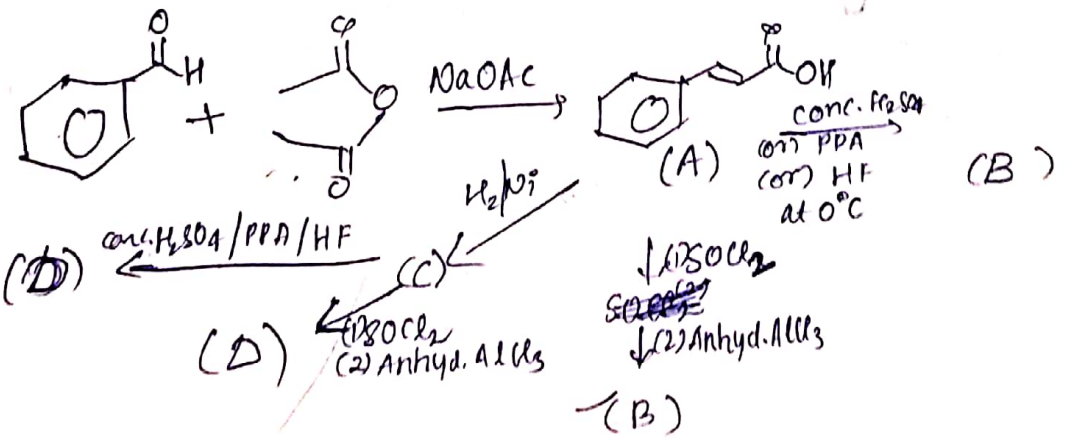


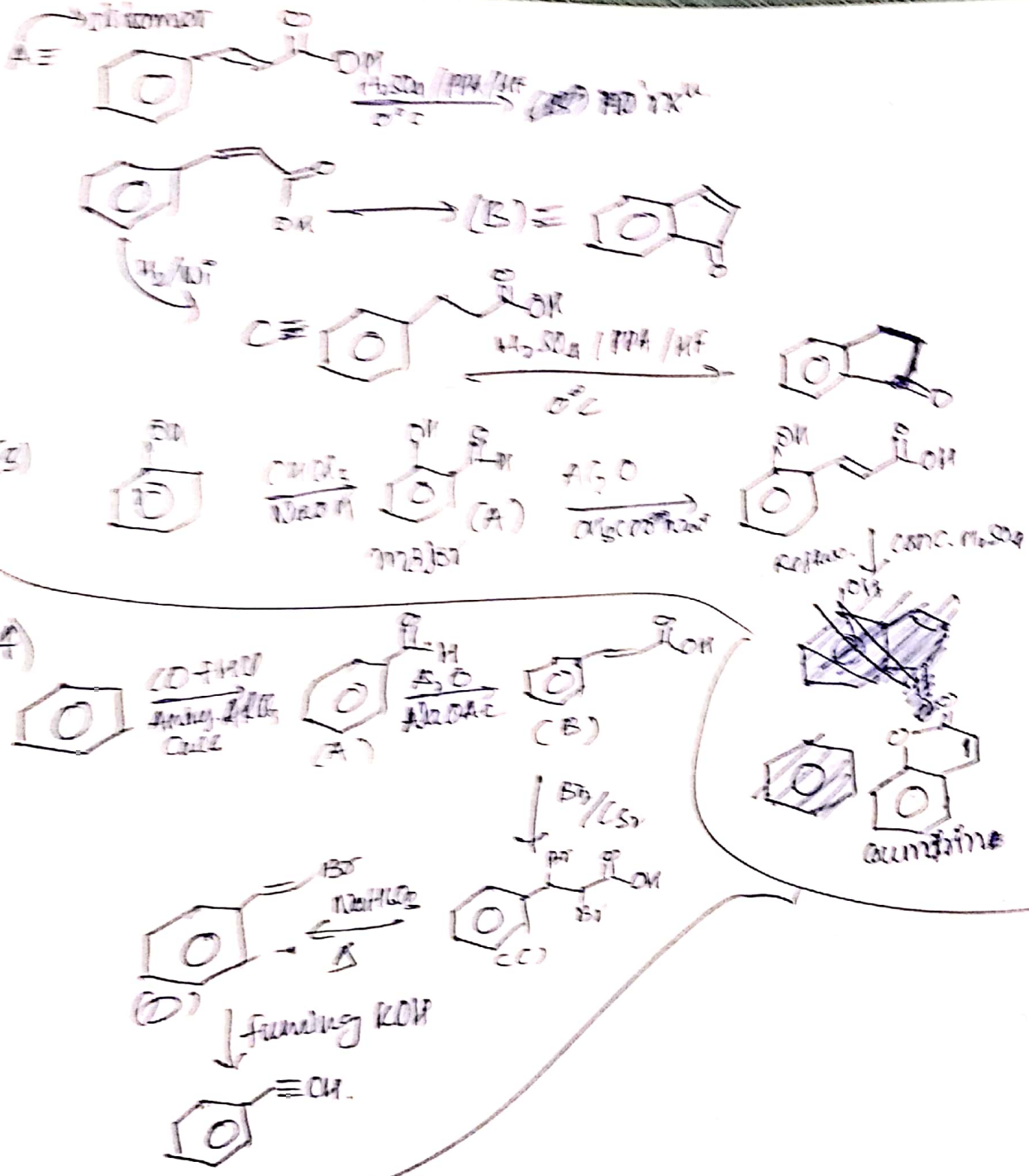
Example :-

(1)



(2)

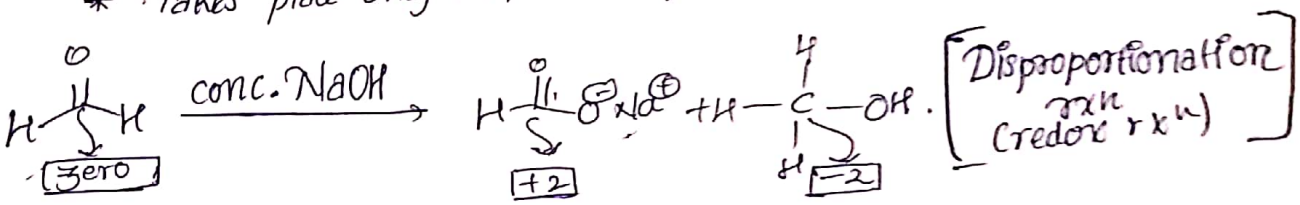




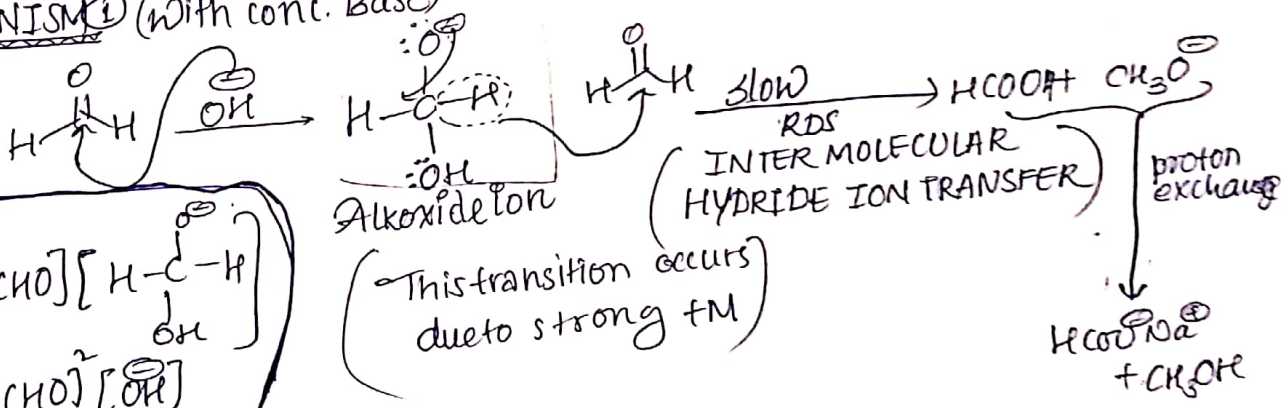
Rxns due to absence of α-Hydrogens

(1) Cannizaro rxn

* Takes place only in presence of concentrated base.



MECHANISM (1) (With conc. Base)

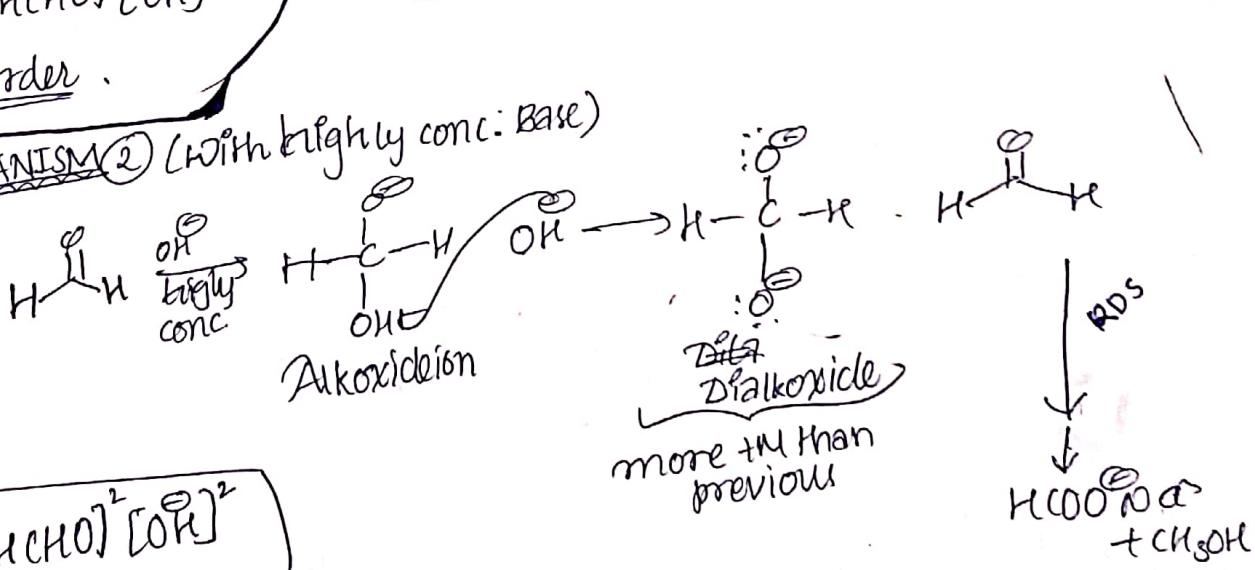


$R \propto [HCHO]\left[H-\underset{\underset{OH}{|}}{C}(O^{\ominus})-H\right]$

$R \propto [HCHO]^2[OH^{\ominus}]$

$\therefore$ 3rd order.

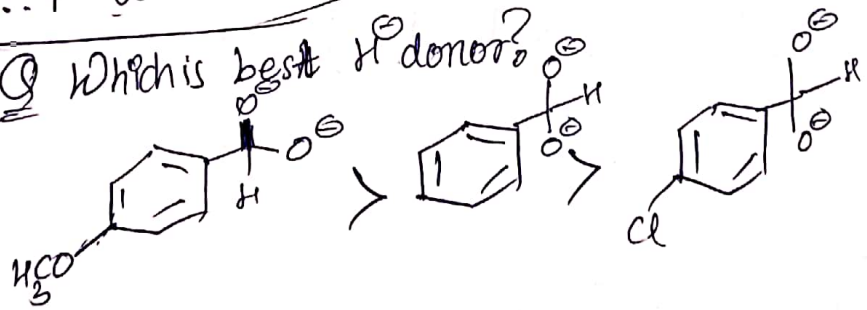
MECHANISM (2) (With highly conc. Base)



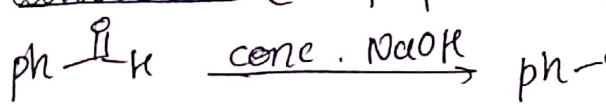
$R \propto [HCHO]^2[OH^{\ominus}]^2$

$\therefore$ 4th order rxn.

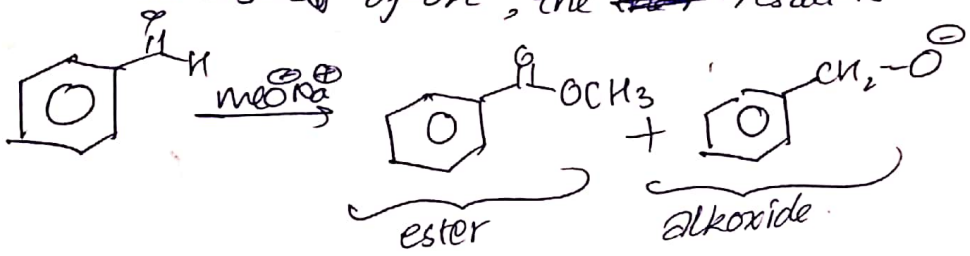
Q Which is best $H^{\ominus}$ donor?



Self-Cannizaro (Disproportionation)

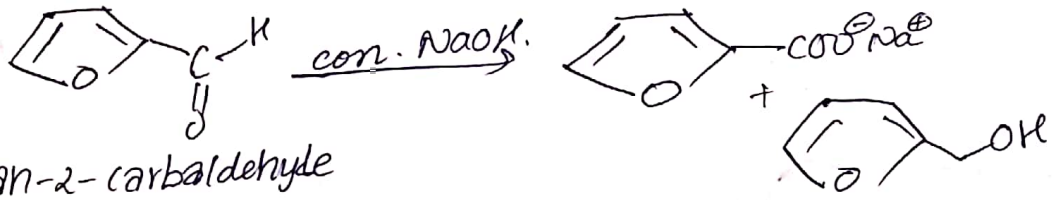


NOTE If alkoxide is base instead of $OH^{\ominus}$, the result is



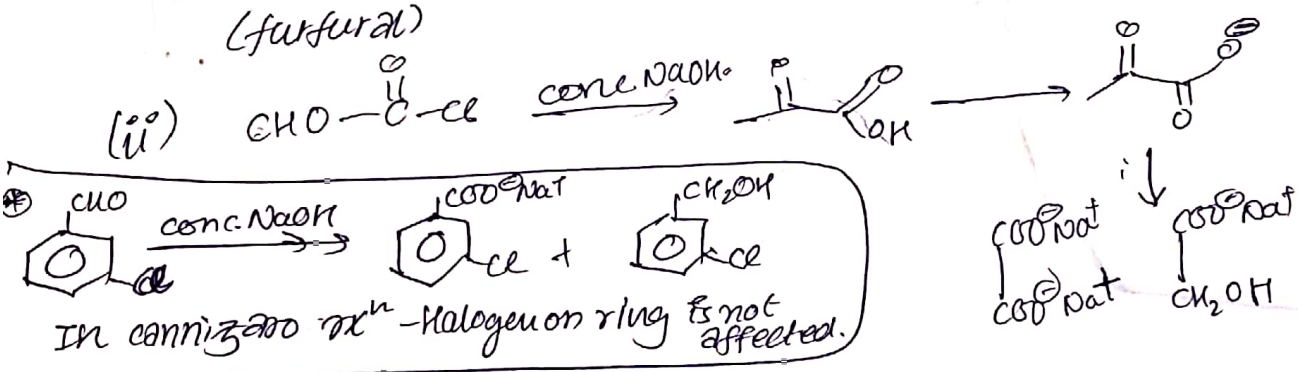
Example:-

(i)



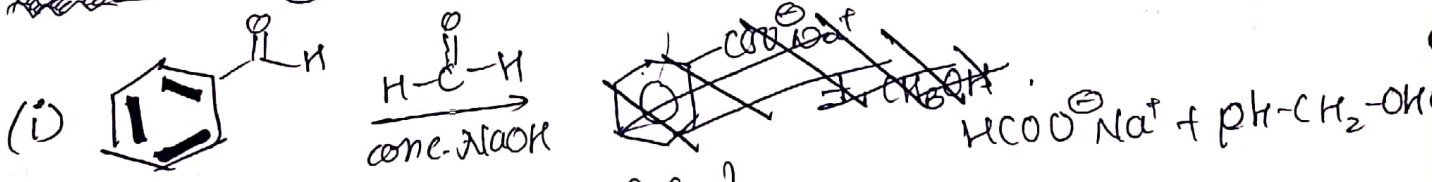
Furan-2-carbaldehyde (furfural)

(ii)



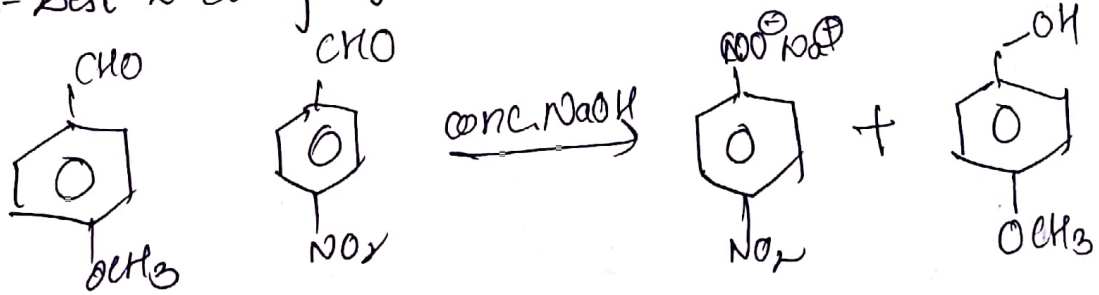
Crossed-cannizaro (Redox rxn)

(i)

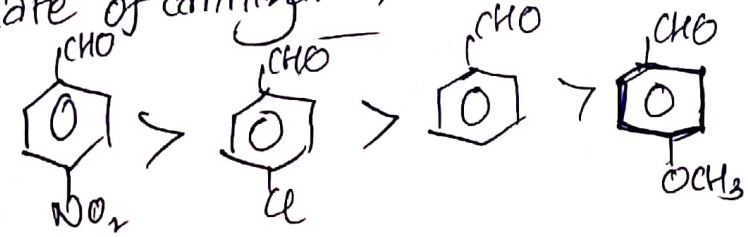


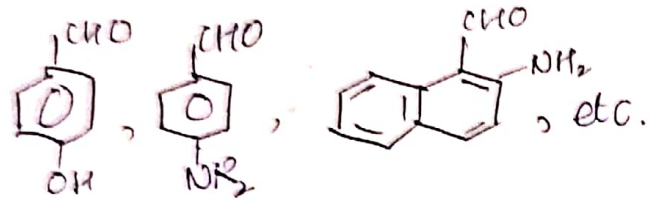
HINT:- Best $E^{\oplus}$ always gets oxidised.

(ii)

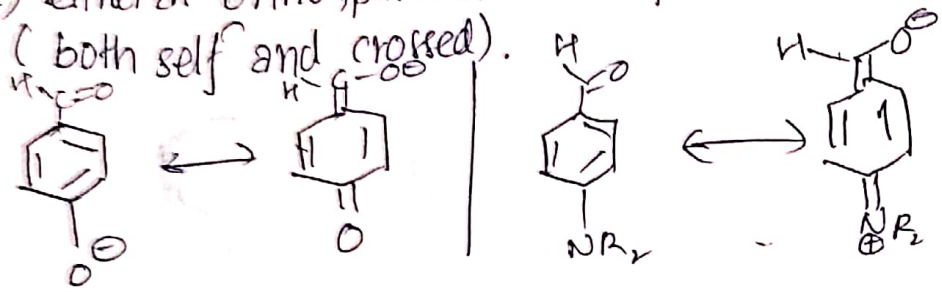


Q Rate of cannizaro rxn.

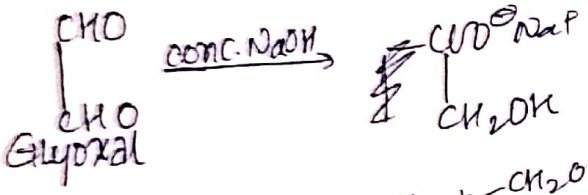


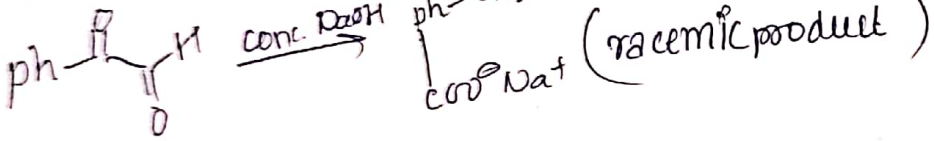
NOTE :- 

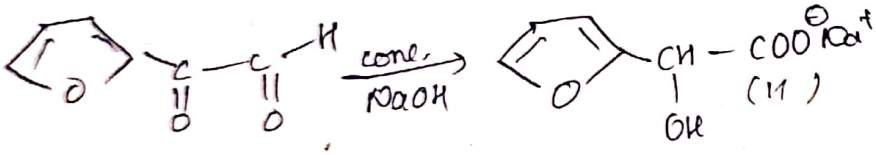
Aryl aldehyde possessing strongly activating groups ($COOH$, NR_2, NHR, NH_2, ...) either at ortho, para or both of them doesn't give Cannizaro rxn (both self and crossed).



Intramolecular Cannizaro

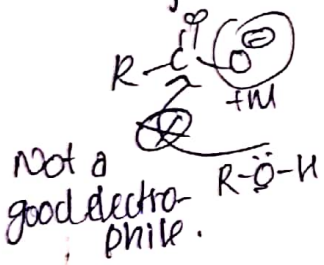
(i) 

(ii) 

(iii) 

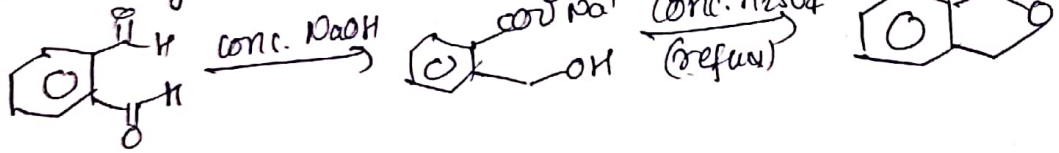
Q Why esters are not obtained in cannizaro rxn?

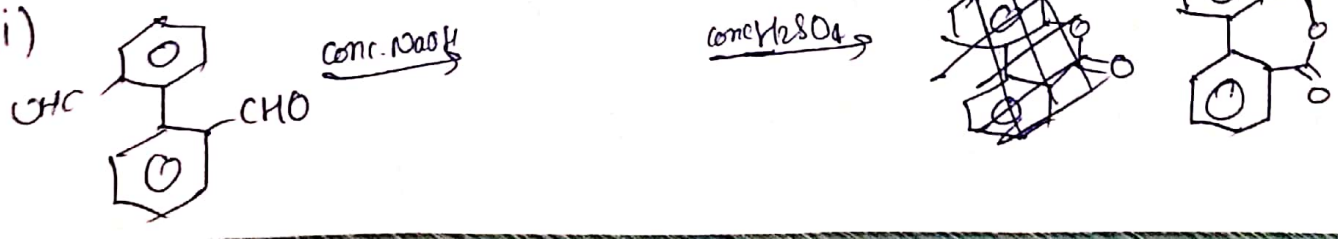
Since, esterification doesn't take place in basic medium.

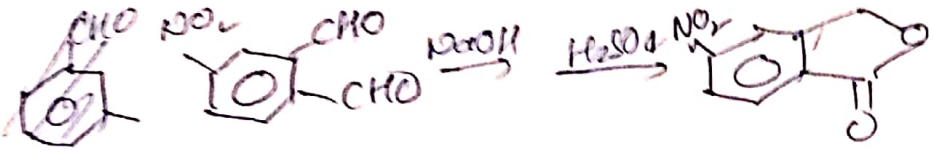


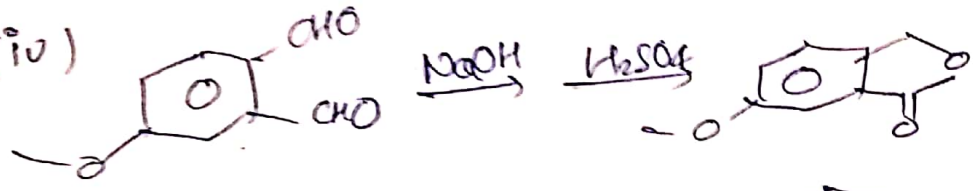
Not a good electrophile.

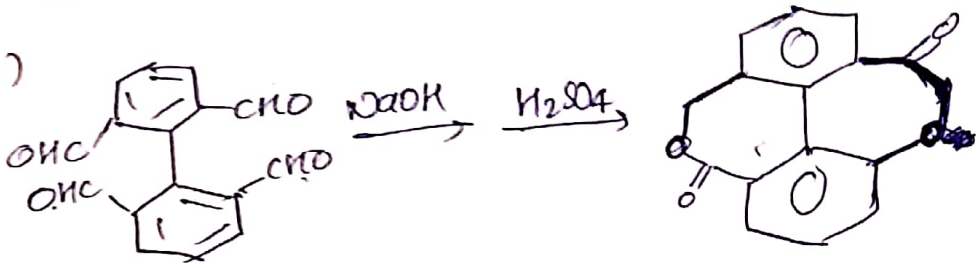
Q How to get ester :-

(i) 

(ii) 

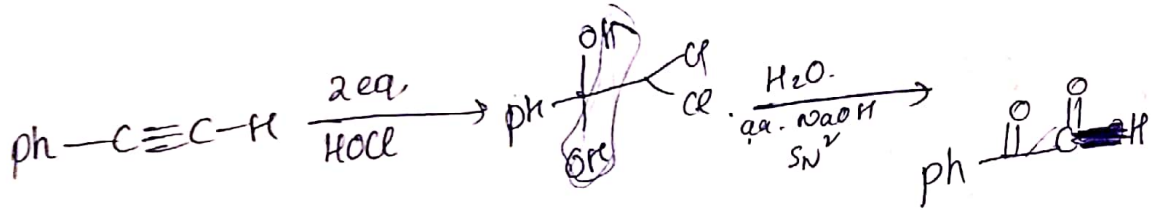
(iii) 

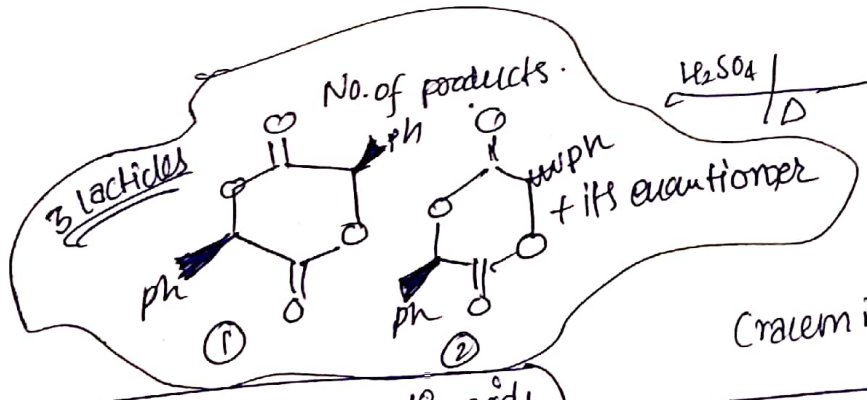
(iv) 

(v) 

Coming soon Adv

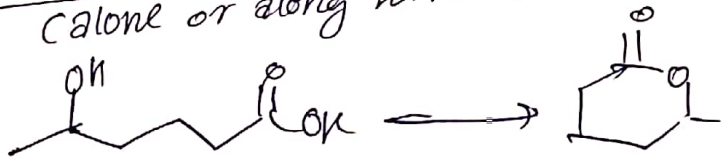
PASSAGE

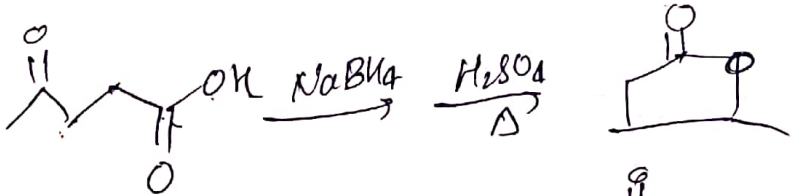


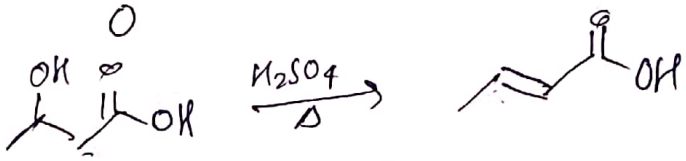


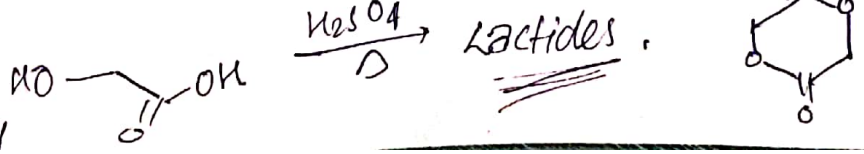
Heating of hydroxy carboxylic acids

(alone or along with H_2SO_4)

(i) 

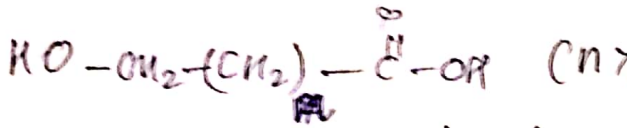
(ii) 

(iii) 

(iv) 

α-hydroxy

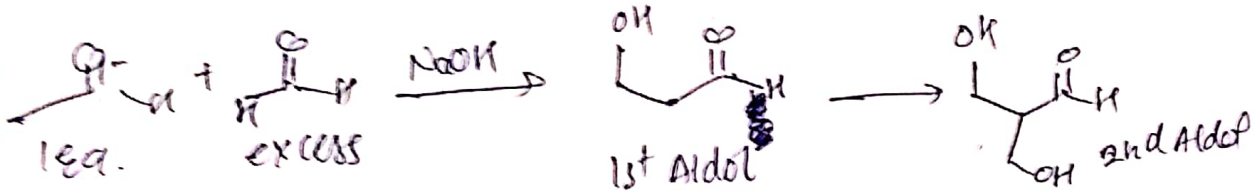
Q



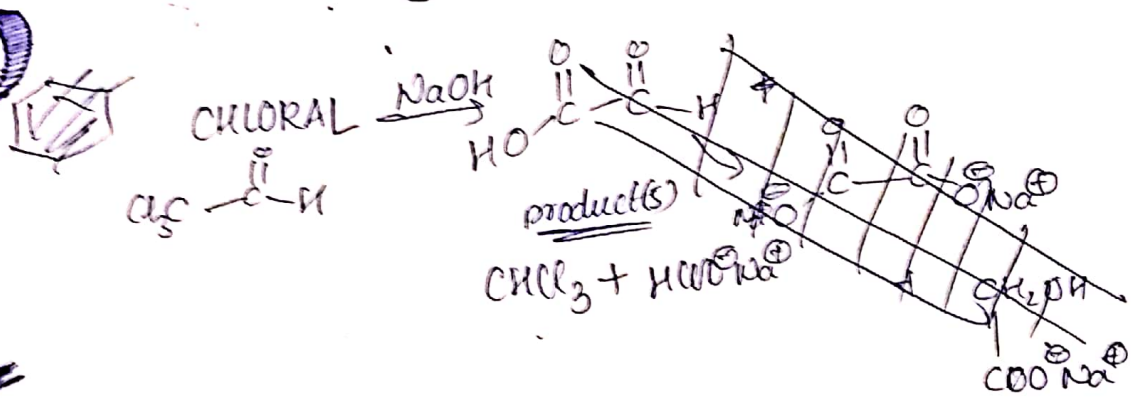
$\xrightarrow{\Delta}$ polyesters.

(2) Tollens rxn (Aldol + Cannizaro)

(i)



Q1



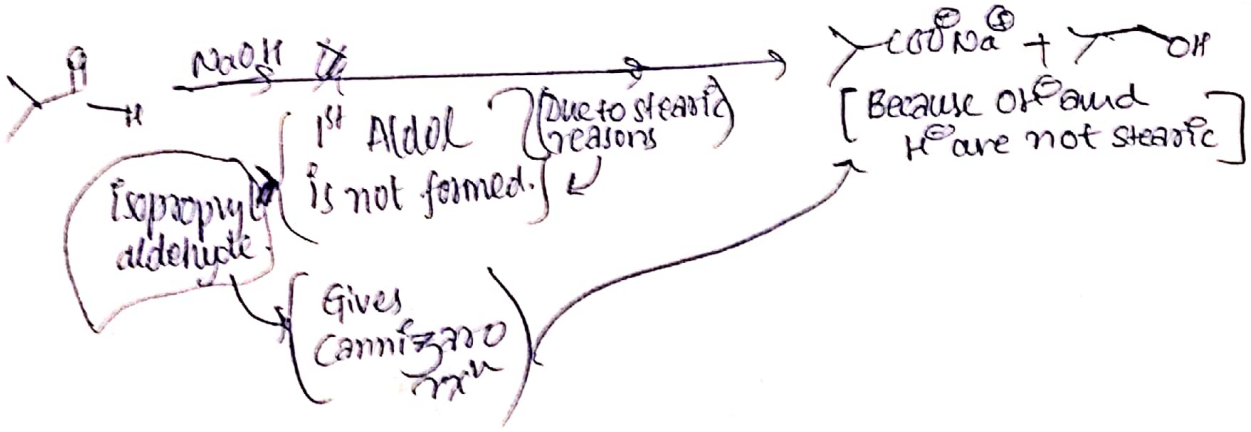
Q

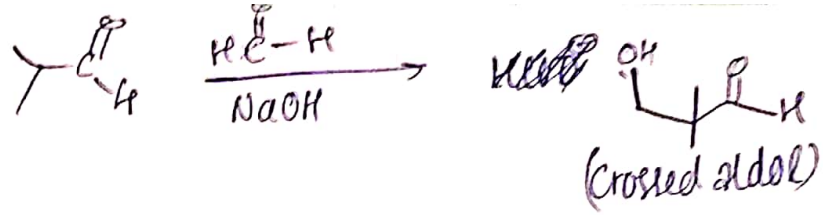
NOT ASKED

$\xrightarrow{NaOH}$ $CH_3-COO^{\ominus}Na^{\oplus}$ + other product?

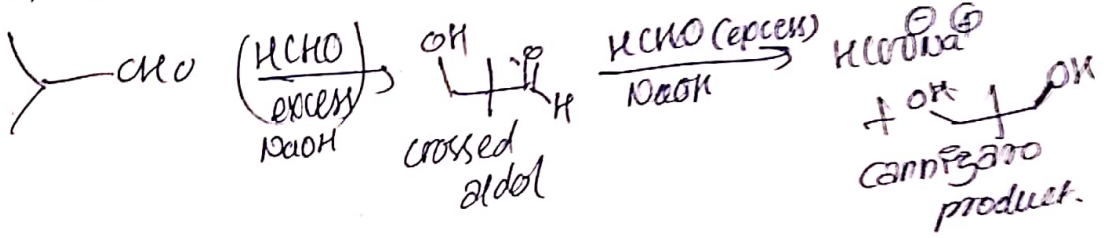
Ans :- CH_3-CH_2-OH

Q

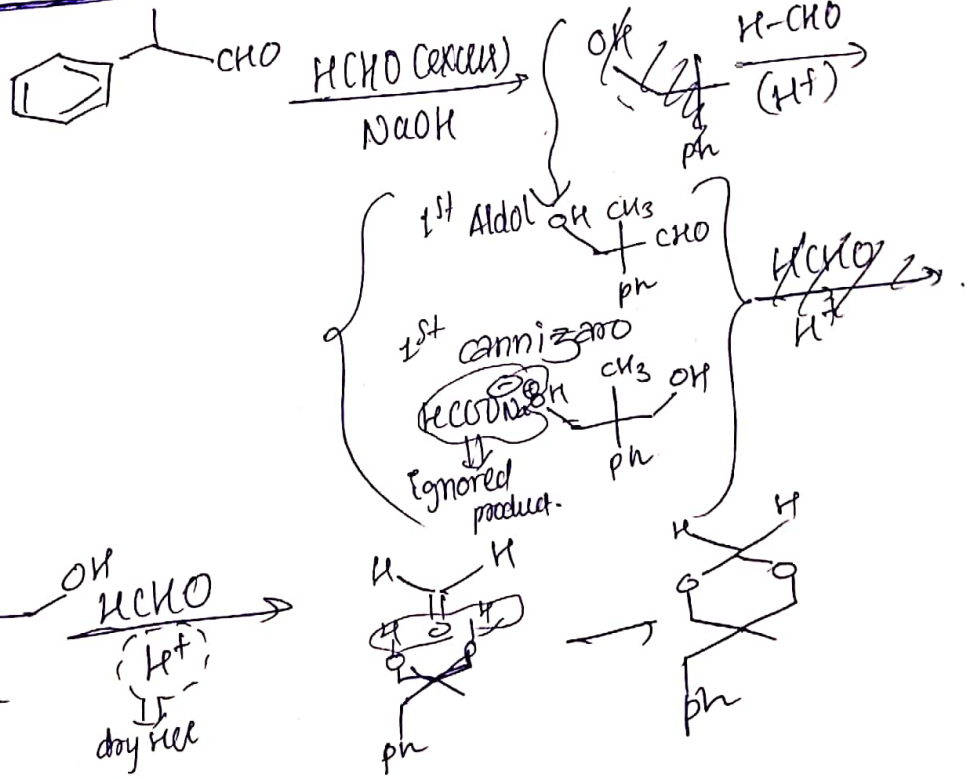


Q 

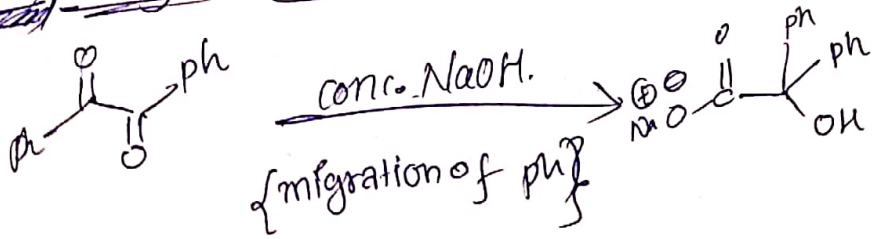
(ii) continued for Tollen's rxn.



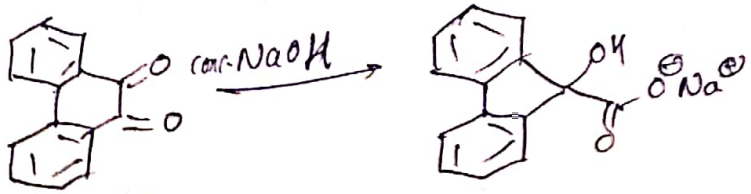
(iii) 2016 Adv-PII



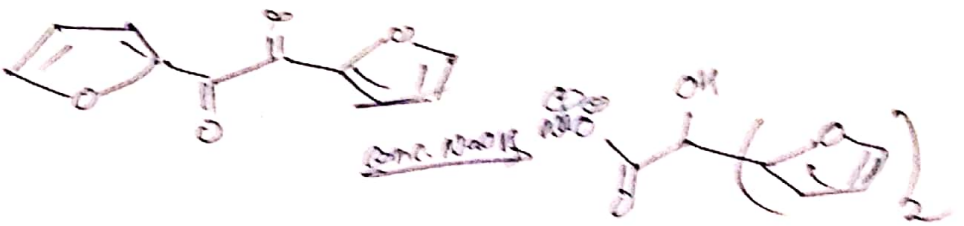
(3) Benzil – salt of Benzilic acid rearrangement.



Examples :- (i)

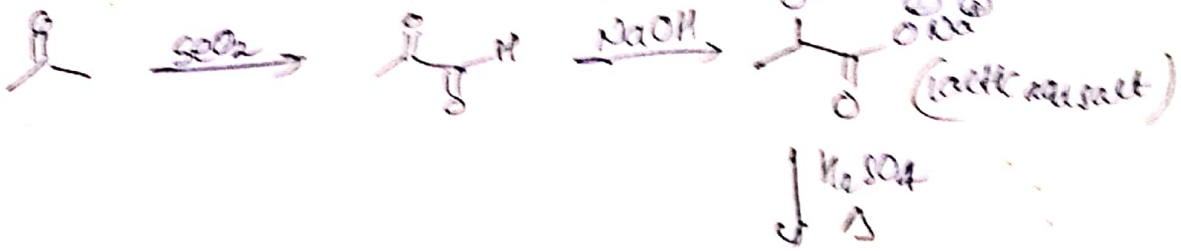


(ii)



(iii)

(iv)

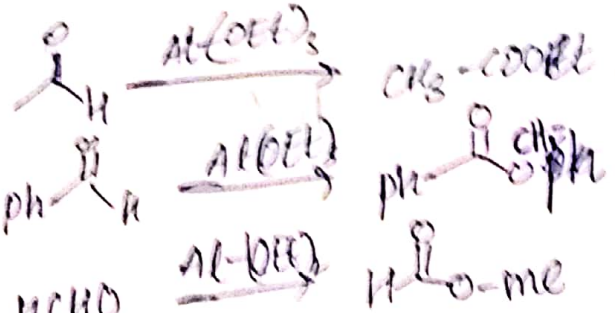


(3) Lactide

(4) TISCHENKO :-

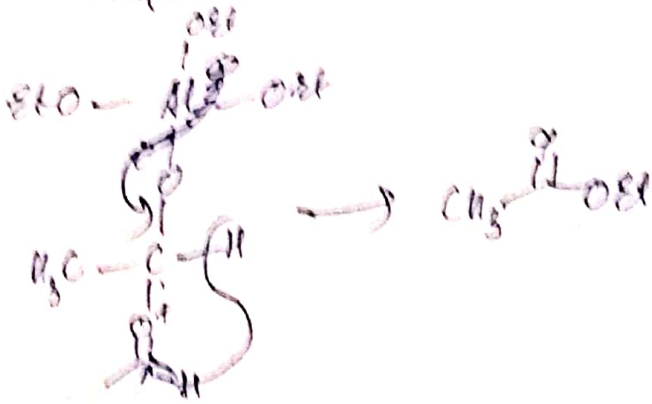
Also known as modern cannizzaro rxn

- Esters are gained directly as products.
- Aldehydes, may or may not possess α-Hydrogens, are converted to corresponding esters by means of aluminium ethoxide.



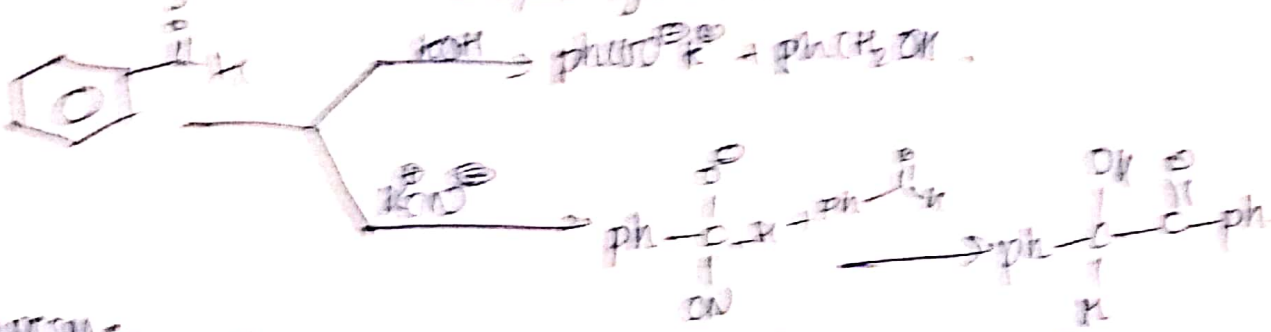
→ Industry prepare bulk amount of ethyl acetate by this way.

→ Hydride ion transfer is observed

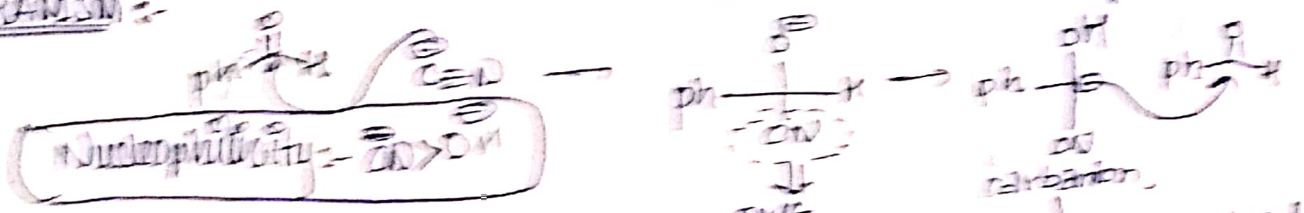


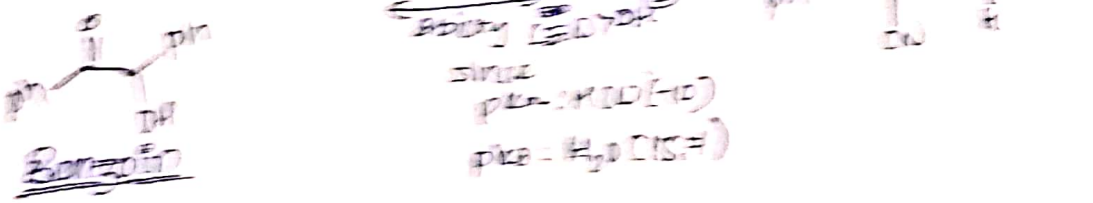
(5) Benzoin condensation

→ Only aromatic aldehydes give this rxn.



MECHANISM :-

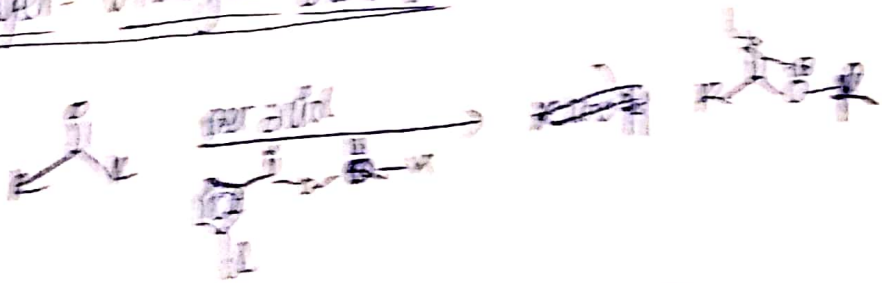




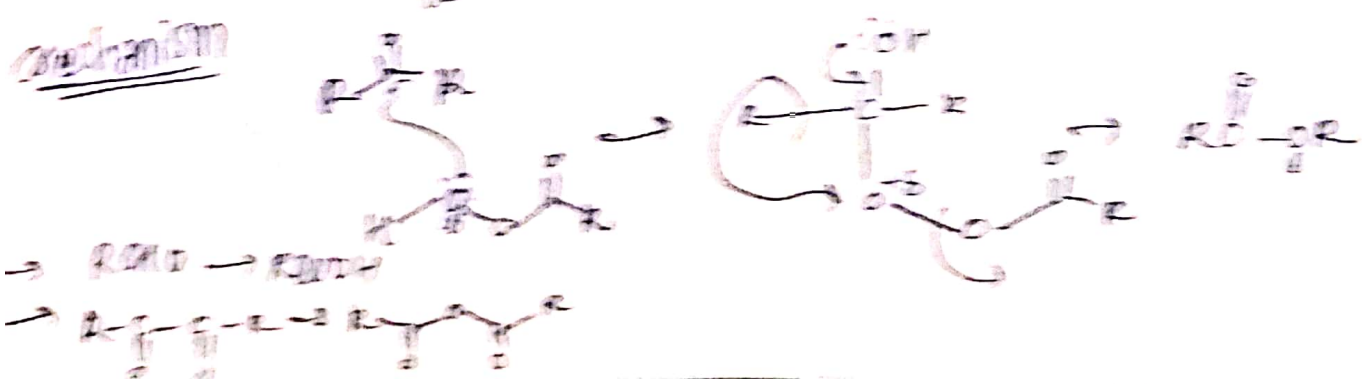
Benzoin

Rxn - II)

(6) Baeyer - Villiger oxidation

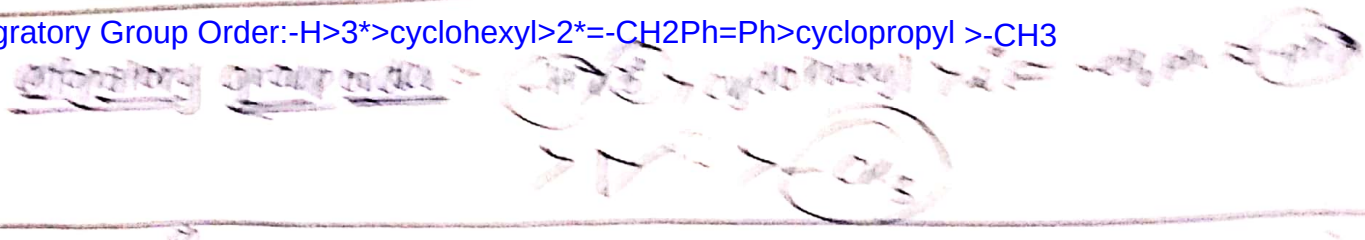


Mechanism



Ex. (i)

Migratory Group Order:-H>3*>cyclohexyl>2*=-CH2Ph=Ph>cyclopropyl >-CH3



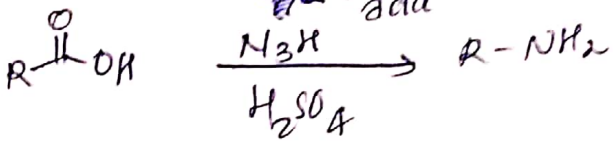
(ii)

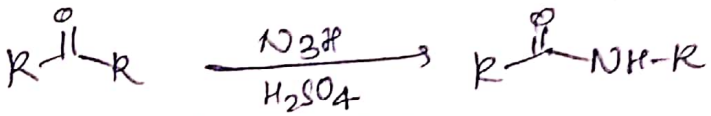
Favorskii Rxn

Mechanism

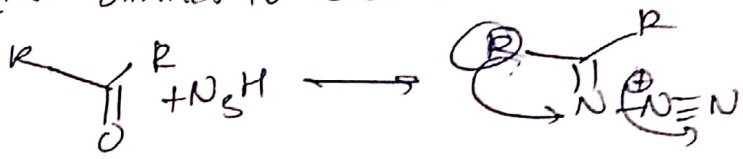
Schmidth Rxn

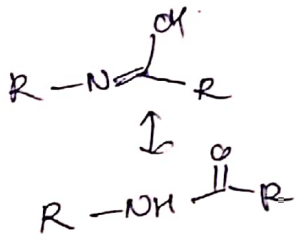
Hydrazoic acid

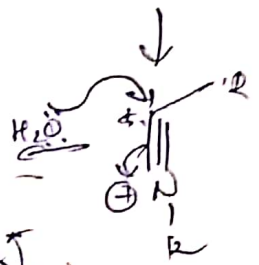




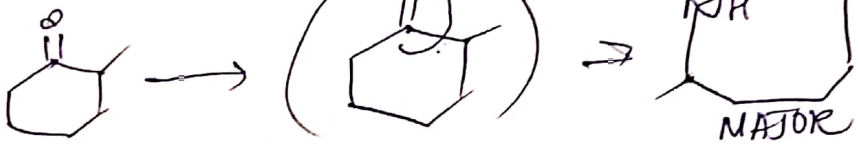
MECHANISM :- similar to Beckmann.







EX:

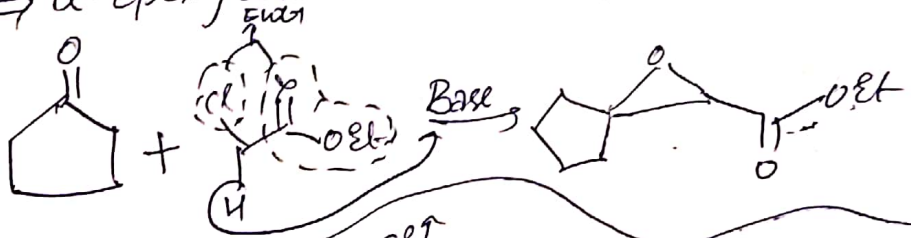


MAJOR

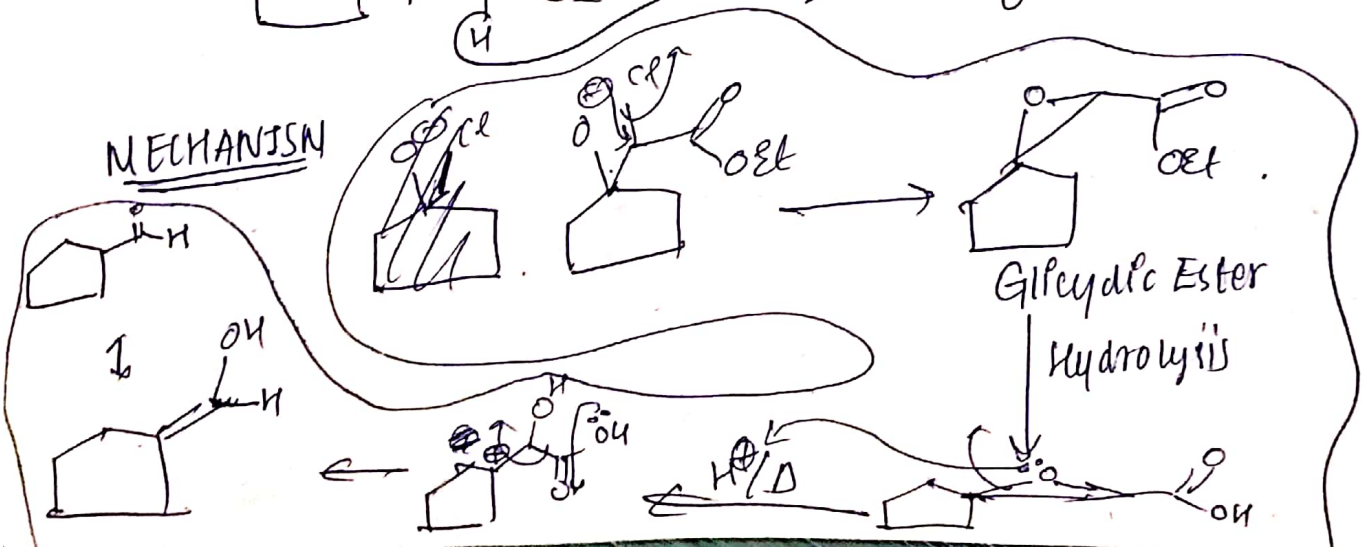
ε-caprolactum

Darzen's Glicydic Ester synthesis :-

⇒ α-epoxy esters are called Glicydic esters.



MECHANISM

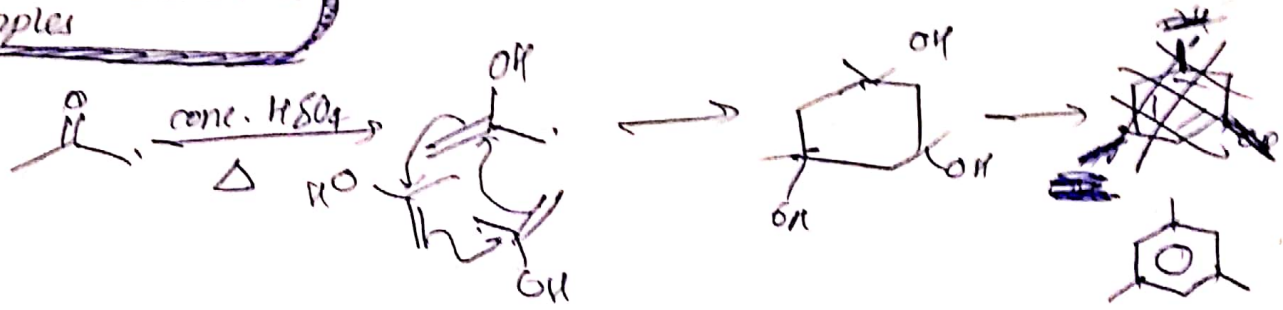


Glicydic Ester

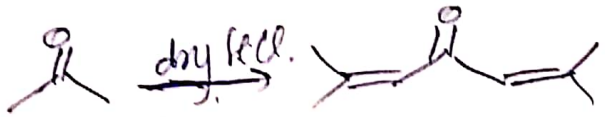
Hydrolysis

Important miscellaneous examples

(1)

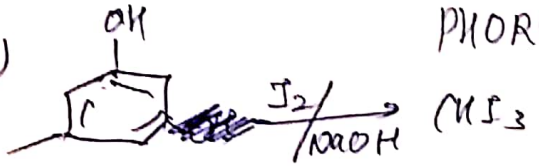


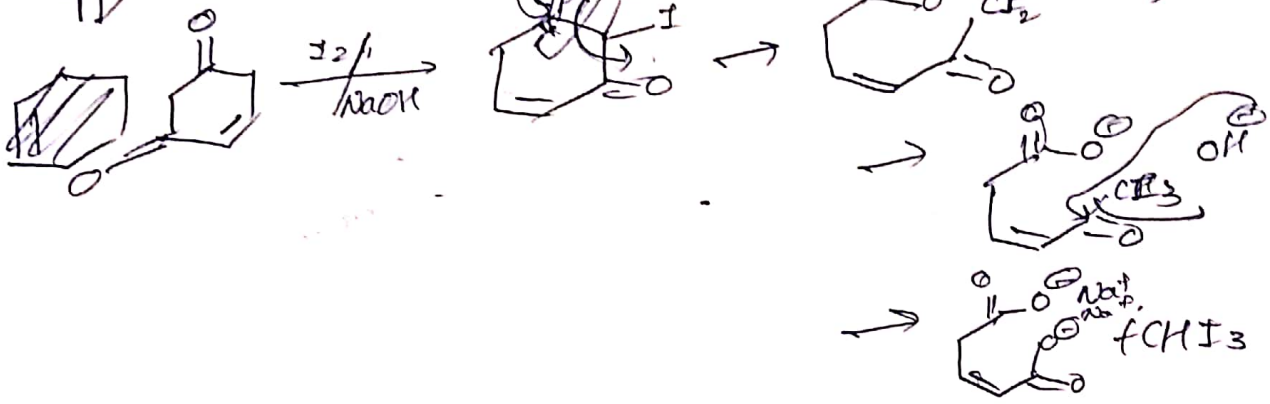
(2)



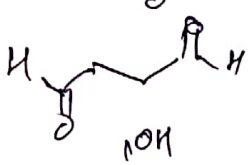
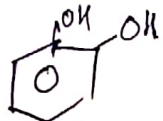
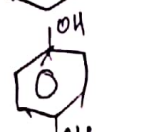
PHORONE

(3)

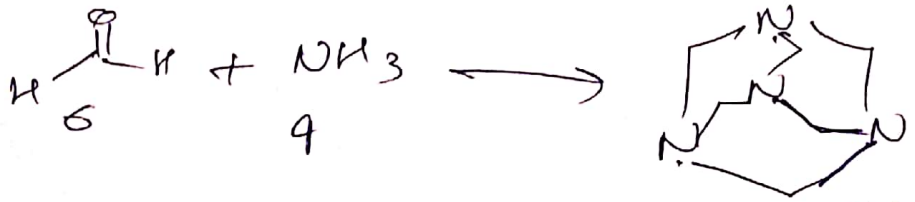




(4)

compound	Tollens	Fehlings
CHO CHO	+	−
CHO COOH	+	—
	+	+
	+	+
	+	+
	+	+
	+	+

Urotropene

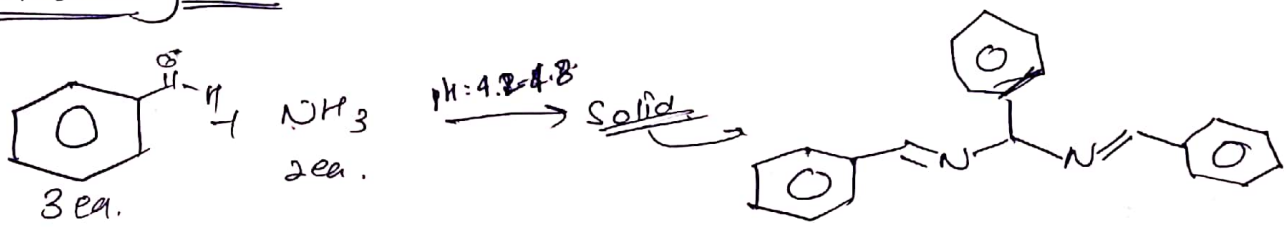


6 + 4 → urotropene

Urotropene
Hexa methylene tetra amine

Imp. for Addn.

HYDROBENZAMIDE

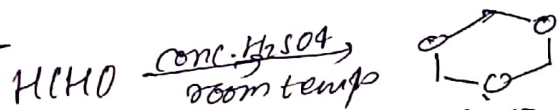


3 eq. + 2 eq. NH_3 → (pH: 4.2–4.8) → Solid

Simple facts

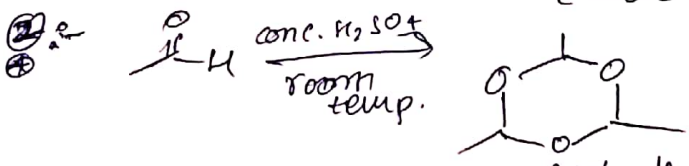
→ Aldehydes (sterically free) ~~soluble~~ shows addition rxns as well as condensation rxns, whereas ketones (sterically hindered) shows condensation rxns only among the molecules.

Ex① :-



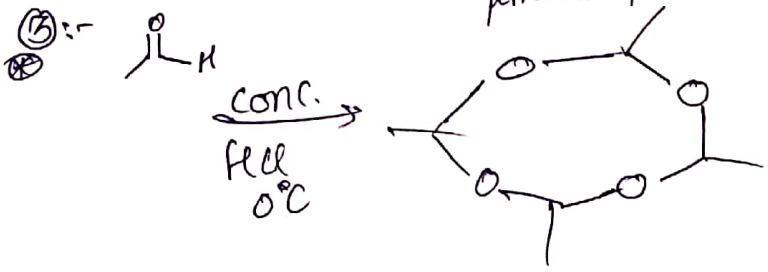
HCHO —(conc. H_2SO_4, room temp)→ 1,3,5-tri oxane (meta formaldehyde)

②:-



—(conc. H_2SO_4, room temp.)→ paraldehyde.

③:-



—(conc. HCl, 0°C)→ metaldehyde.

~~Aqueous formaldehyde on heat~~