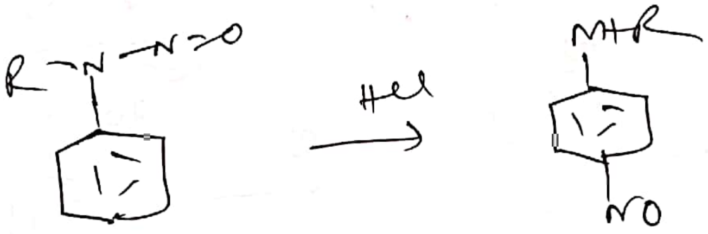
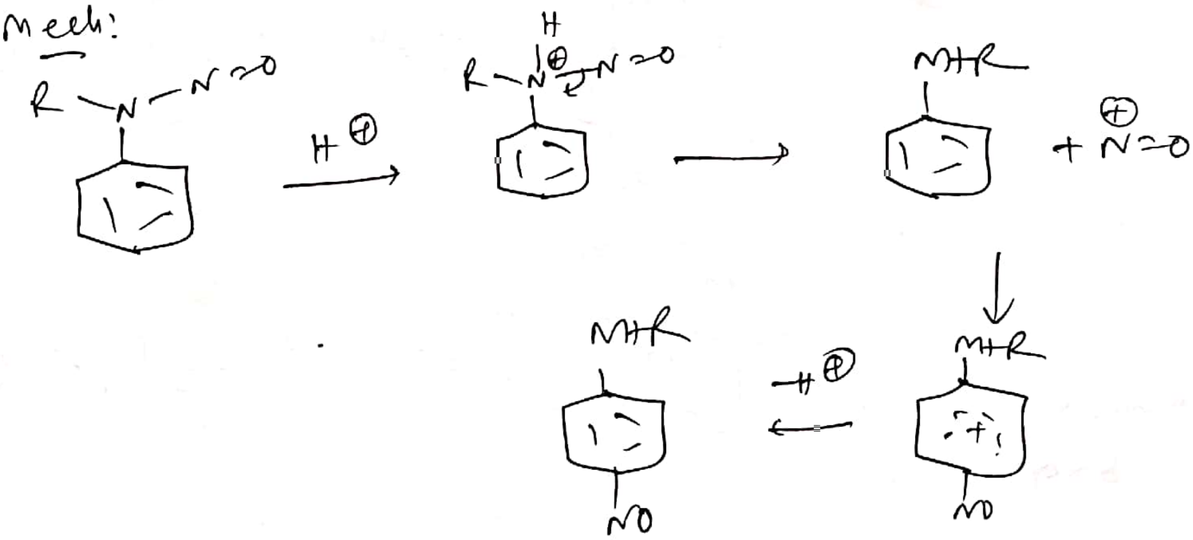
Fischer - Hepp Rearrangement

When N-nitroso derivatives of Secondary aromatic amines are treated with acid, migration of the nitroso group occurs usually at the para position forming the corresponding para nitroso aromatic amines. This rxn known as Fischer - Hepp rxn.



Mech:



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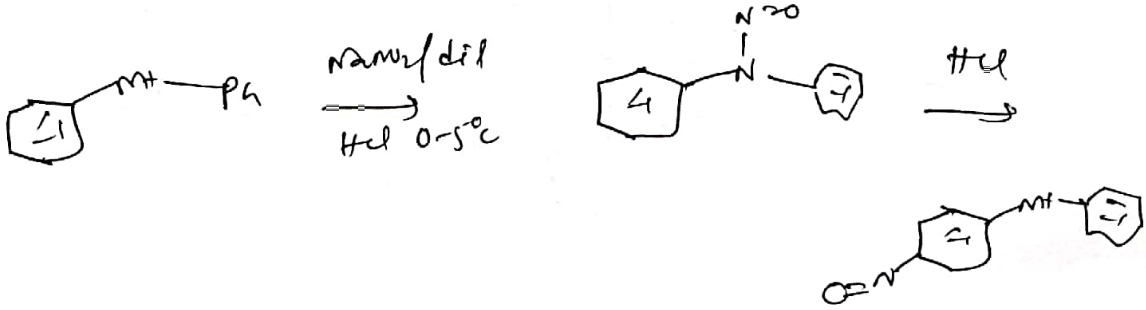
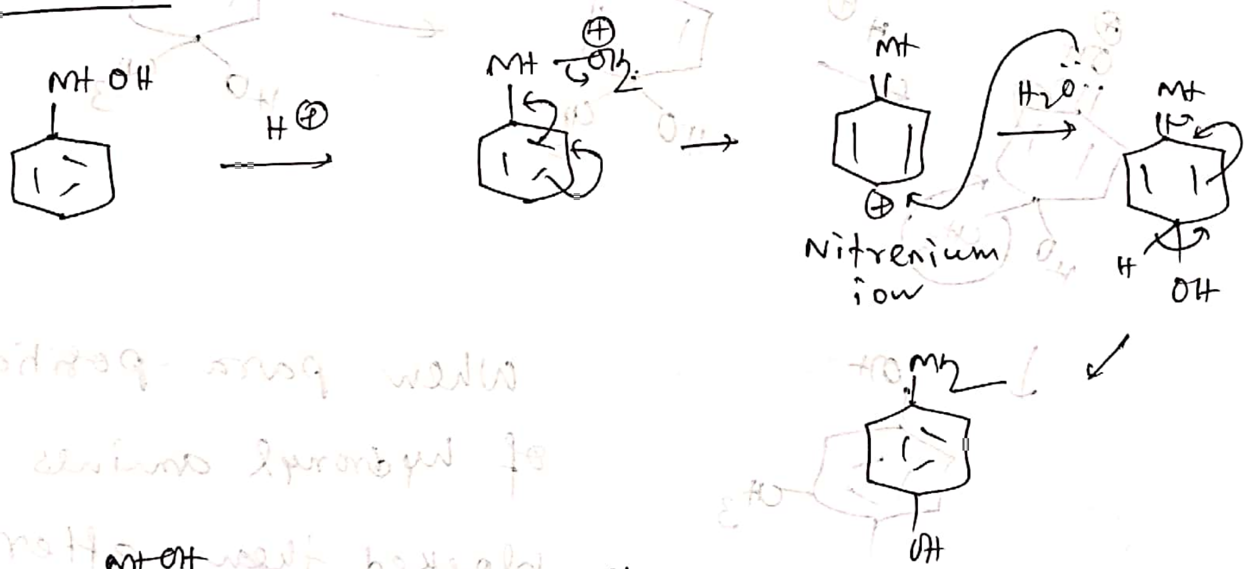


Bamberger Rearrangement

Bamberger rearrangement involves acid-catalyzed rearrangement reaction of aryl hydroxyl amines to para amino phenols.

Mechanism



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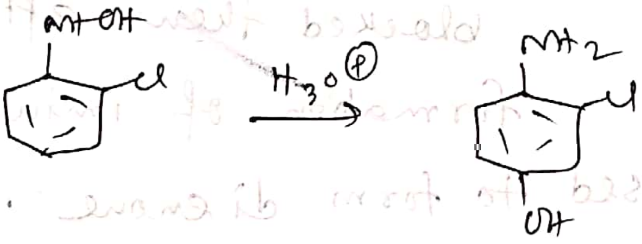

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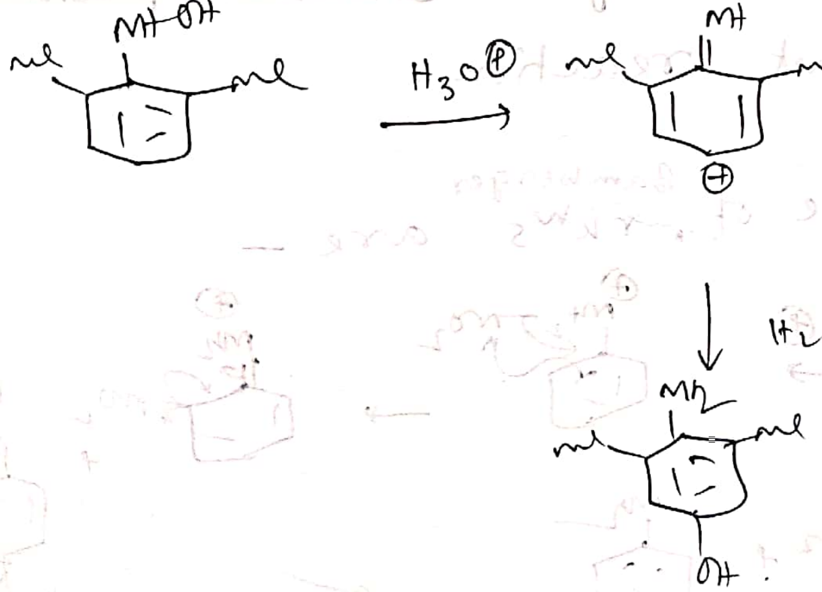
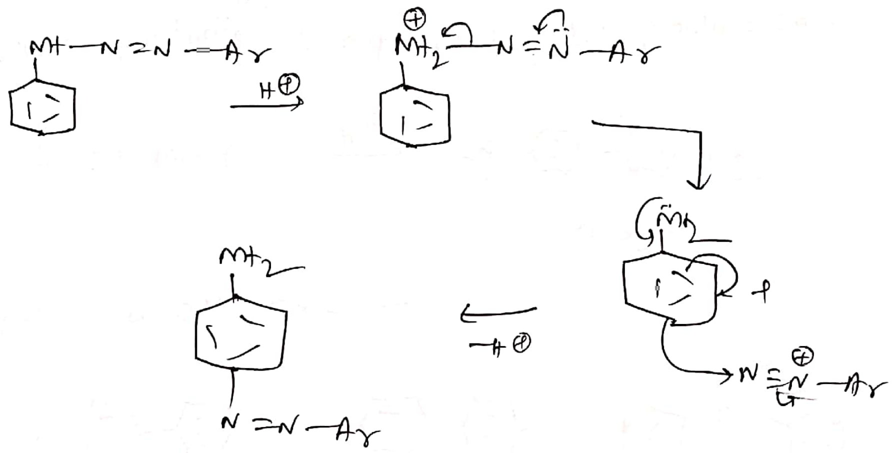


This intermediate is traped.

N-Azo to C-Azo rearrangement reaction

N-Arylazoanilines undergo rearrangement in presence of an acid to produce 4-(2-aryl-diazenyl) aniline. On treatment with acid aryldiazonium ion is formed from the conjugate acid of amine, which migrates to the para position almost selectively.

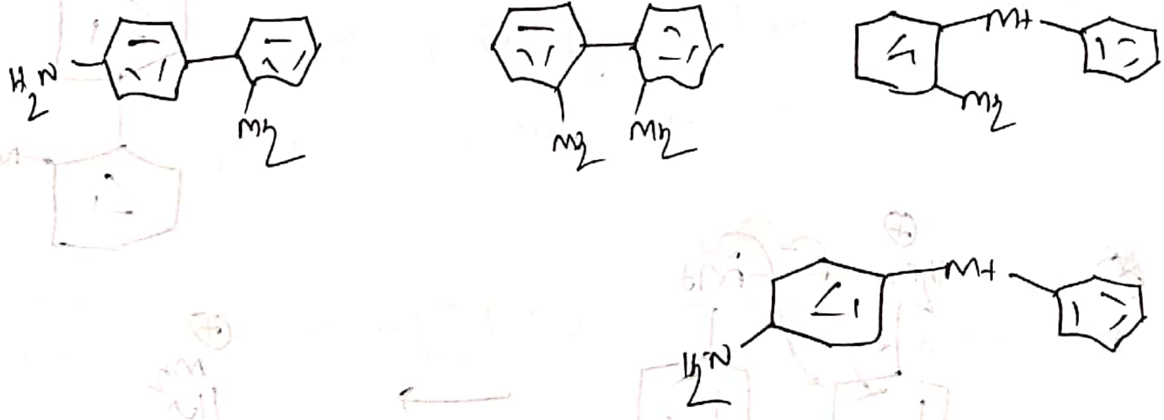


Benzidine - Semidine rearrangement reaction

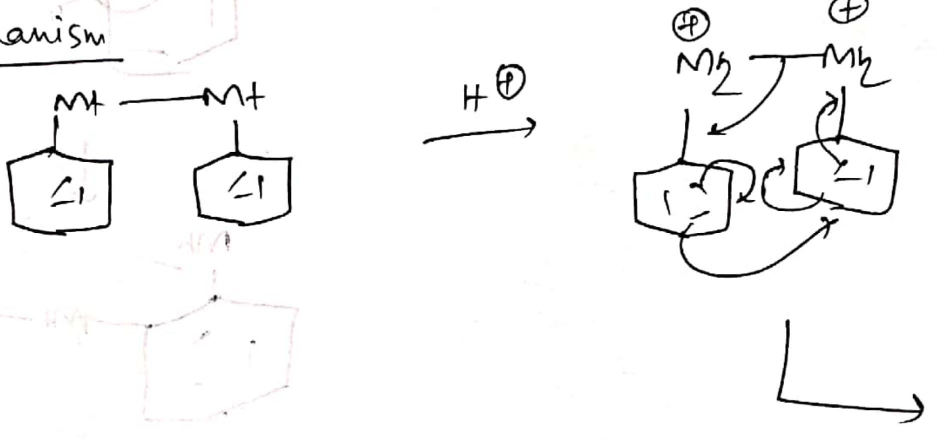
when hydrozobenzene is treated with acids, it rearranges to give about 70% 4,4'-diaminobiphenyl (Benzidine) and about 30% 2,4'-diaminobiphenyl. This reaction is called the benzidine rearrangement. Usually the main product is the benzidine but 4 other products may also be produced.

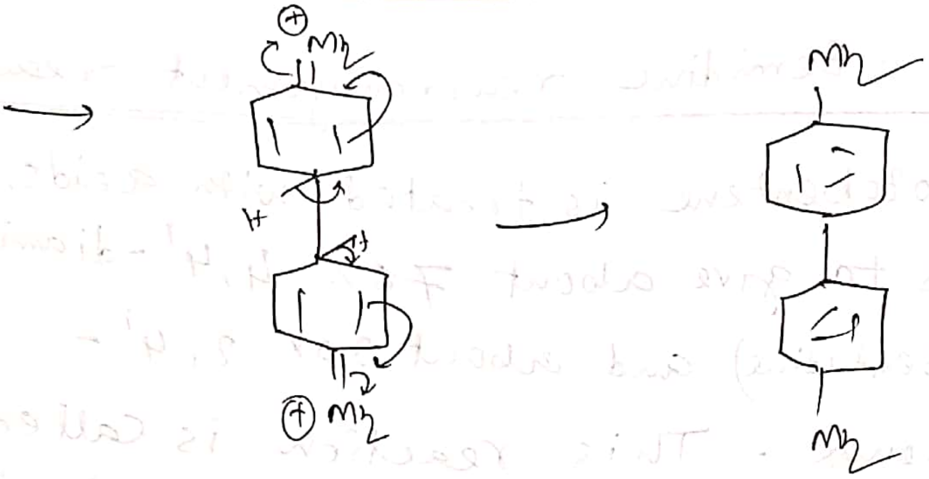
major.

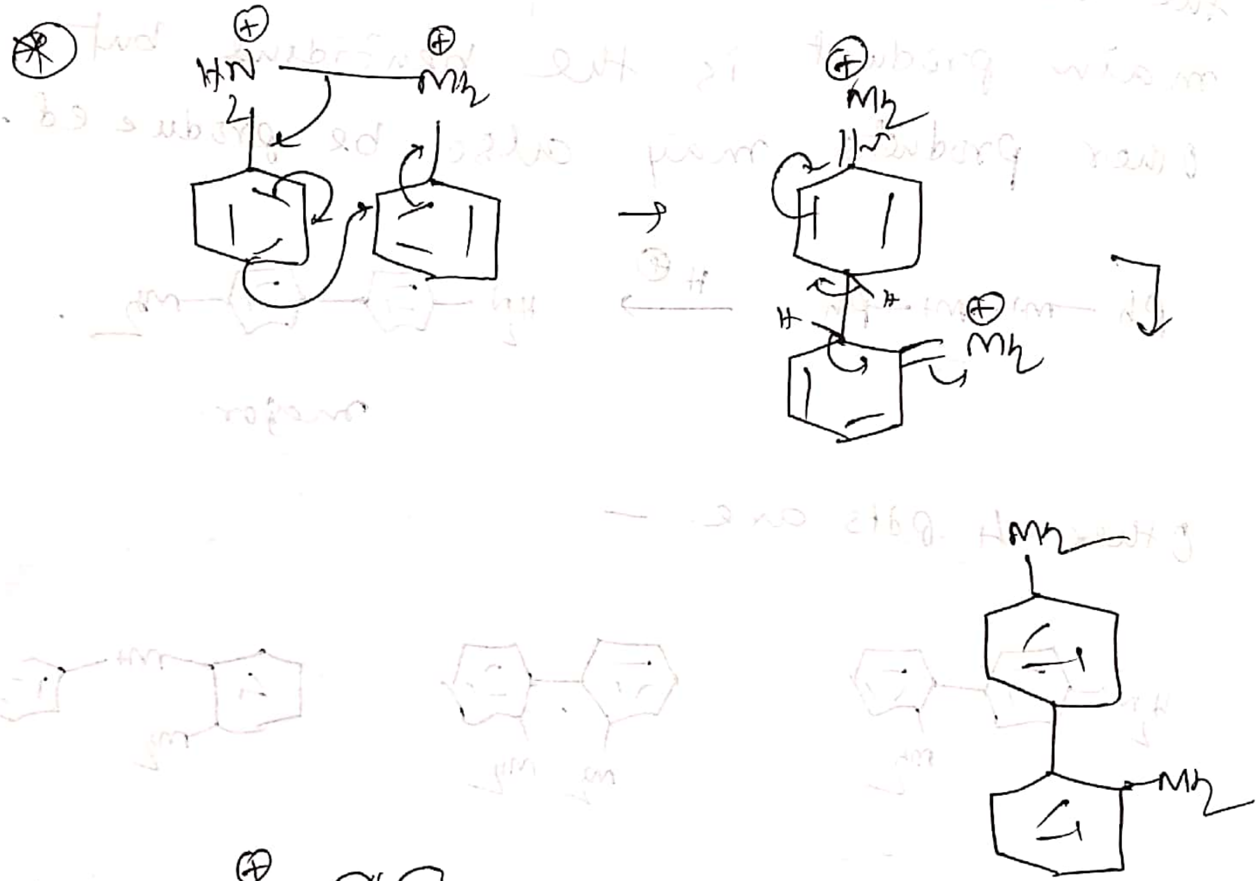
Other 4 pdts are -

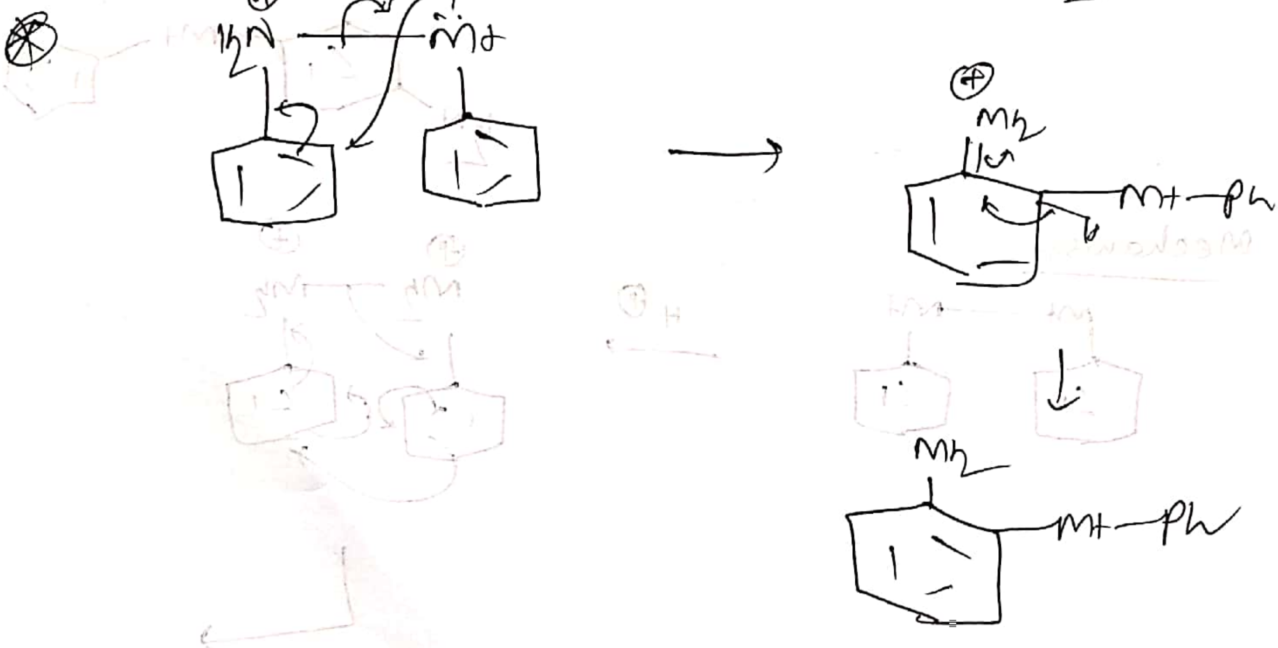


Mechanism



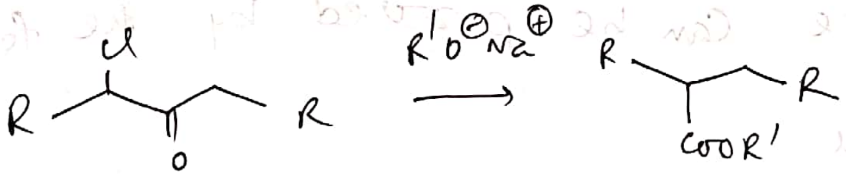

⊕ NH2
H
H
⊕ NH2
NH2
NH2


H2N
⊕ NH2
⊕ NH2
H
H
⊕ NH2
NH2
NH2

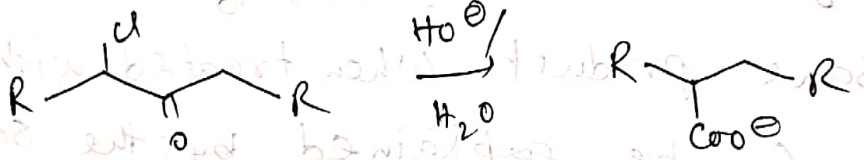

⊕
H2N
NH
⊕ NH2
NH−Ph
NH2
NH−Ph

FAVORSKII REARRANGEMENT

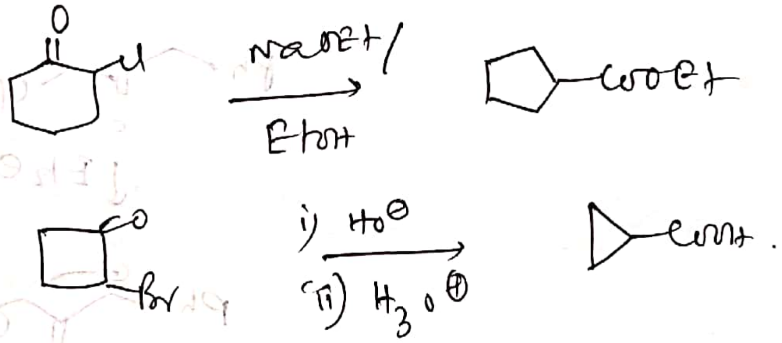
When α-halo ketone is allowed to react with alkoxide ion enolate is formed which then rearranges to the ester via cyclopropanone intermediate.



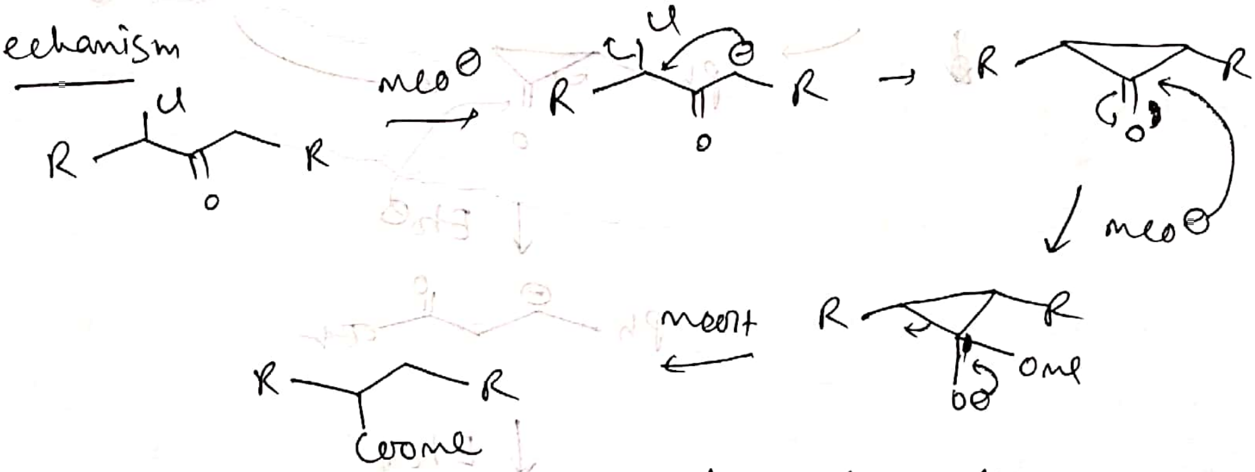
Similarly treatment with $HO^{\ominus}$ produces acid.



Cyclic ketone gives ring contraction product.



Mechanism

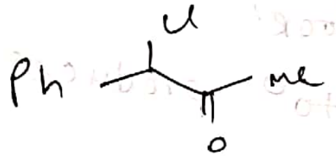


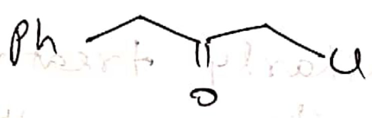
For unsymmetrical α-halo ketone the cyclopropanone intermediate opens to that side which gives stable carbanion.

Alkyl group disstabilize the Carbanion where as aryl group stabilizes it.

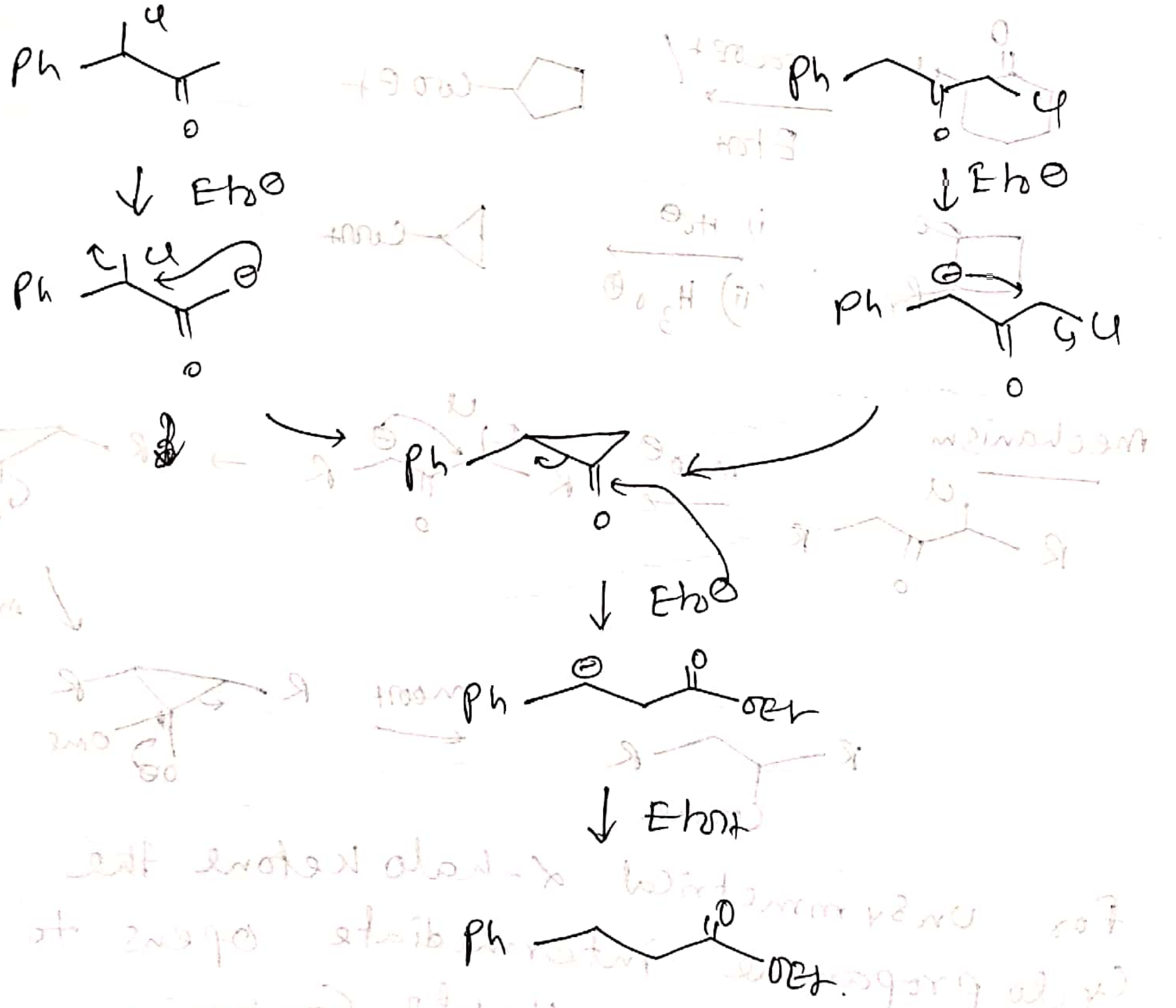
Evidence supporting the mechanism

The reaction proceeds via the Cyclopropanone intermediate Can be proved by the following ways.

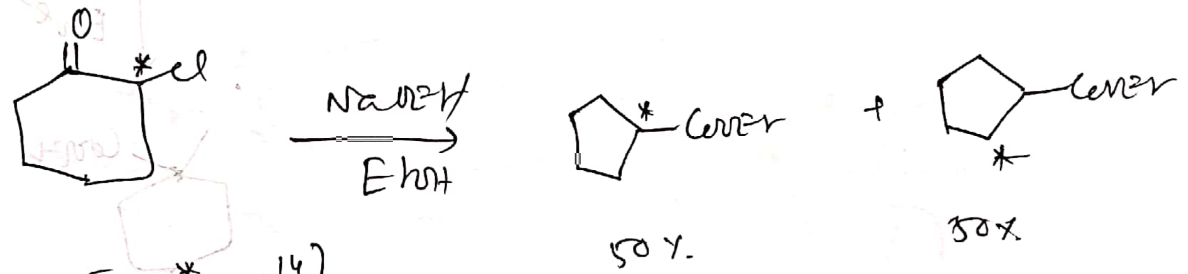
(i) 

and 

give same product when treated with NaOEt. This fact can be explained by the same Cyclopropane intermediate.

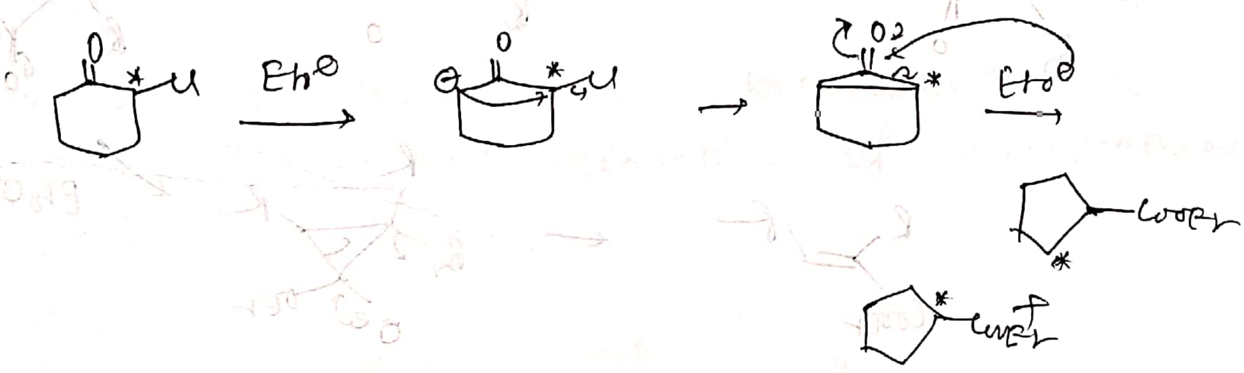


② When 2- chloro cyclo hexane in which Carbon atom connected with chlorine is labelled with C^{14} is allowed to react with NaOEt. it is found that half the C^{14} is at the α- Carbon and half C^{14} is at the β Carbon in the product.



$[C^* = C^{14}]$

This finding demonstrated that the reaction passes through such an intermediate where the α and α' Carbon atom w.r.t. the C=O becomes equivalent. This intermediate is actually a cyclopropanone derivative



③ The intermediate Cyclo propanone is some times isolated.