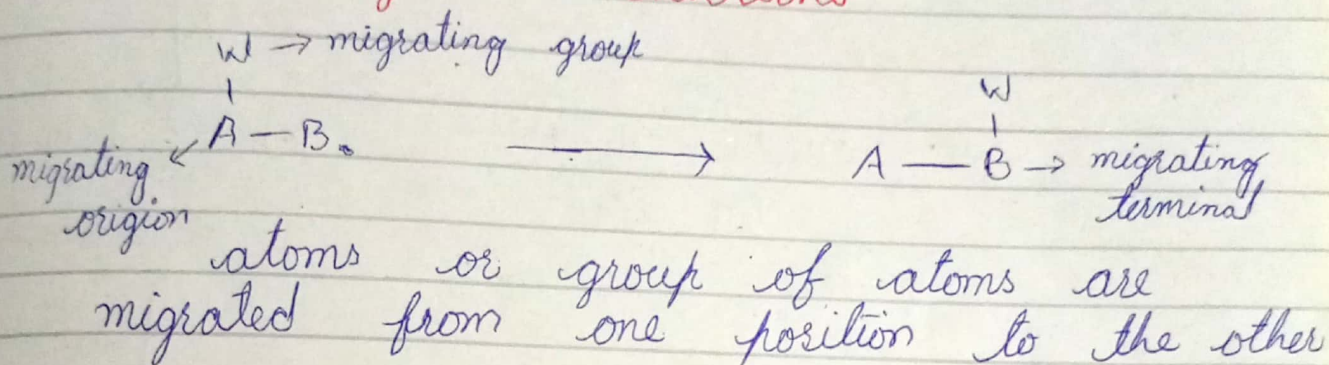


05/09/2019

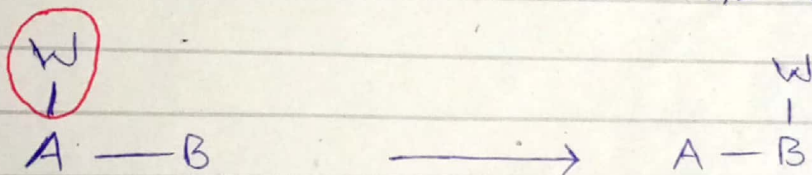
## Reaction Mechanism - II

1. Rearrangement reactions
2. Pericyclic reactions

### Rearrangement reactions

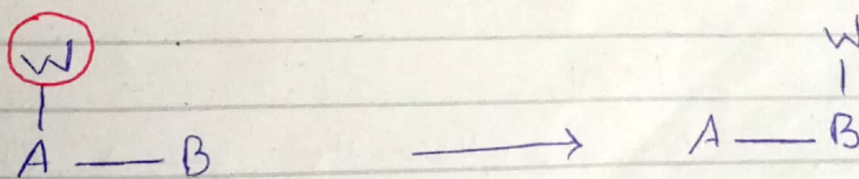


as A and B are adjacent so the rearrangement is termed as 1,2-rearrangements.



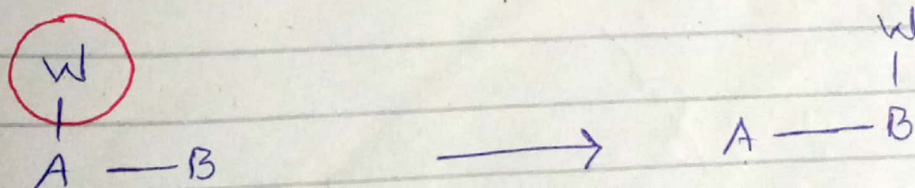
anionotropic

B  $\Rightarrow$  electron deficient  
also called nucleophilic rearrangement.

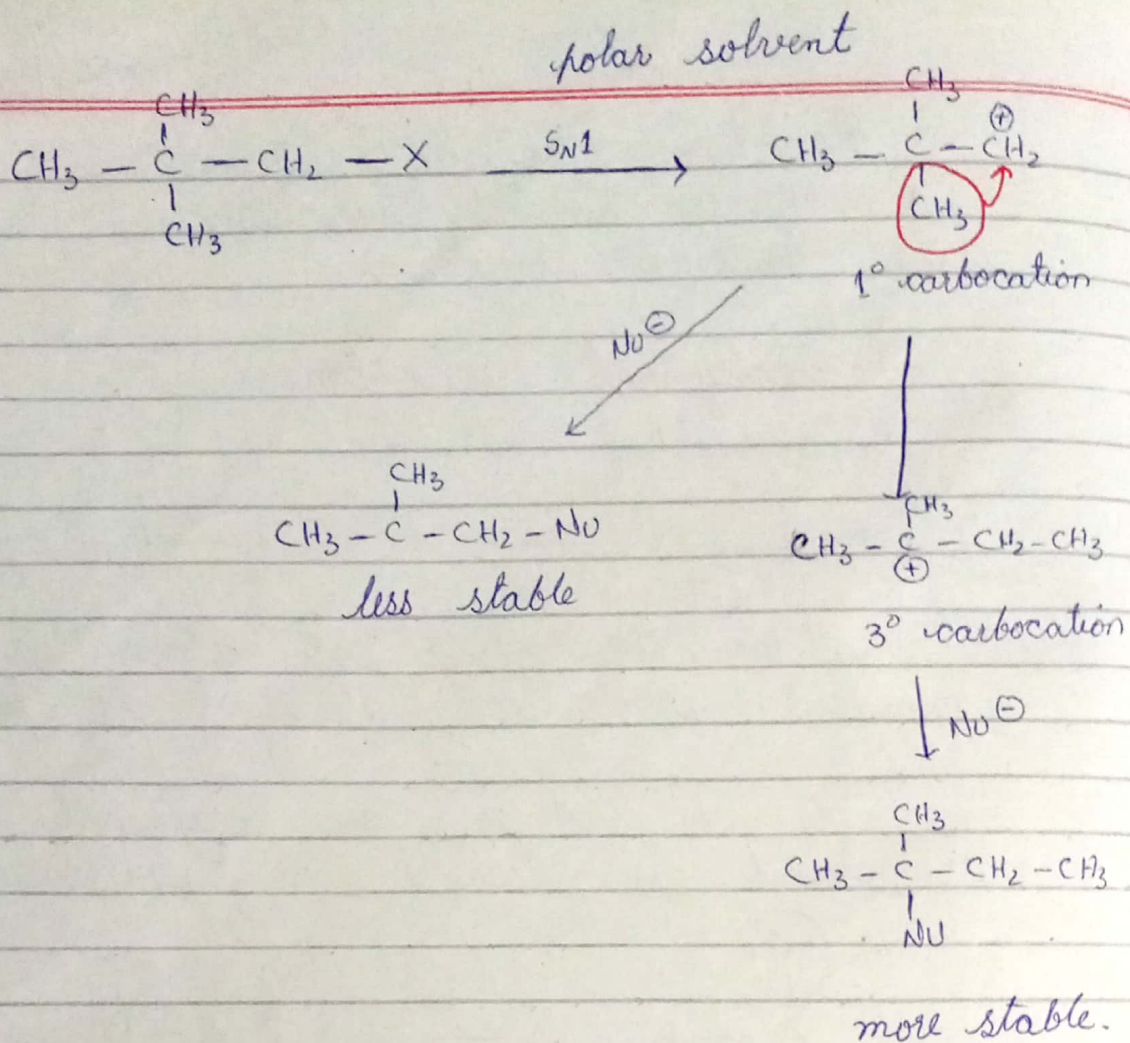


cationotropic

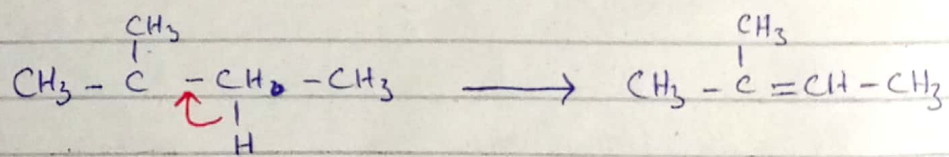
B  $\Rightarrow$  electron efficient



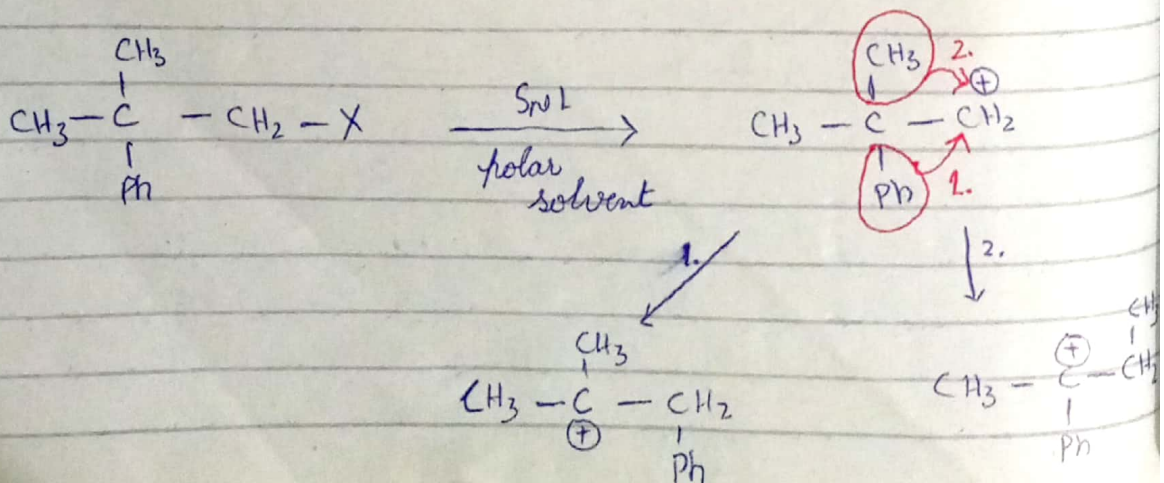
free radical



if we won't have supplied external Nu<sup>⊖</sup>, the system would have sacrificed and undergone elimination.



### Exercise

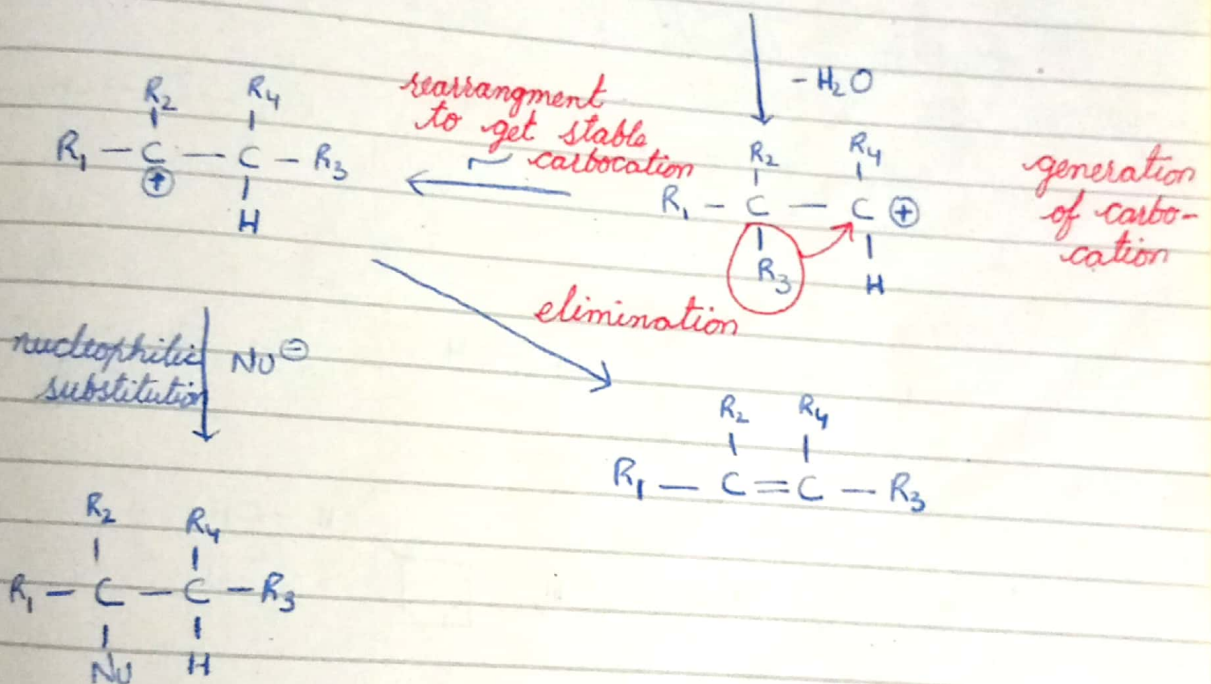
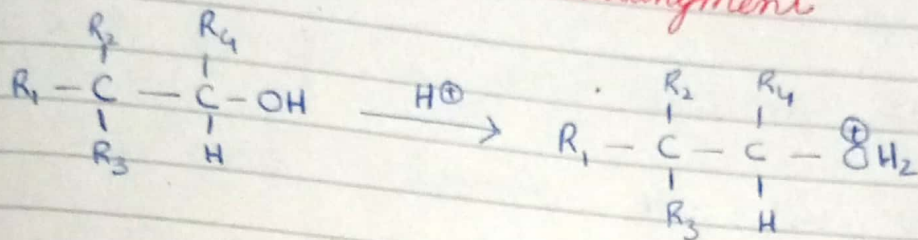




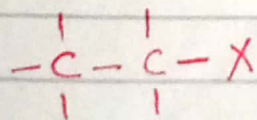
The 2 is more stable because of delocali-  
zation of positive charge over the benzene  
ring.

## Wagner-Meerwein Rearrangement

12/09/2019



carbocations can also be produced from sources other than alcohols-

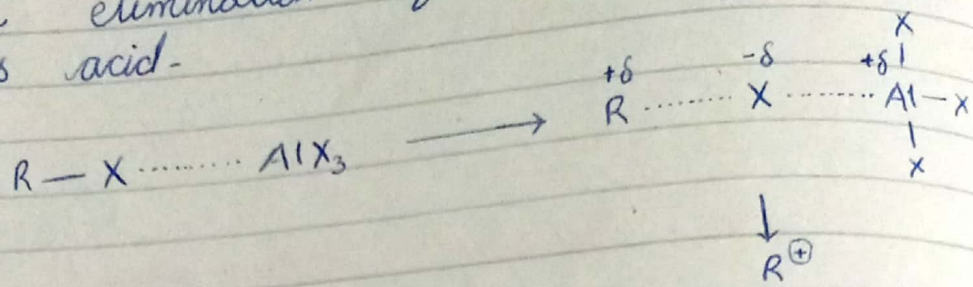


X = OH, Cl, Br, I, OTs

A leaving group takes away the electron. so it must be/have

- i) high electronegativity
- ii) vacant orbitals
- iii) resonance stabilization

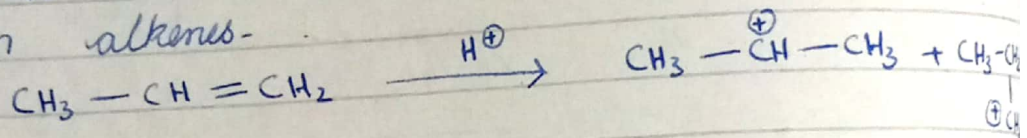
for elimination of halogens, we used Lewis acid-



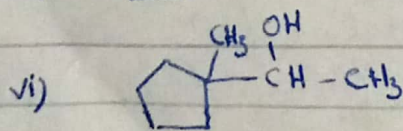
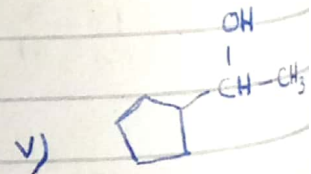
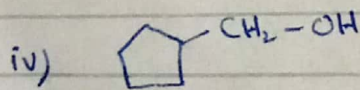
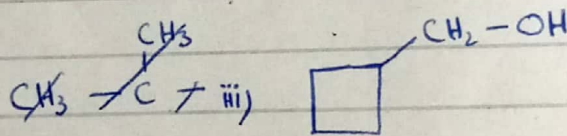
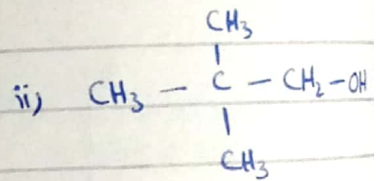
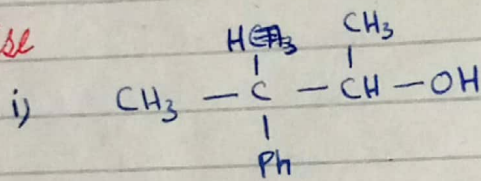
AlX<sub>3</sub> increases the polarity of R-X bond.

Tosylates are themselves good L.G.

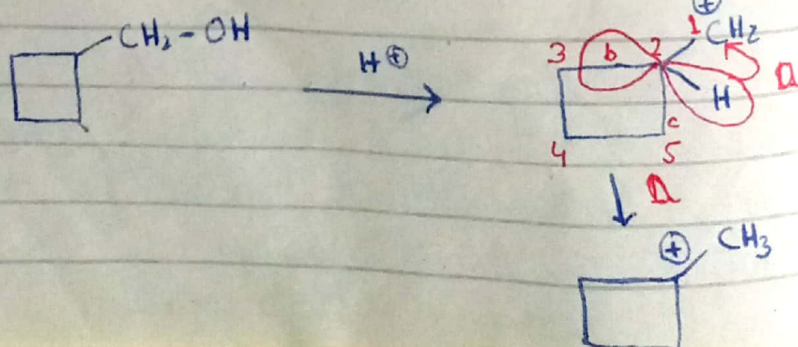
Another method is attack of electrophile on alkenes-



*Exercise*



Ans iii)

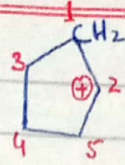




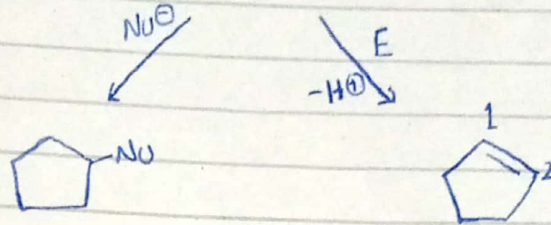
Bredt's rule

the bridgehead carbon is not involved in any reaction

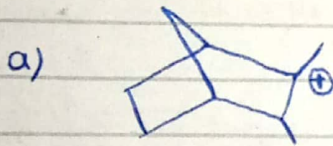
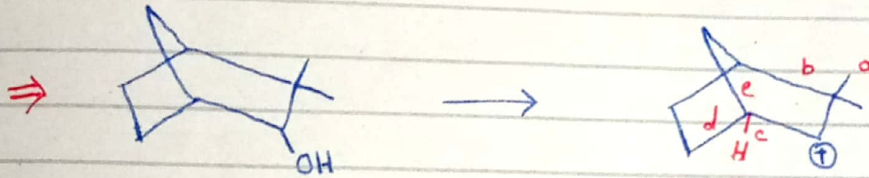
G-migration  
b/c



ring enlargement

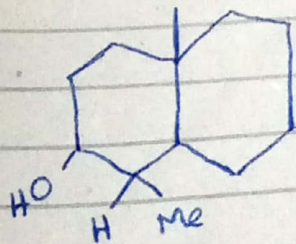


ring strain is being reduced.

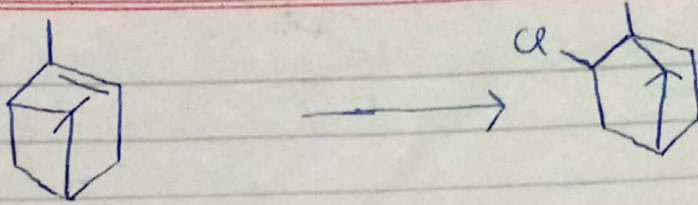


b)

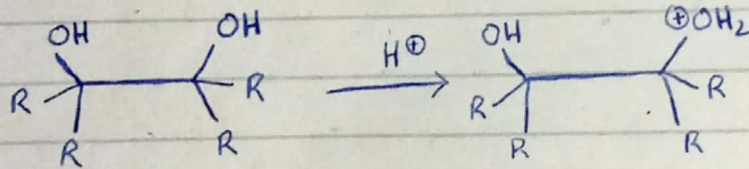
vii)



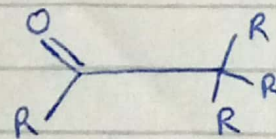
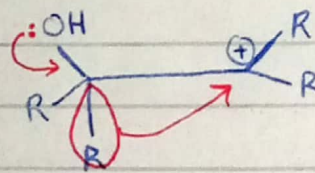
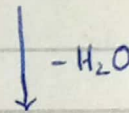
viii)



## Pinacol - Pinacolone Rearrangements

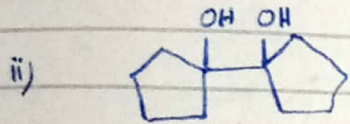
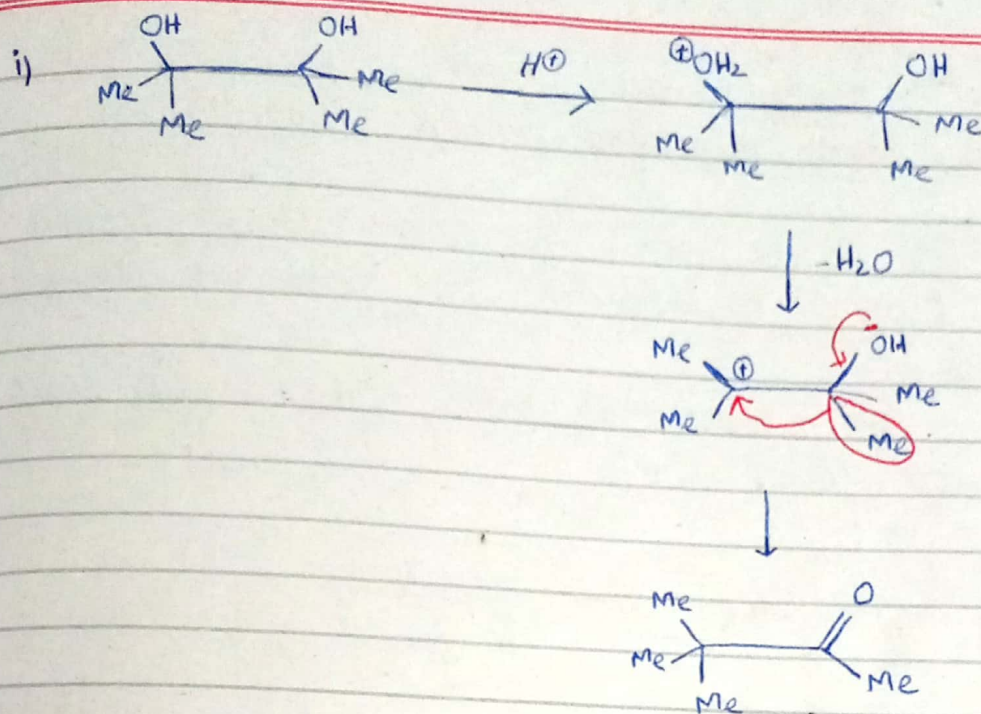


diols

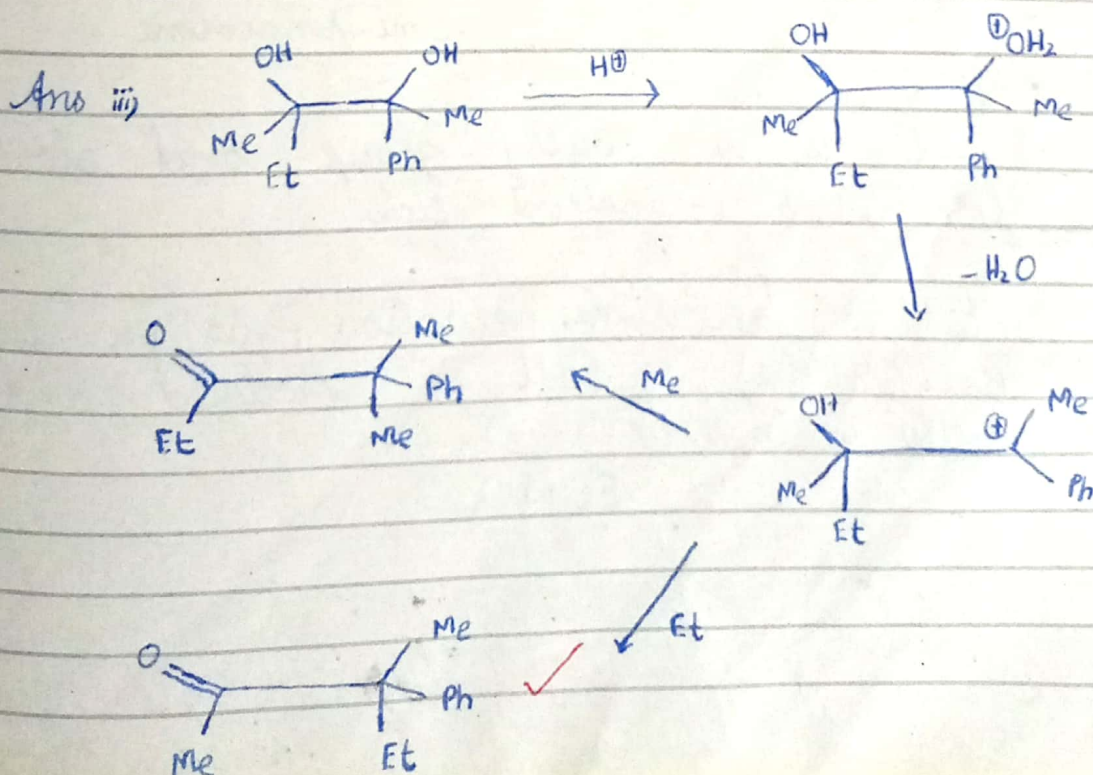
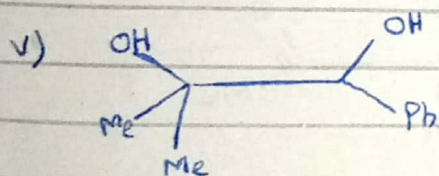
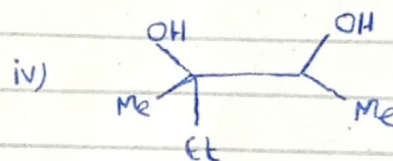
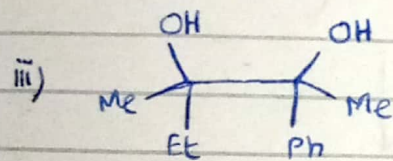


diols can be prepared by oxidation of alkenes using  $\text{KMnO}_4$  /  $\text{OsO}_4$





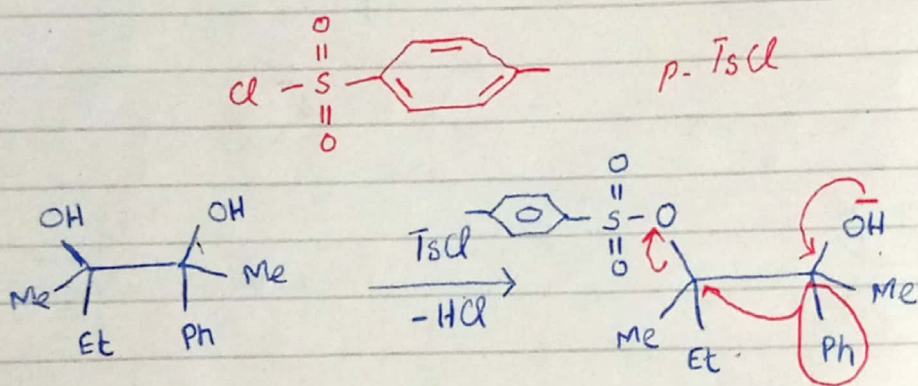
product Wagner-Meerwein



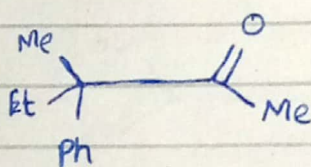
H and phenyl are good migrating groups.  
Et is <sup>better</sup> good migrating group than Me.

That OH will be removed that results  
in more stable carbocation in case of unsym-  
1,2-diols -

we use TsCl. for removing other -OH i.e less stable



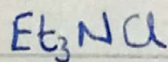
tosylate  
is a good  
L.G.



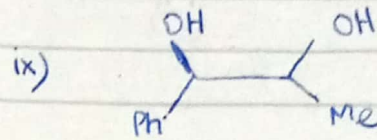
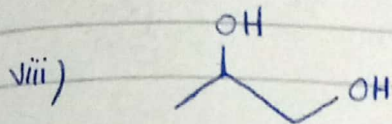
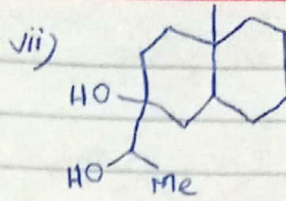
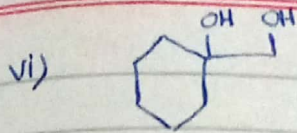
semi-pinacolone

TsCl is a bulky group and looks  
for less hindered side.

It is reversible reaction. so we use  
any Base ( $\text{Et}_3\text{N}$ ) - salt is produced and that  
settles down.

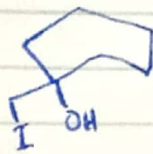




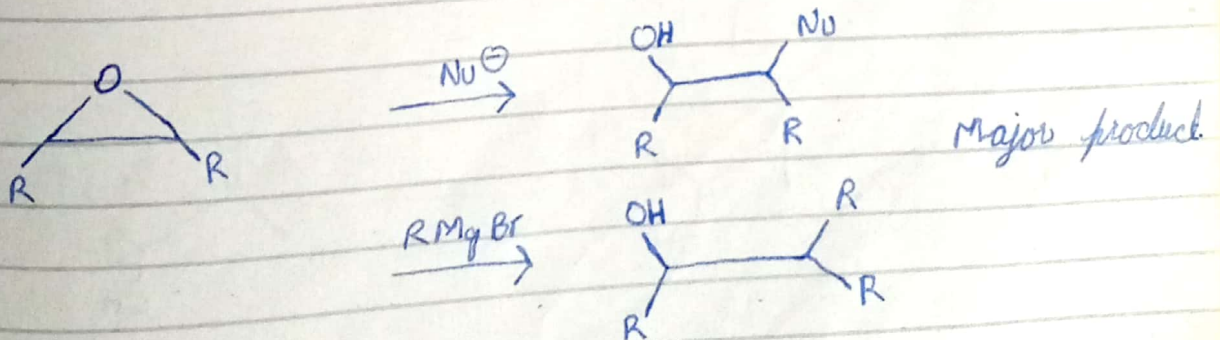
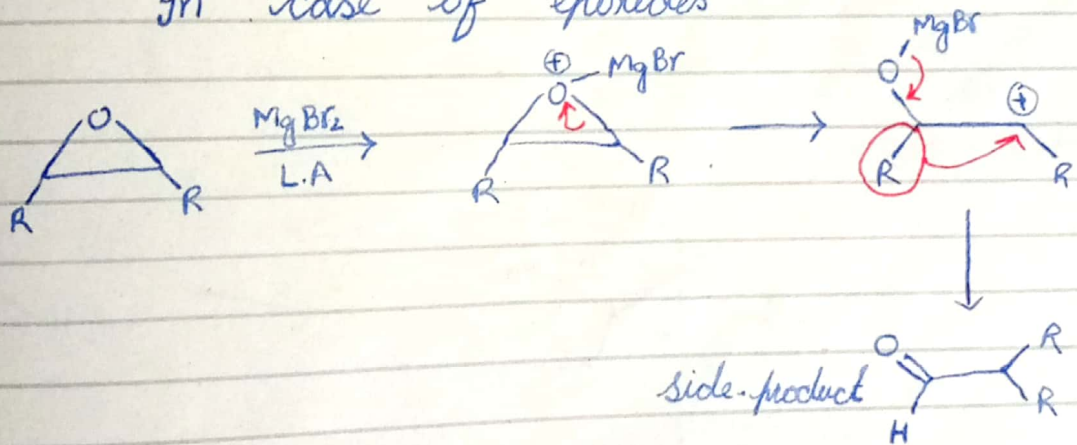


16/09/2019.

If a good L.G. is present at a position adjacent to -OH carrying carbon it is also called pinacol-pinacolone -

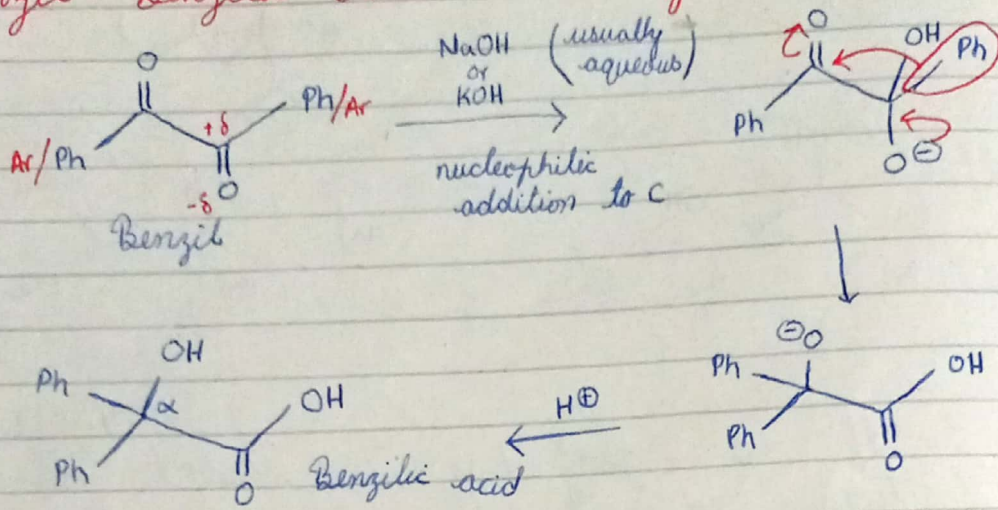


In case of epoxides

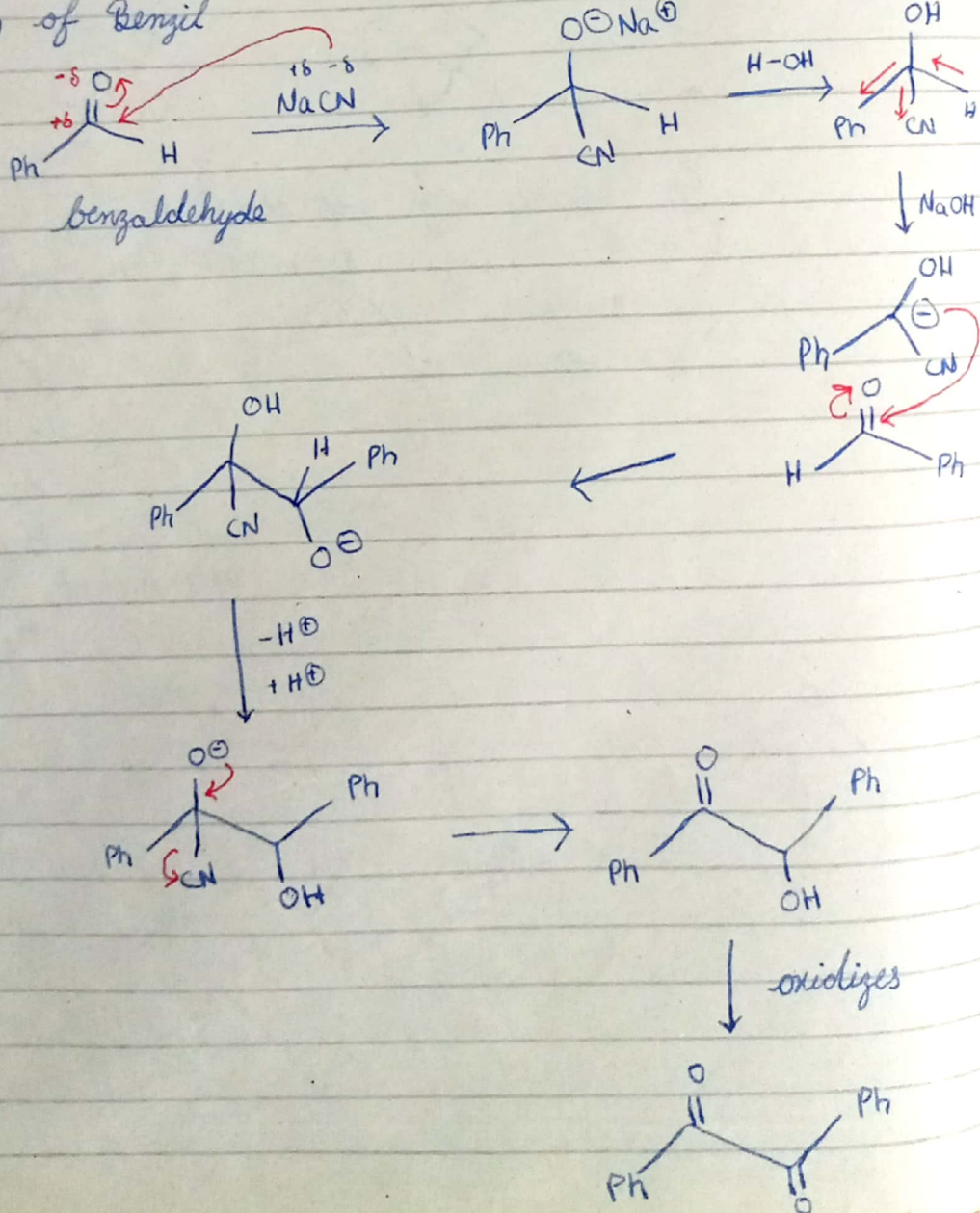


# Benzil - Benzilic Acid Rearrangement

March's 5<sup>th</sup> ed  
1402

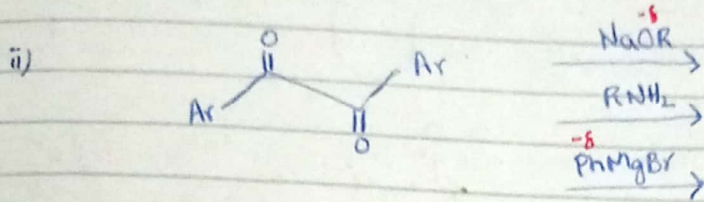
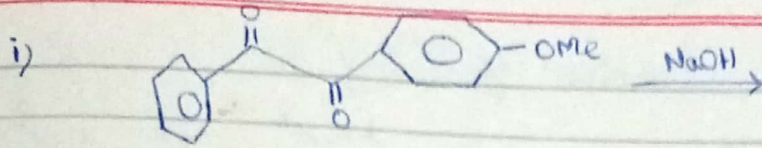


## Preparation of Benzil

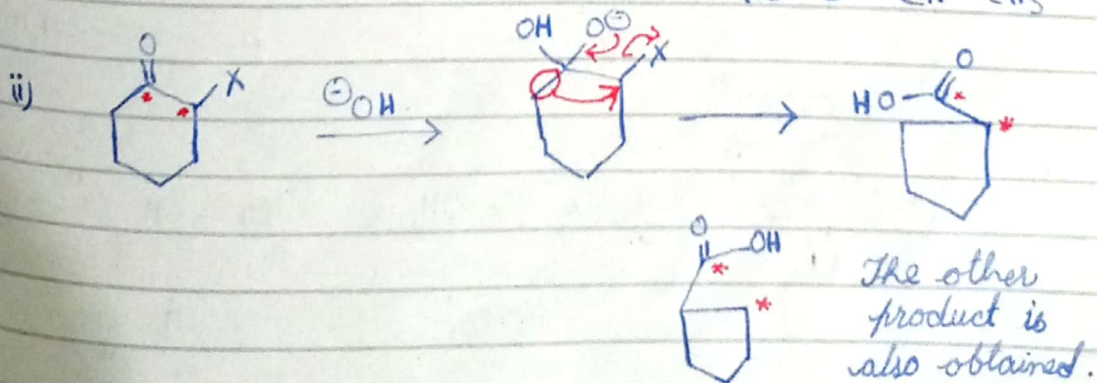
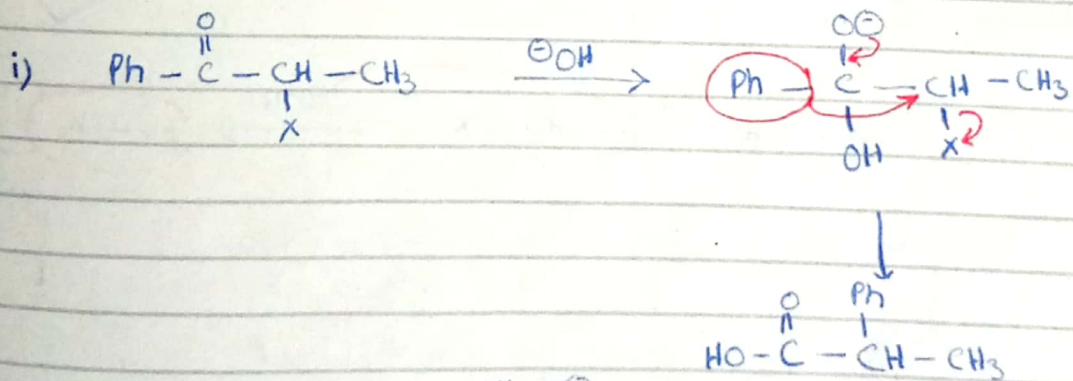
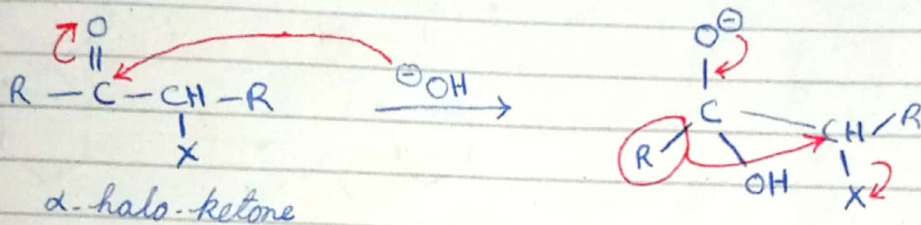




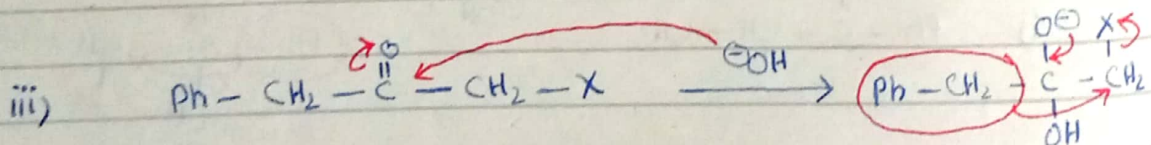
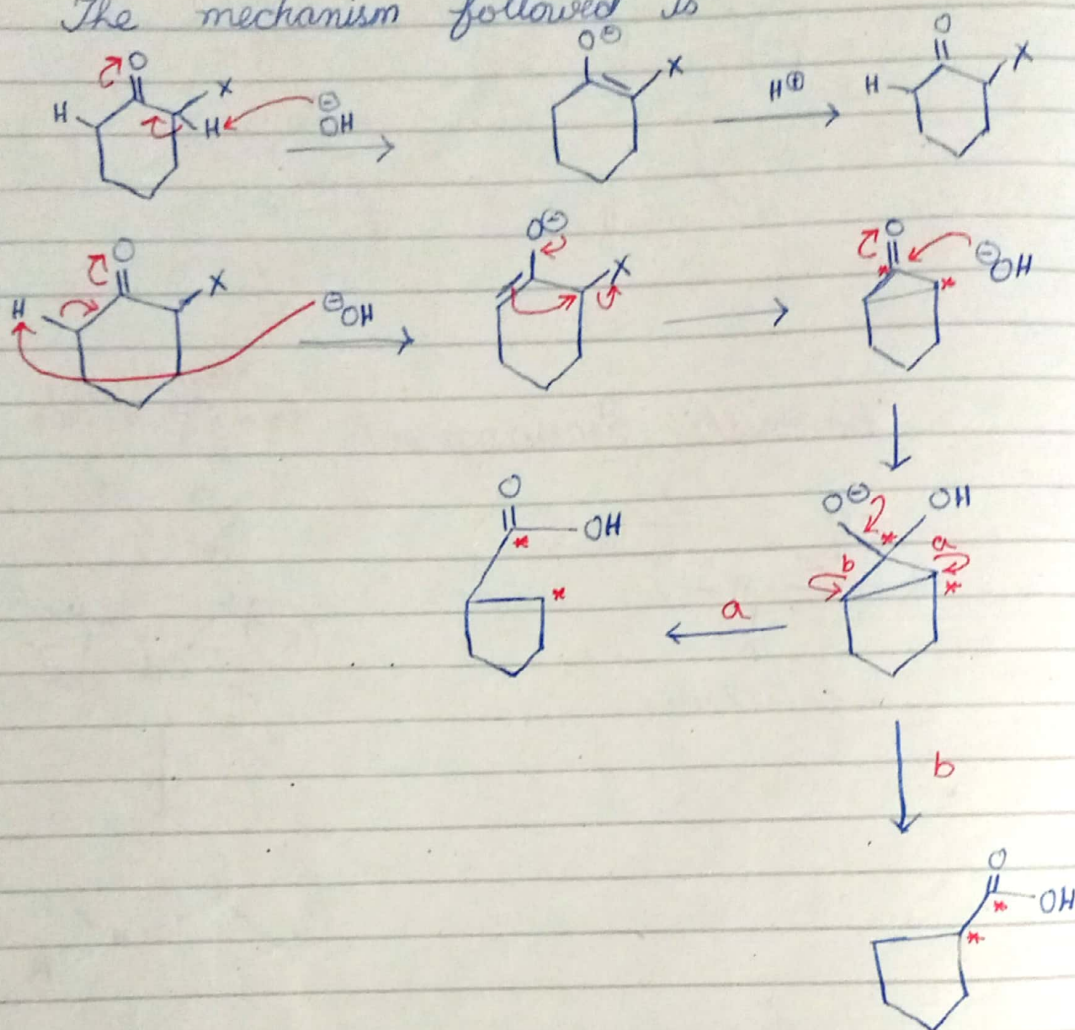
Electrophilic carbon of one benzaldehyde is connected to electrophilic carbon of other. This is done using CN which is then removed.



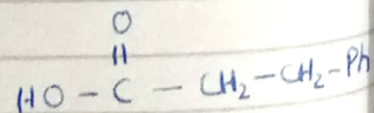
**Favorskii Rearrangement** 19/09/2019  
March's 5th ed 1403



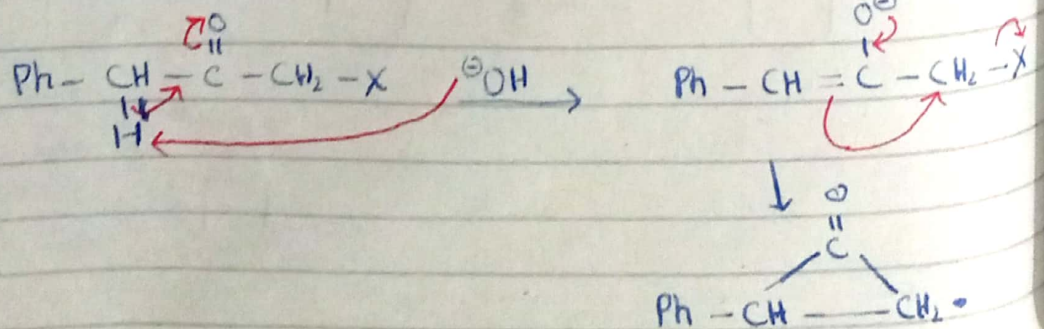
The mechanism followed is



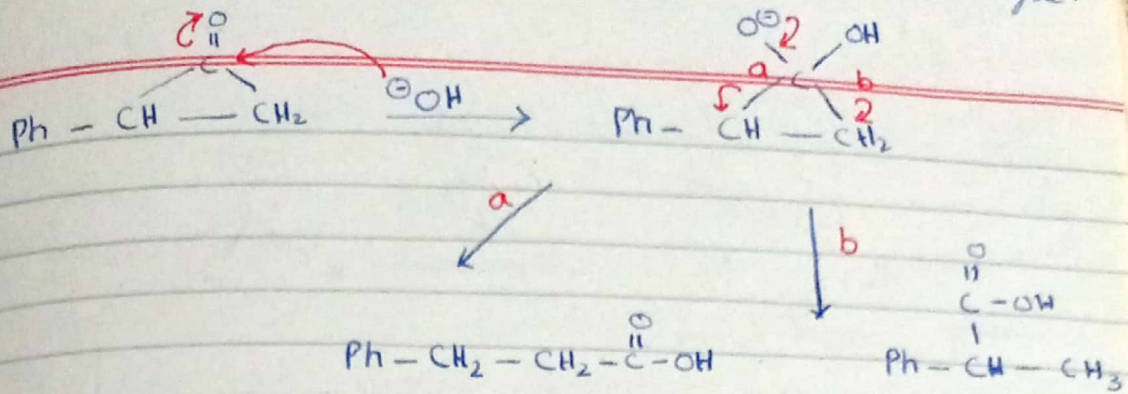
conventional



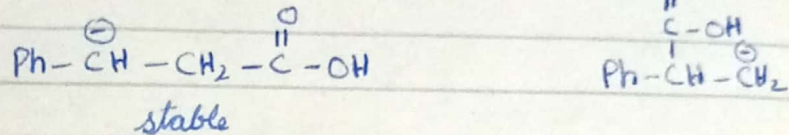
modern



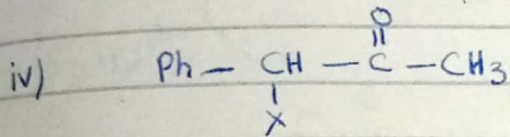




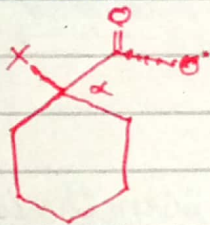
The intermediates involved are



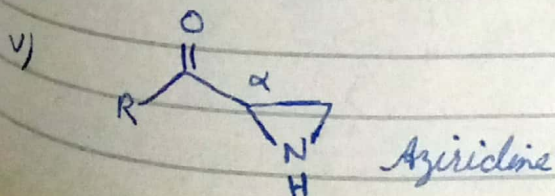
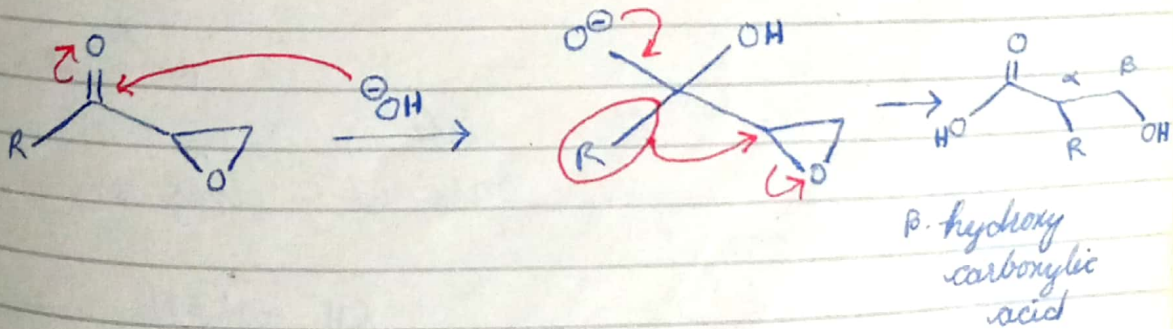
so a is major product.



if no  $\alpha$ -hydrogen is available, conventional mechanism is followed. This situation is called quasi-favorski -



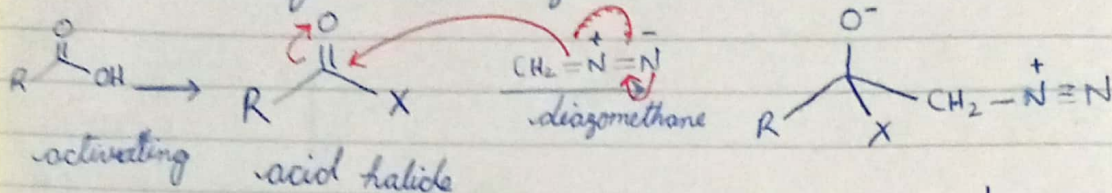
X be any good leaving group like  $\text{OR}^-$ ,  $\text{NH}_2^-$  etc.



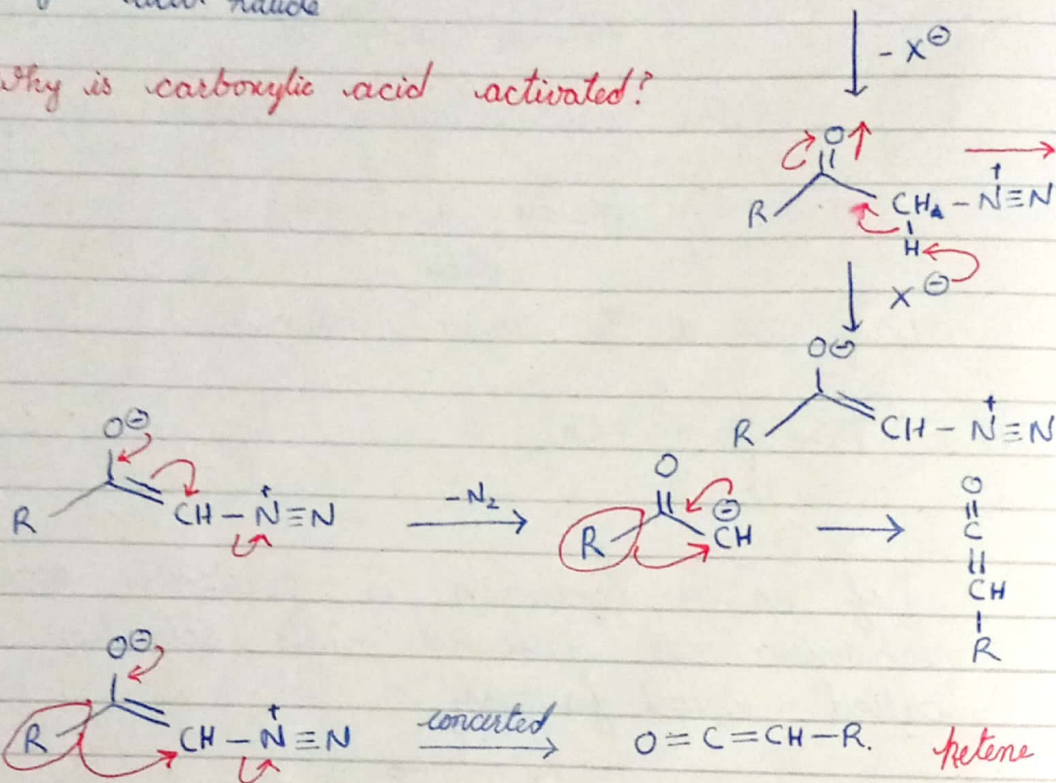
unsaturated groups are E.W.G.

20/09/2019

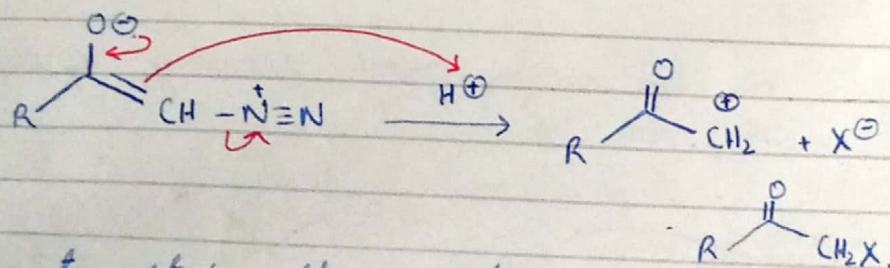
### ✓ Wolf Rearrangement



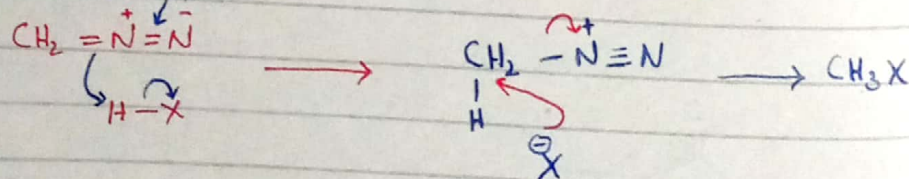
Q Why is carboxylic acid activated?



### Arnold-Ester synthesis

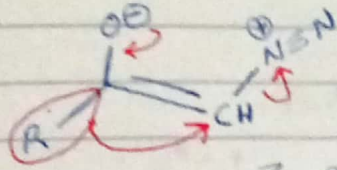


to stop this side reaction, we use base. we use excess of diazomethane

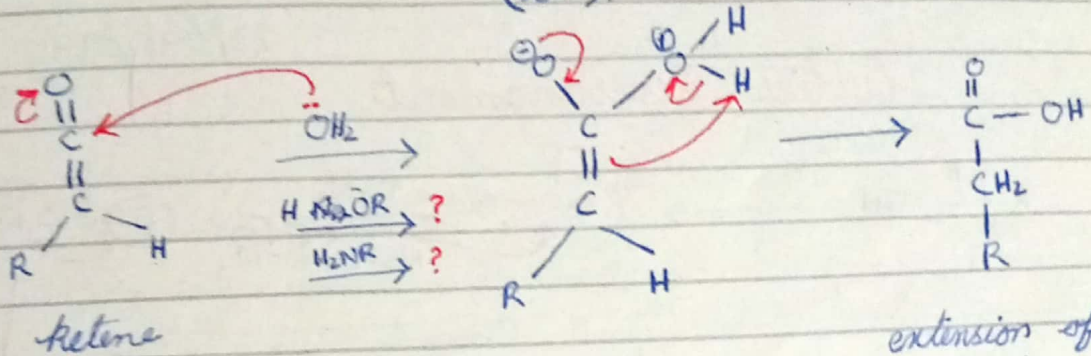




for concerted mechanism

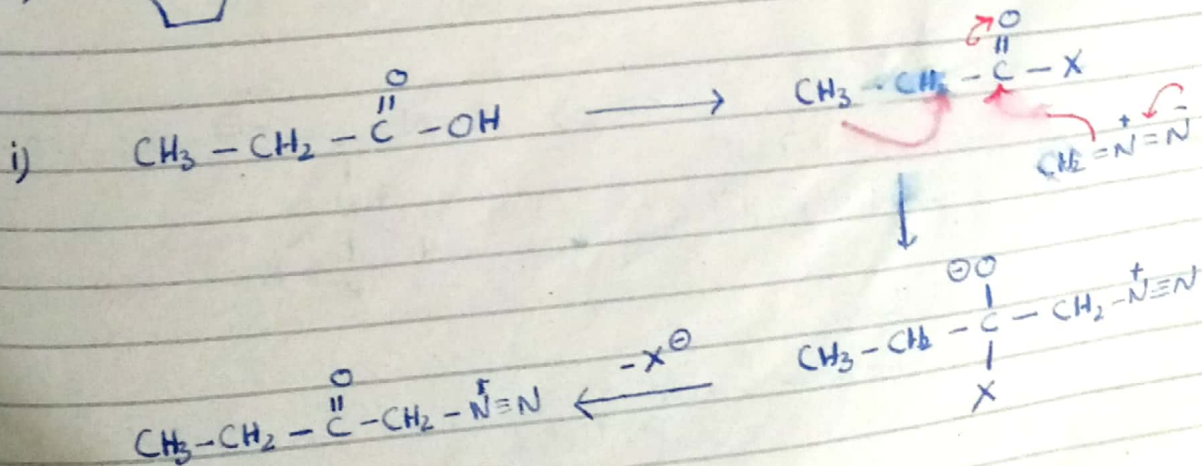
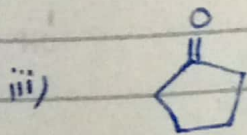
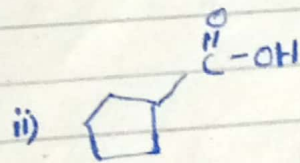
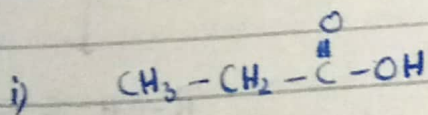
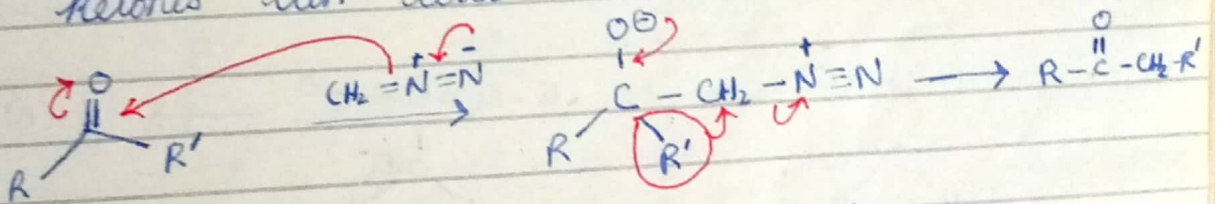


Z-enolate  
anti-periplanar for best elimination  
(180°).

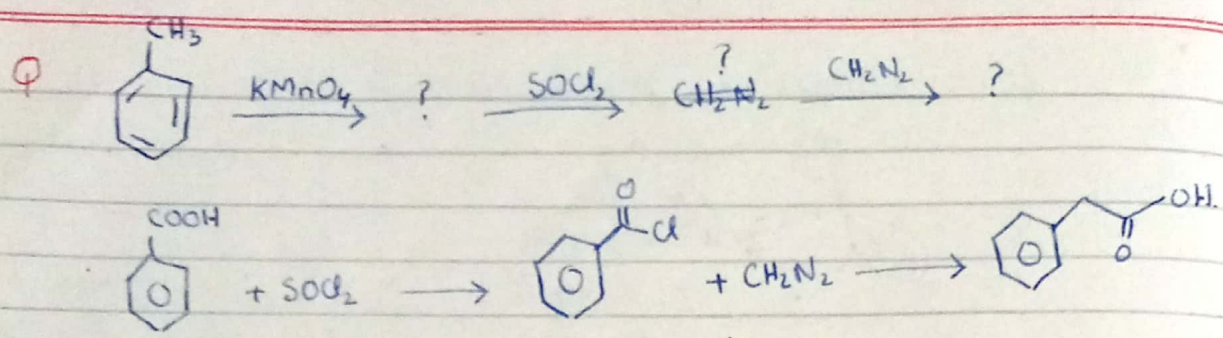


extension of  
carboxylic  
acid -

ketones can also be used.

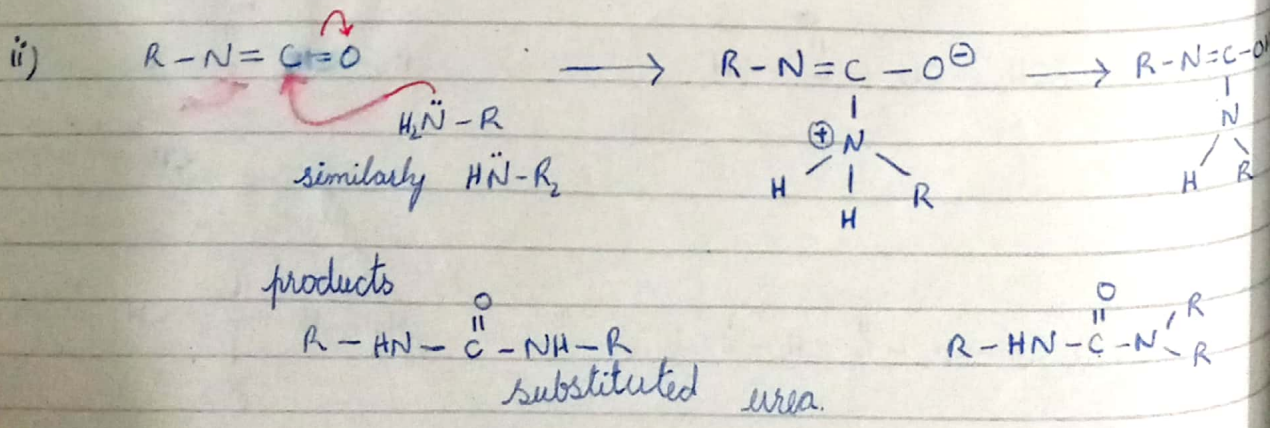
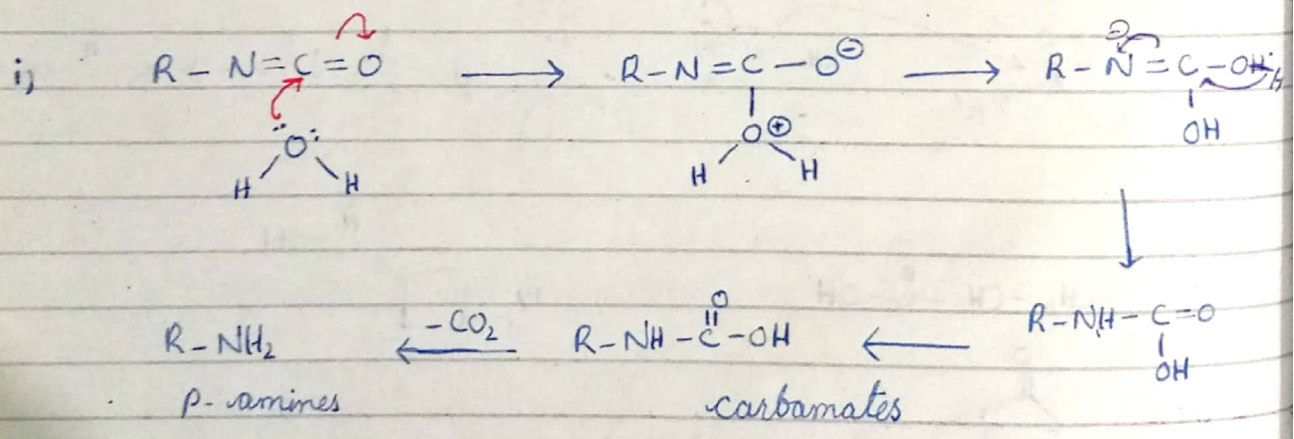
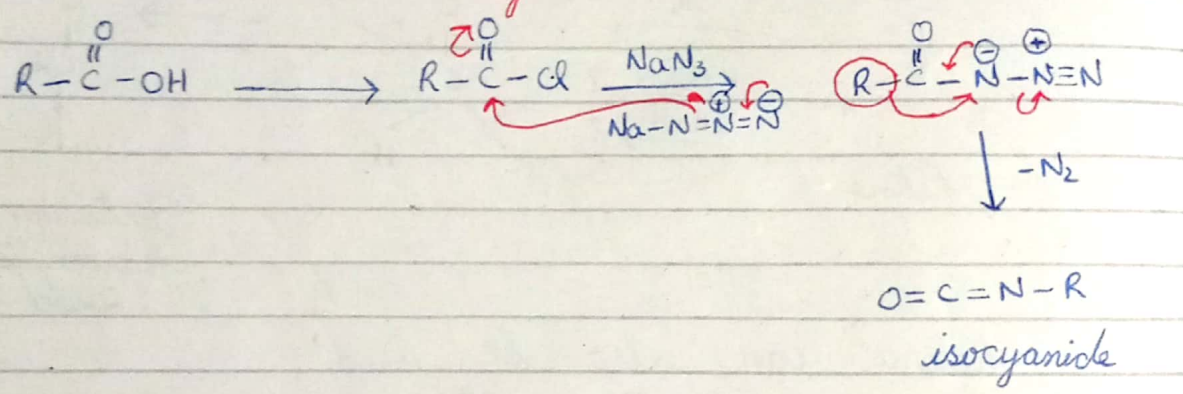


esters don't release CO<sub>2</sub>. They are first hydrolyzed and converted into carboxylic acids -



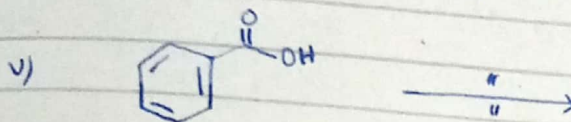
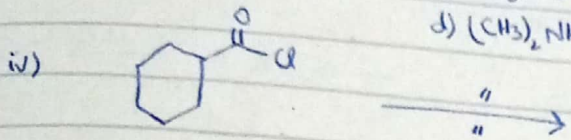
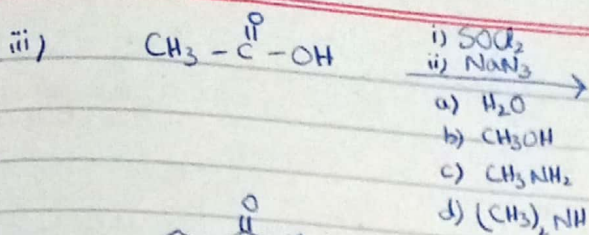
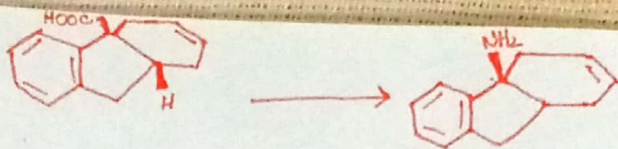
23/09/2019.

✓ Curtius Rearrangement



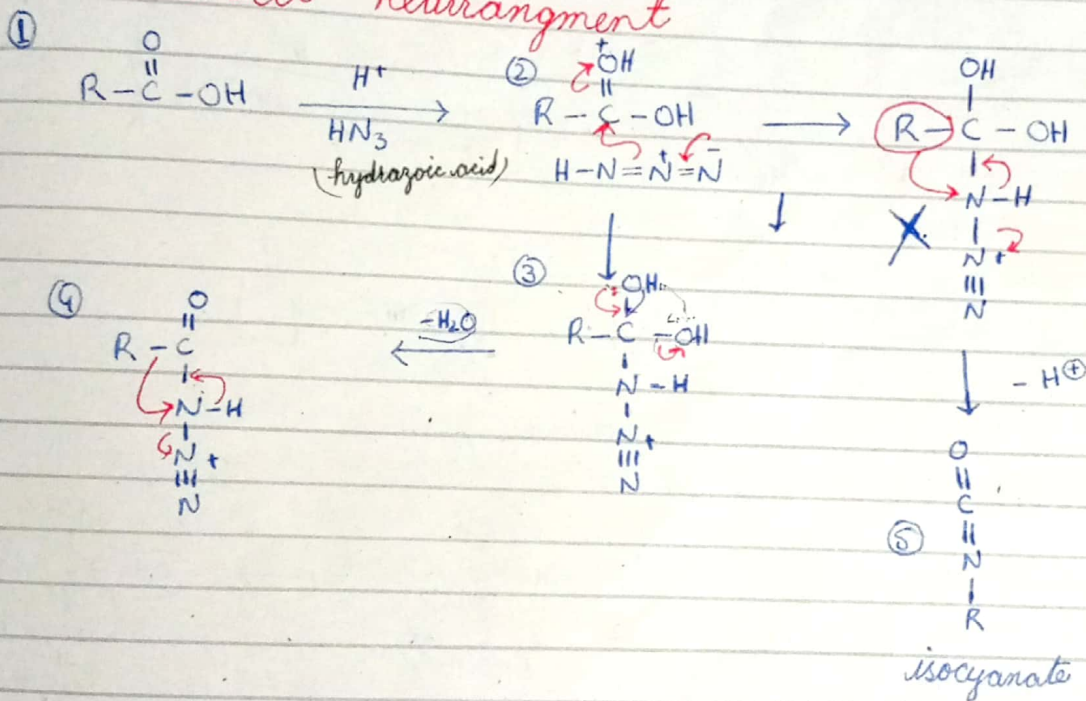


example of Curtius

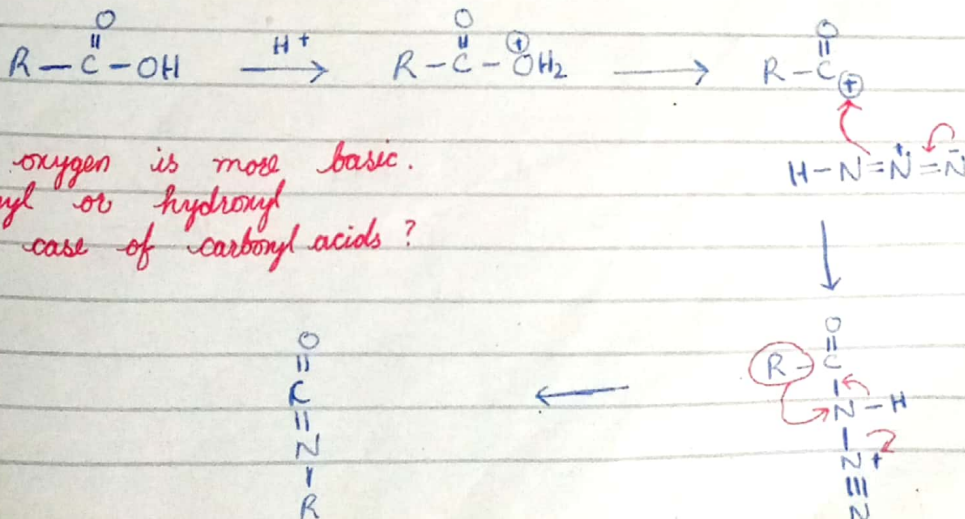


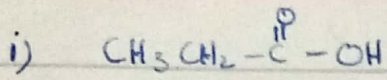
## ✓ Schmidt Rearrangement

26/09/2019

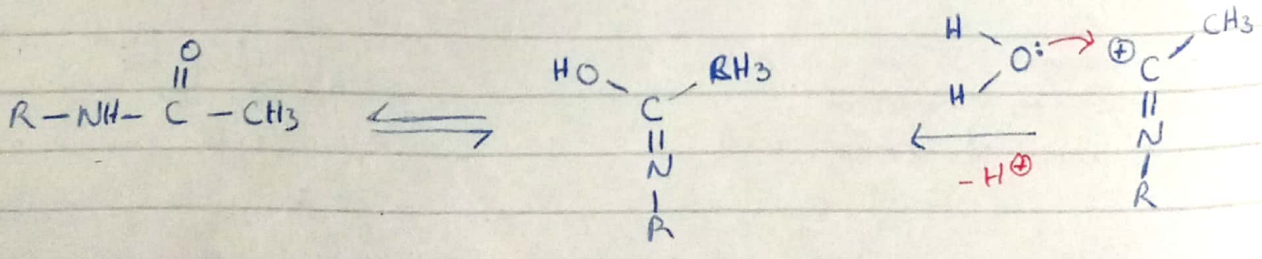
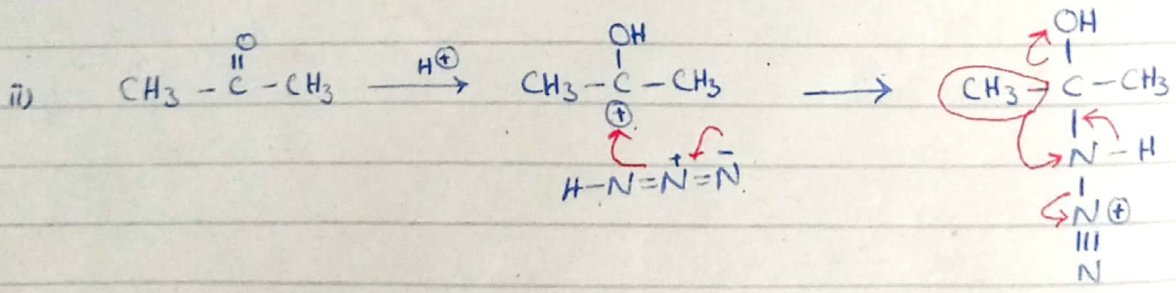
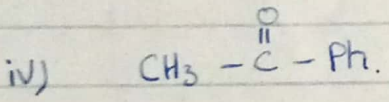
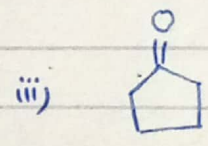
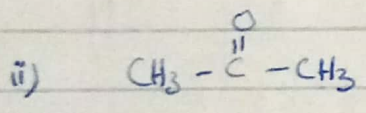
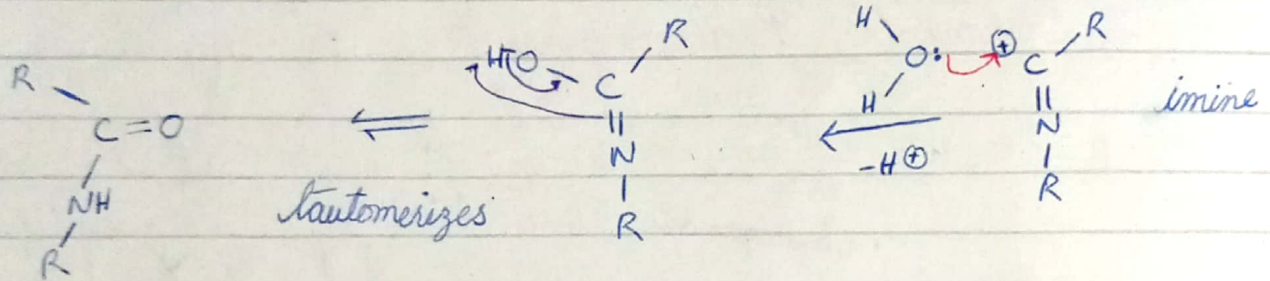
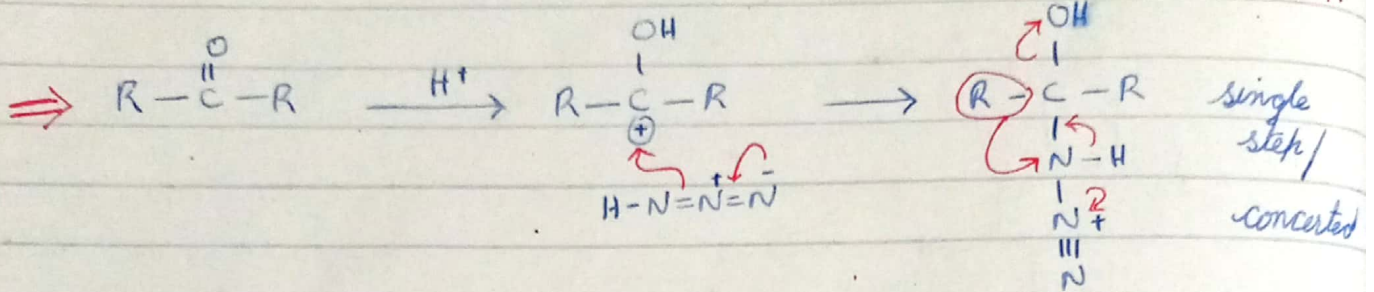


2<sup>nd</sup> mechanism

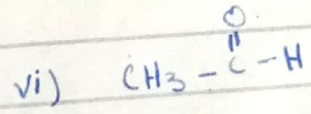
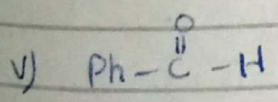
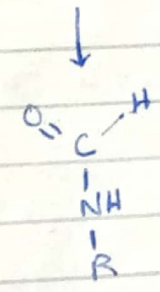
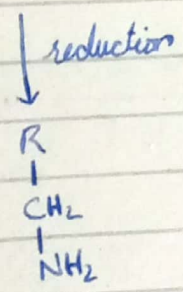
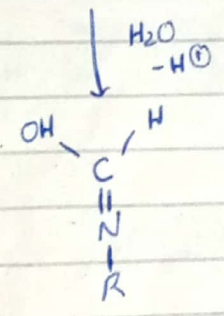
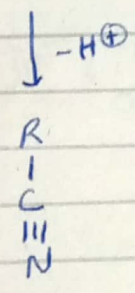
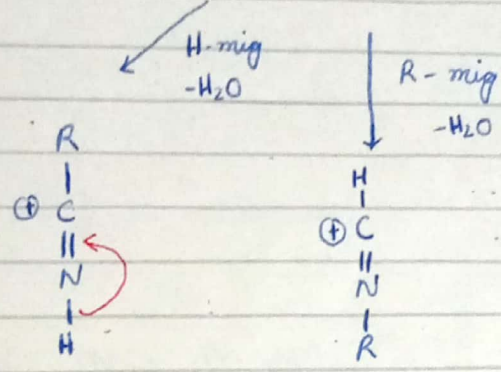
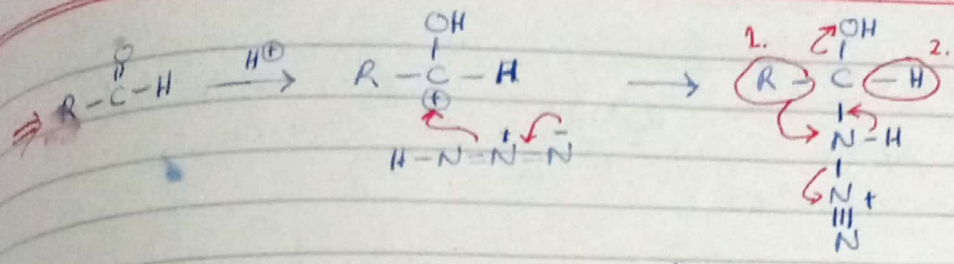




How -OH leaves  
as it is not good  
L.G.?

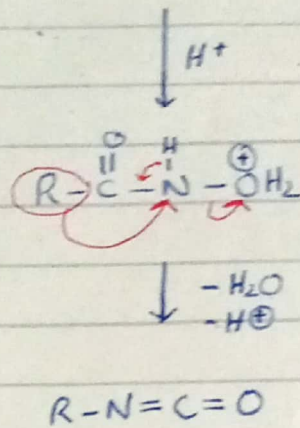
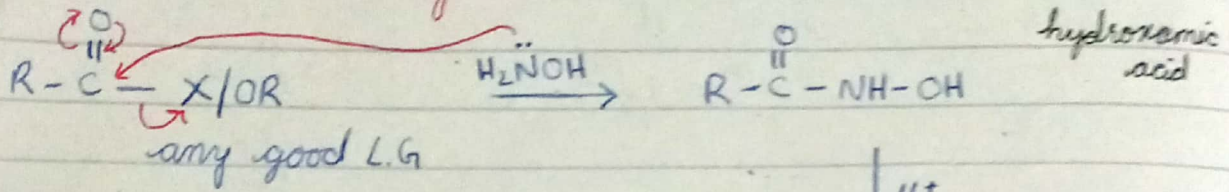




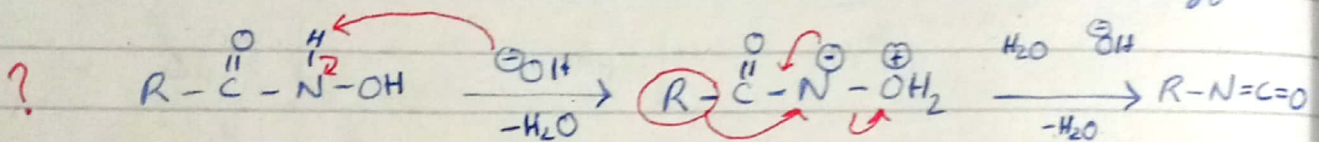


27/09/2019

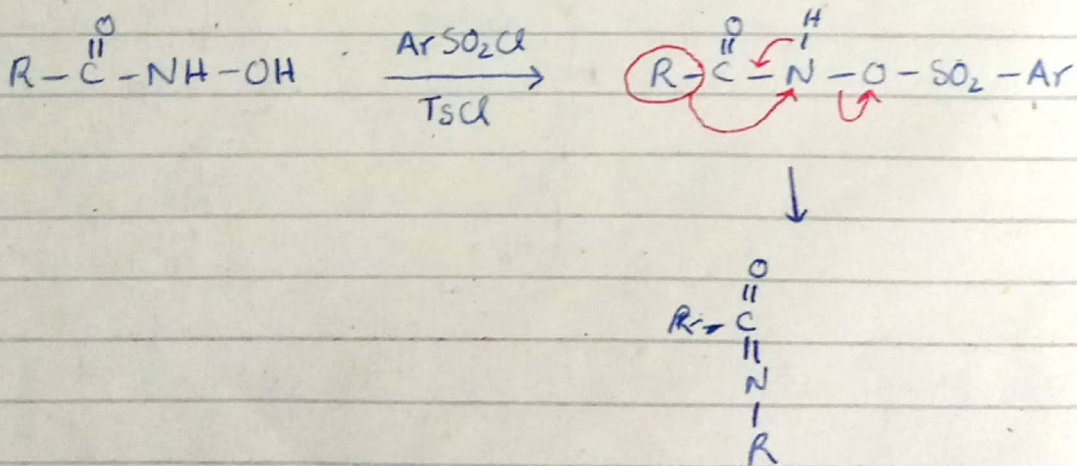
# ✓ Lossen Rearrangement



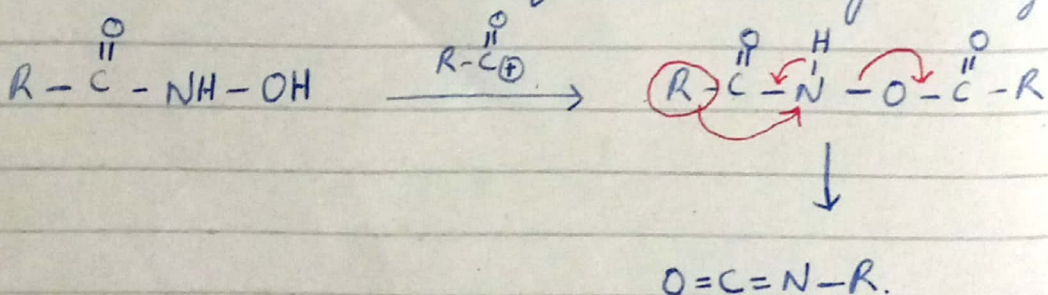
The reaction can also be base catalyzed-



Another modification is



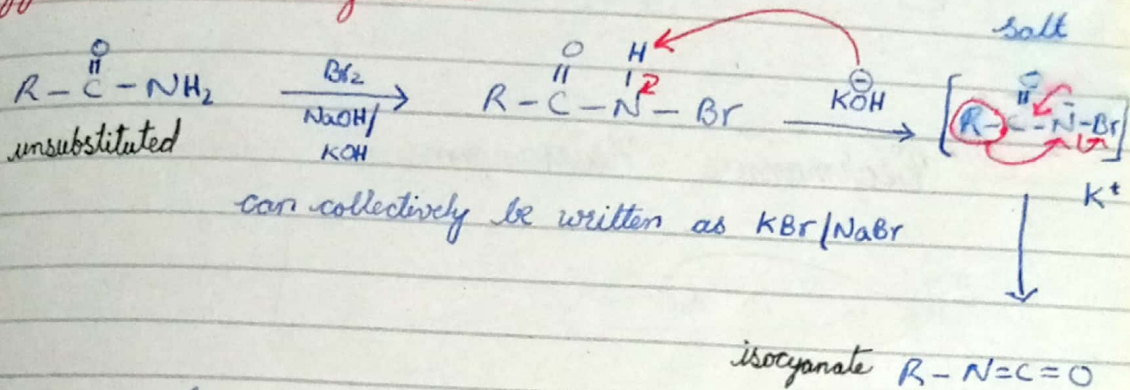
can also be performed using acylation



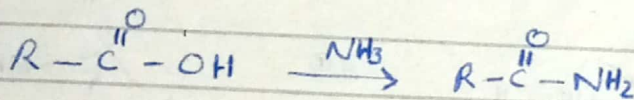


We can catalyze this reaction by adding a small base as a proton has to be extracted -

### Hoffman Rearrangement

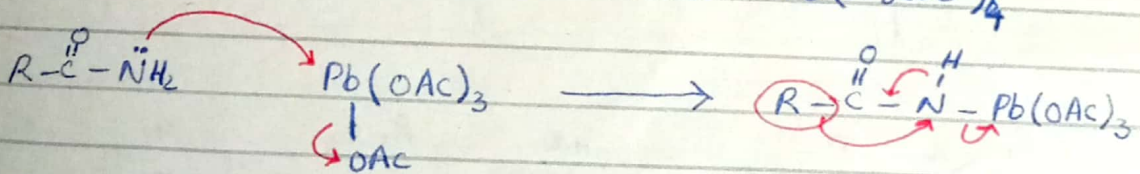


if we have carboxylic acid, we will convert it into amide -

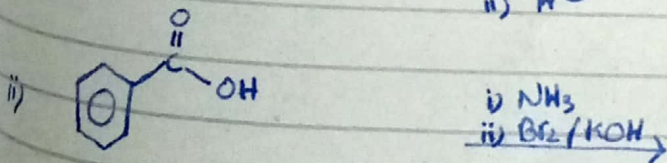
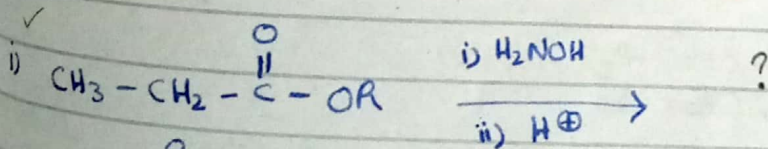


modification is

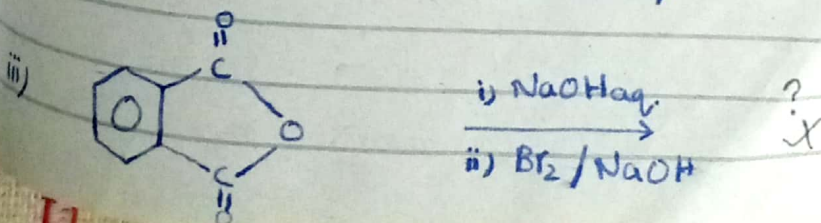
we use  $\text{NaOBr}$  and  $\text{Pb}(\text{CH}_3\text{COO}^-)_4$



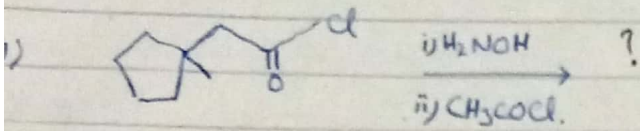
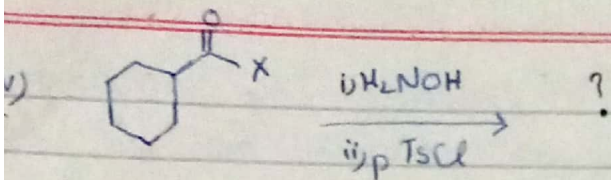
\*  $\text{Br}_2$  has an irritating smell and so reaction becomes difficult - so to avoid this we use  $\text{NaOBr}$ . The reaction is easy to perform -



Caravon's pg 371.

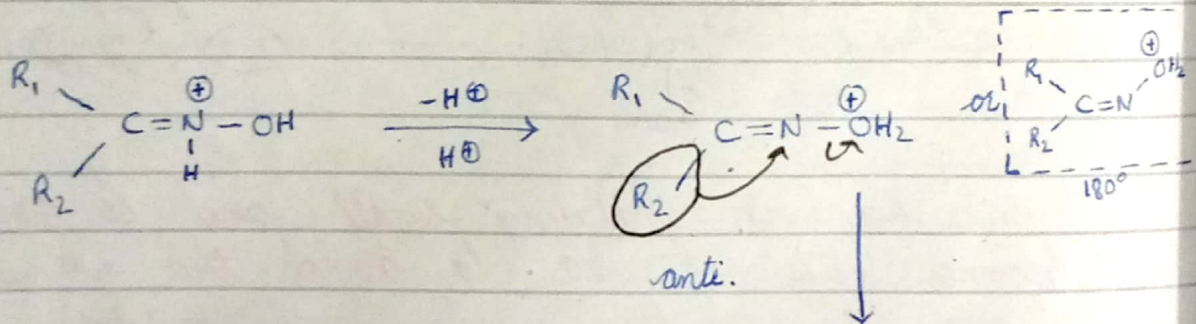
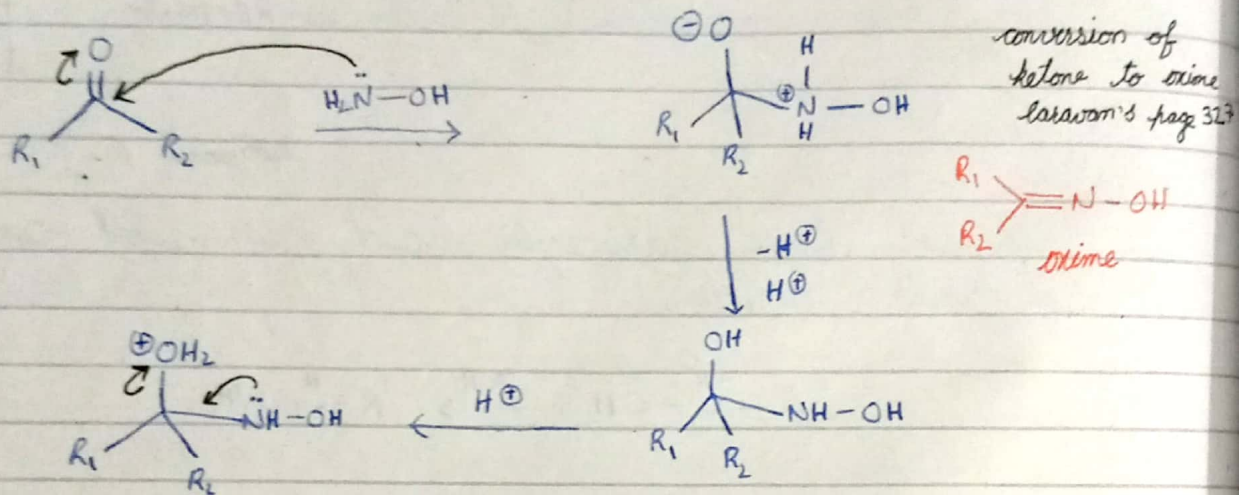


Caravon's Pg 377



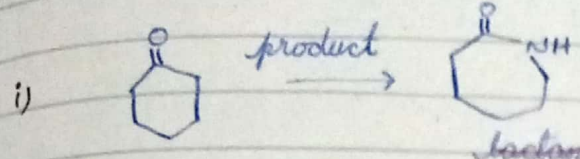
30/09/2019.

✓ Beckmann's Rearrangement *Clayden's 958*

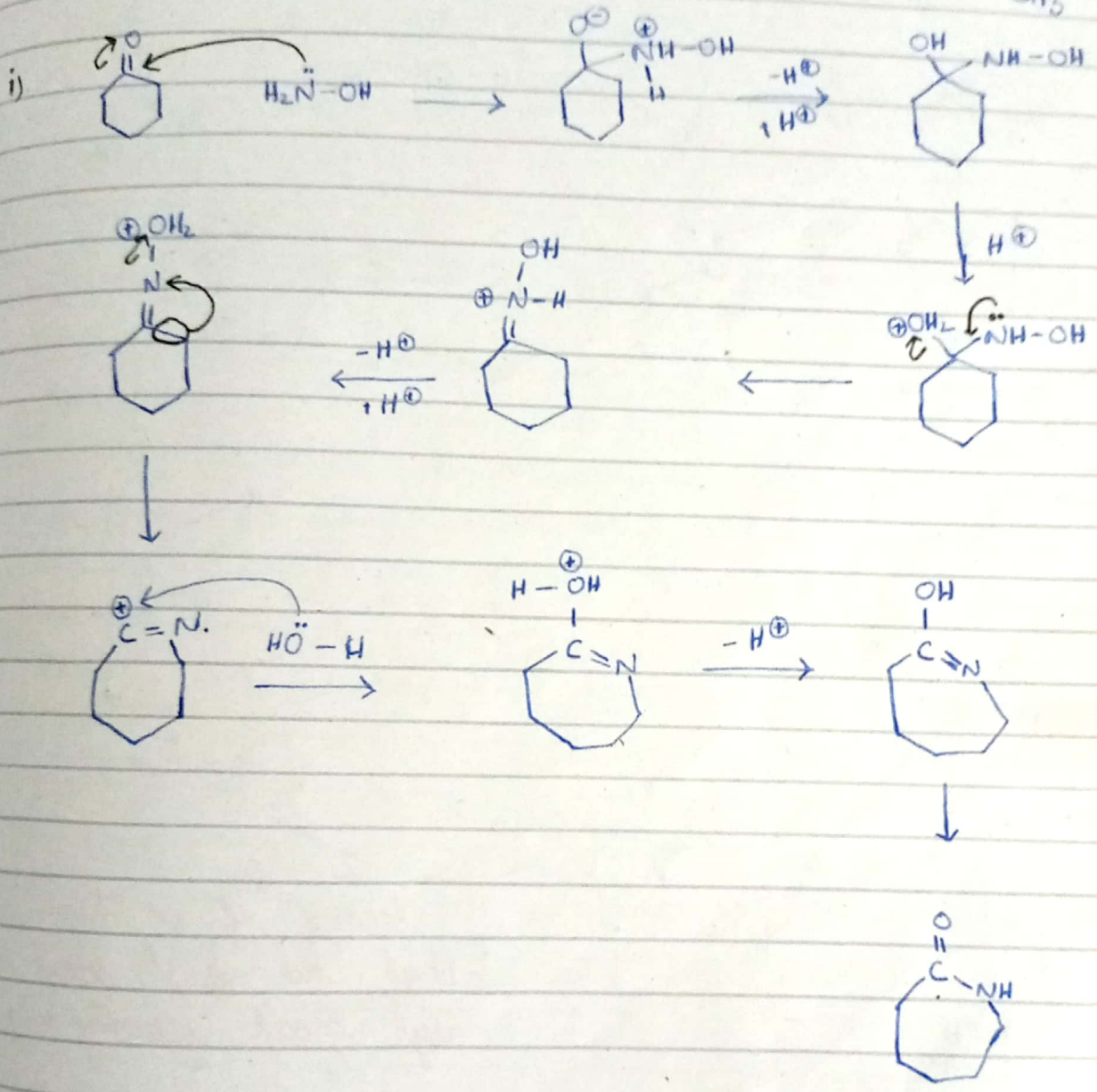




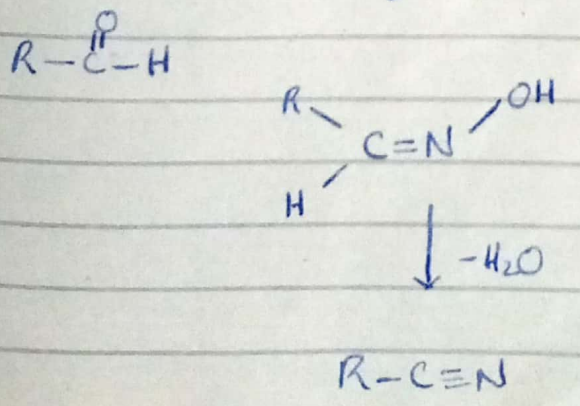
\* This reaction was used to determine the geometry. The R group that was part of ammonia would have been at anti position.



lactams lactams.



in case of aldehydes.

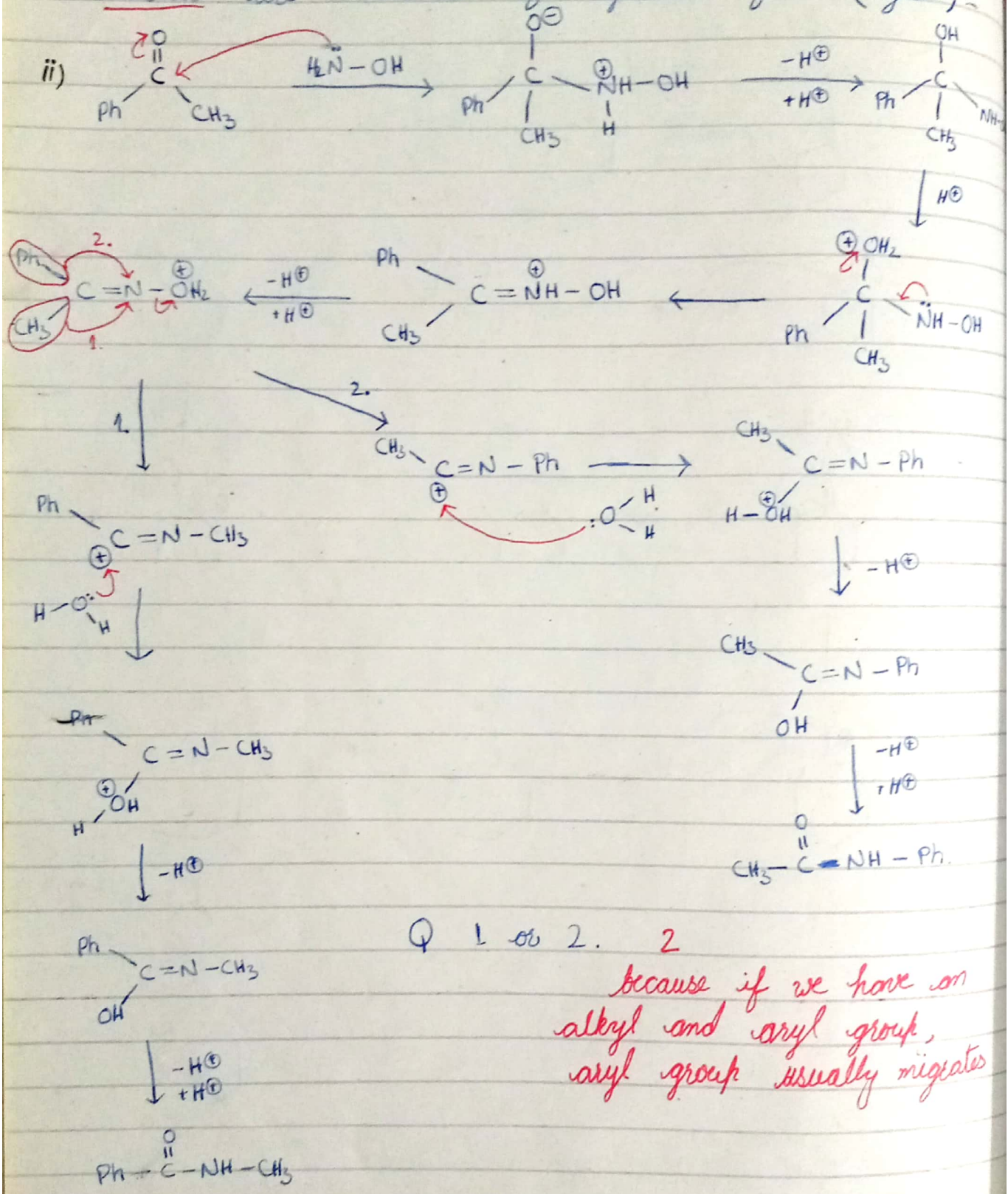


H seldom migrates ....

no migration why beckmann's rearrangement is not observed with oximes from aldehydes?

Lactams

Lactams are monomers of synthetic fibres (nylon) -



Q 1 or 2. 2

because if we have an alkyl and aryl group, aryl group usually migrates

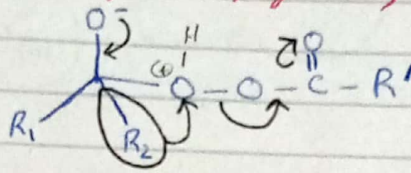
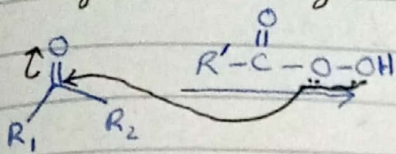


Which oxygen of percarboxylic acid is more nucleophilic?

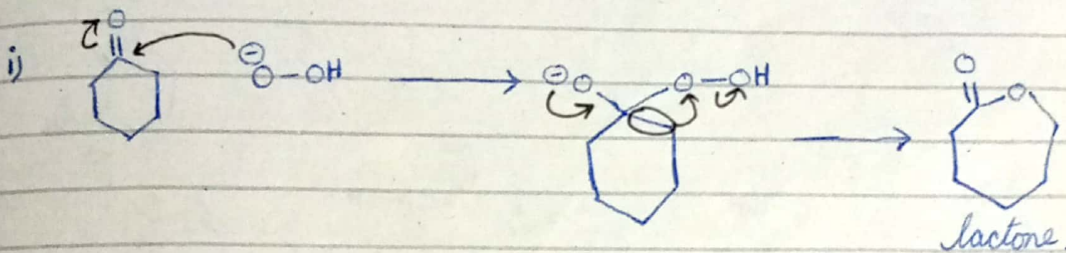
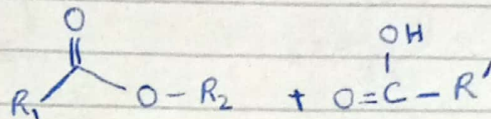
03/00/2019.

✓ Baeyer's villiger

(Clayden's page 953) March's (1368) Ed. 7

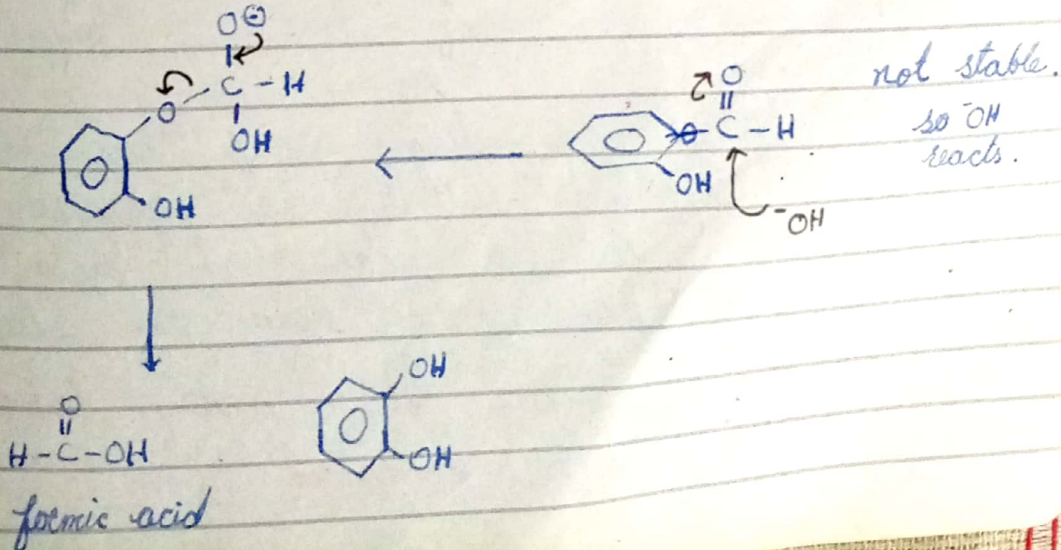
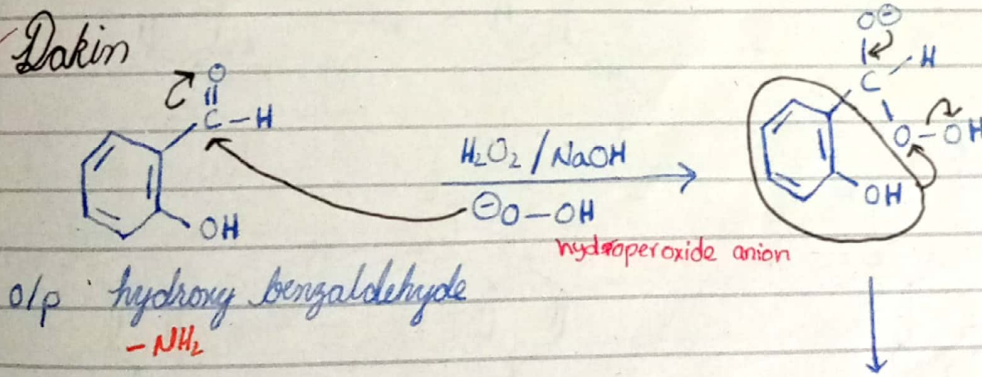


H<sub>2</sub>O<sub>2</sub> can also be used in place of peracids  
 $\text{HO-OH} \xrightarrow{\text{NaOH}} \ominus\text{O-OH}$

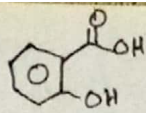
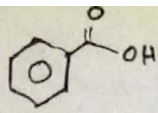


no external reagent is used for leaving -OH, because we used base first that produced water. This water acts as acid and donates a proton to OH.  
 for unsymmetrical ketones, the approximate order of migration is **tert.alkyl > sec.alkyl > aryl > p.alkyl > methyl**

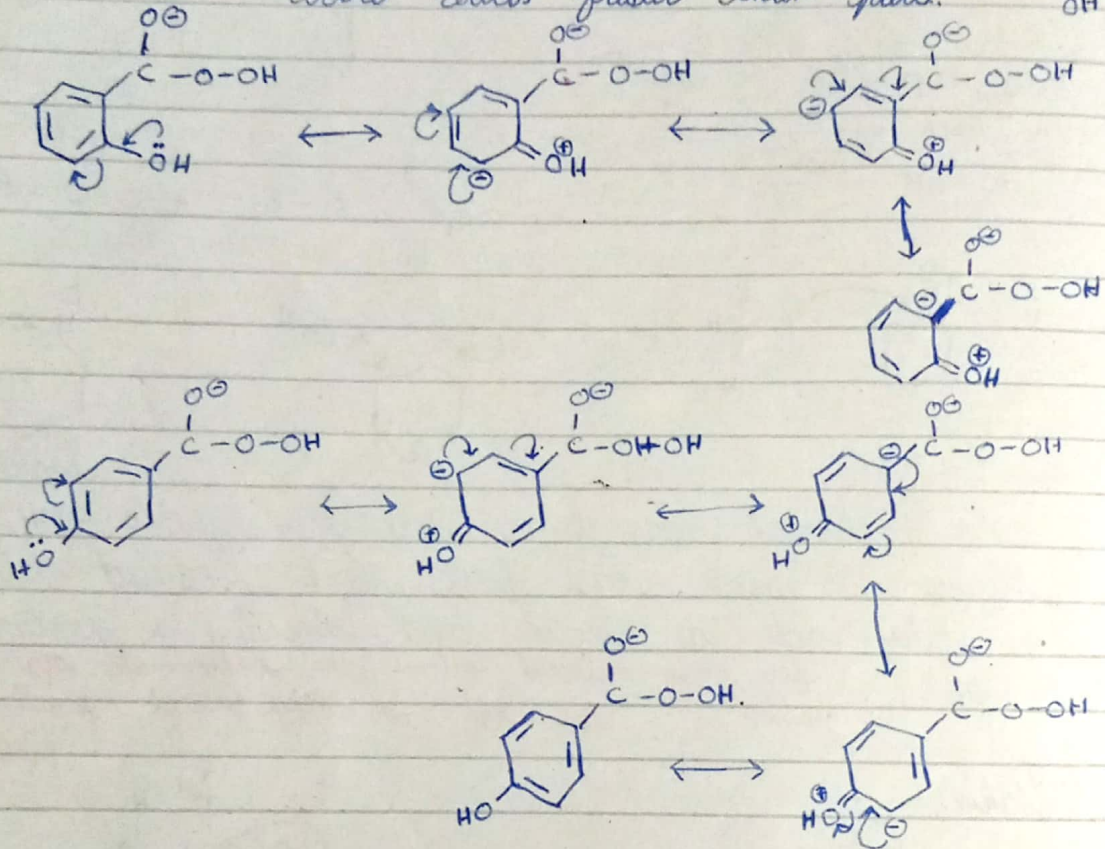
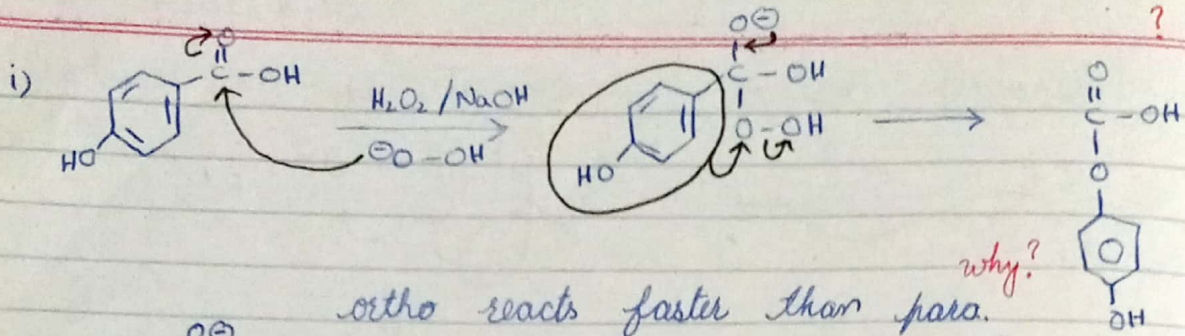
✓ Dakin



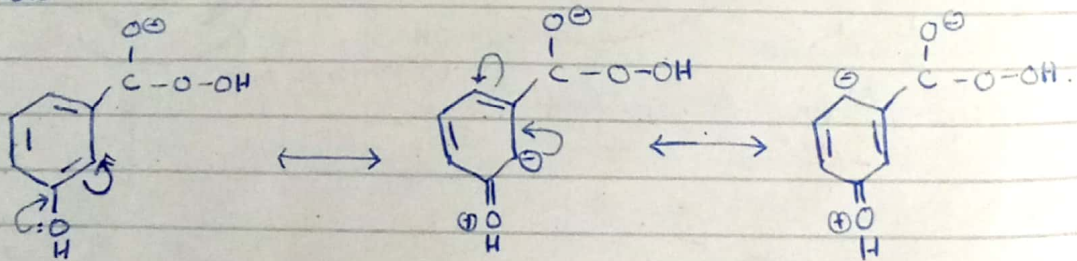




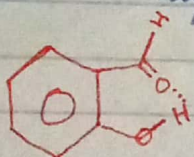
which is more acidic?



meta

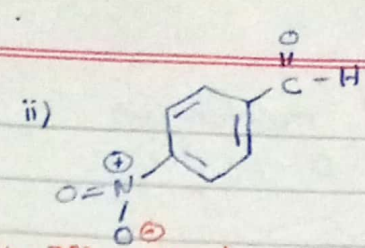
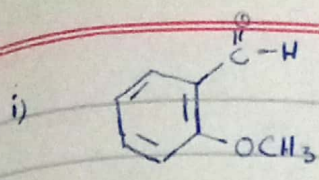


That migrating group has better migrating aptitude that has greater electron density - so in case of meta -H is better migrating group than the other group.



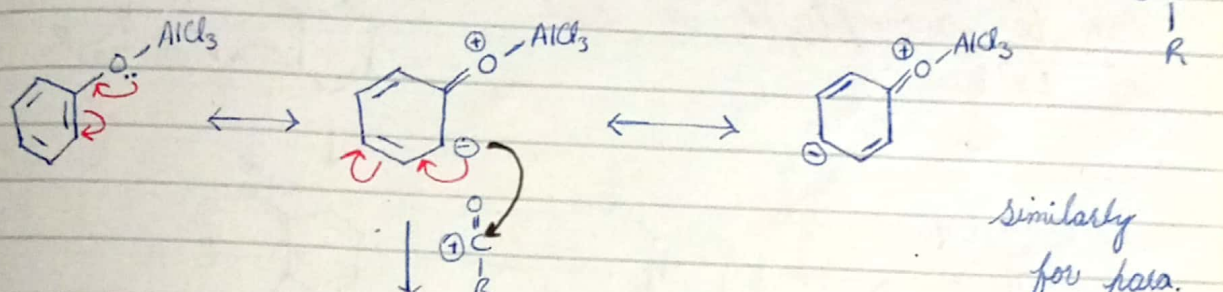
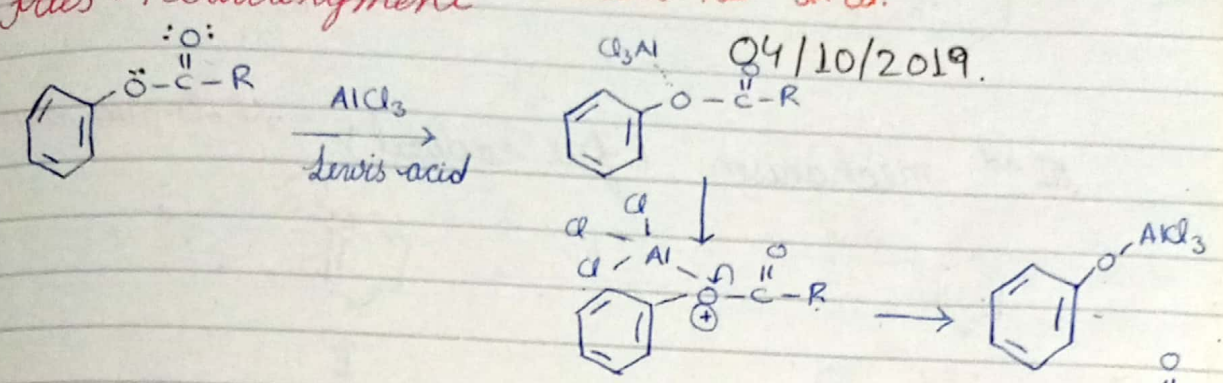
because of H-bonding, carbon's electrophilicity is enhanced.



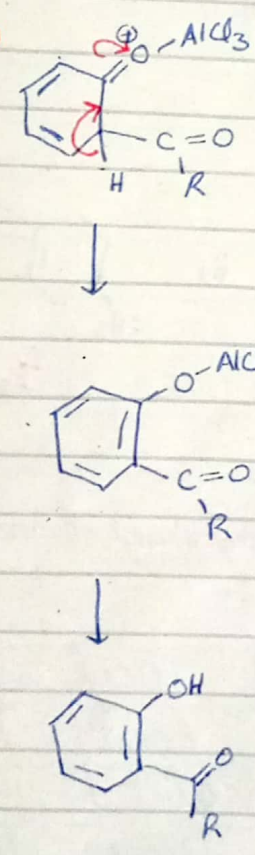


*Fries Rearrangement* March's 752 5th ed.

04/10/2019.



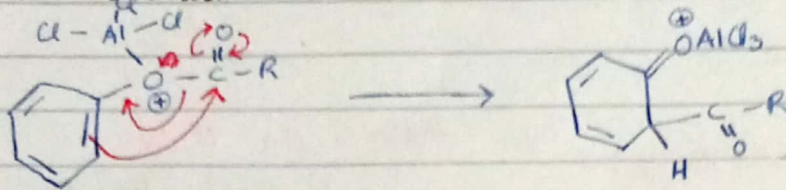
electron withdrawing groups at ring interfere with the reaction.



Q can protic acids be used instead of Lewis acids?

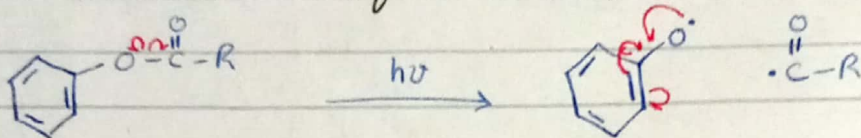
The ortho-para ratio depends on the temperature, solvent and amount of catalyst used.

II<sup>nd</sup> mechanism

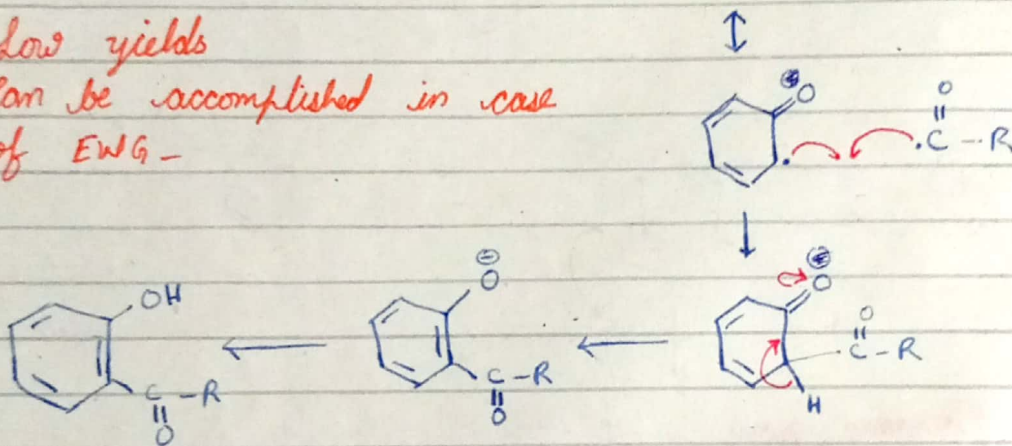


III<sup>rd</sup> mechanism (free radical)

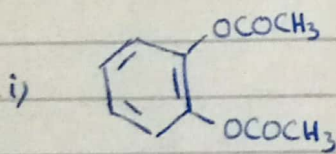
photo-fries rearrangement



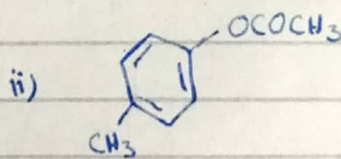
low yields  
can be accomplished in case  
of EWG-



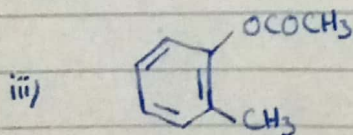
examples.



1,2-diacetonylbenzene



3-methyl phenyl ethanoate.



2-methyl phenyl ethanoate.

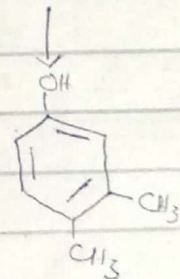
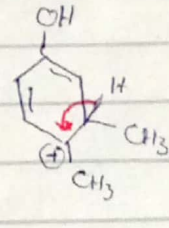
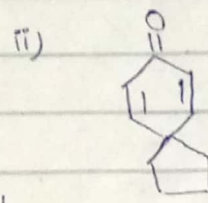
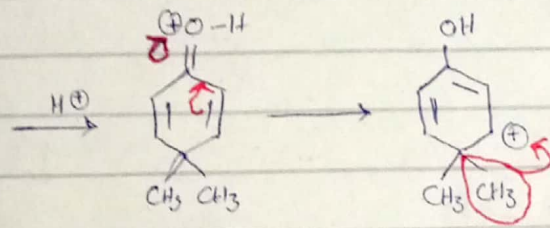
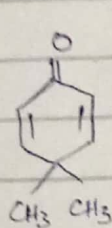
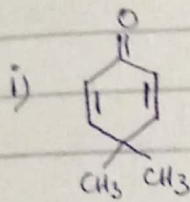
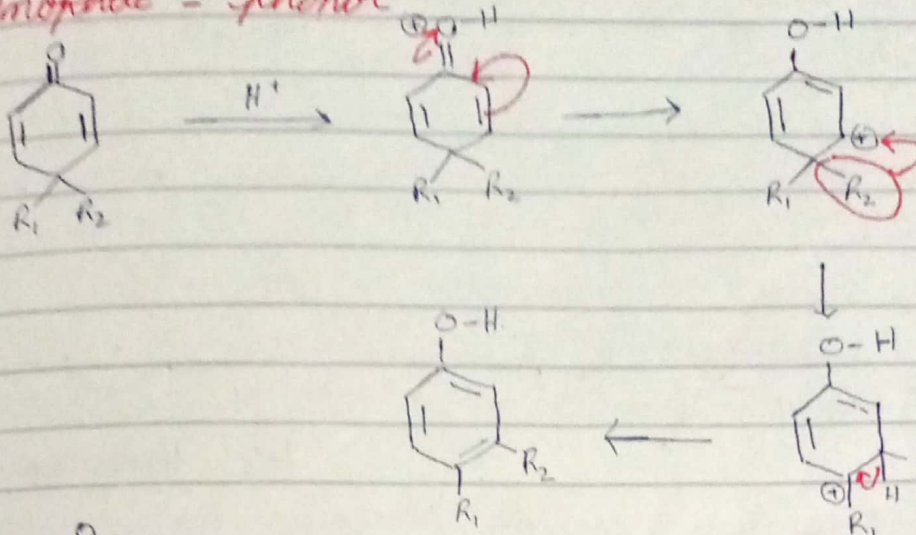
The attack of acyl group occurs at both ortho and para positions - If ortho or para is substituted, the attack will occur at other place that is unsubstituted.



10/10/2019.

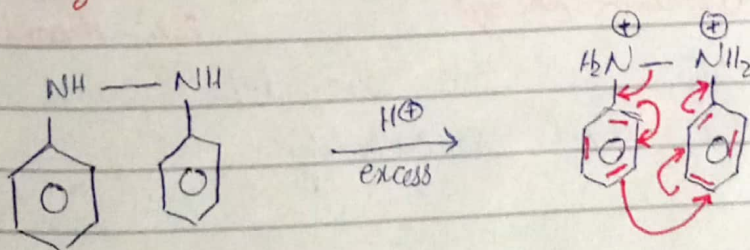
# re. Dieneophile - phenol

March's 5<sup>th</sup> ed 1402



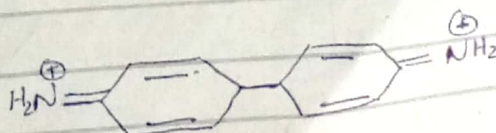
3,4-dimethyl phenol.

# Benzidine (March's 1455) ed 5<sup>th</sup>

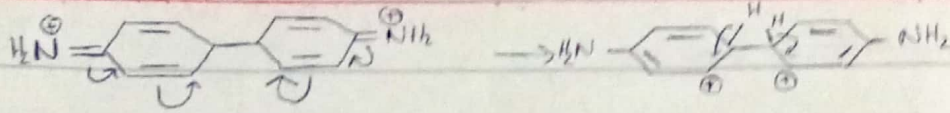
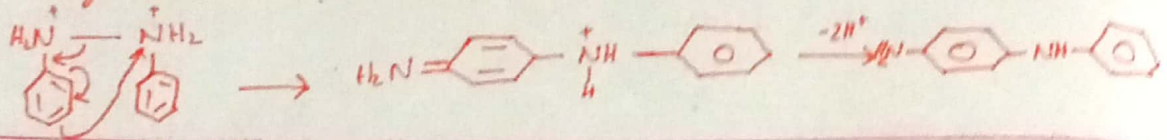


hydrazobenzene

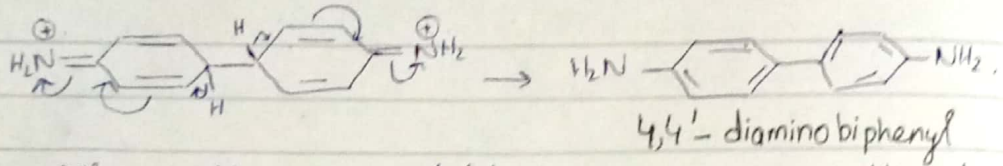
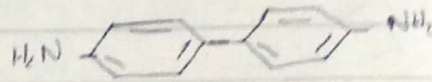
highly unstable



*p*-arylaminoaniline is also formed.

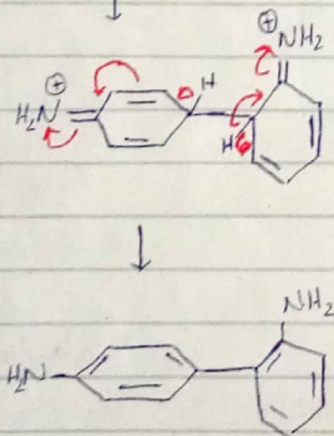
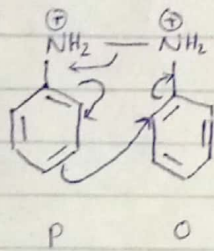


Wrong.

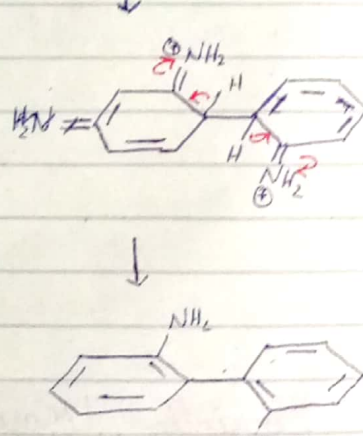
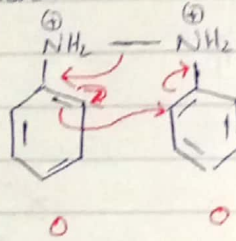


4,4'-diaminobiphenyl  
(benzidine)

The other possibilities are.

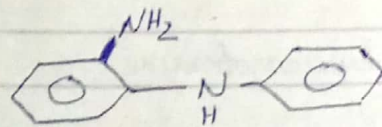
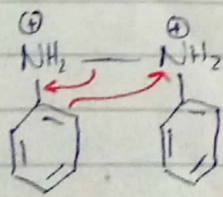


2,4'-diaminobiphenyl



2,2'-diaminobiphenyl

The possibility is less than 1%.  
p-p has most probability.



*p*-arylaminoaniline

