

ALDEHYDES & KETONES

classmate

Date _____

Page _____

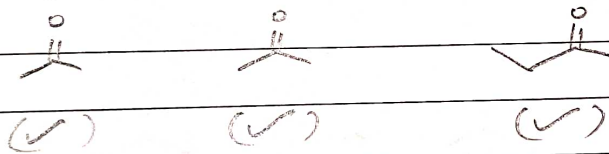
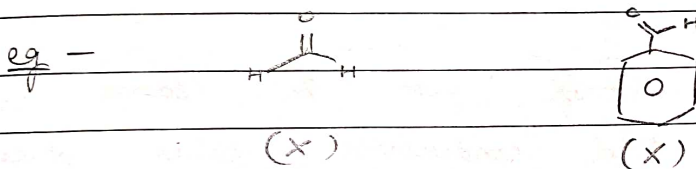
16/06/2023

ALDOL CONDENSATION

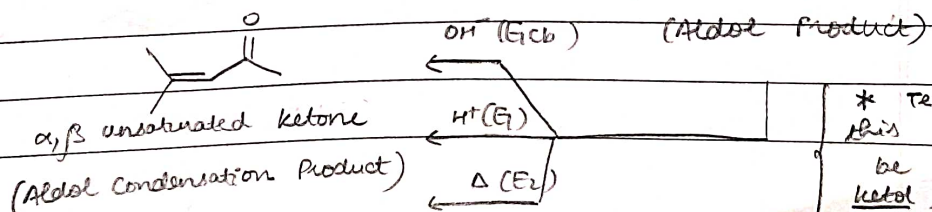
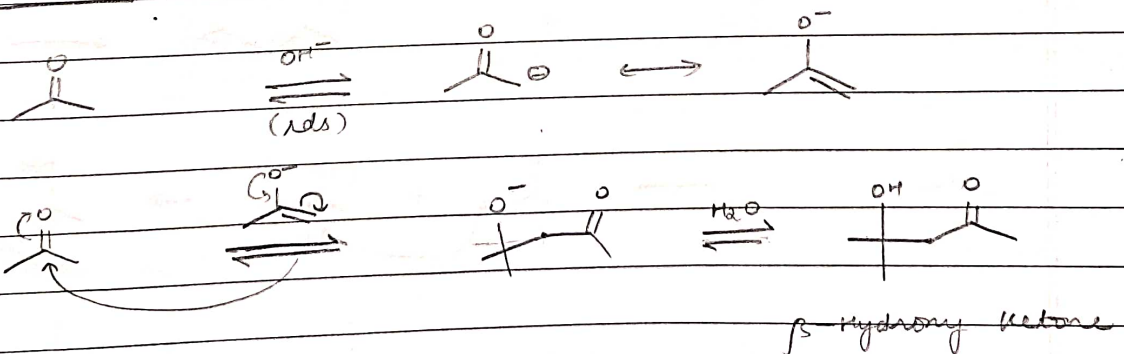
Condⁿ: Aldehyde or Ketone having at least one α -Acidic Hydrogen

Medium

- Acidic - H^+ , conc. H_2SO_4 , H_2SO_4
- Basic - OH^- , $NaOH$, dil. $NaOH$, KOH , $Ca(OH)_2$, $Ba(OH)_2$, Na_2CO_3 , K_2CO_3



→ Mechanism (Basic Medium)

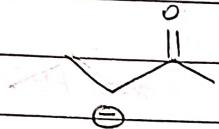


* technically this should be called ketol, but convention

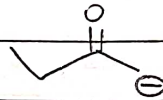
NOTE: 1. T₁D Product — Stability of enolate ion

Kinetic Product — Stability of C[⊖]

eg



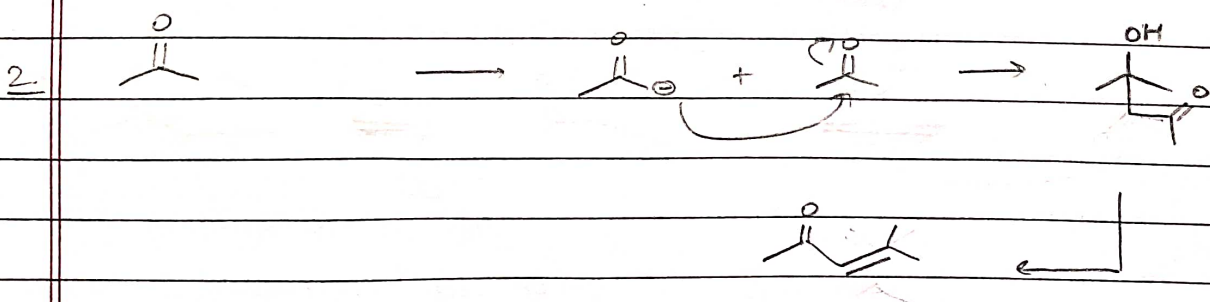
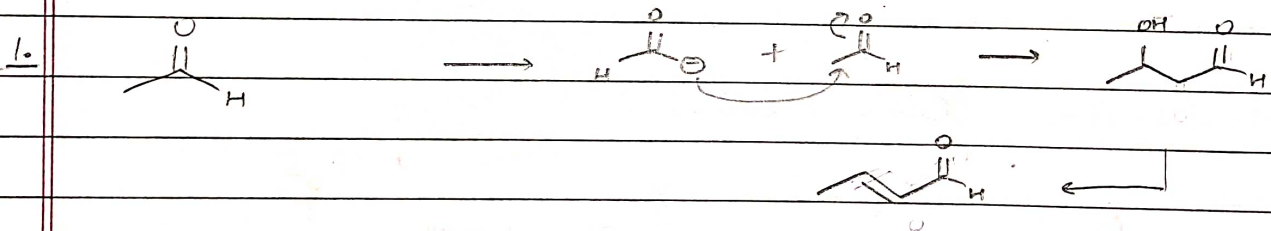
(For T₁D product)



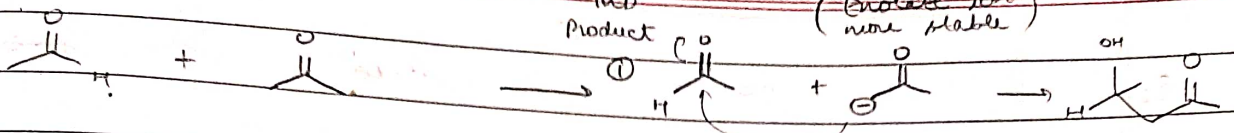
(for kinetic product)

2. When 2 carbonyl grps in same comp, intramolecular Aldol condensation takes place which results in ring formation.

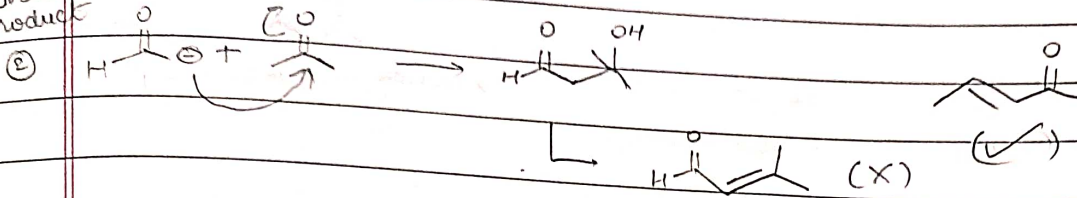
Q. Write mechanism & product.



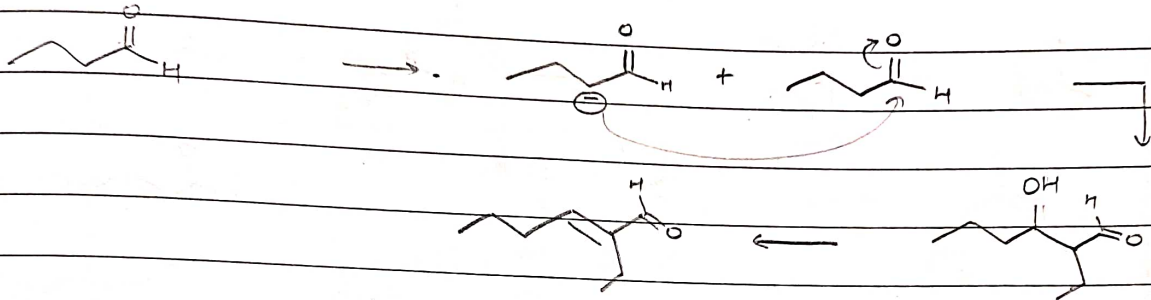
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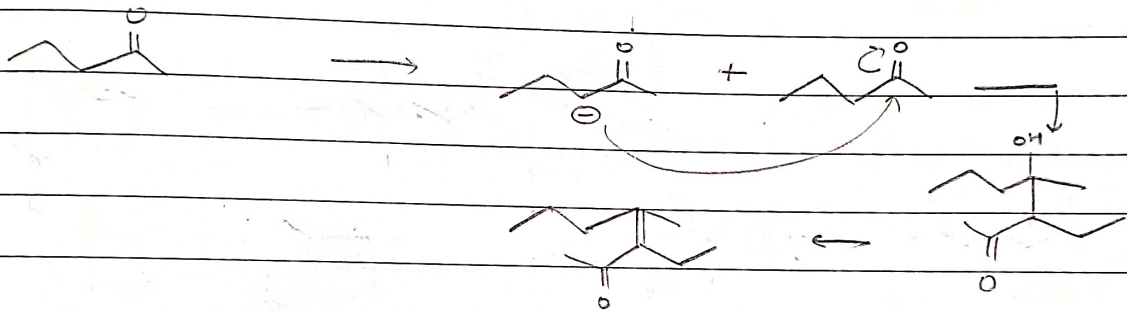
Kinetic product



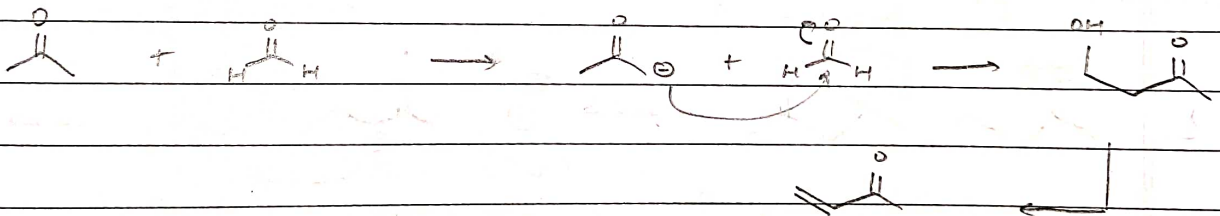
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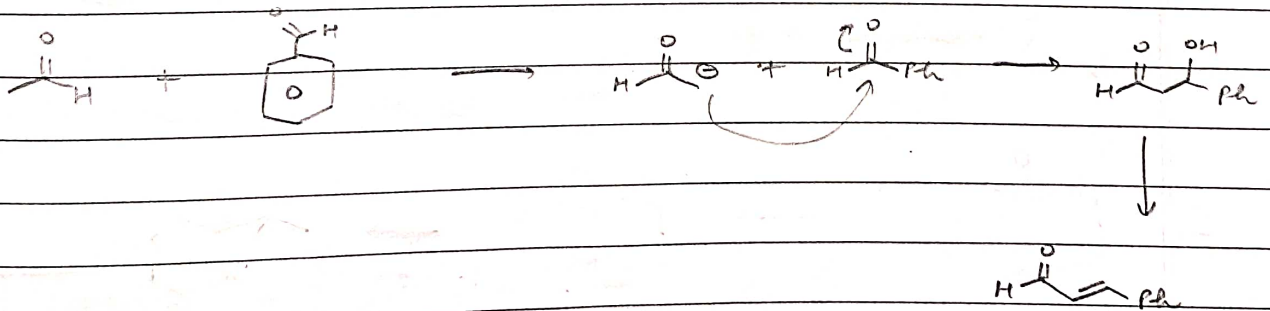
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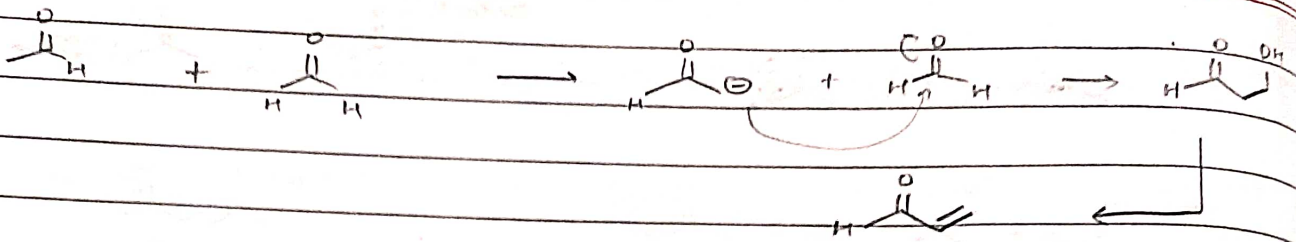
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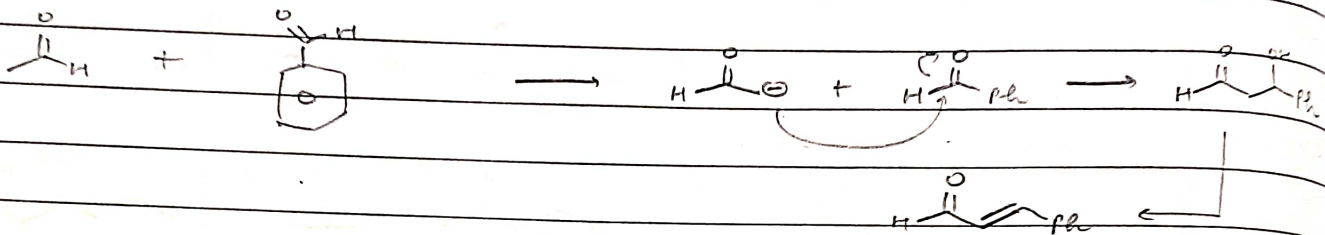
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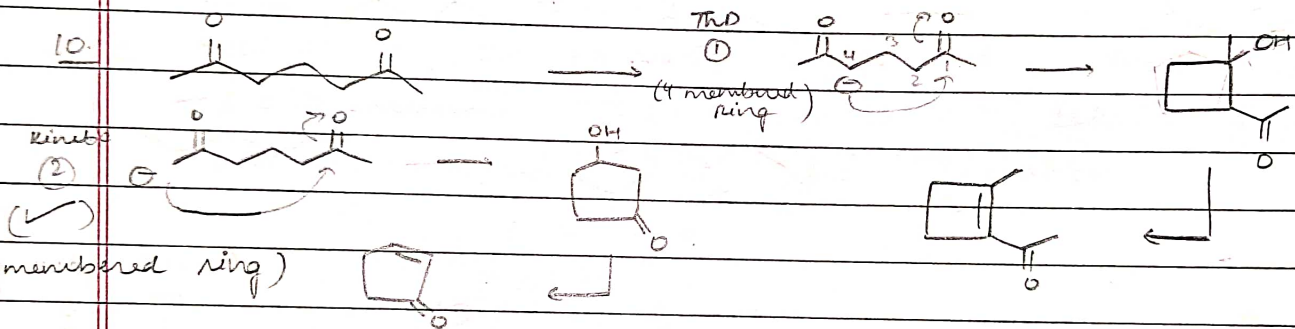
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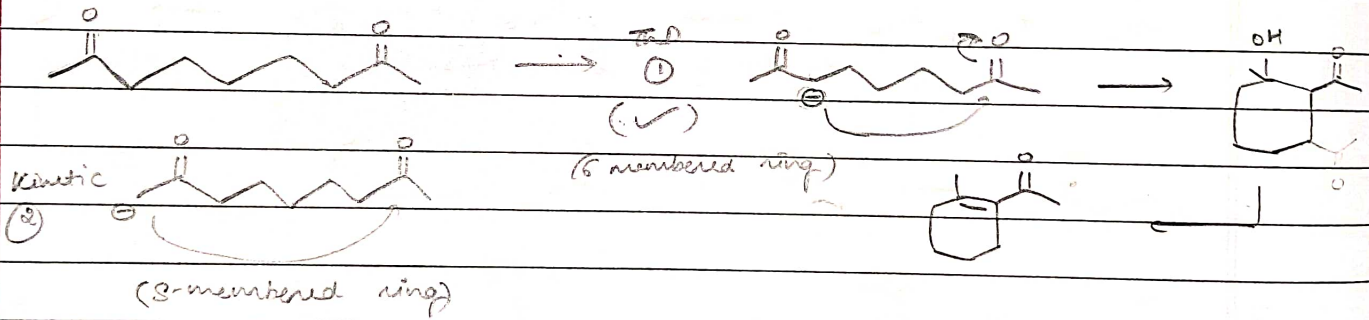
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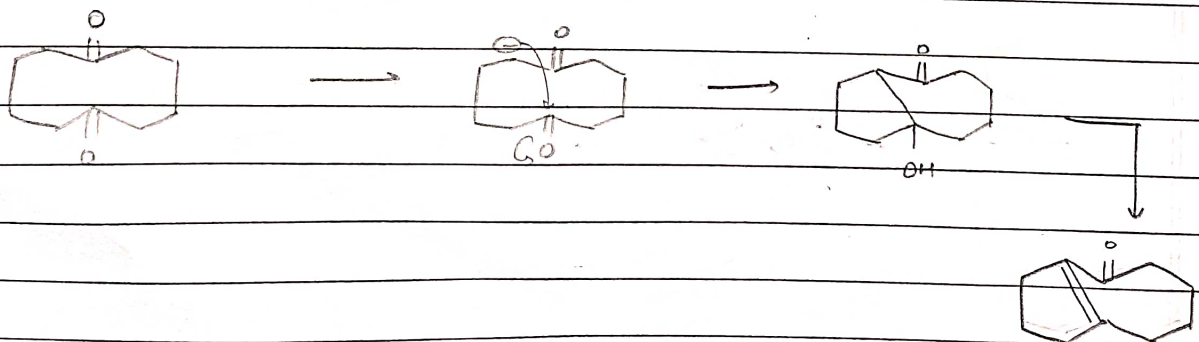
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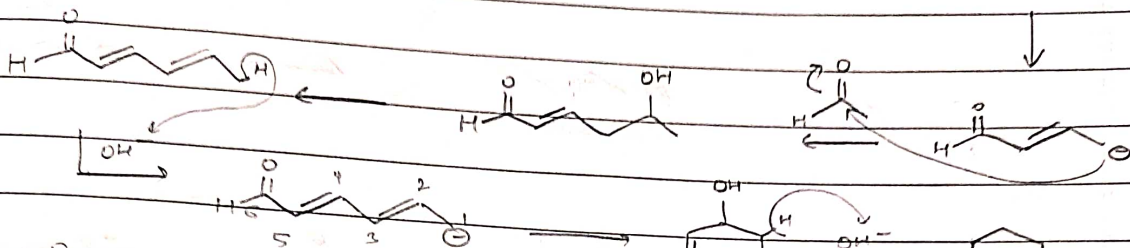
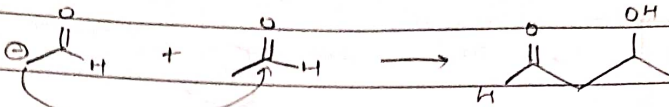
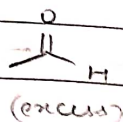
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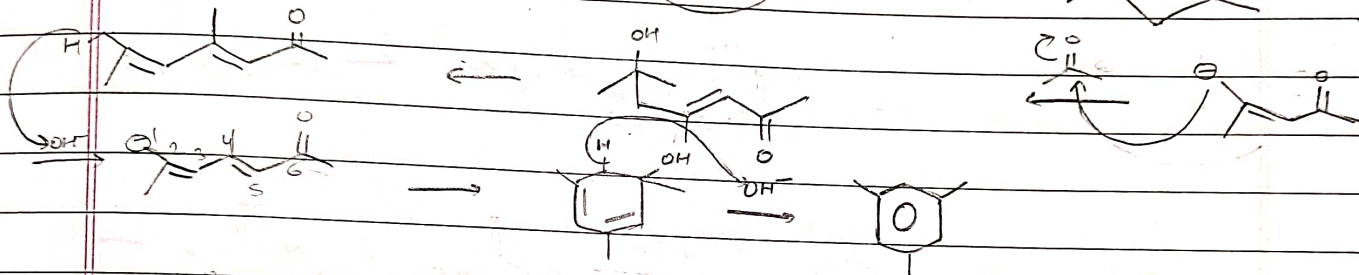
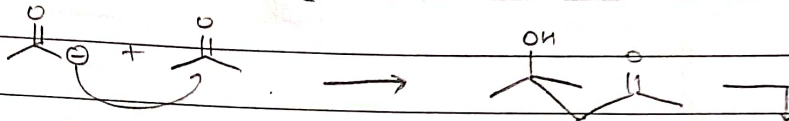
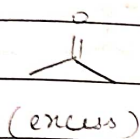
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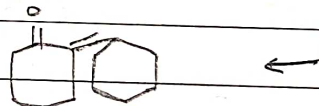
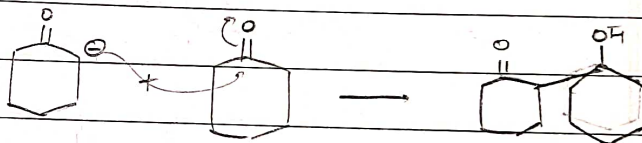
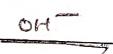
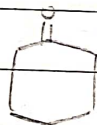
★ 13.



★ 14.



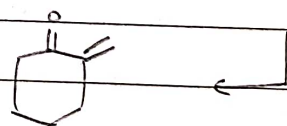
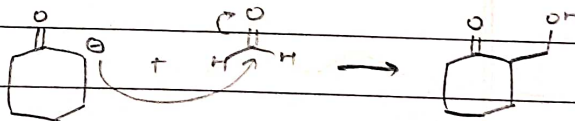
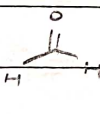
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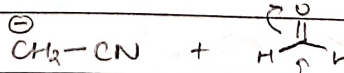
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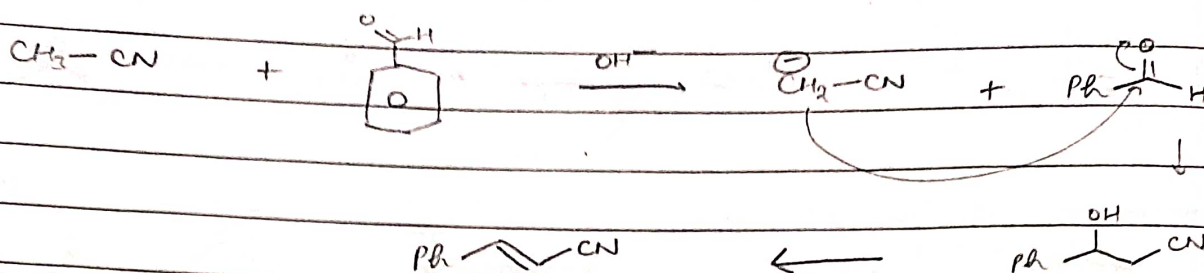
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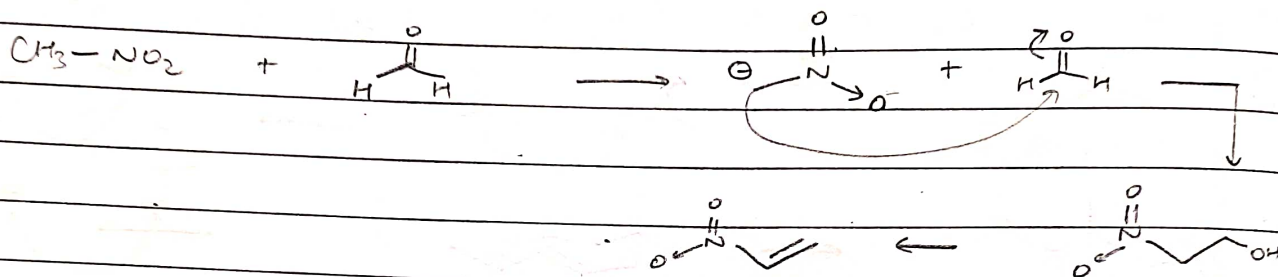
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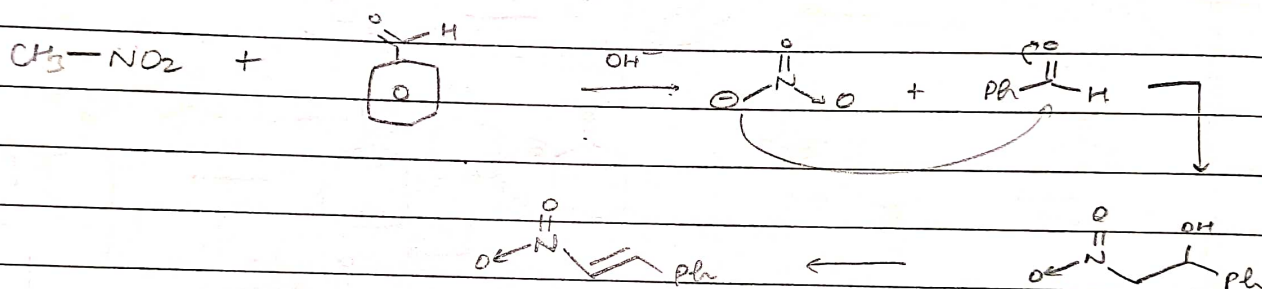
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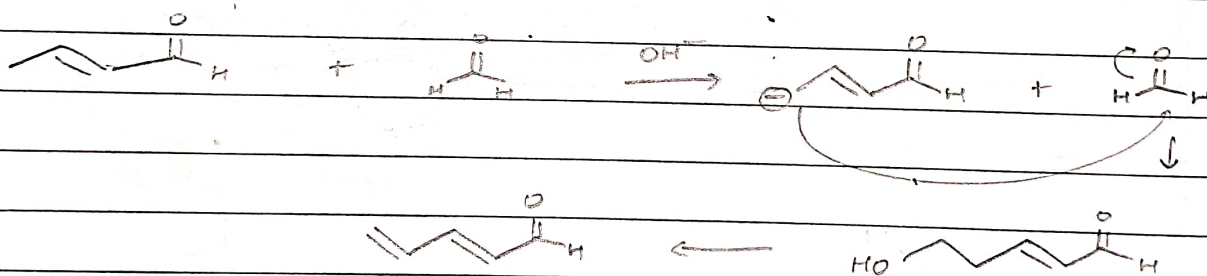
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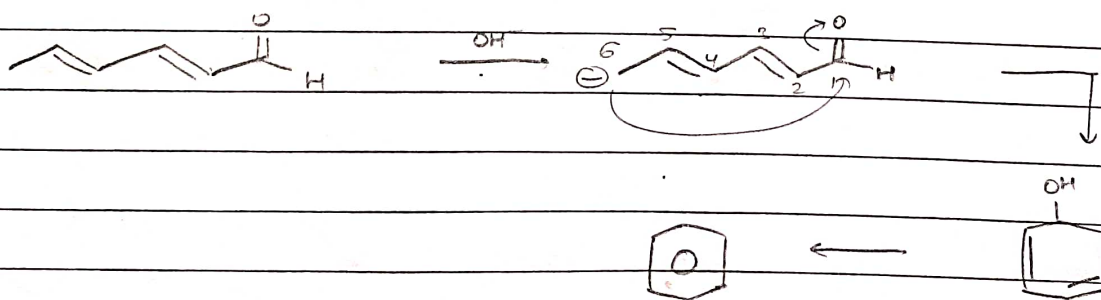
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* 21.



22.

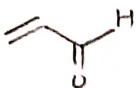


(RI)

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+

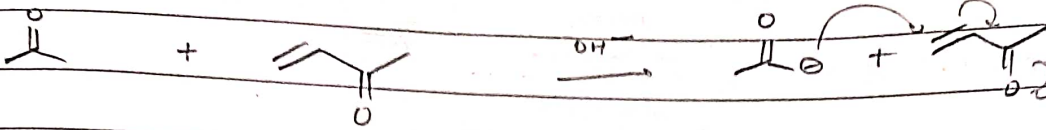


→ (See Remarks)

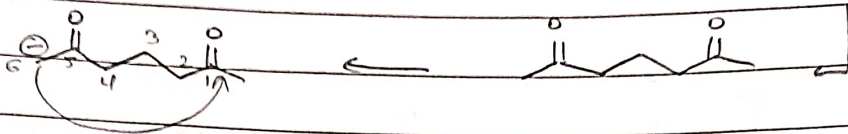
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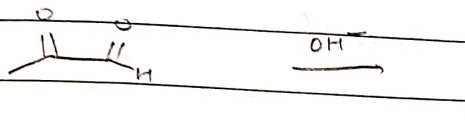


OH

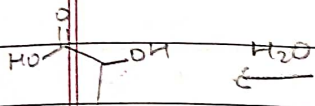
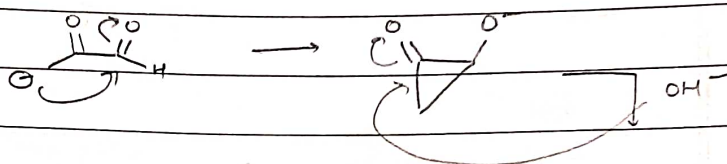


(R II)

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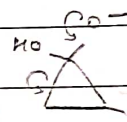
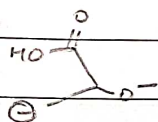
OH⁻



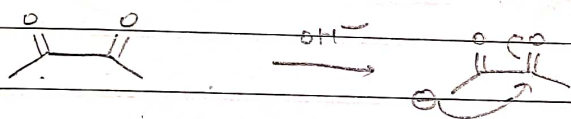
H₂O



H⁺
exchange

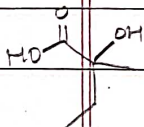
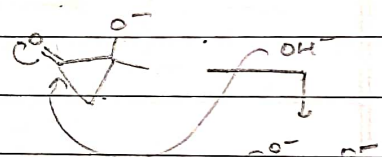


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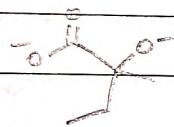


OH⁻

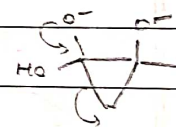
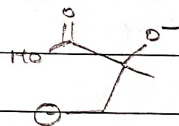
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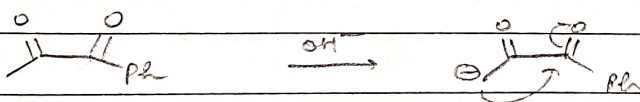
H₂O



H⁺
exchange

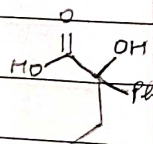
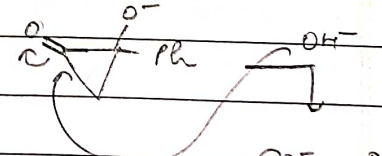


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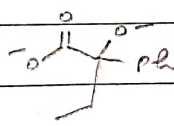


OH⁻

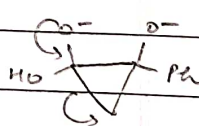
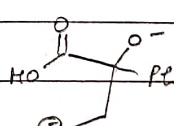
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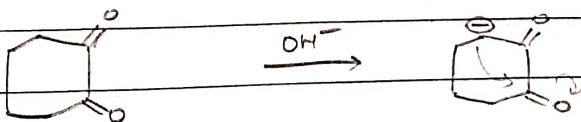
H₂O



H⁺
exchange

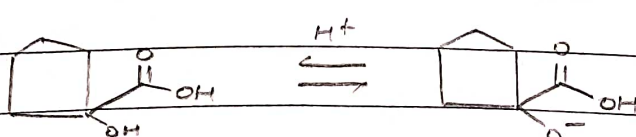
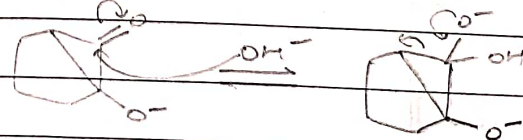


★ 27.



OH⁻

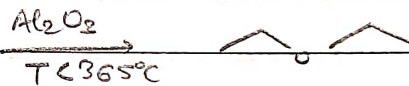
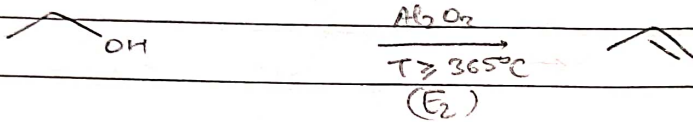
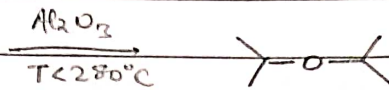
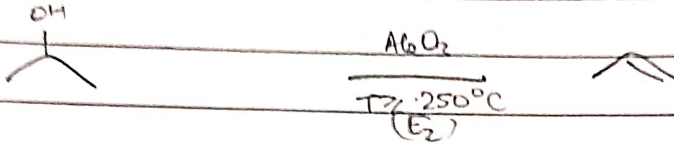
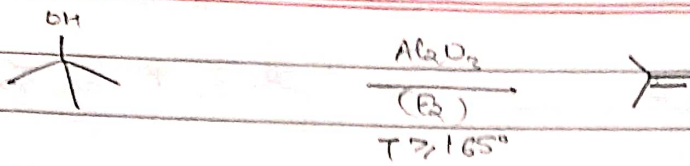
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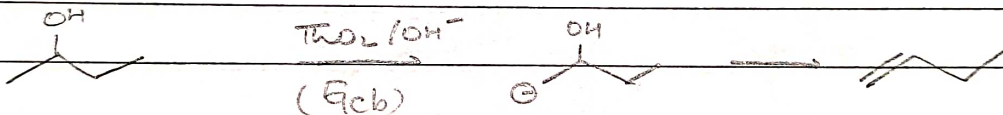
H⁺



NOTE: ①



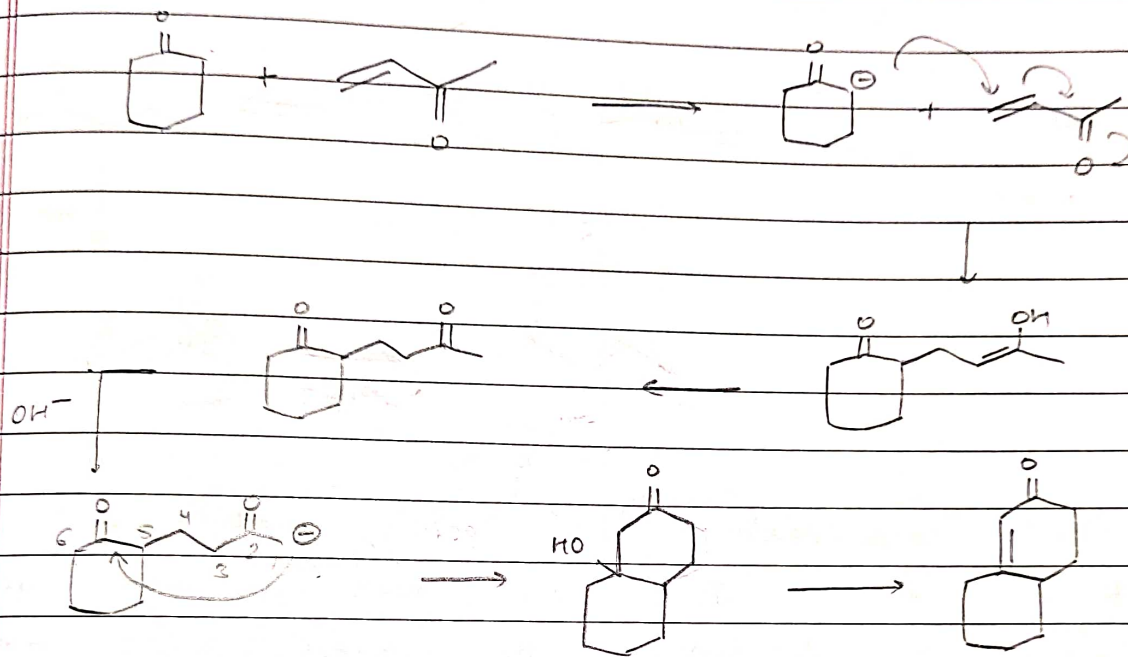
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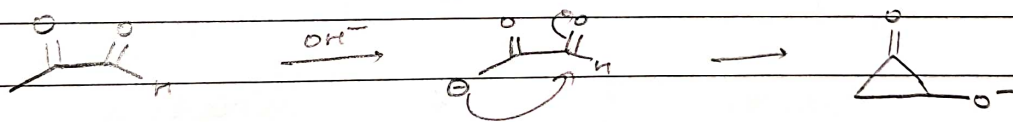
REMARKS:

(I) Robinson Annulation

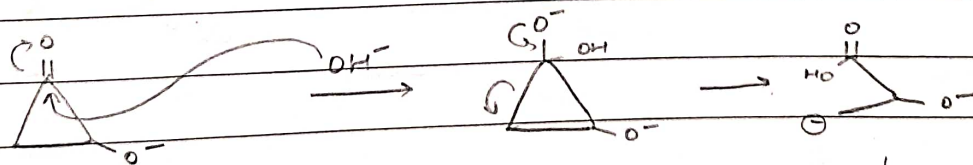
= Michael Addⁿ + Aldol Condensation
(1,4 Addⁿ)



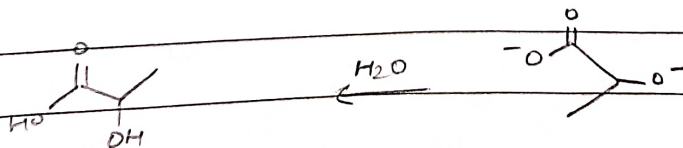
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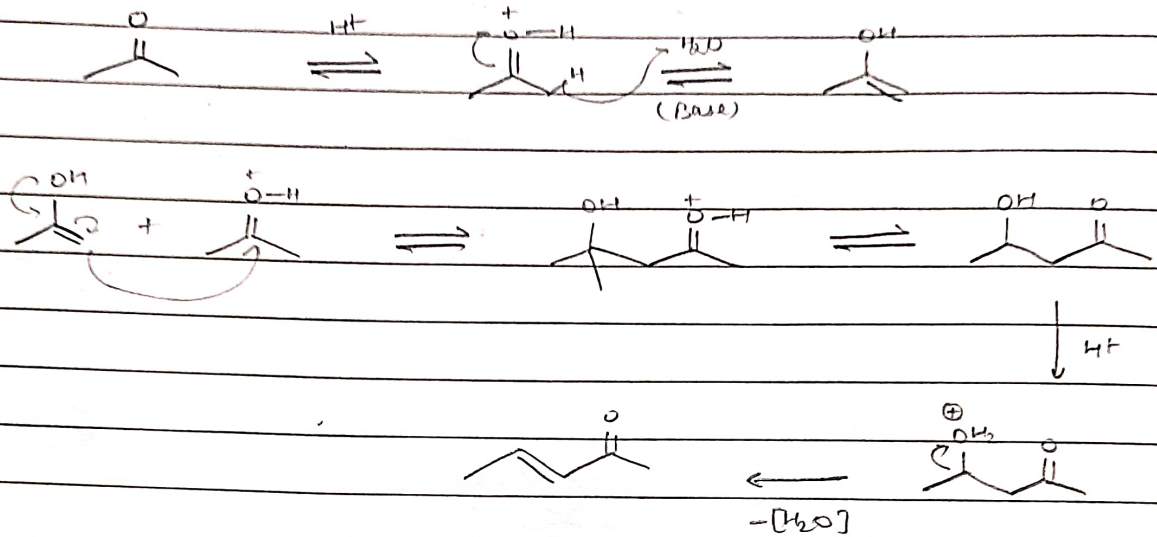
Whenever such triangular cyclic intermediate formed, Nu addⁿ or subⁿ by OH⁻



H⁺ exchange



→ Mechanism (Acidic Medium)

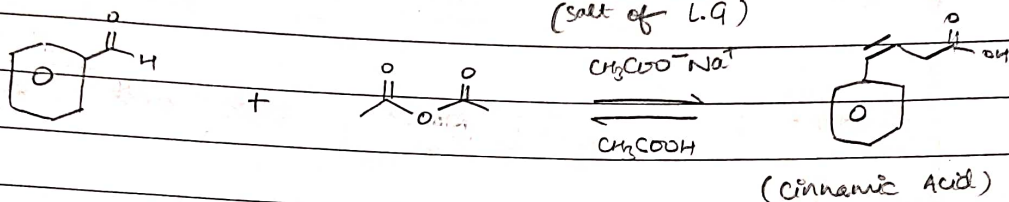


NOTE: Aldol condensation in acidic medium is better than that in basic medium as base has tendency to remove acidic $-H$ & form product kinetically. In acidic medium however, yield of kinetic product is less.

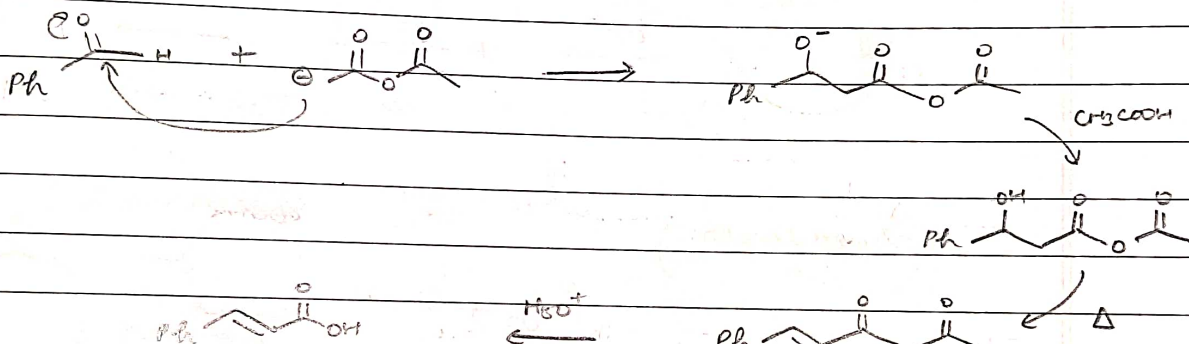
PERKIN REAⁿ

Condⁿ: Non- enolic Aldehyde

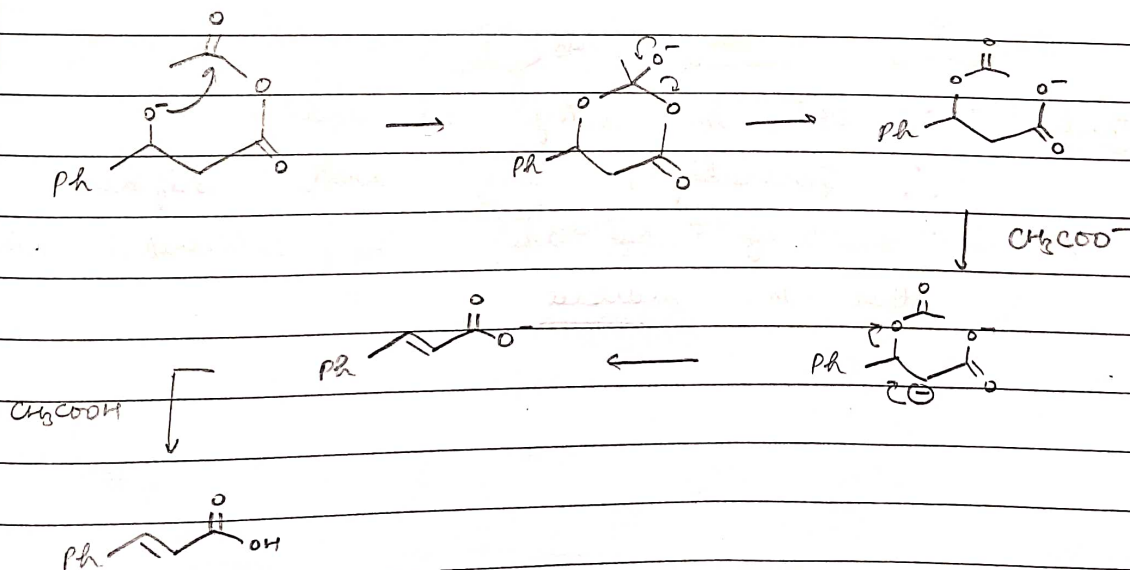
* This is taken as it. Nu addⁿ on CH2=O does not take place



Mechanism



This mechanism is not correct.

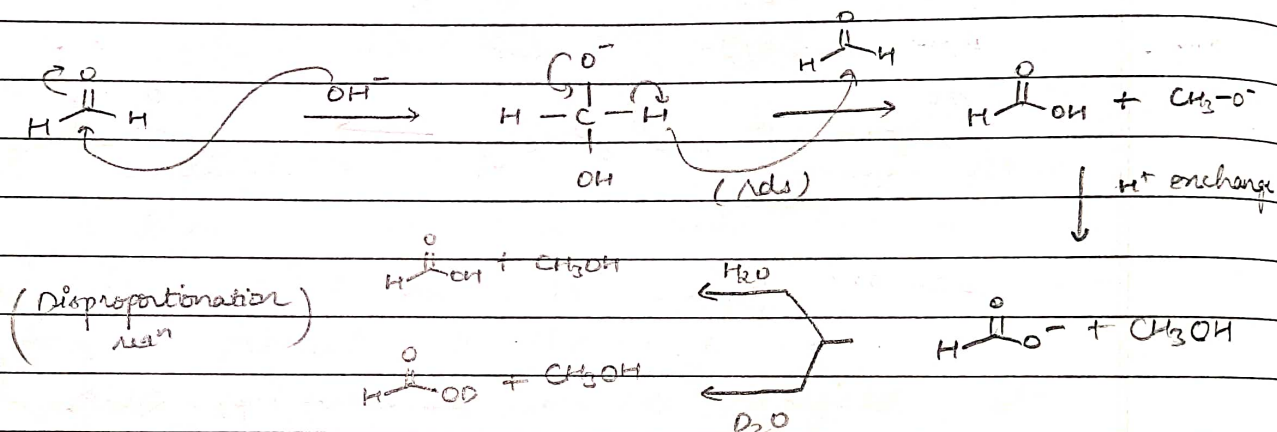


CANNIZZARO'S REAⁿ

Condⁿ : 1. Aldehyde with no α -acidic H
 2. In rds, H/O⁻ should transfer

Reagents : 50% NaOH, 50% KOH, NaOH, KOH, OH⁻

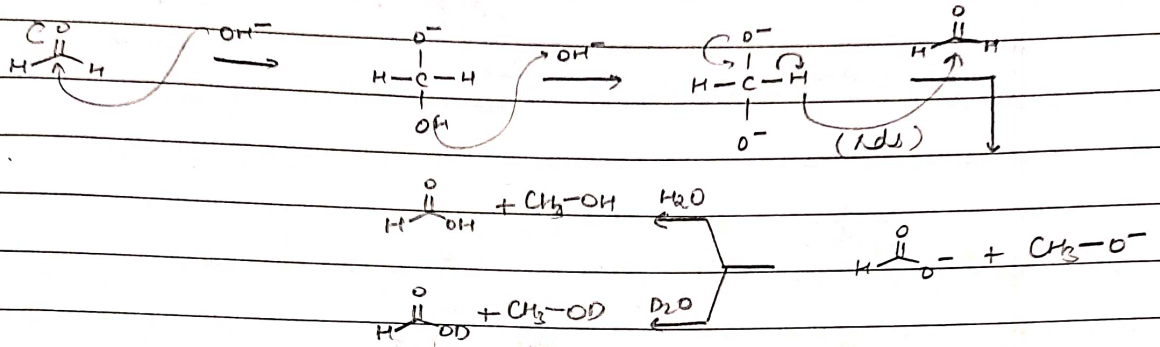
Case I: Normal conc. of OH⁻



NOTE: $\text{ROR} \propto [\text{HCHO}]^2 [\text{OH}^-]^1 \Rightarrow \text{Order} = 3$

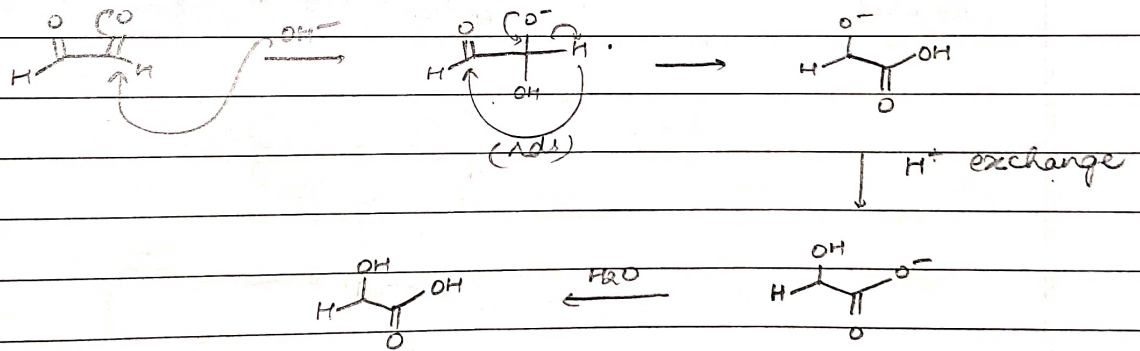
Trick : \therefore OH⁻ is doing Nu addⁿ.
 \therefore Generally, comp with higher rate of Nu addⁿ is oxidised, while other is reduced

Case II : Higher conc. of OH^- (eg - 50% NaOH)



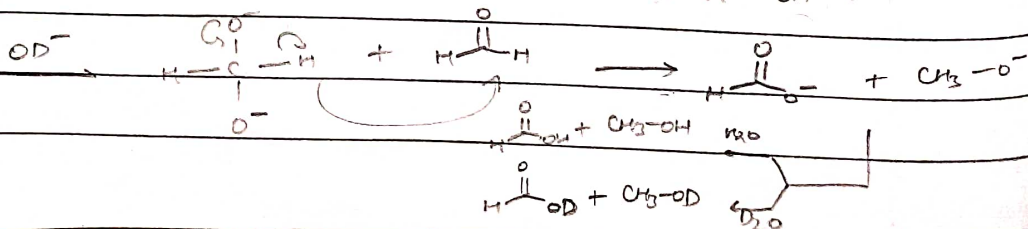
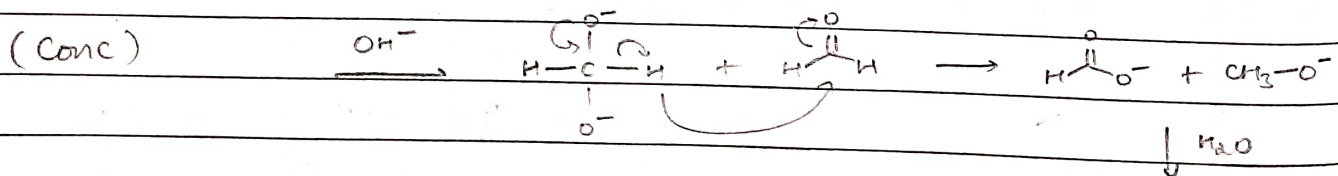
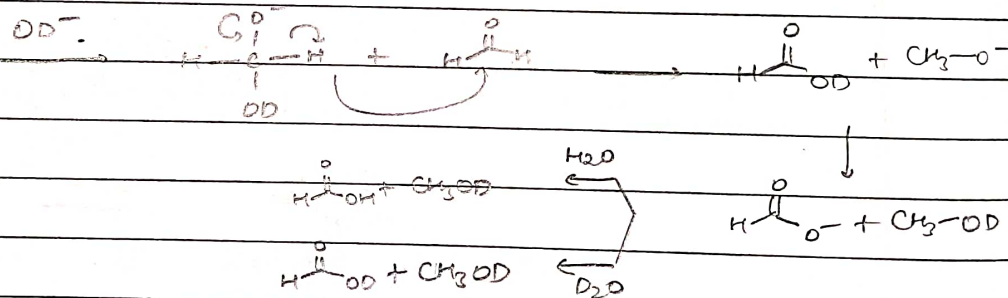
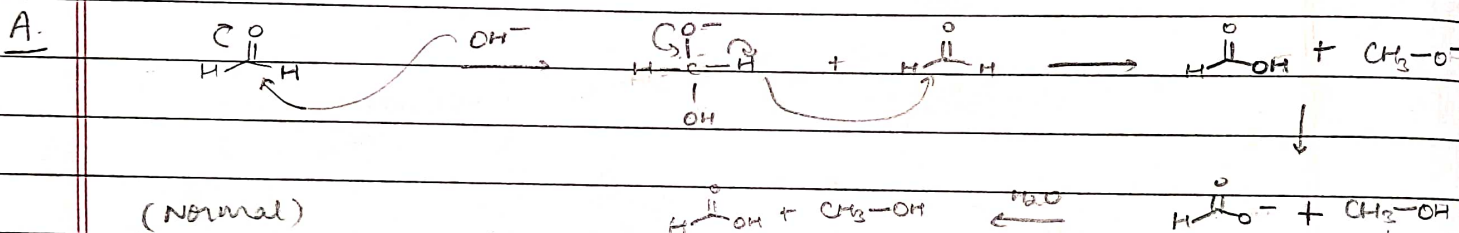
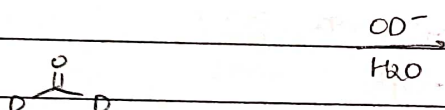
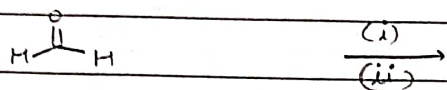
NOTE: $\text{ROR} \propto [\text{H}_2\text{C}=\text{O}]^2 [\text{OH}^-]^2 \Rightarrow \text{Order} = 4$

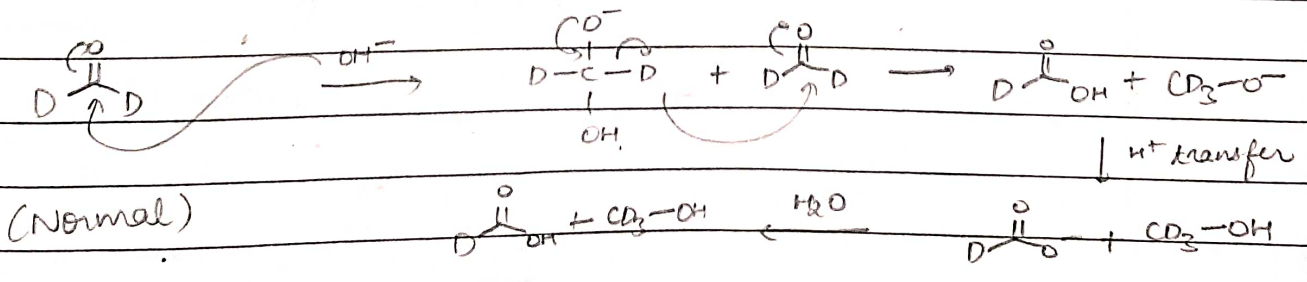
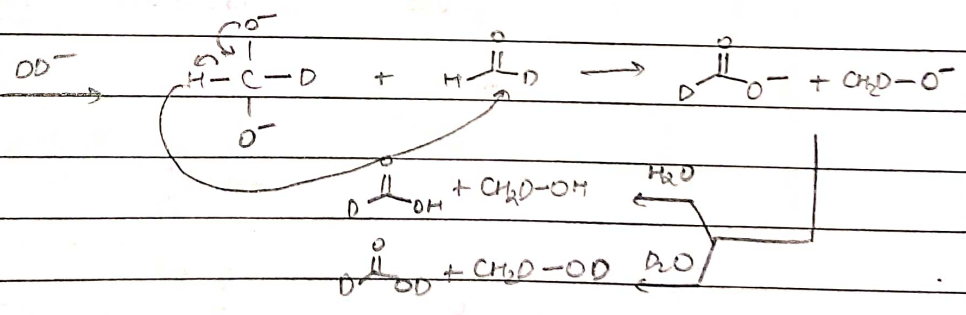
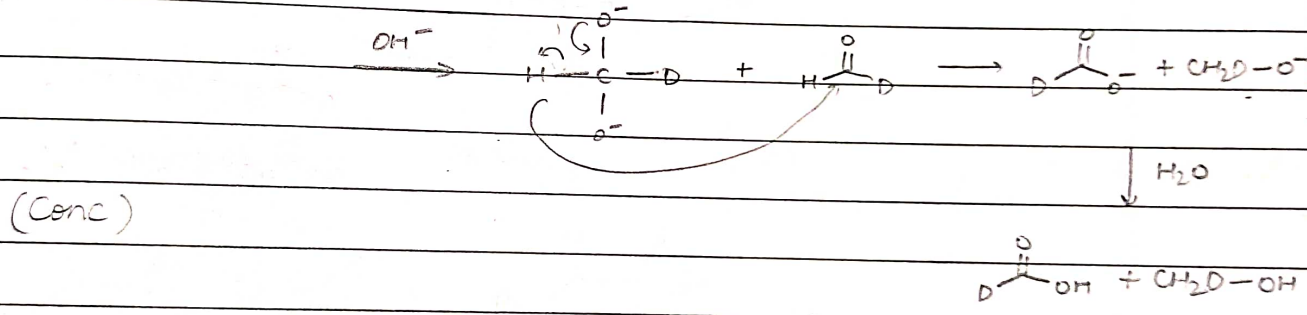
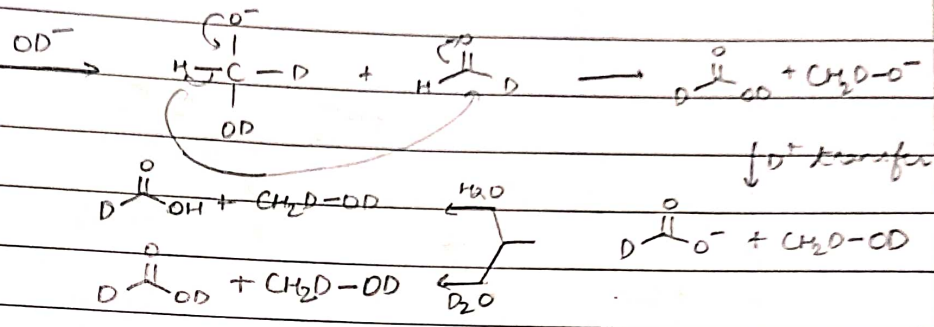
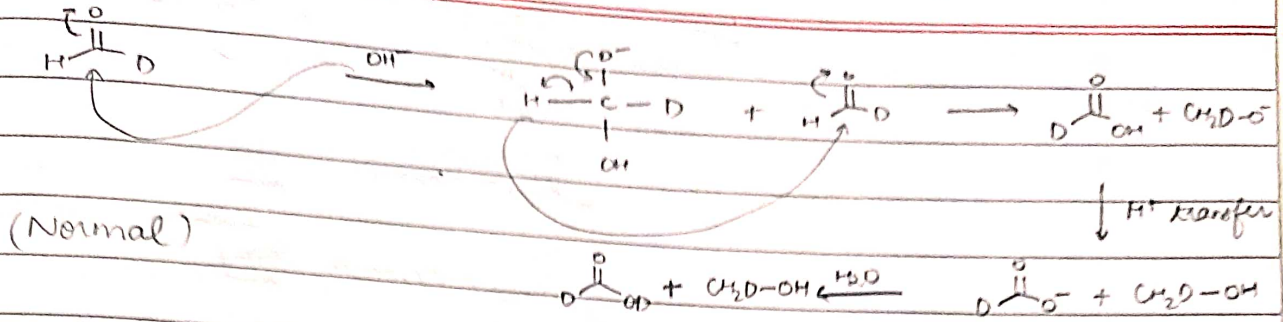
Case III : Intramolecular redⁿ

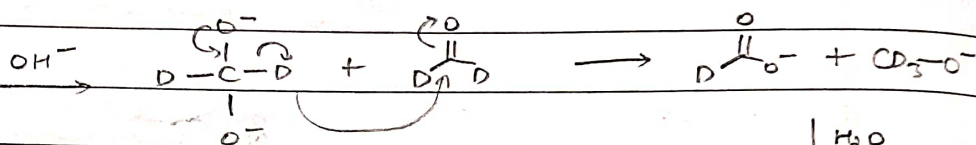
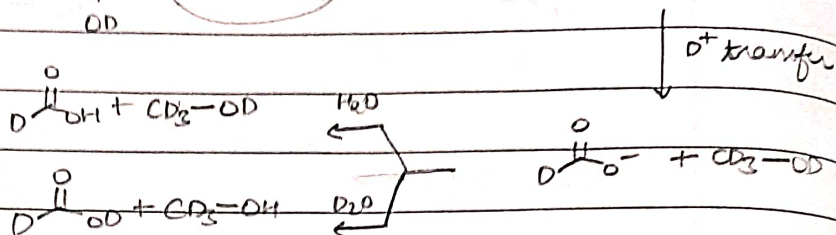
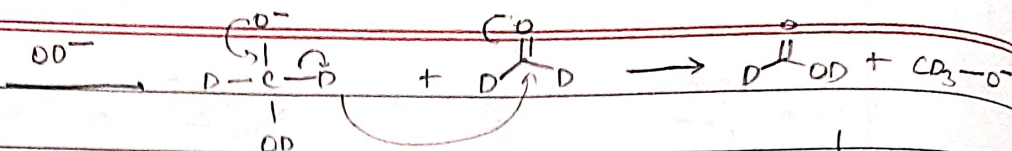


NOTE: $\text{ROR} \propto [\text{Ph-CO-CHO}] [\text{OH}^-] \Rightarrow \text{Order} = 2$

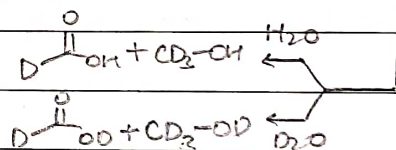
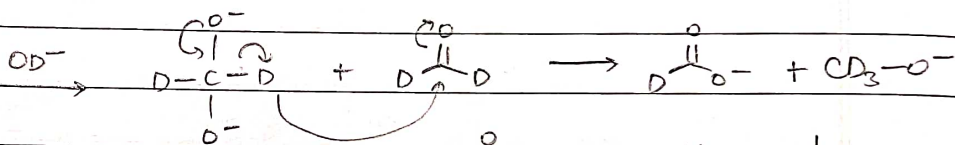
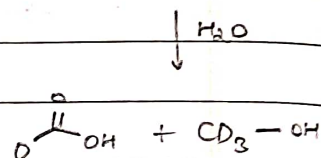
Q. Write mechanism (both normal & conc. cases)





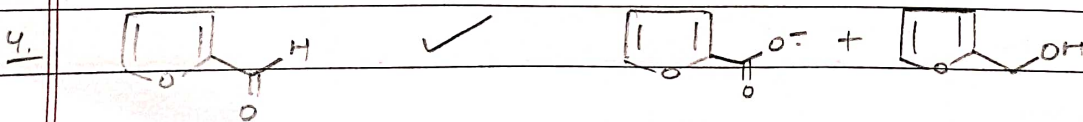
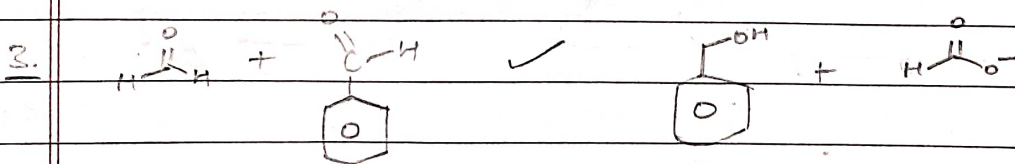
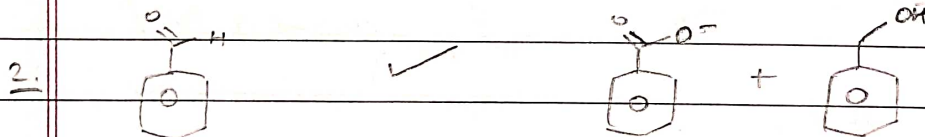


(conc)



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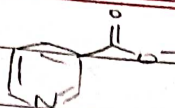
Q. Which give Cannizzaro reactⁿ.



5.



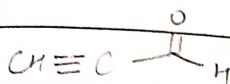
✓



+



★ 6.

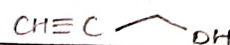


✓

(X)

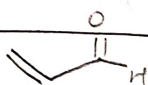


+



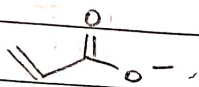
Acidic H & cross conj.

★ 7.



✓

(X)



+



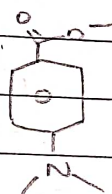
Cross conj.

★ 8.

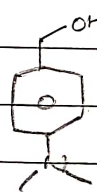


✓

(X)



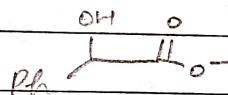
+

Highly activating grp \Rightarrow ROR(Nu addⁿ)

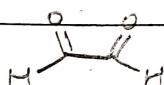
9.



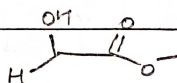
✓



10.



✓



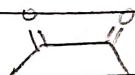
11.



X

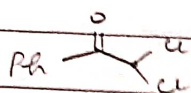
(Acidic -H)

12.

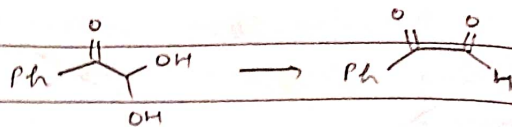


X

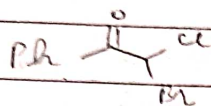
★ 13.



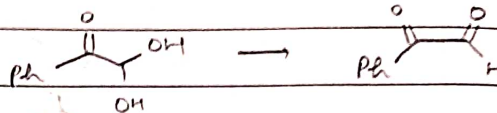
X (✓)



★ 14.



X (✓)

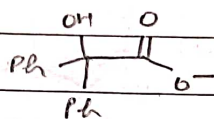


(R-I)

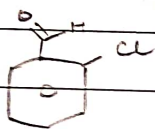
★ 15.



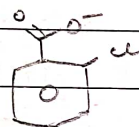
X



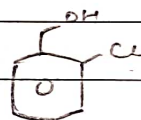
16.



✓

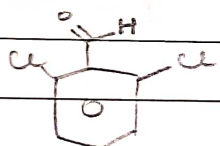


+

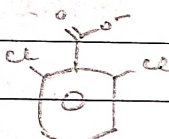


(R-II)

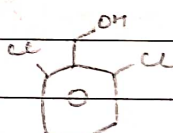
★ 17.



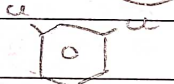
✓



+



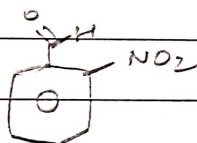
(X)



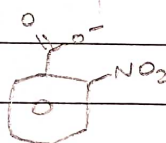
+



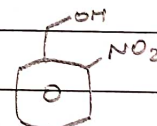
18.



✓

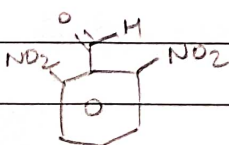


+

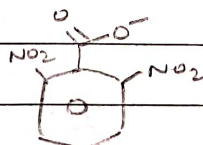


(R-II)

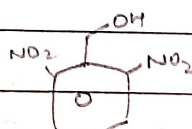
★ 19.



✓



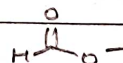
+



(X)



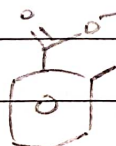
+



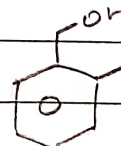
20.



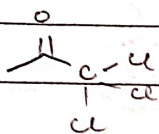
✓



+



28.

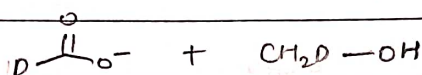


X

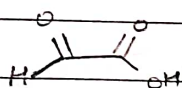
29



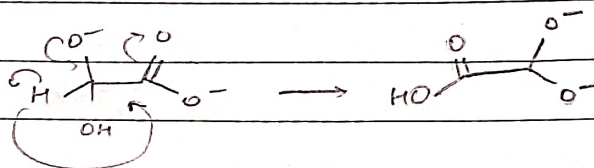
✓



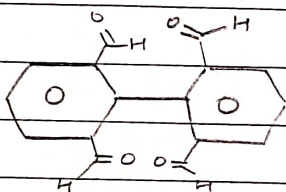
30.



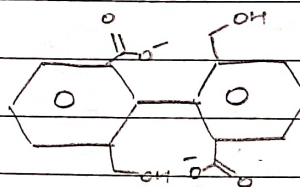
✓



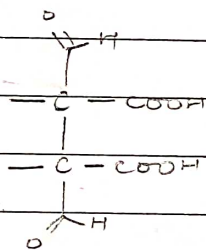
31.



✓

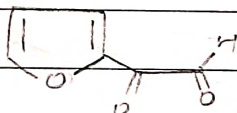


32.

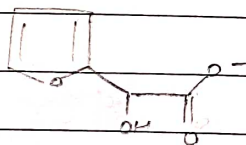


✓

33.

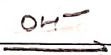
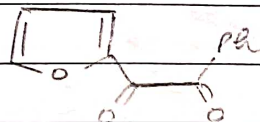


(✓)

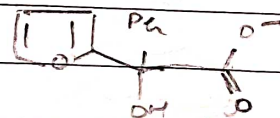
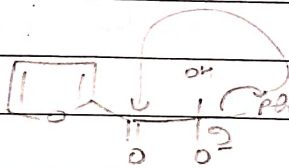


(R-I)

34.

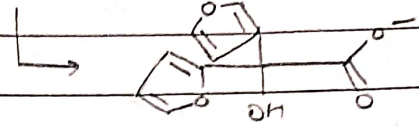
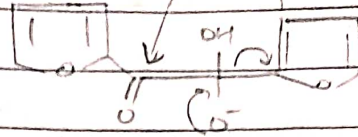
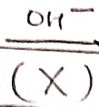
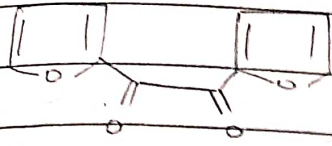


(X)

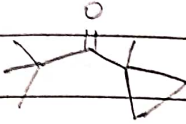


(R-I)

35.

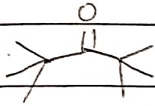


36.



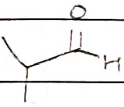
X

37.



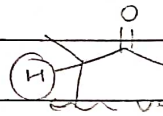
X

* 38.



X

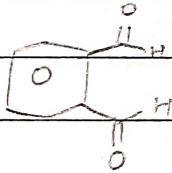
(✓)



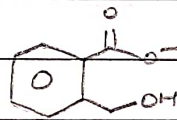
very less acidic

This comp. gives 95% Cannizzaro & 5% Aldol

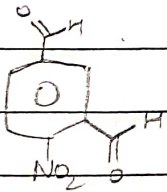
39.



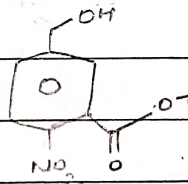
✓



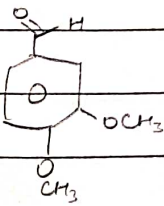
40.



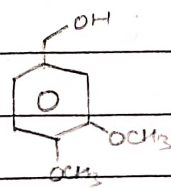
✓



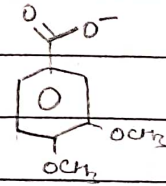
41.



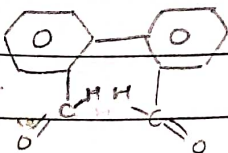
✓



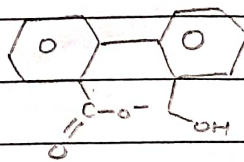
+

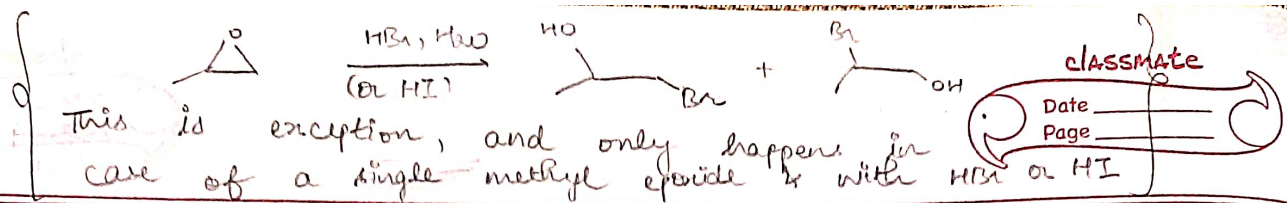


42.



✓

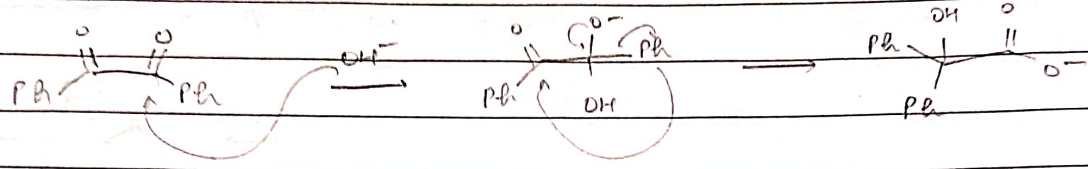




CLASSMATE
 Date _____
 Page _____

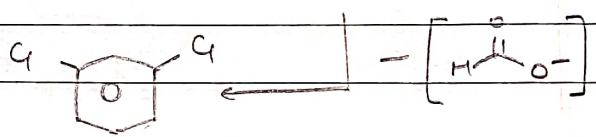
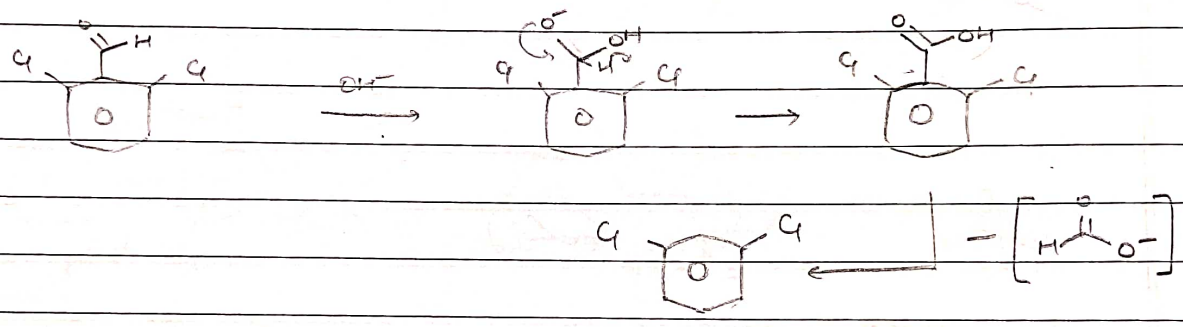
REMARK: I. Benzylic Rearrangement

(Q 5, 34, 35)



This takes place in case of any aromatic group (see 34 & 35)

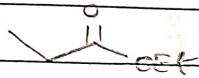
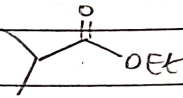
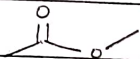
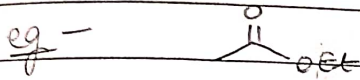
II.
(Q 17, 19)



22/06/2023

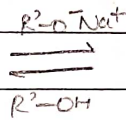
CLAISEN ESTER CONDENSATION

Condⁿ: Ester + 2 α -acidic H

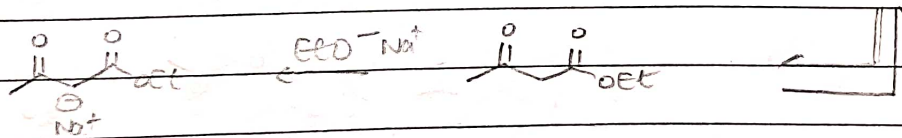
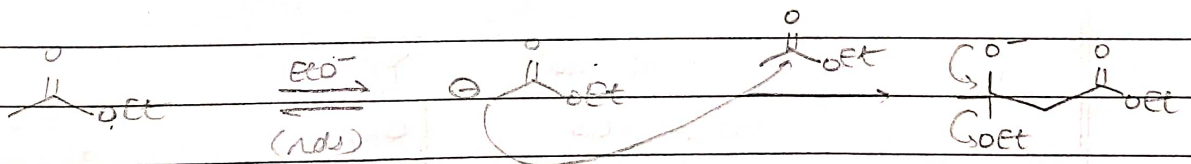


X

✓

 β keto ester

Mechanism



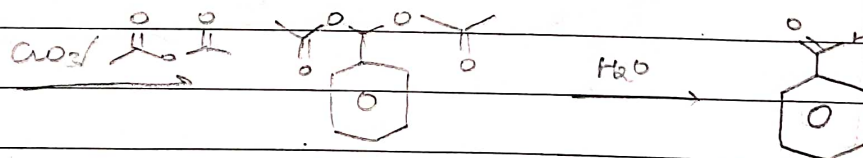
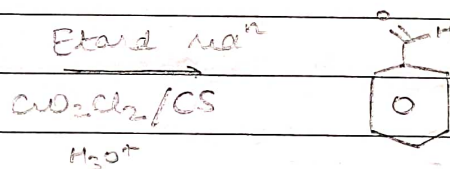
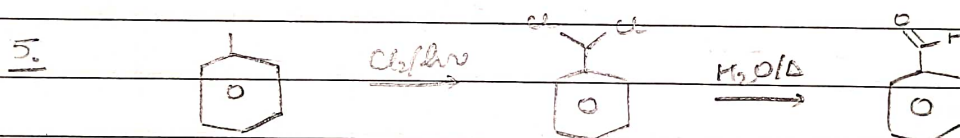
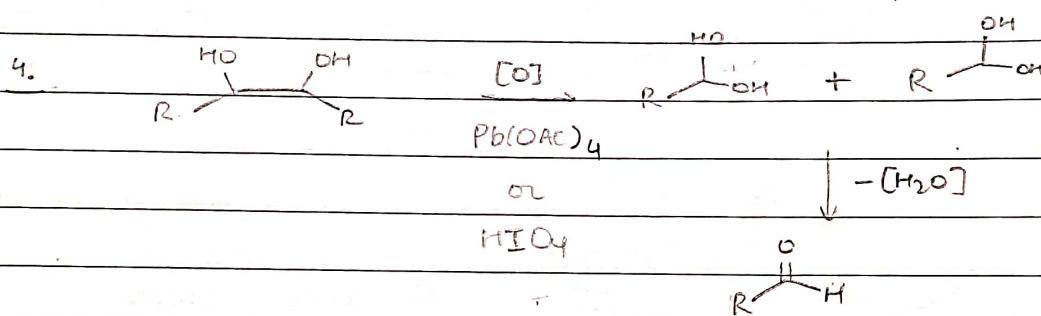
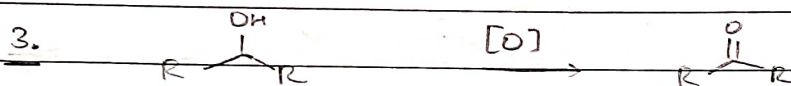
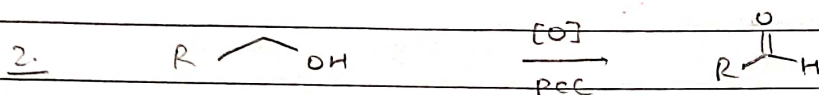
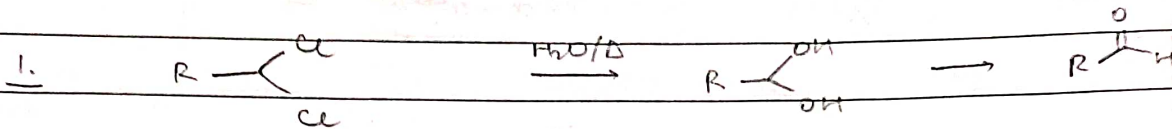
NOTE:

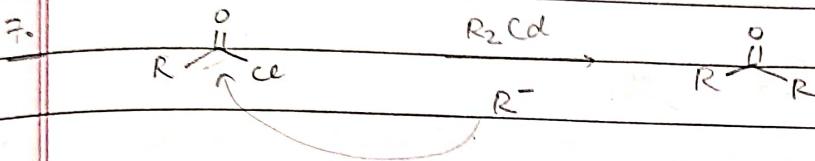
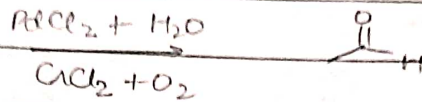
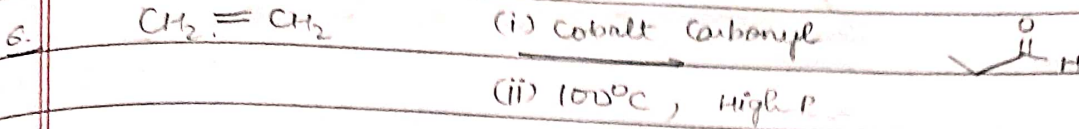
All steps are reversible.

So to drive the reⁿ fwd, salt is removed.

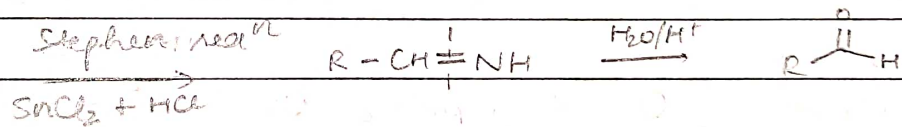
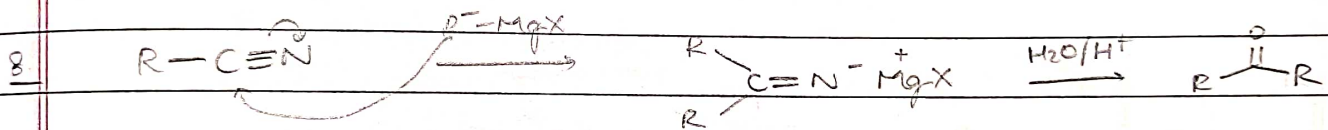
This is why 2 α -acidic H-atoms are required.

27/06/2023

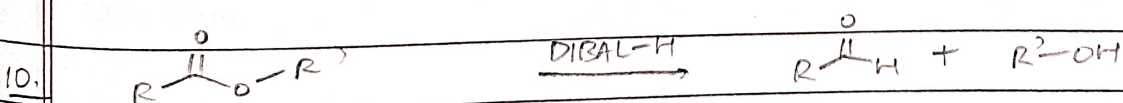
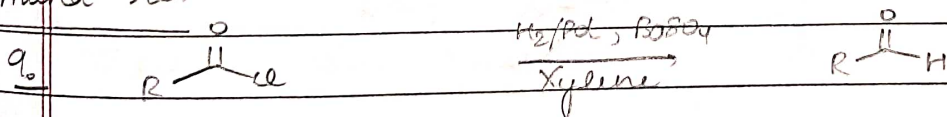
PREPⁿ OF ALDEHYDES & KETONES

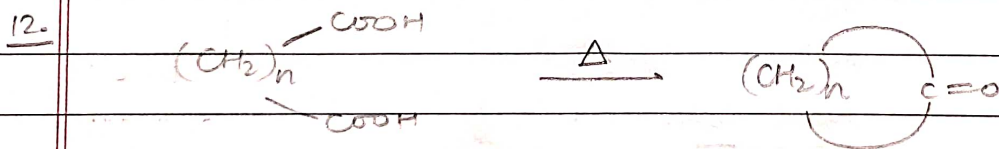
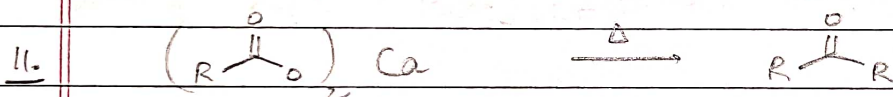
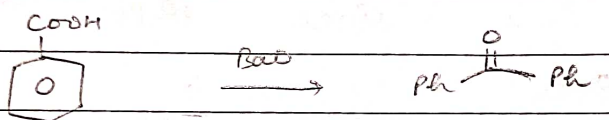
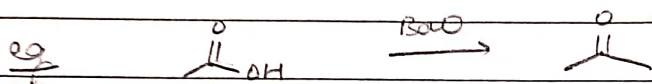
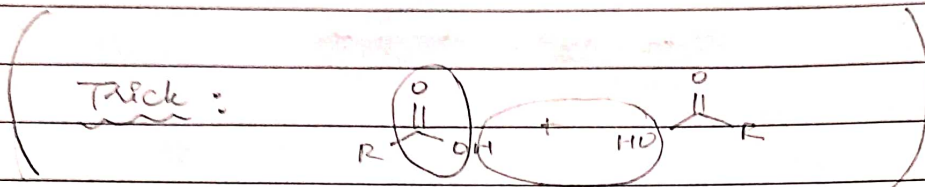
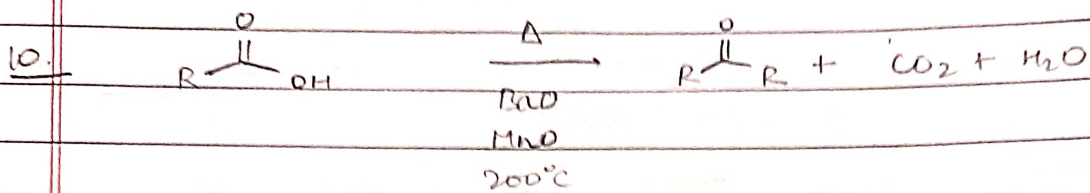


(Reaction stops here since this R^- is soft Nu)



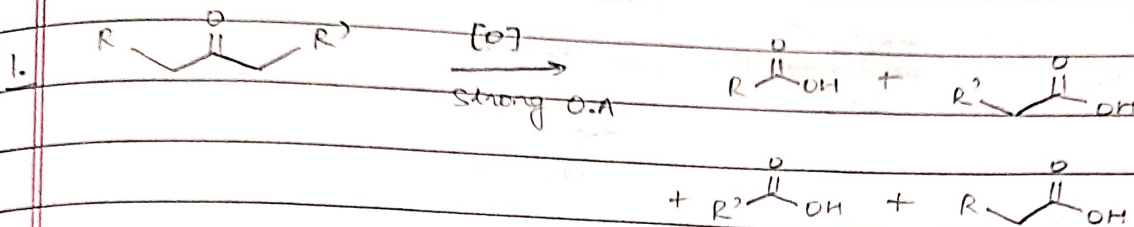
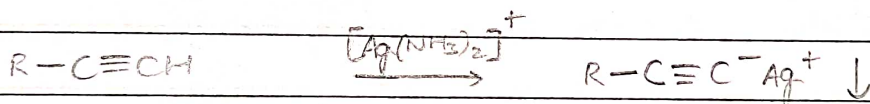
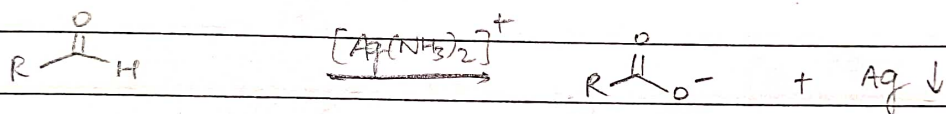
Rosenmund reagent





$$n = 4, 5$$

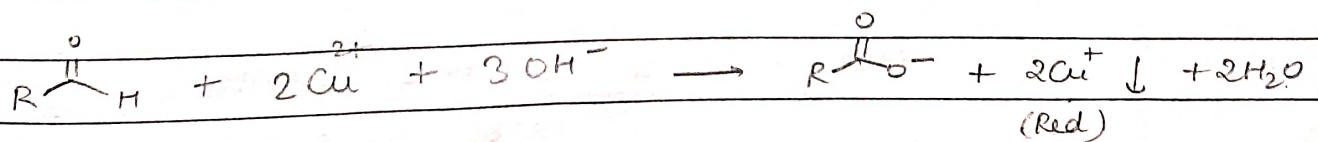
REACTIONS OF ALDEHYDES & KETONES

→ Oxidⁿ• Tollen's reagent — $[\text{Ag}(\text{NH}_3)_2]^+$ Selective O.A. : only Aldehyde to Acid

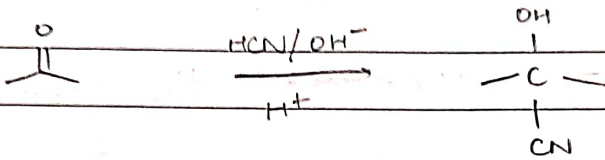
• Fehling solⁿ — 50% Ag_2SO_4
50% NaOH + Sodium Potassium
Tartarate

These give Cu^{2+} ions in solⁿ. (Rochelle Salt)

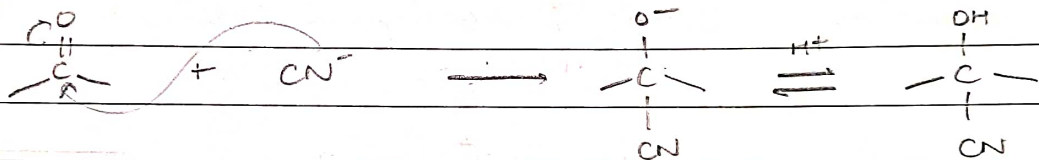
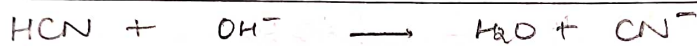
Selective O.A. : only Aliphatic Aldehyde to Acid.



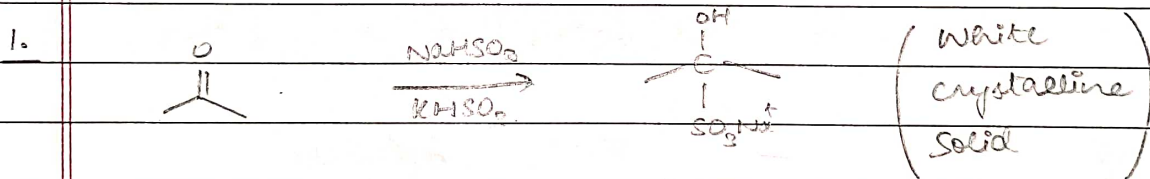
→ Cyanohydrin formation



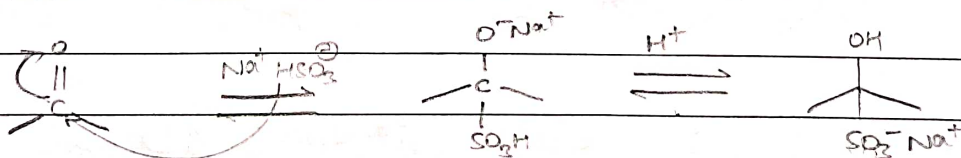
Mechanism



→ Addⁿ

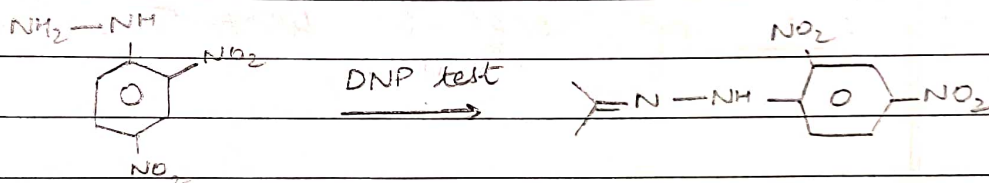
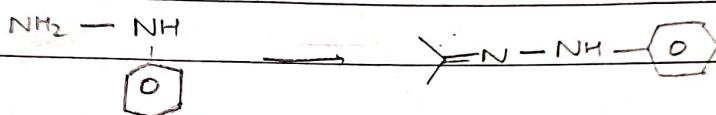
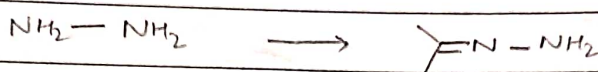
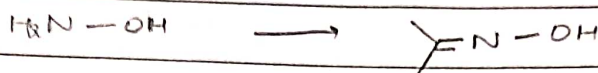
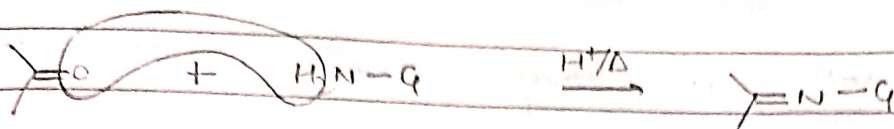


Mechanism

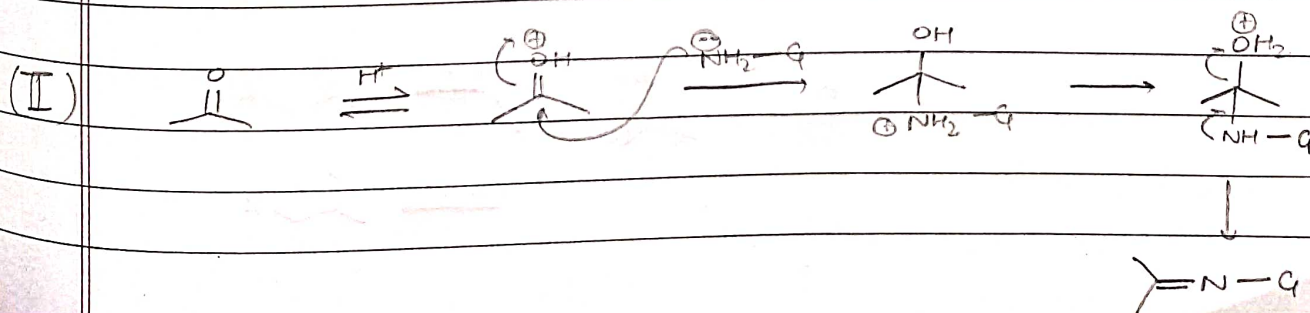
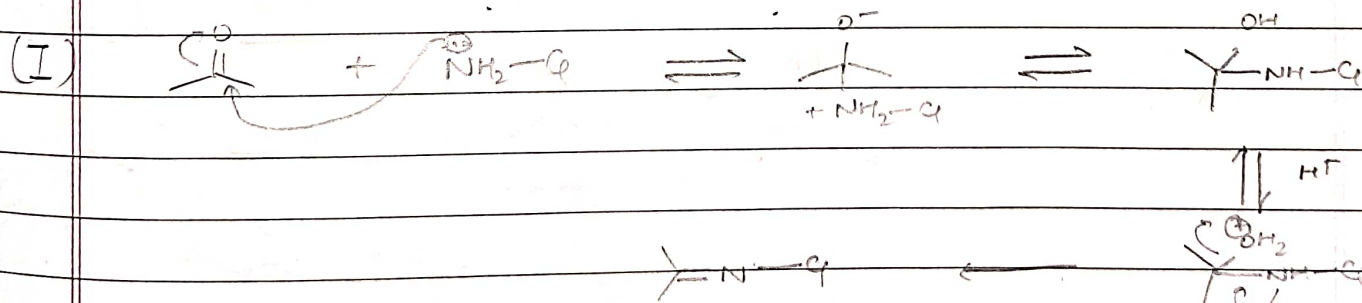


NOTE: All aldehydes & methyl ketones give this test (with #C ≤ 6)

2.

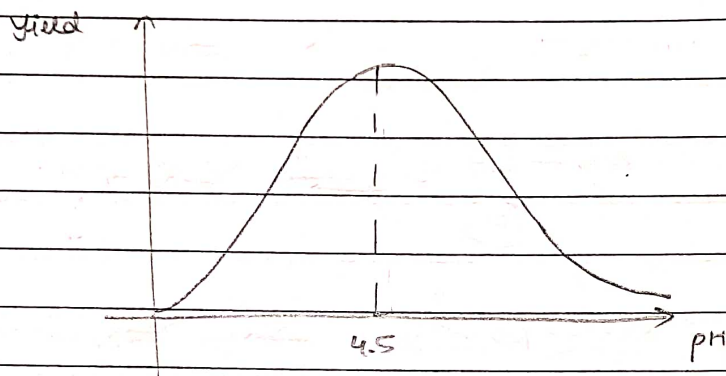
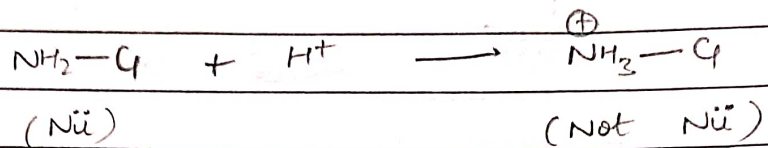


Mechanism



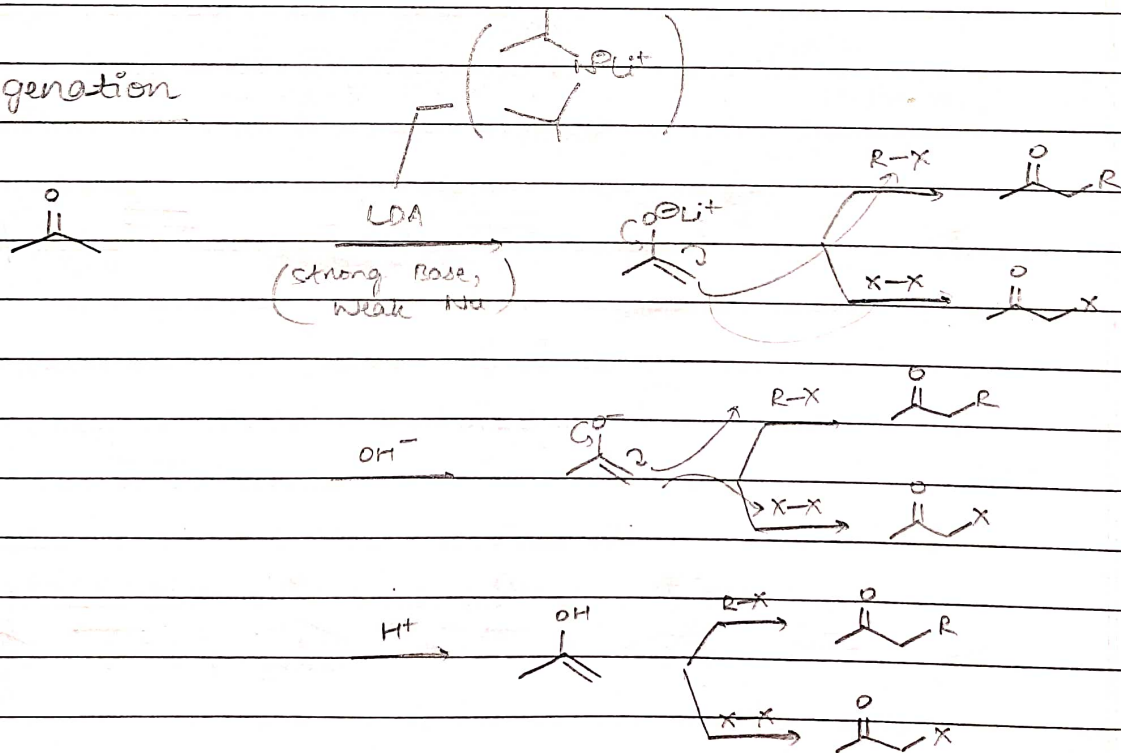
NOTE: This rxn is very sensitive to pH.

since

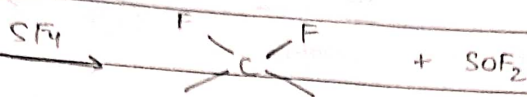
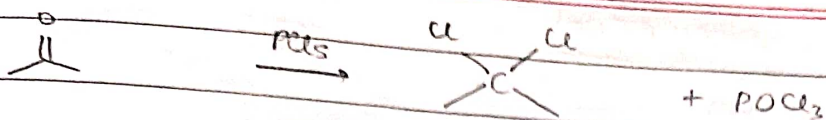


Best pH range : 4 to 5

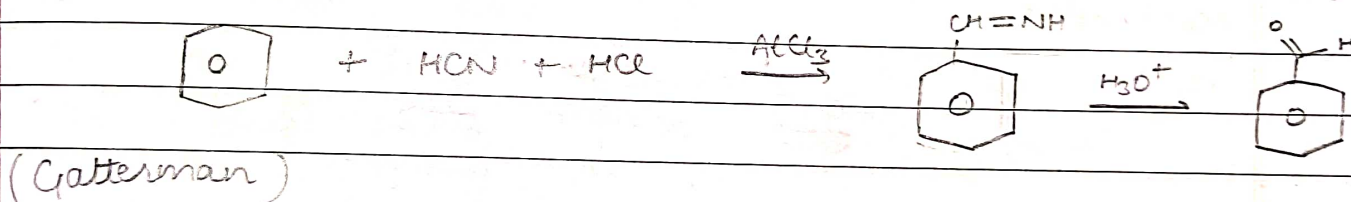
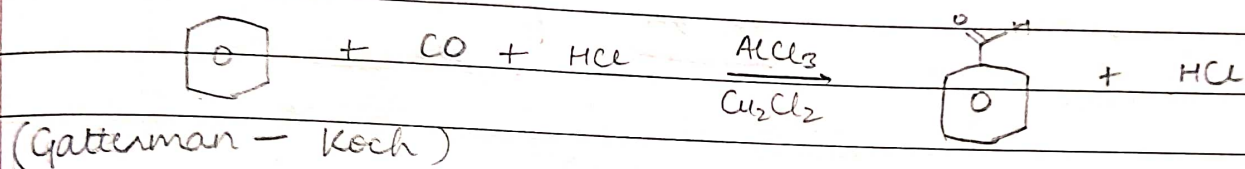
→ Halogenation

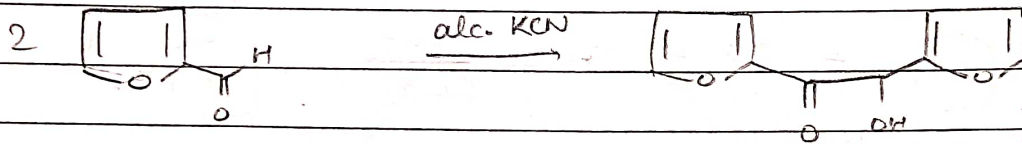
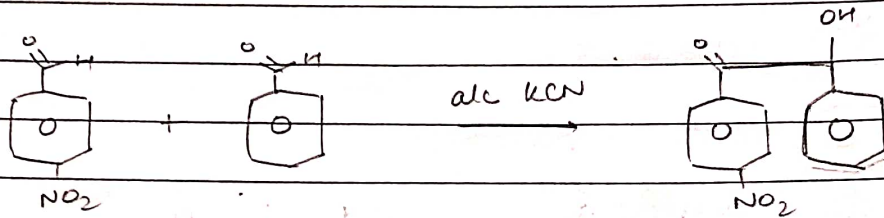
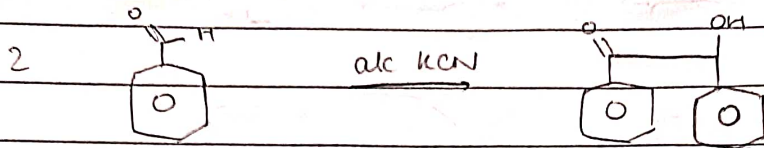
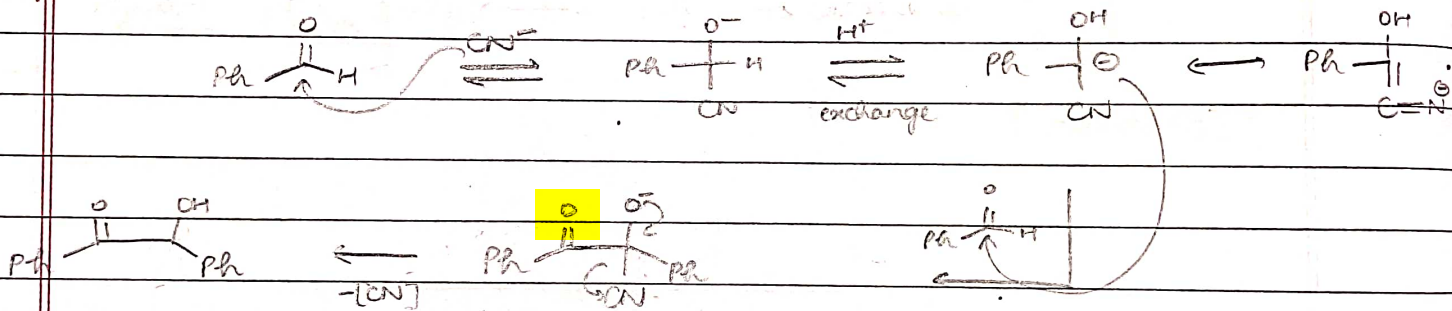


NOTE:



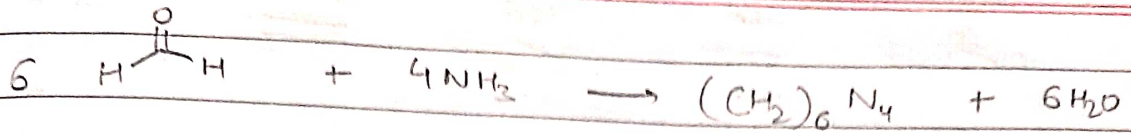
→ Aldehyde Synthesis



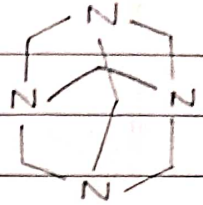
BENZOIN CONDENSATIONMechanism

(Trick: Ketone on the ring whose rate of Nu⁻ addⁿ is greater)

NOTE:

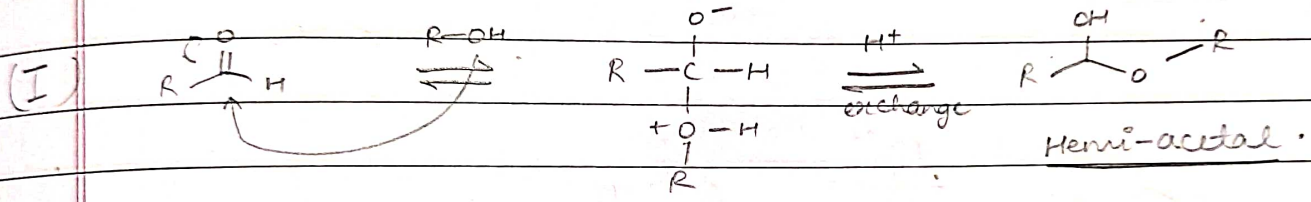


urotropine



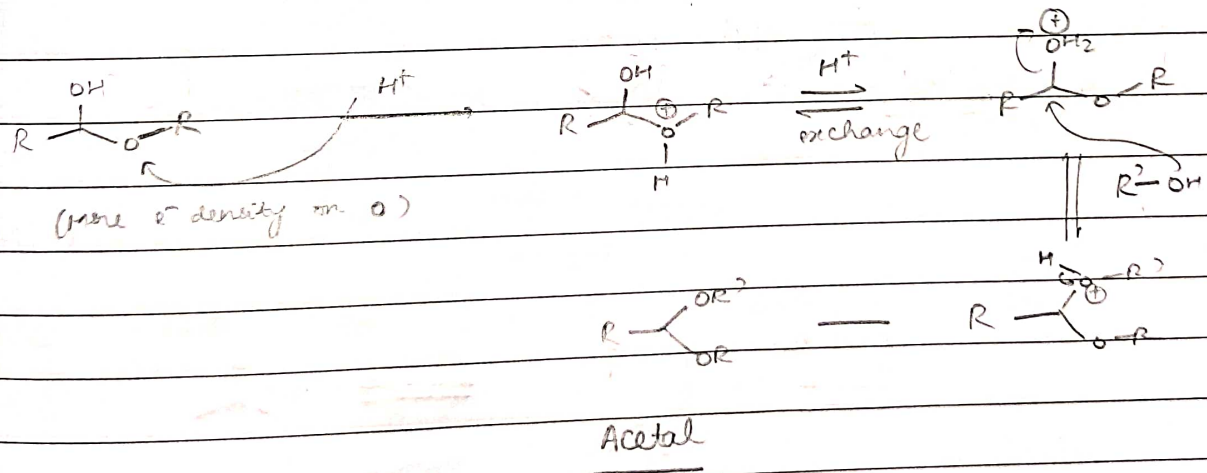
28/06/2023

PREPⁿ OF ACETAL & HEMIACETAL

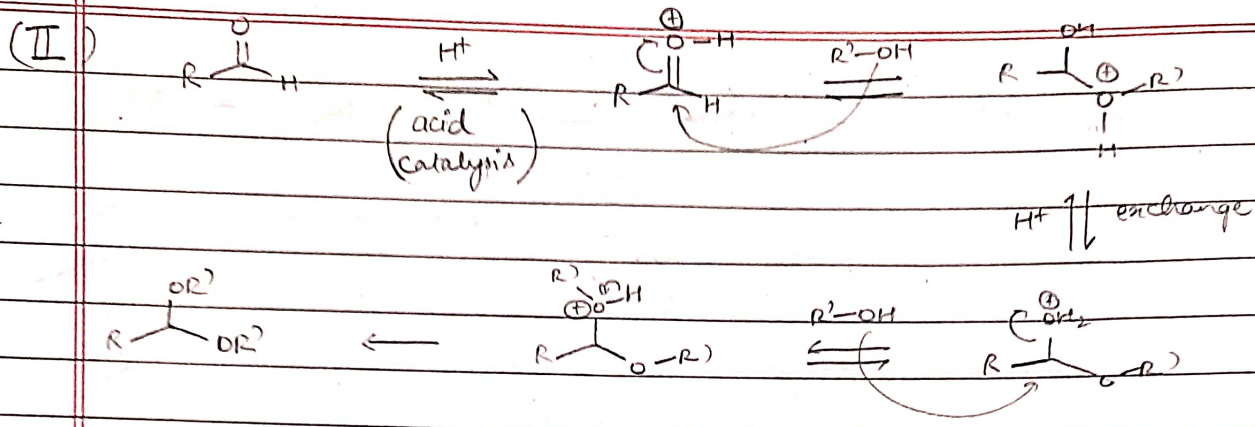


Rean stops here.

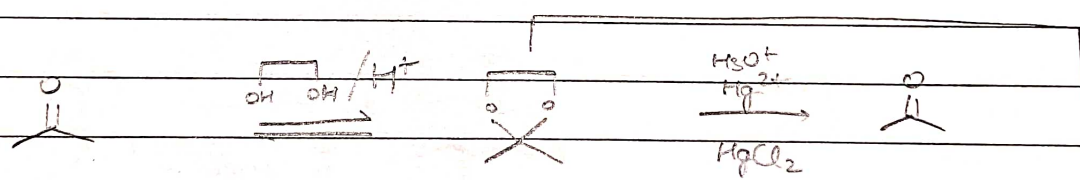
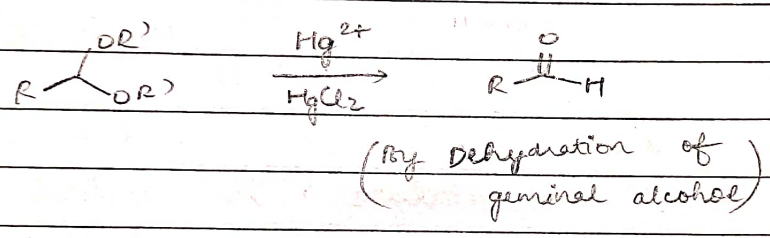
If we further catalyse it with acid (eg- dry HCl).



(more e density on O)

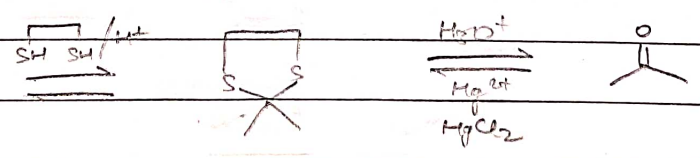


NOTE: Unlike in (I), reac^n does not stop at hemi-acetal



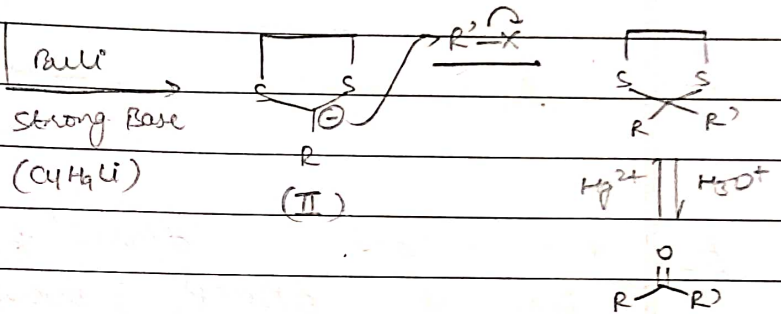
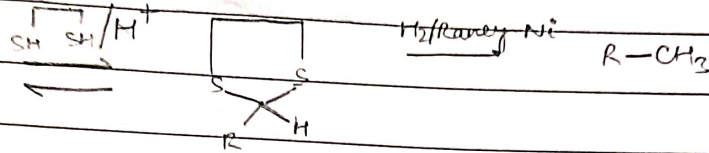
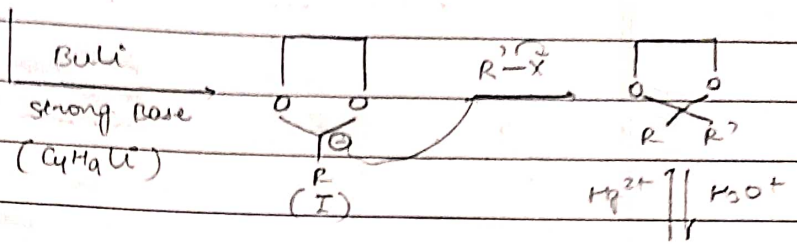
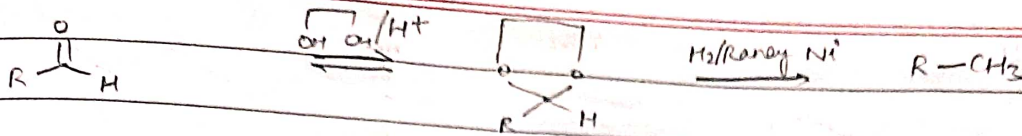
Cyclic Acetal or ketal

$\text{H}_2/\text{Raney Ni}$



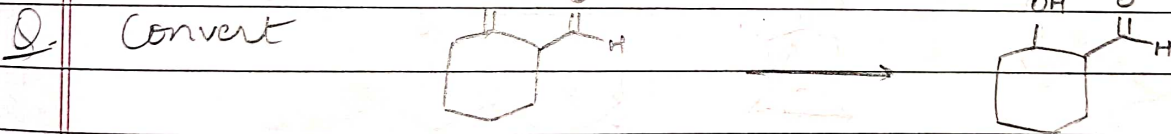
$\text{H}_2/\text{Raney Ni}$



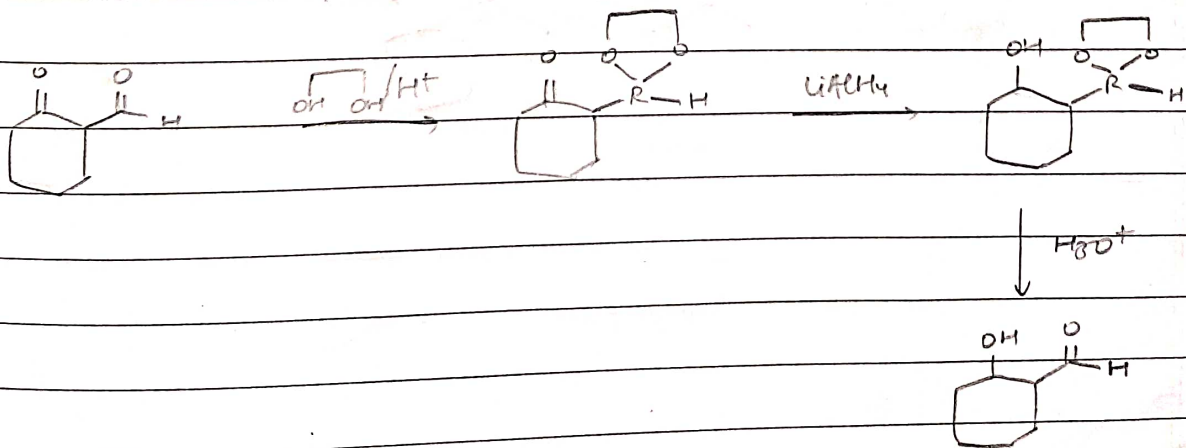


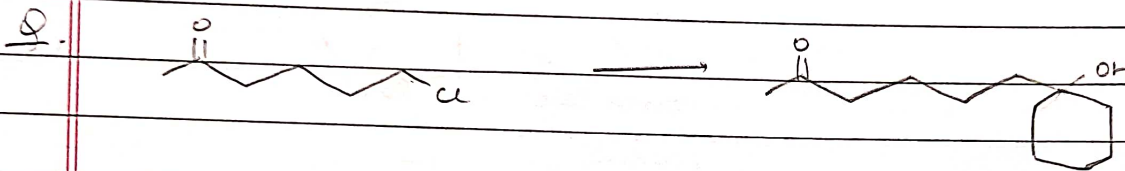
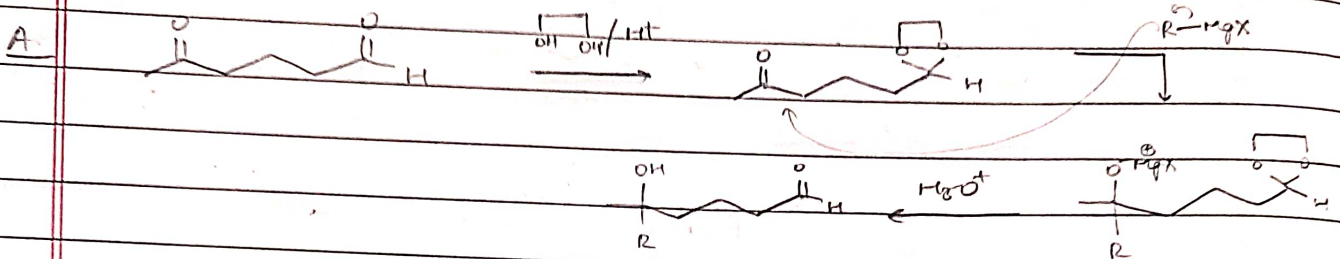
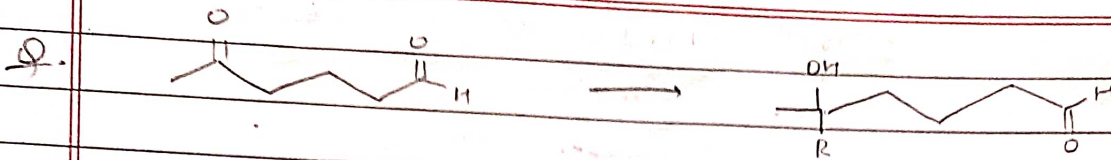
Stability : (II) > (I) (Vacant orbital in S).

Nucleophilicity : (I) > (II) (\ominus involved in resonance with S)

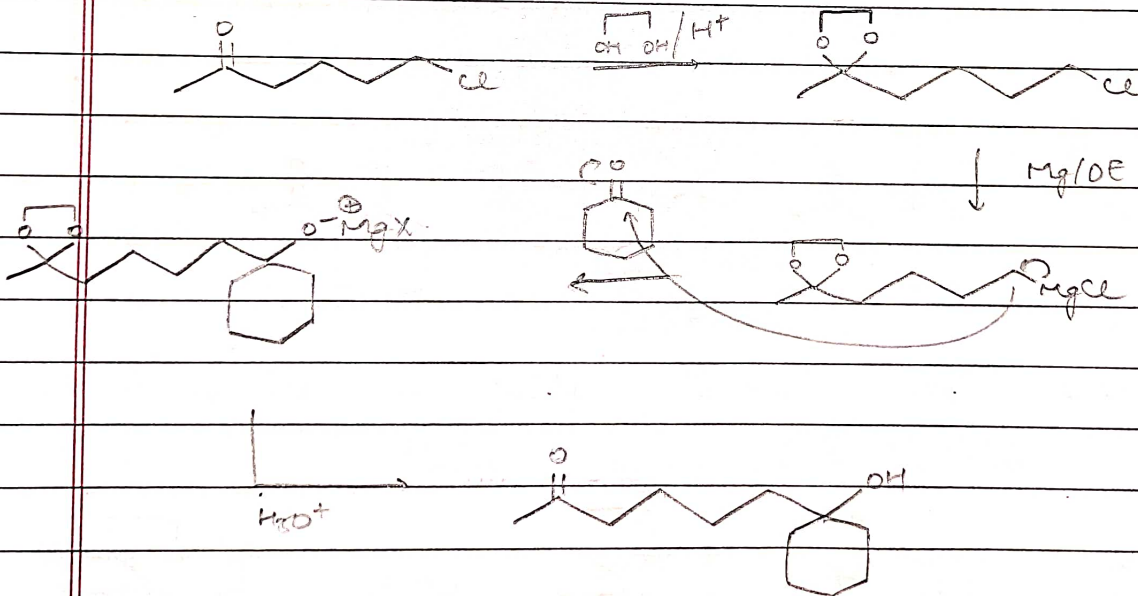


A. We need to protect aldehyde using ketal before adding R-A

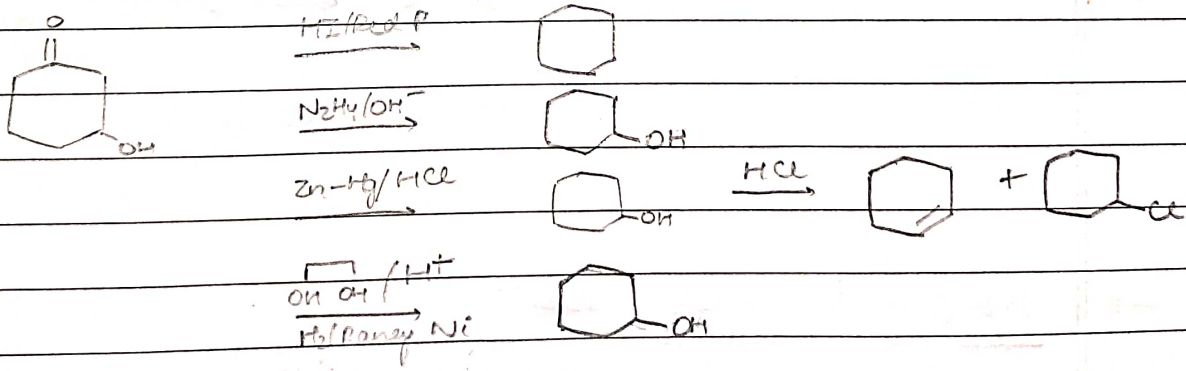
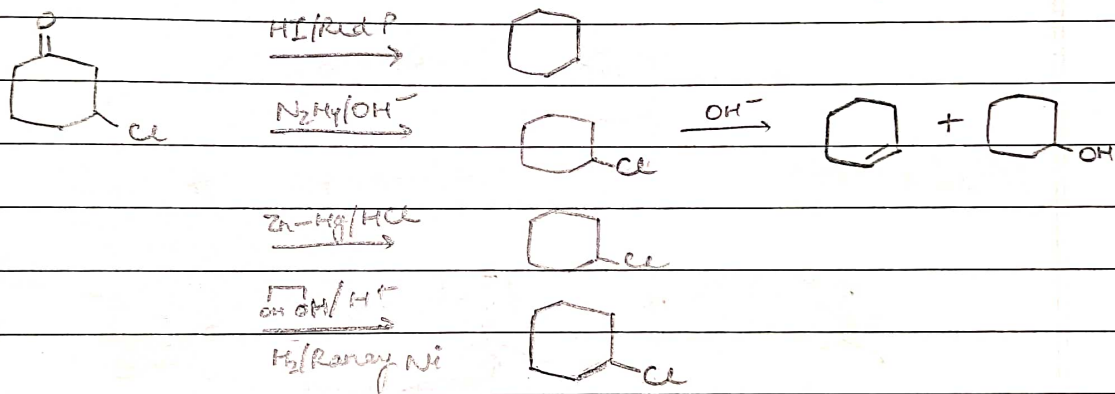
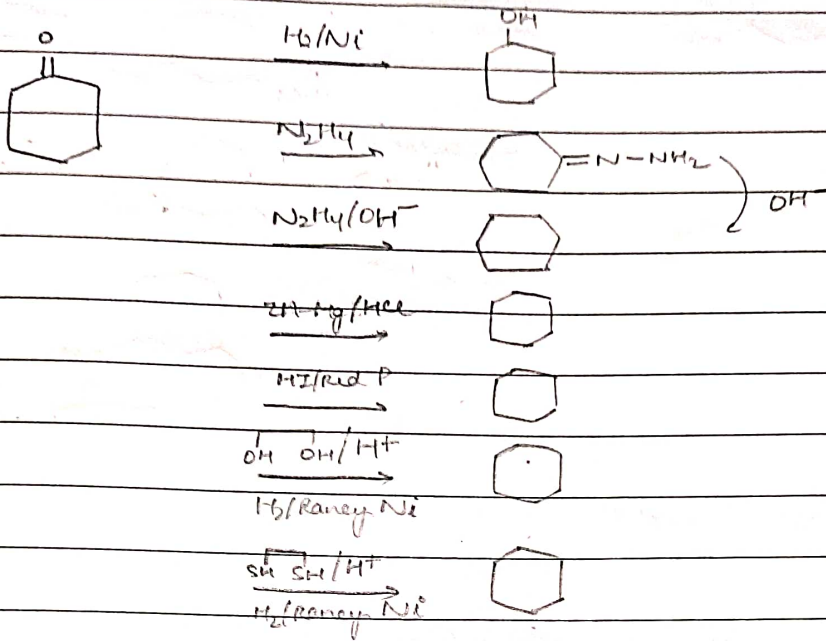


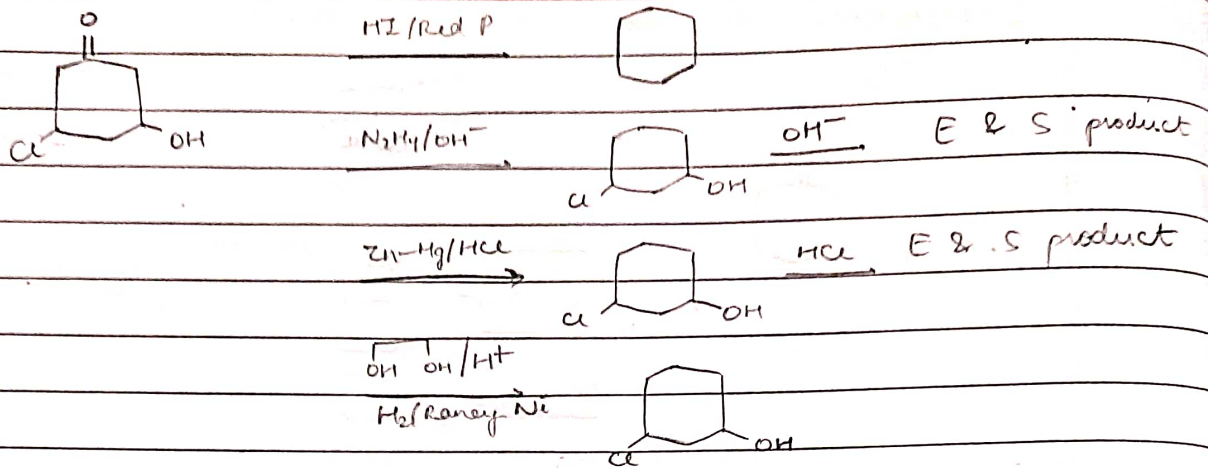


A. We cannot directly add Mg/DE as internal attack would occur. Hence we protect the ketone first.

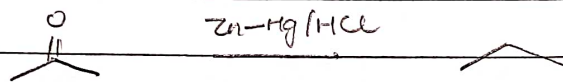


CLEMENSON & WOLF - KISHNER REDⁿ

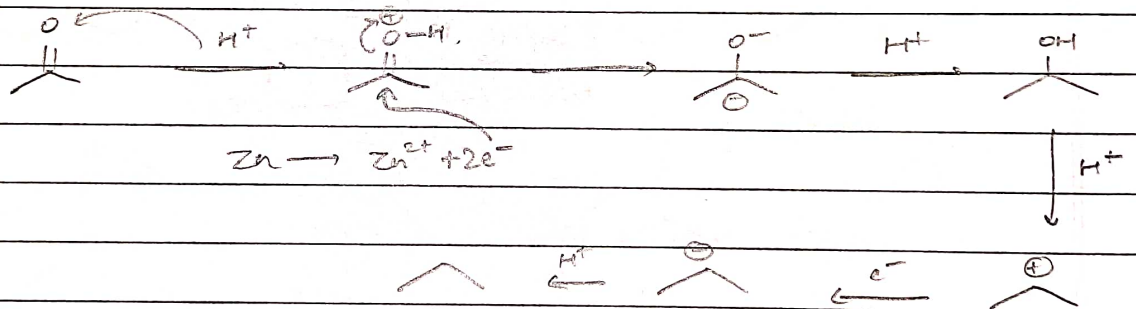




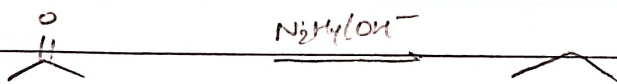
→ Clemenson redⁿ



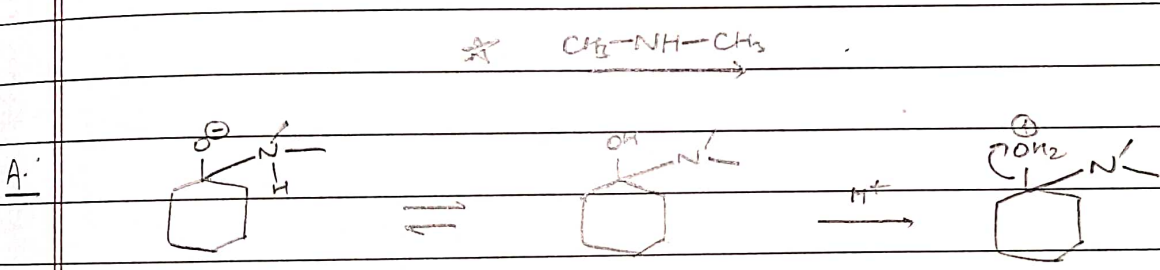
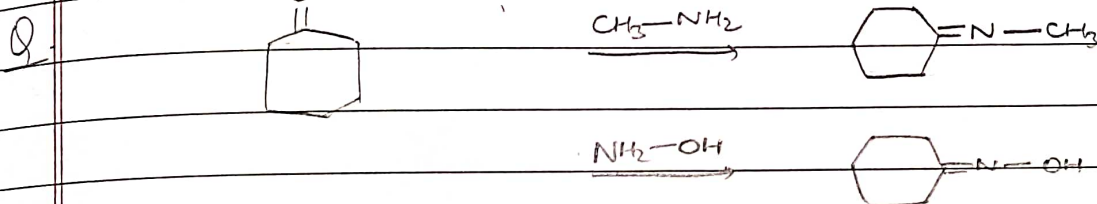
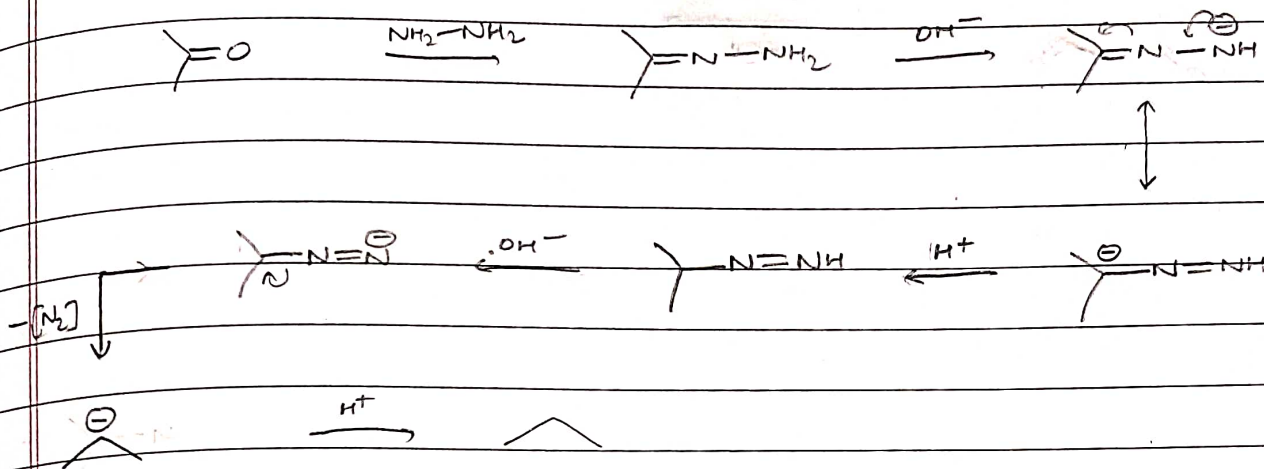
Mechanism



→ Wolf-Kishner redⁿ

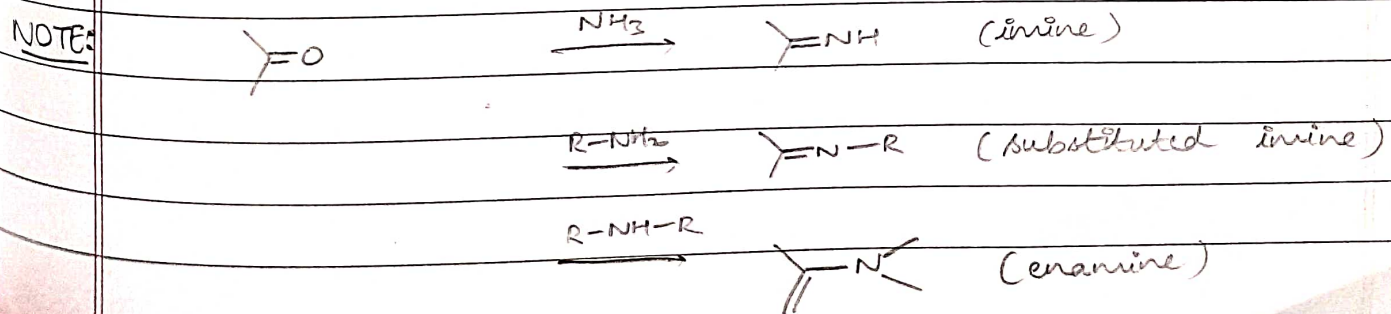


Mechanism



Now, lp of N cannot attack on \oplus created as there is not -H which can leave.

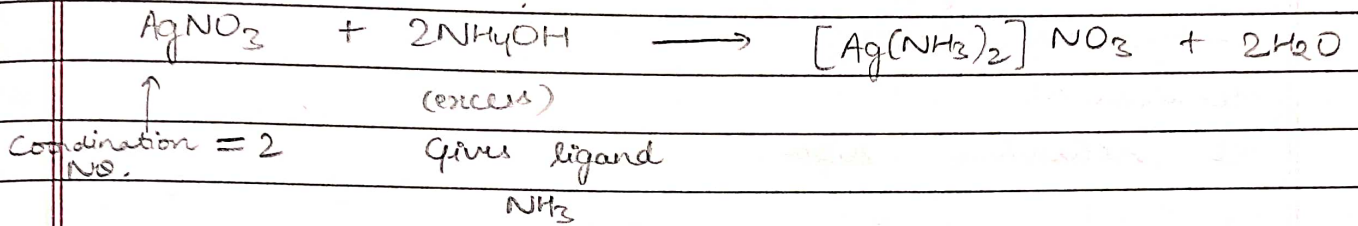
Therefore elimination occurs. i.e. C1CCC(CC1)C(=O)C is formed



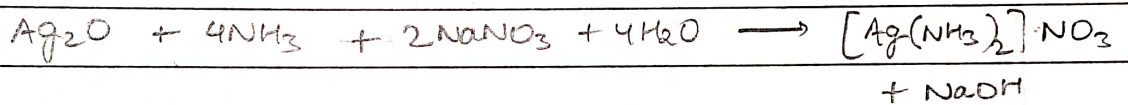
04/07/2023

TOLLEN'S REAGENT (Ammonical Silver Nitrate)

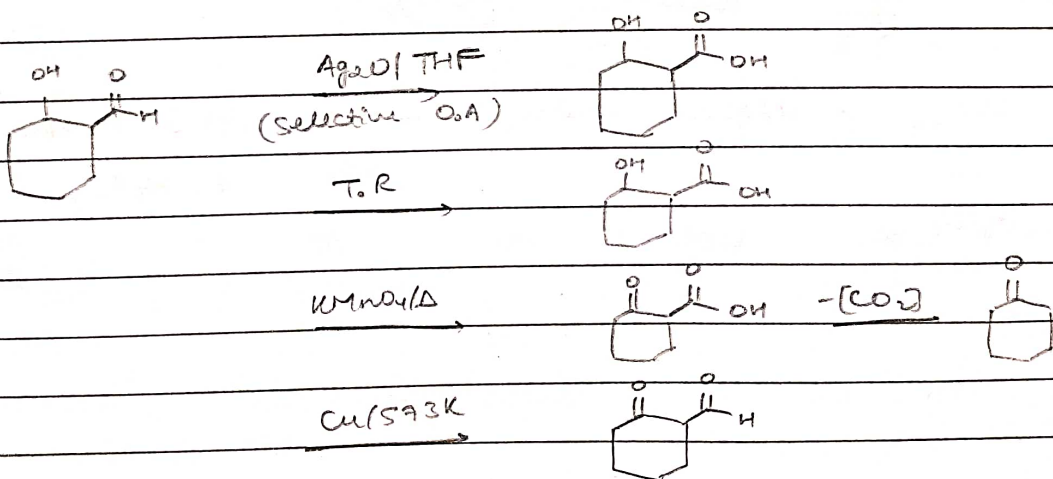
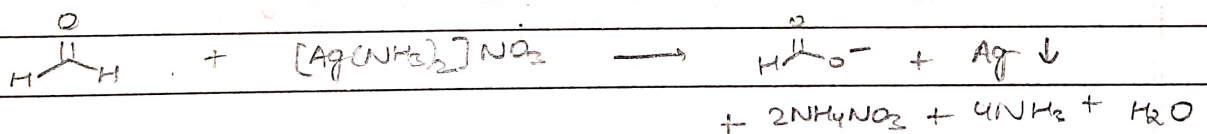
Type I : $\text{NH}_4\text{OH} + \text{AgNO}_3$



Type II : $2\text{AgNO}_3 + 2\text{NaOH} \longrightarrow \text{Ag}_2\text{O} (\text{s}) + 2\text{NaNO}_3 + \text{H}_2\text{O}$



T.O.R is selective O.A



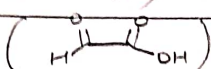
Compounds which give +ve Tollen's test

All aldehydes

All terminal alkynes

Formic acid

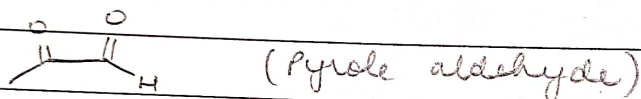
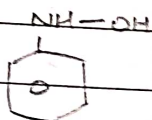
Glyoxal ()

Glyoxal acid ()

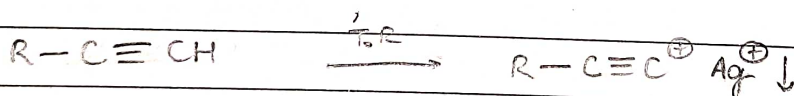
α -Hydroxy ketones

Hemiacetal

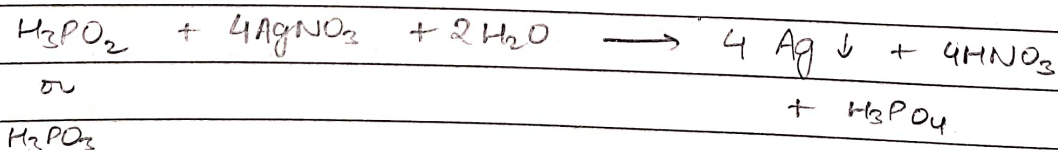
All reducing sugar

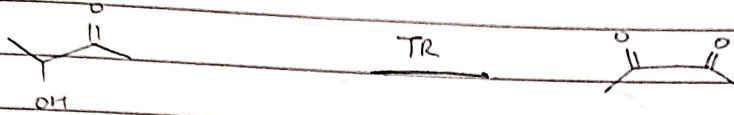


NOTE: (1) Terminal alkynes give Tollen's test but not silver mirror test.

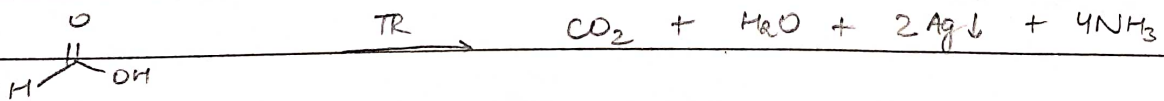
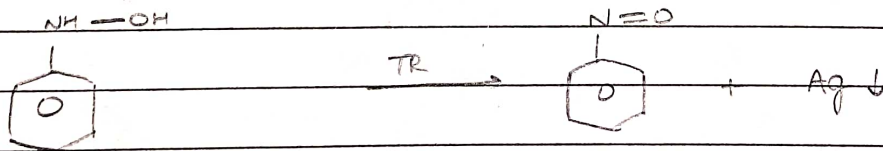
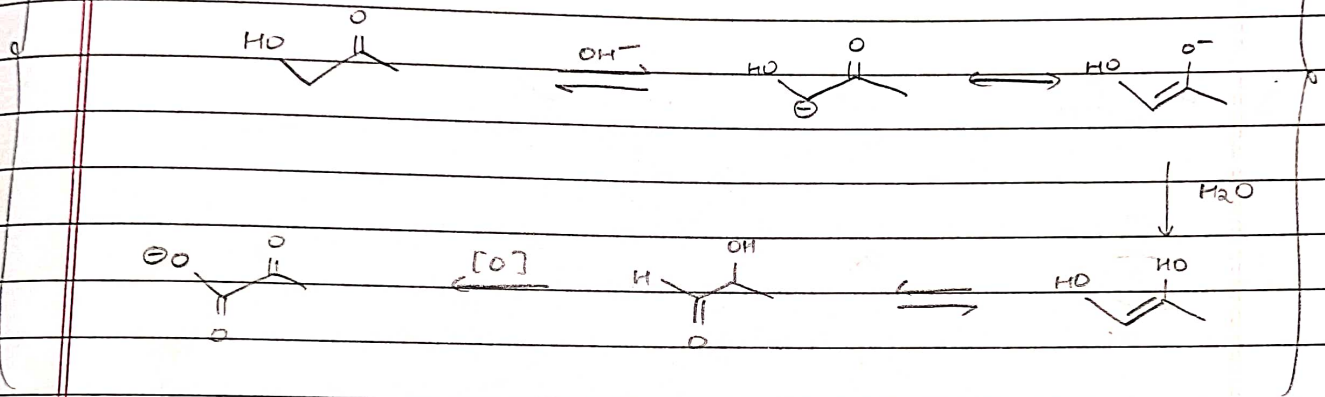


(2) H_3PO_2 & H_3PO_3 give silver mirror test but not Tollen's test.





Mechanism



Q	Compound	Tollen's Test	Silver Mirror Test	Fehling's Test
<u>1.</u>	<chem>H-C(=O)-H</chem>	✓	✓	✓
<u>2.</u>	<chem>CH3-C(=O)-H</chem>	✓	✓	✓
<u>3.</u>	<chem>HO-CH2-C(=O)-H</chem>	✓	✓	✓
<u>4.</u>	<chem>O=C1C(O)C(O)C(O)C1O</chem>	X	X	X
<u>5.</u>	<chem>O=C1C(O)C(O)C1O</chem>	X	X	X
* <u>6.</u>	<chem>O=C1C(O)C(O)C1O</chem> \rightleftharpoons <chem>O=C1C(O)C(O)C1O</chem>	X (✓)	X (✓)	✓
* <u>7.</u>	<chem>HO-C(=O)-OH</chem>	✓	✓	✓
<u>8.</u>	<chem>CH3-C(=O)-OH</chem>	X	X	X
<u>9.</u>	<chem>CCCC(=O)OH</chem>	X	X	X
* <u>10.</u>	<chem>H3PO3</chem>	X	✓	X
* <u>11.</u>	<chem>H3PO2</chem>	X	✓	X
<u>12.</u>	<chem>H3PO4</chem>	X	X	X

13

X

X

X

14

X

X

X

15

✓

X

X

16

X

X

X

17

✓

X

X

18

X

X

X

19

✓

X

X

20

✓

X

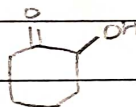
X

21

X

X

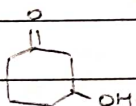
X

22

✓

✓

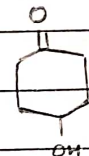
✓

23

X

X

X

24

X

X

X

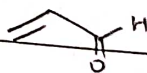
25

✓

✓

✓

26.

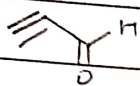


✓

✓

✓

27.



✓

✓

✓

28.

Glucose

✓

✓

✓

29.

Fructose

✓

✓

✓

30.

Sucrose

X

X

X

31.

Maltose

✓

✓

✓

32.

Lactose

✓

✓

✓

33.

Starch

X

X

X

34.

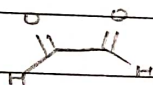
Cellulose

X

X

X

* 35.



✓

✓

X

* 36.



✓

✓

X

37.



X

X

X

(R-I)

* 38.



X

X

✓

(R-I)

* 39.



(✓)

(✓)

X

(R-I)

* 40.



✓

✓

✓

(R-I)

* 41.



✓

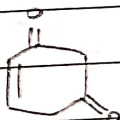
✓

X

(X)

(X)

42.

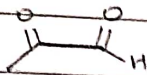


X

X

X

43



✓

✓

✓

44

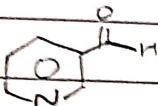


✓

✓

X

45

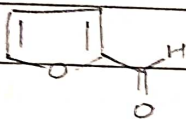


✓

✓

X

46

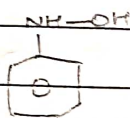


✓

✓

X

47

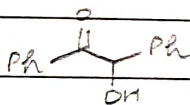


✓

✓

X

48



✓

✓

✓

49

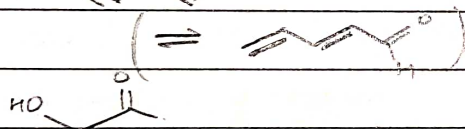


✓

✓

✓

50



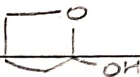
✓

✓

✓

(R-I)

★ 51



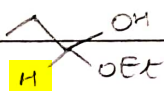
✓

✓

✓

(R-I)

★ 52



✓

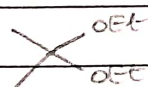
✓

X

(X)

(X)

53



X

X

X

54



✓

✓

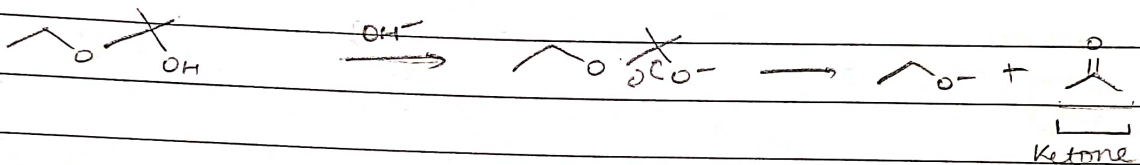
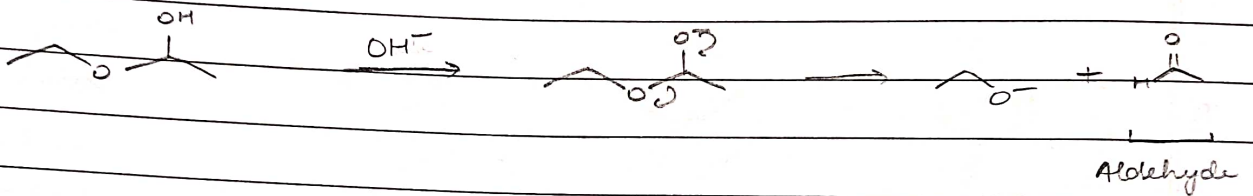
✓

NOTE:

① All mono & disaccharides except sucrose give Tollen's, Silver Mirror Test & Fehling's test

REMARK:

Q 38-41 & 51

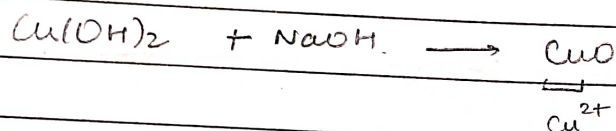


FEHLING'S TEST

Fehling solⁿ → Blue colour, not ppt

→ Fehling (A) (50%) - Aq. CuSO_4

→ Fehling (B) (50%) - $\text{NaOH}/\text{NH}_4\text{OH}$ + Sodium Potassium
Tartarate
(Rochelle's salt)



Cu^{2+} precipitates (blue), to avoid which, Rochelle's salt is added, which forms complex with it.

In test $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ (Red)

Compounds which give Fehling's test

All aldehydes except aromatic aldehydes

Formic Acid

α -Hydroxyketones

Hemiacetal

All mono & disaccharides (except sucrose)

BENEDICT'S TEST

Same as Fehling's Test

→ Benedict (A) - aq. CuSO_4

→ Benedict (B) - NaOH + Sodium Potassium Citrate

SCHIFF'S TEST

Dil. solⁿ of rosocyanine hydrochloride in water has red or magenta colour.

When SO_2 gas passed through solⁿ, magenta colour disappears

When aldehyde added to this solⁿ, magenta colour reappears

All aldehydes except those having intramolecular H-bonding give Schiff's test.

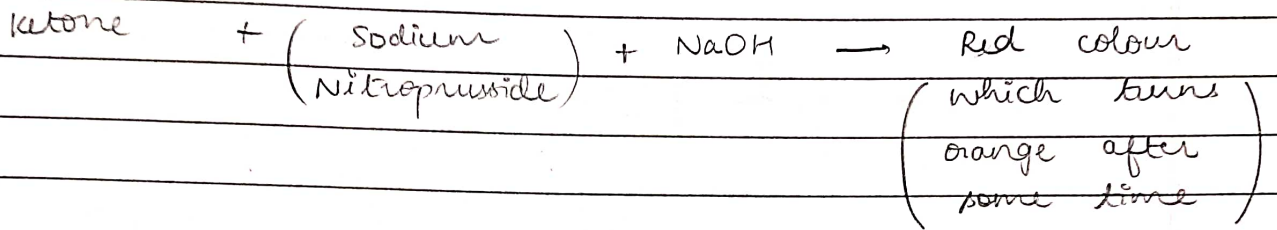
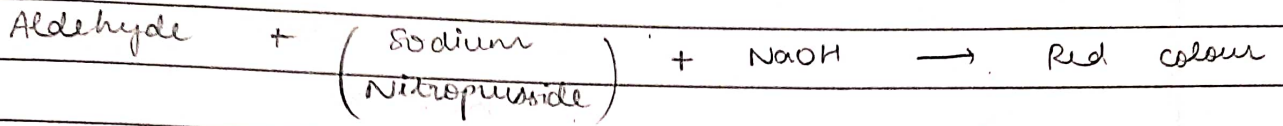
Formic acid ✓

Vanillin X

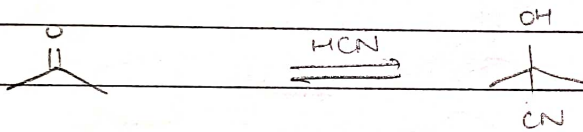
Glucose X

Fructose X

SODIUM NITROPRUSSIDE TEST

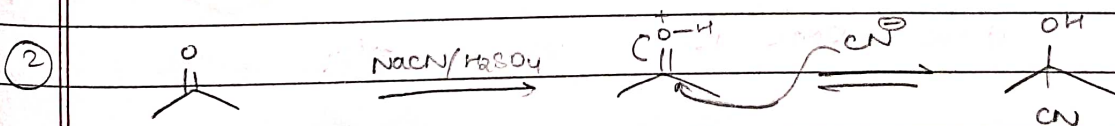
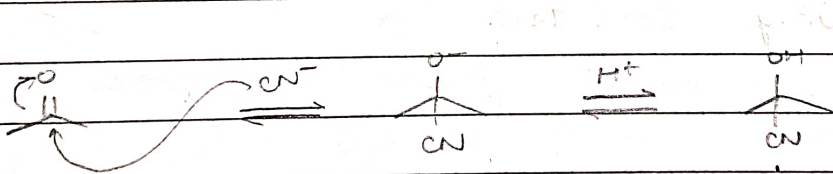
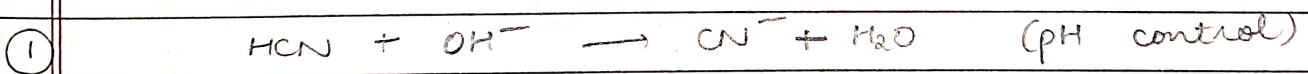


CYANOHYDRIN

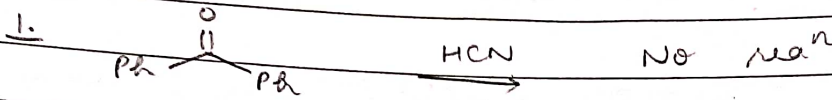


But this method gives poor yield as HCN is weak acid.

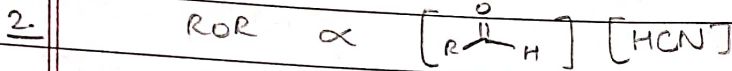
To get good yield, there are 2 ways.



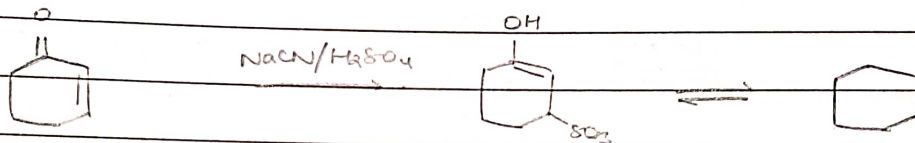
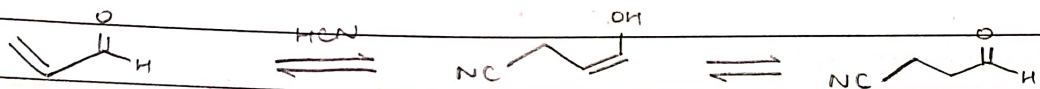
NOTE:



due to steric hindrance



3. (1,4) addⁿ favoured

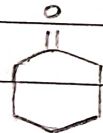


SODIUM METABISULPHITE TEST

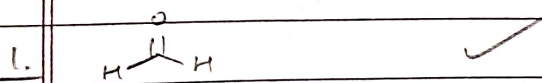


Comps. giving SMS Test

All aldehyde except glucose & fructose
Methyl ketones with #C ≤ 6 &



Q Which give SMS Test



13.



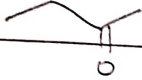
✓

14.



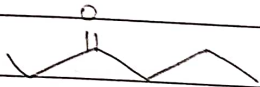
✓

15.



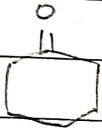
✓

16.



X

★ 17.



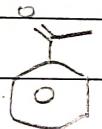
✓

18.



✓

★ 19.



✓

10.



X

11.

Glucose

X

12.

Fructose

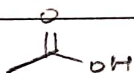
X

13.

Sucrose

X

14.



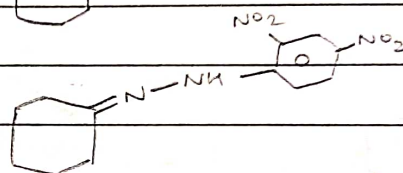
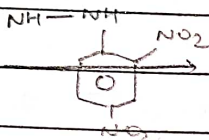
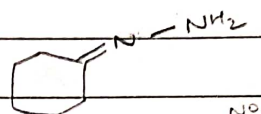
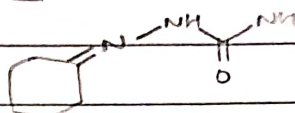
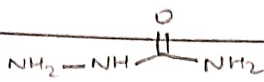
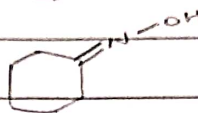
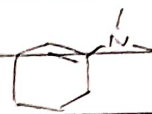
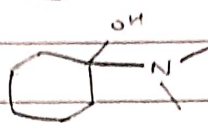
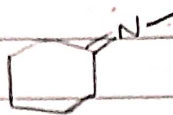
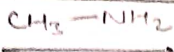
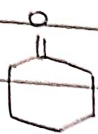
X

15.



X

16

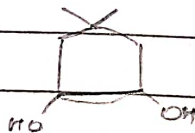
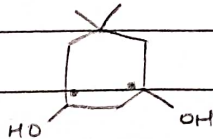
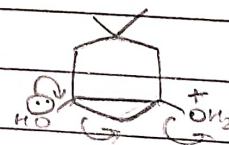
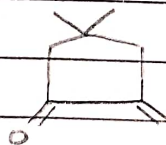
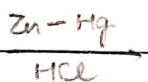
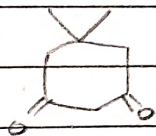
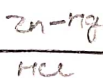
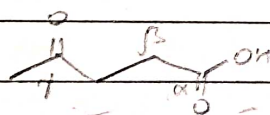


(Brady's Reagent)

MISCELLANEOUS REAⁿ_A

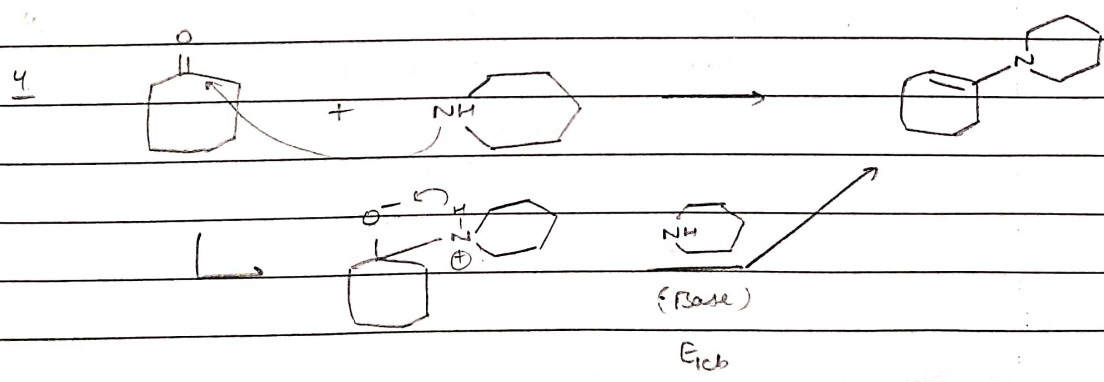
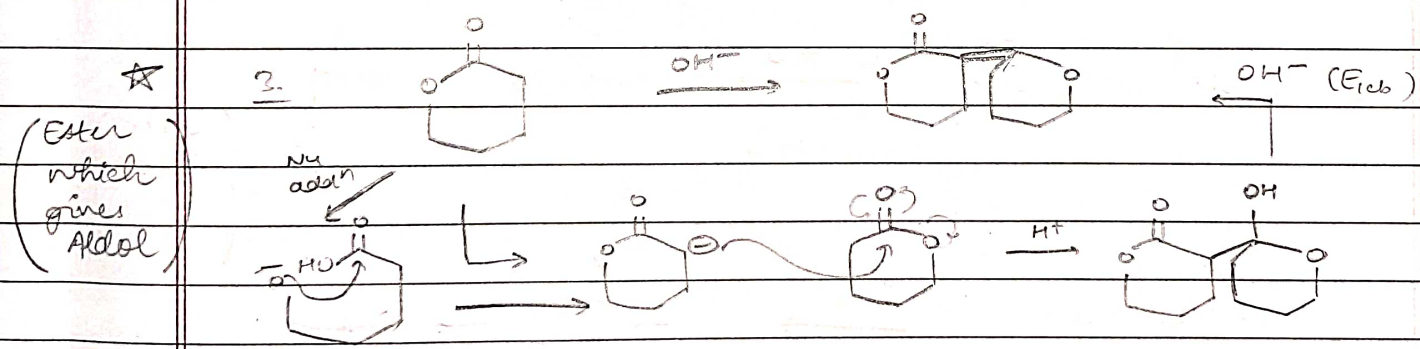
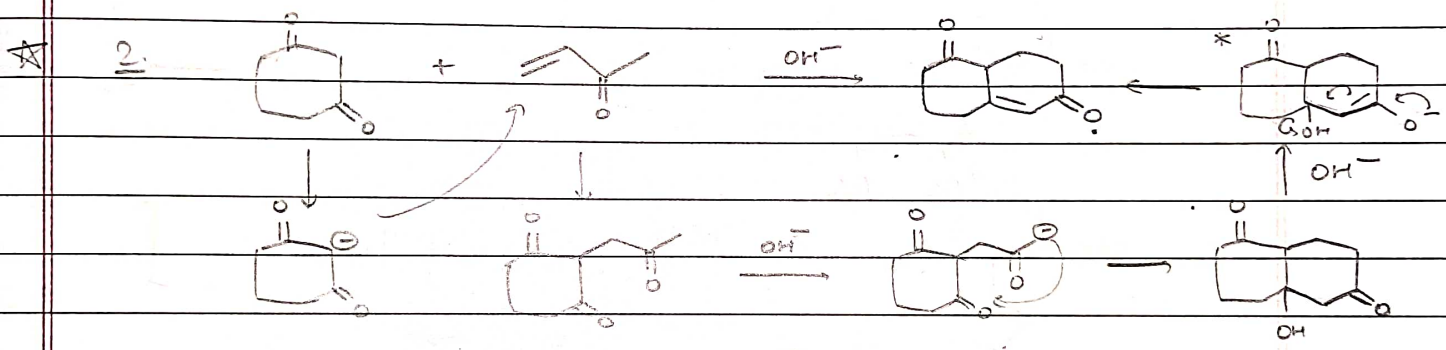
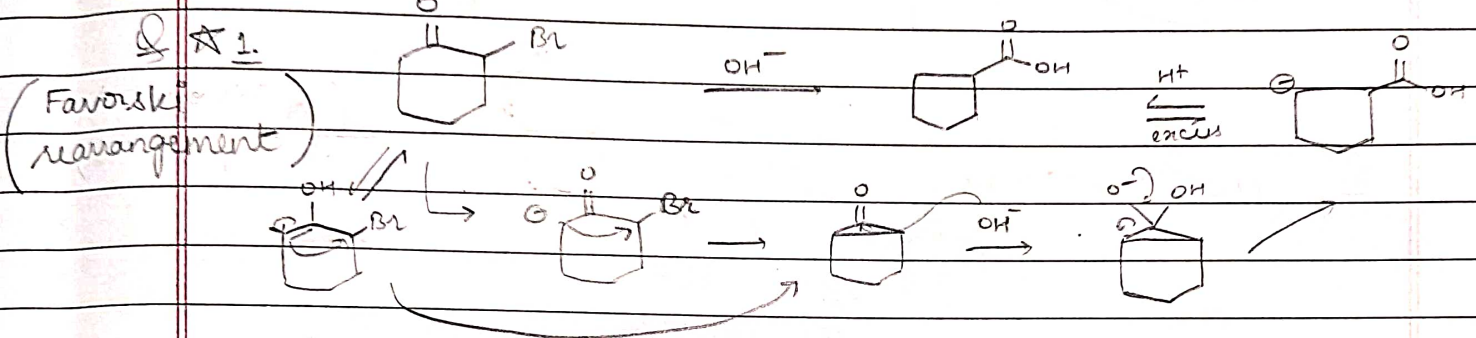


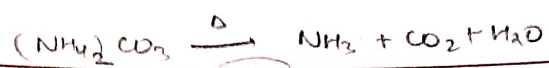
NO REAⁿ



H^+

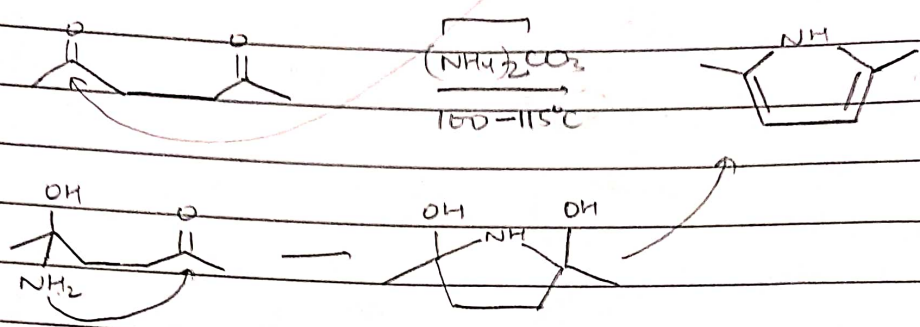
* O=C1C=CC(O)CC1 is not favourable



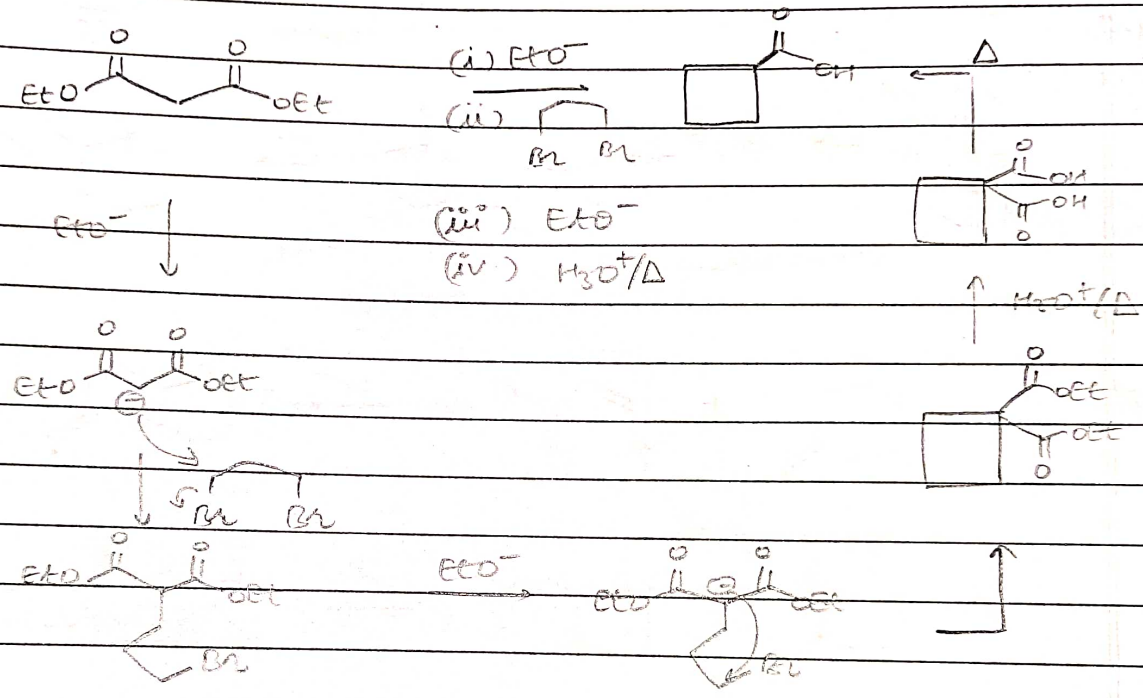


Q.

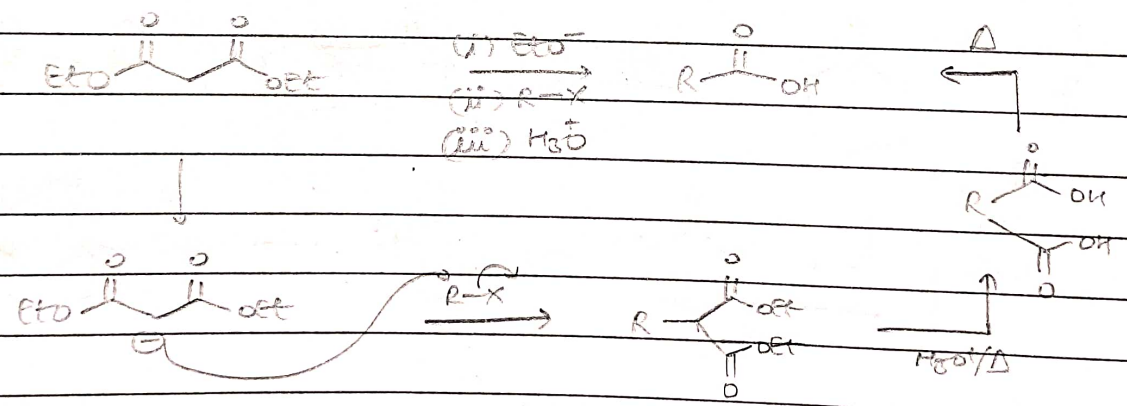
1.

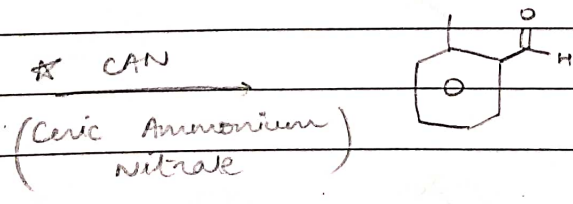
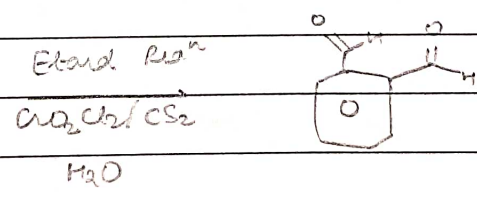
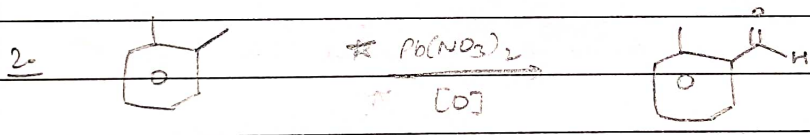
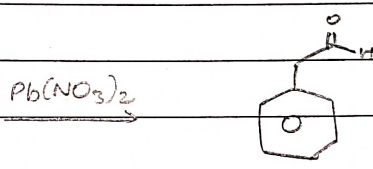
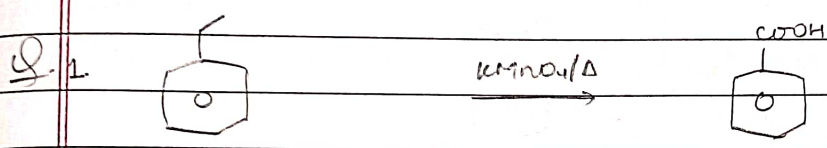
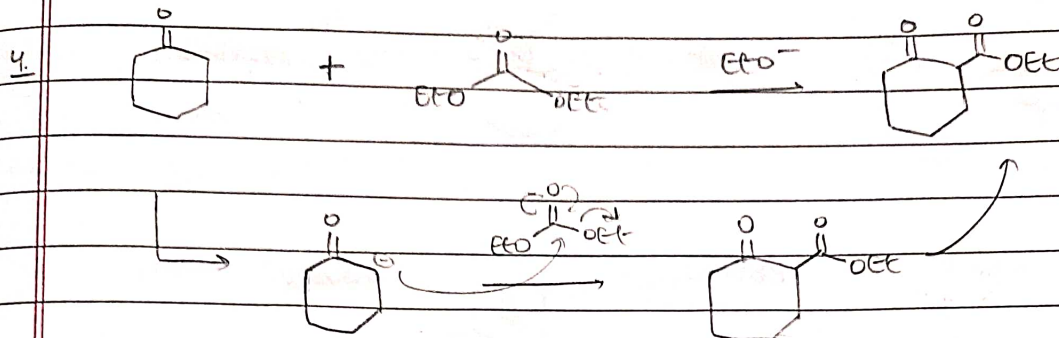


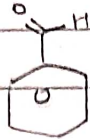
2.



3.






 $\xrightarrow{\text{CAN}}$

 $\xrightarrow{\text{Pb(NO}_2)_2}$

 $\xrightarrow[\text{H}_2\text{O}]{\text{CrO}_2\text{Cl}_2/\text{CS}_2}$


Q Which give Claisen Ester Condensation?

1.



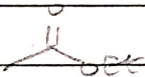
X

2.



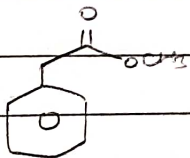
✓

3.



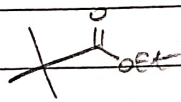
✓

4.



✓

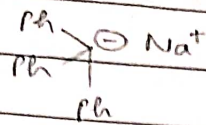
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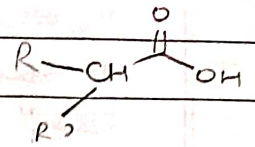
X

NOTE: Claisen Ester Condensation

with



in

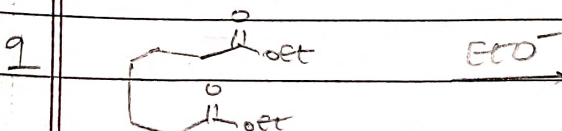
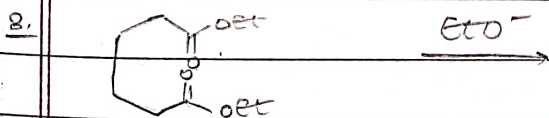
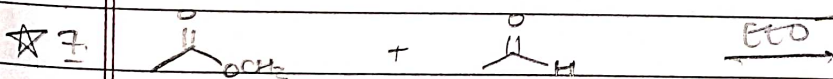
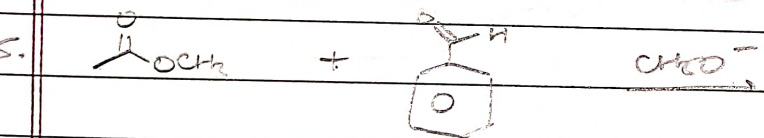
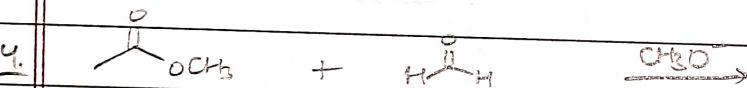
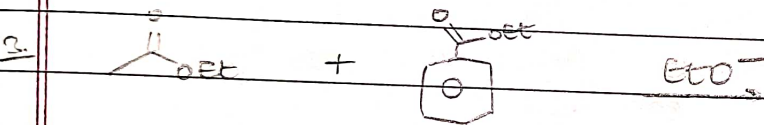
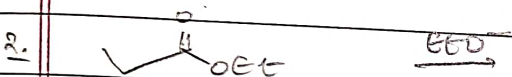
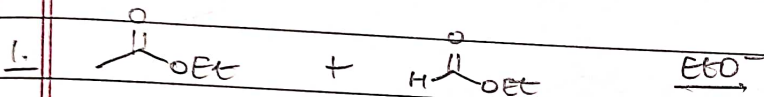


is irreversible

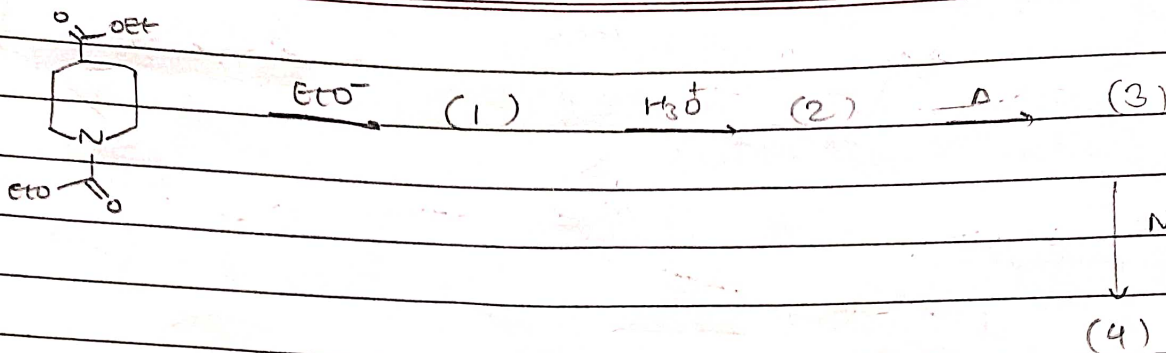
(at least one acidic H)

06/07/2023

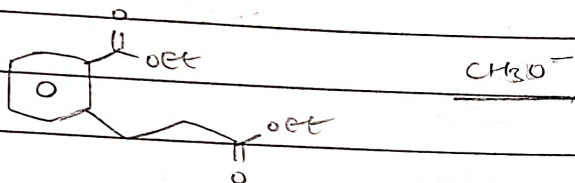
Q Write product with mechanism.



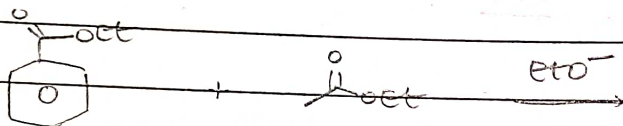
★ 10



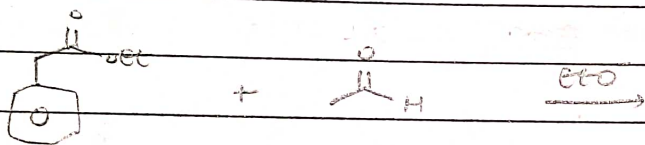
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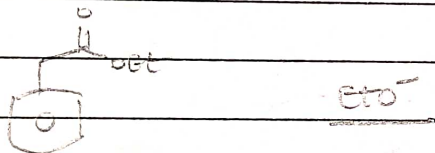
12



★ 13



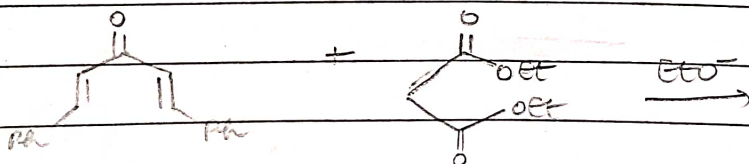
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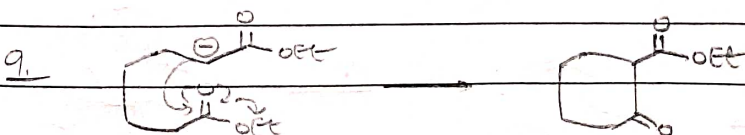
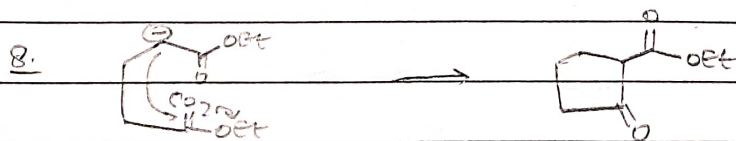
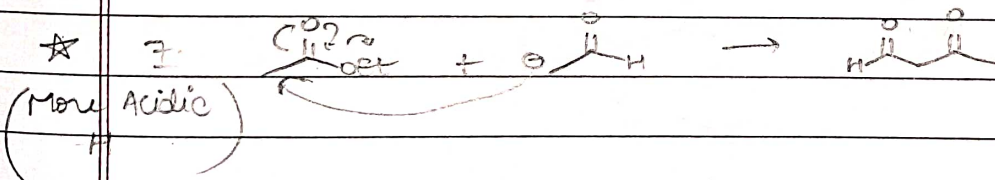
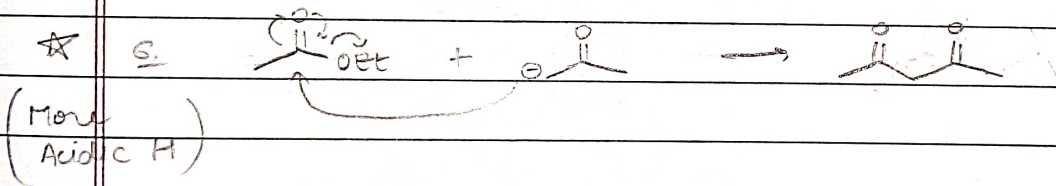
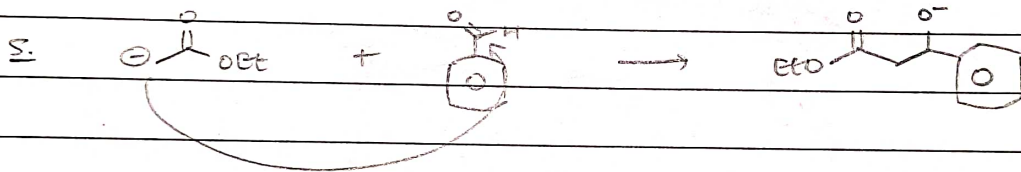
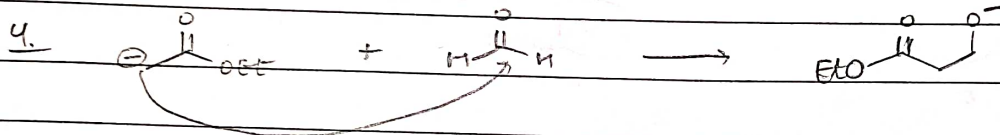
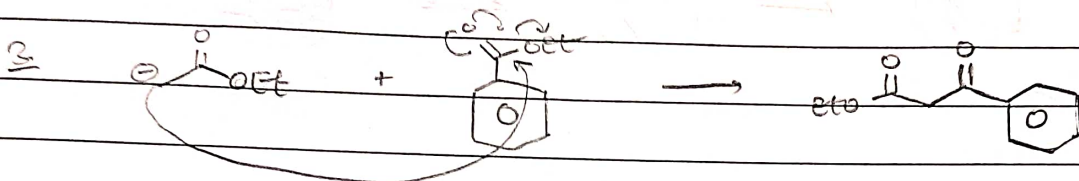
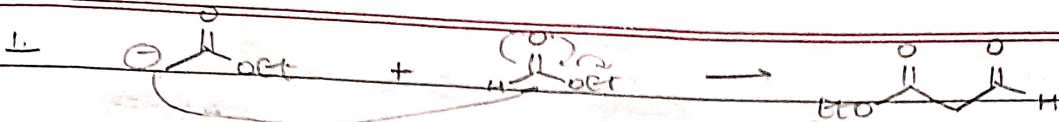
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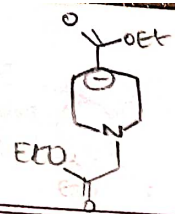


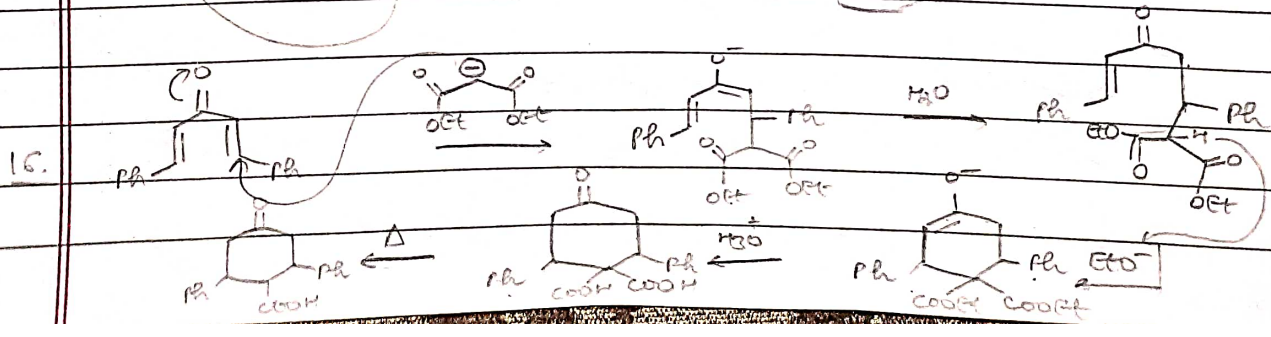
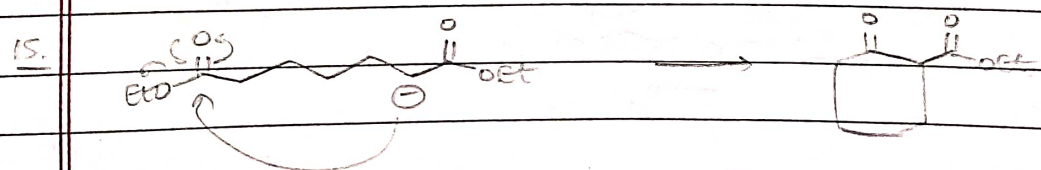
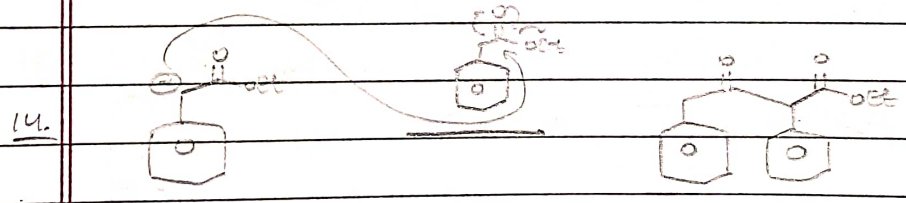
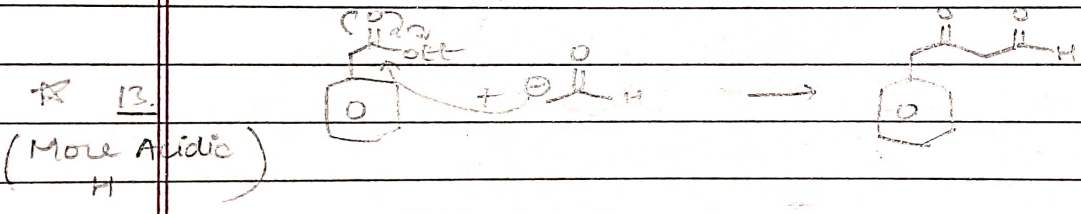
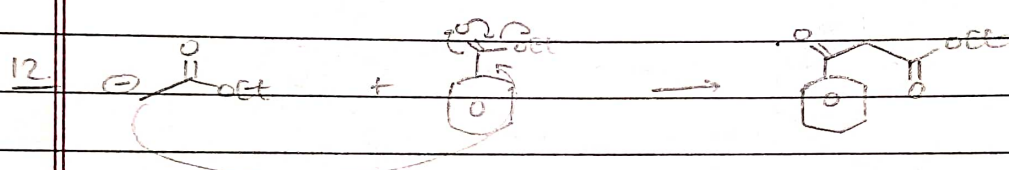
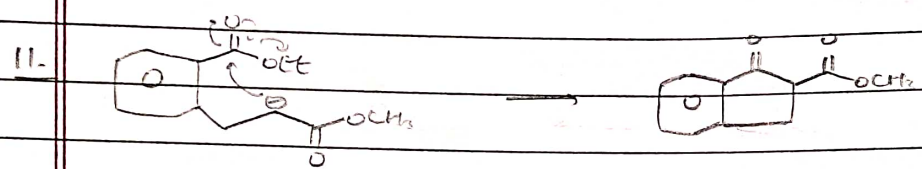
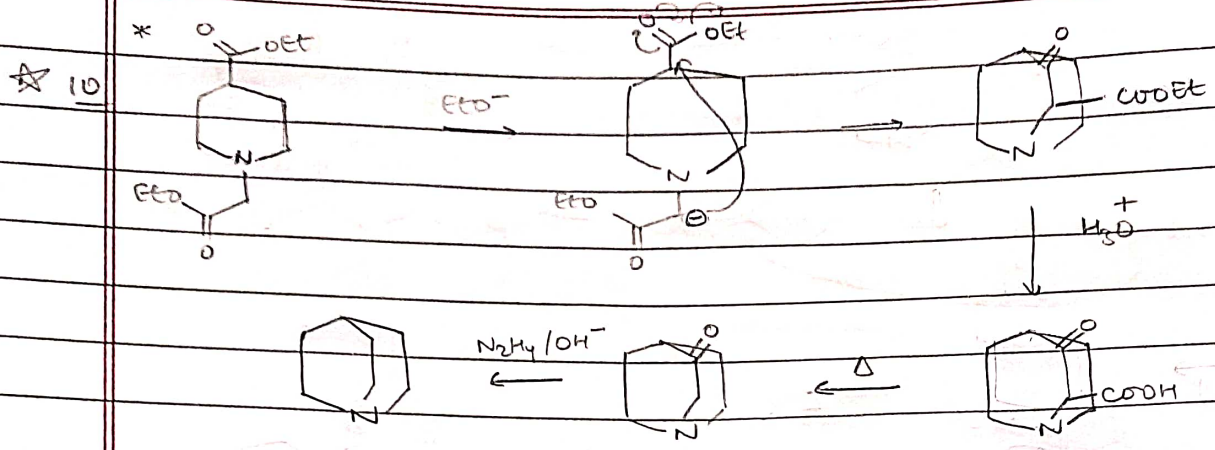
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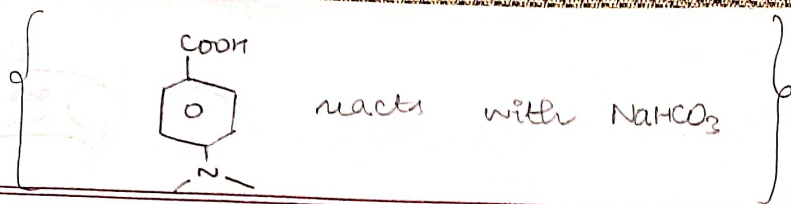


A



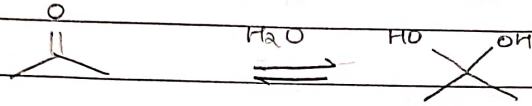
*  *not formed as near reversible & 2 α -H not present*





11/07/2023

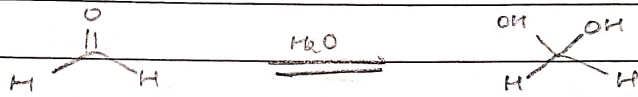
GEM DIOLS



Generally, gem diols are unstable, so eqnⁿ goes bwd.

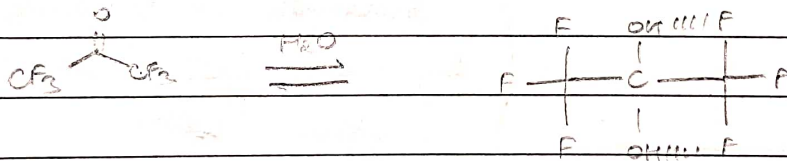
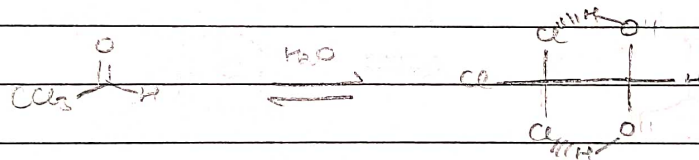
Stable gem diols :-

1.



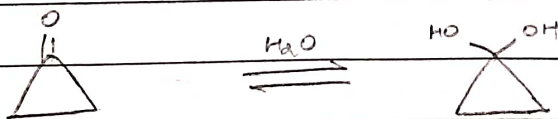
Rate of Nu addⁿ extremely high

2.



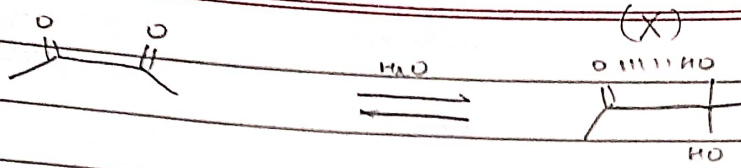
(Intramolecular H-bonding)

3.

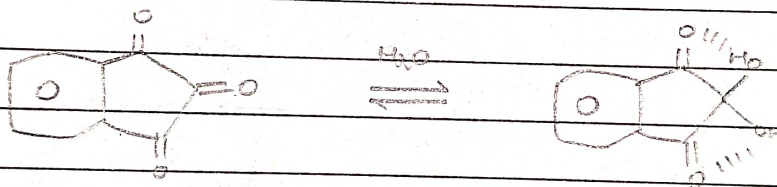
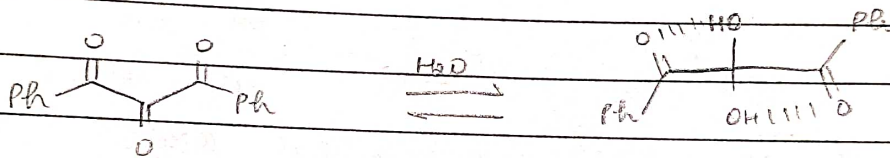
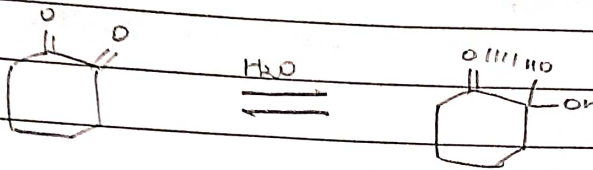


(less ring strain)

4.

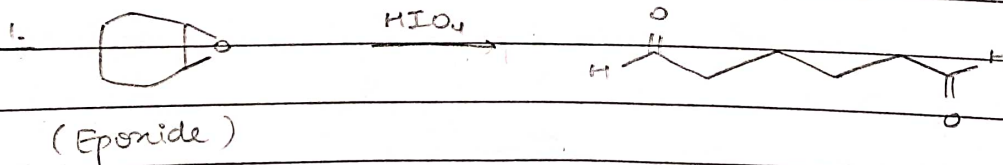


Not stable as no H-bonding
due to free rotation

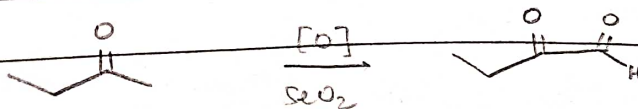
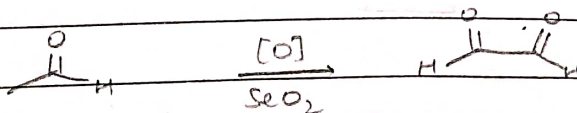


(Intramole. H-bonding
due to lack of
free rotⁿ.)

NOTE:

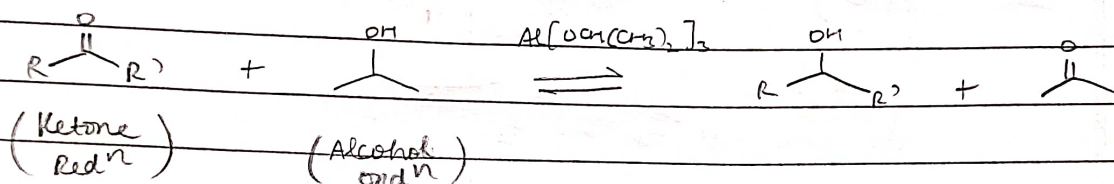


2.



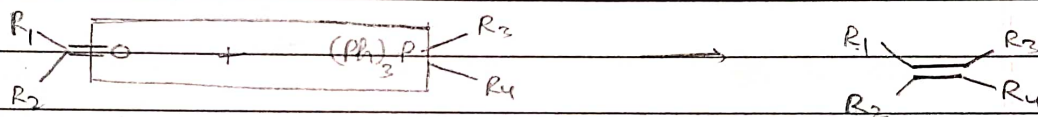
MISC REAⁿS

- Meerwein - Ponnendorf - Verley Redⁿ (MPV) -

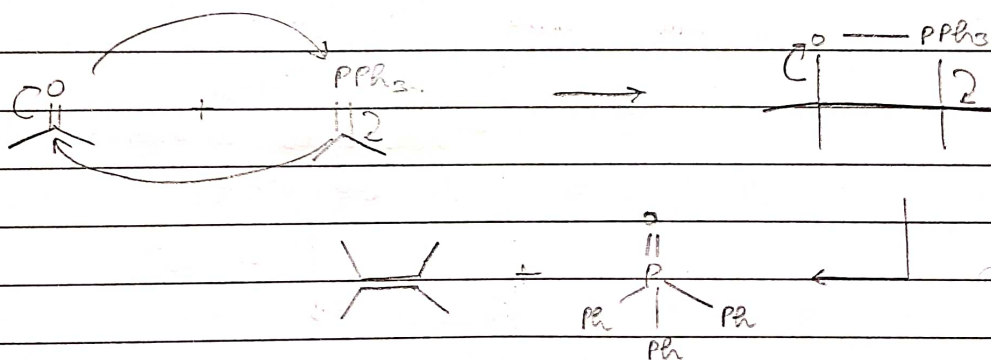
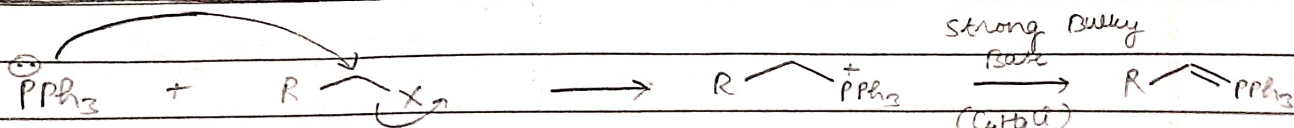


Reverse of this rxn is known as Oppenauer's rxn

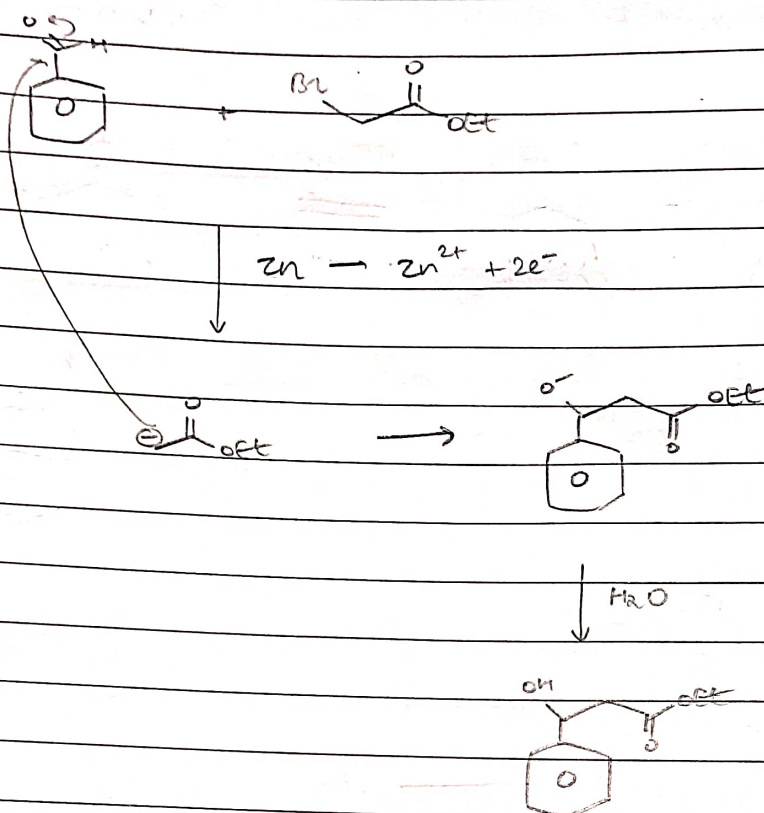
- Wittig Reaⁿ -



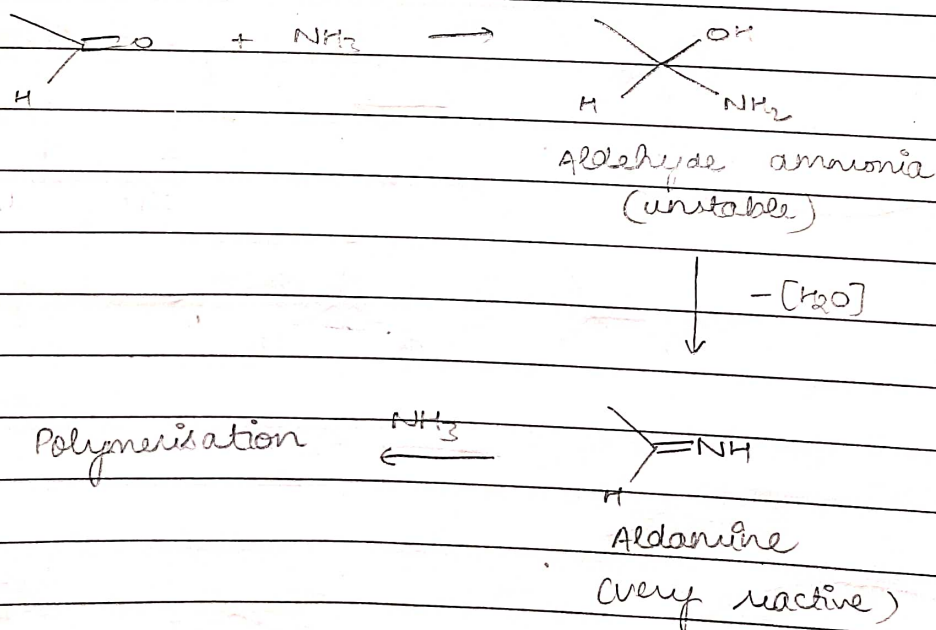
Mechanism

Prepⁿ of Ph₃P=C<

Reformatski rean

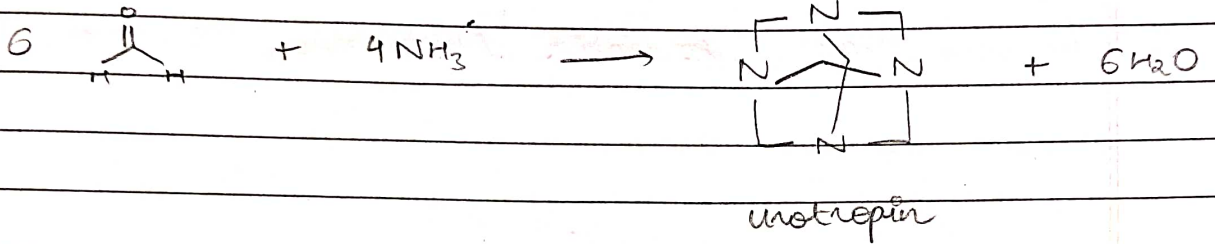


REAⁿ OF AMMONIA & ALDEHYDE

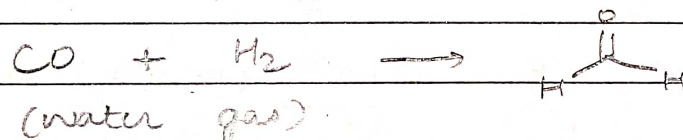


NOTE:

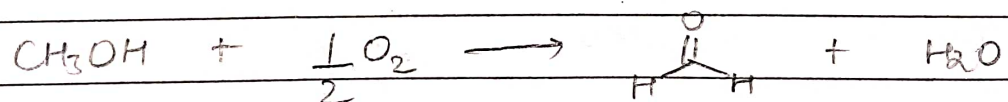
Reaⁿ b/w NH_3 & HCHO does not form aldehyde, but gives hexamethylenetetramine, used in medicine as a urinary antiseptic under the name Urotropin.

FORMALDEHYDE→ Prepⁿ

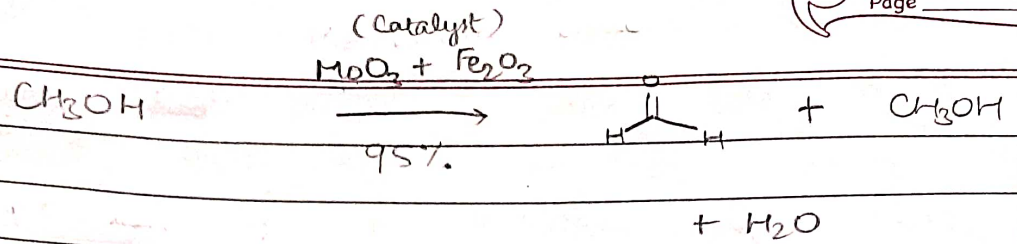
- ① Redⁿ of CO - At low P through electric discharge of low intensity



- ② Oxdⁿ of CH_3OH - Mix of CH_3OH vapour and air passed over heated Cu or Ag

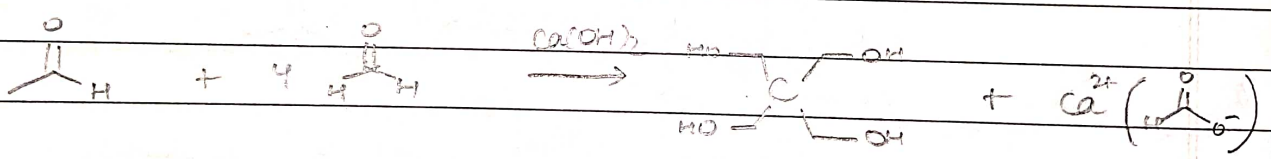
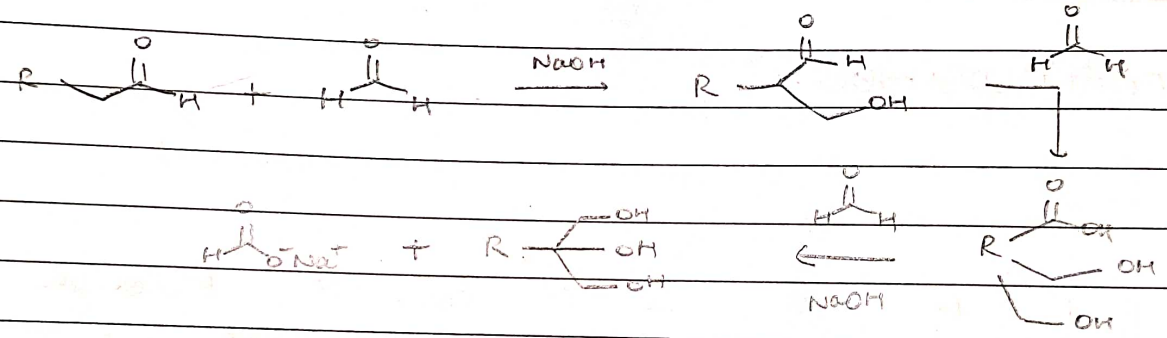


3



The mix is freed from excess of methanol by distillation, which results in a mix known as formalin (40% HCHO, 8% CH₃OH, 52% H₂O)

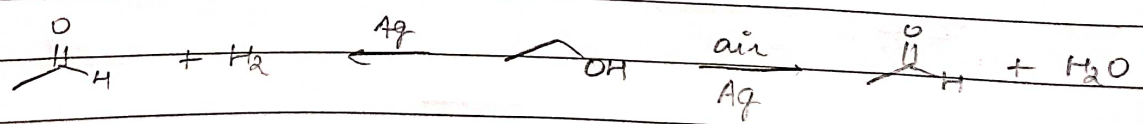
→ Condensation Reaⁿ



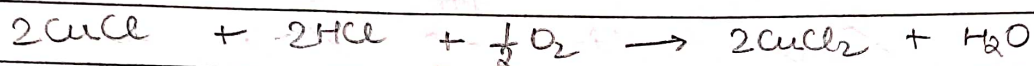
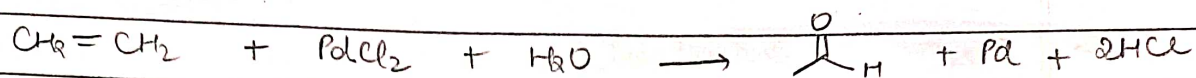
ACETALDEHYDE

→ Prepⁿ (Industrial)

① Air oxidⁿ of CH_3OH - At 300°C



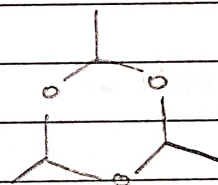
② At 50°C



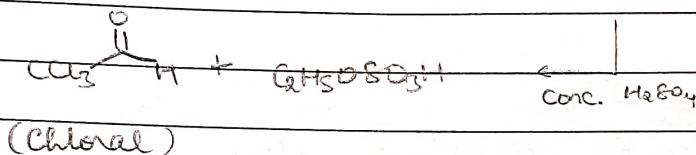
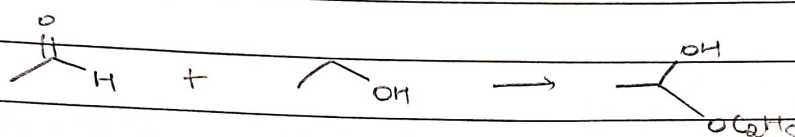
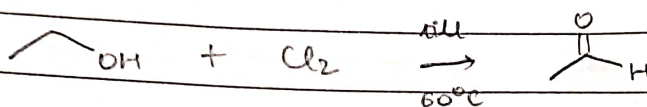
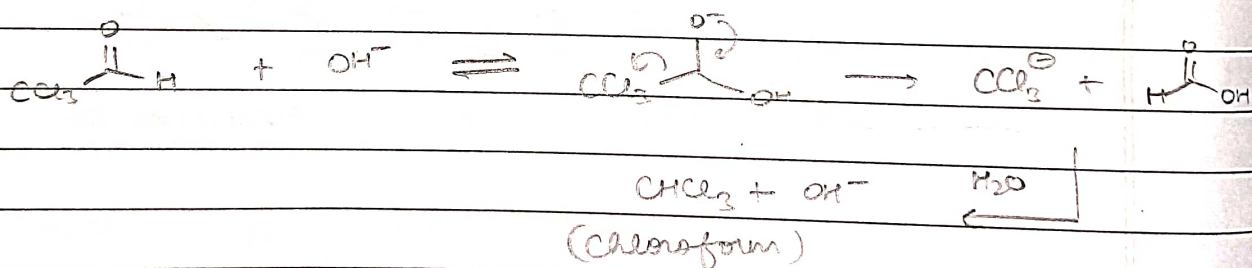
→ Physical props

- Colourless
- Pungent smelling liq.
- B.P = 21°C

→ Polymers



Paraaldehyde

CHLORAL→ Prepn (Industrial)Chlorination of $\text{C}_2\text{H}_5\text{OH}$ -→ Rean① With Alkali -② With Acids -