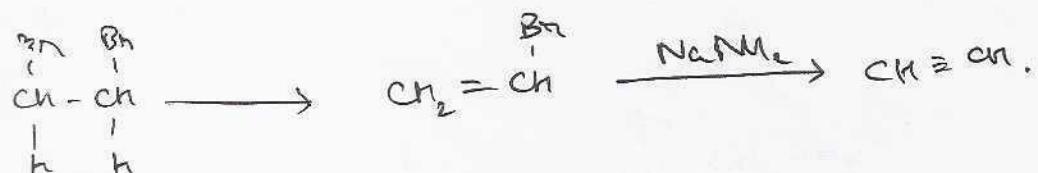
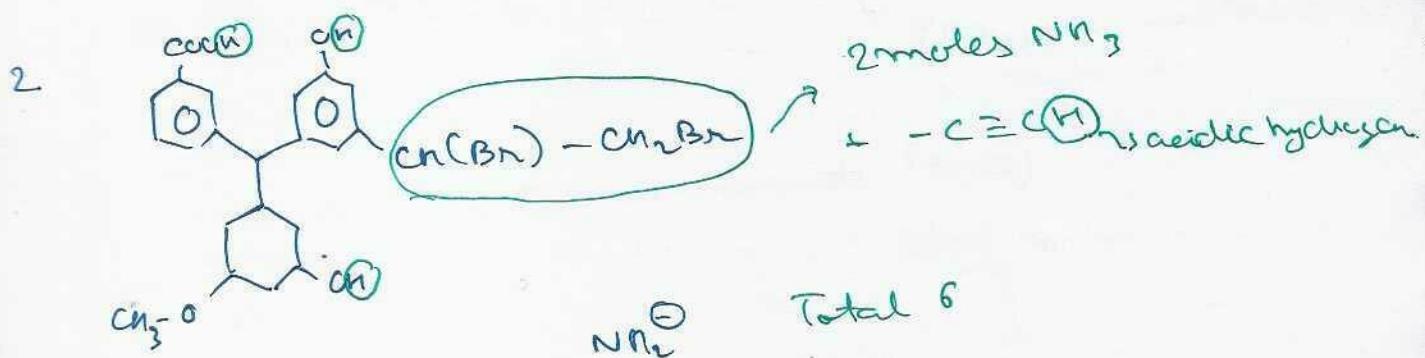
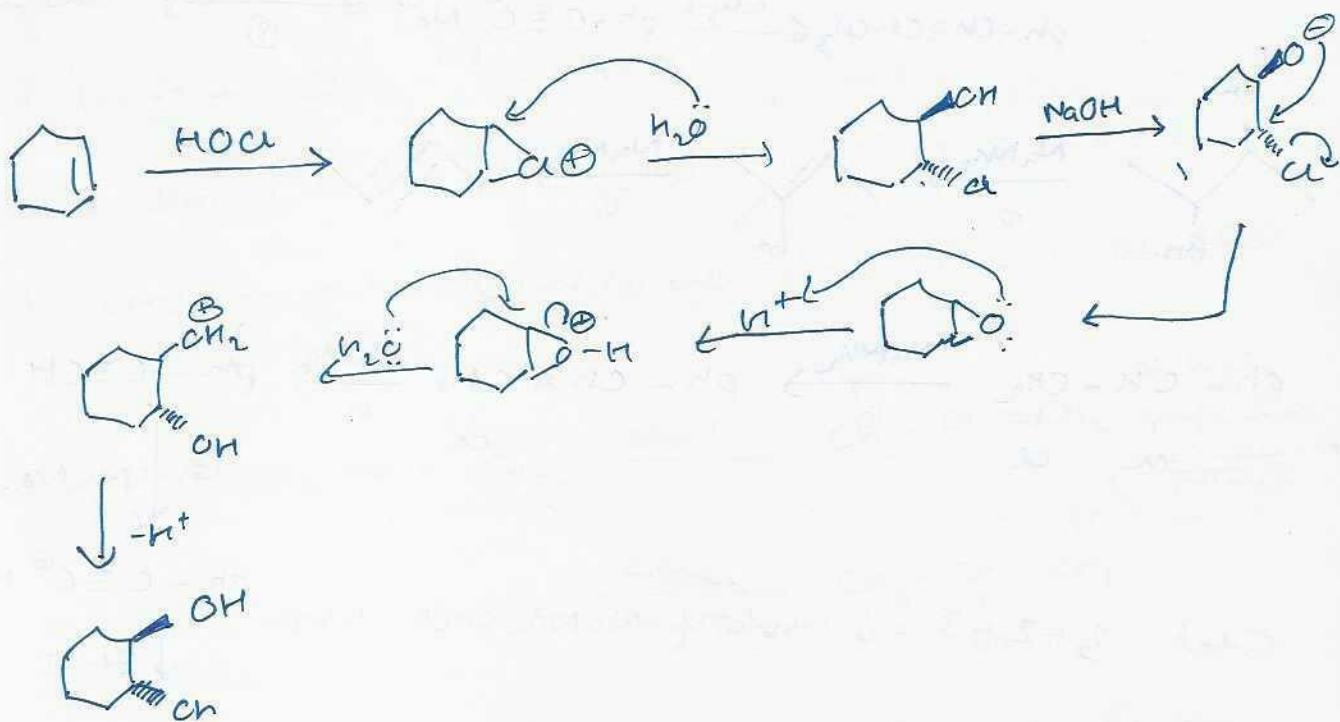
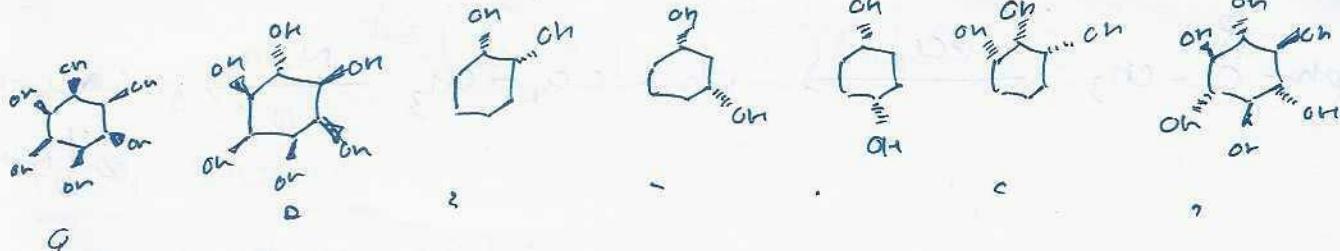


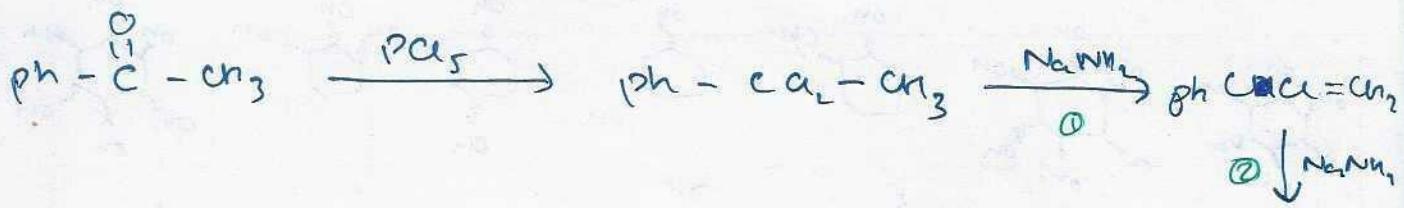
I N D E X

NAME: Shibashish
Mukhopadhyay STD.: _____ SEC.: _____ ROLL NO.: _____ SUB.: _____

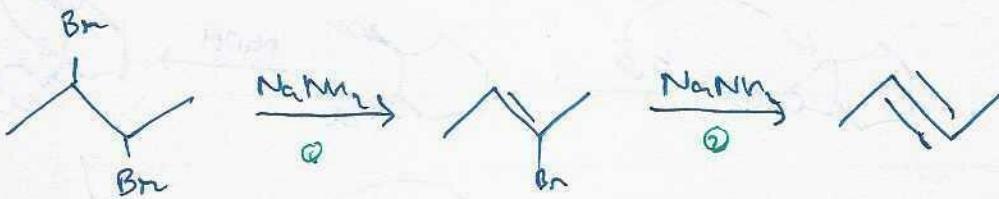
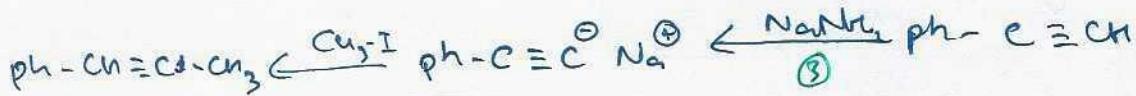


-N=N- is weakly deactivating group.

↳ ortho-para directing.

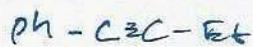
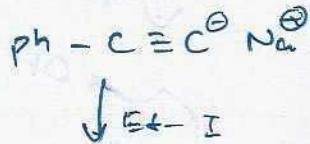
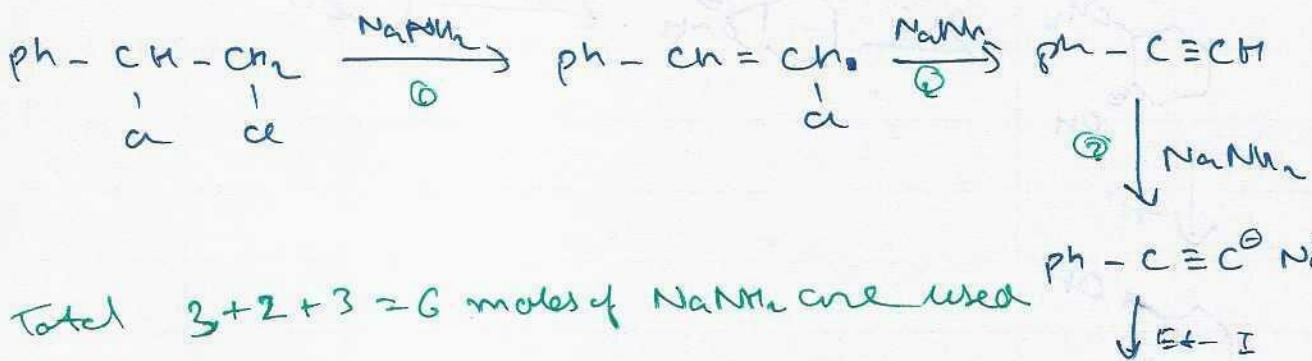


1. F



B

C



CH₃

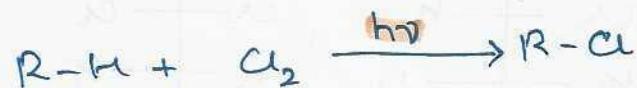
Ran *

CH

ALKYL HALIDES

1. FROM ALKANES

Free Radical Substitution.

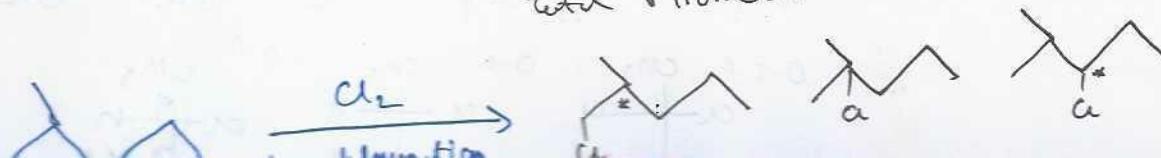
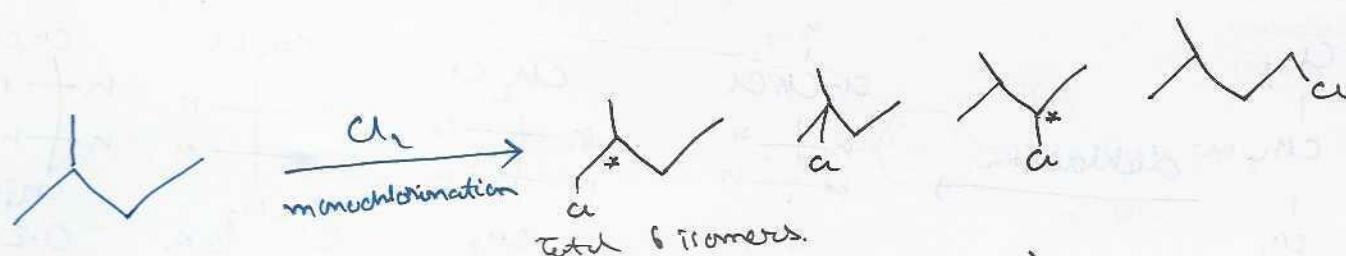
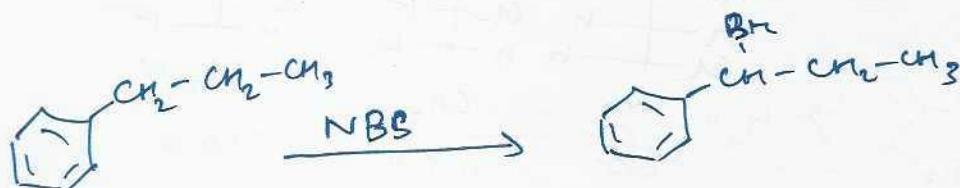
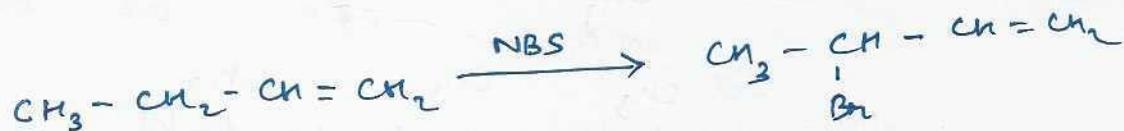
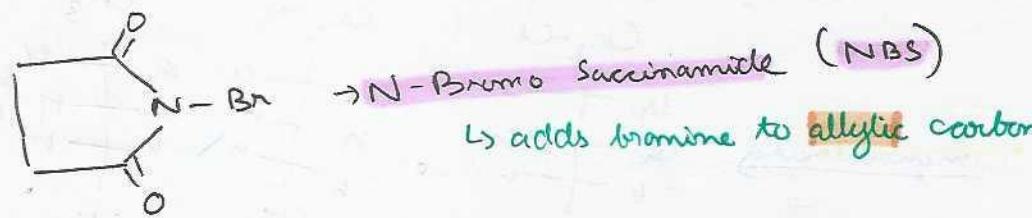
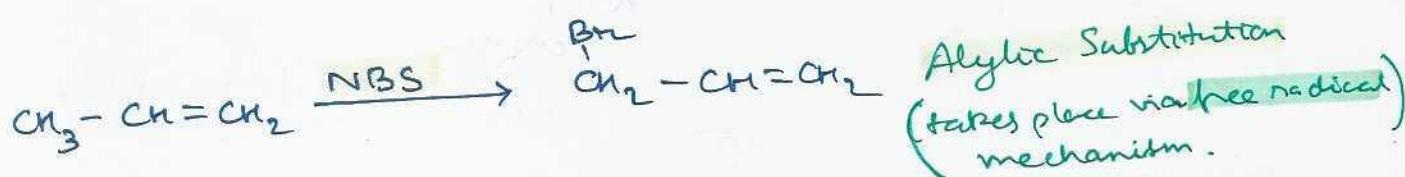
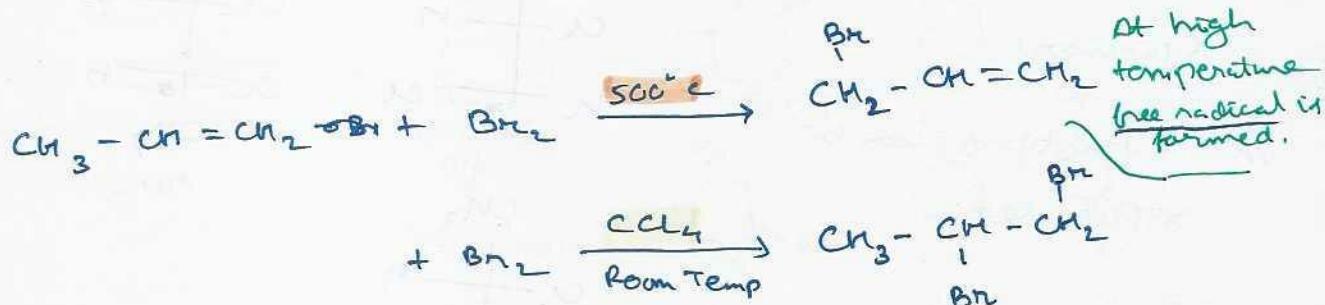


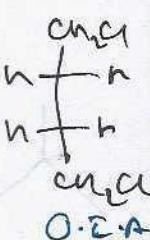
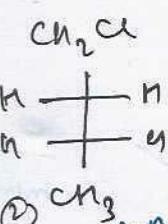
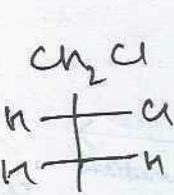
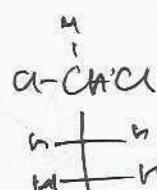
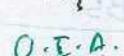
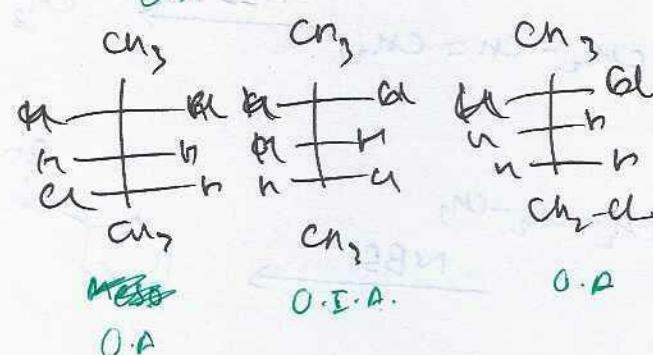
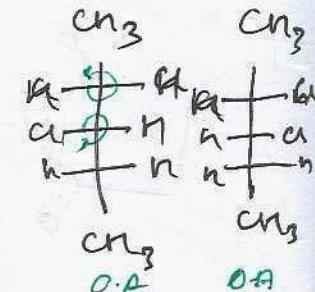
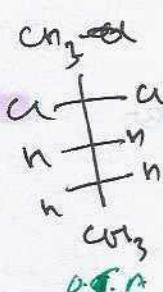
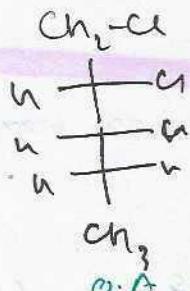
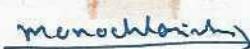
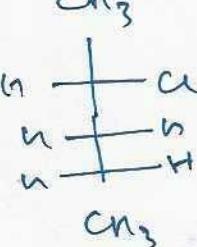
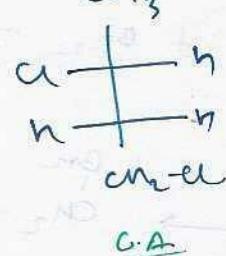
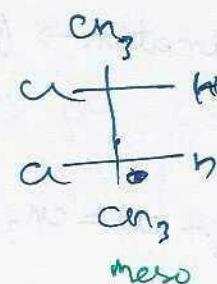
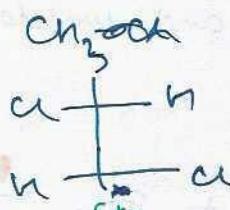
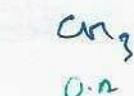
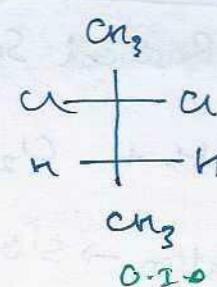
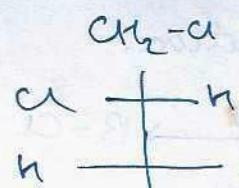
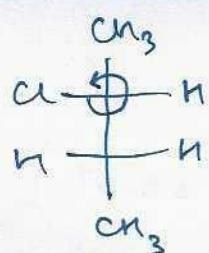
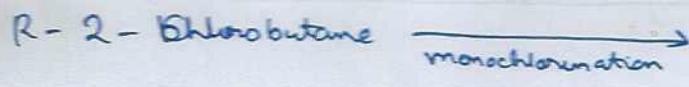
Bromination \rightarrow slow and selective

$$1^\circ : 2^\circ : 3^\circ = 1 : 3.8 : 5$$

Chlorination \rightarrow fast and unselective

$$1^\circ : 2^\circ : 3^\circ = 1 : 82 : 1600$$

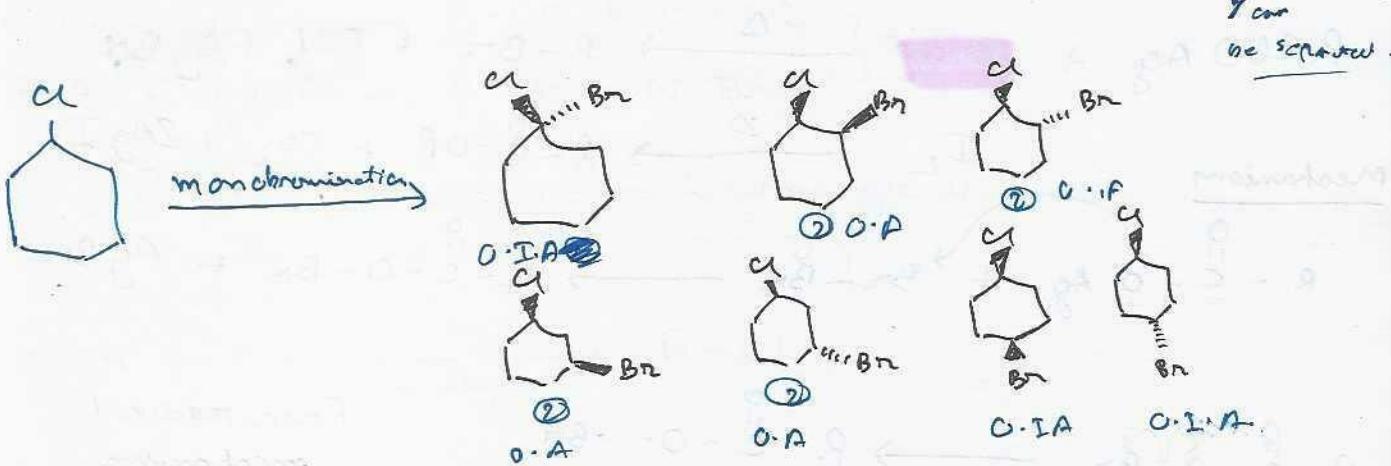
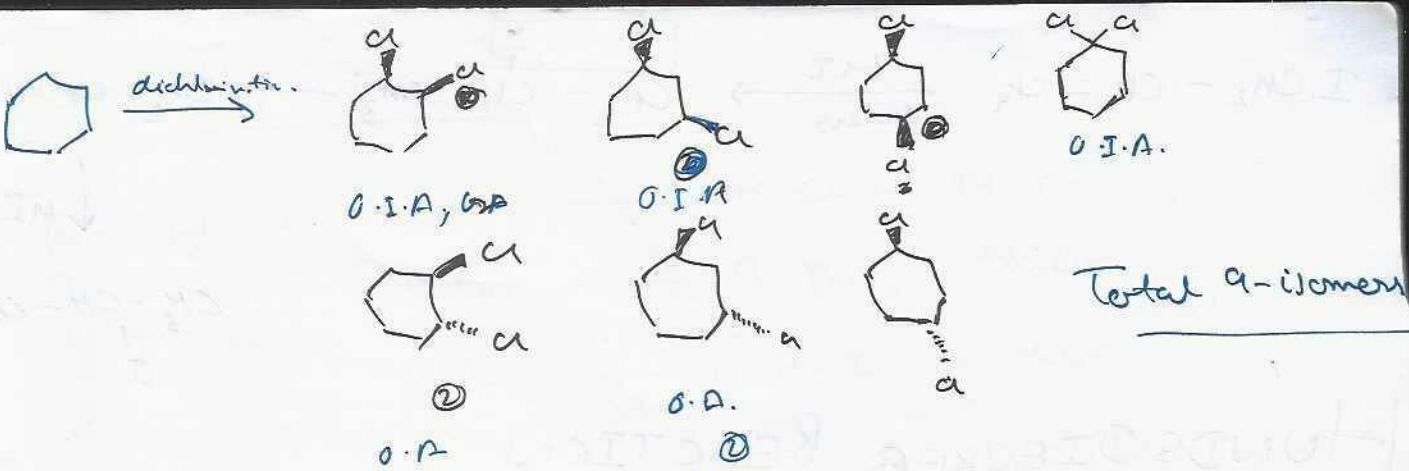




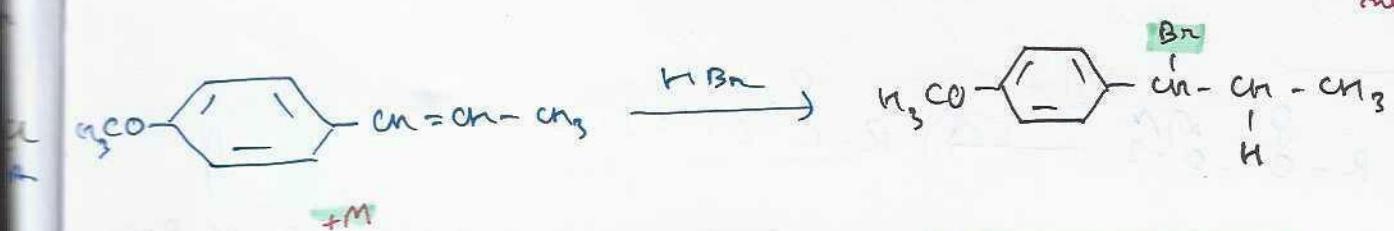
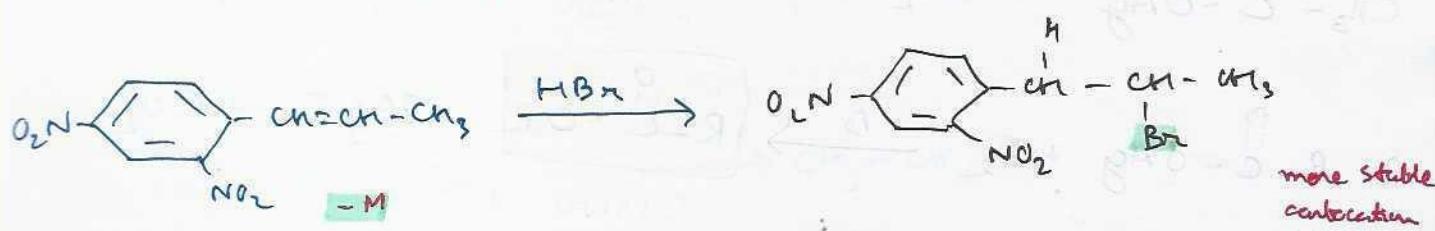
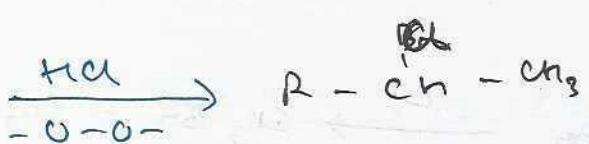
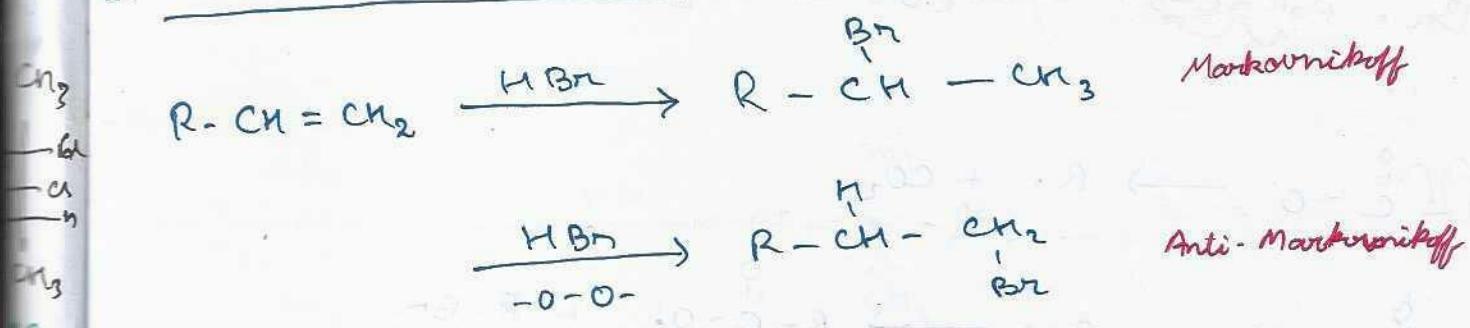
2. FR

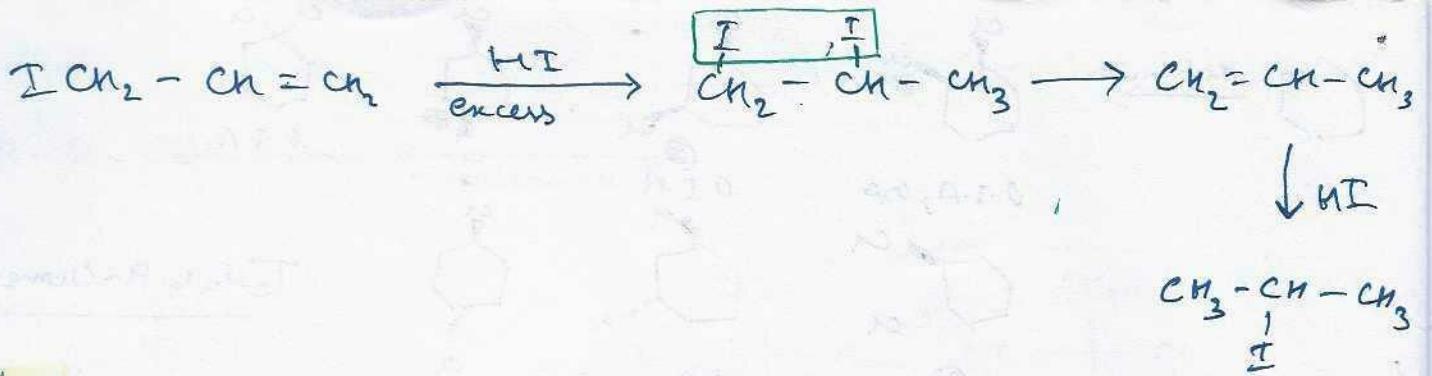
R.

O₂N

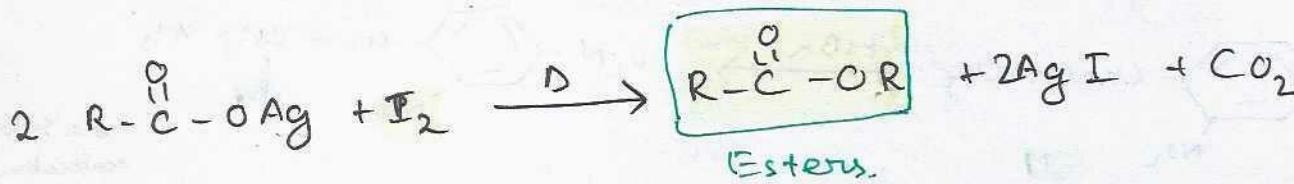
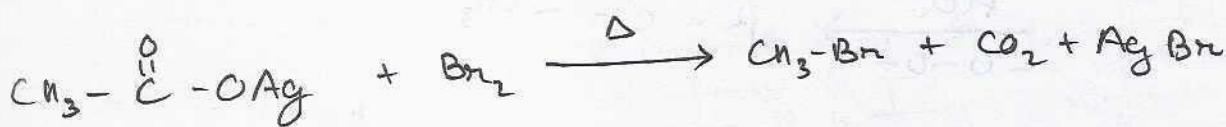
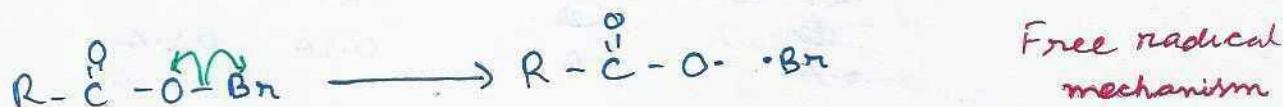
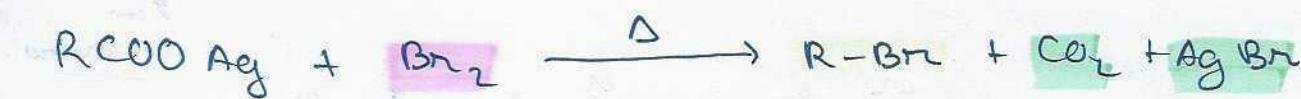


2. FROM ALKENES



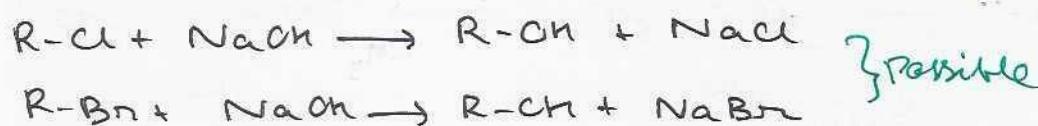
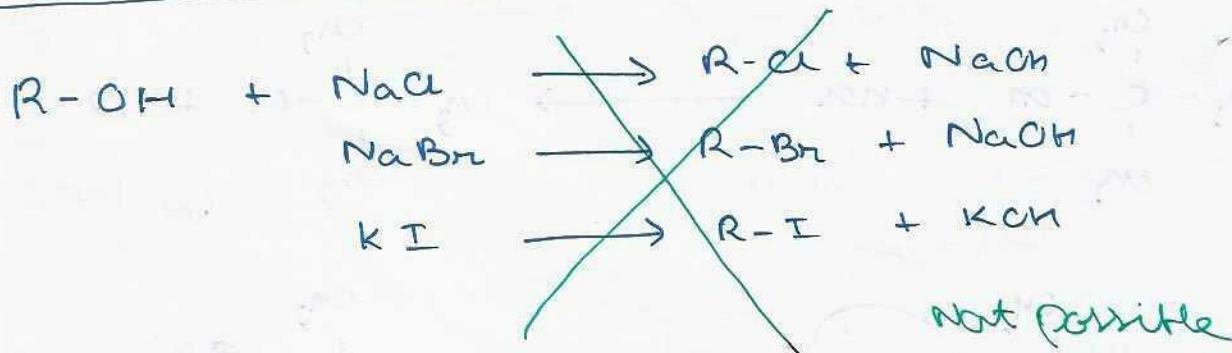


HUND'S DIECKER REACTION

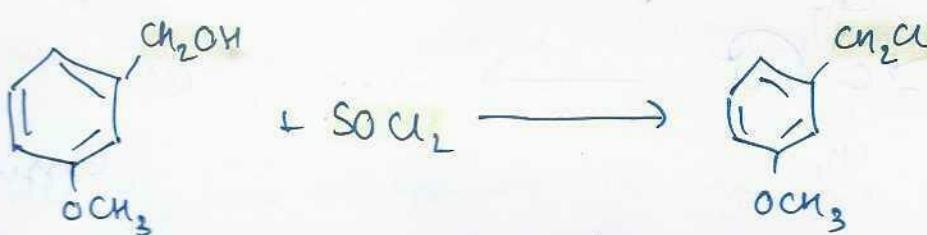
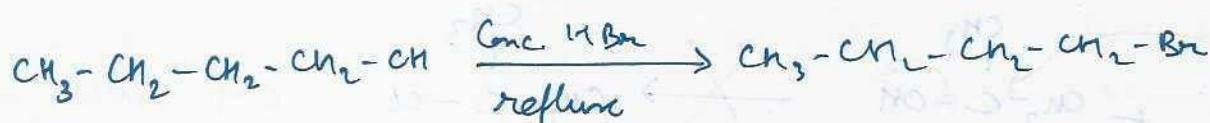
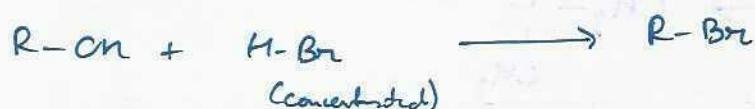
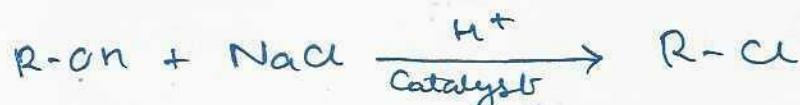


$\text{I} \cdot + \text{I} \cdot \longrightarrow \text{I}_2$ which was not the case with Br.

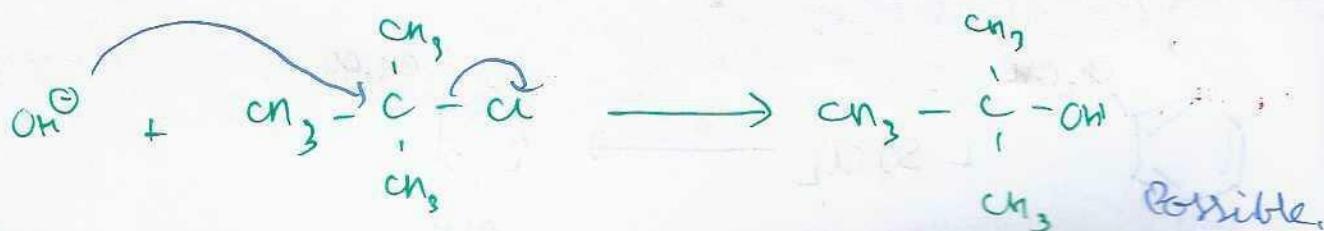
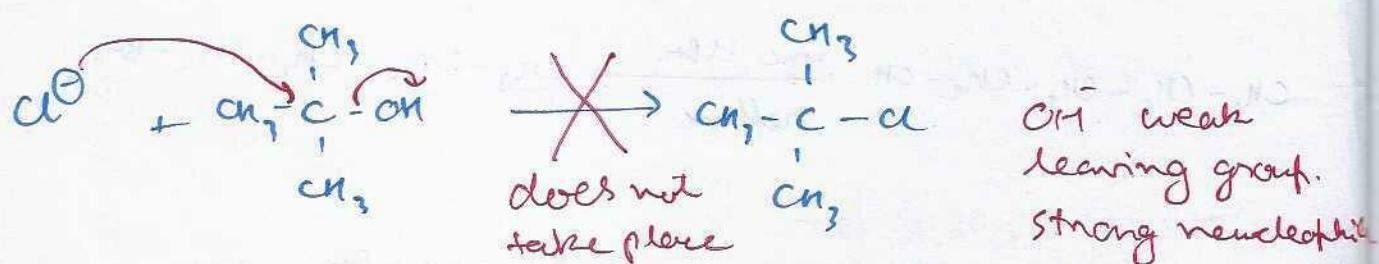
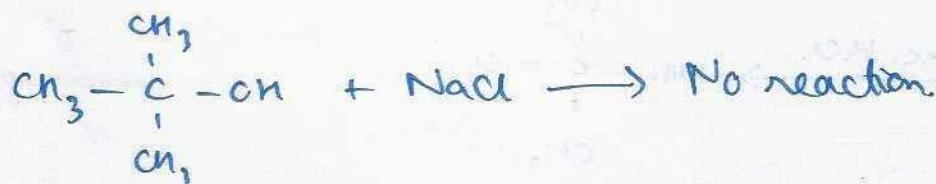
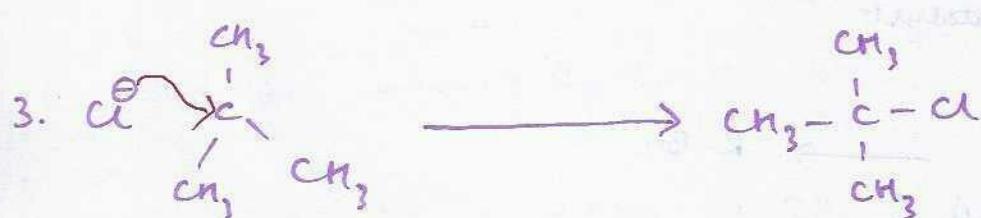
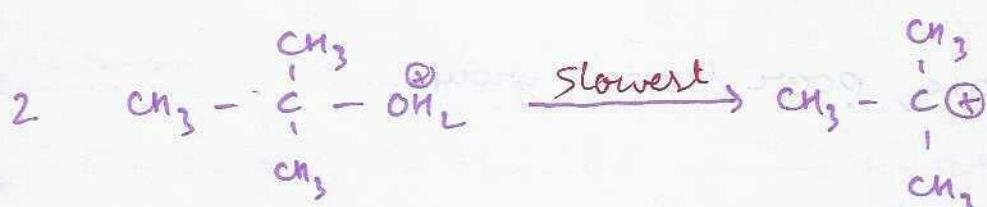
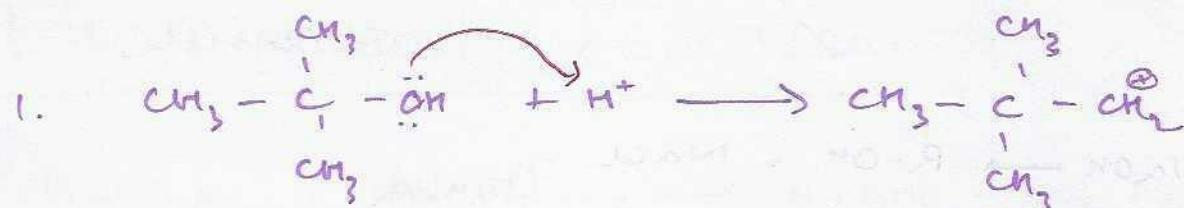
FROM ALCOHOLS

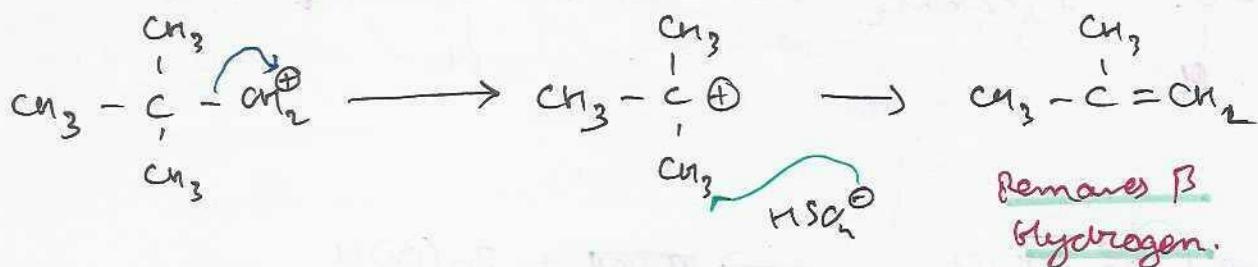
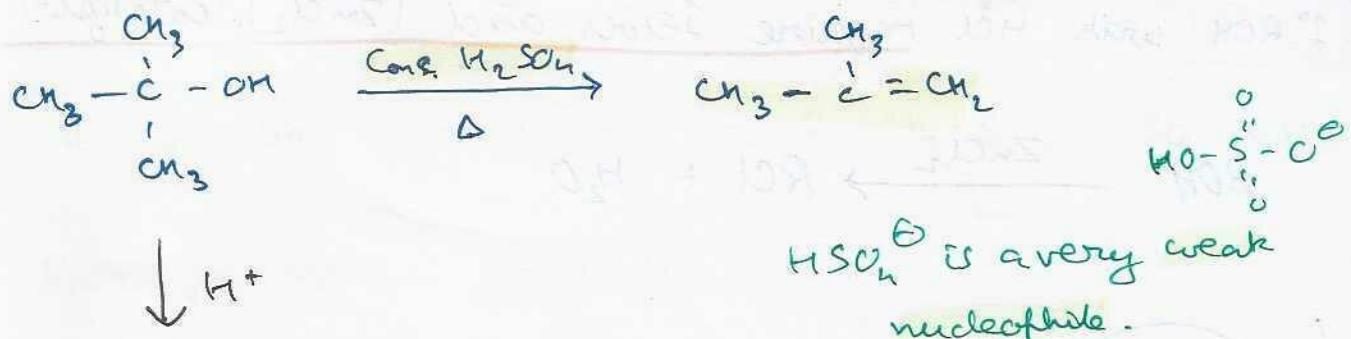


OH^- strong base, poor leaving group.



Mechanism





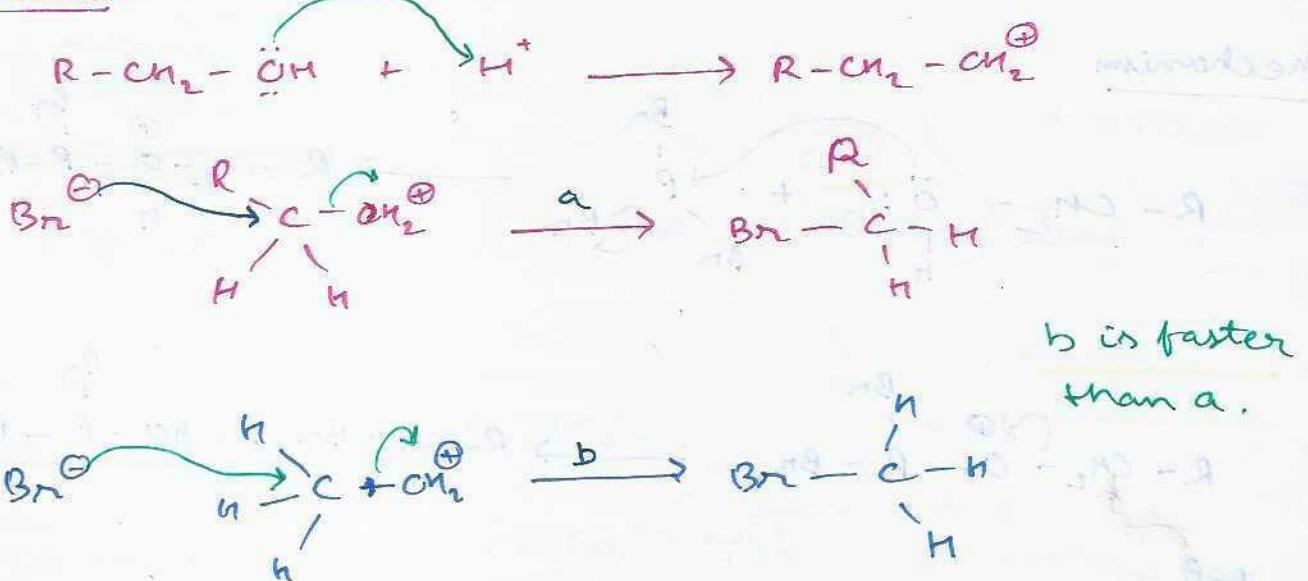
$3^\circ \text{RON} > 2^\circ \text{RON} > 1^\circ \text{RON} \xleftarrow{\text{MeOH}} S_{N}2$

$S_{N}2 \quad S_{N}2 \quad S_{N}2$

Does not take place
reactivity with HCl/ZnCl_2 via this mechanism.



Mechanism

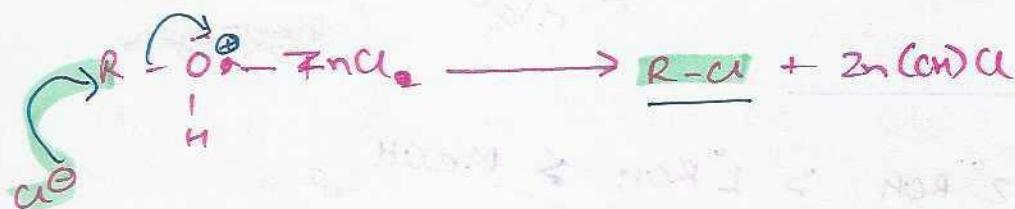
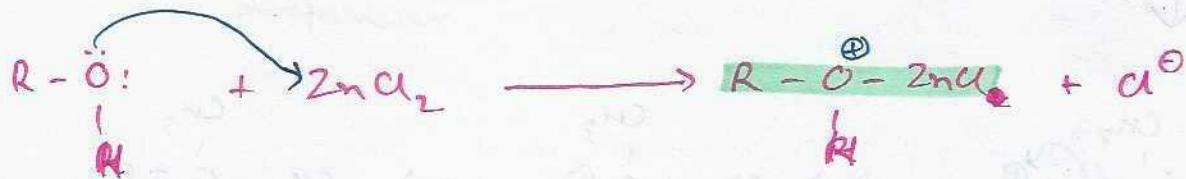


Nucleophiles $\boxed{\text{HI} > \text{HBr} > \text{HCl}}$ HF is unreactive.

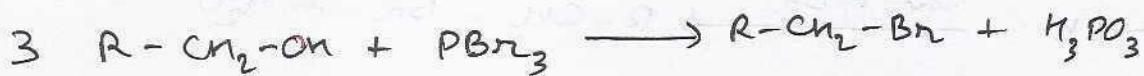
HCl requires catalyst when reacting with 1°RON and MeOH.

because Cl^{\ominus} does not easily attack

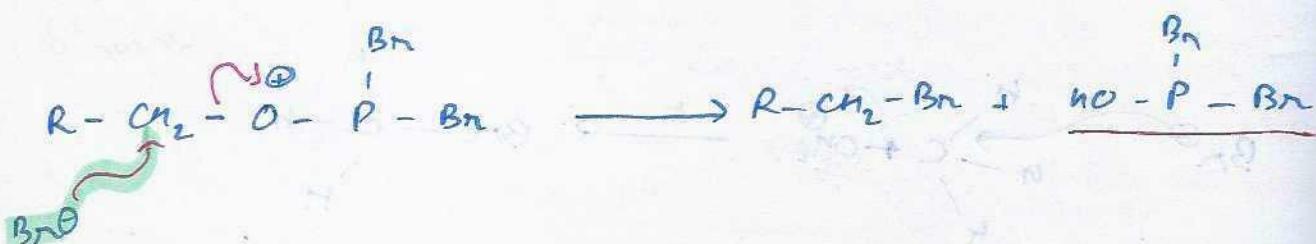
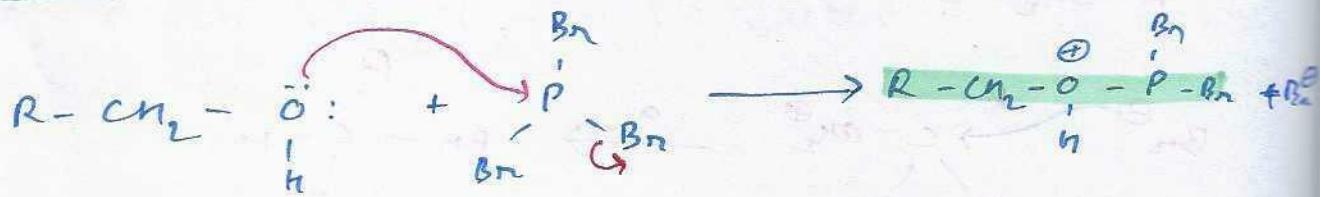
1° ROH with HCl require Lewis acid ($ZnCl_2$) catalyst.



With PBn_3 ,



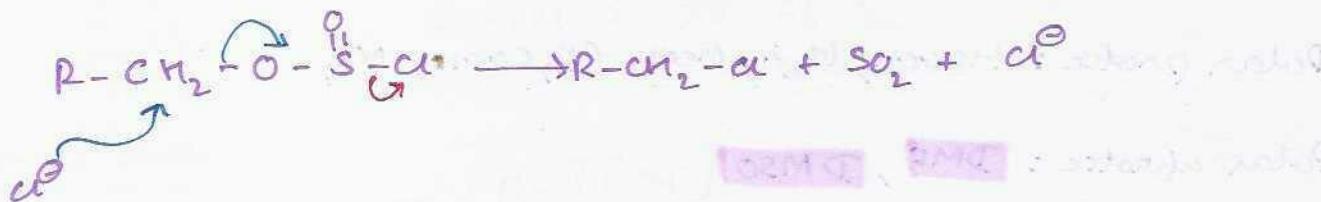
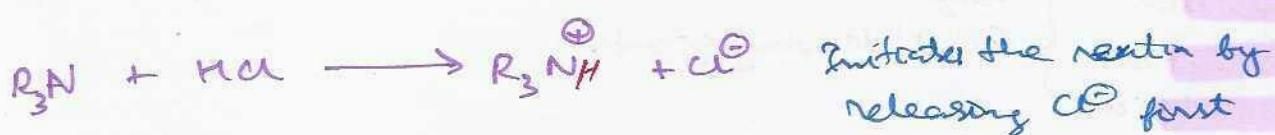
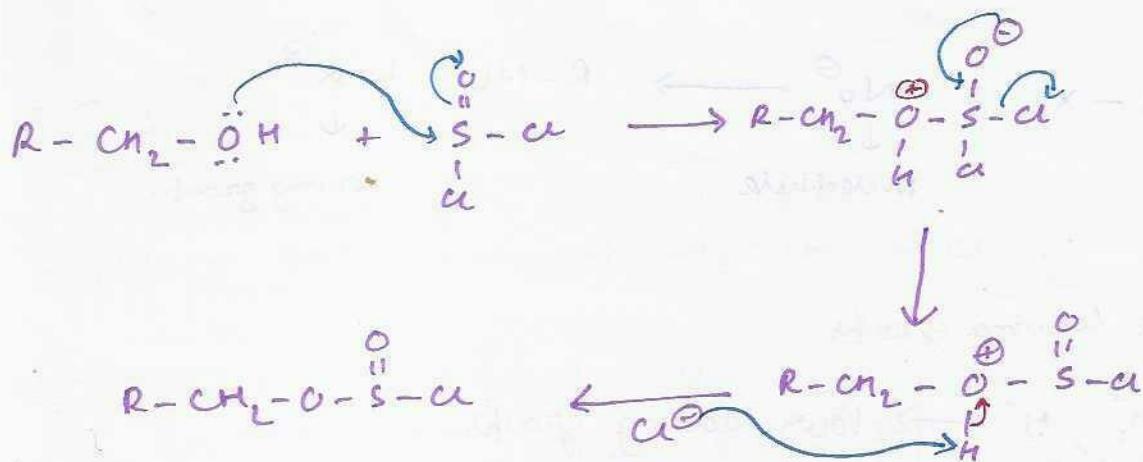
Mechanism



With SOCl_2



3° amine + HCl \rightarrow catalyzed the reaction.



PROPERTIES OF ALKYL HALIDES

+ R_nE

$\text{R}-\text{F} < \text{R}-\text{Cl} < \text{R}-\text{Br} < \text{R}-\text{I}$ Boiling point.



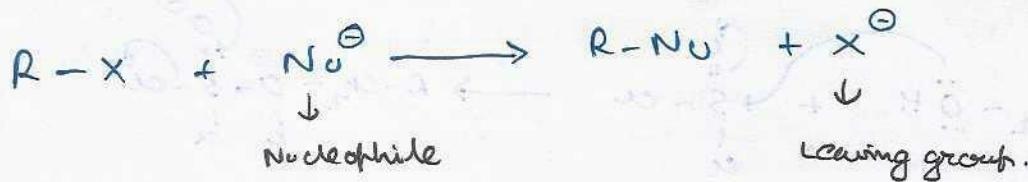
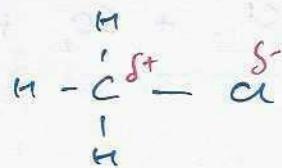
$M = exd$

distance
is more
than CH_3F .
more bond
length.

But $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$.

Does not occur here.

CHEMICAL PROPERTIES



$\text{X}^- \rightarrow$ good leaving groups

$\text{OH}^-, \text{F}^-, \text{CN}^-, \text{H}^- \rightarrow$ Poor leaving groups

Tosylate ion
Triflate ion
Methylate ion } very
Good leaving groups

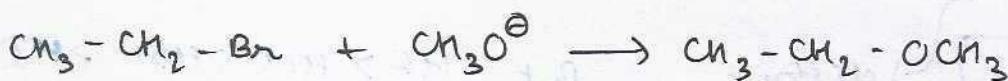
Polar protic: $\text{HCOOH}, \text{H}_2\text{O}; \text{MeOH}, \text{CH}_3\text{COOH}, \text{NH}_3$

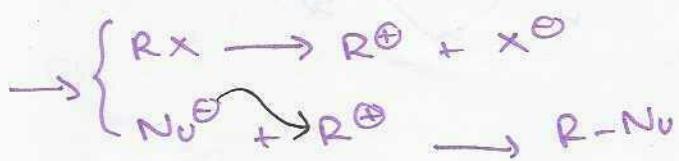
Polar aprotic: DMF, DMSO

Polar Protic Nucleophilicity: $\text{F}^{\ominus} < \text{Cl}^{\ominus} < \text{Br}^{\ominus} < \text{I}^{\ominus}$

due to solvation

Polar Aprotic Nucleophilicity: $\text{F}^{\ominus} > \text{Cl}^{\ominus} > \text{Br}^{\ominus} > \text{I}^{\ominus}$

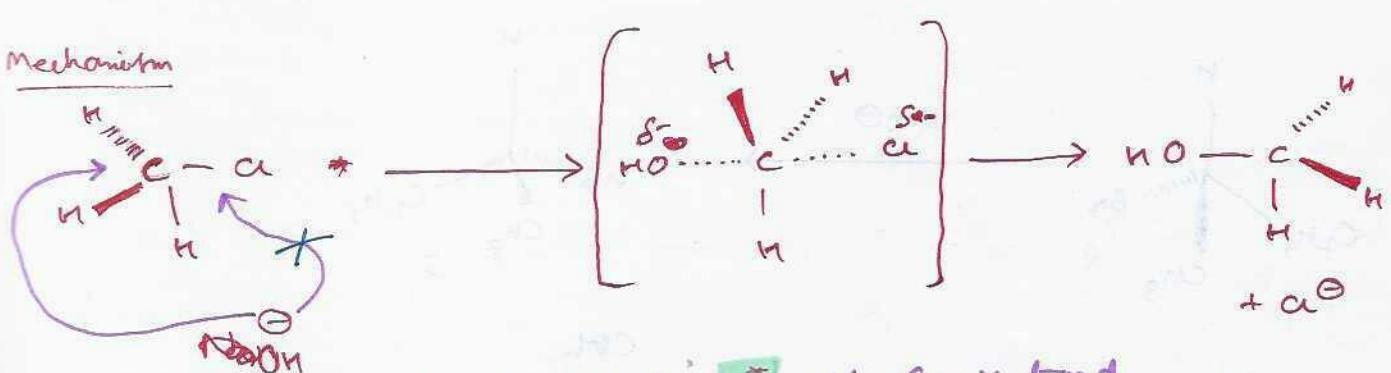




S_N^2



Mechanism

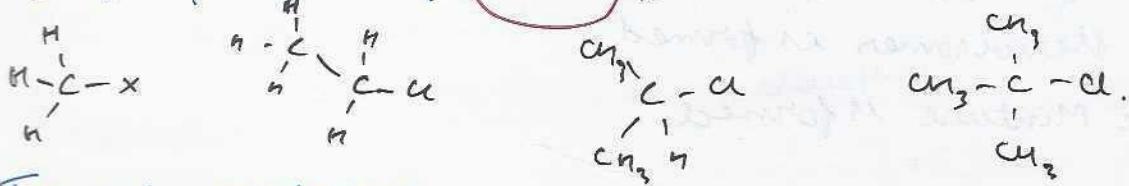


OH^\ominus attacks at σ^* of C-X bond.
(previously vacant)

'Single Step'



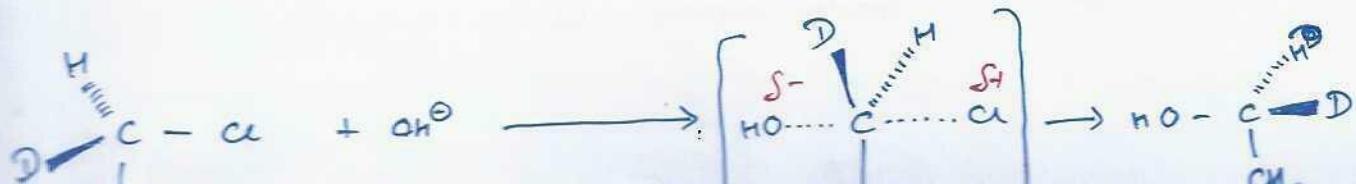
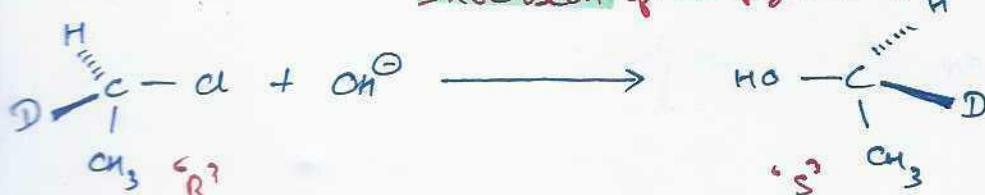
- Strong Nucleophile $\rightarrow NS^\ominus, CH_3O^\ominus, NH_2^\ominus$
- Polar aprotic (Polar aprotic solvents can solvate them) nucleophile

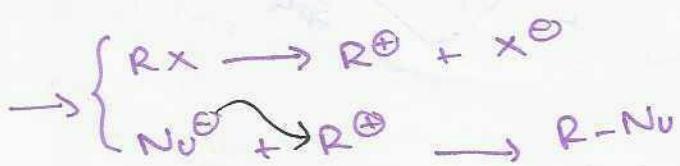
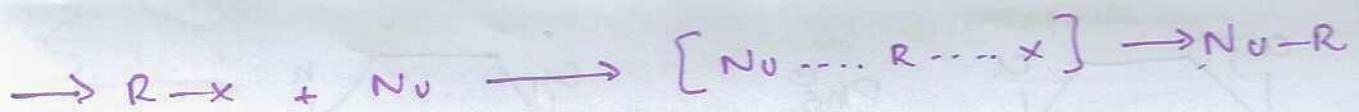


- Transition state is formed. No intermediate.

STEREOCHEMISTRY

Inversion of Configuration. \rightarrow (Not always)

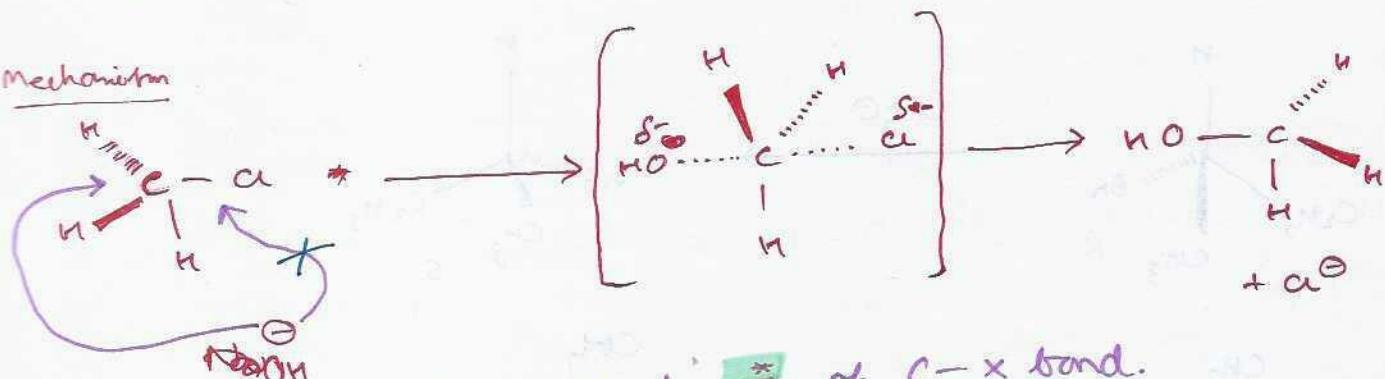




S_N2



Mechanism

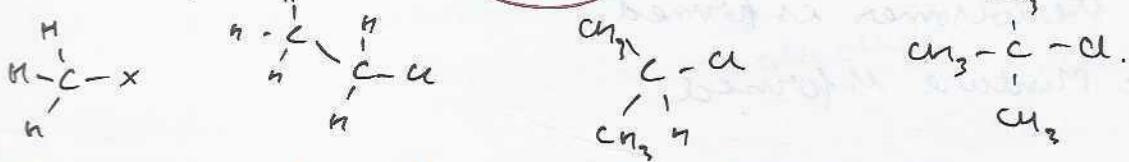
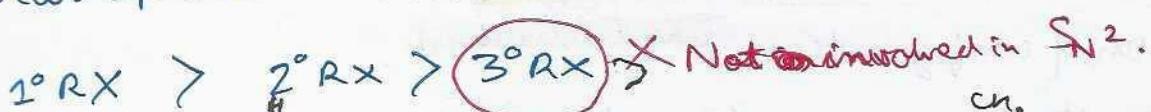


OH^- attacks at σ of C-X bond.
 (previously vacant)

"Single Step"



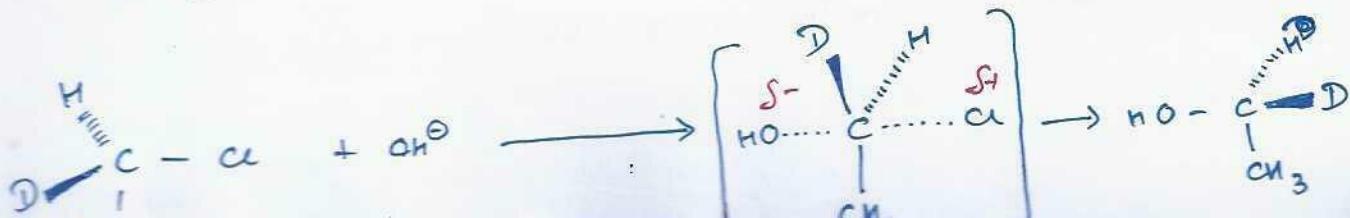
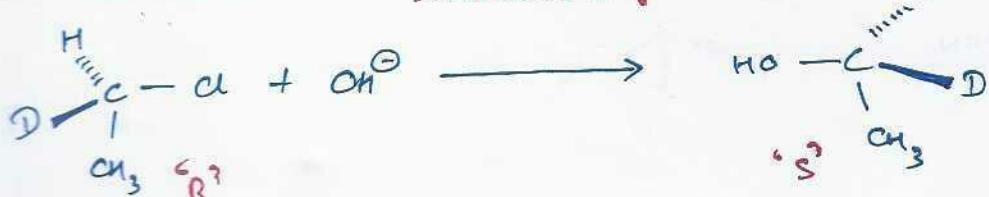
- Strong Nucleophile $\rightarrow HS^-, CH_3O^-, NH_2^-$
- Polar aprotic (Polar aprotic solvents can solvate them) nucleophile

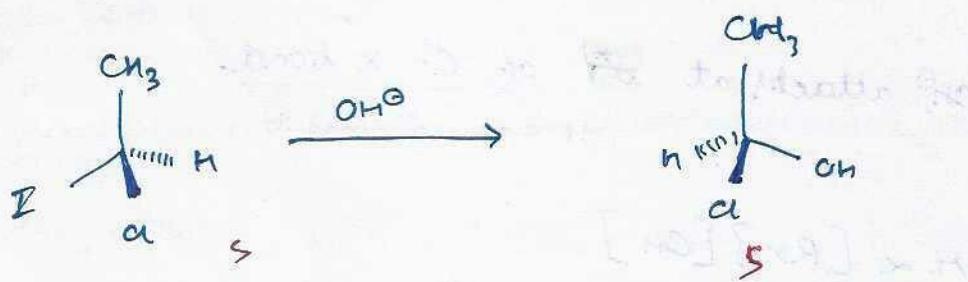
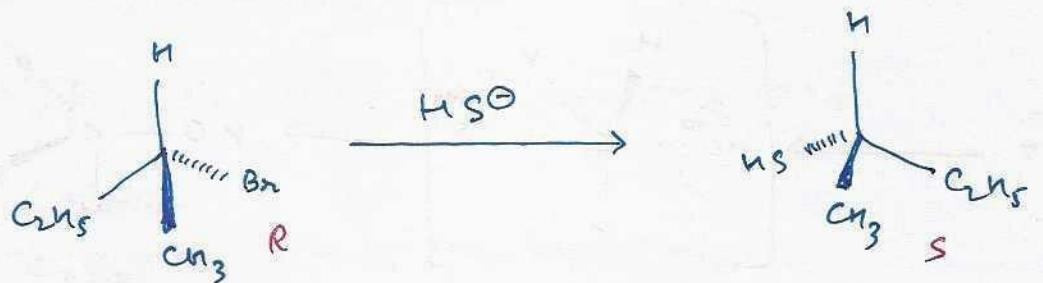
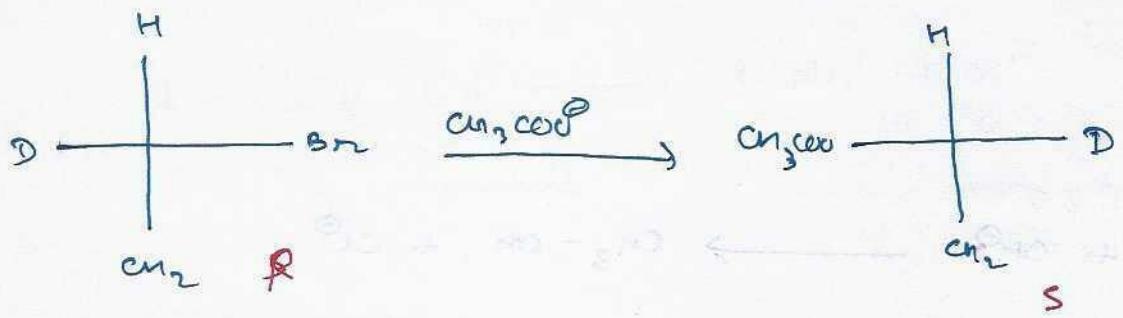
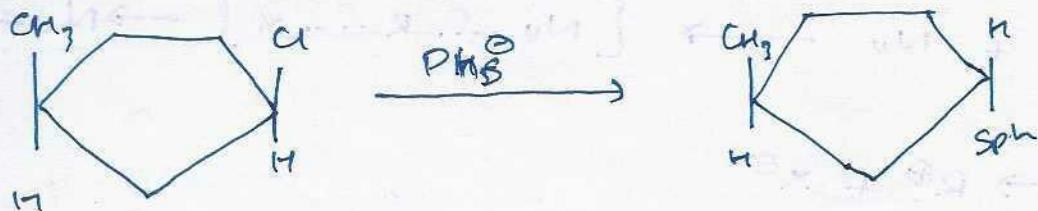


- Transition state is formed. No intermediate.

STEREOCHEMISTRY

Inversion of Configuration. \rightarrow (Not always)





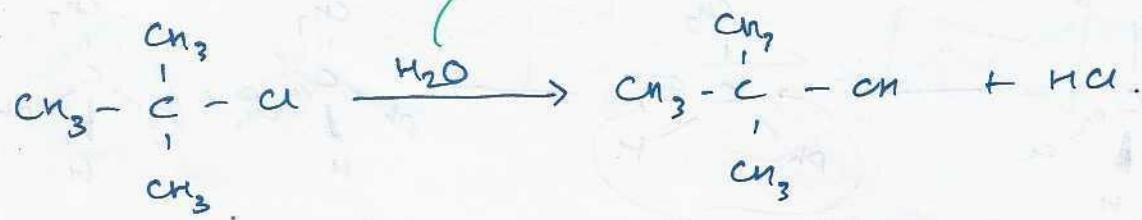
Q In S_N2 reaction always

a) Inversion of configuration (Not always).

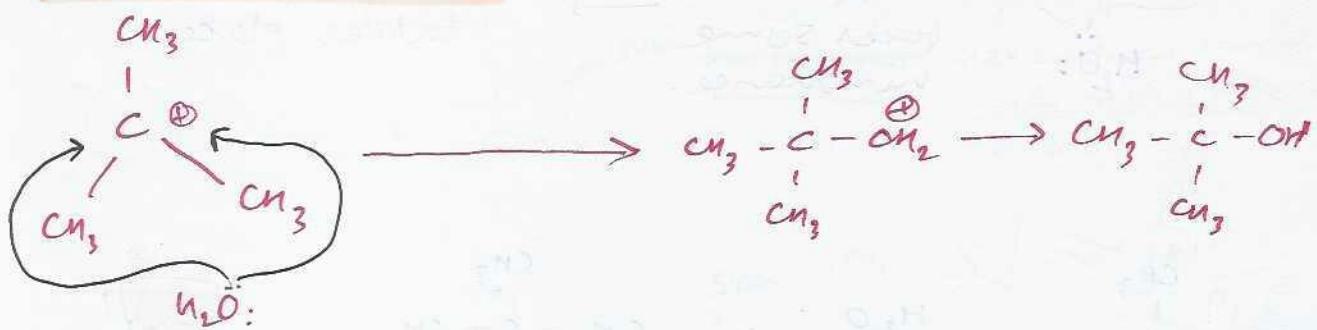
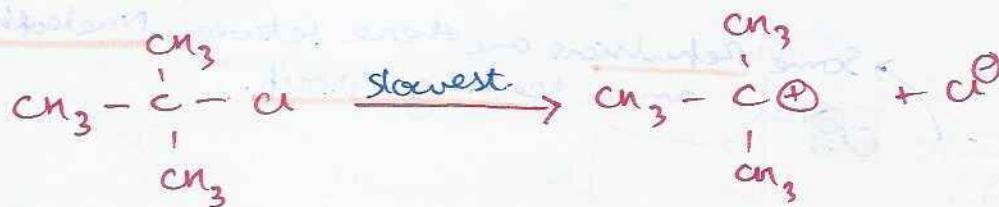
~~b)~~ Single stereoisomer is formed

c) Racemic Mixture is formed

S_N^1



Mechanism



$\propto [Rx]$ Unimolecular.

Carbocation intermediate

Two step process

does not undergo.

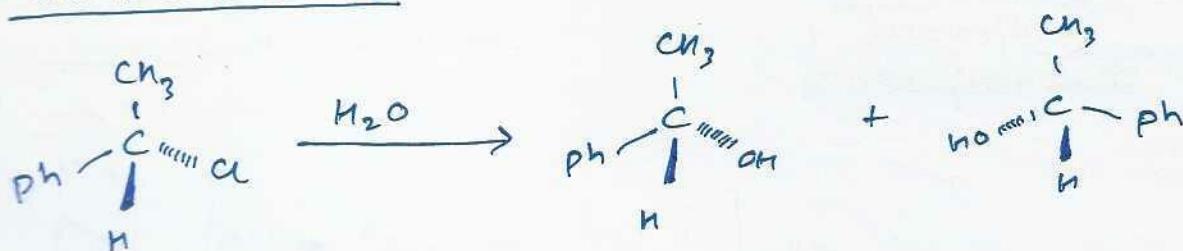
$3^\circ \text{RX} > 2^\circ \text{RX} > 1^\circ \text{RX}$ [$3^\circ \text{Carbocation} > 2^\circ \text{Carbocation} > 1^\circ \text{Carbocation}$]

Polar Protic solvent.

Solvolytic. (Solvent acts as nucleophile).

Weak Nucleophile.

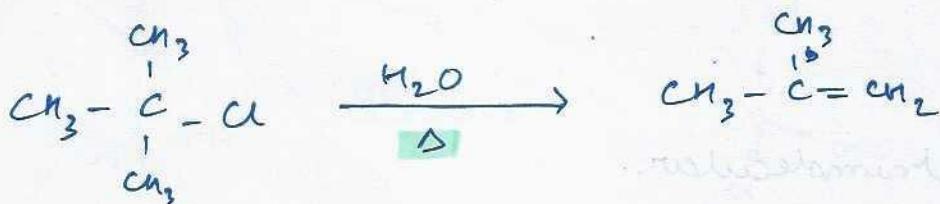
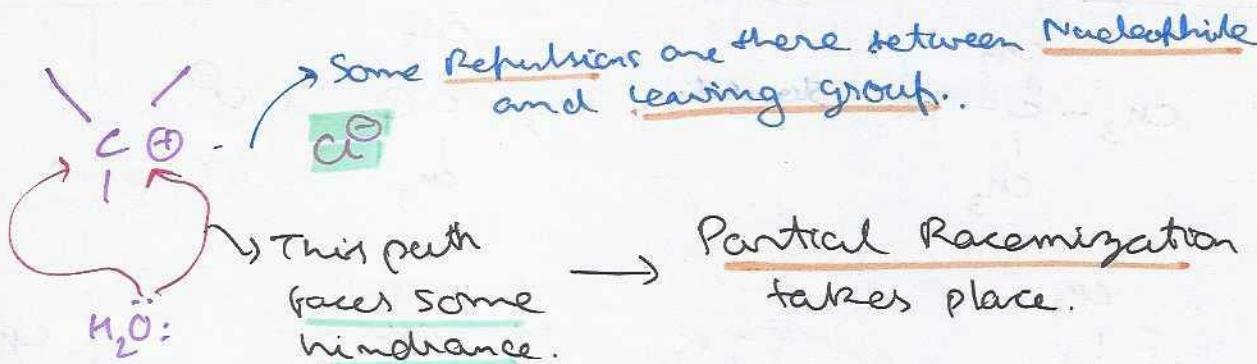
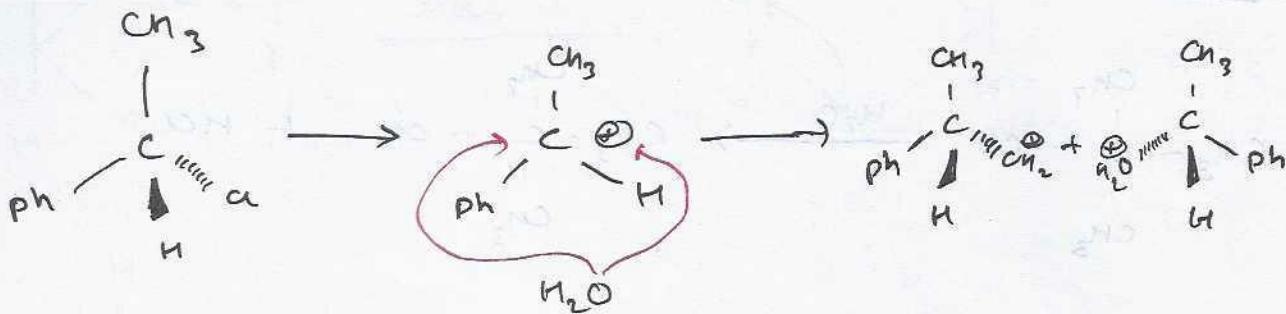
STEREOCHEMISTRY



Partial or complete racemization takes place.

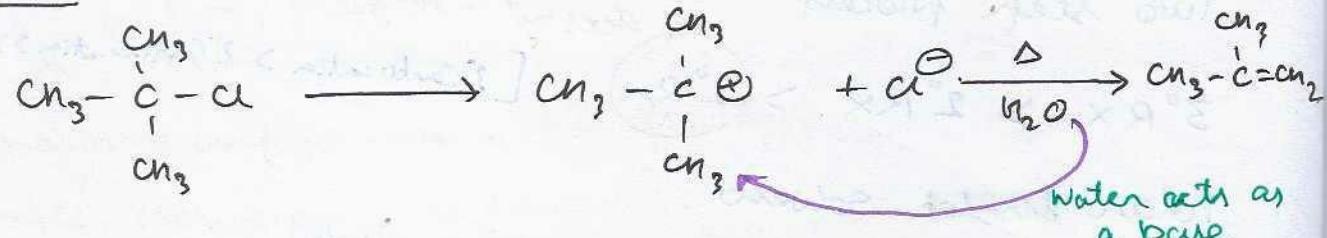
Mechanism

SUB



E₂

Mechanism



- Elimination needs more activation energy.
- It is entropically favoured as one more extra product is formed.

Leave

the

In the

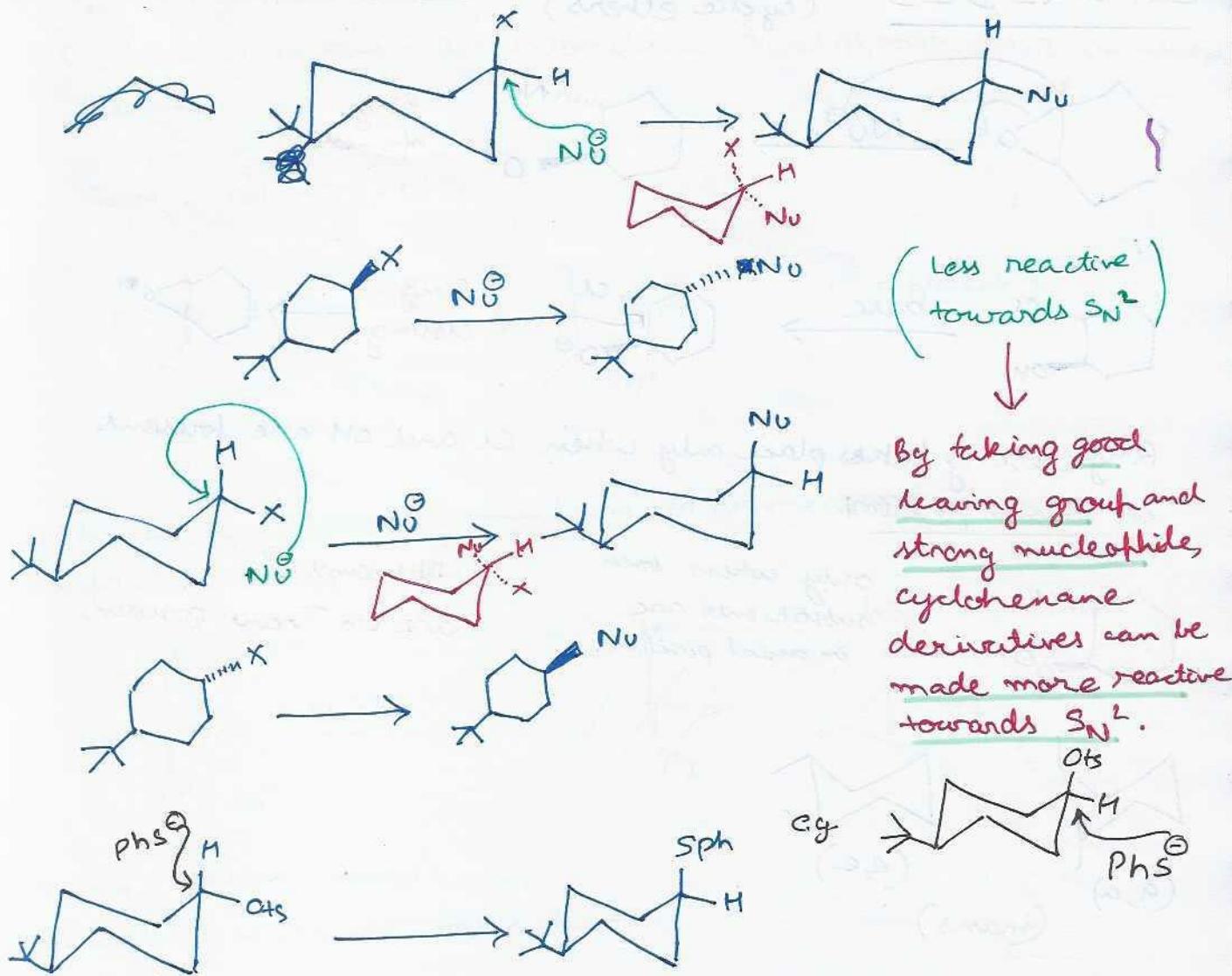


Repel
hydro
Grou

n

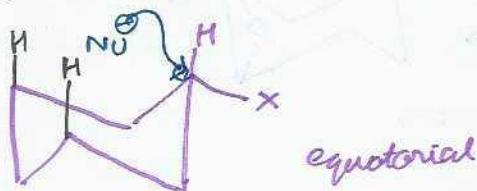
130

SUBSTITUTION IN CYCLOHEXANE DERIVATIVES

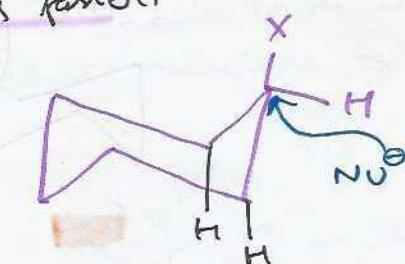


Leaving group present at axial position more reactive than leaving group present in equatorial position.

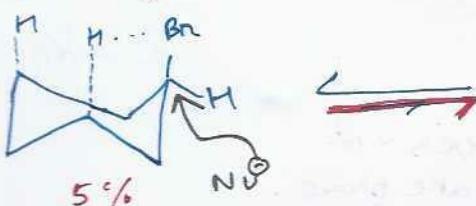
In the above example, 31 times faster.



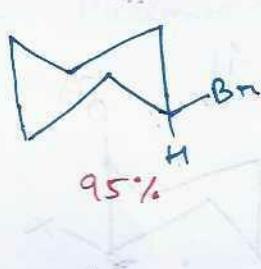
Repulsions between axial hydrogen and nucleophile.
Crowding takes place.



Repulsions are not present.
No crowding.
More favored.



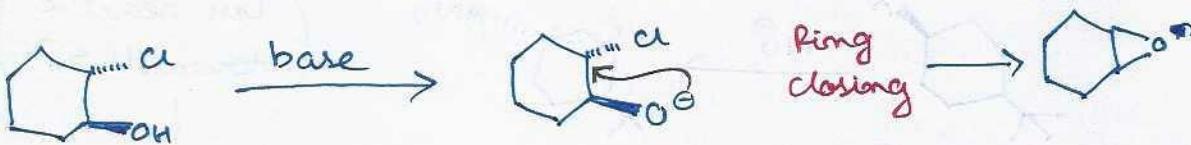
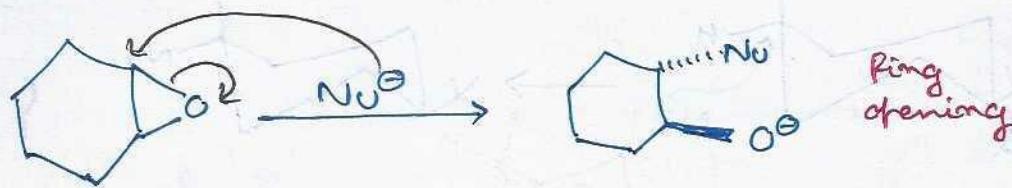
1,3 diaxial interactions
Less stable



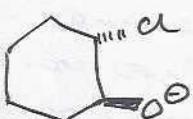
As percentage composition is less, reactivity is slowed down.

EPOXIDES

(cyclic ethers)



Ring closing takes place only when Cl and OH are present in trans position.

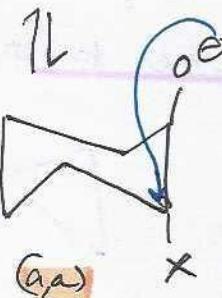
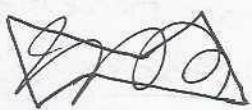


only when both
substituents are
in axial position.

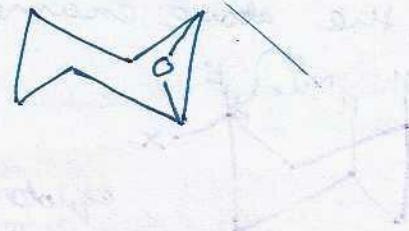
Nu^- and O^\ominus
are in Trans position



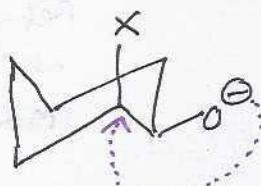
Not possible



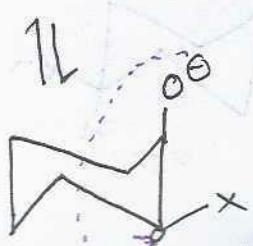
Not possible



Cis



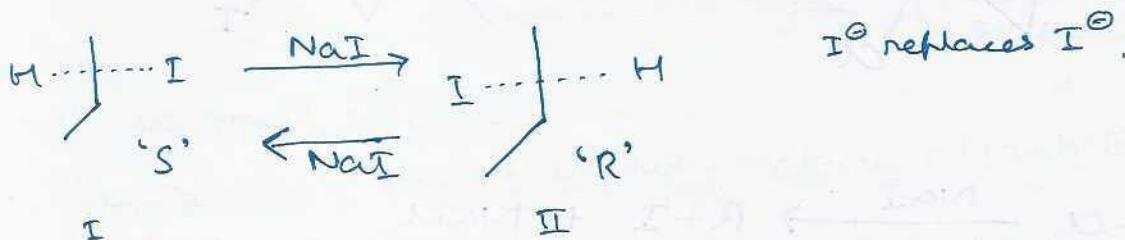
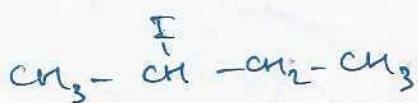
Does not
take place



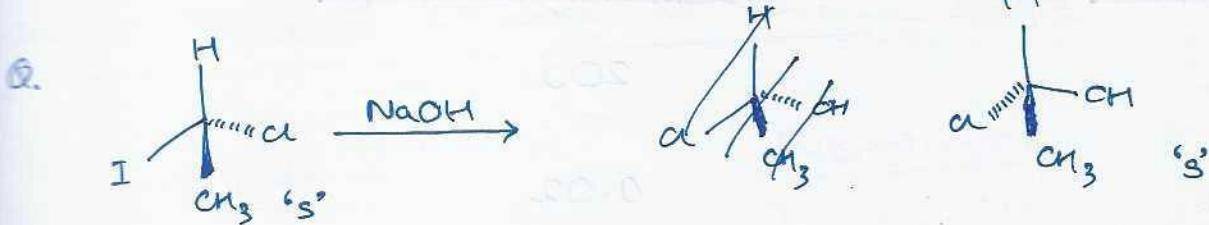
Does not
take place.

Q. Optically active - 2 - iodide

Optically active - 2 - iodobutane treated with NaI in ~~ether~~ acetone.



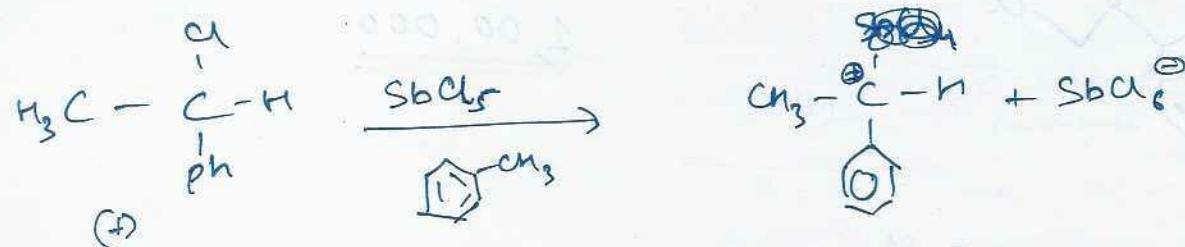
Ultimately, racemic mixture is formed.
(Optical activity lost).



In S_{N}^2 reaction always

- Inversion of configuration takes place
- Enantiomer formed
- Racemic mixture formed
- Single stereoisomer formed.

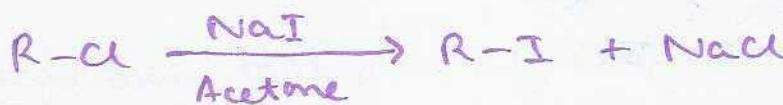
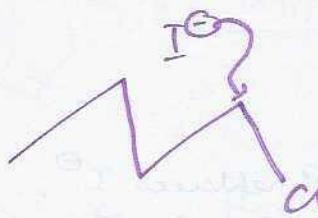
Q. (+) - 2 - chloro - 2 - phenylethane on reaction with SbCl_5 in the presence of Toluene gives racemic mixture by forming



RELATIVE REACTIVITY OF ALKYL CHLORIDES WITH IODIDE

Q.

Ion By S_N^2

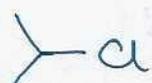


Compound

Selective Reactivity



200



0.02



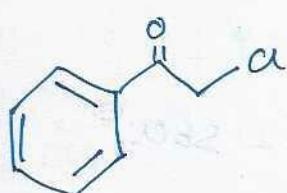
79



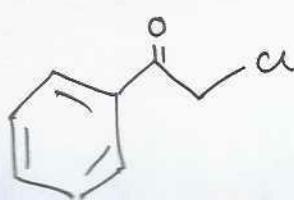
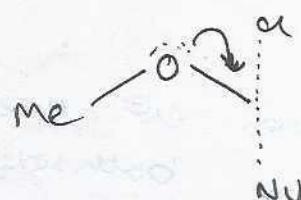
200



970



1,00,000

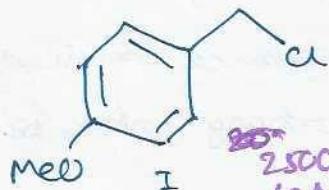


π CO group interaction with σ C-Cl

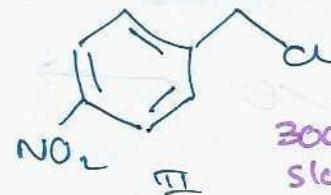
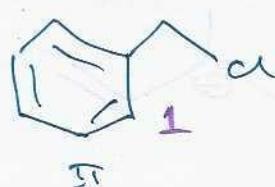
makes it highly reactive.

DIIDE

Q.



25°
2500 times
faster



3000 times
slower.

Reaction towards S_N^2 .



(Resonance
stabilisation)

S_N^2 : III is most reactive.

NO₂ decreases electron density making attack by nucleophile easy.

REACTIVITY OF ALKYL CHLORIDES TOWARDS SOLVOLYSIS

IN 50% AQUEOUS ETHANOL at 40°C

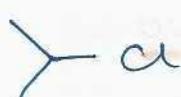
S_N^1

Compound

Reactivity



0.07



0.12



21,000

Tertiary
carbocation is
more stable than
allylic carbocation.



91

(2° carbocation in
resonance structure)



1



1,30,000

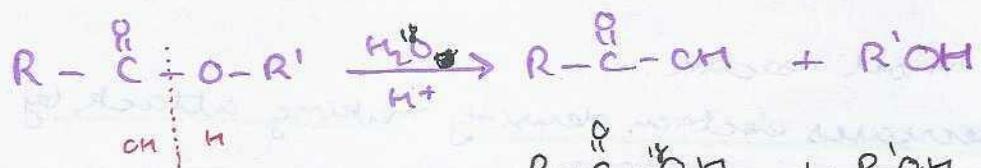


7,700



- Resonance stabilisation
- Tertiary carbocation.

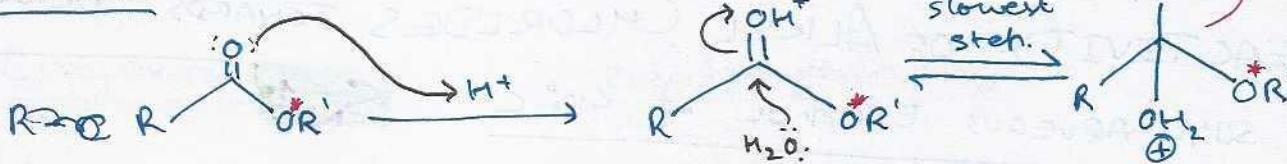
S_N1 REACTION IN ESTERS



sp^3 hybridisation
more steric hindrance.

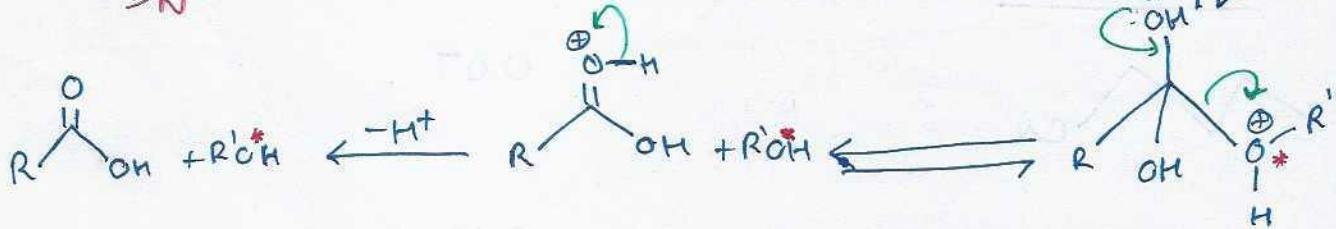


Mechanism

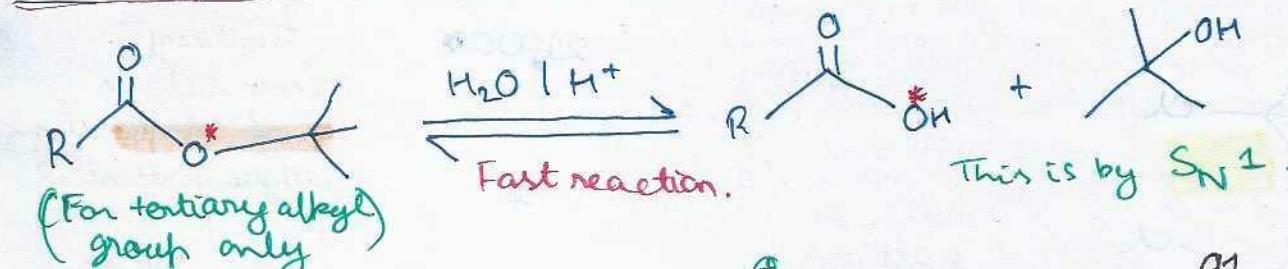


$\text{H}_2\text{O} \rightarrow$ weak nucleophile, can't attack directly.

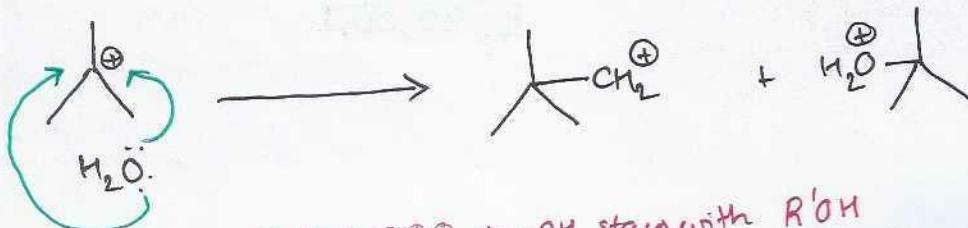
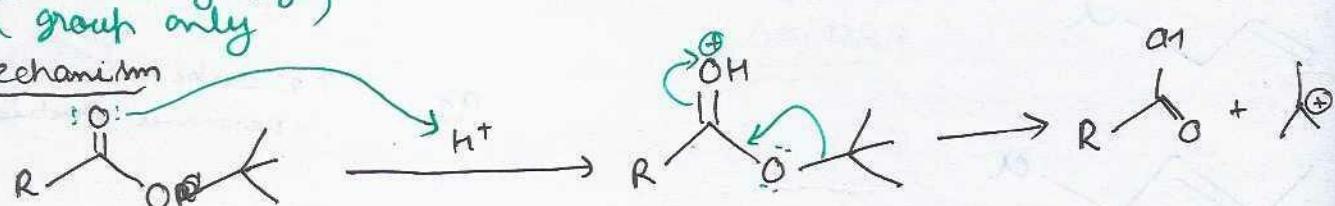
S_N2



If bulkiness of alkyl group increases, reactivity decreases

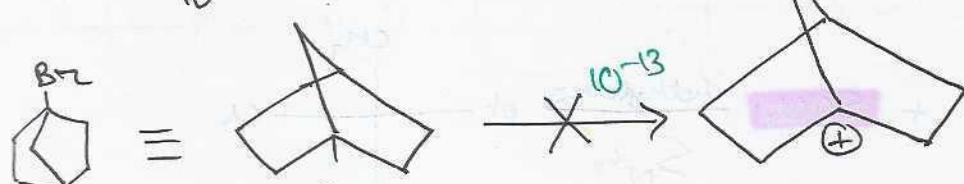
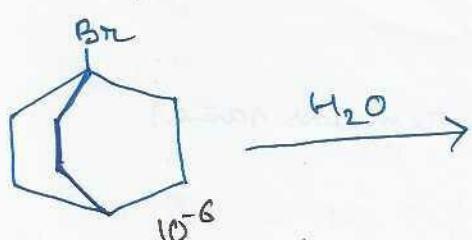
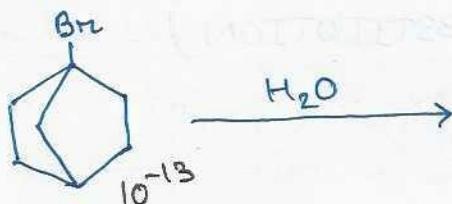


Mechanism

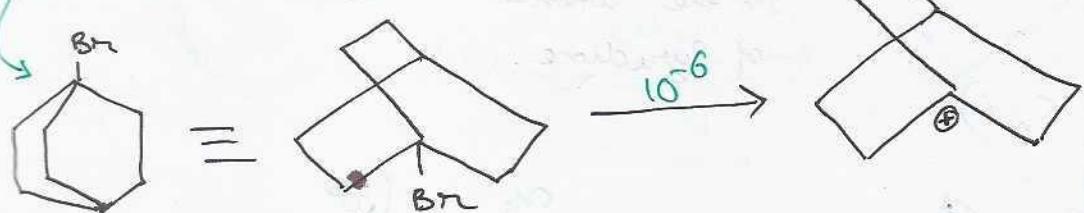


$S_N2 \rightarrow -\text{O}^+\text{O}$ in -OH stays with $\text{R}'\text{OH}$

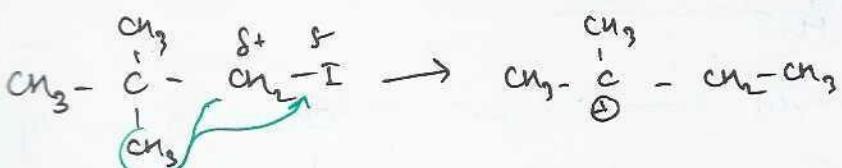
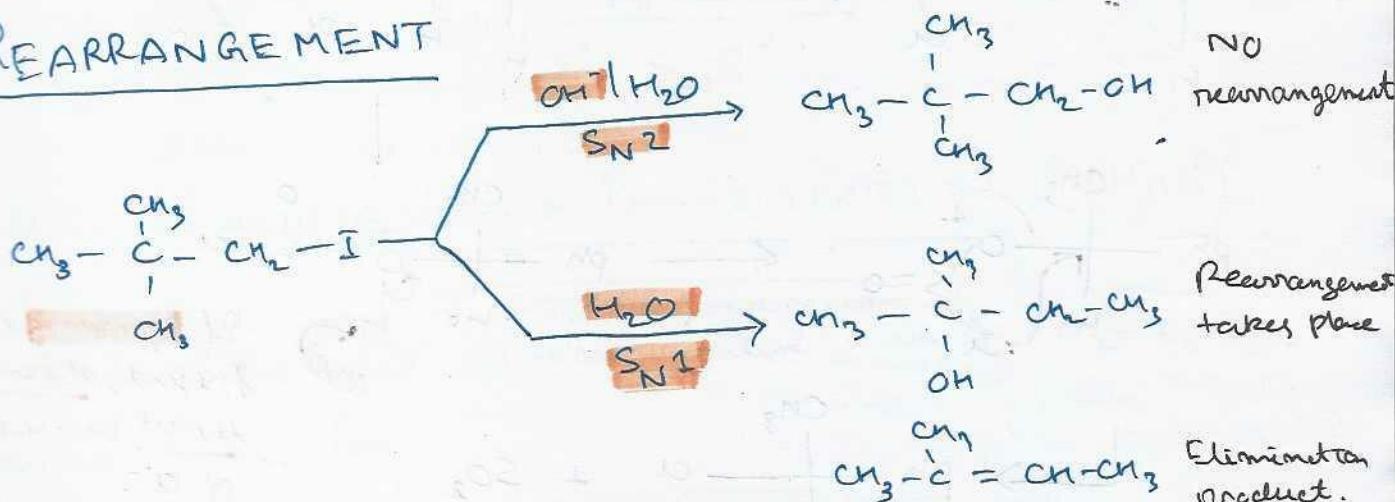
$S_N1 \rightarrow \text{O}$ in -OH stays with $\text{R}-\overset{\text{O}^-}{\underset{\text{(tert-butyl)}}{\underset{\text{C}}{\underset{\text{OH}}{\underset{|}{\text{H}}}}}}$



Cannot undergo S_N^1 or S_N^2 .



REARRANGEMENT

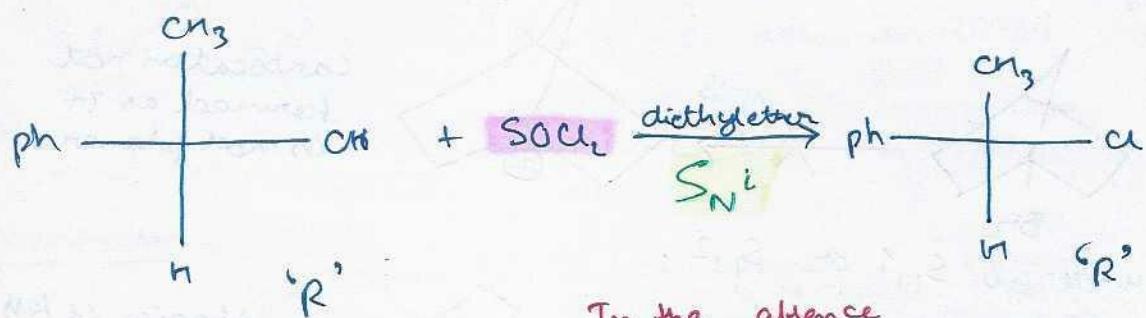


S_N^i (INTERNAL NUCLEOPHILIC SUBSTITUTION)

$S_N^2 \rightarrow$ Inversion

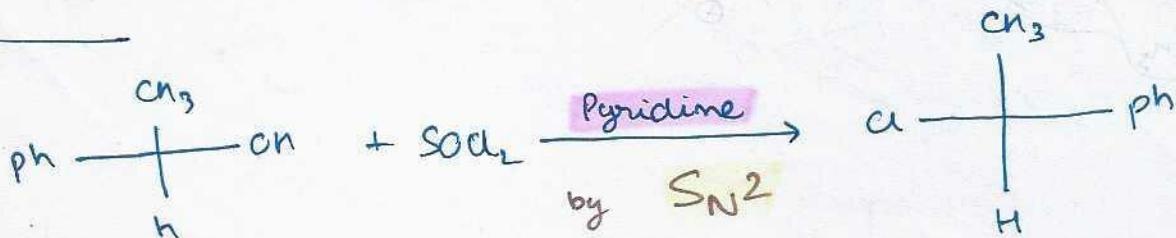
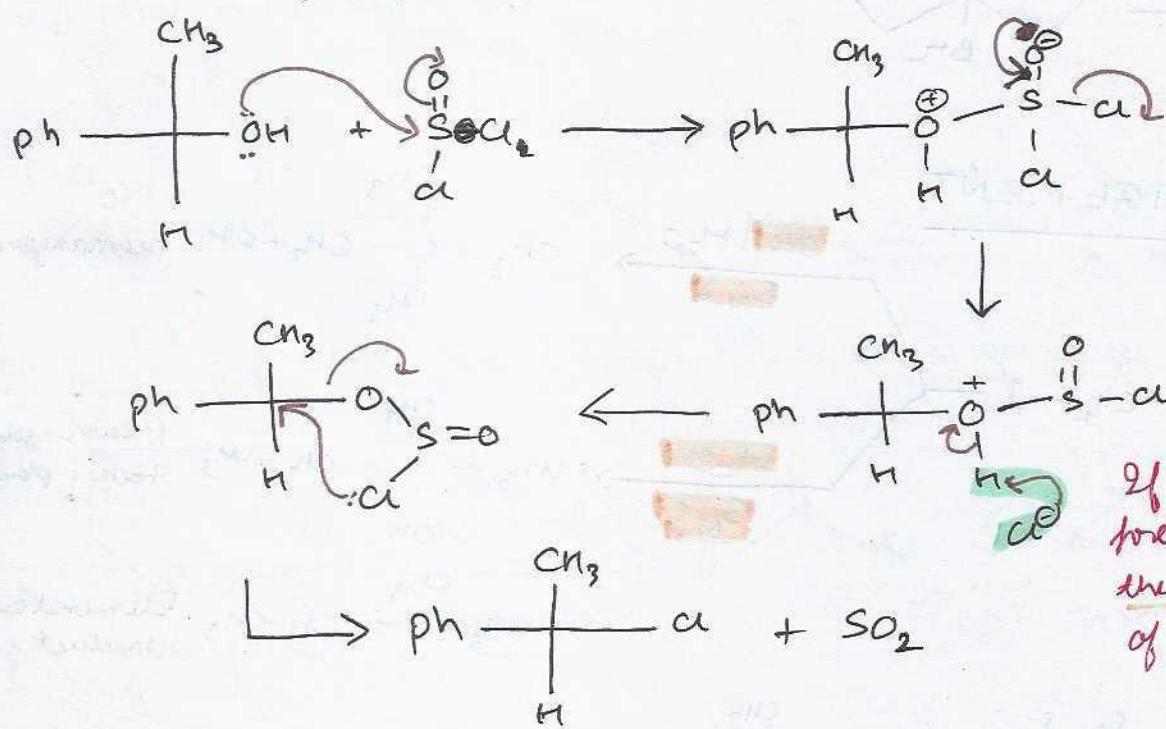
$S_N^1 \rightarrow$ Racemisation

$S_N^i \rightarrow$ Retention (Configuration remains same)



In the absence
of Pyridine.

Mechanism (S_N^i)

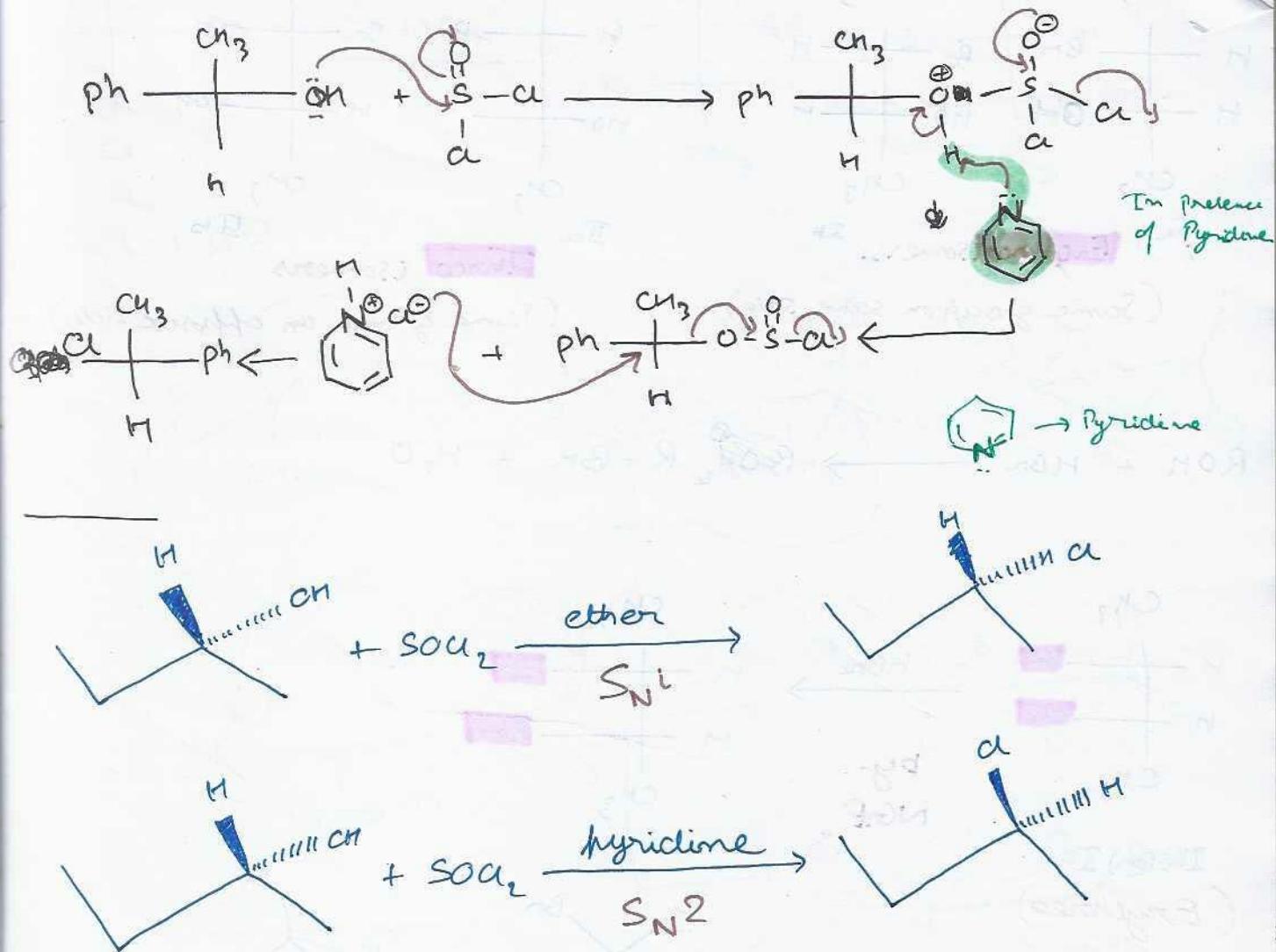


Pyridine acts as a base and removes the H^+ ion; in the place of Cl^- .

Cl^- is left and behaves as a nucleophile, attacks from back side

~~so H^+ is removed. S_N^2 is not shown~~

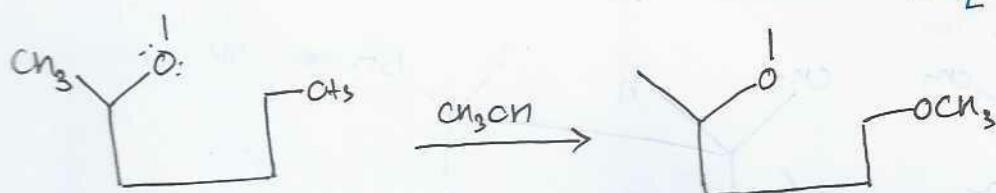
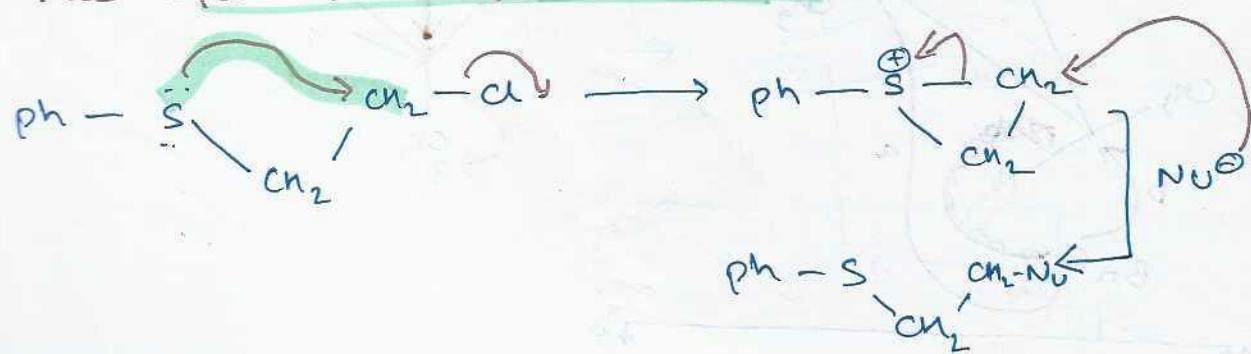
Mechanism (S_N2)



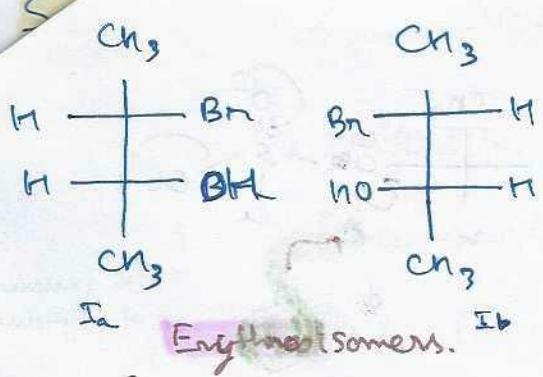
NEIGHBOURING GROUP PARTICIPATION (NGP)

$\text{Ph-S-CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ is more reactive than $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Cl}$ towards substitution.

Due to participation of Sulfur atom.

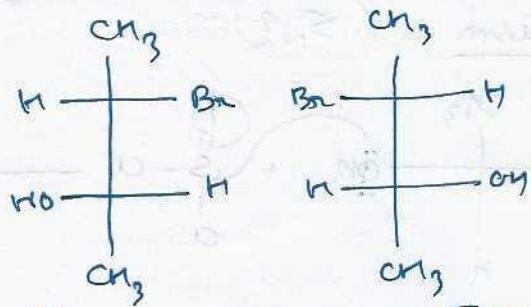


Elements having lone pair or electrons participate.



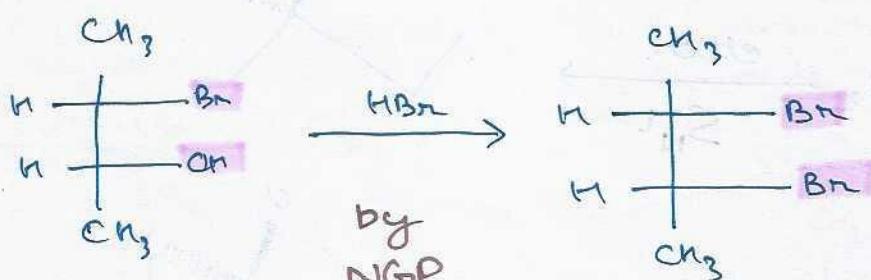
Erythroisomers.

(Same group on same side)

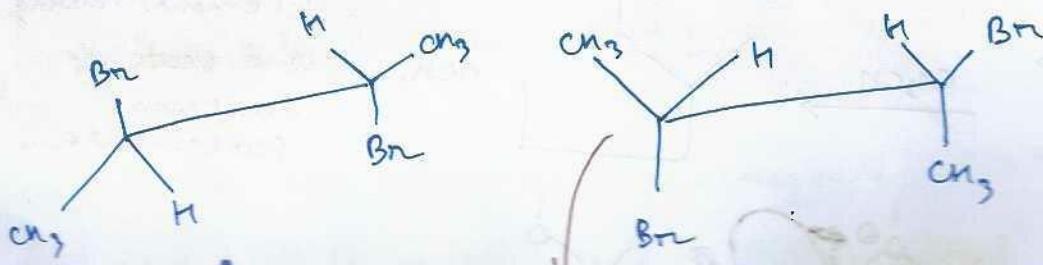
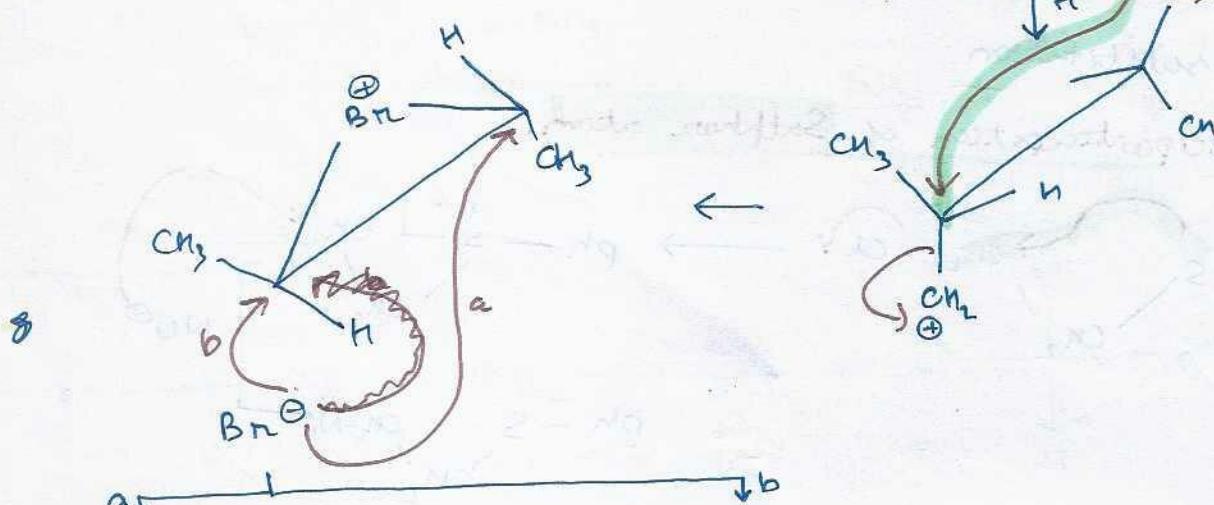
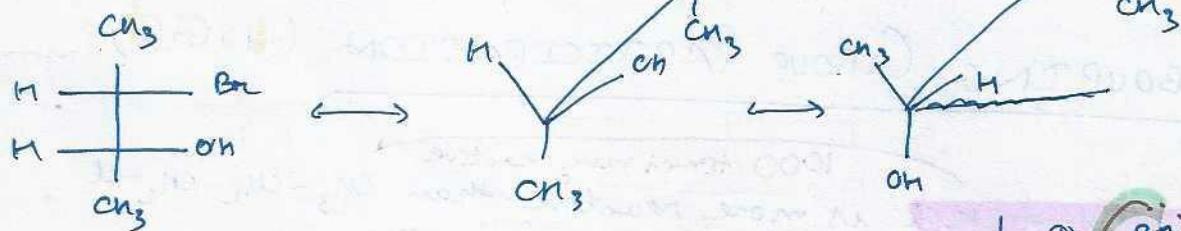


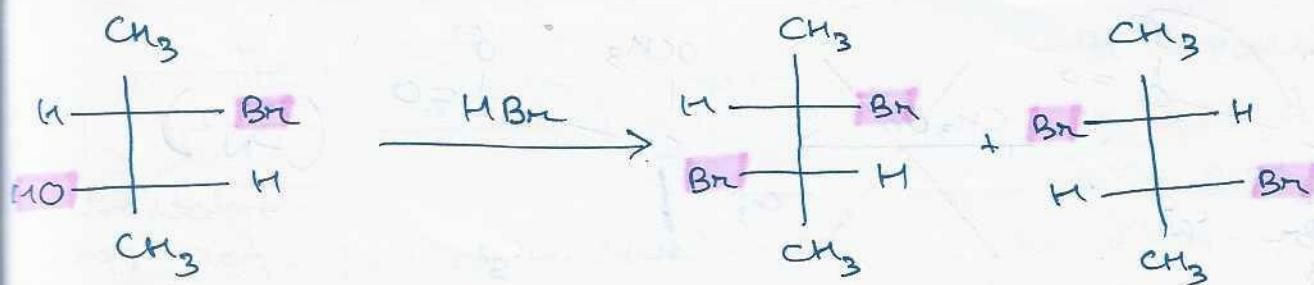
Threo isomers

(Same group on opposite side)



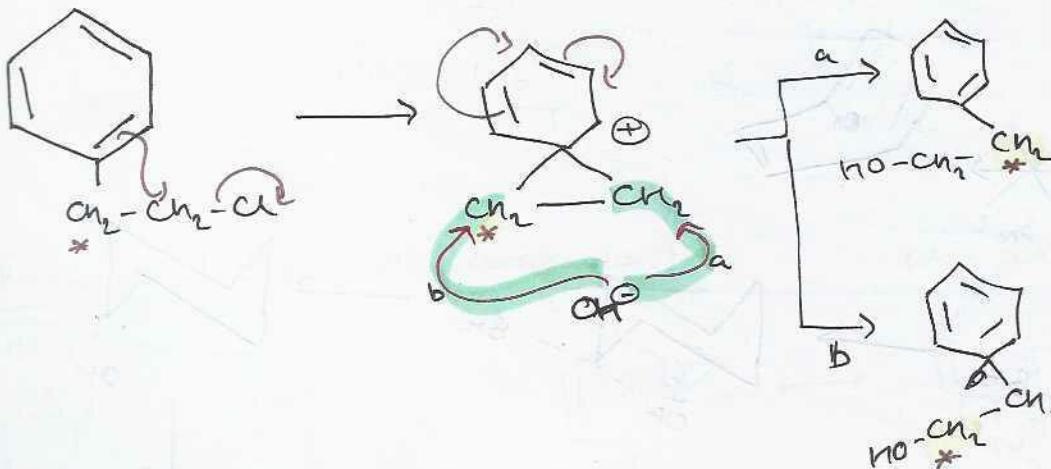
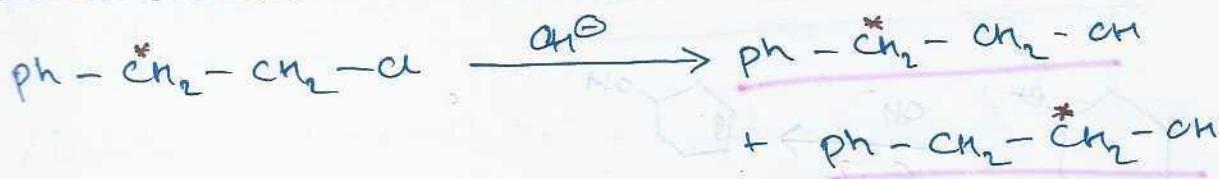
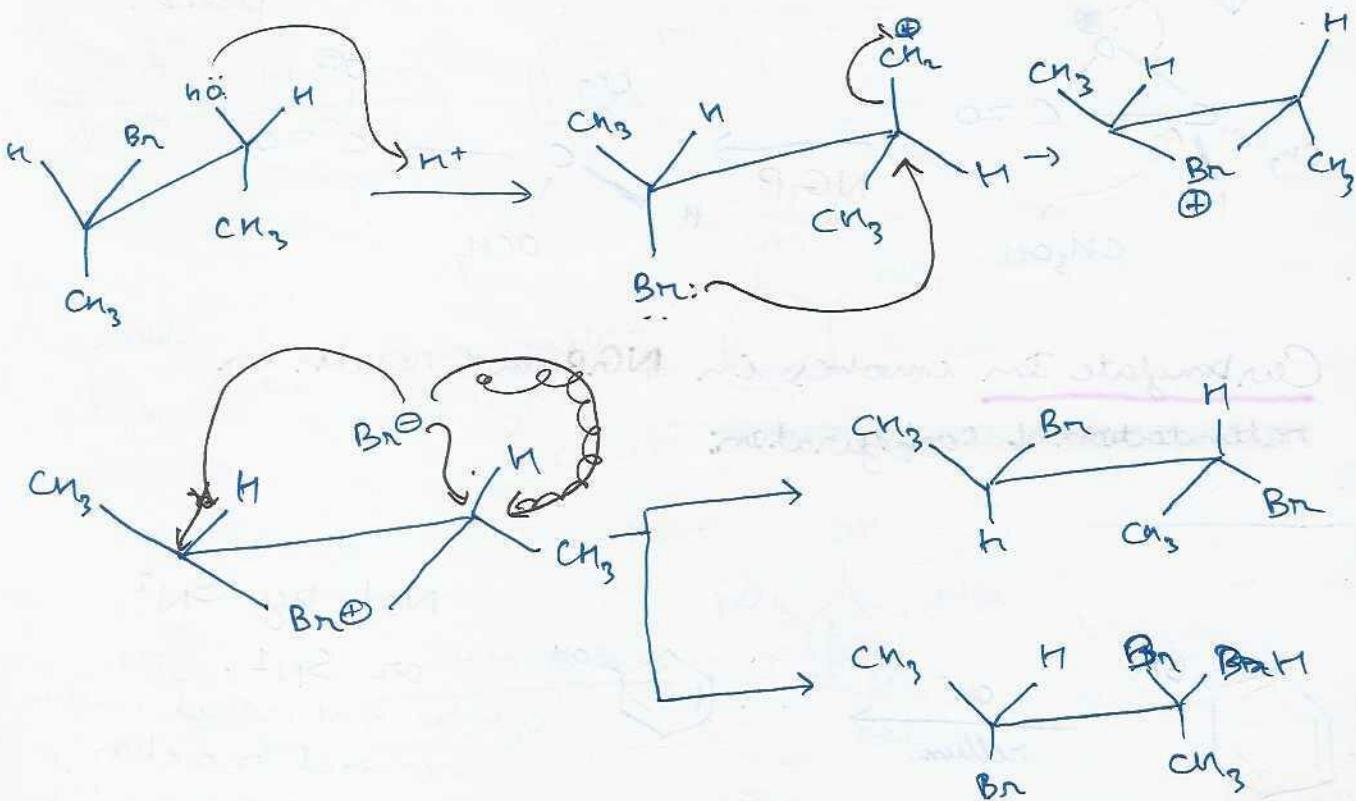
Ia (or) Ib
(Erythro)

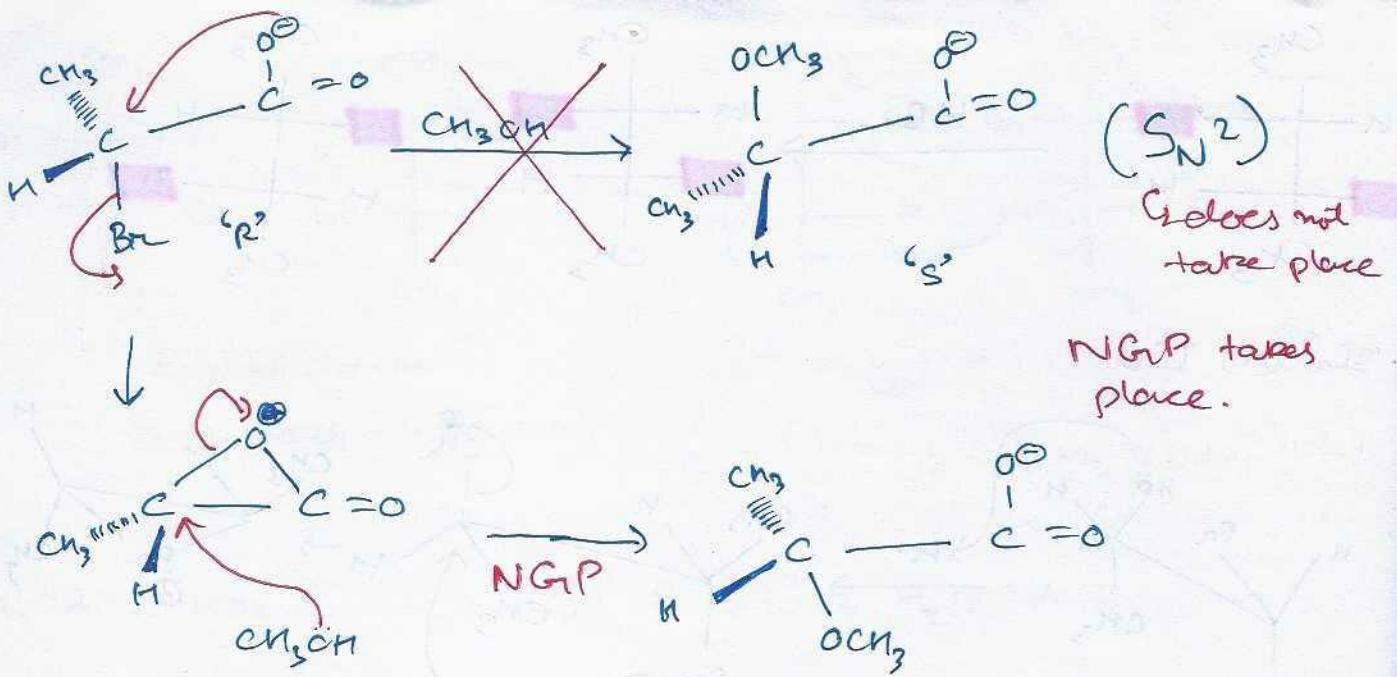




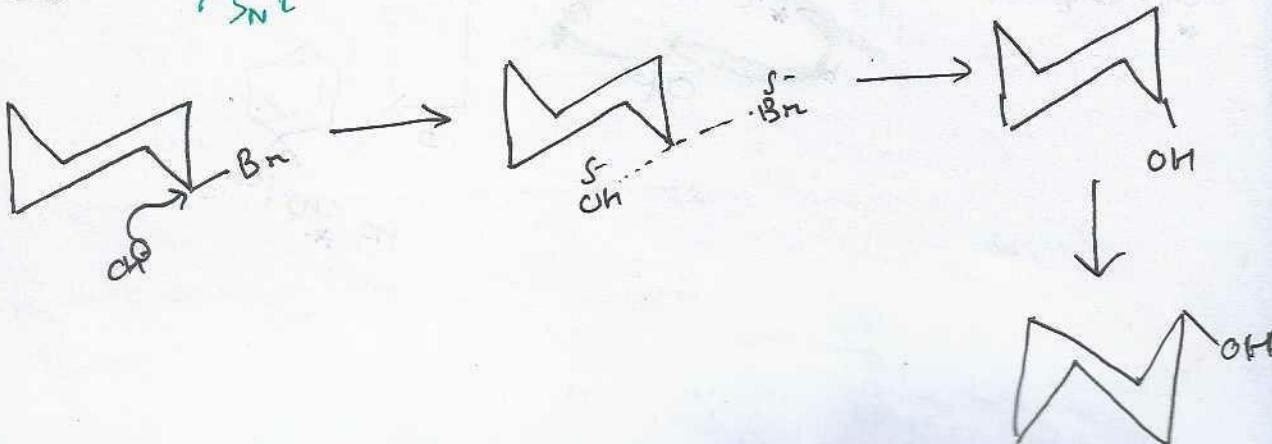
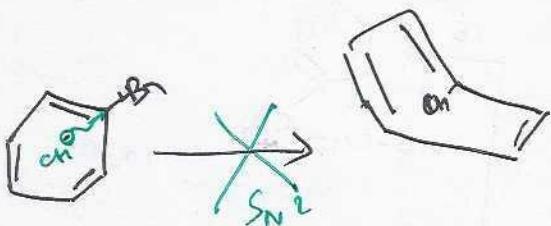
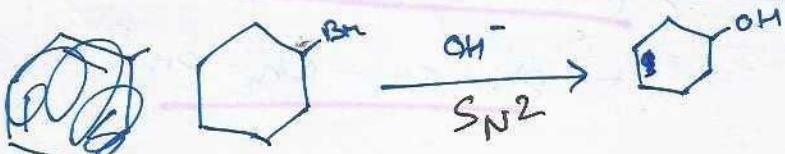
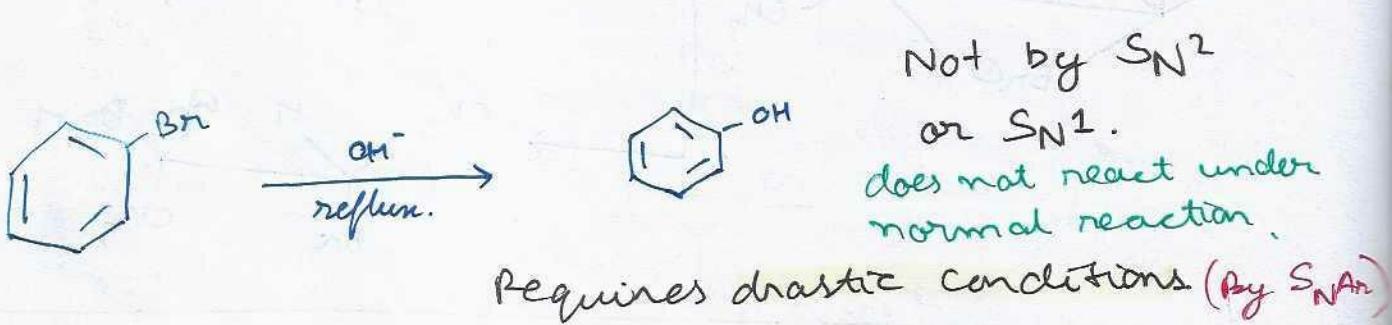
IIa (or) IIb

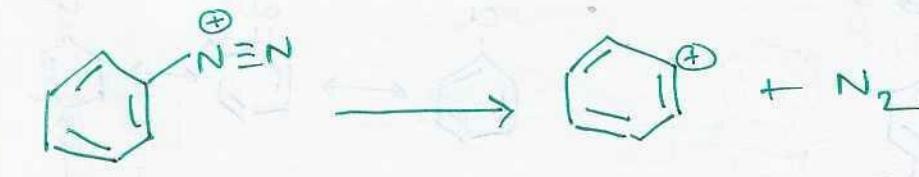
(de)





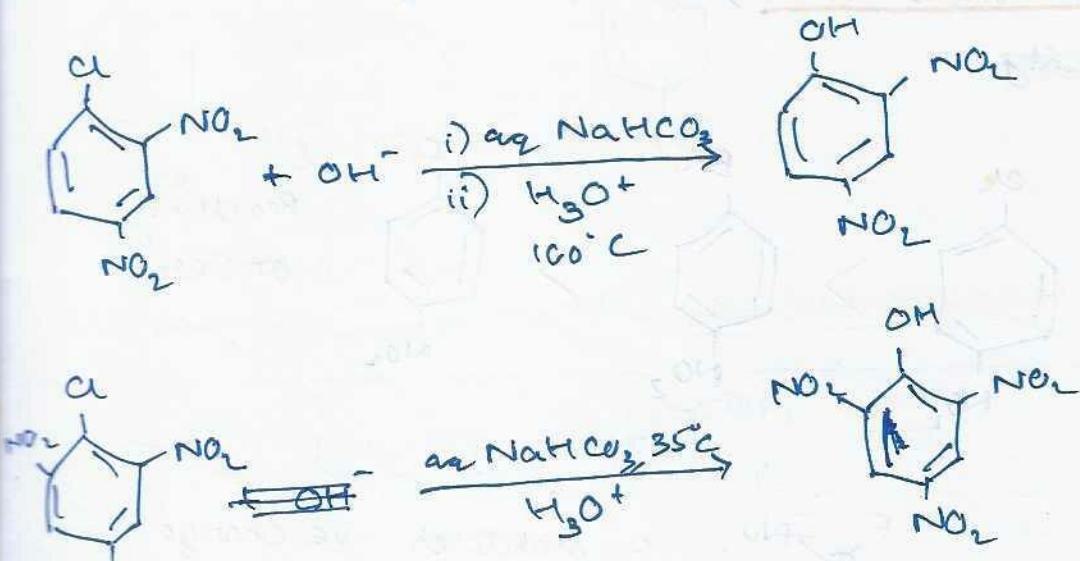
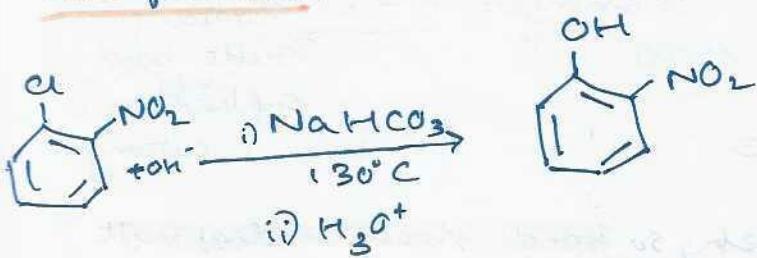
Carbonylate Ion involves in NAC and results in retention of configuration.





It is possible
as $\text{N}=\text{N}$ is a
very good leaving
group.

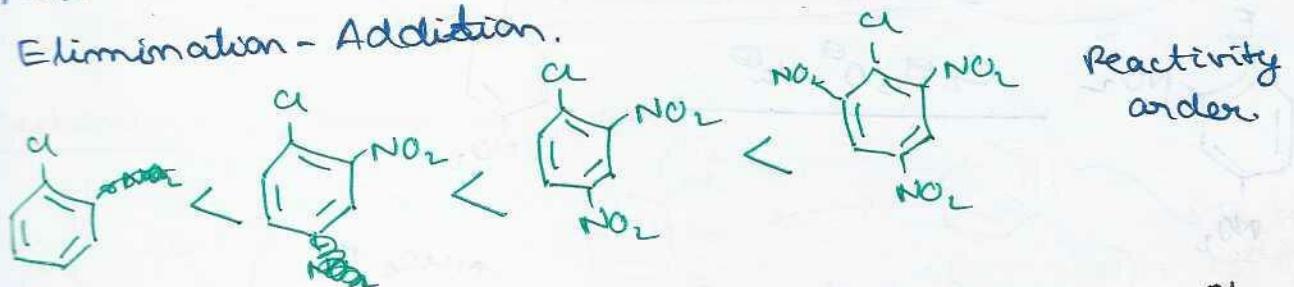
Otherwise phenyl carbocation is
not formed.



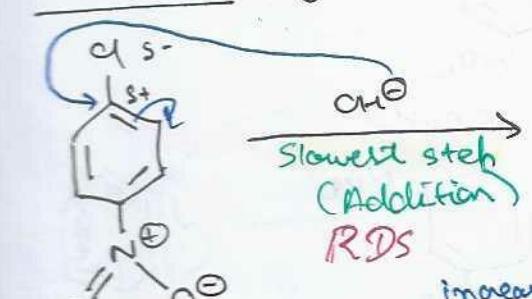
AROMATIC NUCLEOPHILIC SUBSTITUTION ($S_{\text{N}}\text{Ar}$)

① Addition - Elimination

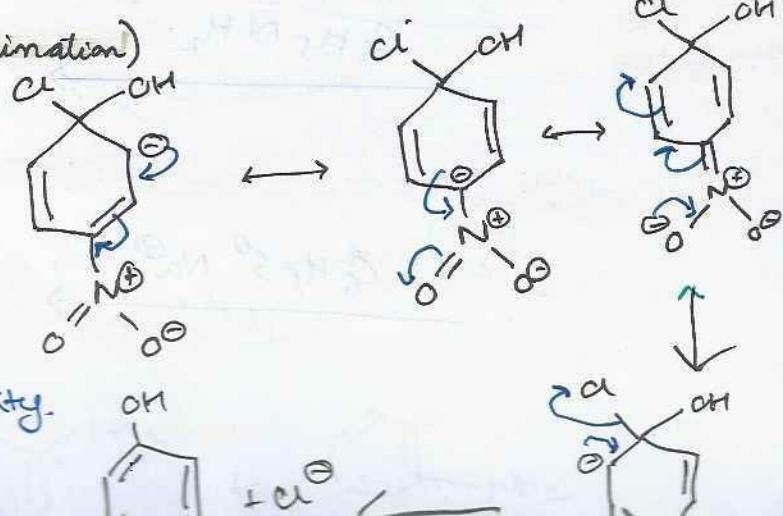
② Elimination - Addition.

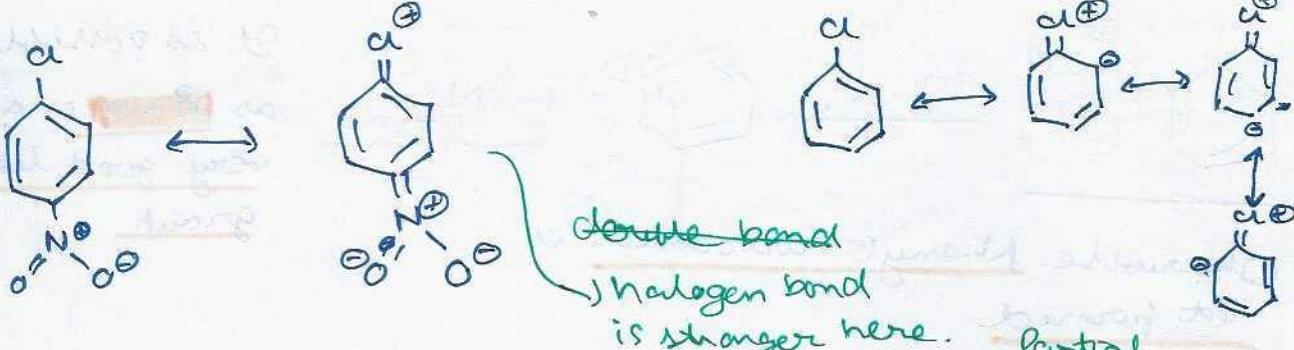


mechanism (Addition-Elimination)



Negative charge is
increased reactivity.

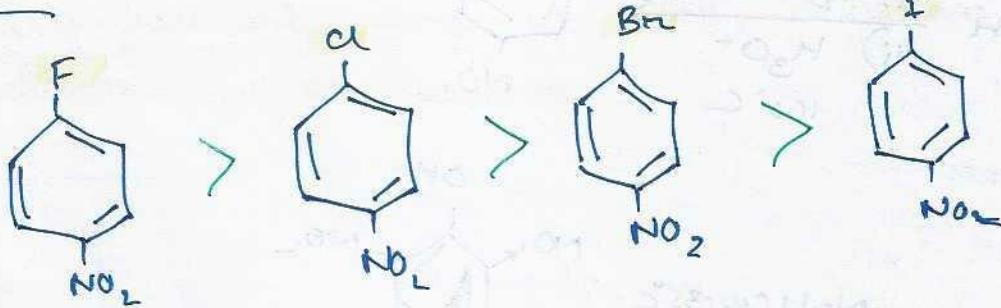




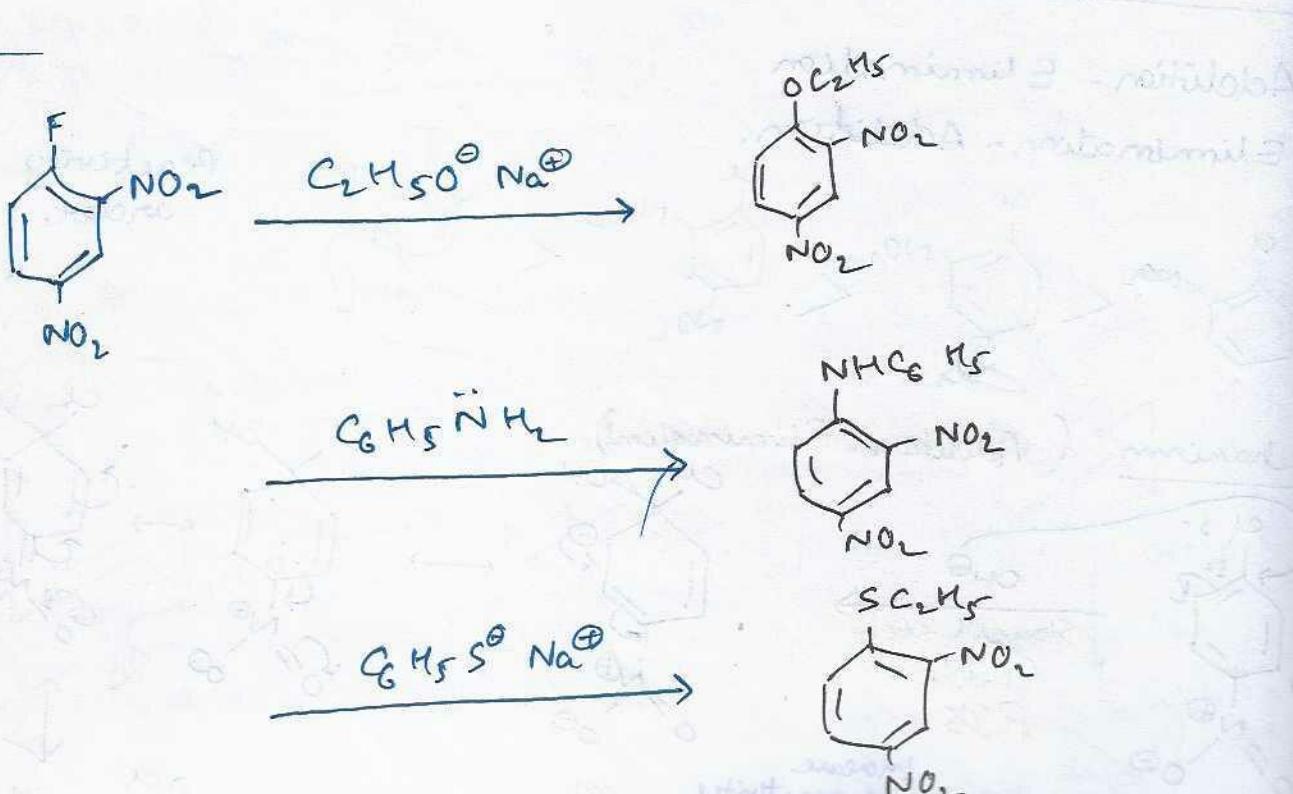
Slowest step addition of OH^-

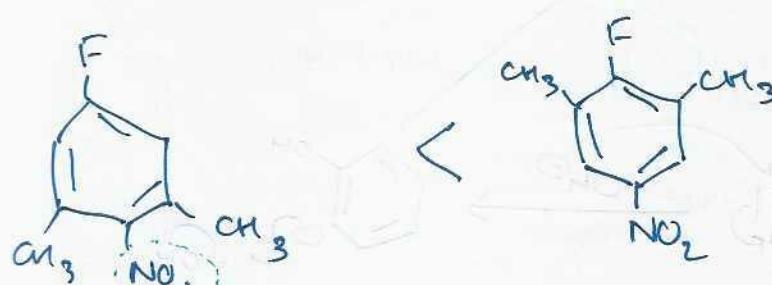
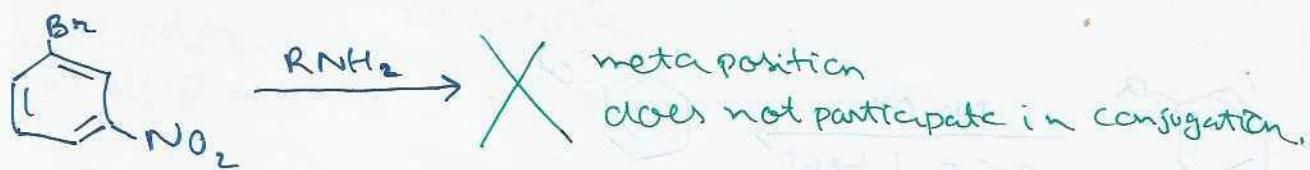
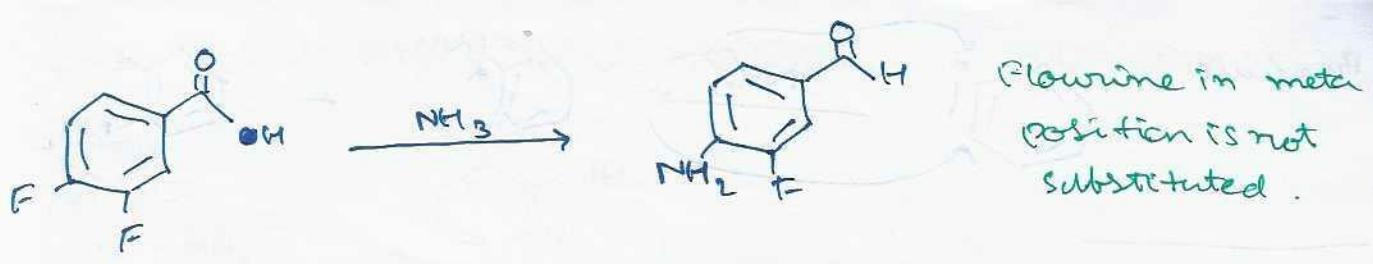
Elimination of Cl^- is last step, so bond strength does not influence reactivity.

Partial Double bond explanation is wrong-



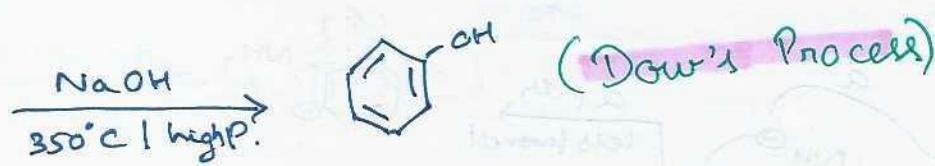
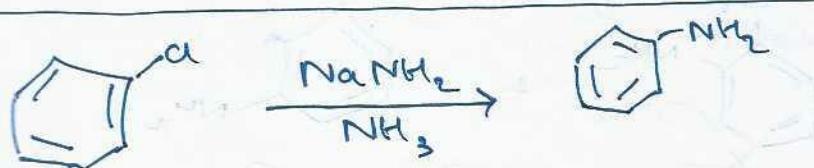
Reactivity order.





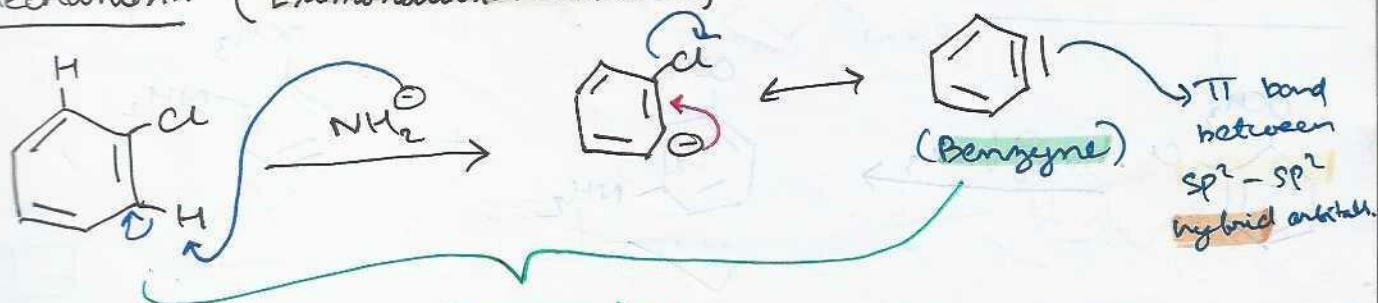
out of plane

All previous reactions are addition-elimination type

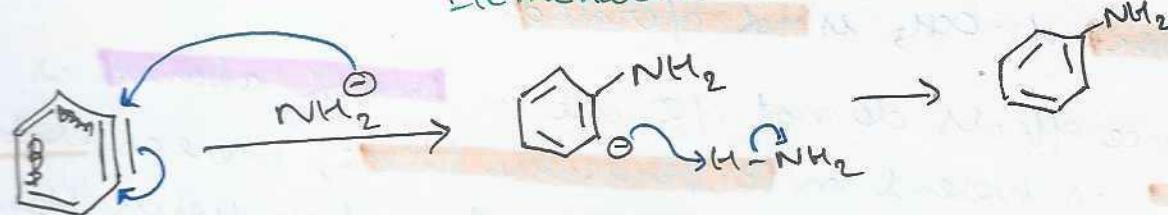


These reactions are elimination-addition type.

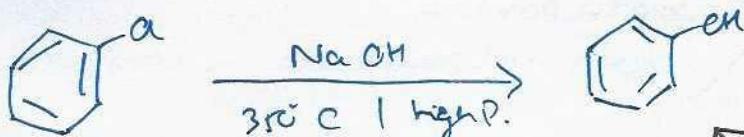
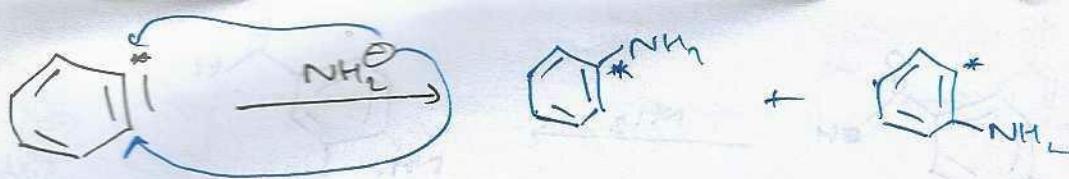
Mechanism (Elimination-Addition)



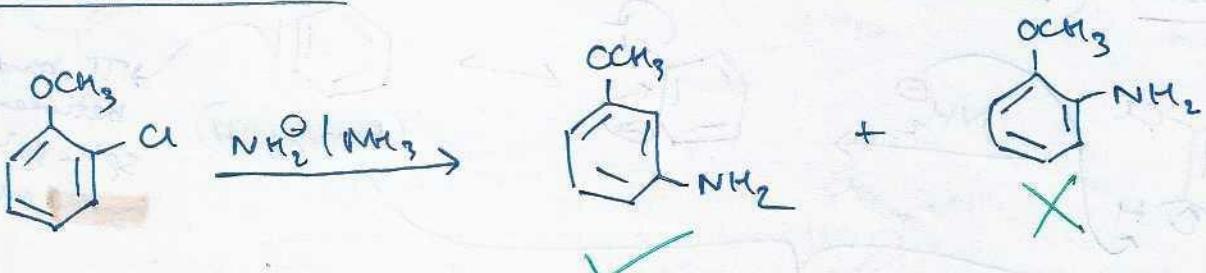
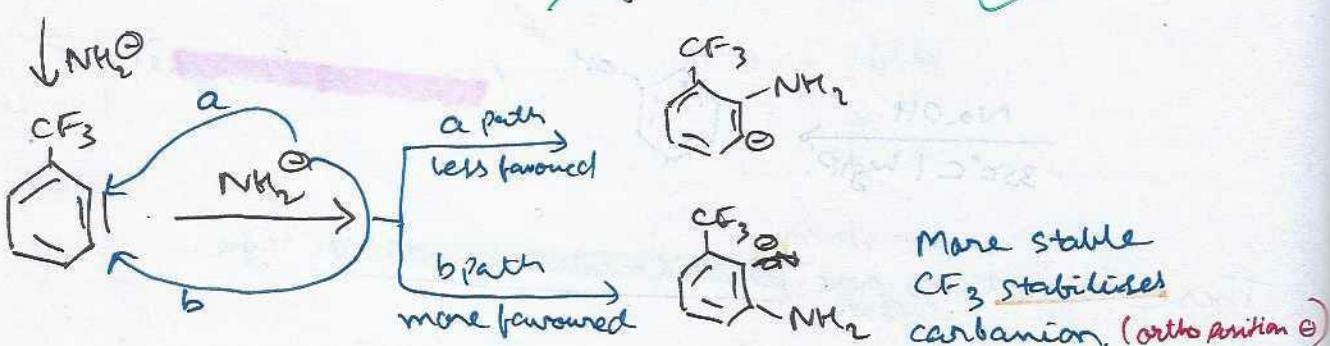
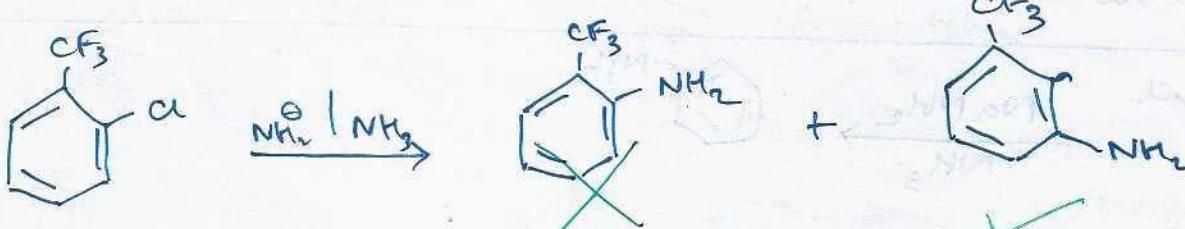
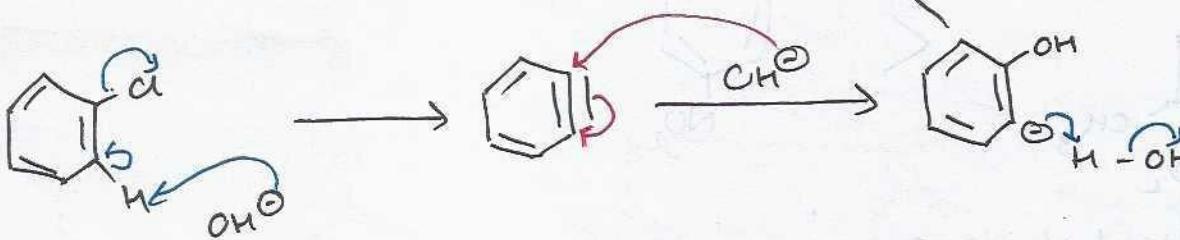
Elimination



Because



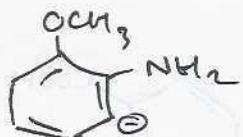
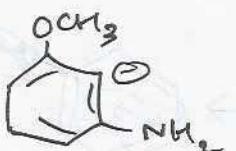
Mechanism



+M effect of $-\text{OCH}_3$ is not operated.

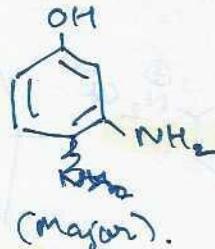
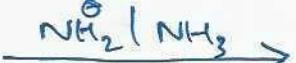
Resonance effects do not operate in benzyl carbocation as lone pair is present in perpendicular plane, whereas electro pair is present in sp^2 orbital of carbon which lies in plane of benzene ring.

Only effect +I, -I effect operates.

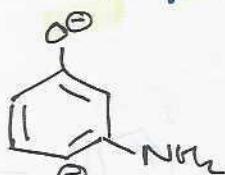
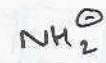


Stabilised by
-I effect.

Less stable.

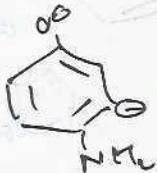


(Major).

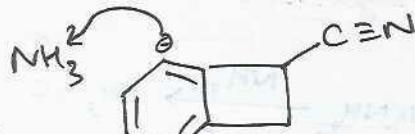
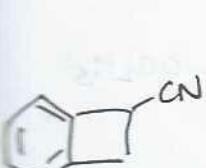
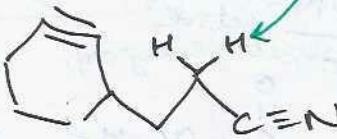
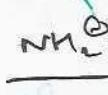
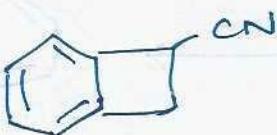
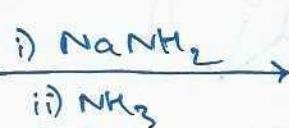
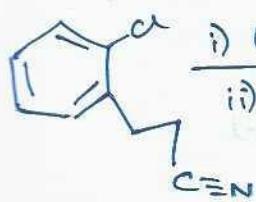


more the separation between -ve charges, more is the stability.

O^+ shows +I effect.

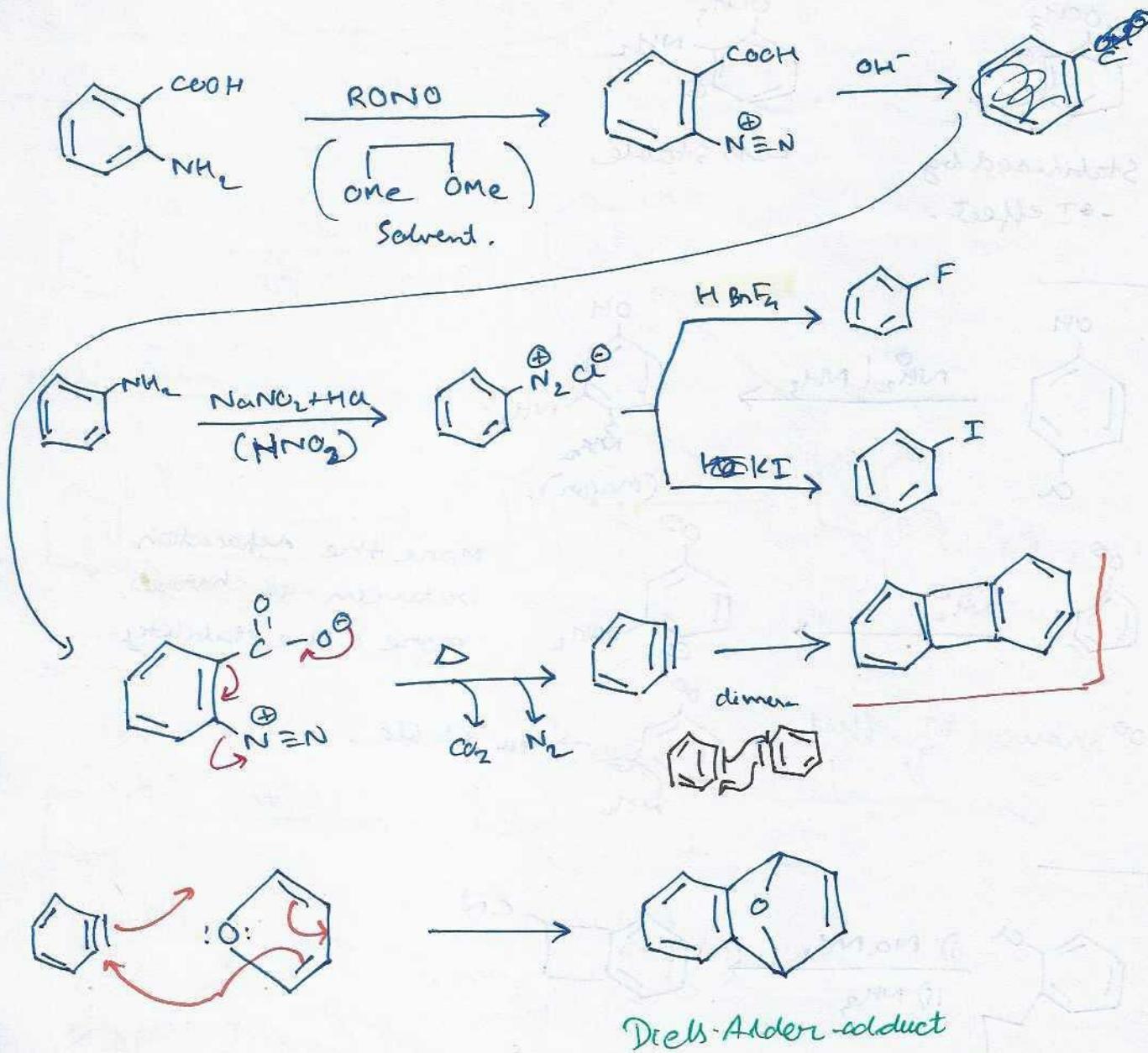


→ less stable.

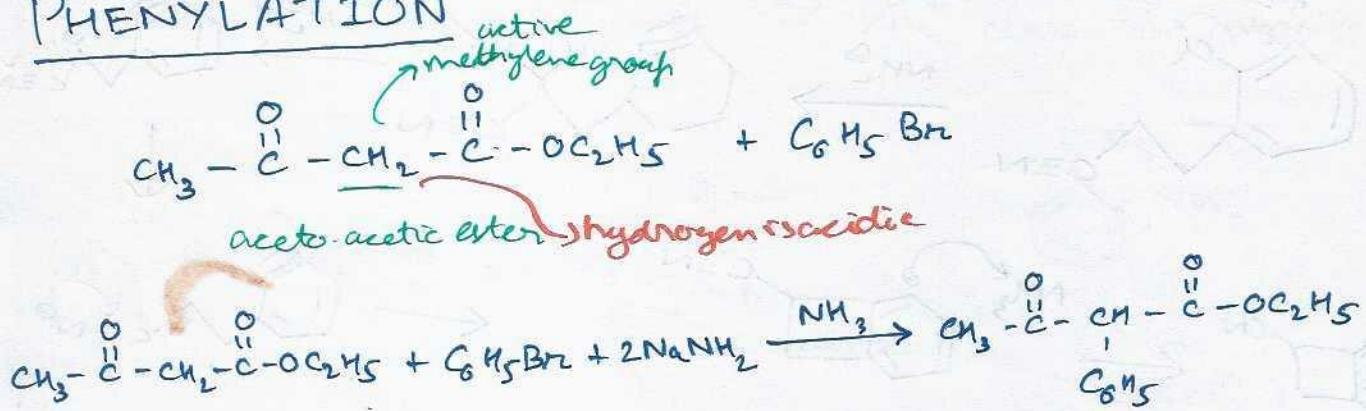


EVIDENCE FOR BENZYNE MECHANISM

2nd

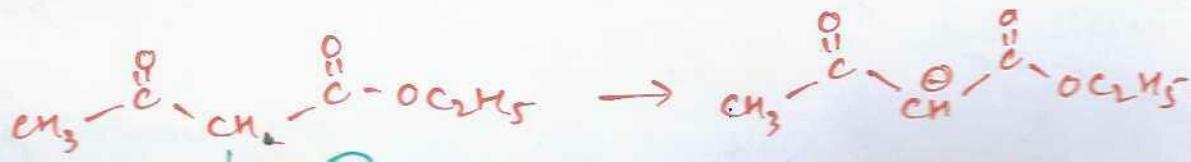


PHENYLATION

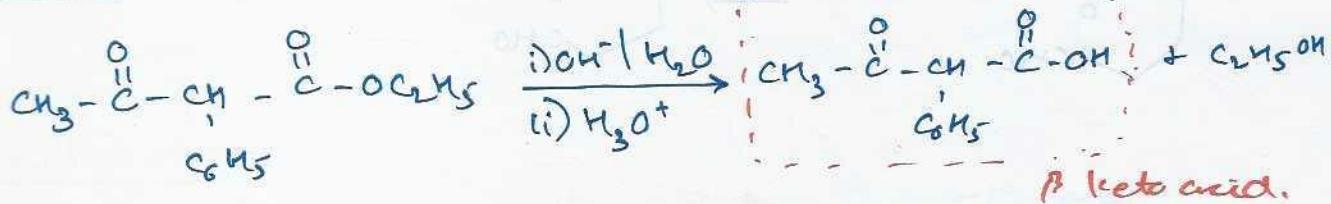
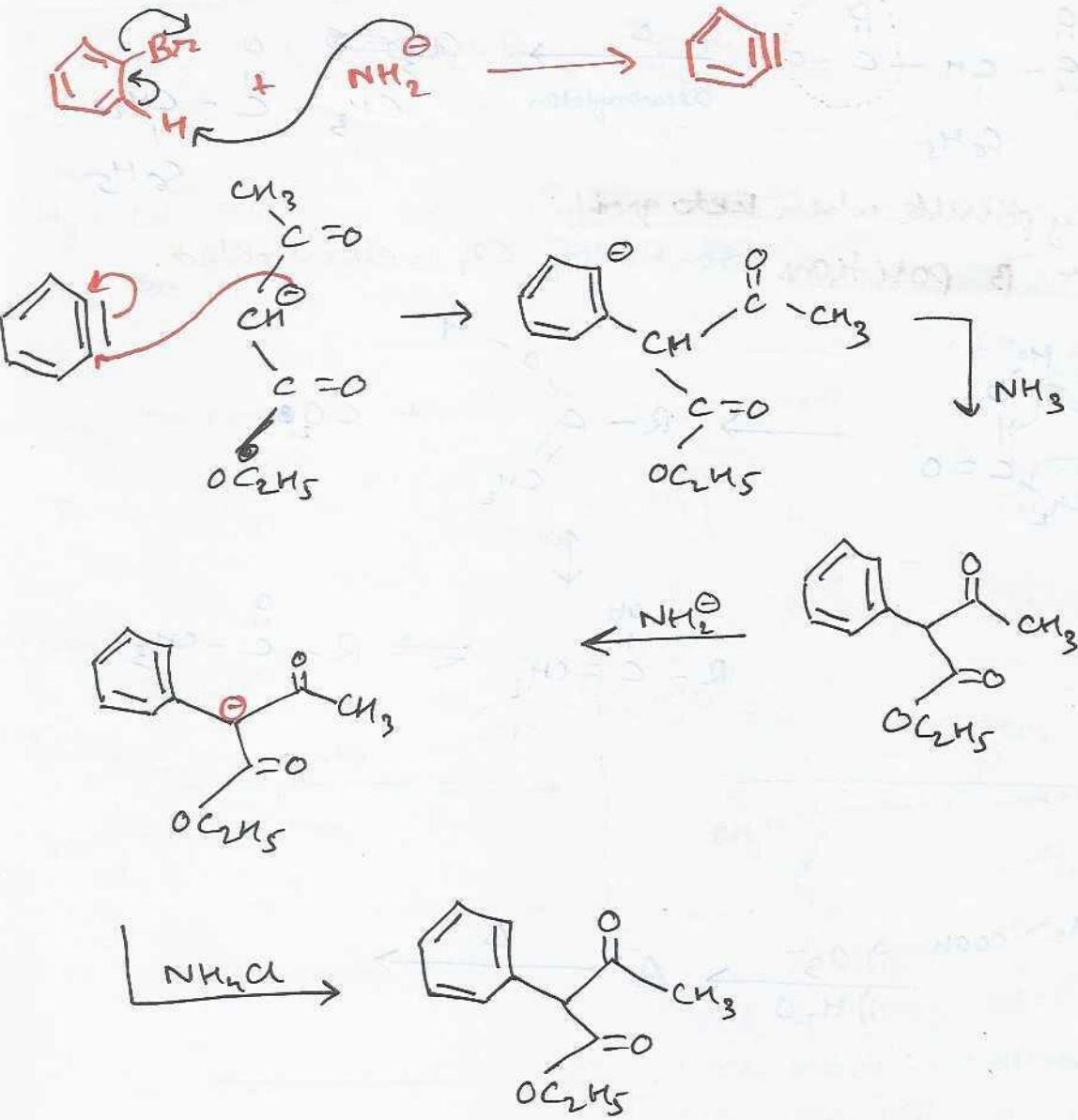


Takes place via Benzyne Mechanism

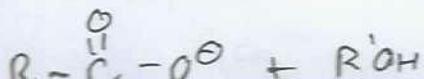
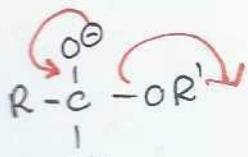
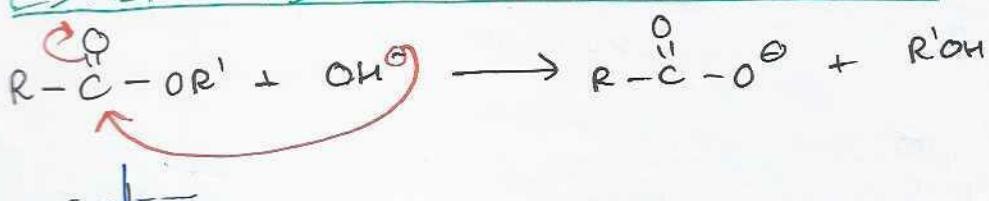
1 equivalent of NH_2^+ ion removes acidic hydrogen from ester

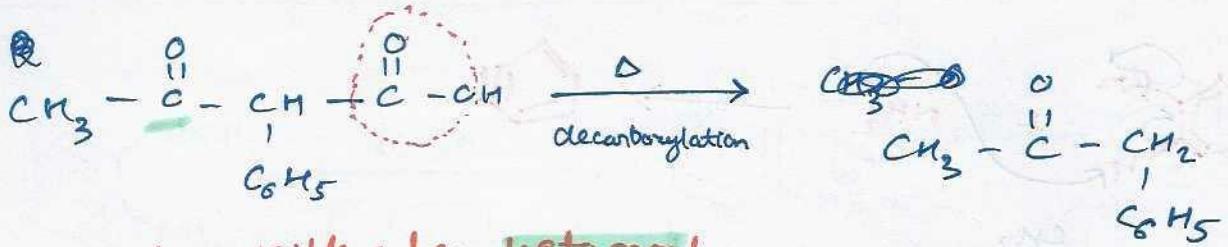


2nd equivalent NH_2^0 forms Benzene.



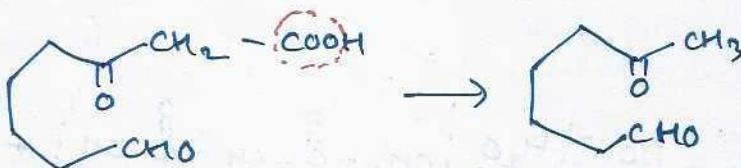
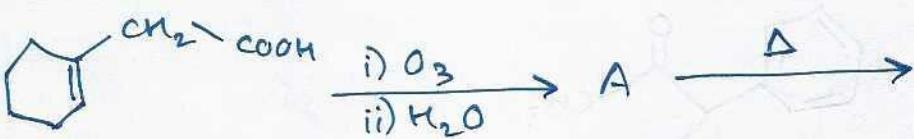
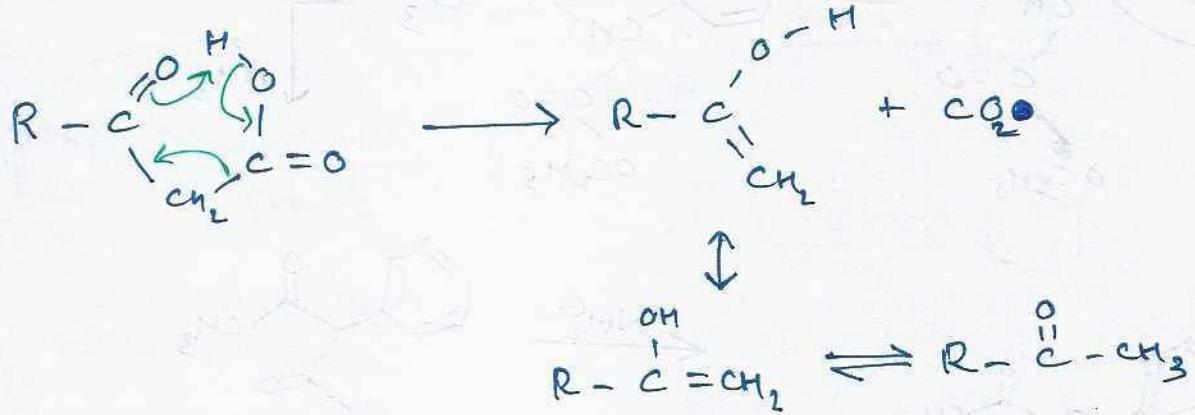
ESTER HYDROLYSIS IN BASIC MEDIUM





only possible when **keto group**

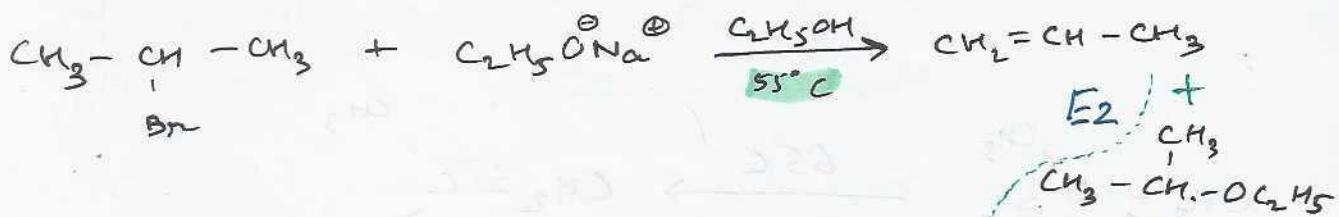
in β position. \rightarrow on heating CO_2 is eliminated.



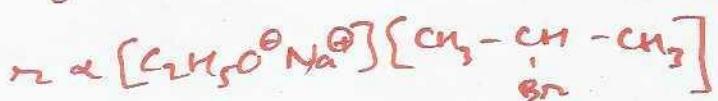
ELIMINATION

E_2 E_1 E_1CB

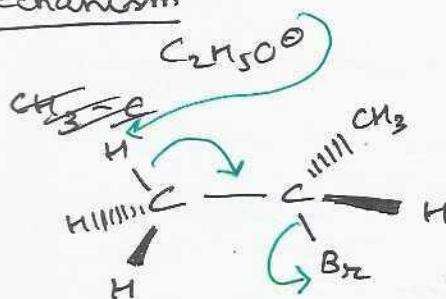
Pyrolytic



Strong base $\rightarrow \text{NH}_2^\ominus, \text{RO}^\ominus$ E_2 is favoured.

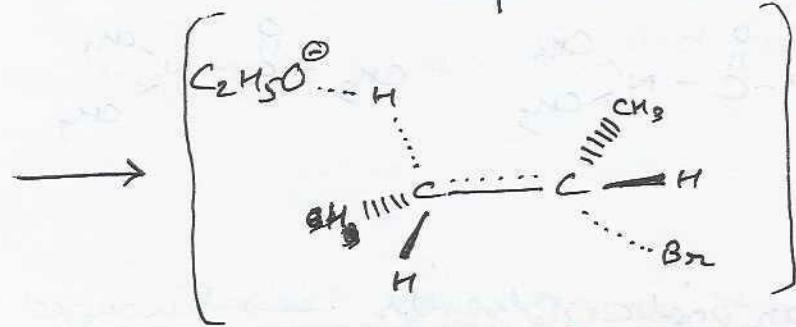


E_2 Mechanism



Anti-periplanar

Thus, tertiary alkyl halides are more reactive towards E_2 .



Alkene like transition state.

More substituted alkene like transition state is more stable

E_1

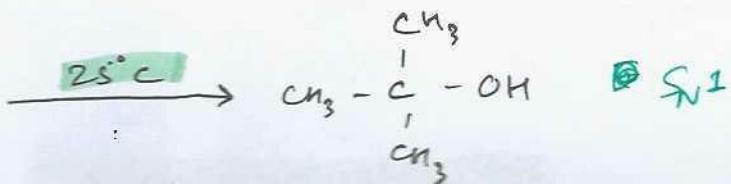
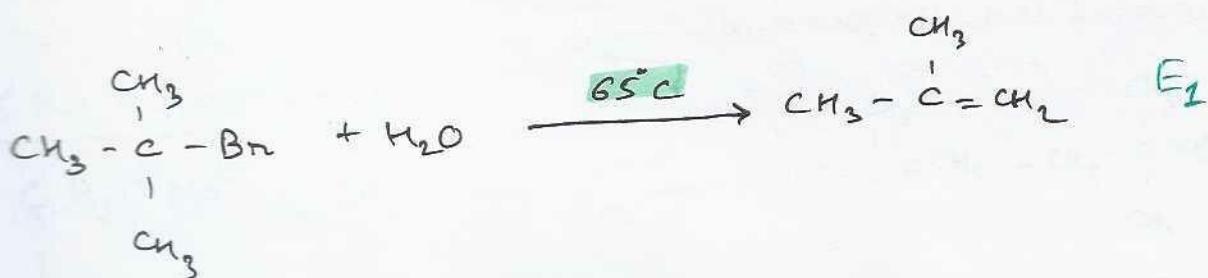
Mechanism

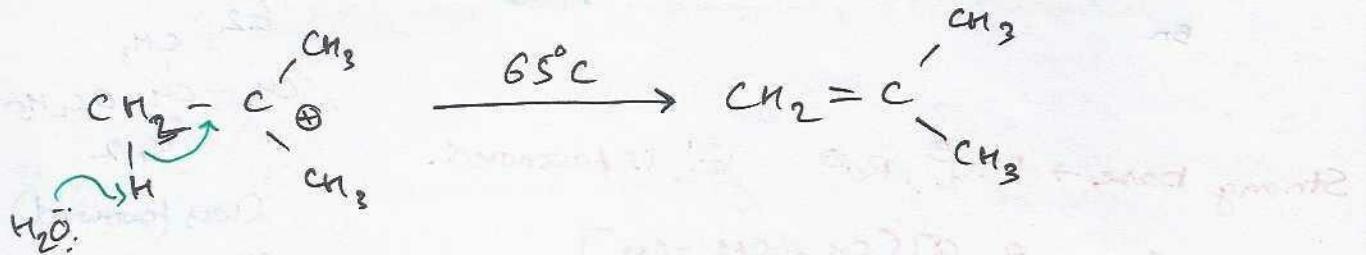
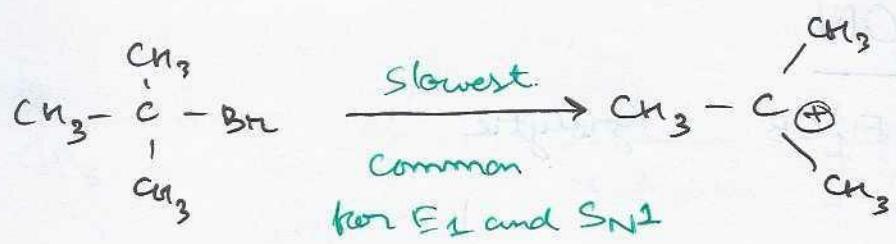
Not possible in primary alkyl halide.

~~$n \propto [3^\circ \text{ ROX}]$~~

High temperature $\xrightarrow{?}$ Favoured
 Tertiary alkyl halide

$n \propto [3^\circ \text{ RX}]$





Polar aprotic Solvents \rightarrow Favoured for $S_{N}2$



Polar protic solvents \rightarrow Favoured for E_1

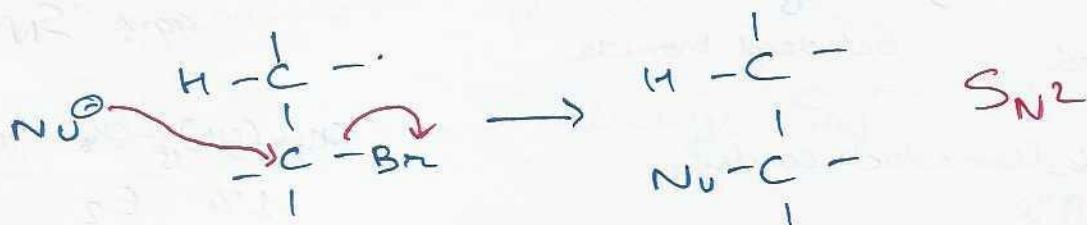
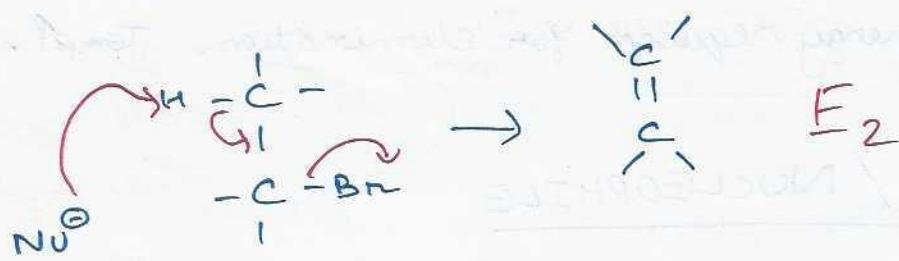
$1^\circ R$

$2^\circ R$

$3^\circ R$

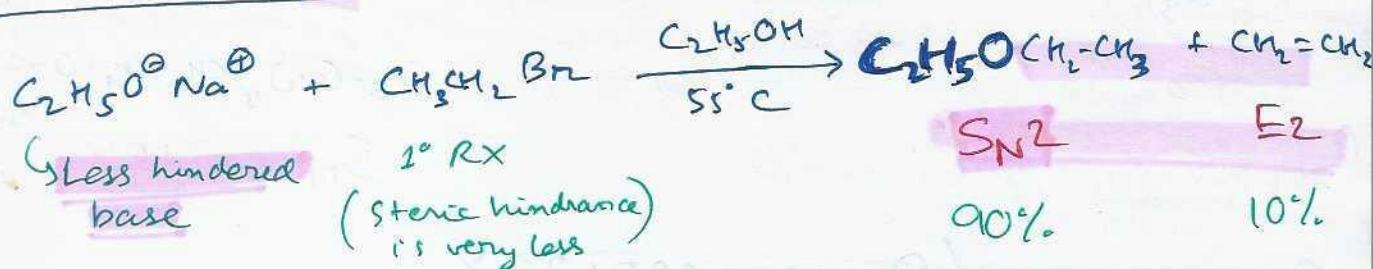
C_2

S_N2 and $E2$

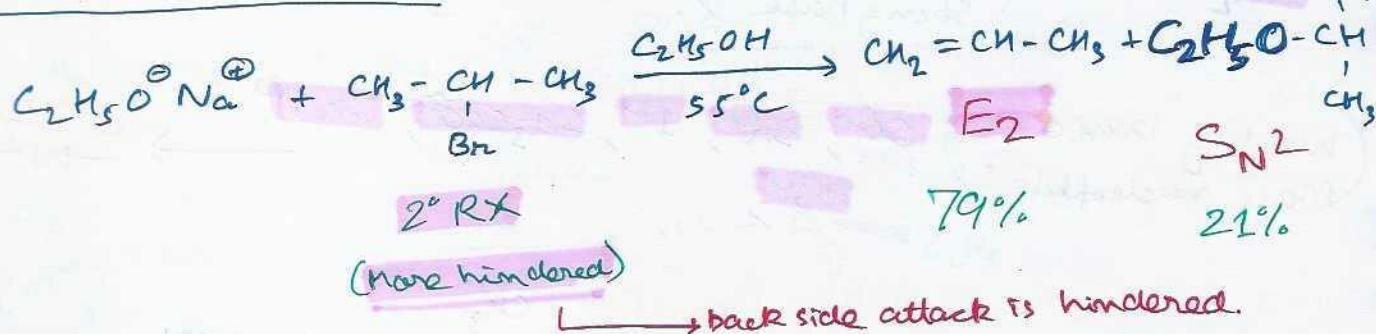


Strong nucleophile or strong bases favour E_2 and $S_{\text{N}}2$.

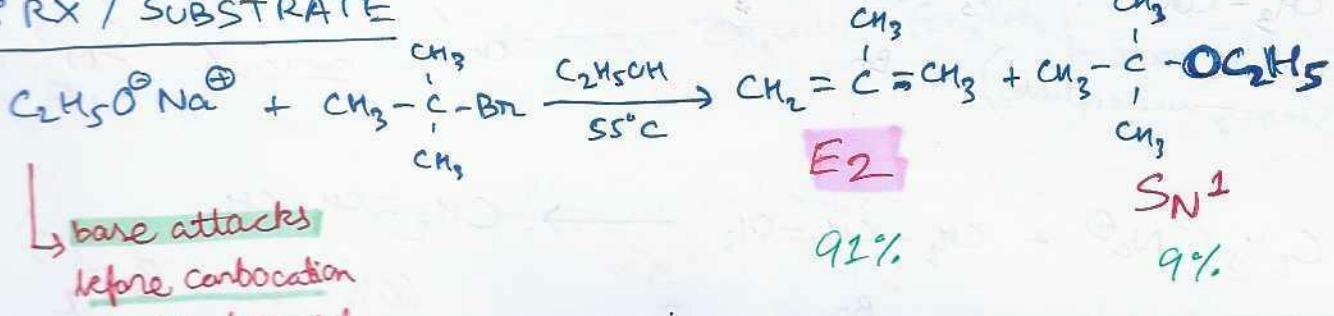
1°RX / SUBSTRATE



2°RX / SUBSTRATE



3°RX / SUBSTRATE

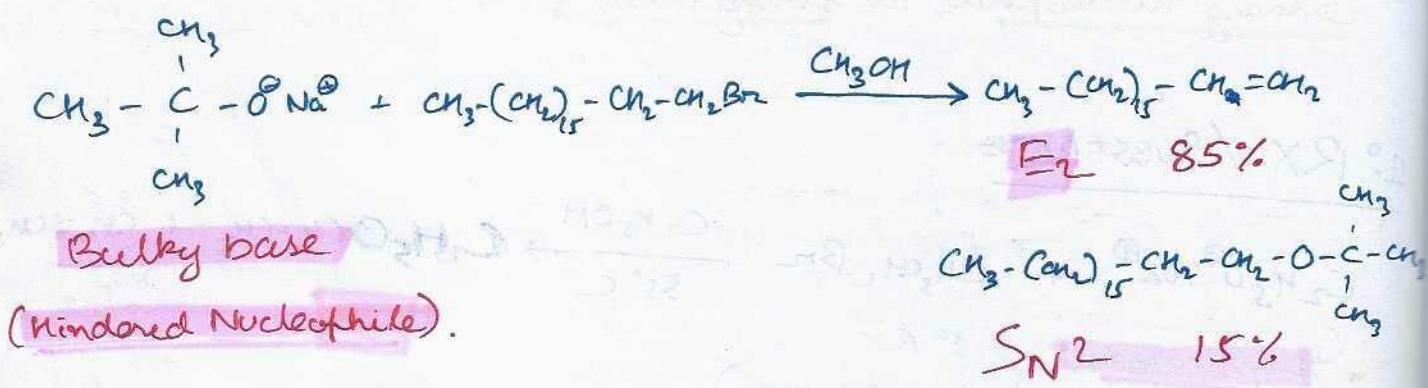
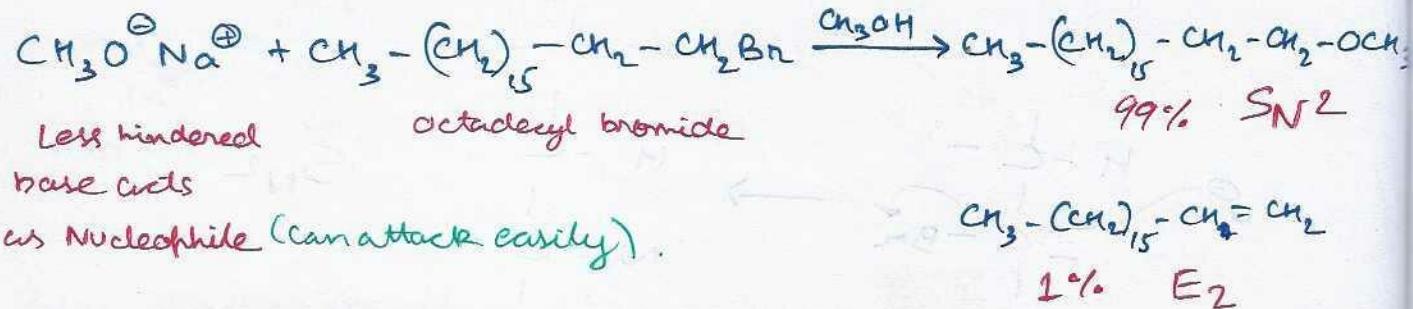


E_1 and E_2

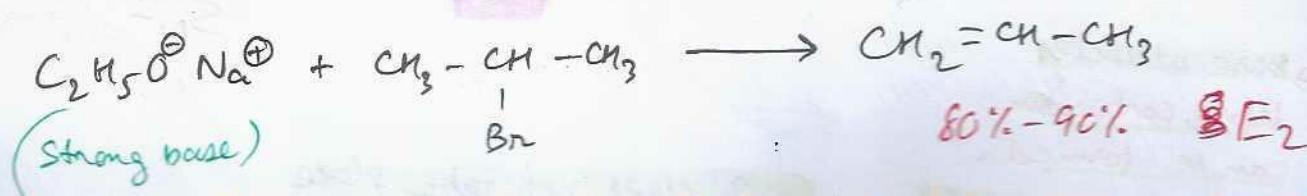
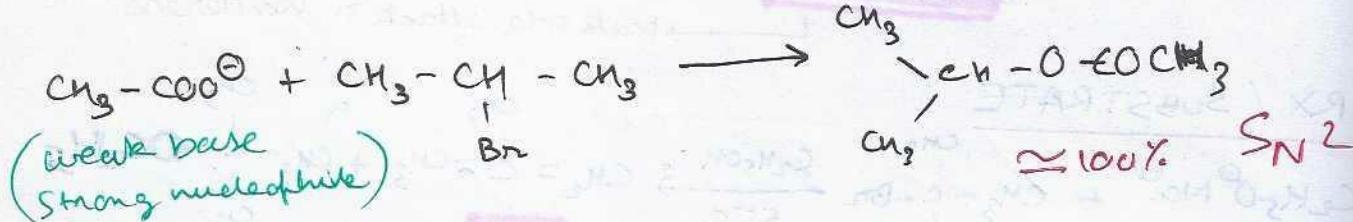
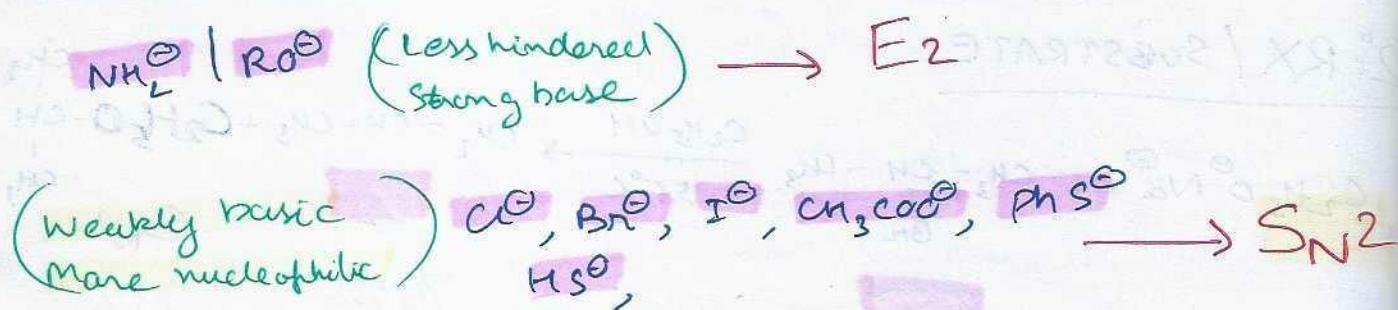
TEMPERATURE

High activation energy required for elimination. Temp↑.

SIZE OF BASE / NUCLEOPHILE



BASICITY / POLARIZABILITY



E₁ vs. S_N1

3° RX are more favoured for E₁ and S_N1
 Polar Protic Solvent
 Weak Base

High Temperature → E₁

Low Temperature → S_N1

Methyl halide (CH₃X) → always S_N2

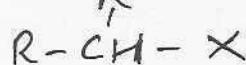
1° RX



S_N2 | E₂

less hindered base
SN2 does not take place

2° RX



S_N2 | E₂

weak base (nucleophile)
H⁰, I⁰, B_n⁰

Strong base R₂O, NHR

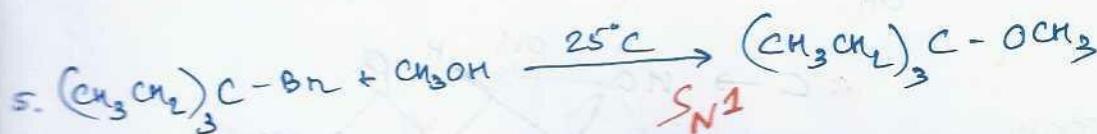
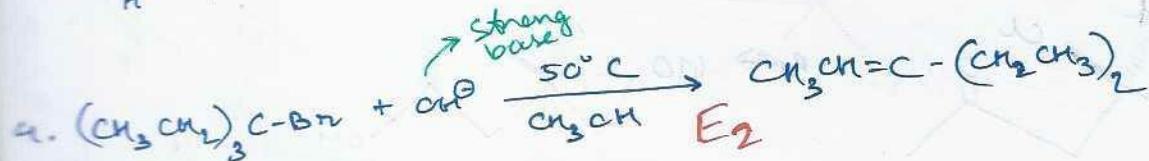
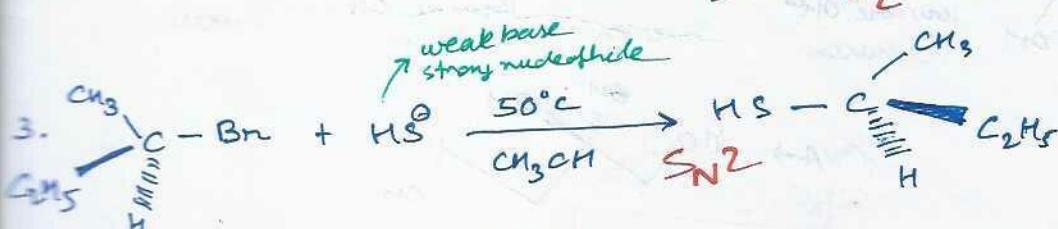
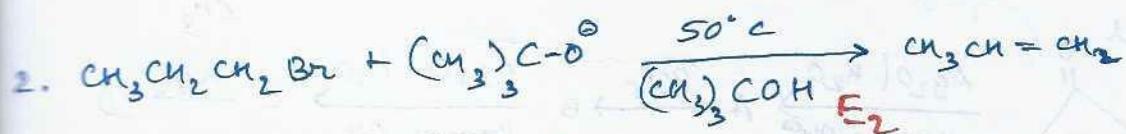
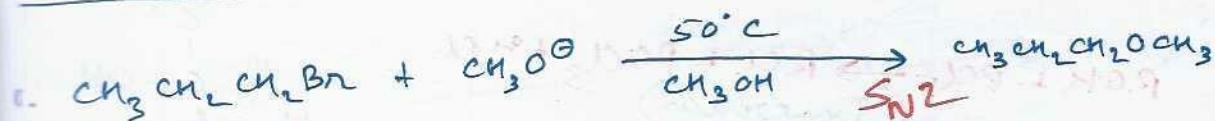
3° RX

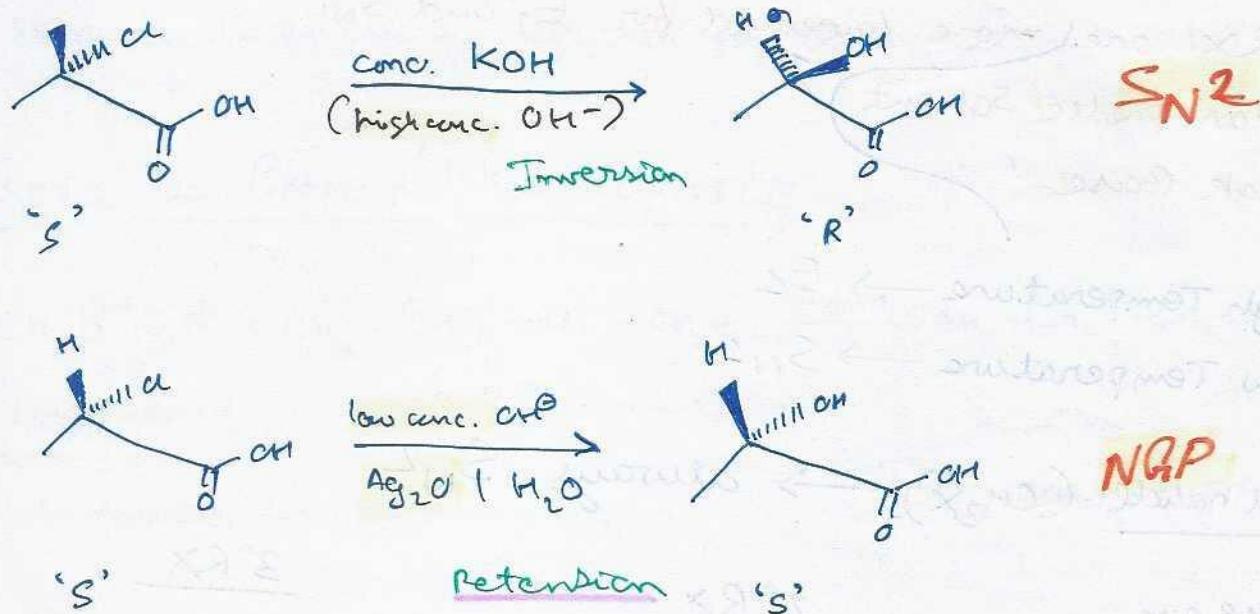
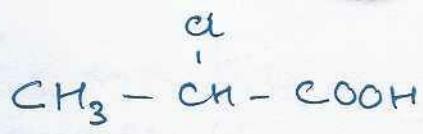
S_N1: Polar protic solvent.
Low temperature

E₁: Polar protic solvent.
High temperature

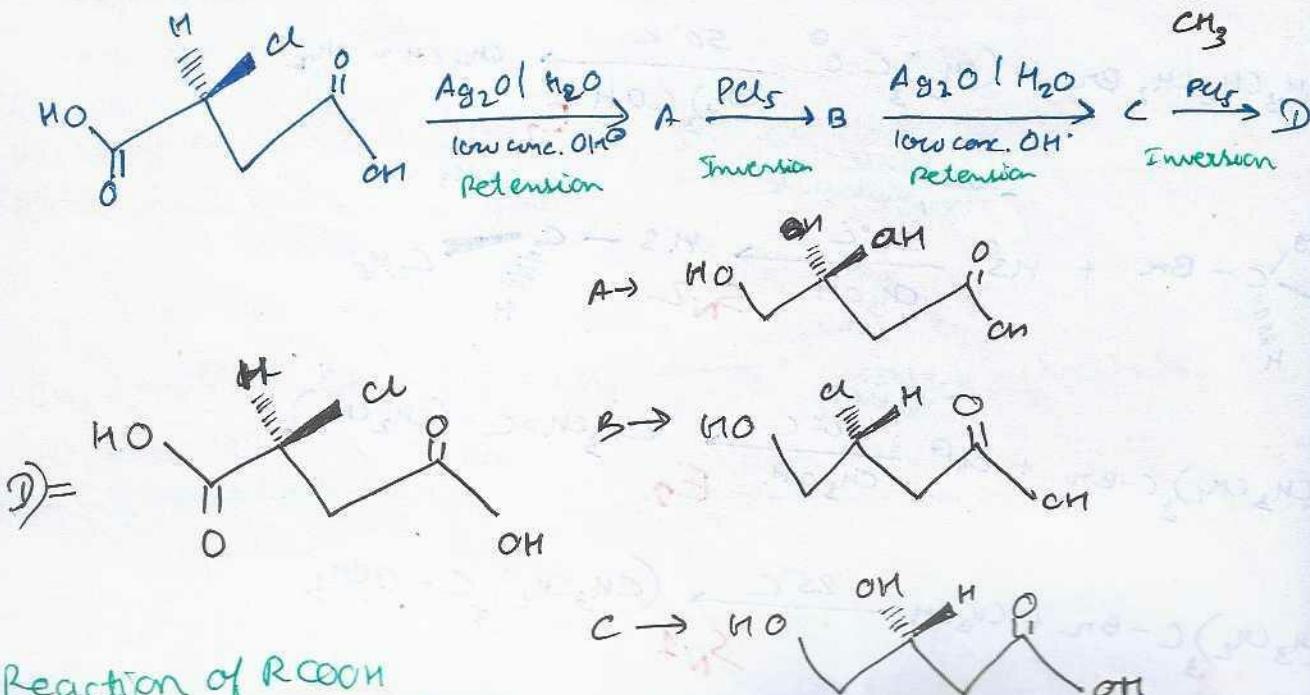
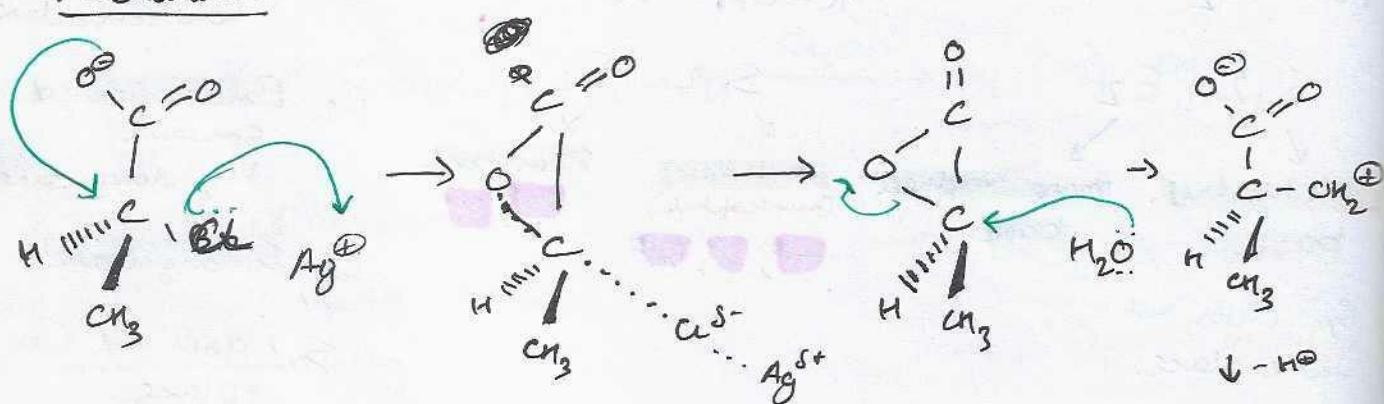
E₂: Strong base

S_N2 does not take place

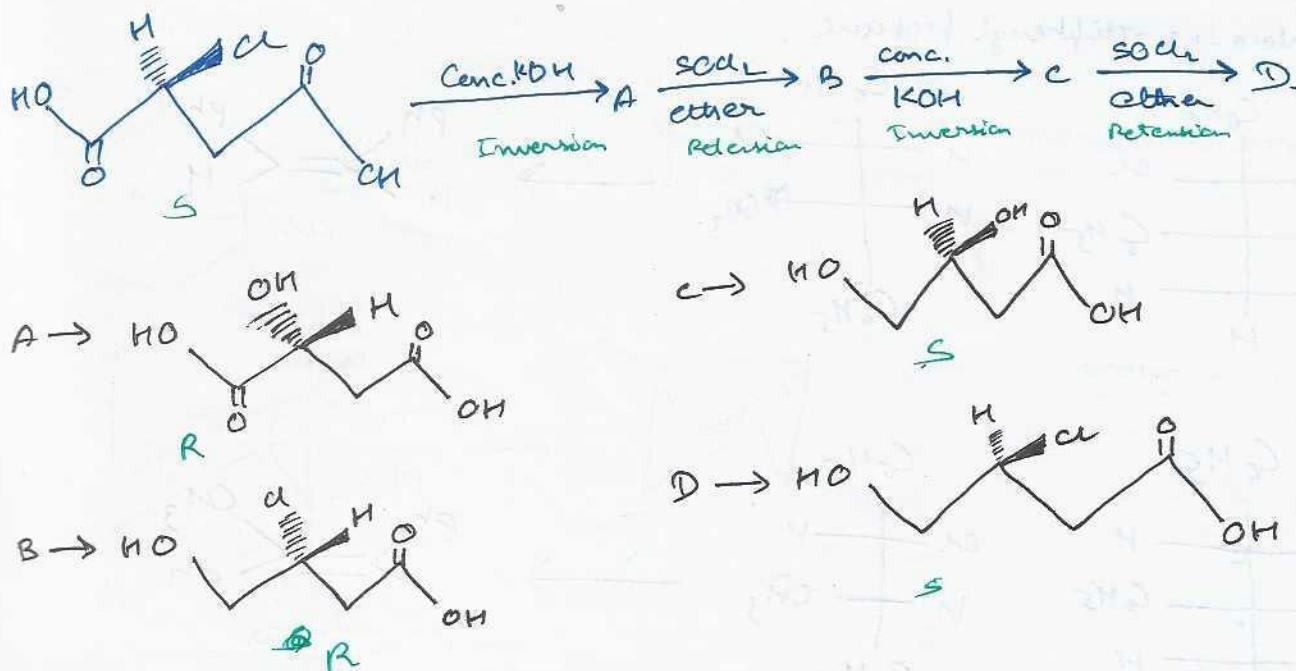




↳ mechanism

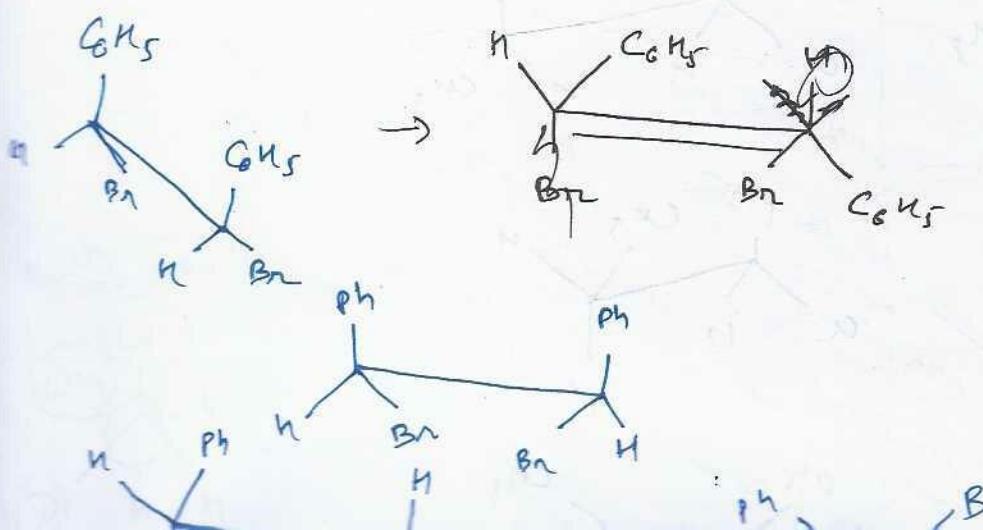
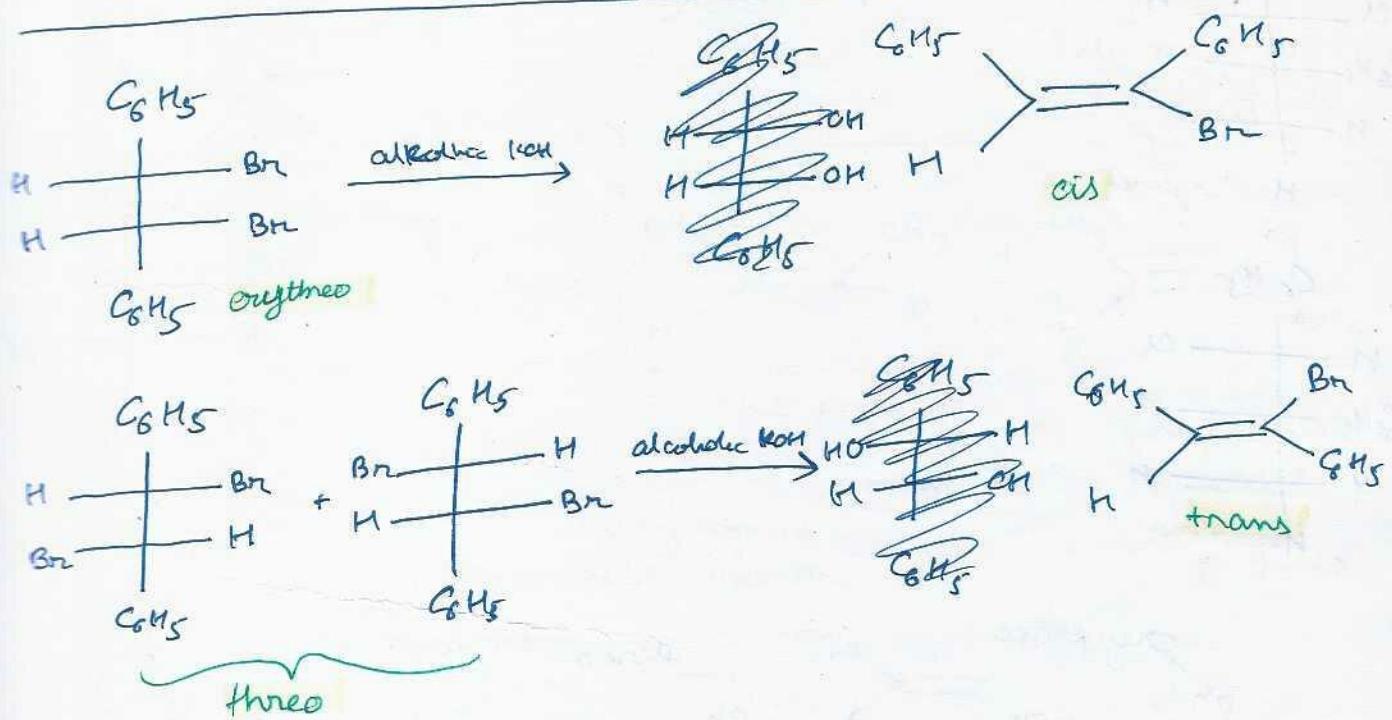


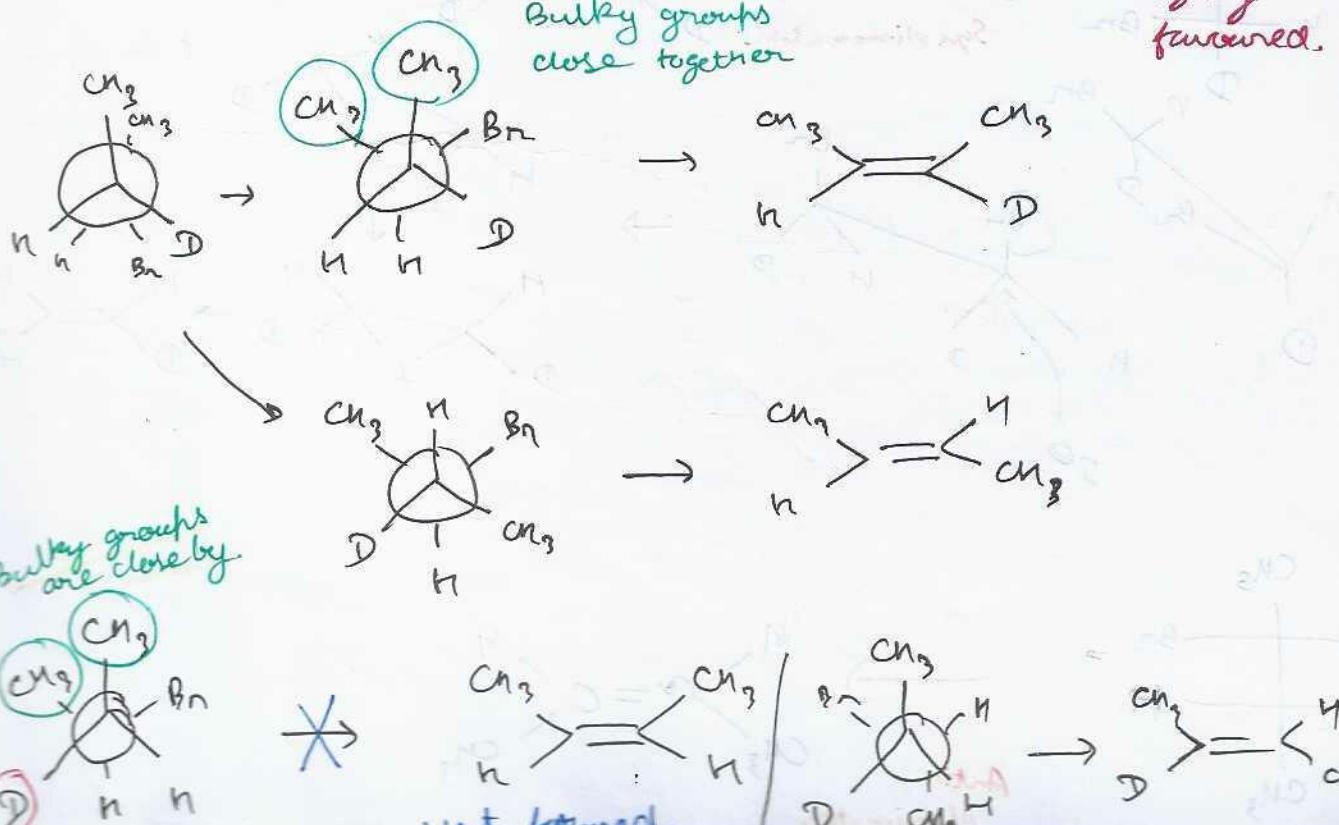
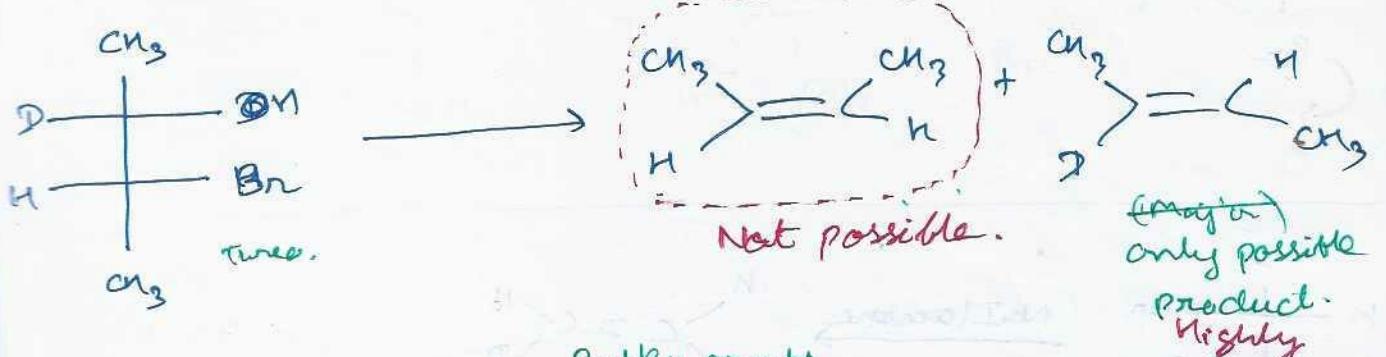
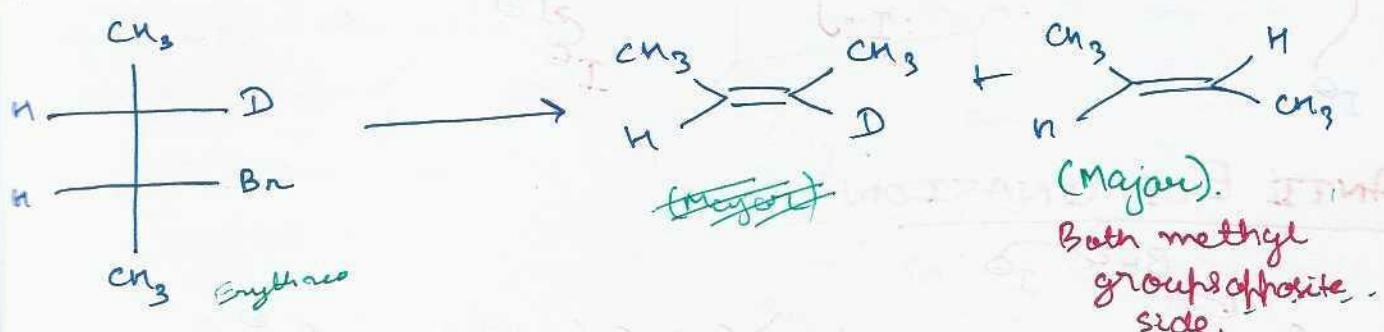
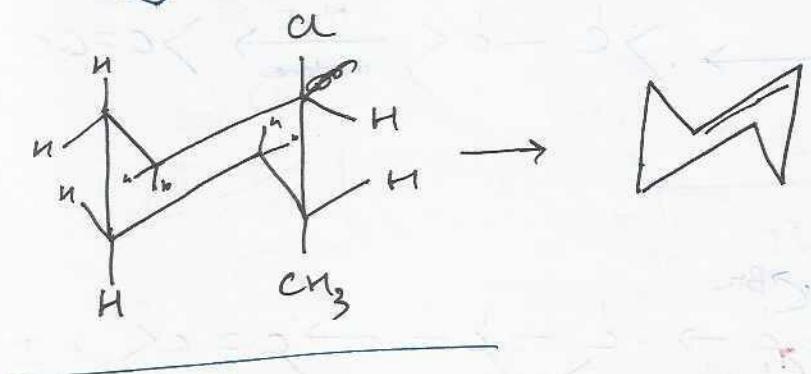
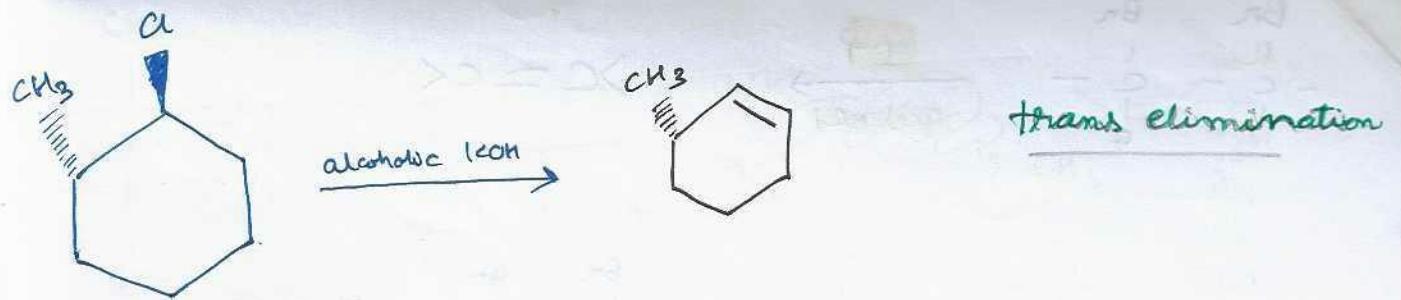
Reaction of RCOOH
with PCl_5 not considered.

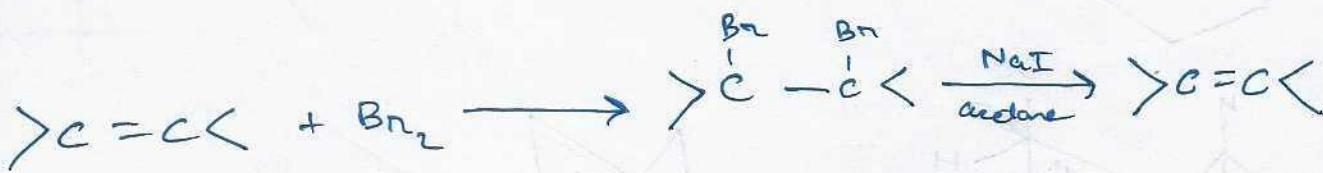


Reaction of RCOOH with SOCl_2 is not considered.

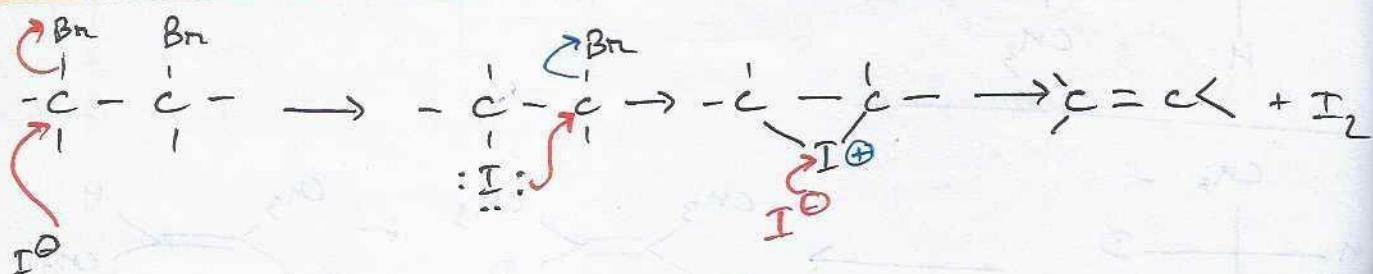
STEREOCHEMISTRY OF E₂ (ANTI ELIMINATION)



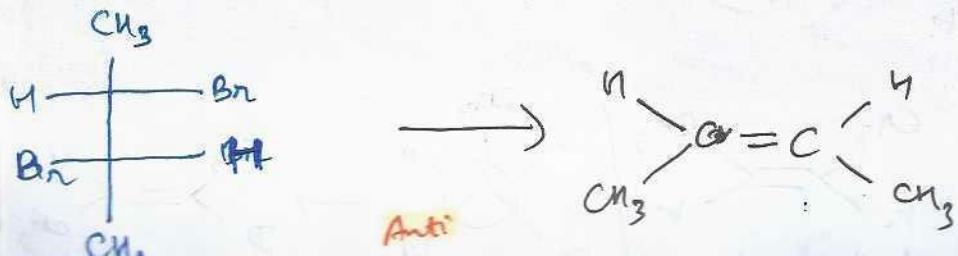
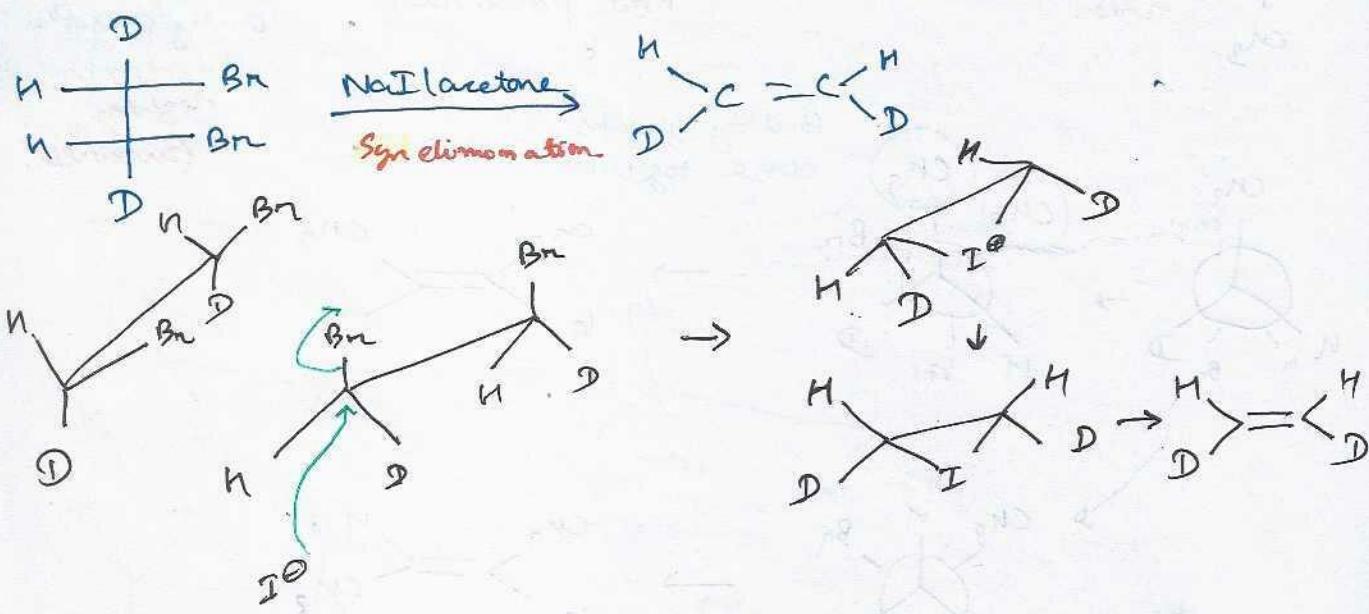
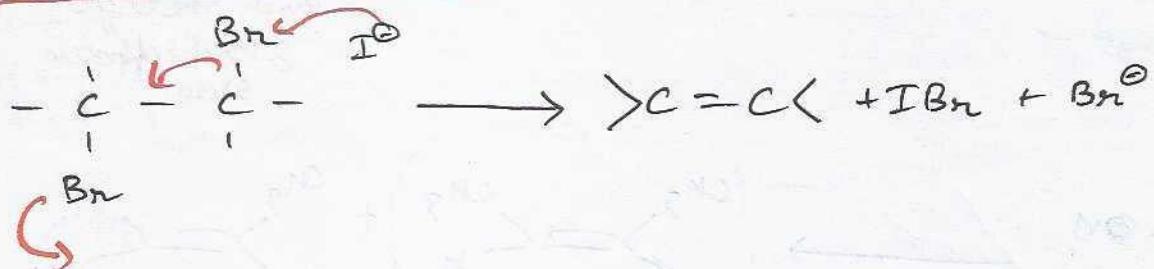


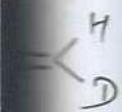
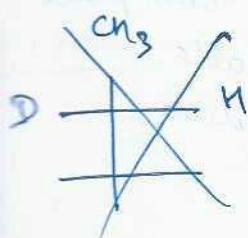
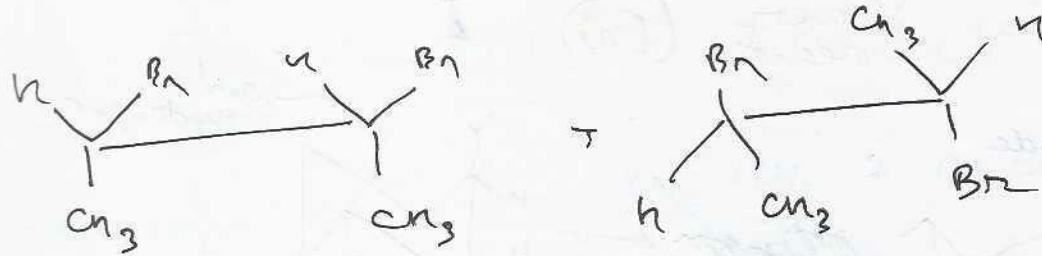
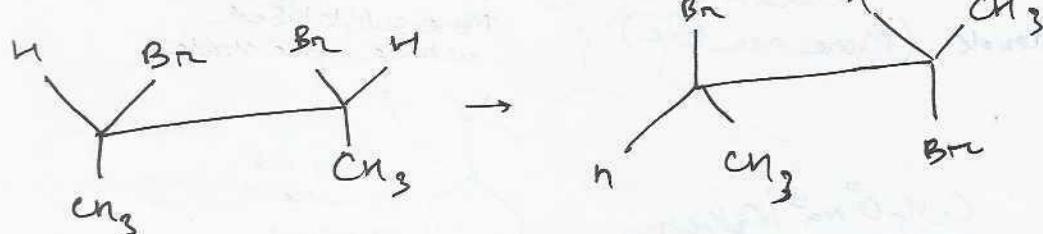
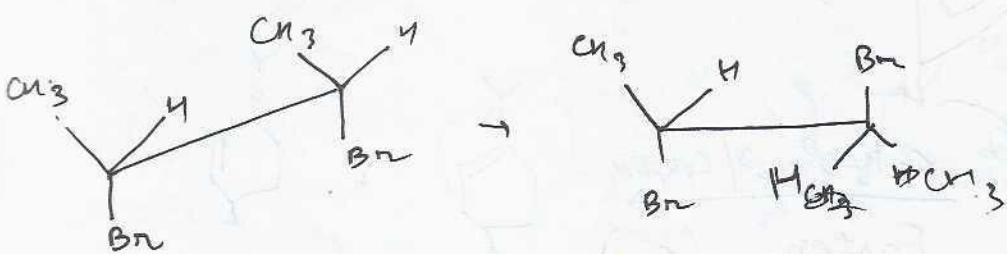
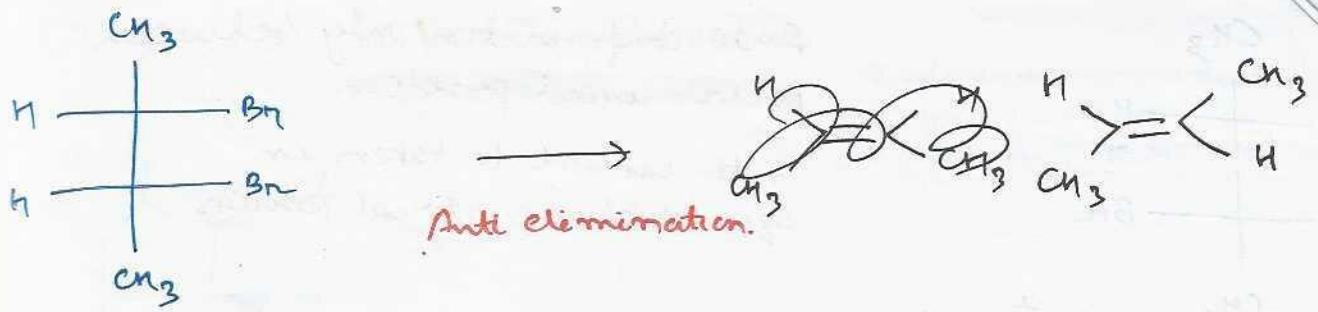


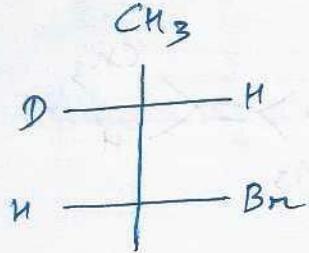
SYN ELIMINATION



ANTI ELIMINATION

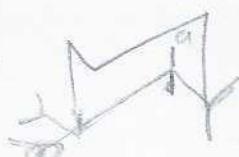
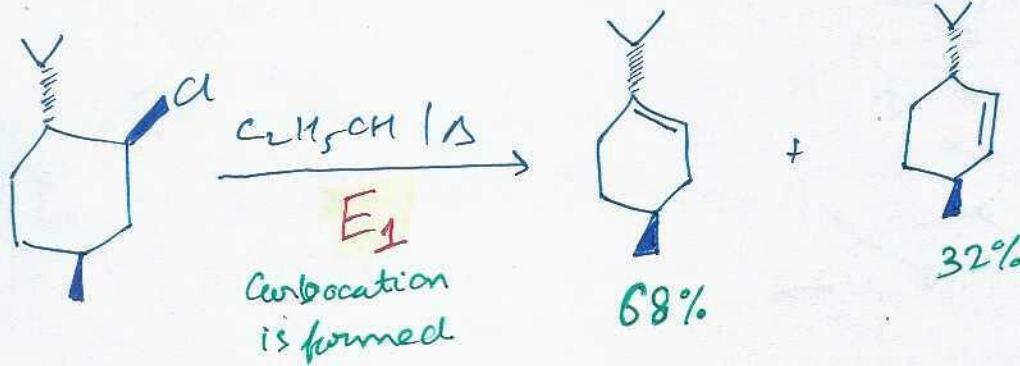
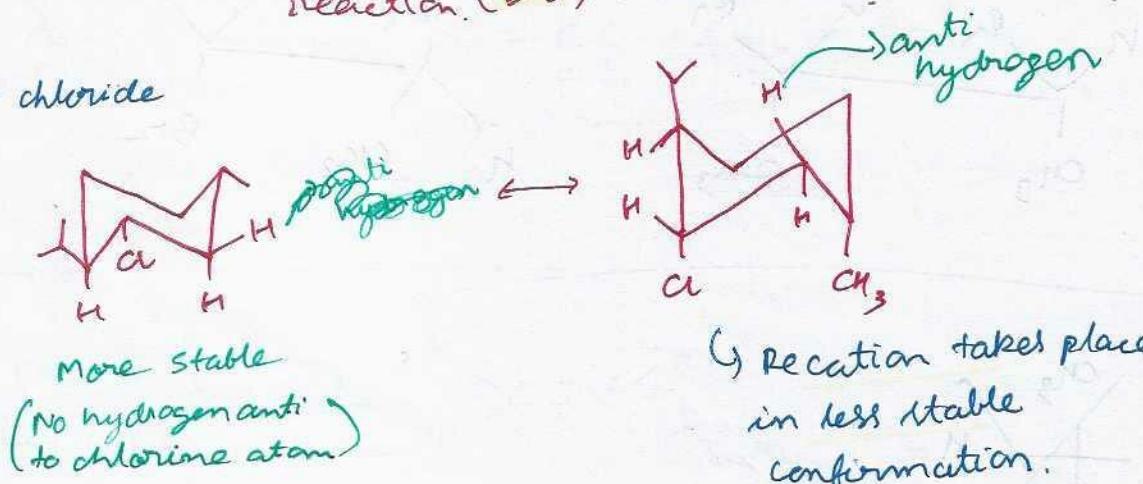
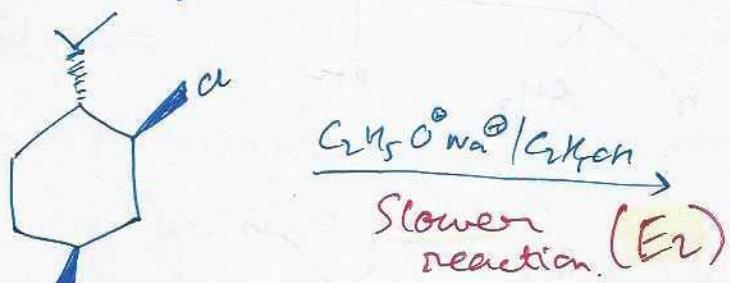
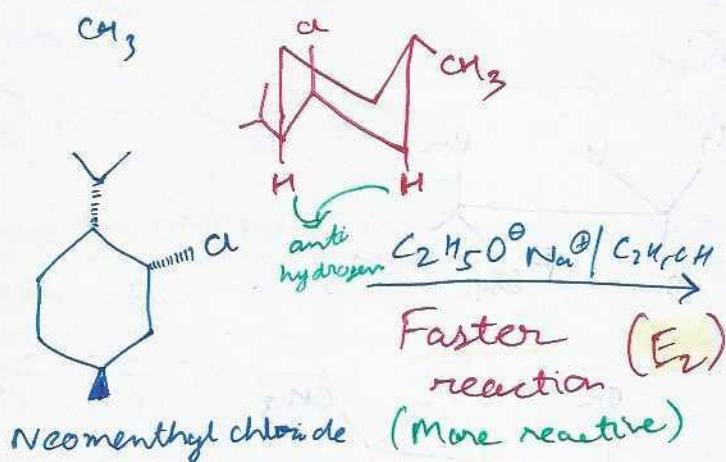






Anti-conformation only between axial-axial position.

Anti cannot be taken in equatorial-equatorial position.

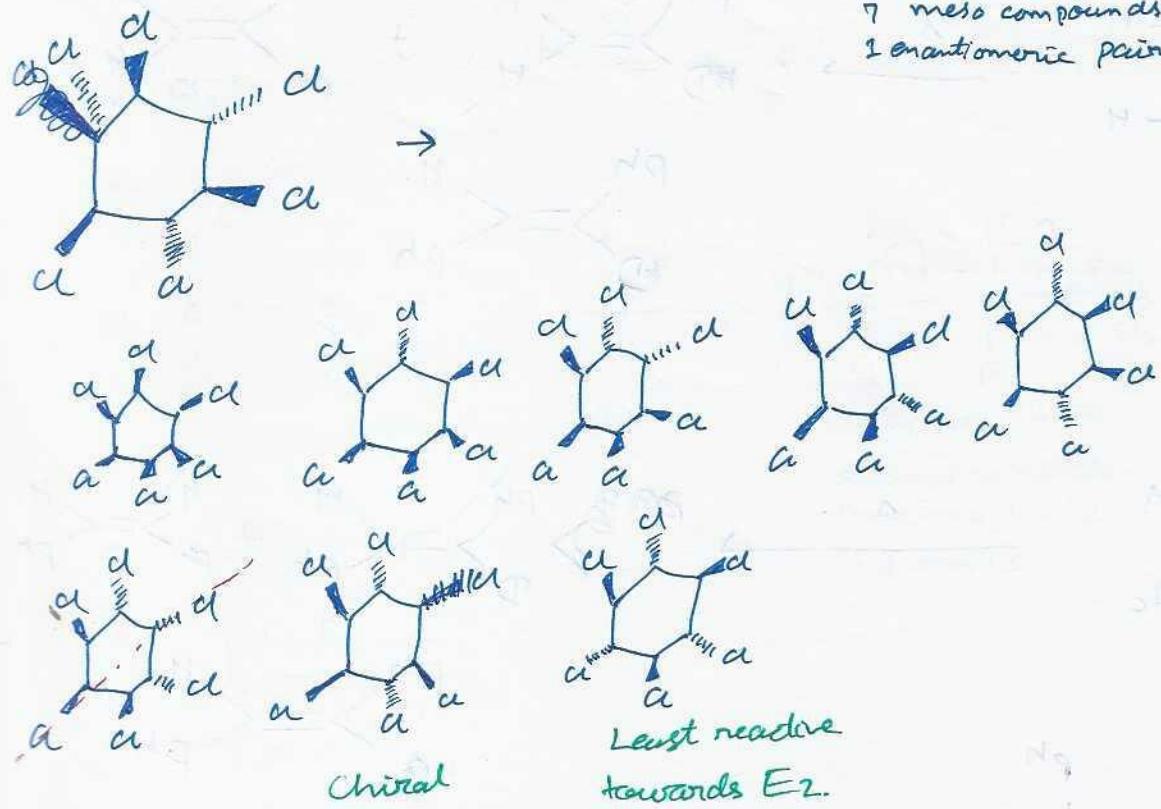


1,2,3,4,5,6 - hexachlorocyclohexane.

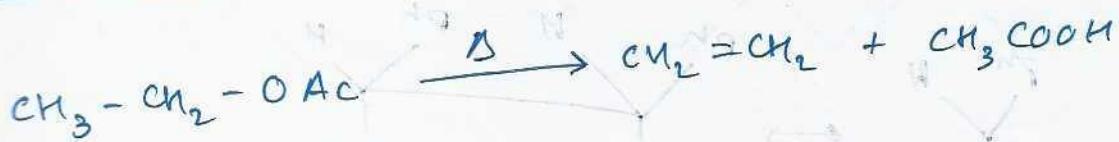
9 stereo isomers are possible

7 meso compounds.

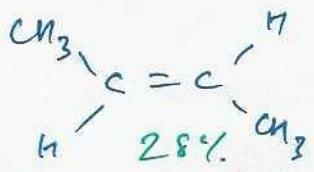
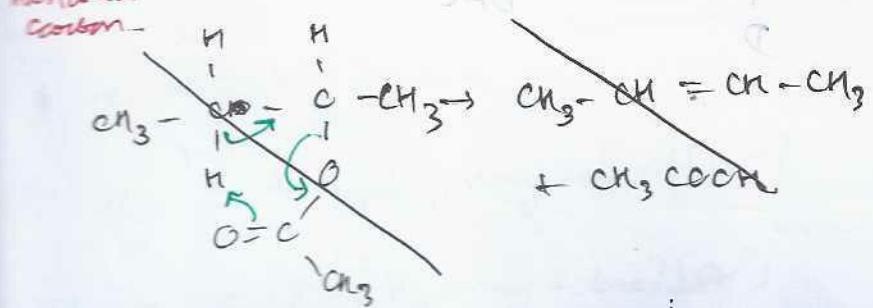
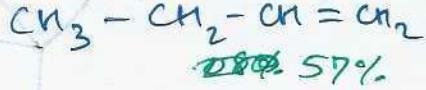
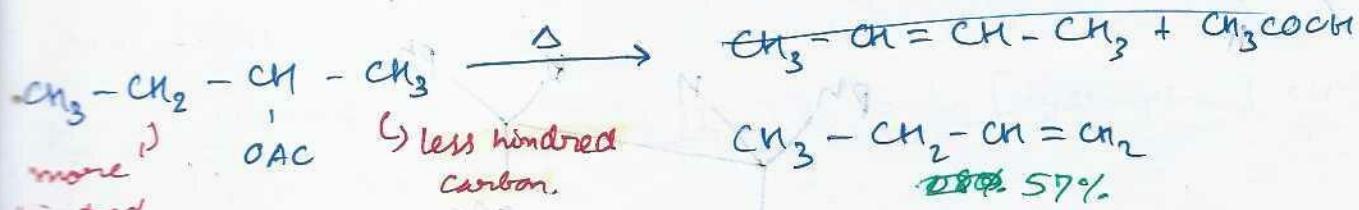
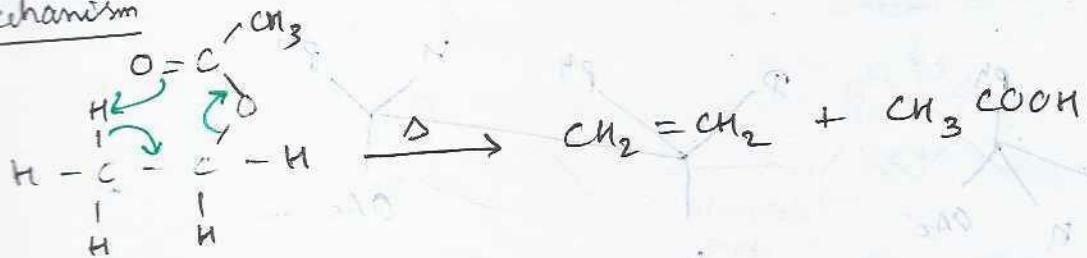
1 enantiomeric pair



SYN ELIMINATION (PYROLYTIC)

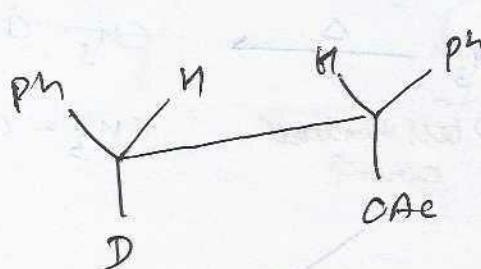
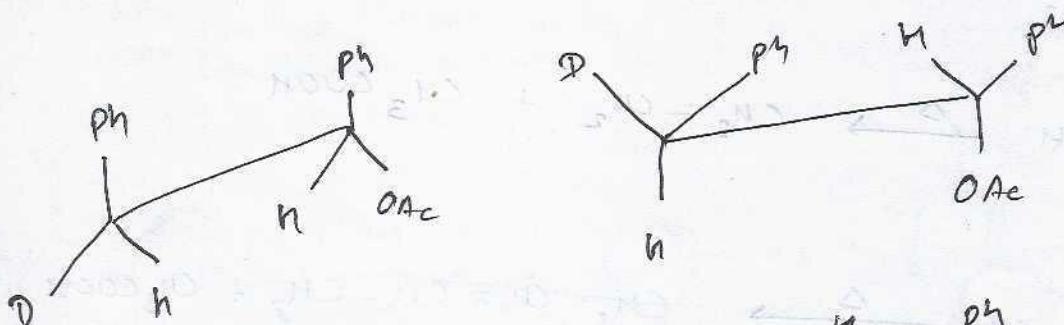
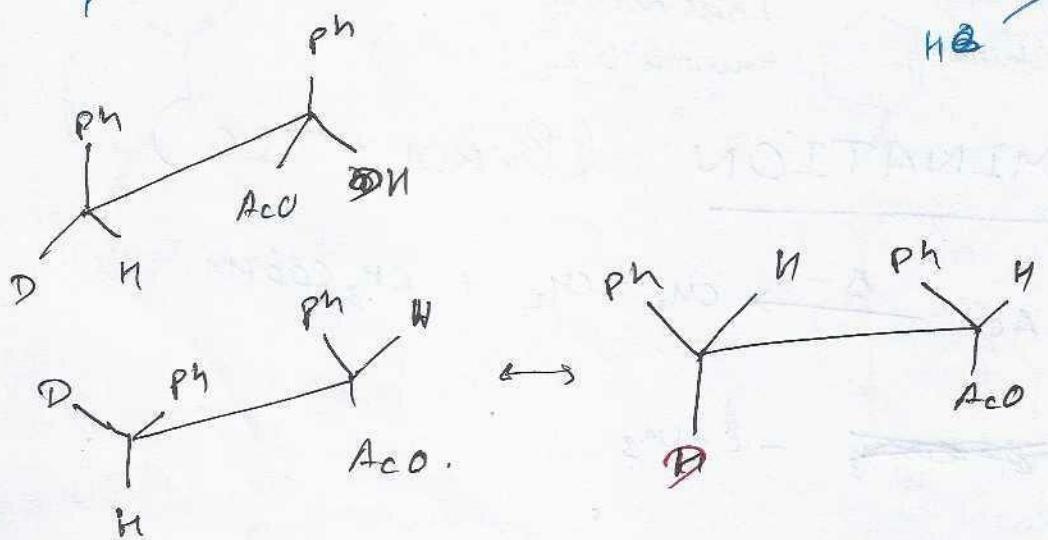
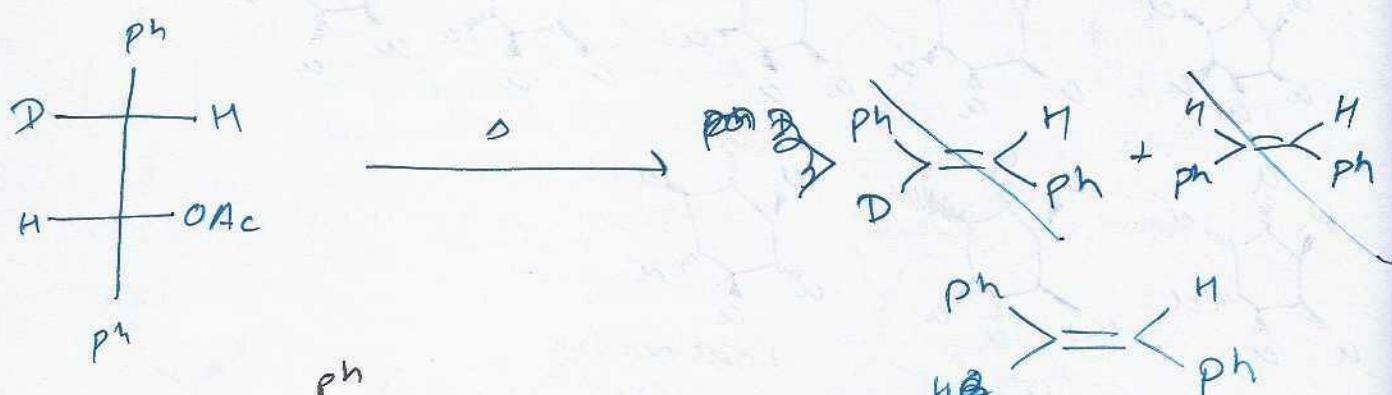
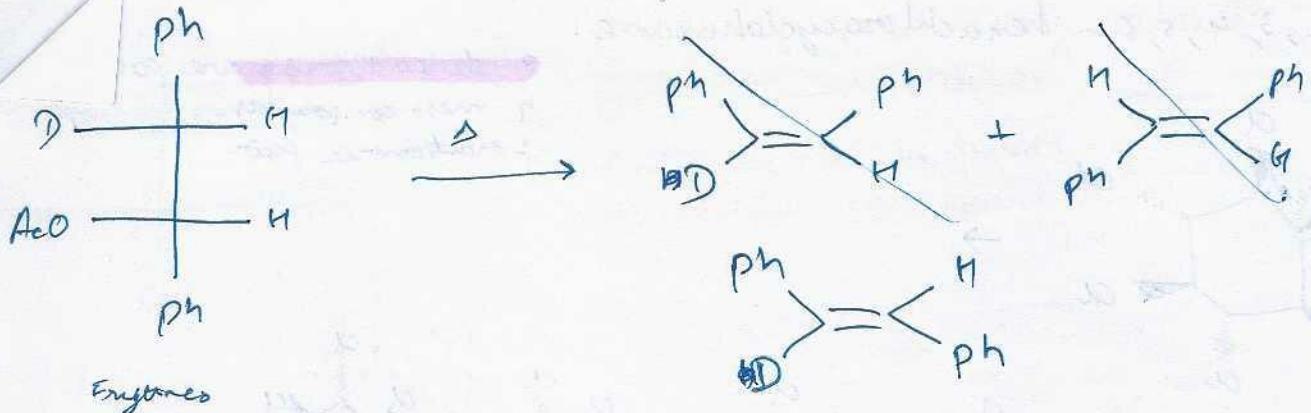


Mechanism



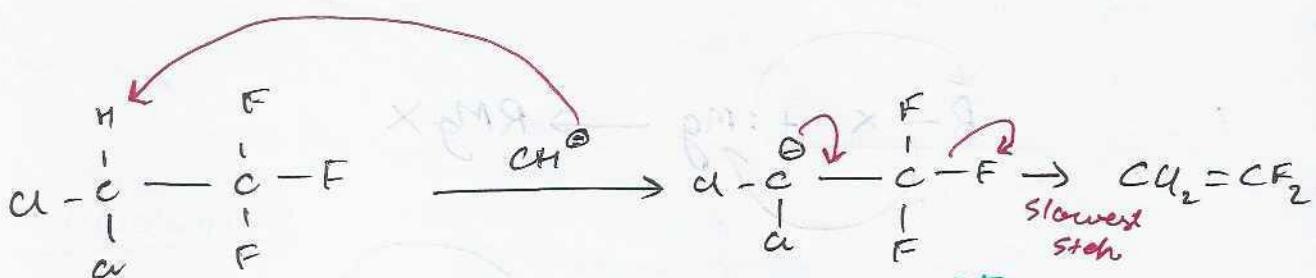
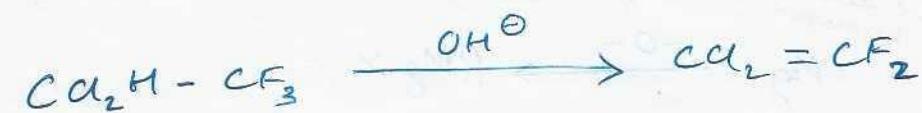
bulky groups opposite side

less in bulk growth.



E1 CB

Elimination via conjugate base formation.

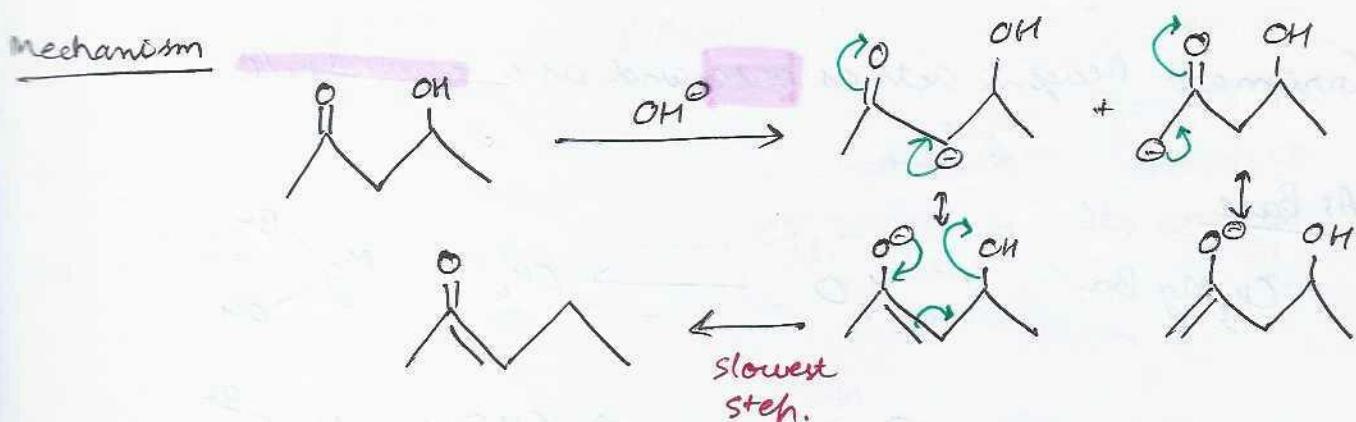


α [Bcarbanion]

$$k_{eq} = \frac{[\text{Carbanion}]}{[\text{RX}][\text{OH}^-]}$$



Mechanism



α [Enolate ion]

$$k_{eq} = \frac{[\text{Enolate ion}]}{[\text{Hydroxy ketone}][\text{OH}^-]} \Rightarrow [\text{Enolate}] = k_{eq} [\text{Hydroxy ketone}][\text{OH}^-]$$

$\alpha = k [\text{Enolate Ion}]$

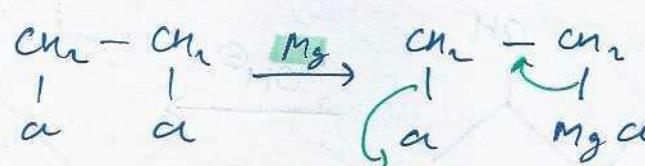
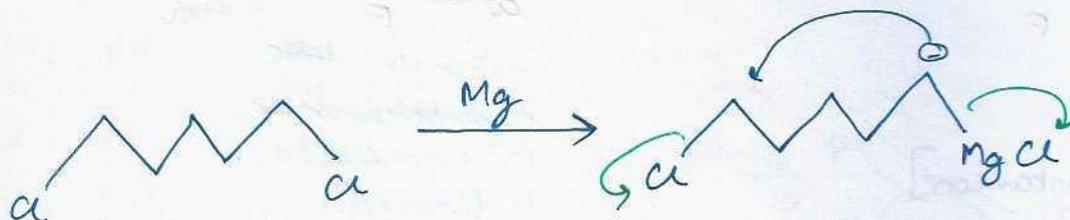
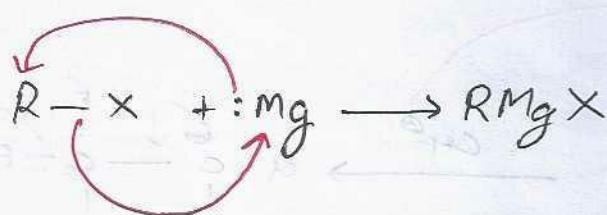
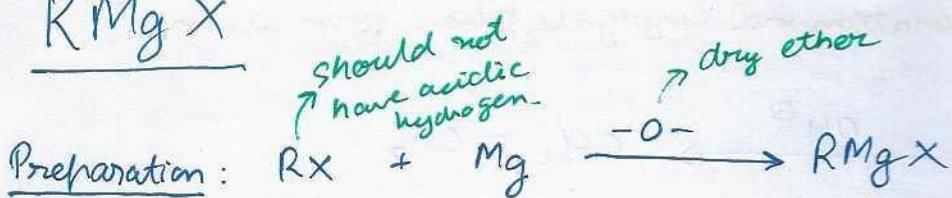
$$\therefore \alpha = k \cdot k_{eq} [\text{Hydroxy ketone}][\text{OH}^-]$$

$$\therefore \alpha = k' [\text{Hydroxy ketone}][\text{OH}^-]$$

$E_1 CB \rightarrow$ unimolecular

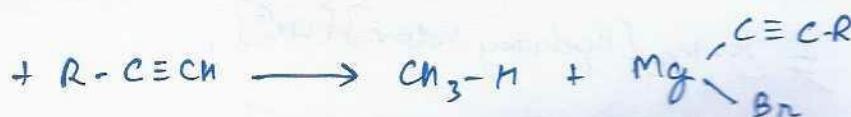
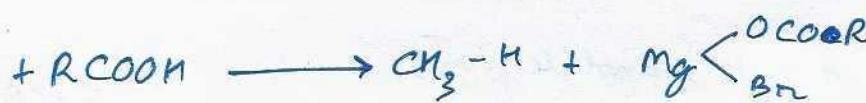
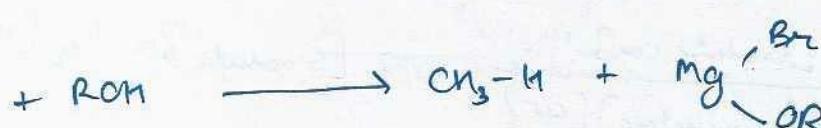
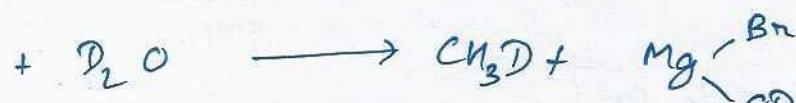
2nd order.

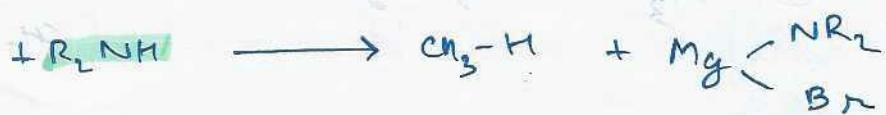
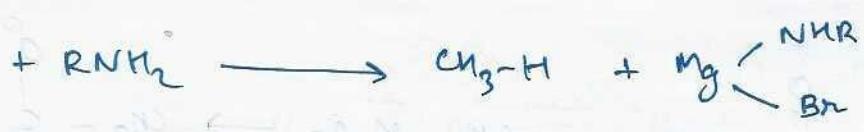
R Mg X



Grignard Reagent acts as **base**, and as a **nucleophile**.

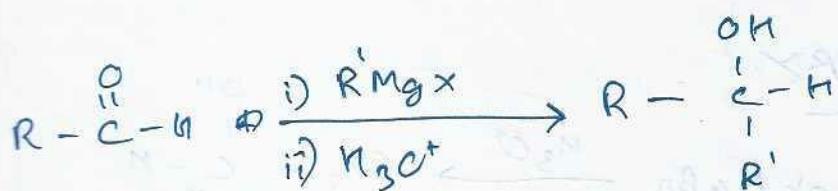
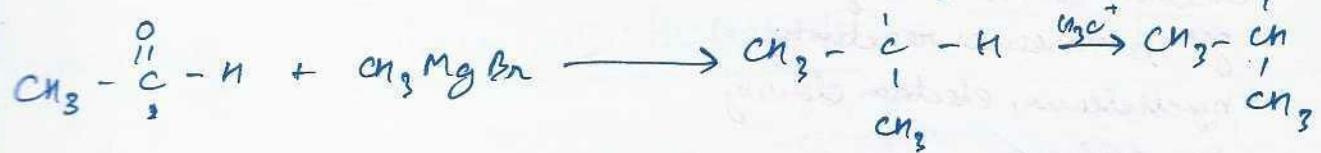
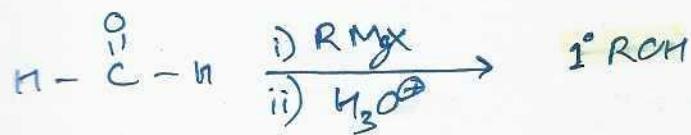
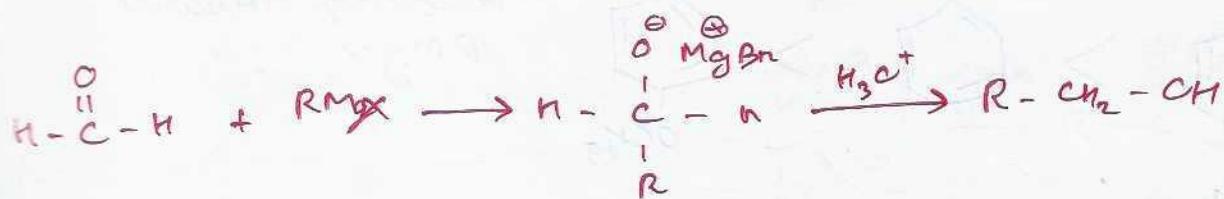
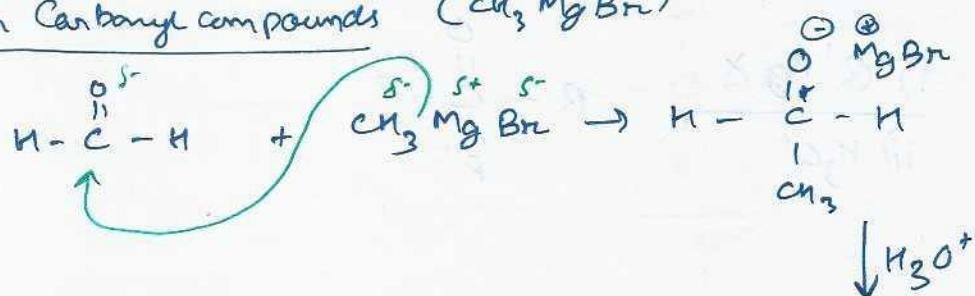
As Base



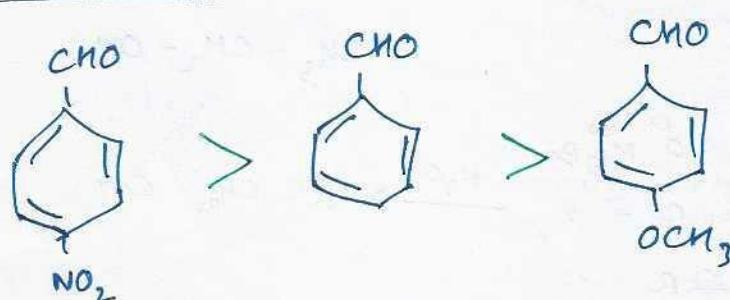
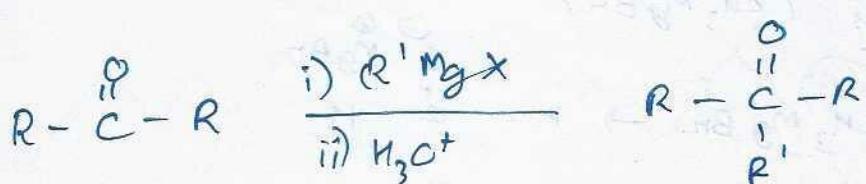
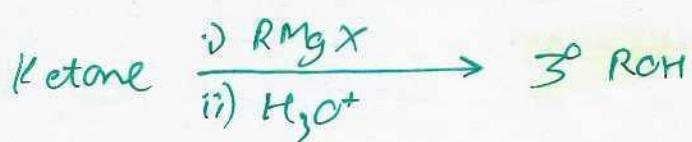
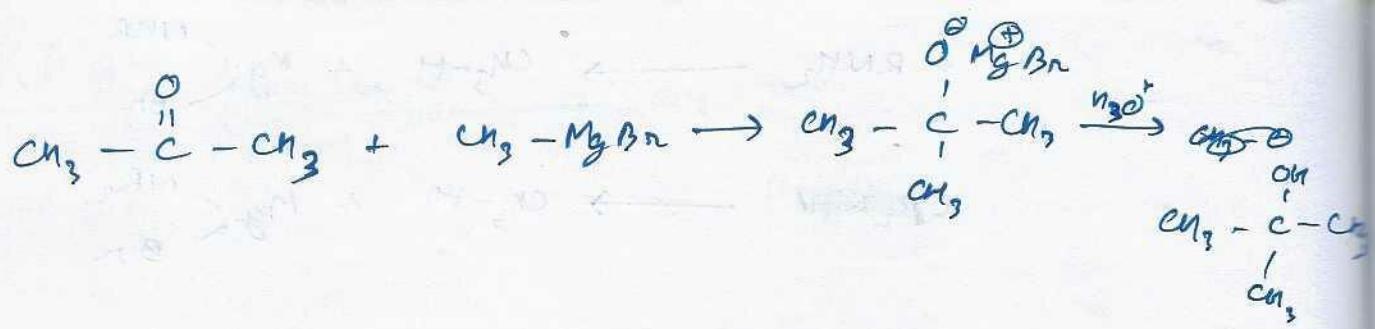


As a Nucleophile

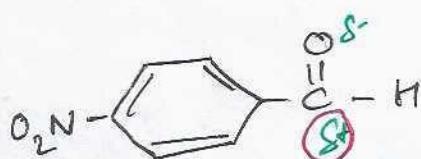
with Carbonyl compounds (CH_3MgBr)



Any aldehyde, other than formaldehyde $\xrightarrow[\text{ii)}]{\text{i)}} RMgX \quad 2^\circ ROH$

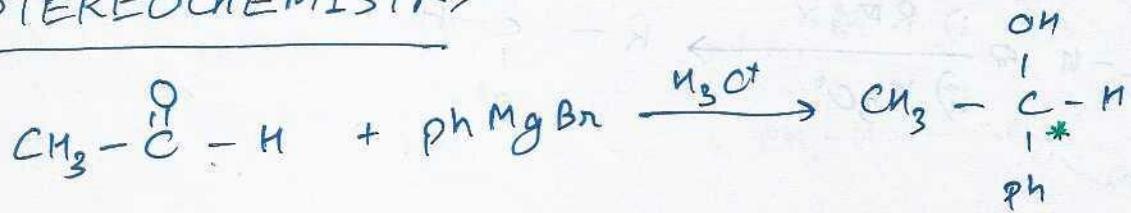


Reactivity towards
RMgX.

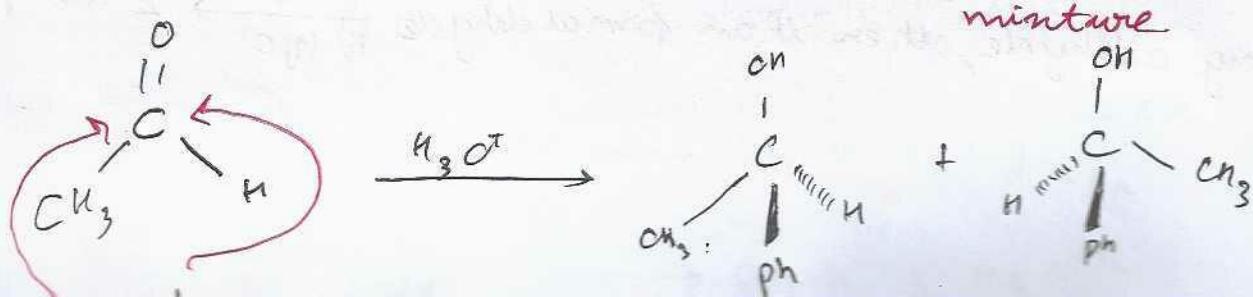


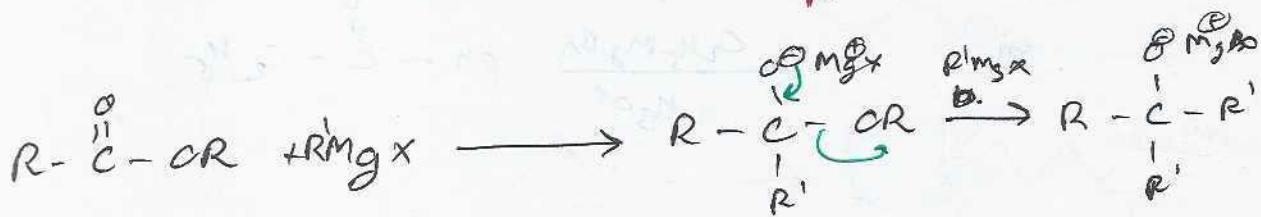
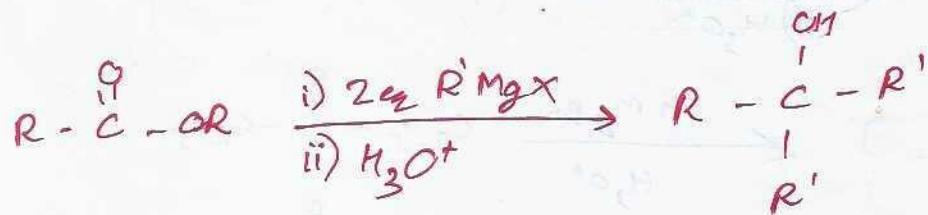
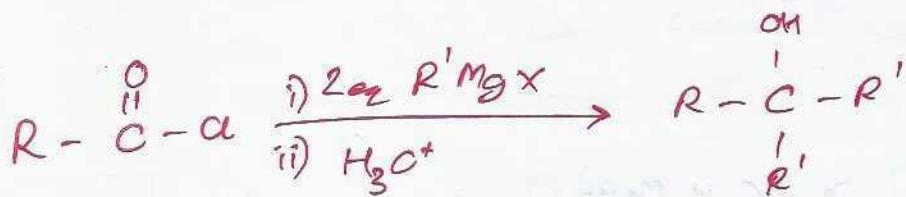
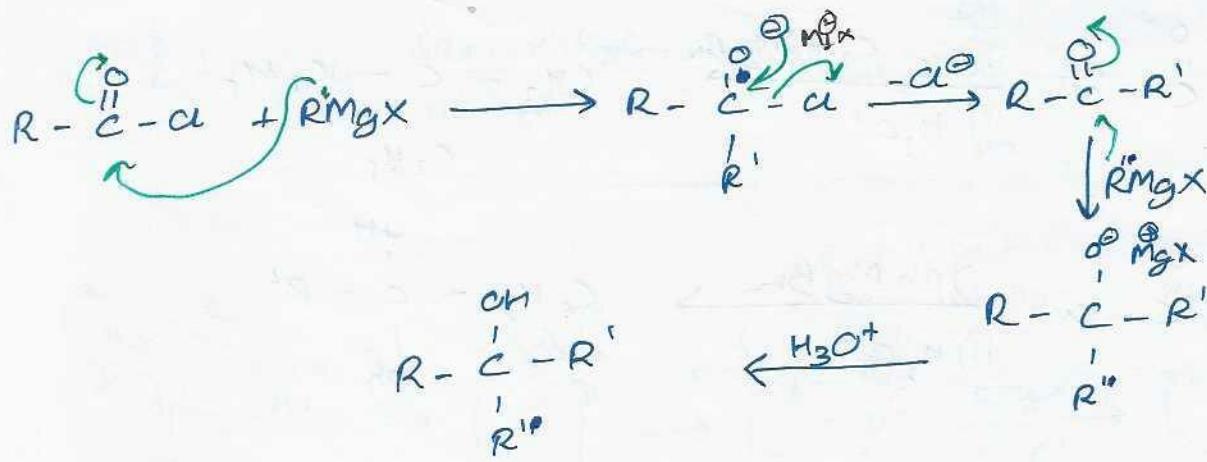
4-electron withdrawing group increases reactivity by decreasing electron density on carbon.

STEREOCHEMISTRY

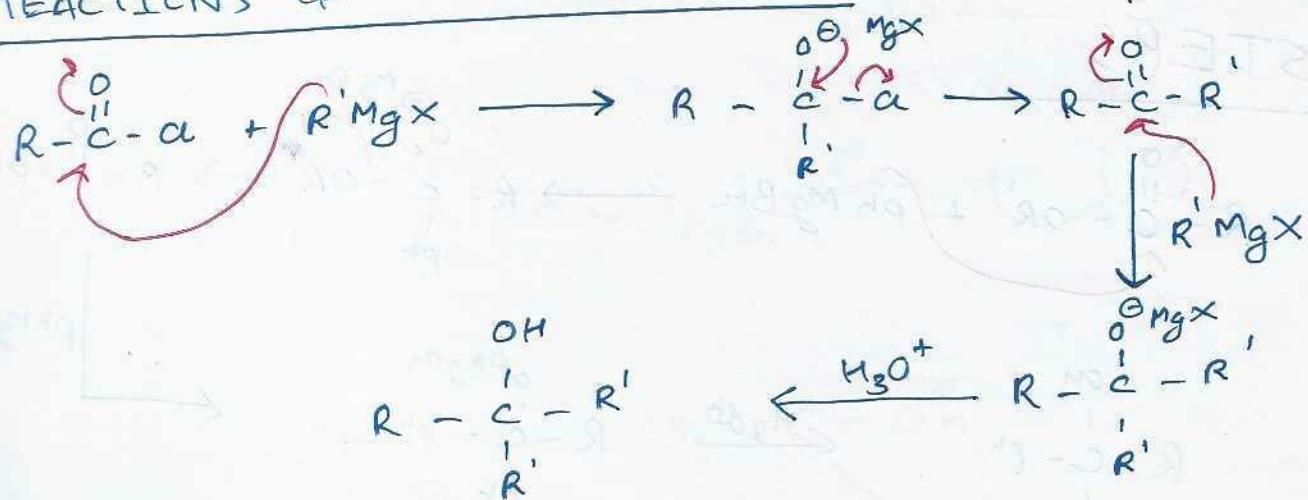


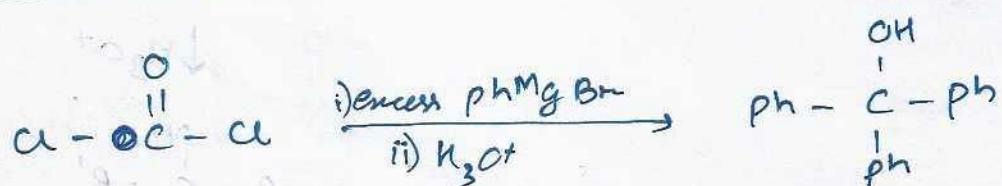
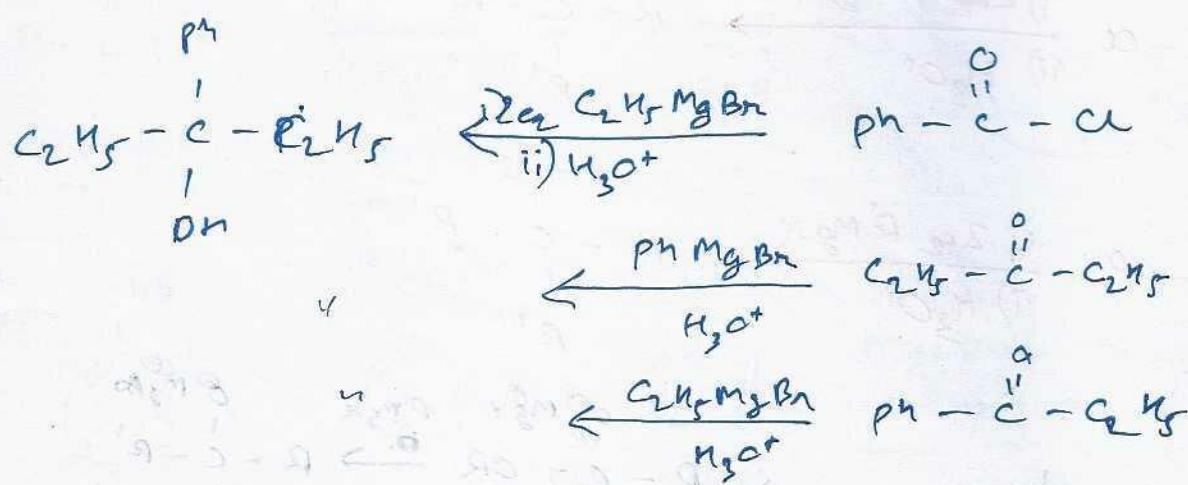
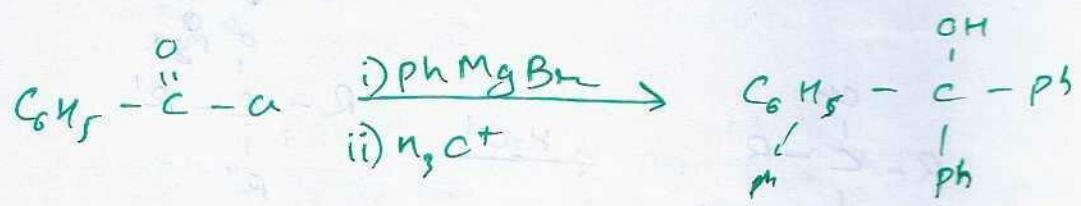
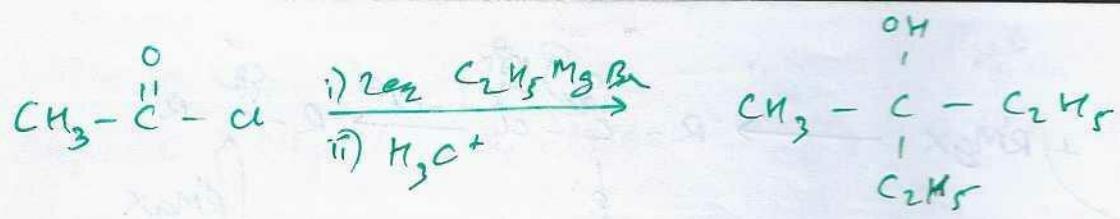
Forms racemic mixture



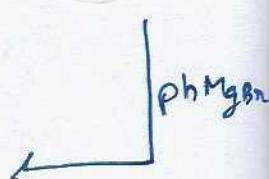
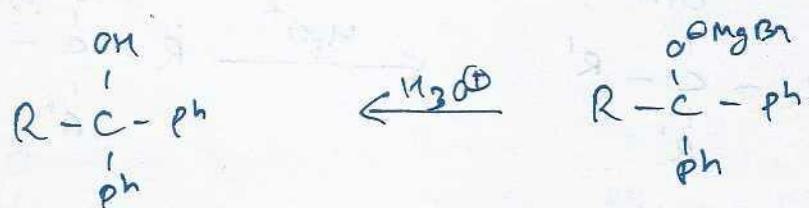
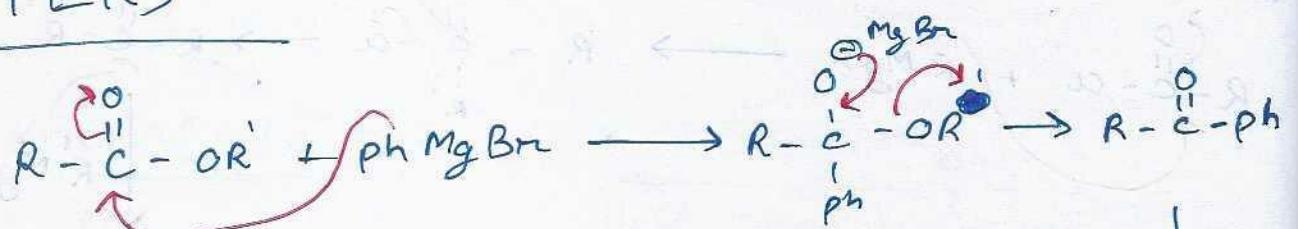


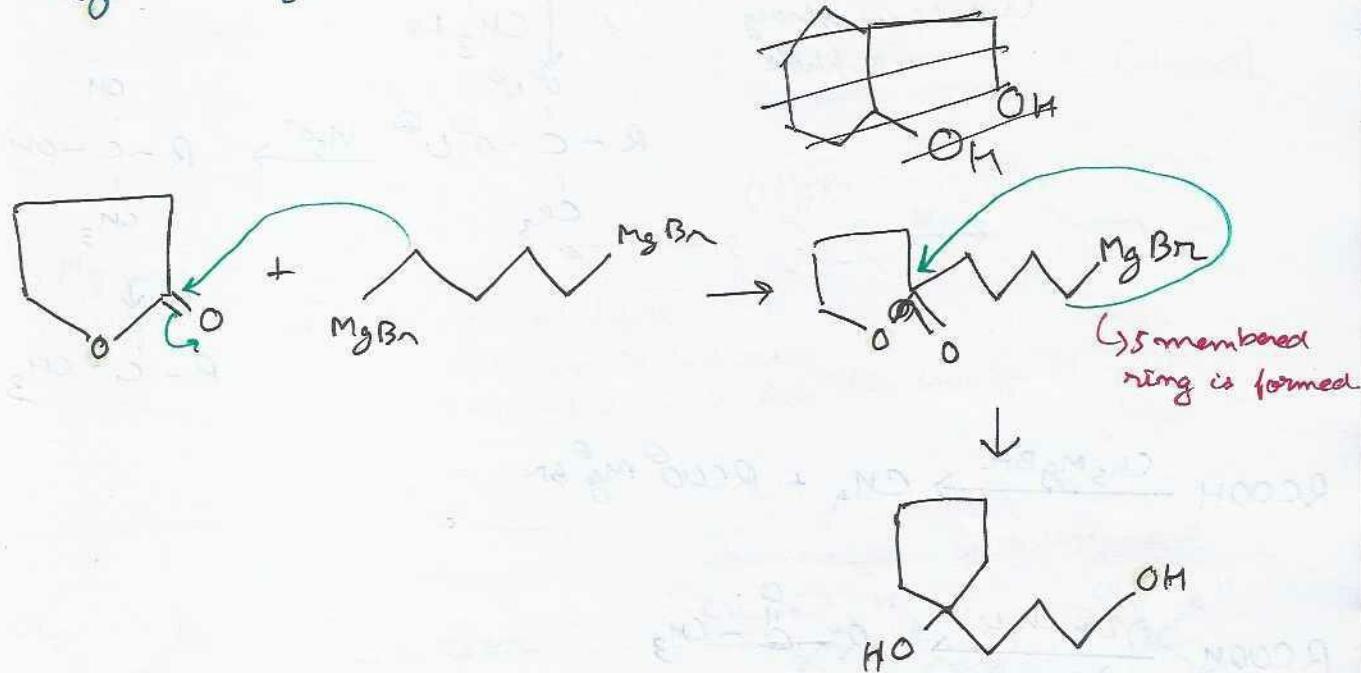
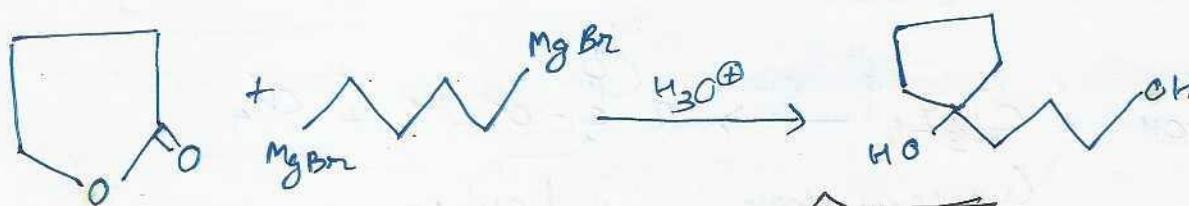
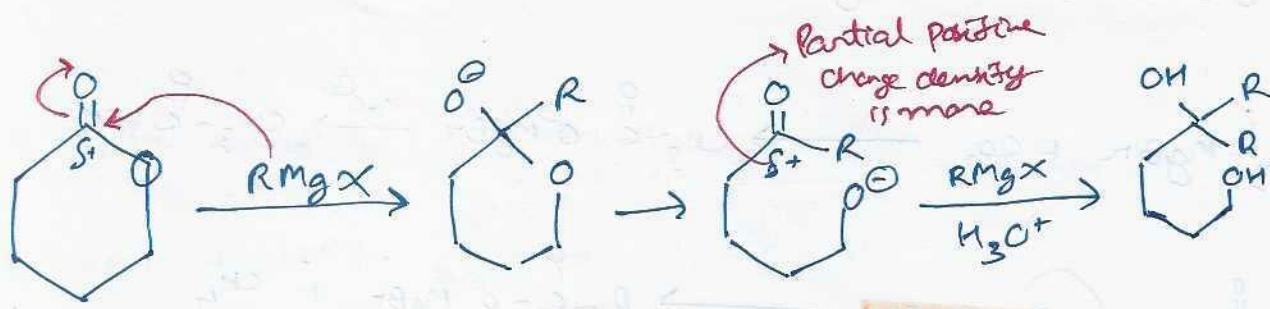
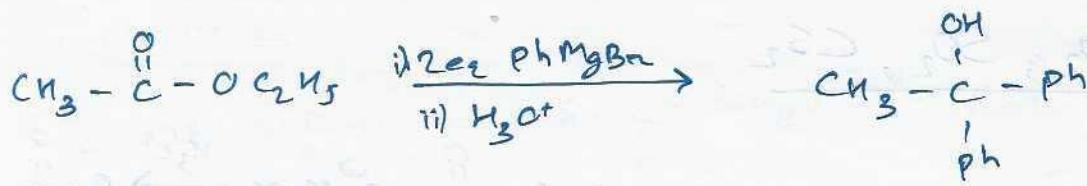
REACTIONS OF GRIGNARD REAGENT



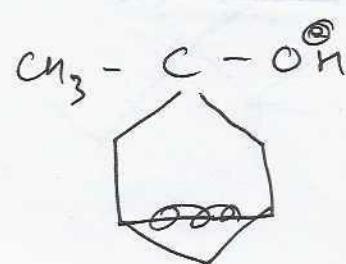
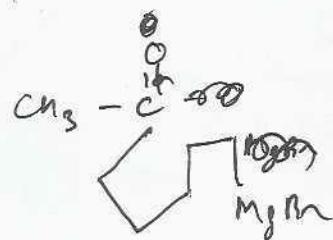


ESTERS

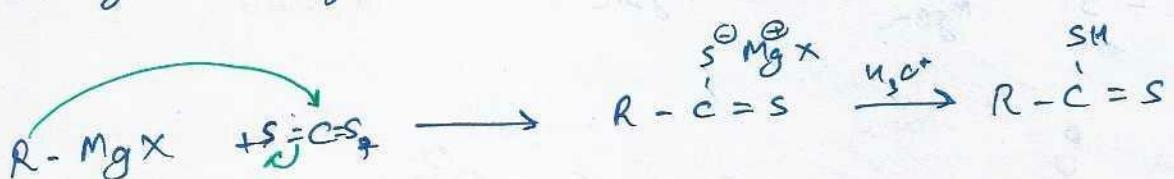
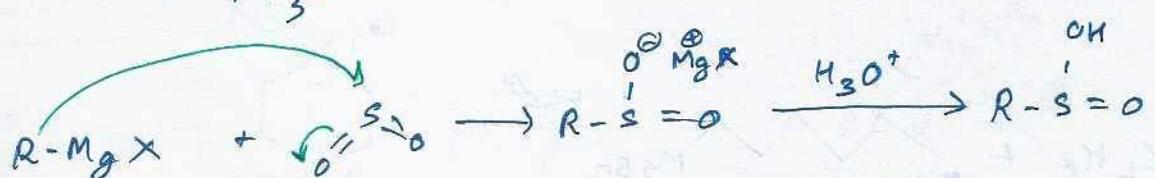
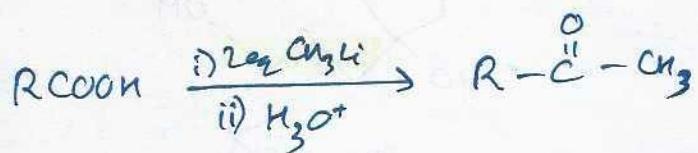
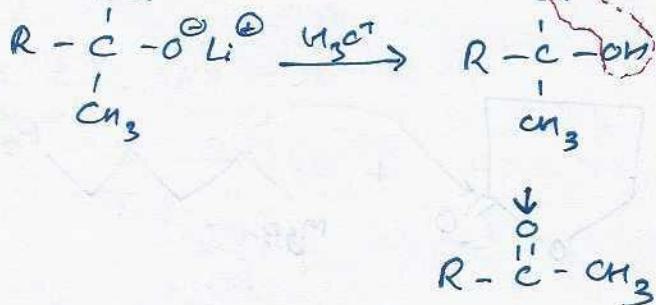
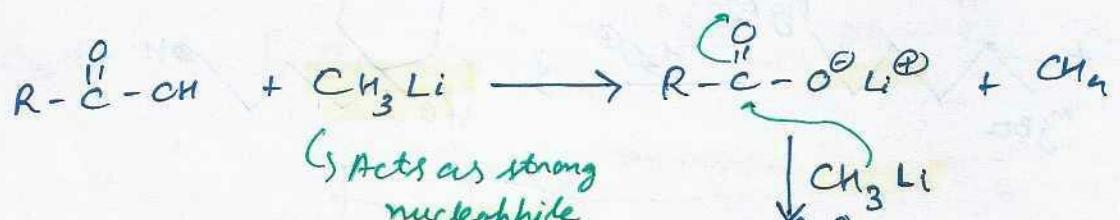
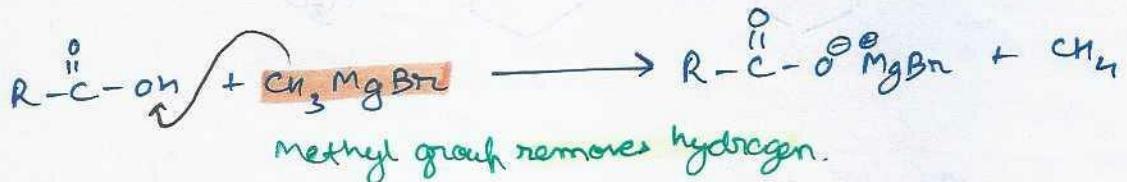
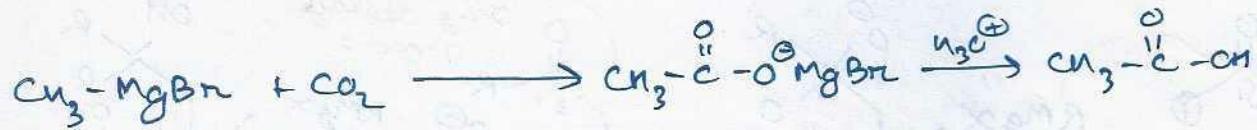
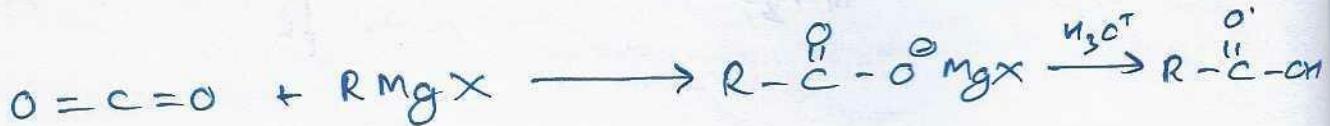




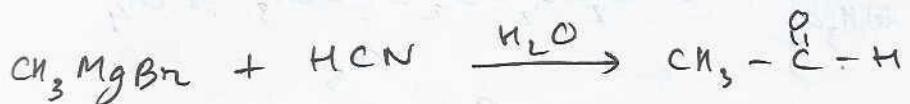
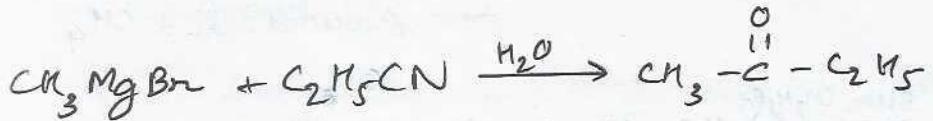
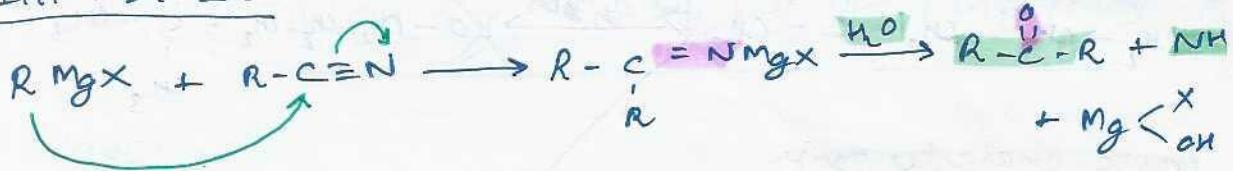
PhMgBr



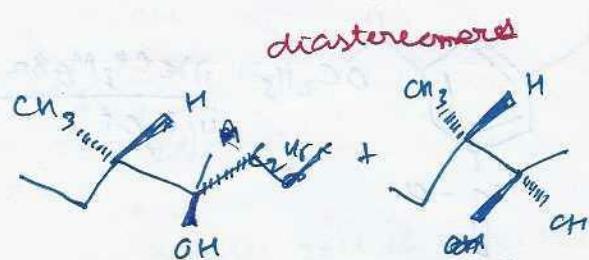
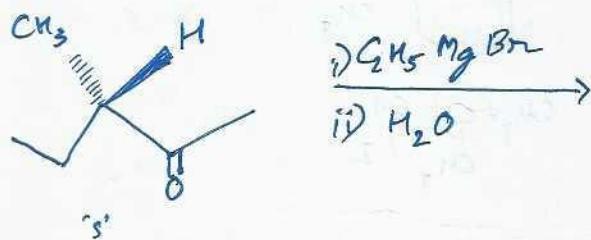
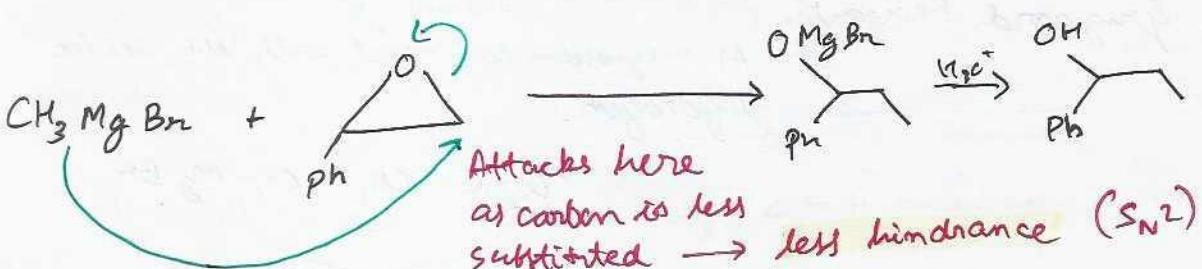
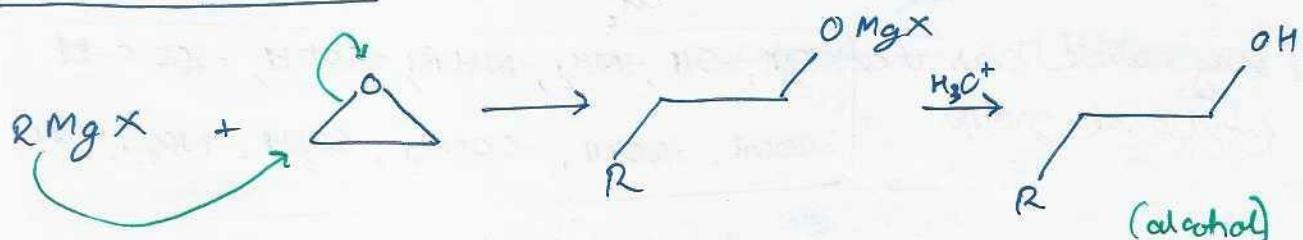
WITH CO_2 , SO_2 , CS_2



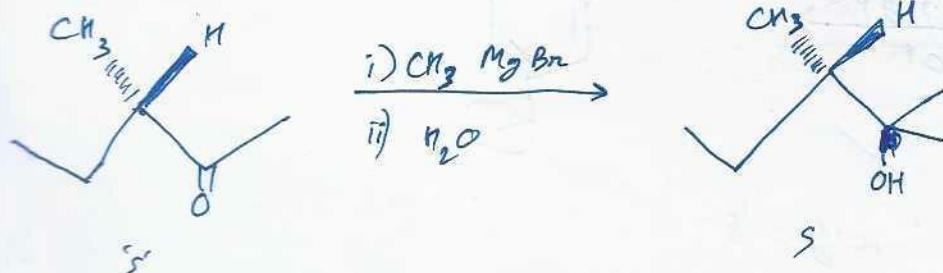
WITH NITRILES

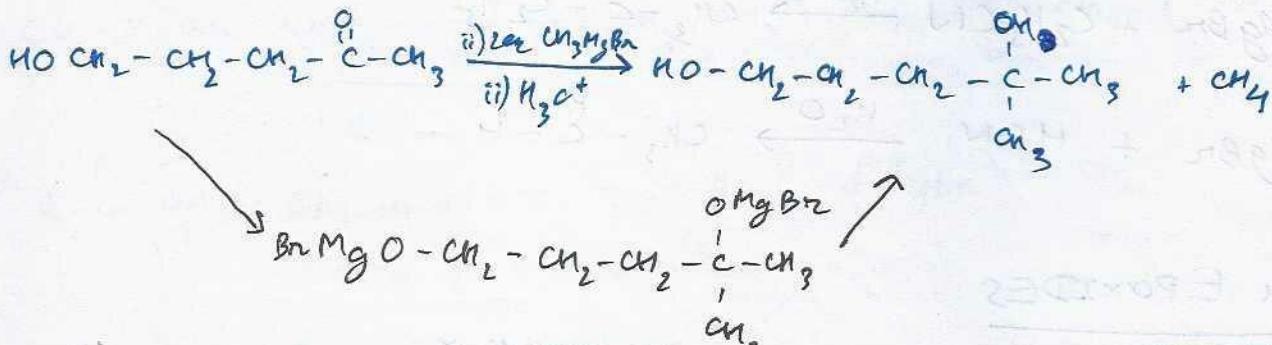
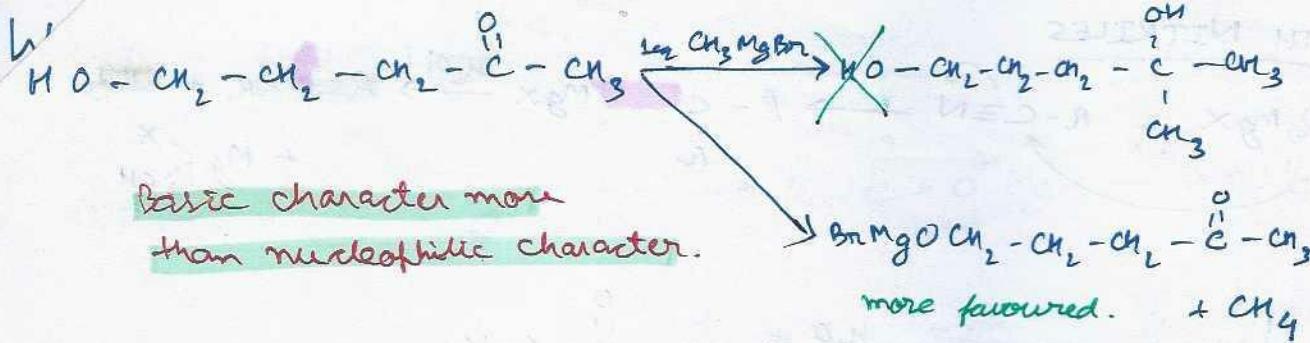


WITH EPOXIDES



Two chiral S,S centres are present



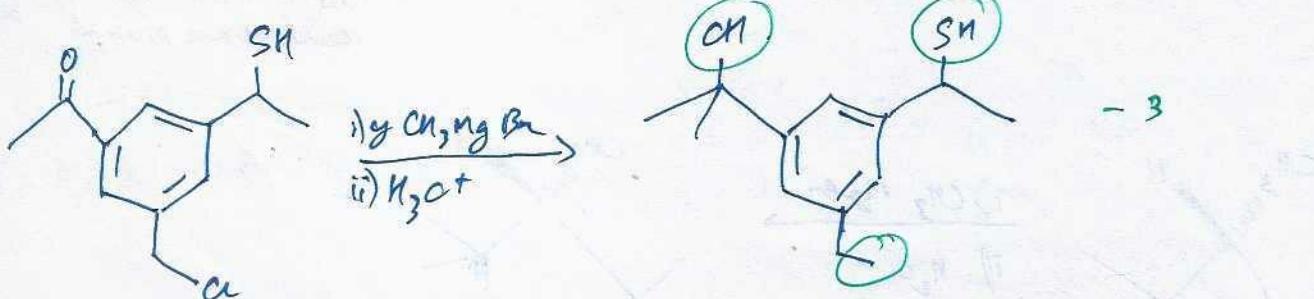
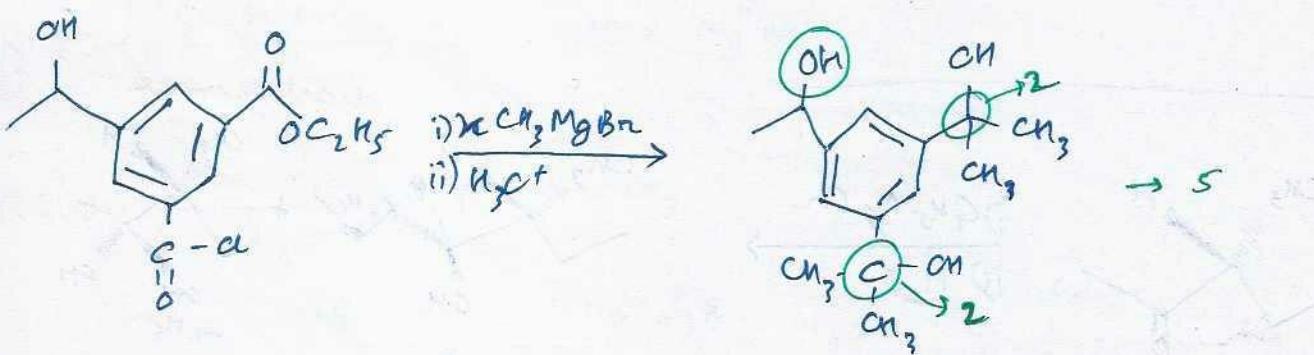
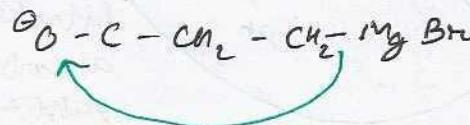


If alkyl halide has these functional groups

$-\text{OH}, -\text{SH}, -\text{NH}_2, -\text{NHR}, -\text{COOH}, -\text{C}\equiv\text{C-H}$
 $- \text{COOR}, -\text{COCl}, -\text{CONH}_2, \text{SO}_3\text{H}, \text{NO}_2, -\text{CN}$

We cannot use these alkyl halides to prepare Grignard Reagent.

As magnesium can react with the acidic hydrogen.



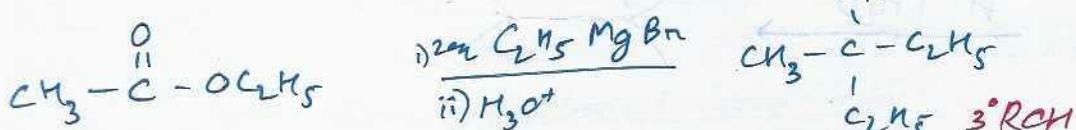
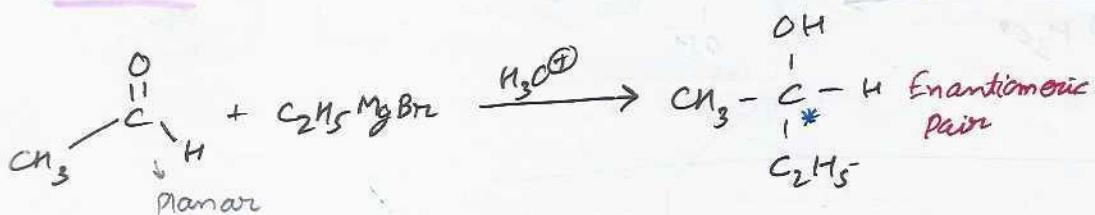
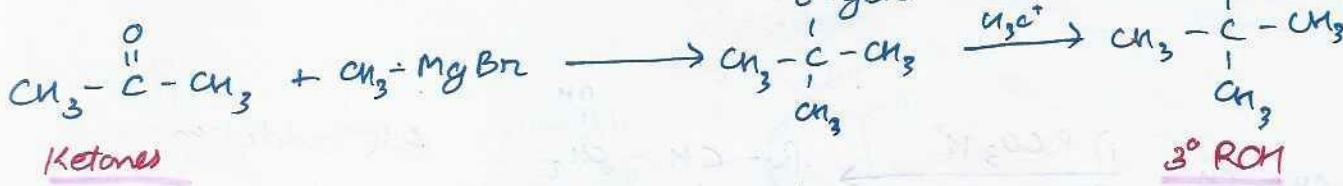
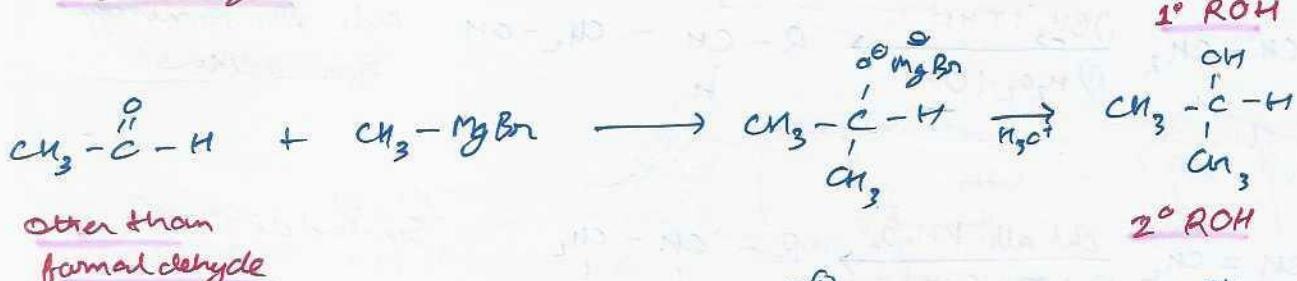
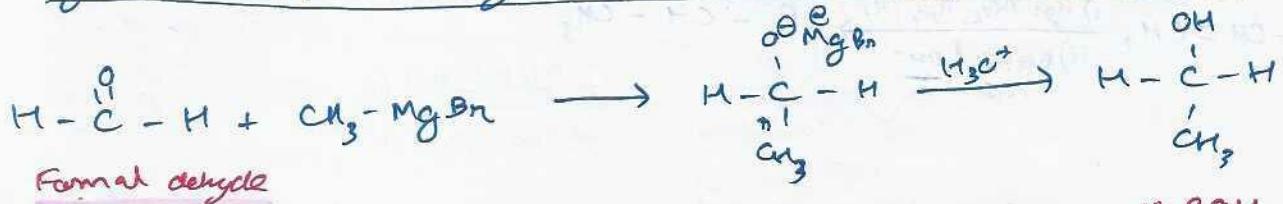
$$n+y=8$$

ALCOHOLS, PHENOLS, ETHERS

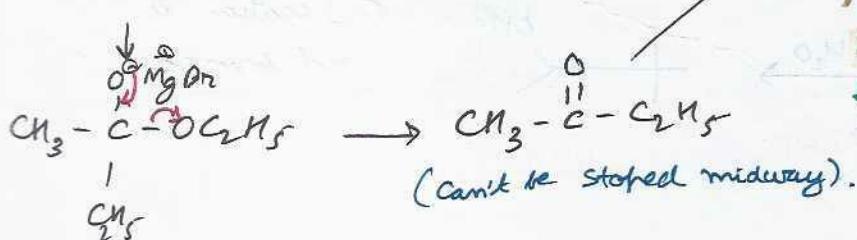
ALCOHOL

1. From Grignard Reagent

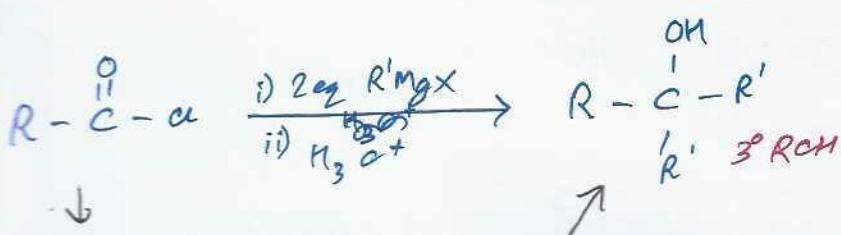
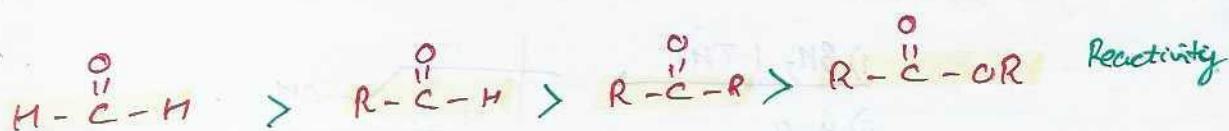
a. By reaction of carbonyl compounds with Grignard reagent.



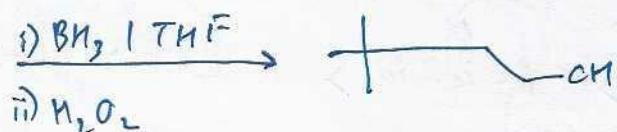
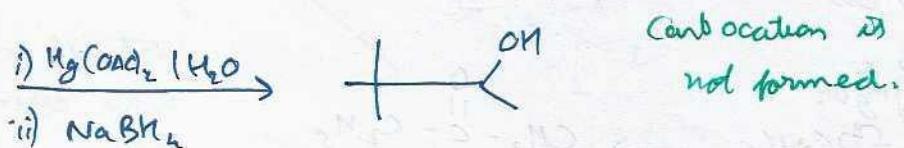
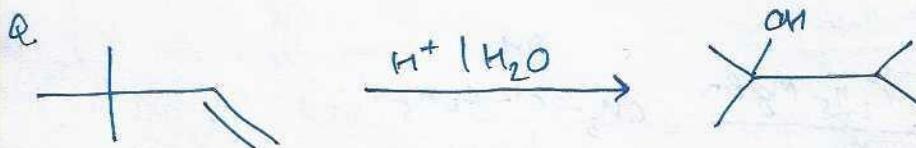
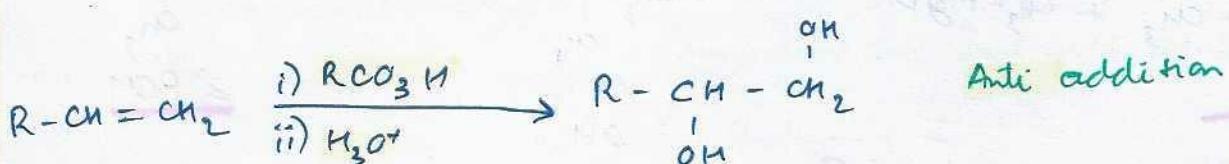
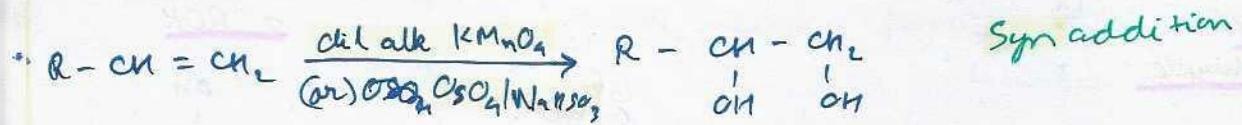
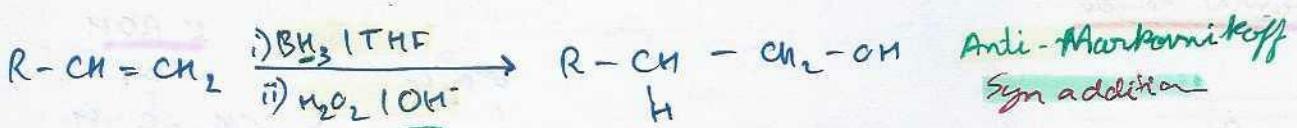
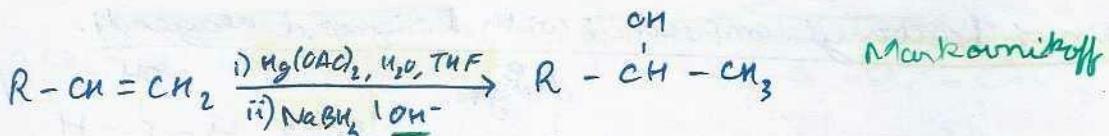
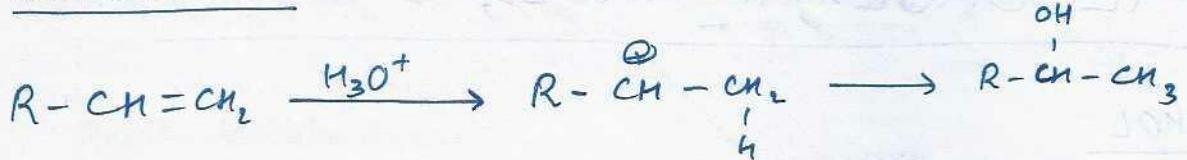
Esters



Ketones will be more reactive than esters. ($\text{as-OC}_2\text{H}_5 < \text{C}_2\text{H}_5$).



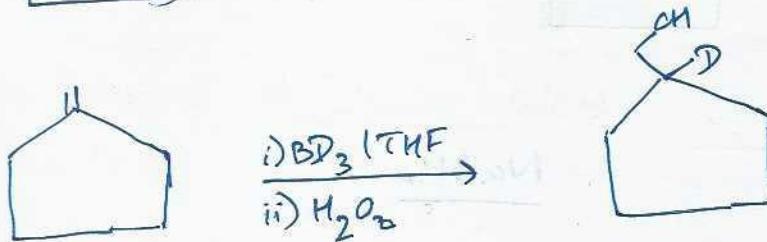
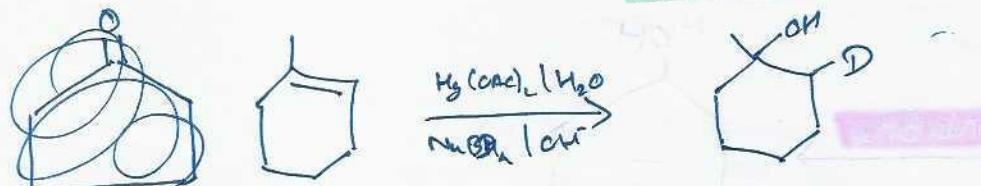
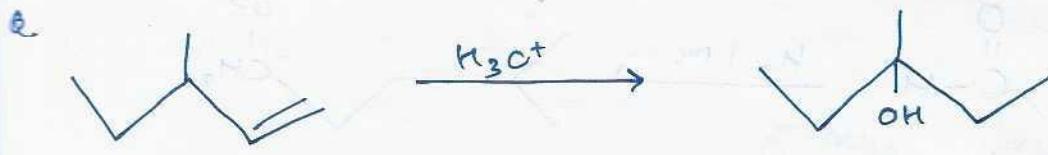
2. From alkenes



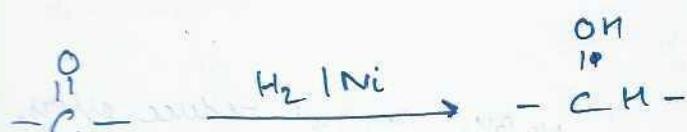
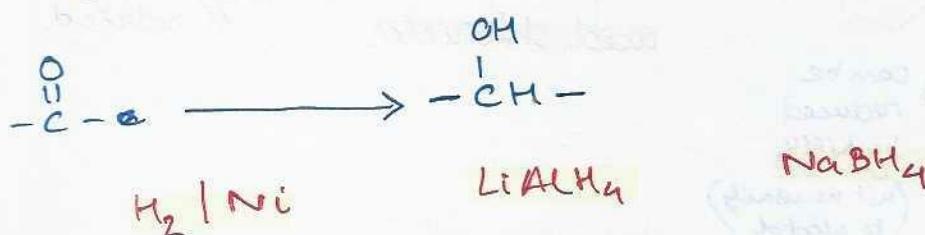
3. B

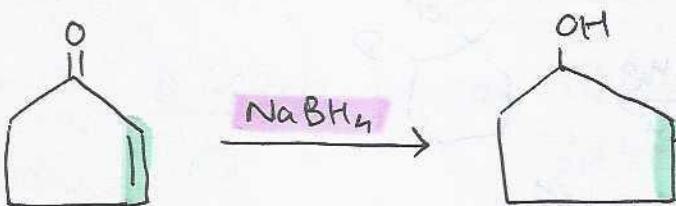
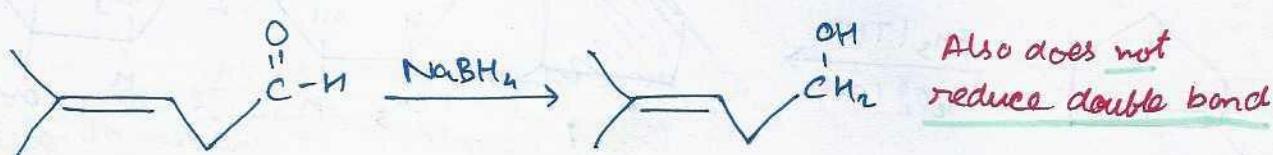
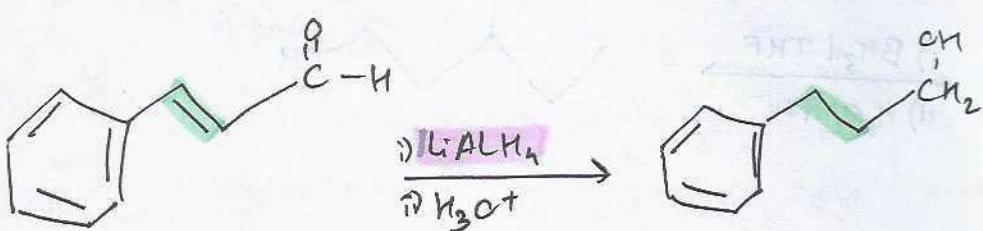
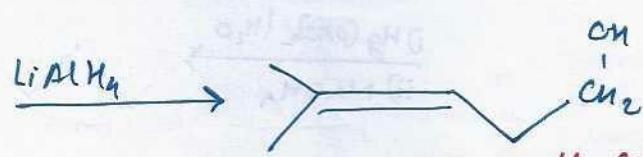
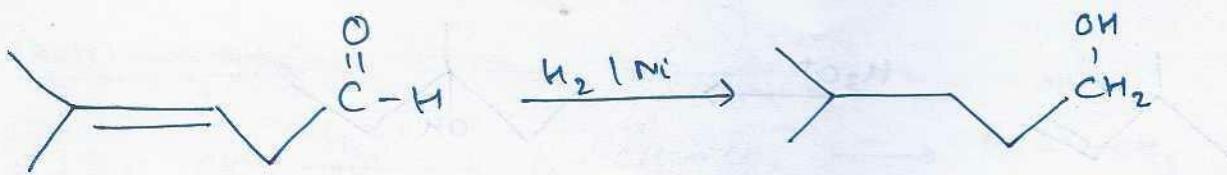
O
 C

O
 C



3. By the reduction of Carbonyl Compounds





LiAlH₄

aldehydes
ketones
esters
carboxylic acid
amides → amines
acid chlorides
alkyl ~~halides~~ halides → alkanes
nitriles → amines

→ can be reduced by LiAlH₄
(not necessarily)
to alcohol

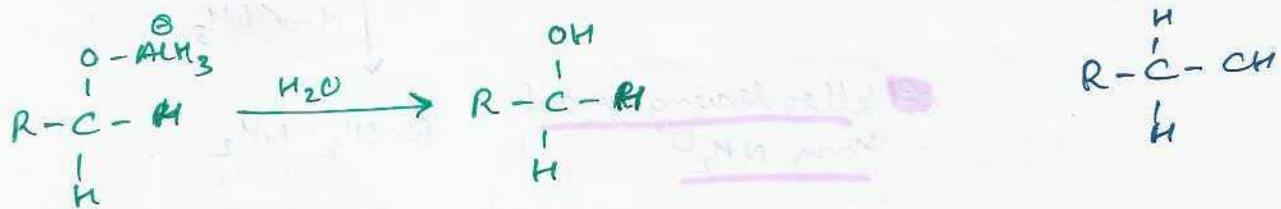
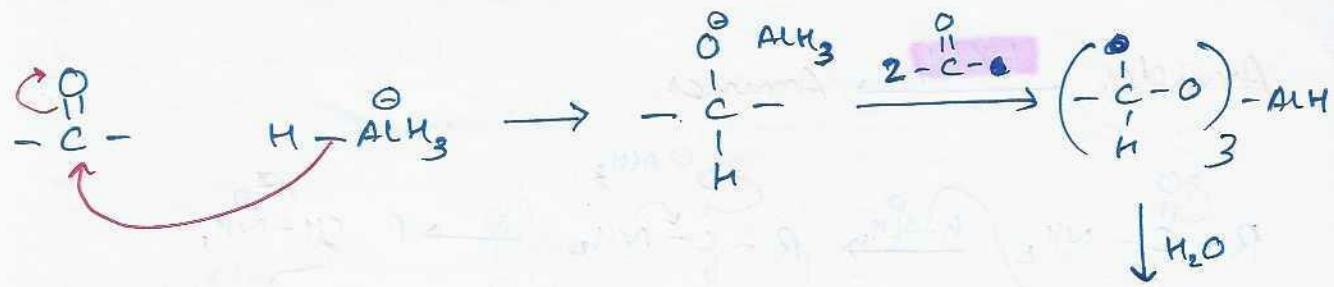
NaBH₄

aldehydes
ketones
acid chlorides → alcohols
(remaining can't be reduced)

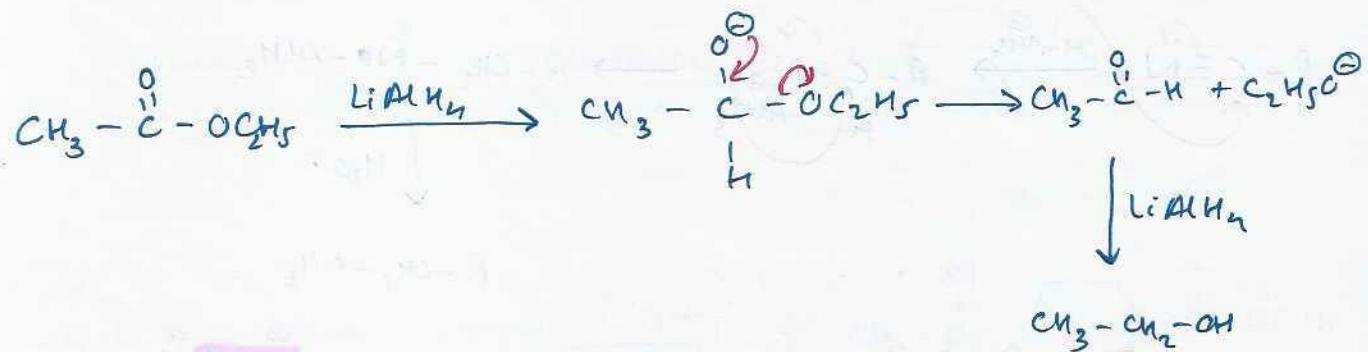
NaBH₄ cannot reduce esters.

$\text{LiAlH}_4 > \text{NaBH}_4$

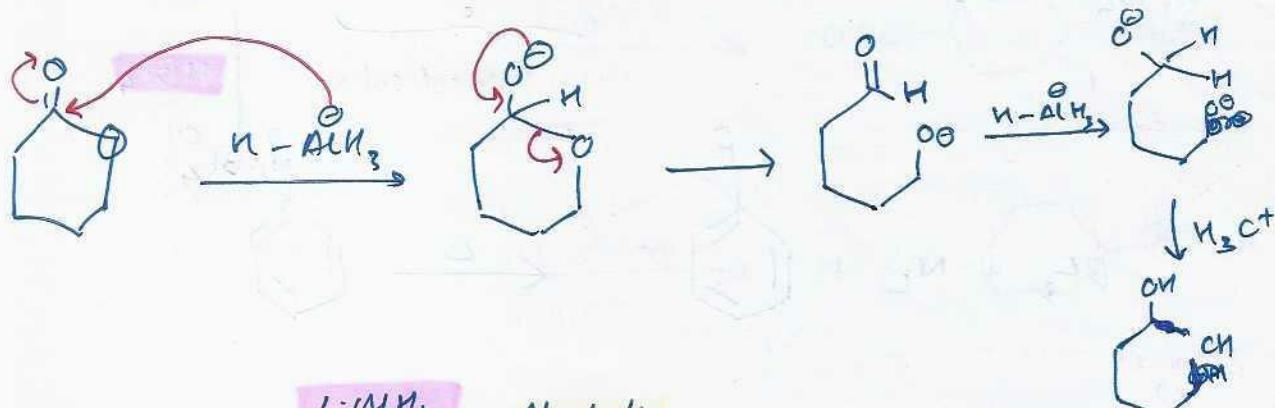
reducing strength.



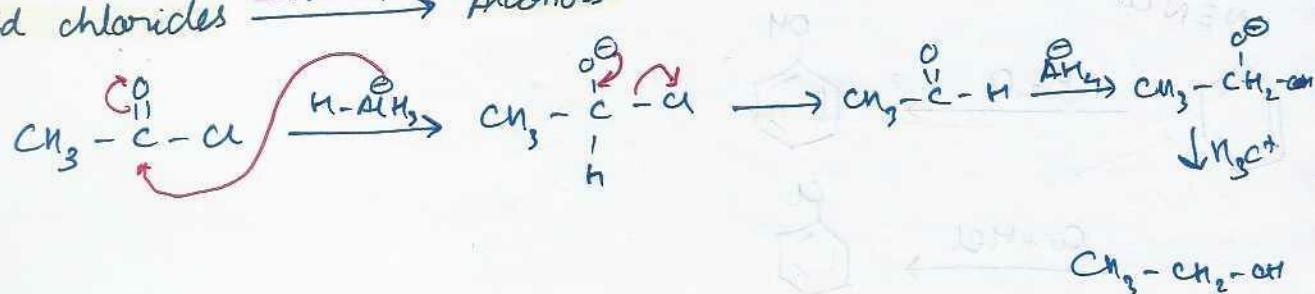
Esters $\xrightarrow{LiAlH_4}$ Alcohols

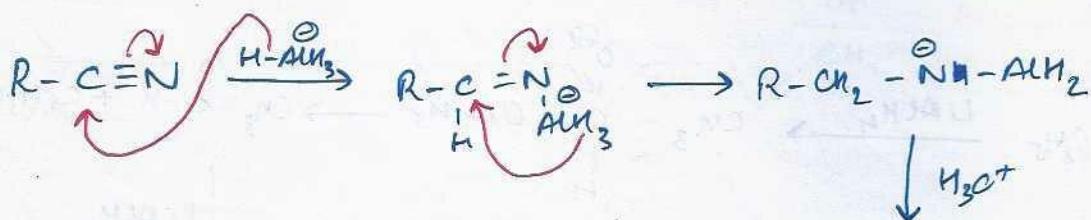
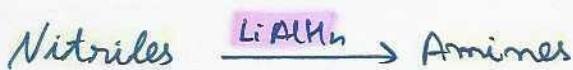
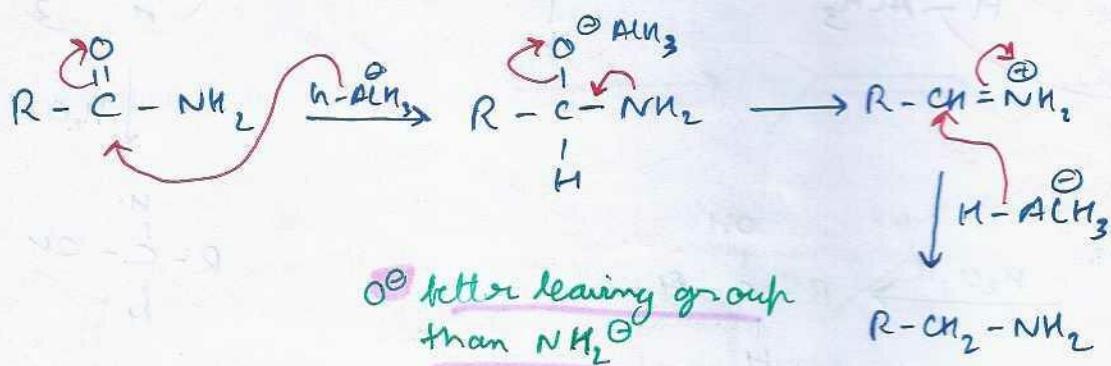
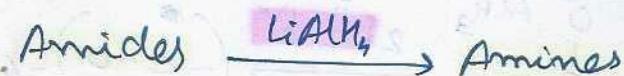
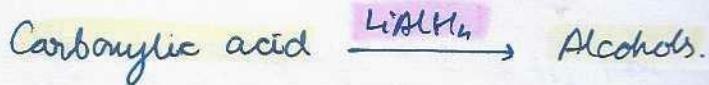


Cyclic esters $\xrightarrow{LiAlH_4}$ diols.
(Lactones)

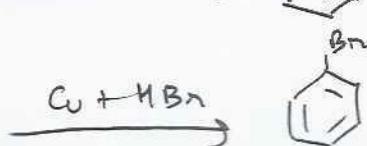
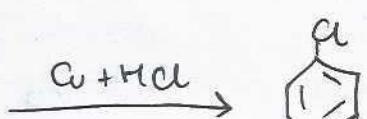
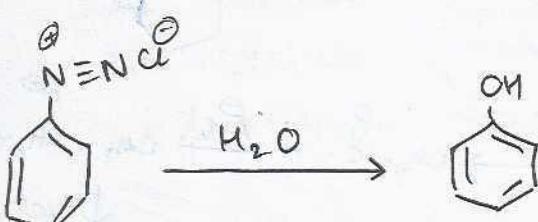
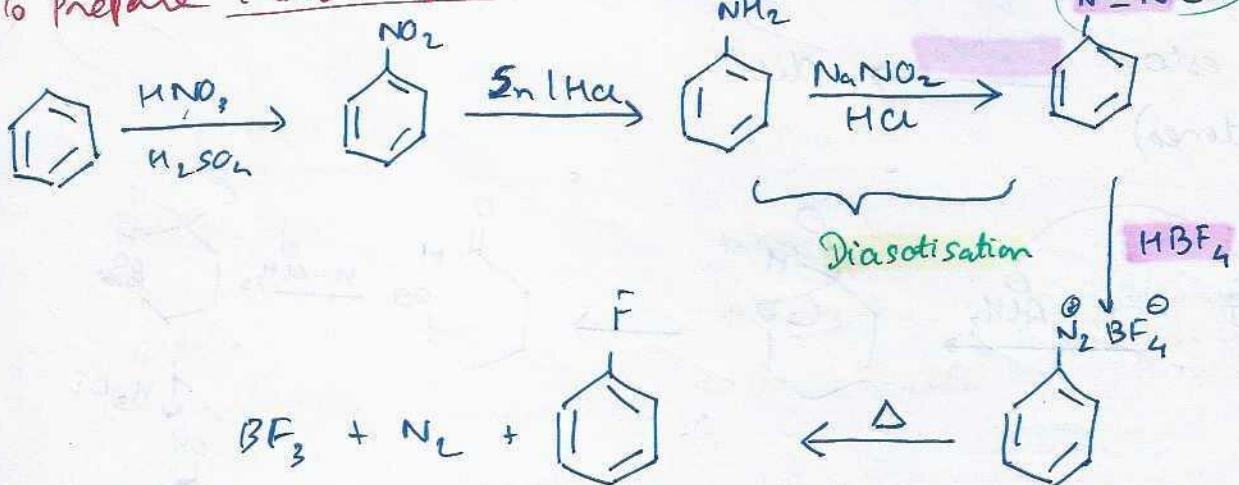


Acid chlorides $\xrightarrow{LiAlH_4}$ Alcohols

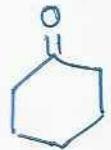




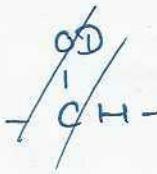
To Prepare Floro Benzene



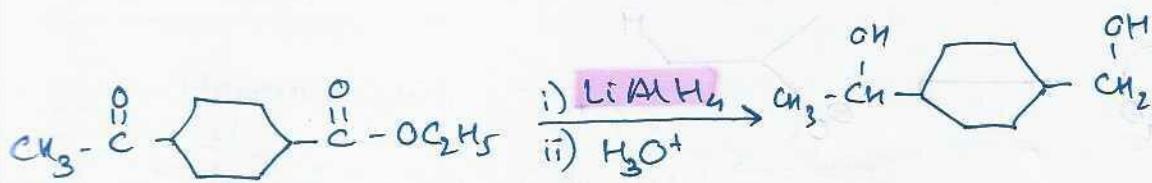
Li AlH₄



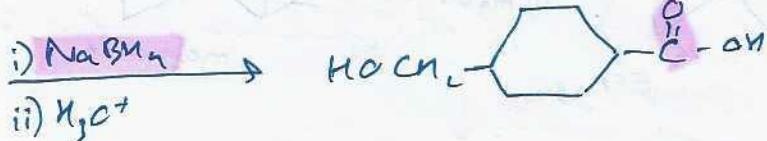
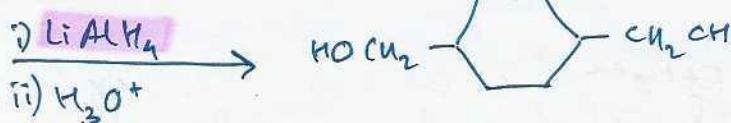
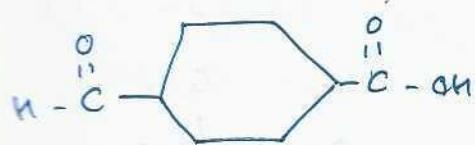
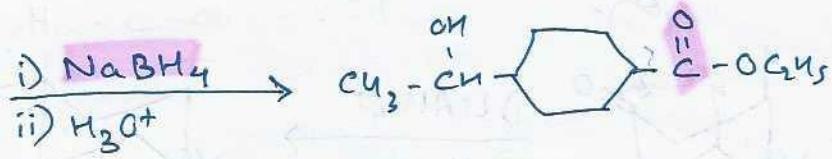
i) LiAlH₄
ii) H₃O⁺



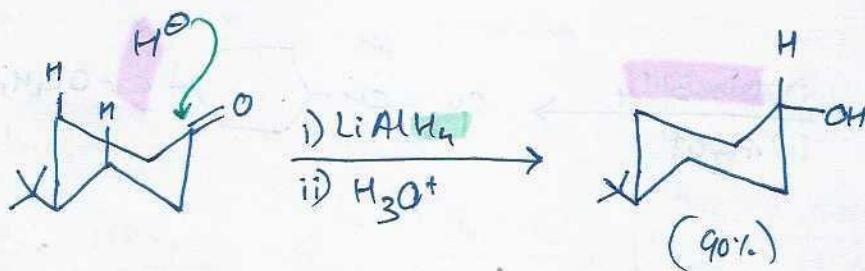
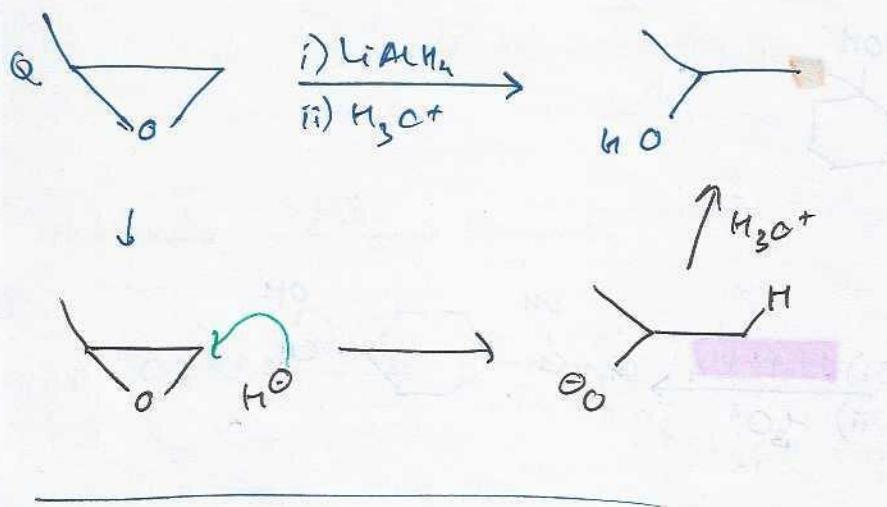
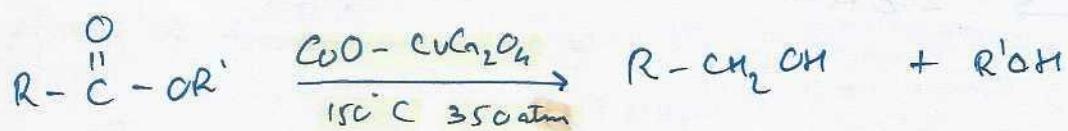
i) LiAlD₄
ii) H₃O⁺



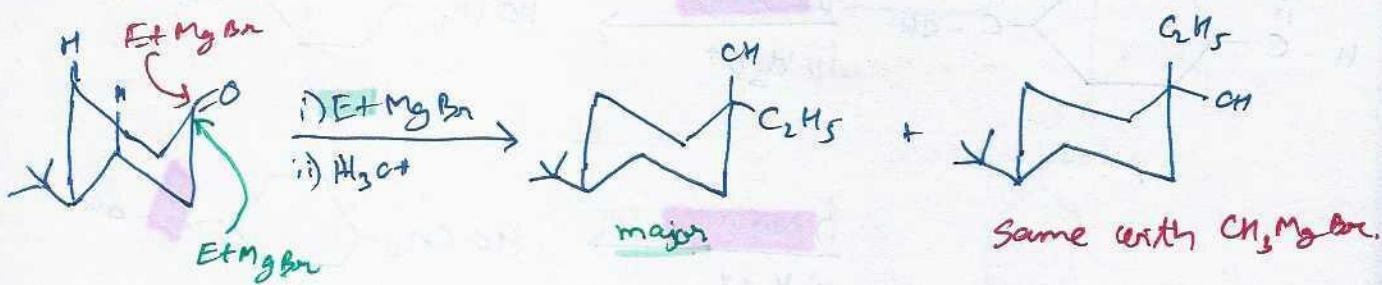
→ very
good
leaving
group.



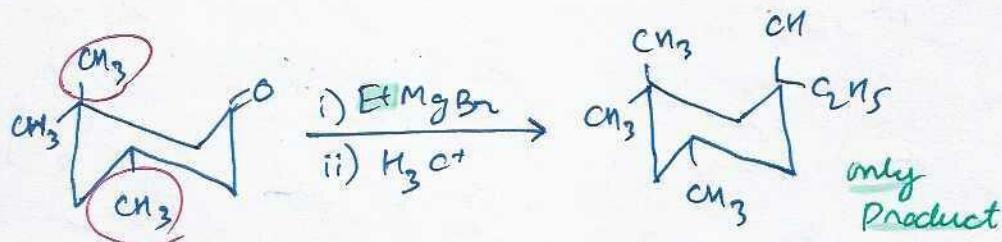
HYDROGENALYSIS



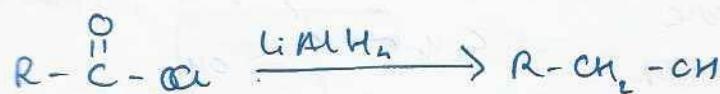
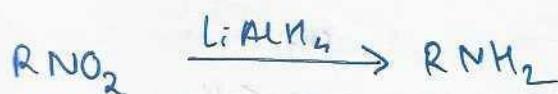
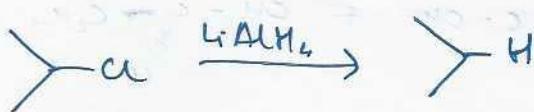
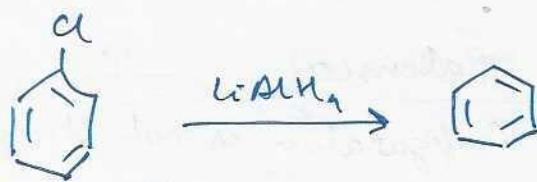
H_2^{\ominus} is not bulky group, so 1-3 dienial interactions are less.



1-3 dienial interactions.



more repulsion as compared to H.

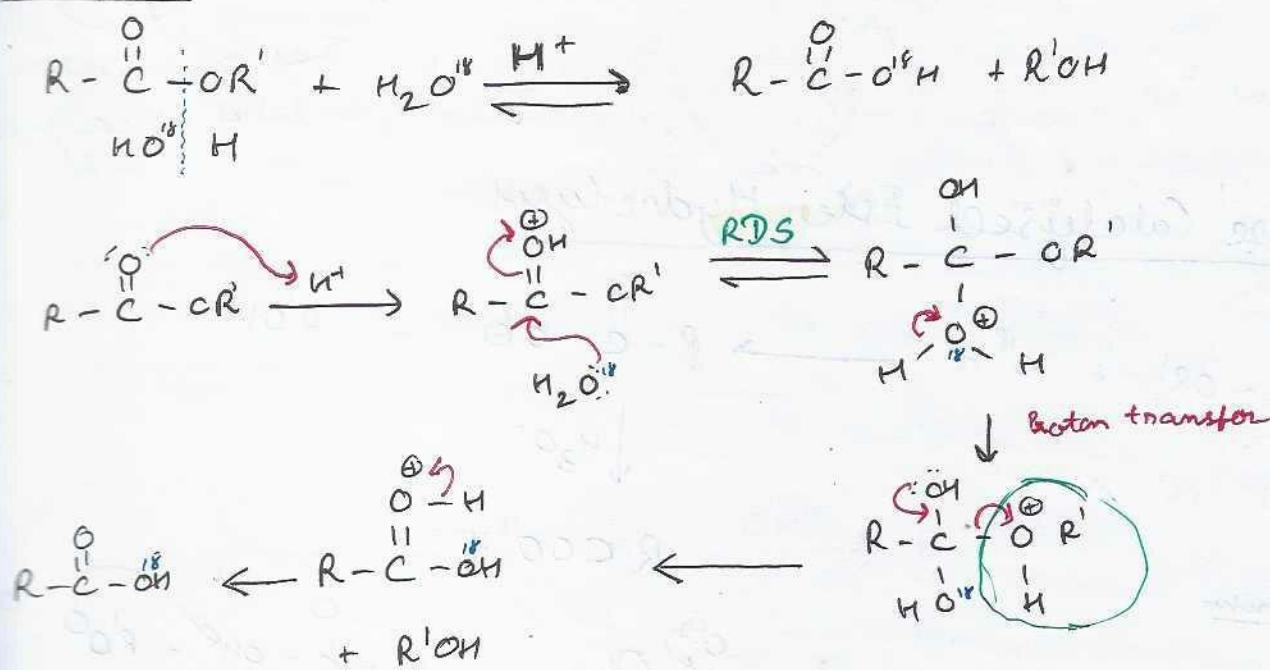


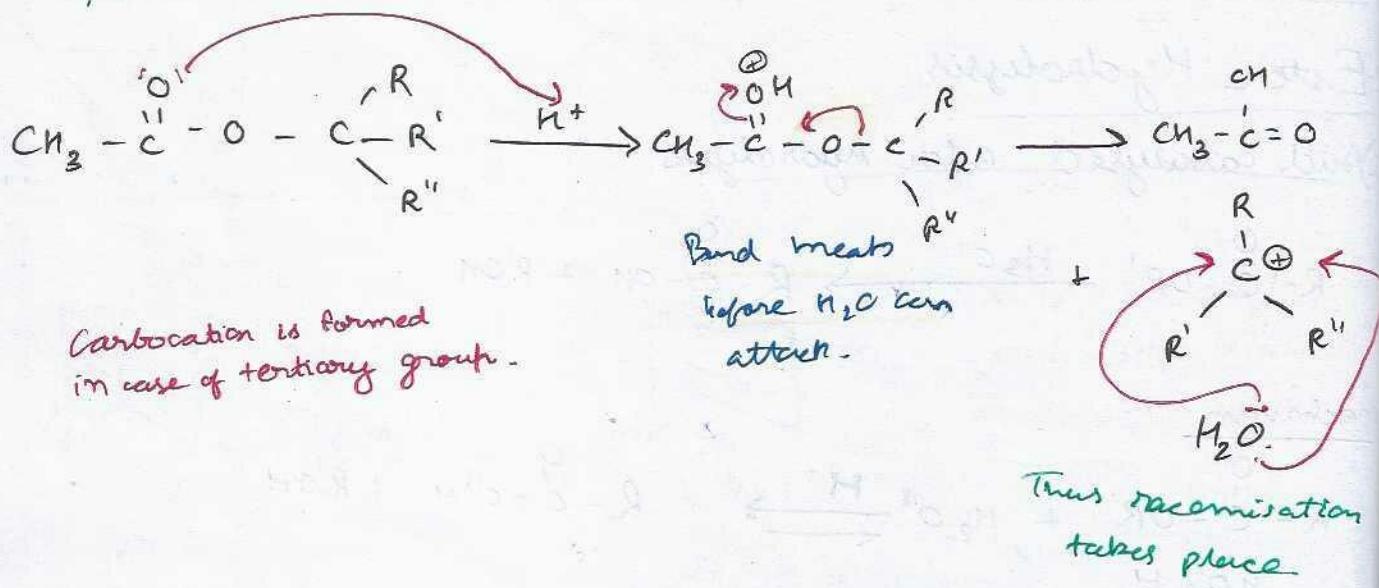
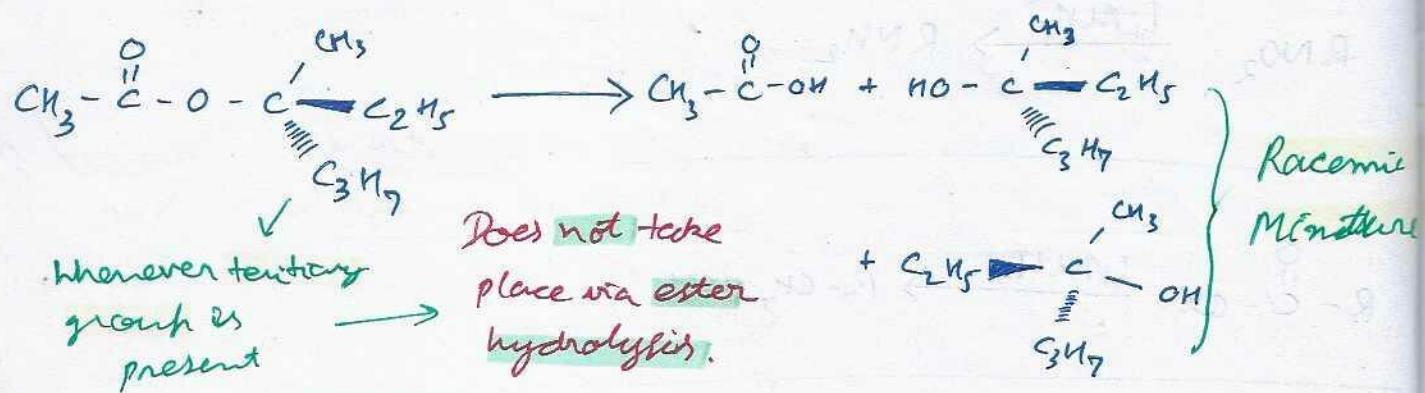
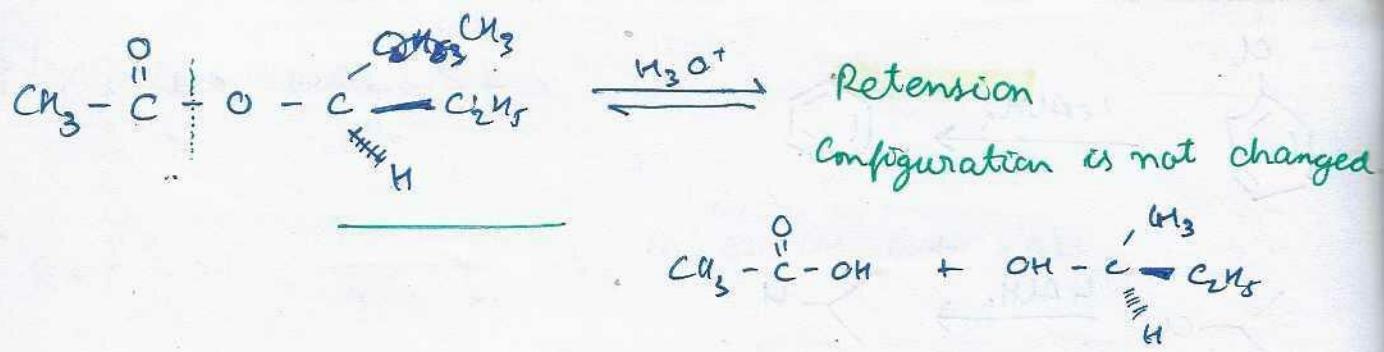
Ester Hydrolysis.

Acid catalysed ester hydrolysis.

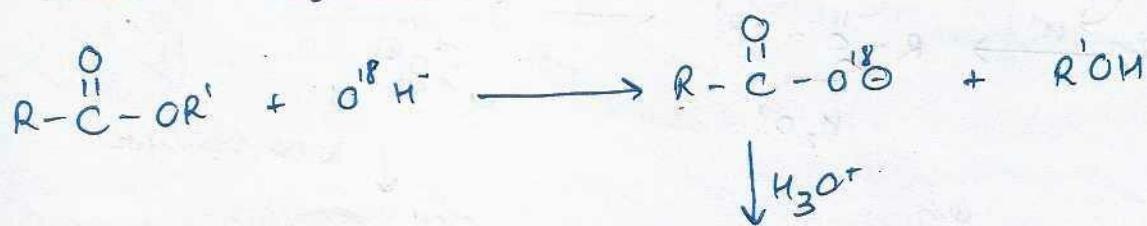


mechanism

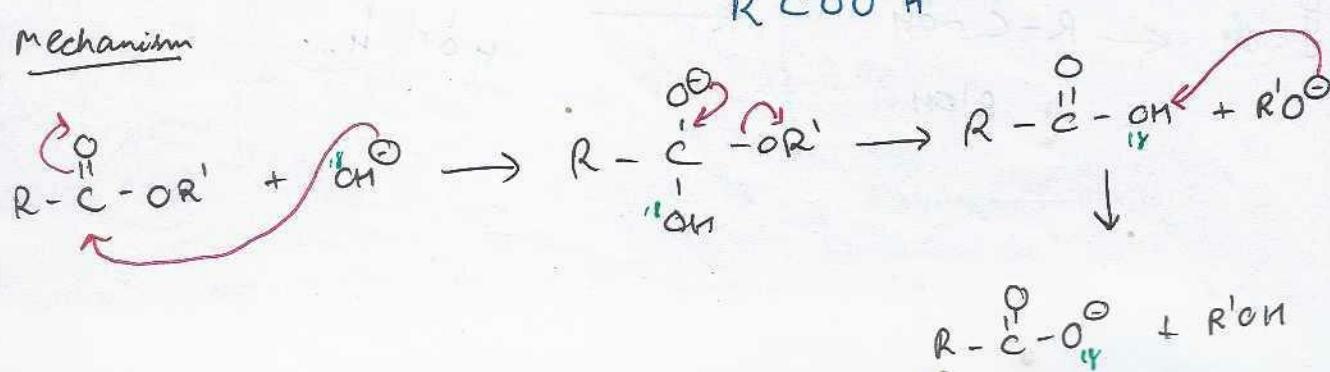




b) Base Catalysed Ester Hydrolysis

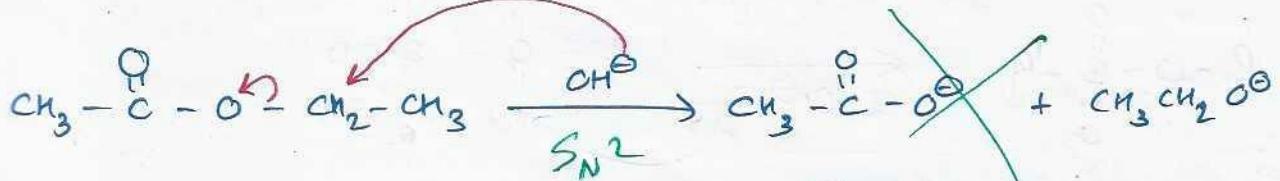
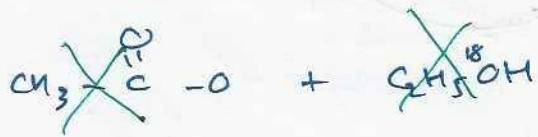


Mechanism





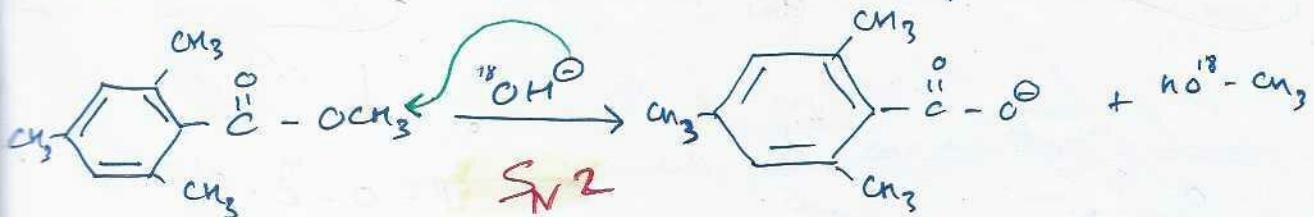
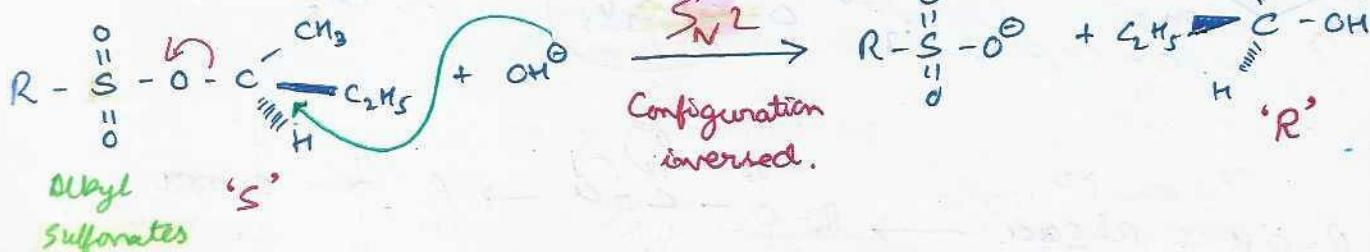
changed.



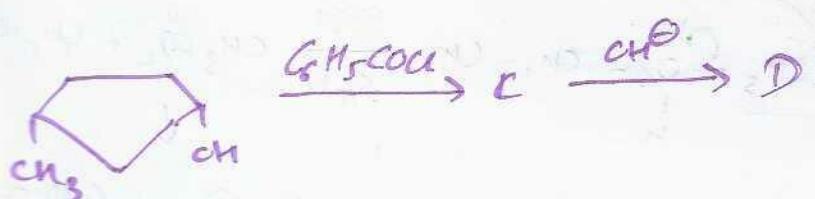
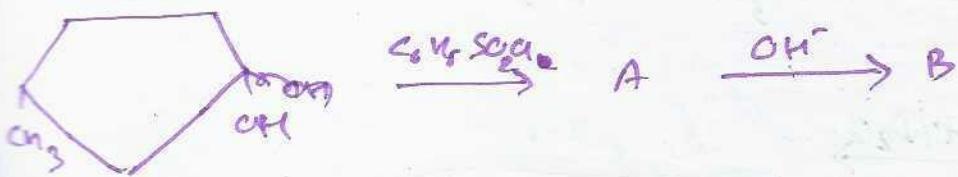
These products are not formed.

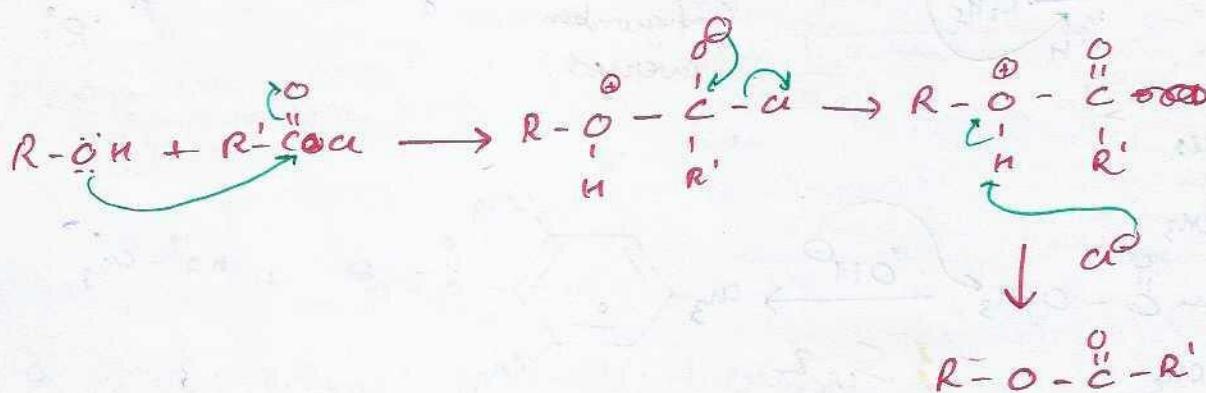
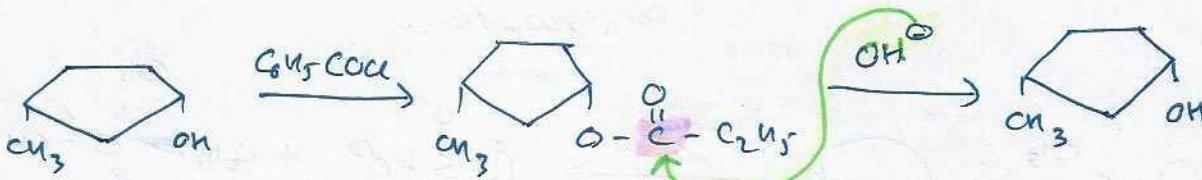
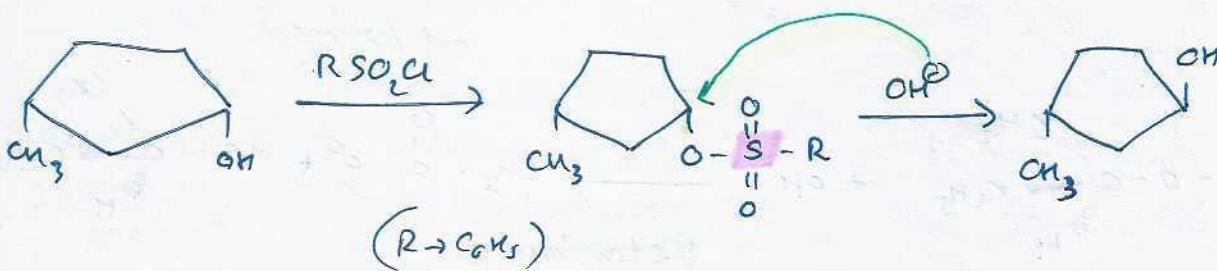
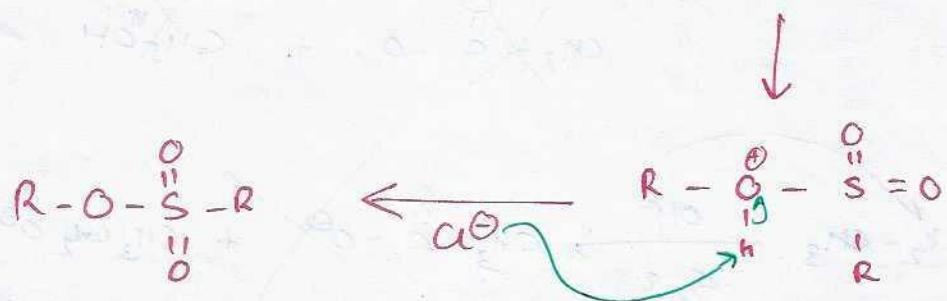
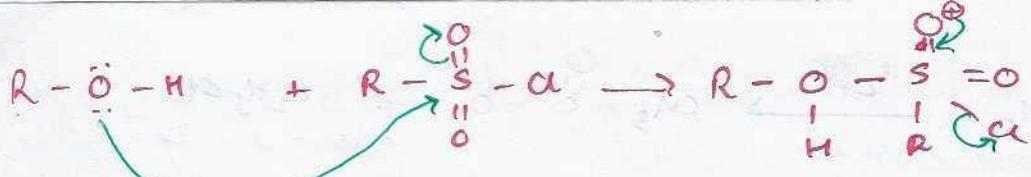


Retention of configuration.

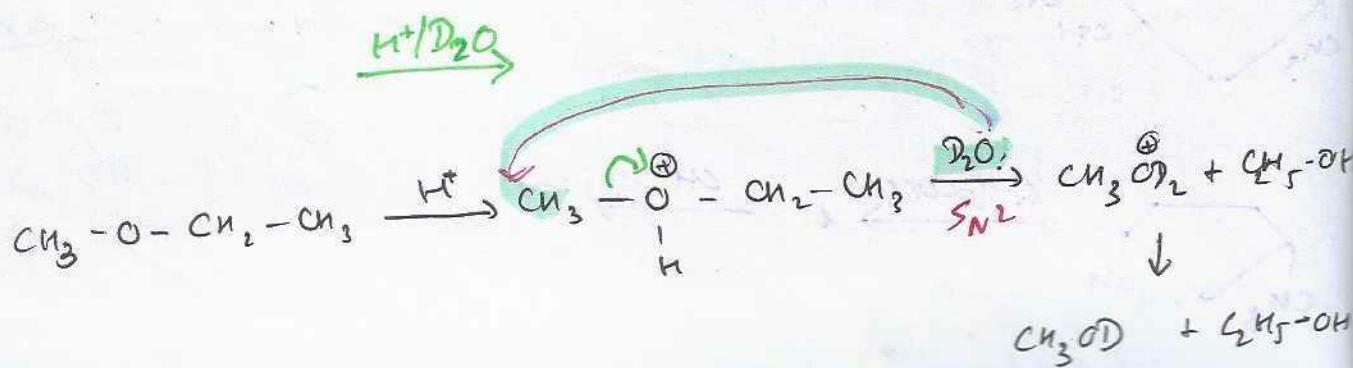


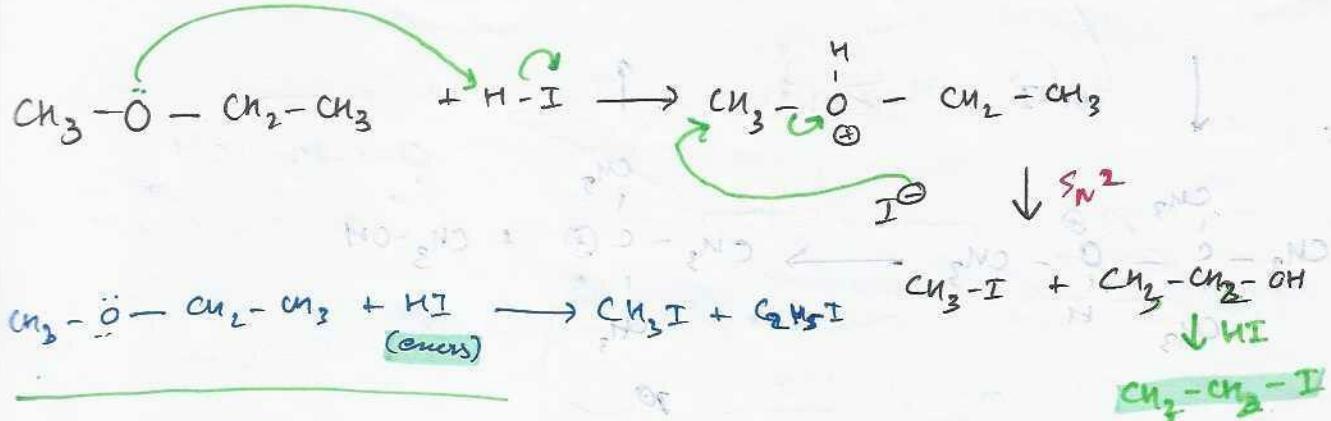
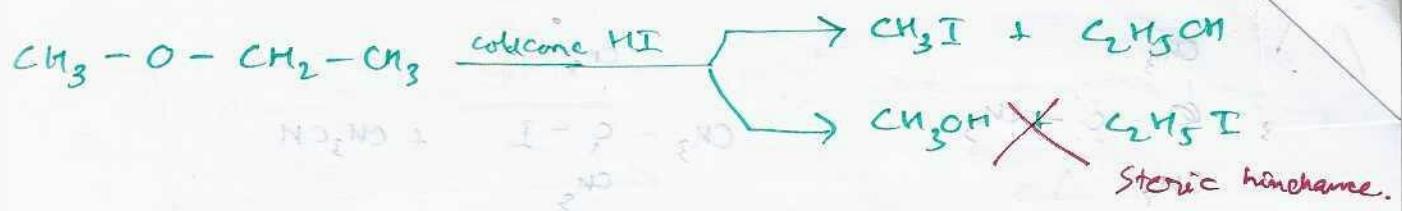
Steric hindrance prevent the formation of tetrahedral intermediate.



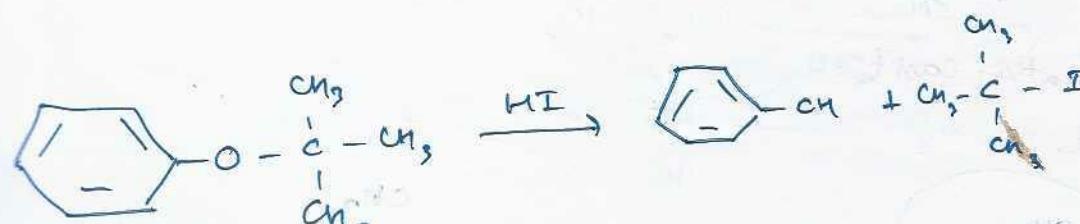
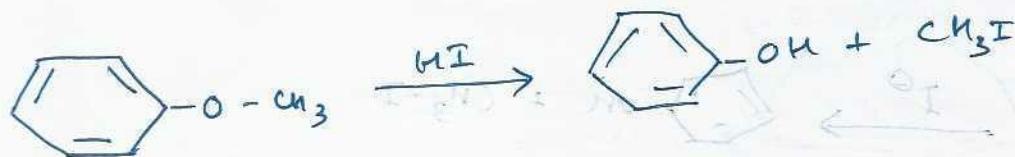
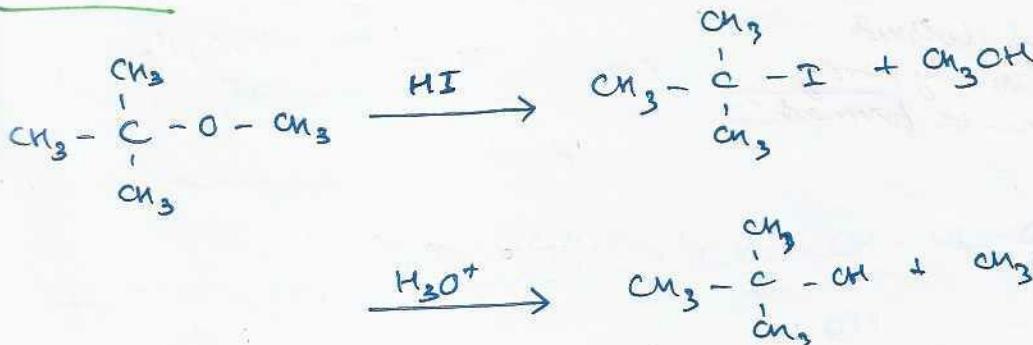
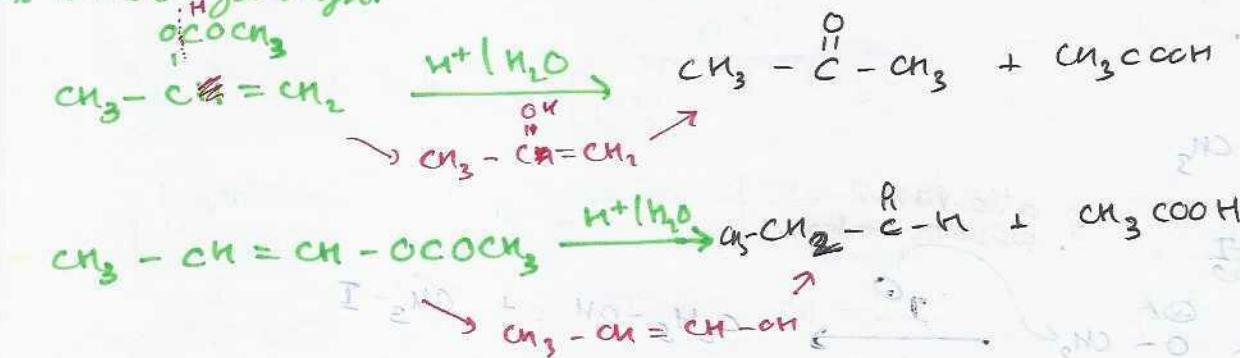


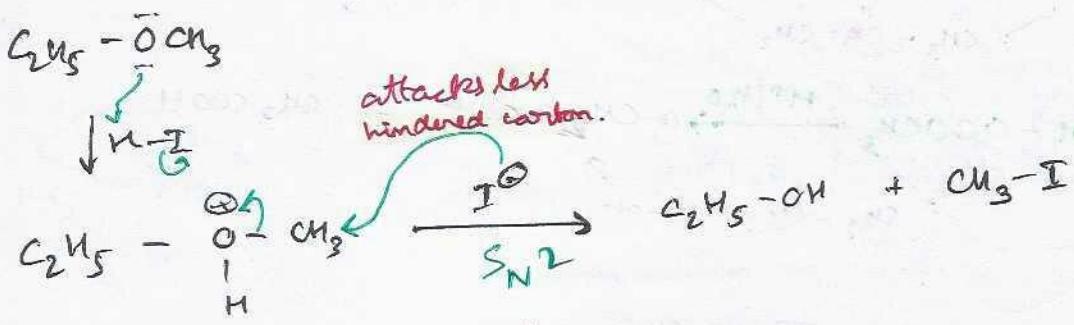
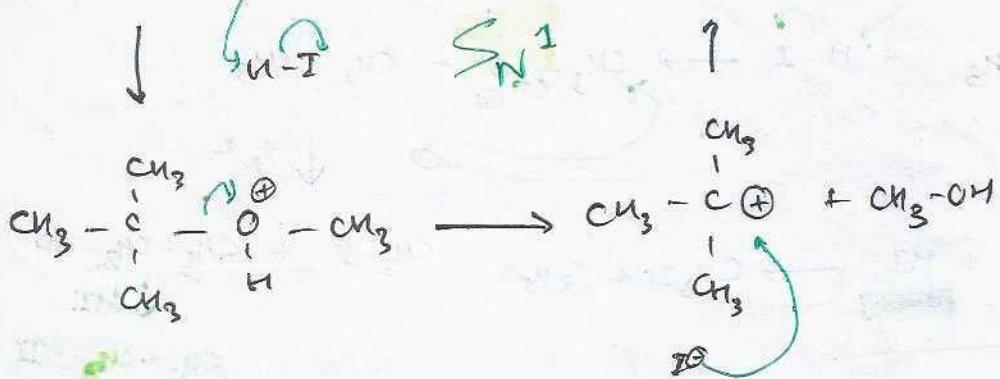
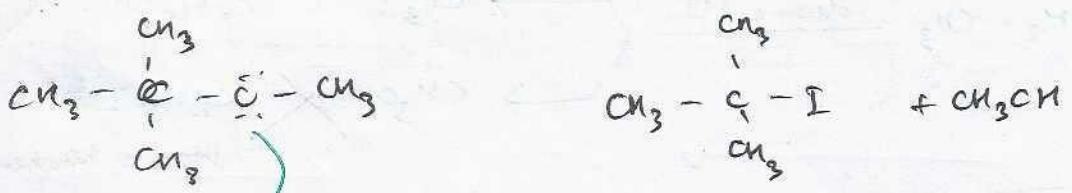
4. From Ethers Hydrolysis



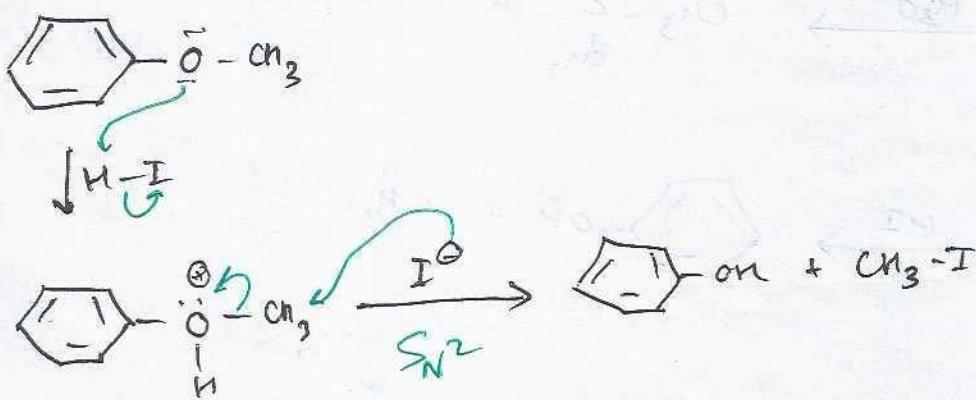


* Ester hydrolysis

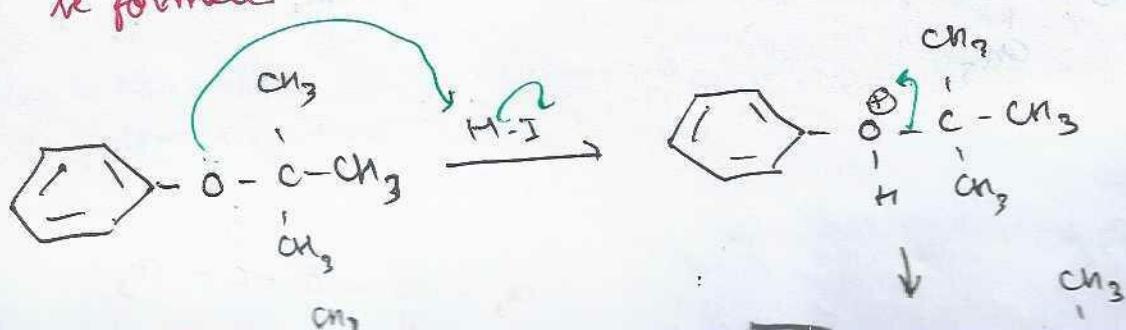


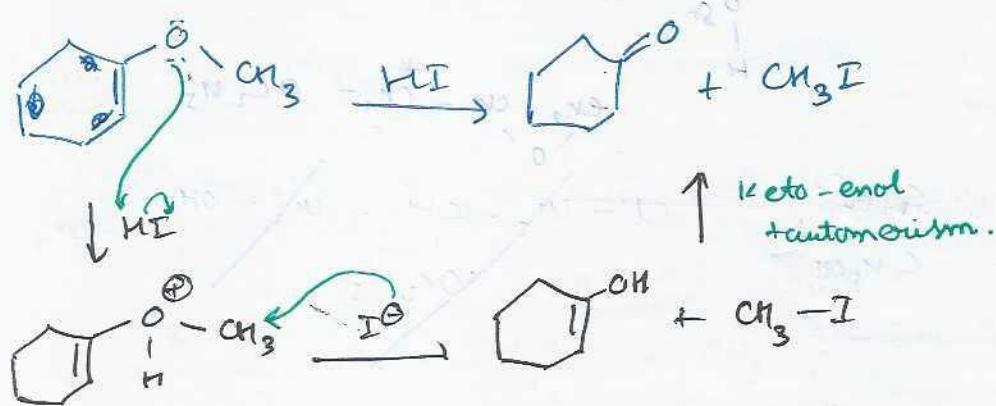
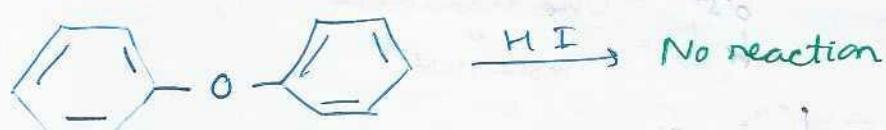
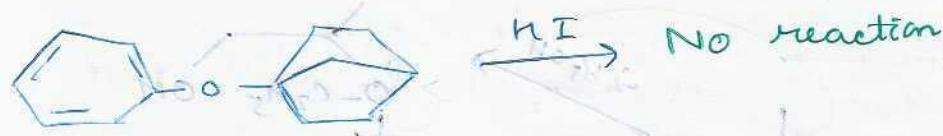
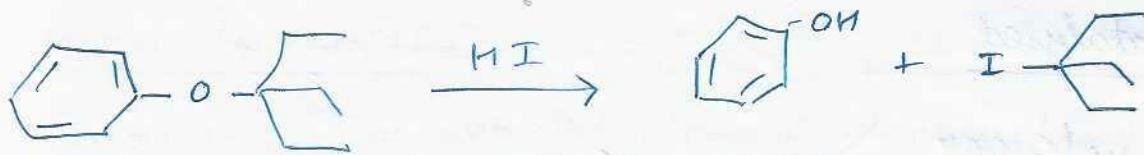


Bond breaking does not take place. As only primary carbocation can be formed



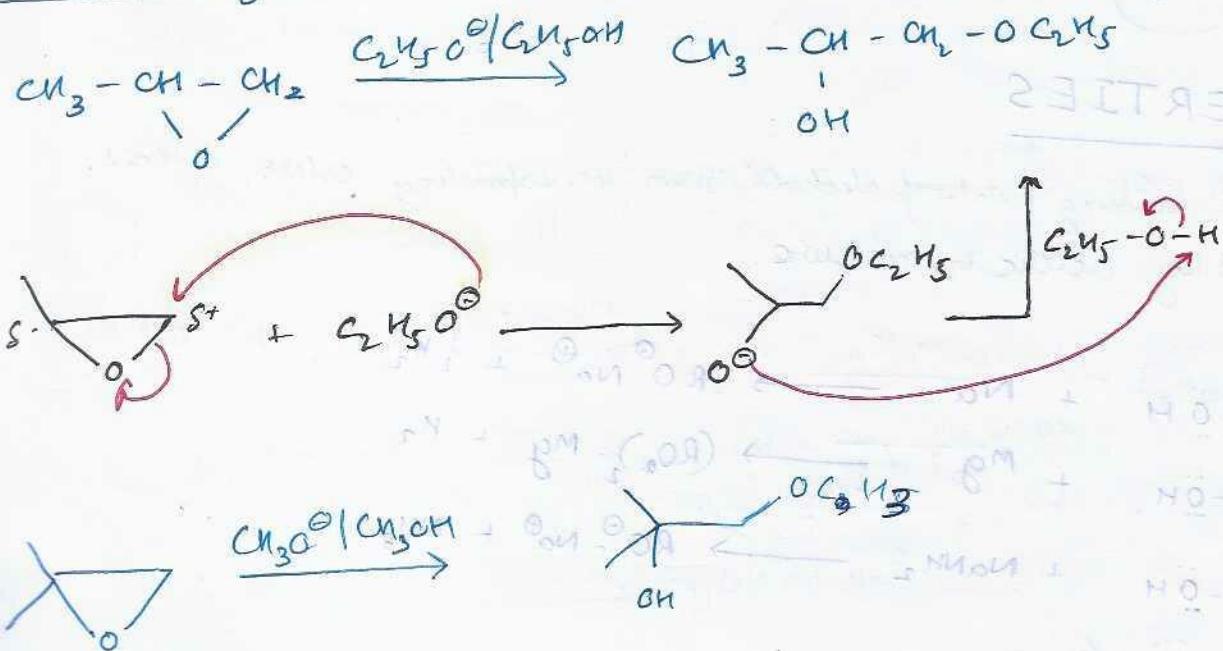
Phenyl carbocation can't be formed



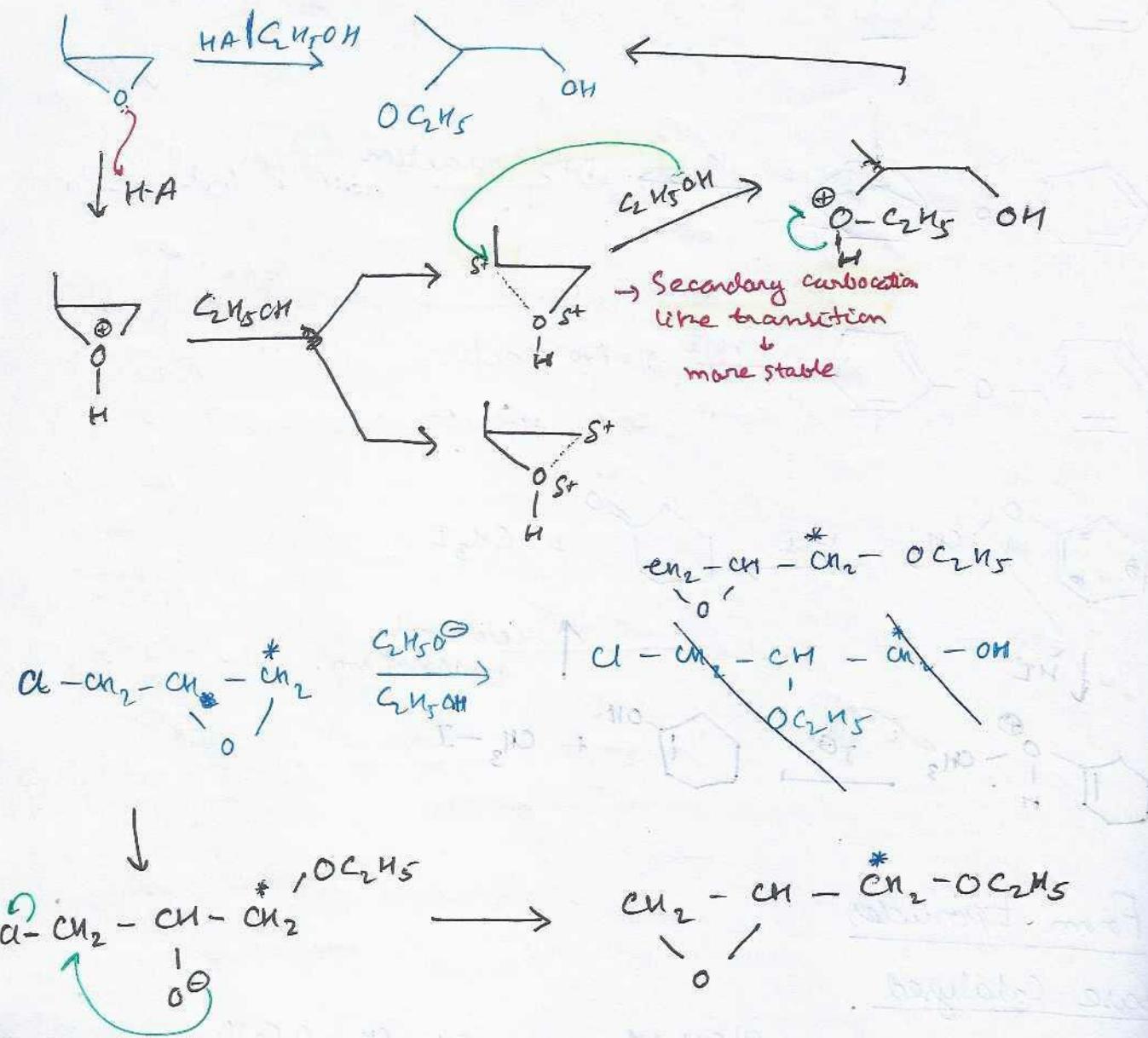


b. From Eponides

Base Catalysed

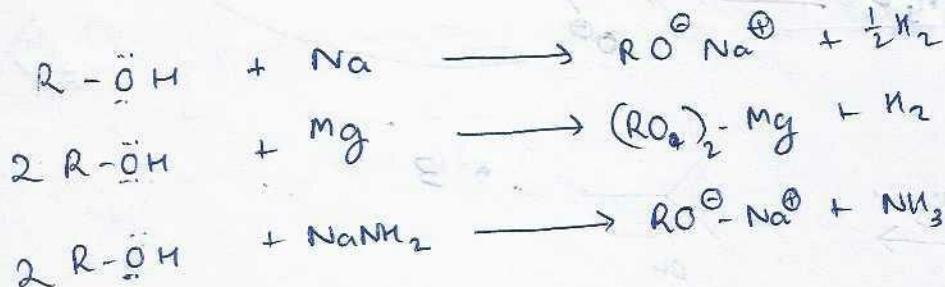


Acid catalysed



PROPERTIES

- Higher boiling point of alcohols than corresponding esters, ketones.
- Slightly acidic in nature.



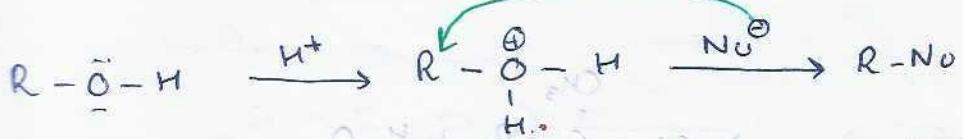
$\text{H}_2\text{O} > \text{R-OH}$ acidic character

Exception: $\text{CH}_3\text{-OH} > \text{H}_2\text{O}$

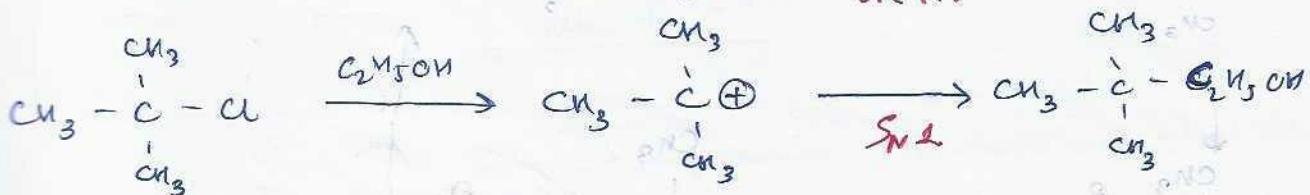
$\text{H}_2\text{N} > \text{NH}_3 > \text{CH}_2=\text{CH}_2 > \text{CH}_3-\text{CH}_3$ Acidic character

CHEMICAL PROPERTIES

Alcohols can act as both electrophiles and nucleophiles.

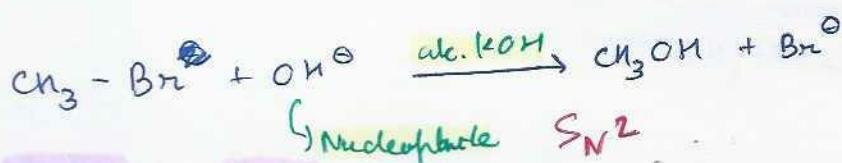
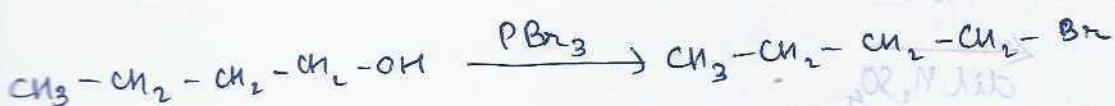
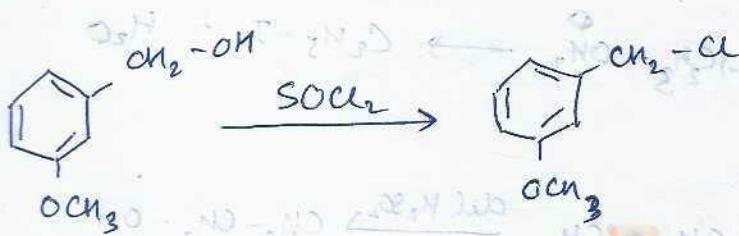
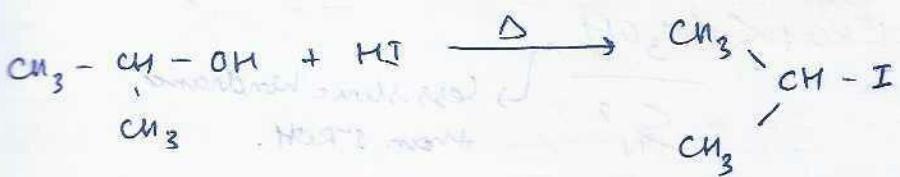
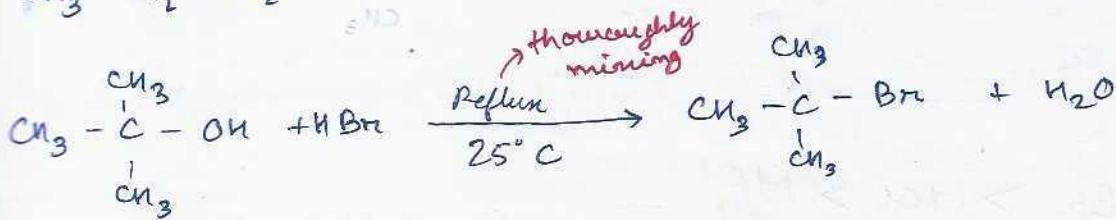
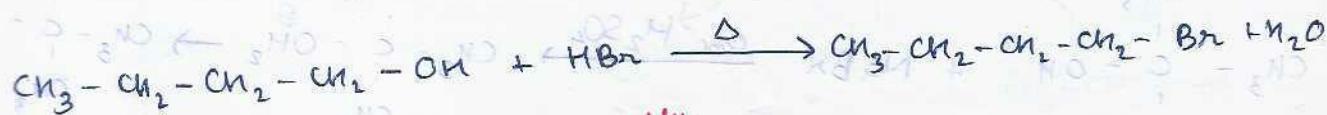


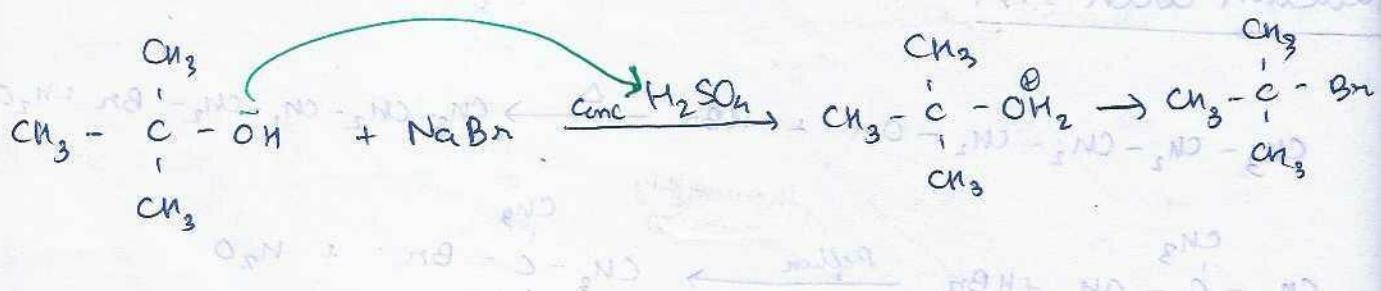
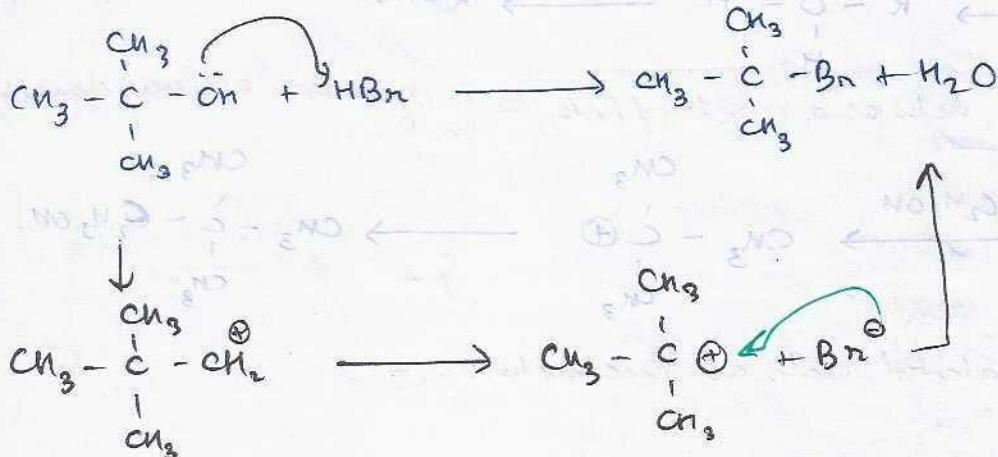
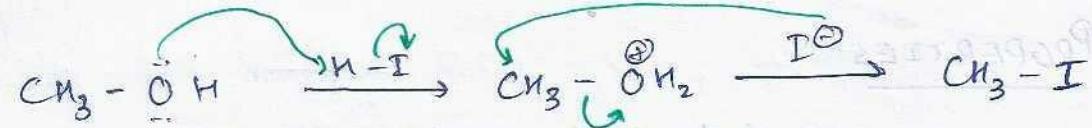
Here, alcohol acts as a electrophile, as it decreases electron density on R.



Here, alcohol acts as nucleophile.

Reaction with HX





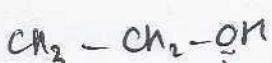
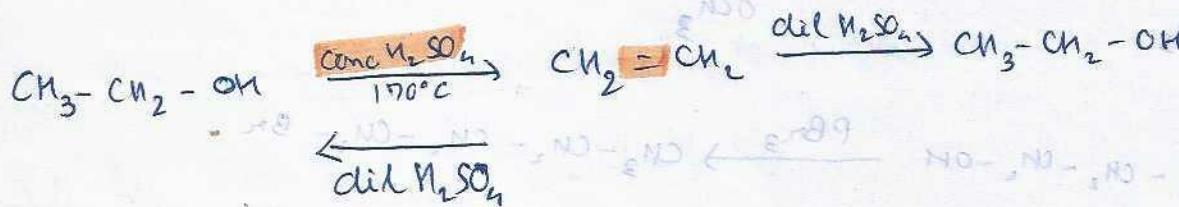
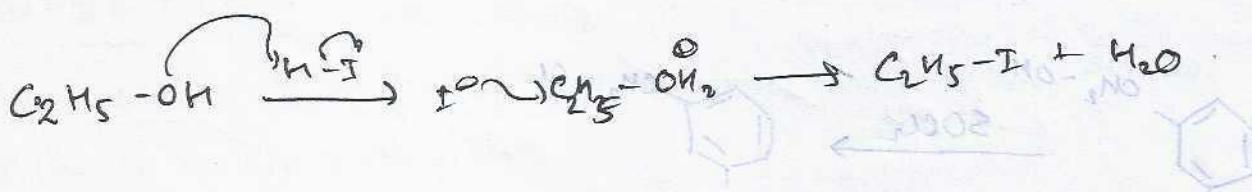
$\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

Reactivity order

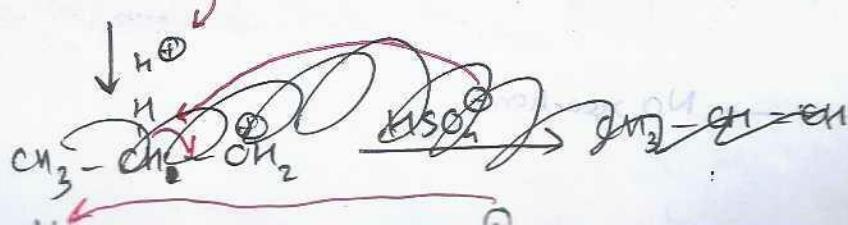
$3^\circ \text{ROH} > 2^\circ \text{ROH} > 1^\circ \text{ROH} < \text{CH}_3\text{OH}$

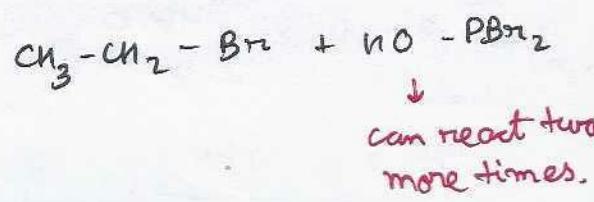
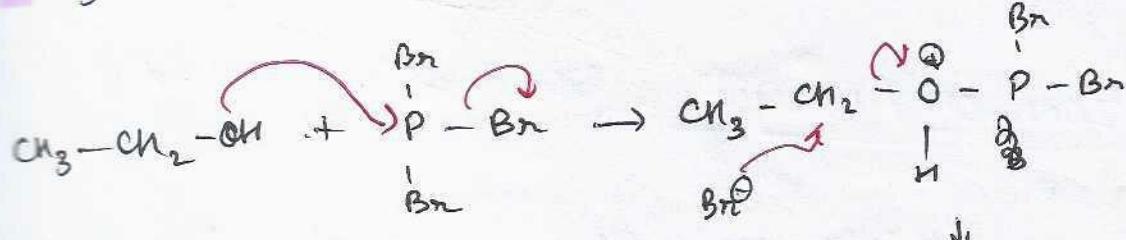
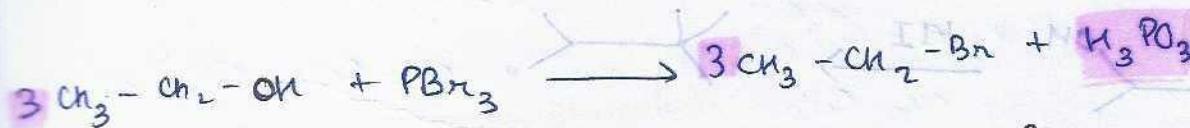
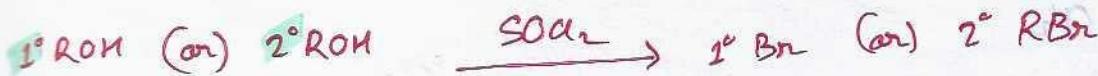
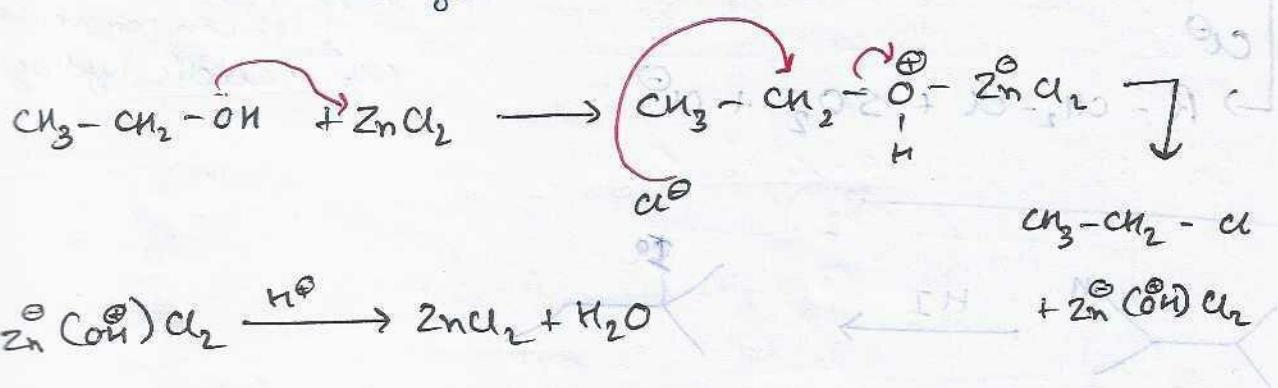
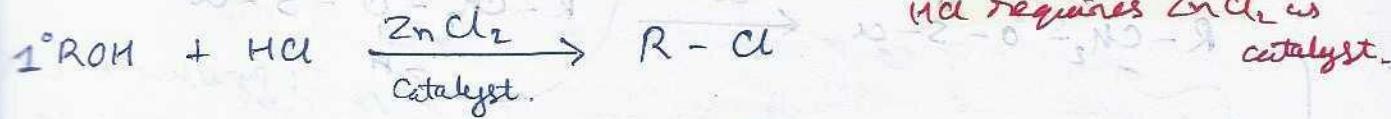
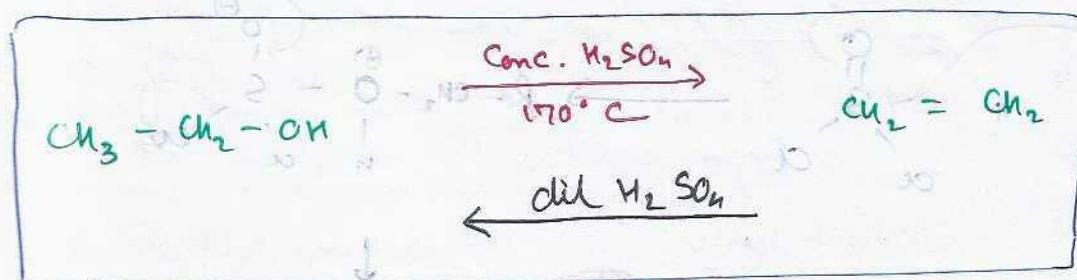
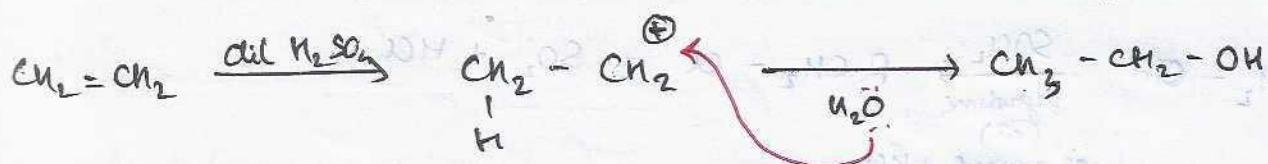
S_N^2

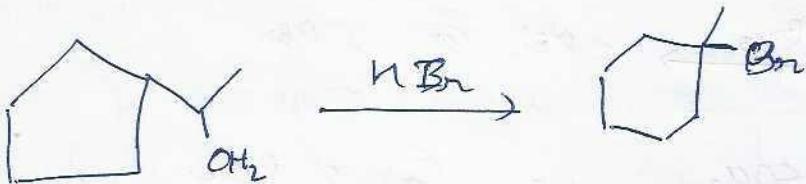
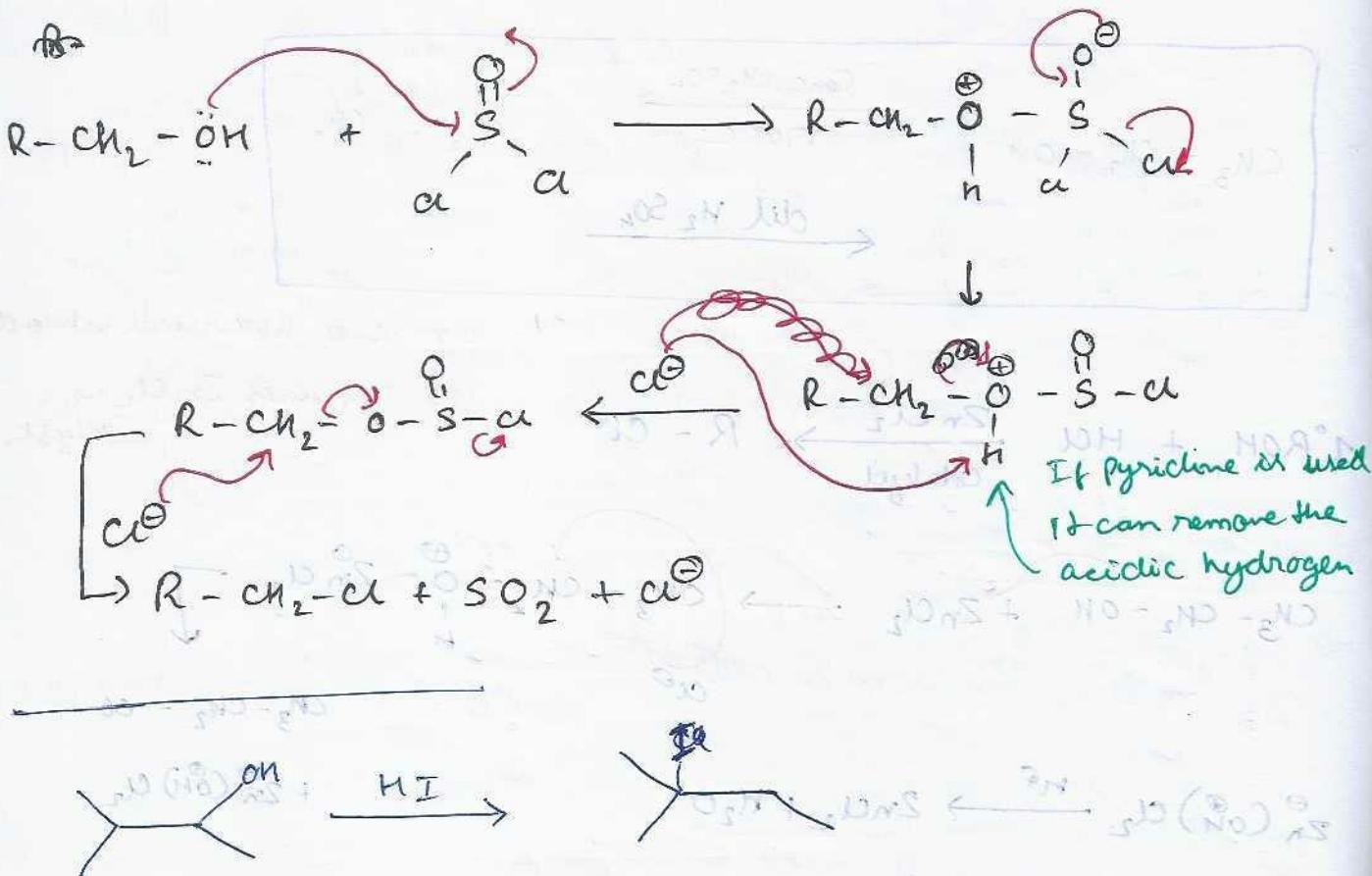
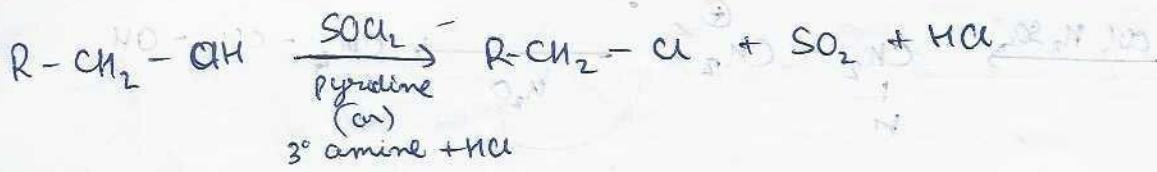
less steric hindrance than 1°ROH .



HSO_4^- is not a strong nucleophile.

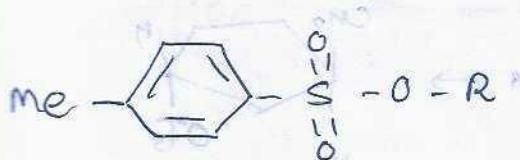




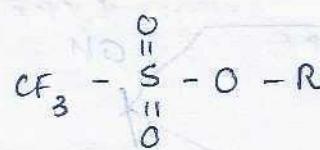


Tosylate, Mesylate, Triflate ions

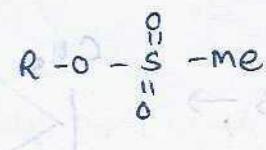
Alkyl sulfonate ester formation.



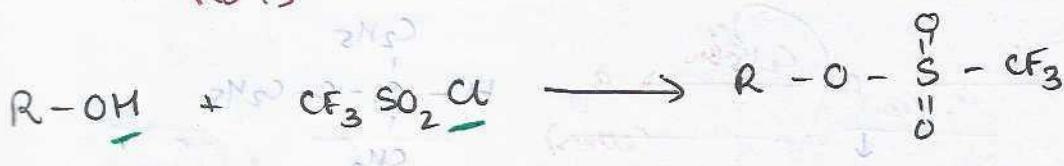
p-methyl tosylate
(alkyl tosylate)
RO₂S



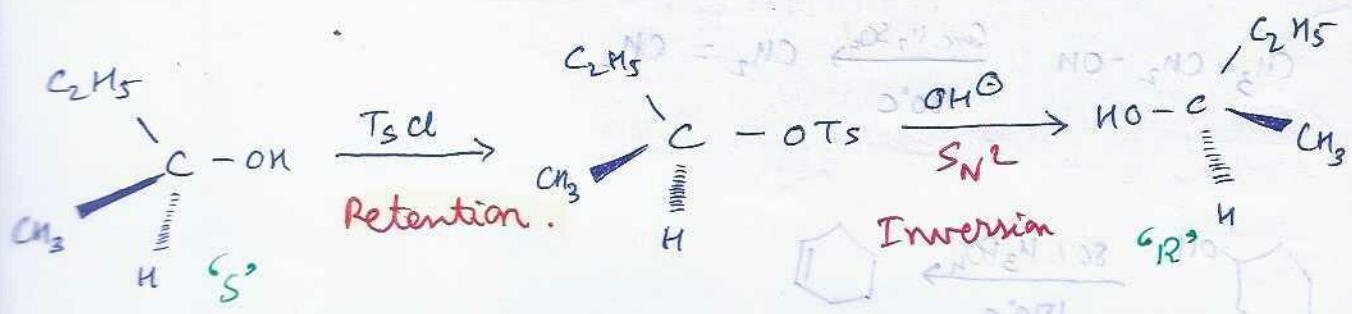
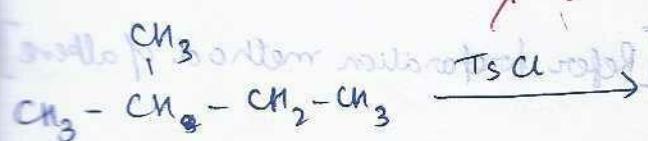
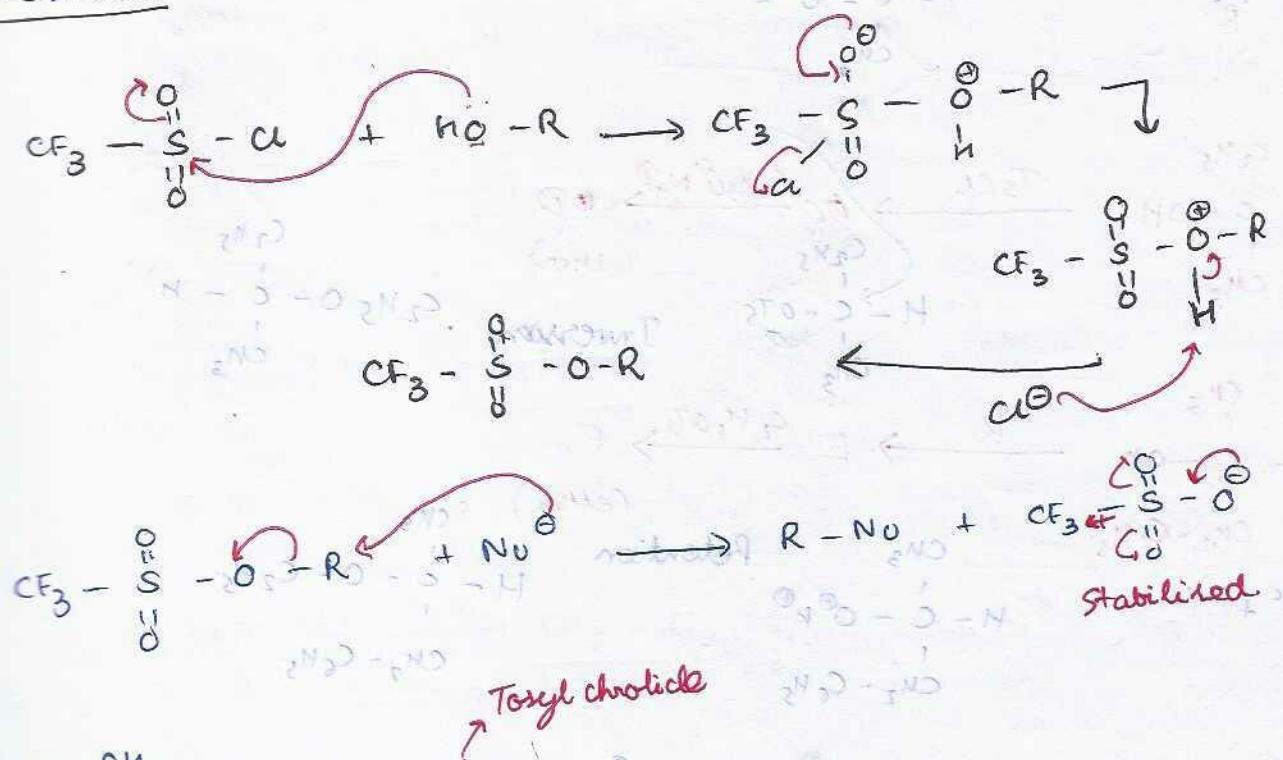
alkyl triflate
RO₂Tf

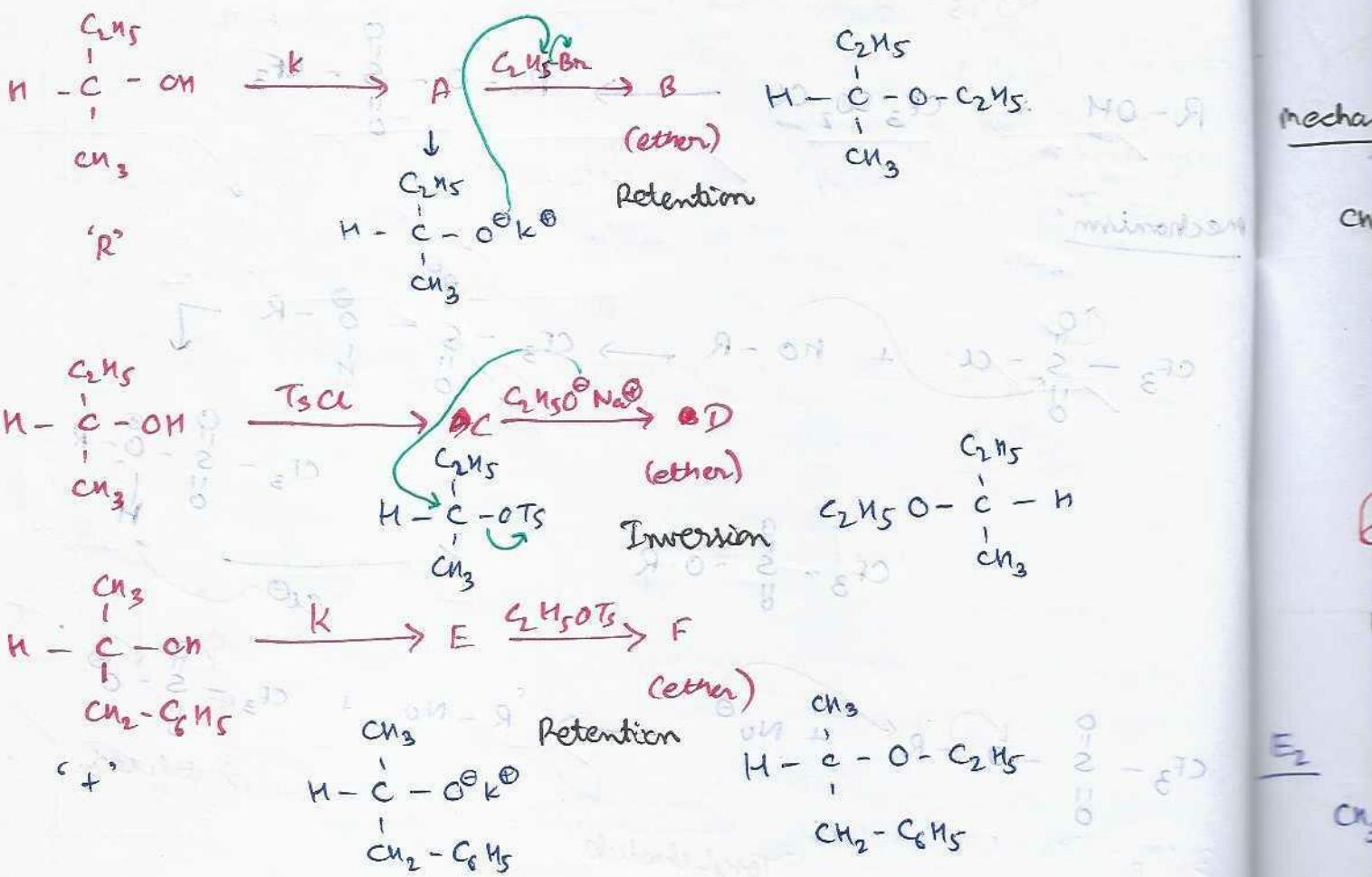
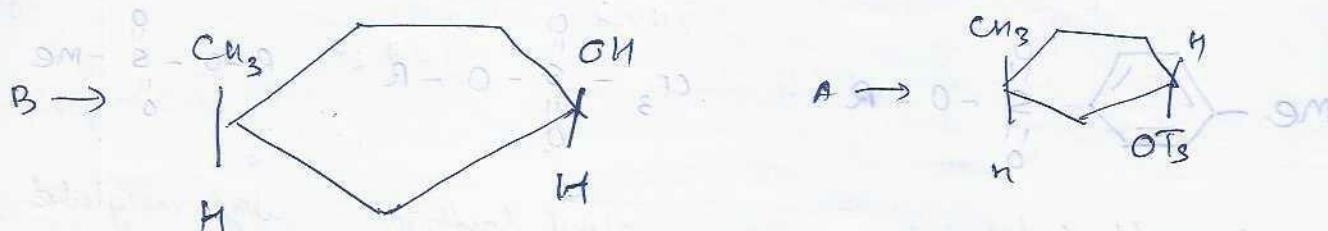
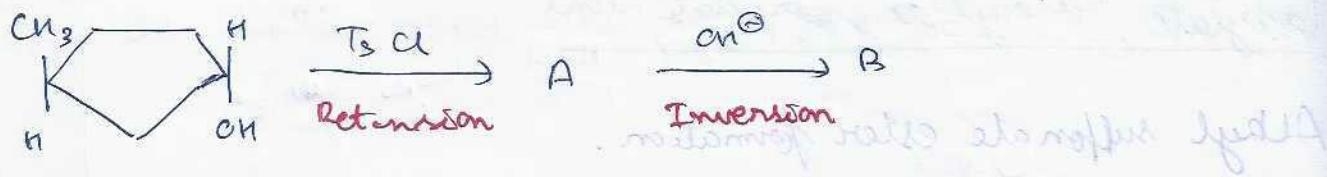


alkyl mesylate
RO₂MS

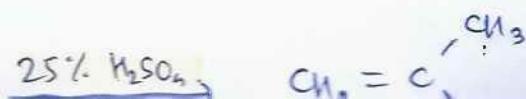
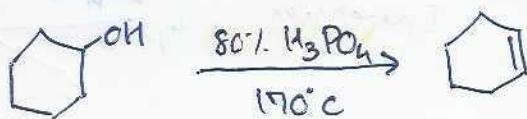
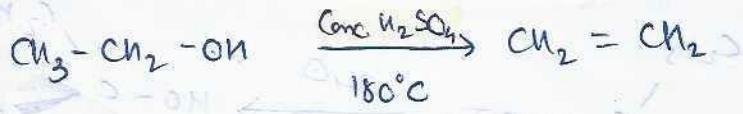


mechanism





DEHYDRATION OF ALCOHOLS [Refer preparation method of alkene]

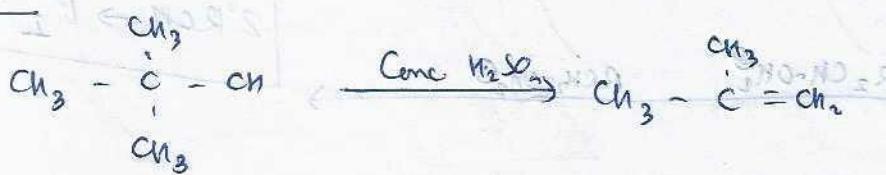


3° ROH and 2° ROH $\xrightarrow[\text{catalyst}]{\text{with } \text{H}^+}$ E_1 mechanism

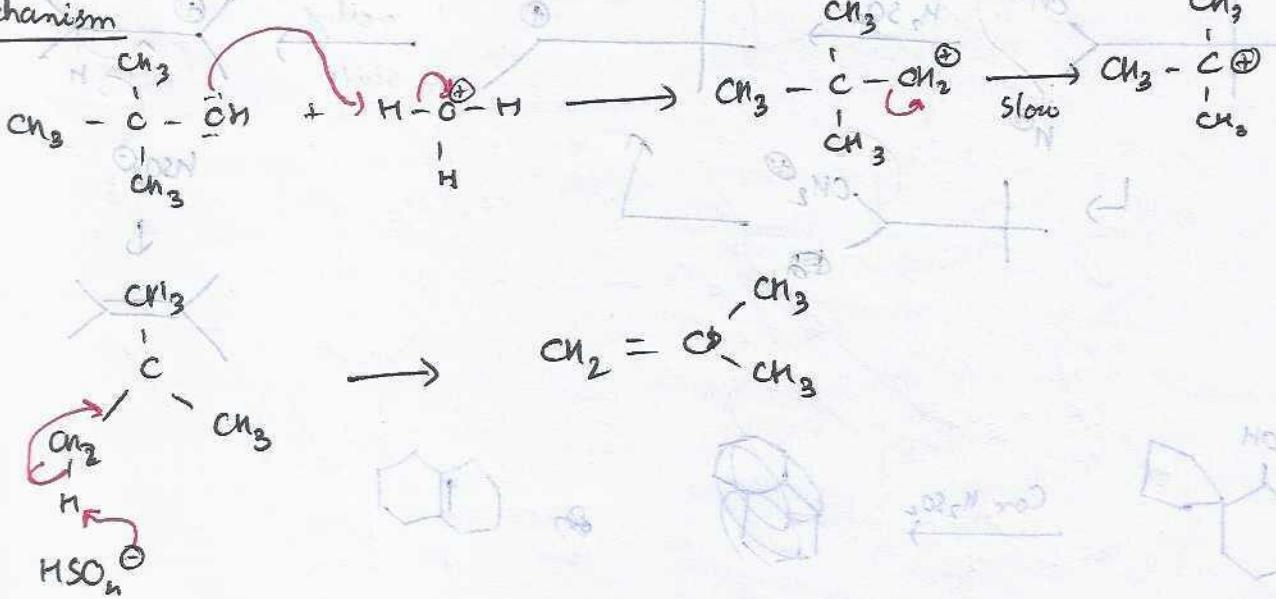
1° ROH $\xrightarrow[\text{catalyst}]{\text{with } \text{H}^+}$ E_2 mechanism.

(dilute H_2SO_4 would give alcohol)

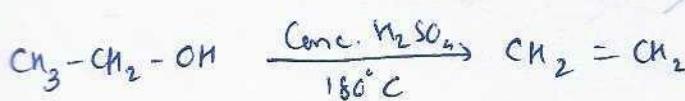
E_1



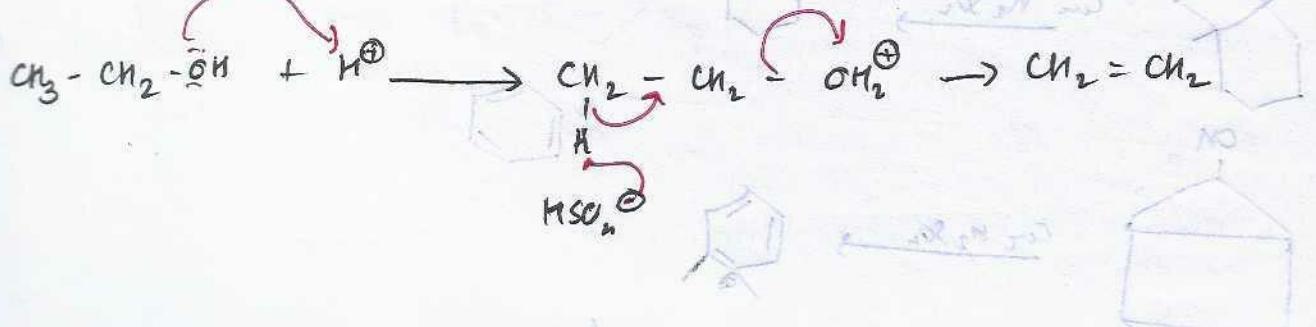
mechanism

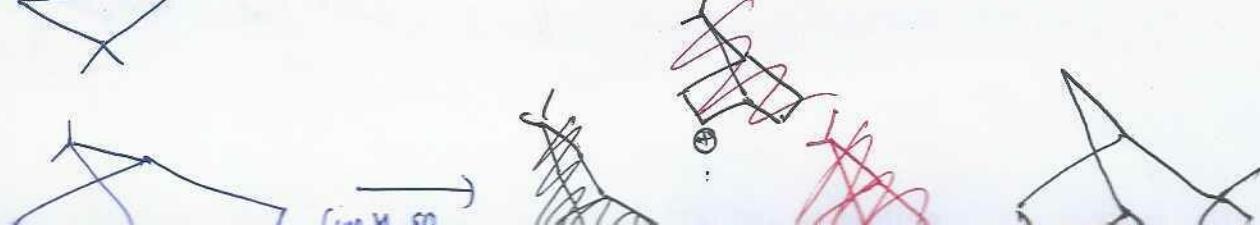
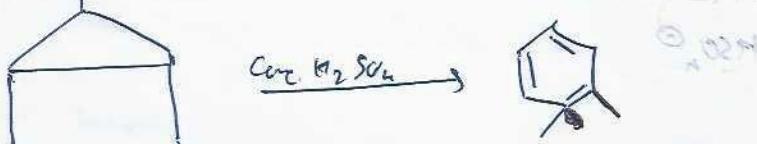
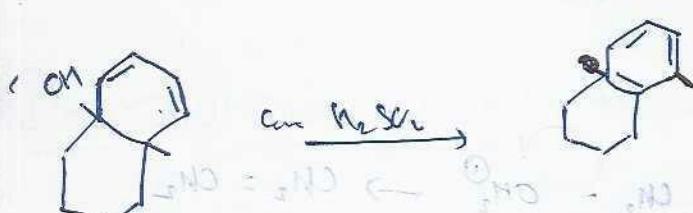
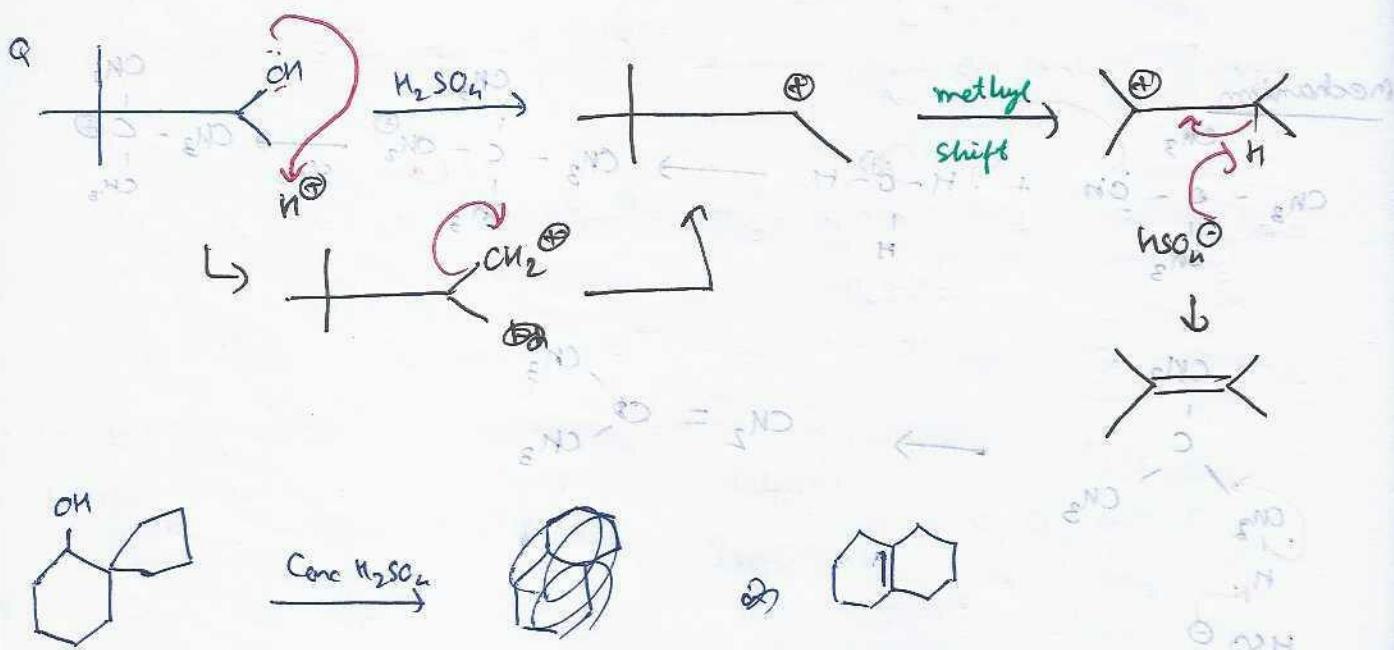
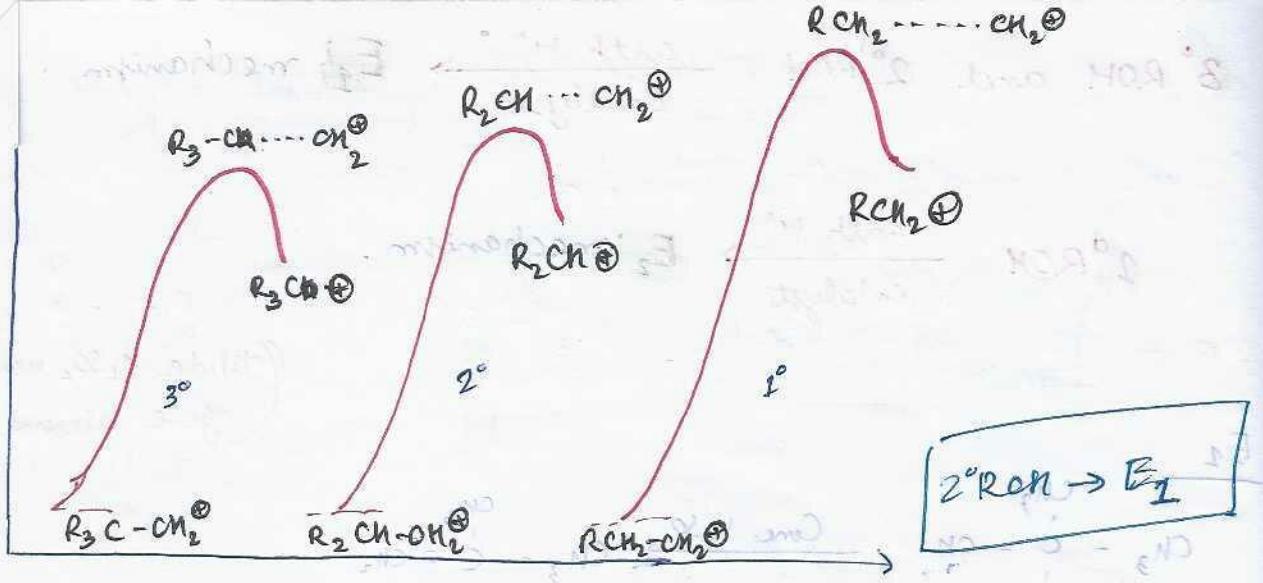


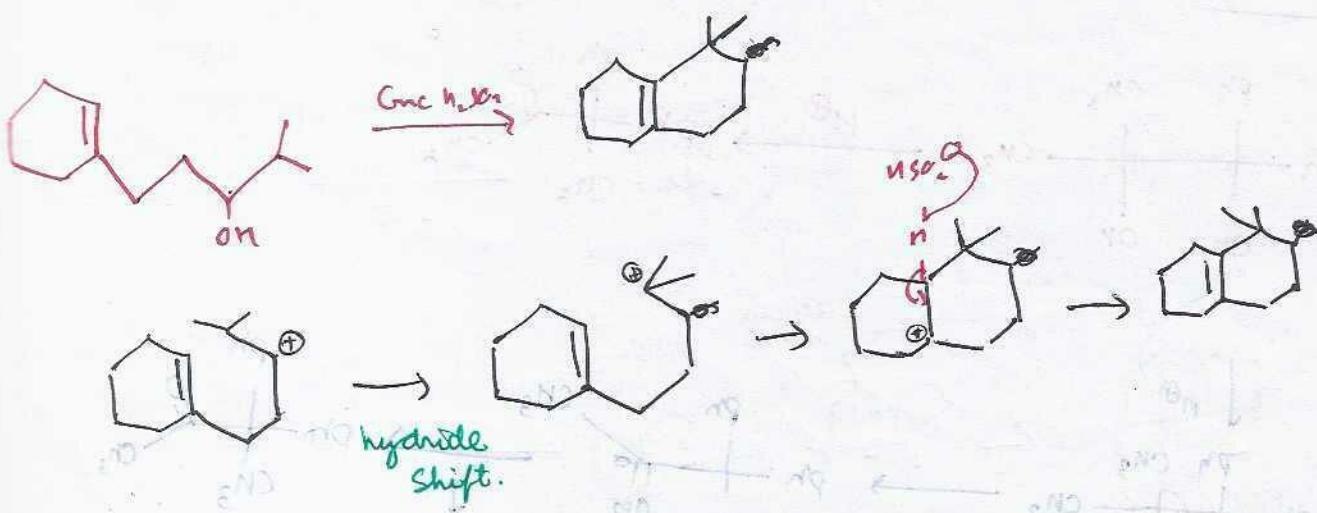
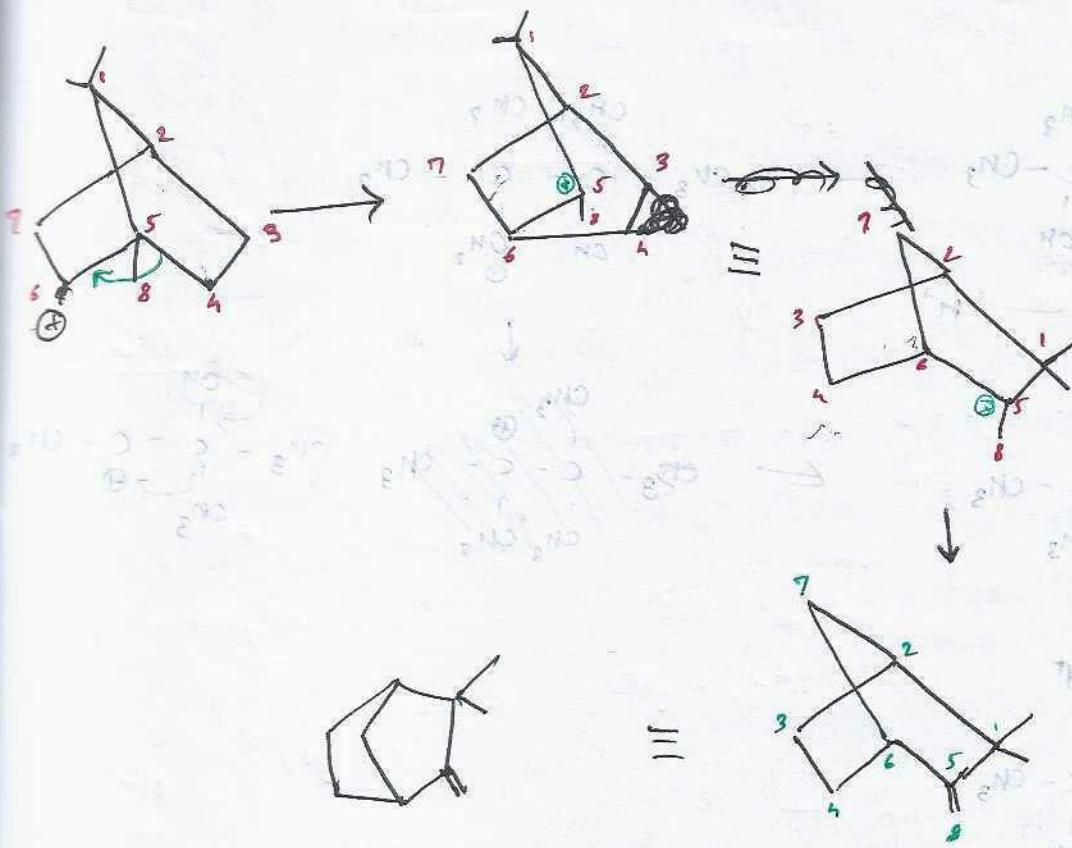
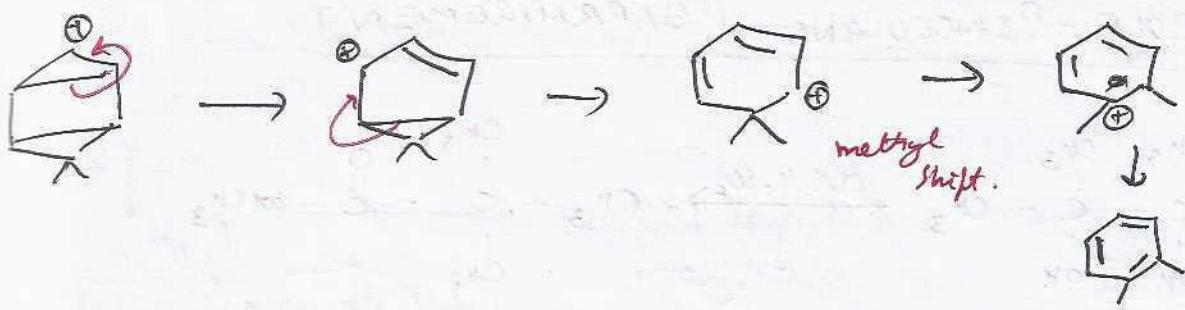
E_2



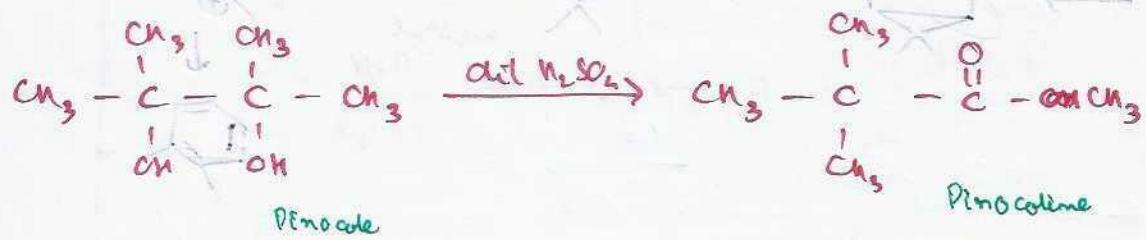
[alkene] mechanism



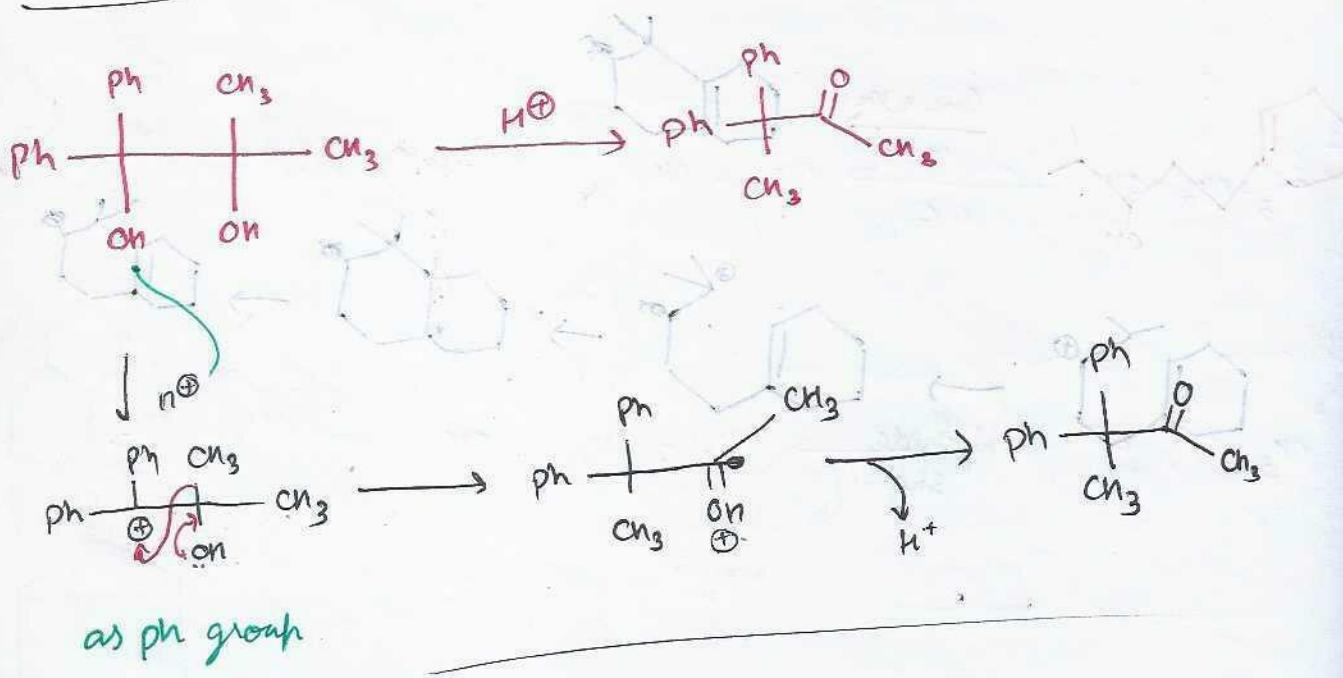
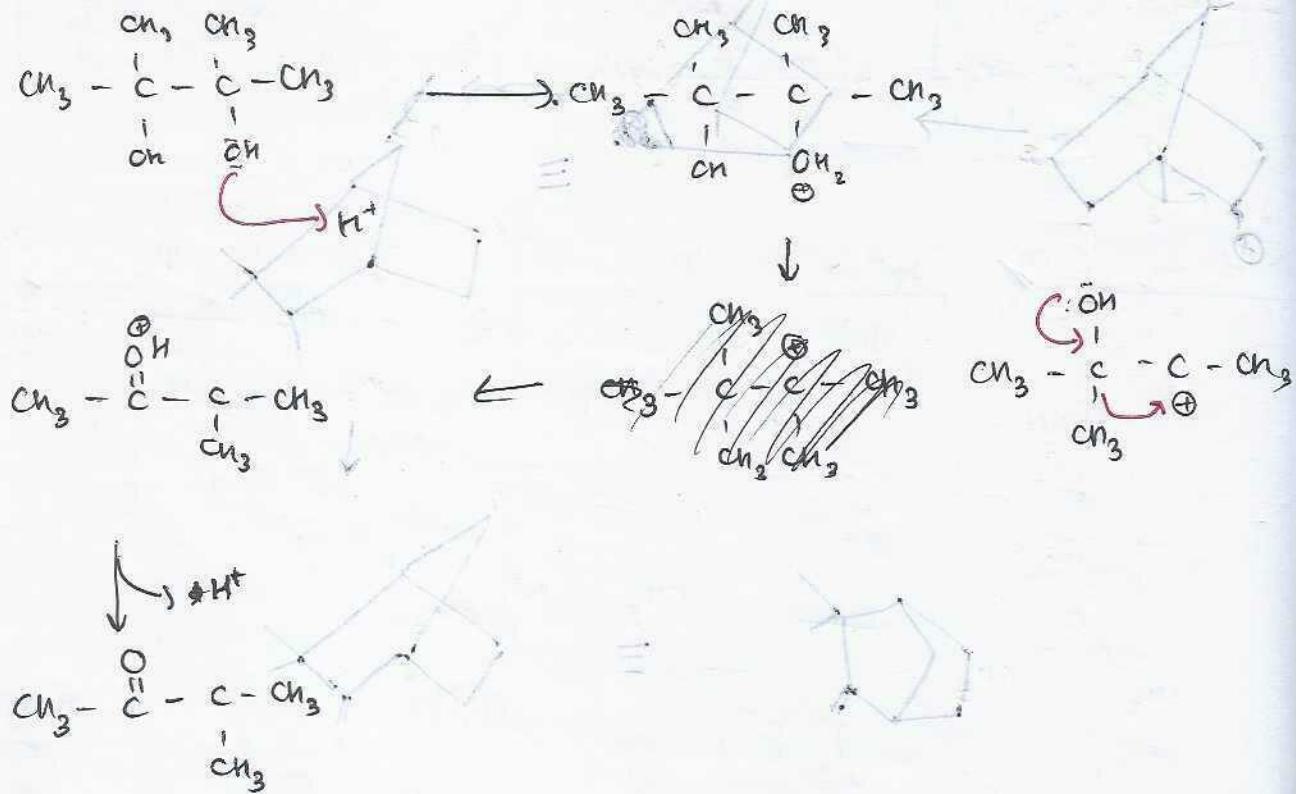




PINOCOLE - PINCOLINE REARRANGEMENT

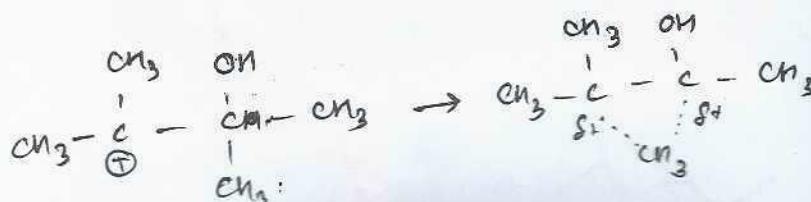


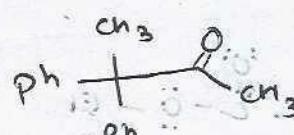
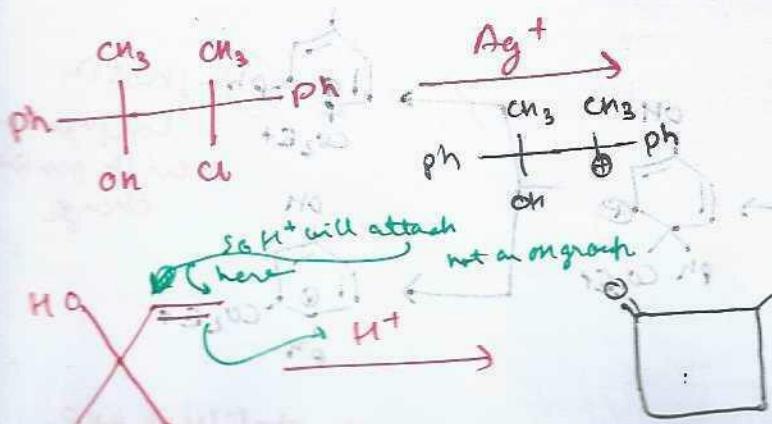
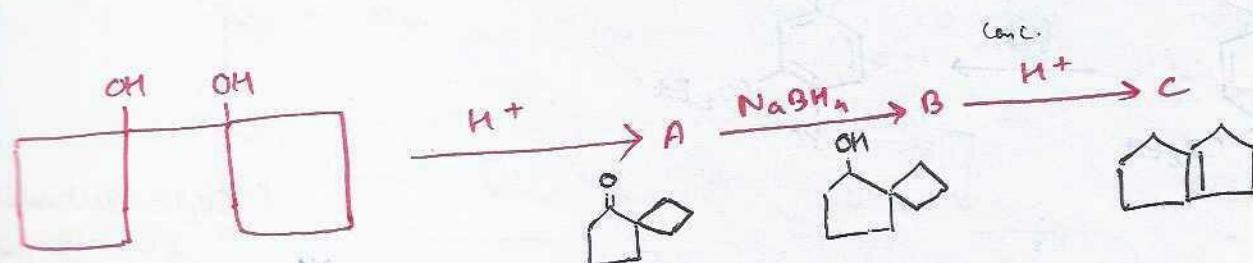
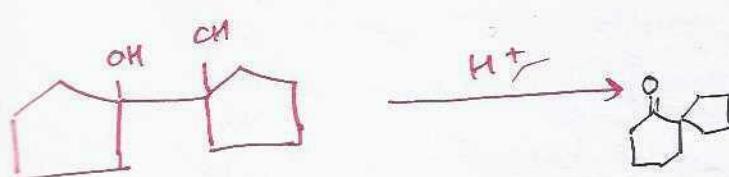
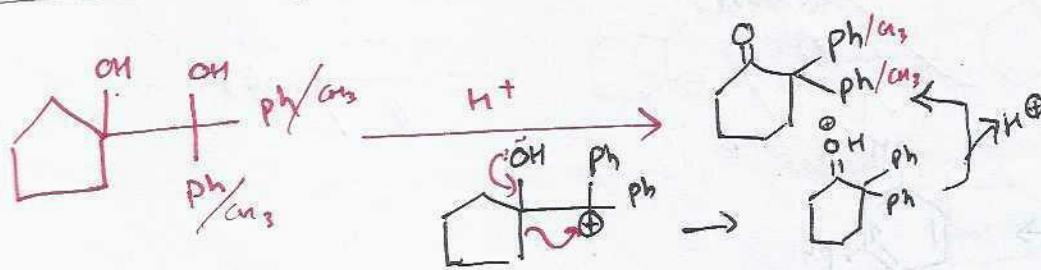
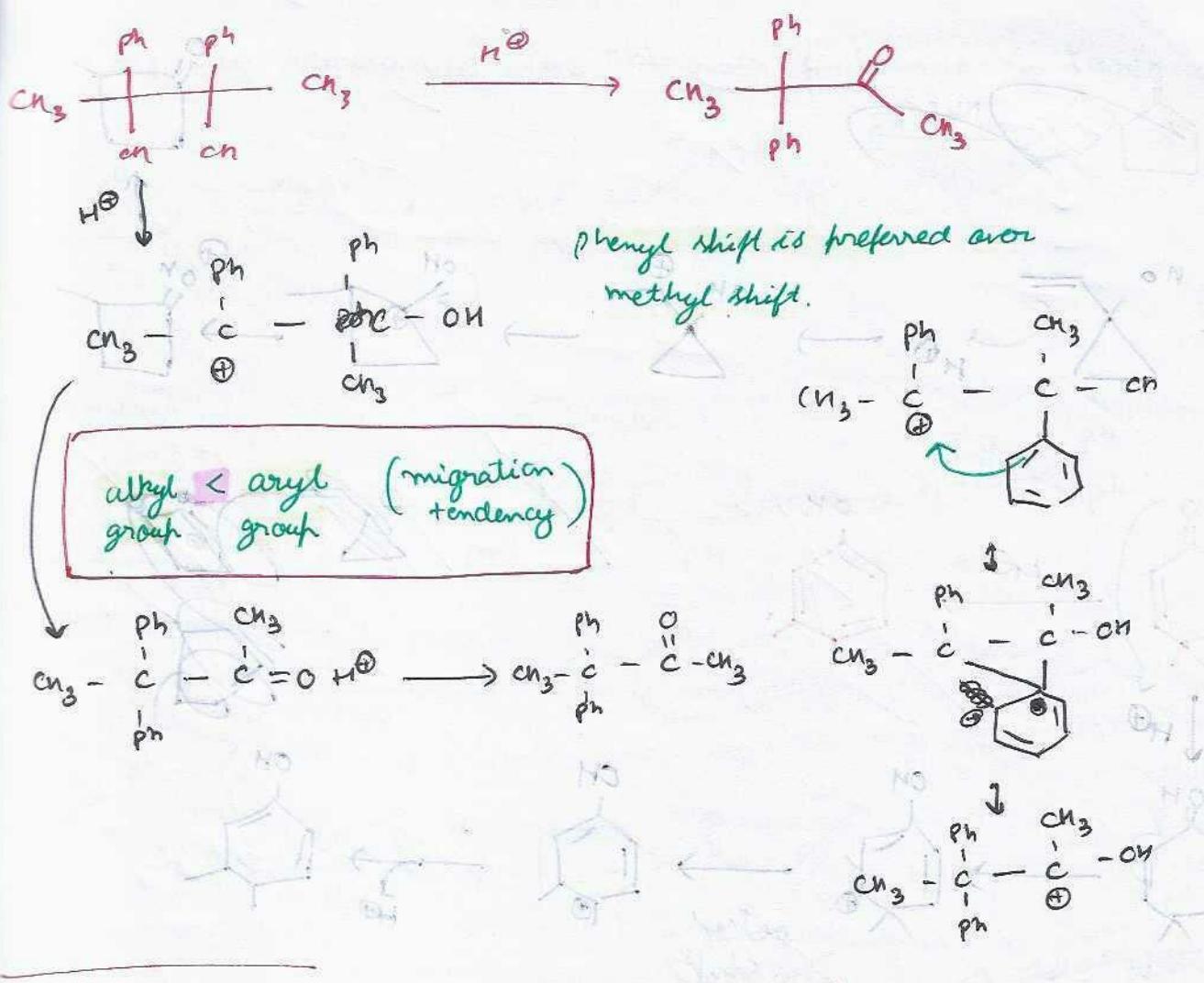
Mechanism

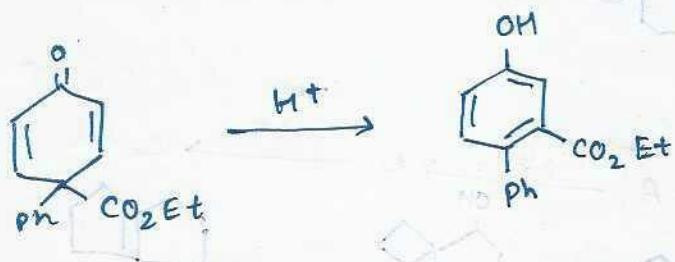
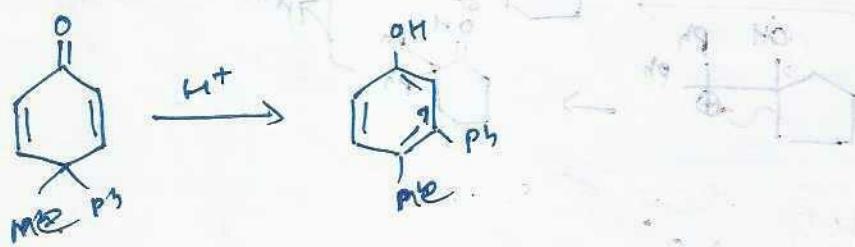
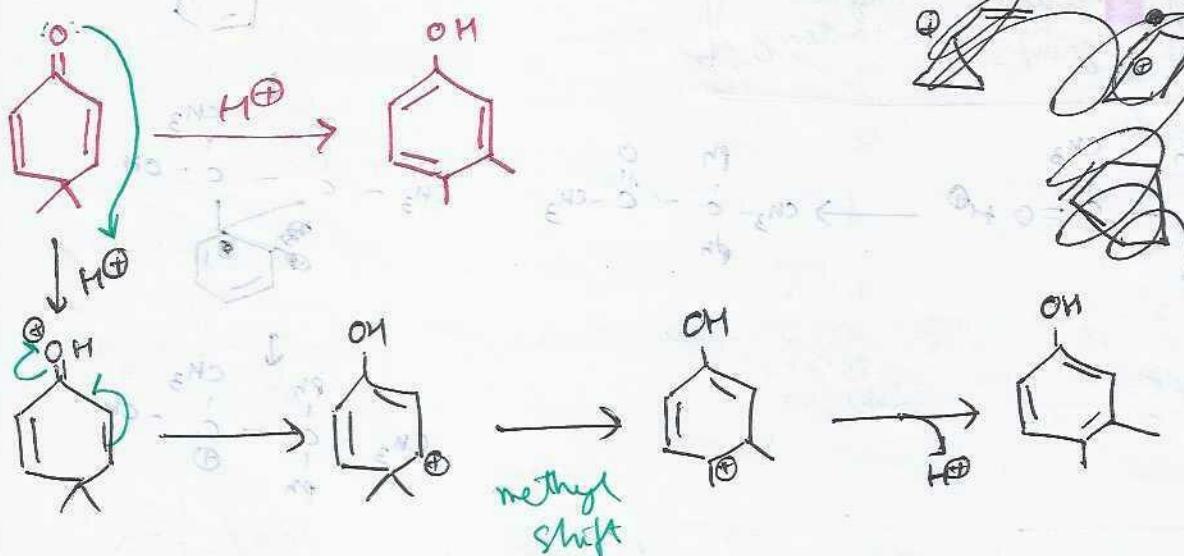
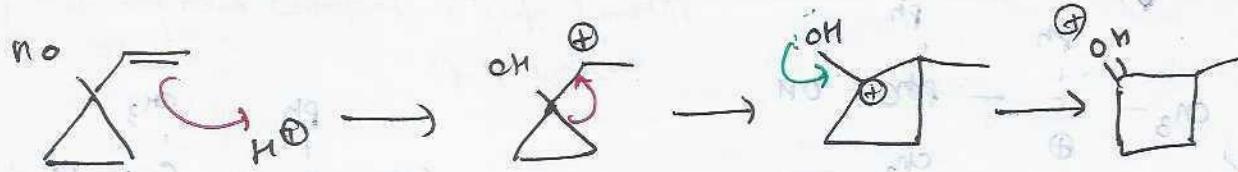


as ph group

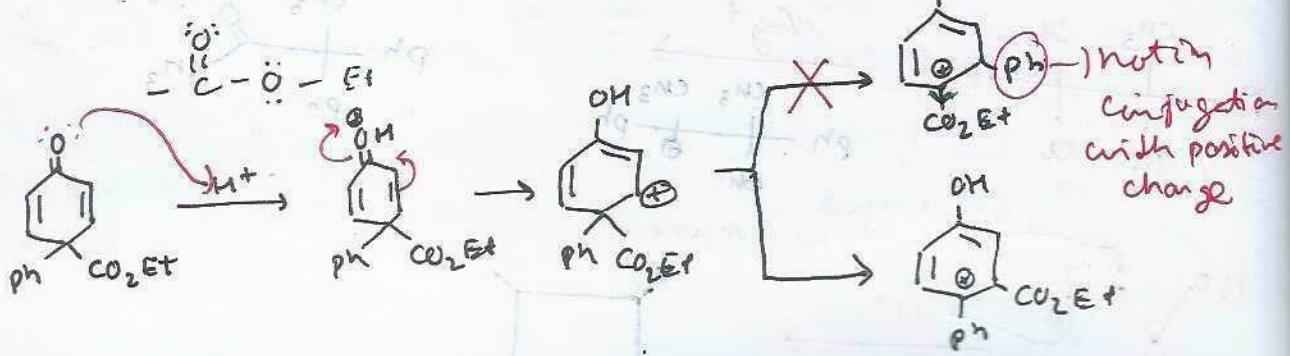
can stabilize
the carbocation.



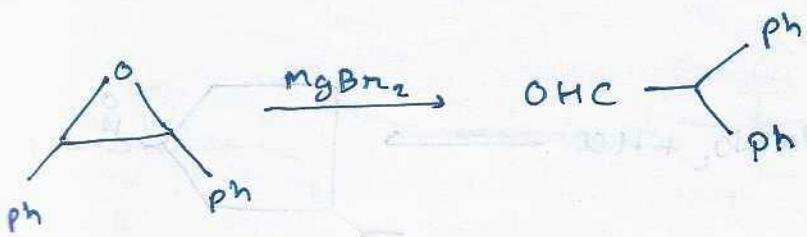




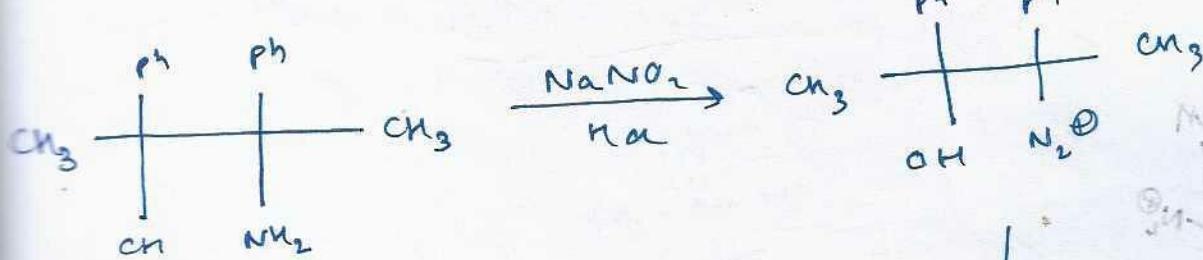
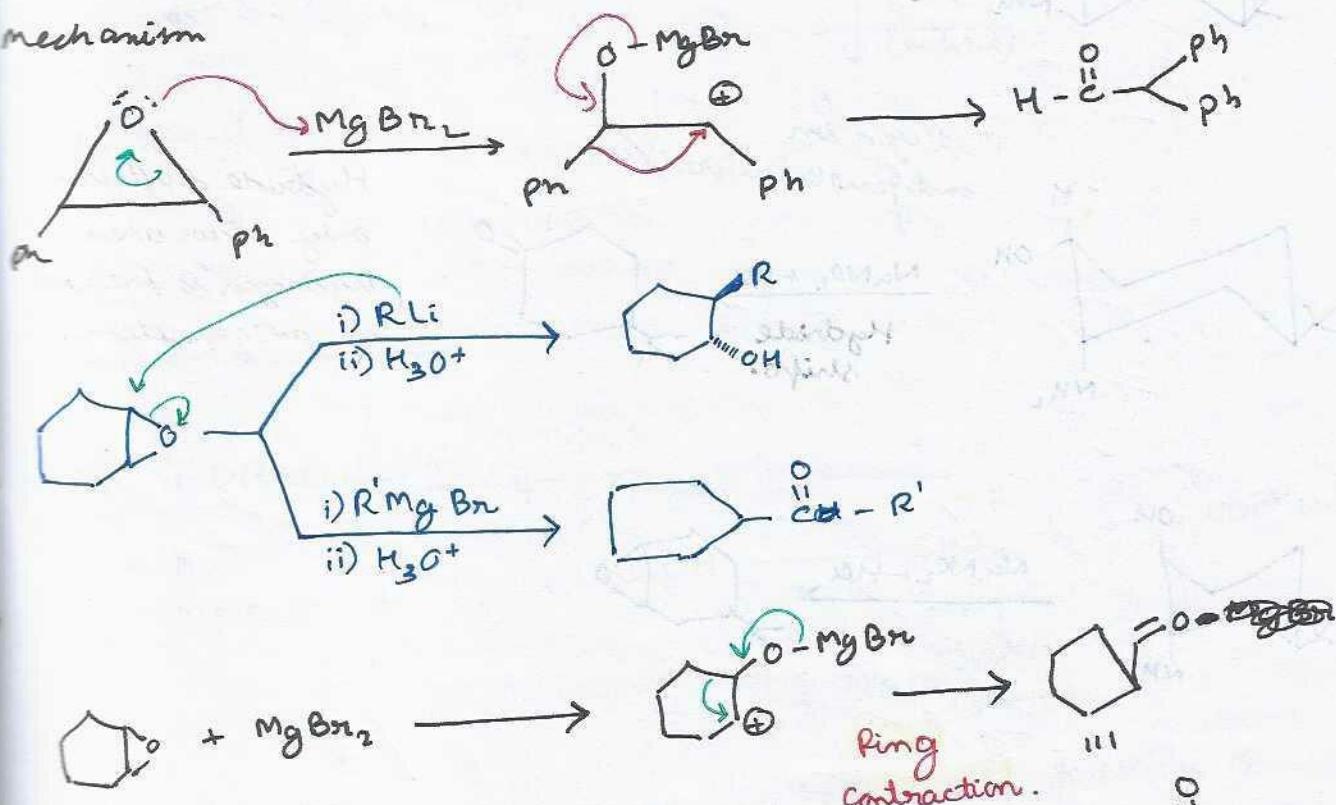
CO_2Et destabilizes
+ve charge



Epoxydides can rearrange like Pinacole fashion with Lewis acids.



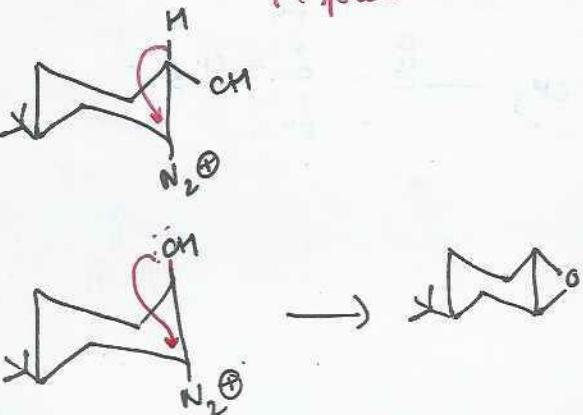
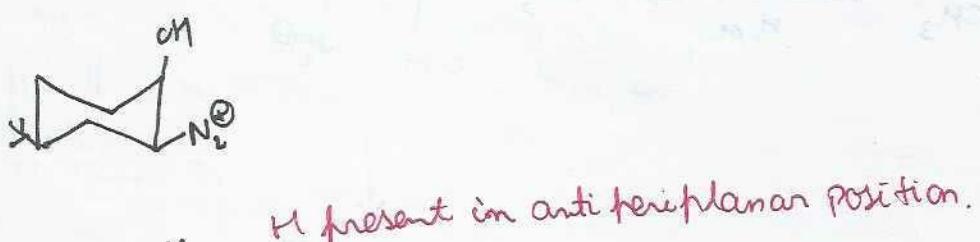
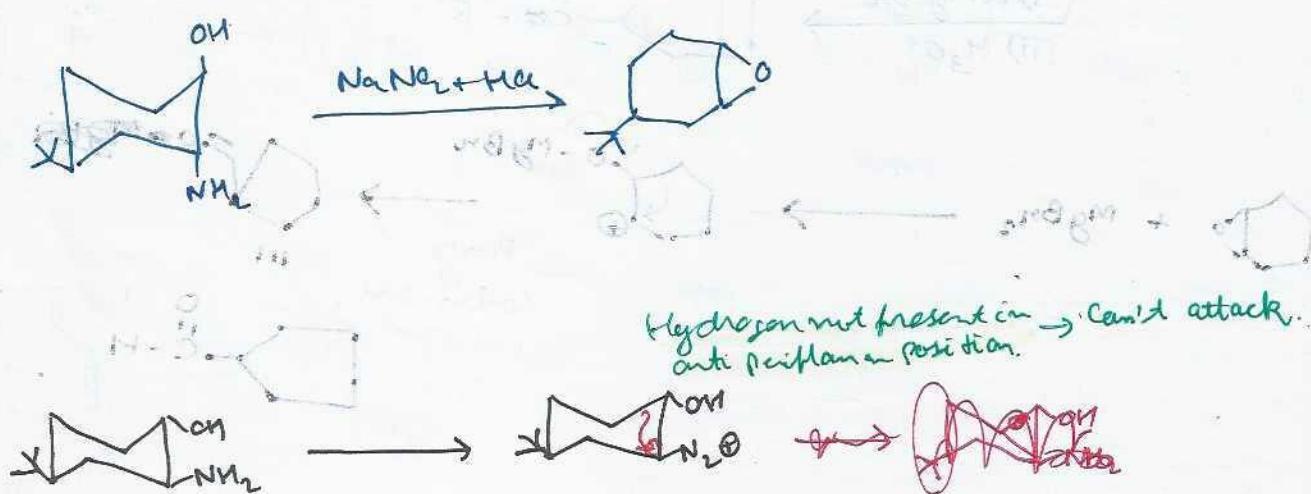
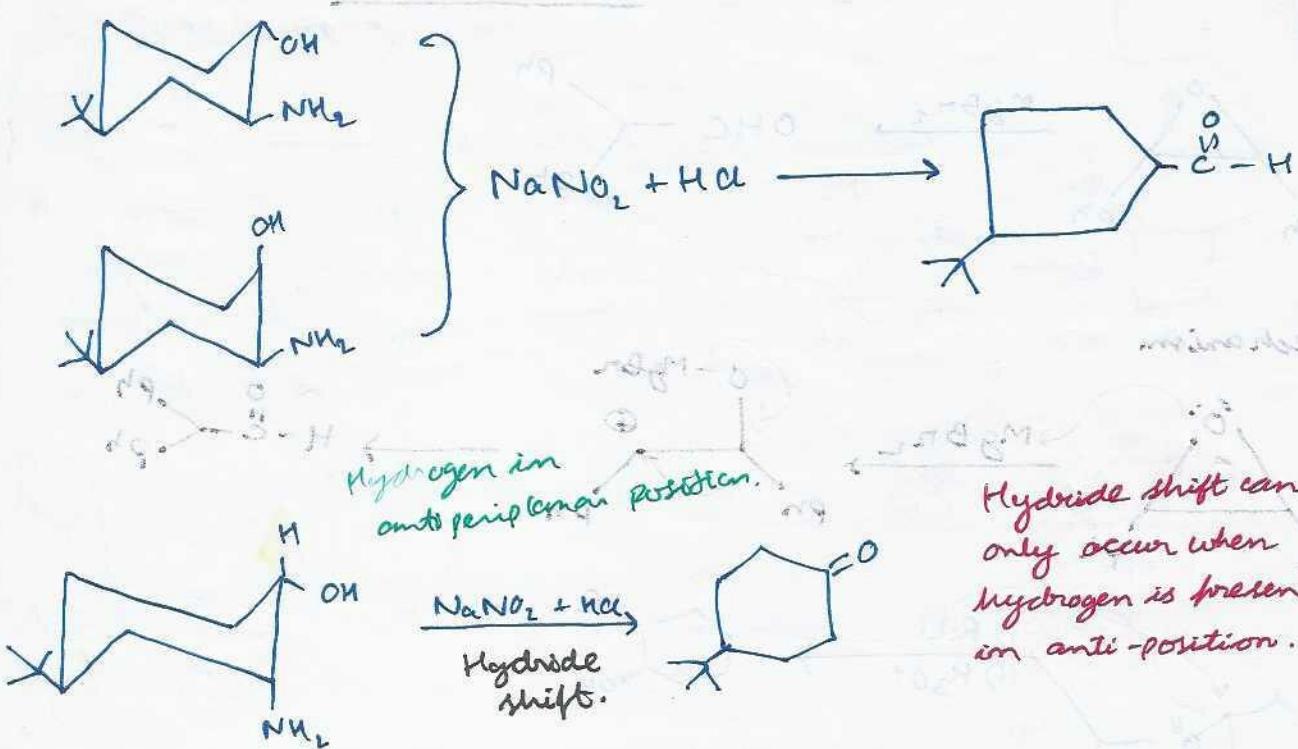
mechanism



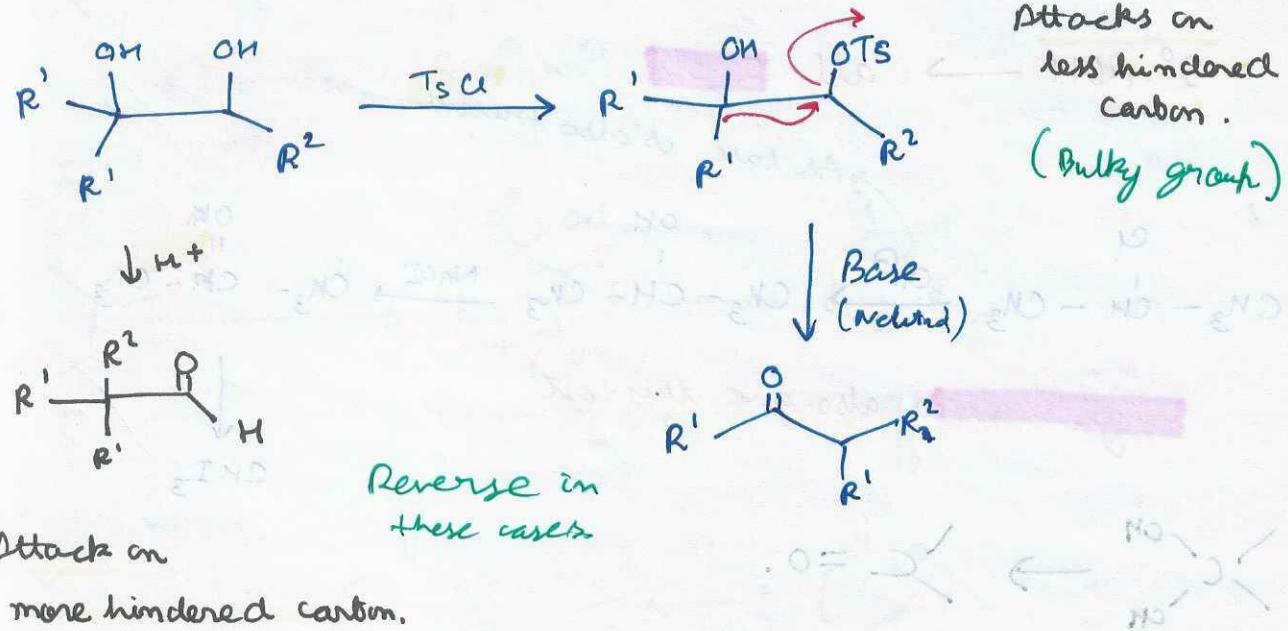
switches
charge

\rightarrow
projection
 \rightarrow positive
 \rightarrow 2

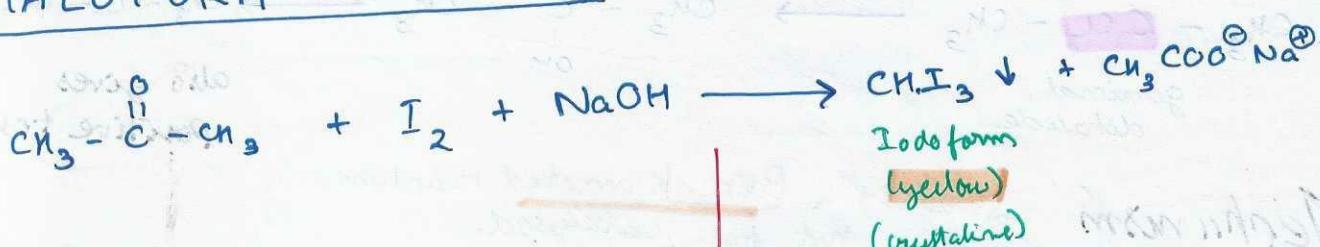
SE



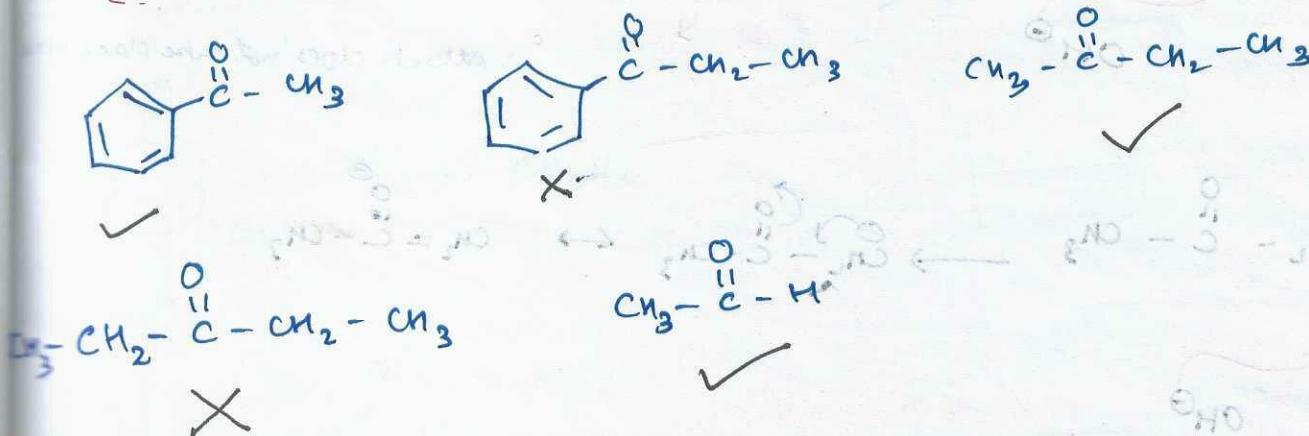
SEMI PINOCOLE REARRANGEMENT



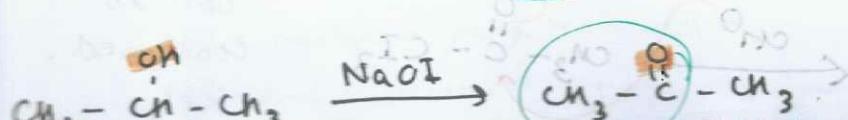
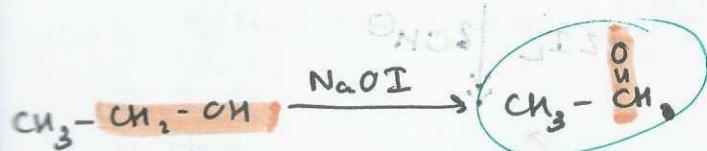
HALOFORM REACTIONS



$\text{CH}_3-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_3$ methyl keto group. Used to identify presence of
methyl keto group.



Mechanism

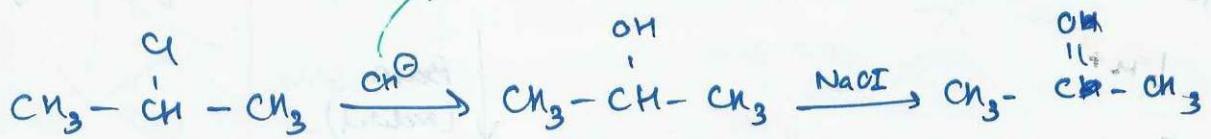


So these alcohols give positive test.

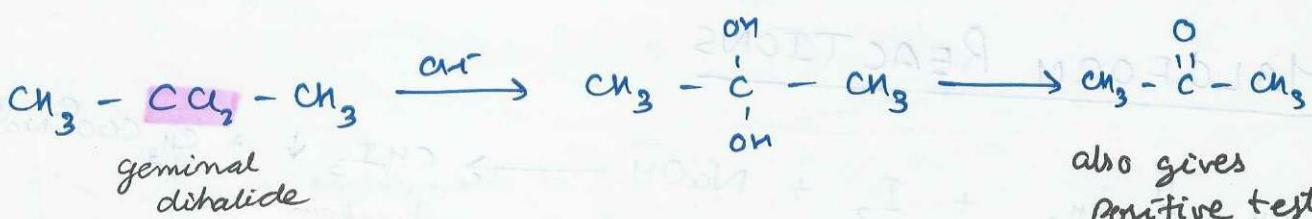
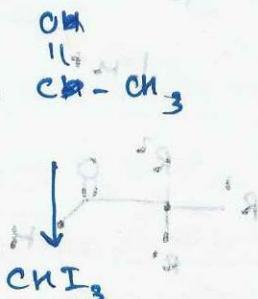
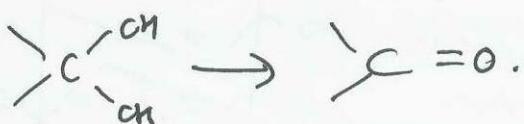
oxidises
 $1^\circ \text{ ROH} \rightarrow \text{C}_2\text{H}_5\text{OH}$ only

$2^\circ \text{ ROH} \rightarrow$ all 2-ols.

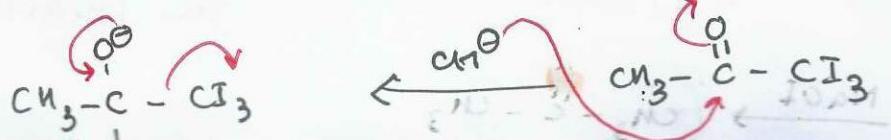
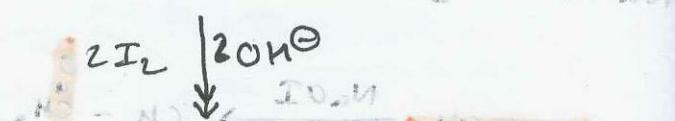
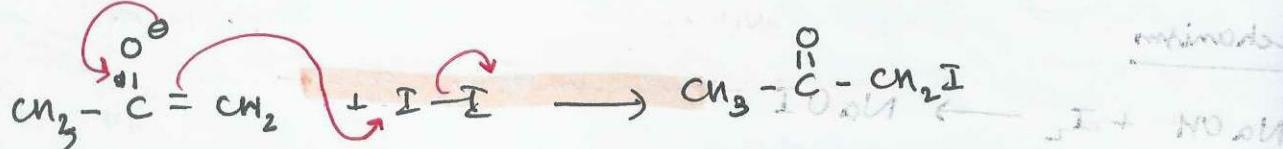
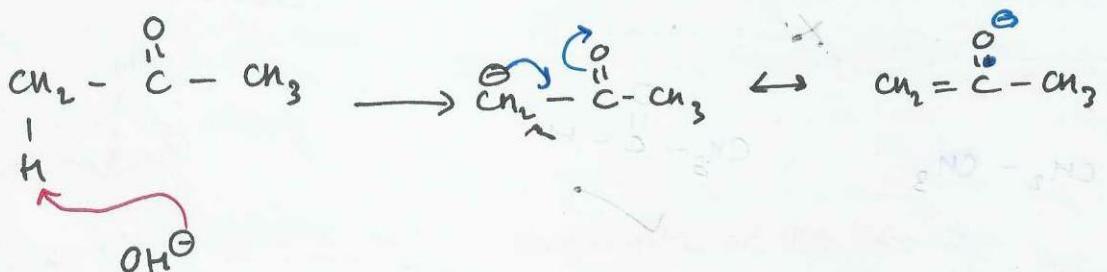
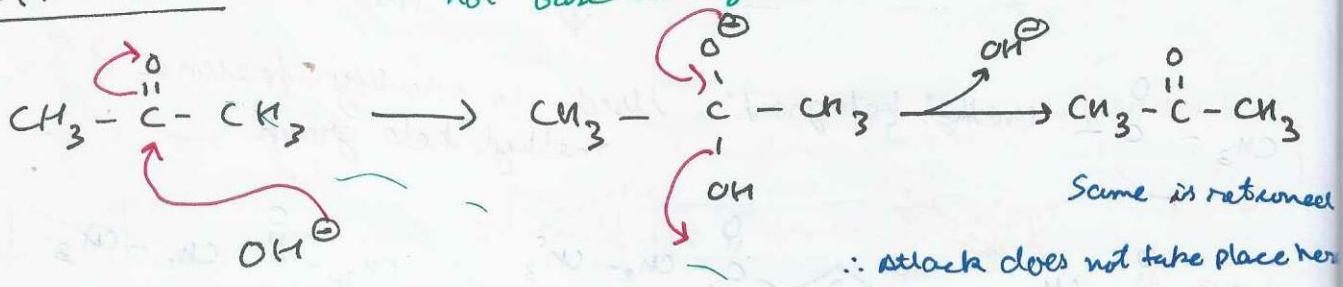
As base is also present



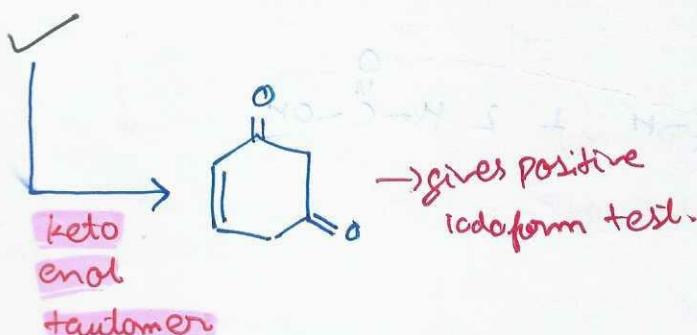
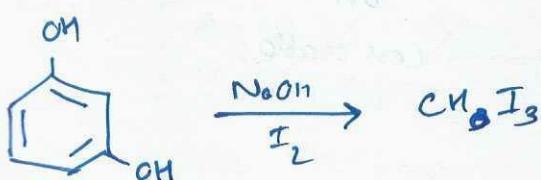
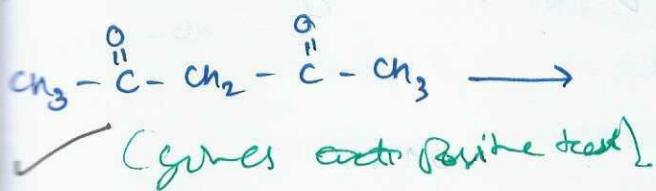
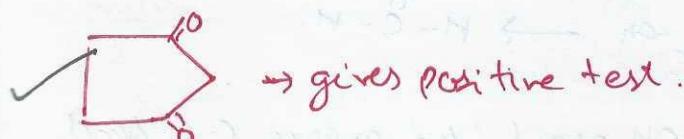
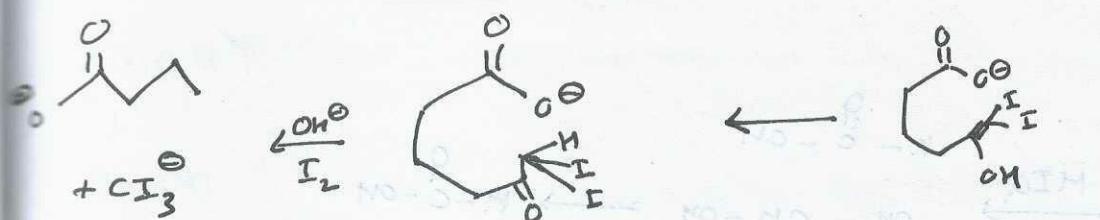
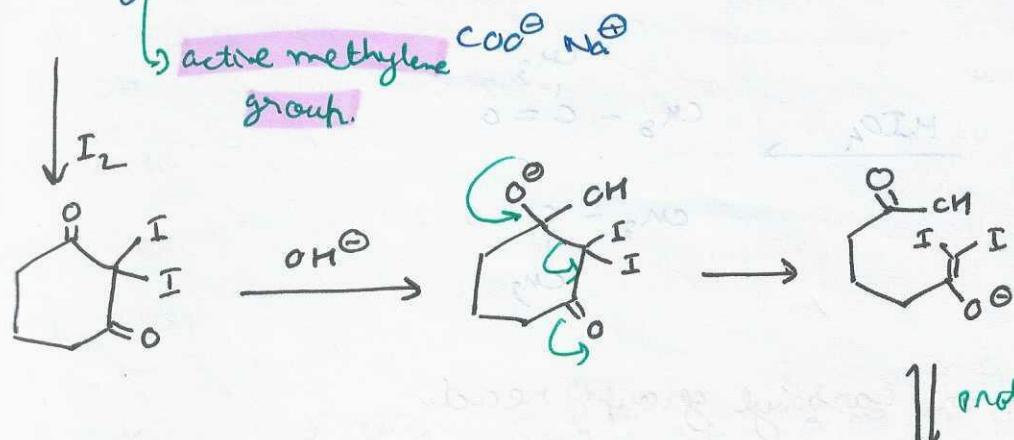
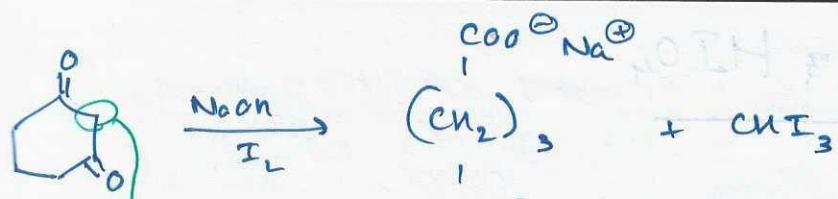
Alkyl halides also give this test.



Mechanism \rightarrow It is a Base promoted reaction.
not base catalysed



OH^- is consumed.



methyl keto group

$\text{CH}_3, \text{CH}_2\text{OH}$
2-ols

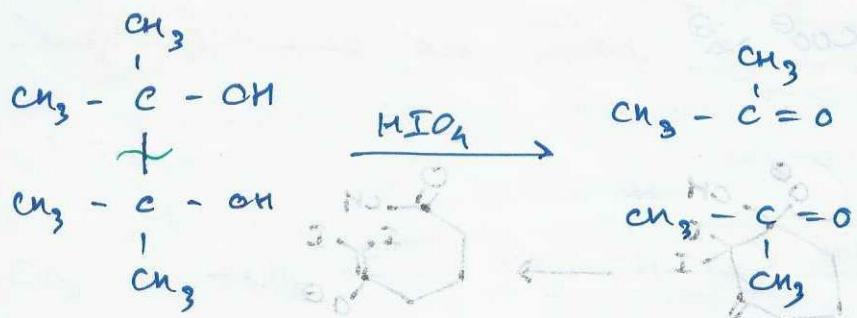
alkyl halides

active methylene group molecules

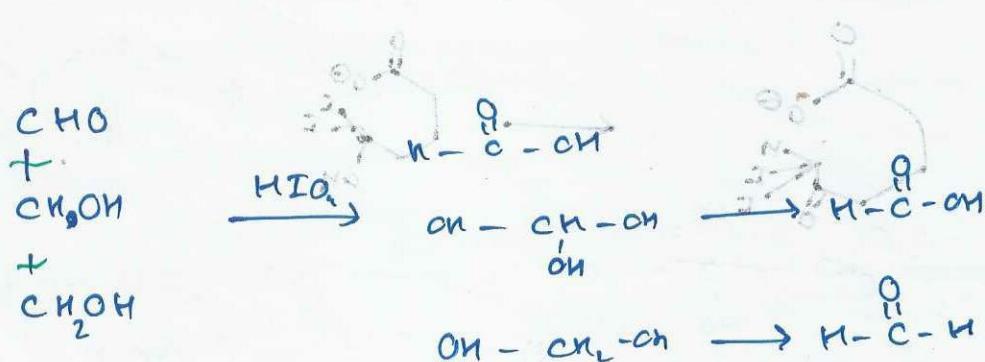
keto- and tautomers

} Positive haloform test.

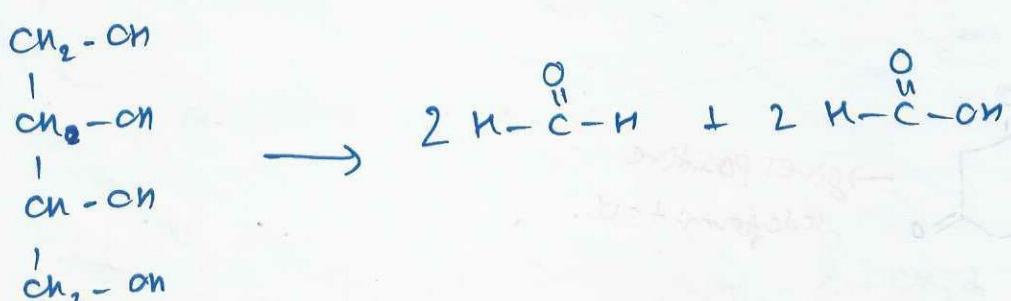
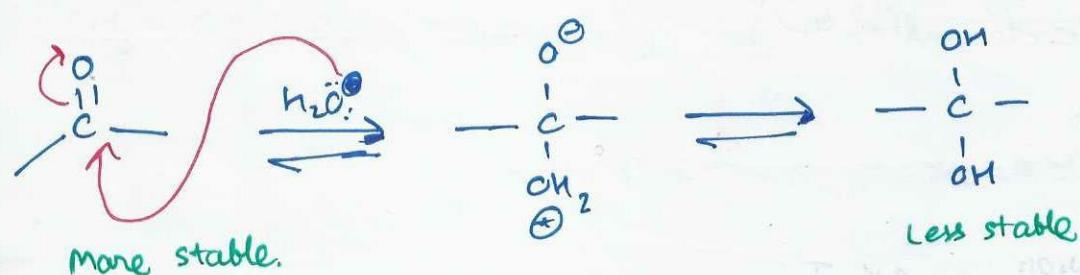
OXIDATION BY HIO_4

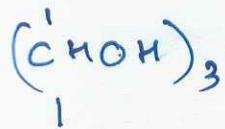
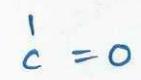
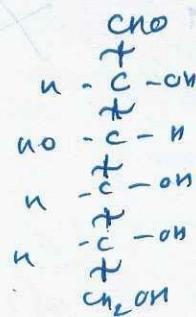
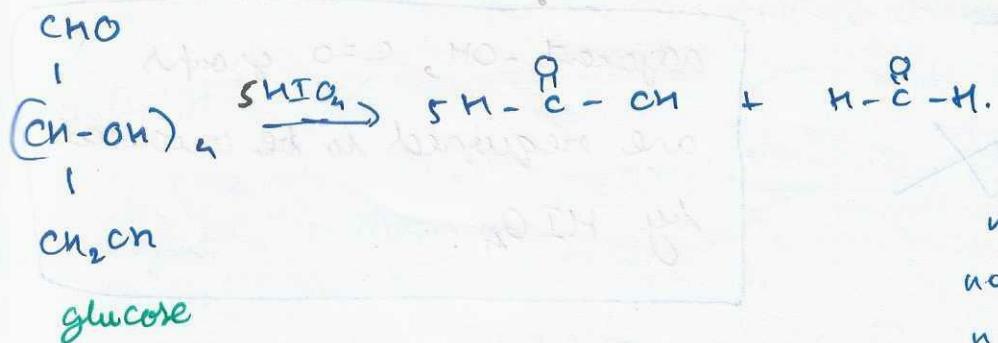


Continuous OH or || carbonyl groups react.

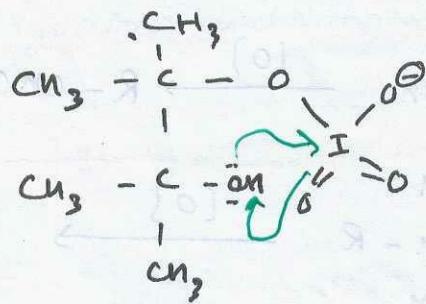
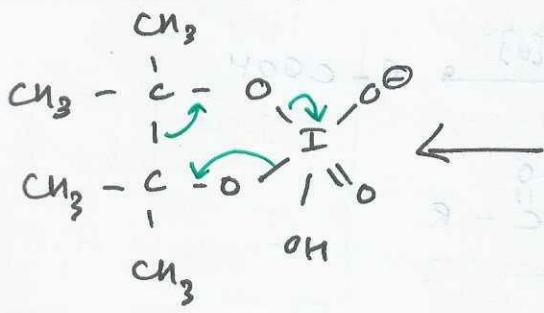
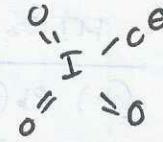
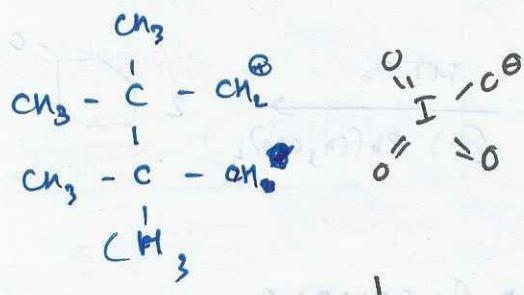
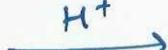
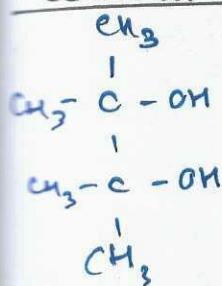


Break C-C bond and add OH group for every C-C bond broken.



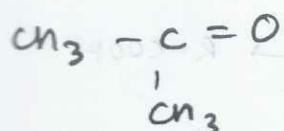
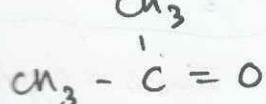


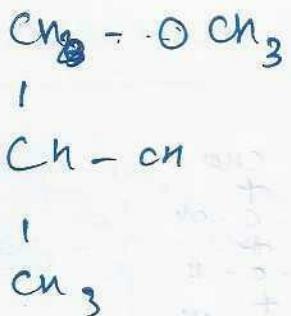
Mechanism



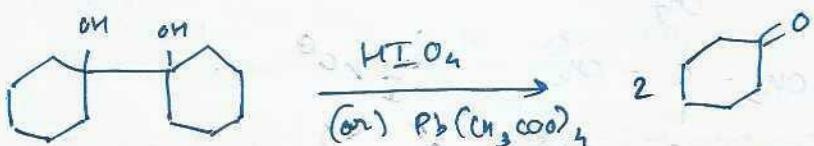
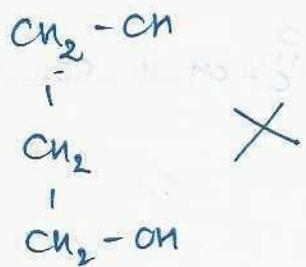
mole

For one bond broken, one mole
of HIO_4 is used.

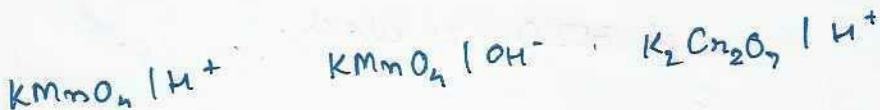
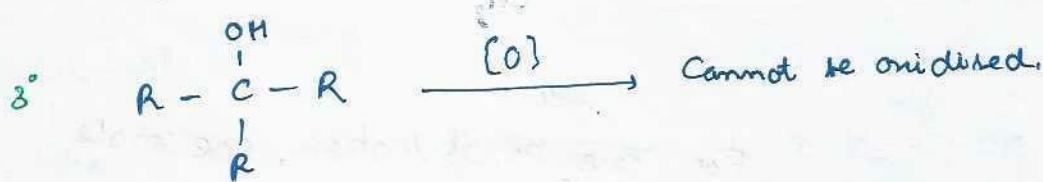




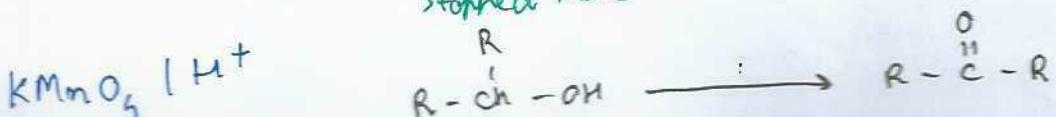
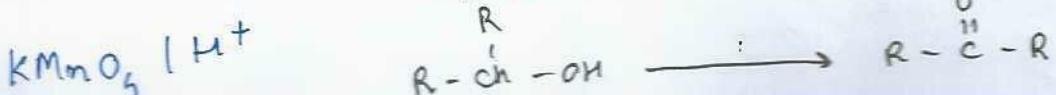
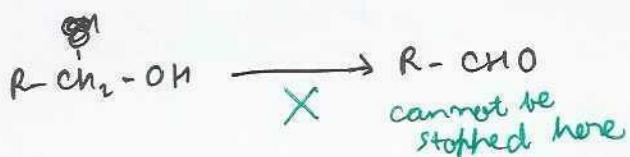
adjacent -OH, C=O groups
are required to be oxidised
by HIO_4 .

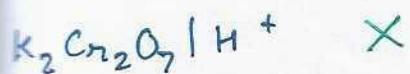


OXIDATION OF ALCOHOLS



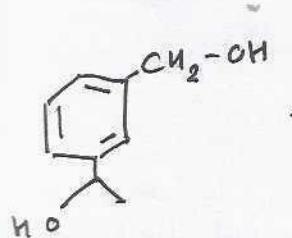
$\text{CrO}_3 / \text{acetone} / \text{dil H}_2\text{O}$
Jones's reagent





Tone's reagent

in certain cases ✓



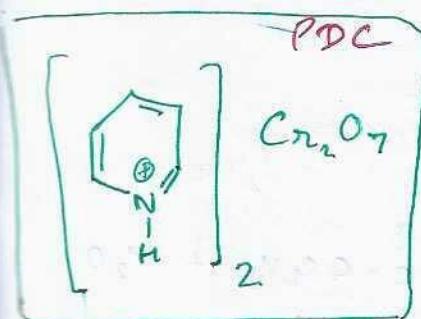
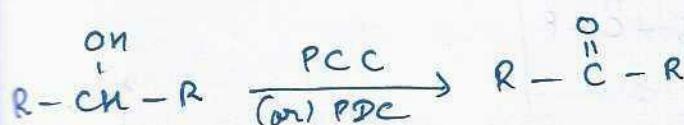
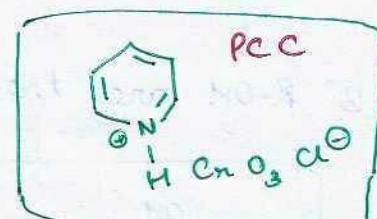
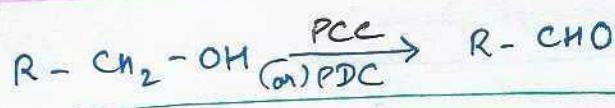
Aldehyde is formed

when in conjugation
with double bond



This cannot be stopped at
aldehyde.

PCC → Pyridine chloro chromate.



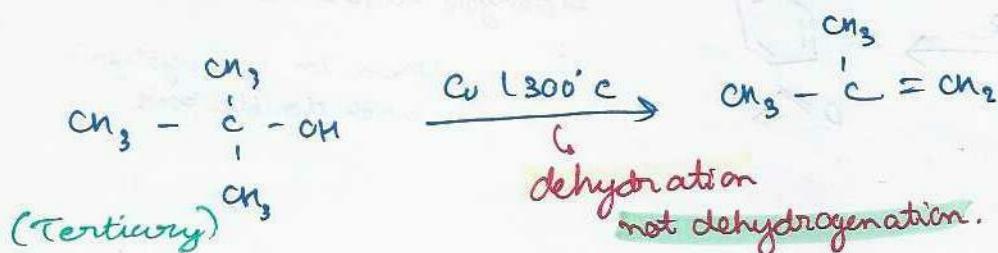
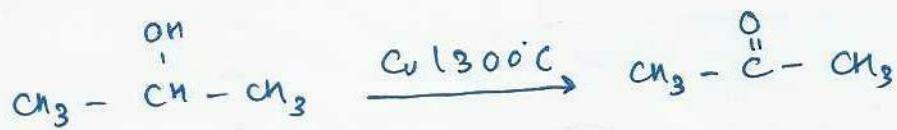
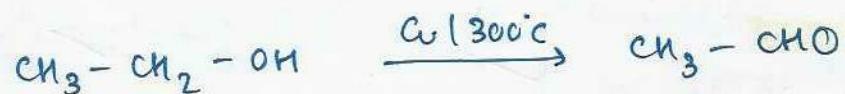
PDC → Pyridine di chromate.

[In non aqueous solutions]

PD C ✓ X ✓

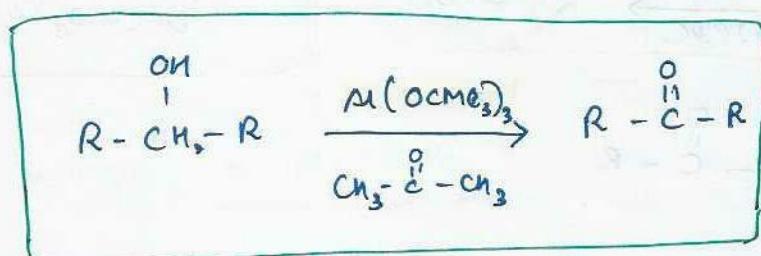
PCC ✓ X ✓

Cu | 300°C \rightarrow dehydrogenation

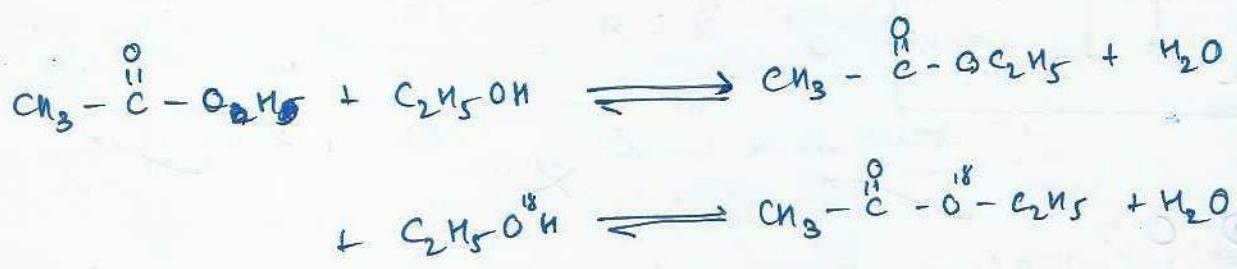


OPENNAUER OXIDATION

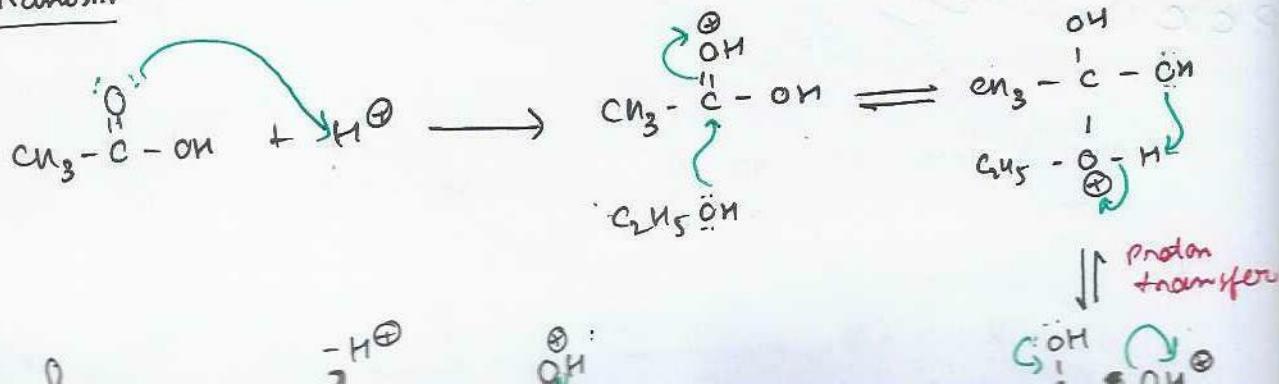
2° R-OH are treated with



ESTERIFICATION



Mechanism

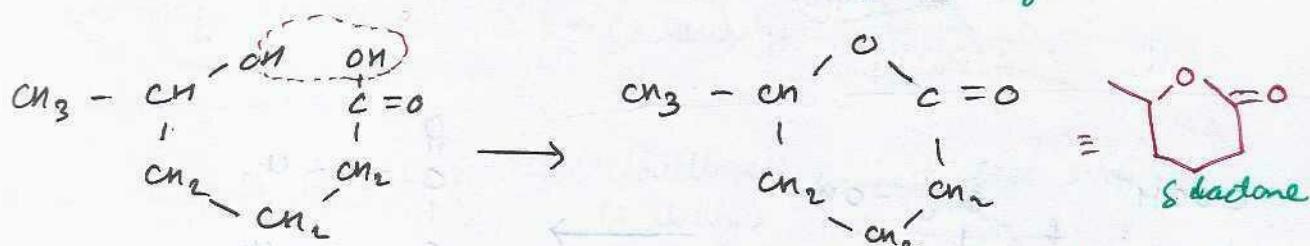
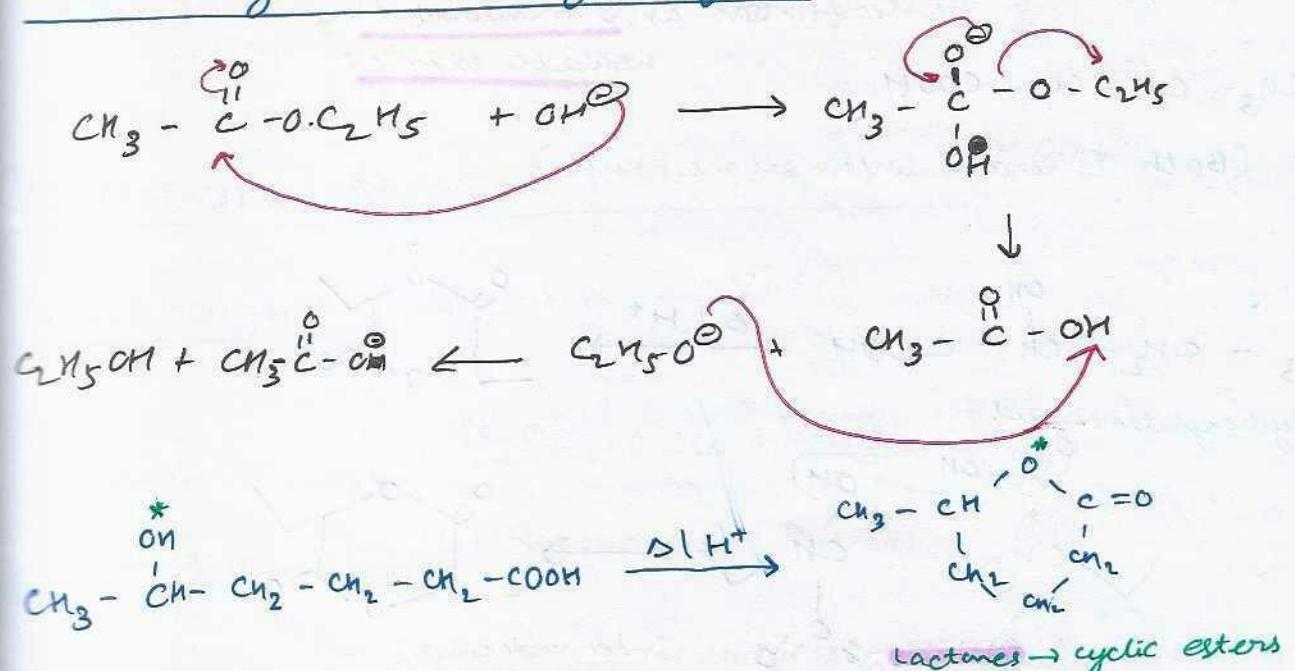


Base Catalyzed Esterification is not possible



so cannot react.

Base Catalysed Ester hydrolysis



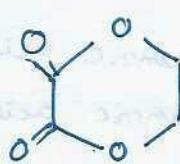
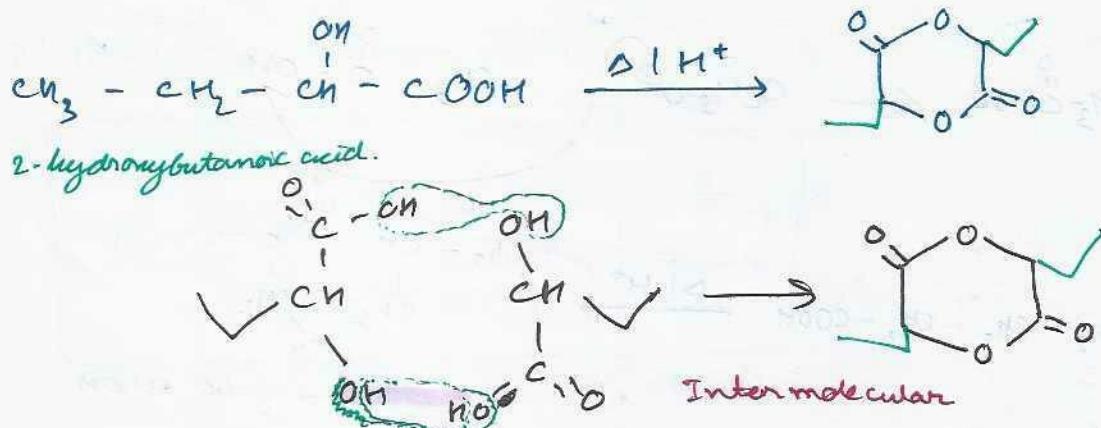
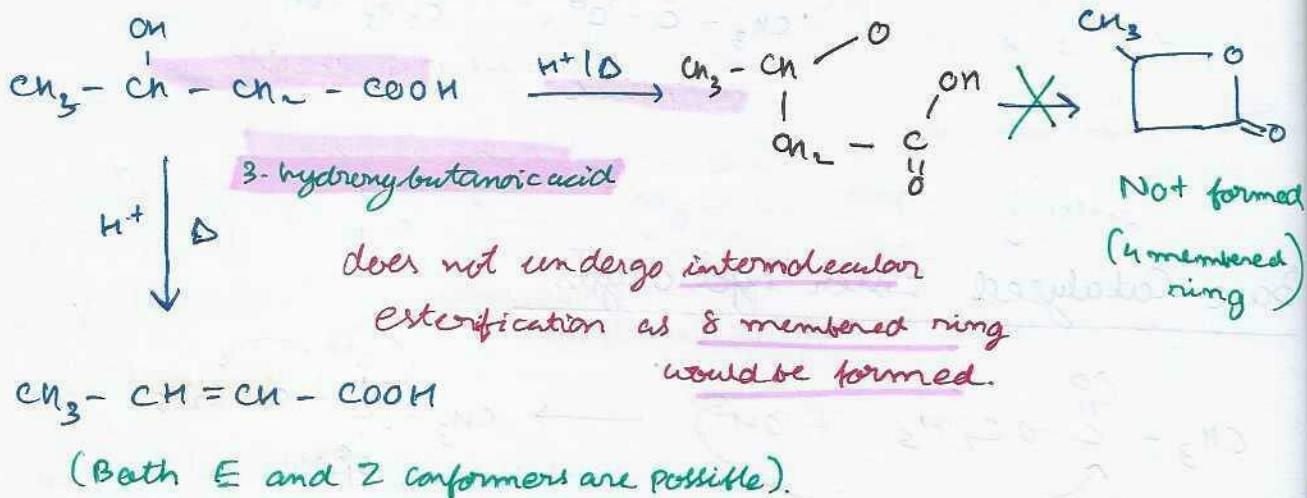
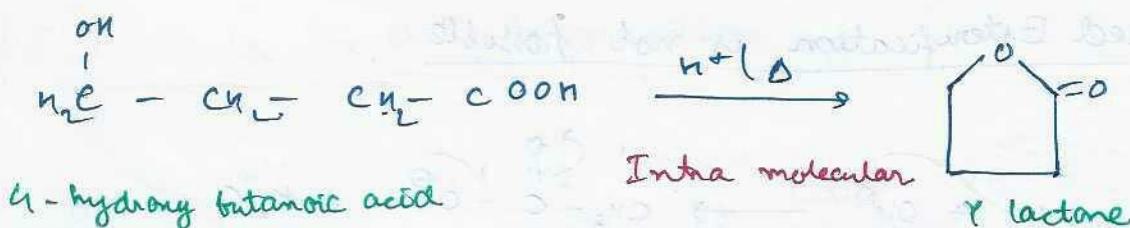
5 and 6 membered rings are stable. \therefore they are formed.

4 - hydroxy butanoic acid

3 - hydroxy butanoic acid

2 - hydroxy butanoic acid

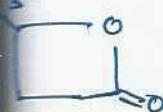
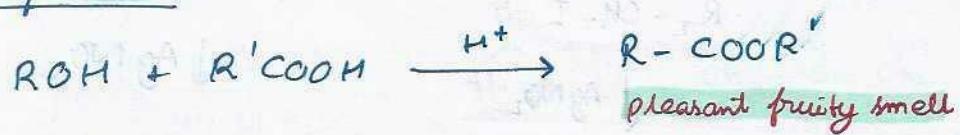
monomer
for



IDENTIFICATION OF ROH

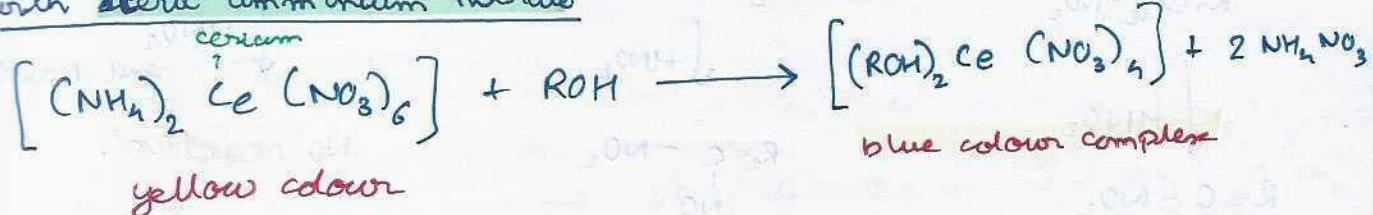


esterification



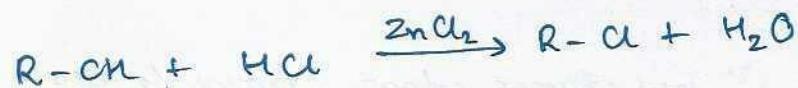
Not formed
(membered
ring)

with ceric ammonium nitrate



DISTINGUISH BETWEEN 1° ROH, 2° ROH and 3° ROH

Lucas reagent : Conc. HCl + $ZnCl_2$



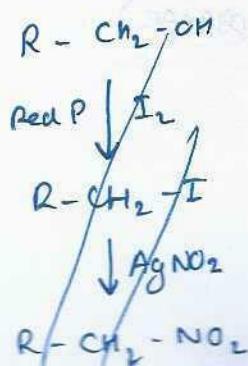
Rate of reactivity $3^\circ ROH > 2^\circ ROH > 1^\circ ROH$

Lucas test

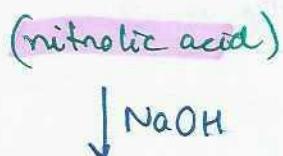
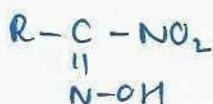
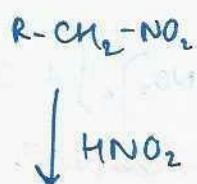
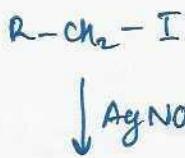
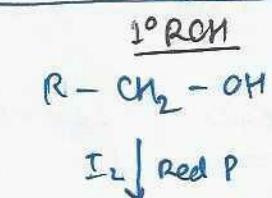
- Lucas reagent + 3° ROH \longrightarrow cloudiness (turbidity) is formed immediately.
 \downarrow insoluble
- Lucas reagent + 2° ROH \longrightarrow cloudiness (turbidity) formed after 5 min
- Lucas reagent + 1° ROH \longrightarrow no turbidity (primary alkyl chloride soluble)

Victor Mayer Test

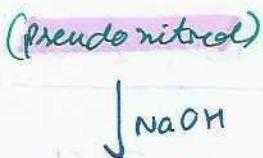
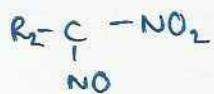
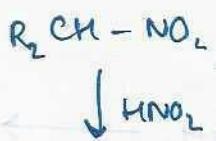
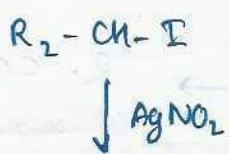
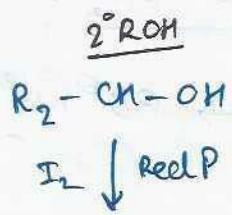
1° ROH
 \downarrow Red P / I_2
R-I



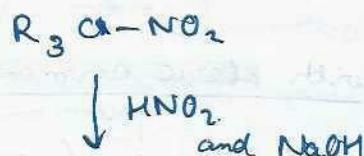
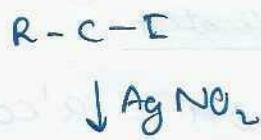
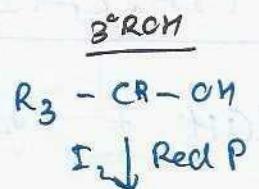
Victor Mayer Test



Blood red colour.

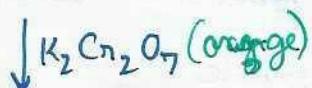


Blue colour

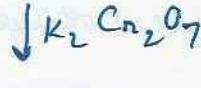


No reaction.

Dichromate Test



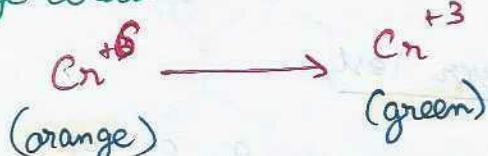
carboxylic acid
with same No. of
carbon atoms is formed



No reaction.

$\text{Cr}^{+3} \rightarrow$ green colour

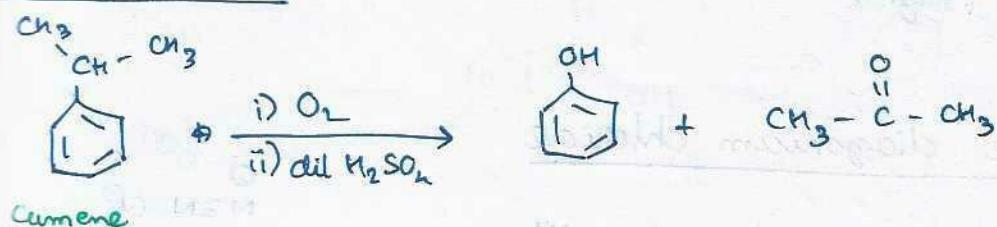
$\text{Cr}^{+6} \rightarrow$ orange colour



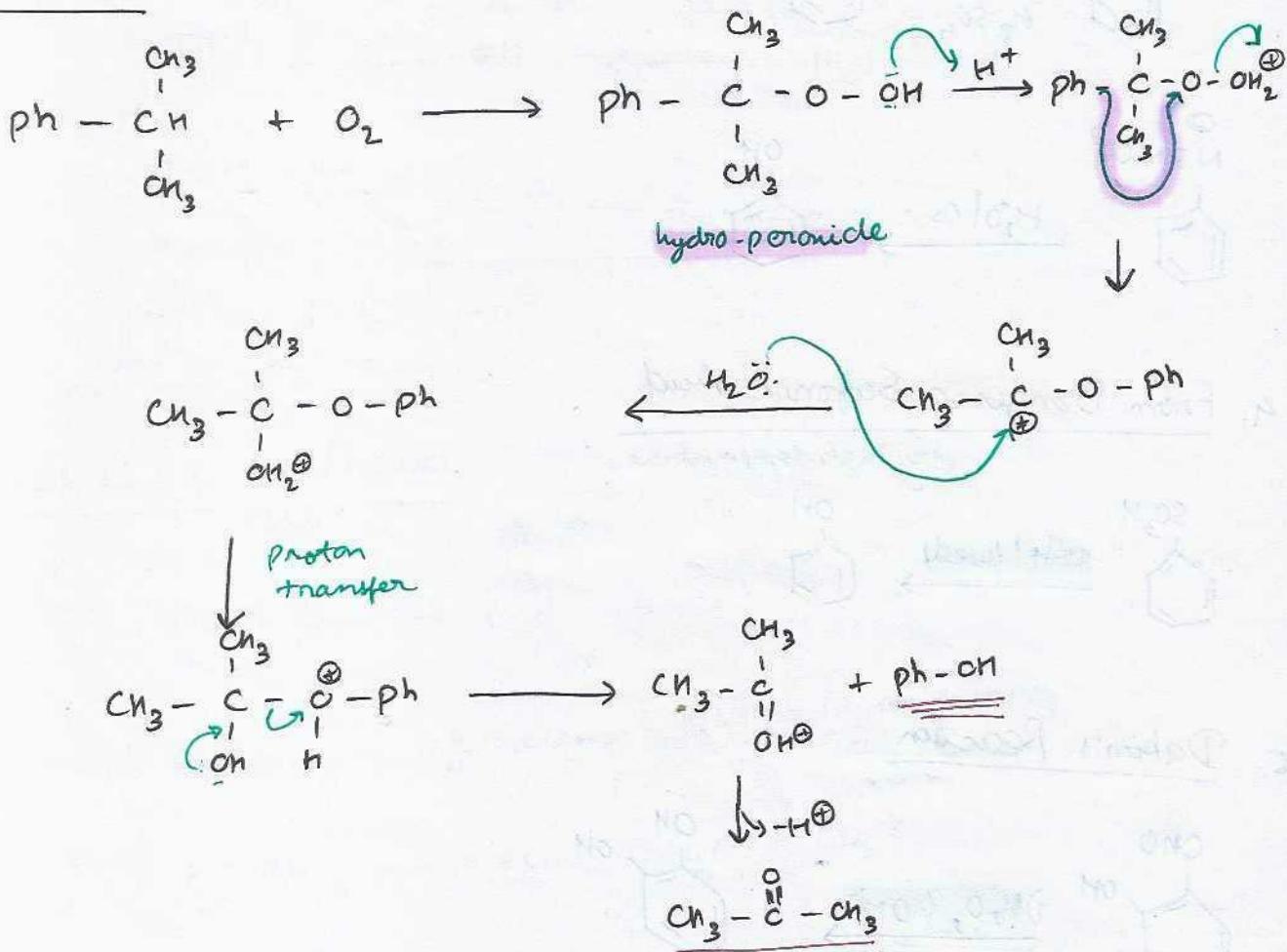
PHENOL

PREPARATION

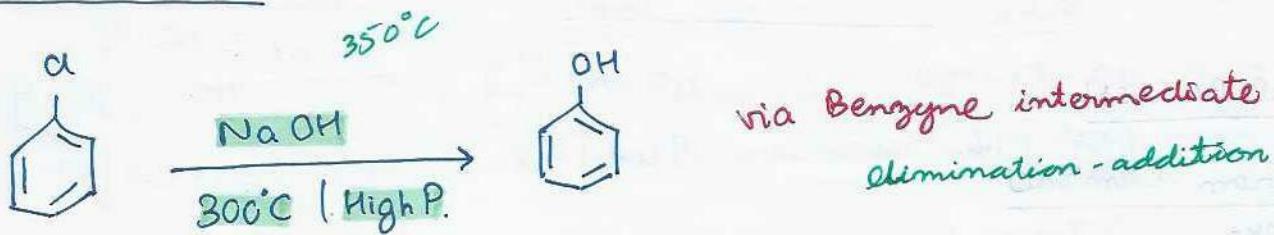
From Cumene



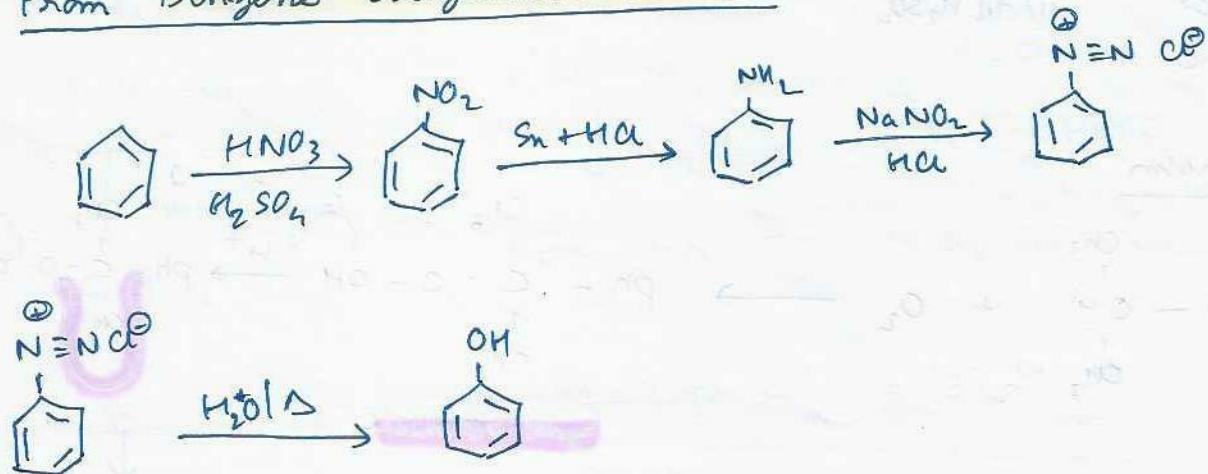
Mechanism



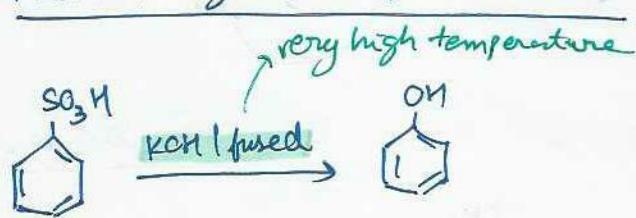
2. Dow's Process



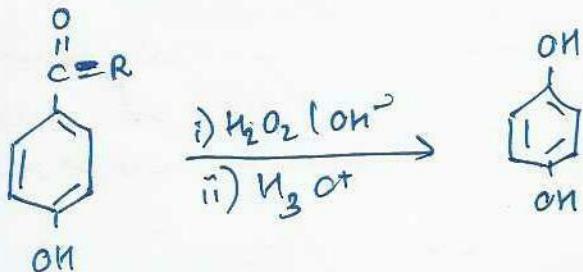
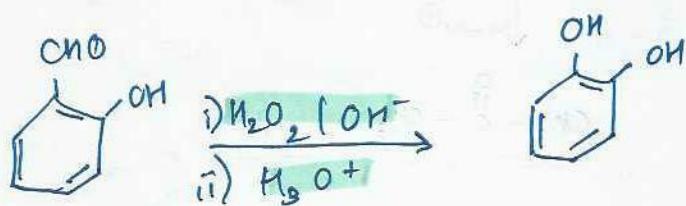
3. From Benzene diazonium chloride



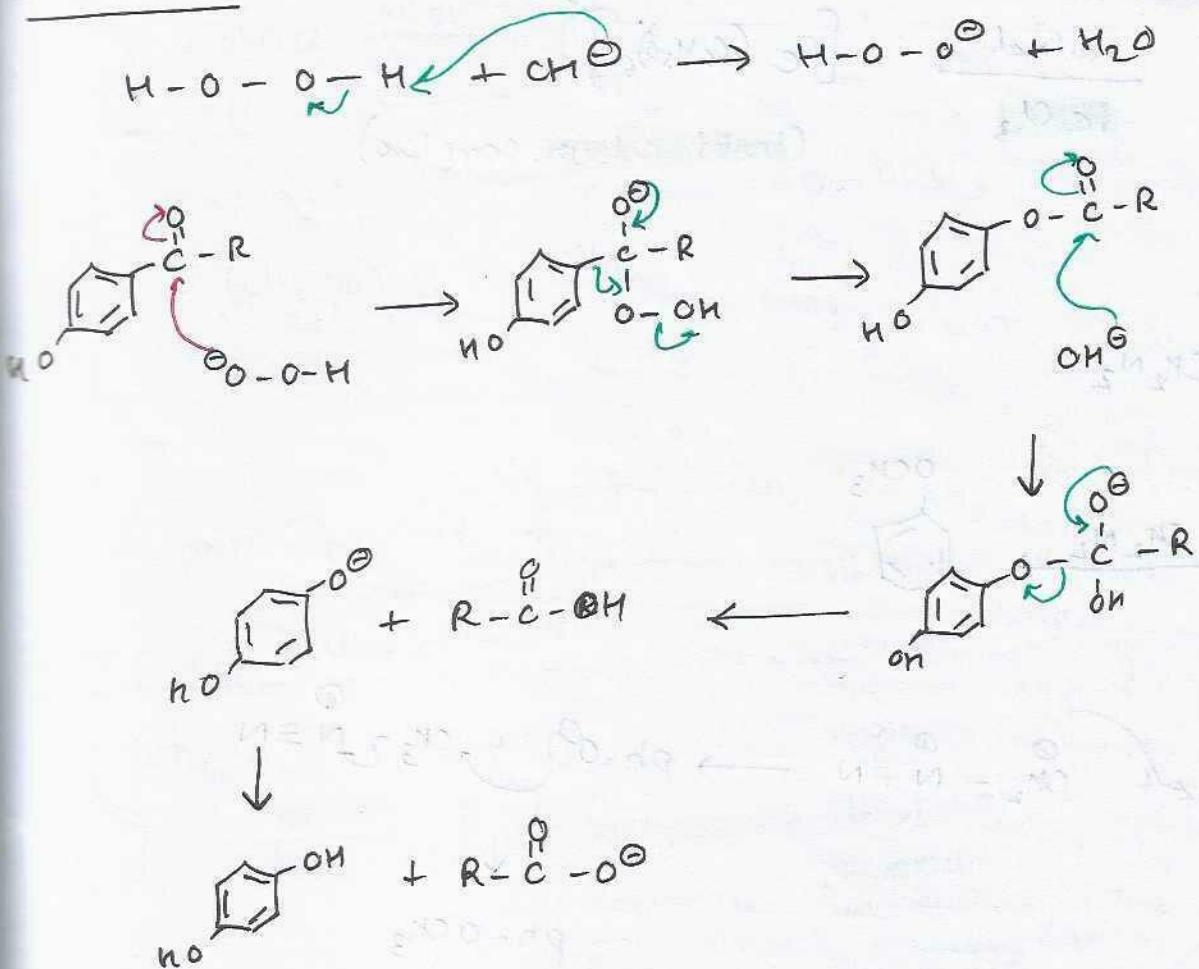
4. From Benzene Sulfonic Acid



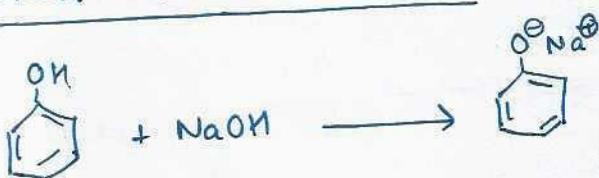
5. Dakin's Reaction



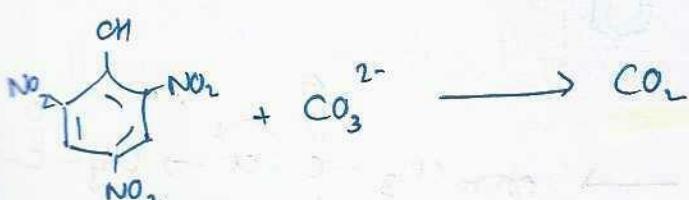
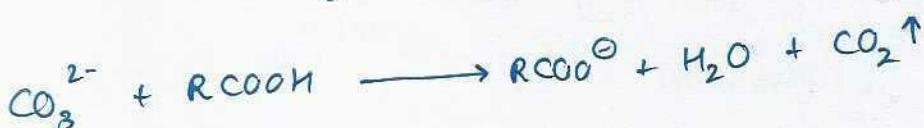
Mechanism



PROPERTIES OF PHENOL

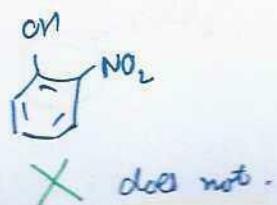
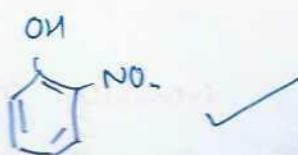


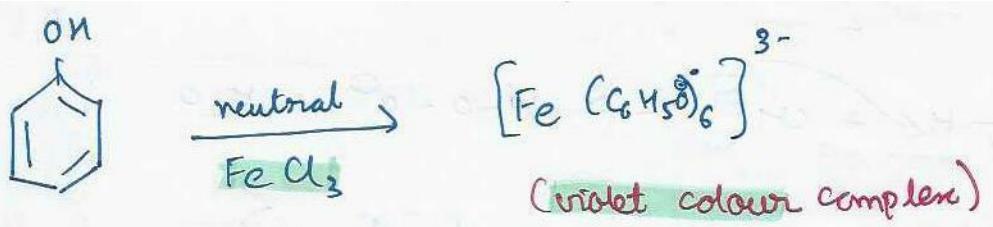
Phenol cannot give effervescence with Na_2CO_3 or NaHCO_3 .



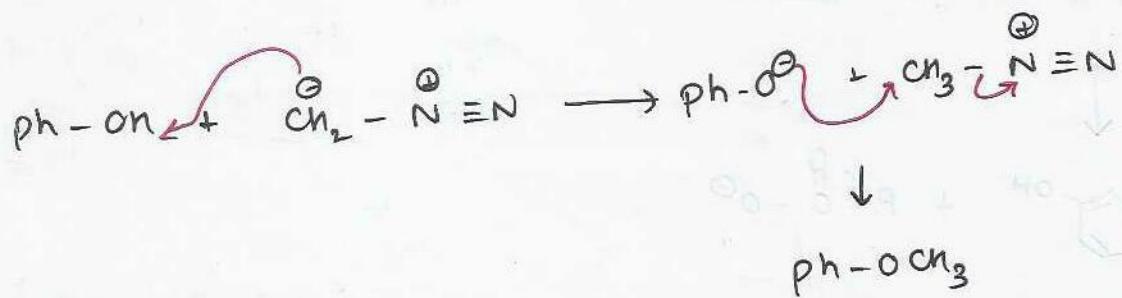
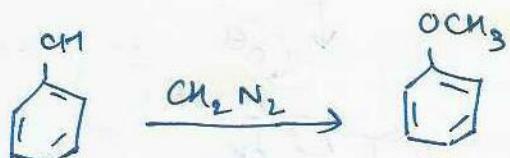
Picric acid

(more acidic than acetic acid)

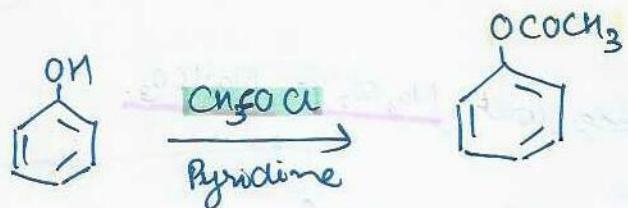




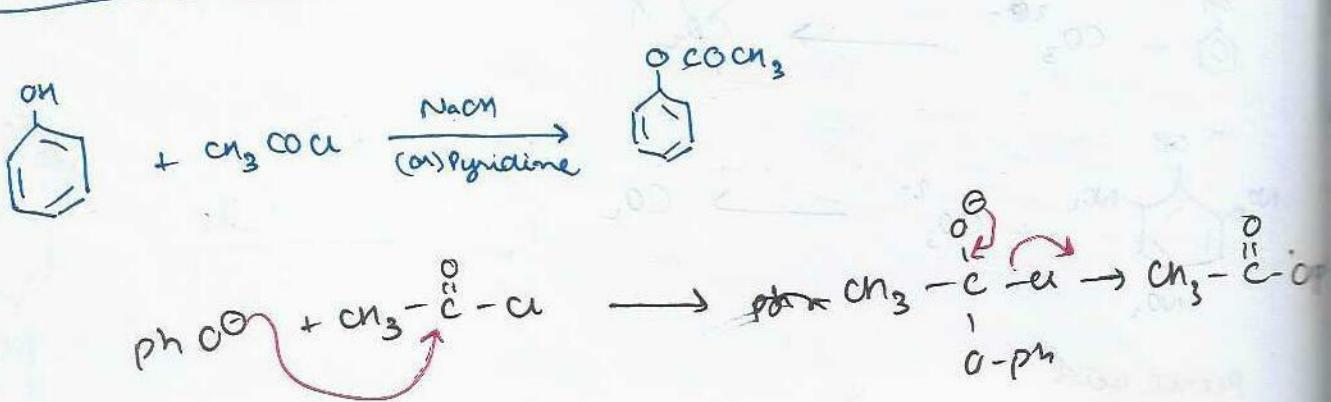
with CH_2N_2



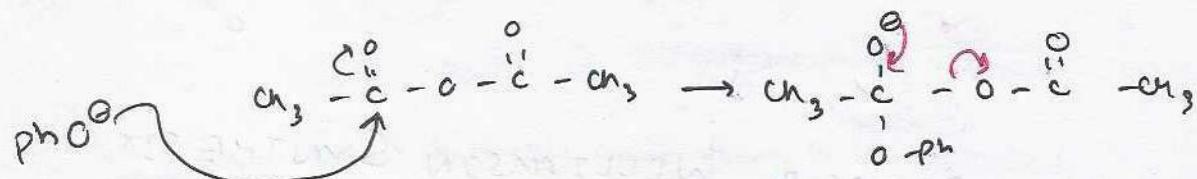
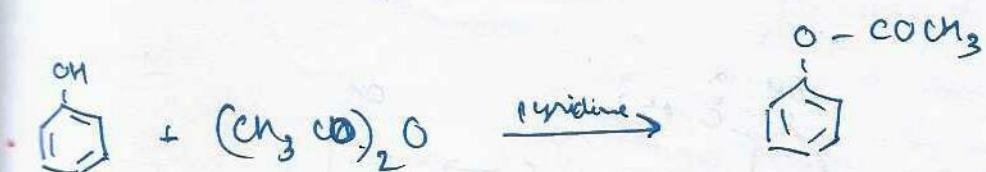
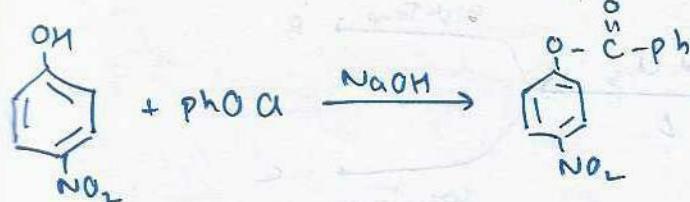
with acetyl chloride



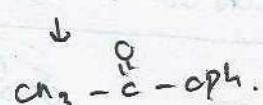
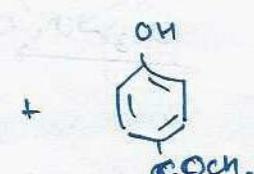
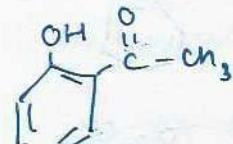
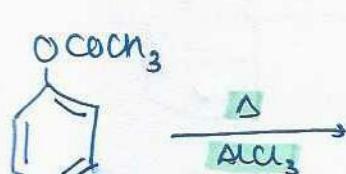
Formation of Ester



Normally there are
multiple methods to



FRIES REARRANGEMENT

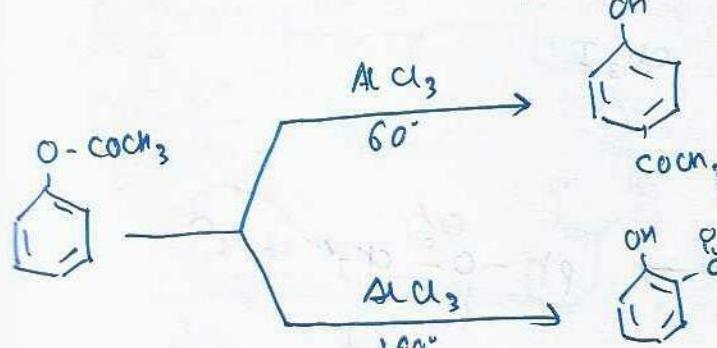


At high temperature

160°C
major

At low temperature

60°
major

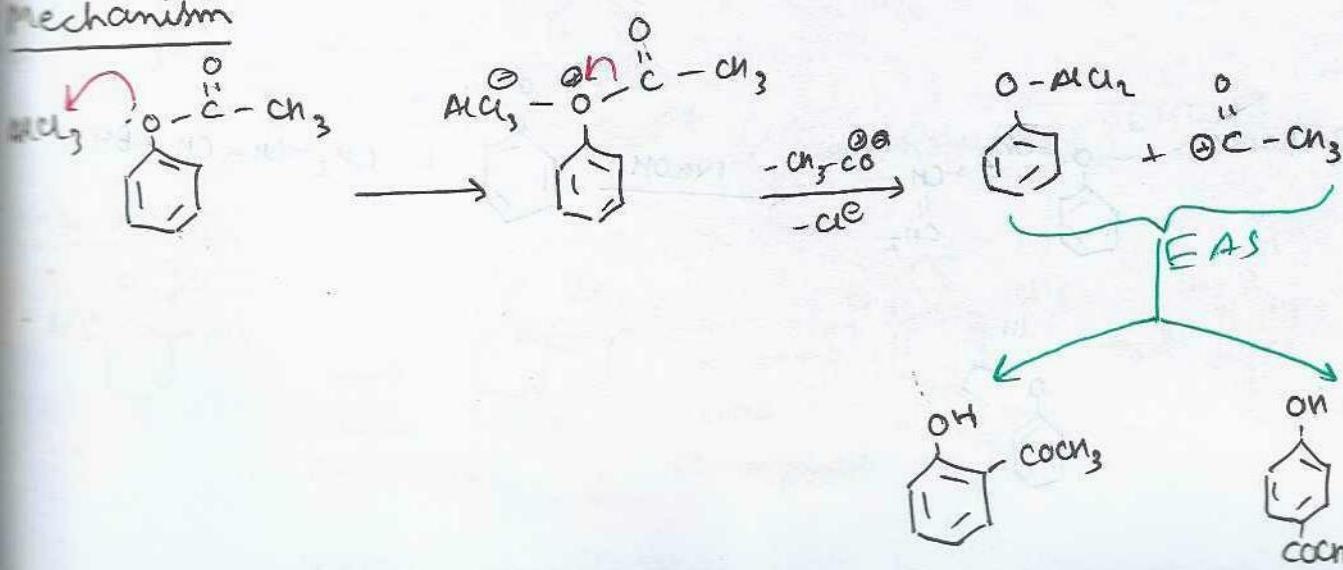


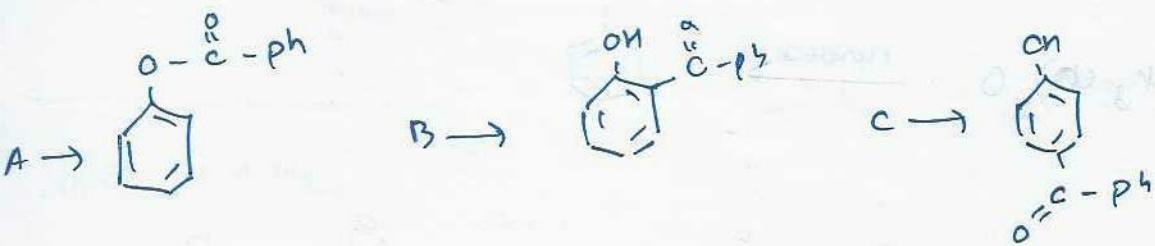
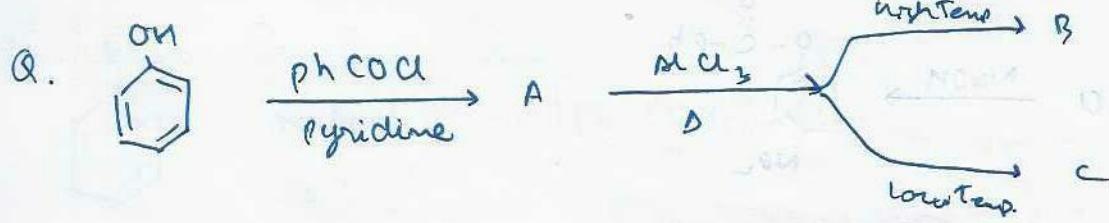
(kinetically controlled)

→ forms intramolecular
hydrogen bonding.

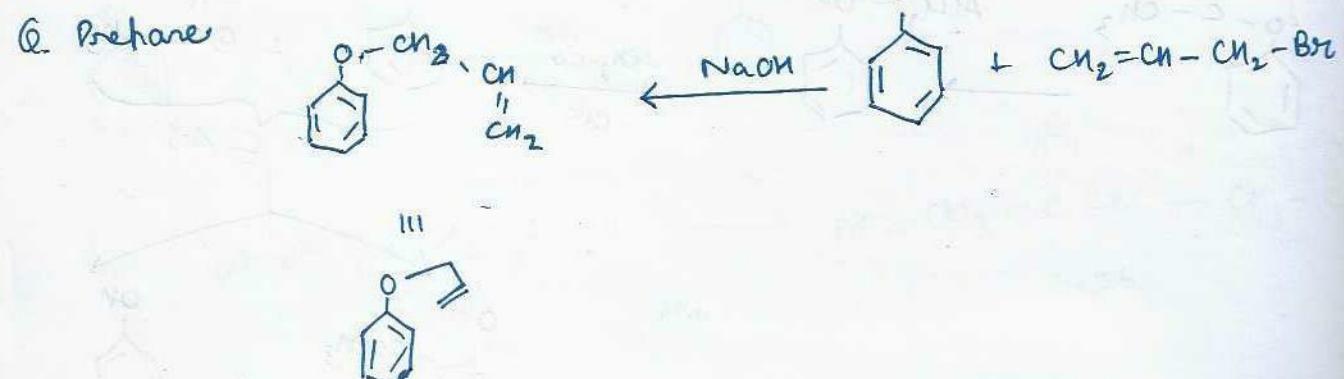
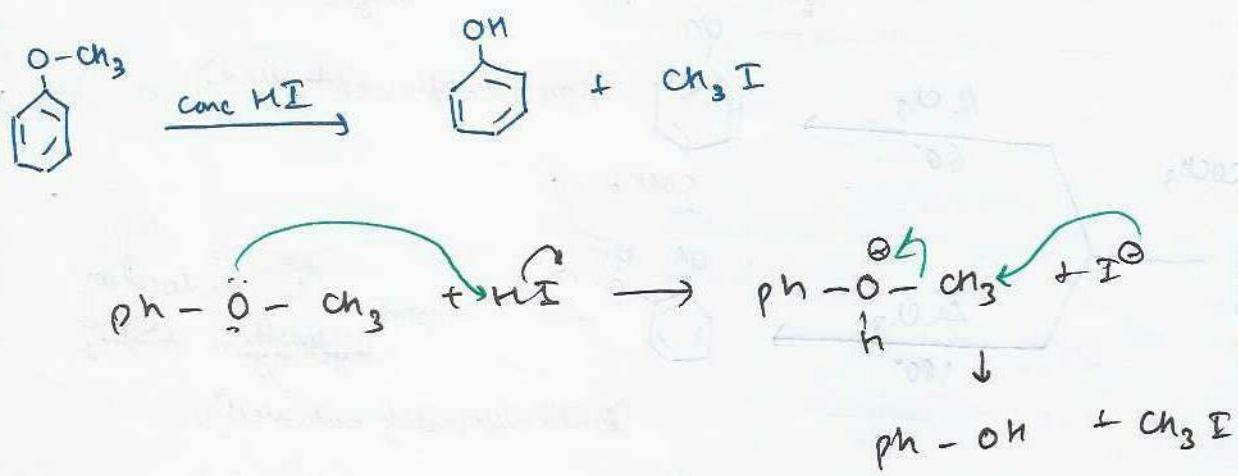
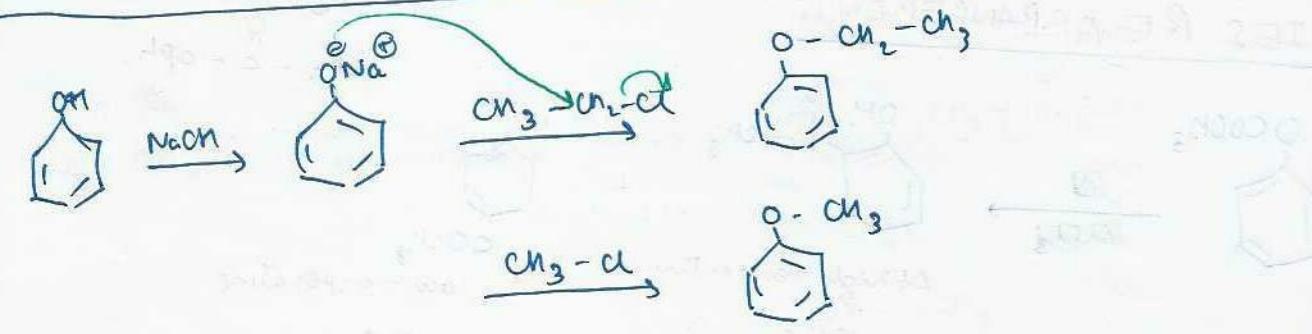
(thermodynamically controlled).

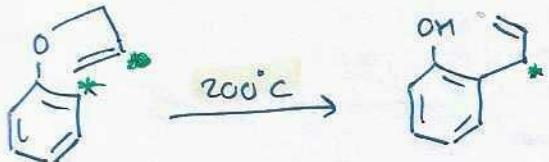
Mechanism





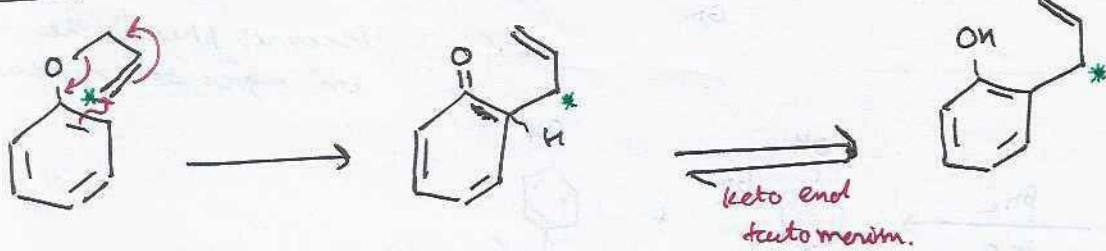
FORMATION OF ETHERS BY WILLIAMSON SYNTHESIS



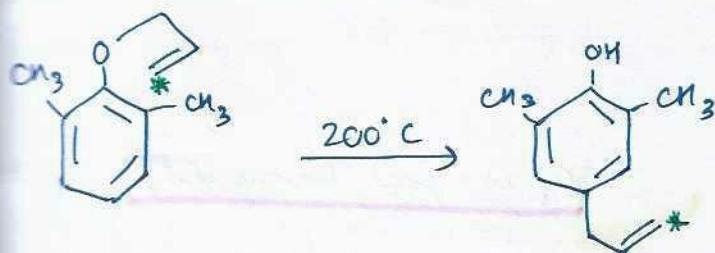
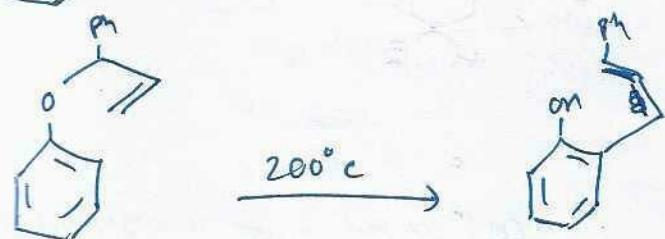
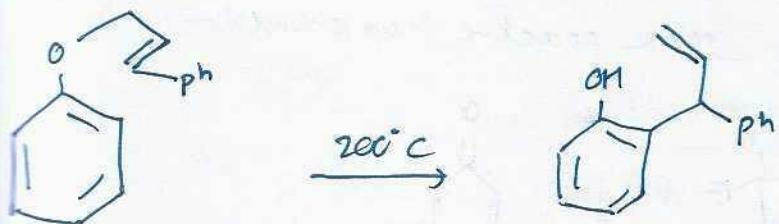
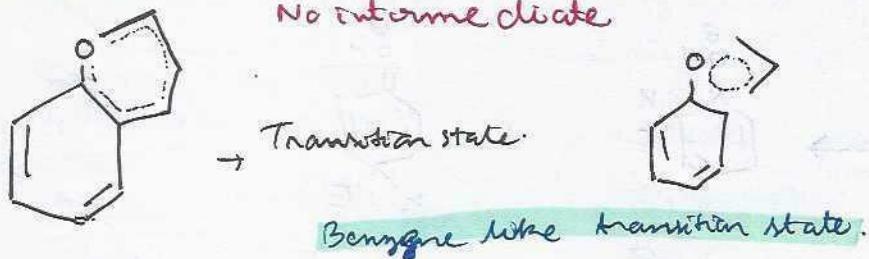


CLAISEN REARRANGEMENT

Mechanism

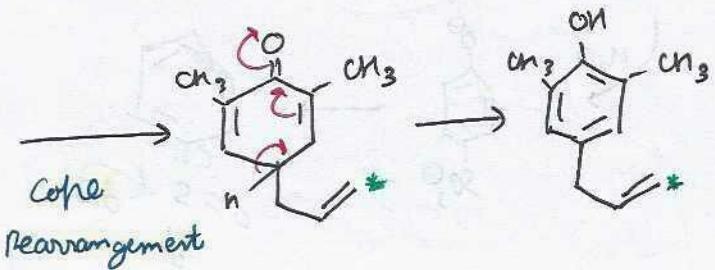
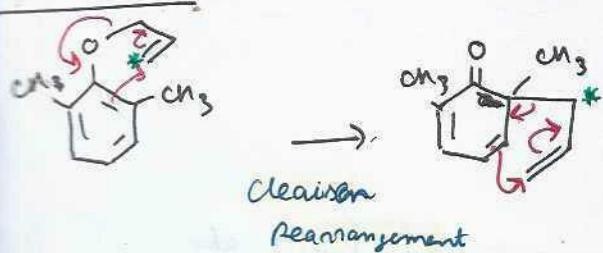


Consented Reaction: Occurs through transition state.
No intermediate

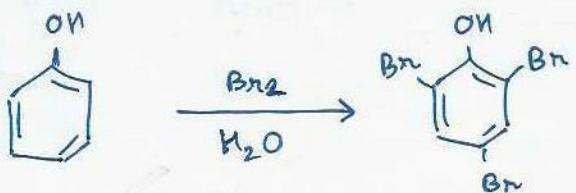


COPP REARRANGEMENT

Mechanism

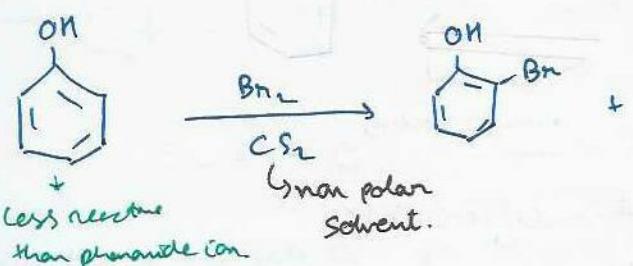


REACTIONS DUE TO RING

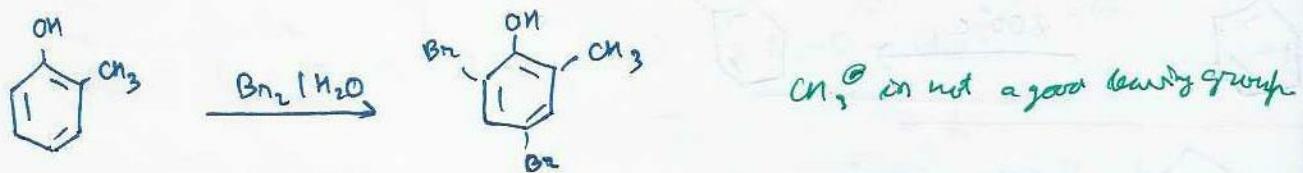
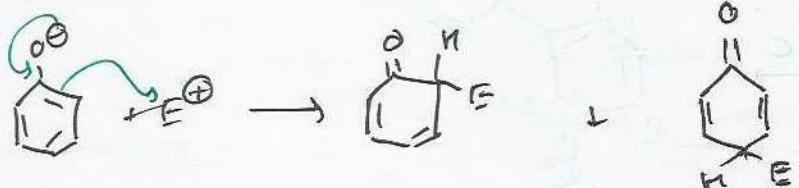
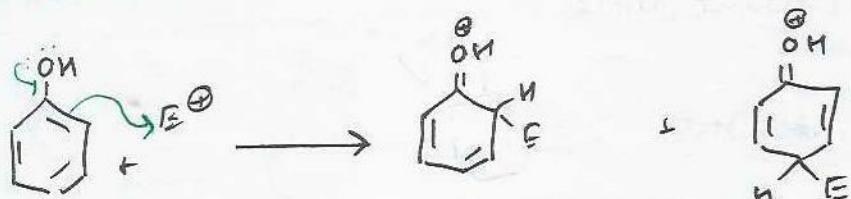


[Phenol more reactive than Benzene].

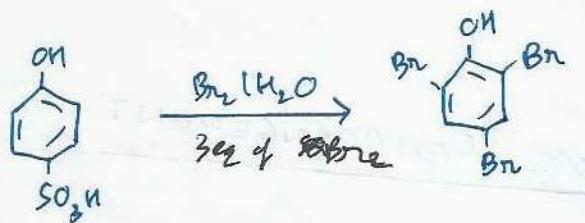
becomes phenoxide ion
in aqueous medium.



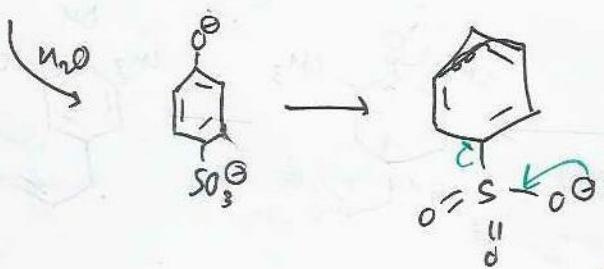
major \rightarrow as Br is bulky group.



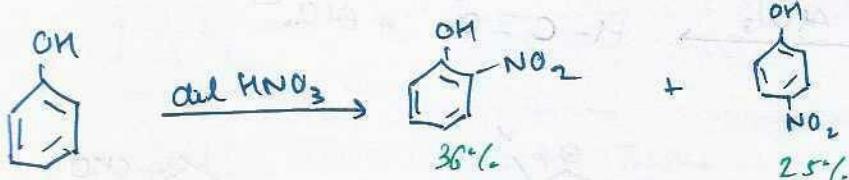
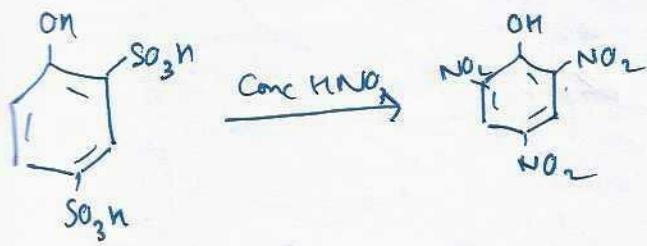
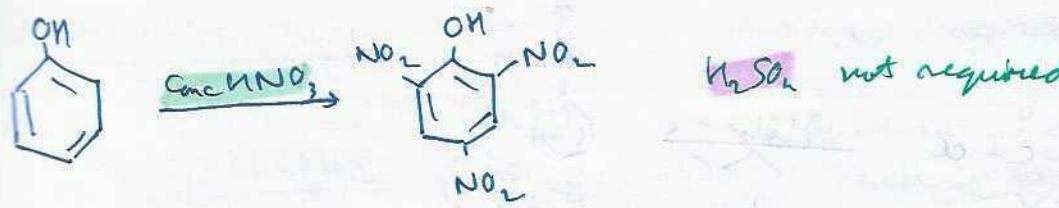
CH_3^+ is not a good leaving group



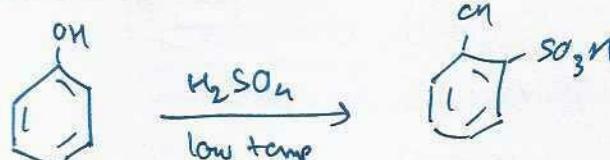
SO_3^- is a good leaving group.



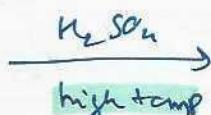
If COON group is present at
ortho or para position, it is



SULPHONATION



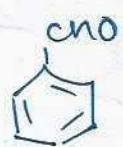
$\text{20}^\circ\text{C}$



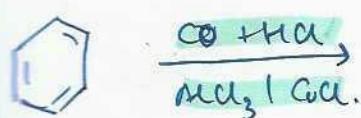
100°C

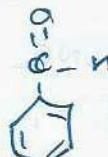
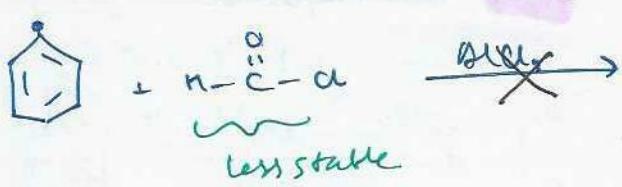
Steric hindrance is more dominating than attack by H-bonding

Q How many show H-bonding

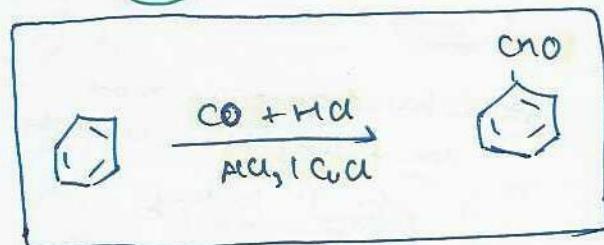
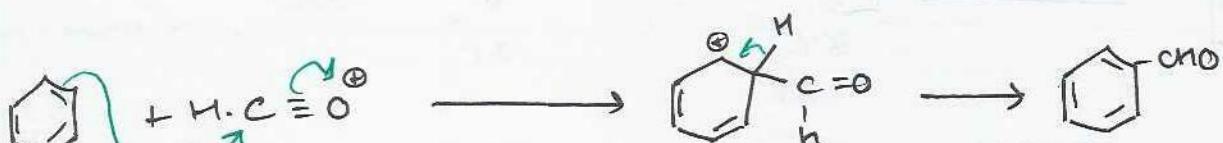
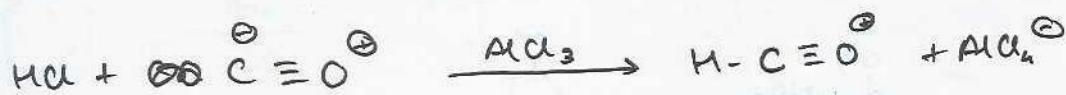
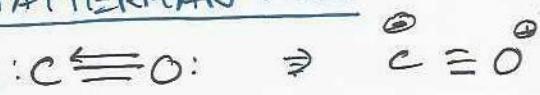


Curtissman Koch

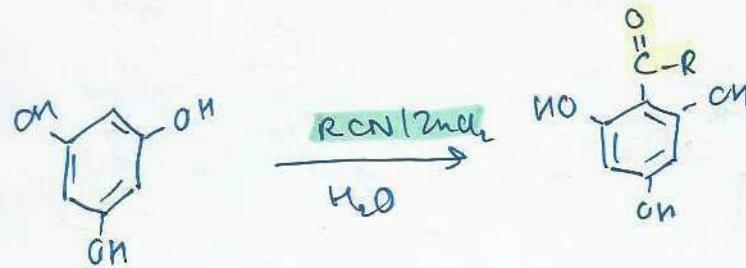
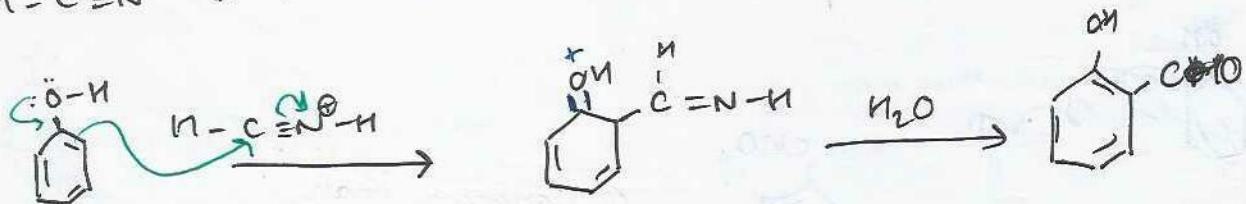
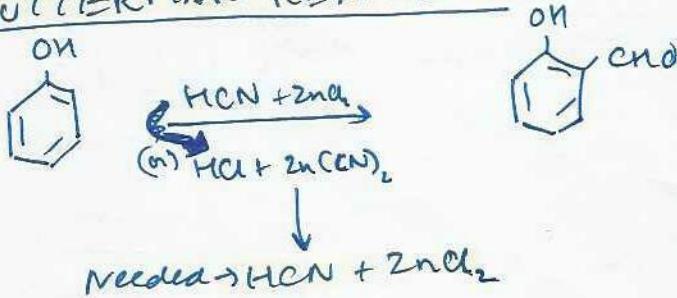




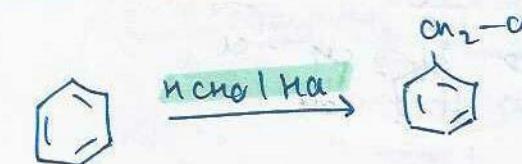
GATTERMAN KOCH



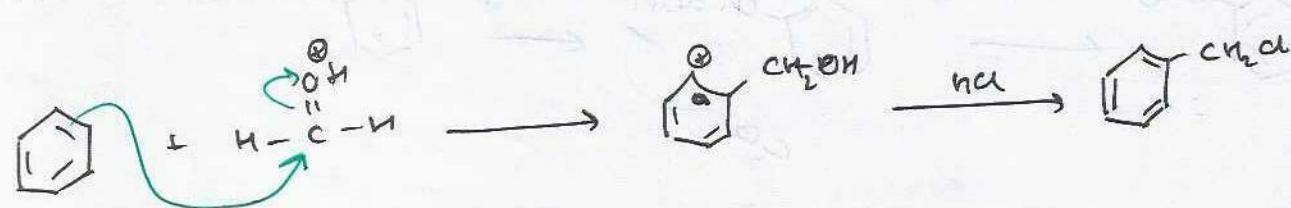
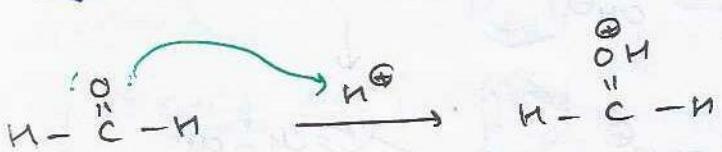
GATTERMAN REACTION



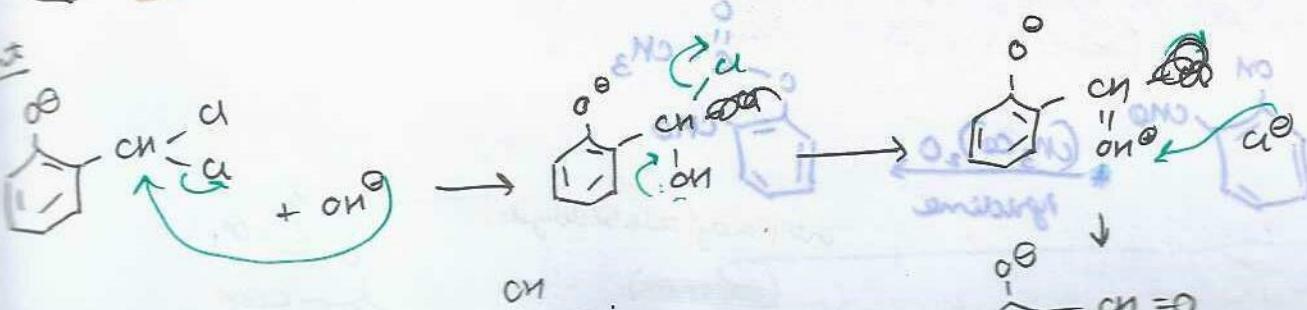
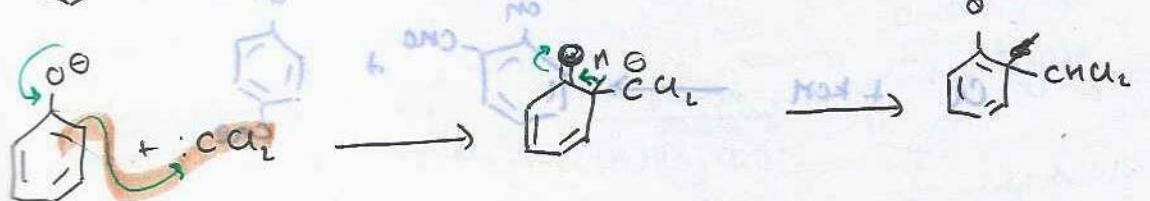
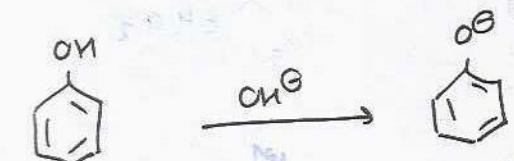
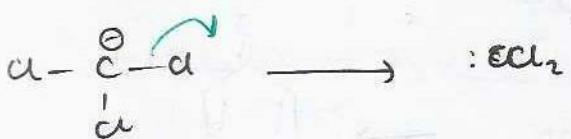
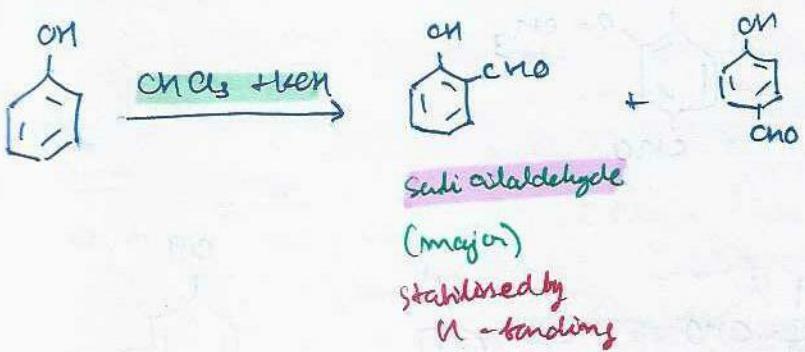
CHLOROMETHYLATION



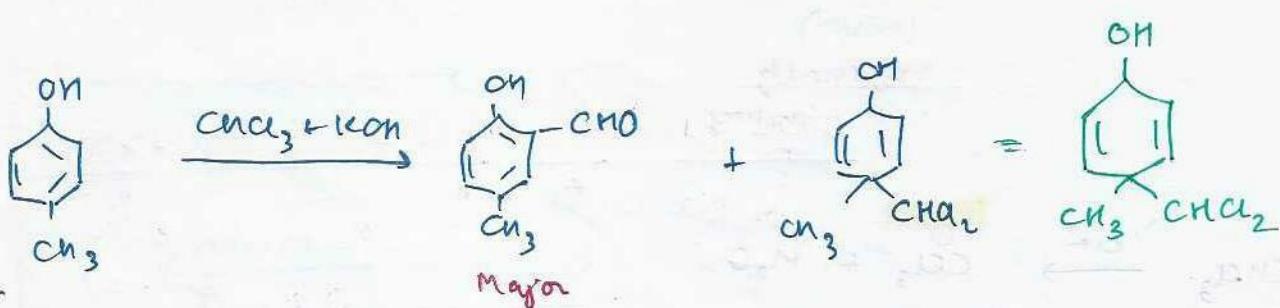
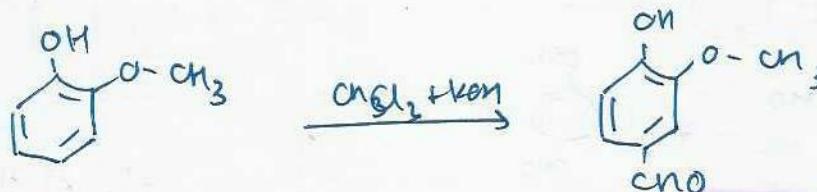
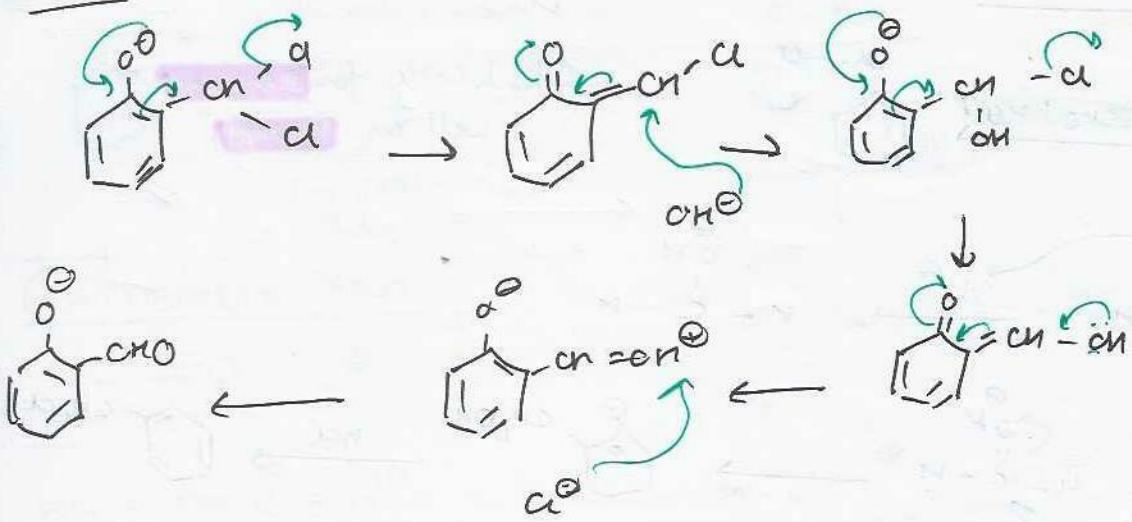
Applicable for Benzene as well as Phenol



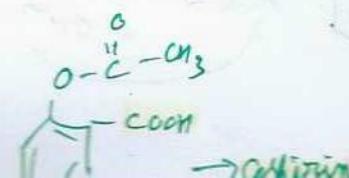
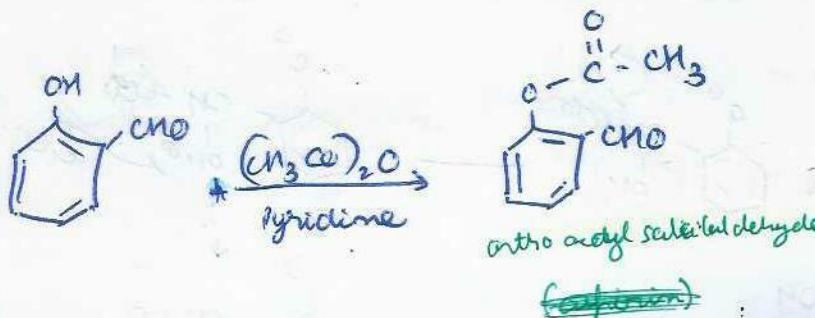
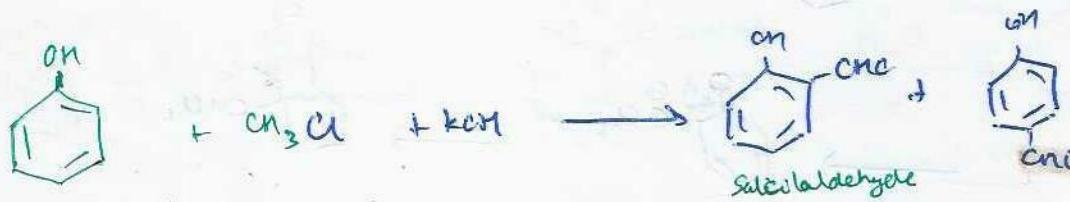
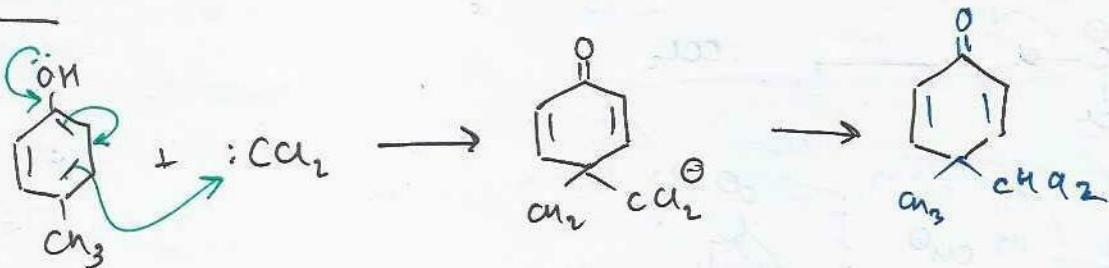
RIEMER - TIEMANN's REACTIONS

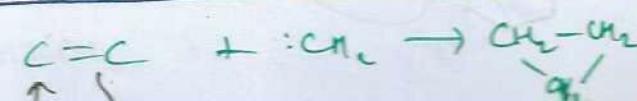
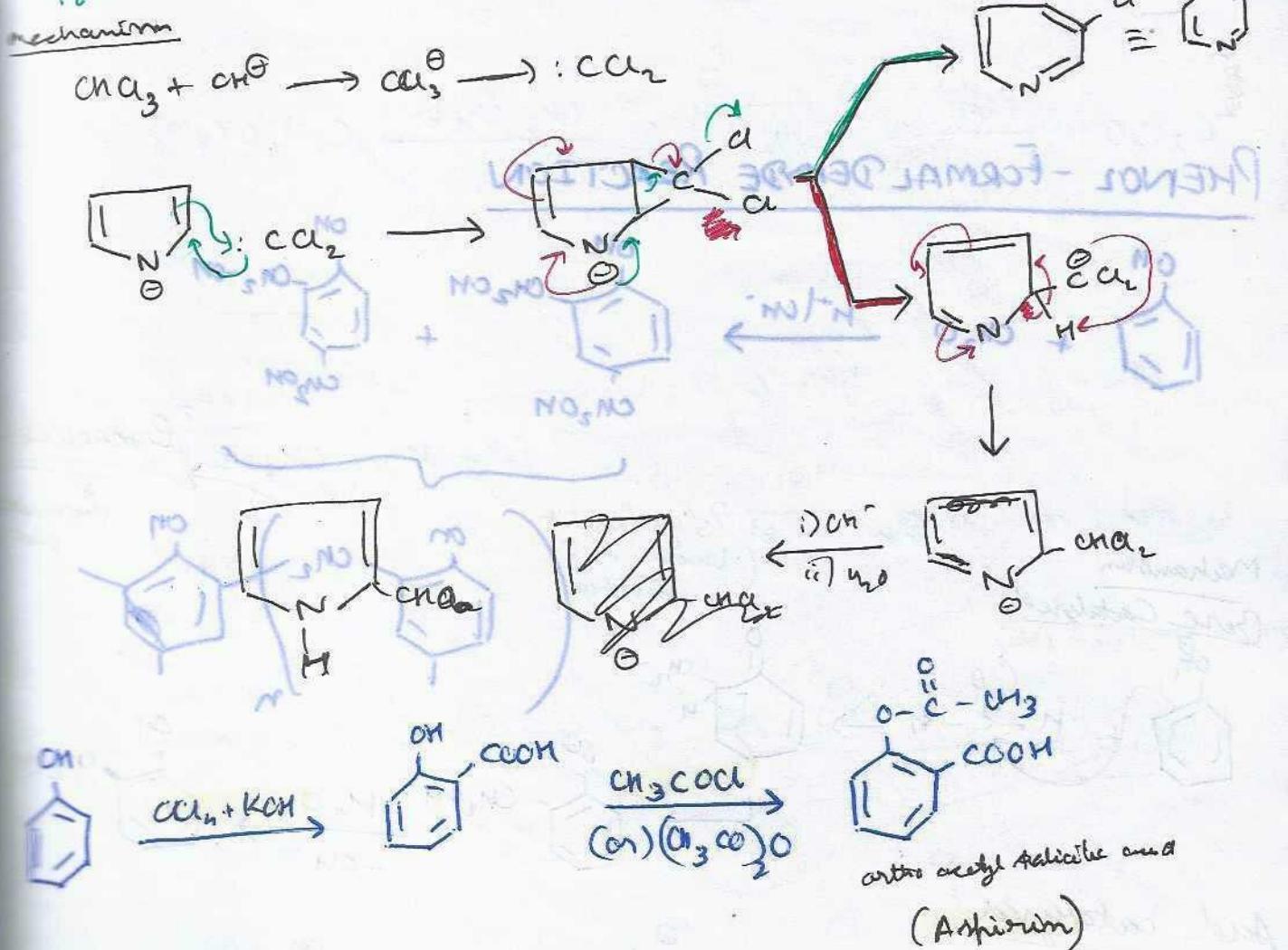
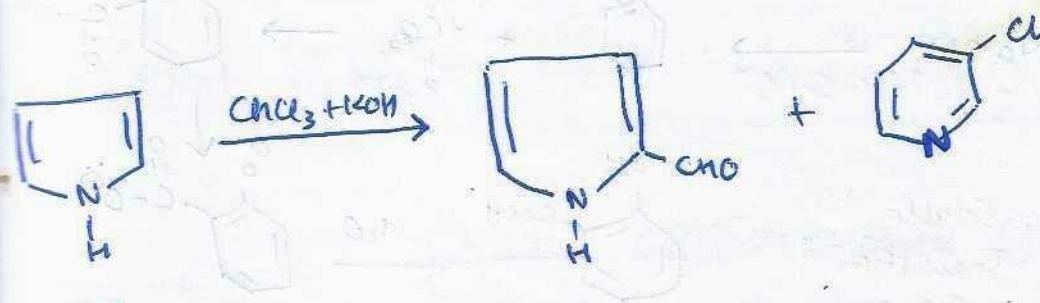
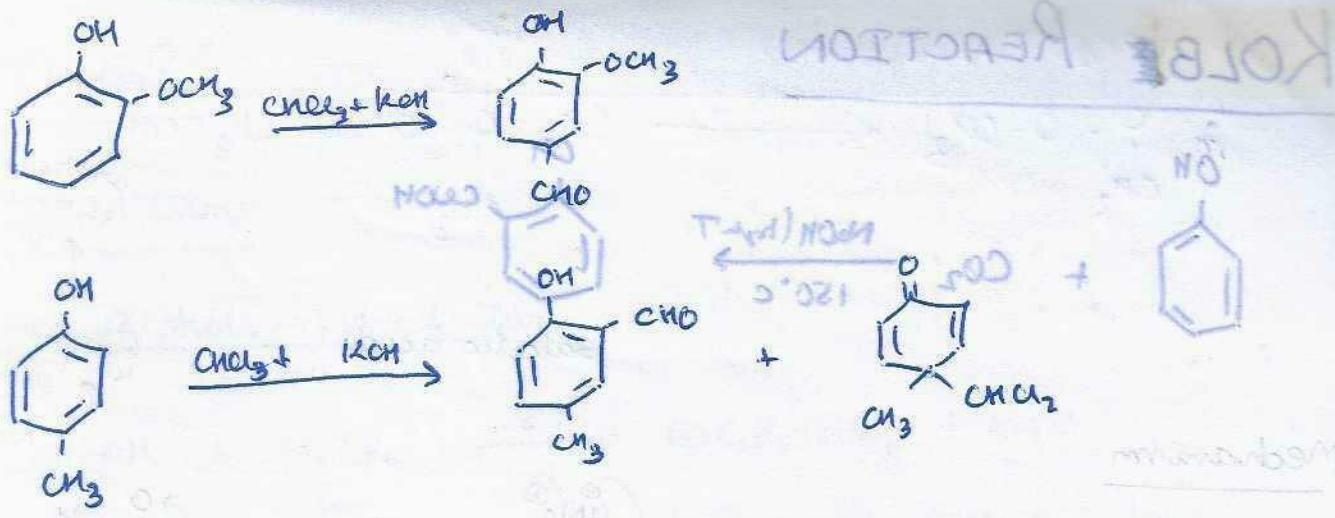


Funk

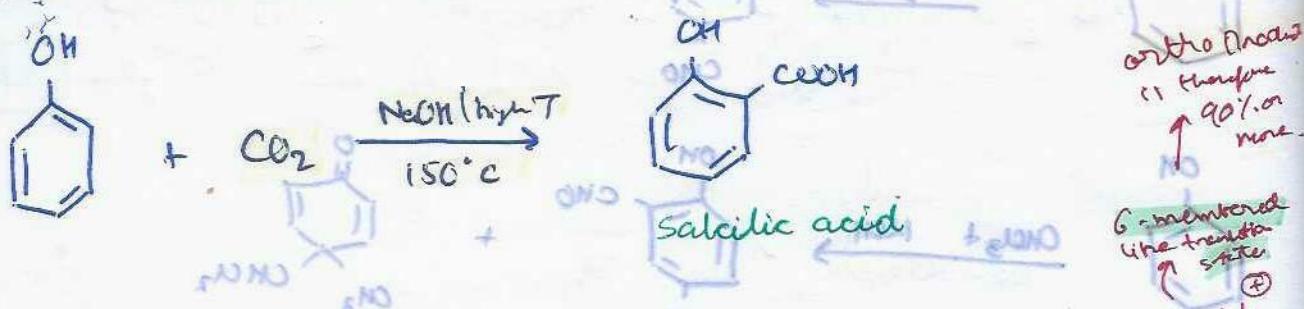


Mechanism

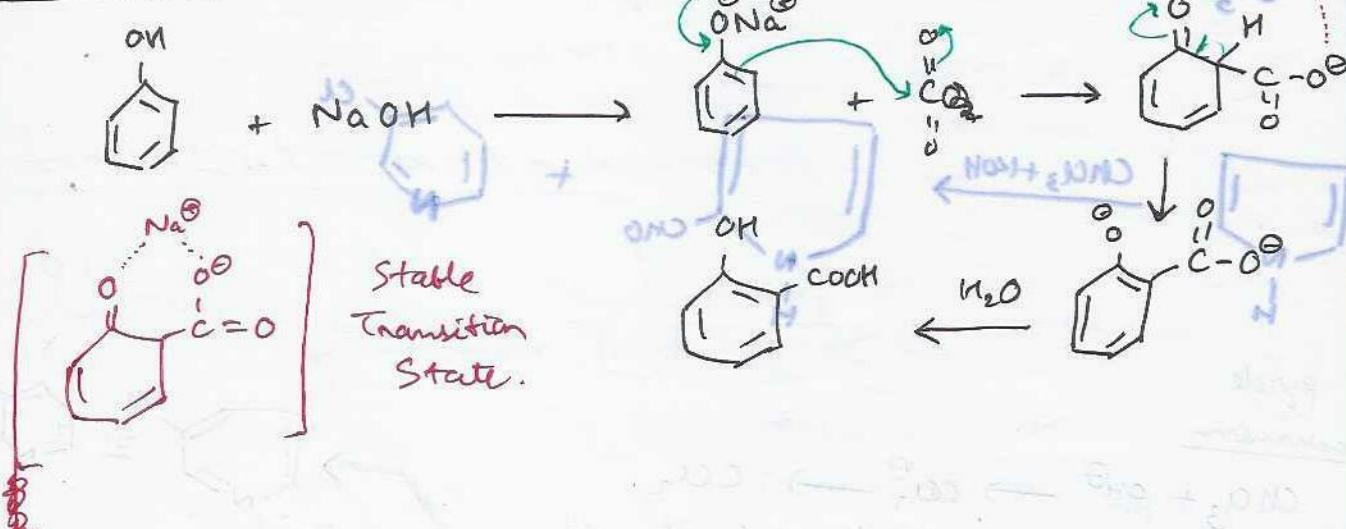




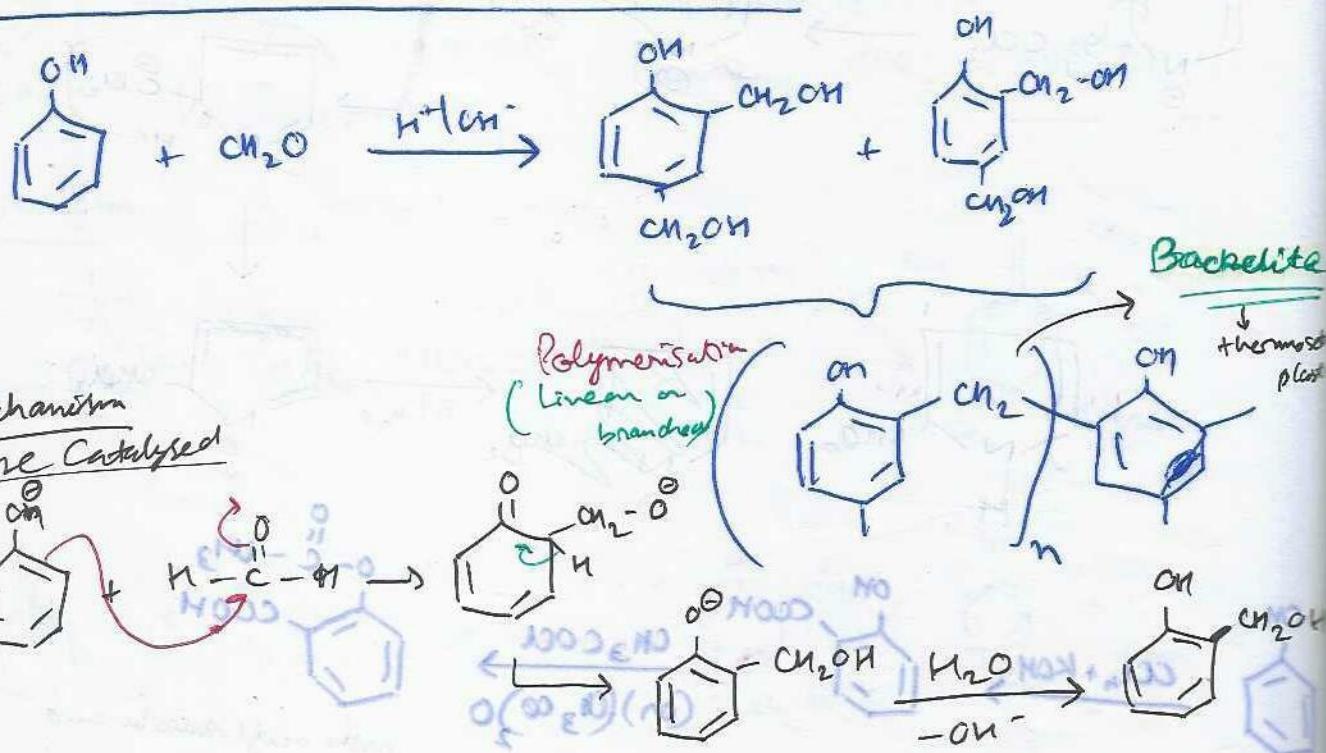
KOLBE REACTION



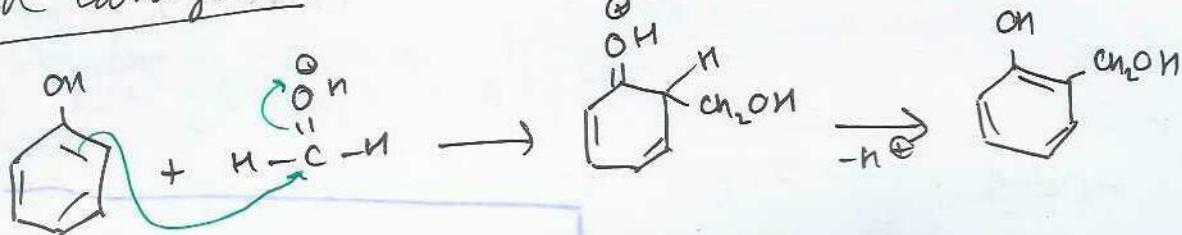
Mechanism



PHENOL - FORMALDEHYDE REACTION



acid catalysed



ETHERS

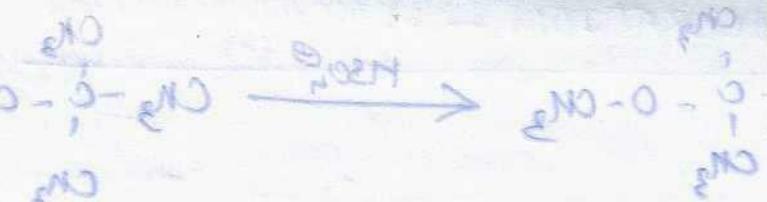
no Product
because
90% or
more.

interior
reaction
sites
② Na

C-O⁻

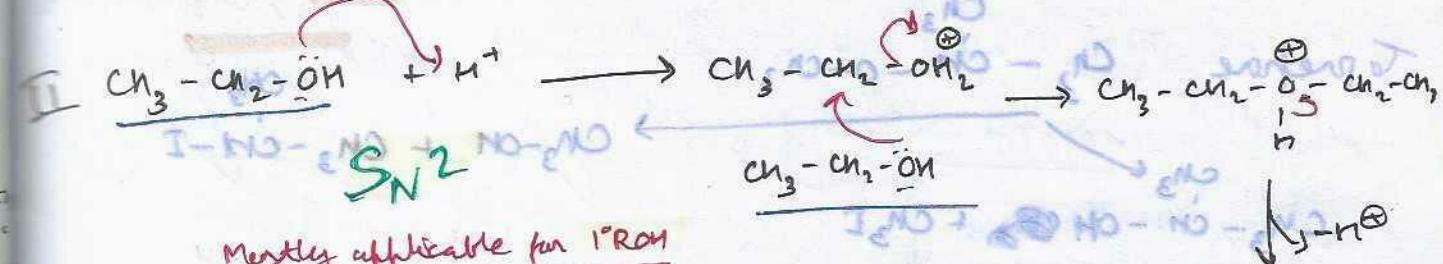
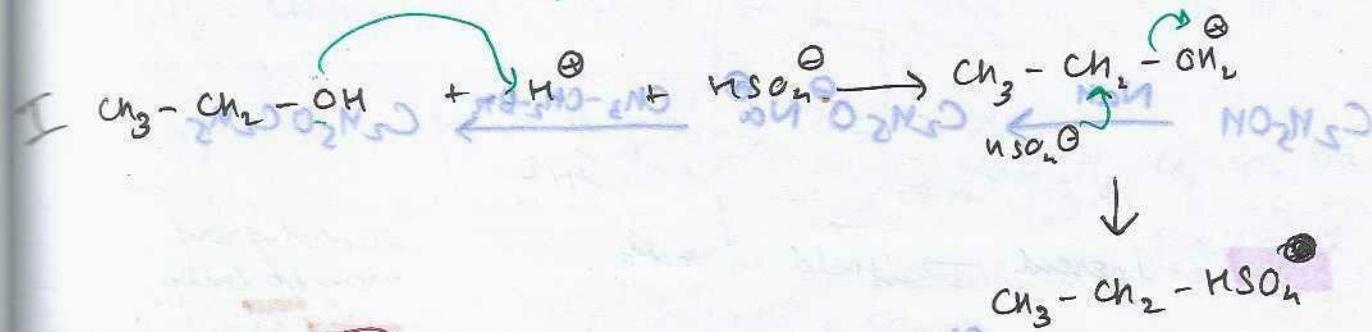
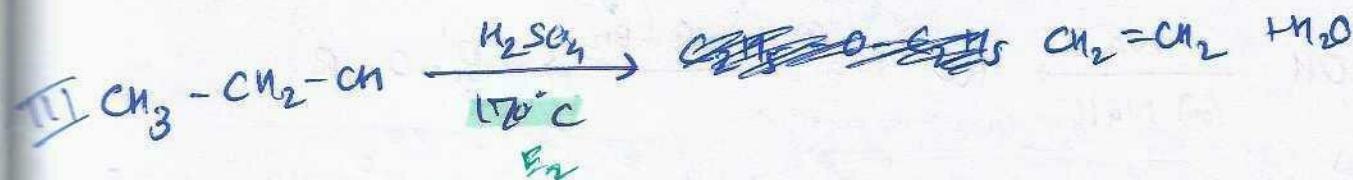
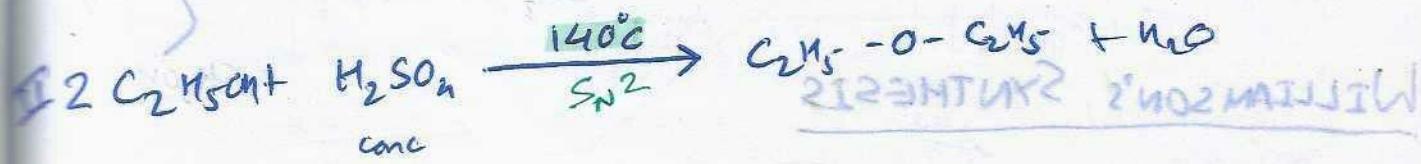
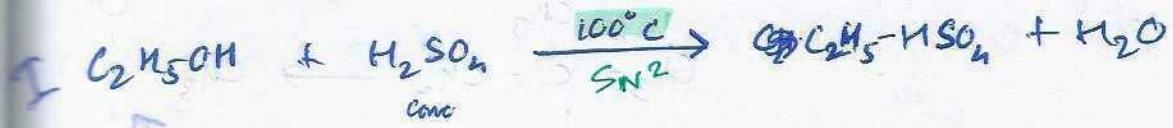
e-

solvent
thermoset
plastic

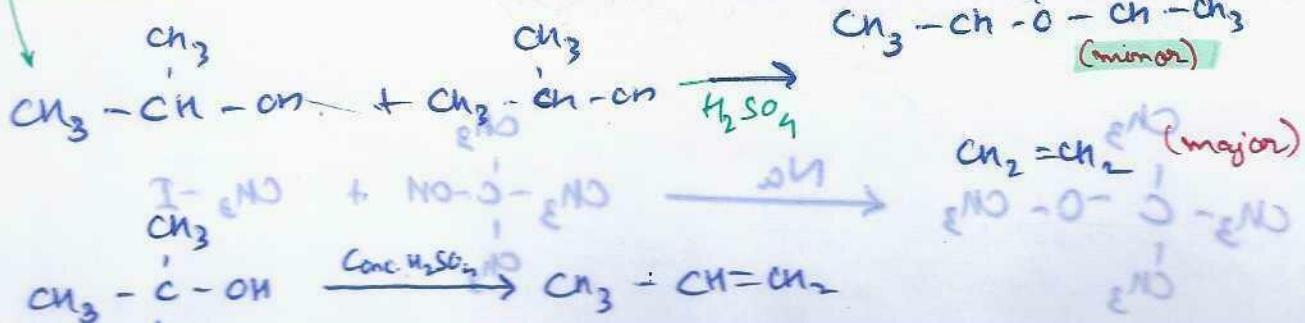
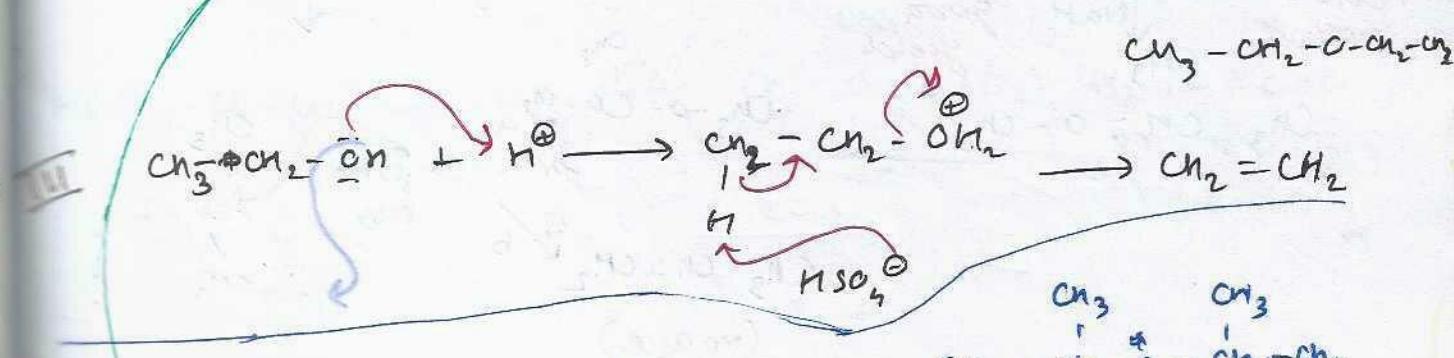


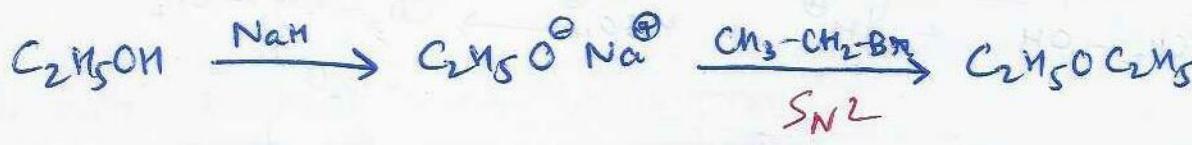
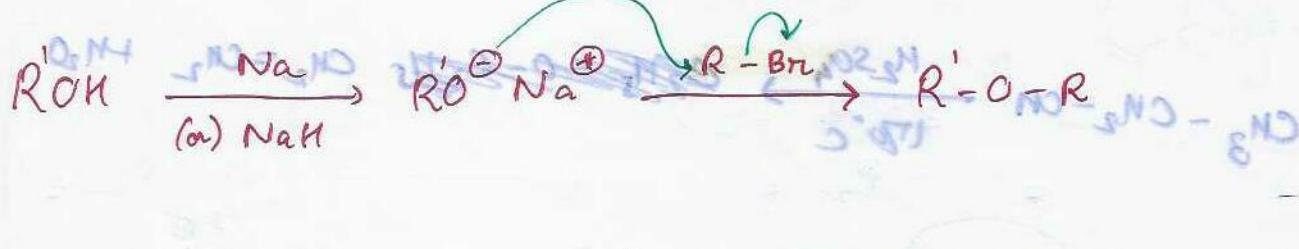
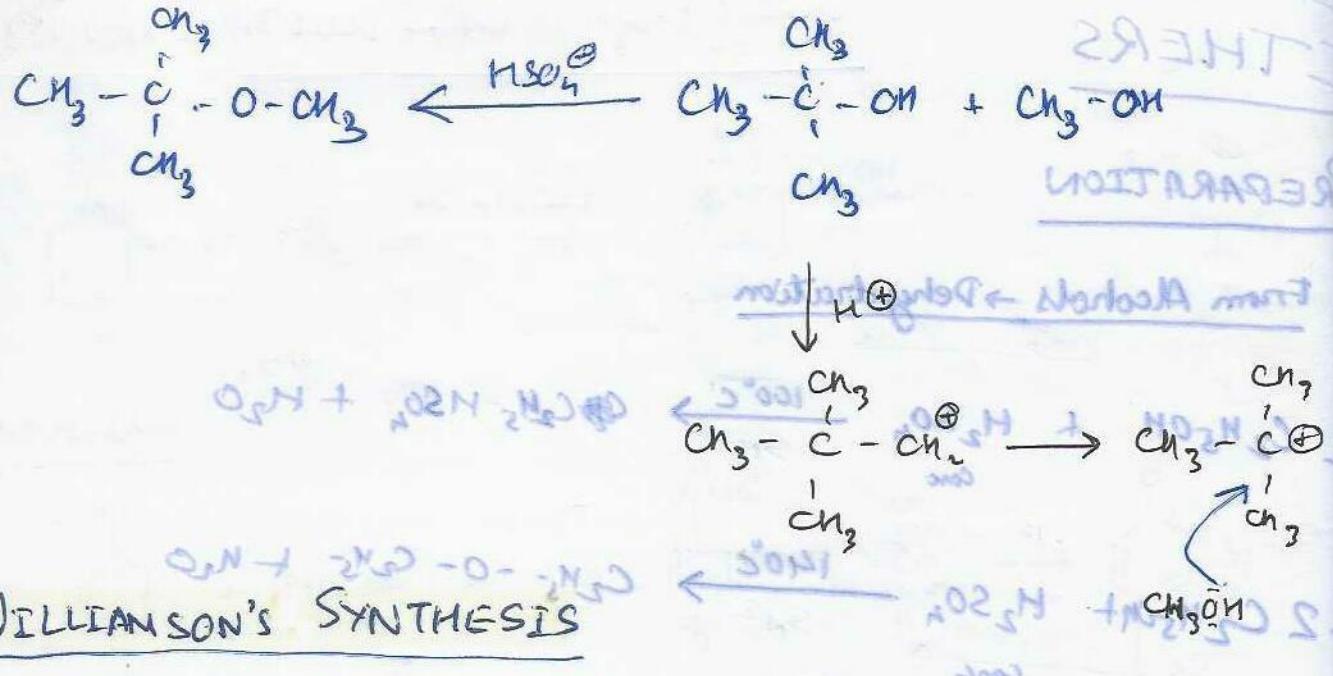
PREPARATION

From Alcohols → Dehydration



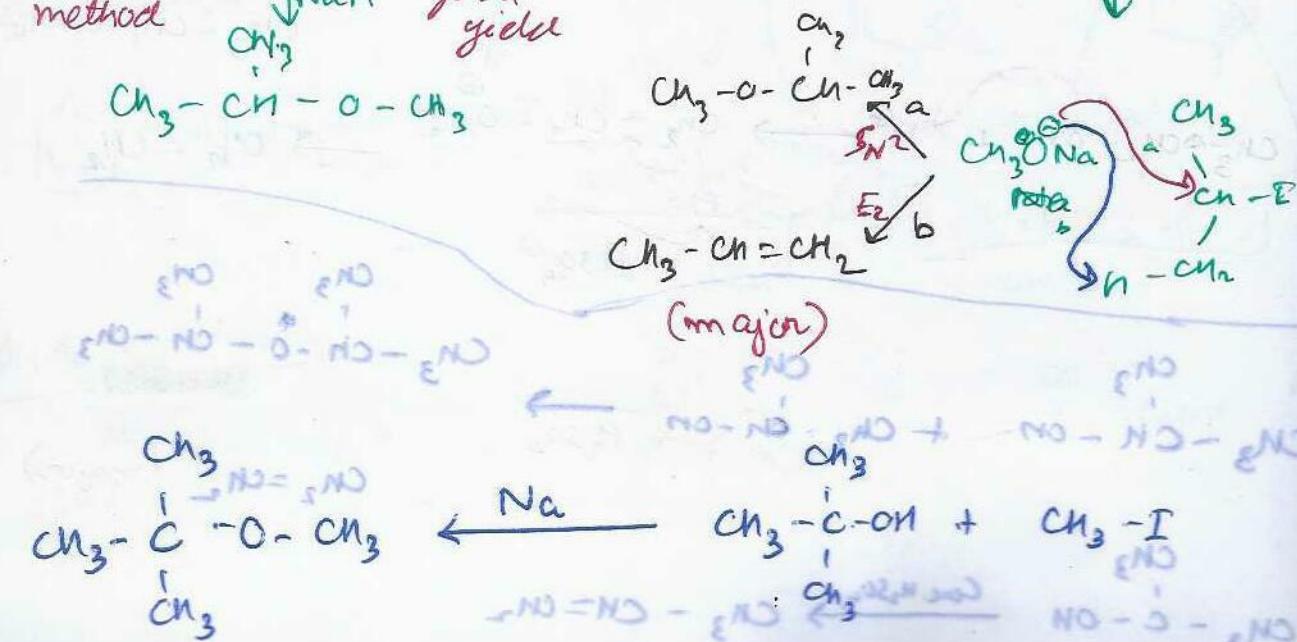
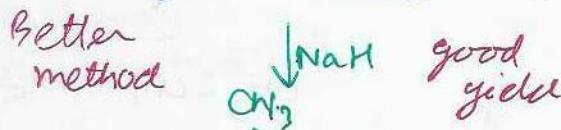
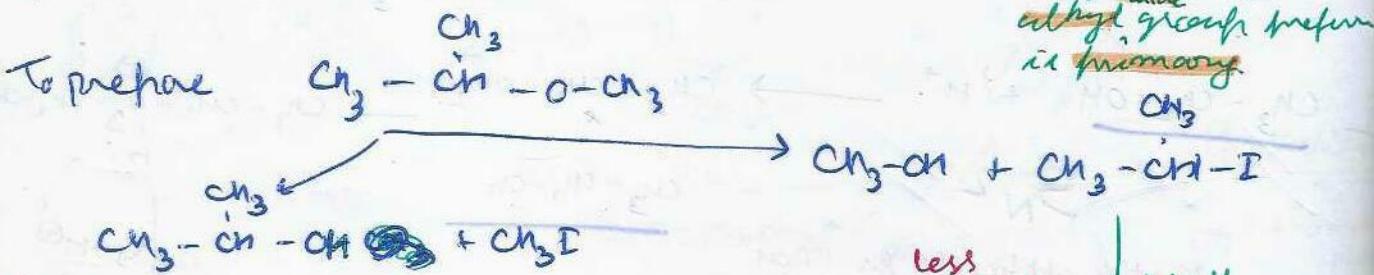
Mostly applicable for 1°ROH

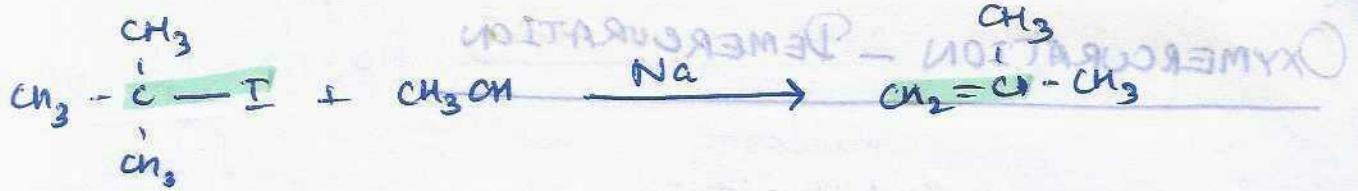




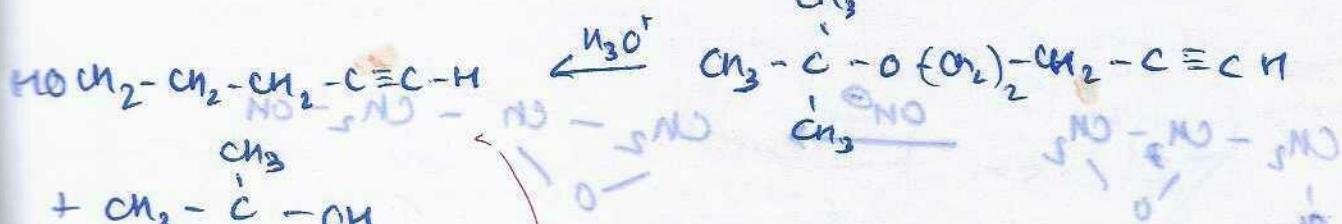
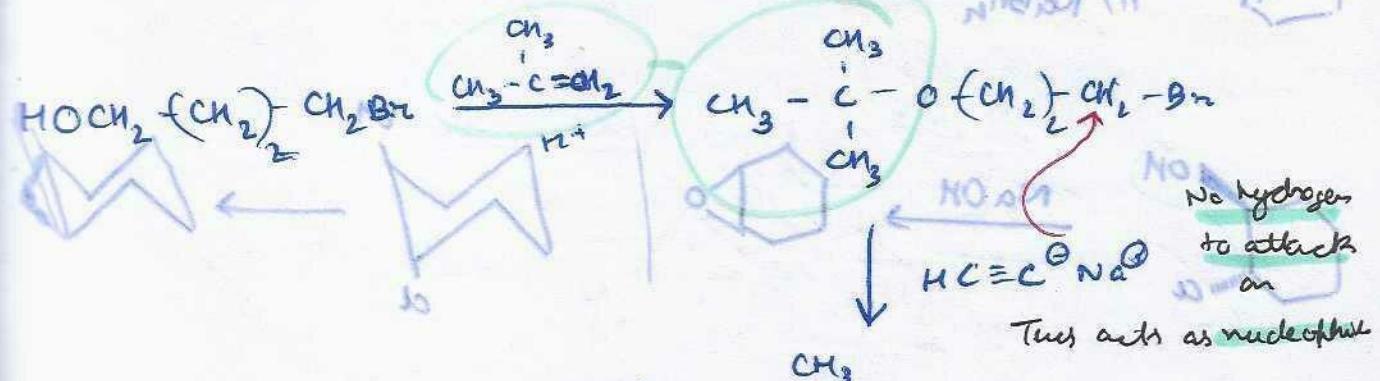
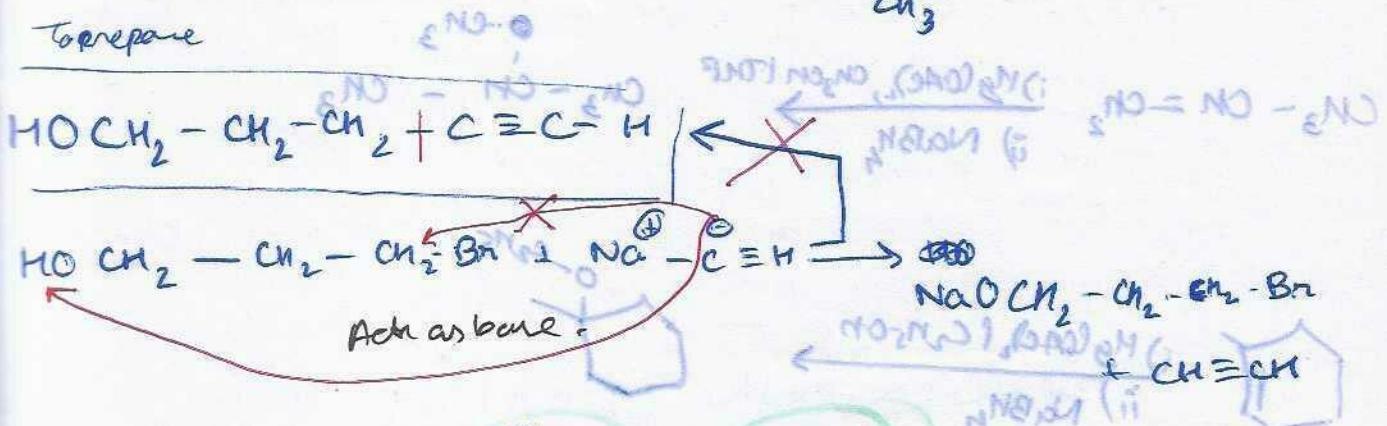
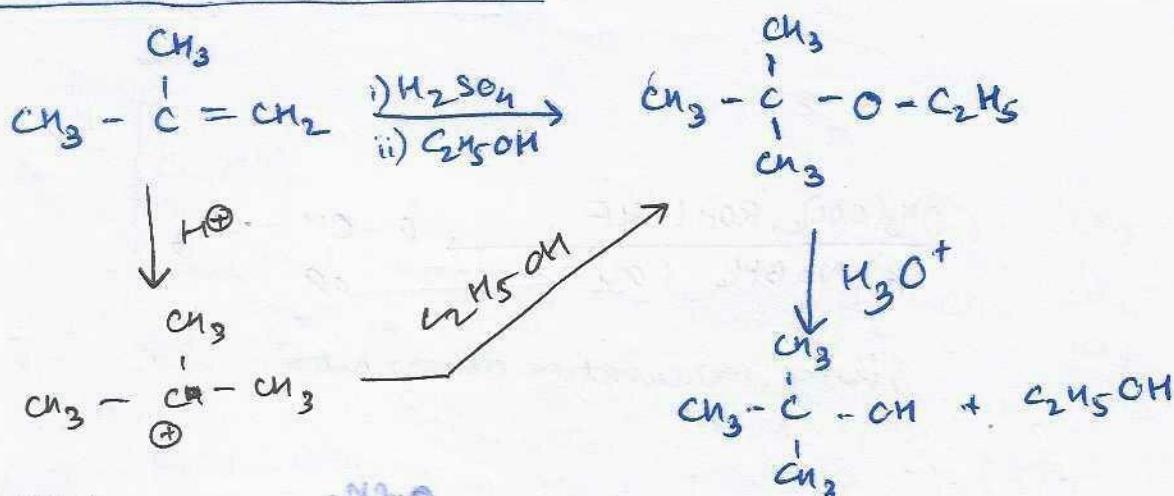
If I^-RX is present \rightarrow yield is more.

alcohol group
may be bulky,
ethyl group when
is primary

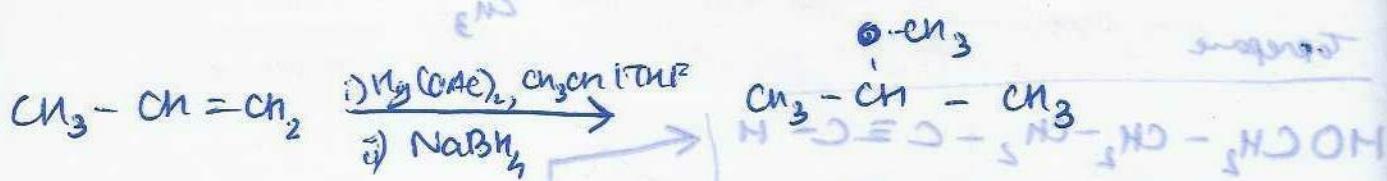
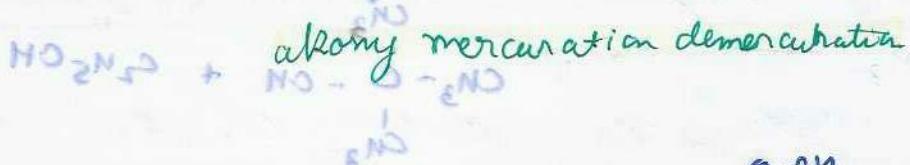
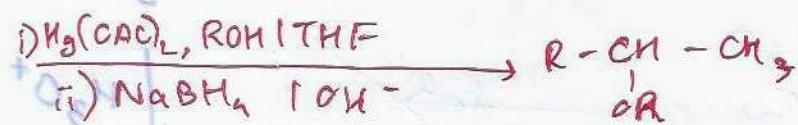
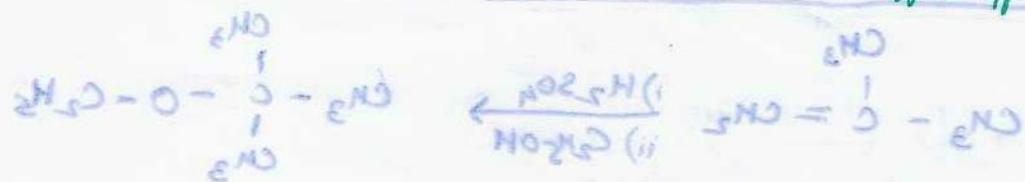
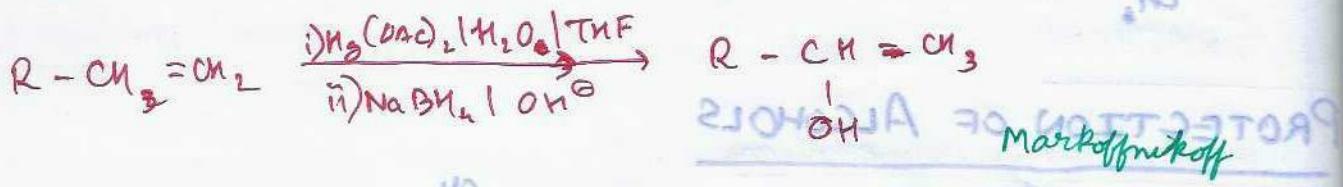




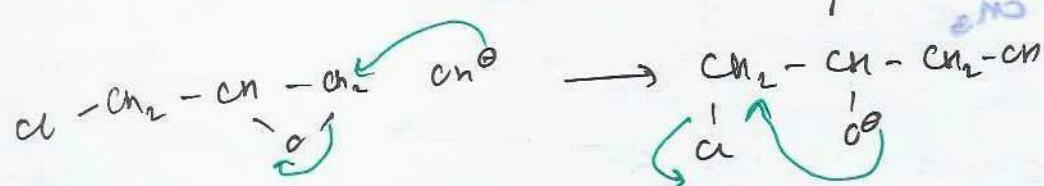
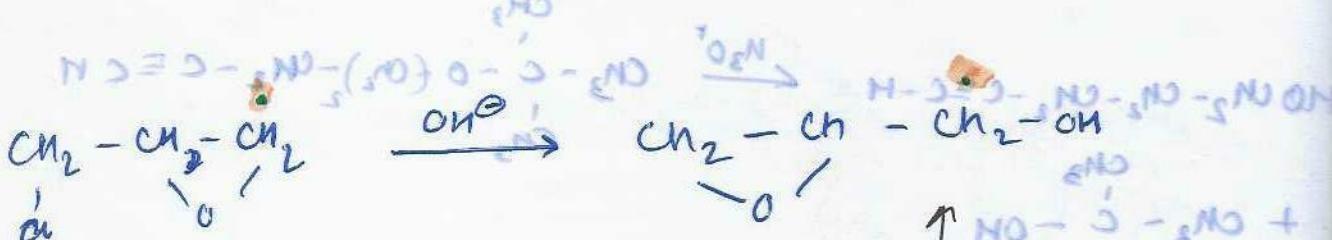
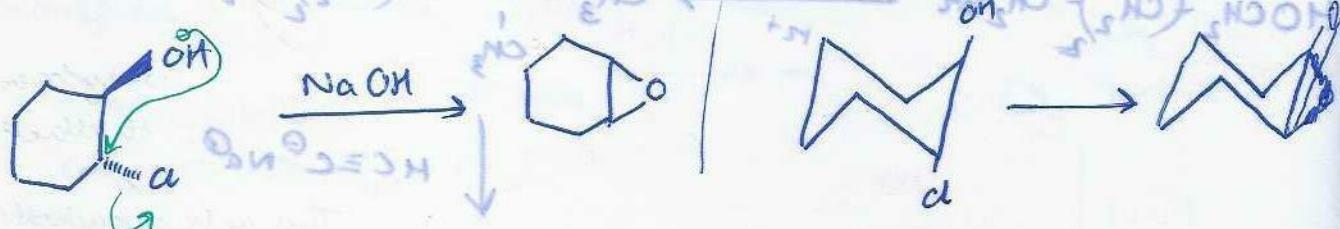
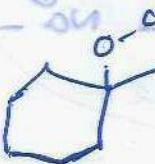
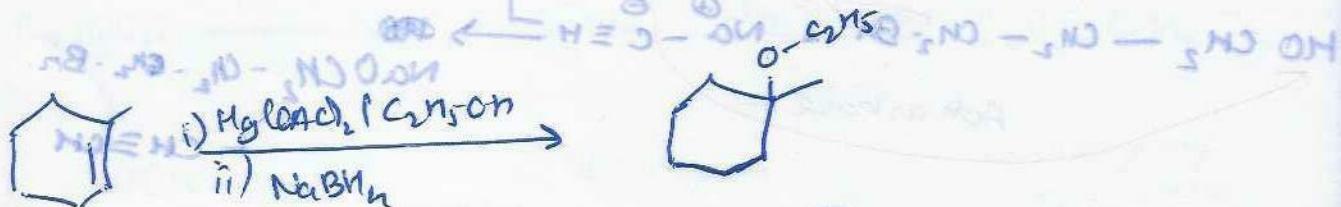
PROTECTION OF ALCOHOLS

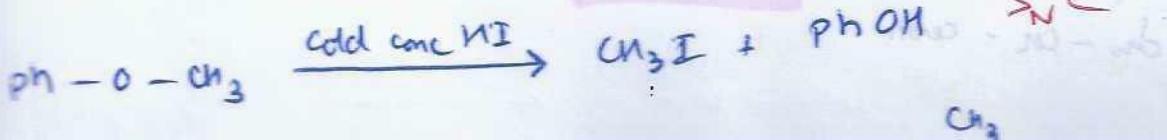
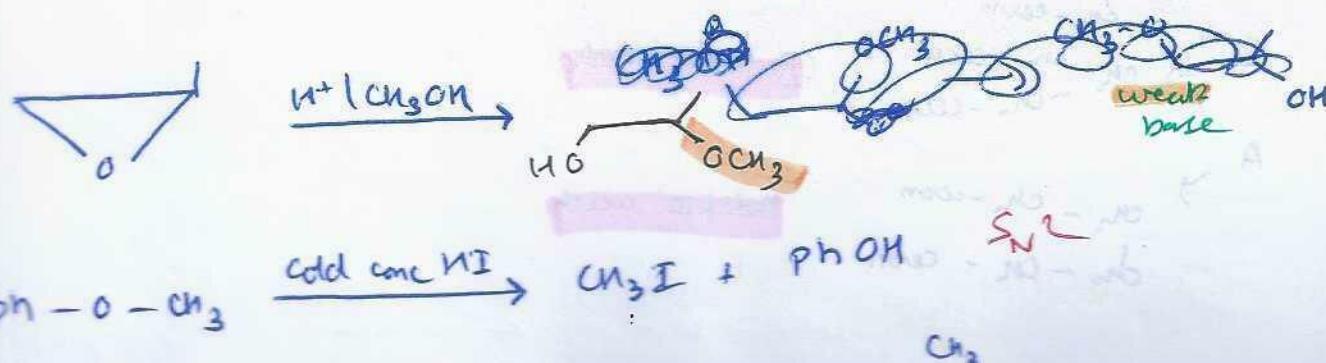
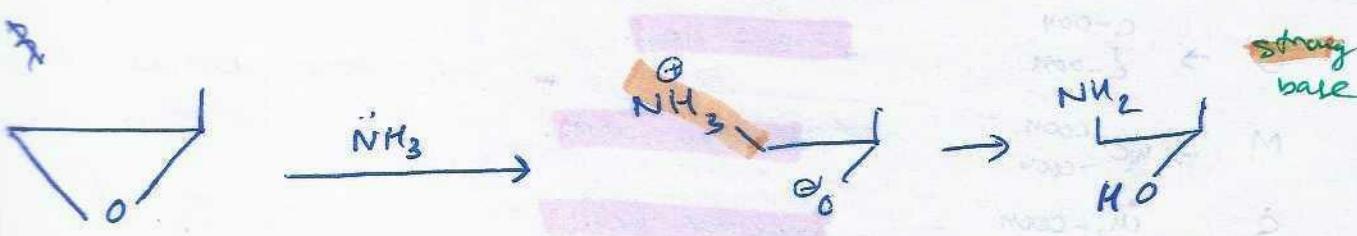
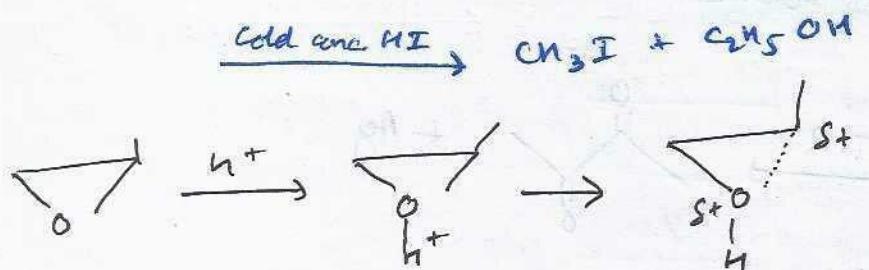
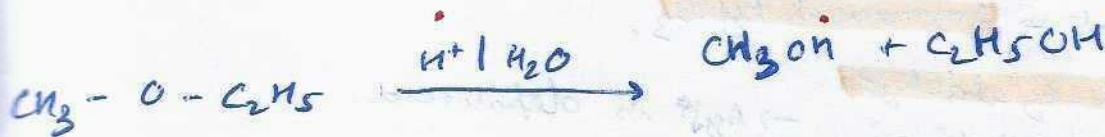
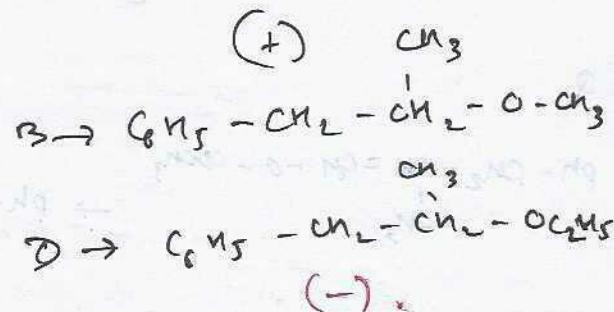
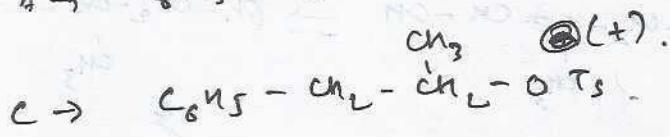
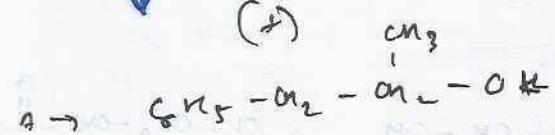
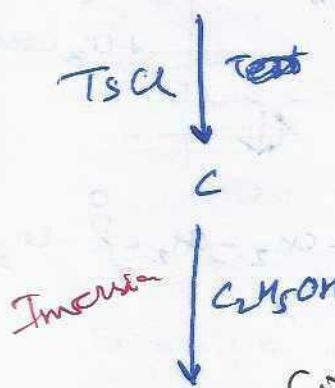
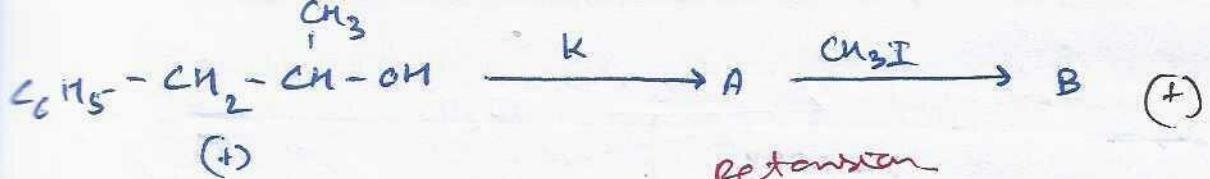


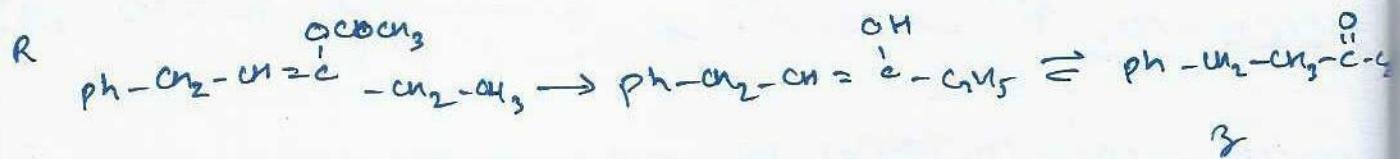
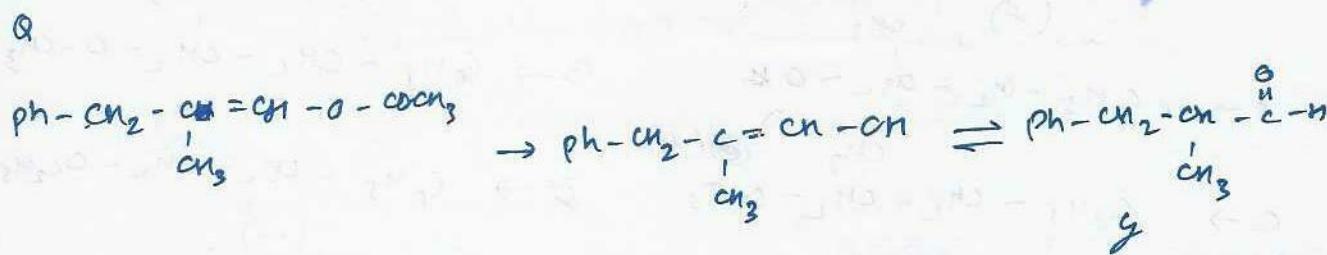
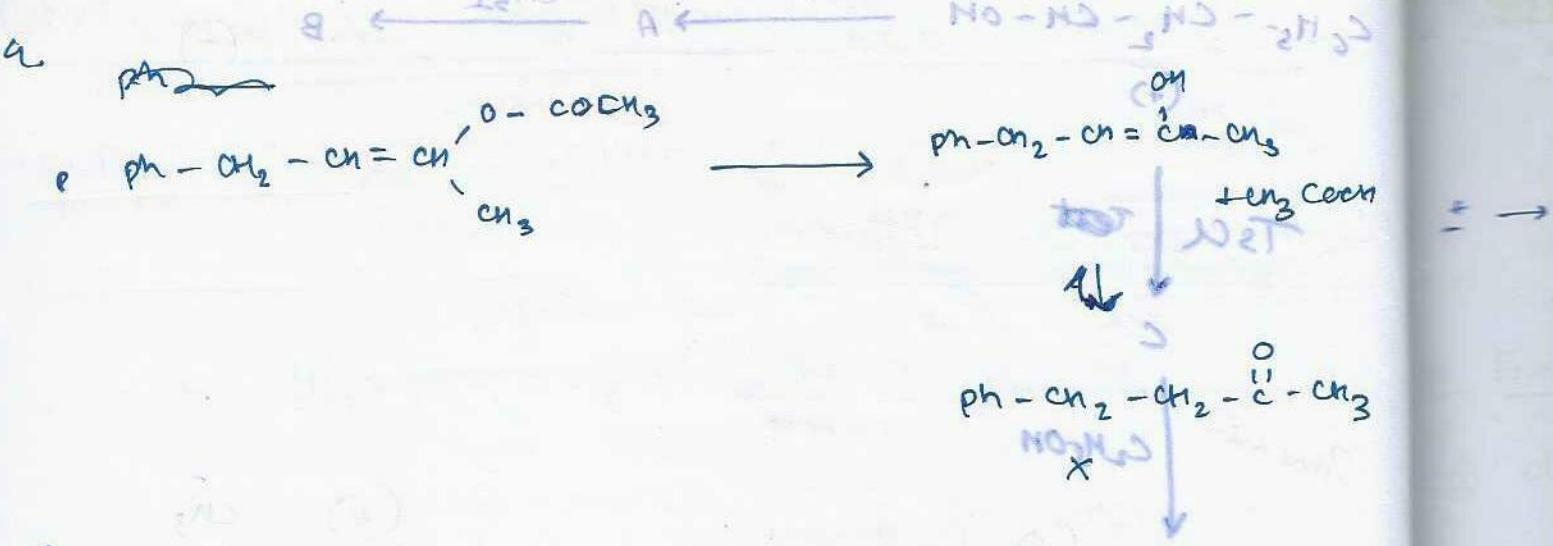
OXYMERCURATION - DEMERCURATION



tert-butyl

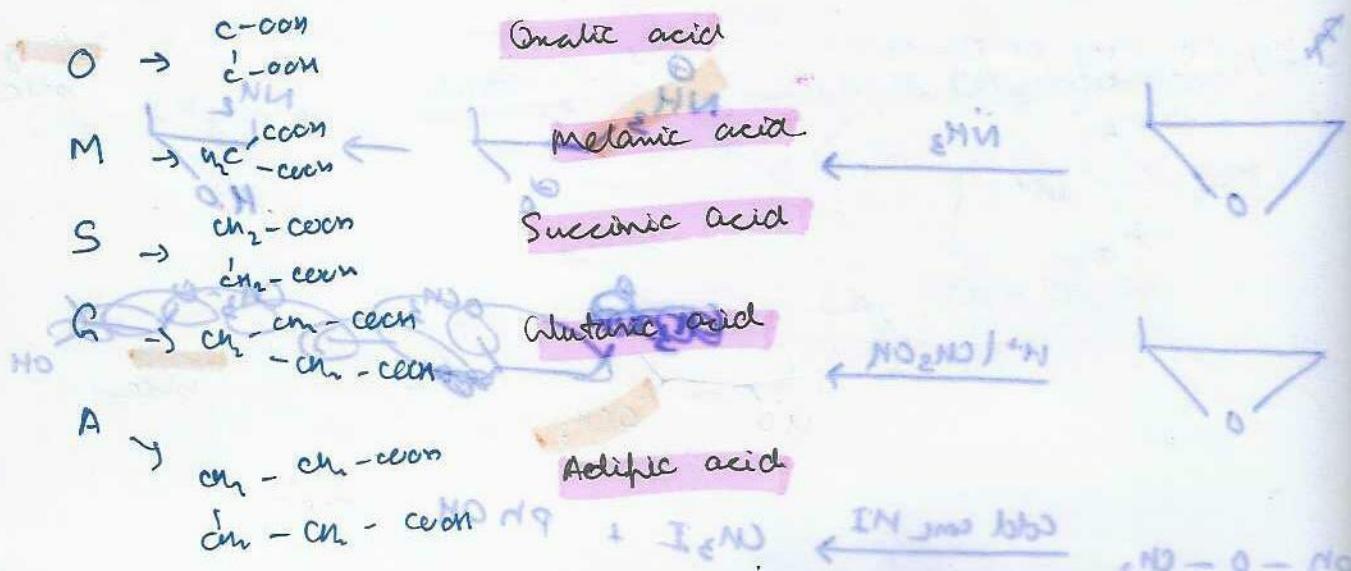
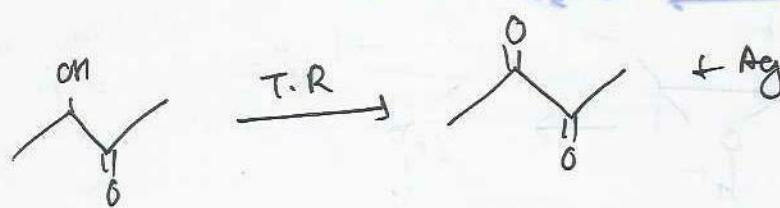


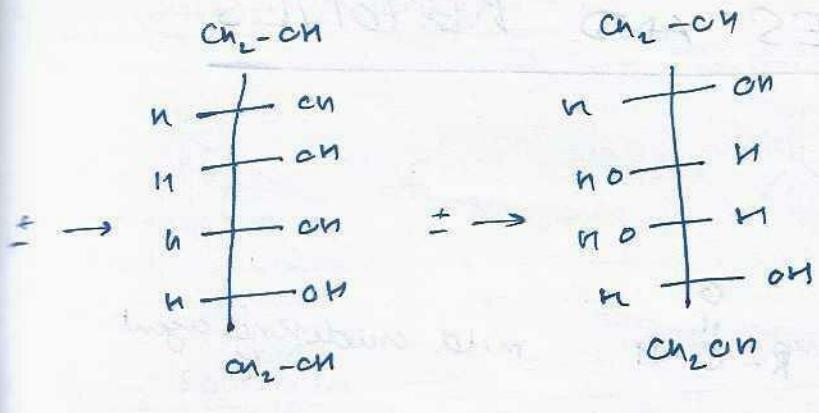




Tollen's Reagent \Rightarrow Ammonical AgNO_3 .

Positive test by aldehyde. $\rightarrow \text{Ag}^{+}$ is deposited. $\text{2H}_2\text{O} - \text{O} - \text{gNO}$
 Negative for ketone.





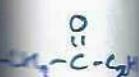
DEPOLARIZATION

Burkhardt

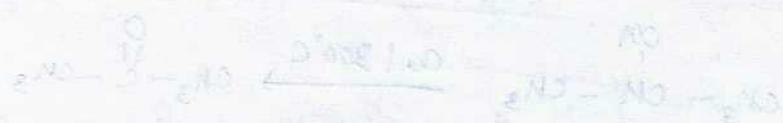
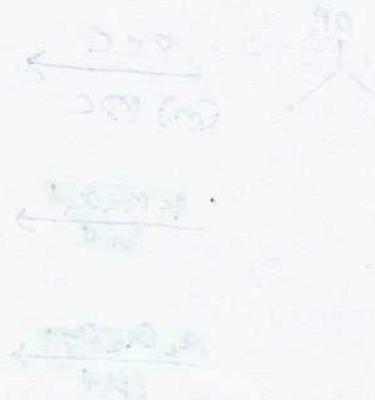
Dose
Dose (2)

NO₂-CH₂-CH₂-NO₂

The mechanism of NO₂
absorption



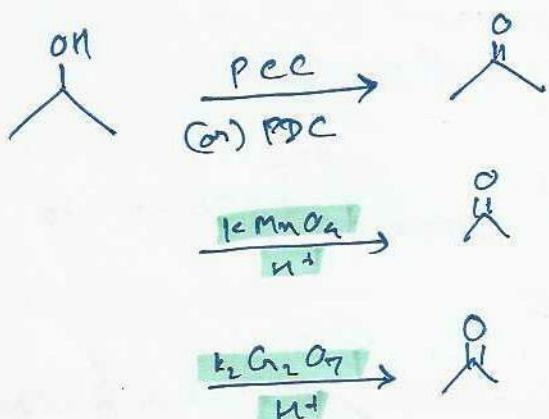
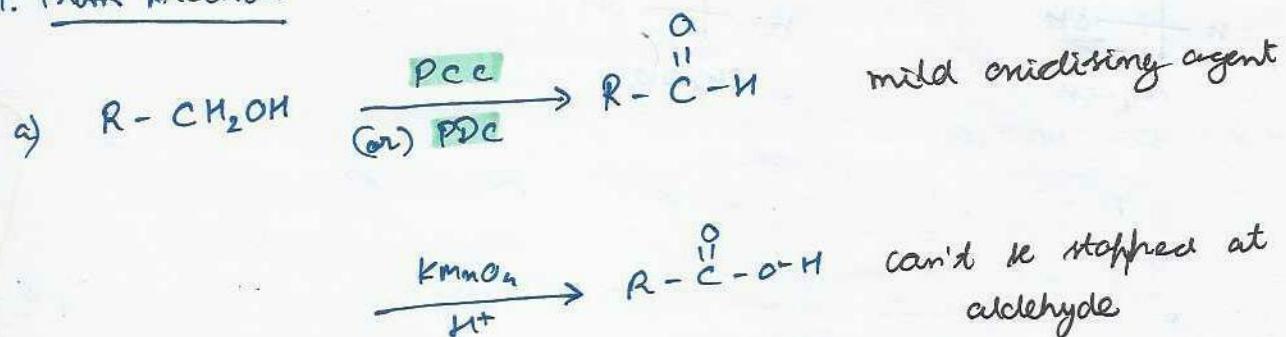
-ENJ



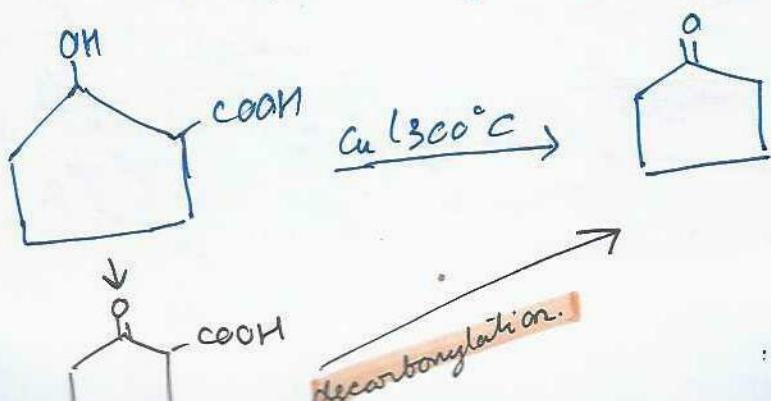
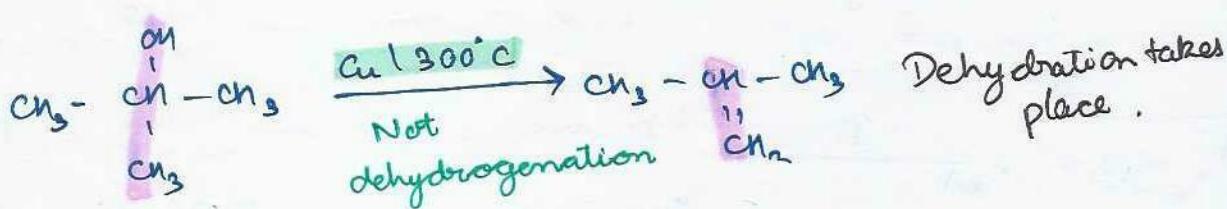
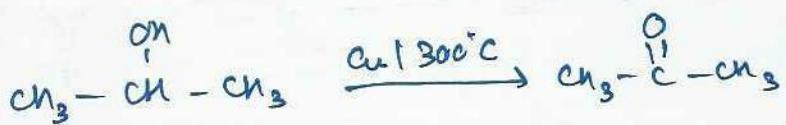
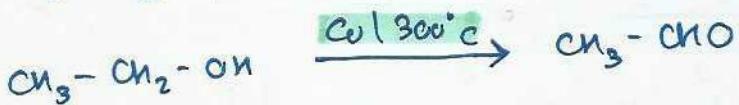
ALDEHYDES AND KETONES

PREPARATION

1. From Alcohols

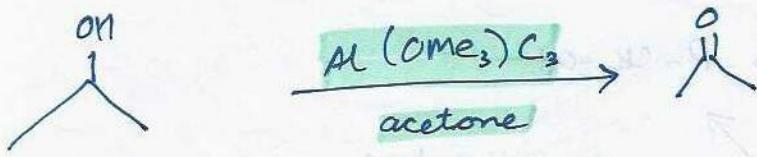


b) Dehydrogenation-



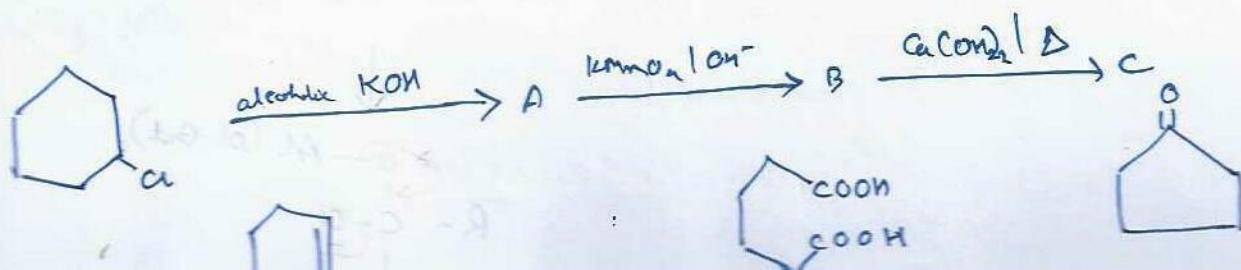
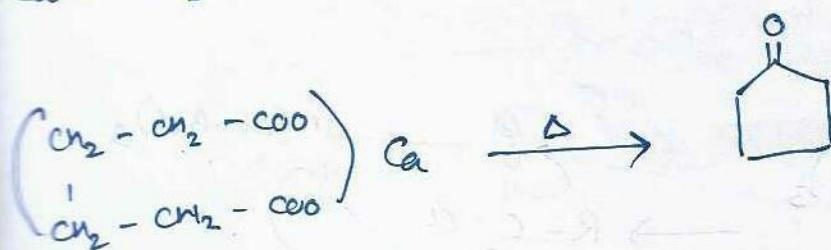
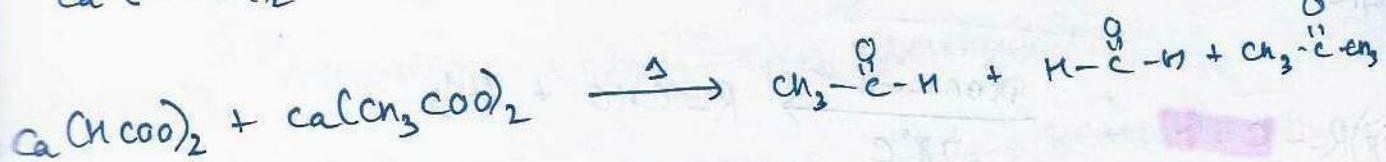
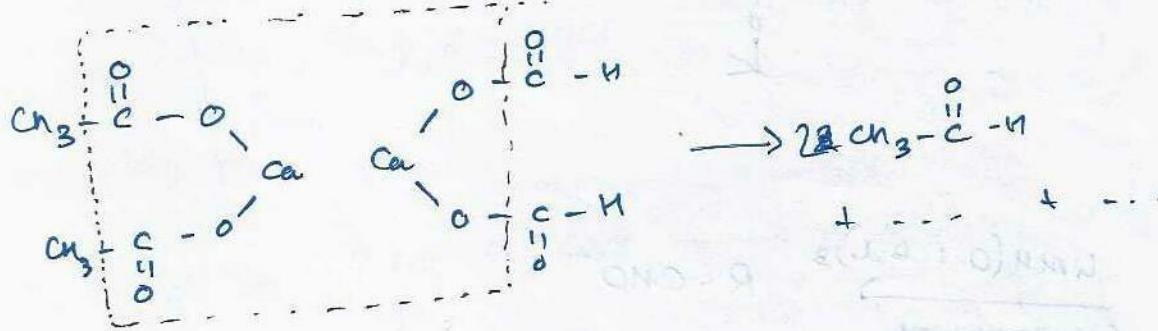
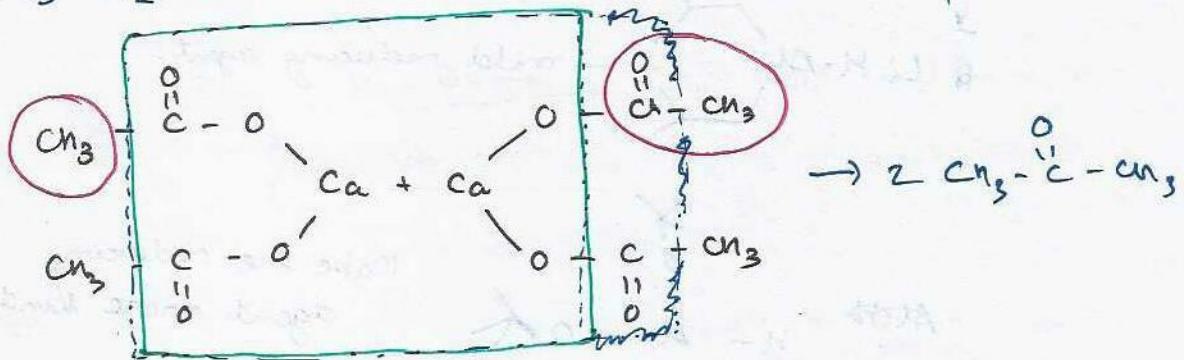
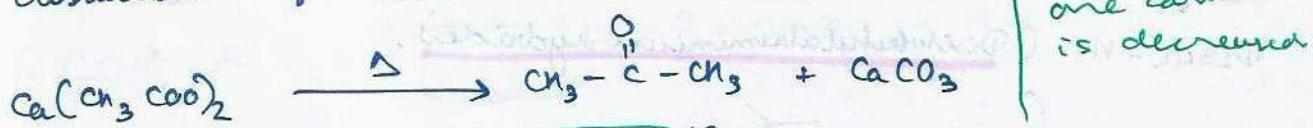
Oppenear Oxidation

$\text{Al}(\text{OCH}_3)_3$

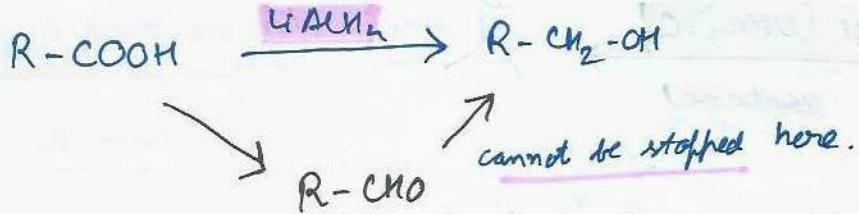


From Carbonylic acid and Derivatives

- a) distillation of calcium salts of carbonylic acid

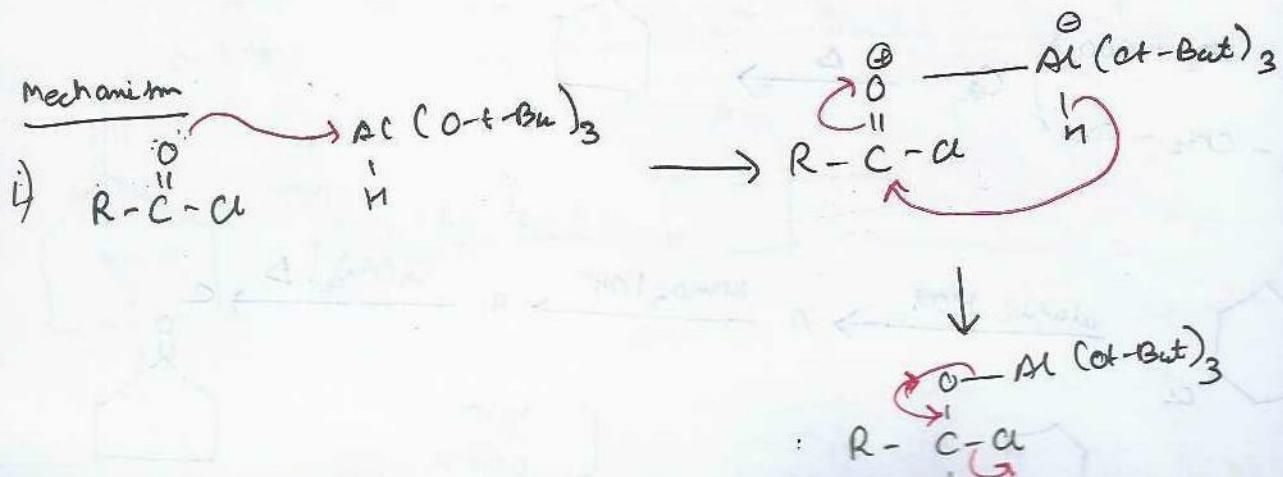
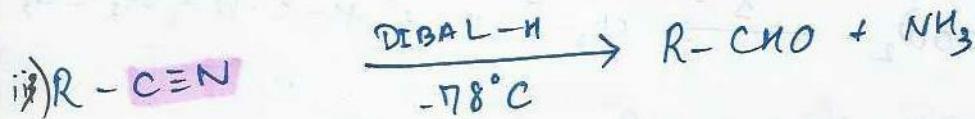
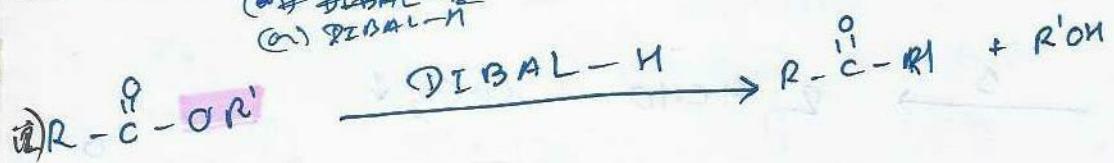
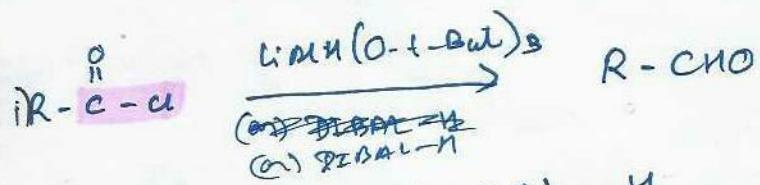
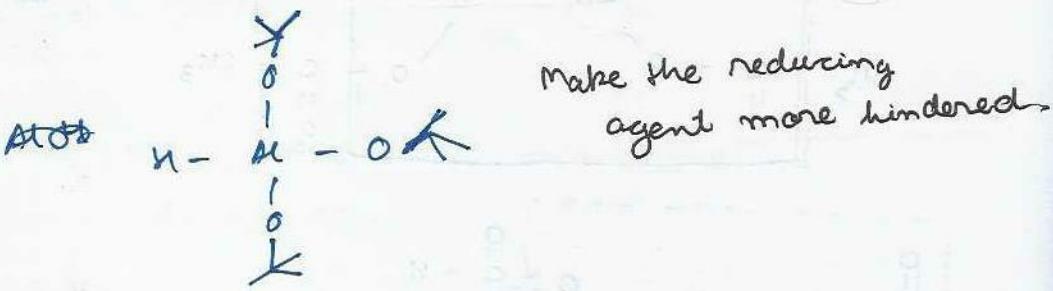
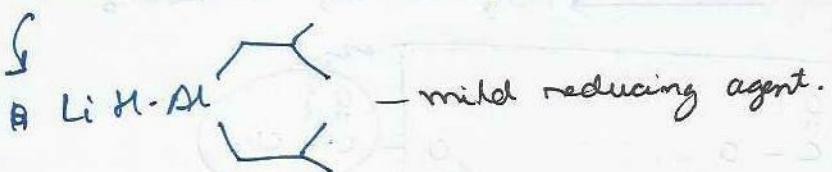


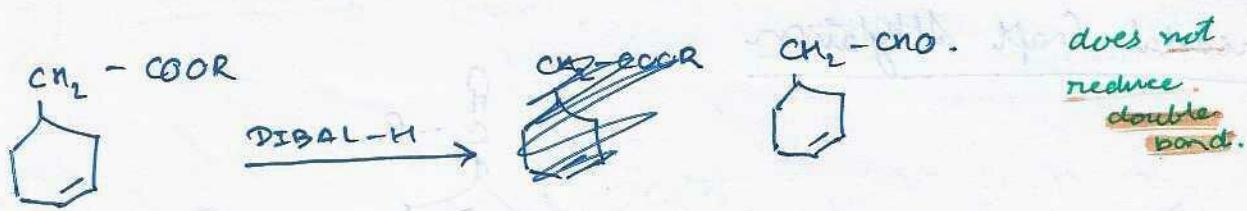
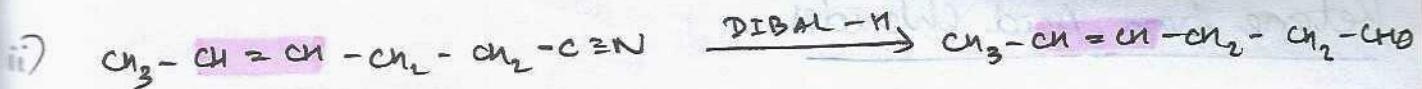
b) From Carbonylic Acid Derivatives



Mild reducing agents should be used.

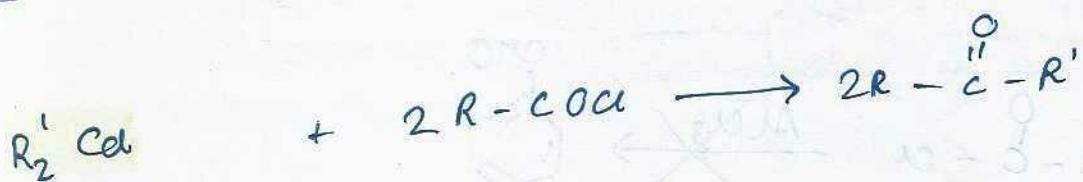
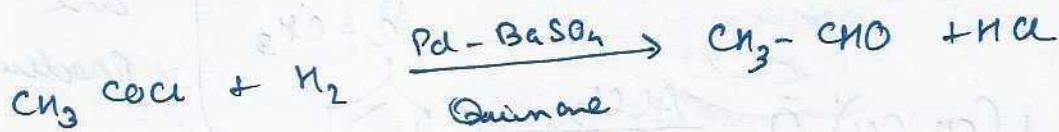
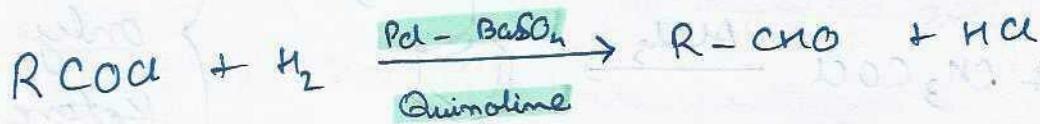
↓
DIBAL-H (Diisobutylaluminium hydride):



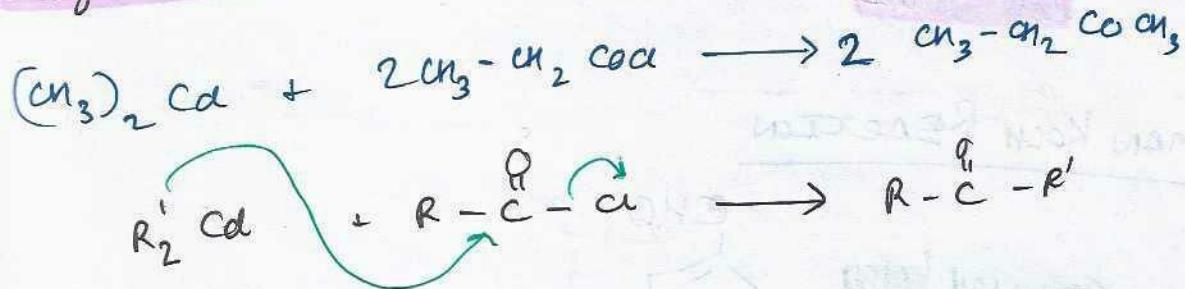


Rosenmund Reduction (Only for aldehyde)

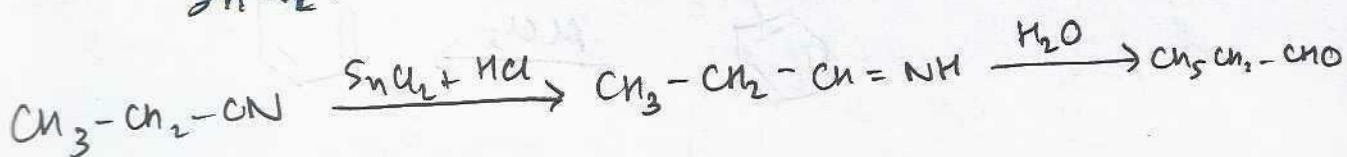
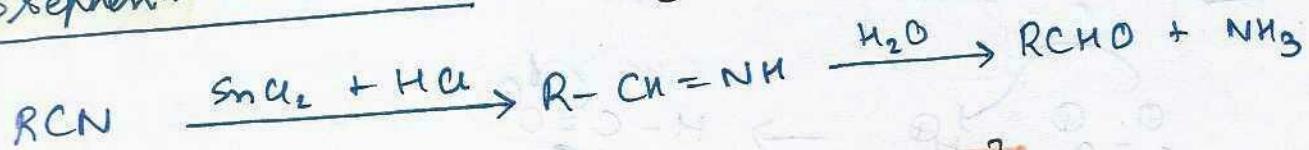
Applicable for acid chlorides only



Dialkyl cadmium



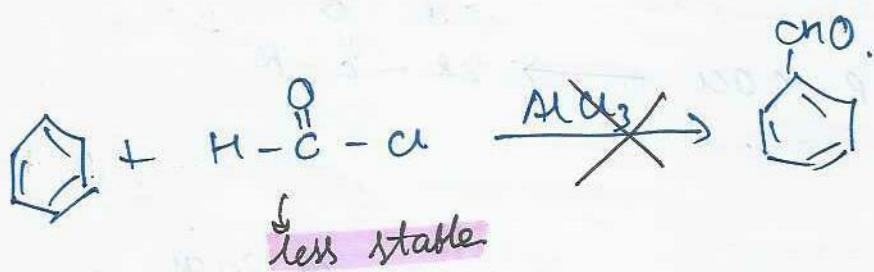
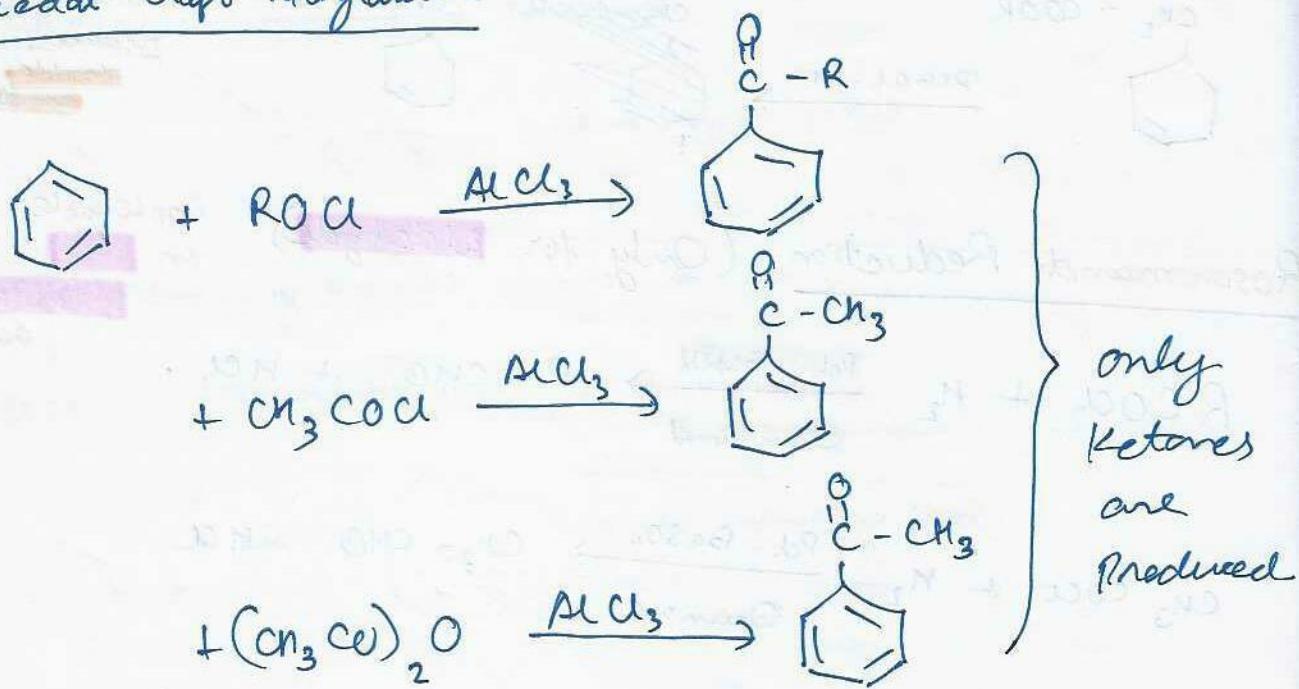
Stephen's Reduction (Only for aldehyde)



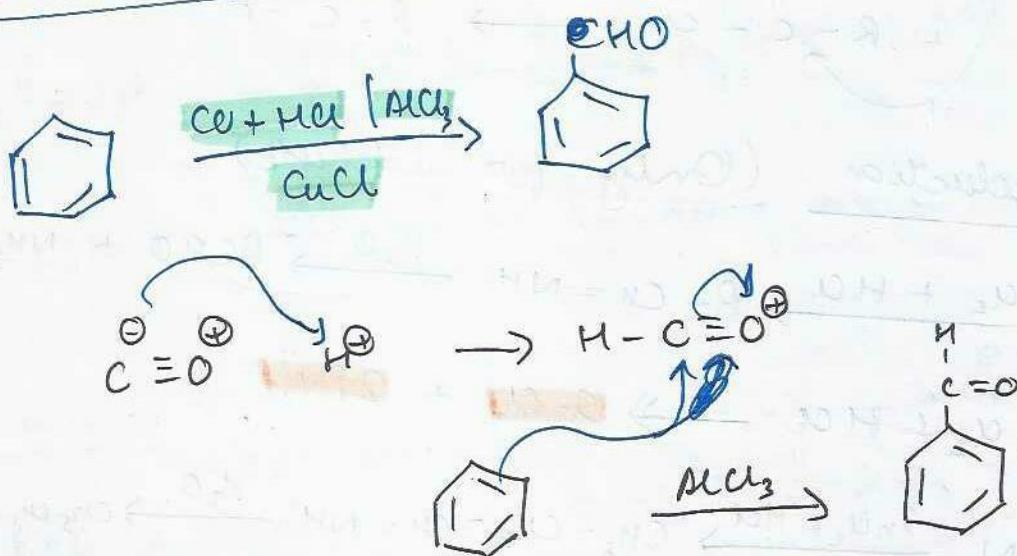
What is the role of dissociation
formaldehyde bond breaking

Ketone from Acid Chlorides

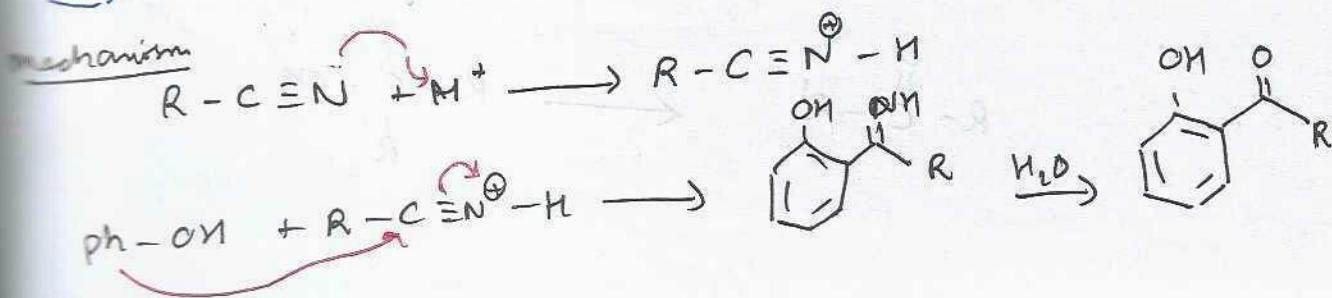
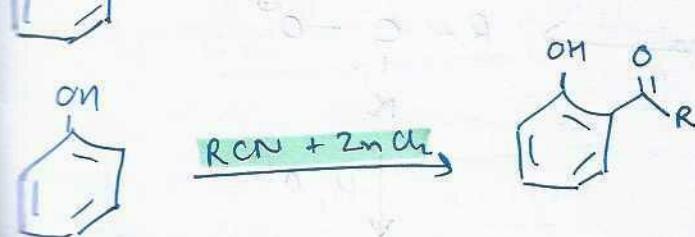
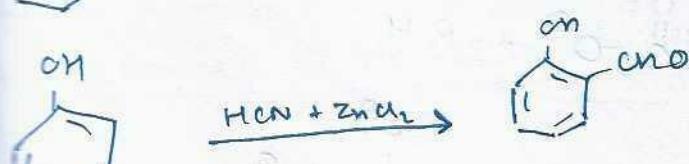
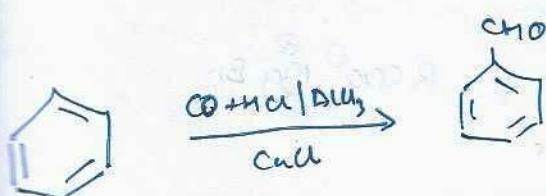
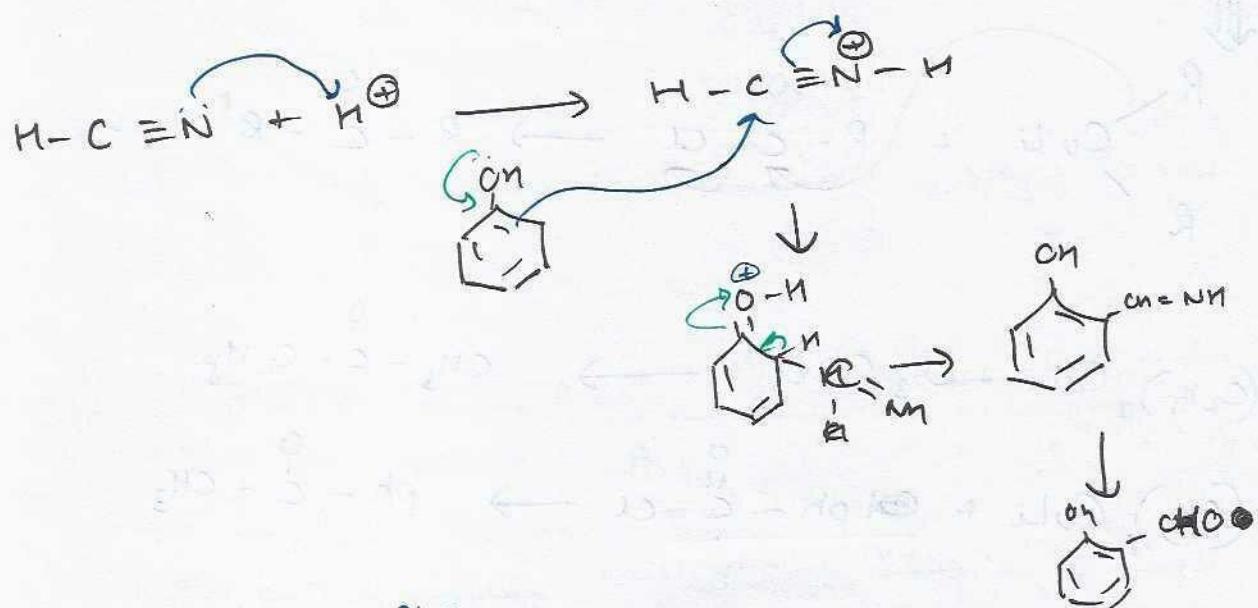
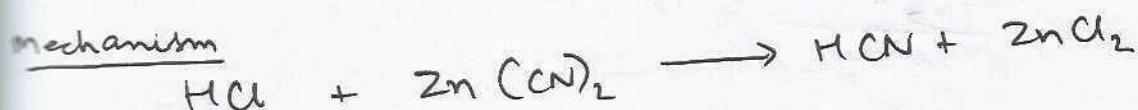
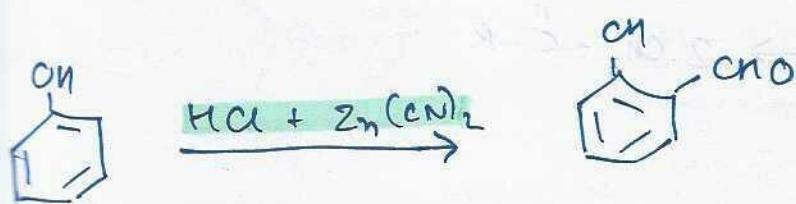
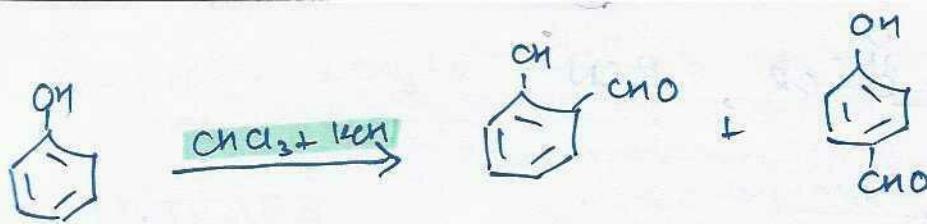
Friedel-Crafts Alkylation

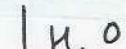
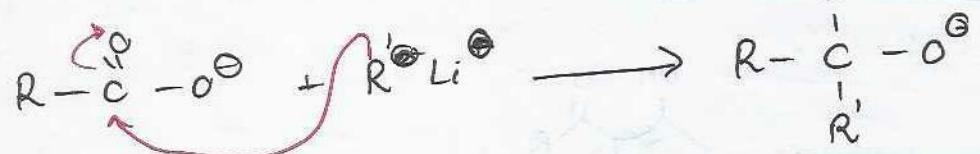
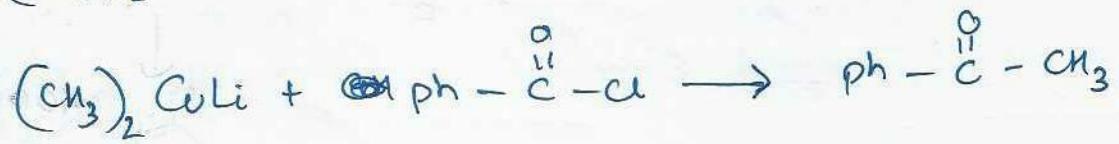
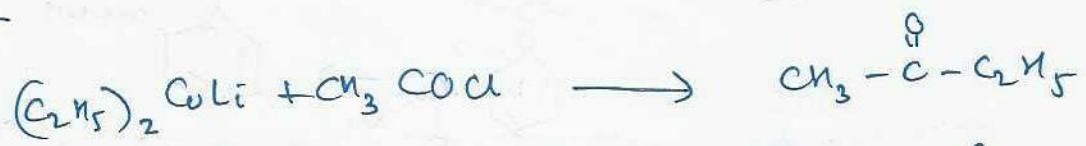
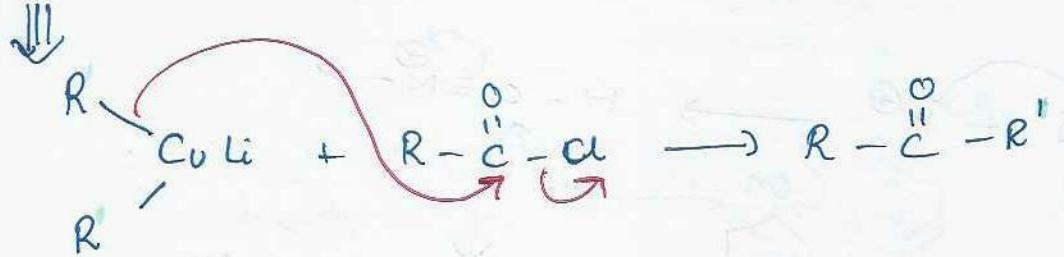
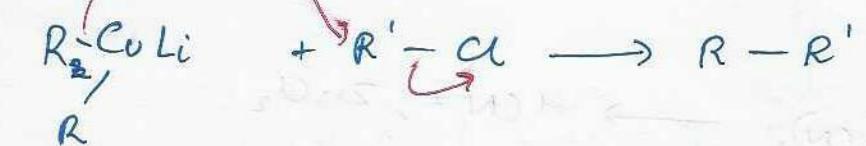
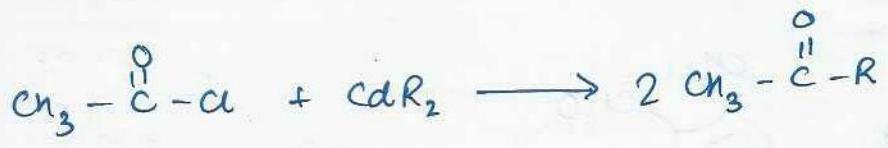
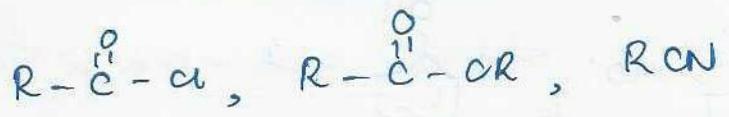


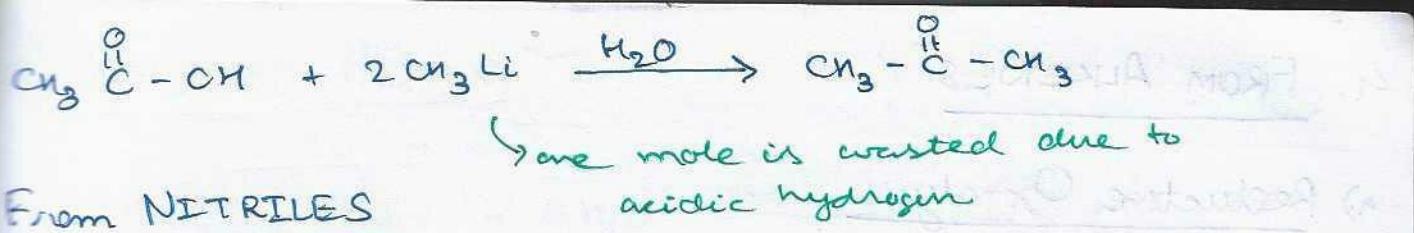
GUTTERMAN-Koch REACTION



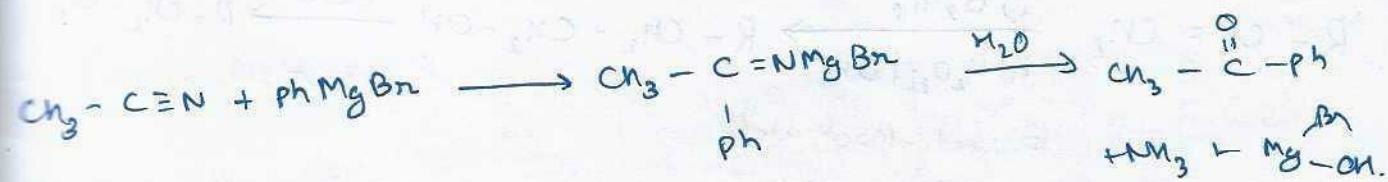
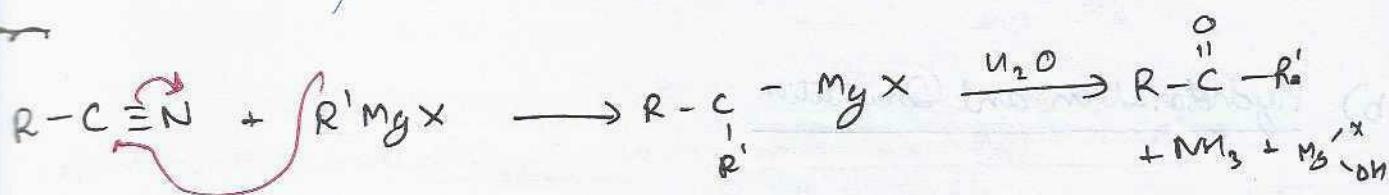
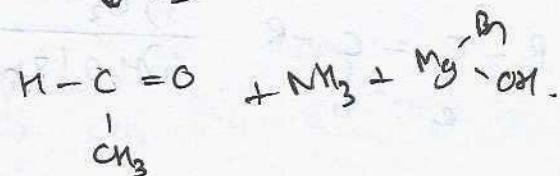
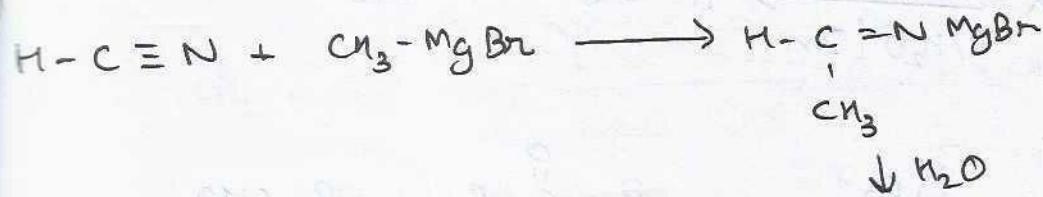
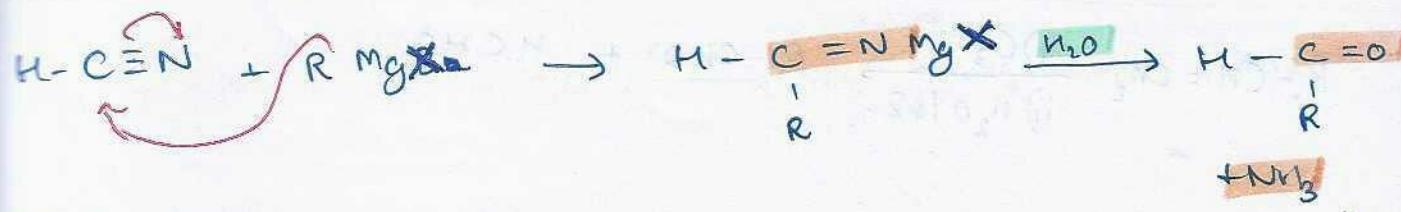
Not applicable for phenol as AlCl_3 attacks the OH group and deactivates the ring.



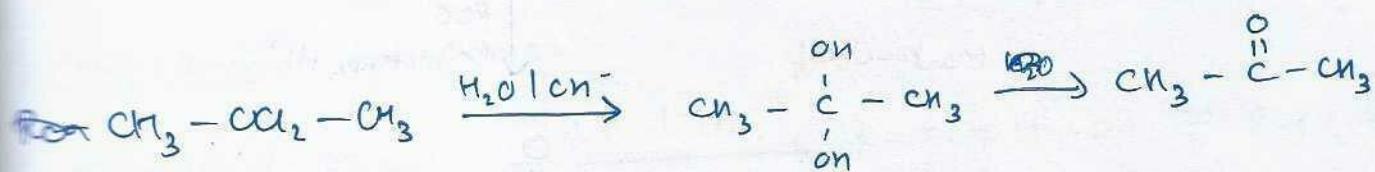
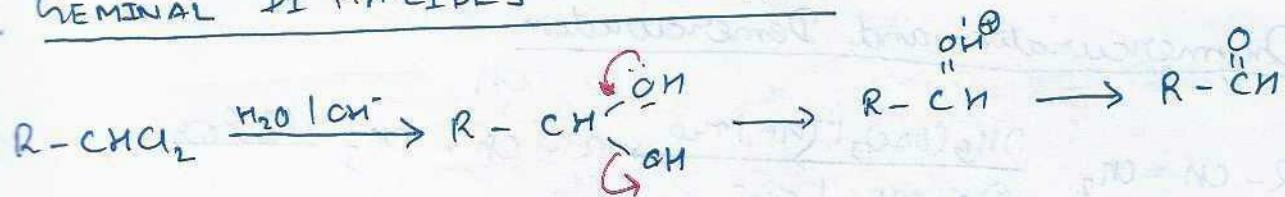




From NITRILES

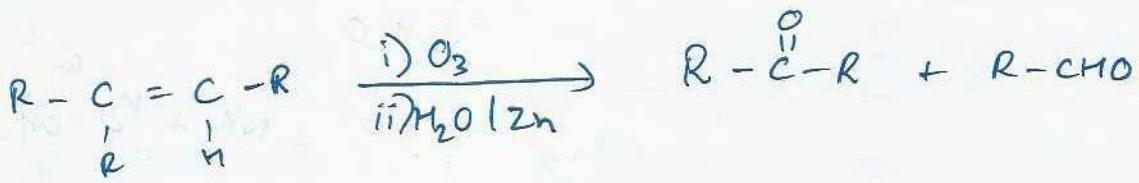
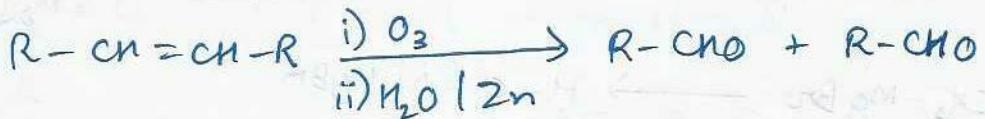


3. GEMINAL DI HALIDES HYDROLYSIS

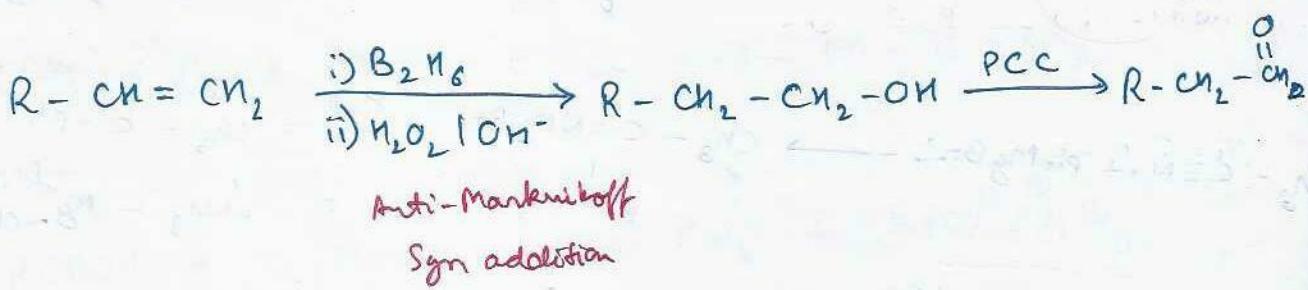


4. FROM ALKENES

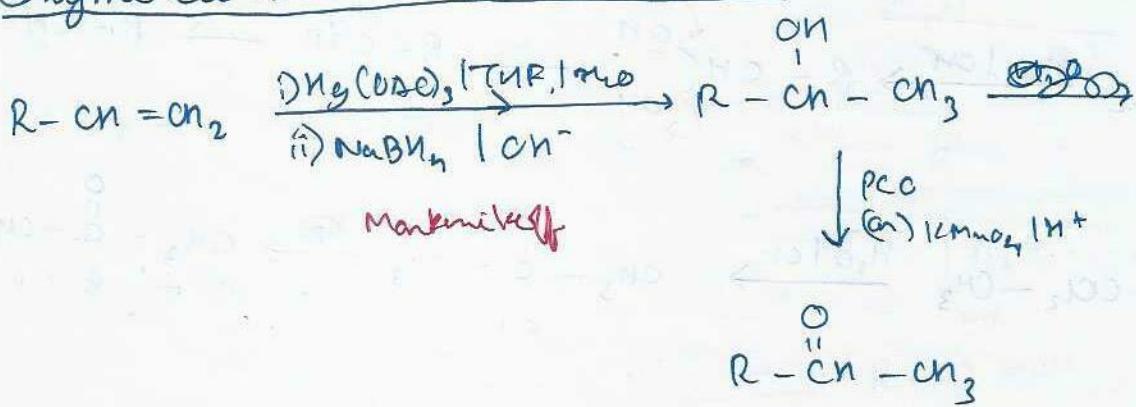
a) Reductive Ozonolysis



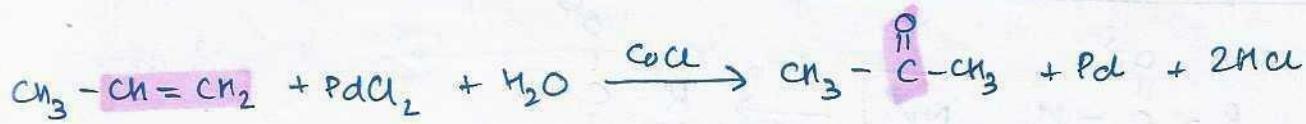
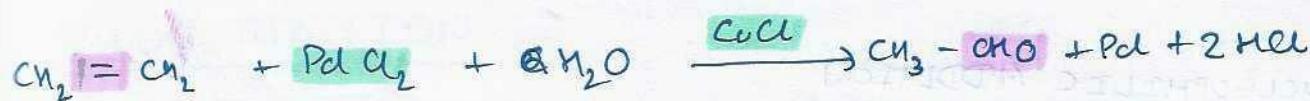
b) Hydroxylation and Oxidation



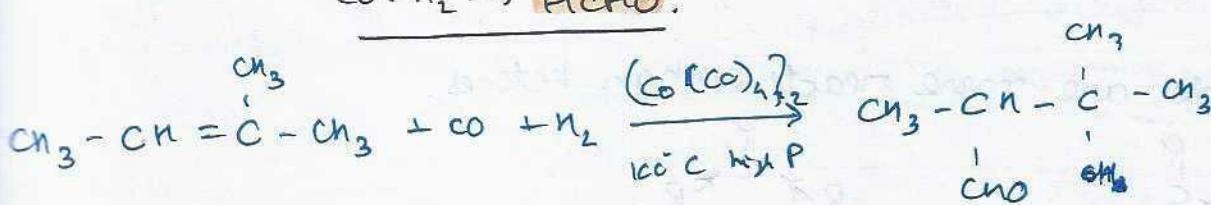
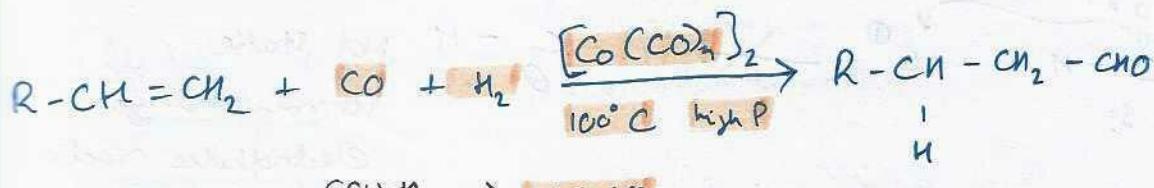
c) Oxymercuration and Demercuration



a) WALKER's PROCESS

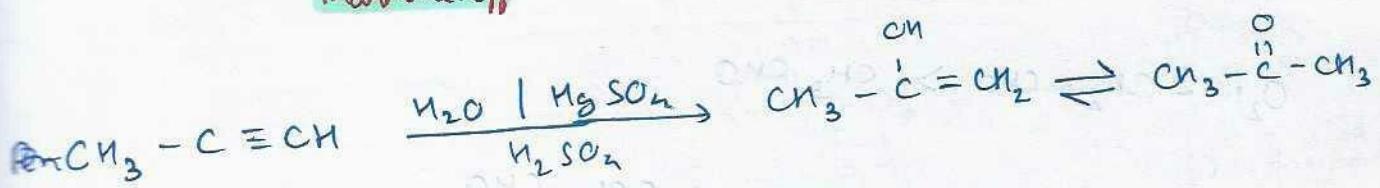
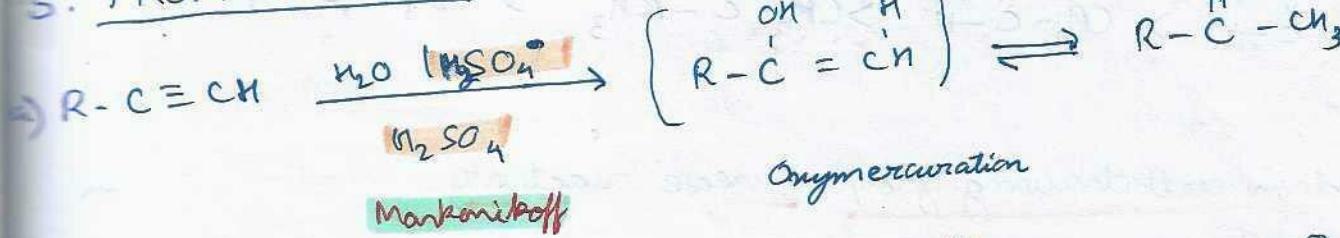


e) OXOPROCESS (only for ~~terminal~~ aldehydes) ~~→ terminal~~

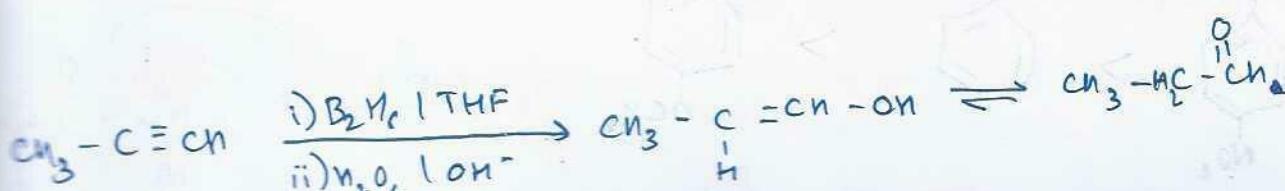
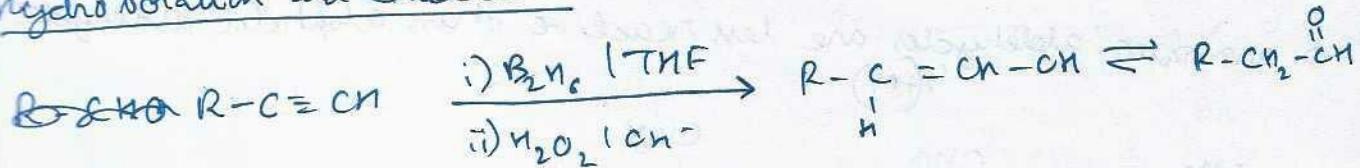


↓
Addition of formaldehyde as per Anti Markonikoff's rule.

5. FROM ALKYNES

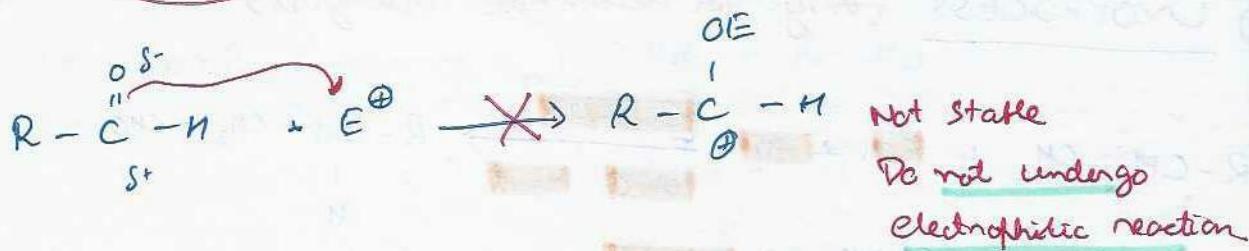
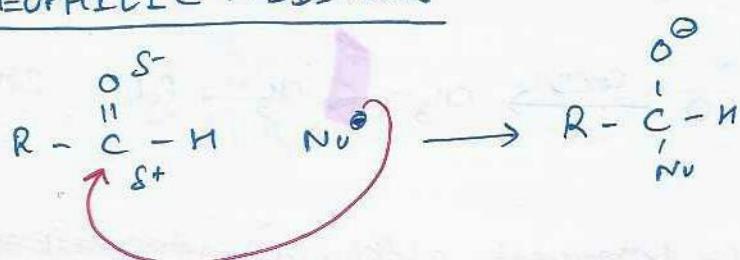


6) Hydroboration and Oxidation



PROPERTIES OF CARBONYL COMPOUNDS

NUCLEOPHILIC ADDITION

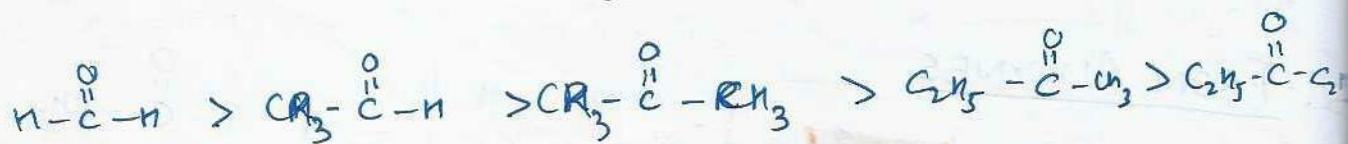


- Aldehydes are more reactive than ketones.

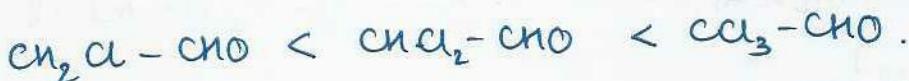
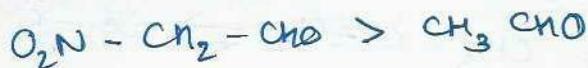


→ less steric hindrance.

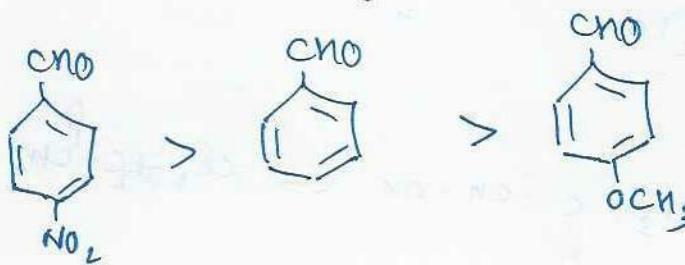
→ Alkyl group is +I group, they increase electron density on C.



- Electron withdrawing group increase reactivity

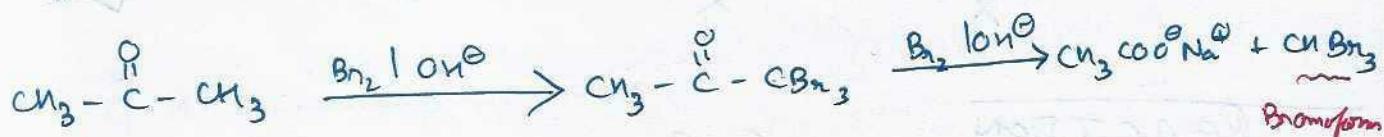
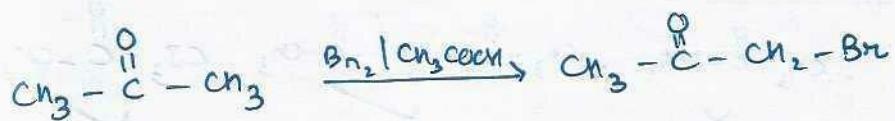
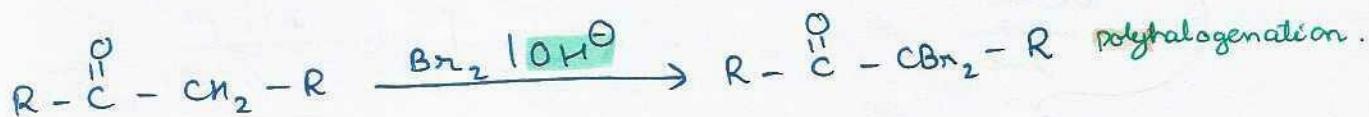
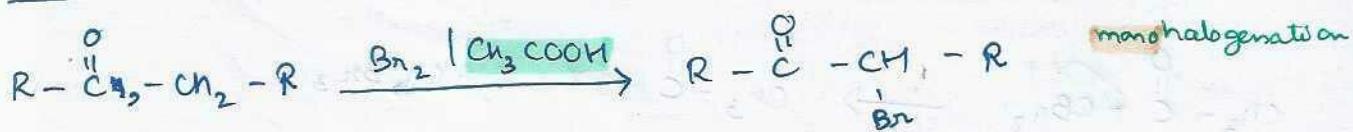


→ aromatic aldehydes are less reactive than aliphatic aldehydes.
(para)

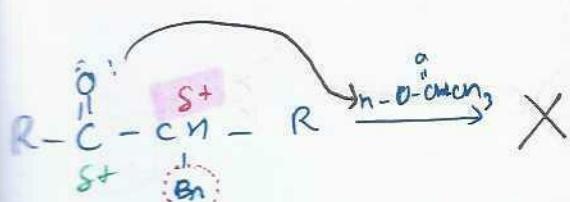
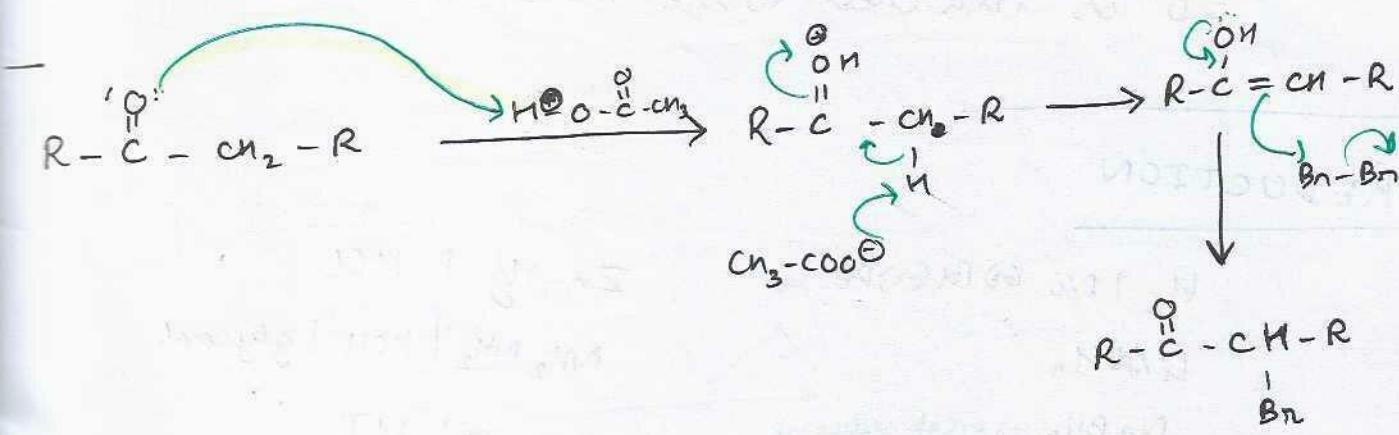
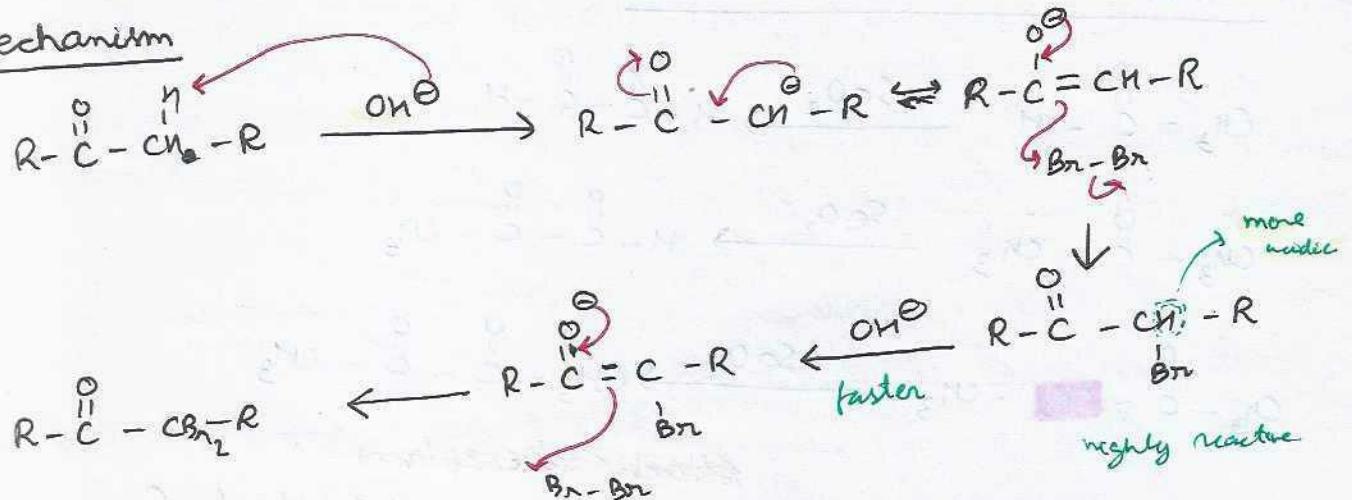


I REACTION DUE TO α -HYDROGEN

a) HALOGENATION

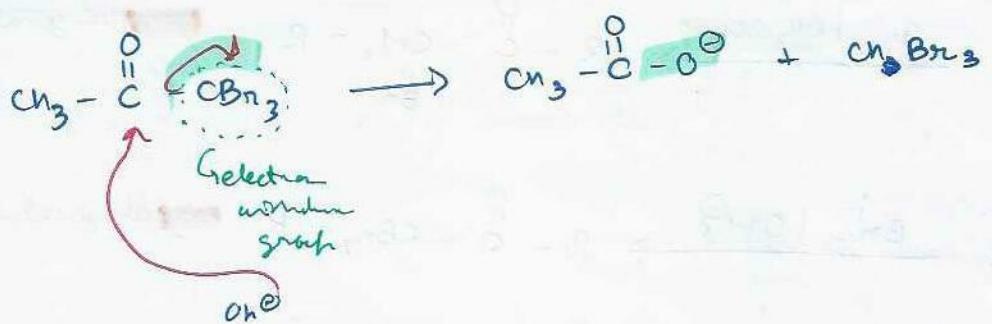
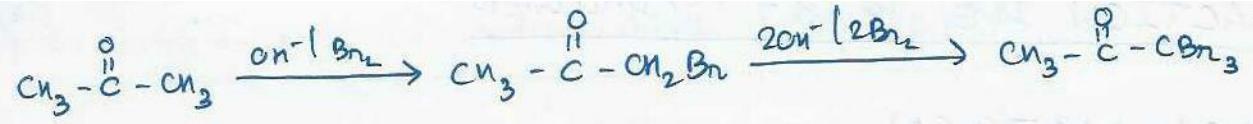


Mechanism



transition state

Two adjacent partial positive charges make it less stable for reactivity



Ide form Reaction: $\text{CH}_3 - \overset{\text{O}}{\underset{\text{H}}{\text{C}}} - \text{OC}_{2\text{H}_5}$, $\text{CH}_3 - \overset{\text{O}}{\underset{\text{H}}{\text{C}}} - \text{NH}_2$, $\text{CH}_3 - \overset{\text{O}}{\underset{\text{H}}{\text{C}}} - \text{CH}_2 - \overset{\text{O}}{\underset{\text{H}}{\text{C}}} - \text{CH}_3$, $\text{Cl}_3 - \overset{\text{O}}{\underset{\text{H}}{\text{C}}} - \text{CH}_3$

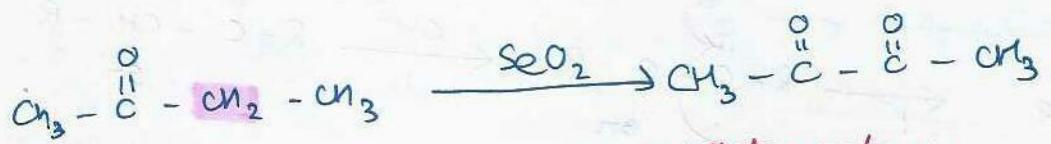
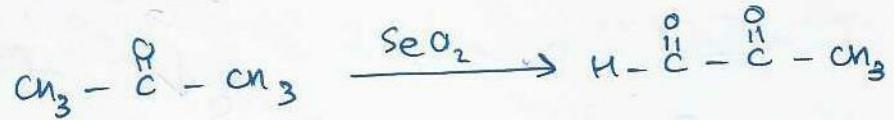
X

X

✓

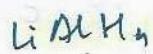
✓

2. REDUCTION WITH SeO_2

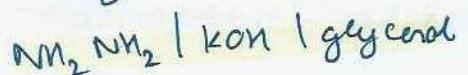
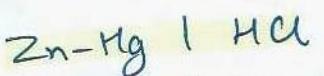


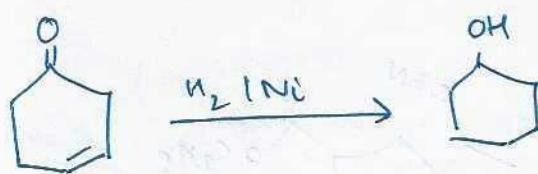
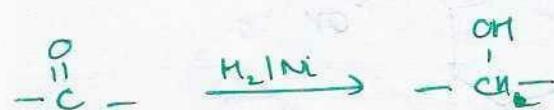
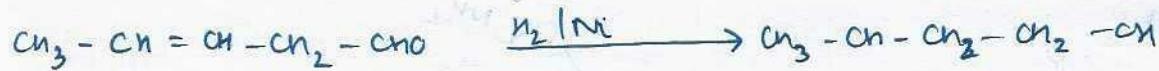
~~Attack at less substituted~~
= O or attached to the more substituted C.

REDUCTION

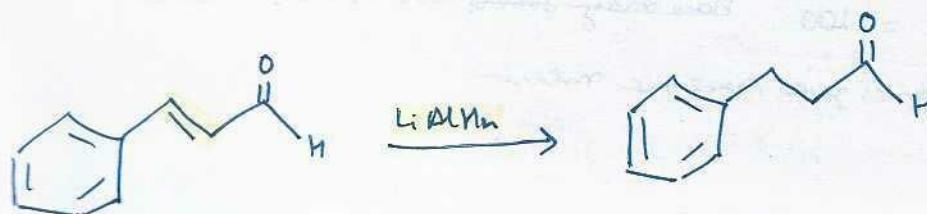
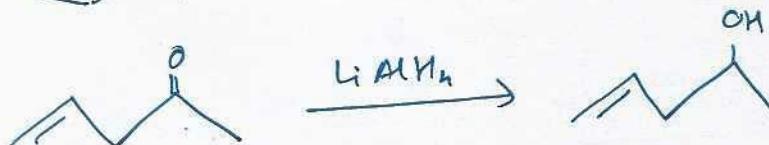
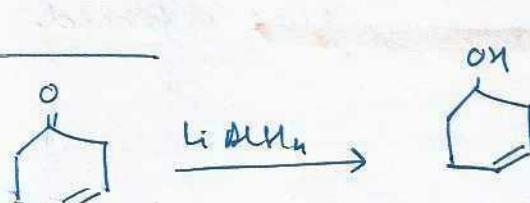


$\text{NaBH}_4 \rightarrow$ weak reducing agent.

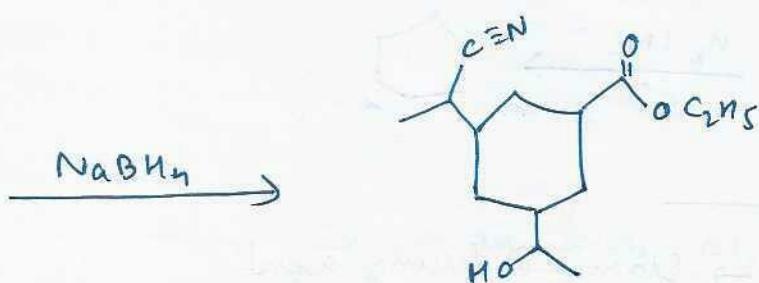
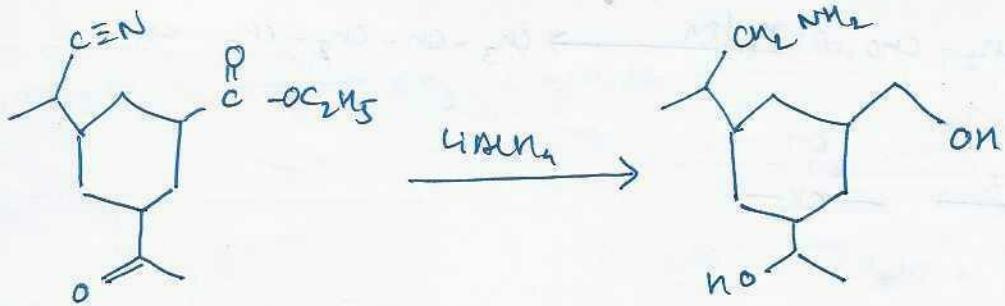




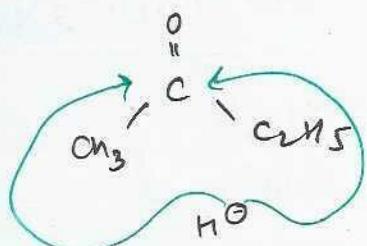
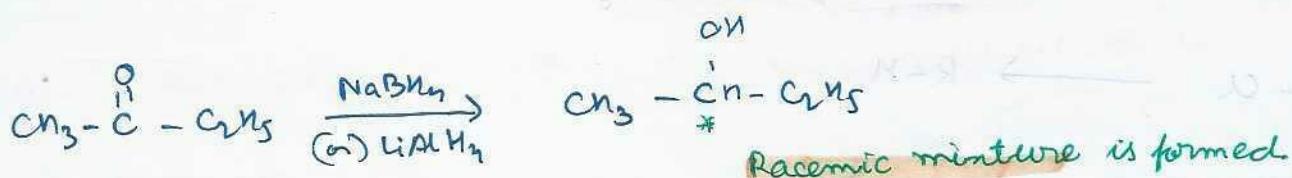
LiAlH_4 → Strong Reducing agent.



Reduces double bond when in conjugation.



NaBH4



Q. Ketone, molecular weight = 100. How many isomers All isomers treated with NaBH4, How many ketones give racemic mixture

Isobutyl isomers

Methylpropyl isomers

$$C_n H_{2n} = 100 - 16 = 84$$

$$n=8,$$

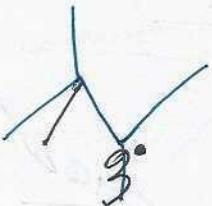
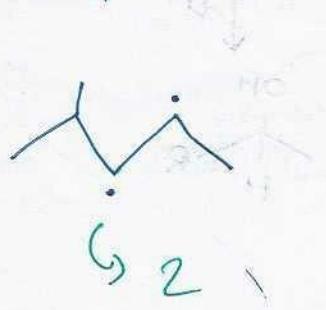
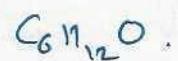
REDUC

1. Zn - I

2. NH2

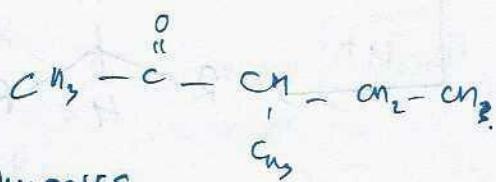
3. Red

CLEMIE



$$1-1=0$$

$$\text{Total} = 6 - 2 = 5$$



REDUCTION OF CARBONYL COMPOUNDS TO ALKANES

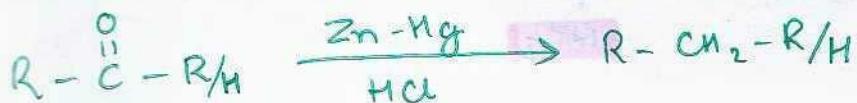
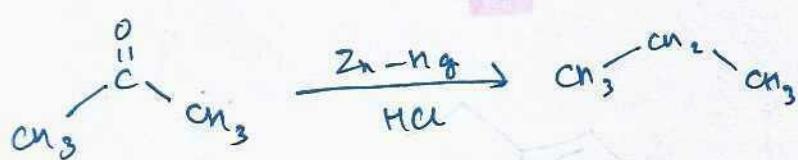
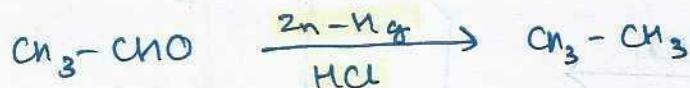


1. $\text{Zn-Hg} | \text{HCl} \rightarrow$ Clemens's Reagent Reduction

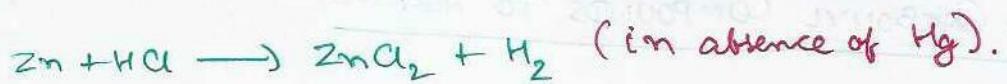
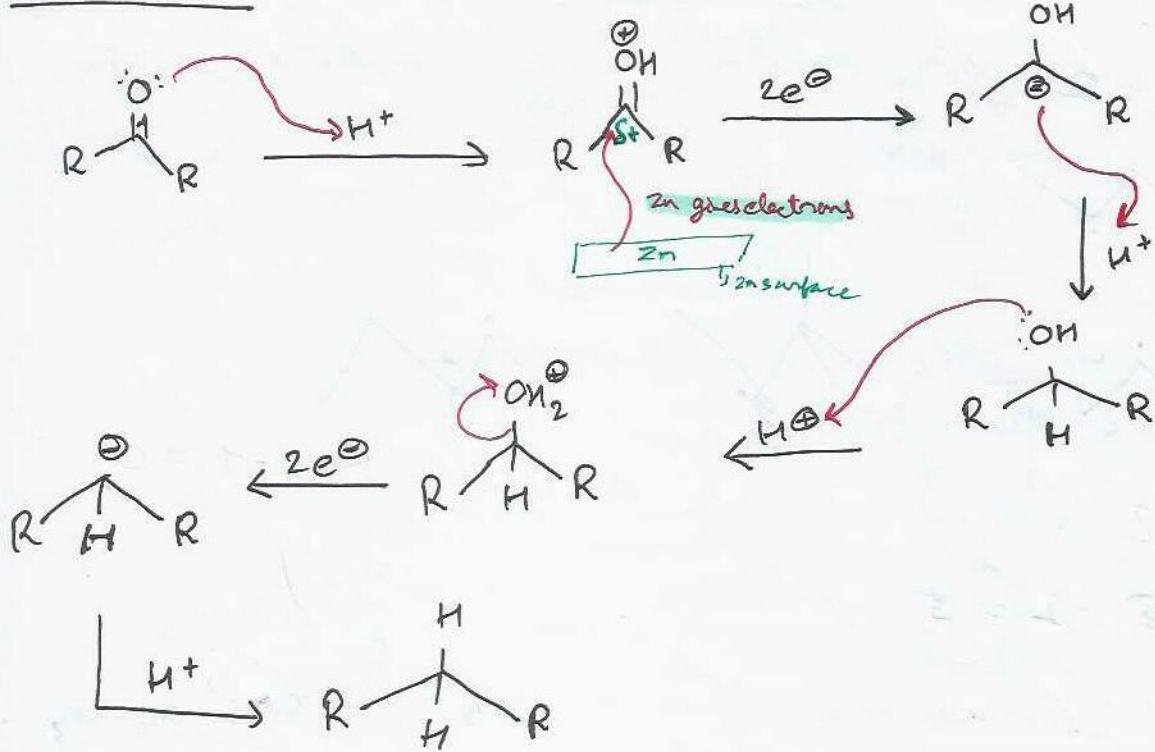
2. $\text{NH}_2-\text{NH}_2^+ \text{ ion}^-$, ethylene glycol, $\Delta \rightarrow$ Wolff-Kishner Reduction.

3. Red P | HI \rightarrow

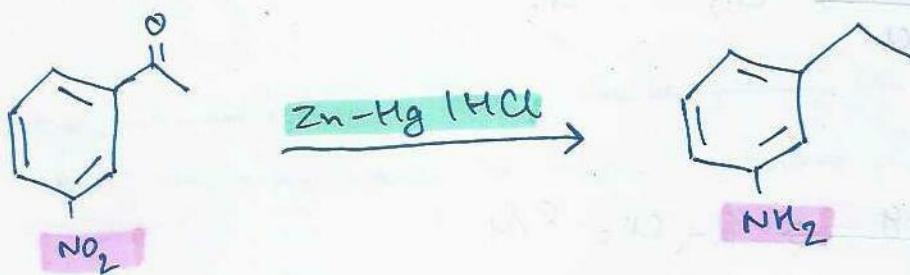
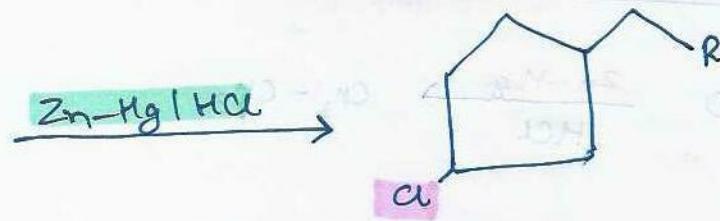
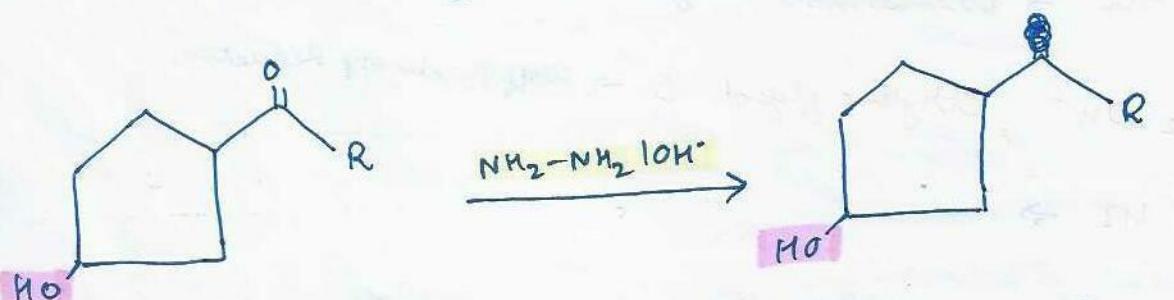
CLEMENS'S REDUCTION



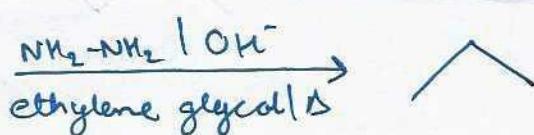
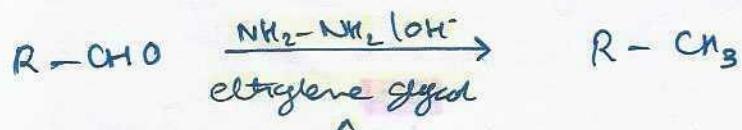
Mechanism



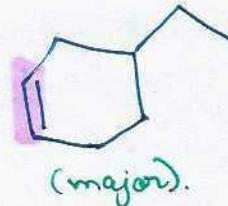
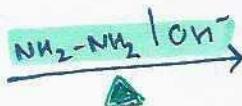
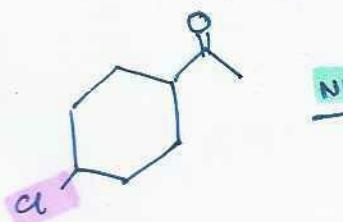
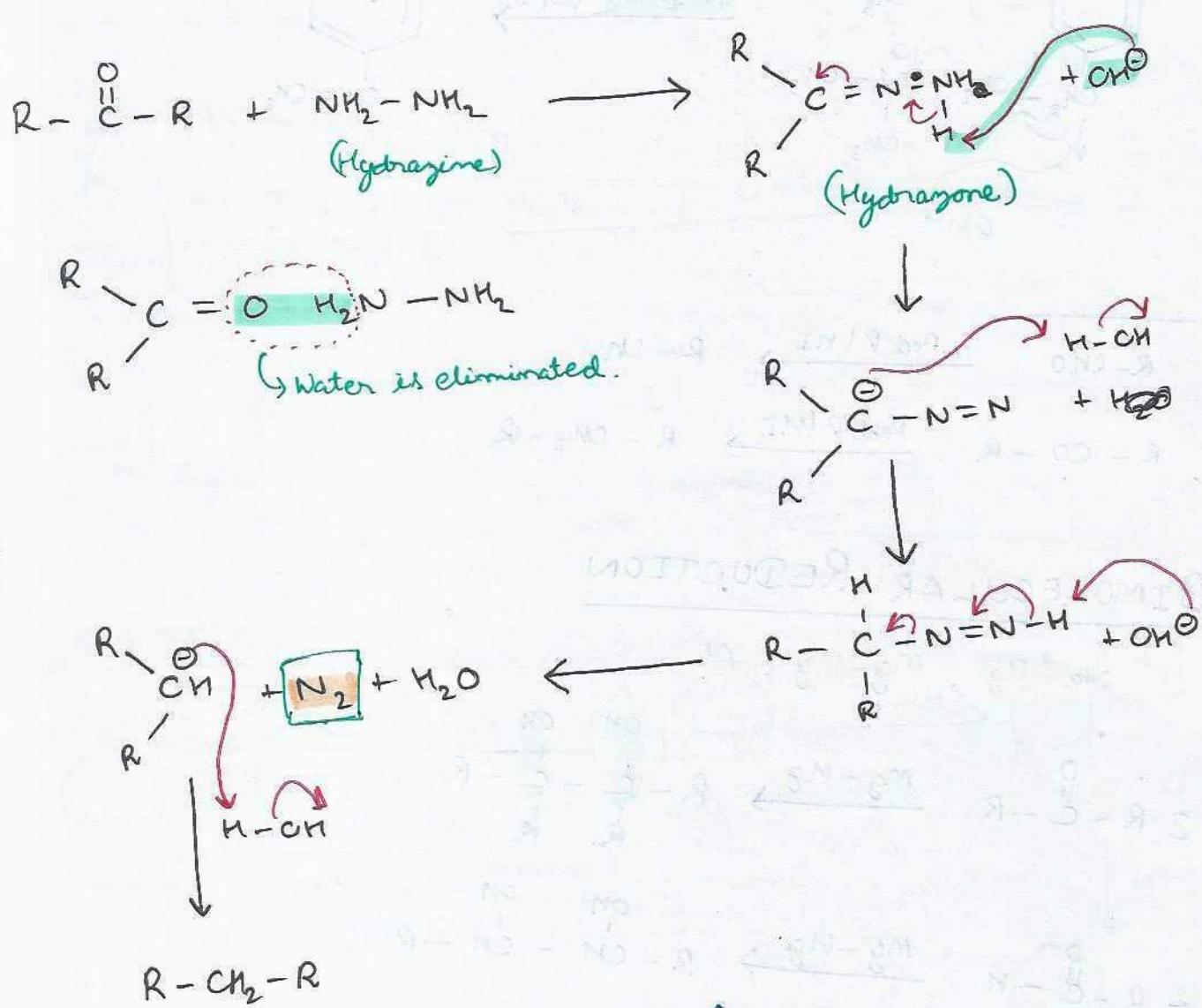
Mercury is added, flow of electrons from Zn metal can be controlled. These electrons are given to the carbon atom and not to H^+ .



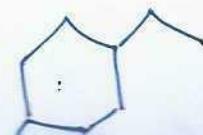
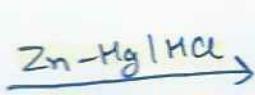
WOLF KISHNER REDUCTION

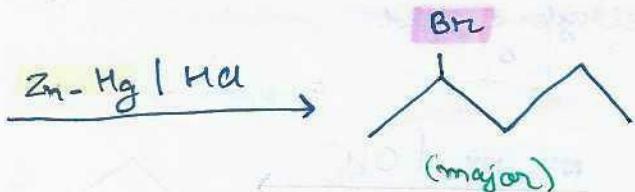
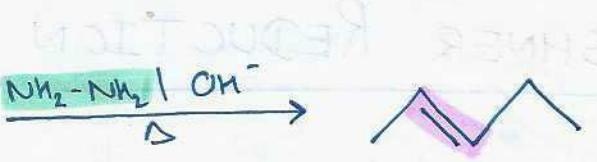
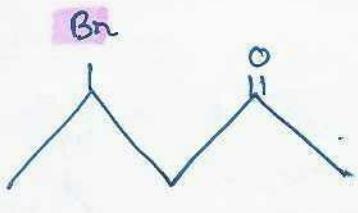


Mechanism

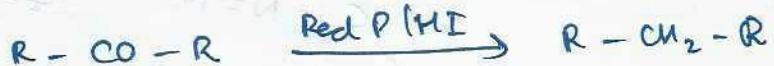
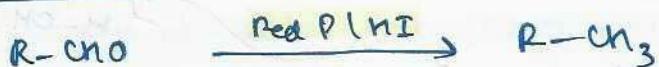
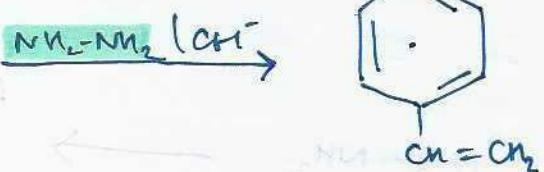
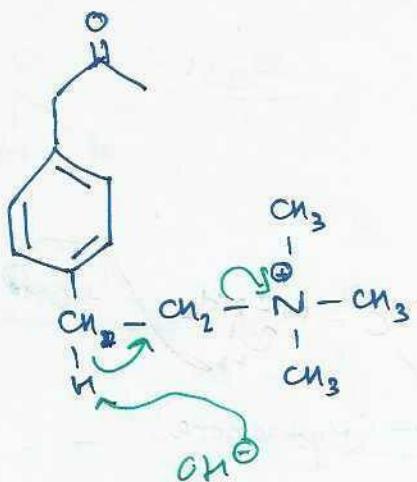


+ Substitution product (negligible)



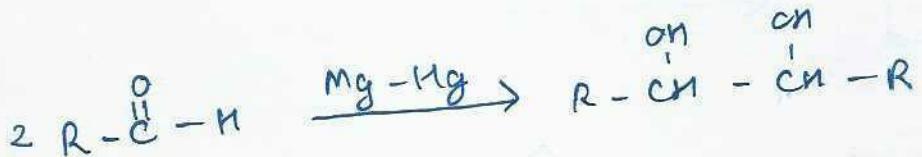
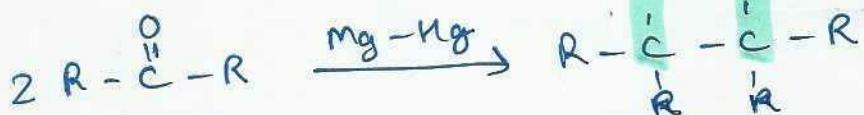


Substitution
product
is negligible

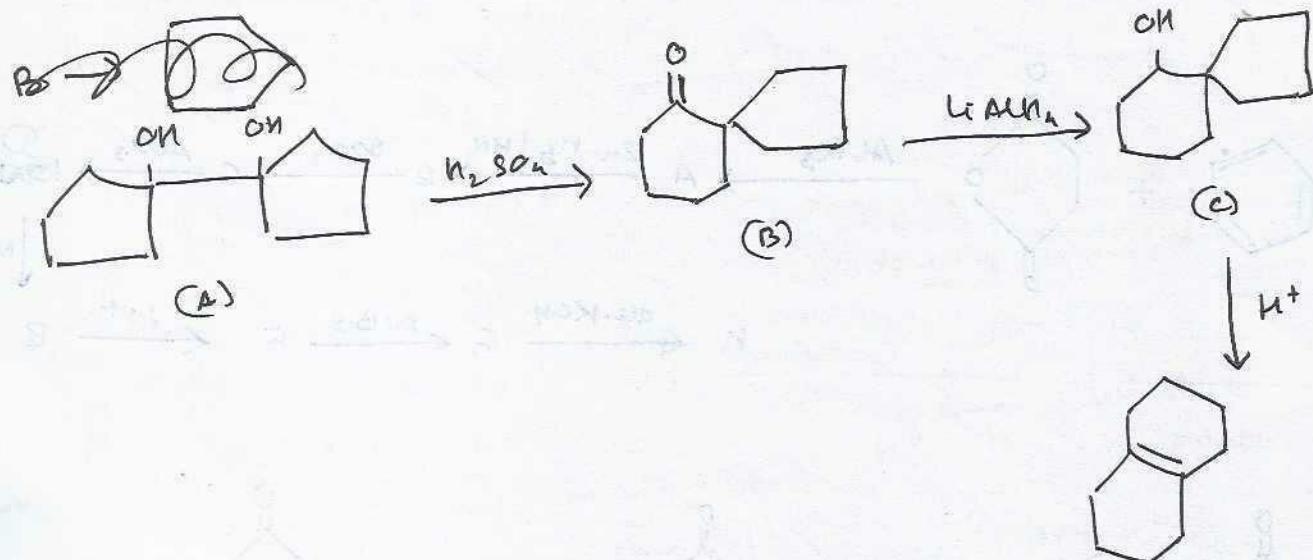
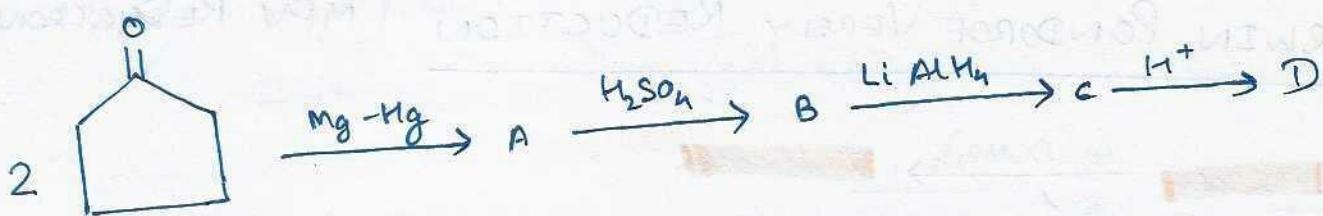
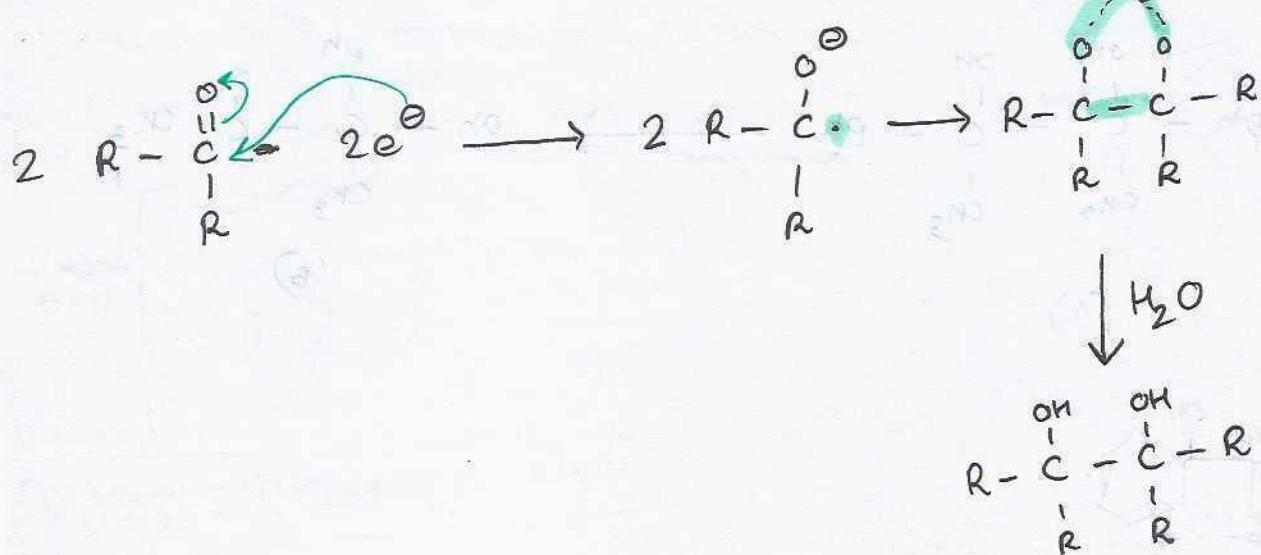
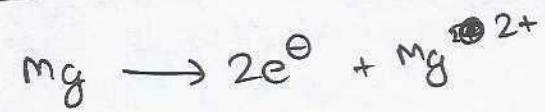


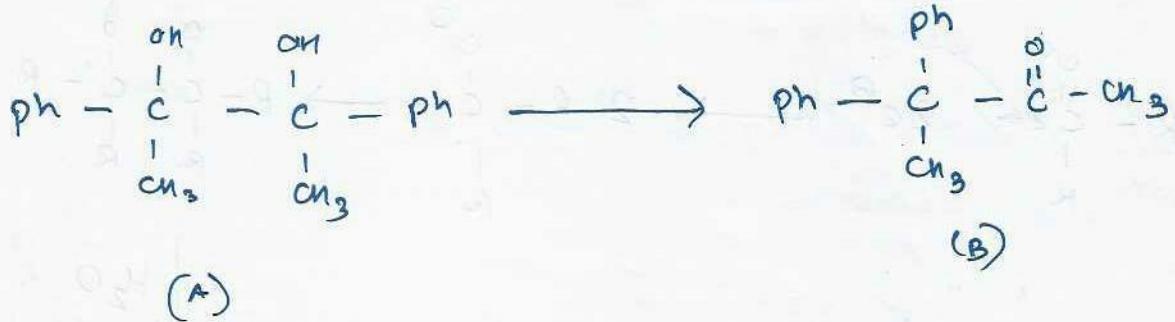
BIMOLECULAR REDUCTION

Na-Hg, Mg-Hg, Al



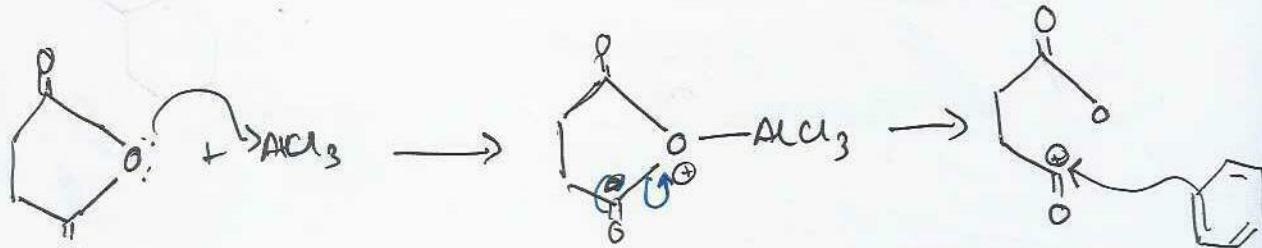
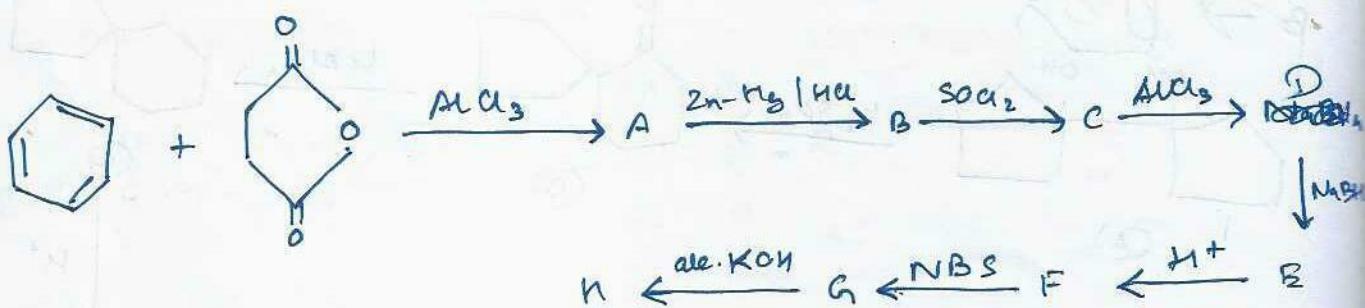
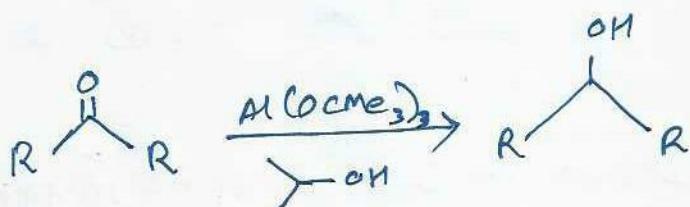
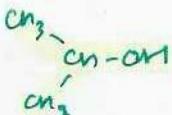
Mechanism

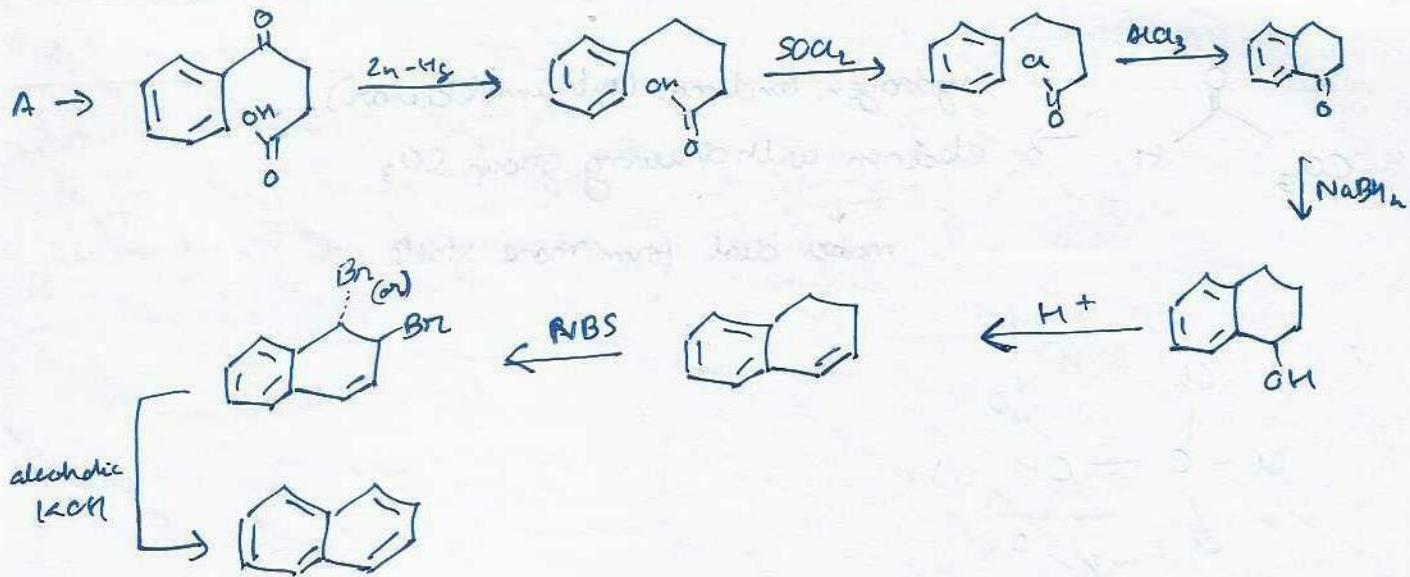




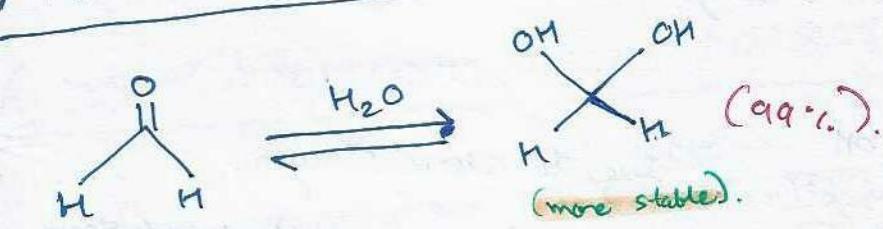
MERWIN PONDOROF VERELY REDUCTION (MPV REDUCTION)

Ketones $\xrightarrow{\text{Al}(\text{OCMe}_3)_3}$ 2° Alcohol

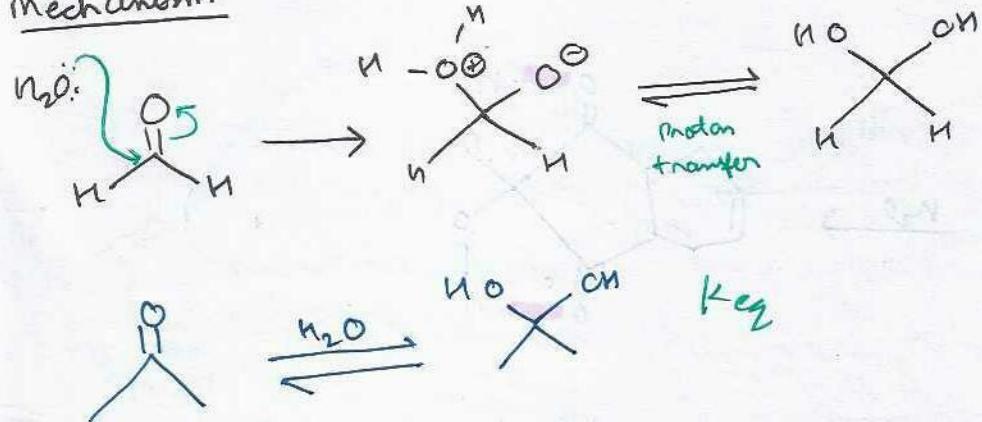




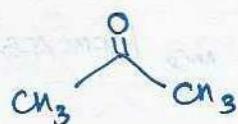
ADDITION OF H_2O



Mechanism



More K_{eq} value more tendency to form diol.



10^{-3}

less steric hindrance

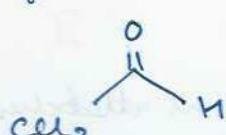


1.06

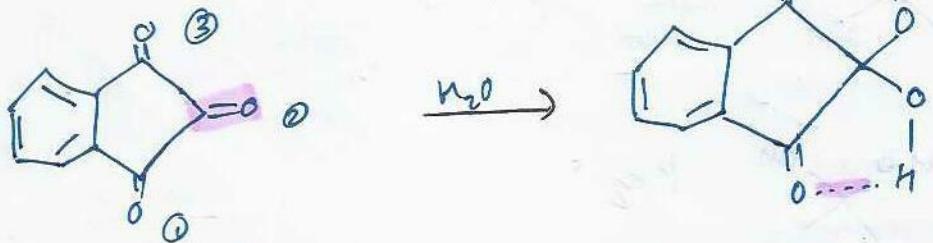
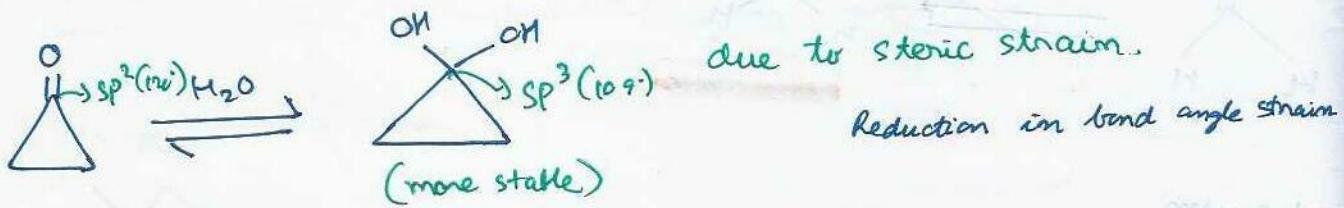
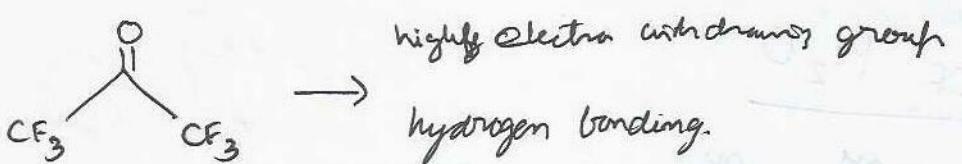
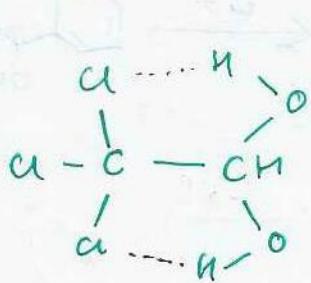
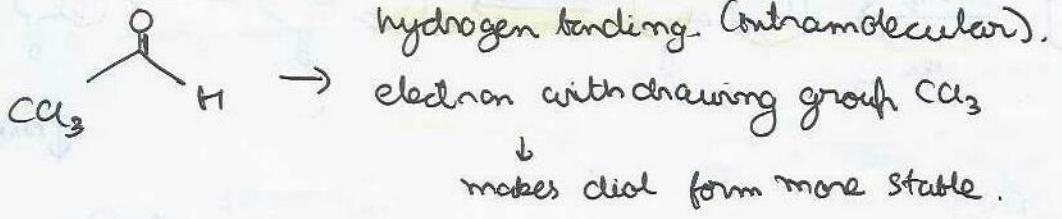


2200

Stable in diol form.



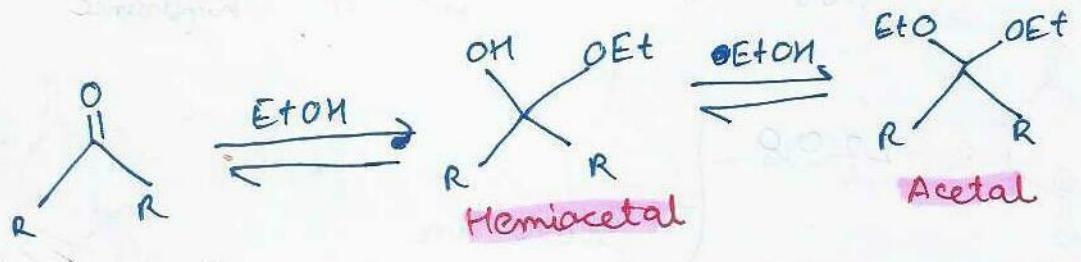
2000



① and ③ are involved
in conjugation with benzene ring

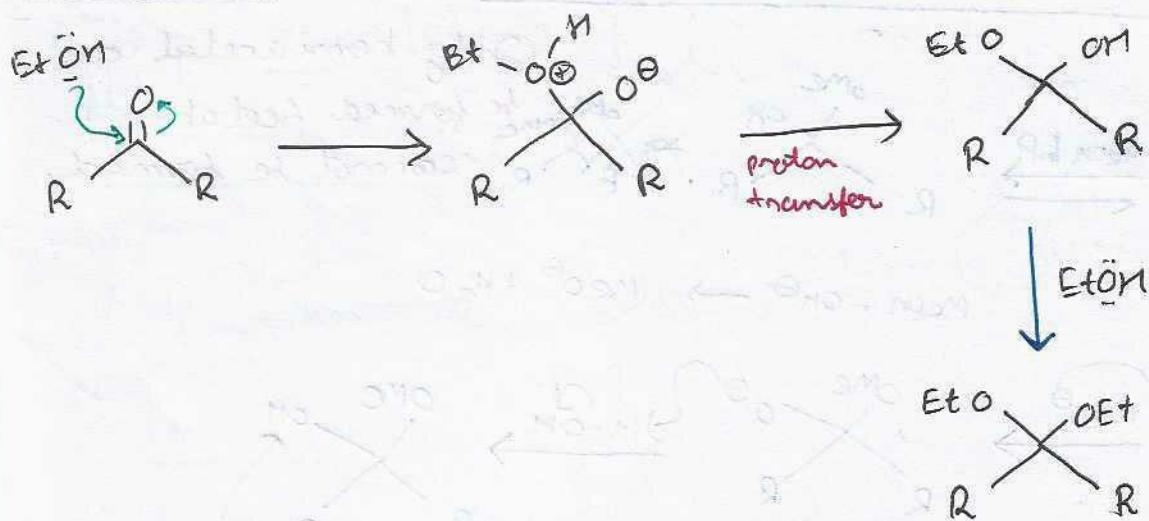
② is hydrolysed.

ADDITION OF ALCOHOLS (FORMATION OF ACETAL AND HEMIACETAL)



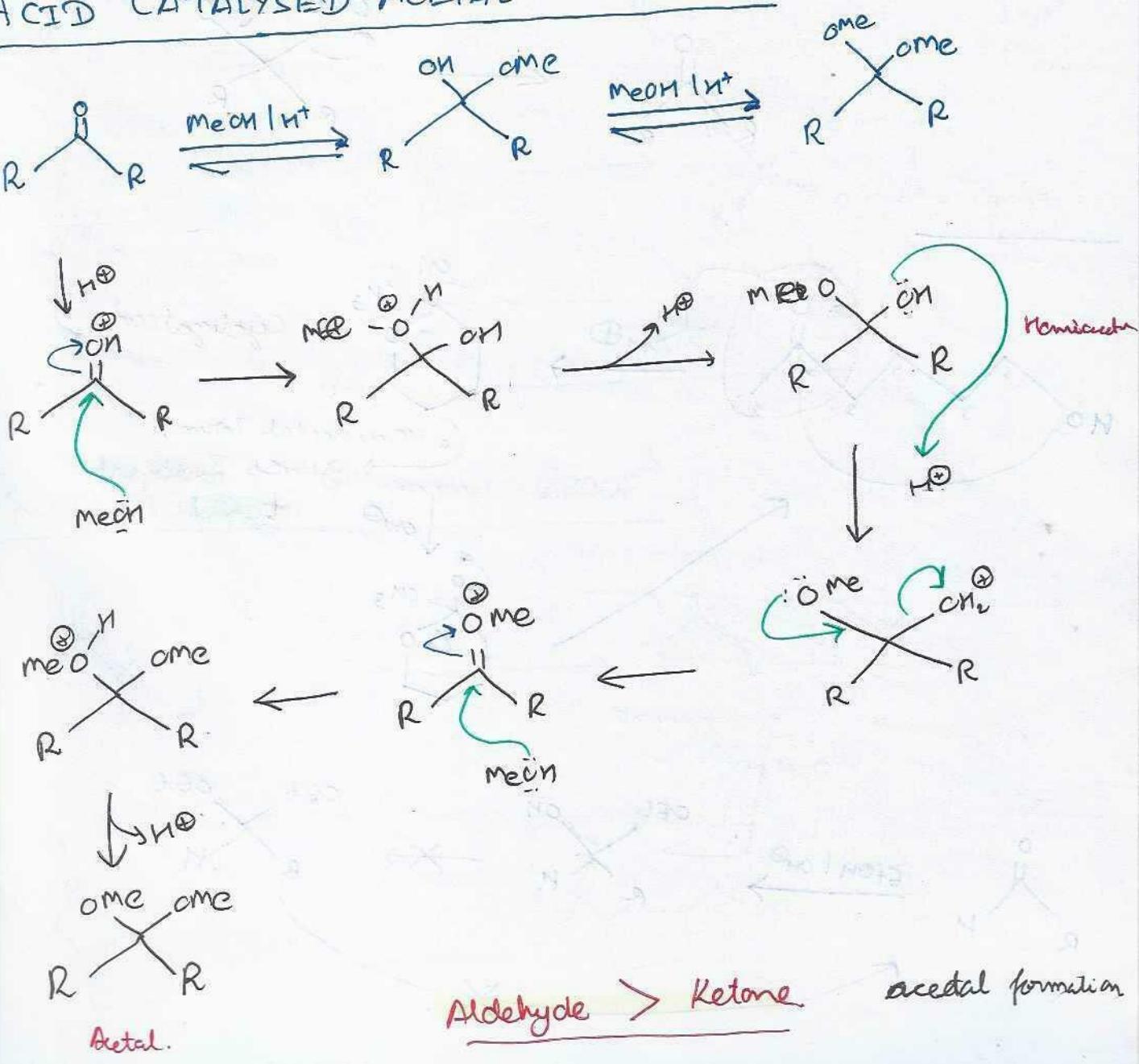
Acetal - On single same carbon, two single bonded oxygen atoms attached to alkyl groups are present.

Mechanism

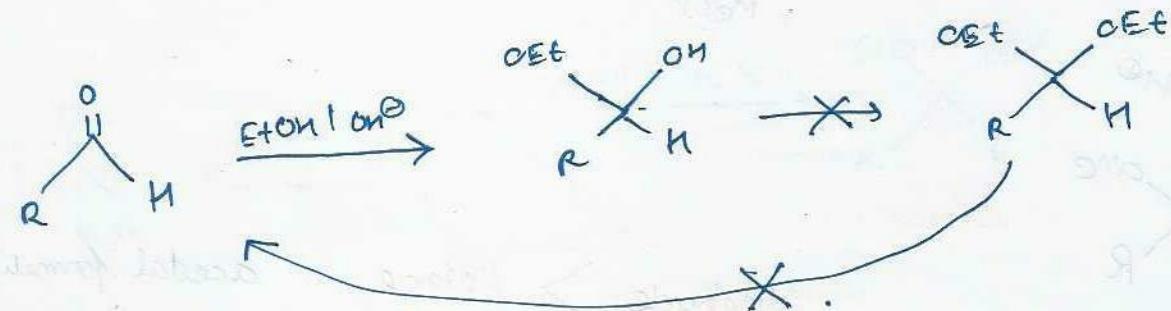
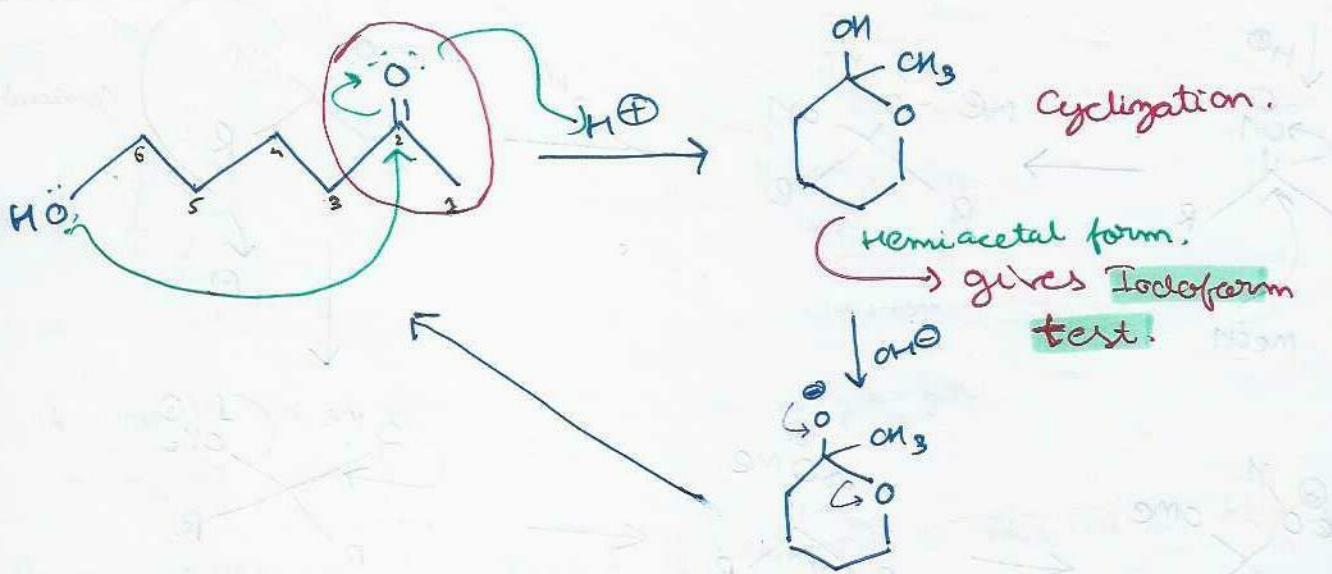
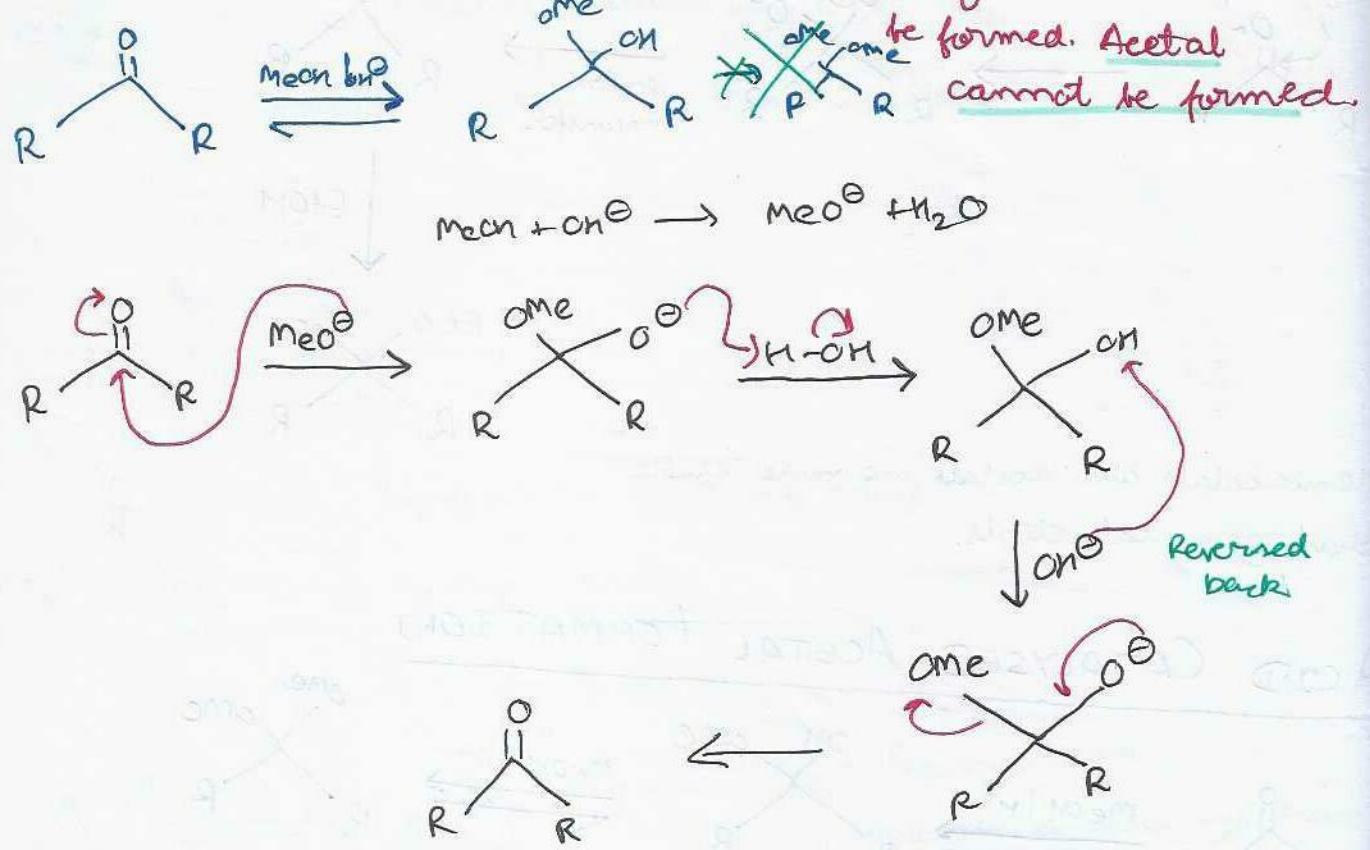


Hemiacetals and acetals are more stable than geminal diols.

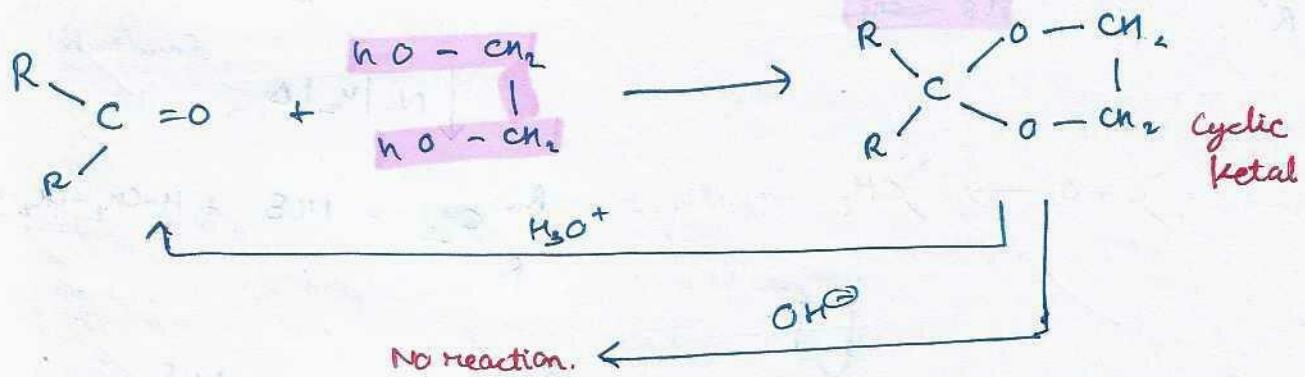
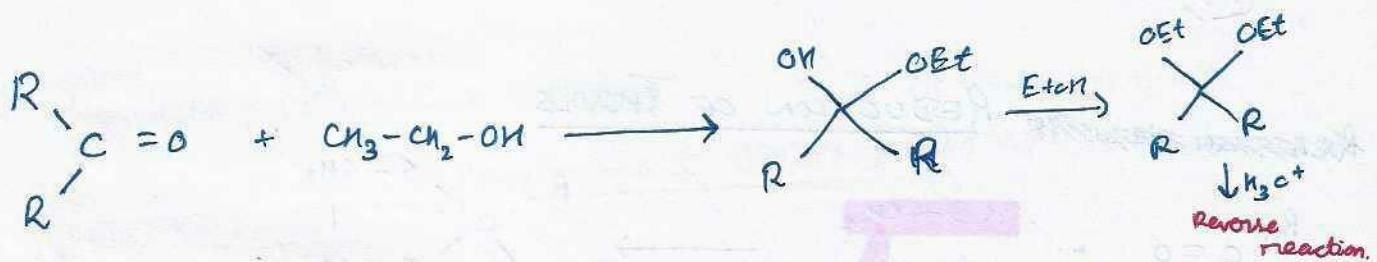
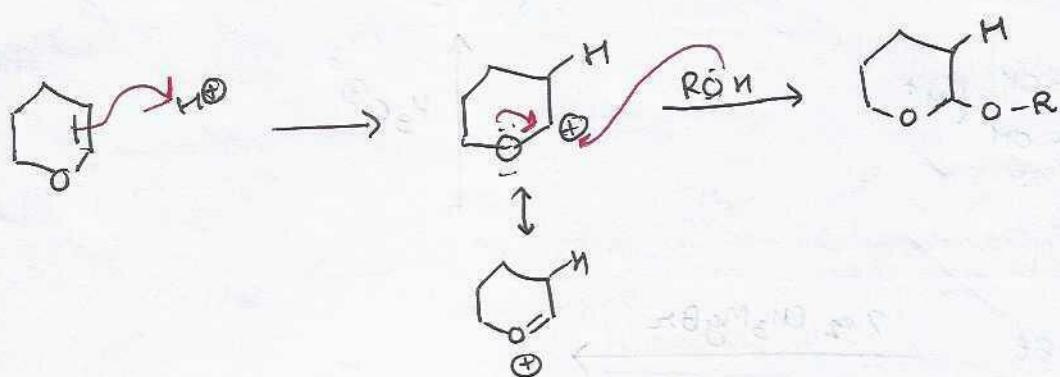
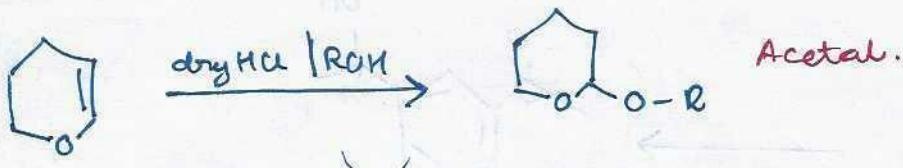
ACID CATALYSED ACETAL FORMATION



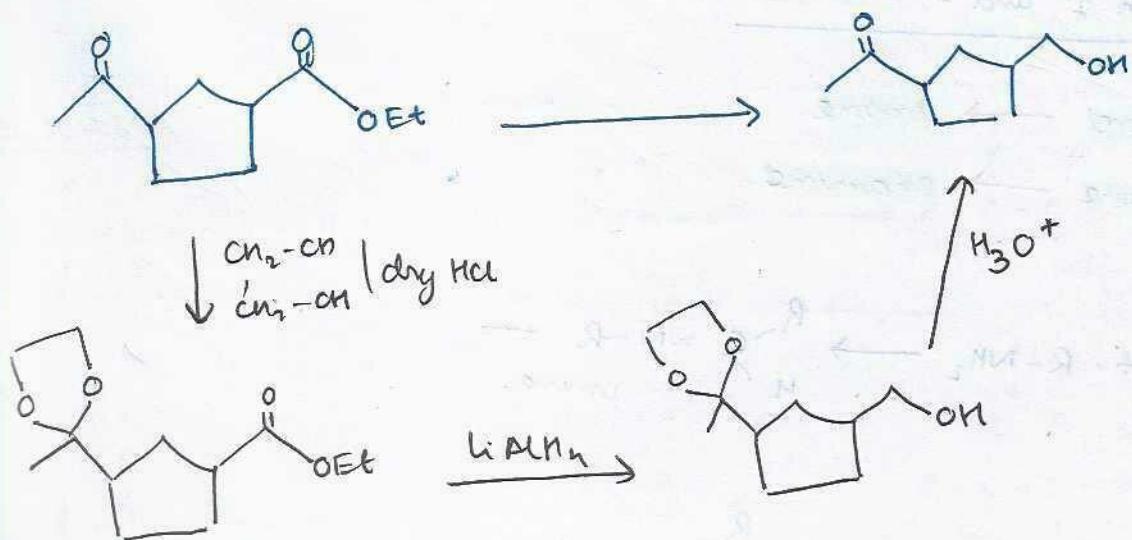
BASE CATALYSED ACETAL FORMATION

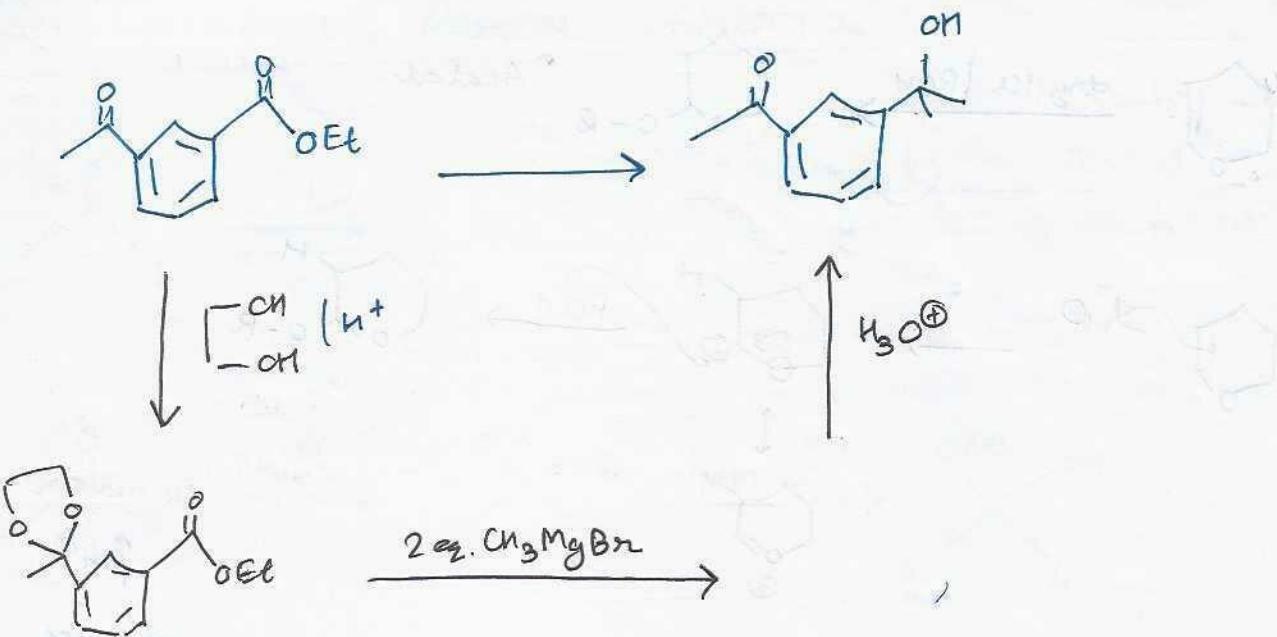


thus, Hemiacetals are not converted to ac aldehydes.

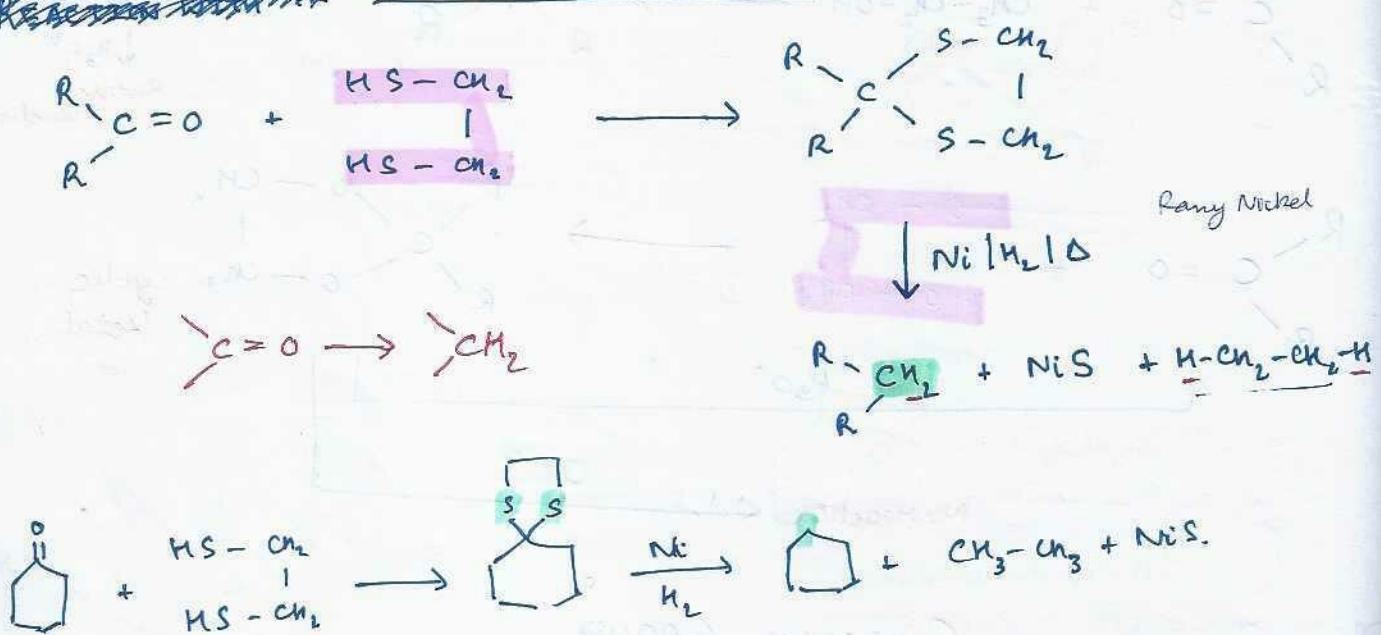


PROTECTION OF CARBONYL GROUP

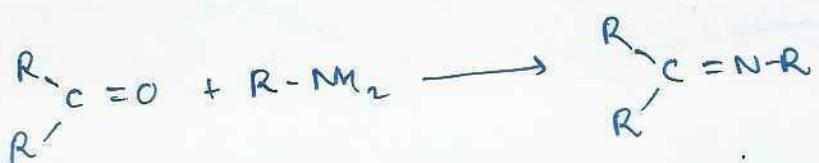
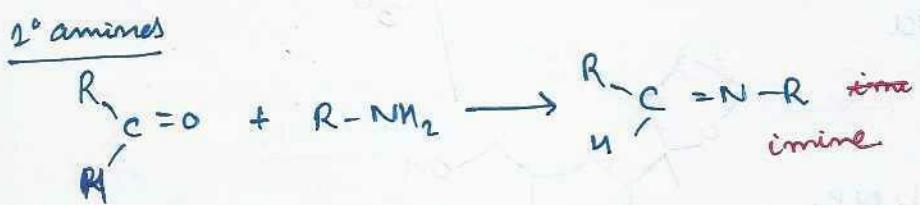
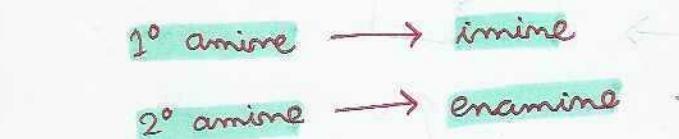




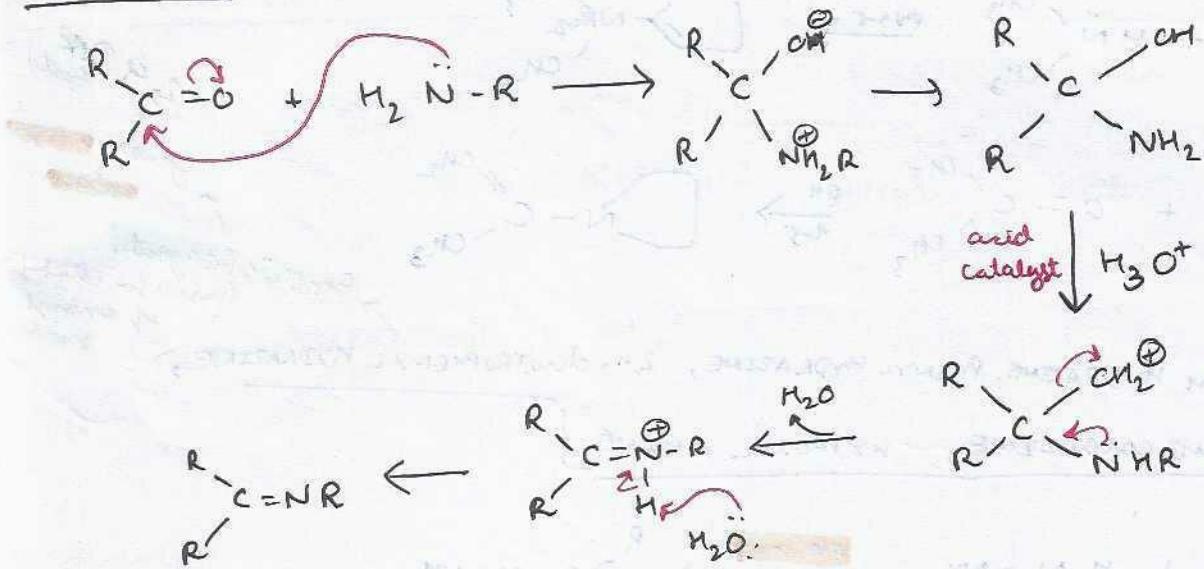
REDUCTION OF TRIOLS



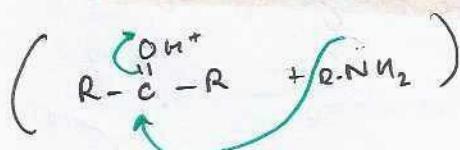
REACTION WITH 1° and 2° AMINES



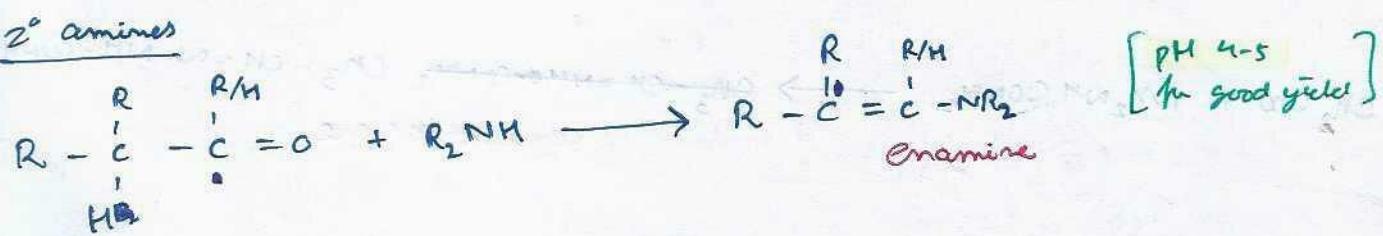
Mechanism



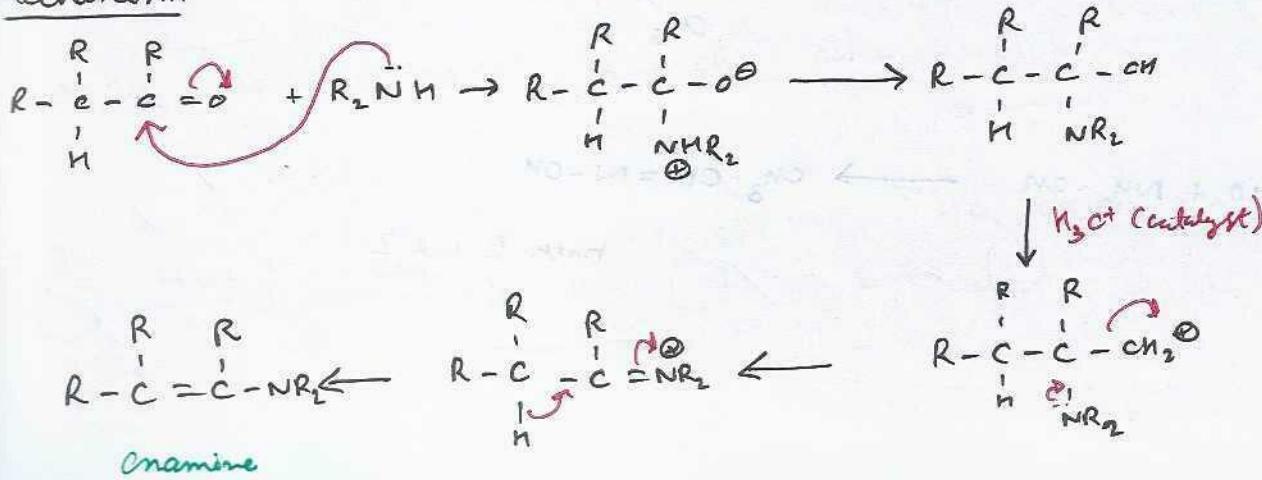
In strong acid; $\text{RNH}_2 \xrightarrow{\text{H}^+} \text{RNH}_3^+$ } optimum pH of 4-5
is preferred.
In weak acid; can't tolerate amine alcohol

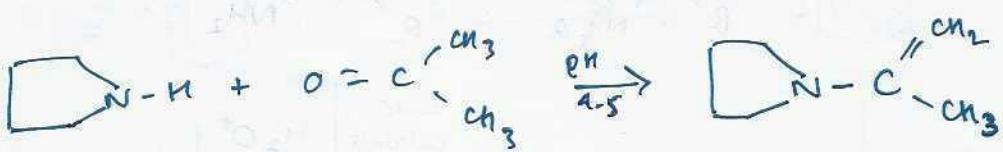


2° amines



Mechanism





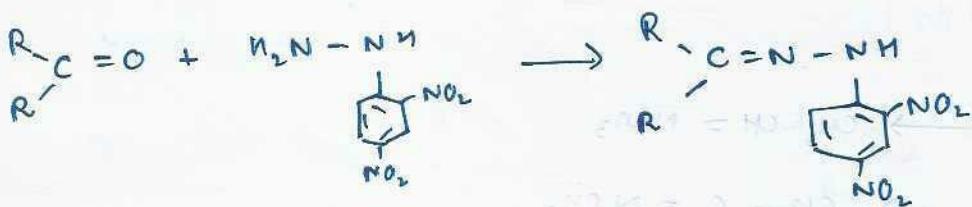
REACTION WITH HYDRAZINE, PHENYL HYDRAZINE, 2,6-dinitroPHENYL HYDRAZINE,
SEMI HYDROXYL AMINE, SEMI CARBAZINE,



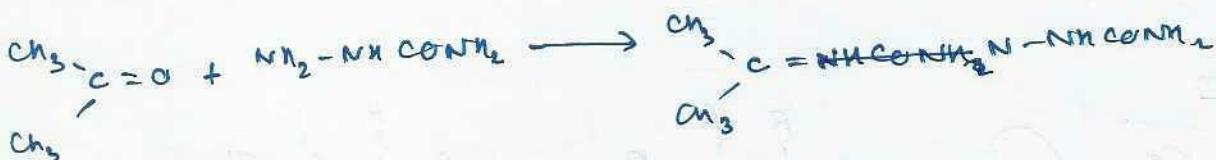
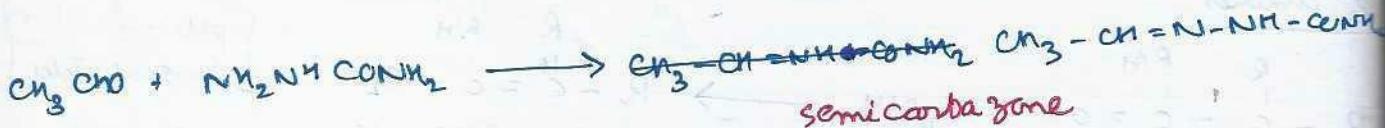
aldehyde hydrazone



ketone phenyl hydrazone



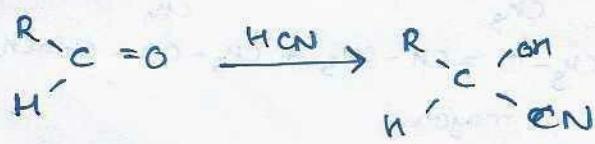
(2,4 DNP test) → gives orange colour



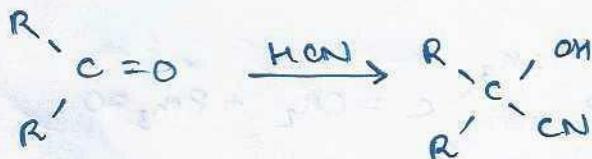
bath E and 2

(2,4 DNP test)
gives orange colour
Brady's Reagent
(used for identification of carbonyl group)

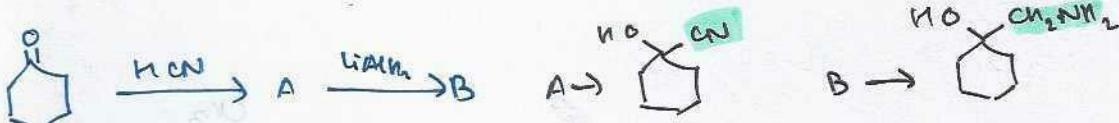
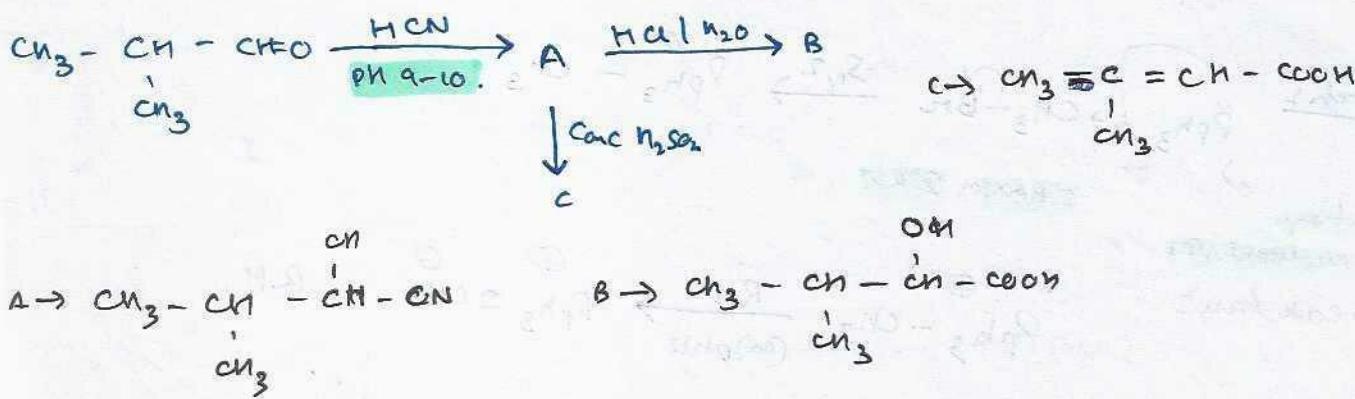
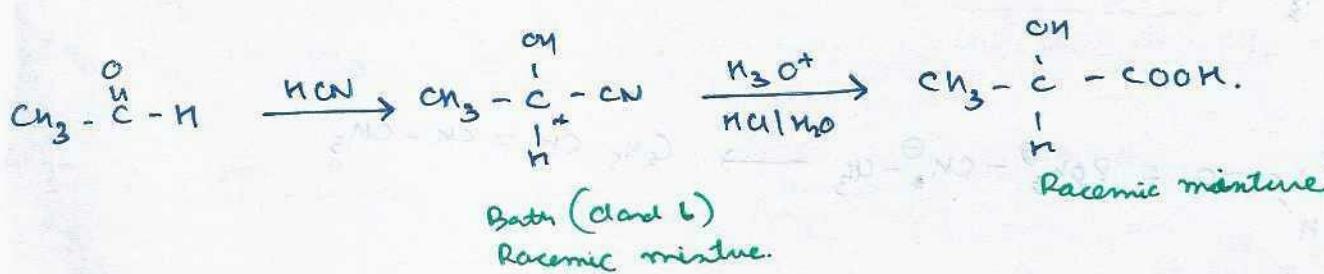
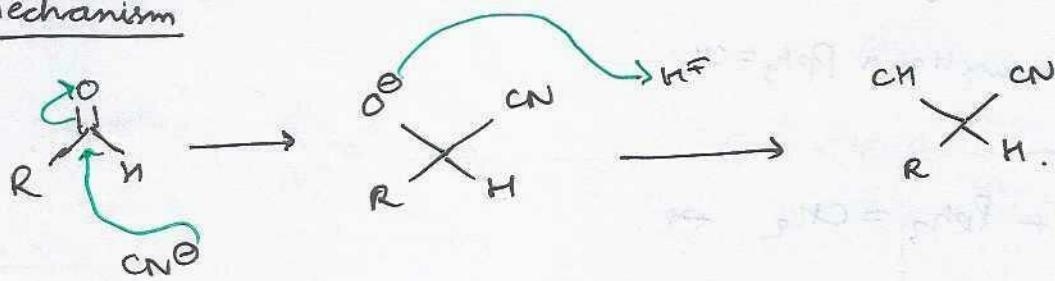
REACTION WITH HCN



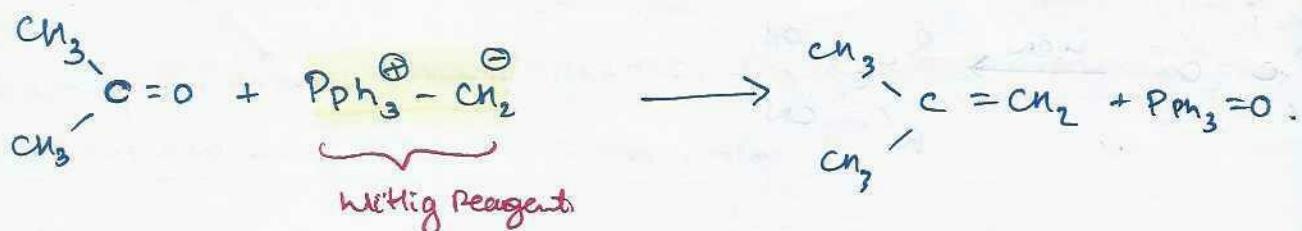
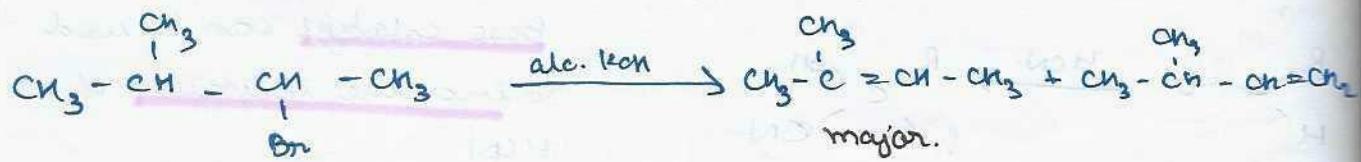
Base catalyst can be used to increase ionization of HCN



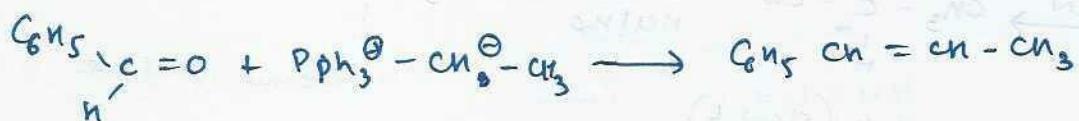
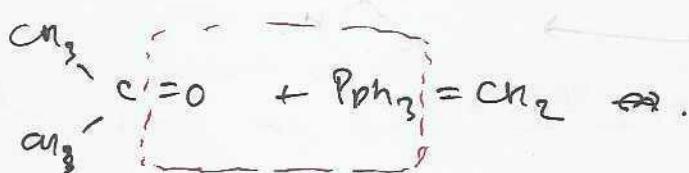
Mechanism



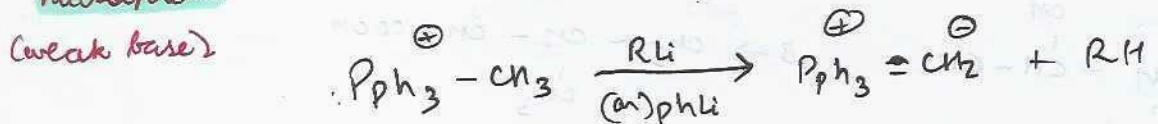
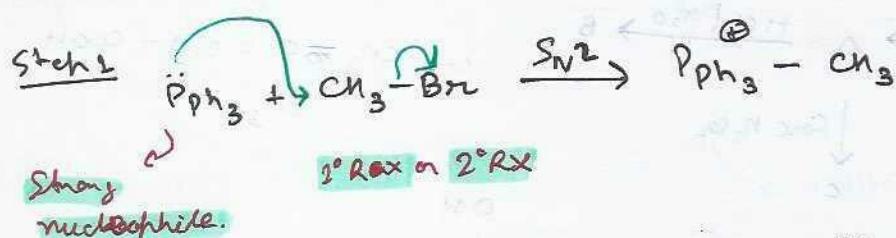
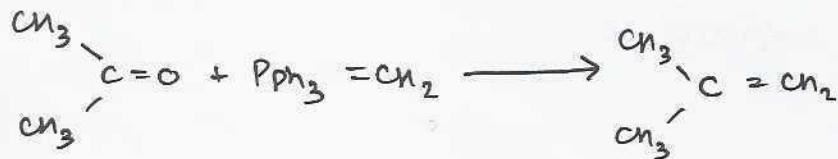
WITTIG REACTION (single product, without rearrangement).



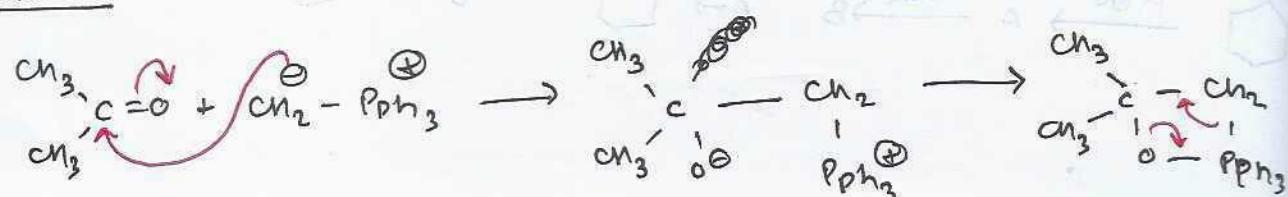
also write as $\text{PPh}_3=\text{CH}_2$

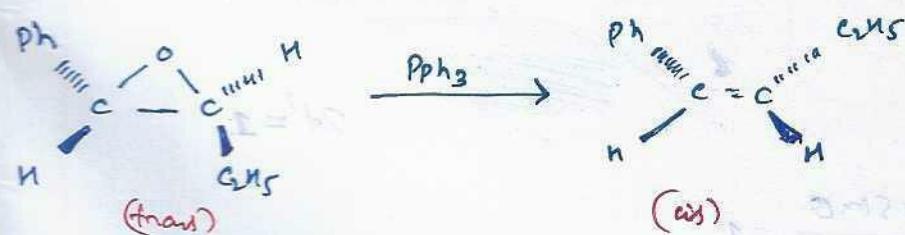
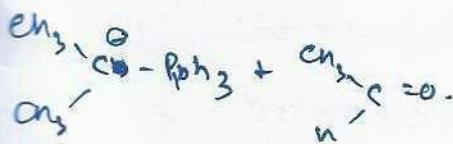
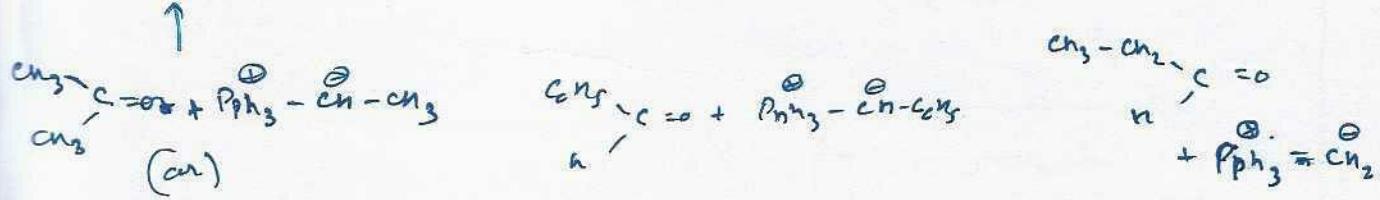
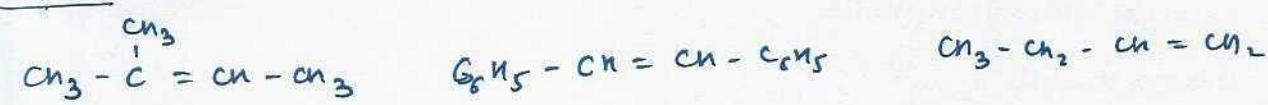
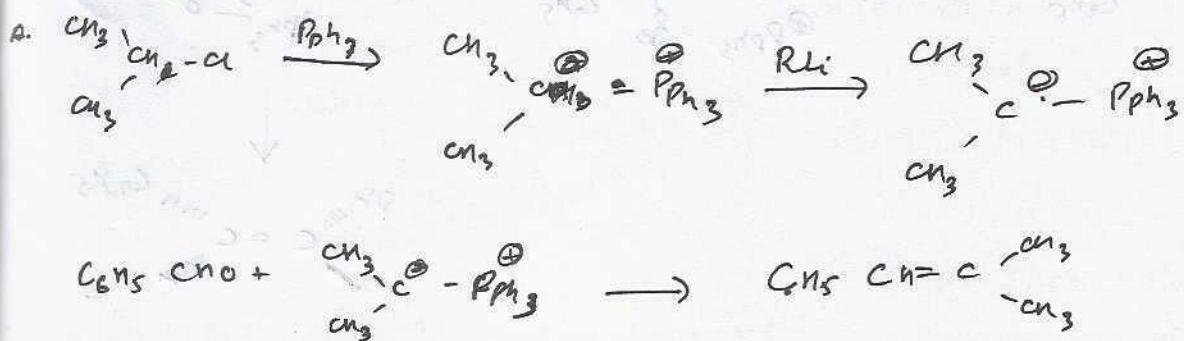
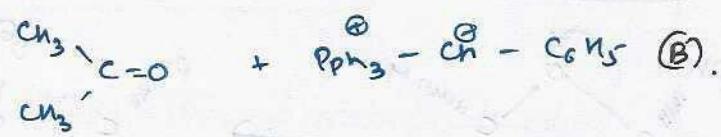
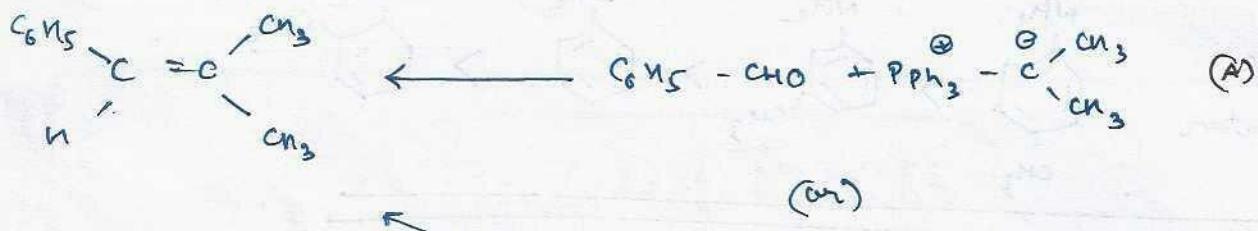


Preparation of Wittig Reagent

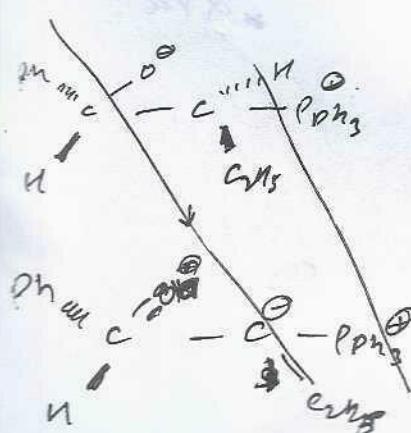


Mechanism

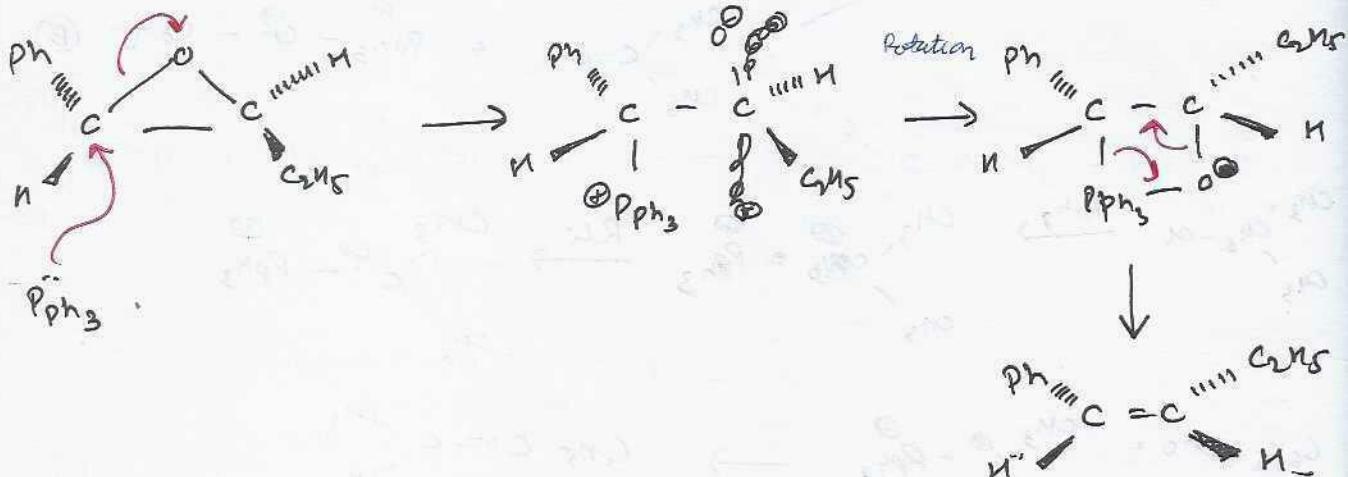
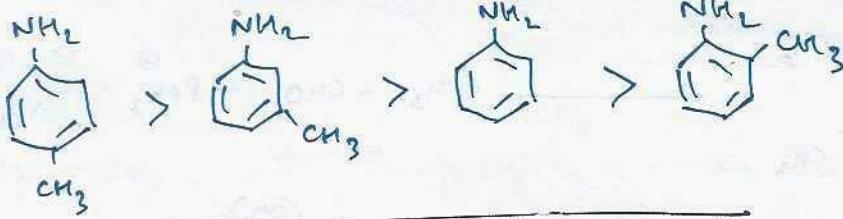




(mechanism on next page)



Basic
character



$$nC_V \Delta T = \Delta U$$

$$C_V =$$

$$\tan \theta (2t^2 - 1) = 0$$



$$2d^2 = 1$$

$$\frac{x \cos \theta}{2\sqrt{a} \sin \theta} + \frac{y \sin \theta}{\sqrt{a}} = 1$$

$$x \propto \sqrt{a}$$

$$\frac{\cos \theta}{2\pi}$$

$$\cos \theta$$

$$1$$

