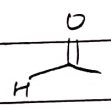
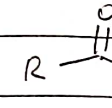
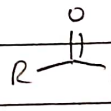
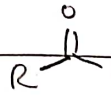
25/05/2023

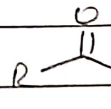
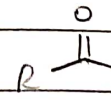
ALCOHOLS, PHENOLS & ETHERS

NUCLEOPHILIC ADD^{n}

- Carbonyl Comp —  ,  ,

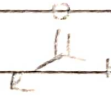
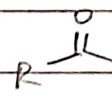
  Any comp containing –CO grp.

   ,  ,

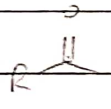
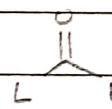
   , 

Types —

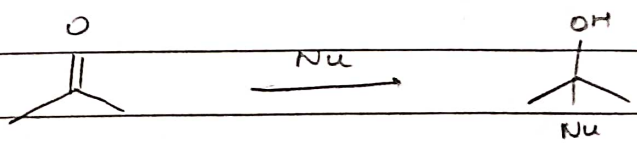
→ Pure — Nu L.G adj to –CO grp

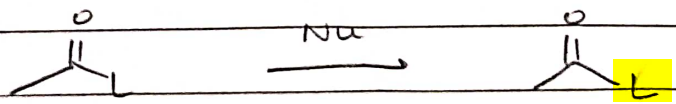
 ,  , 

→ Impure — L.G adj. to –CO grp

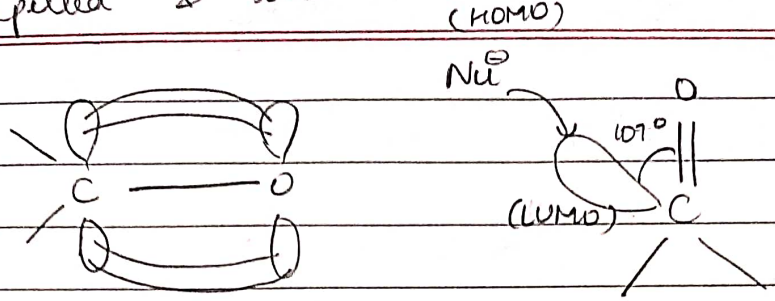
 , 

- Rean



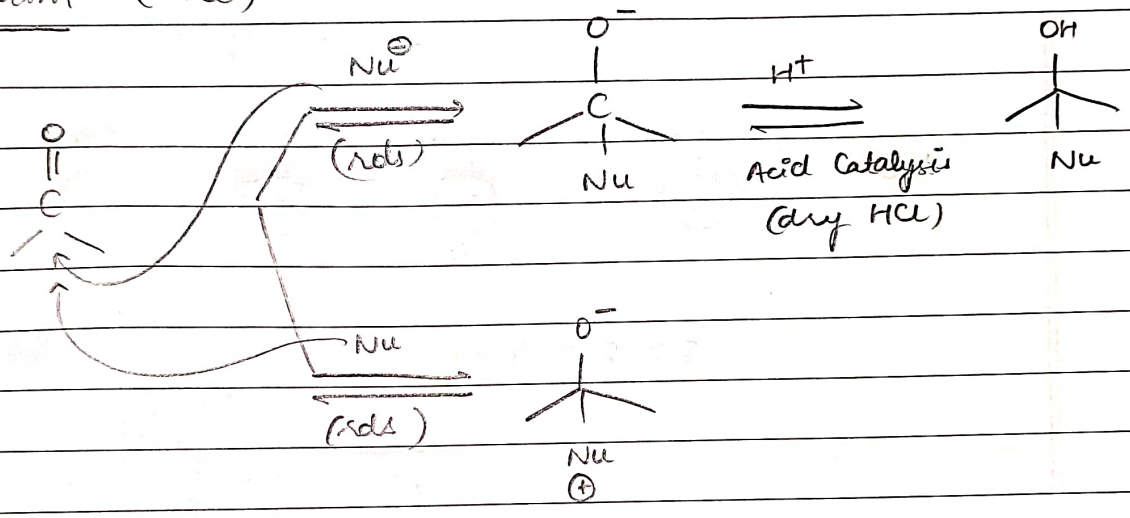


Actually, $Nu^{\ominus}$ attacks at 107° angle to $-CO$ bond, due to which πe^- are repelled & bond breaks.

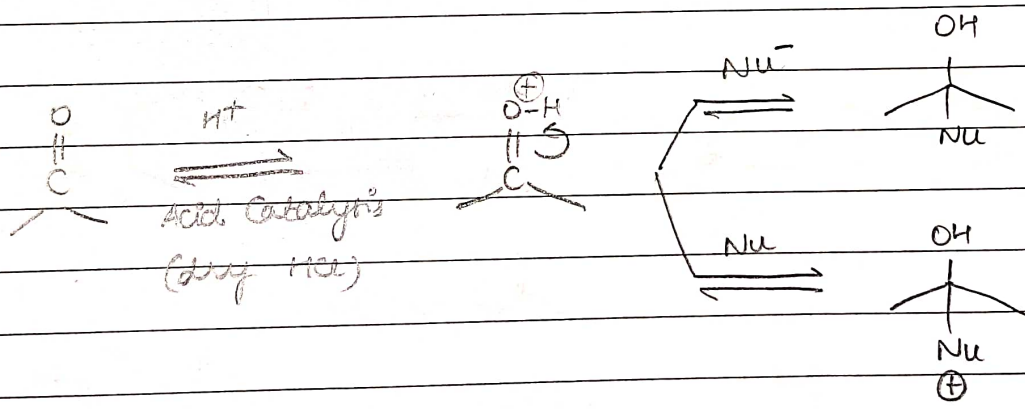


→ Mechanism (Pure)

(I)



(II)

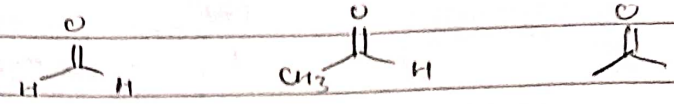


ROR(II) > ROR(I)

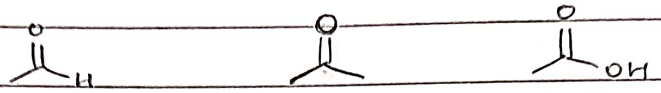
NOTE: ① ROR $\propto$ (ENG or C)

$\propto \frac{1}{\text{(Steric Hindrance)}}$

Eg –

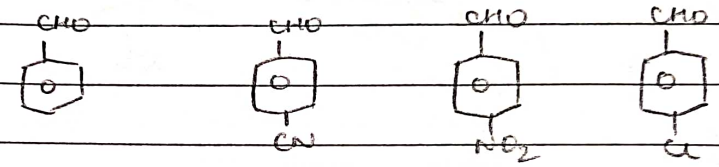
(i) 

1 > 2 > 3

(ii) 

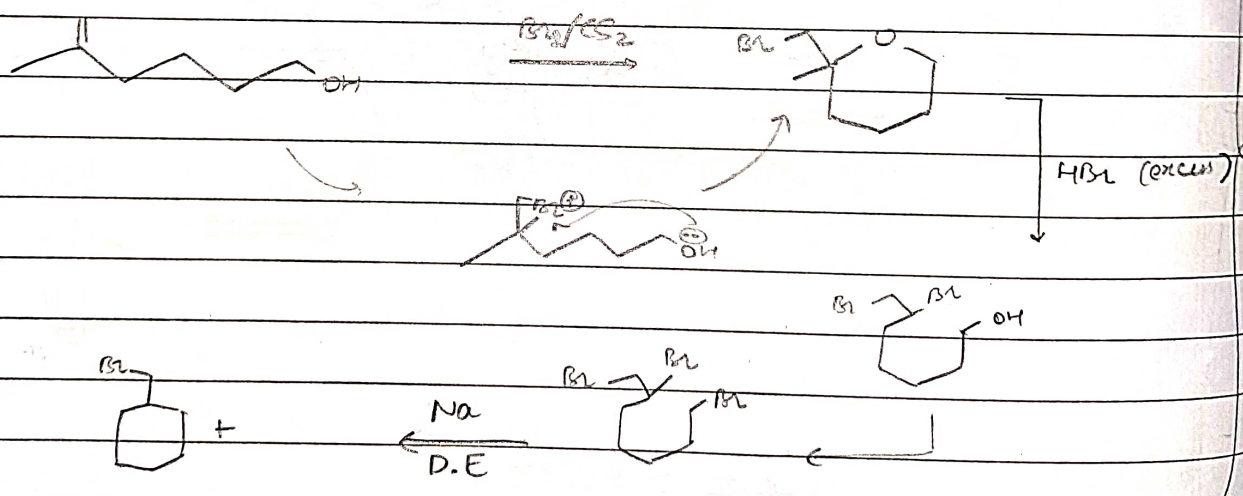
1 > 2 > 3

└ (H⊕ off of –OH)

(iii) 

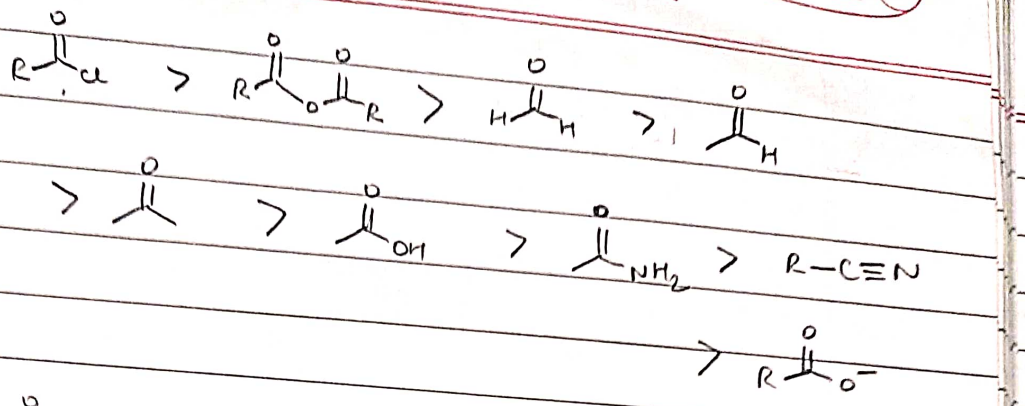
3 > 2 > 4 > 1

Q

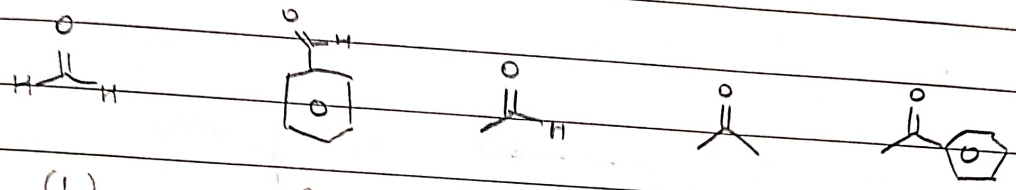


26/05/2023

(2) Rate of Nu Add^n :



Q

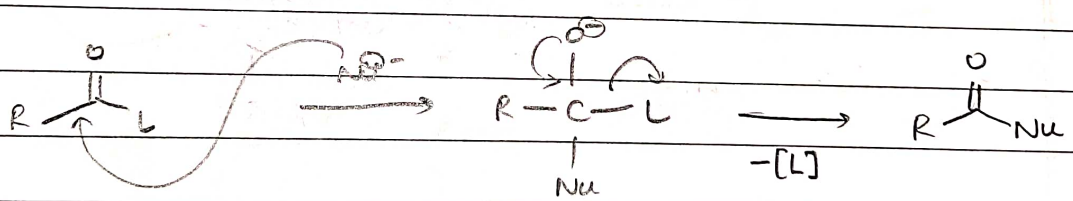


(I) (II) (III) (IV) (V)

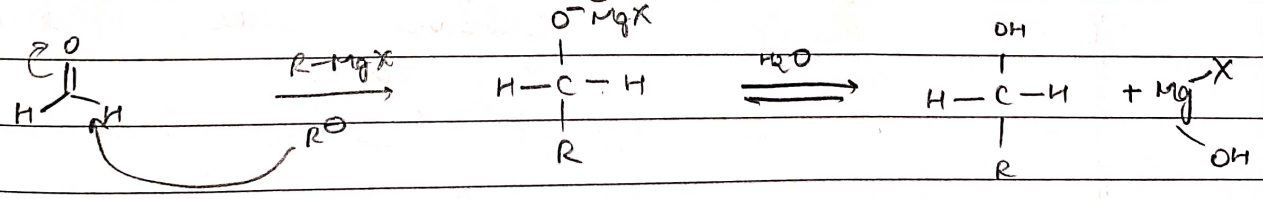
order of rate of Nu add^n

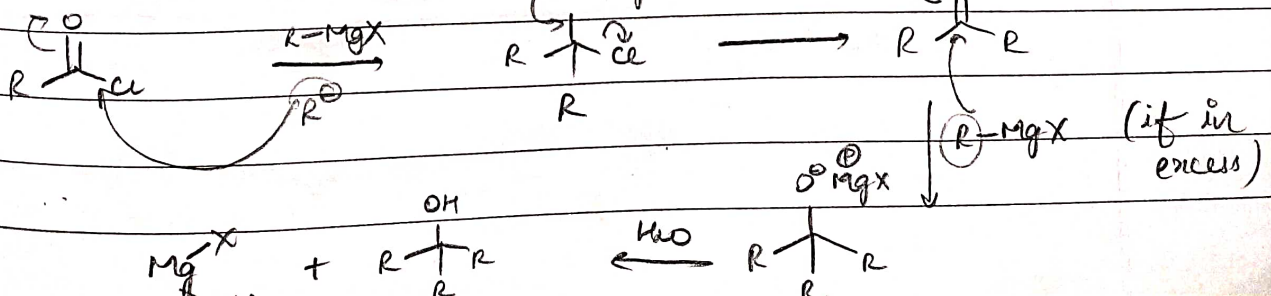
A.

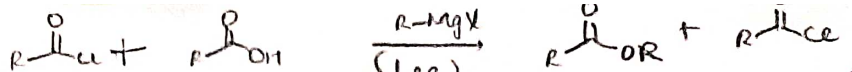
→ Mechanism (Ampure)



eg



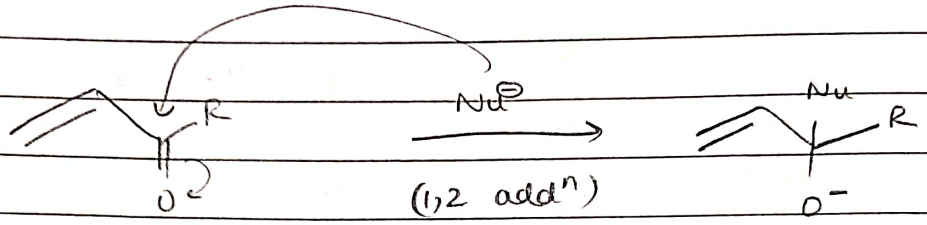


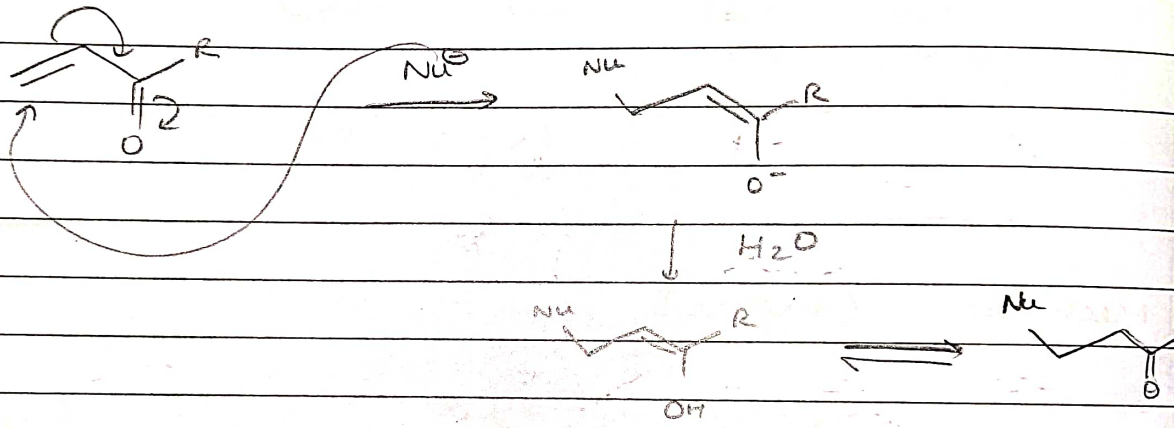
If  (1 eq)

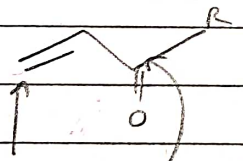
because ⊖ species first behave like base.

So rate of rxn with R-MgX : 

→ (1,2) V/s (1,4) addn







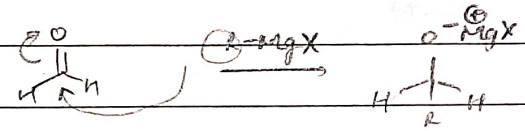
Soft E⊕ Hard E⊕

Here since C=O bond polarity is more, it behaves like Hard E⊕

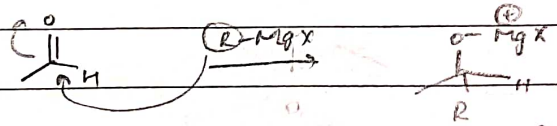
Generally, Hard E⊕ & Soft E⊕ react with Hard Nu⊖ & Soft Nu⊖ respectively.

Source	Nü$^{\ominus}$	Nature
$R-MgX$	R^-	Hard
$R-Li$	R^-	Hard
$RMgX + Cu$	R^-	Soft
R_2CuLi	R^-	Soft
$Ph-MgX$	Ph^-	Soft
$LiAlH_4$	H^-	Hard
$NaBH_4$	H^-	Soft

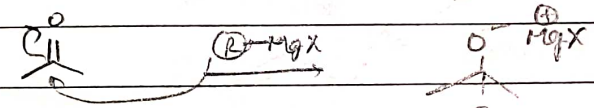
Q. 1.



2.



3.



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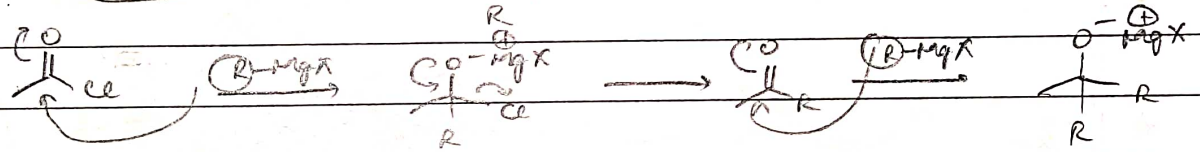
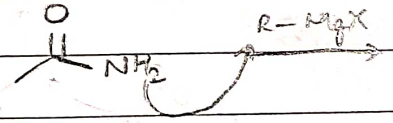


☆ 5.



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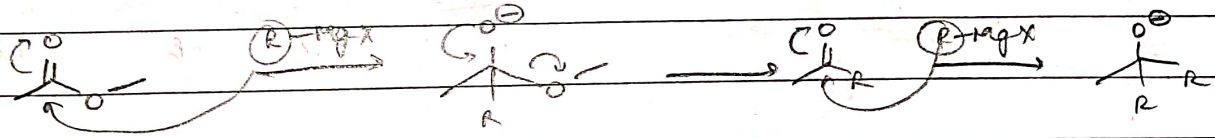

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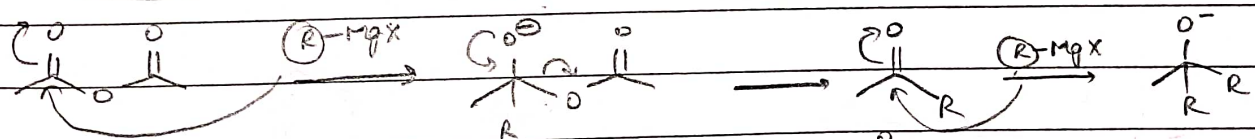

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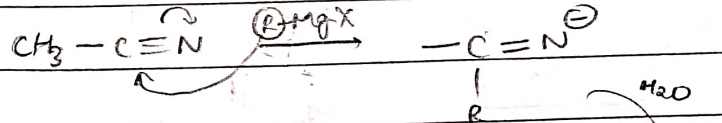
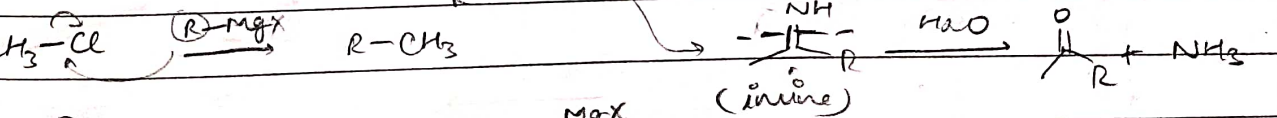


☆ 9.



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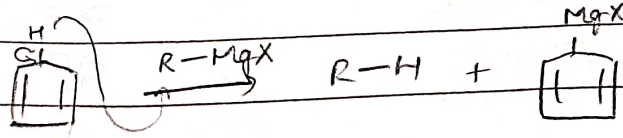
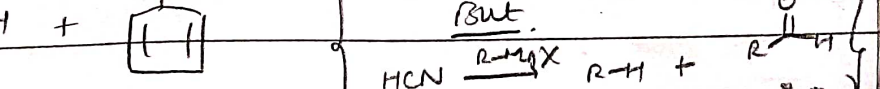
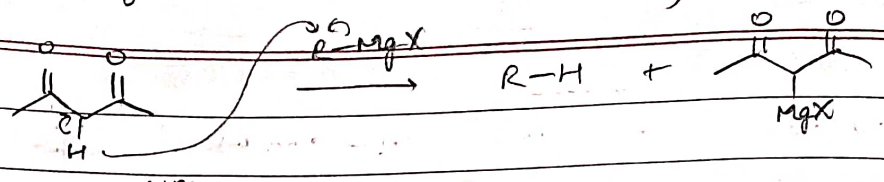


But.



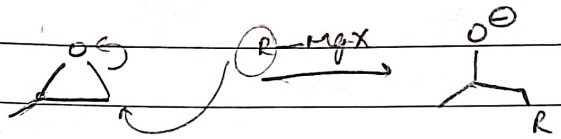
{ H of $-CH_3$ is never acidic
H- of NH_3 & $-NH_2$ is acidic }

11. 

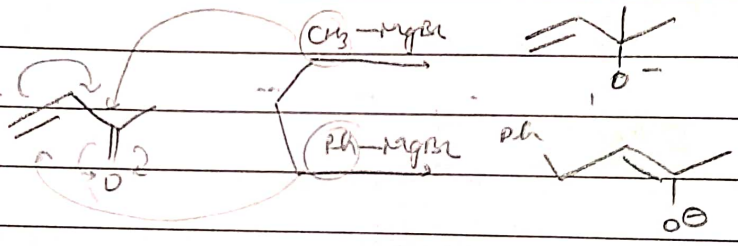
12. $CH_2(NO_2)(CN) \xrightarrow{R-MgX} R-H$

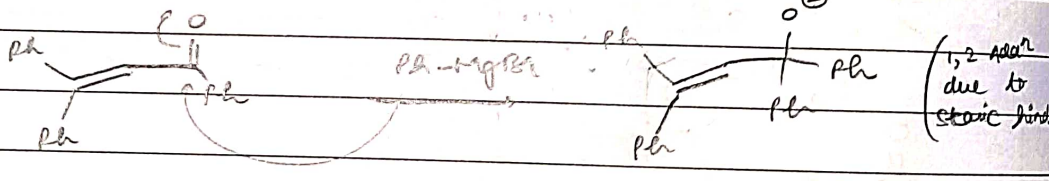
13. $CH_3-C\equiv CH \xrightarrow{R-MgX} R-H$

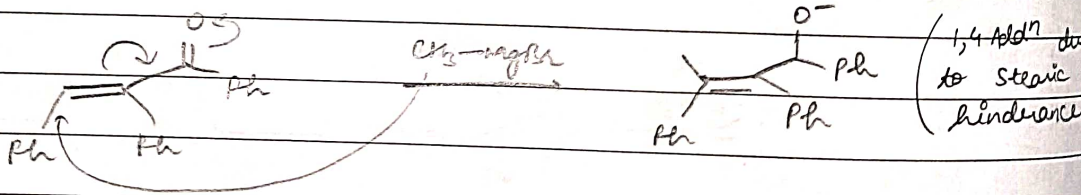
14. $CH_3-OH \xrightarrow{R-MgX} R-H$

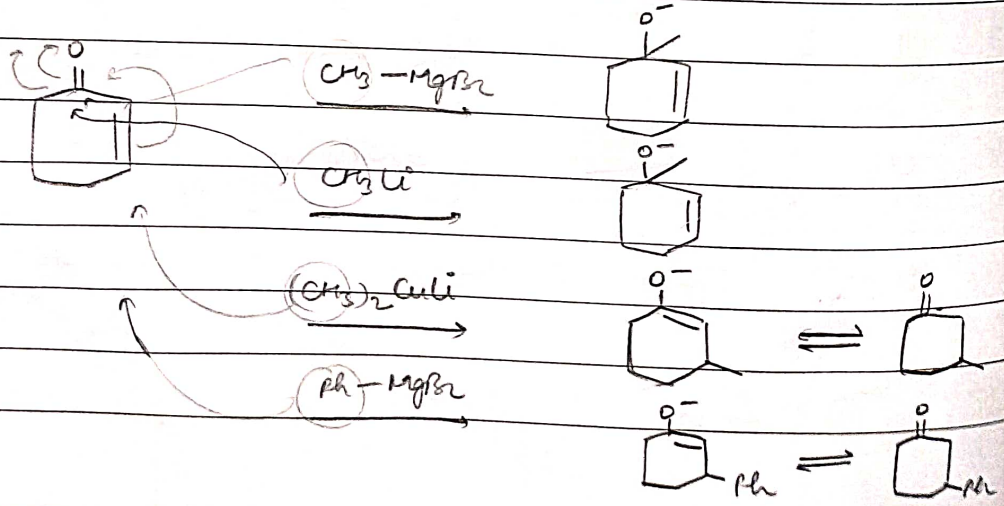
15. 

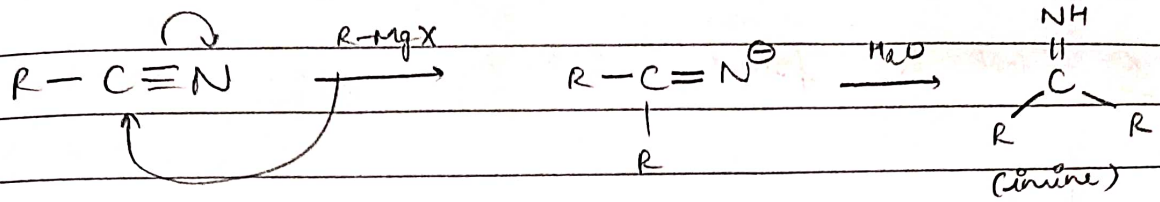
☆ 16. $NH_3 \xrightarrow{R-MgX} R-H$

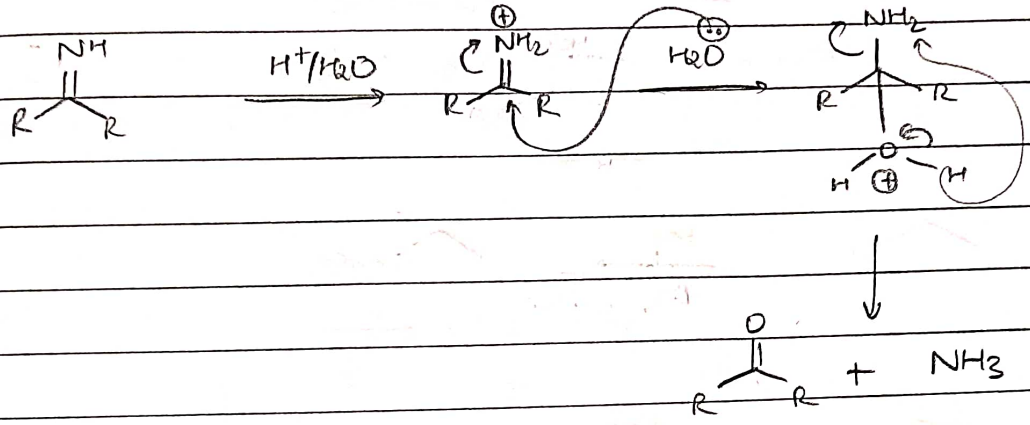
Q 1. 

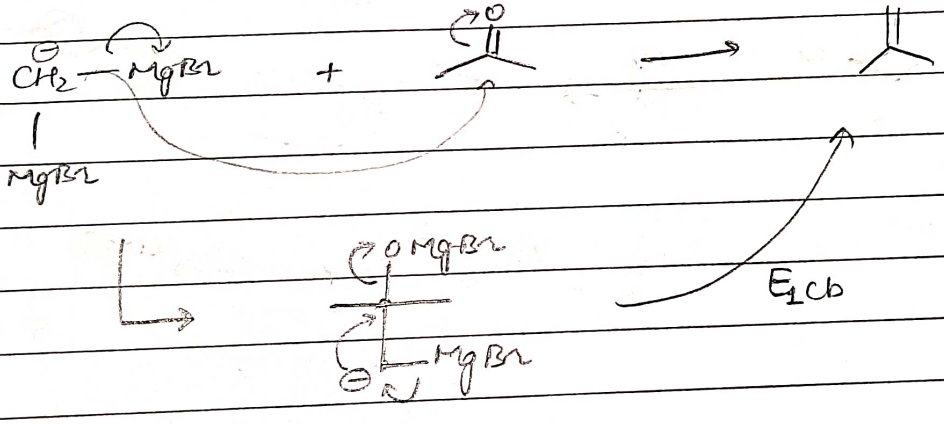
☆ 2. 

☆ 3. 

4. 

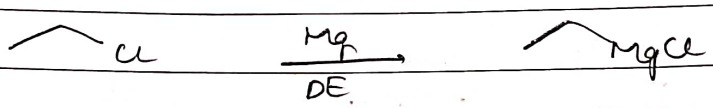
NOTE: ① 

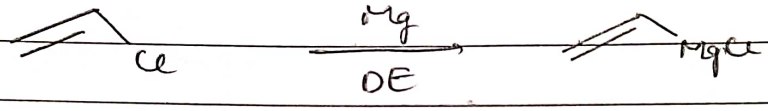


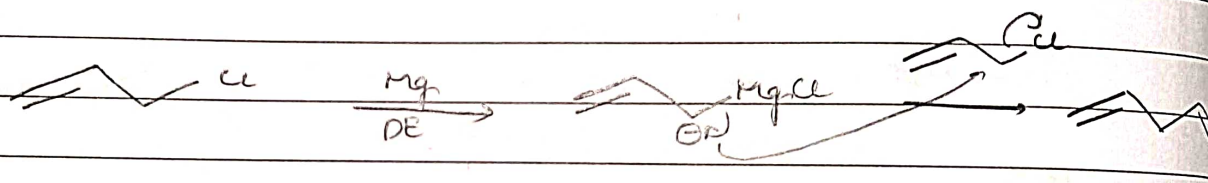
★ ② 

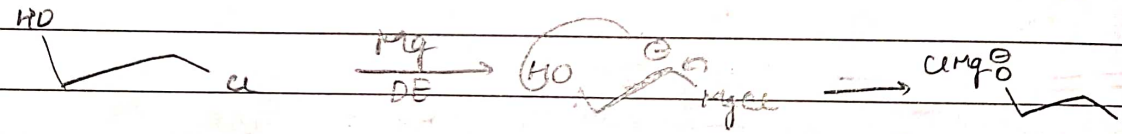
Q Which forms G.R ?

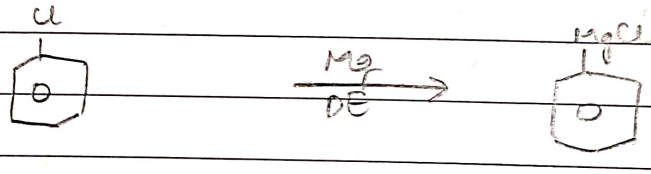
1. $CH_3-Cl \xrightarrow[DE]{Mg} CH_3-MgCl$

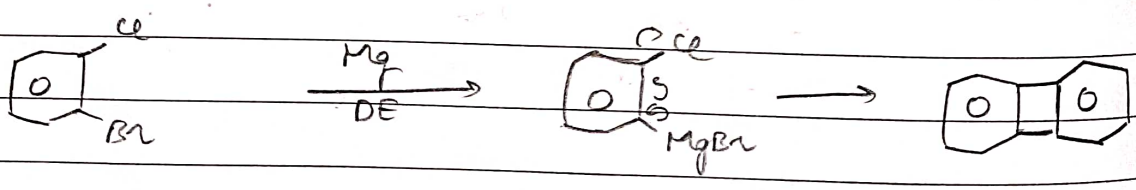
2. 

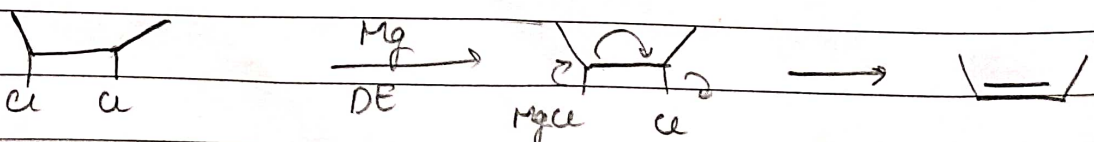
3. 

4 

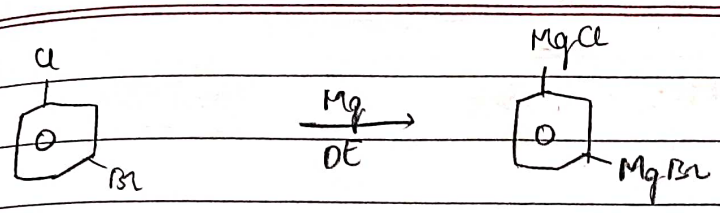
☆ 5. 

6. 

7. 

8. 

9



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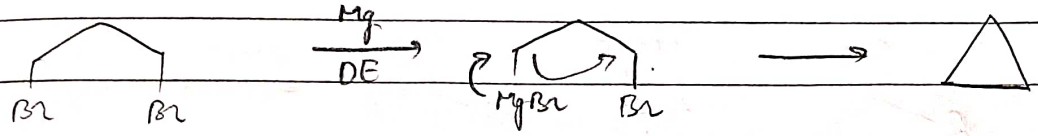
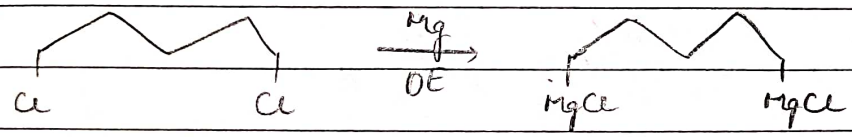


11



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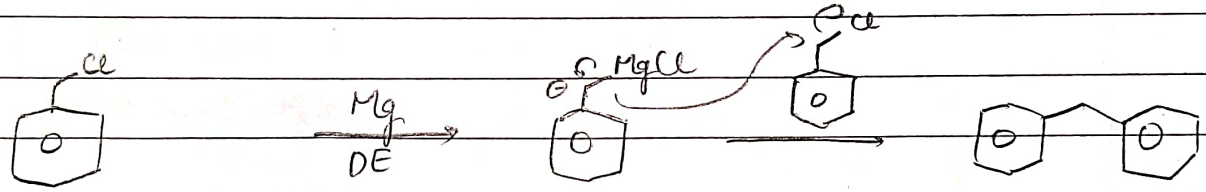

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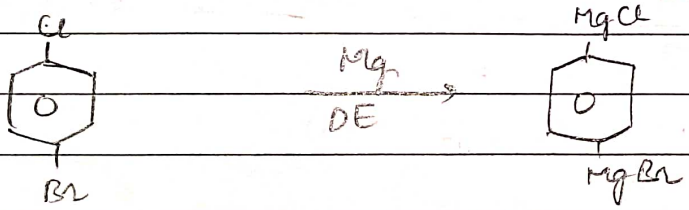

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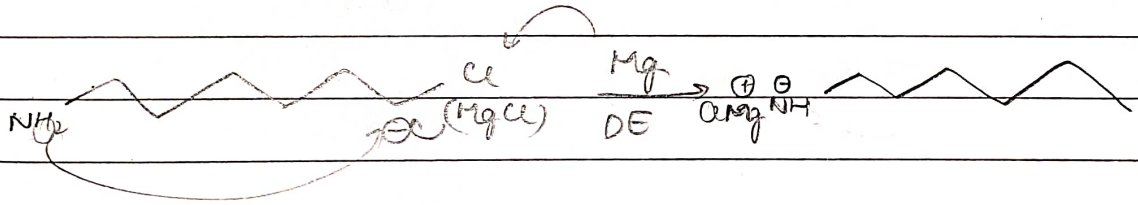

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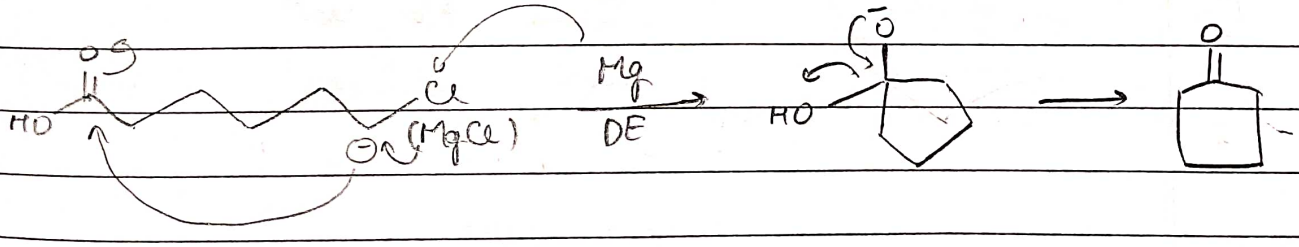

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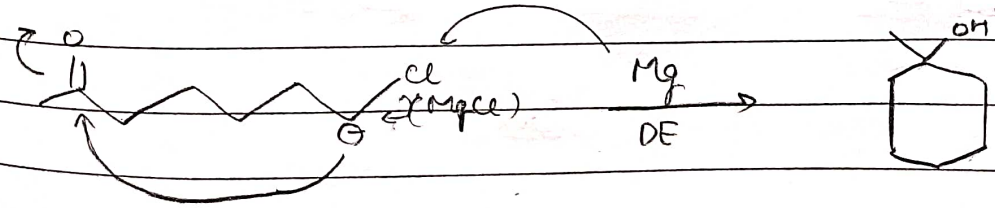

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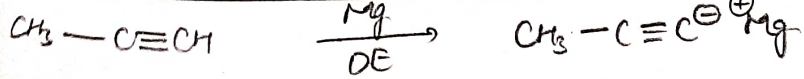
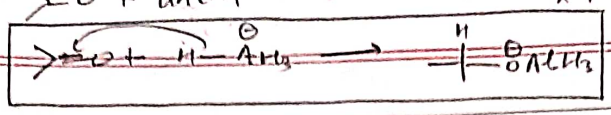


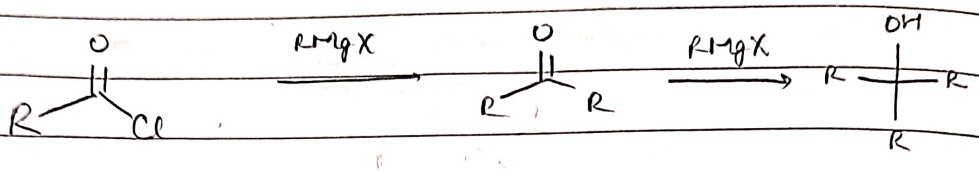
Actually σ-bond of $NaBH_4$ & $LiAlH_4$ act as Nu, since cov. bond b/w central atom

4. $>C=O + LiAlH_4 \longrightarrow (R_2CHO)_4Al \xrightarrow[\times 4]{H_2O} 4.\ R-CH-OH + Al(OH)_4$

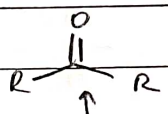


NOTE: ① Compound with acidic H cannot form G.R.

②

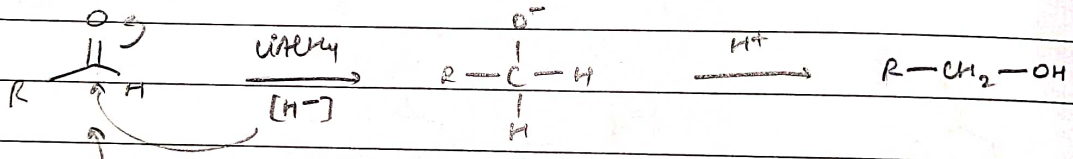


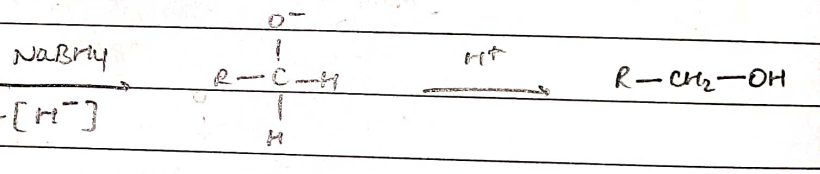
R_2CuLi / R_2Cd



Hard E⊕ & Soft Nu⊖ ⇓ Rxn stops here!

③





③ $-C=C-$ / $-C\equiv C-$ $\xrightarrow{LiAlH_4}$ No rxn

$\xrightarrow{NaBH_4}$ No rxn

④ $-C\equiv C- \xrightarrow[CCl_4]{LiAlH_4 \text{ or } NaBH_4} -C=C-$

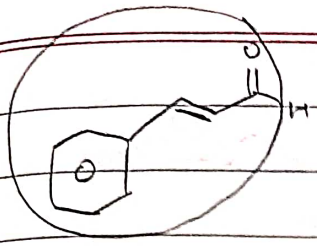
(Transition metal)

Cinnamic System

{ Ni reduces all comps except -COOH

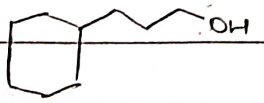
classmate Date Page

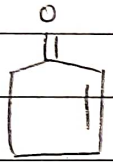
⑤ only in cinnamic system
- Ring
- db
- carbonyl

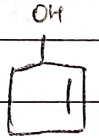


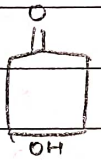
$NaBH_4$ → 

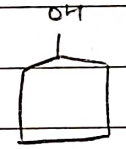
$LiAlH_4$ → 

H_2/Raney-Ni (powdered form of Ni) → 

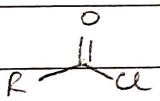
⑥ 

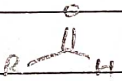
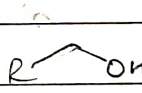
$LiAlH_4$ →  (1, 2 add^n)

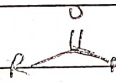
$NaBH_4$ (1,4 add^n) → 

$NaBH_4$ →  (100%)

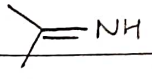
$NaBH_4$ + $CeCl_3$ → 

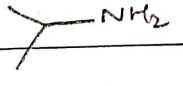
⑦ 

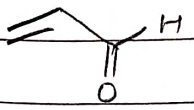
$LiAlH_4$ →  → 

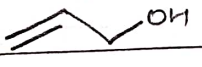
$NaBH_4$ →  → 

(even though soft Nu)

⑧ 

$NaBH_4$ → 

⑨ 

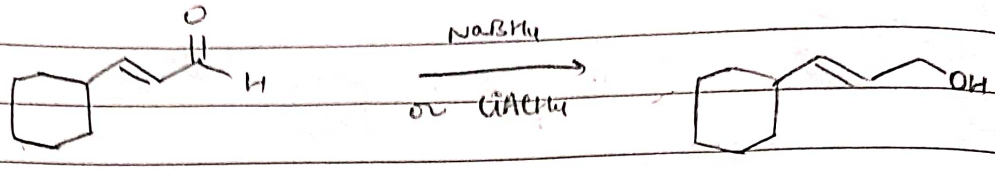
$LiAlH_4$ or $NaBH_4$ → 

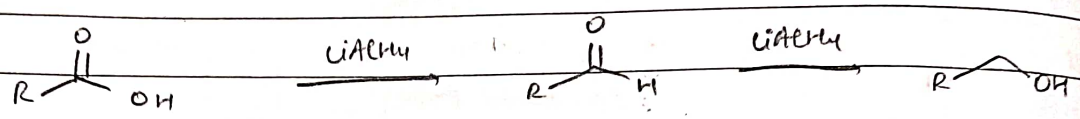
↳ (even though soft Nu)

In gaseous phase : $RO^- < OH^-$

aq. medium : $RO^- > OH^-$

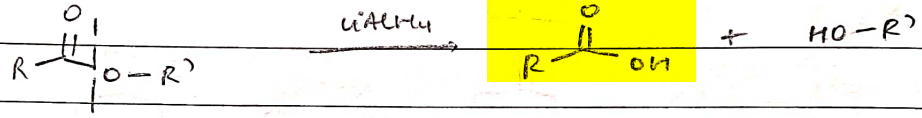
(nucleophilicity)

(10) 

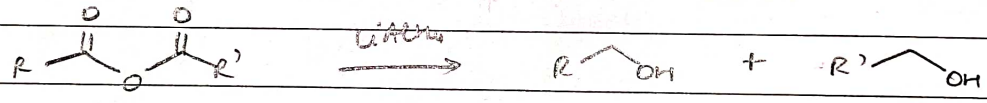
(11) 

$NaBH_4$ → No rean

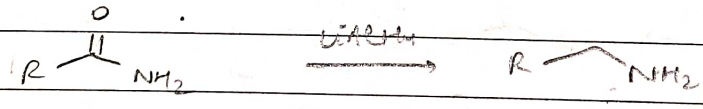
(since OH^- poor Nu & $NaBH_4$ poor source)

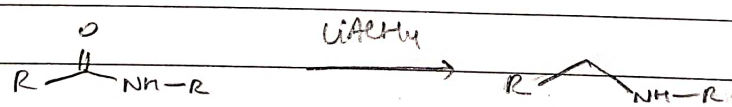
(12) 

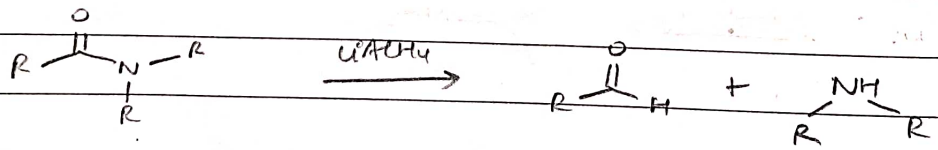
$NaBH_4$ → No rean

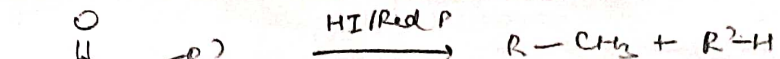
(13) 

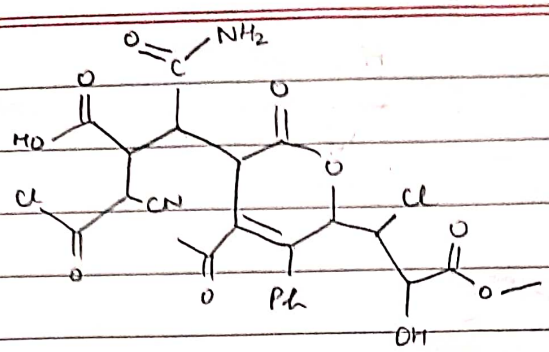
$NaBH_4$ → No rean

(14) 



☆ 





Q.

CH_3-MgBr (1)

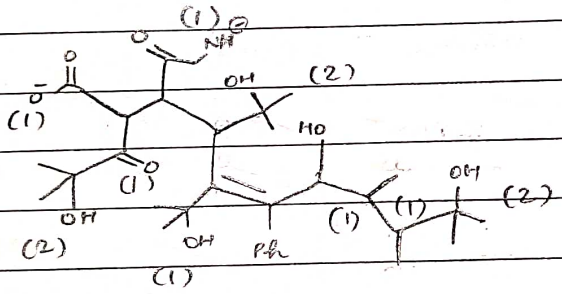
HI/Red P (2)

$LiAlH_4$ (3)

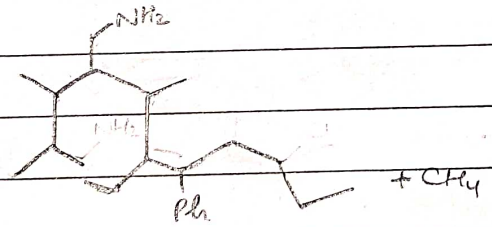
$NaBH_4$ (4)

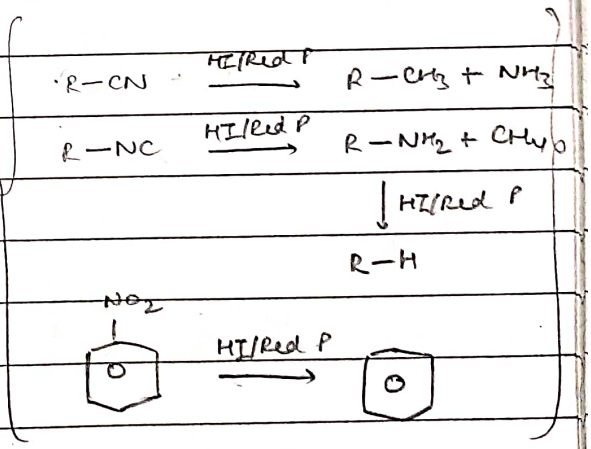
H_2/Raney Ni (5)

A. (1)

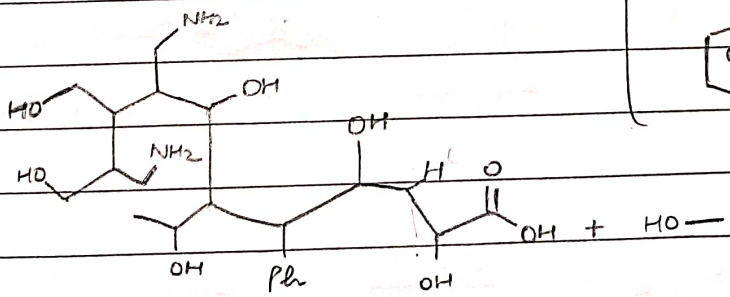


(2)

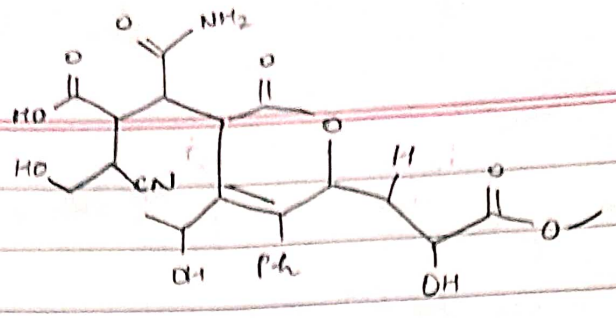




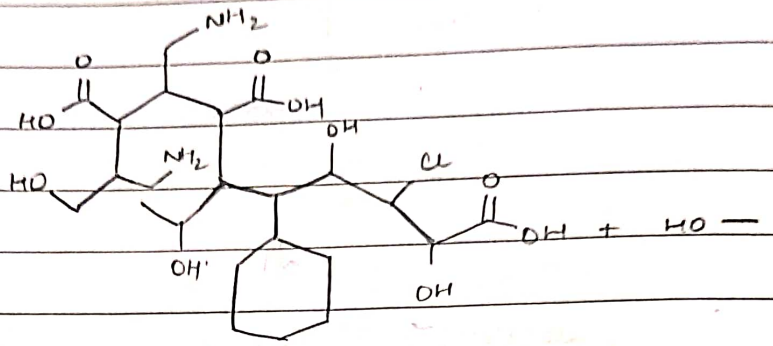
(3)



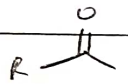
(4)



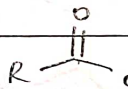
(5)



HALOFORM REAⁿ



$\xrightarrow{X_2/OH^-}$



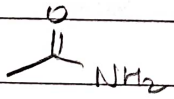
$+ CHX_3$

Haloform

$\xrightarrow[\text{(greenish yellow)}]{Cl_2/OH^-}$  $+ CHCl_3$ (colourless liq.)

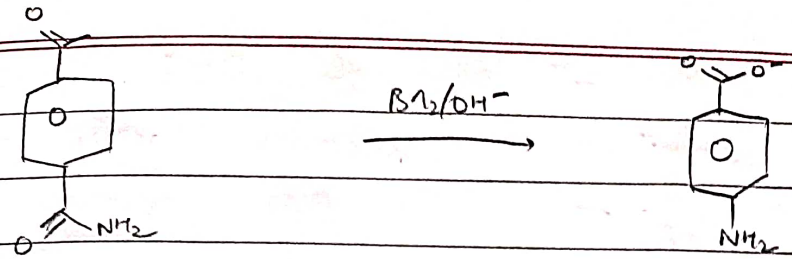
$\xrightarrow[\text{(Red)}]{Br_2/OH^-}$  $+ CHBr_3$ (Red/colourless liq.)

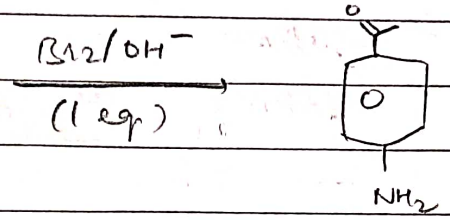
$\xrightarrow[\text{(Violet)}]{I_2/OH^-}$  $+ CHI_3 \downarrow$ (Yellow ppt.)

NOTE: 1. 

$\xrightarrow{X_2/OH^-}$ $-NH_2$

2.





(since H of $-NH_2$ more acidic than $-CH_3$)

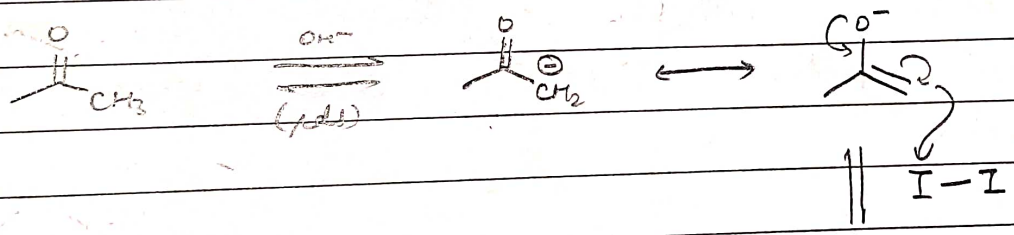
3. Reagents : X_2/OH^- (KOH, $NaOH$, $Ca(OH)_2$, $Ba(OH)_2$, Na_2CO_3)

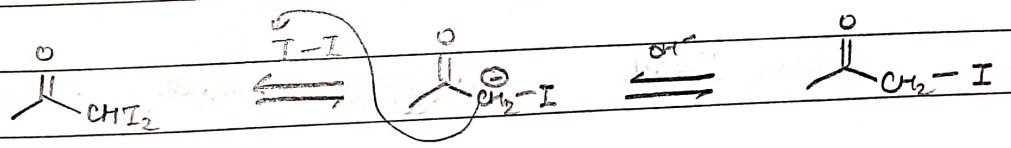
($X = Cl, Br, I$)

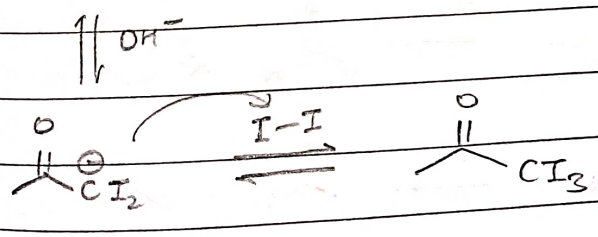
OX^- ($NaOX$, KOX)

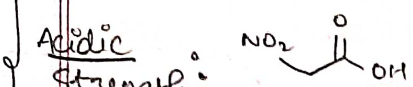
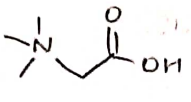
Any source which produces X_2/OH^-

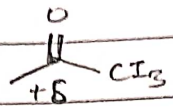
Mechanism



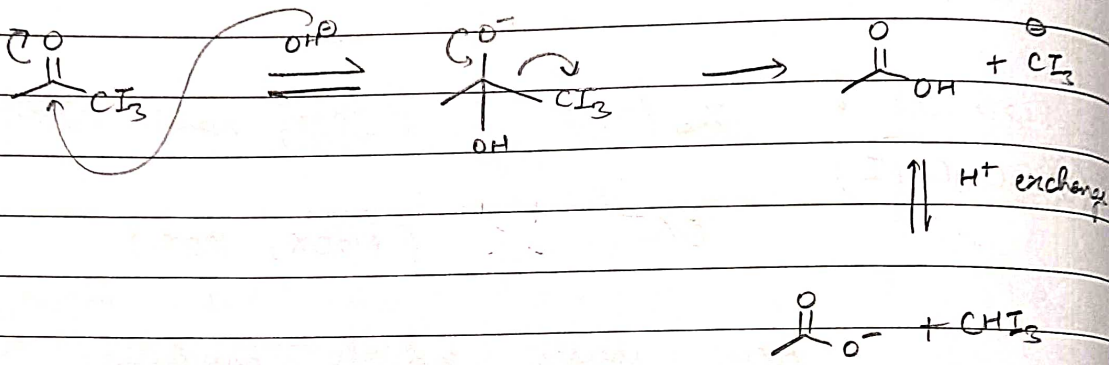




Acidic Strength :  > 

Now, due to -I eff of 3-I & carbonyl group,  becomes very good E⊕ centre.

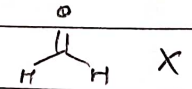
Hence, OH^- behaves as a Nü, instead of base, taking H of CH_3

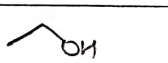
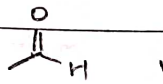


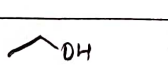
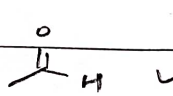
→ Haloform / Iodoform Test

Condⁿ : Any comp. (not necessarily carbonyl comp.) which gives CHI_3 on rxn with I_2/OH^- will give Iodoform test.

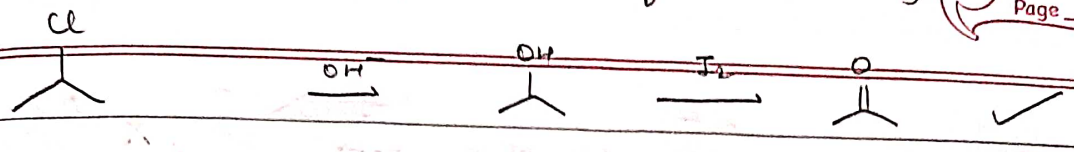
Q. Which give +ve Iodoform test.

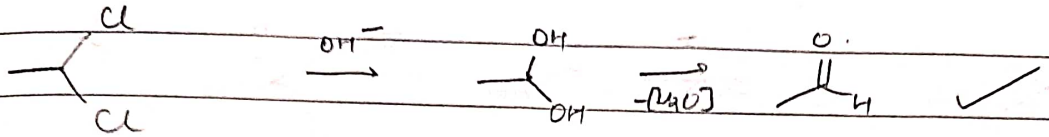
1. $CH_3-Cl \xrightarrow{OH^-} CH_3-OH \xrightarrow{I_2}$  X

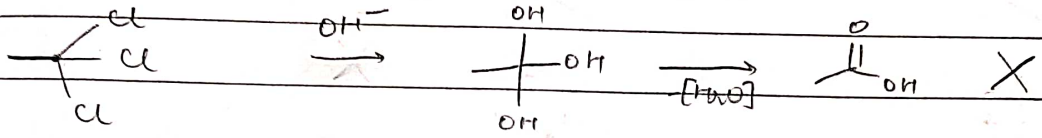
2.  $\xrightarrow{OH^-}$  $\xrightarrow{I_2}$  ✓

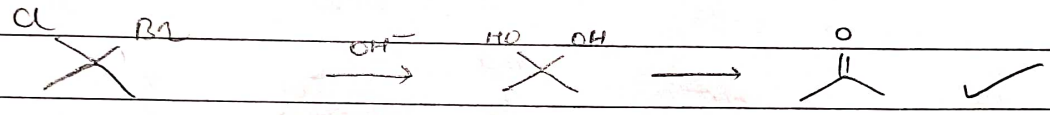
3.  $\xrightarrow{OH^-}$  $\xrightarrow{I_2}$  ✓

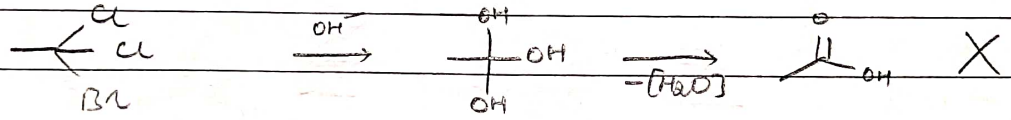
{ OH is the only 1° Alcohol which gives Iodoform test }

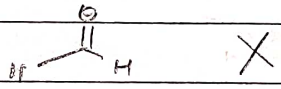
4. 

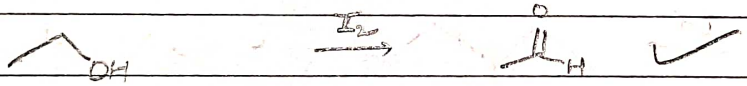
5. 

6. 

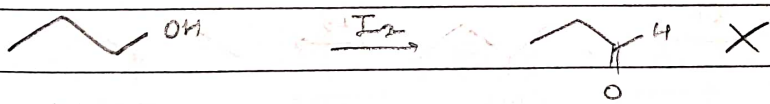
7. 

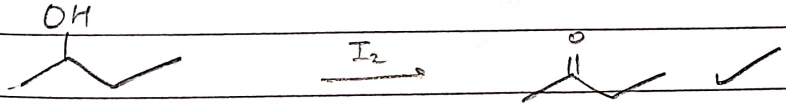
8. 

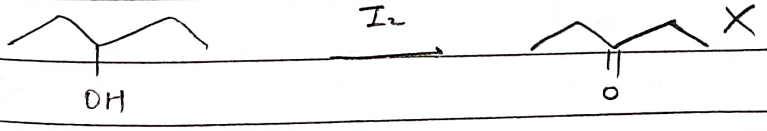
9. CH_3-OH $\xrightarrow{I_2}$ 

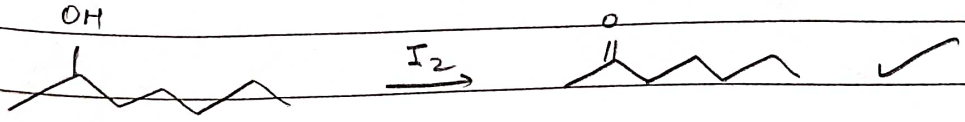
10. 

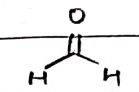
11. 

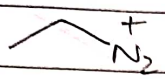
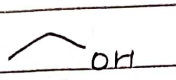
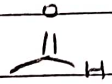
12. 

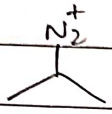
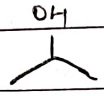
13. 

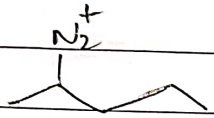
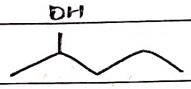
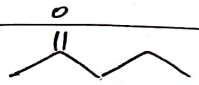
14. 

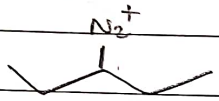
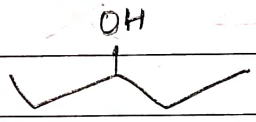
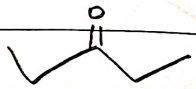
15. 

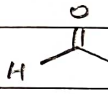
16. $CH_3-N_2^+ \xrightarrow{OH^-} CH_3-OH \xrightarrow{I_2}$  X

17.  $\xrightarrow{OH^-}$  $\xrightarrow{I_2}$  ✓

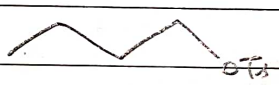
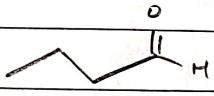
18.  $\xrightarrow{OH^-}$  $\xrightarrow{I_2}$  ✓

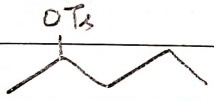
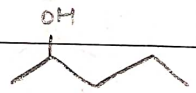
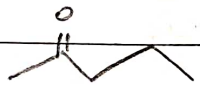
19.  $\xrightarrow{OH^-}$  $\xrightarrow{I_2}$  ✓

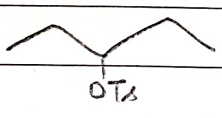
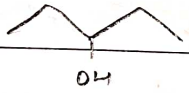
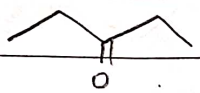
20.  $\xrightarrow{OH^-}$  $\xrightarrow{I_2}$  X

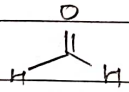
21. $CH_3-OTs \xrightarrow{OH^-} CH_3-OH \xrightarrow{I_2}$  X

22.  $\xrightarrow{OH^-}$  $\xrightarrow{I_2}$  ✓

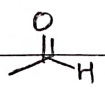
23.  $\xrightarrow{OH^-}$  $\xrightarrow{I_2}$  X

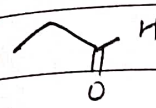
24.  $\xrightarrow{OH^-}$  $\xrightarrow{I_2}$  ✓

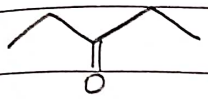
25.  $\xrightarrow{OH^-}$  $\xrightarrow{I_2}$  X

26.  X

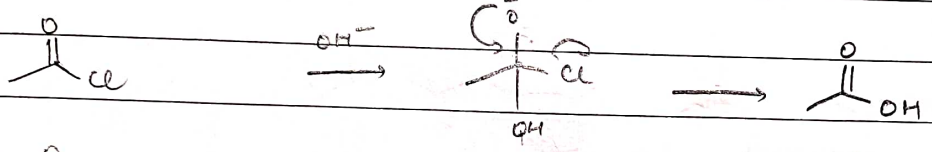
27.  ✓

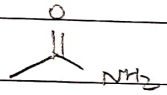
28.  ✓

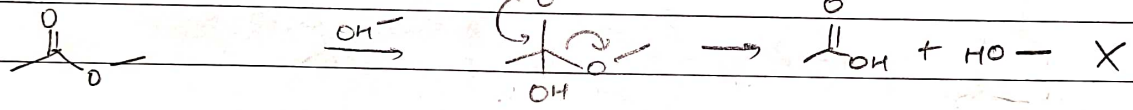
29.  ✗

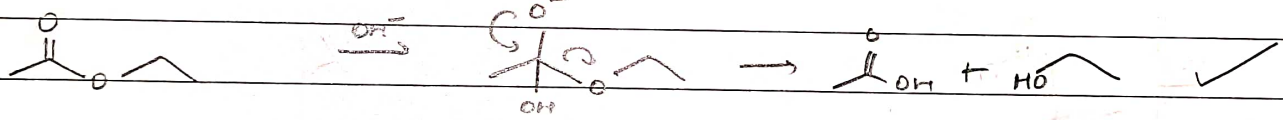
30.  ✗

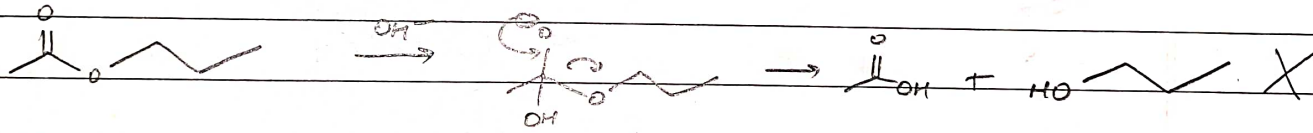
31.  ✗ (OH^- snatches acidic H of $-OH$)

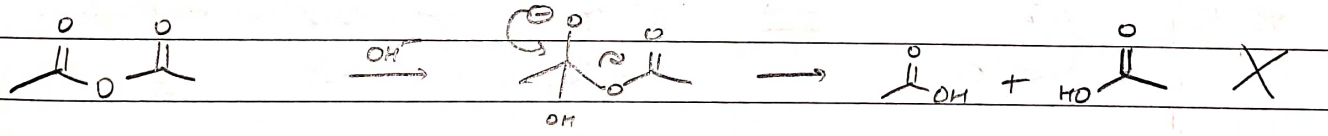
32.  ✗

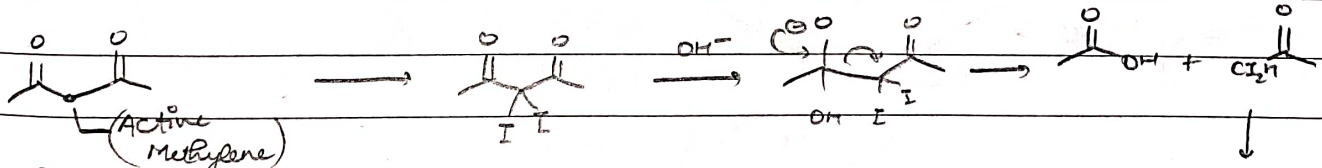
33.  ✗

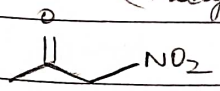
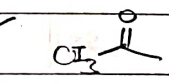
34.  ✗

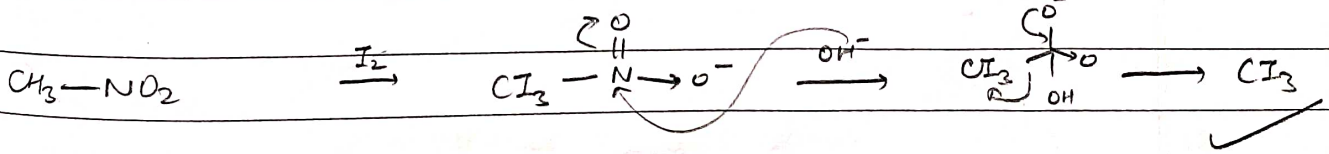
35.  ✓

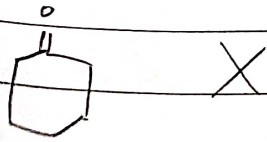
36.  ✗

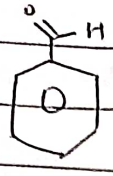
37.  ✗

☆38. 

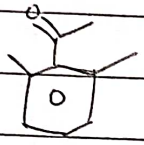
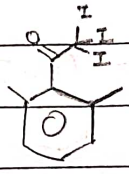
39.  ✓ ✓ 

40.  ✓

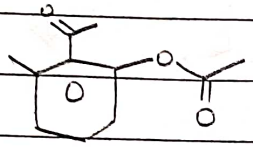
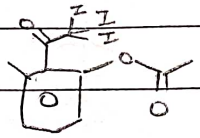
41.  ✗

42  ✗

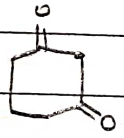
43.  ✓

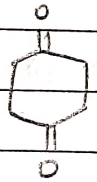
44.  I_2 →  (✗)

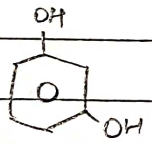
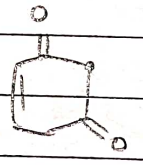
NO Nu addn due to steric hindrance

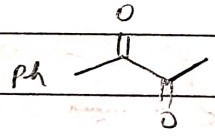
45.  I_2 →  (✗)

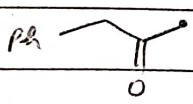
NO Nu addn due to steric hindrance

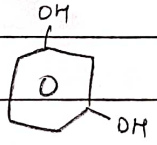
46.  ✗ (✓) Active Methylene

47.  ✗

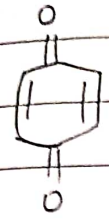
☆ 48  ⇌  ✓ (Active Methylene)

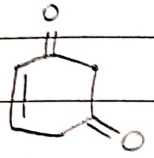
49  ✓

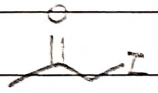
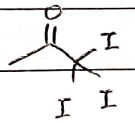
80  ✗ (✓)

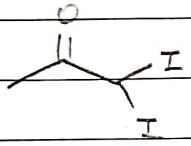
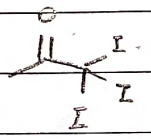
51.  (Same as 48.)

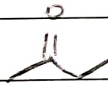
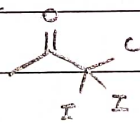
52.  ✗

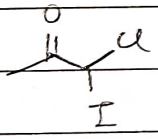
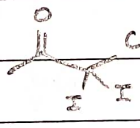
53.  ✗

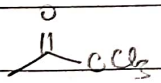
54.  ✓ Active Methylene

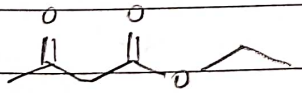
55.  ✓ ( formed)

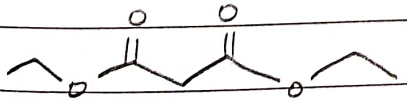
56.  ✓ ( formed)

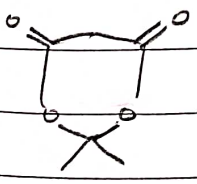
57.  ✗ ( formed)

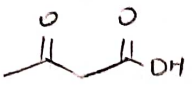
58.  ✗ ( formed)

59.  ✗

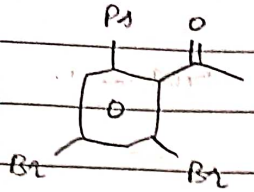
★ 60.  ✗ (Even though Active Methylene, due to steric hindrance, no Nu add^{n} of $-OH^{-}$)

61.  ✗ (Steric hindrance)

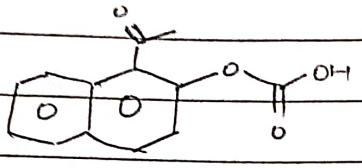
62.  ✗ (Steric hindrance)



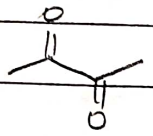
✓

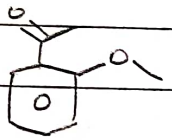
63. 

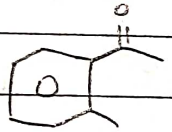
✓ (X) (Steric hind.)

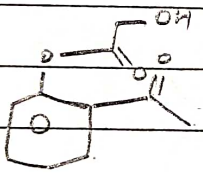
64. 

X (Steric hind.)

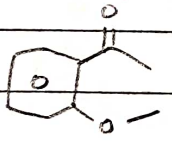
65. 
✓

66. 
X

67. 
X (✓)

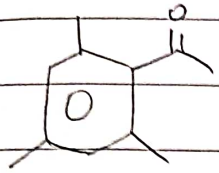
68. 

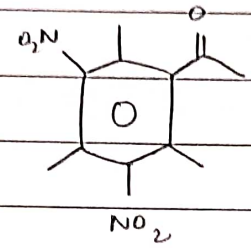
X (✓)

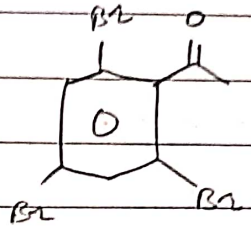
69. 
X (✓)

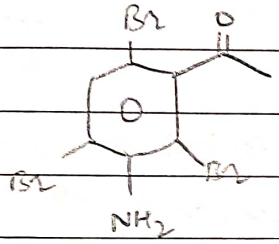
02/06/2023

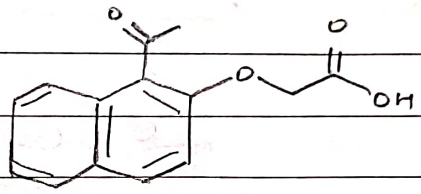
NOTE: 1. Comps. which give (-ve) Iodoform test.

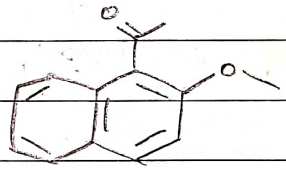




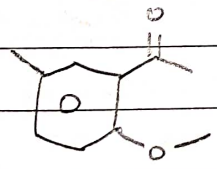


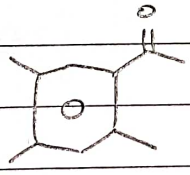


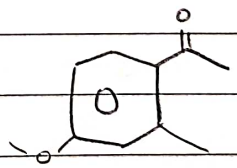


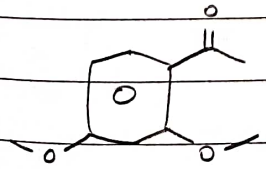


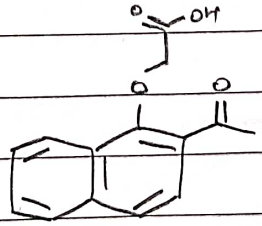
2. Comps. which give (+ve) Iodoform test

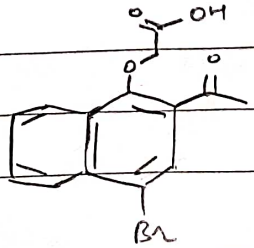












PREPⁿ OF ALCOHOL (From Amines)

$R-NH_2 \xrightarrow[[HNO_2]]{NaNO_2+HCl} R-OH$

$\xrightarrow[[HNO_2]]{NaNO_2+H_2SO_4} R-OH$

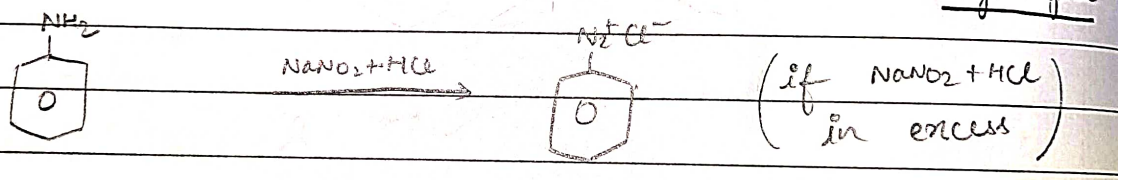
But,

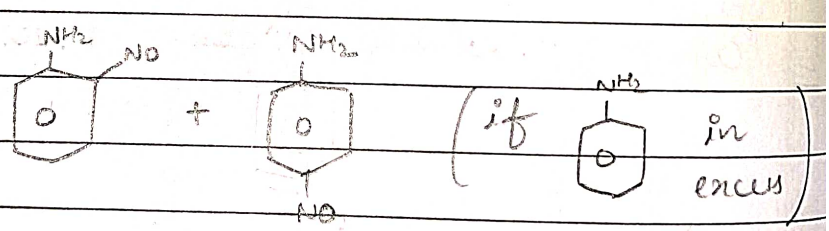
$CH_3-NH_2 \xrightarrow[[HNO_2]]{NaNO_2+HCl} CH_3-O-CH_3$ (major) + CH_3-OH (minor)

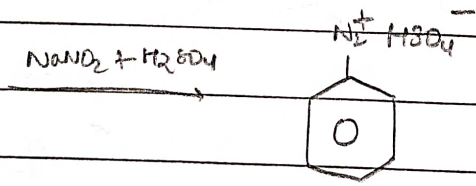
$\xrightarrow[[HNO_2]]{NaNO_2+H_2SO_4} CH_3-OH$ (major) + CH_3-O-CH_3 (H_2SO_4 hydrolyses $-O-$)

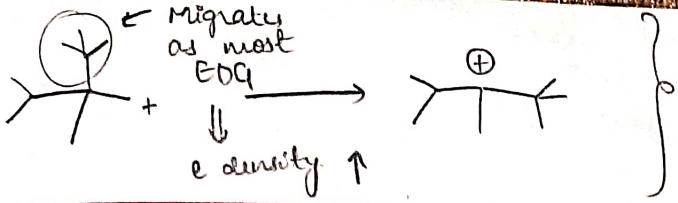
$\xrightarrow{NaNO_2/\text{excess } HCl} CH_3-O-NO + N_2 + 2H_2O$

* in presence of dil. H_2SO_4, $-O-$ & $-O-NO$ will be hydrolysed









classmate
Date
Page

10/6/2023

Mechanism

1°: $R-NH_2 + HO-N=O \xrightarrow{\text{Nu addn}} R-NH-N=O$

$R-NH-N=O \rightleftharpoons R-N=N-OH$

$R-N=N-OH \xrightarrow{H^+} R-N=N-\overset{\oplus}{O}H_2$

$R-N=N-\overset{\oplus}{O}H_2 \longleftarrow R-N\equiv\overset{\oplus}{N}$

if $R = \text{Ar}$ & $T = 0-5^\circ C$,

$R-N_2^\oplus$ can be isolated.

otherwise

$R-N_2^\oplus \xrightarrow{H_2O\,(Nu)} R-OH + N_2$ (major)

$\xrightarrow{H_2O\,(Base)}$ Alkene

(Present in sys. as $NaNO_2 + HCl$ used)

$\xrightarrow{NO_2^-} R-NO_2 + R-ONO$

$\xrightarrow{Cl^-} R-Cl$

$\xrightarrow{ROH} R-O-R$

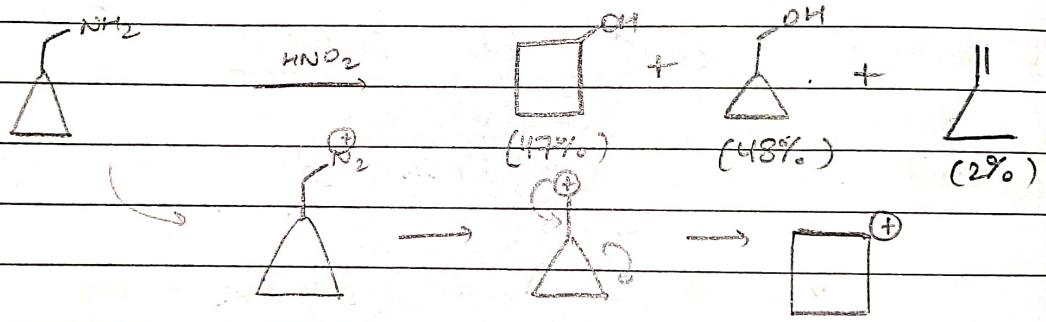
2°: $R_2NH + HO-NO \longrightarrow R_2N-N=O$

3°: $R_3N + HNO_2 \longrightarrow [R_4N]^+ NO_2^-$

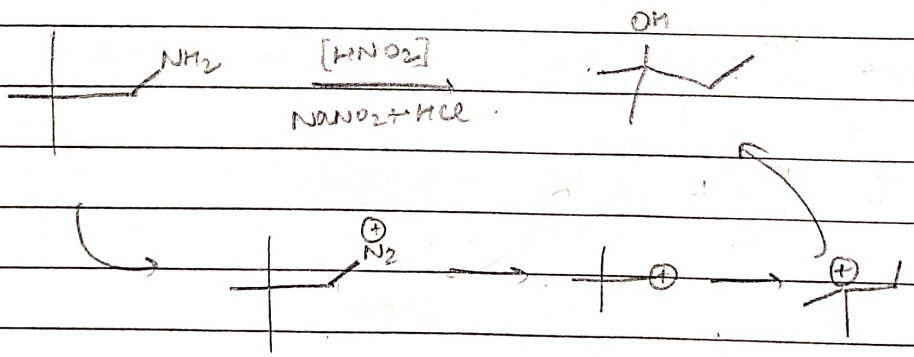
* if $\xrightarrow[H_2O]{\Delta}$ R–OH.

But do not consider this.
Only 1° –NH_2 form –OH.

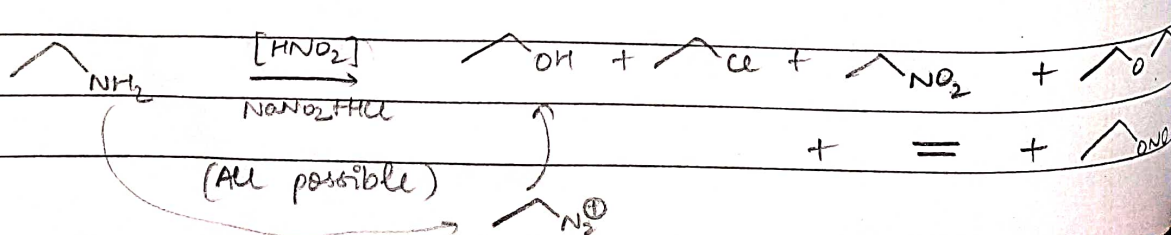
Q. (i)



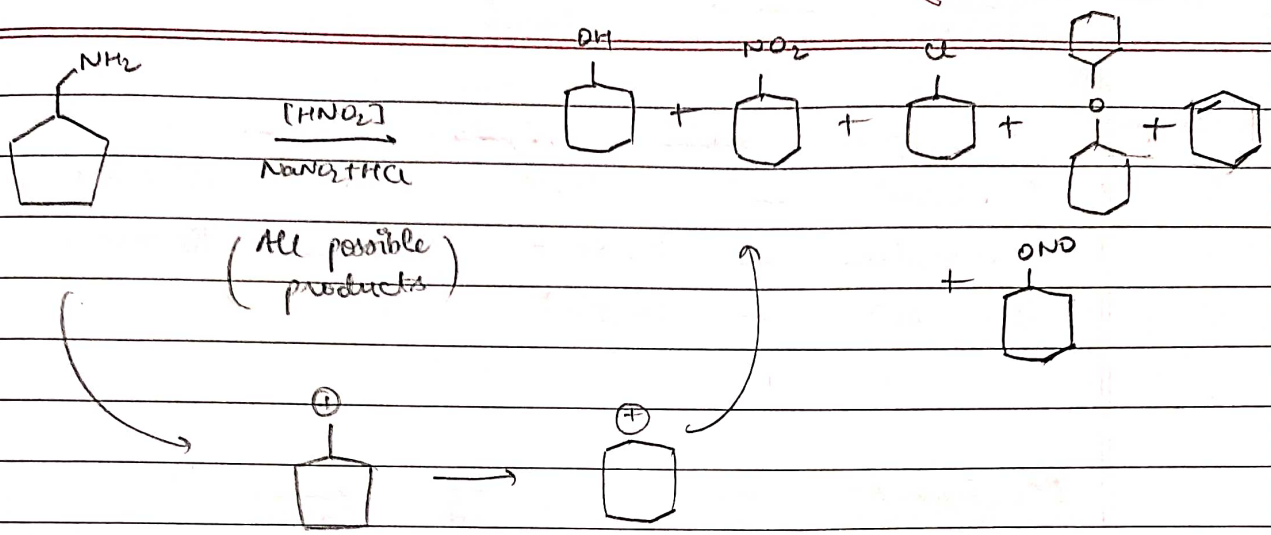
(ii)



(iii)

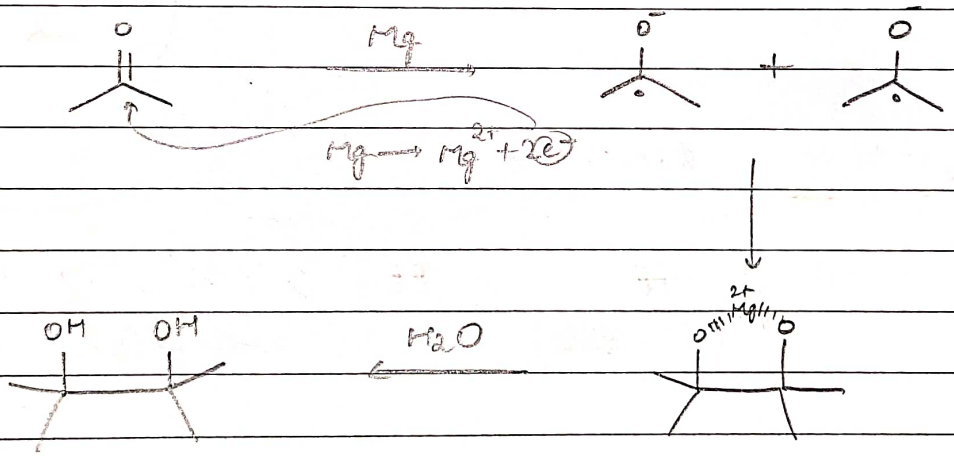


(iv)

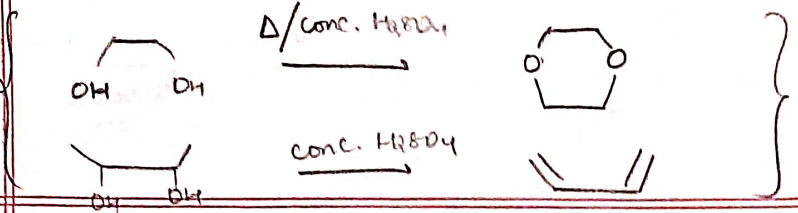


PINNACOL & PINNACOLENE REARRANGEMENT

→ **Formation**



(Pinnacol)

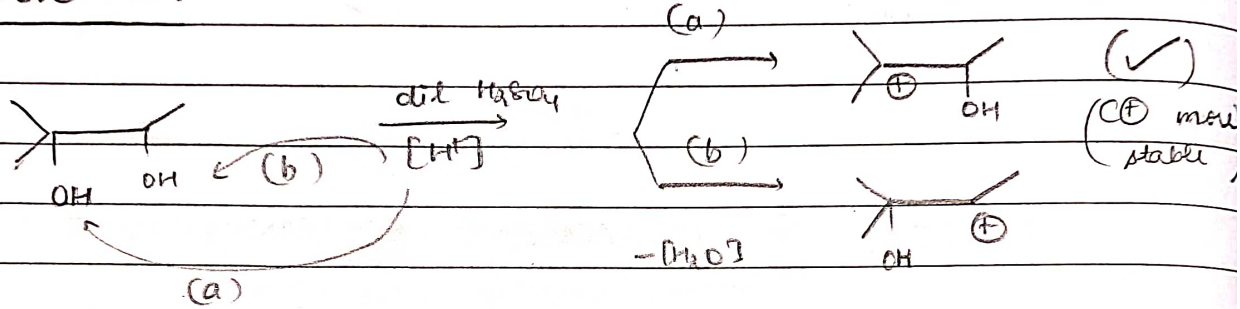


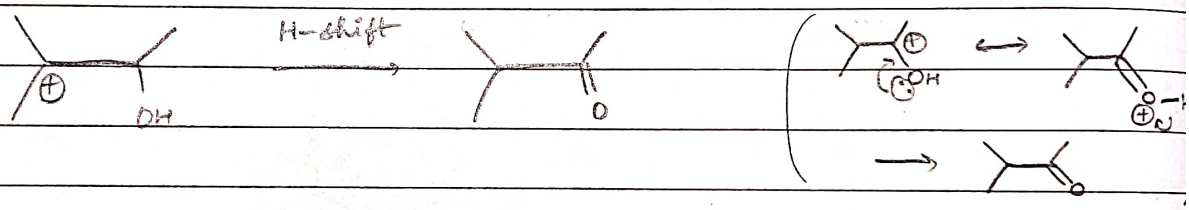
Pinnacole — Reactant (Vicinal dihalide)

Pinnacoline — Product (Aldehyde / Ketone)

dil acid — Reagent

Mechanism





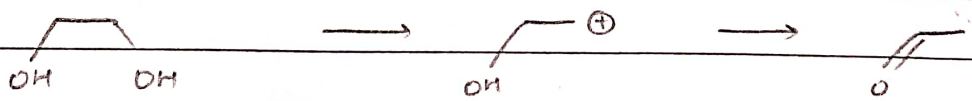
NOTE: Migrating tendency

$H^- > D^- > Ph^- > Ph^- > Ph^- > 3^\circ > 2^\circ > 1^\circ$

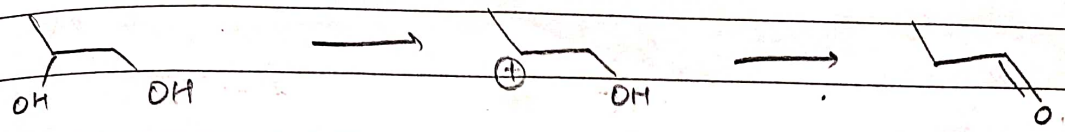
(with EDG) (with EWG) — Methyl

Q. Write the mech. & product

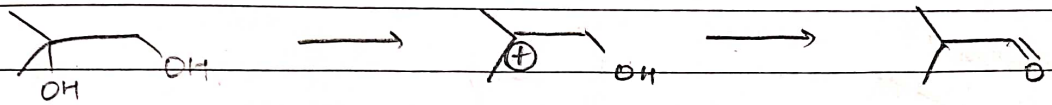
1.



2.



3.



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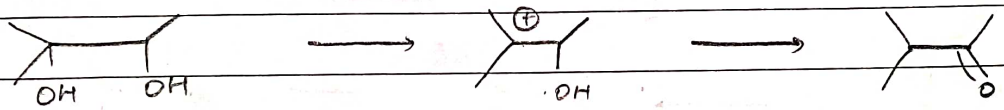

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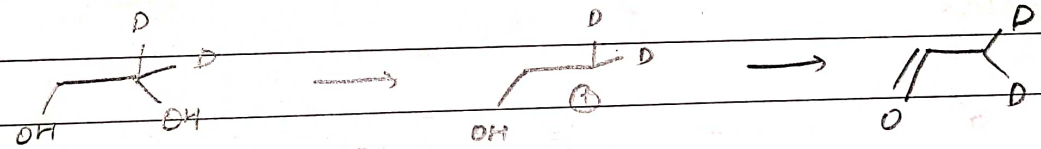

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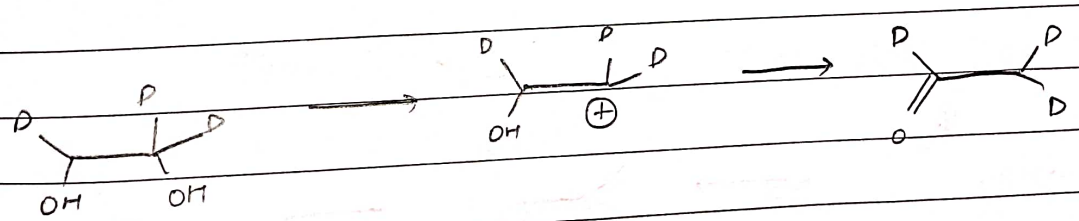

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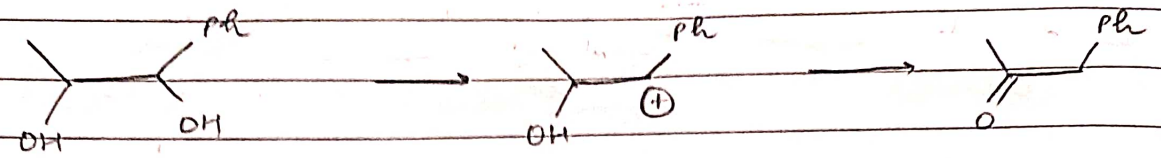

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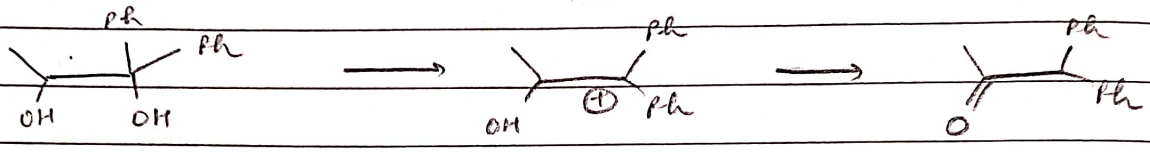

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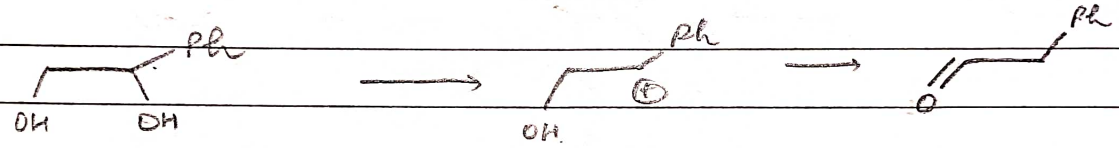

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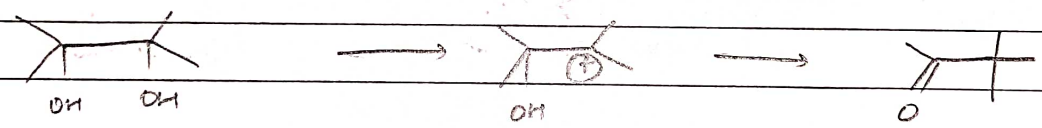

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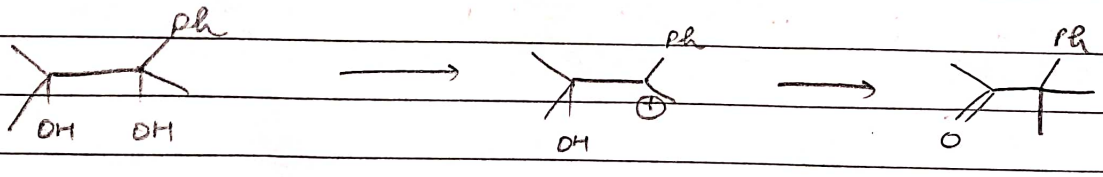

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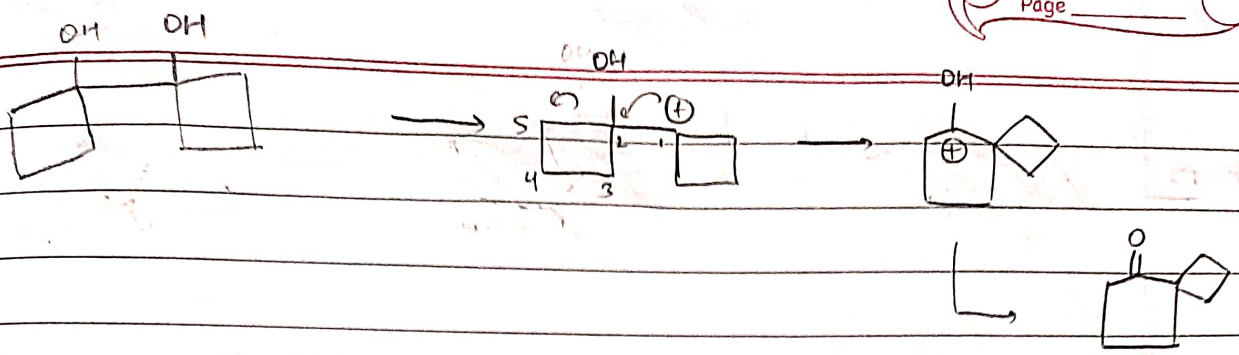

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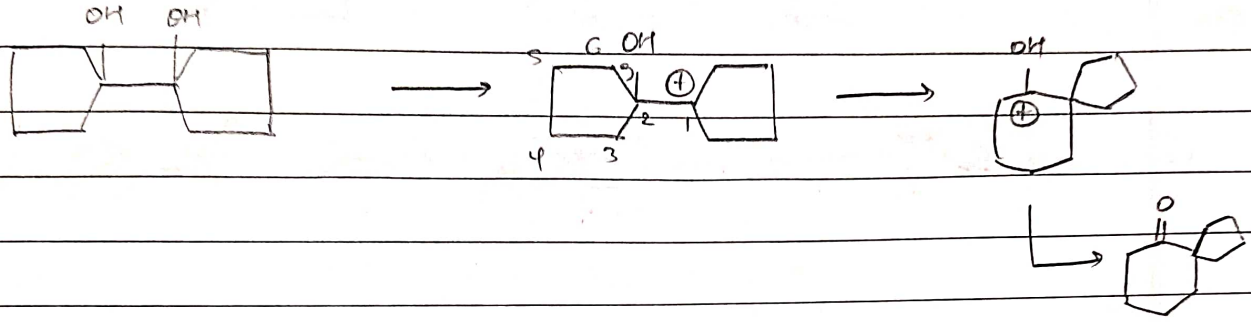

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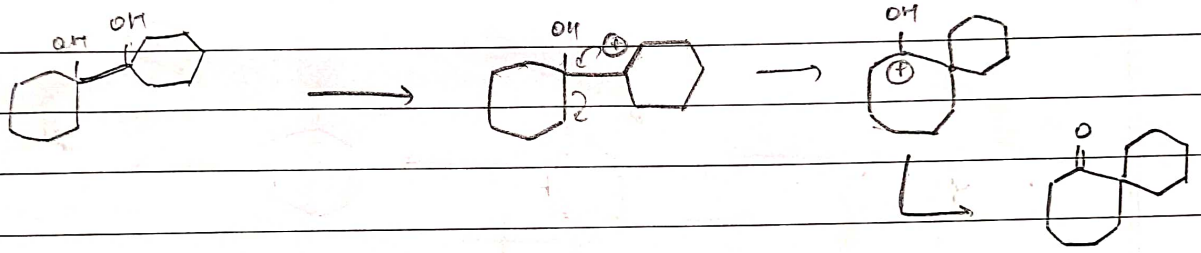

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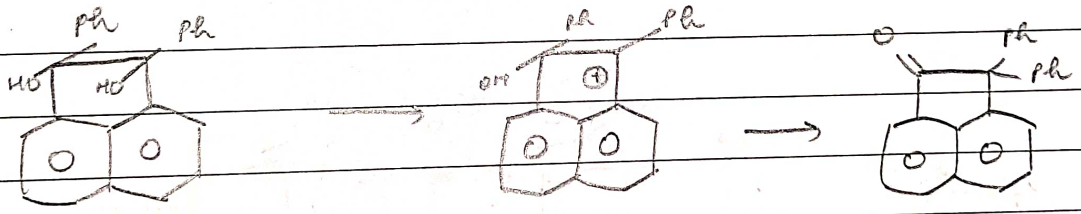

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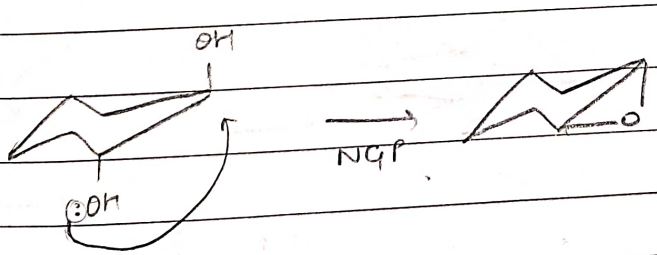
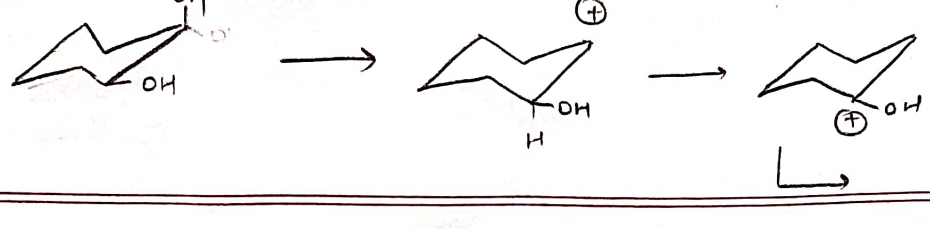
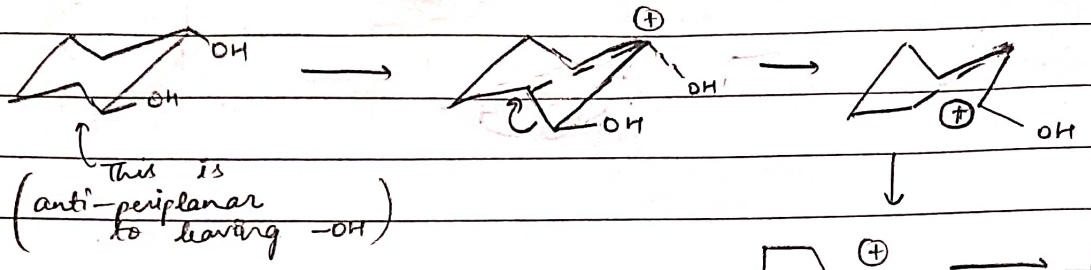
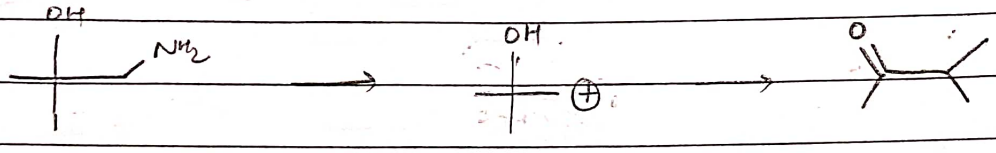
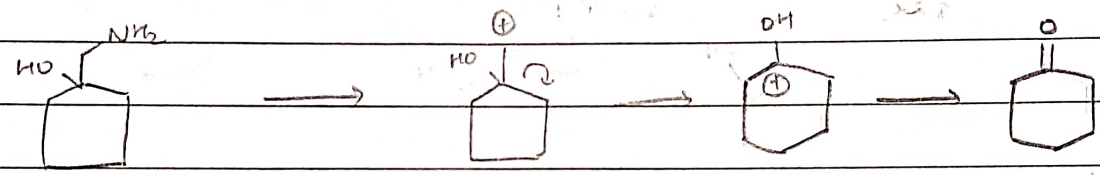


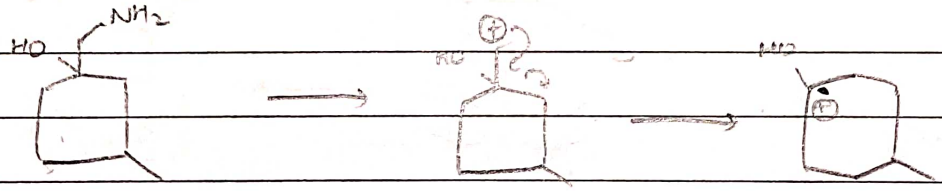
☆ 

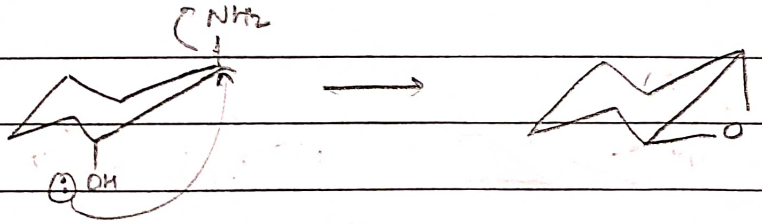
☆ 17. 

(HNO_2 in all $-NH_2$ comps.)

18 

19. 

20. 

21. 

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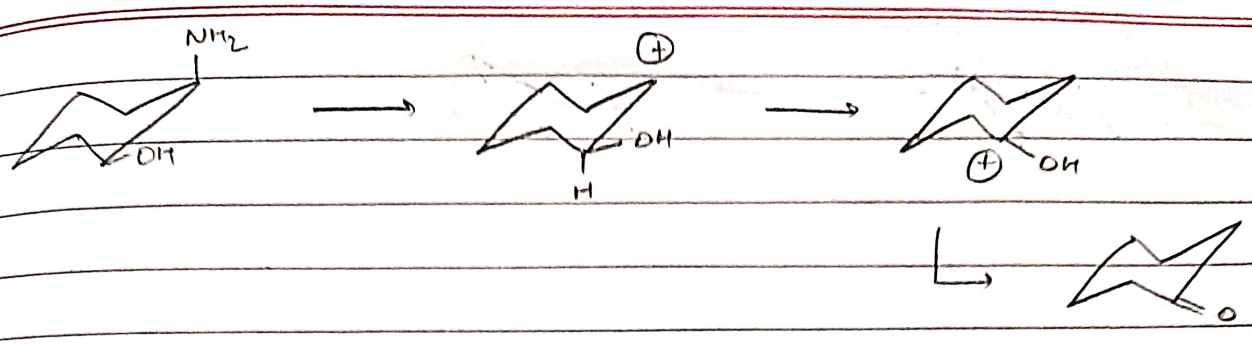

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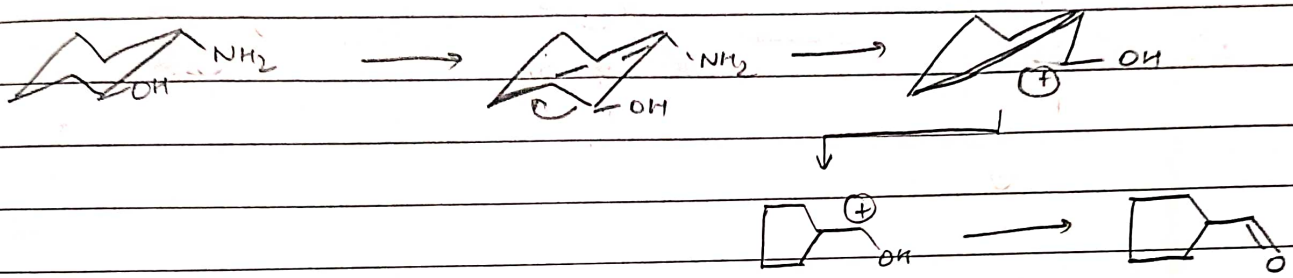
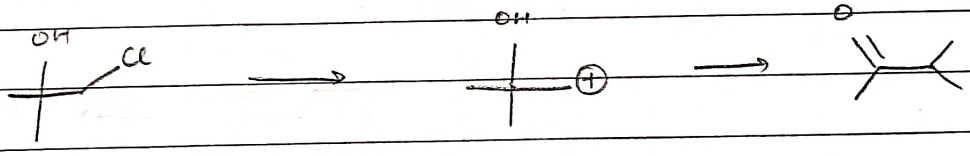


(AgNO3 in all -Cl comps)

24.



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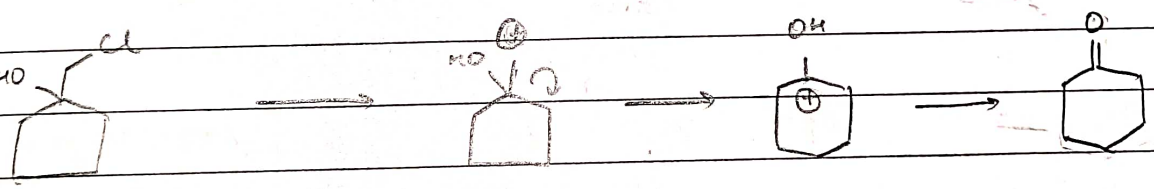

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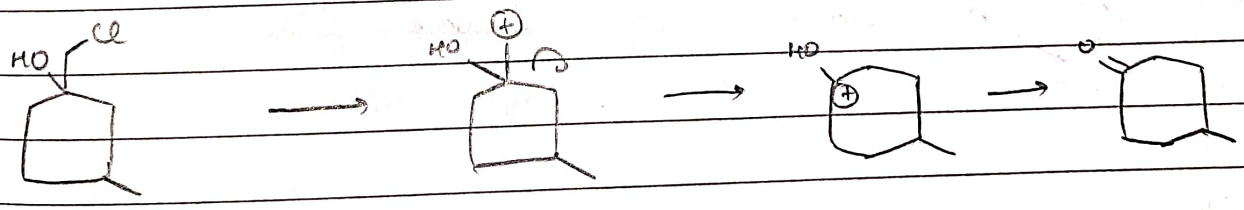

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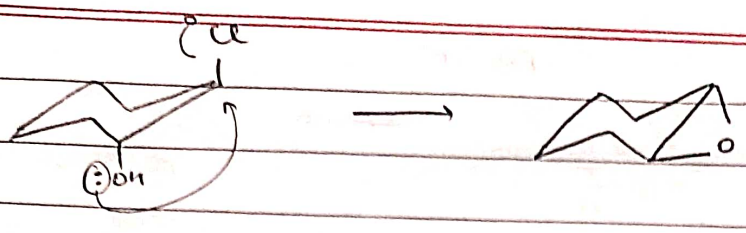

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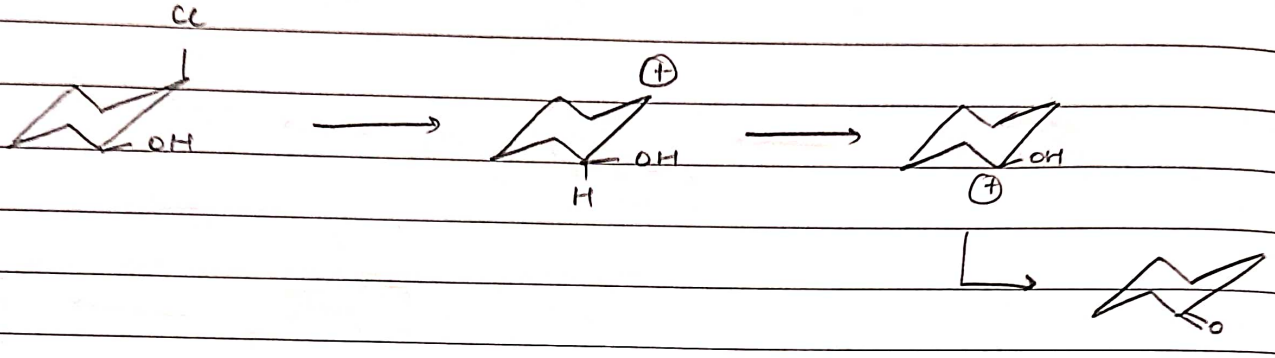

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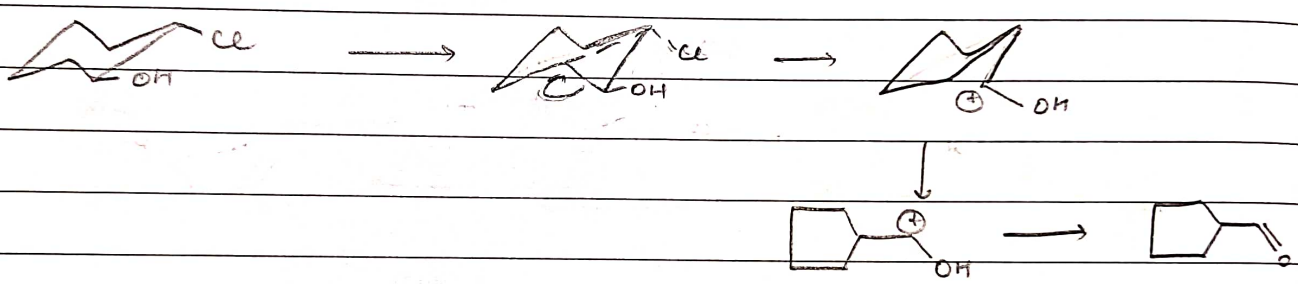


NOTE: 1) In cyclohexane, C⊕ formed at axial first, then eq.

2) Migration of grp in C⊕ rearrangement happens only if grp is Anti-periplanar to leaving grp.

3) NO pinnacolene in trans diol since —OH does NGP attack.

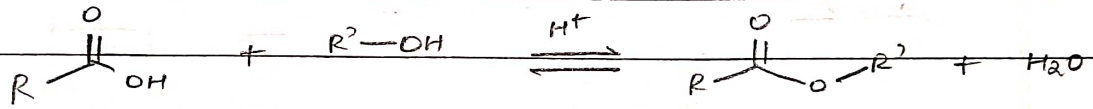
$$R-OH \xrightarrow{Na} R-O^- Na^+ + H_2$$

$$\xrightarrow{Ca} (R-O)_2 Ca + H_2$$

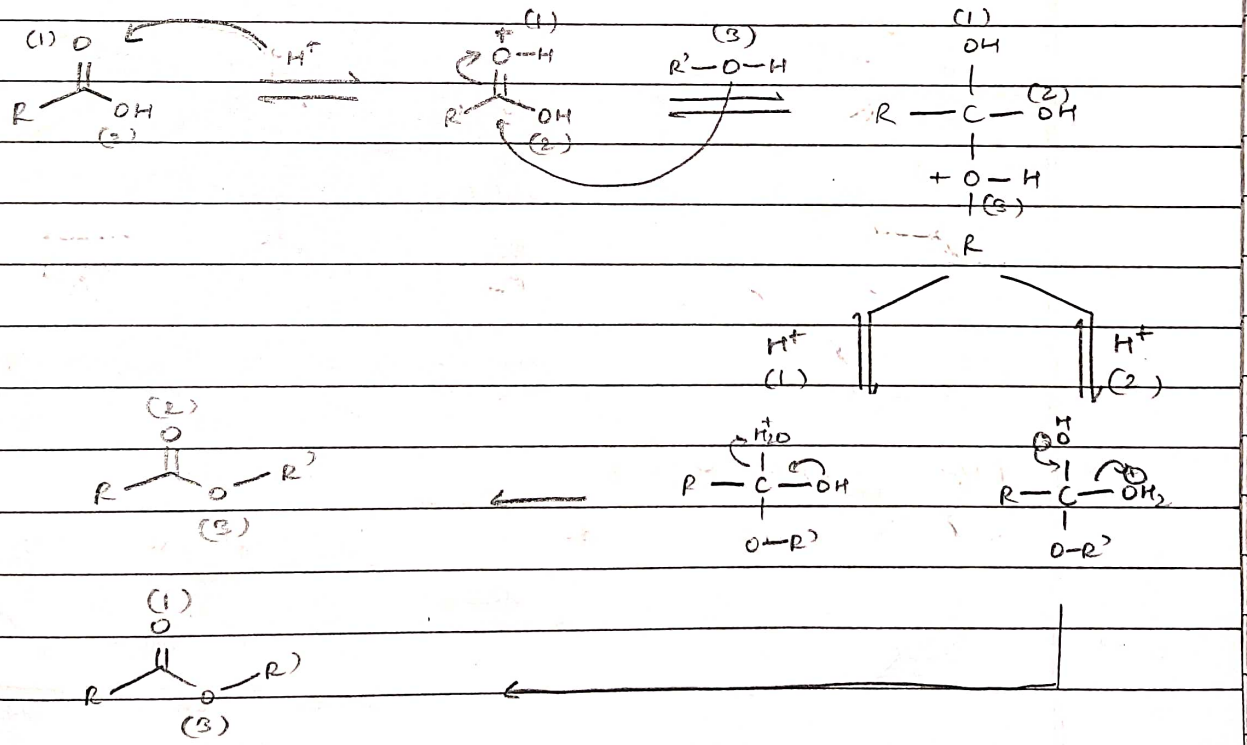
$$\xrightarrow{Al} (R-O)_3 Al + H_2$$

Reactivity : $1^\circ > 2^\circ > 3^\circ$ (alcohol)

ESTERIFICATION



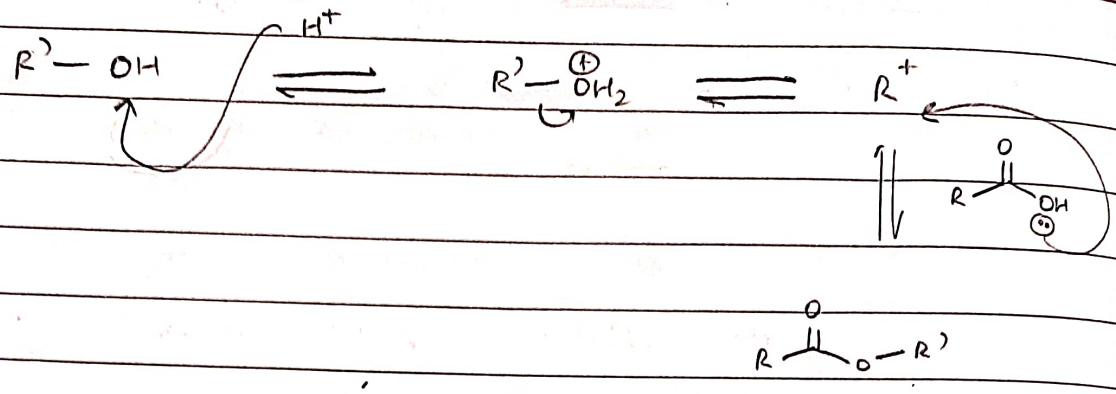
Case-I : ($R'-1^\circ, 2^\circ$)



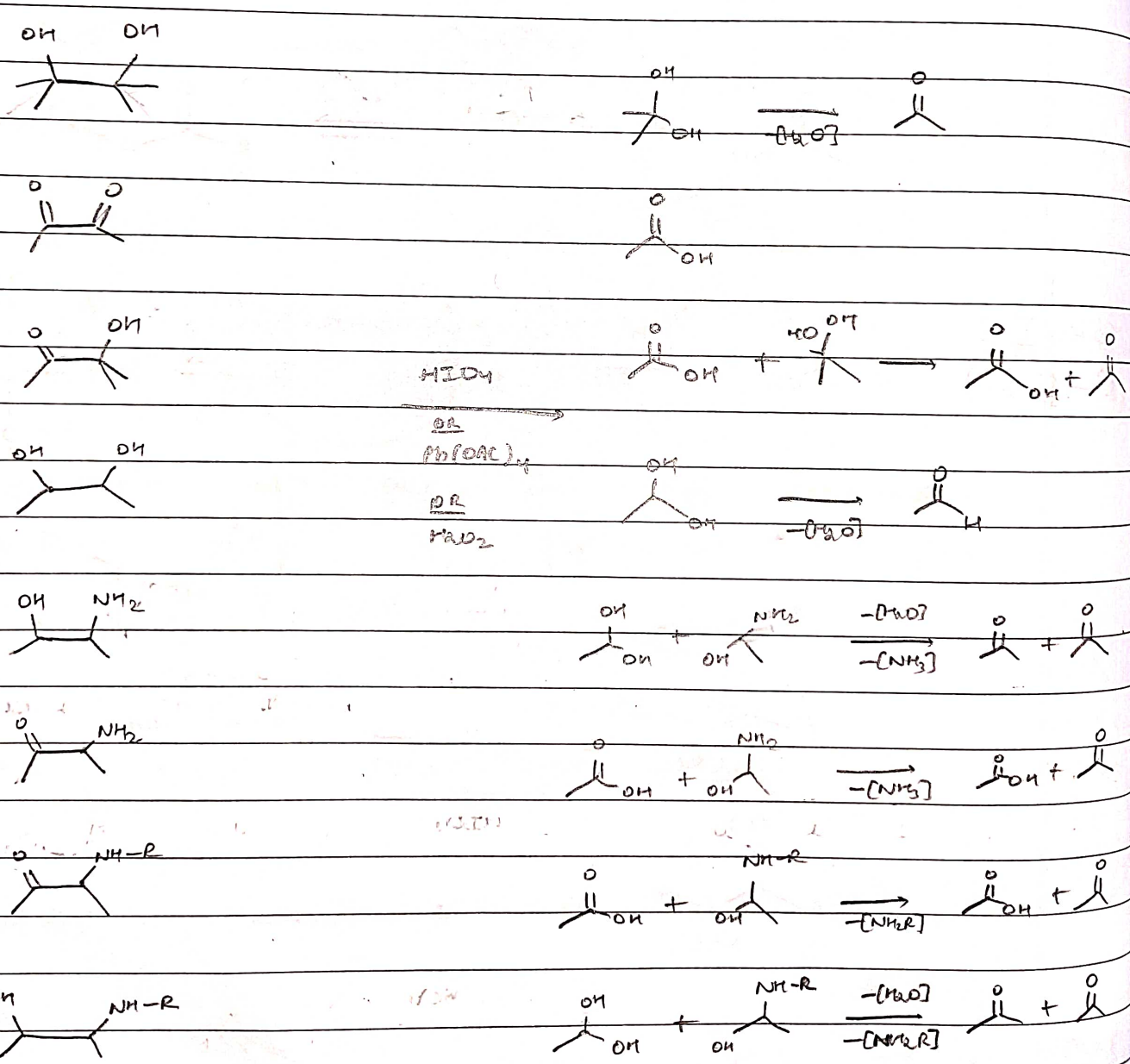
NOTE:
1. All steps reversible
2. Retention product formed
(stereochemistry of R & R' retained)

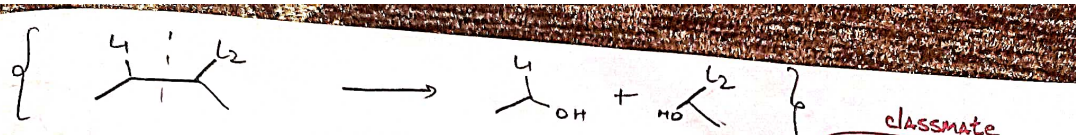
Case II :

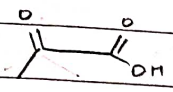
(R' – 3°)



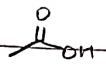
NOTE: Racemic mixture formed



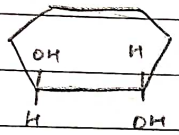


NOTE: 1. 

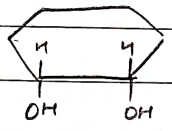
HIO_4 → No Mn^{n}

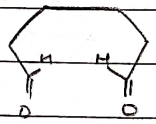
$Pb(OAc)_4$ →  + CO_2 + H_2O

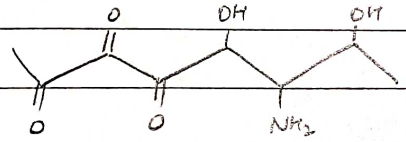
2. If cyclic diol, Mn only takes place if -cis diol

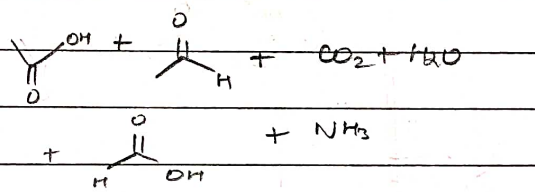


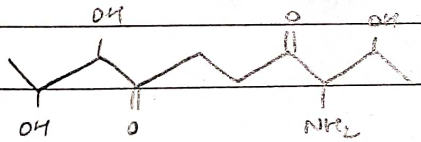
HIO_4 → No Mn^{n}

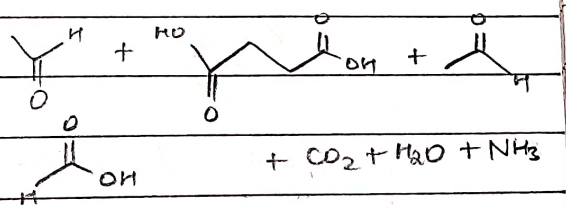


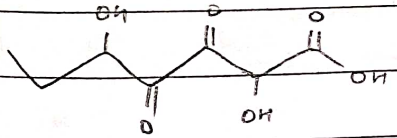
HIO_4 → 

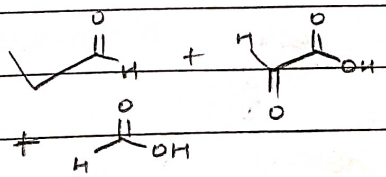
Q 1. 

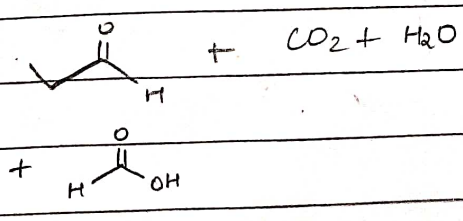
HIO_4 or $Pb(OAc)_4$ → 

2. 

HIO_4 or $Pb(OAc)_4$ → 

3. 

HIO_4 → 

$Pb(OAc)_4$ → 

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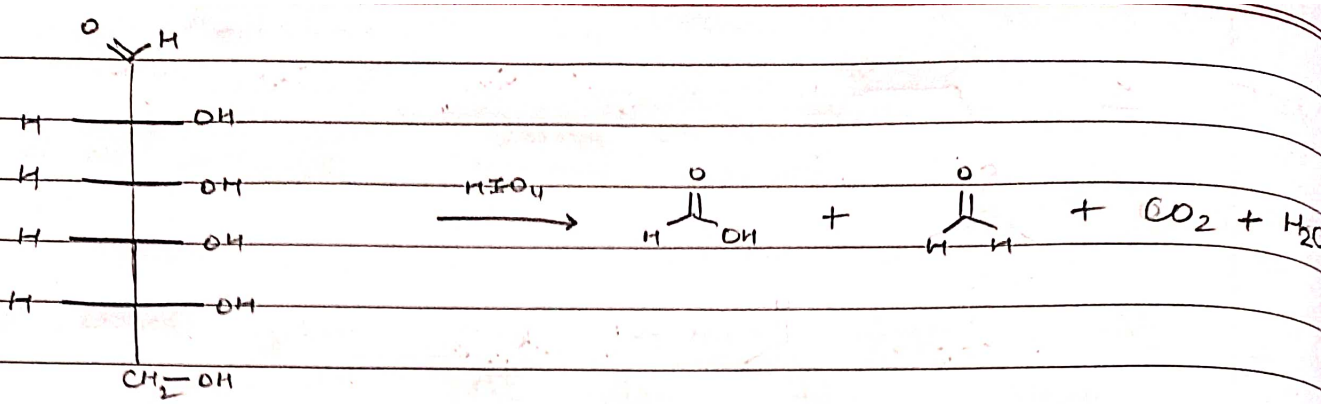
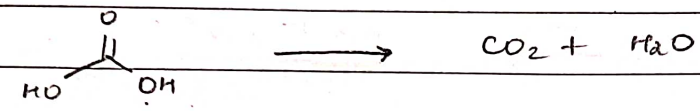
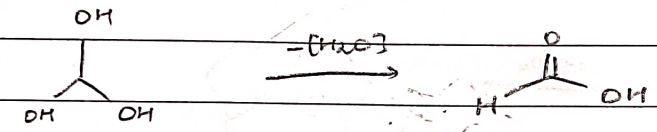
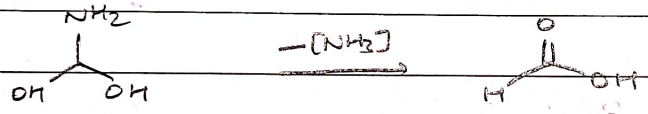


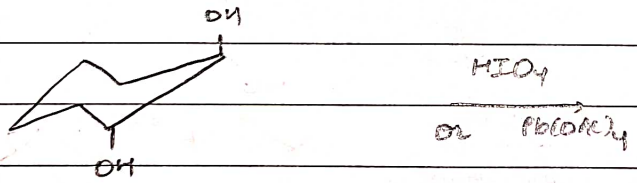
NOTE:





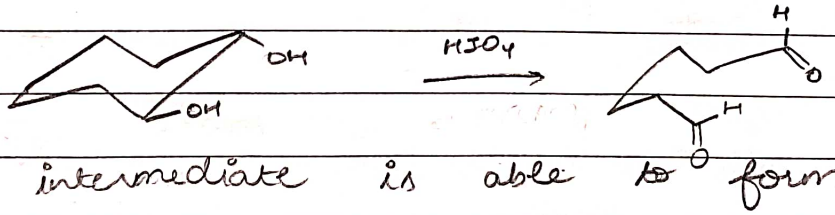


NOTE:



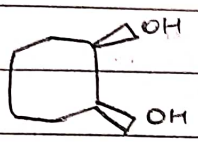
Cyclic intermediate is formed in rea^n.
Here, since both -OH in an. post, cyclic intermediate is not able to form.

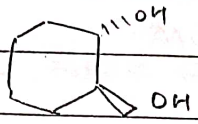
However,

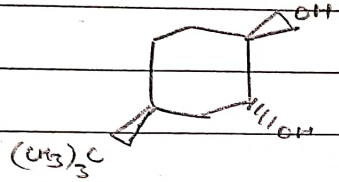


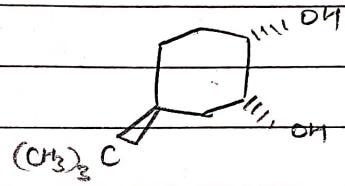
since cyclic intermediate is able to form.

★Q Which of the following will not react with HIO_4 ?

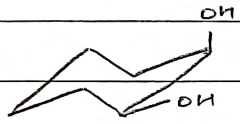




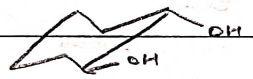




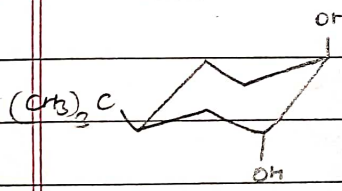
A.



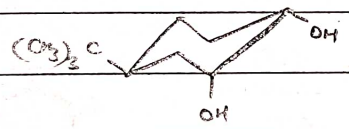
(Cis) ✓



(Even though trans, can form cyclic intermediate) ✓



(X)



(Cis) ✓

OXIDATION OF ALCOHOL

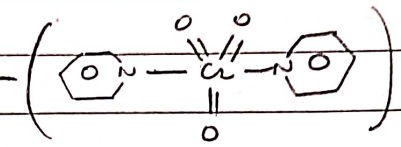
$\xrightarrow{[O]}$

PCC

PDC

$K_2Cr_2O_7/\Delta$

Collin's Reagent



Cold $K_2Cr_2O_7/H^+$

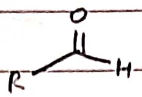
anhyd CrO_3

$Cu/573K$

$Ag/573K$

NBS

NCS

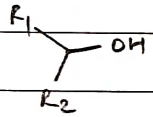


$\xrightarrow{[O]}$

conc $KMnO_4/\Delta$

conc HNO_3

CrO_3/H_2SO_4 (John's Reagent)



$\xrightarrow{[O]}$

PCC

PDC

$K_2Cr_2O_7/\Delta$

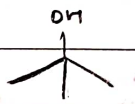
$KMnO_4/\Delta$

conc $KMnO_4$

acidic $KMnO_4$

hot $K_2Cr_2O_7/H^+$

CrO_3/H_2SO_4 (John's Reagent)

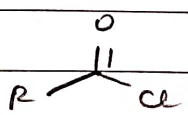


$\xrightarrow{[O]}$

Cu or Ag

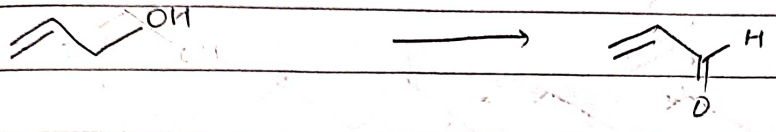
573 K

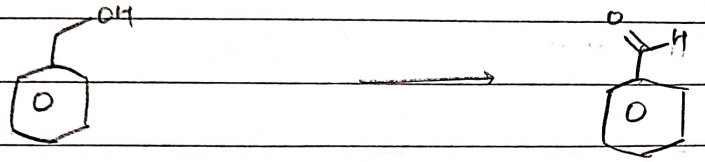
NOTE:



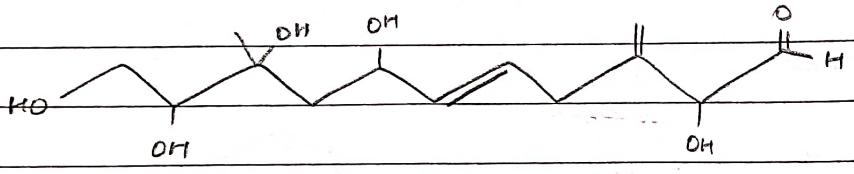
$\xrightarrow{H_2/Pd}$

NOTE: John's Reagent & MnO_2 are selective reagents





Q



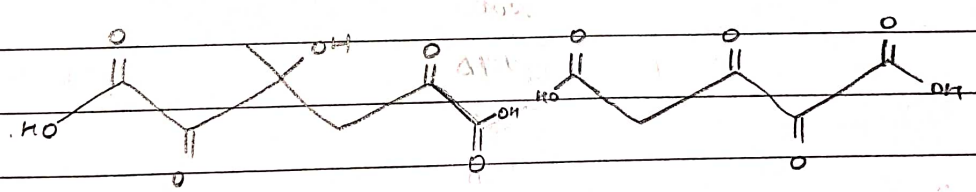
[O] (1)
Hot $KMnO_4$

$Cu/573K$ (2)

PCC, PDC, CrO_3 (3)

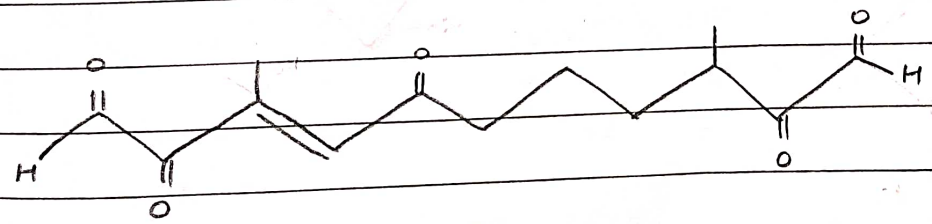
MnO_2 (4)

A. ★ 1.



$+ CO_2$

2.



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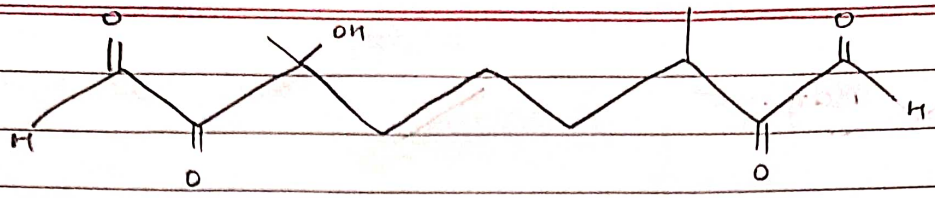

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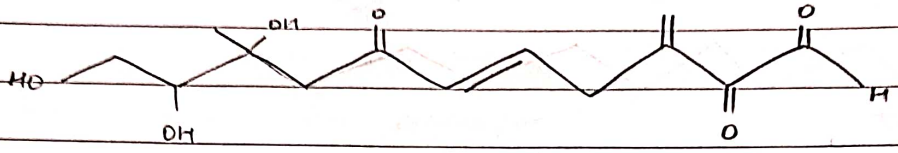
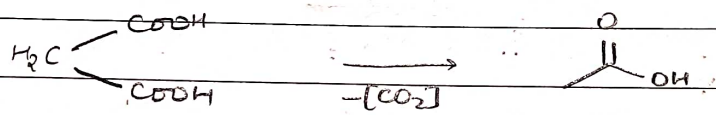
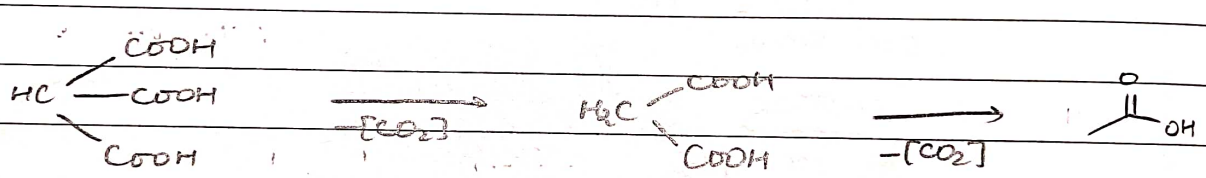


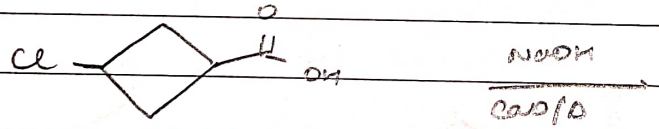
→ DE-CARBOXYLATION (W/O magent)

(I) Geminal acids

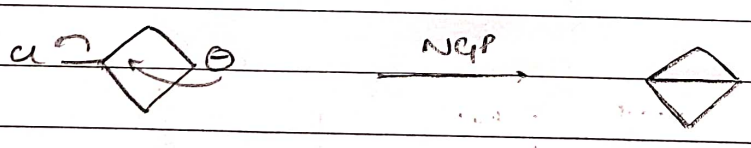




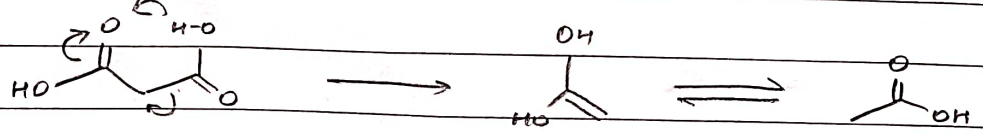
Q



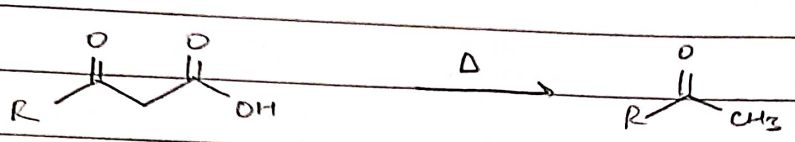
A.

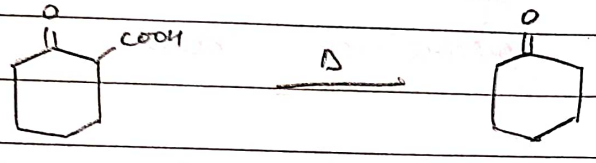


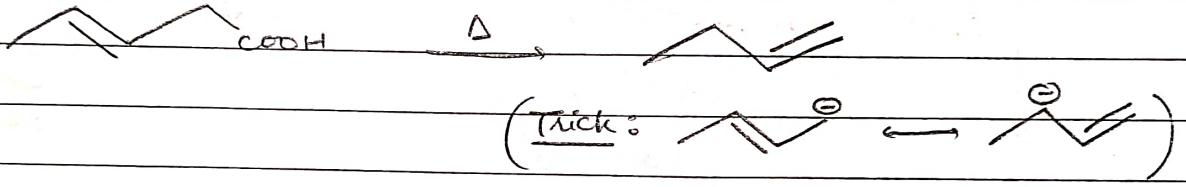
Mechanism

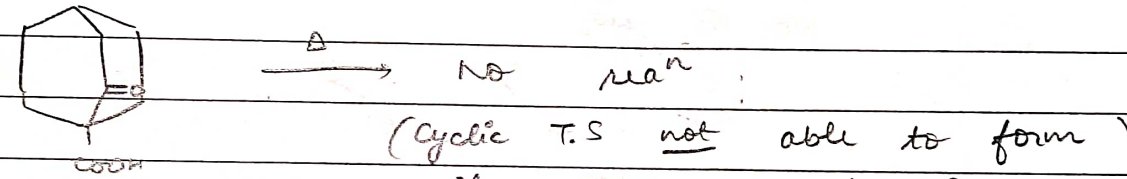


(II) β- Keto Acids



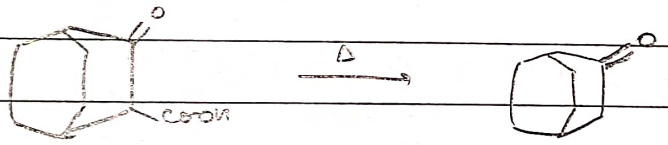




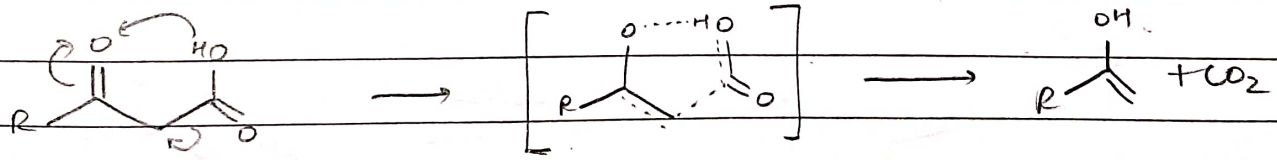


No ma^n

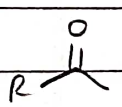
(Cyclic T.S not able to form if −COOH on bridge head C)



Mechanism



Cyclic T.S



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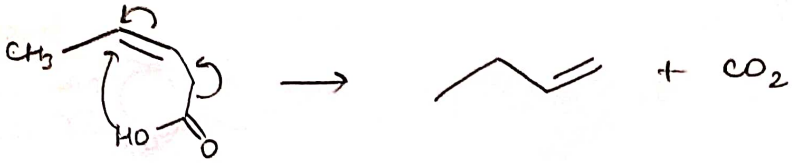
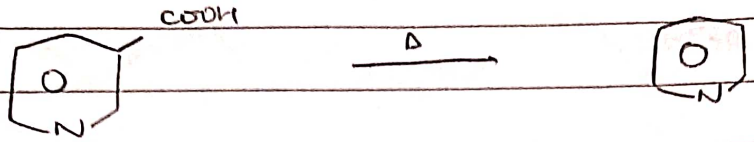


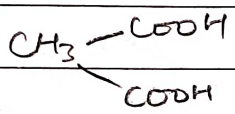
NOTE:

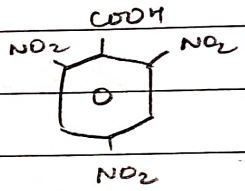


Q. Give order of soda-lime decarboxylation of the following acids.

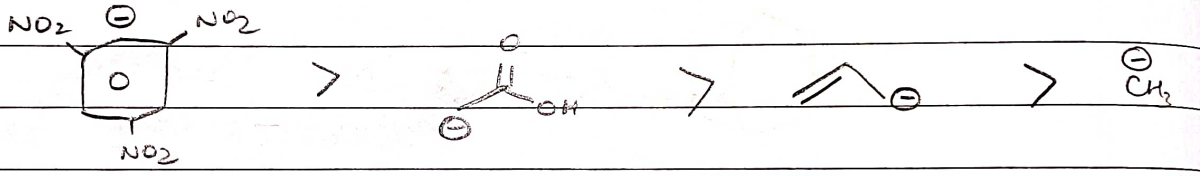
(I) CH_3-COOH

(II) 

(III) 

(IV) 

A.

stability: 

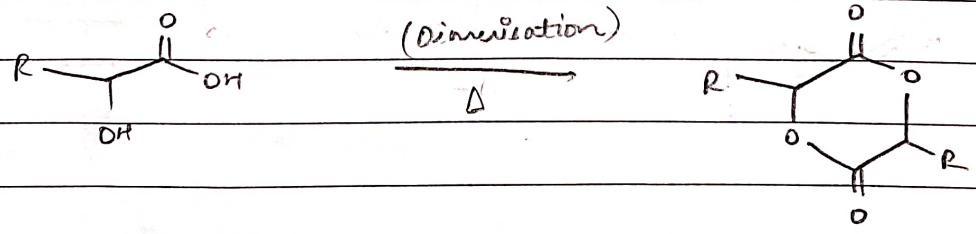
(Heavy-I) (Resonance with O) (Resonance)

$\Rightarrow$ (IV) > (III) > (II) > (I)

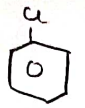
HEATING EFFECTS

(I) Hydroxy Carboxylic Acids

- α

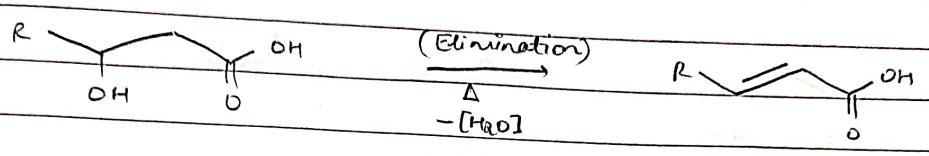


R–X $\xrightarrow[Zn/NaOH \\ Zn/CH_3COOH \\ Zn/Cu]{Zn/HCl}$ R–H

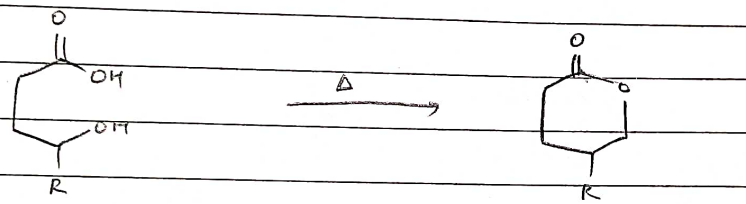


$\xrightarrow{Zn/HCl}$

- **β**



- **γ, δ ...**

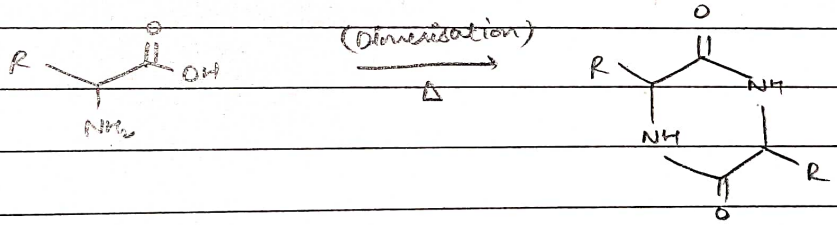


cyclic Ester
(Lactone)

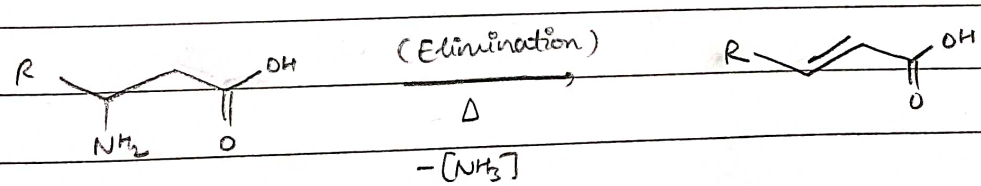
$\ominus CH_2$

(II) Amino Acids

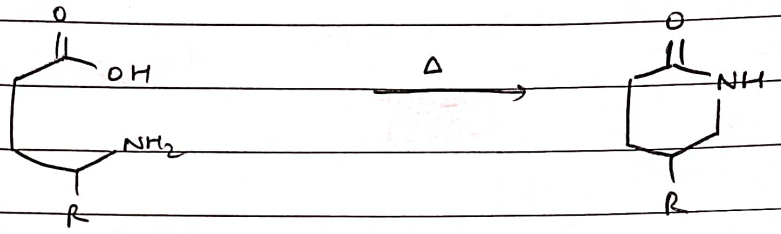
- **α**



- **β**

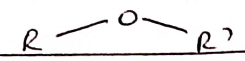


- γ, δ ...



Cyclic Amide
(Lactam)

ETHERS



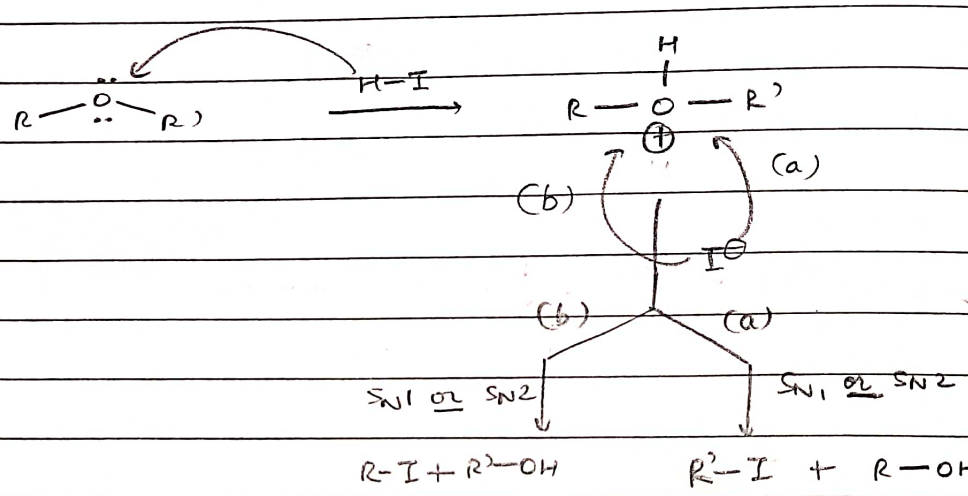
$\xrightarrow{HI}$ (Anhyd. HI / Hyd. HI / conc HI / dil. HI) (or HBr, HCl)

$R-OH + R'-I$

OR

$R-I + R'-OH$

Mechanism



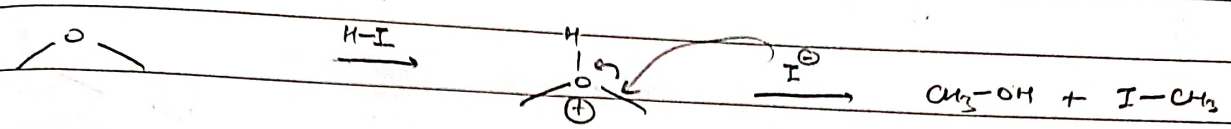
NOTE: 1. No cyclic intermediate ⟹ Nü attacks acc. to steric hindrance

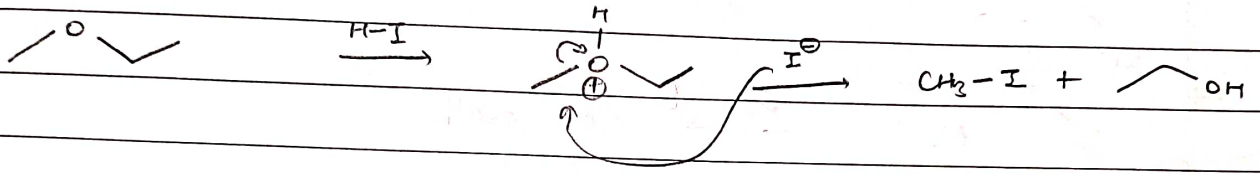
* (if S_N1 not taking place)

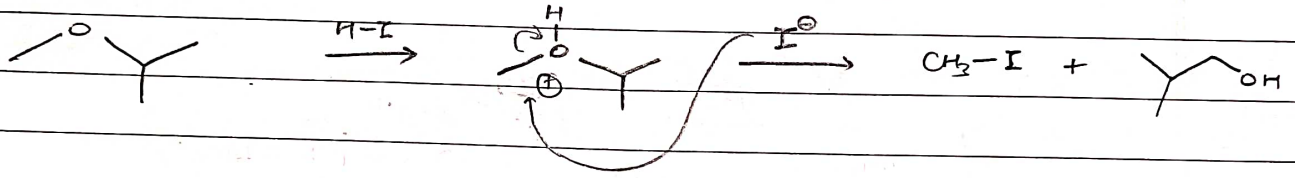
2. If R_1 and R_2 : – 1°/2° } S_N2 followed
– 3° + PAS (anhyd. HI) }

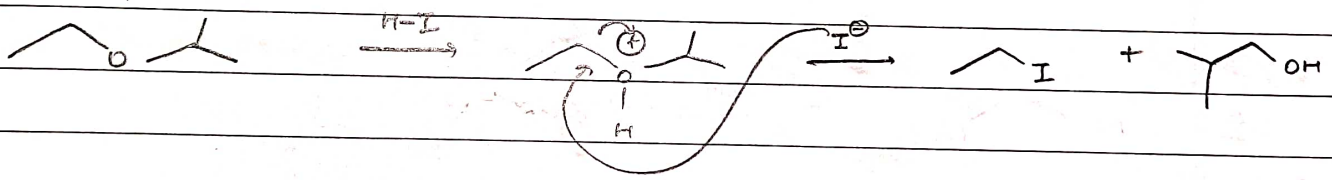
R_1 or R_2 : – 3° + PPS } S_N1 followed
– Resonance stabilised }

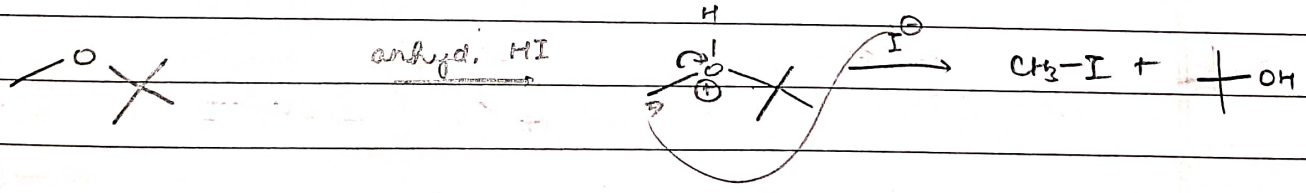
Q. Write mechanism & product.

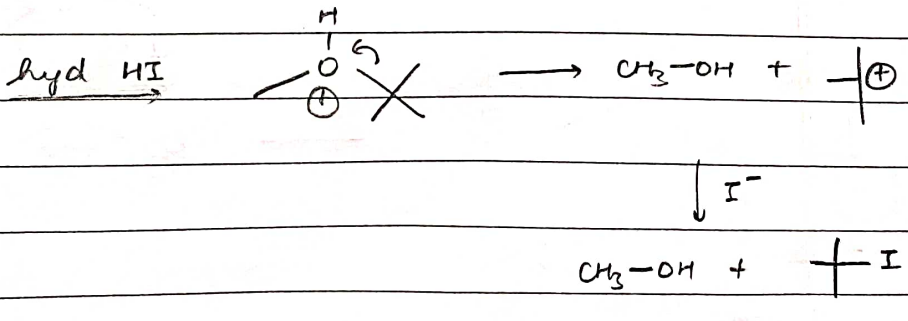
1. 

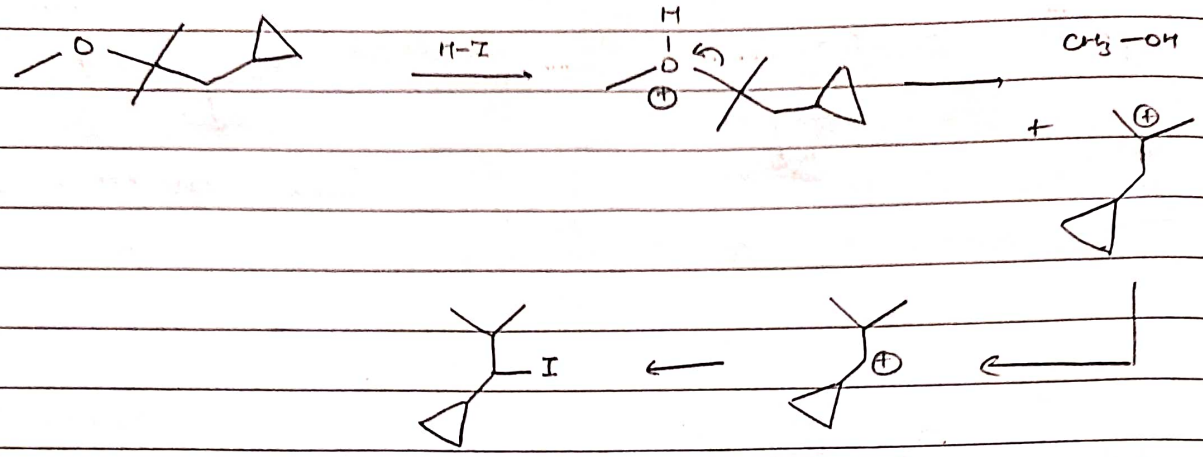
2. 

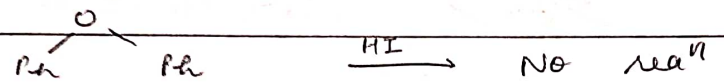
3. 

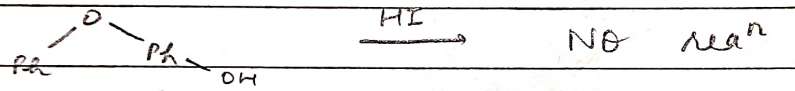
4. 

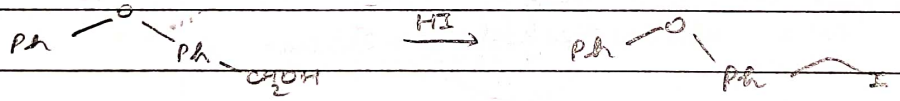
5. 



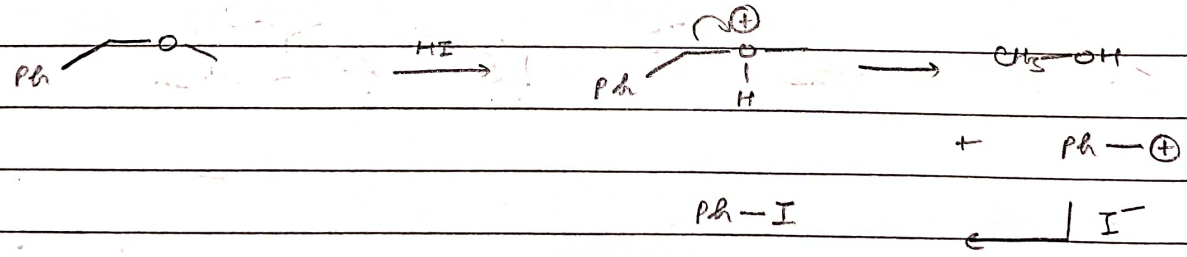
6. 

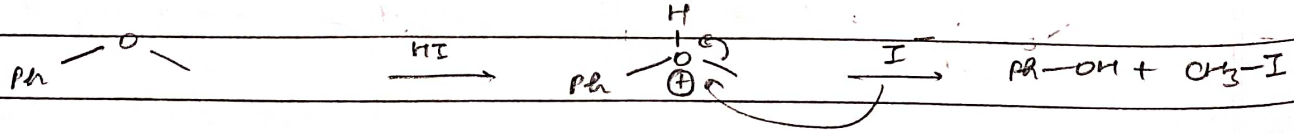
7. 

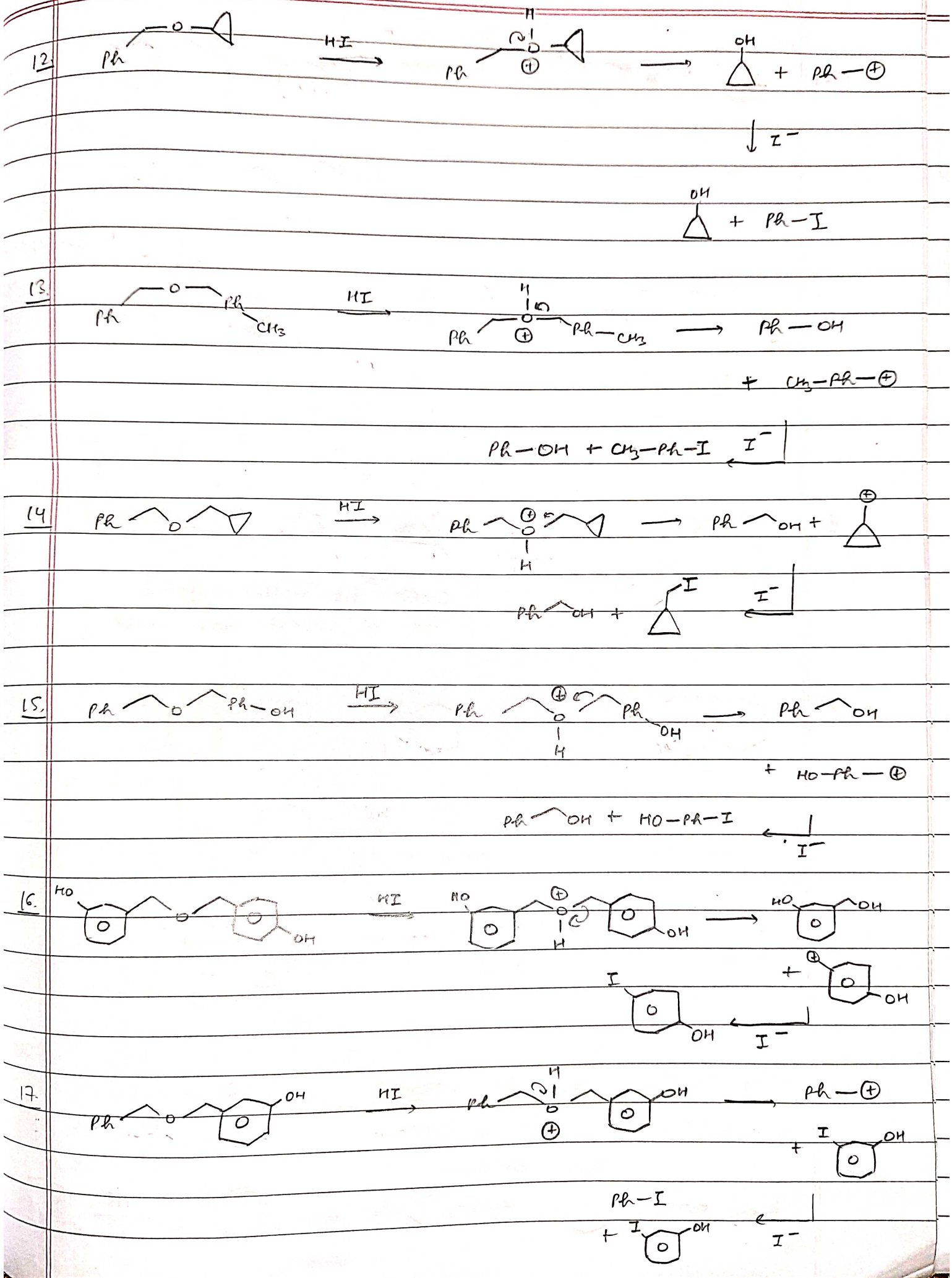
8. 

9. 

(S_N1)

10 

11. 


12.
HI
OH
+ Ph—⊕
I⁻
OH
+ Ph—I
13.
HI
Ph—OH
+ CH₃—Ph—⊕
Ph—OH + CH₃—Ph—I
I⁻
14
HI
Ph—OH +
OH +
I
I⁻
15.
HI
Ph—OH
+ HO—Ph—⊕
Ph—OH + HO—Ph—I
I⁻
16.
HO
OH
HI
HO
OH
OH
+
I
OH
I⁻
17.
OH
HI
Ph—⊕
+
I
OH
Ph—I
+
I
OH
I⁻

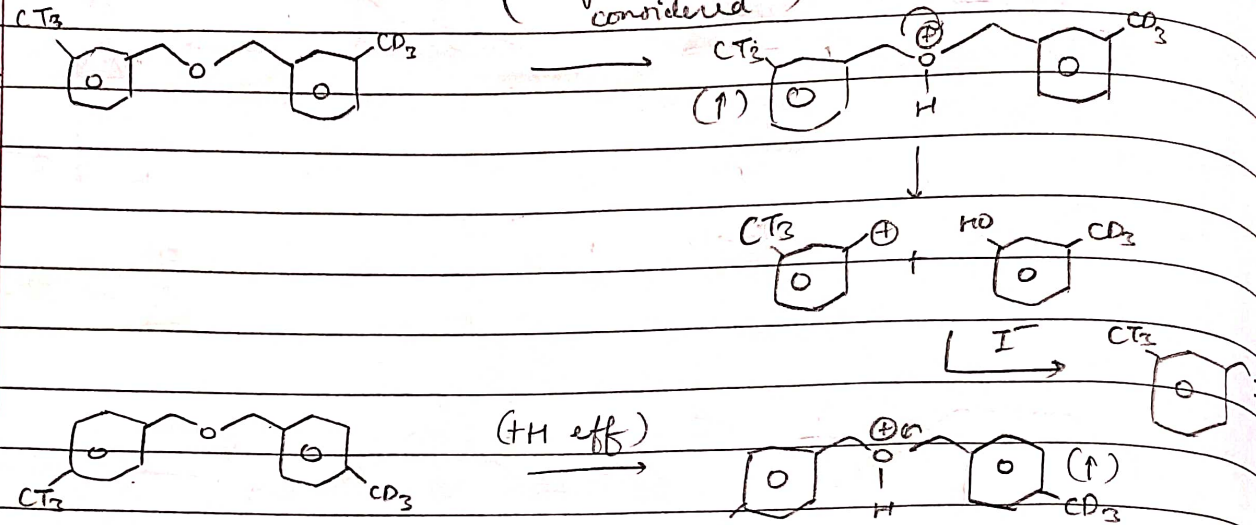
B.S : C–T > C–D > C–H

+I : $-CT_3 > -CD_3 > -CH_3$

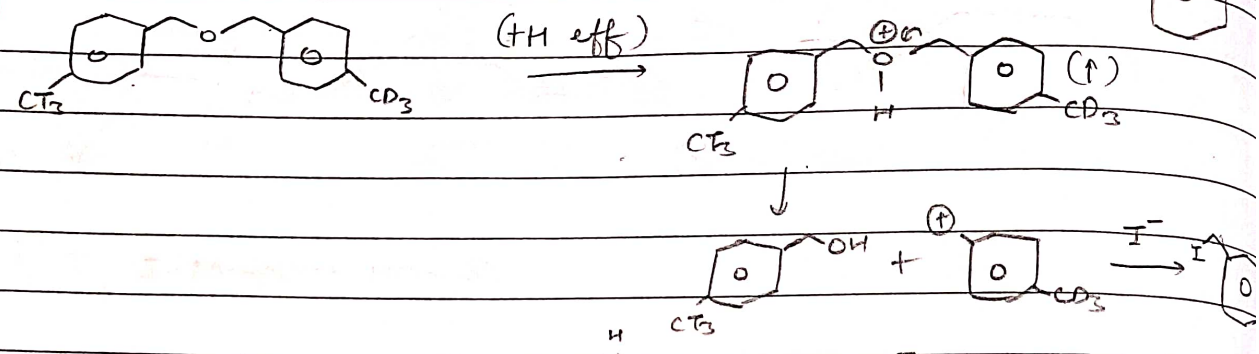
+H : $-CT_3 < -CD_3 < -CH_3$ ($\propto \frac{1}{B.S}$)

(only +I effect considered)

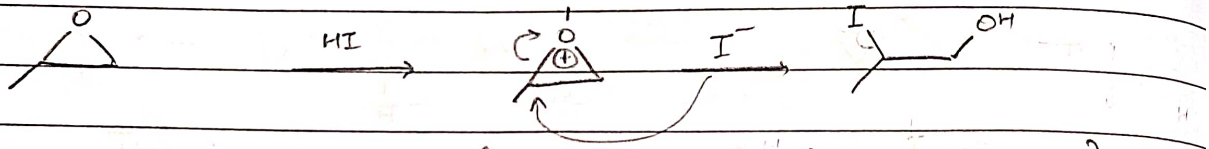
18.



19.

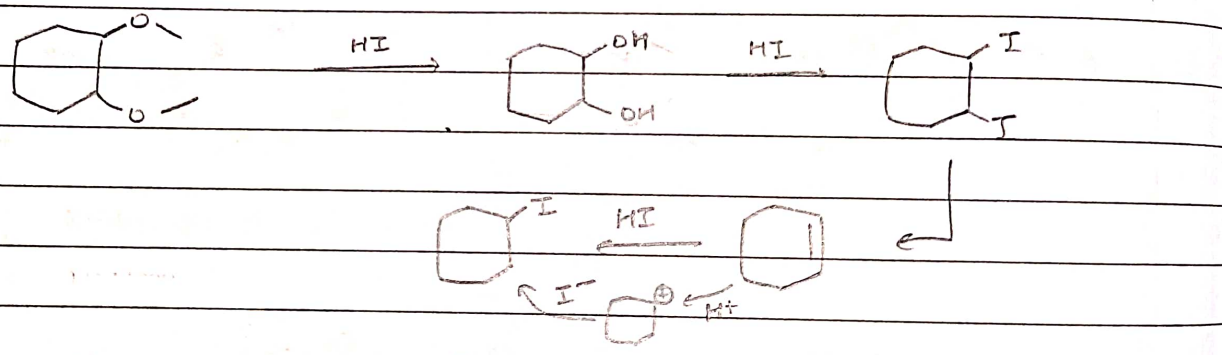


20.

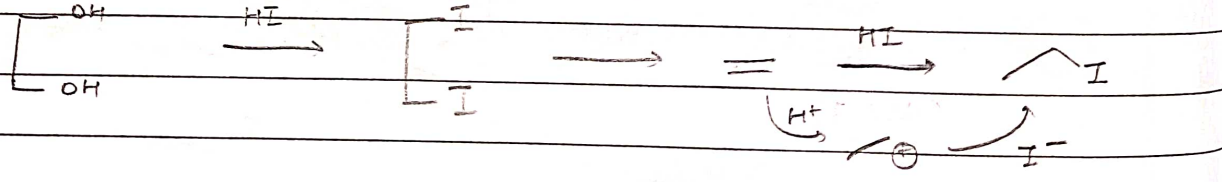


{ Cyclic intermediate ⊕ ⇒ ⊕ charge more stable }

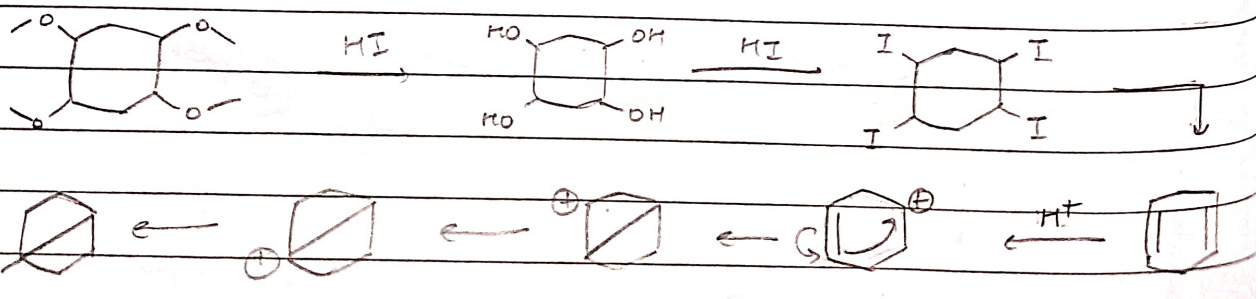
☆ 21.

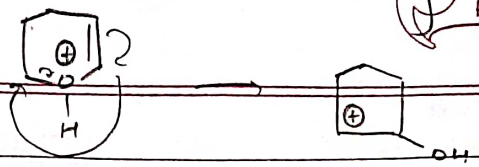


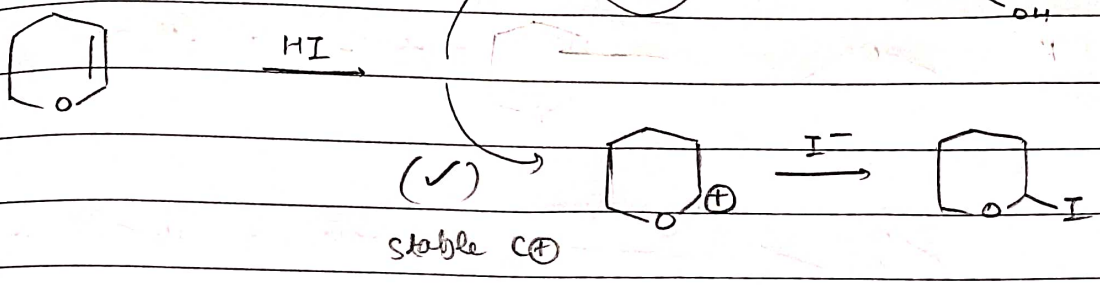
☆ 22.



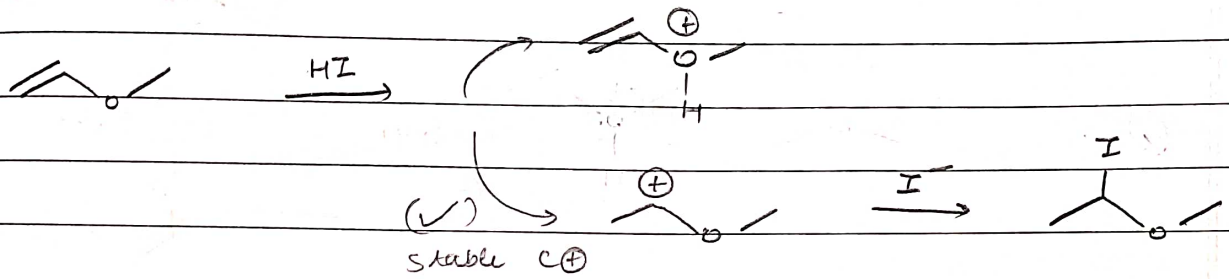
☆ 23.





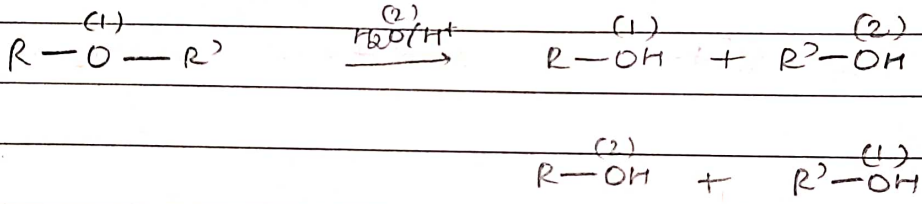


★ 24

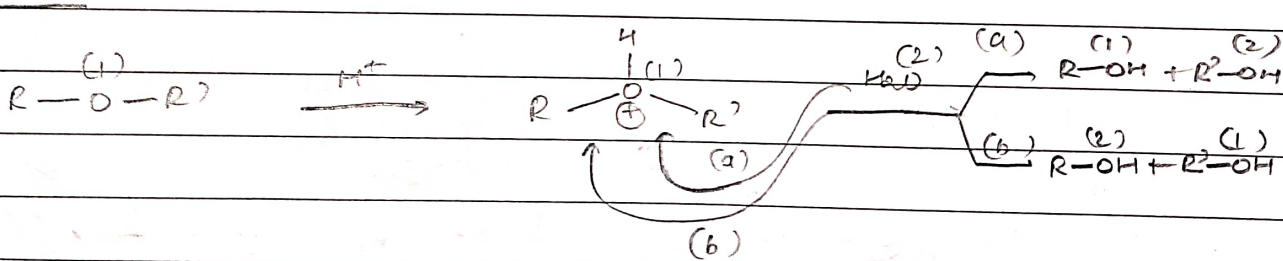


★ 25

→ **Hydrolysis of Ester**

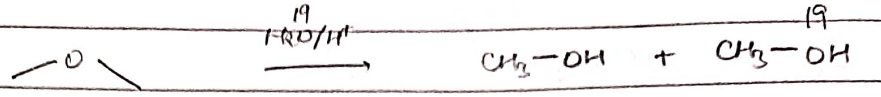


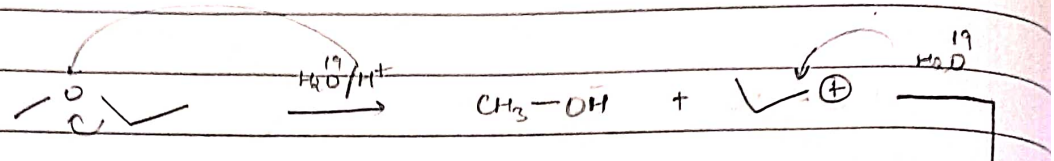
Mechanism

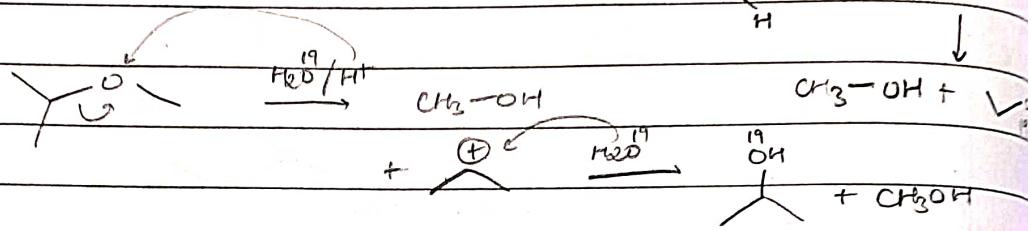


NOTE: If R & R' → 1° ⇒ S_N2

S_N1 in rest of the cases

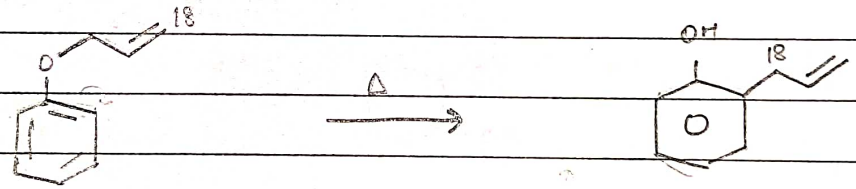
eg (i) 

(ii) 

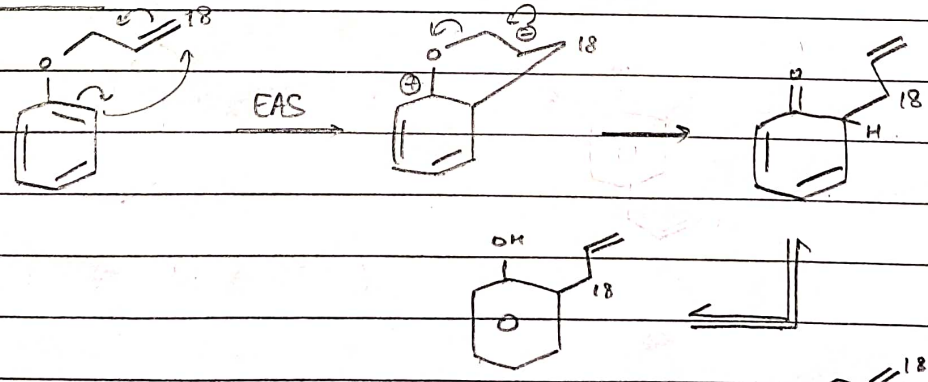
(iii) 

→ Claisen rearrangement

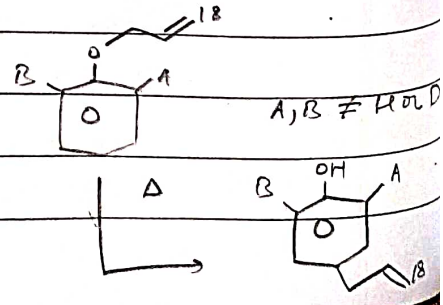
(in aryl–allyl or aryl–aryl ethers)



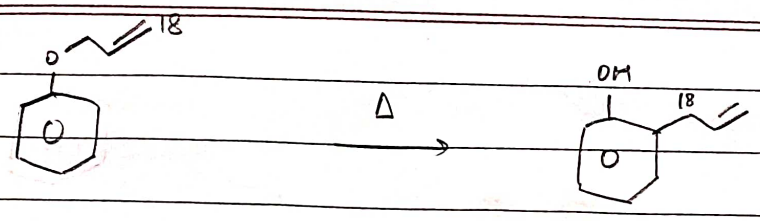
Mechanism

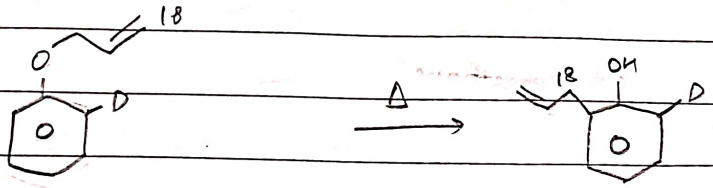


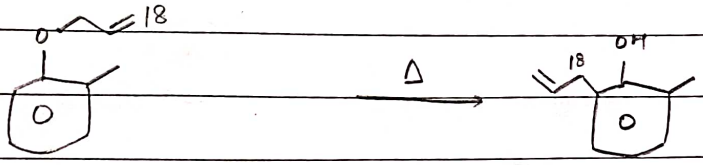
But, if ortho post blocked, i.e tautomerism not able to take place ⇒ (EAS happens again) ⇒

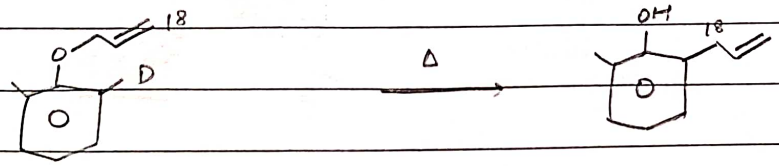


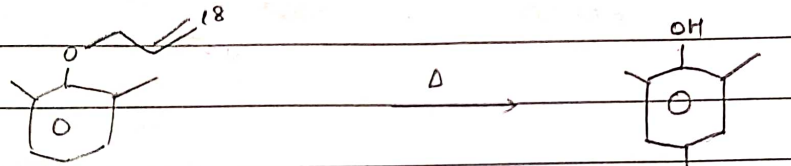
eg –

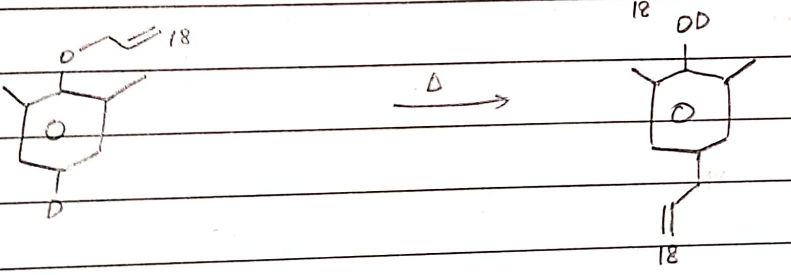






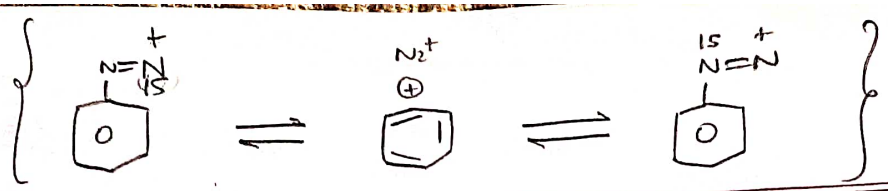




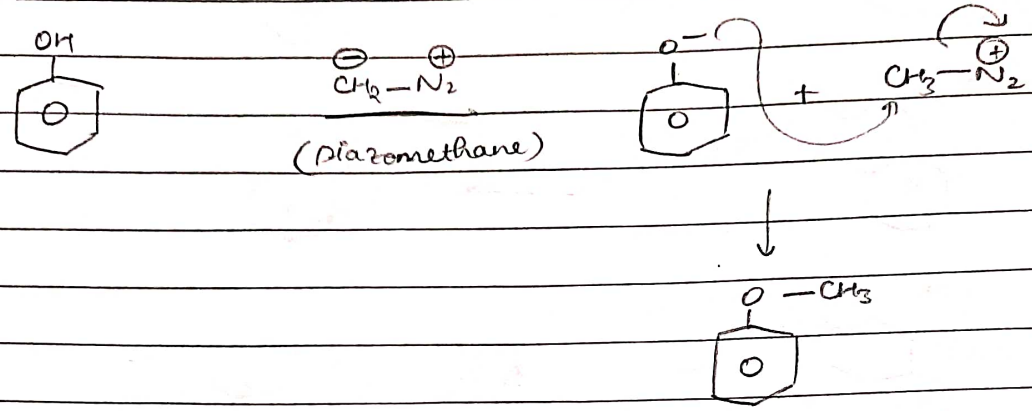


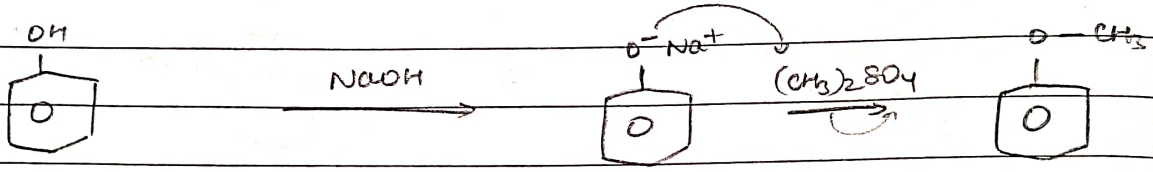
☆

NOTE: If H & D present, the one with better leaving tendency transferred in tautomerism (i.e -H)



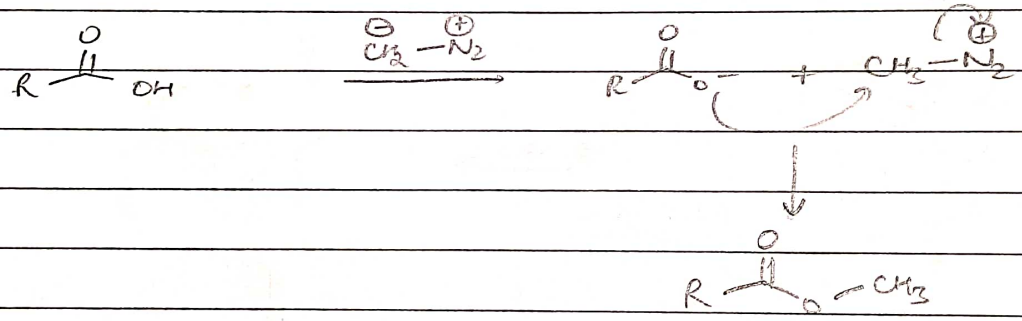
PHENOL





$NaHCO_3$ → No reaⁿ

NOTE: 1.

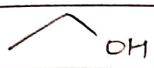


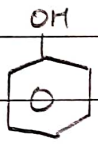
2. Any comp. with acidic H & pKa ≤ 7.23 reacts with $NaHCO_3$.

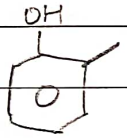
(pKa of orthonitrophenol)

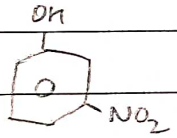
Q. Which gives CO_2 on rea^n with $NaHCO_3$?

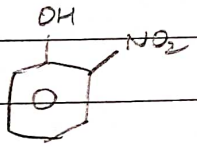
1. CH_3-OH ✗

2.  ✗

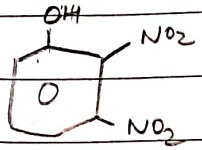
3.  ✗

4.  ✗

5.  ✗

6.  ✓ pKa = 7.23

7.  ✓ pKa = 7.14

8.  ✓

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Date
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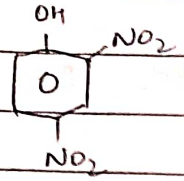
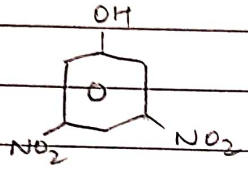
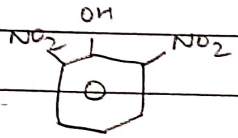
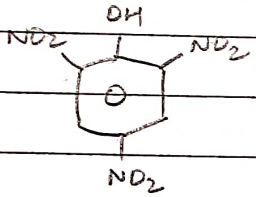
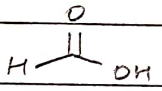
9.  ✓

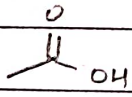
☆ 10.  (✓) pka = 6.73

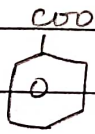
11.  ✓

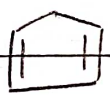
12.  ✓

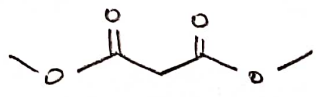
13.  ✓

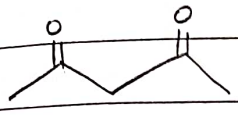
14.  ✗

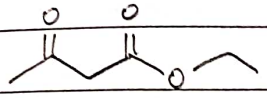
15.  ✓

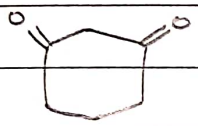
16.  ✓

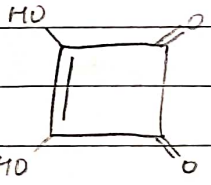
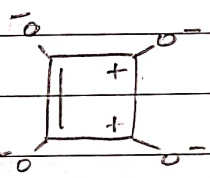
17.  ✗

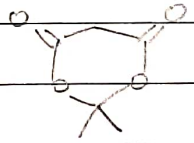
 × pKa = 15.57

18.  × pKa = 13.33

19.  ×

20.  ×

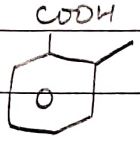
★ 21.  (✓)  Aromatic ⇒ Highly acidic

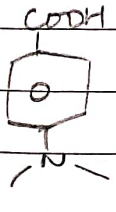
★ 22.  (X) pKa = 7.32

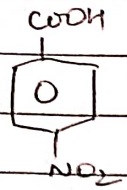
23. H_2SO_4 ✓

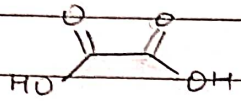
24. HCN ×

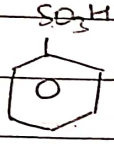
25. $CH_3-C\equiv CH$ ×

26.  ✓

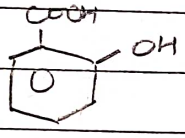
★ 27  (X) (Highly activating -N grp.)

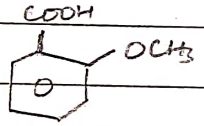
28.  ✓

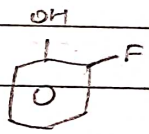
29.  ✓

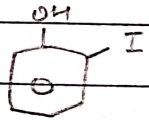
30.  ✓

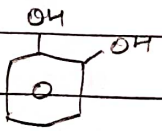
31. HCl ✓

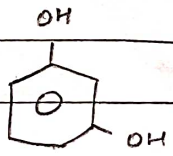
32.  ✓

34.  ✓

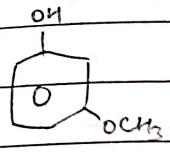
35.  ✗

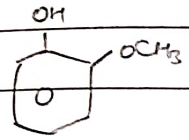
36.  ✗

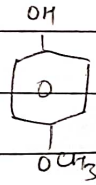
37.  ✗

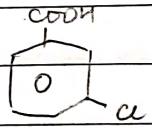
38.  ✗

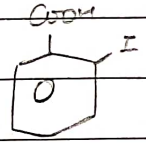
39.  ✗

40.  ✗

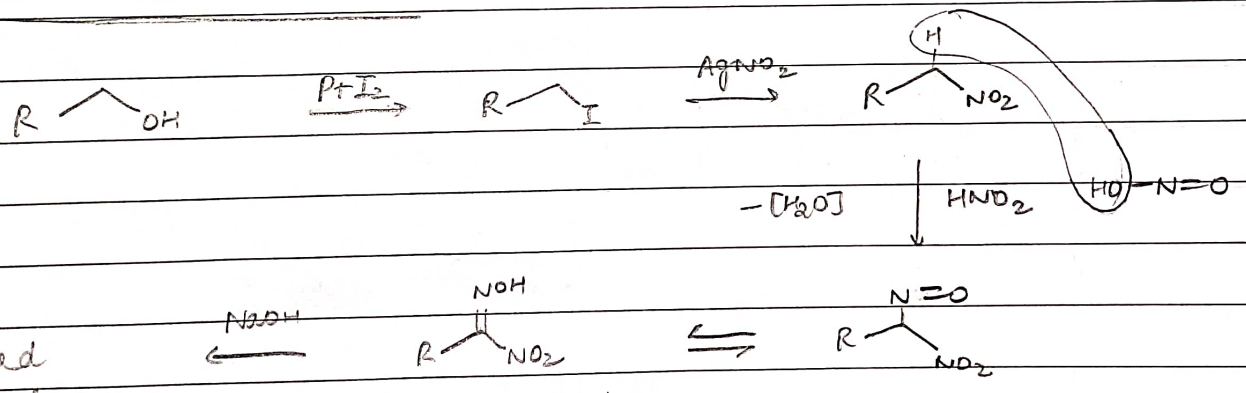
41.  ✗

42.  ✗

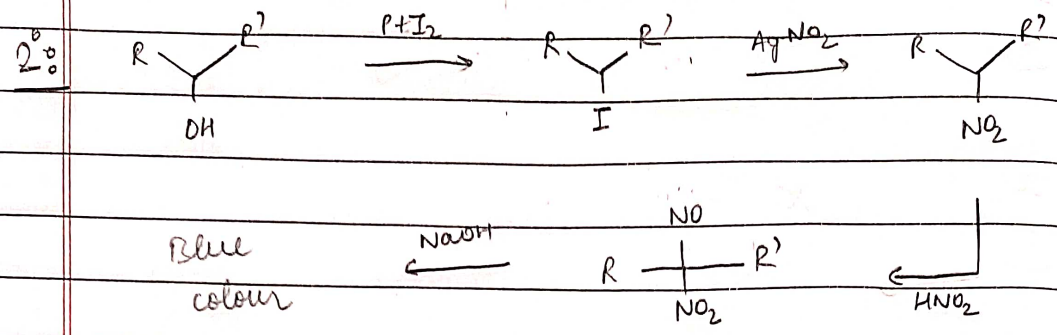
43.  ✓

44.  ✓

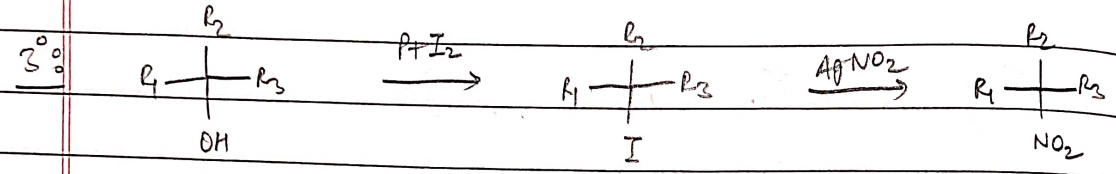
VICTOR – MAYER TEST

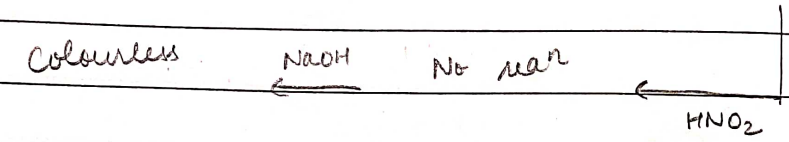
1°: 

Nitrolic Acid



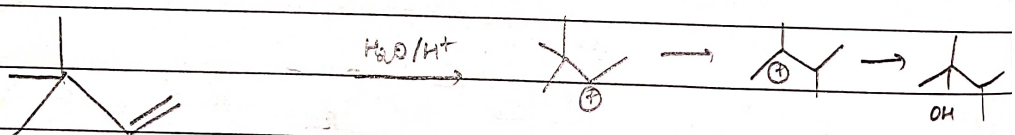
Pseudonitrolic Acid

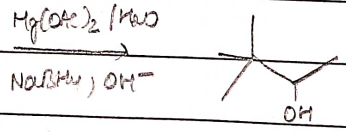


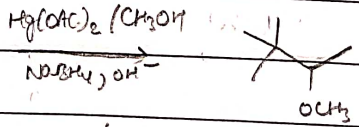


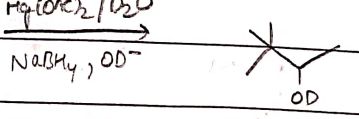
PREPⁿ OF ALCOHOL

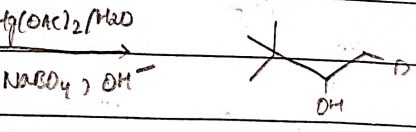
→ Hydroboration & OMDM



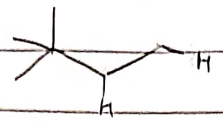






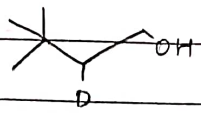


B_2H_6/THF
CH_3COOH

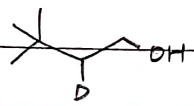


B_2H_6/THF
H_2O_2/OH^-

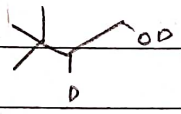
B_2D_6/THF
H_2O_2/OH^-



B_2D_6/THF
H_2O_2/OD^-

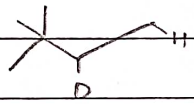


B_2D_6/THF
D_2O_2, OH^-

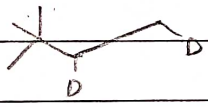


B_2D_6/THF
D_2O_2/OD^-

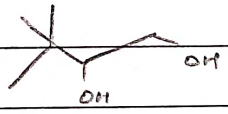
B_2D_6/THF
CH_3COOH



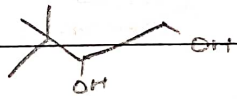
B_2D_6/THF
CH_3COOD



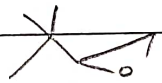
Cold dil $KMnO_4$



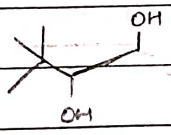
OsO_4 / $NaHSO_3$
H_2O



RCO_3H/CCl_4



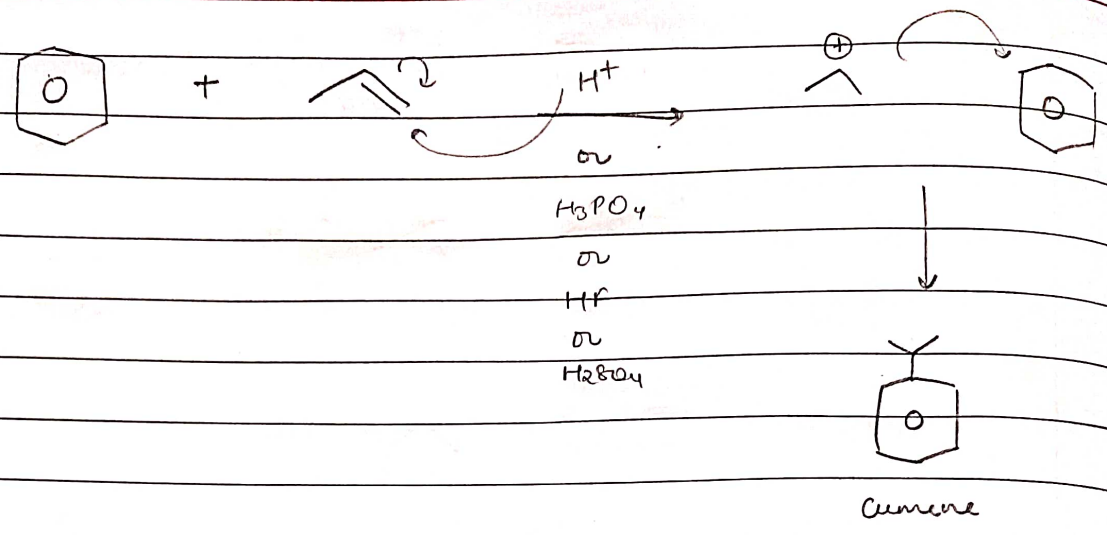
RCO_3H/H_2O



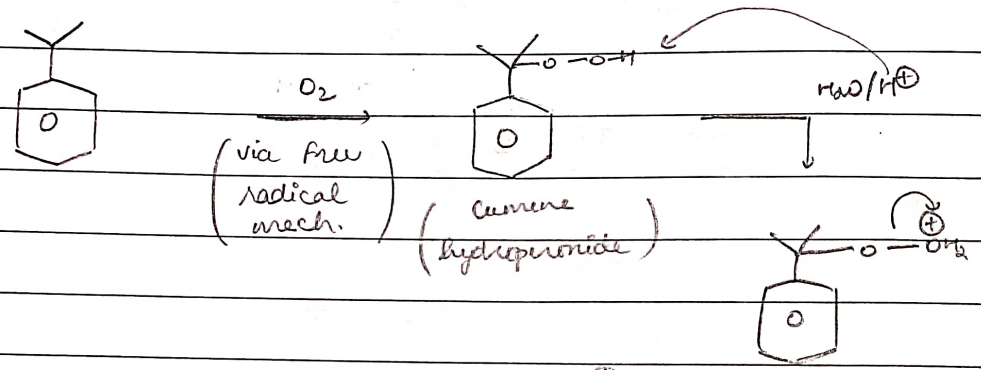
NOTE: 1. H comes from B_2H_6 in hydroboration & OH comes from H_2O_2

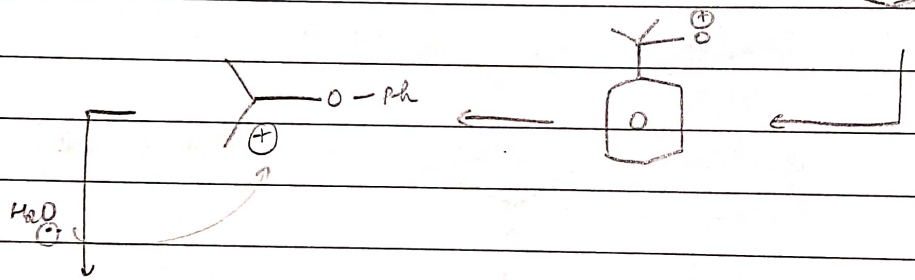
2. H comes from $NaBH_4$ in OMDM & OH comes from H_2O

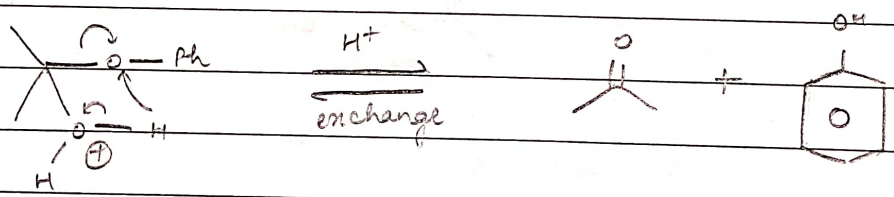
PREPⁿ OF PHENOL (From Cumene)



Cumene

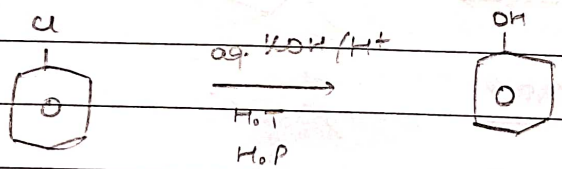




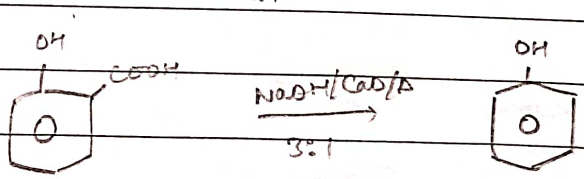


NOTE:

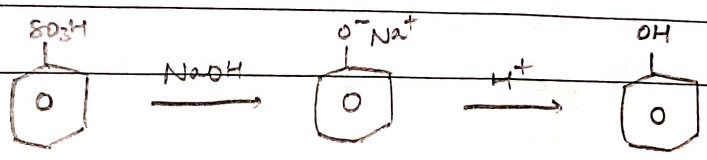
(i)



(ii)



(iii)



PREPⁿ OF ETHER

$$2\,R-OH \xrightarrow[(Anhy.\ Alcl_3)]{H_2SO_4/\Delta} R-O-R + H_2O$$

eg  $\xrightarrow[T=180°C]{H_2SO_4}$ =

$\xrightarrow[T=140°C]{H_2SO_4}$ 

→ Reaⁿ with peroxide

On standing in contact with air, most aliphatic ethers are converted slowly into unstable peroxides

The presence of peroxide is indicated by formation of a red colour when the ether is shaken with aq. soln of Ammonium sulfate & Potassium thiocyanate

$$\text{Peroxide} + Fe^{2+} \longrightarrow Fe^{3+} \xrightarrow{SCN^-} Fe(SCN)_n^{(3-n)-}$$

$(n = 1 \text{ to } 6)$

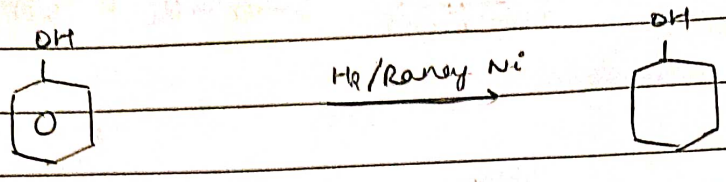
Peroxides can be removed from ethers in a no. of ways :-

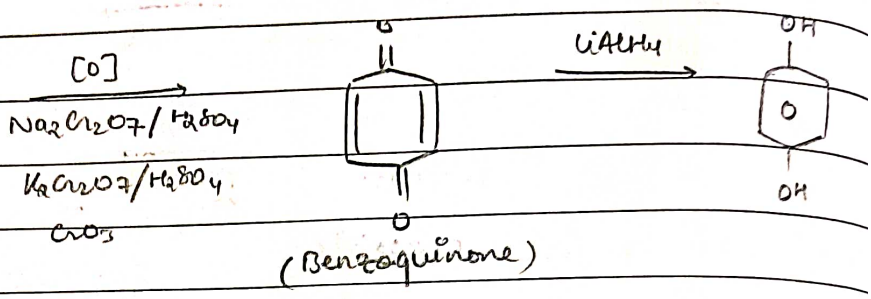
- Washing with sol'n of Fe^{2+} ion (which reduces peroxide)
- Distillation from conc. H_2SO_4 (which oxidizes peroxides)

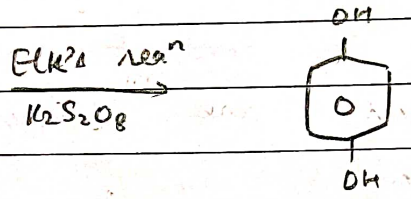
NOTE: For prepⁿ of Grignard reagent, ether must be free of traces of water & alcohol.

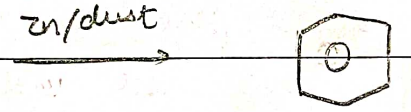
This absolute ether is prepared by distillation of ordinary ether with conc. H_2SO_4 (which removes water, alcohol & peroxides) & storing over Na metal

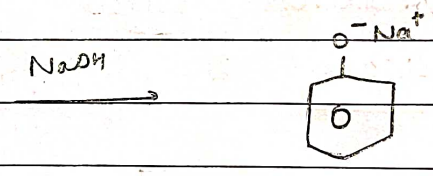
REA^{n}s OF PHENOL





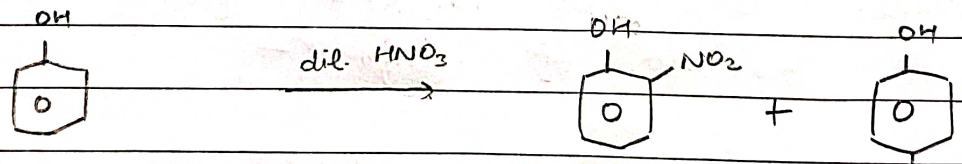


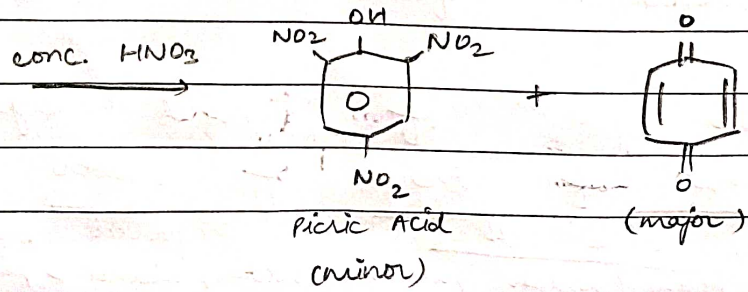


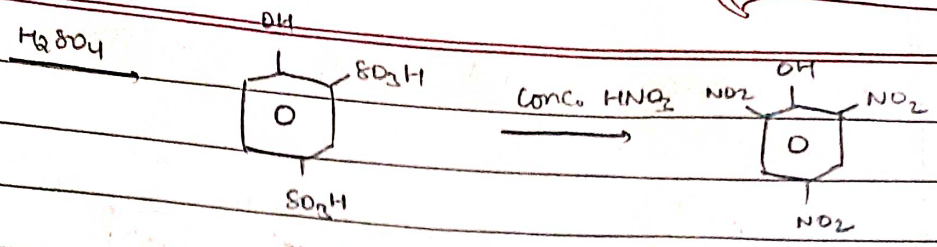


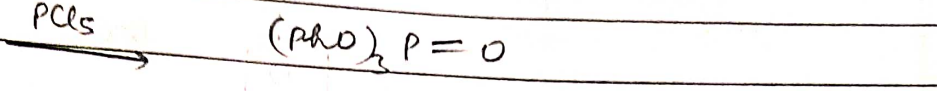
$NaHCO_3$ → No reaⁿ

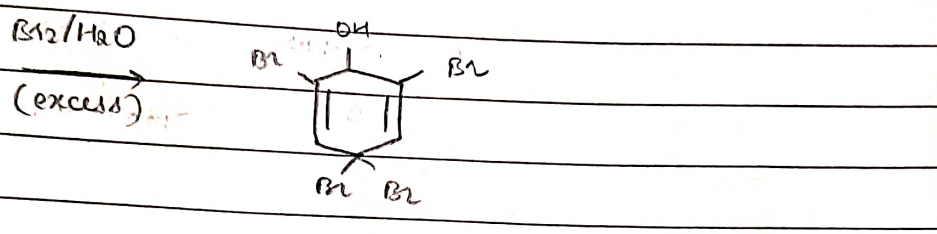
→ EAS

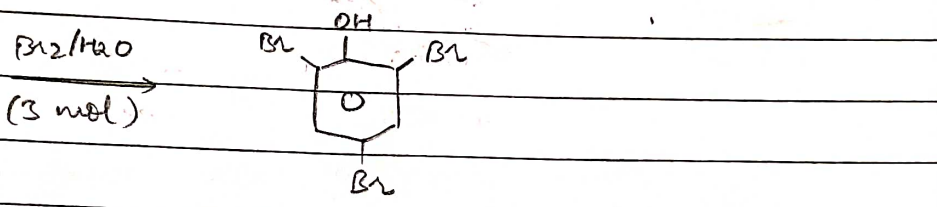


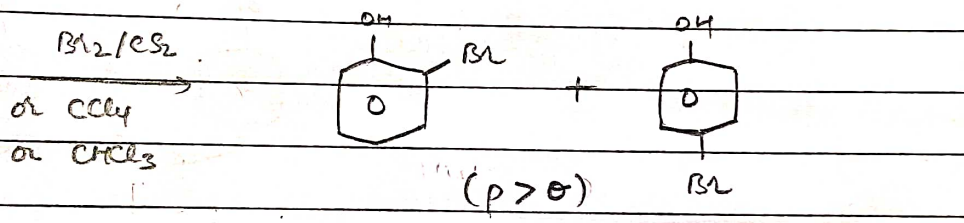


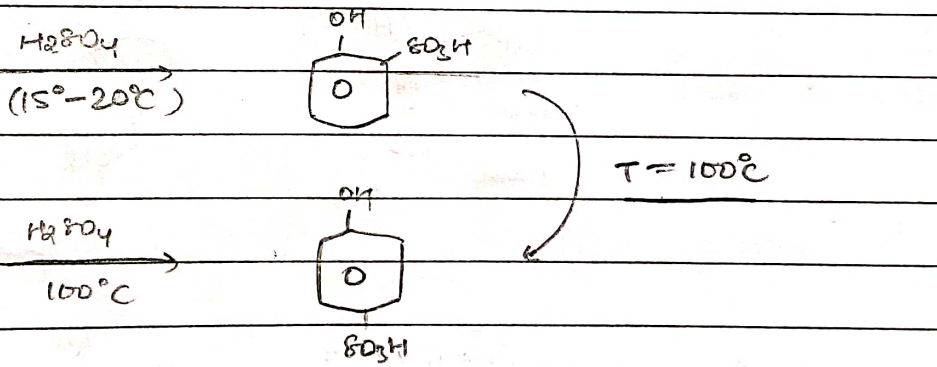

H_2SO_4
OH
SO_3H
O
SO_3H
Conc. HNO_2
OH
NO_2
NO_2
O
NO_2


PCl_5
$(PhO)_3P=O$

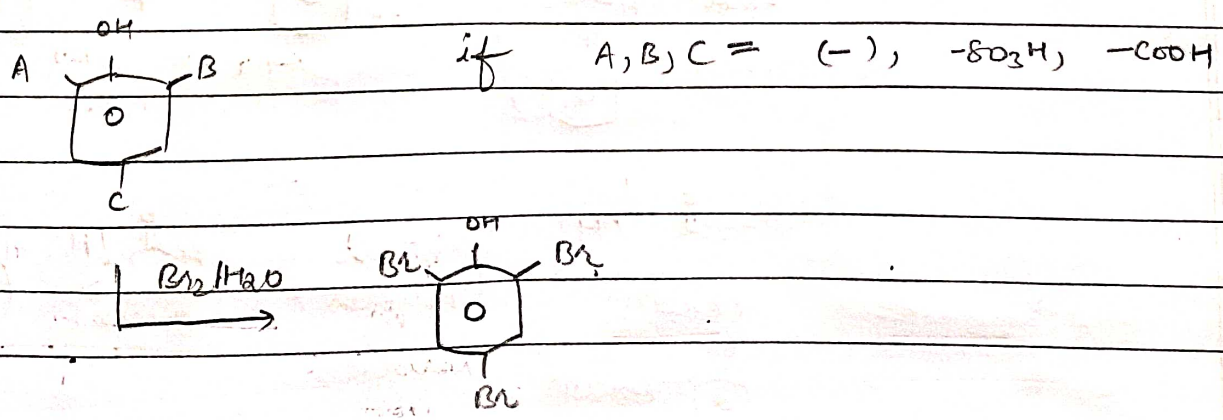

Br_2/H_2O
(excess)
OH
Br
Br
Br
Br


Br_2/H_2O
(3 mol)
OH
Br
Br
O
Br


Br_2/CS_2
or CCl_4
or $CHCl_3$
OH
Br
O
+
OH
O
Br
(p > o)

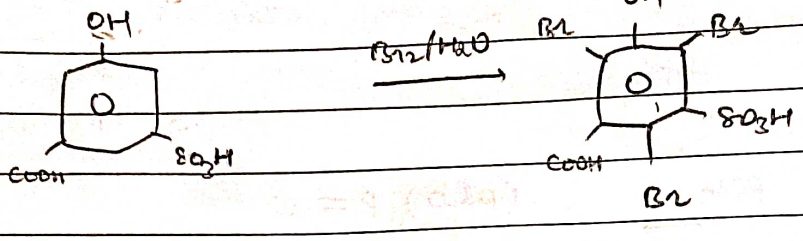

H_2SO_4
(15°–20°C)
OH
SO_3H
O
T = 100°C
H_2SO_4
100°C
OH
O
SO_3H

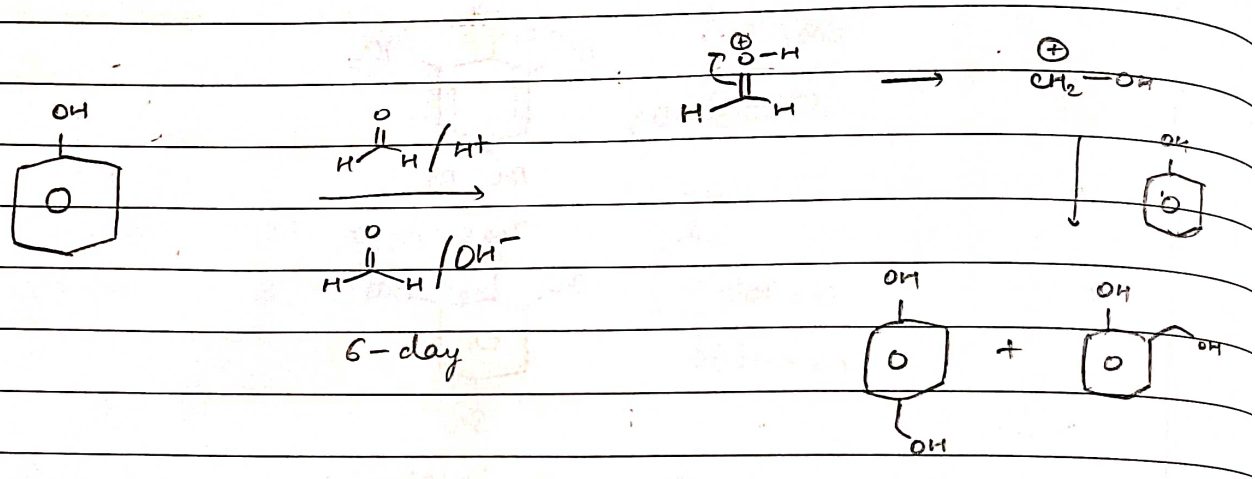
NOTE:

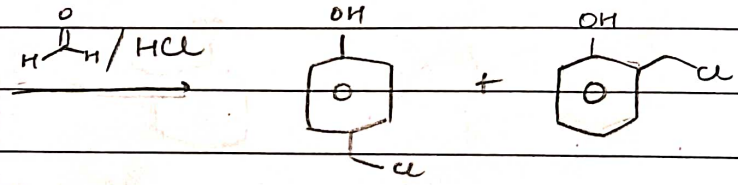

OH
A
B
O
C
if A, B, C = (–), $-SO_3H$, $-COOH$
Br_2/H_2O
OH
Br
Br
O
Br

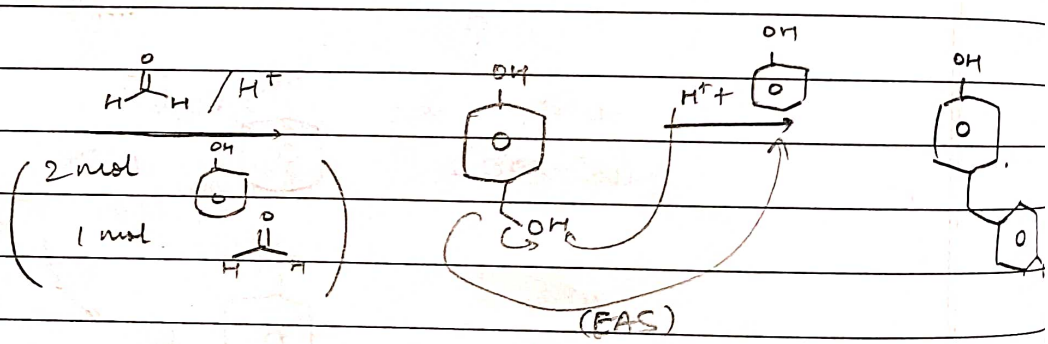
2. Meta posts are unaffected

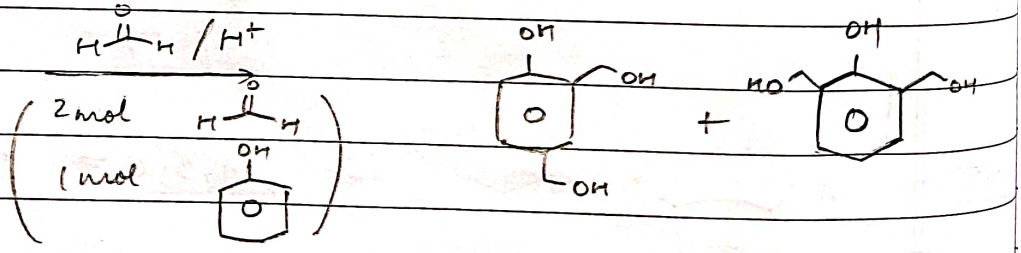
eg –

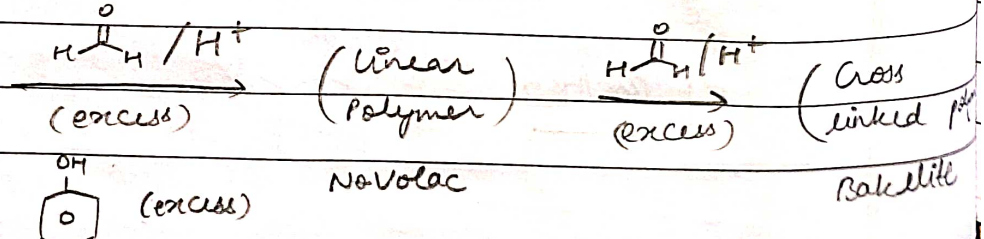


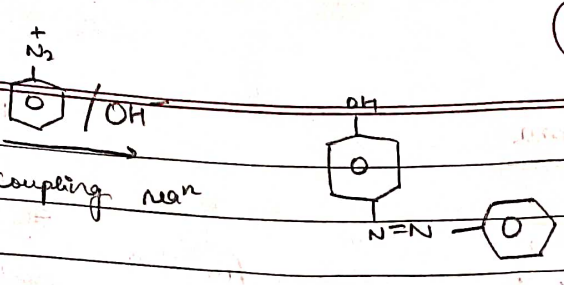




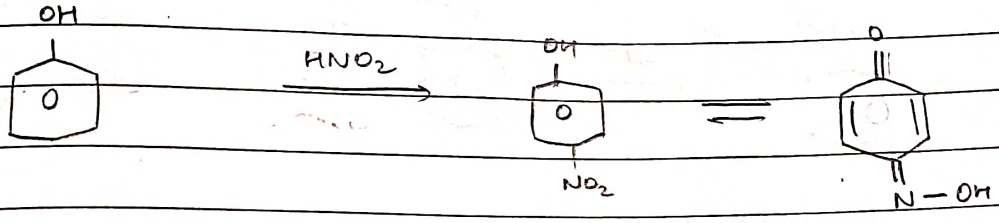




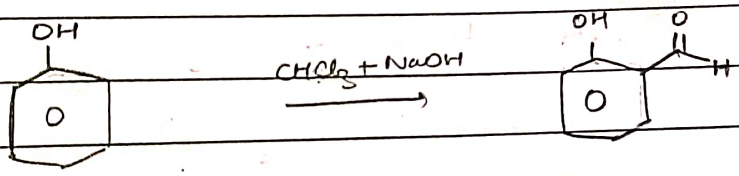




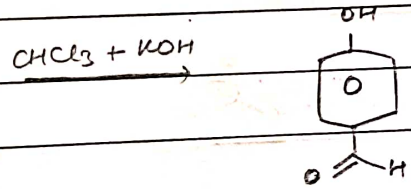
(orange dye)



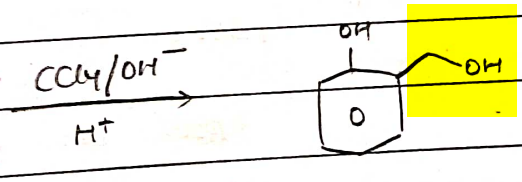
- Reimer – Tiemann Reaⁿ (RTR)

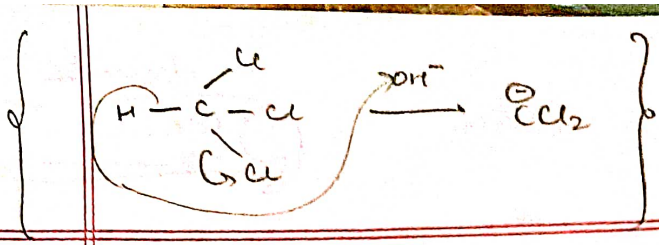


(Salicylaldehyde)



(* since Chelation Effect not strong due to large size of K⊕)



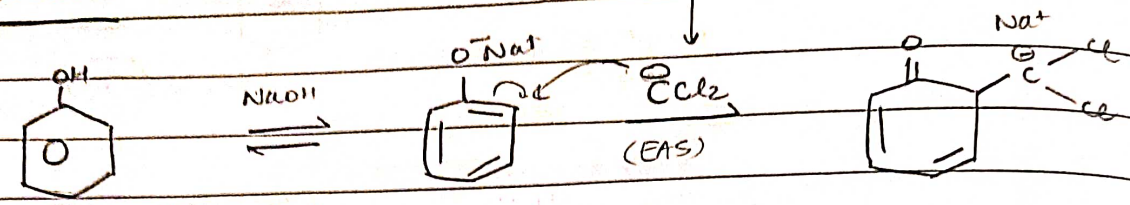


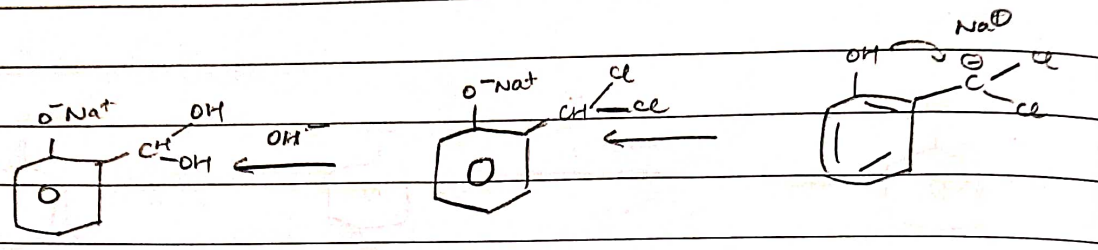
(1,1 Elimination)

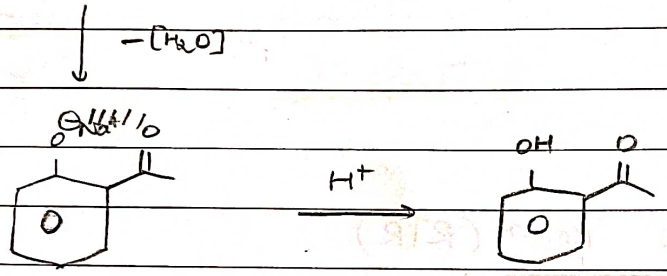
$CHCl_3 + OH^- \longrightarrow \ddot{C}Cl_2$

(Chloro carbene)

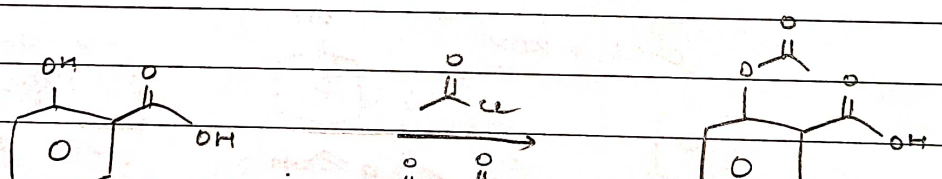
Mechanism







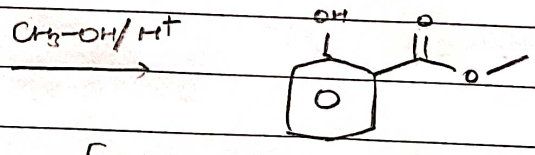
(chelating eff)



Pyridine

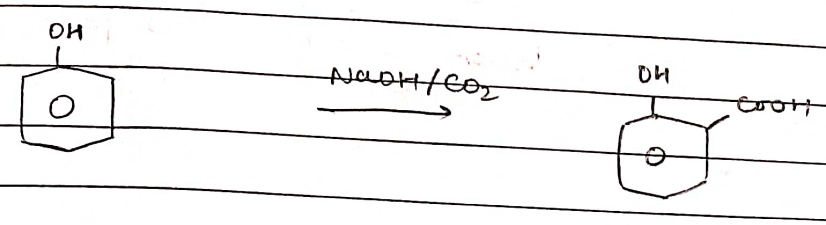
(Aspirin)

[Acid does not react with Acid Derivative]

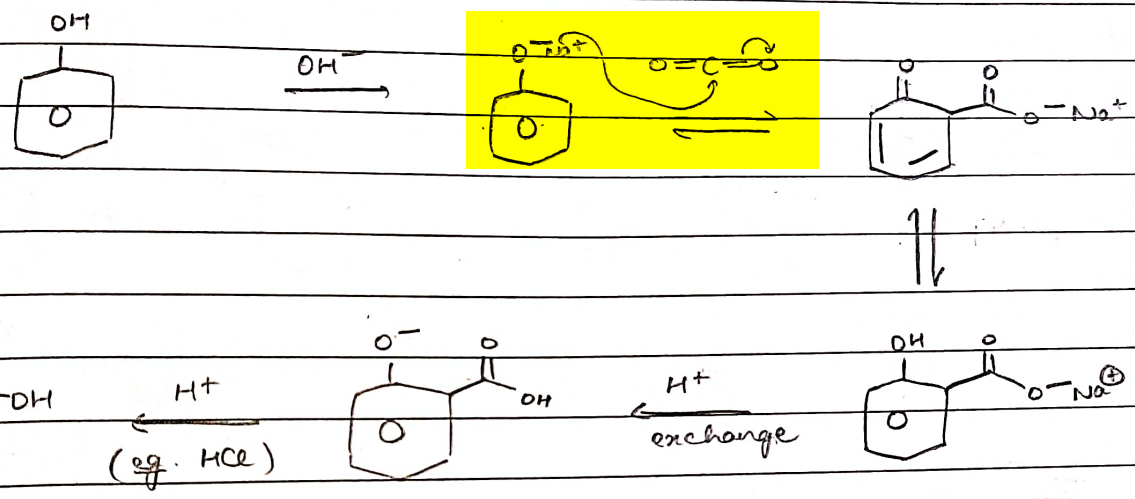


[-OH does not react with -OH]

- Kolbe's rean

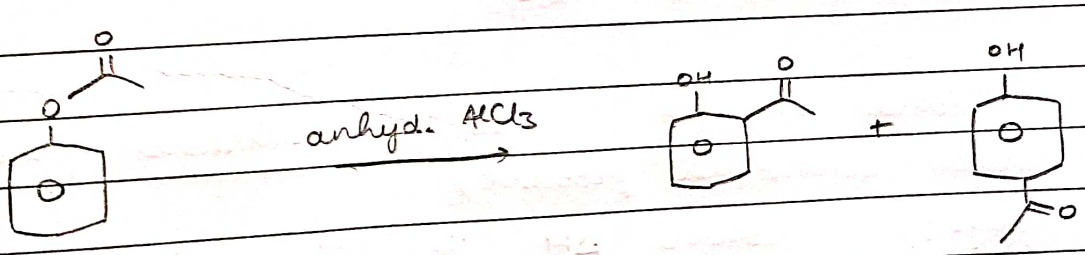


Mechanism



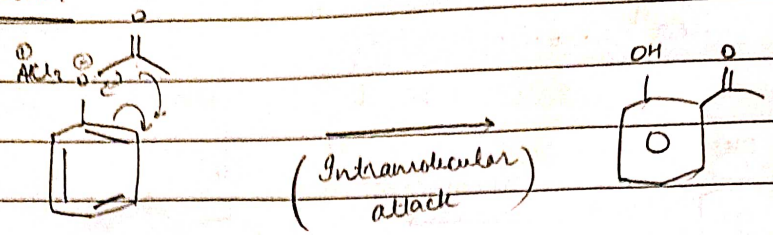
16/06/2023

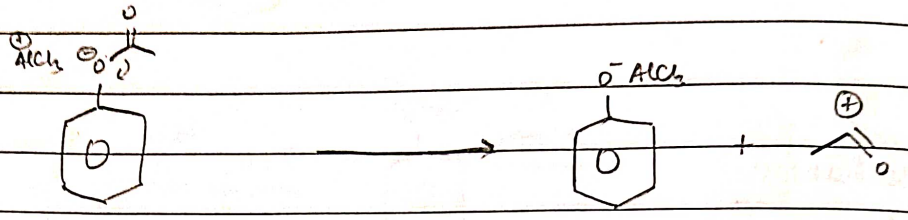
- Fries rearrangement



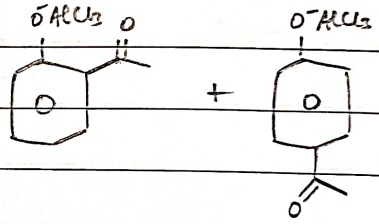
* (Here $AlCl_3$ goes to O instead of C=O, so that EAS can take place)

Mechanism





EAS

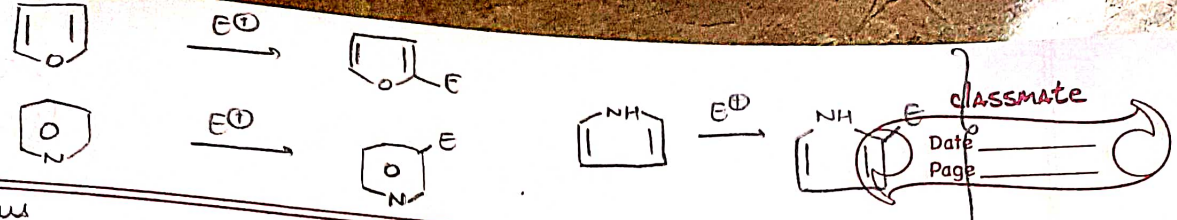


NOTE: 1. The ortho isomer has higher vapour pressure because of chelation, OH---O= & is steam volatile

2. In para isomer, there is intermolecular H-bonding with H_2O

3. Para isomer is exclusive product @ 25°C (rate controlled product)
Reason: lower ΔH & its formation is reversible

4. Ortho isomer is chief product @ 165°C (Eq-controlled product)
Reason: Higher ΔH & stabilized by chelation.



RTR Miscellaneous

Rxn's