Date: 19/04/08.
Saturday.

Named Reactions
(Paper I and paper II)

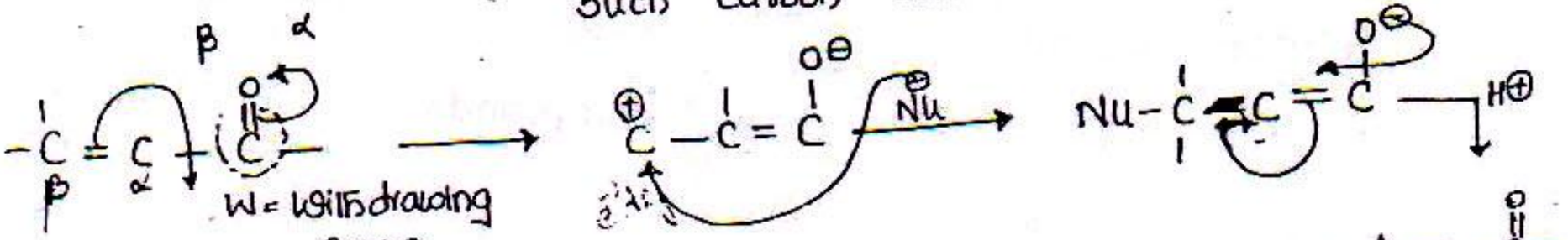
I. paper-II ***. Named reactions :—**

i) Michael additions (or) Michael reactions.

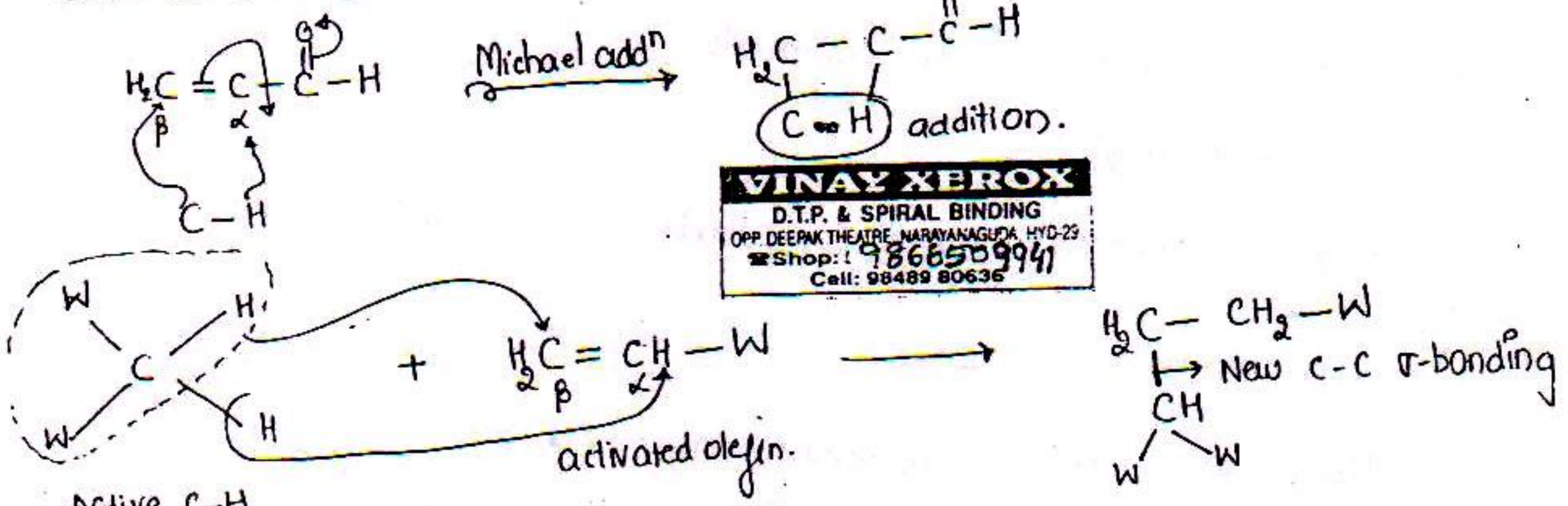
→ Addition of active C-H function at α-β-unsaturated olefin or activated olefin in basic medium called michael reaction/addition

→ New carbon-carbon bond developed at β-position of activated Olefin.

Suppose $\overset{\beta}{C}=\overset{\alpha}{C}-W$ β(C_2)-carbon becomes more electron deficient such carbon called activated carbon.

i.e 

Over-all reaction:

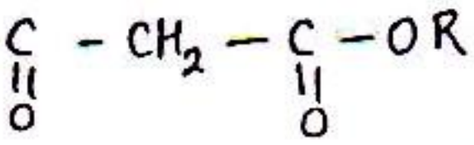


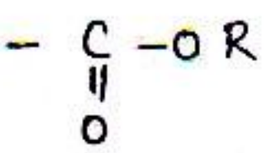
Michael donors: They should readily ionise into carbanion and proton.

RO_2N-CH_2 , RO_2C-, CH_2- , $-\overset{O}{\overset{\|}{C}}-CH_2$,

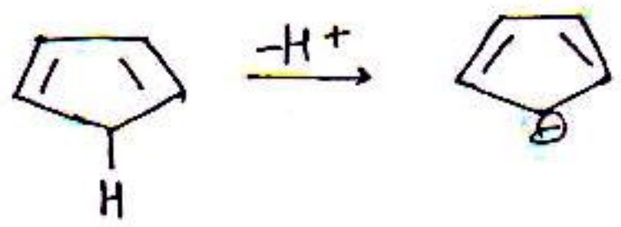
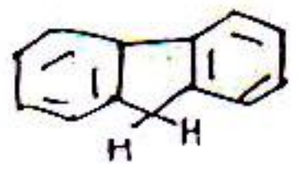
$HO-\overset{O}{\overset{\|}{C}}-CH_2-$, β-diketo $-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-$

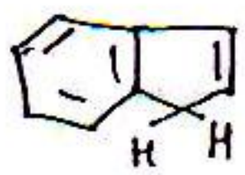
β-Nitro carbonyl compound : $-RO_2N-CH_2-\overset{O}{\overset{\|}{C}}-$

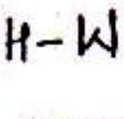
β- Keto ester 

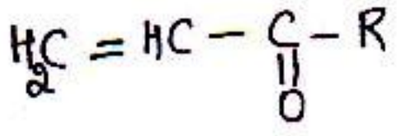
β- cyano esters 

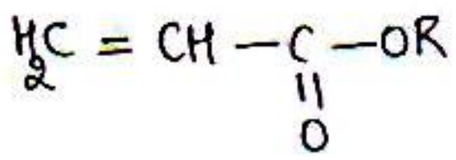
→ Will increase in number of withdrawing group, acidic strength increases.

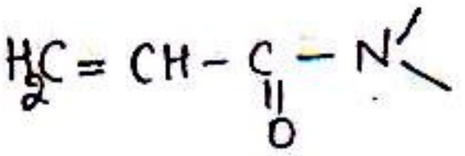
Cyclopentadiene  Flourene 

Indene 

Michael acceptors : 

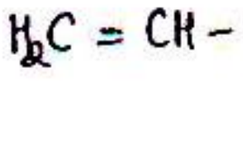
→ α, β- unsaturated carbonyl compounds 

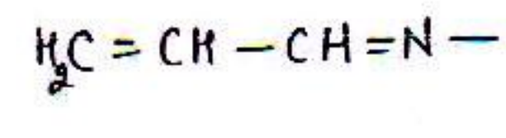
→ α, β unsaturated esters 

→ 

→ α, β unsaturated Nitro compounds

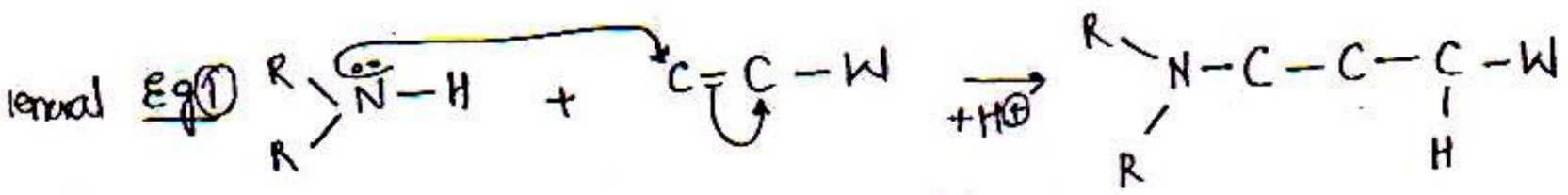
($CH_2=CH-NO_2$)

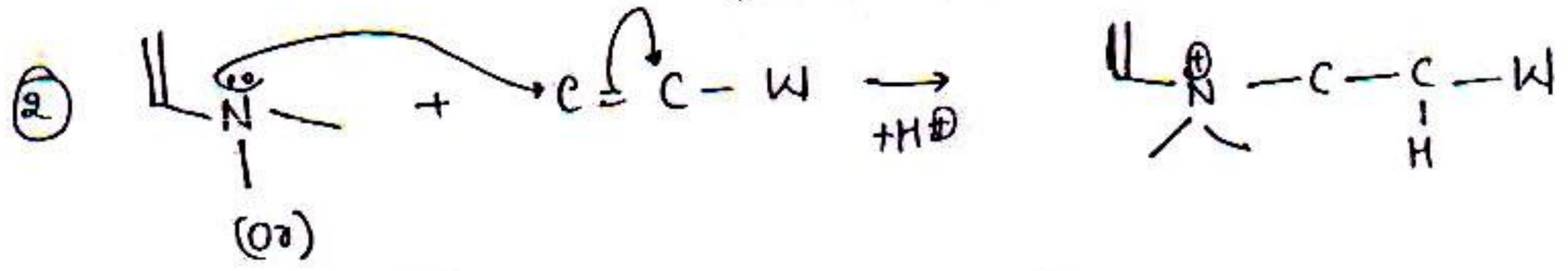
→ α, β-unsaturated cyano compounds 

→ α, β- unsaturated amines 

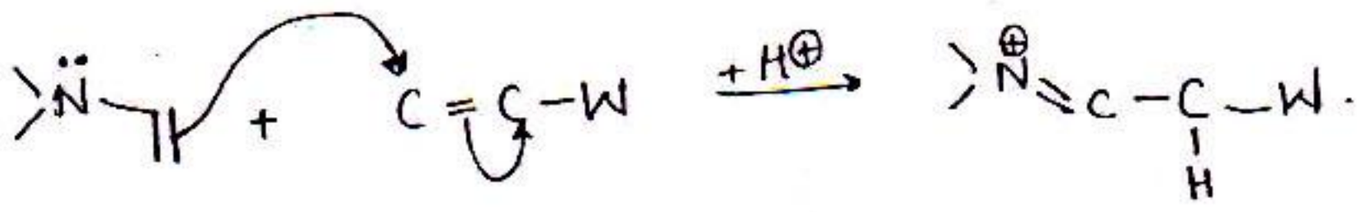
Here all the β- positions are electron deficient.

→ Amines and Enamines also can be used as michael donor

General Eq ① 

② 

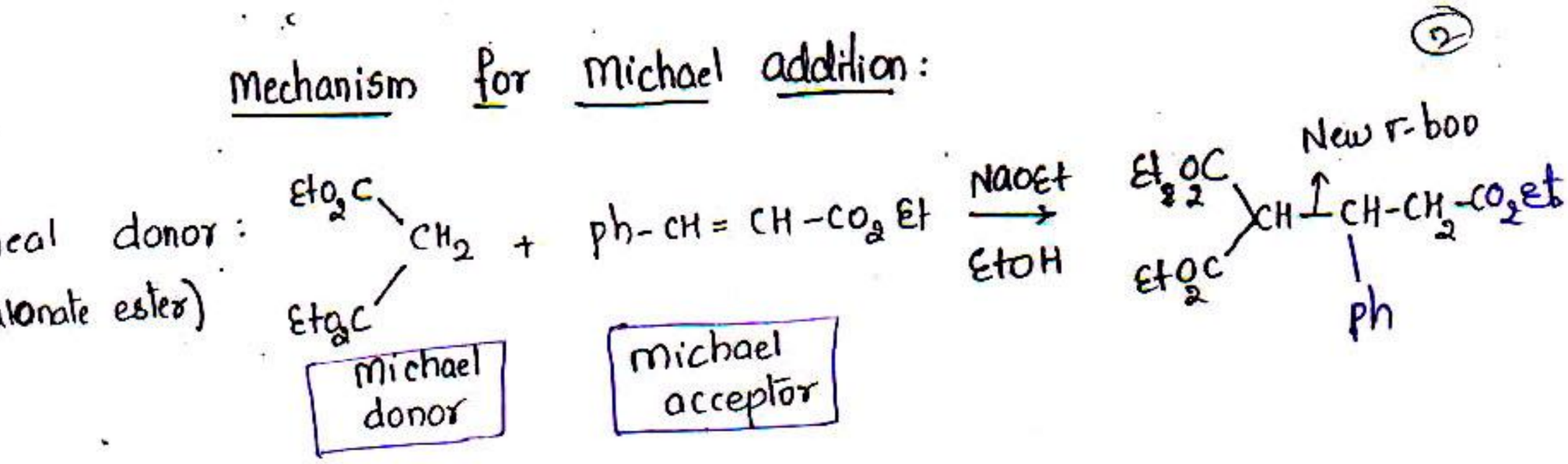
(or)



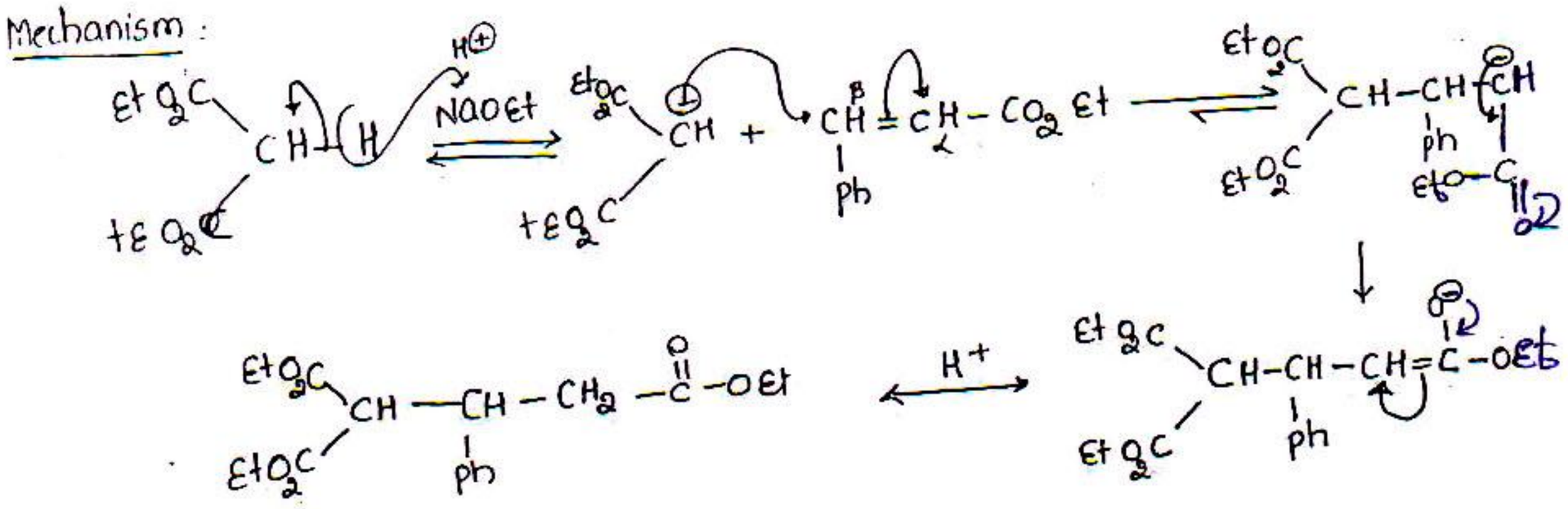
21/04/08
Monday

Mechanism for Michael addition:

Meheal donor: (malonate ester) + ph-CH=CH-CO_2Et $\xrightarrow[EtOH]{NaOEt}$

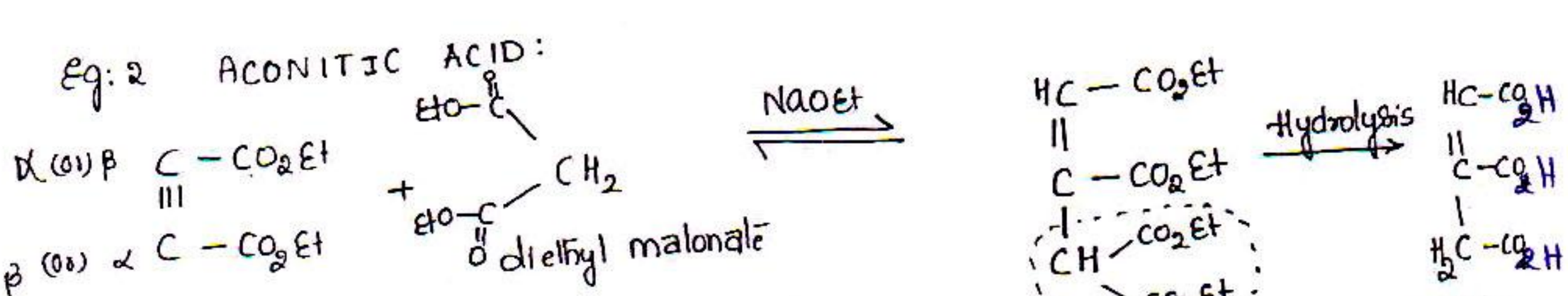


Mechanism:

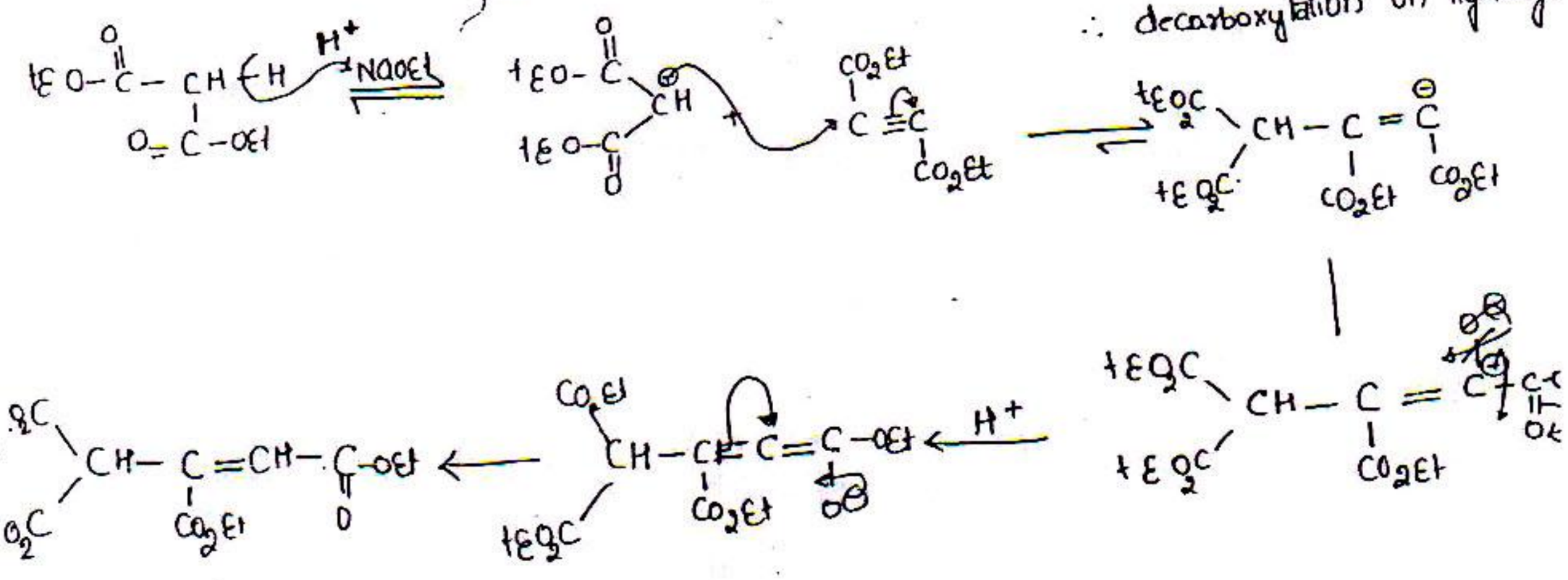


M. adduct.

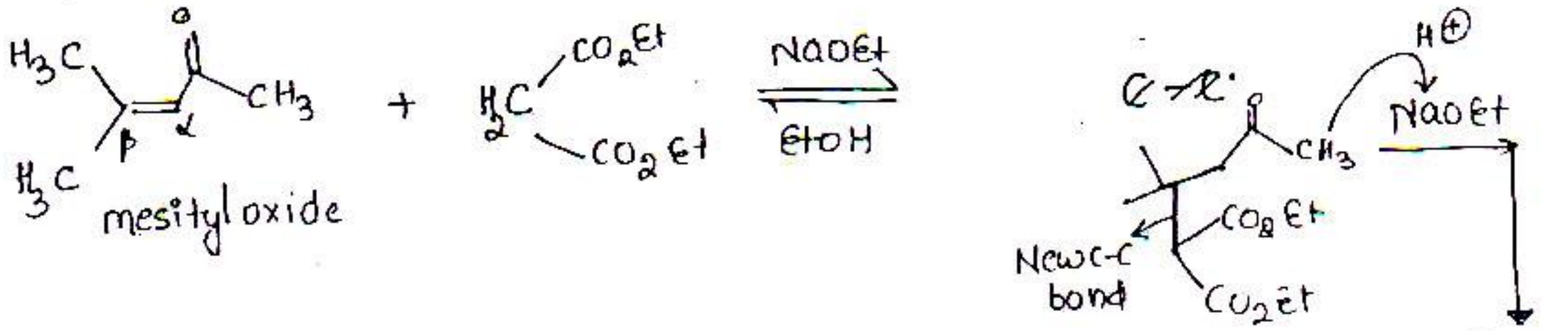
Eg: 2 ACONITIC ACID:



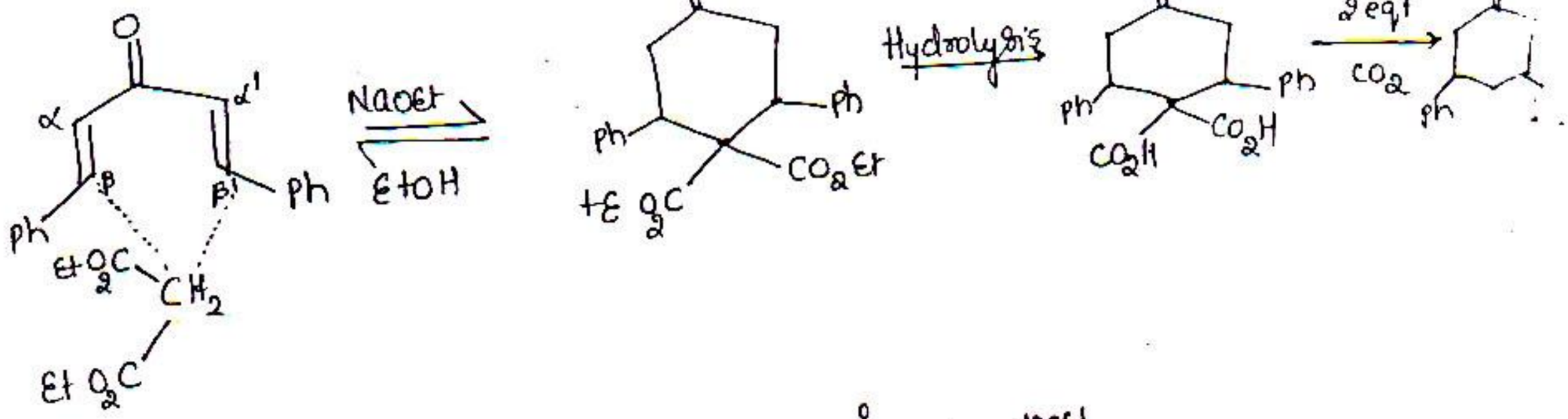
Mechanism:



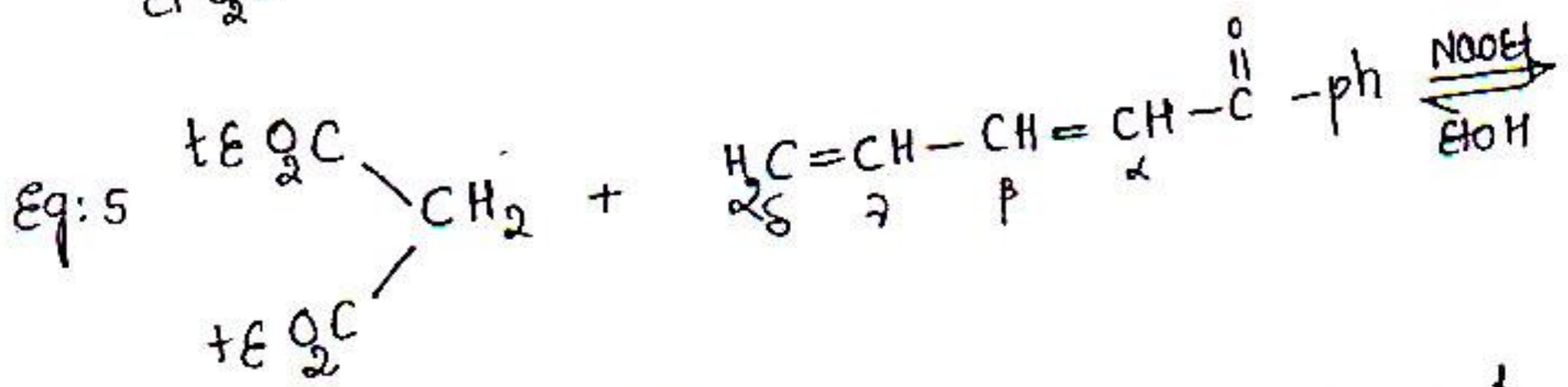
Eq: 3 DIMEDONE FORMATION :



Eq: 4 Double michael additions with in a same molecule.

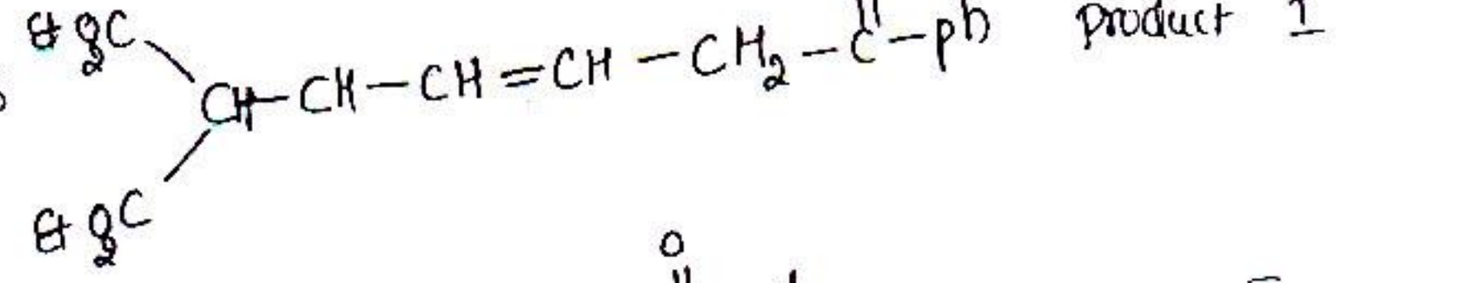


Eq: 5



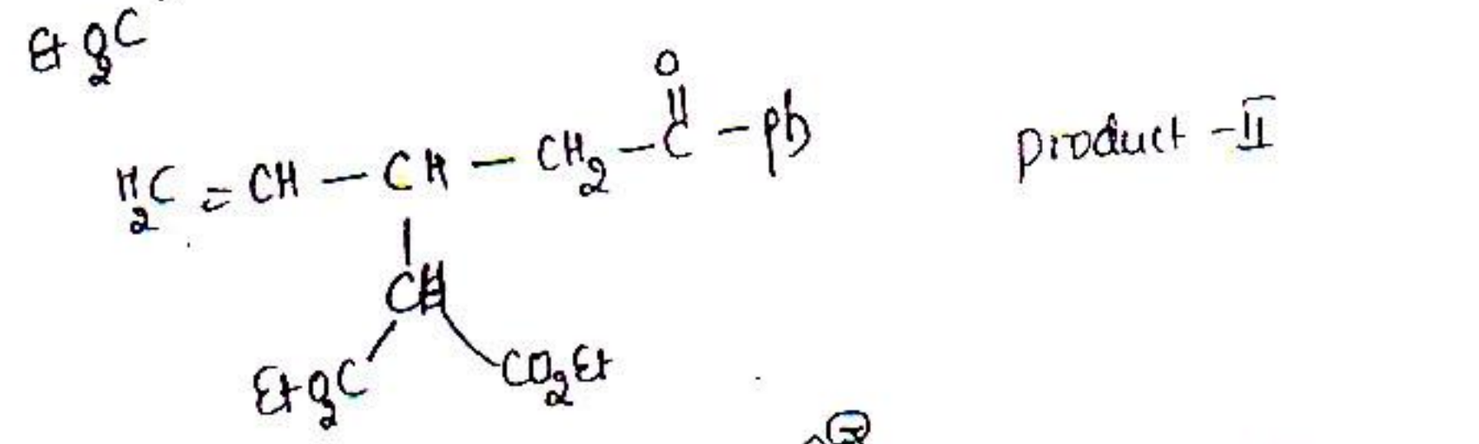
: electron deficient at β & δ - position.

(1) New C-C bond at δ



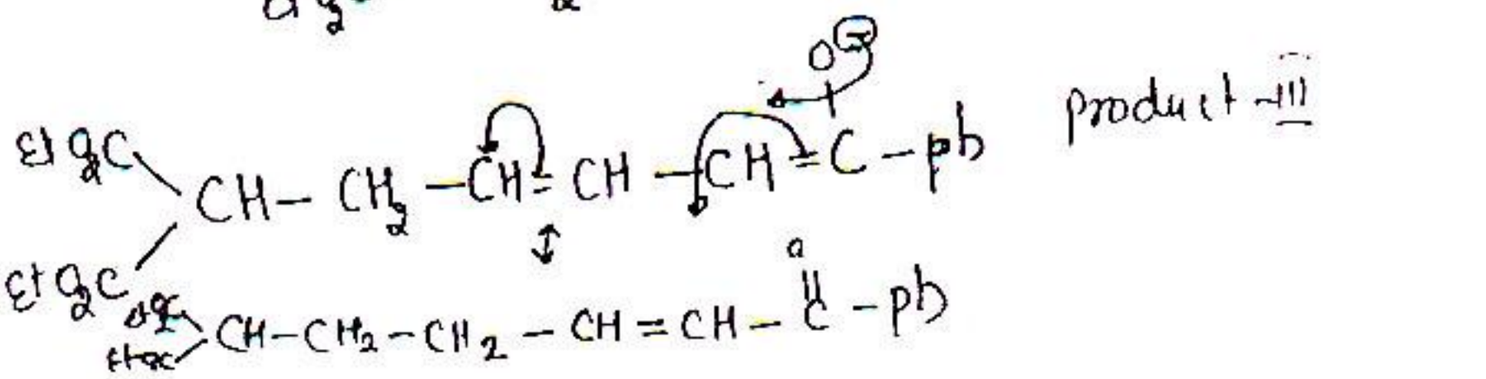
product I

(2) New C-C bond at β



product - II

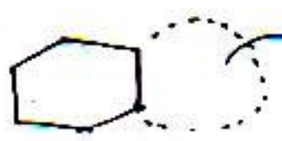
3) New C-C bond at δ



product - III

Robinson ANNULATION's : It is a combination of 2-reactions i/e Michael reaction and aldol condensation or aldol reaction.

ANNULATION : Developing New ring on existing rings called annulations.

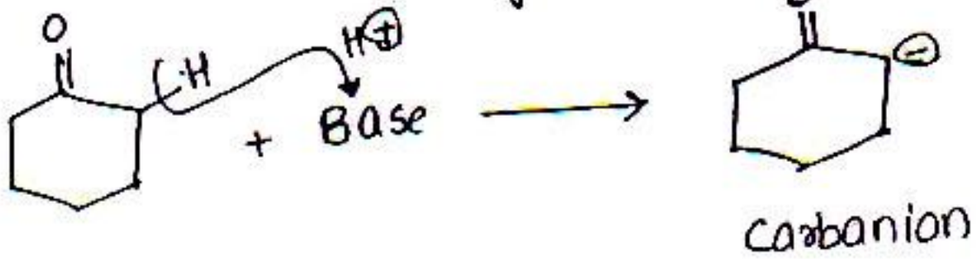


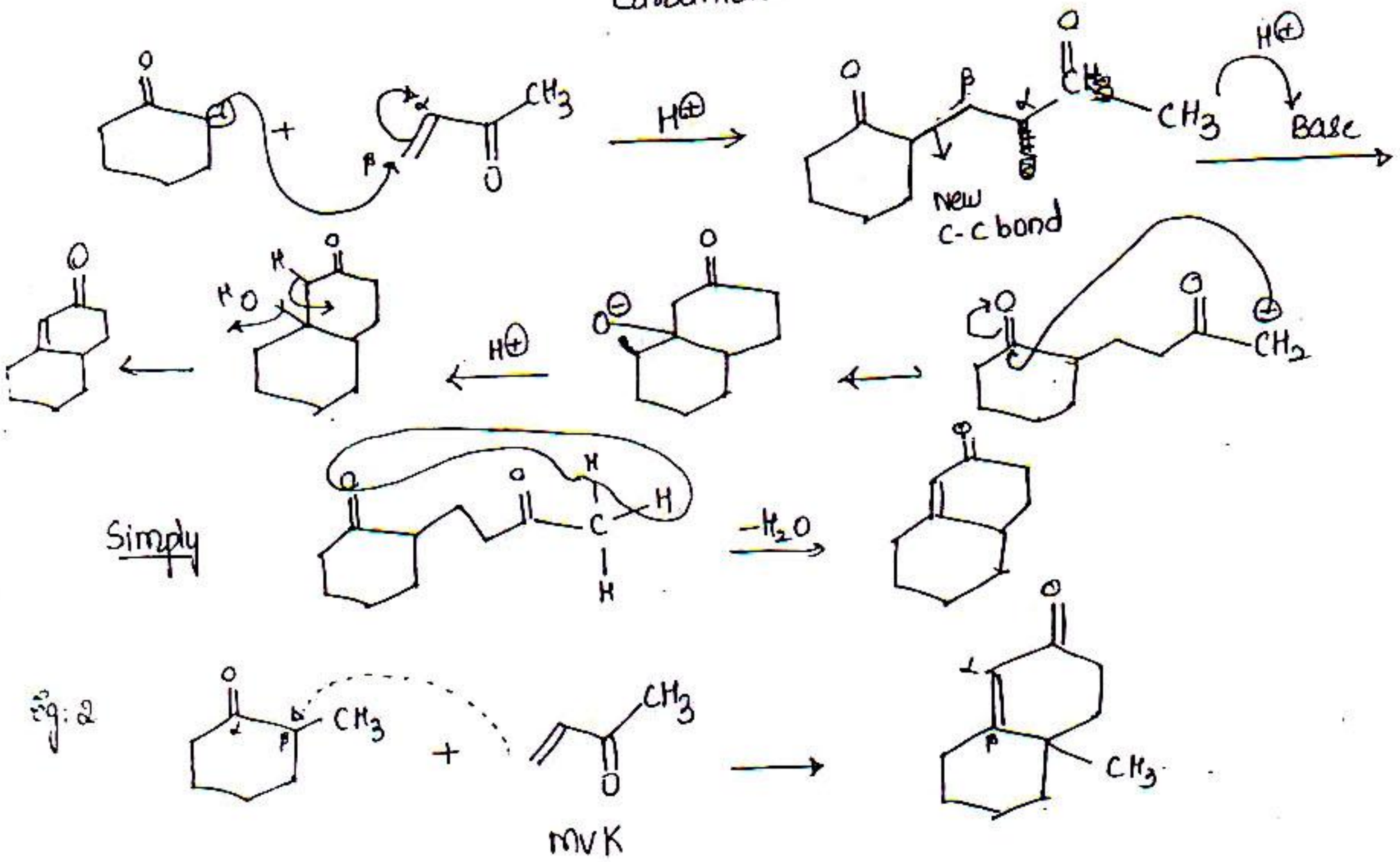
annulation.

Eg: 1.

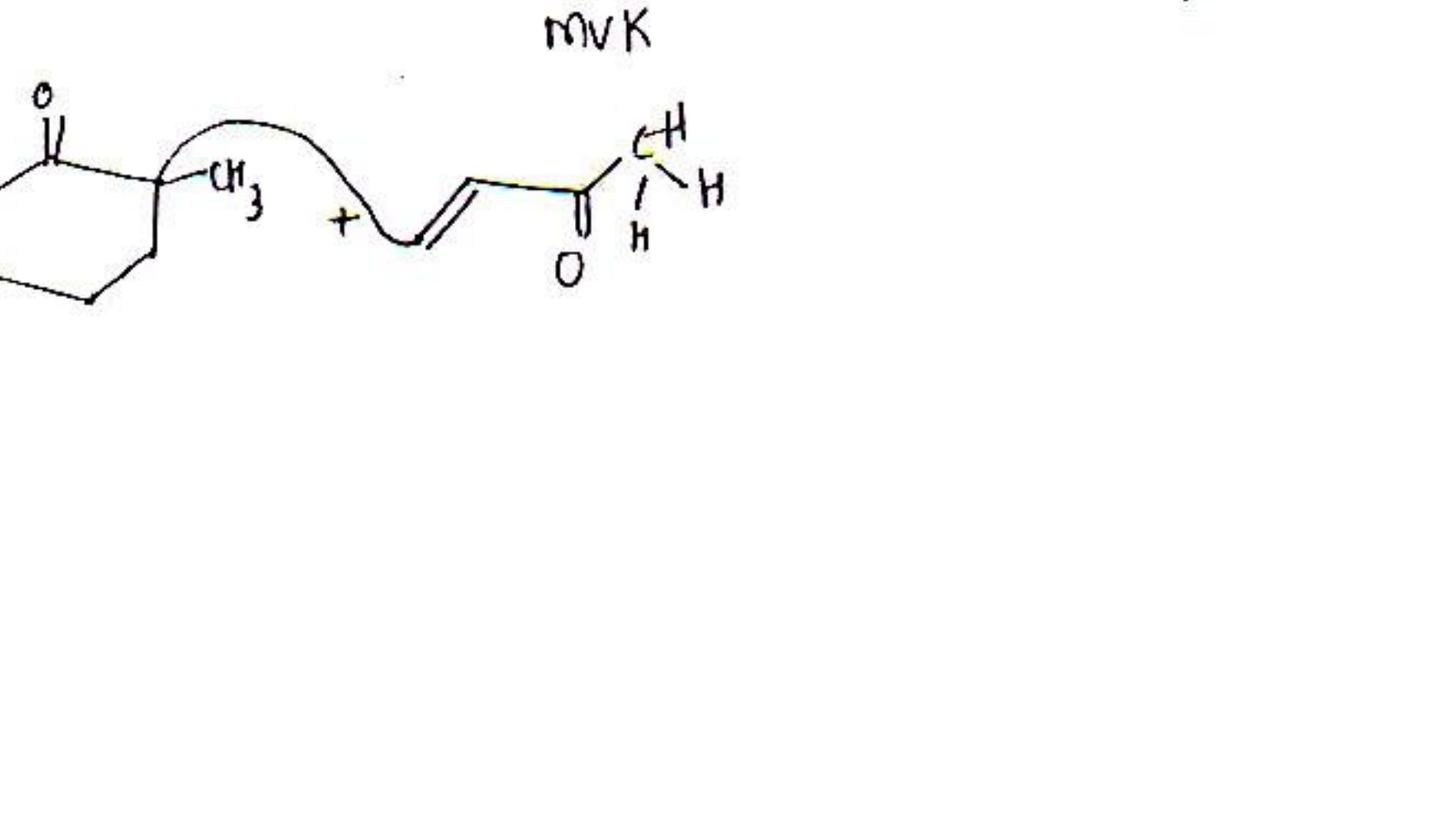
methyl vinyl ketone
(M.V.K)

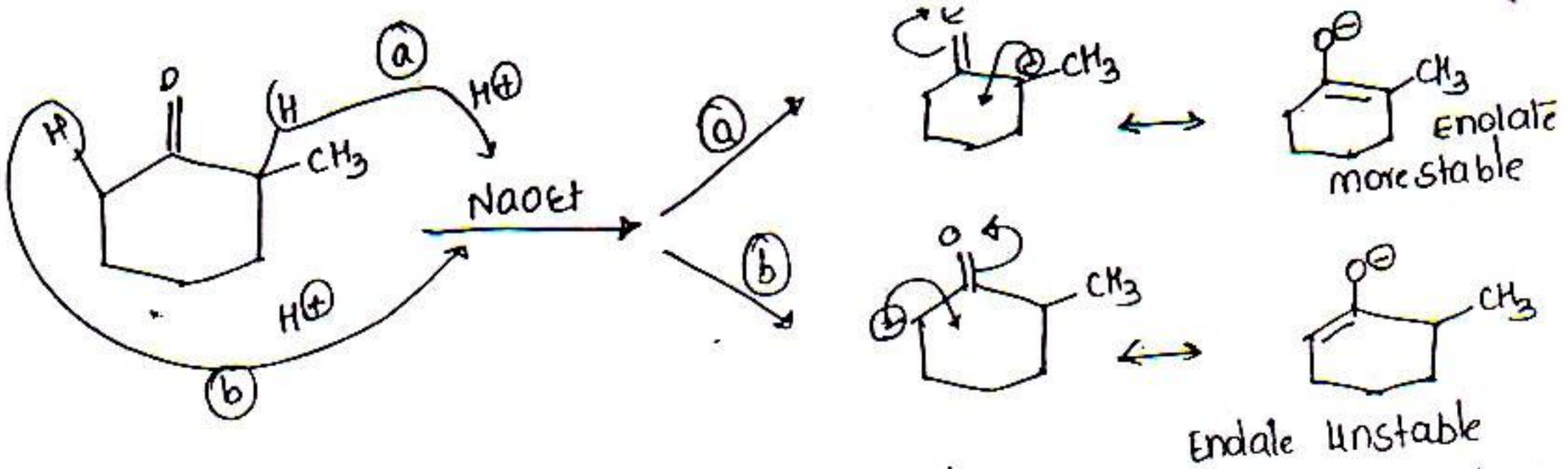
Mechanism : firstly Michael addition.





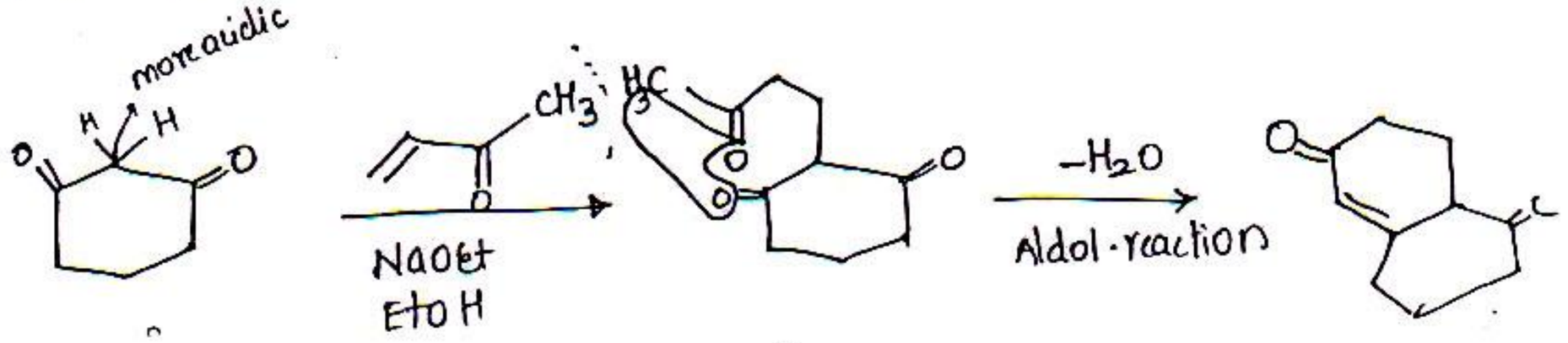
Eg: 2



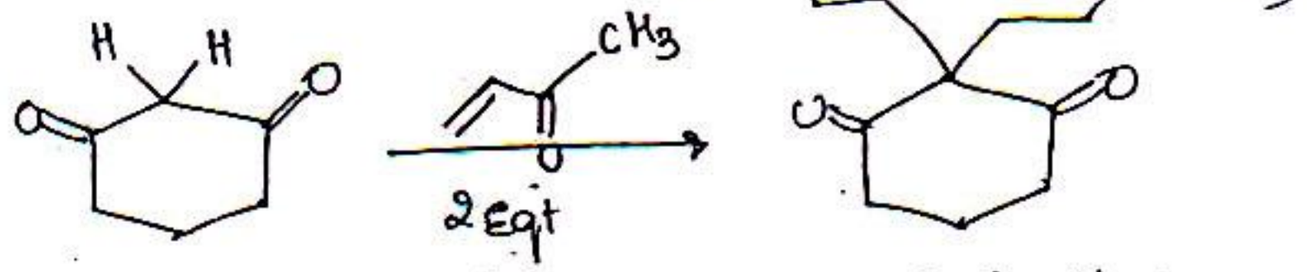


∴ b path is not taken into consideration because of producing unstable enolate.

Eq: 3

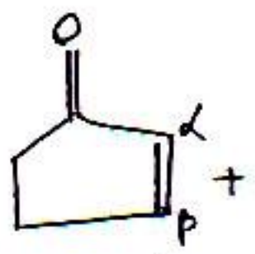


Eq: 4

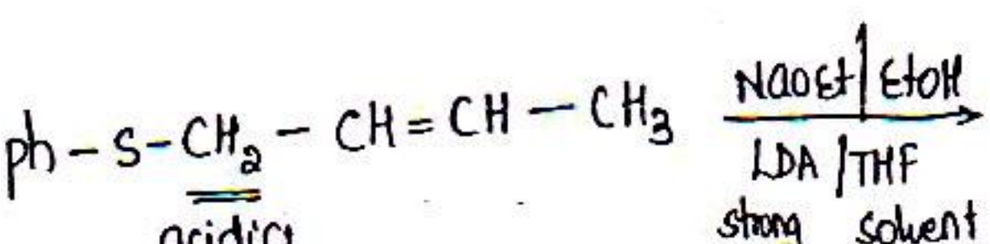


→ No intra-molecular aldol cyclisations. because it gives a strained cyclic system

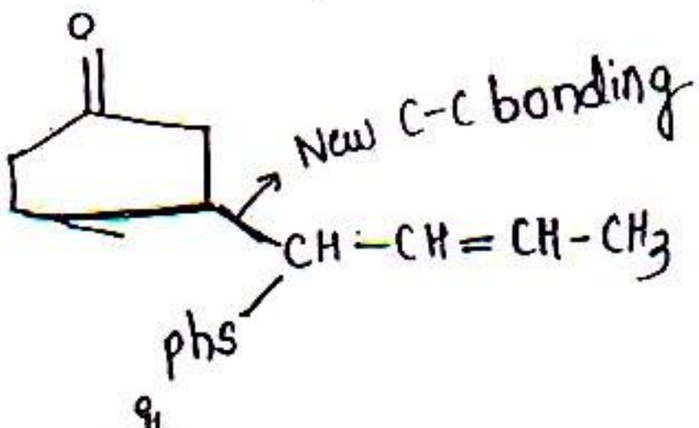
Eq: 5



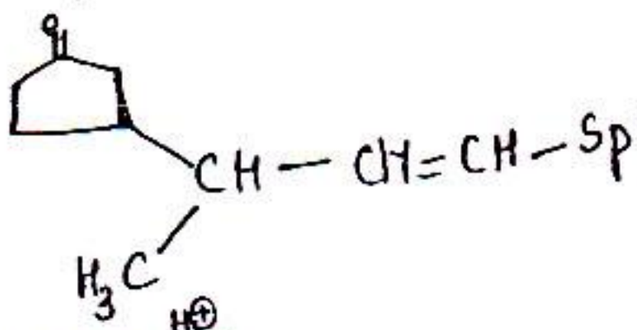
Activated olefin

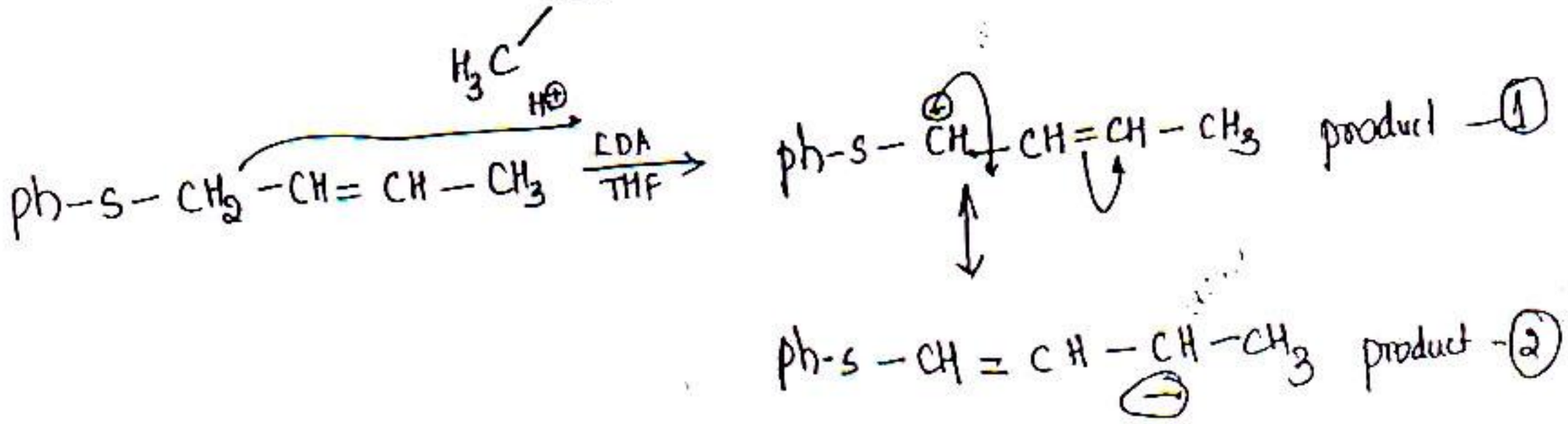


products : 1

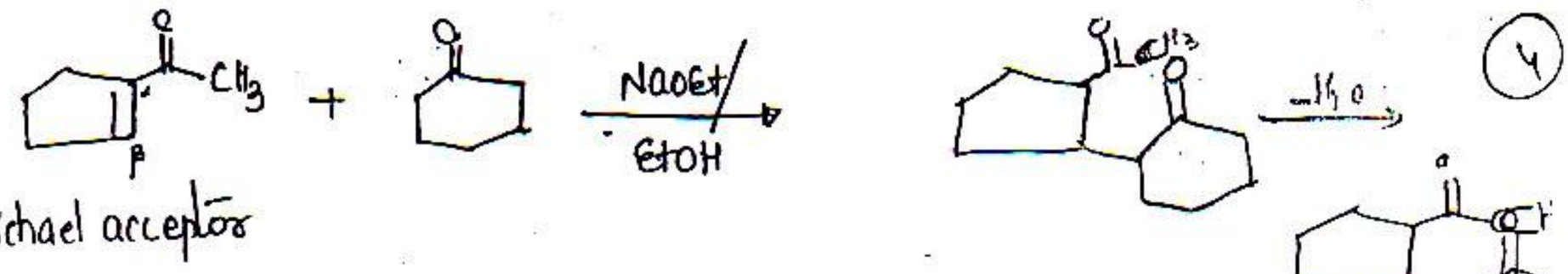


product : 2



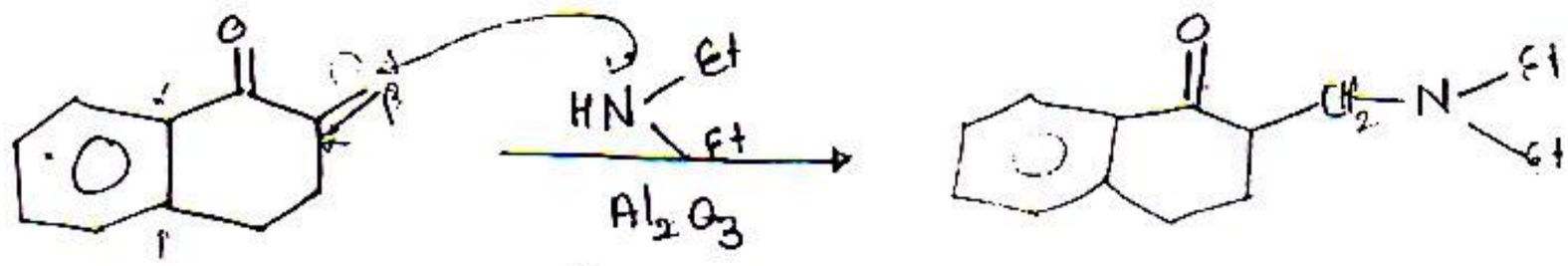


Eg: 6

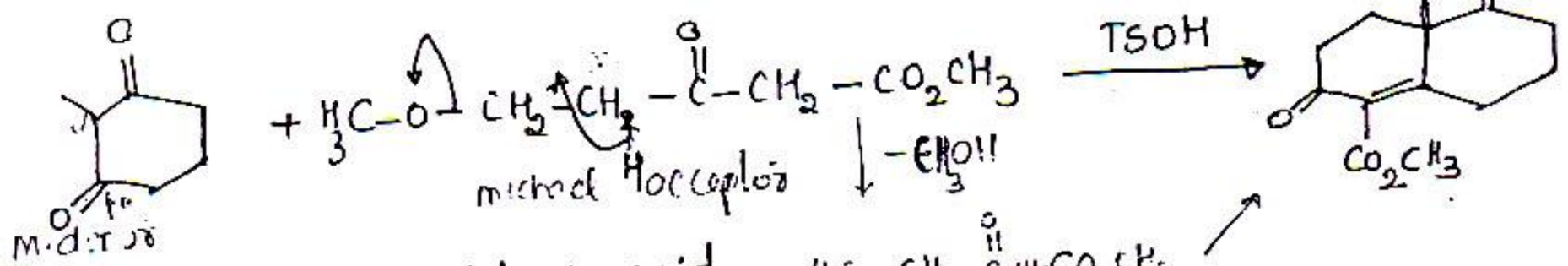


Michael acceptor

Eg: 7

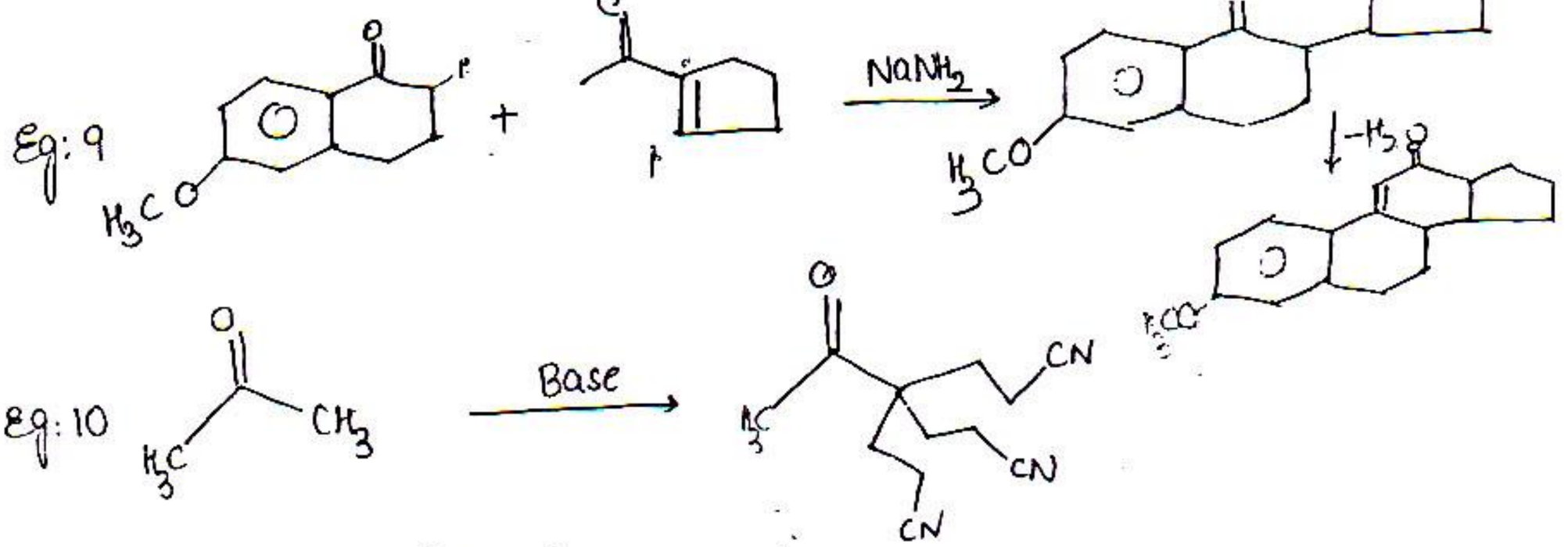


Eg: 8



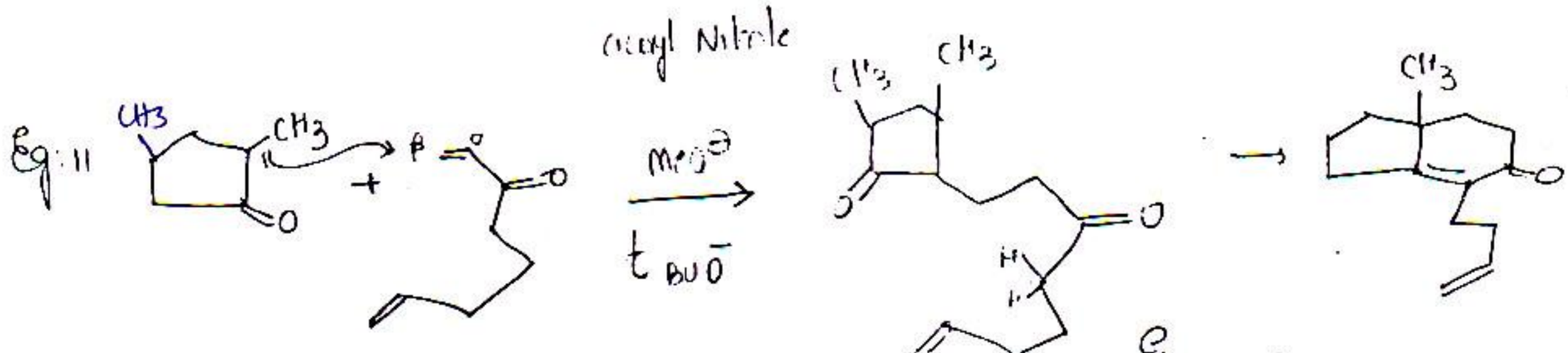
TSOH = p-Toluay sulphonic acid.

Eg: 9

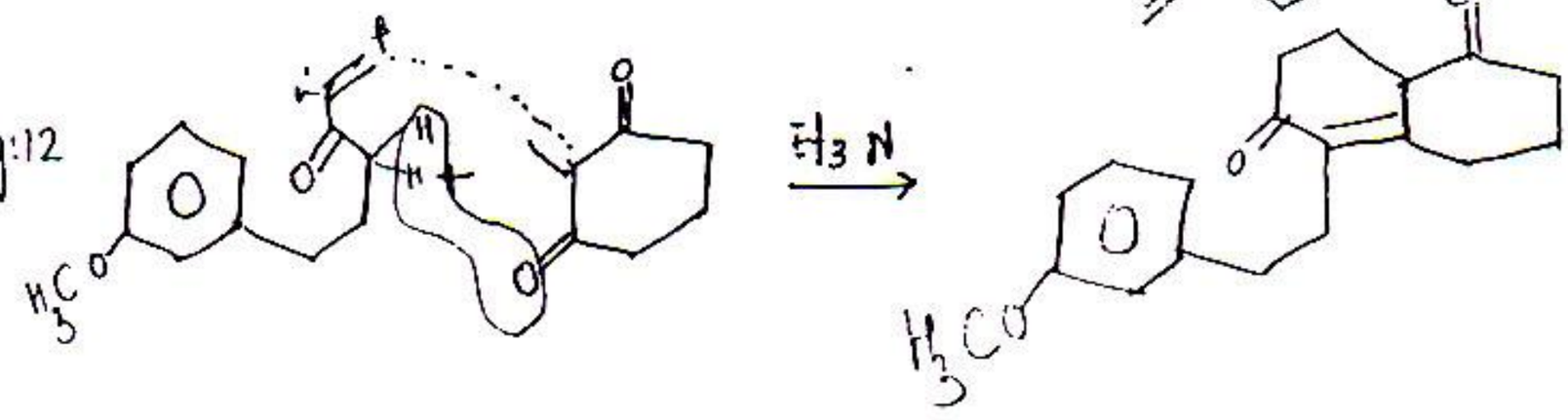


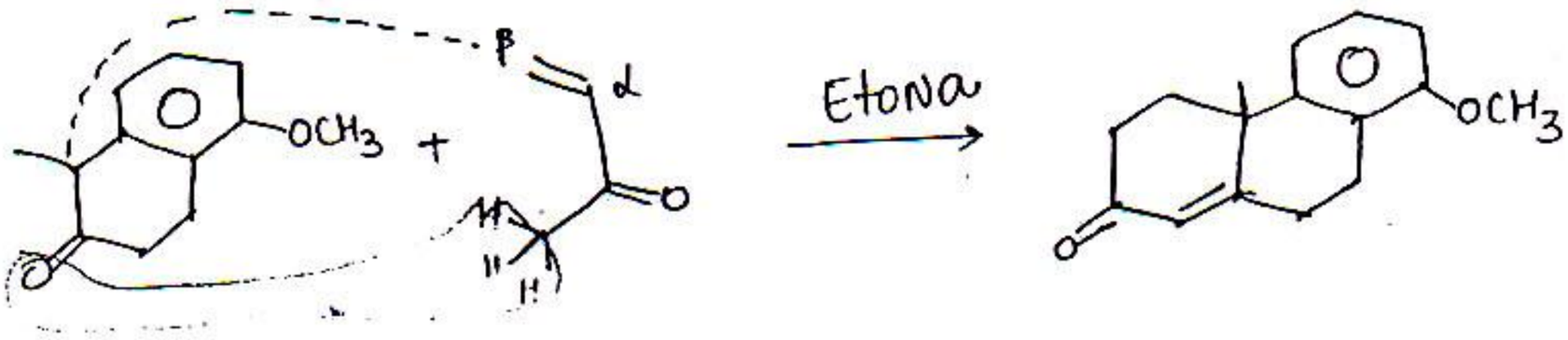
Eg: 10

Eg: 11



Eg: 12



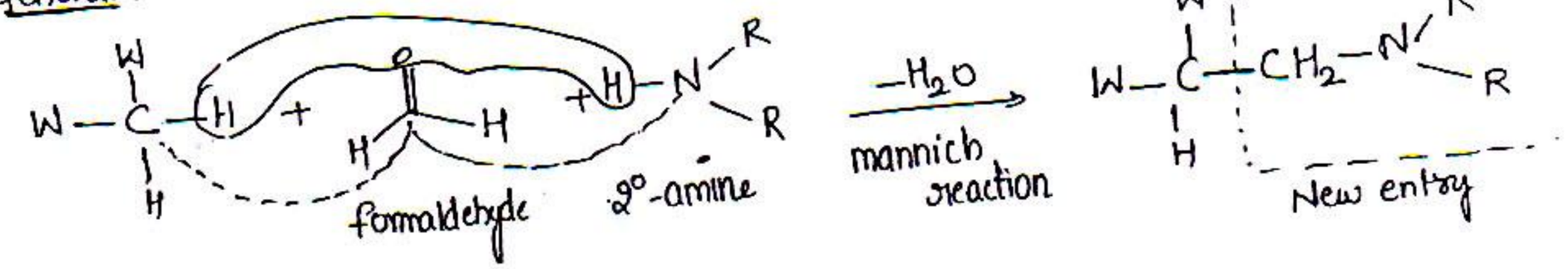


II) MANNICH - Reaction :

Amino - methylations at active positions involving formaldehyde (HCHO) and 2°-Amine called mannich reactions.

Resulting products are mannich bases / mannich salts.

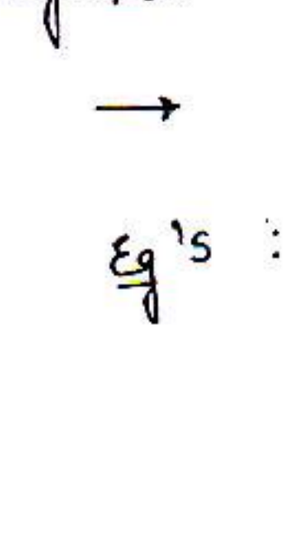
General: Active function → Carbanion + H+.

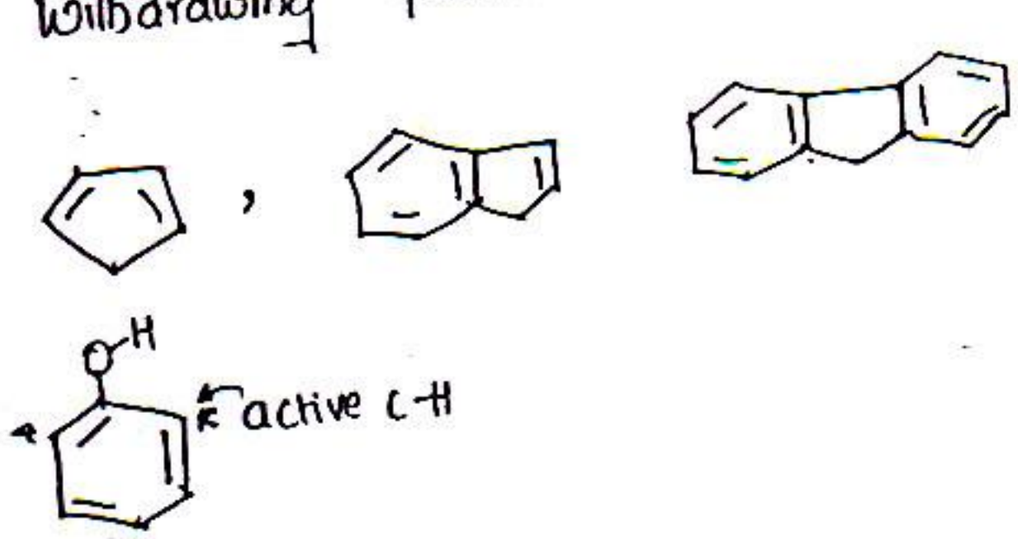


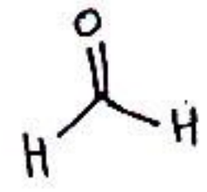
Eg: for active C-H function:

→ C-H group attached to withdrawing function is active C-H

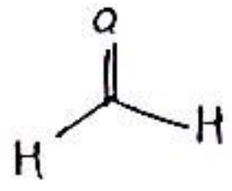
Eg's :



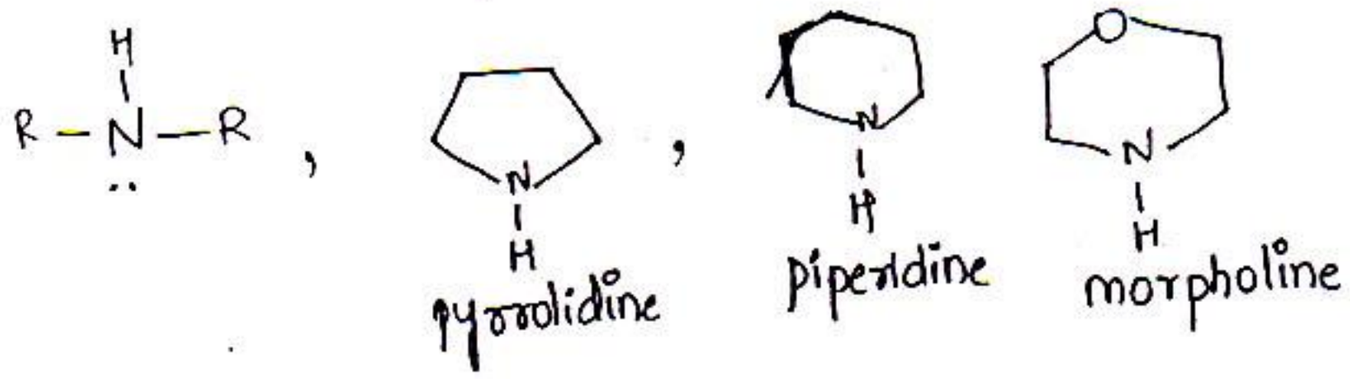


Active C-H function +  + 2°-Amine ⟶ mannich base (or) Amino-methylations at active positions.

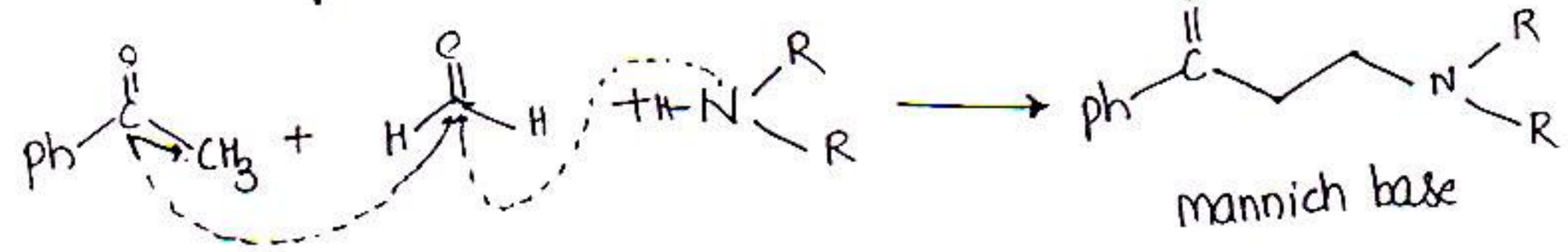
(5)

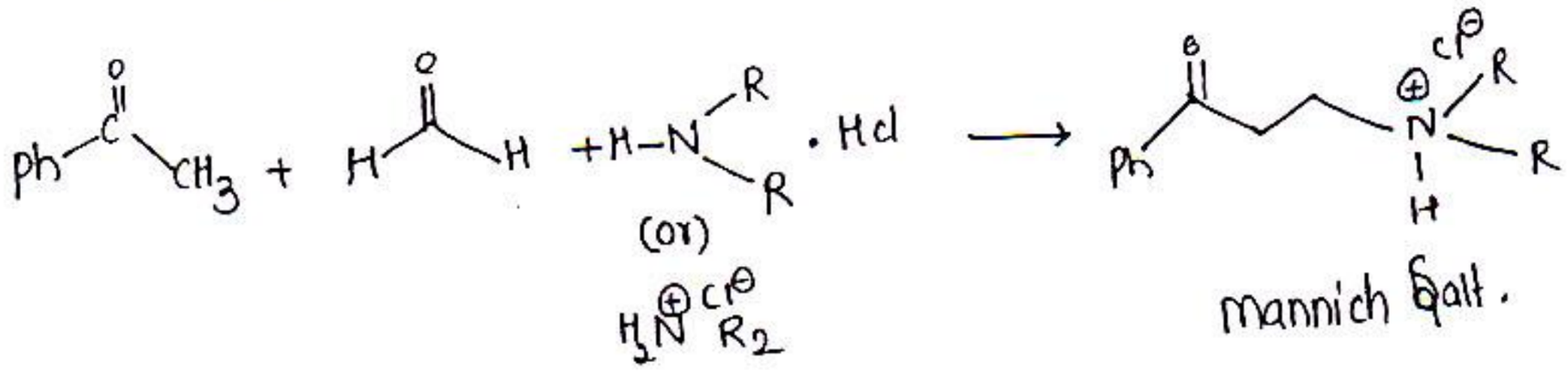
Active C-H function +  + salt of 2°-Amine ⟶ mannich salt.

2°- amines may be cyclic or accyclic.

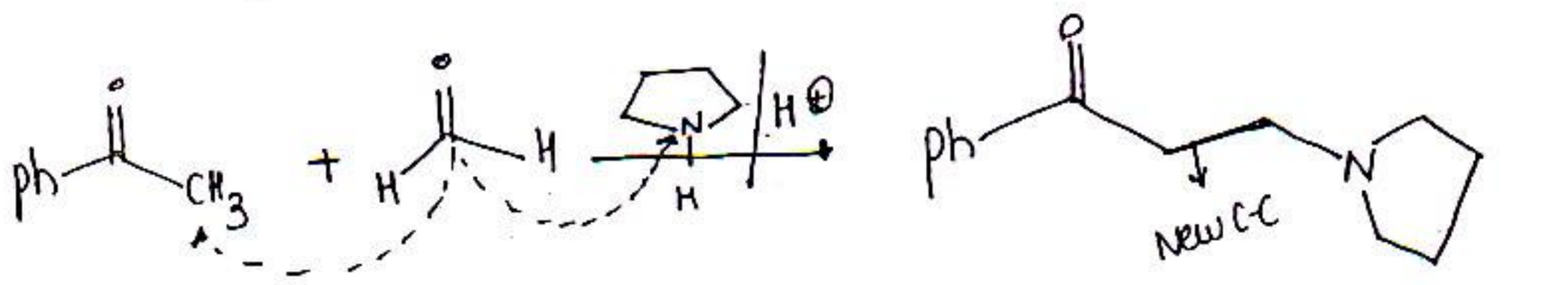


Eq. 1

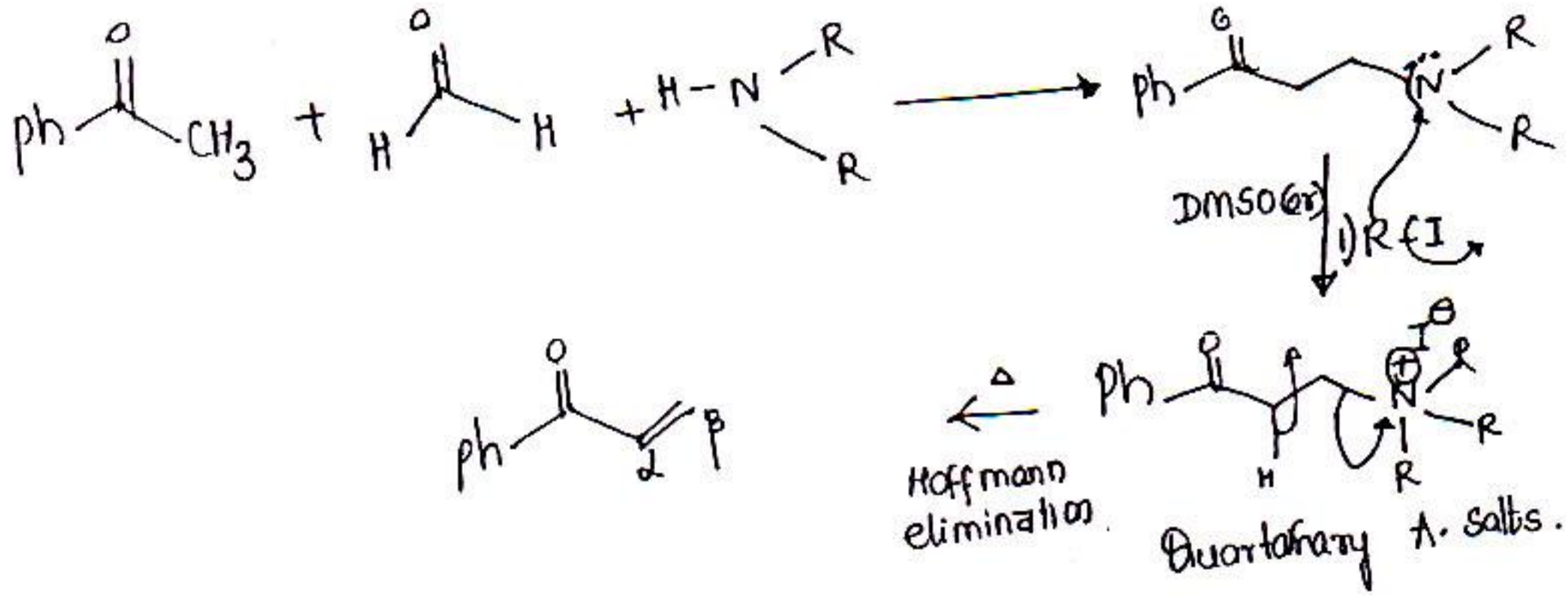


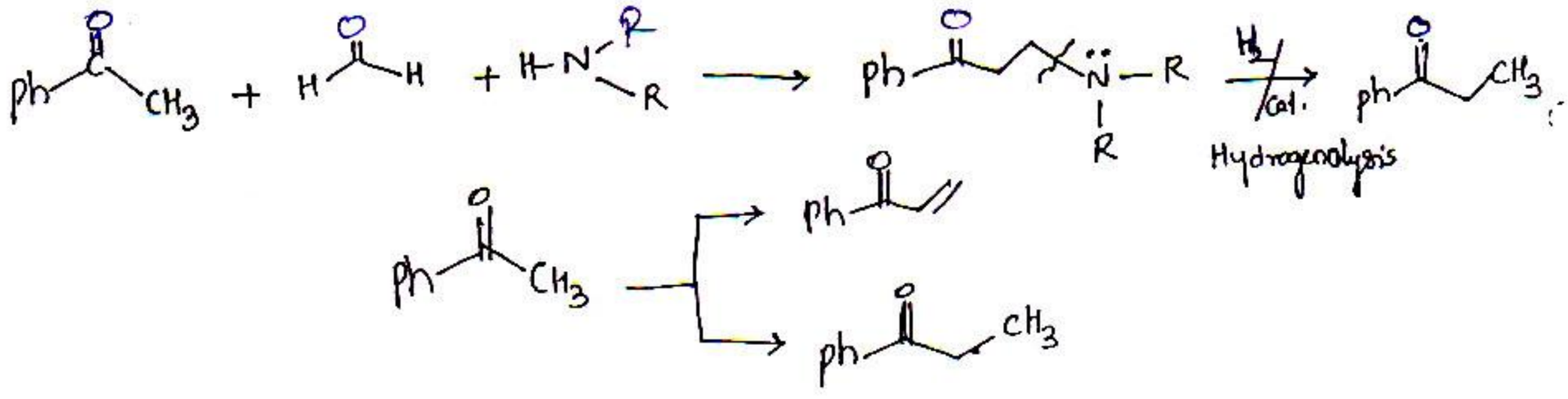


Eq: 2

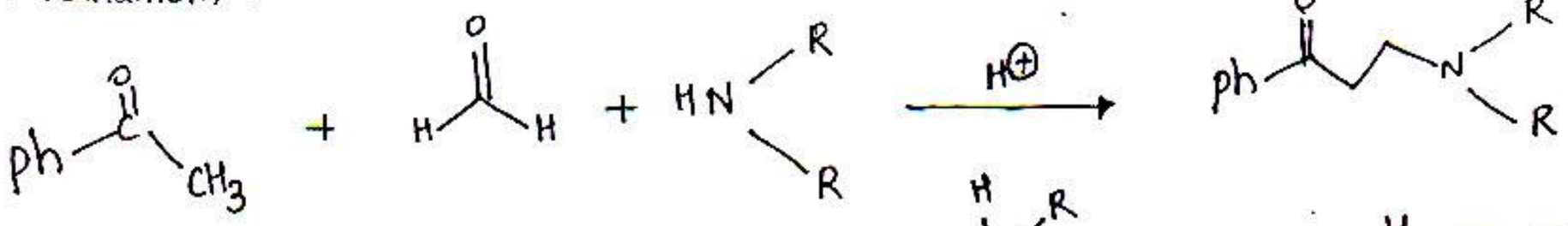


Eq: 3

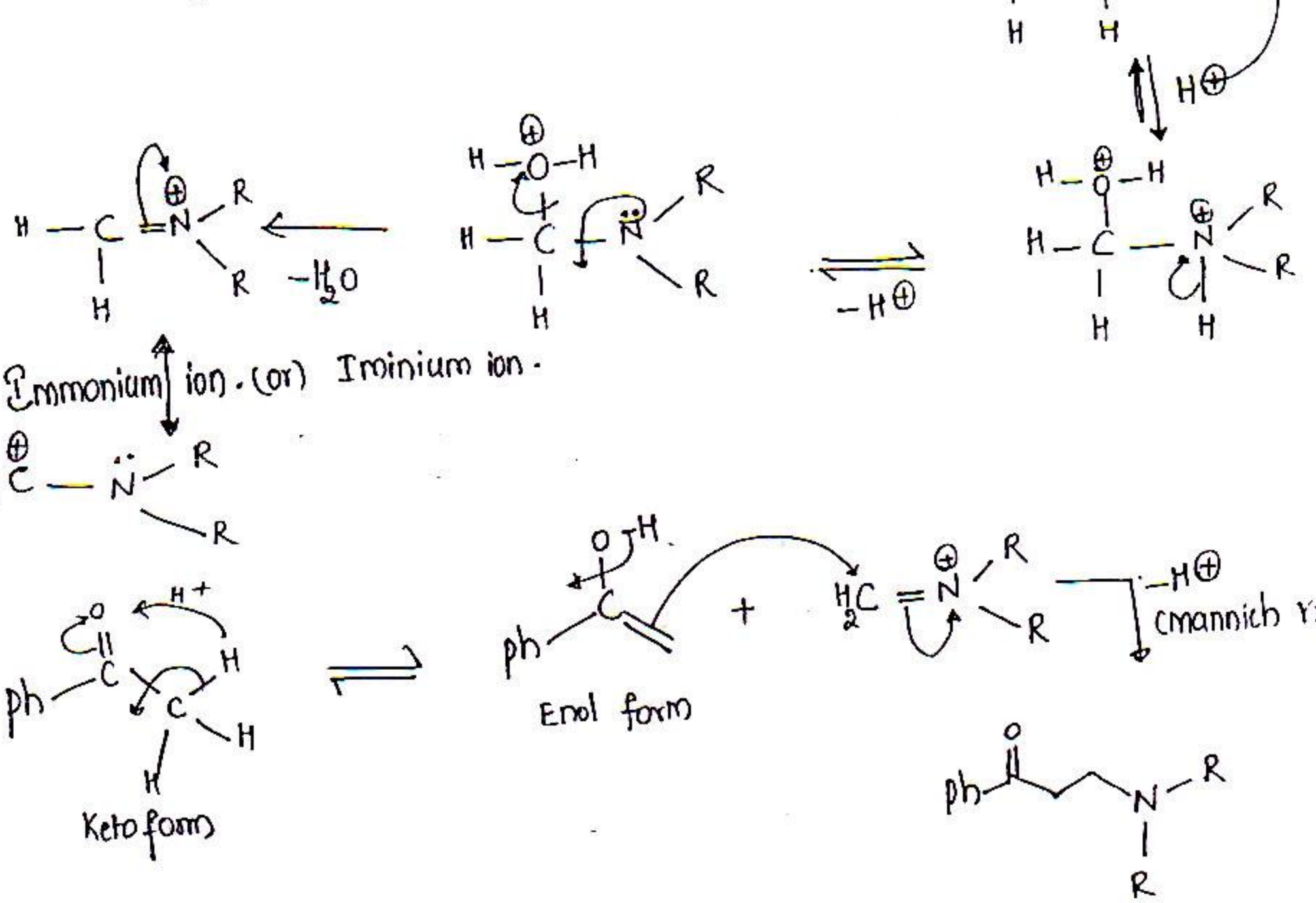




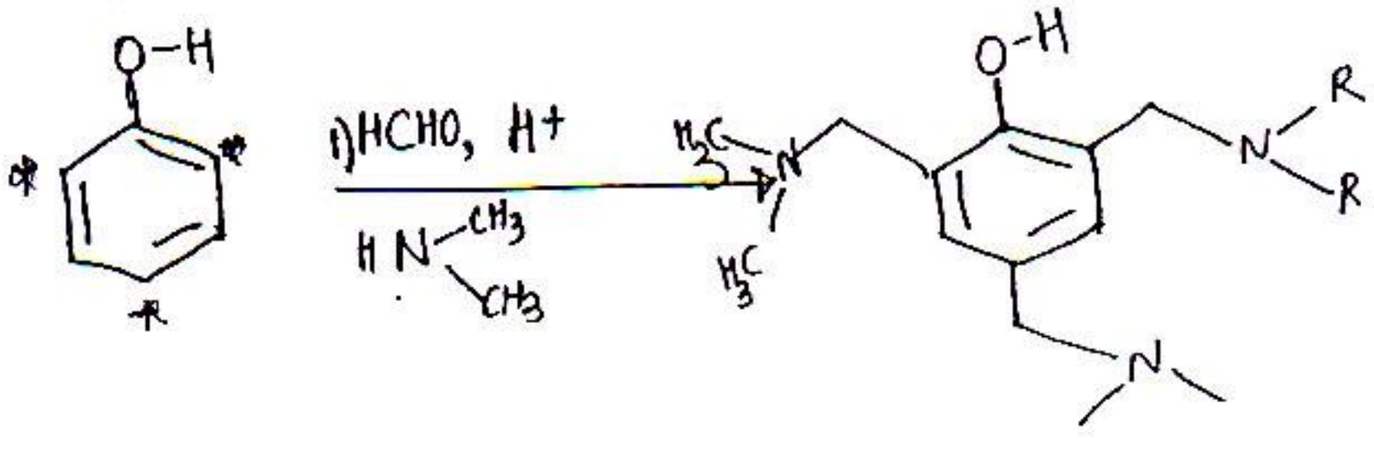
Mechanism :

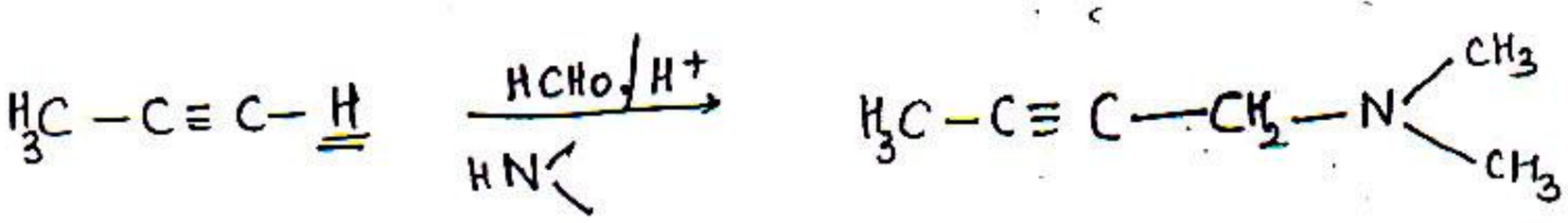


Step: 1 :

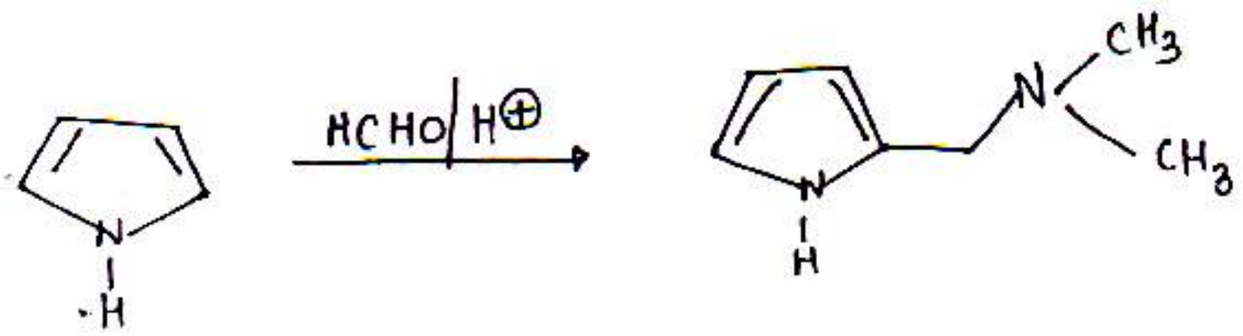


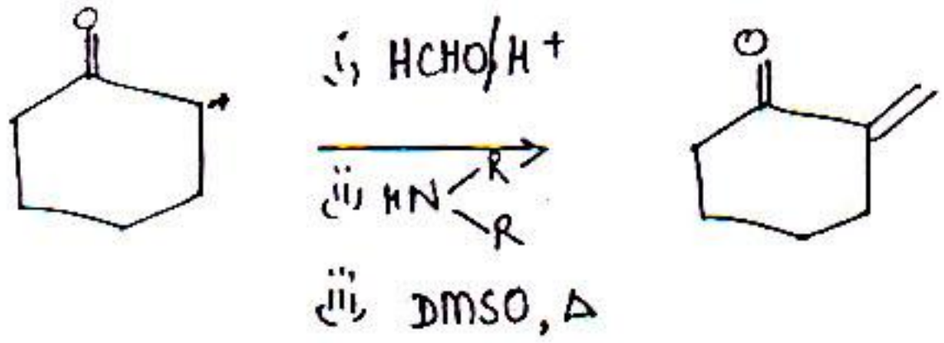
Eg: 4.



Eg: 5 

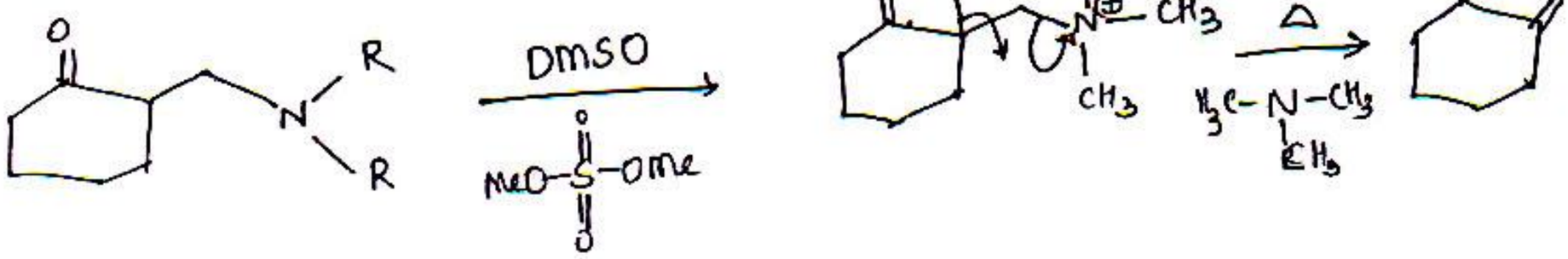
(6)

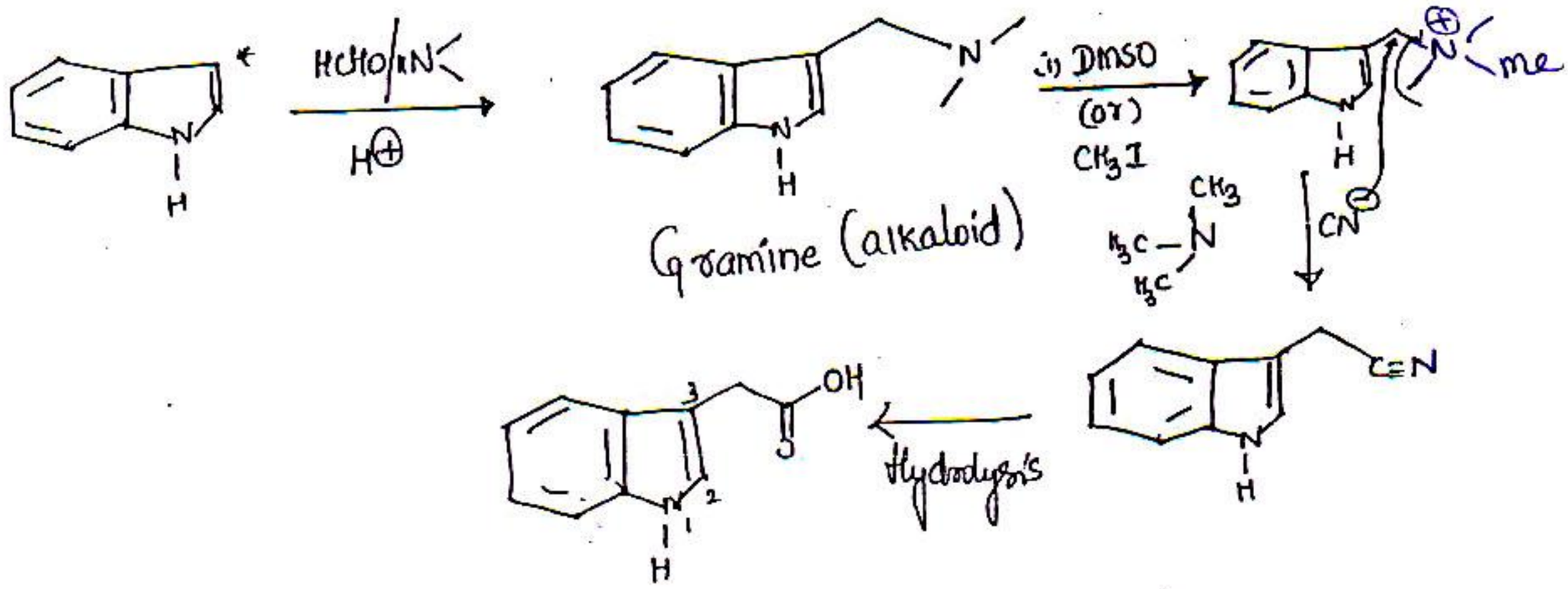
Eg: 6 

Eg: 7 

Explain

i, mannich reaction



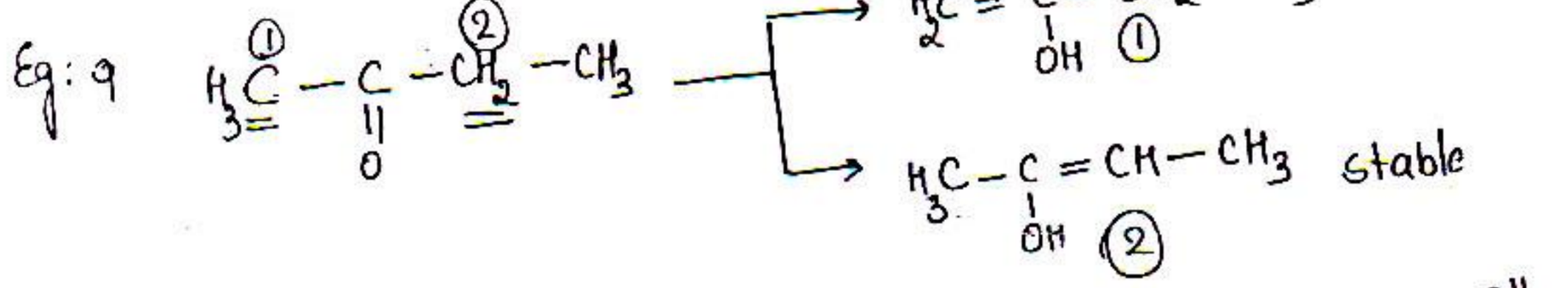
Eg: 8 

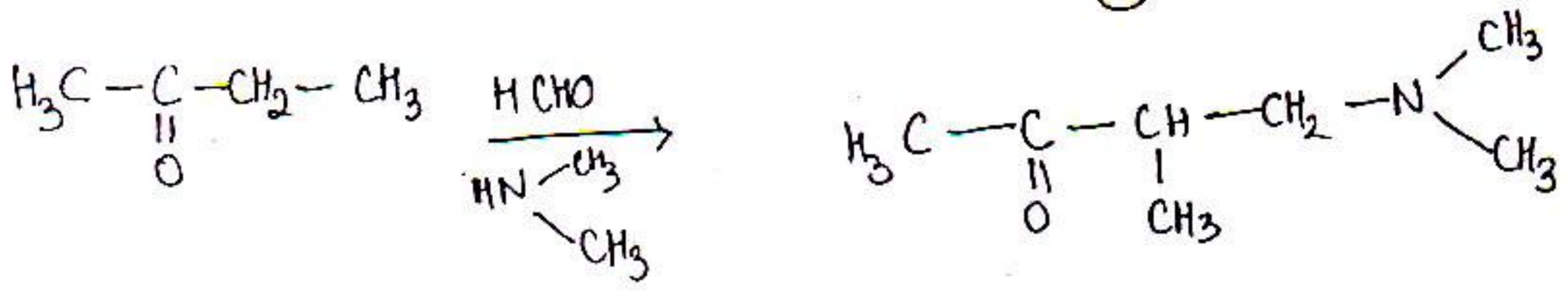
Gramine (alkaloid)

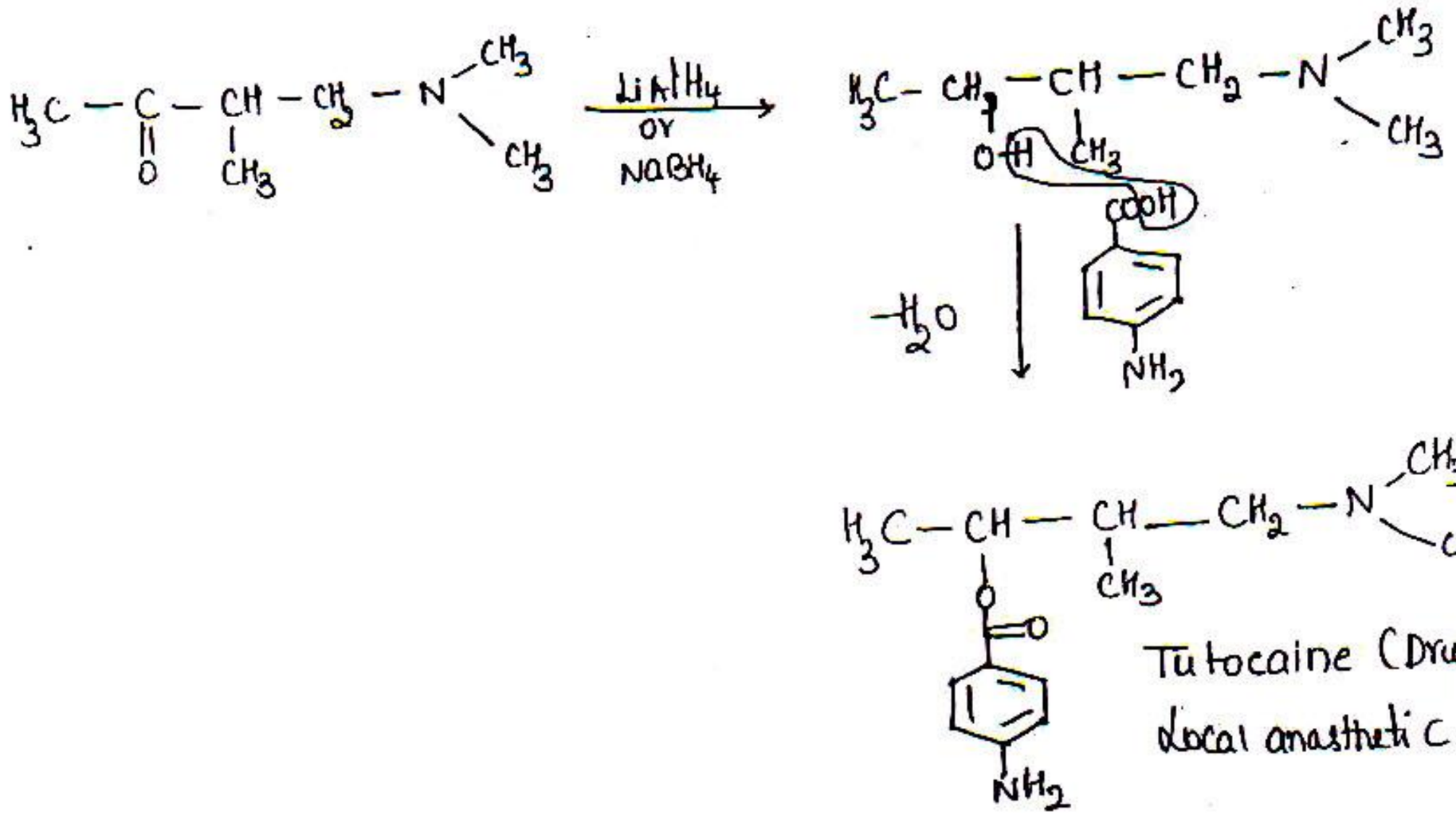
Hydrolysis

Heteroauxin (Indole-3-acetic acid)

(drug)

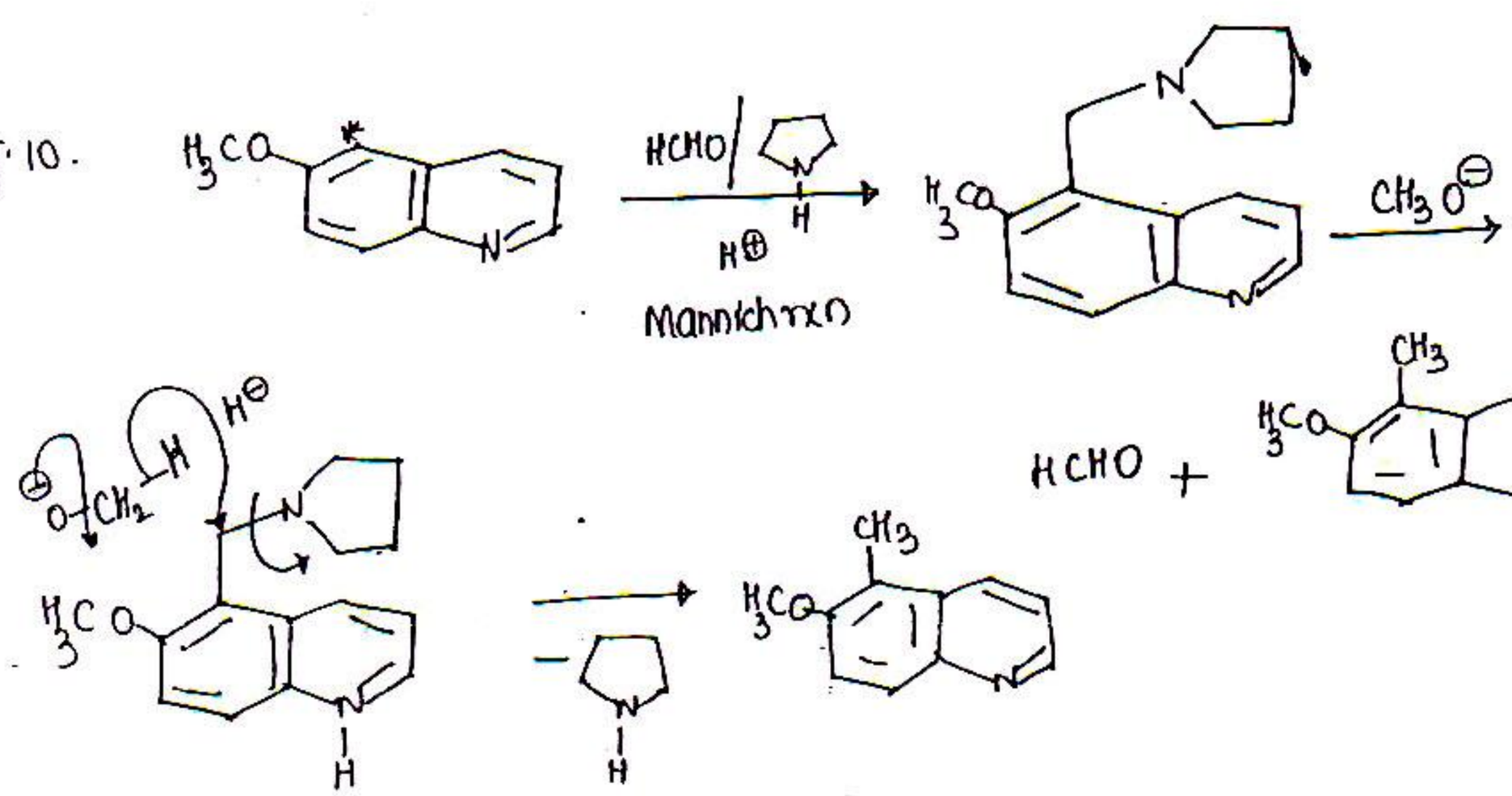
Eg: 9 



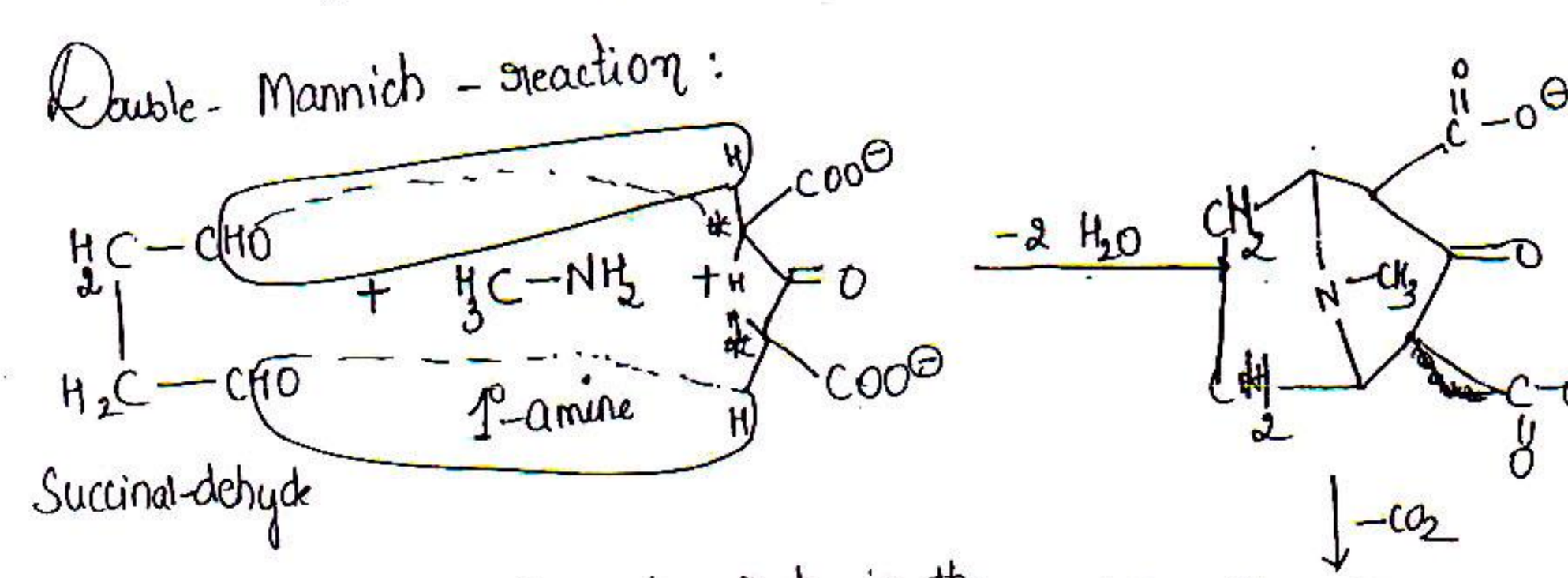


Tutocaine (Drug)
Local anasthetic.

Eg: 10.



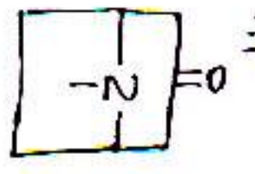
Mannich rxn

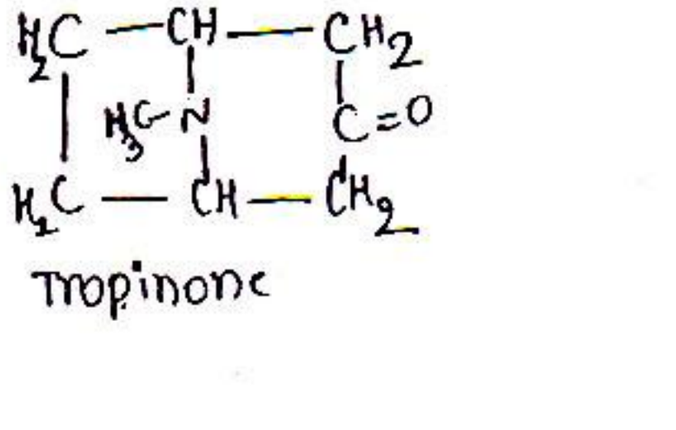


Double - Mannich - reaction :

Succinal-dehyde

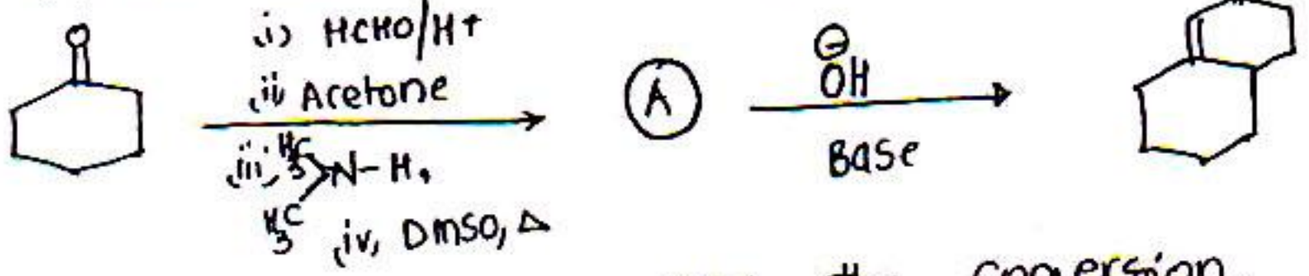
Tropinone one of the intermediate in the proparation of aTropine alkaloid



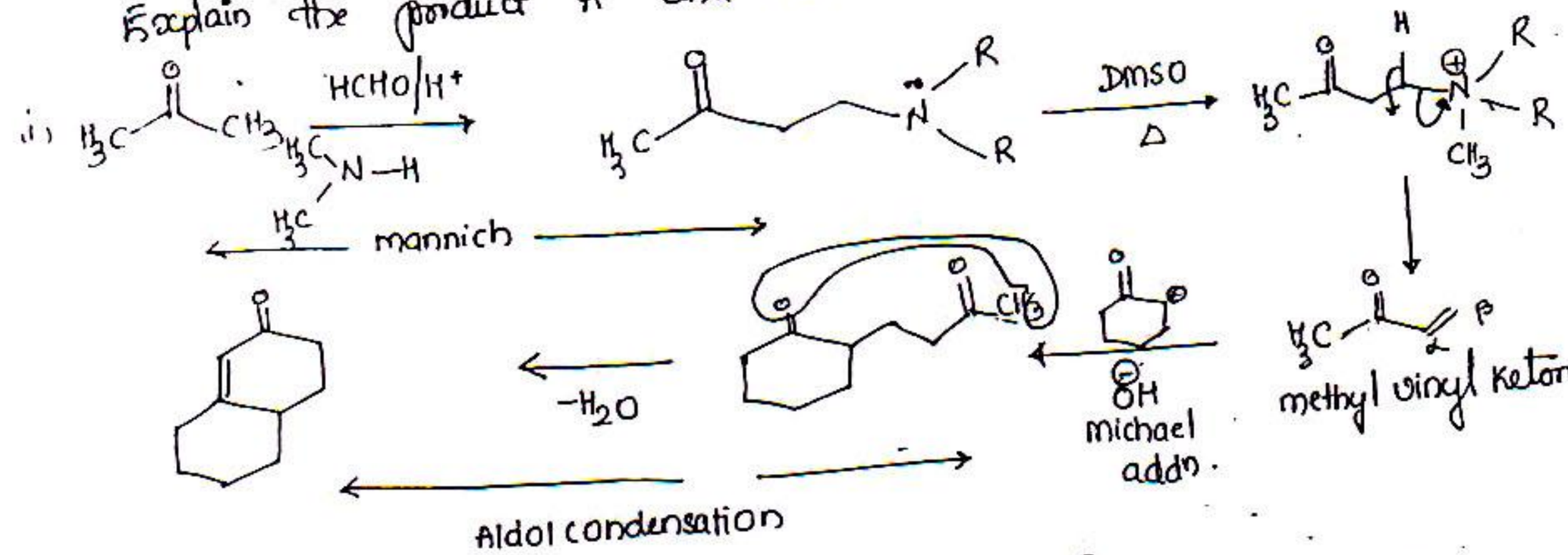


Tropinone

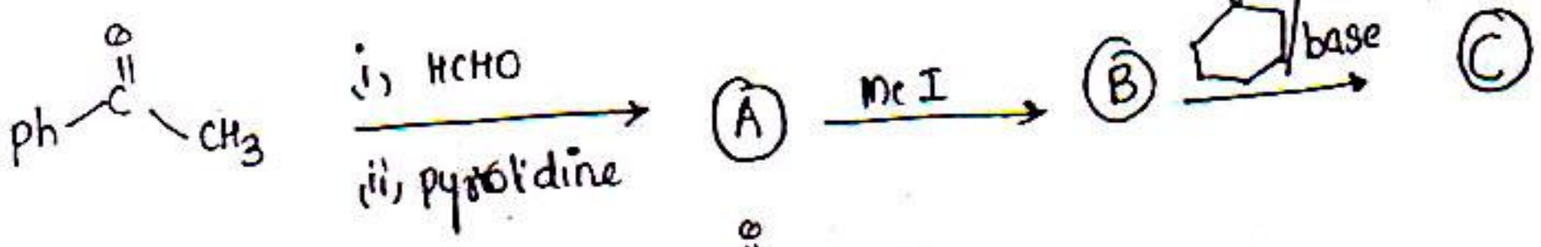
Eg: Mannich reaction + Michael addition + Aldol-reaction.



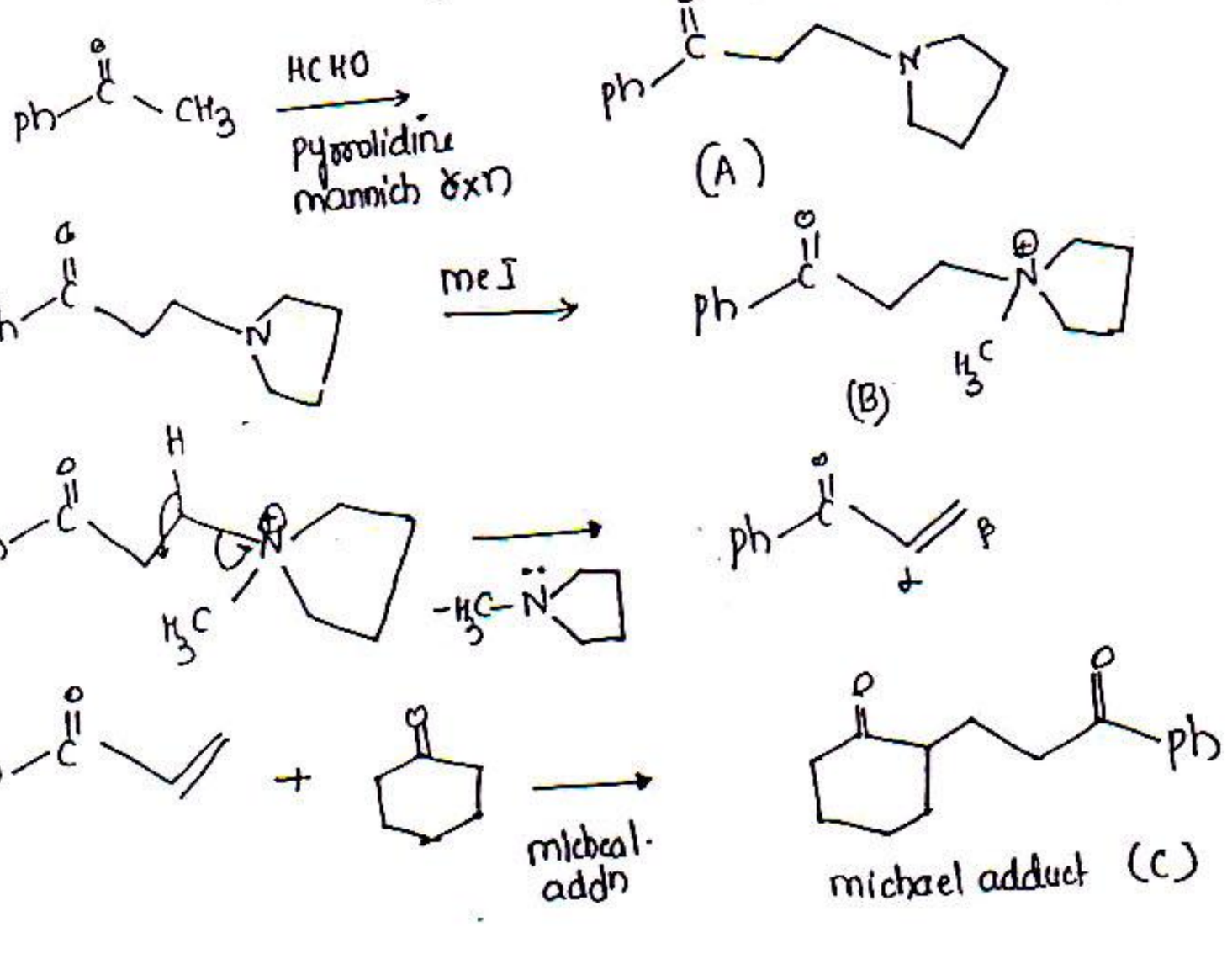
Explain the product A and the conversion.

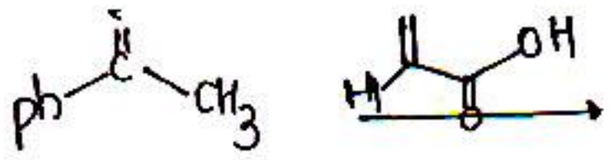


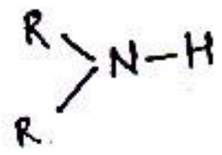
Eg:

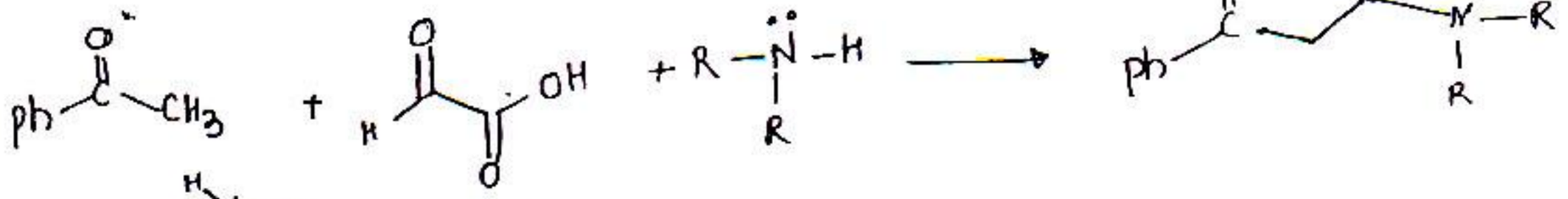


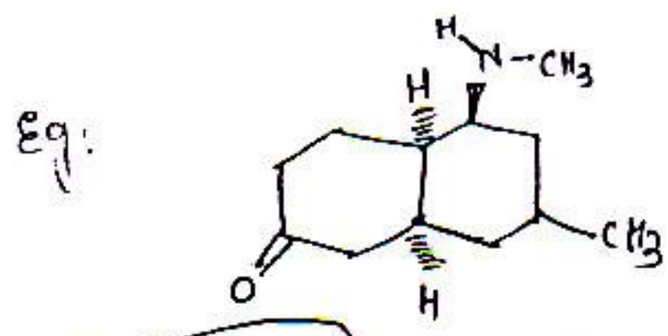
Ans

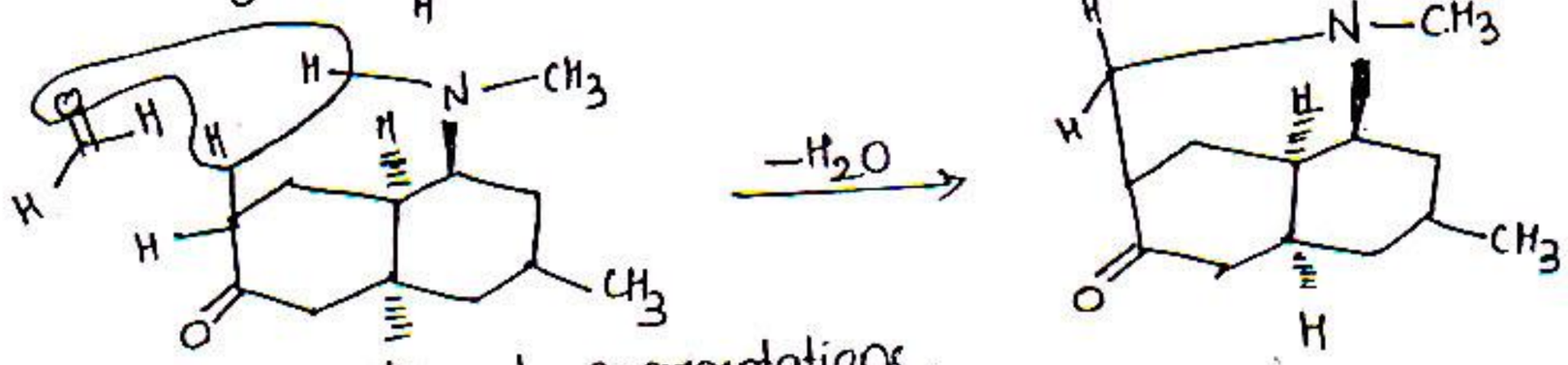


Eg:  Product -



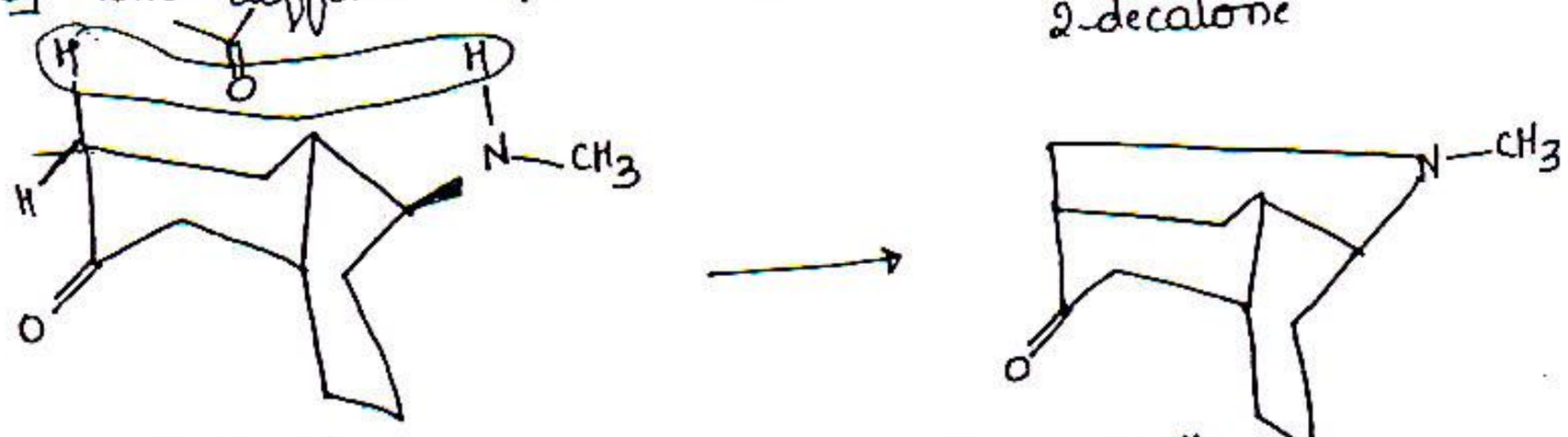


Eg:  ?



same eg with different representations.

2-decalone



cis-decalin

22/04/08
TUESDAY.

STORK – ENAMINE REACTION

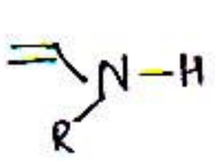
Enol = vinylalcohol  ENE + OL = ENOL

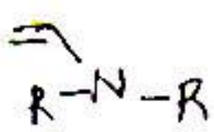
Enamine

Enamine = ENE + amine

amino olefin's

1°. Enamine :

2°. Enamine : 

3°. Enamine : 

Preparation of Enamine :

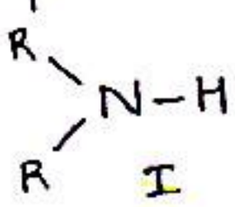
Carbonyl compound + Amine $\overset{H^+}{\rightleftharpoons}$ Enamine

→ Enamine formation is reversible.

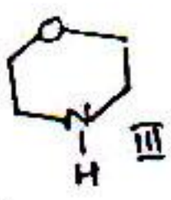
→ carbonyl compound should be alleast with one α-Hydrogen.

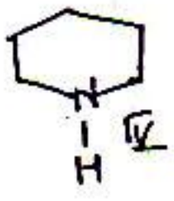
→ $R-\underset{\alpha\text{-position}}{\underline{CH_2}}-\overset{O}{\overset{\|}{C}}-R$ + Amine (acyclic or cyclic) $\rightleftharpoons$ Enamines.

→ Enamines from 2° amines are stable

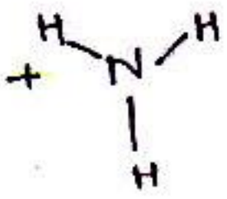
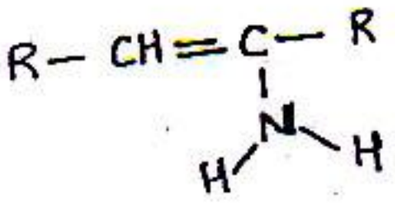
Amines :  I

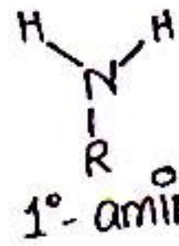
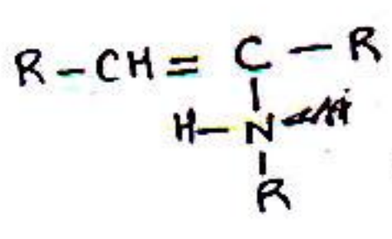
 II

 III

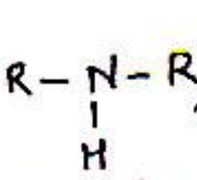
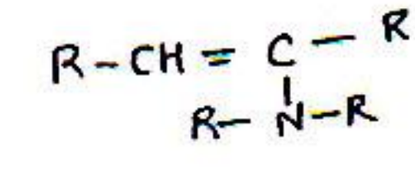
 IV

Reactivity order : I > II > III > IV

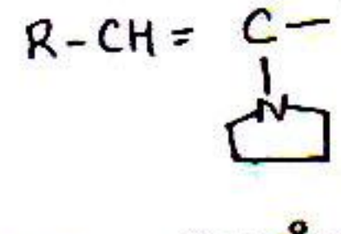
eg: $R-CH_2-\overset{O}{\overset{\|}{C}}-R$ +  $\overset{H^\oplus}{\rightleftharpoons}$  1° enamine (unstable)

eg: $R-CH_2-\overset{O}{\overset{\|}{C}}-R$ +  $\overset{H^\oplus}{\rightleftharpoons}$  unstable.

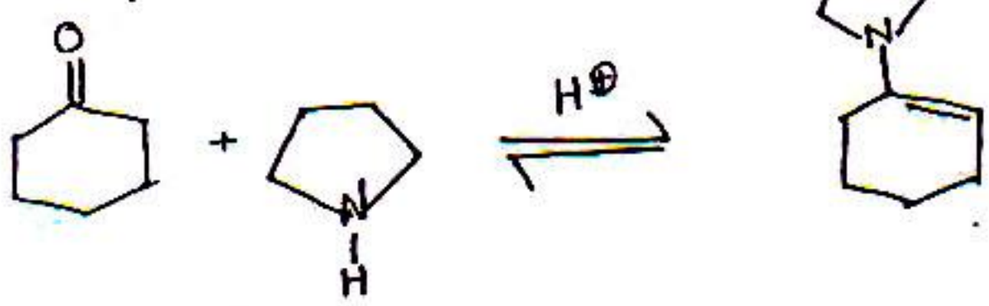
1° amine

eg: $R-CH_2-\overset{O}{\overset{\|}{C}}-R$ +  $\overset{H^\oplus}{\rightleftharpoons}$  (Stable)

2° amine

eg $R-CH_2-\overset{O}{\overset{\|}{C}}-R$ +  $\overset{H^\oplus}{\rightleftharpoons}$  (Stable)

Even cyclic ketones also readily forms enamines.

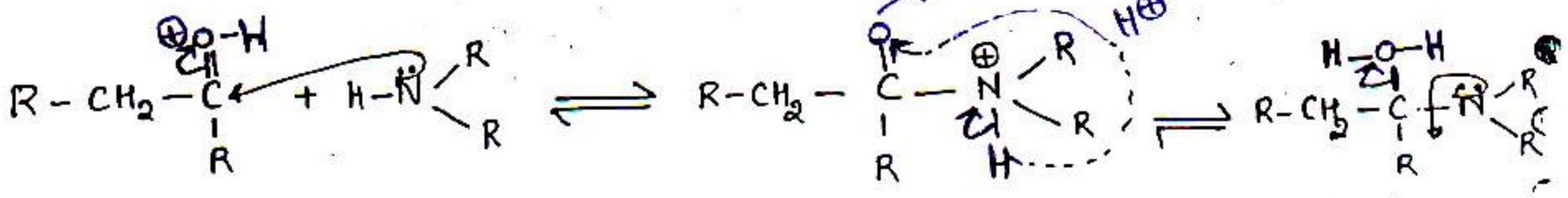


Mechanism:

$R-CH_2-\overset{O}{\overset{\|}{C}}-R$ + $H-\underset{R}{\overset{R}{N}}$ $\overset{H^\oplus}{\rightleftharpoons}$ $R-CH=\underset{R-N-R}{\overset{|}{C}}-R$

Step-1 formation of oxonium ion.

$R-CH_2-\overset{O}{\overset{\|}{C}}-R + H^\oplus \rightleftharpoons R-\overset{\oplus OH}{\overset{|}{C}H_2}-\overset{O}{\overset{\|}{C}}-R$.

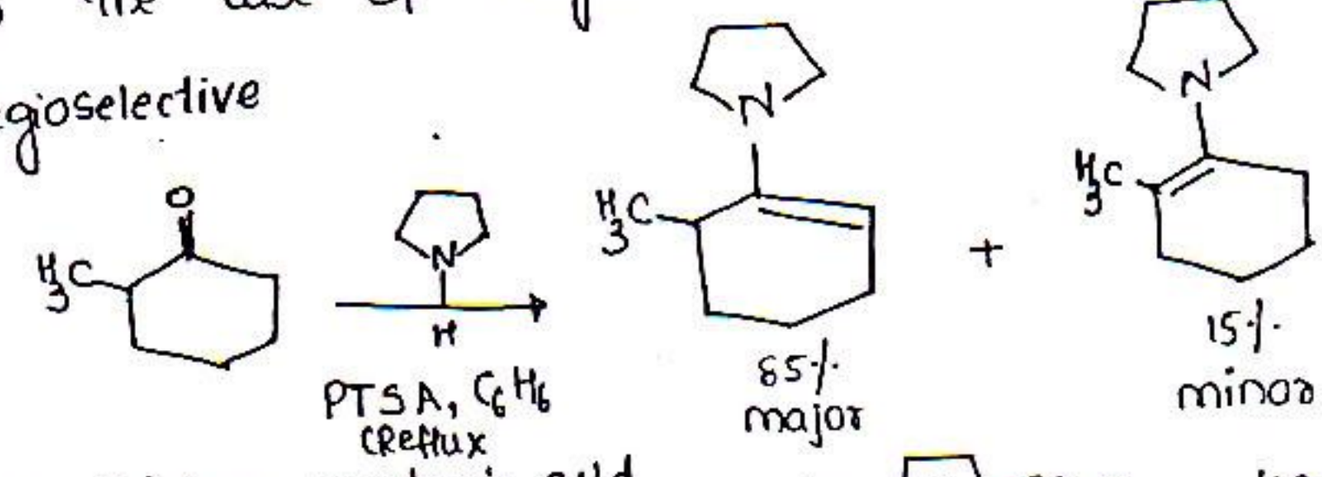


α,β-unsaturated amines
(Enamine)

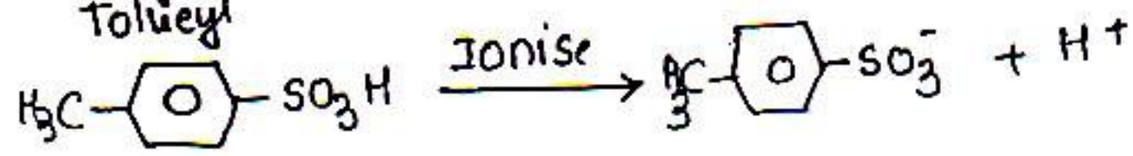
Regioselectivity :

In the case of unsymmetrical Ketones, Enamine formation is regioselective

v.imp ***



para Toluene Sulphonic acid
(or)
para-Tolyl Sulphonic acid
Tolueyl

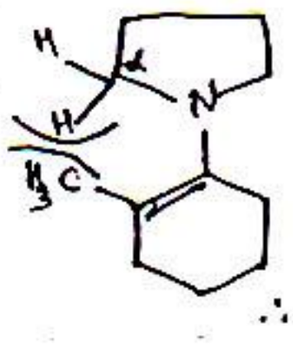


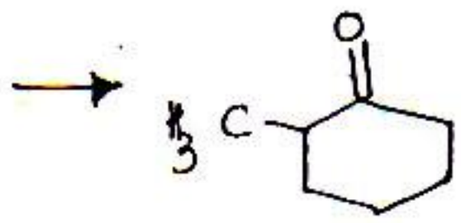
→ Unsymmetrical Ketones forms mixture of Enamines in unequal ratio. Enamine which is less substituted major or predominat product i/e orientation of double bond preferentially at less substituted α-position of carbonyl compound.

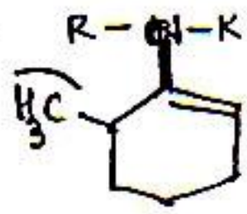
→ Reason :

→ major enamine free from steric interference, because unsaturation (double bond) with small size H

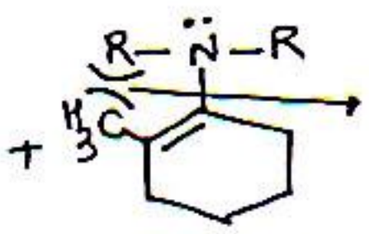
→ In minor enamine there is a steric interference between Bulkier methyl substituent of olefin and α-methylene group of Ammine ~~Nitrogen~~, decreased Resonance or conjugation between lone pair of Nitrogen and π-unsaturation.







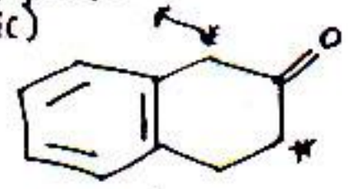
major

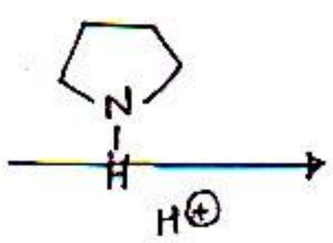


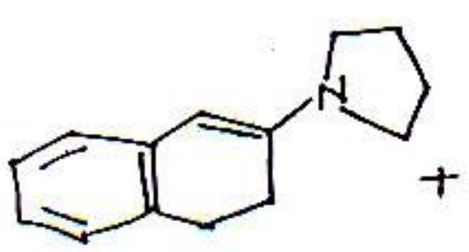
minor

Steric interference.

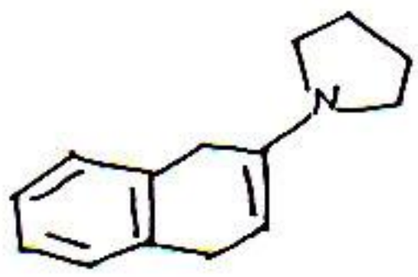
most preferred (benzilic)







major due to conjugation in benzene



minor

STORK - ENAMINE REACTION :

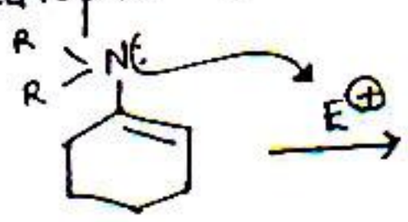
→ Electrophilic attacking at enamine is Stork enamine reaction

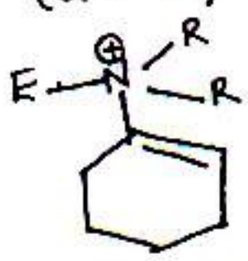
→ There are two Nucleophilic centres in enamine.

Nitrogen is Nucleophilic Centre.

Carbon Nucleophilic centre

→ Electrophile can take (attack) at these two positions.

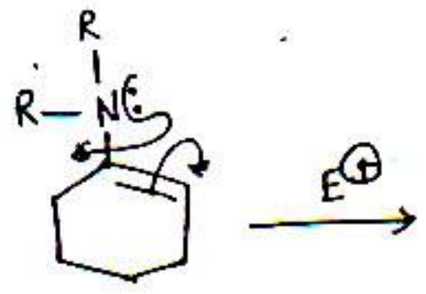


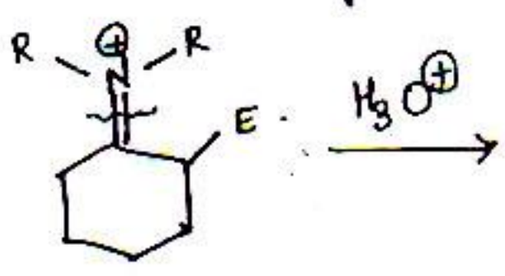


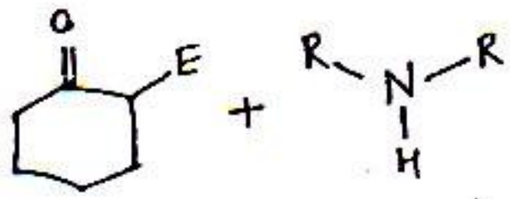
→ dissolves in H_2O.

→ not useful for organic Synthesis.

Quarternary Ammonium.







If $-\overset{|}{C}=\overset{\oplus}{N}-$ ⟶ $\overset{|}{C}=O + H-N-$ → Emonium ion and decomposes into carbonyl and amine functic

Emine on hydrolysis in acidic water

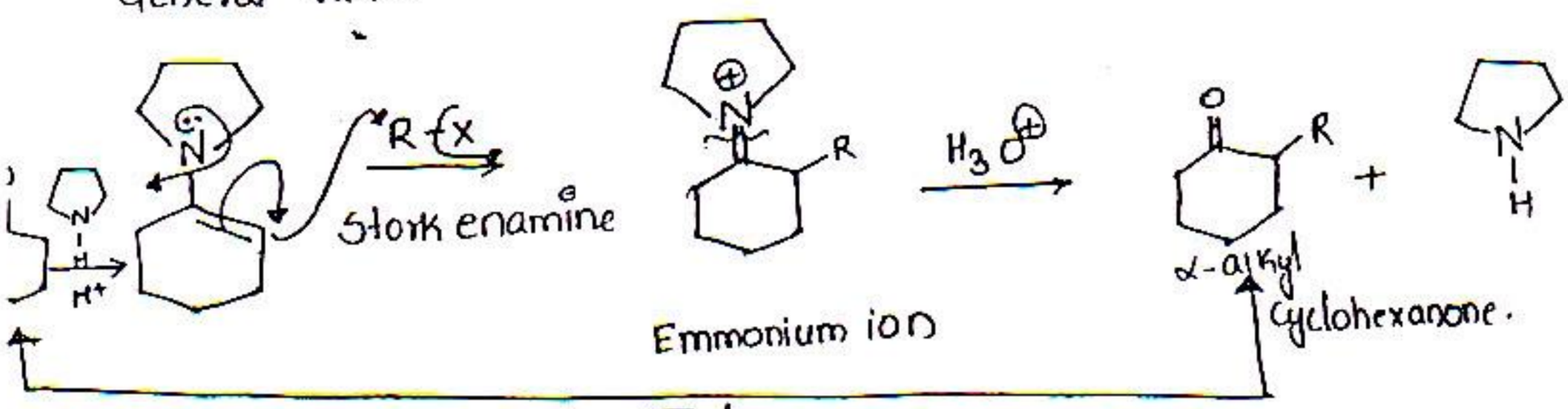
This rxn is useful for organic synthesis

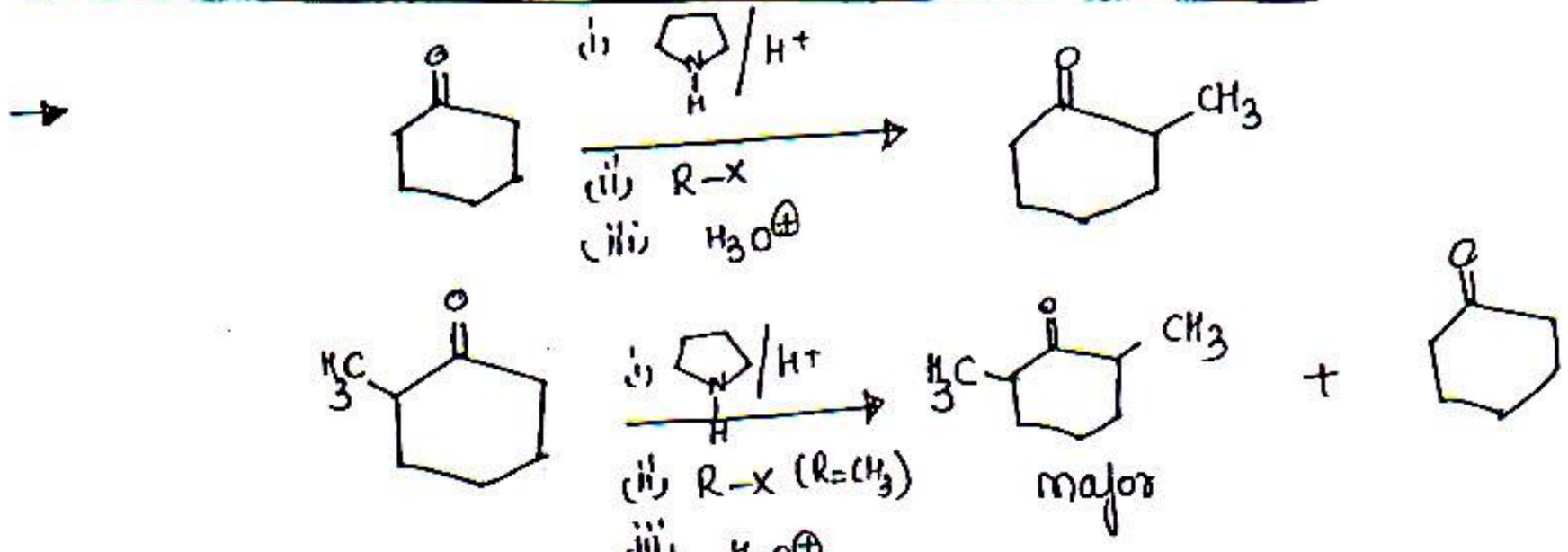
→ In Stork enamine the reaction's taking place at carbon Nucleophile useful for organic synthesis because develops new C–C bonding

Best Electrophiles :

Eg: Carbon electrophiles : $\overset{\oplus}{C}H_3$, $\overset{\oplus}{C}(=O)-R$, $\overset{\oplus}{C}H_2-Ph$, $\overset{\oplus}{C}H_2$

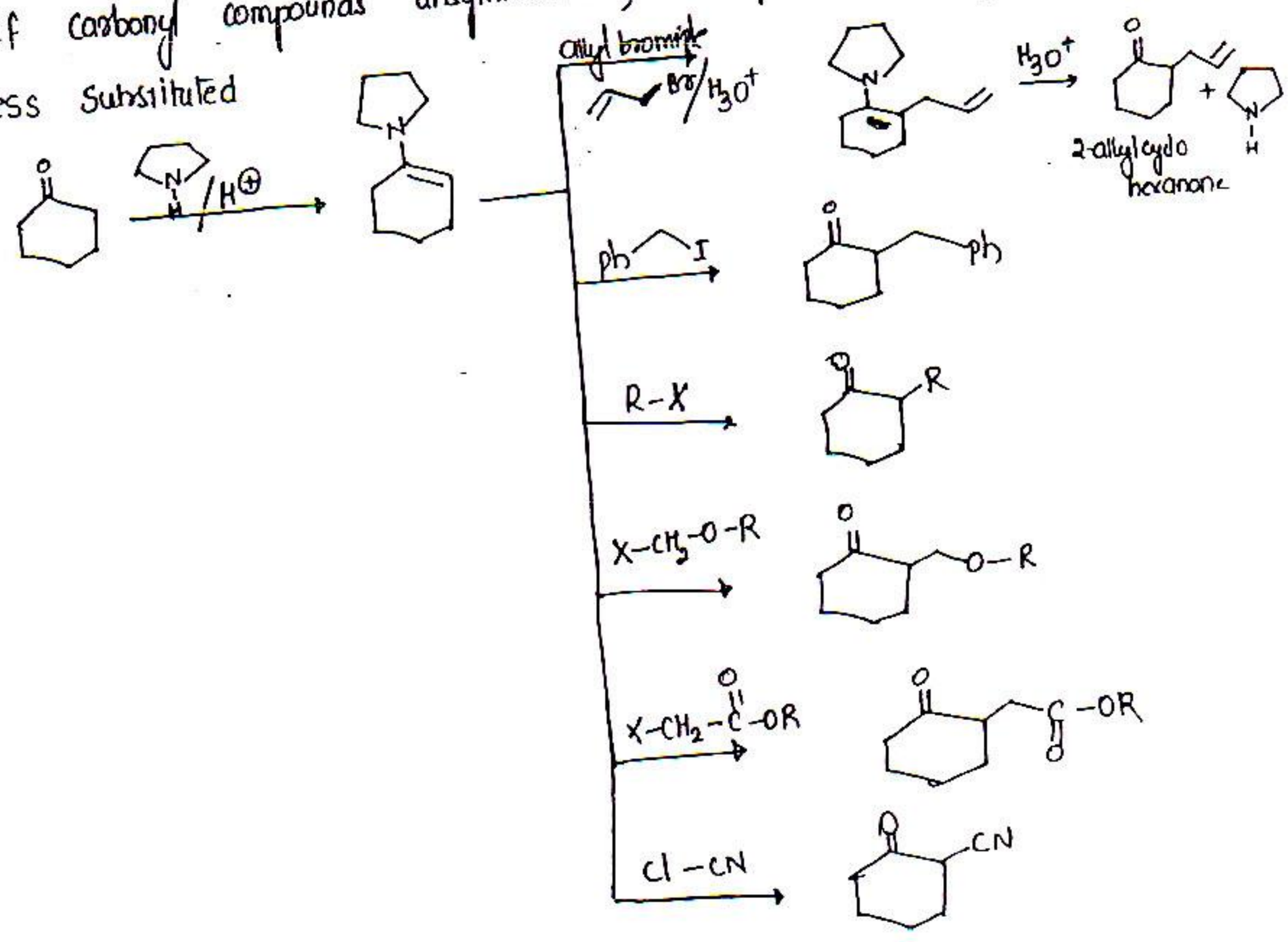
General rxn :

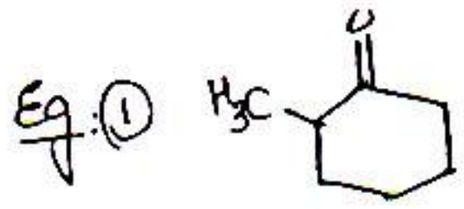
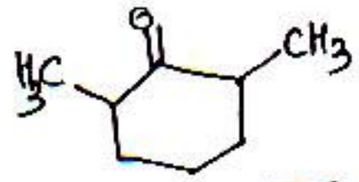


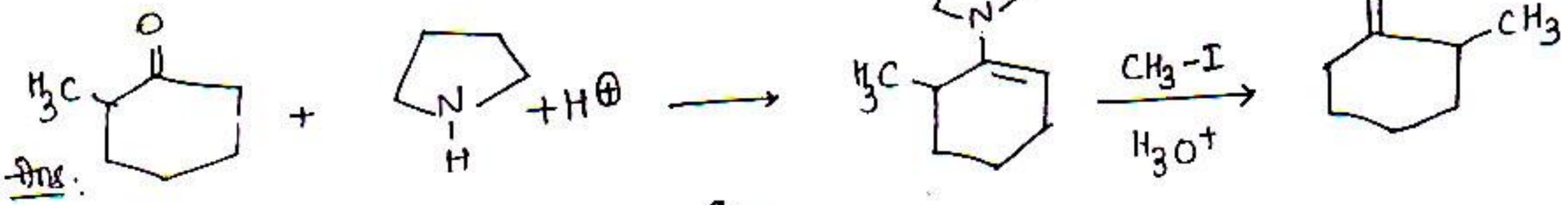


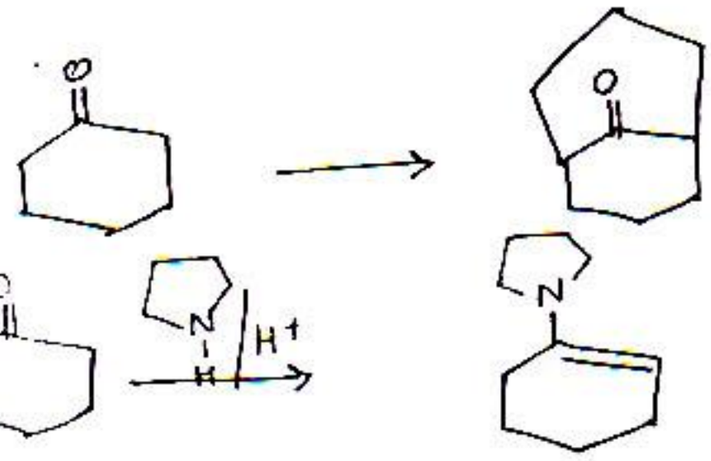
→ Stork enamine rxn's are indirect methods to introduce electrophilic carbon groups at α-position of carbonyl compounds.

→ If carbonyl compounds unsymmetrical, Electrophilic attacking preferentially at less substituted

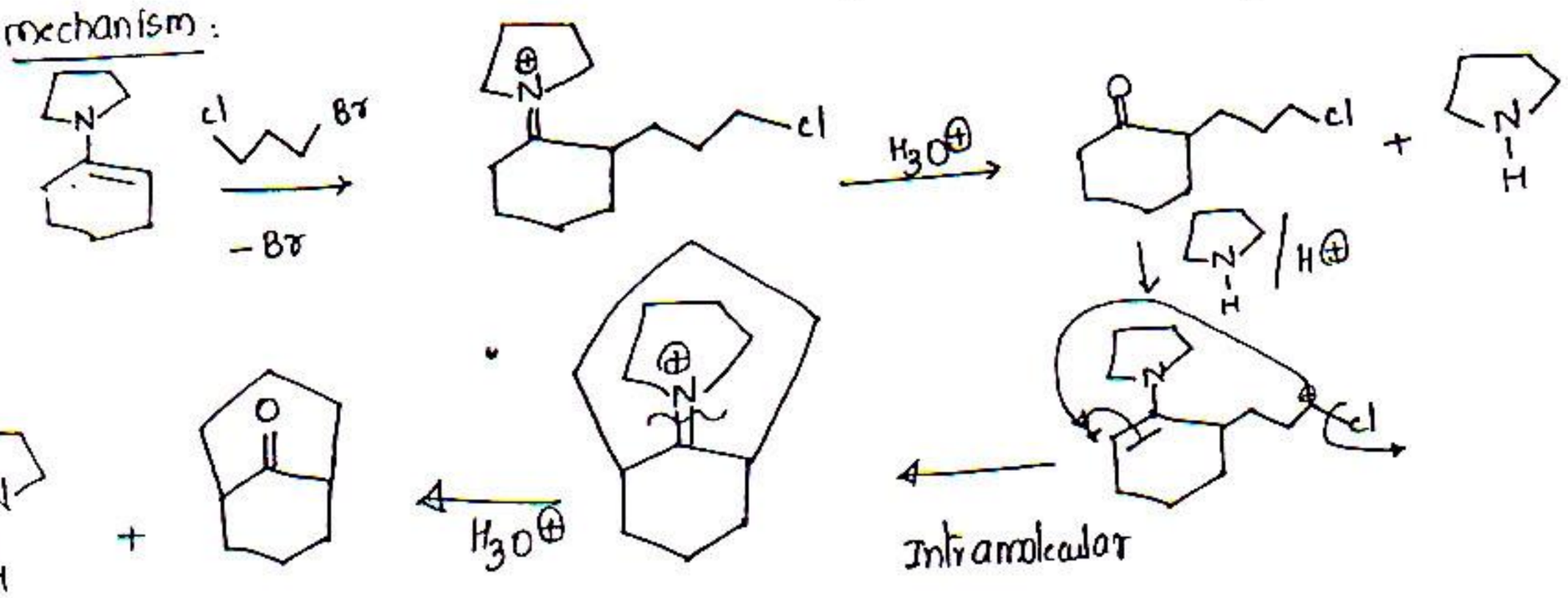


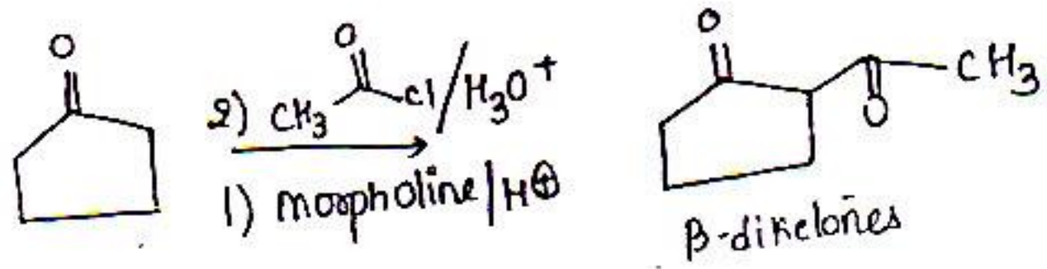
Eg: ①  

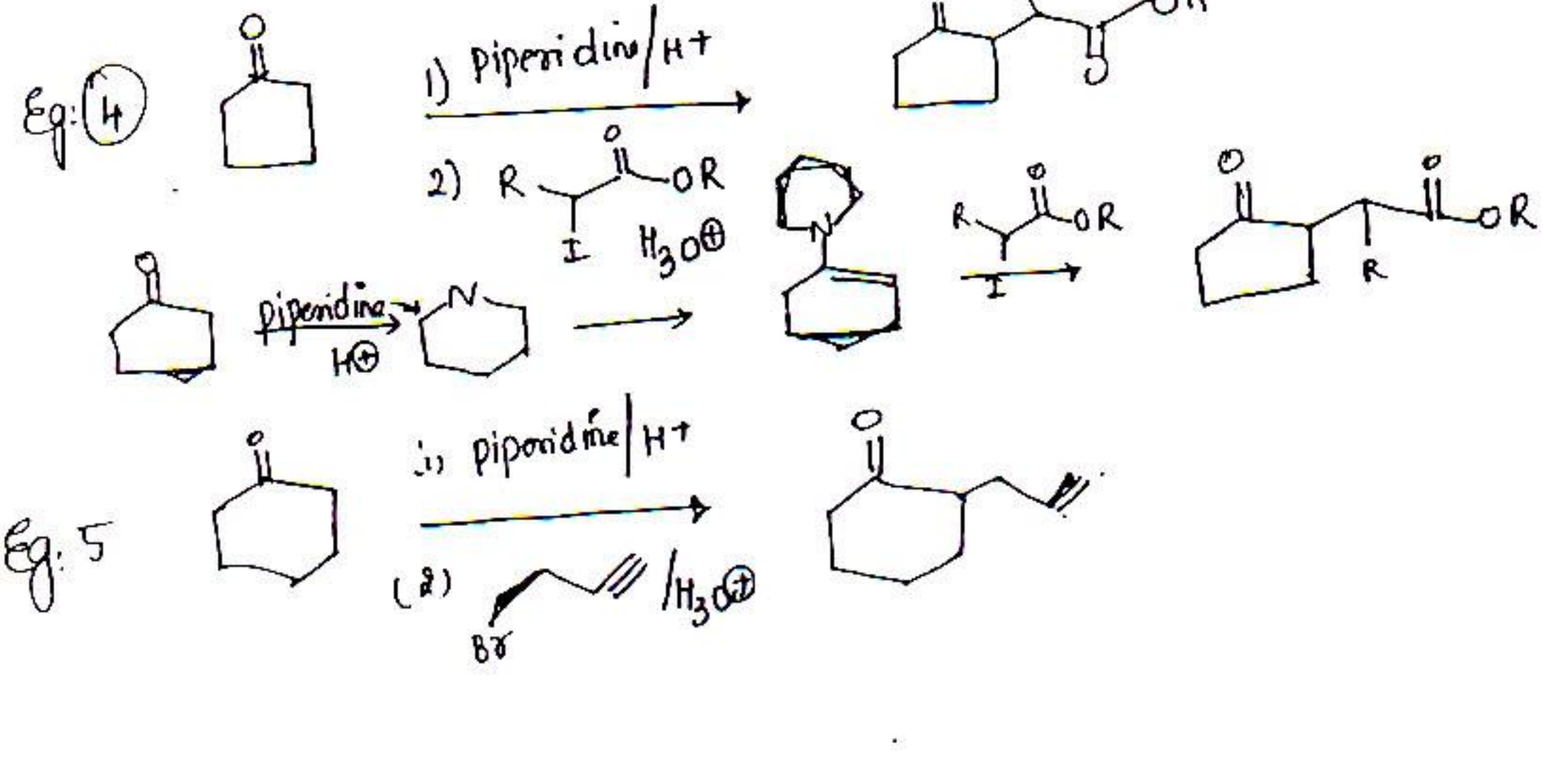
Ans: 

Eg: ② 

Ans:

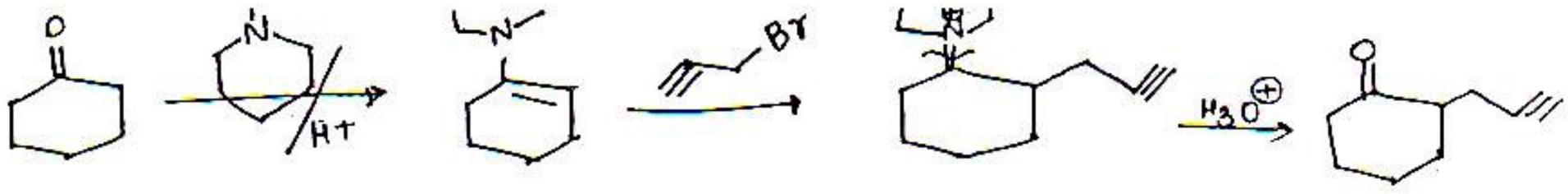
mechanism: 

Eg: ③ 

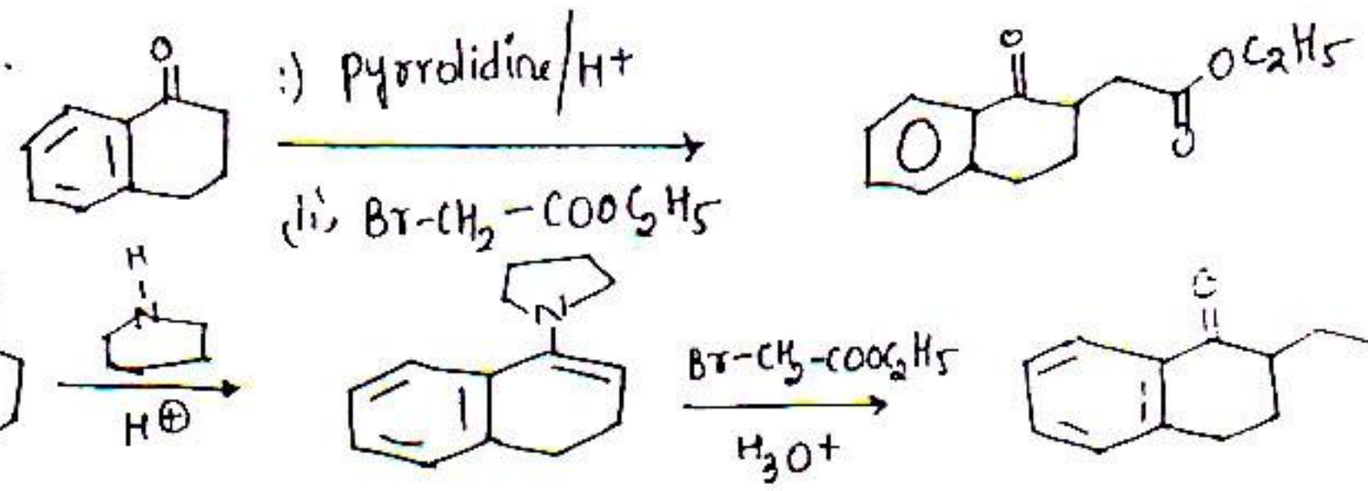
Eg: ④ 

Eg: 5

Ans.

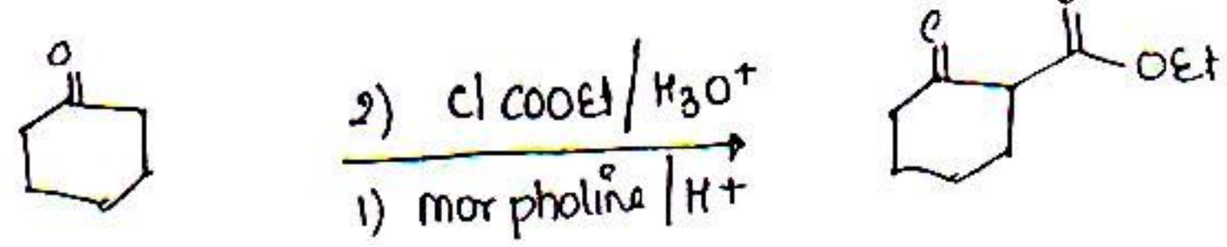


Eg: (6)



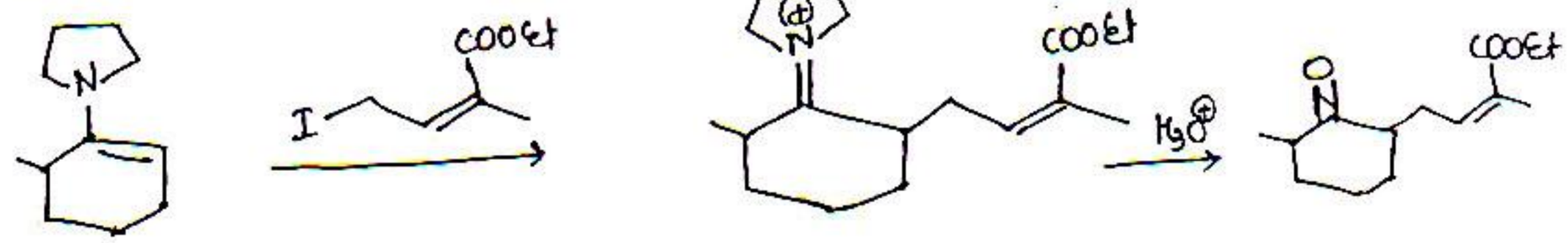
Ans:

Eg: (7)

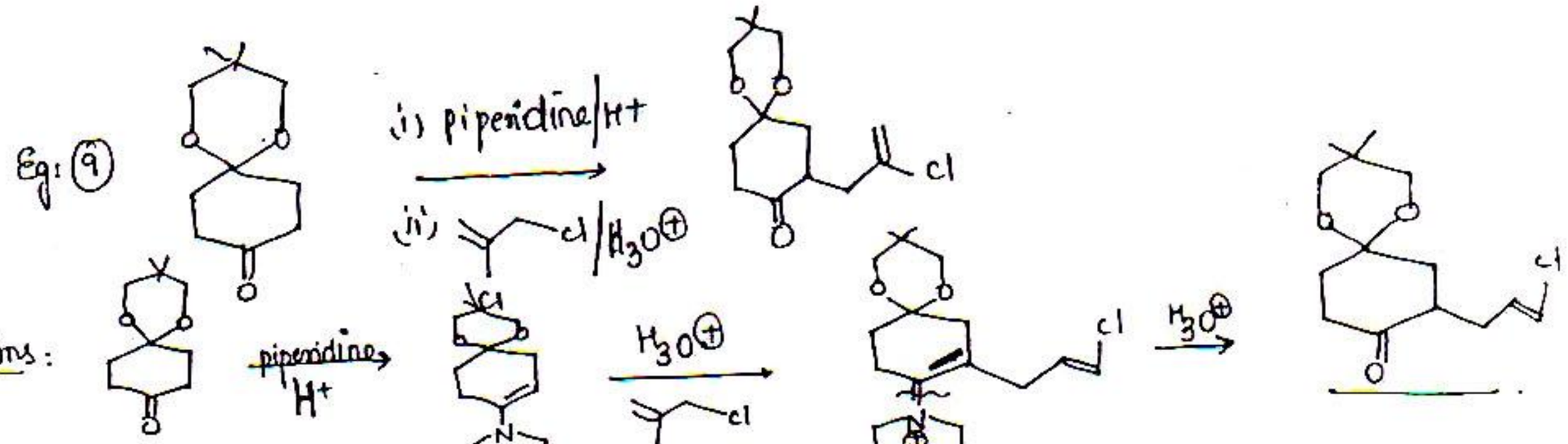


Ans: +

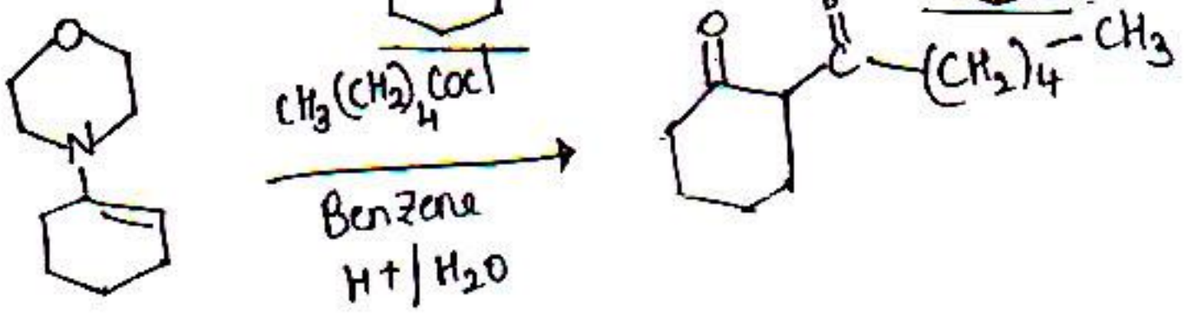
Eg: (8)



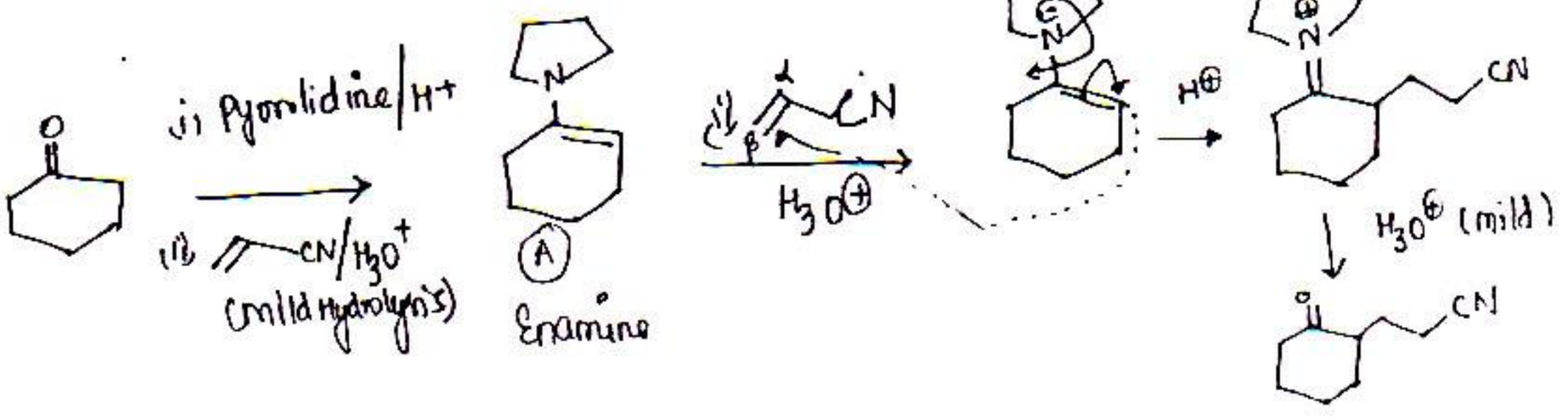
Eg: (9)

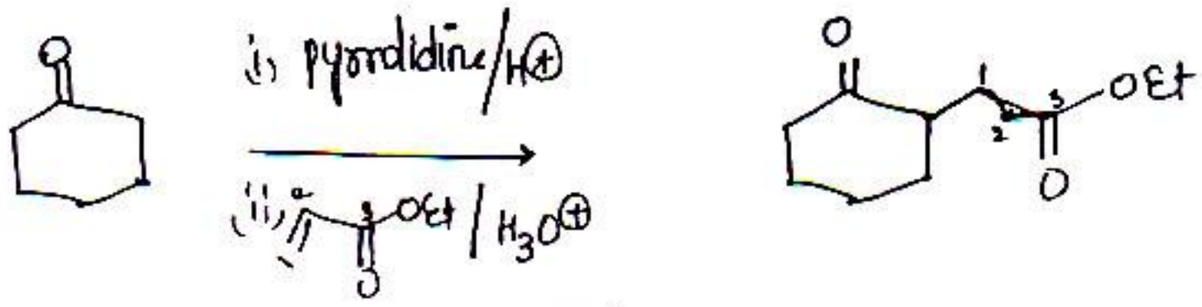


Eg: (10)

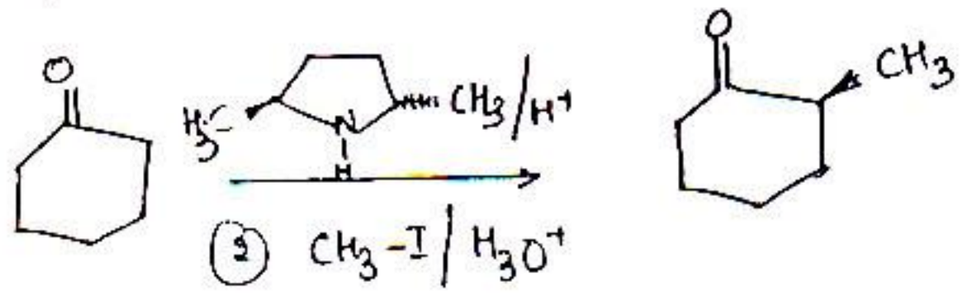


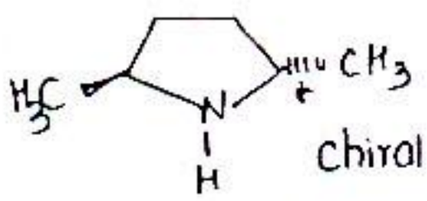
Eg: 11





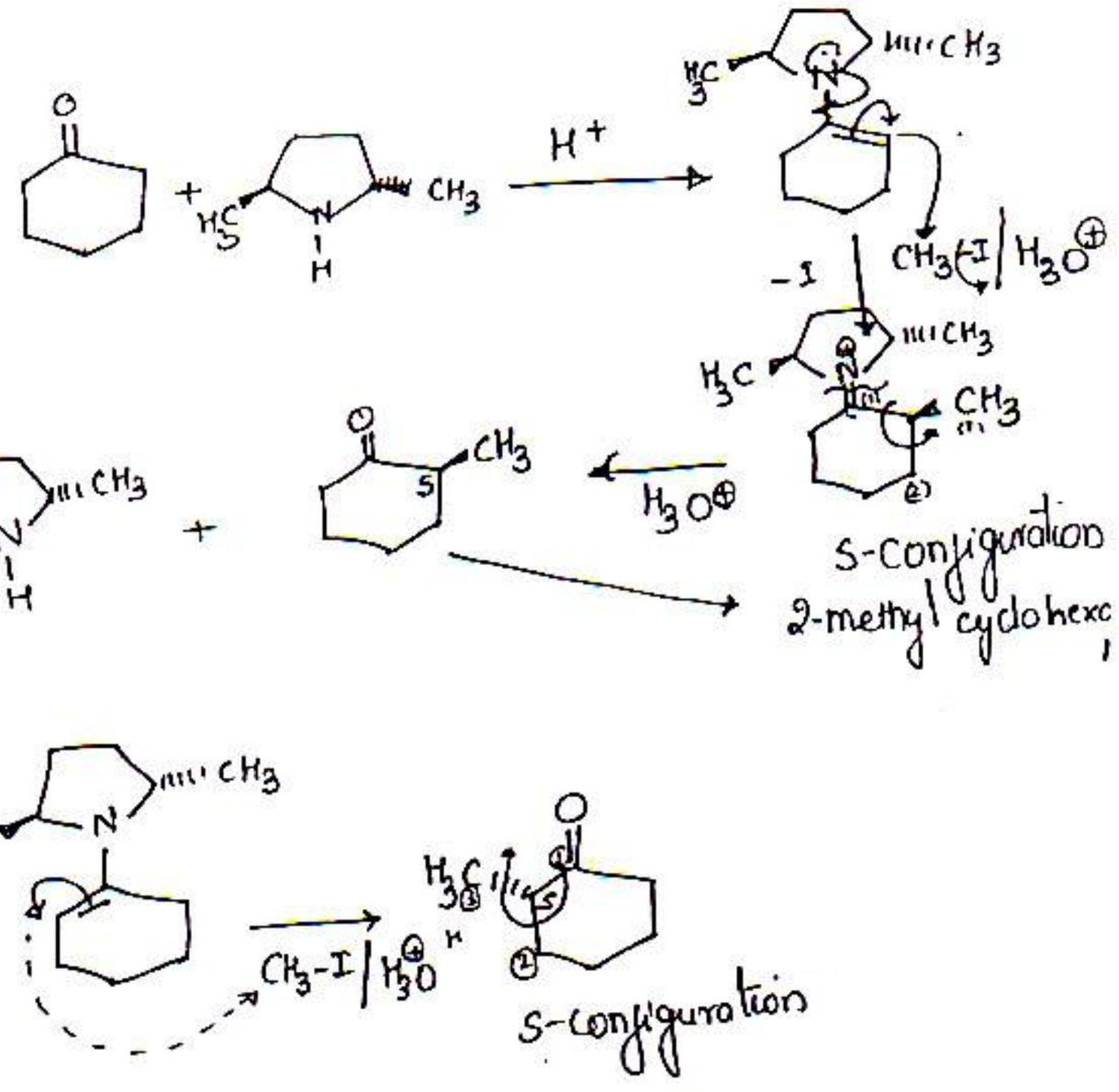
V. Imp ASSymmetric Stork enamine rxn:





→ When the electrophile attacks from back it suffers from steric crowding with the already existing CH_3 on pyrrolidine

∴ It approaches from front side



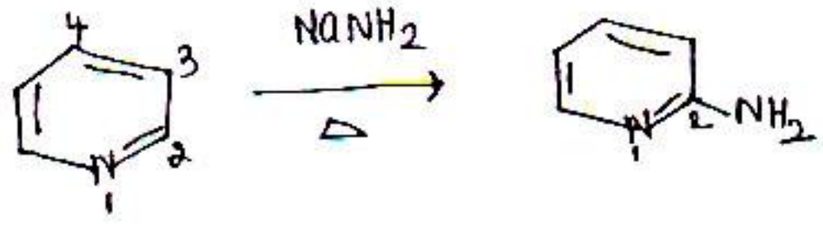
→ Whether double bond orientation at right / left side of Enamine resulting product is same.

CHICHIBABIN – REACTION:

→ Amino methylation at Nitrogen Heterocyclic by using sodium or potassium amides at high temperature is called chichibabin reaction.

→ It is aromatic Nucleophilic substitution.

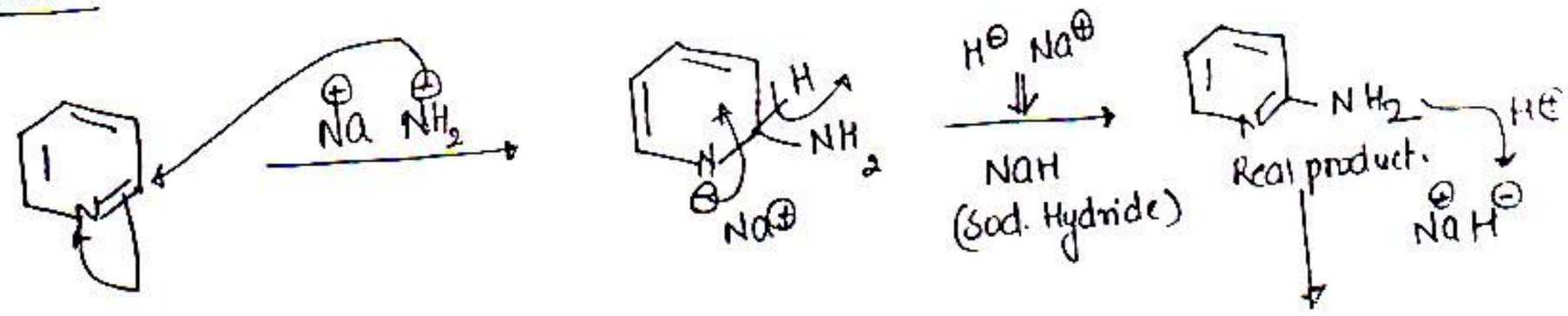
Very good Nitrogen Heterocyclic for chichibabin rxn is pyridine.



→ most predominantly Nucleophilic substitution takes place at C_2 than C_4 because of nearest −I effect. C_3 position is not at all Electrophilic.

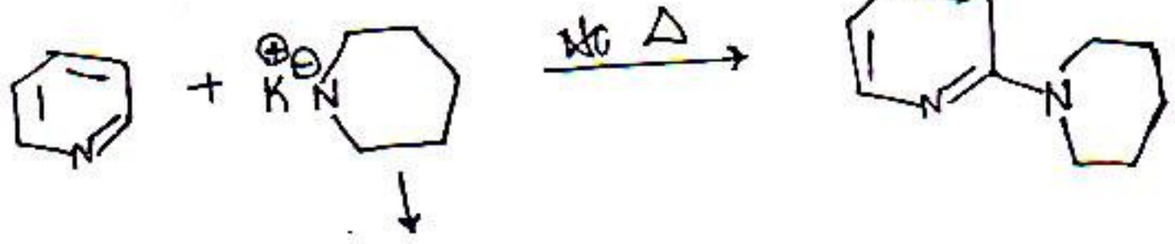
Mechanism :

Eg:1

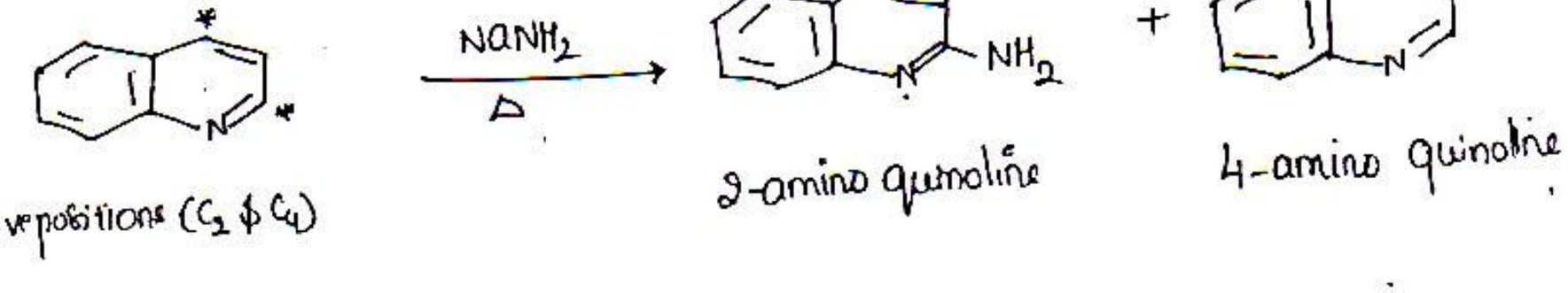


Byproduct.

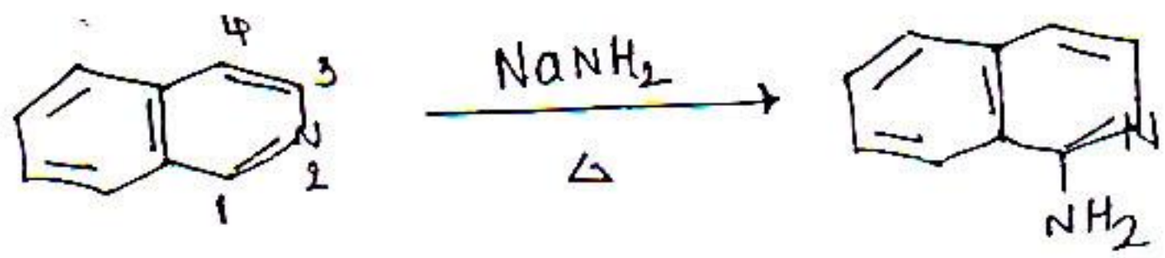
Eg:2



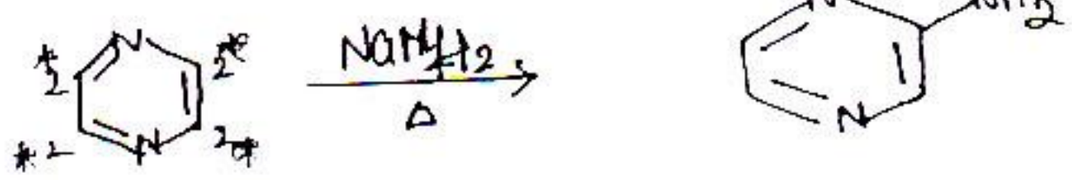
Eg:3

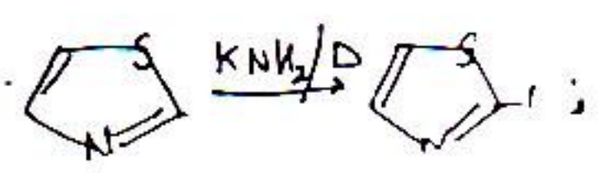


Eg:4

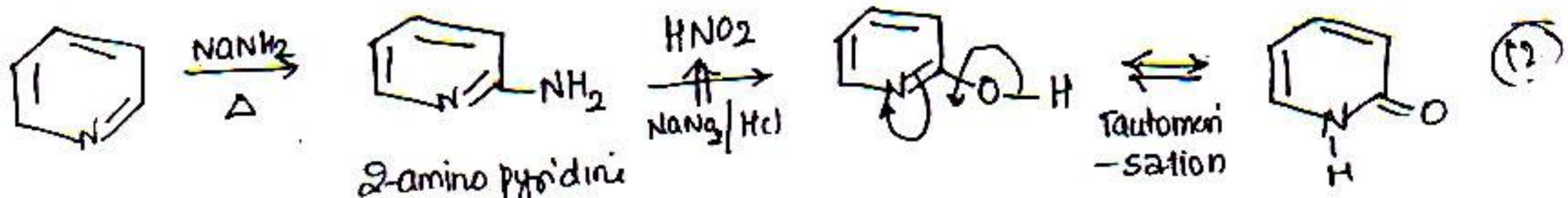


Eg:5



Eg:6 

Eq: 8



(12)

$$R-NH_2 \xrightarrow[HNO_2]{R\text{-}OH} R-OH$$

imp.

SHAPIRO – REACTION :

→ Indirect conversion of carbonyl compound into olefin.

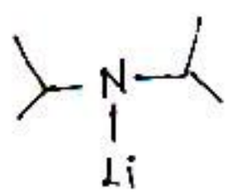
Carbonyl compound $\xrightarrow{Ts\text{-}NHNH_2}$ Tosyl Hydrazone Intermediate $\xrightarrow[\text{2 eq's of strong base}]{\Delta,\ H_3O^{\oplus}\ \text{excess}}$ olefin.

SHAPIRO REACTION

→ Conversion of Tosyl hydrazone of carbonyl compound into olefin with excess or 2 equivalents of strong base called shapiro reaction.

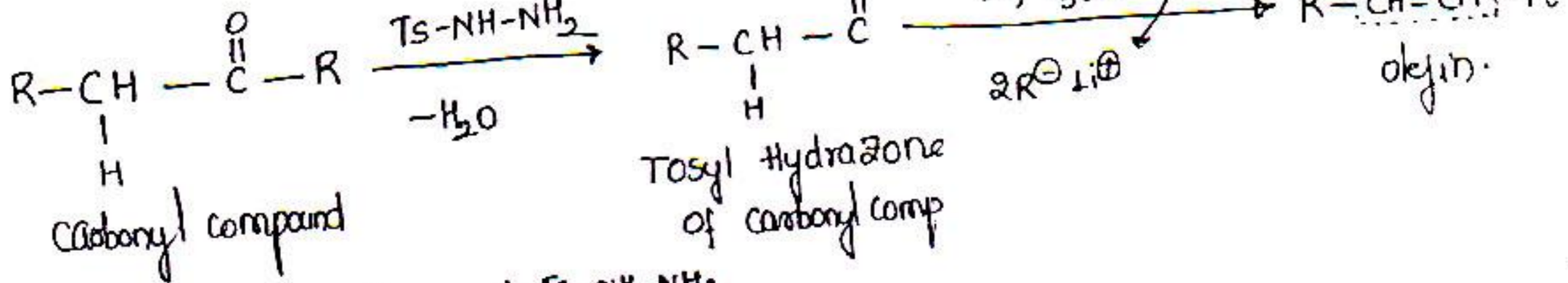
→ Strong bases : Organo dithium Compounds $R^{\ominus}\ Li^{\oplus}$ $CH_3^{\ominus}\ Li^{\oplus}$ $n\text{-}Bu^{\ominus}\ Li^{\oplus}$

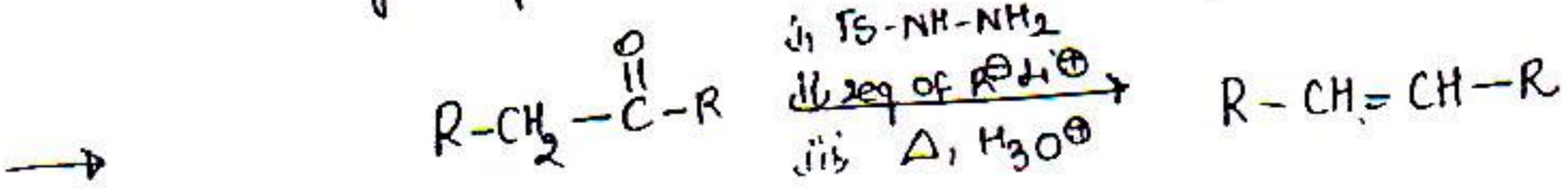
R = CH_3 or n-butyl

Sodamide, ($NaNH_2$) dithium di isopropyl amide  (LDA)

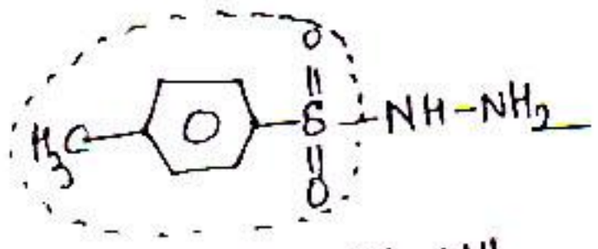
Limitation : Carbonyl compounds should be with al.least with one hydrogen atom at α- position.

→ Carbonyl compounds may be cyclic or acyclic

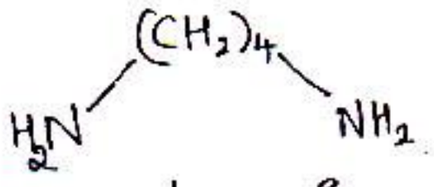
→ 

→ 

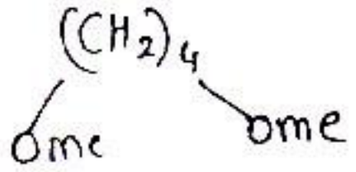
Mechanism :

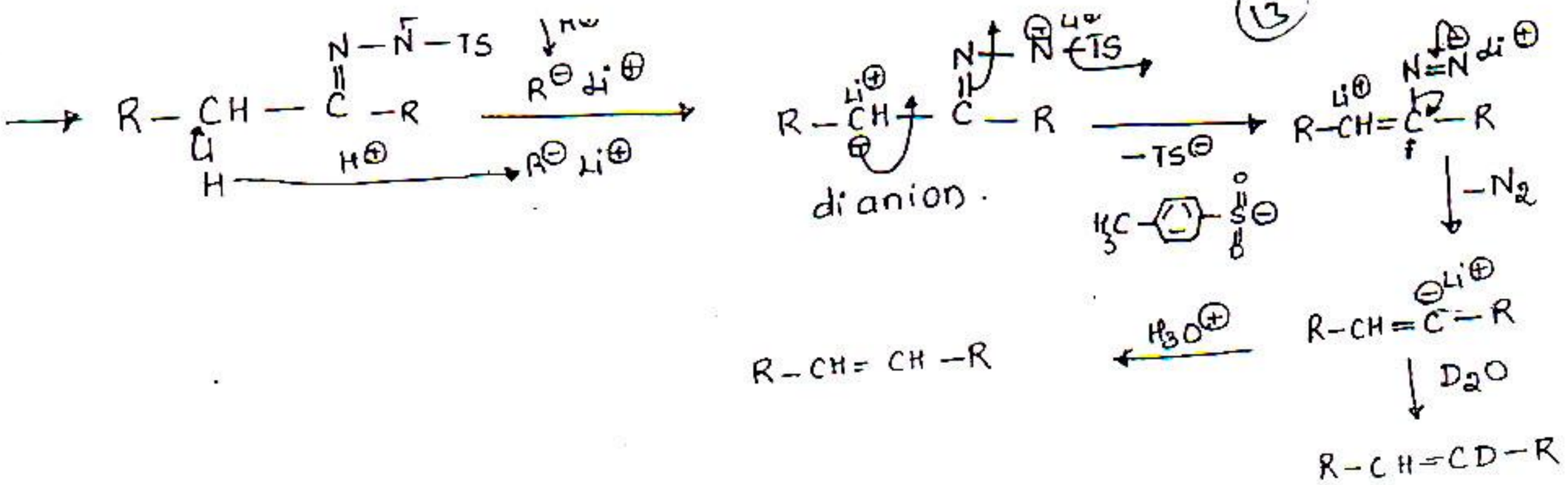
$TS\text{-}NH\text{-}NH_2$ = 

$TS-NH-NH_2$

Solvents : Highly polar Solvents : 

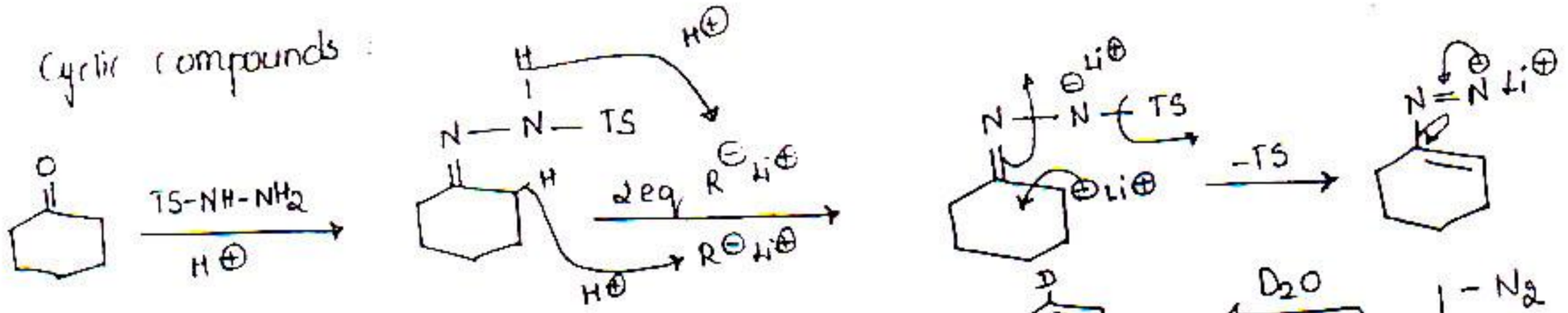
Tetra methylene diamine



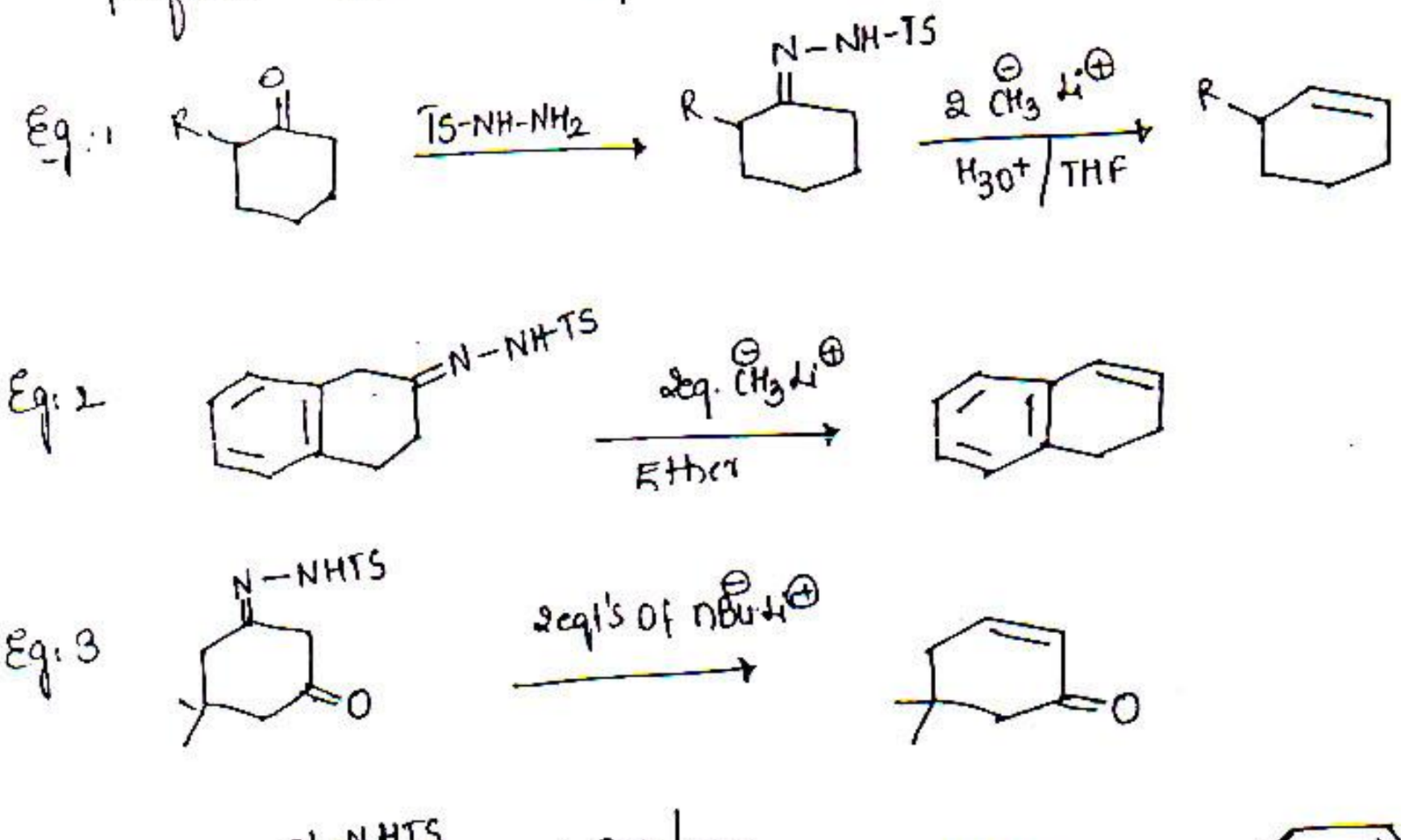


(13)

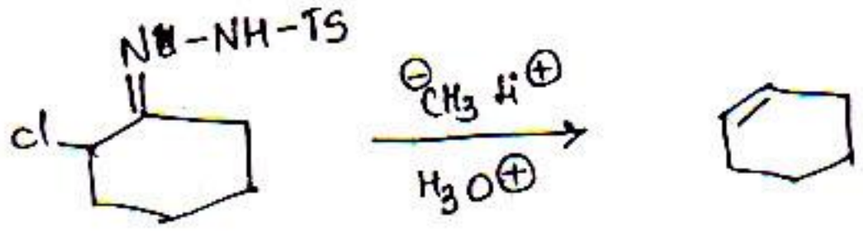
→ Cyclic compounds :



→ In case of unsymmetrical tosyl hydrazones, preferential orientation of double bond at less substituted α-position.



Eg:



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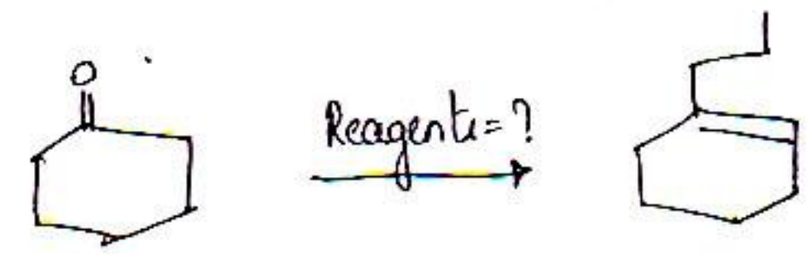

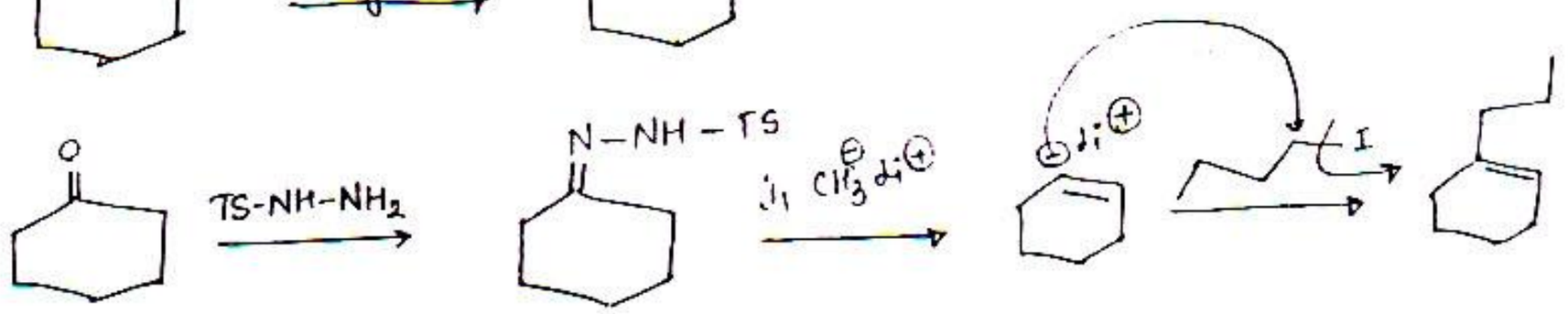

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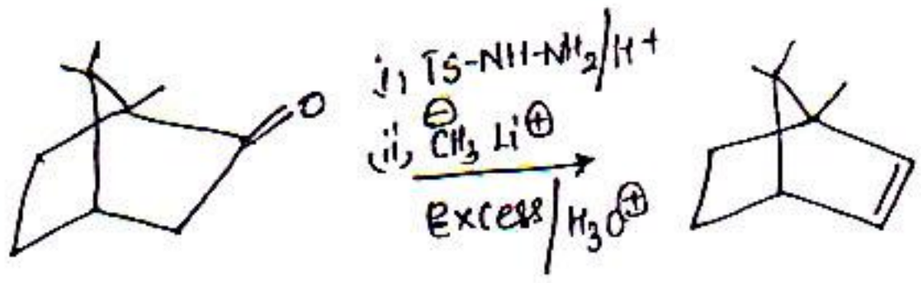
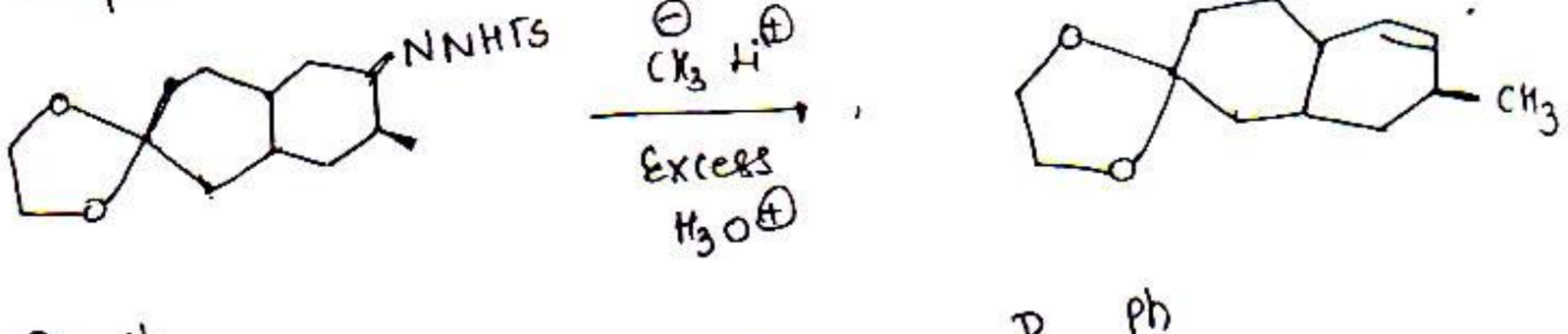


Camphor

Eg:



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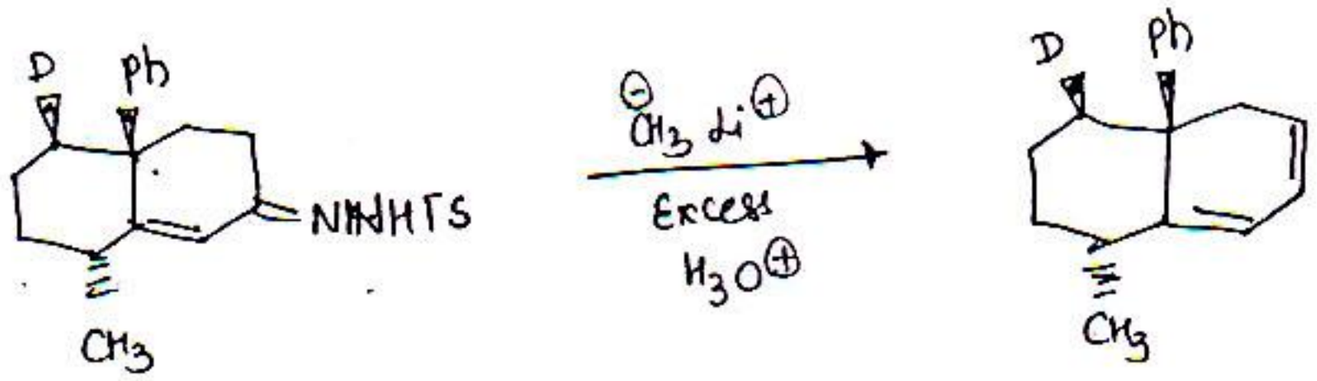


HOFMANN – LOEFFLER – FREYTAG REACTION: HLF - REACTION.

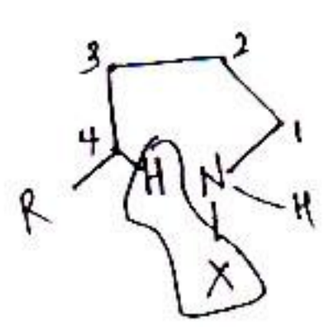
→ Conversion of N-Halo amines having at least one hydrogen atom at C_4 or C_5 positions into 5, or 6-membered Nitrogen Heterocyclic in acidic medium under Thermal or photochemical rxn's called HLF reactions

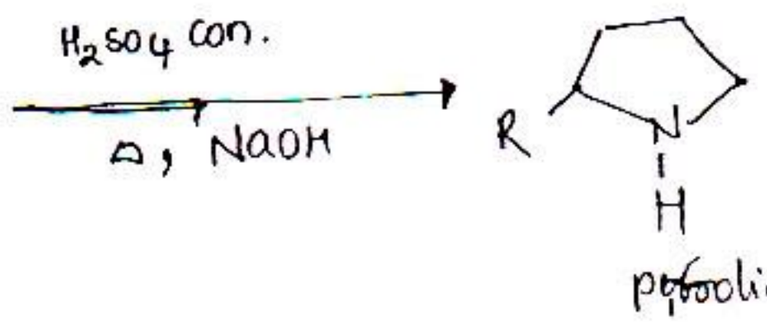
N-Halo amine
Having C_4-H/C_5-H

conc.
1) H_2SO_4/F_3CO_2H
2) $\Delta/h\nu$
3) NaOH

Saturated 5/6-membered Heterocyclic Nitrogen.

Eg:

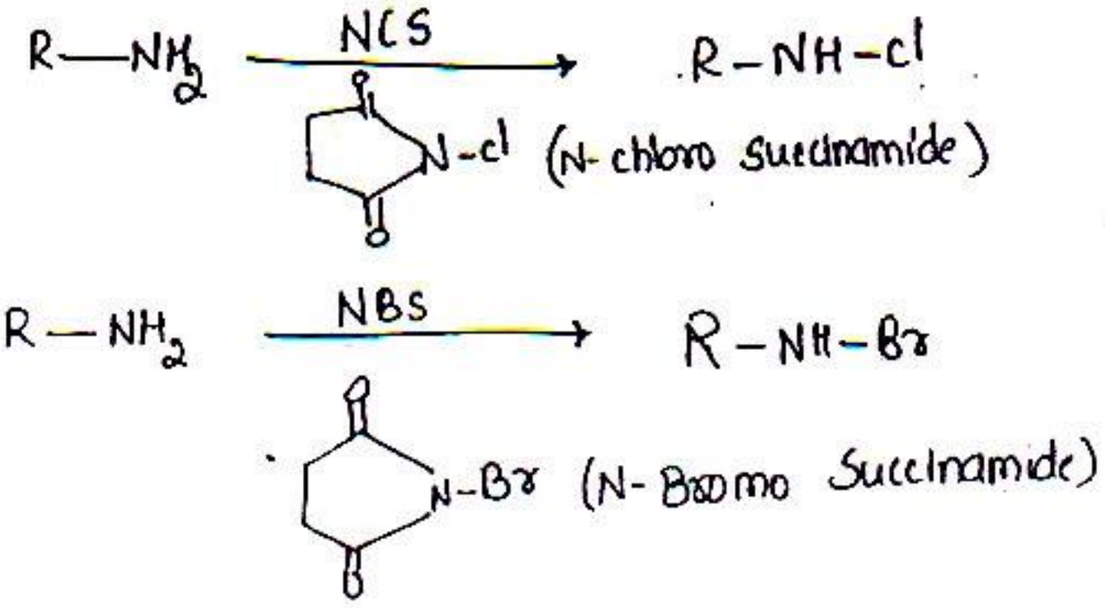




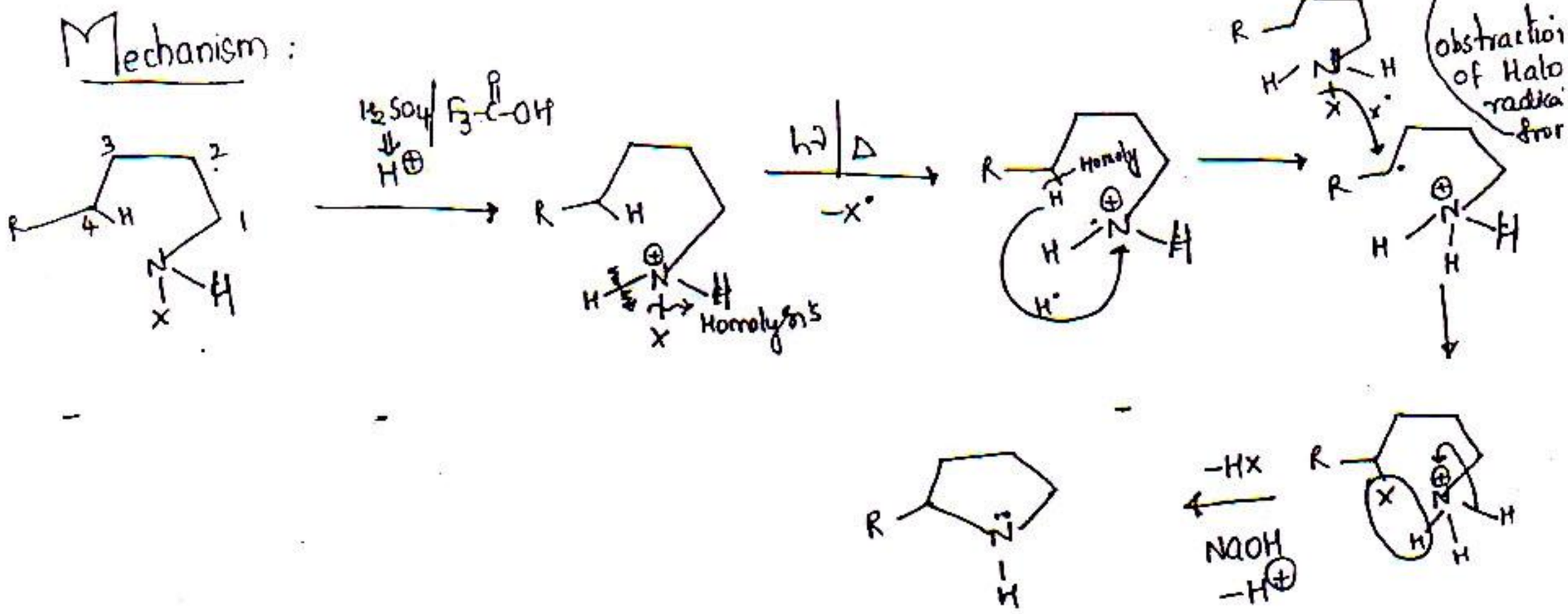
pyrrolidine

X = mostly Cl, Br

preparation of N-haloamine



Mechanism :



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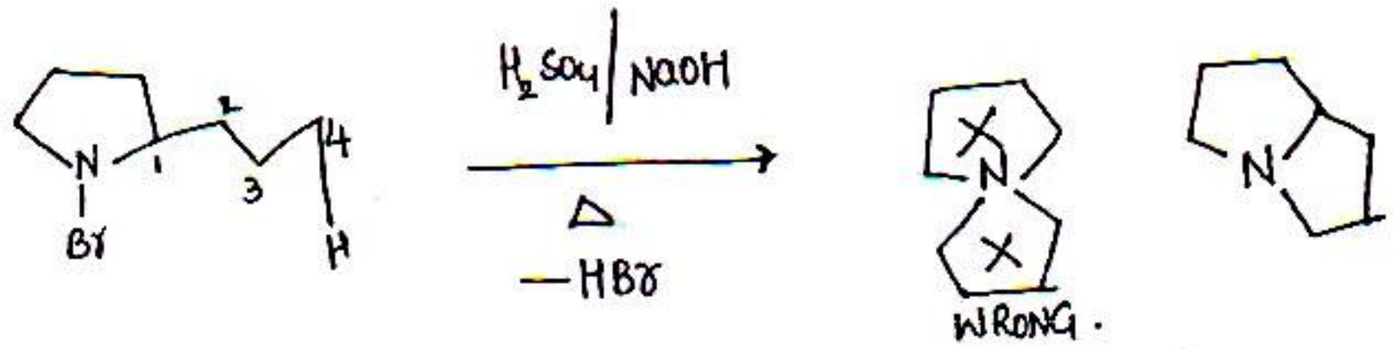
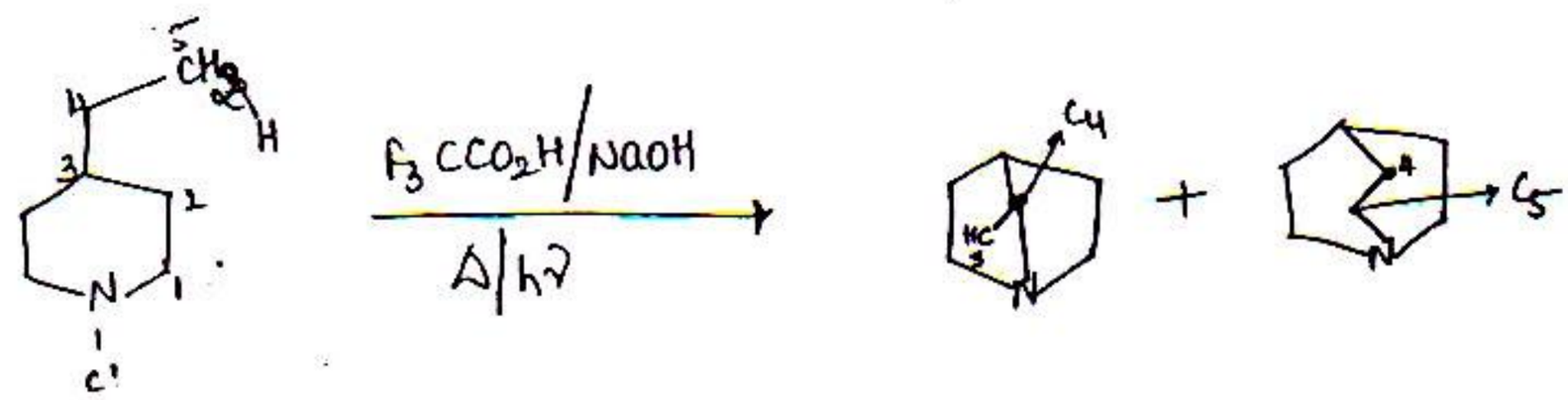
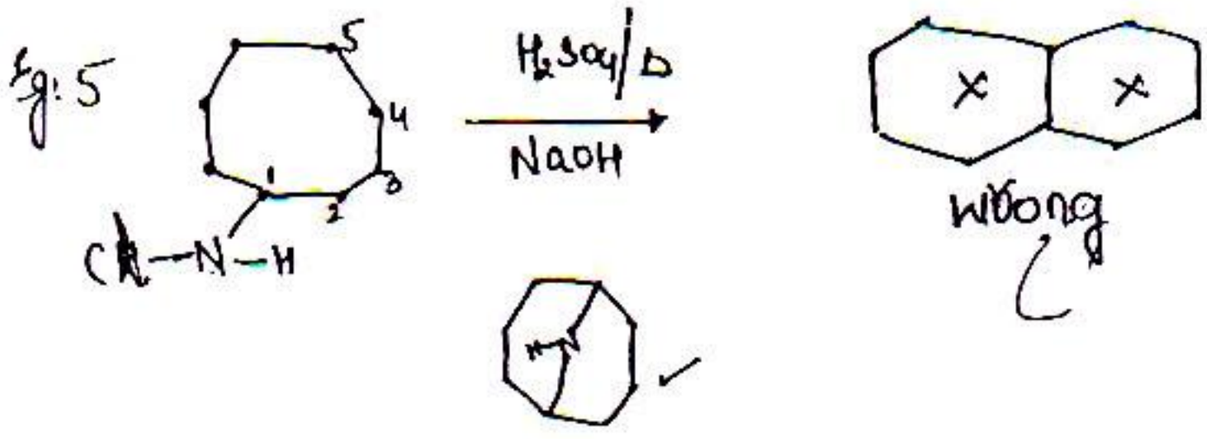


Eg: 2

Eg: 3



Eg: 5



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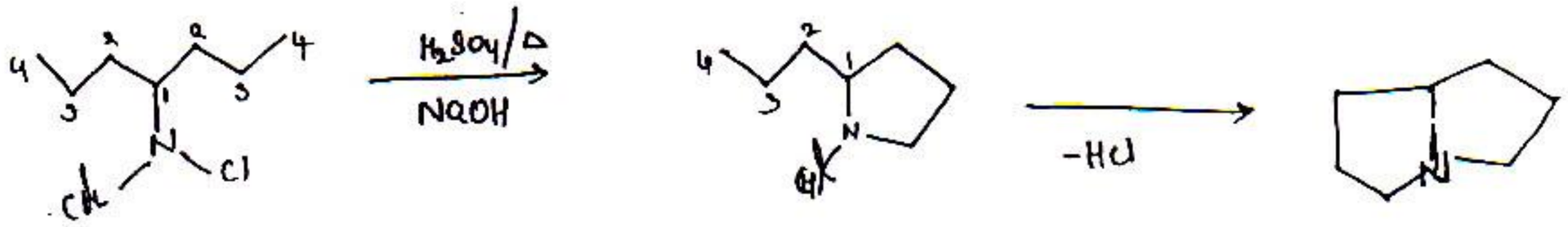

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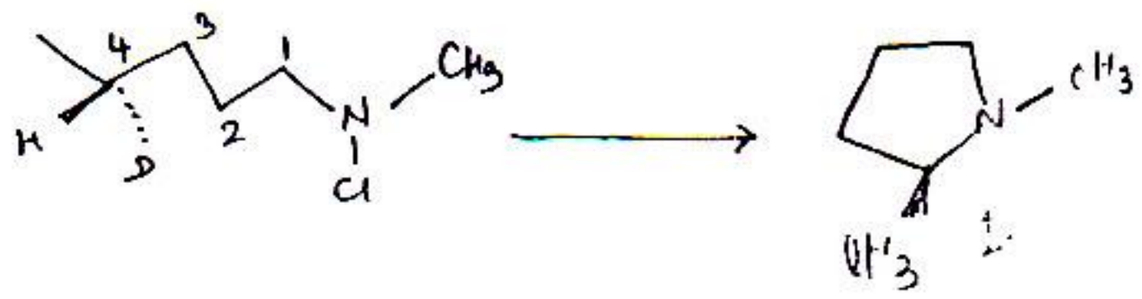

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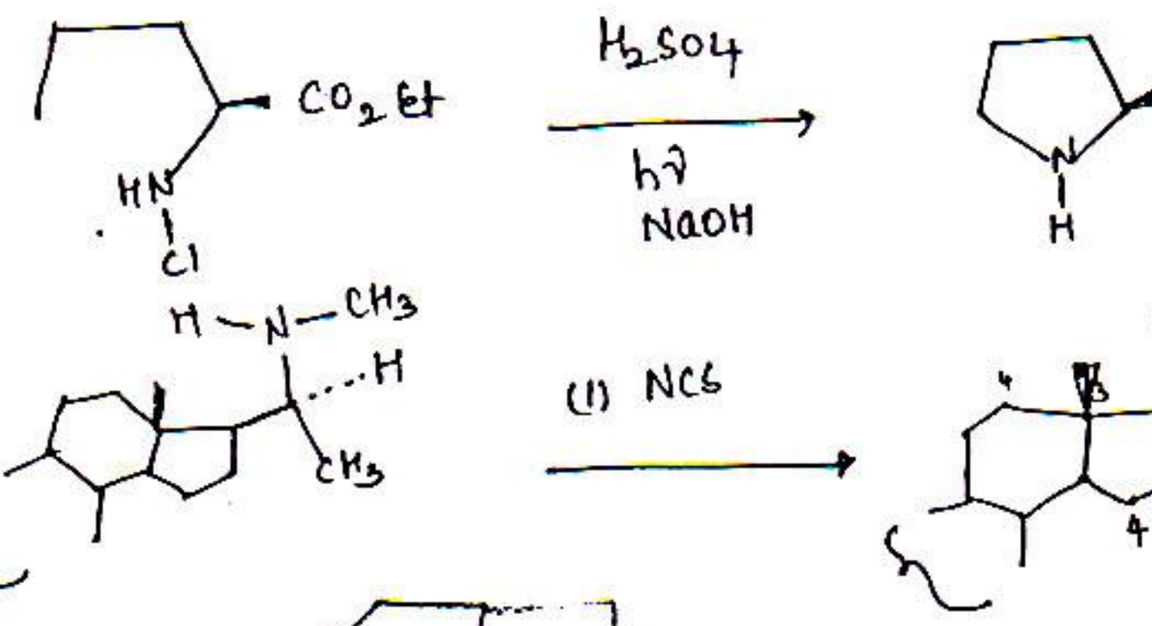
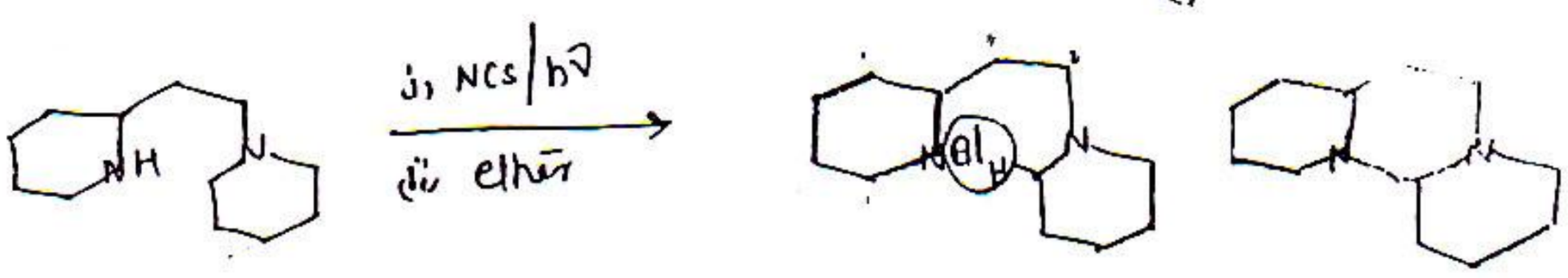


Eg:

Eg:



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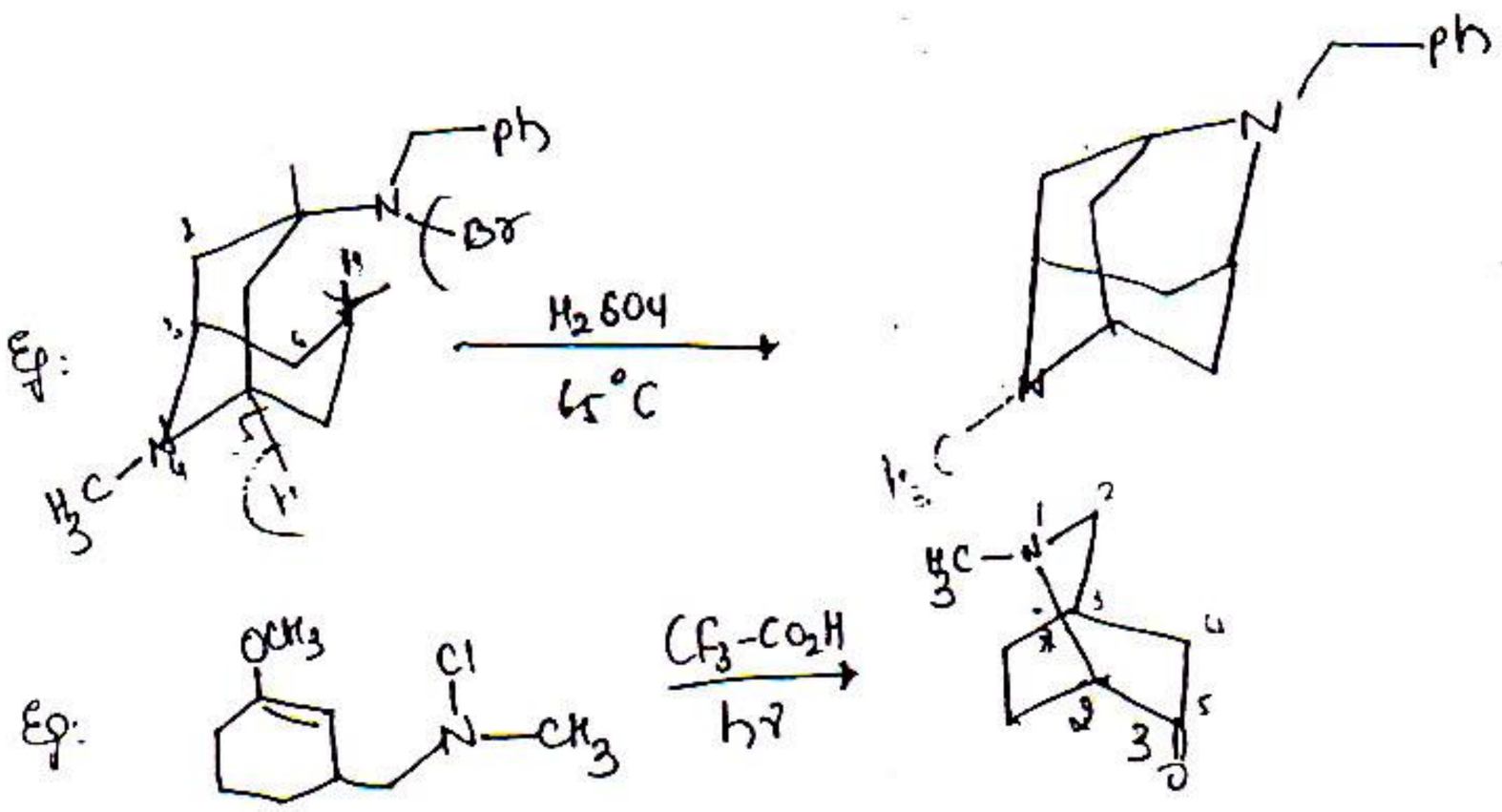
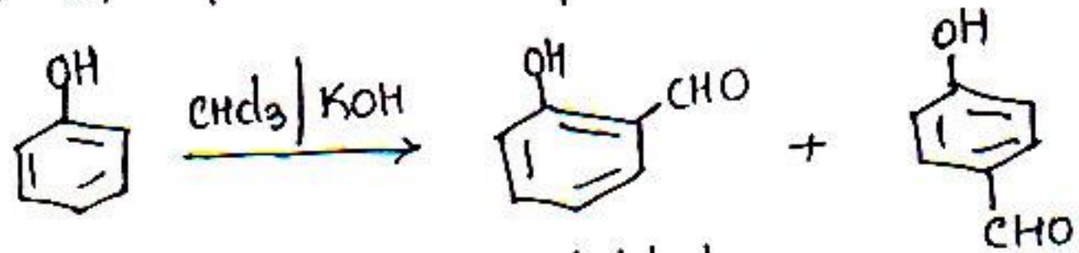


Wed 28/9/08

Paper-I Named reactions.

1) RIEMER–TEIMANN REACTION:

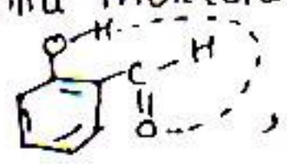
Formylation of phenolic compounds with $CHCl_3$ / KOH, NaOH



Salicyladehyde ← structural isomers → These two products formed with unequal ratio's

∴ The rxn is Regioselective.

→ Intra molecular Hydrogen bonding is developed by ortho product due to In.M.H ortho have low B.p and can be separated by steam distillation.

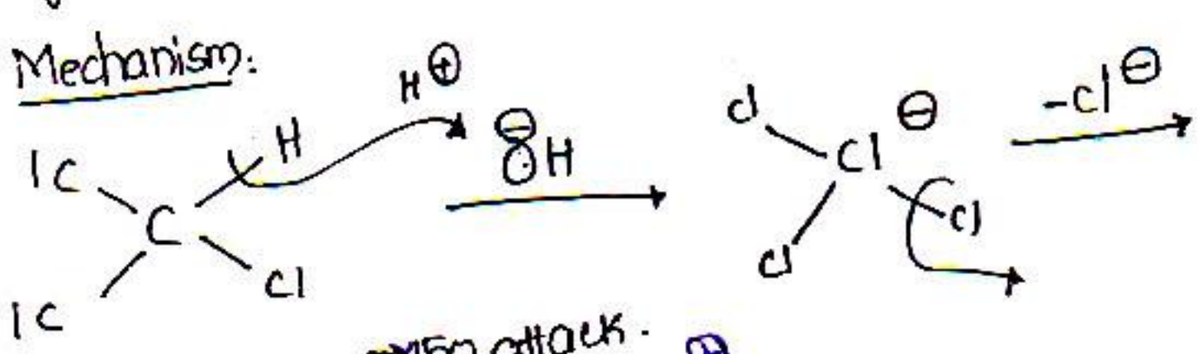


→ Where as para cannot. But para-develop Inter molecular Hydrogen bonding Due to Inter.M.B, it has High boiling point.

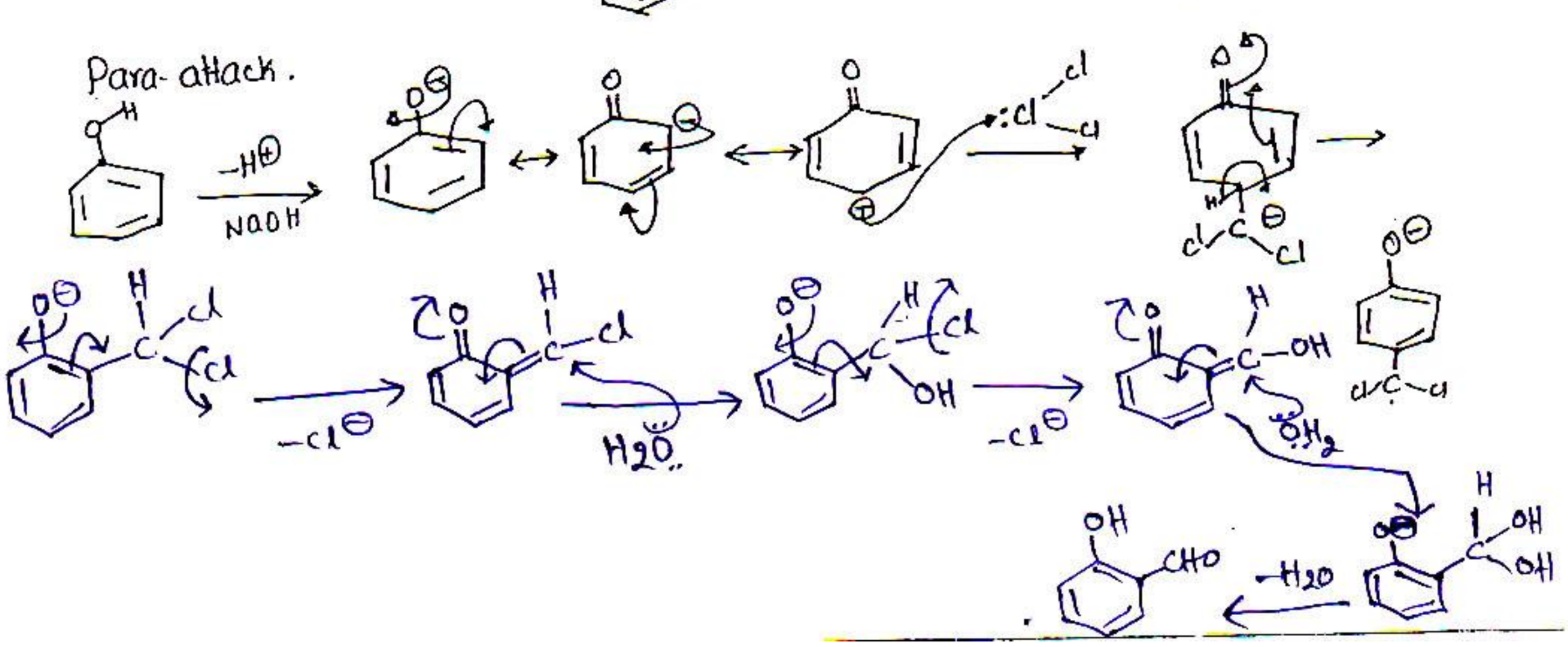
→ I.R can distinguish both Intra & Inter molecular Hydrogen bonding.

→ Products can be identified by 2,4-DNP reagent. Reactant will not give +ve test for 2,4 DNP where as products show +ve Test.

Mechanism:



Para-attack.



→ New C-C bond formation

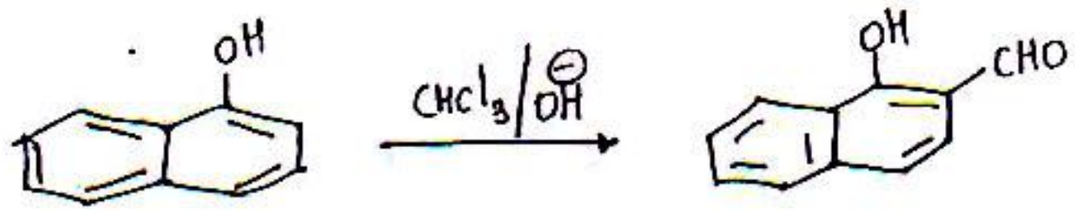
→ Intermediate is dichloro carbene

→ It is an Electrophelic substitution rxn.

→ Involvement of phenoxide anion.

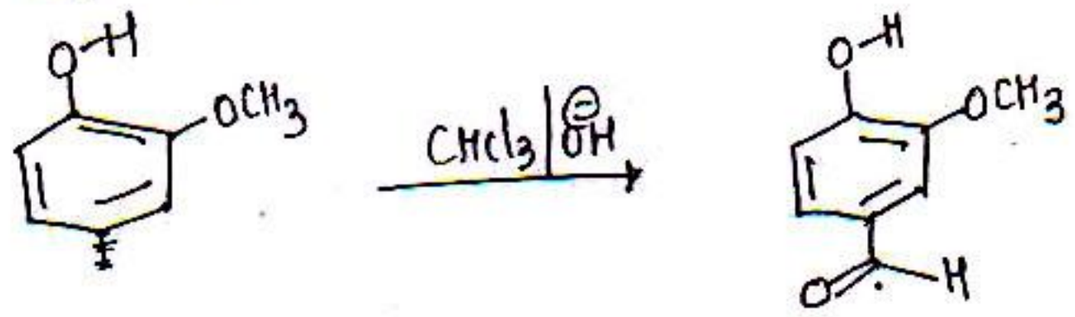
→ It (Riemer- Tiemer rxn) is base catalysed rxn.

Eg: 2.

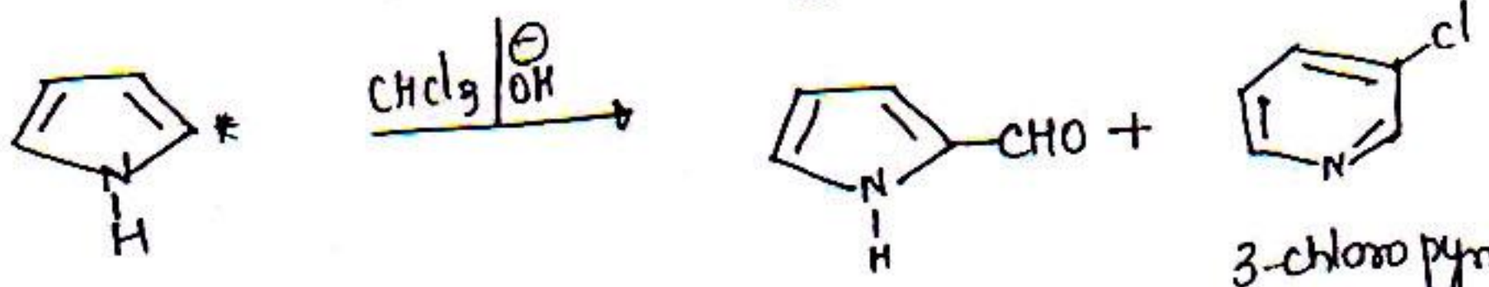


Eg: 3

Eg: 4

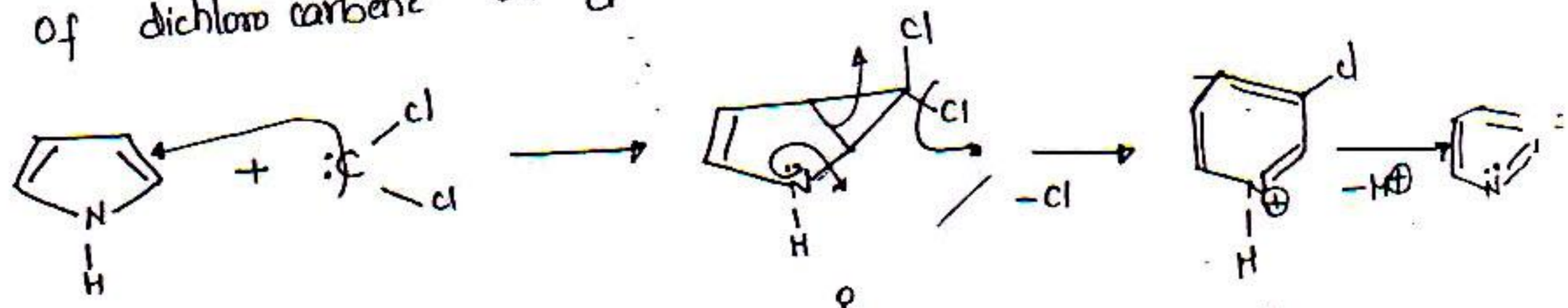


Eg: 5

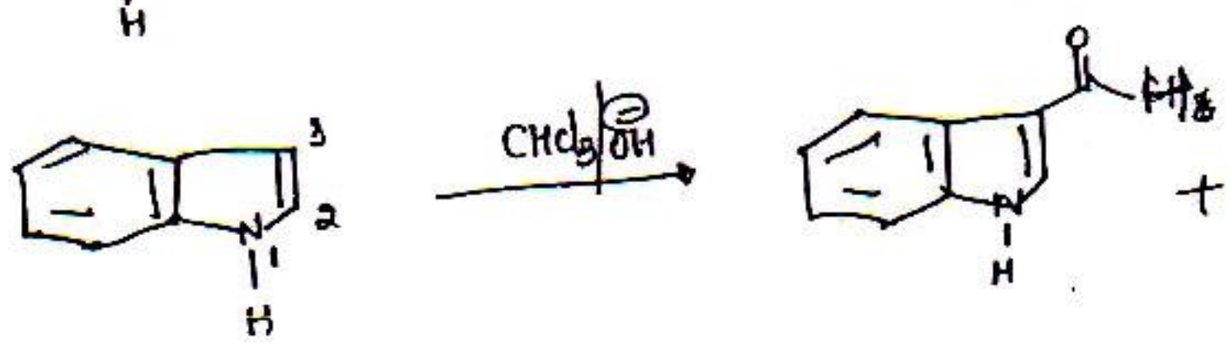


3-chloro pyridine (unexpected product)

The unexpected product is due to the addition rxn of dichloro carbene on duble bond of pyrrole

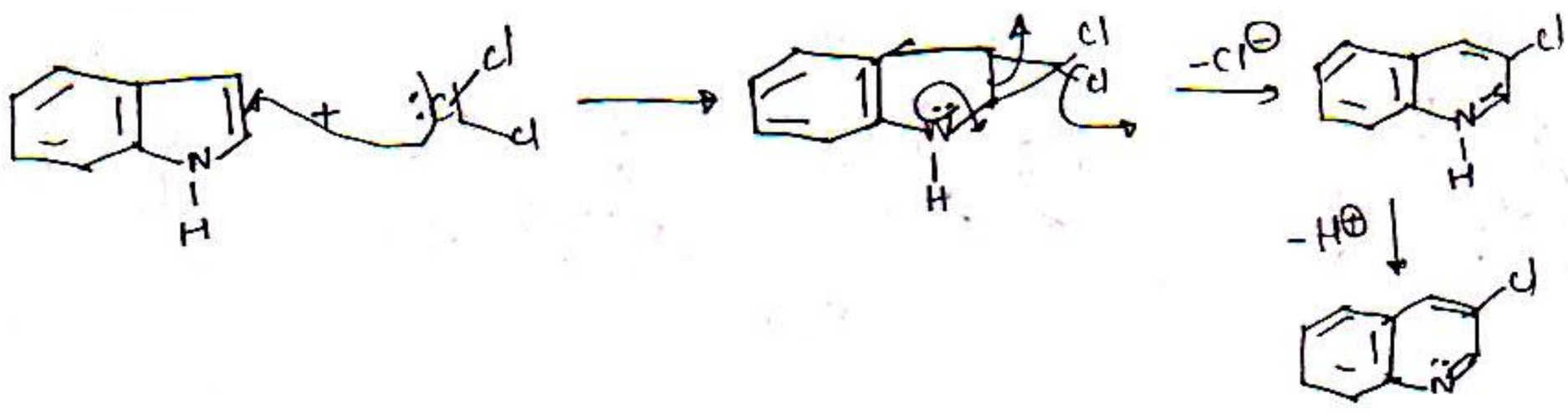


Eg: 6

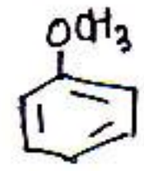


3-chloro quinoline (unexpected product)

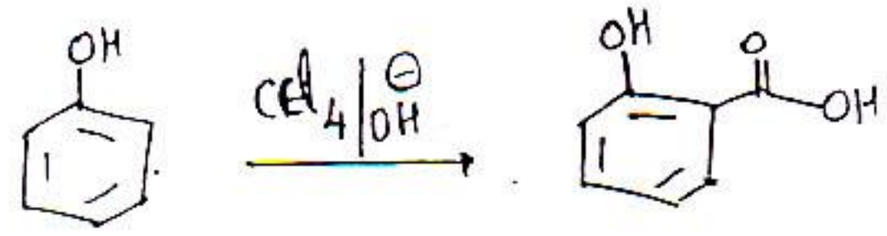
Indole



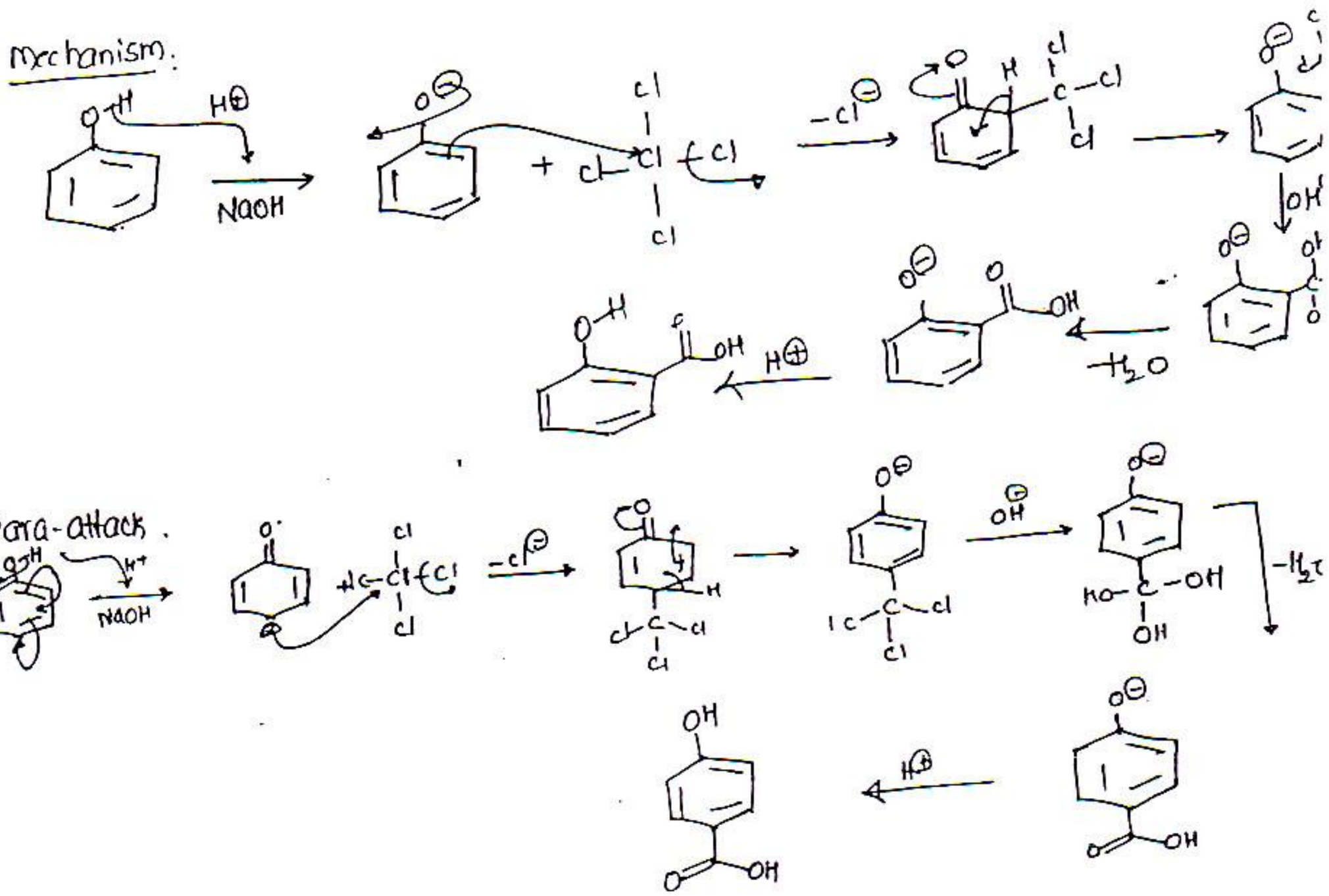
Q) Anisole and Aniline will not undergo R. T. Reaction, why. (4)

A) Anisole  It will not produce phenoxide ion ∴ It cannot undergo R. T. Rxn.

Aniline  → It reacts with carbene and form Isocyanide

Eg: 

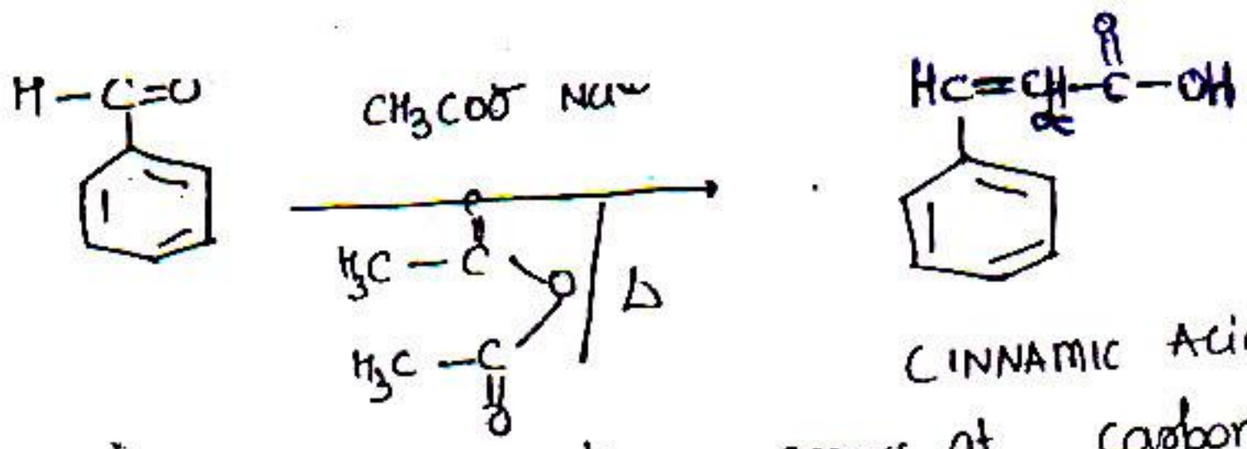
Mechanism:



PERKIN'S REACTIONS:

→ Carbon-Carbon bond formation.
→ Nucleophilic addition at Carbonyl compounds
→ Carbanion intermediate
→ High temperature
→ Salt of Carboxylic acid / Anhydride
→ Conversion of aromatic Acid Hydrid. Aldehydes in to α,β-unsaturated Acid
i.e. Salt of Acid / Anhydride

Eq:1



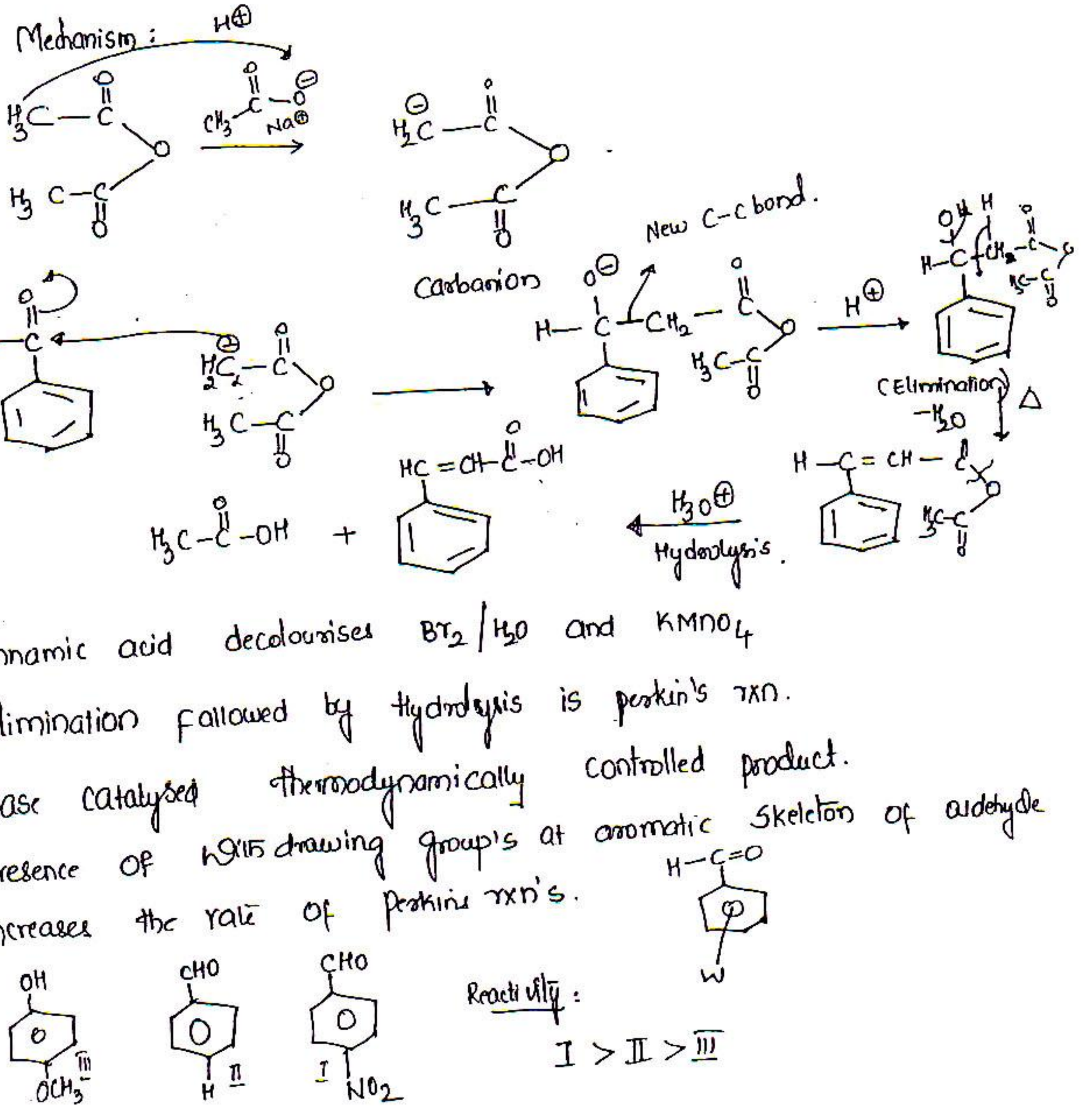
CINNAMIC Acid

→ New C-C bonding formation occurs at carbonyl carbon and α-position of anhydride

→ Salt of carboxylic acid act as base abstracts a proton.

→ If anhydride not used salt of carboxylic acid acts as Nucleophilic centre

Mechanism :



→ Cinnamic acid decolourises Br_2/H_2O and $KMnO_4$

→ Elimination followed by hydrolysis is perkin's rxn.

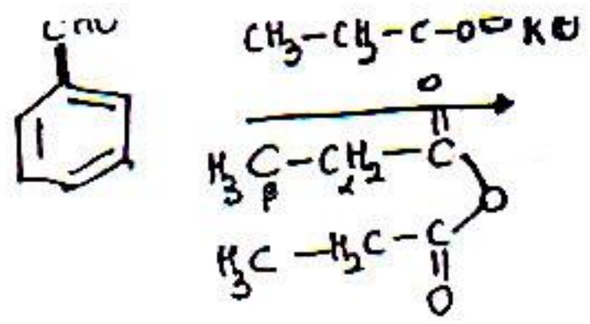
→ Base catalysed thermodynamically controlled product.

Presence of with drawing group's at aromatic skeleton of aldehyde increases the rate of perkins rxn's.

Reactivity :

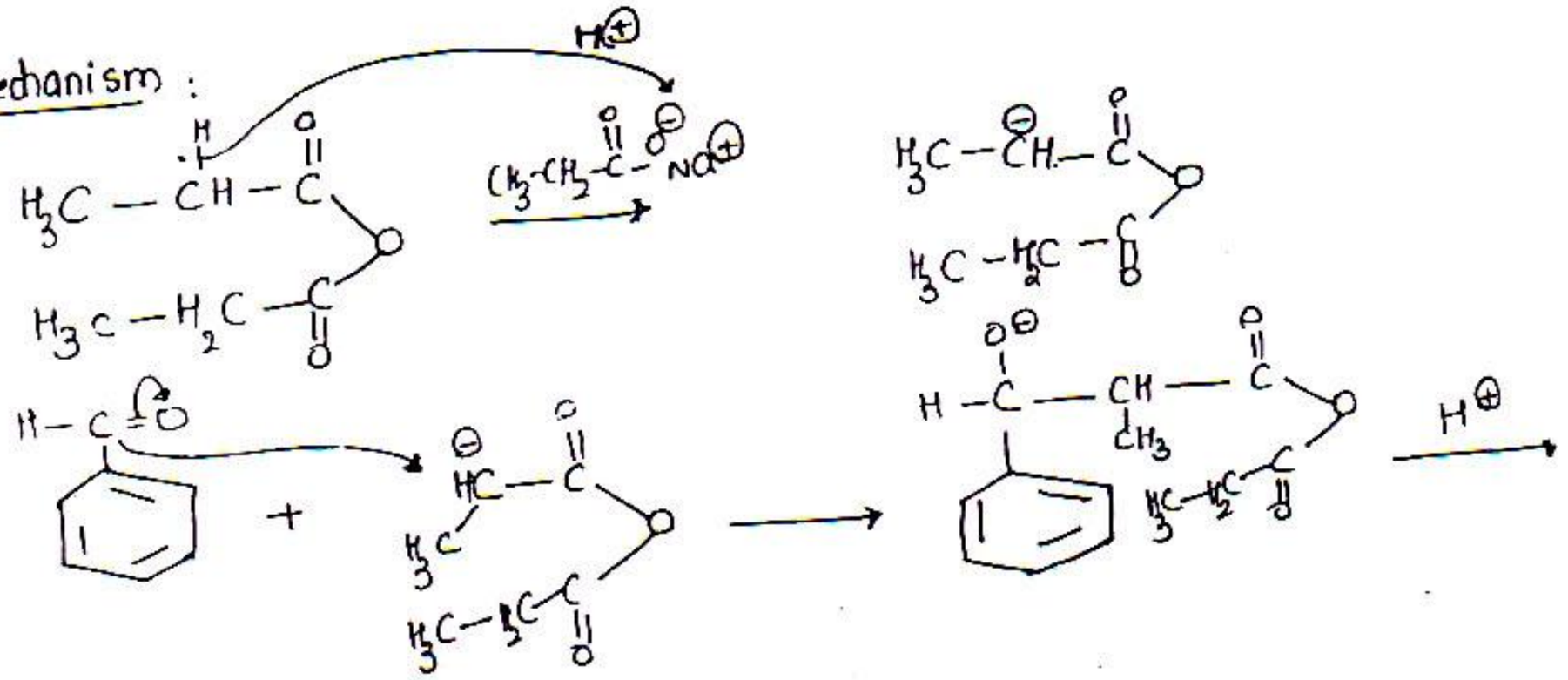
I > II > III

Eg: 2



α- methyl cinnamic acid.

Mechanism :



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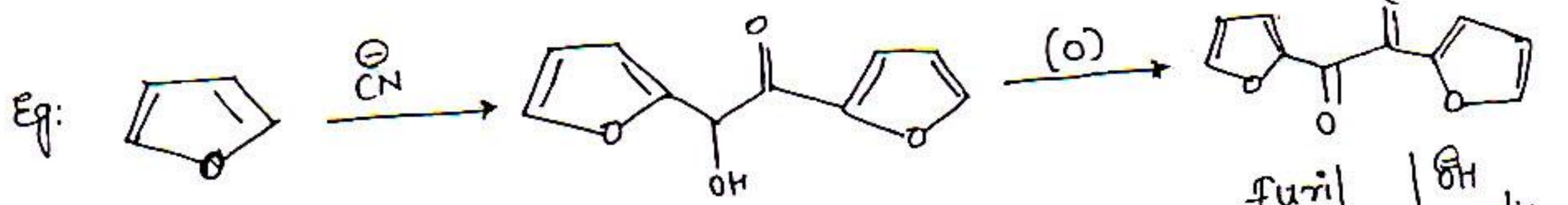

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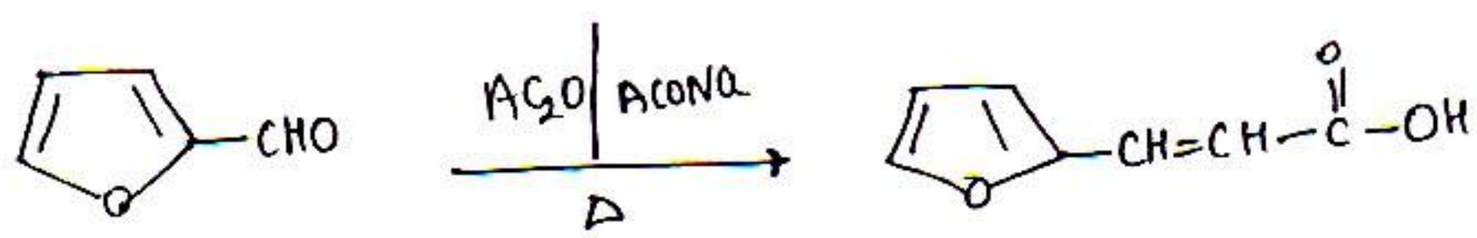

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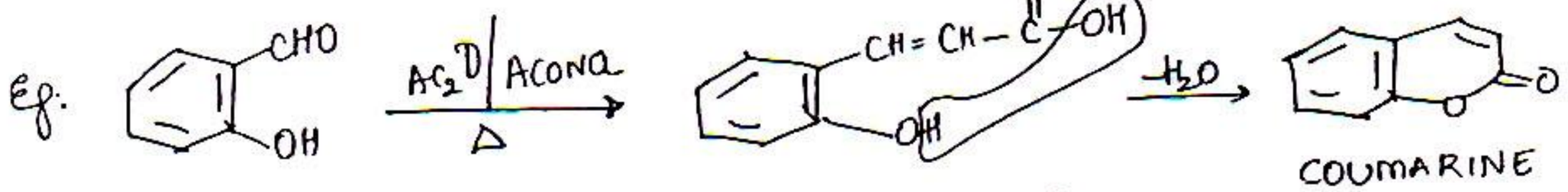

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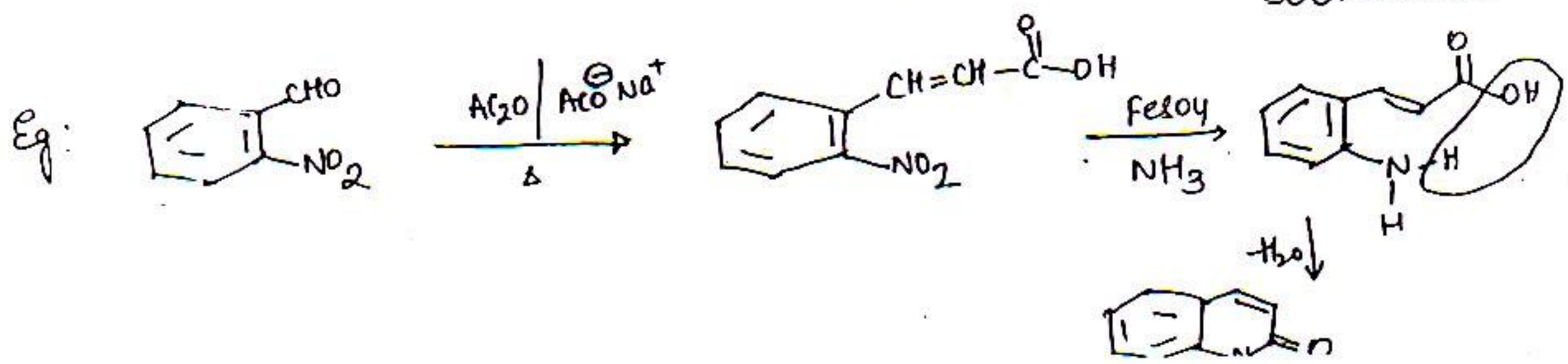

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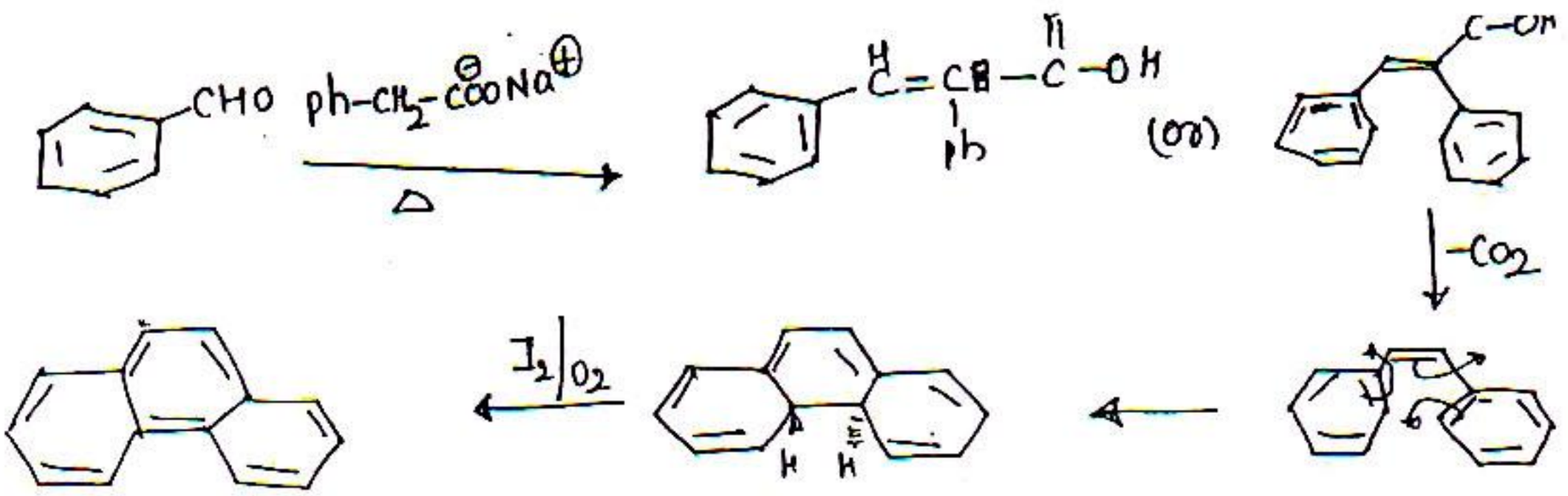

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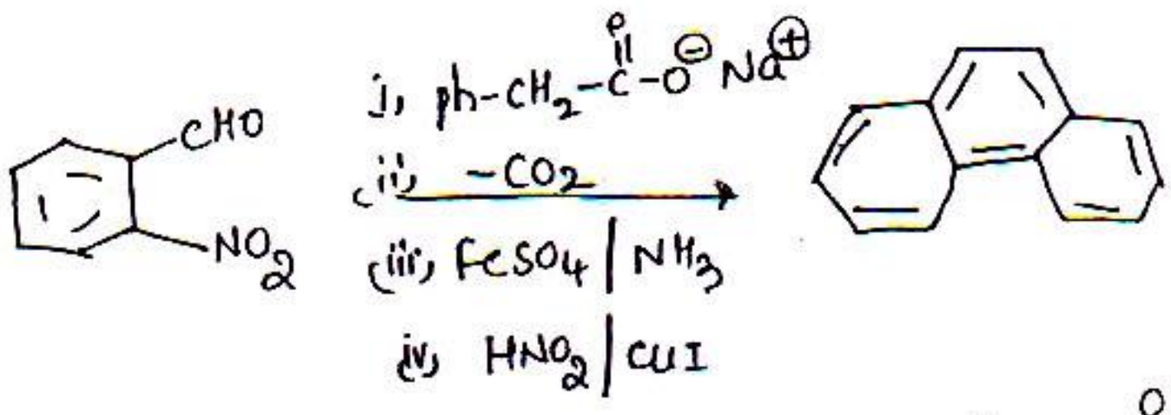

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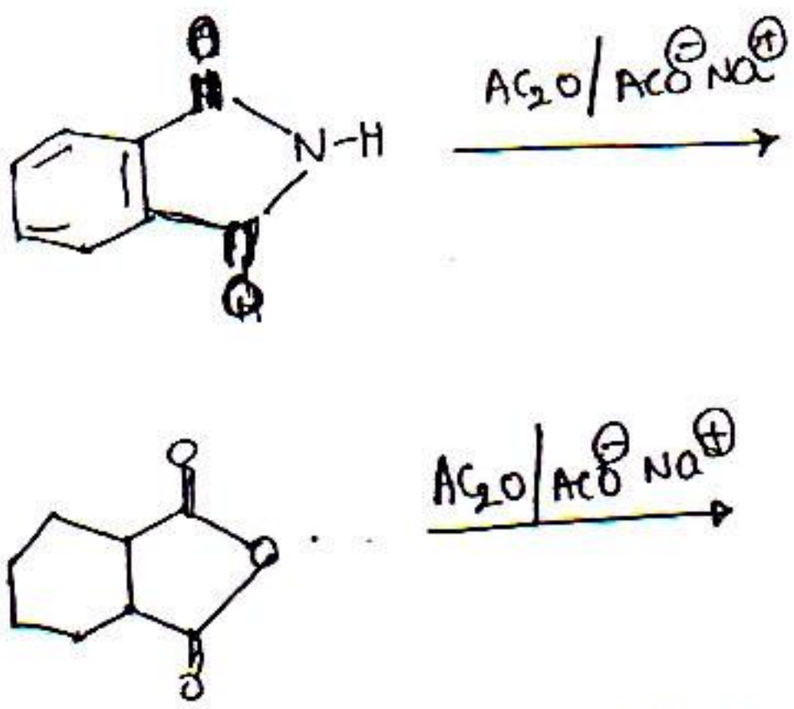
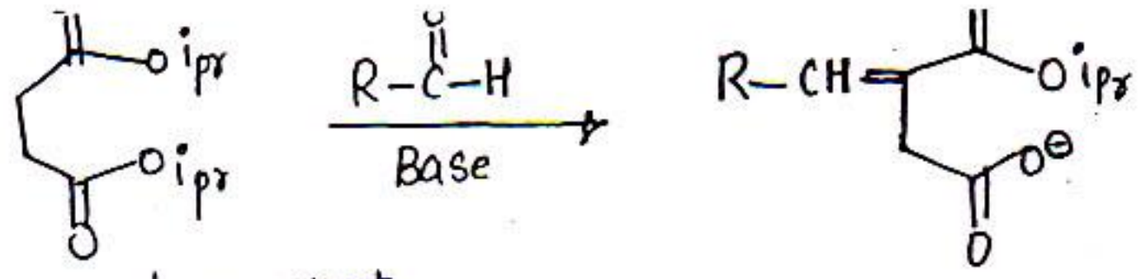


STOBBE CONDENSATION:

→ ~~Addition~~ and elimination is called Condensation.

→ Condensation of aldehydes or ketones, at α-position of dialkyl succinate in basic medium is called stobbe condensation.



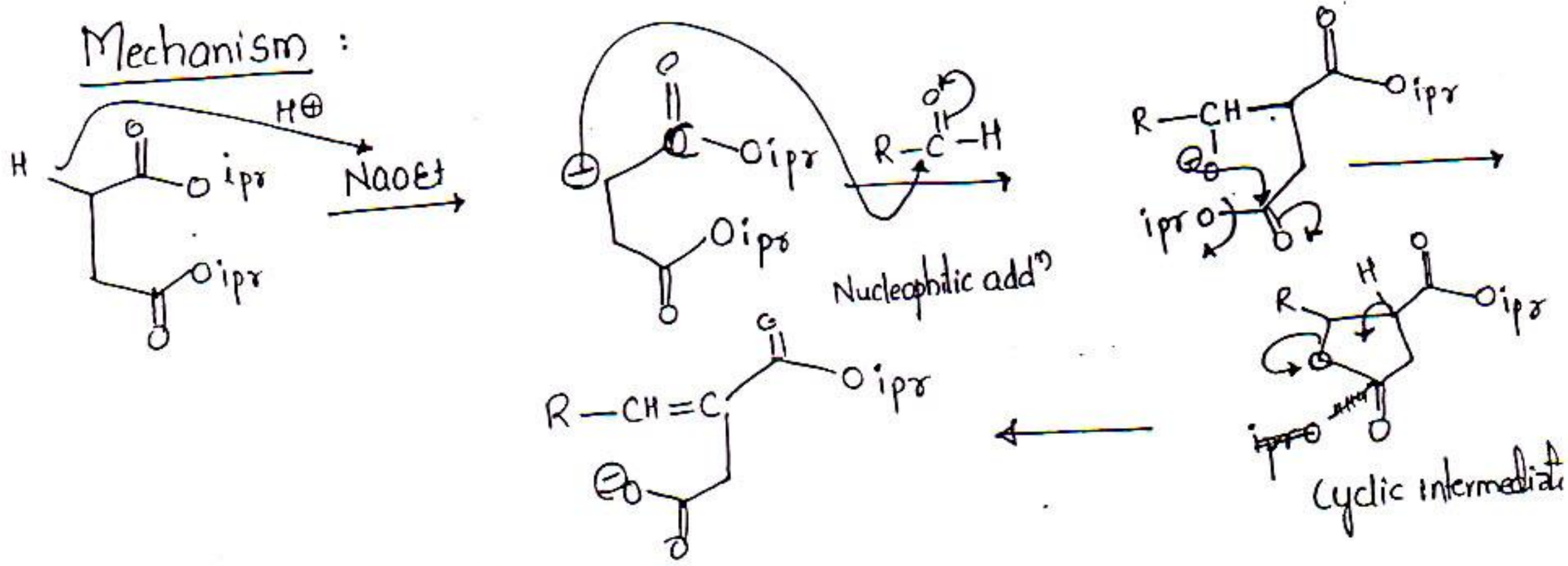
diisopropyl succinate

→ condensation at α-position of ester.

→ one of the ester group get Hydrolysed (ester not attached to double bond hydrolysed.

→ Bases used: NaOEt, NaH $NaNH_2$.

Mechanism :

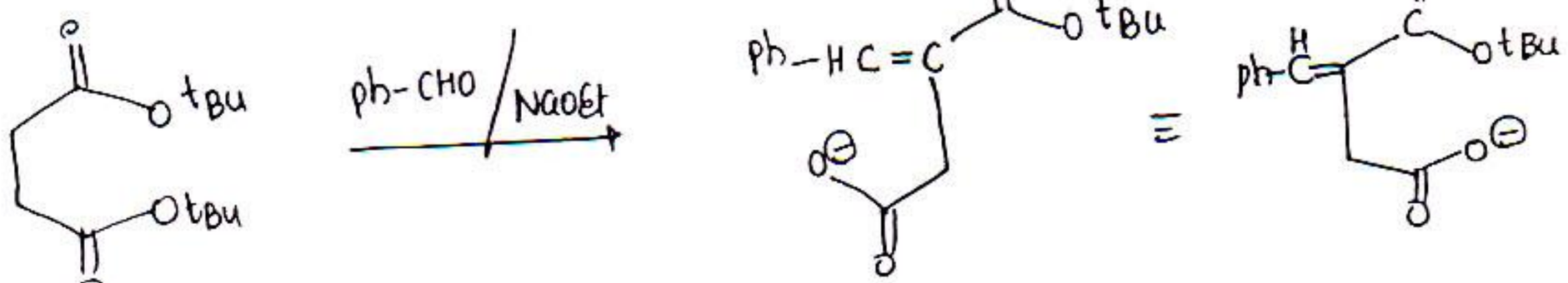


Carbanion Intermediate

Nucleophilic addition at carbonyl function

Cyclic ester intermediate, C-C bond formation.

Eg:



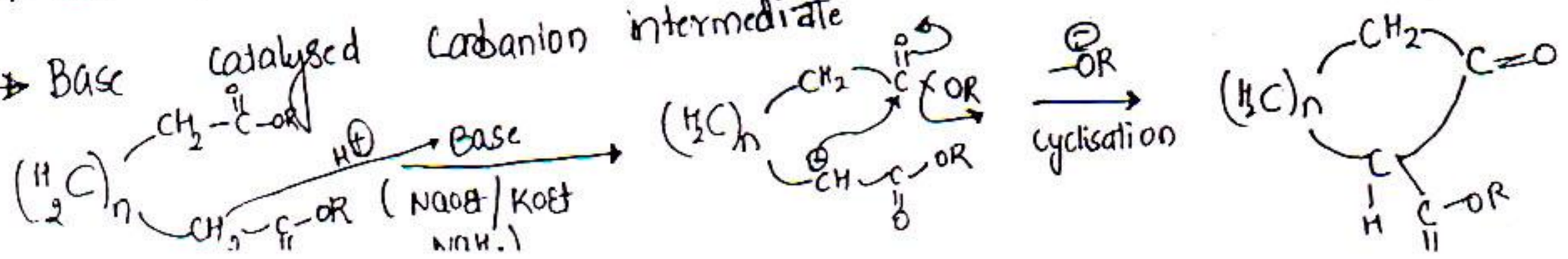
DIECKMAN'S CYCLIZATION'S

→ Method for Synthesis of Alicyclic compounds

→ Intra molecular condensation reactions

→ Base catalysed Carbanion intermediate

Bases: $NaNH_2$, 3° Amine, $\ominus OH$



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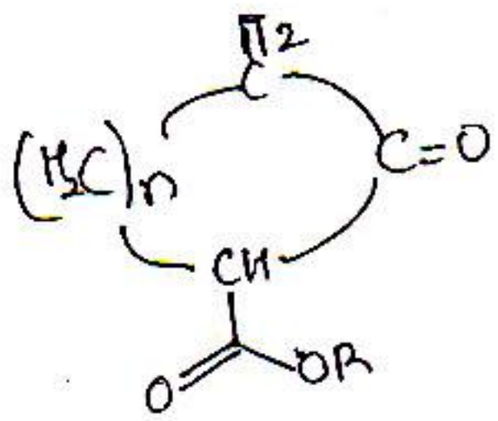
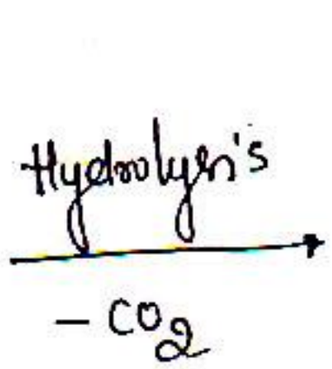
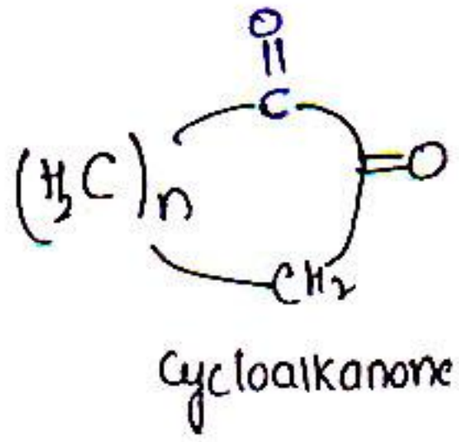
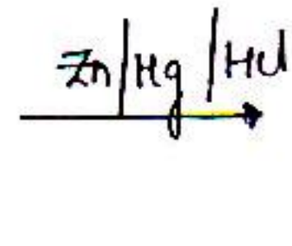
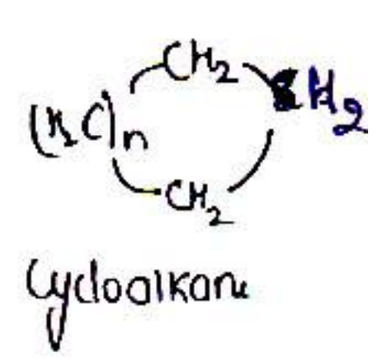






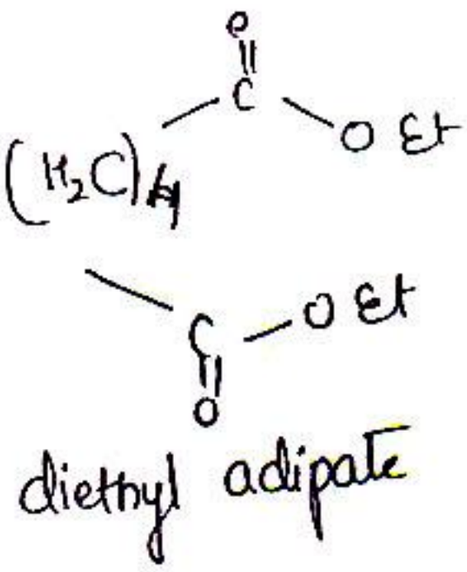
Cycloalkanone



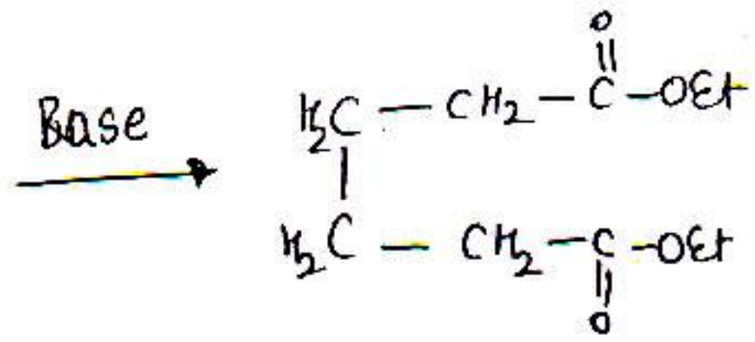


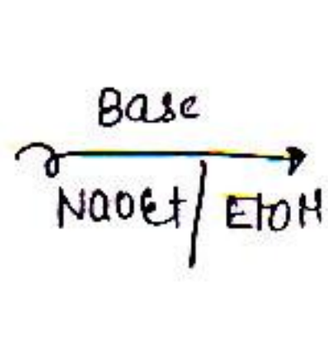
Cycloalkane

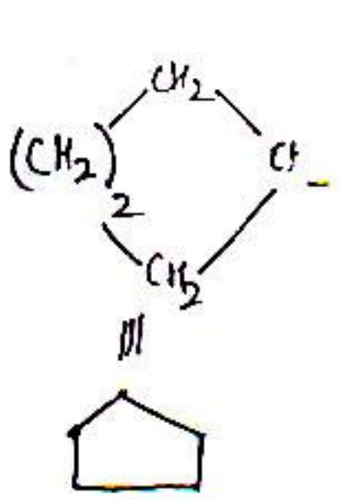
Eg:



diethyl adipate







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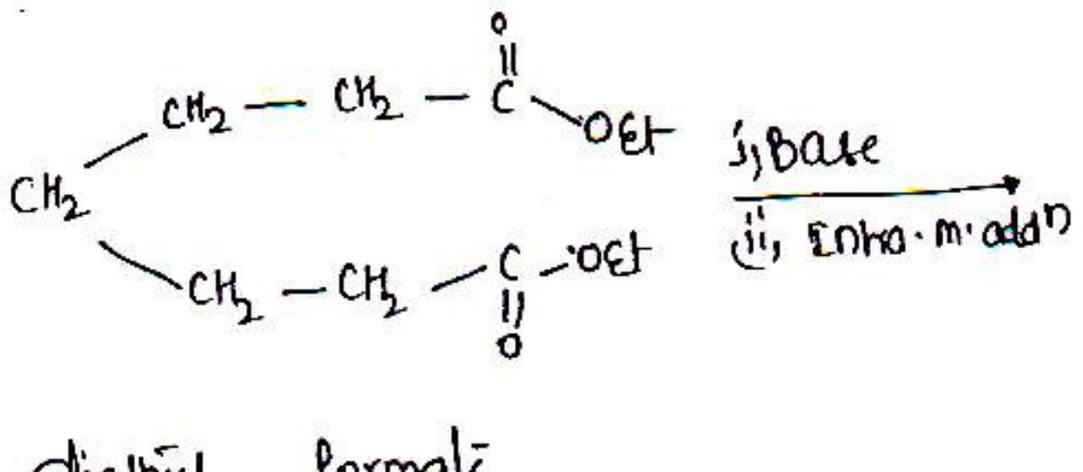
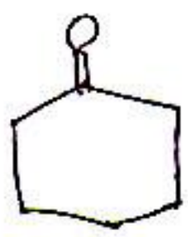
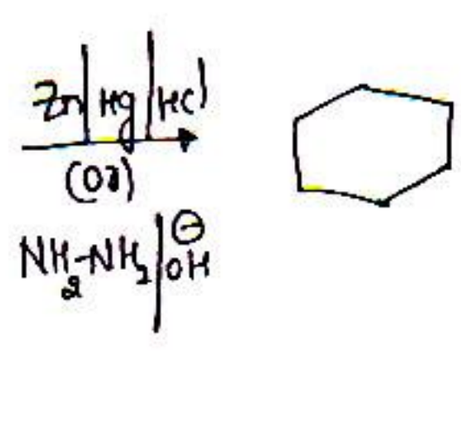


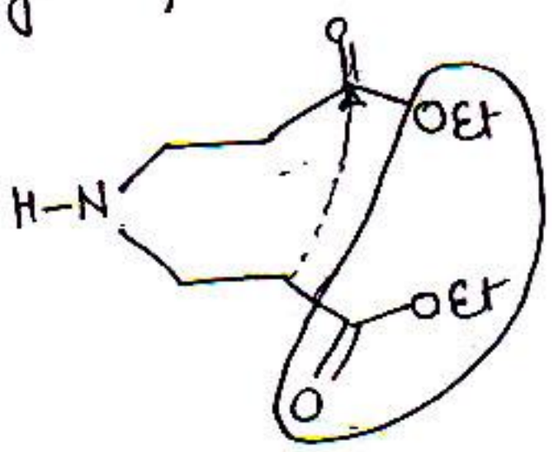


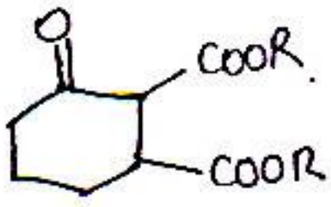


Diethyl formate

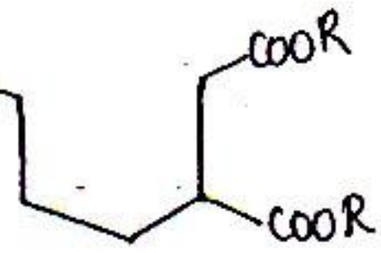
Pet-ether
Hexane
Benzene
Chloroform
Ethyl

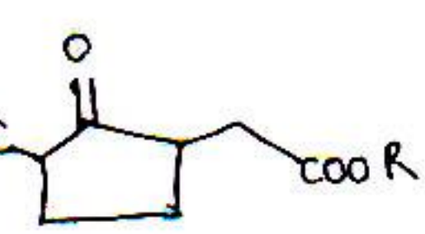
Eg:



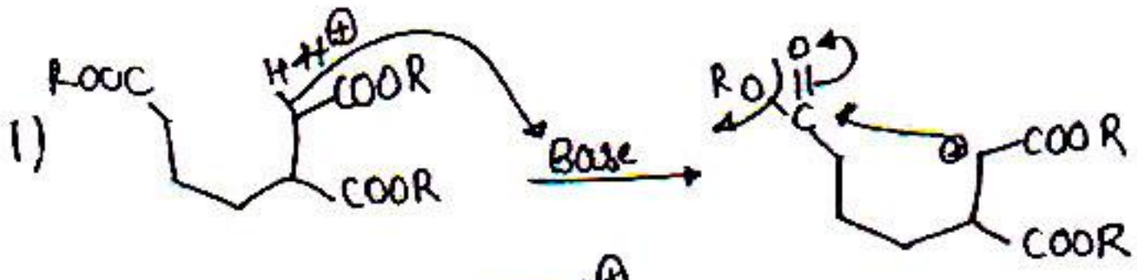


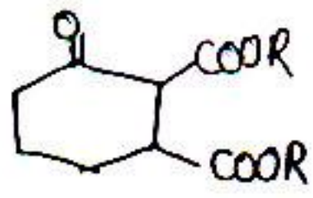
Eg: ROOC COOR COOR





1)





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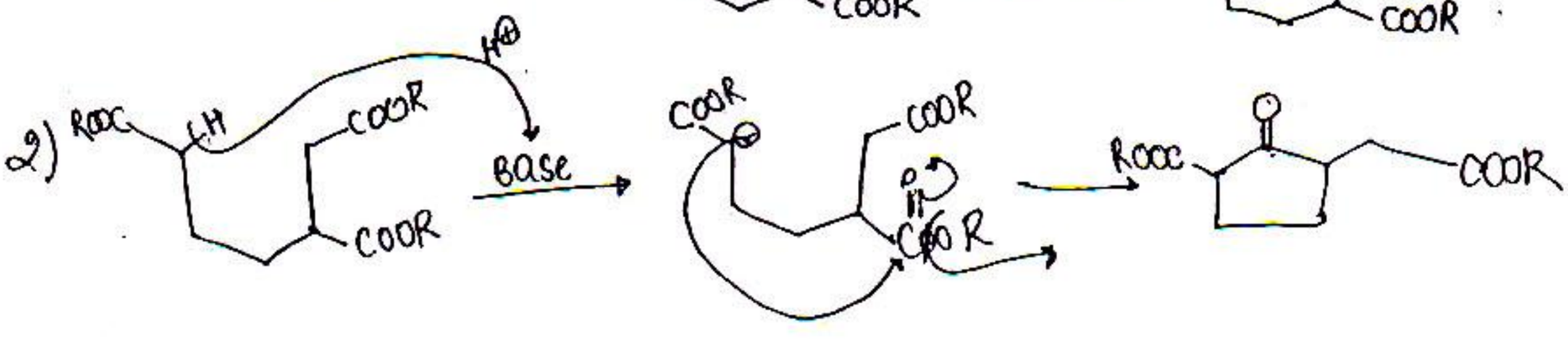
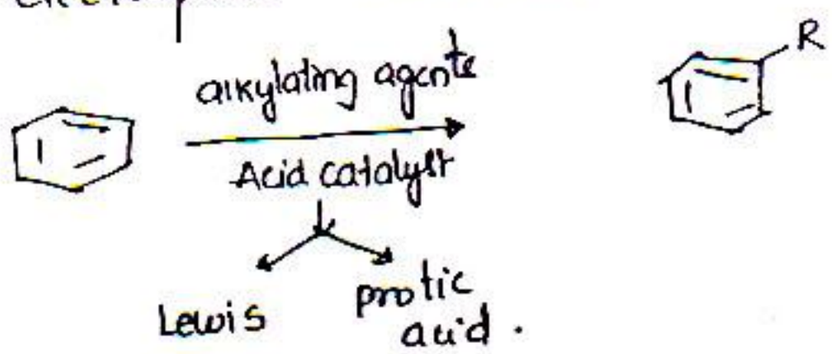


FRIEDEL -CRAFTS ALKYLATION:

→ Introducing of alkyl group at aromatic skeleton using alkylating agents in the presence of lewis acids or protic acids are friedel crafts alkylations.

→ C-C bond formation, Electrophilic substitutions.

→ Attacking electrophile carbocation.



→ Alkylating agents : (i) Halo-alkanes → best, widely used and common.
(ii) Cycloalkane (Cyclopropane)
(iii) Alcohols
(iv) Epoxides
(v) alkenes, alkynes
(vi) Carboxylic acids.

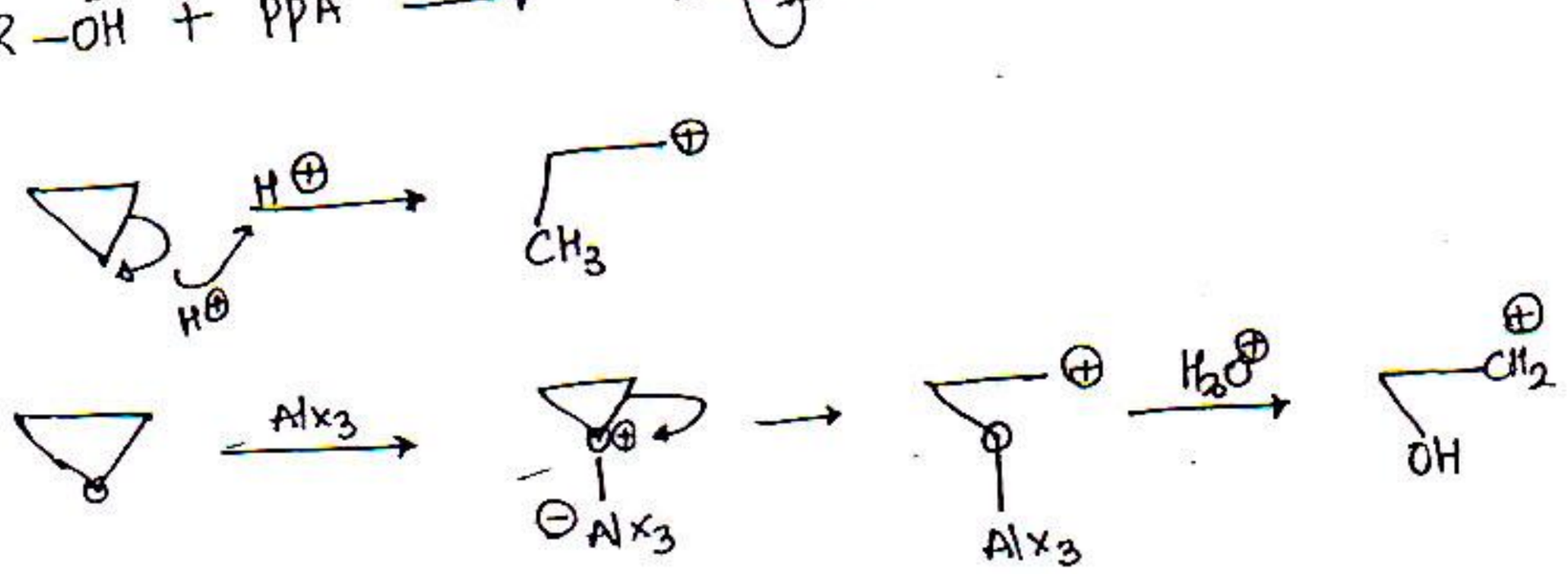
→ Lewis Acids : AlX_3, BX_3, $ZnCl_2$, $SnCl_4$, $SbCl_5$ etc.

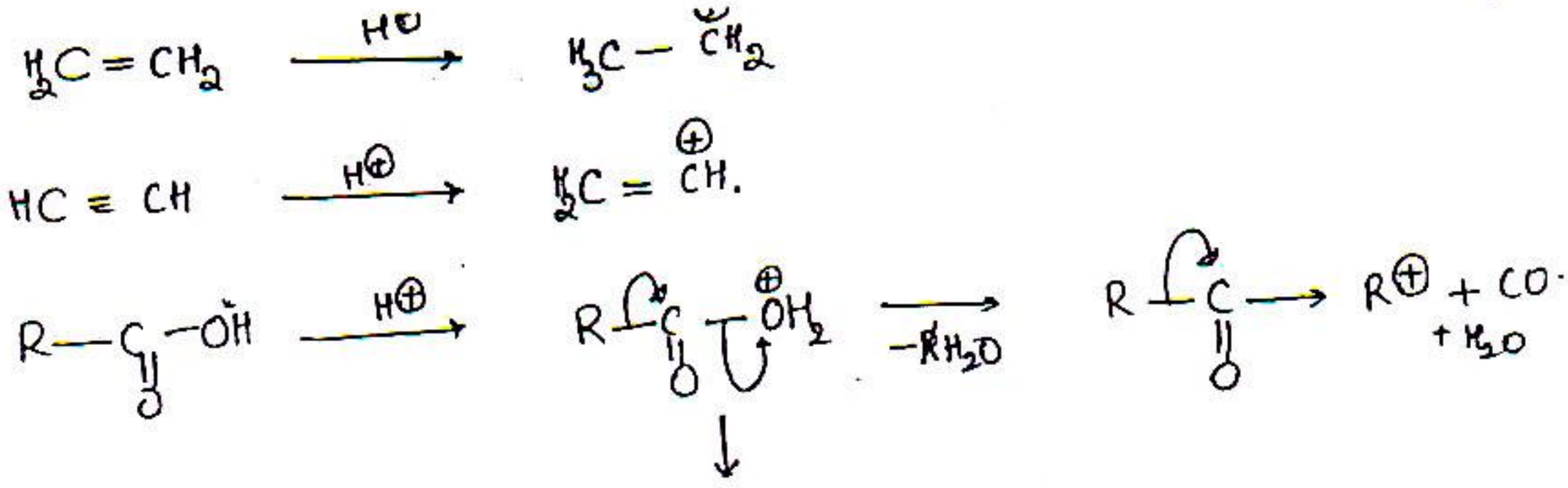
→ protic acids : H_3PO_4, Polyphosphoric Acid (PPA), HNO_3, H_2SO_4

→ Role of acid catalyst : Acid catalyst are helpful for ready / fast generation of Carbocation intermediate from alkylating agent.

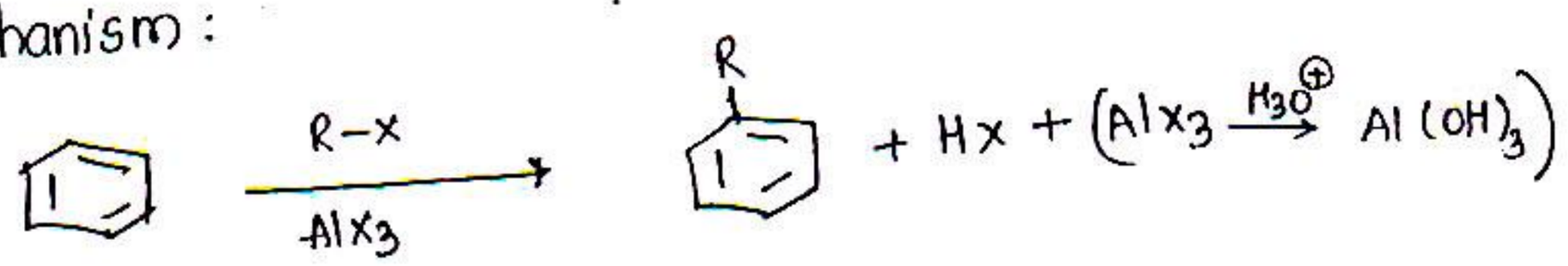
Eg: $R-X + AlX_3 \longrightarrow R-\overset{\oplus}{X}-\overset{\ominus}{Al}X_3 \longrightarrow AlX_4^{\ominus} + R^{\oplus}$

$R-OH + PPA \xrightarrow{H^{\oplus}} R-\overset{\oplus}{O}H_2 \xrightarrow{-H_2O} R^{\oplus} + H_2O$





Mechanism:

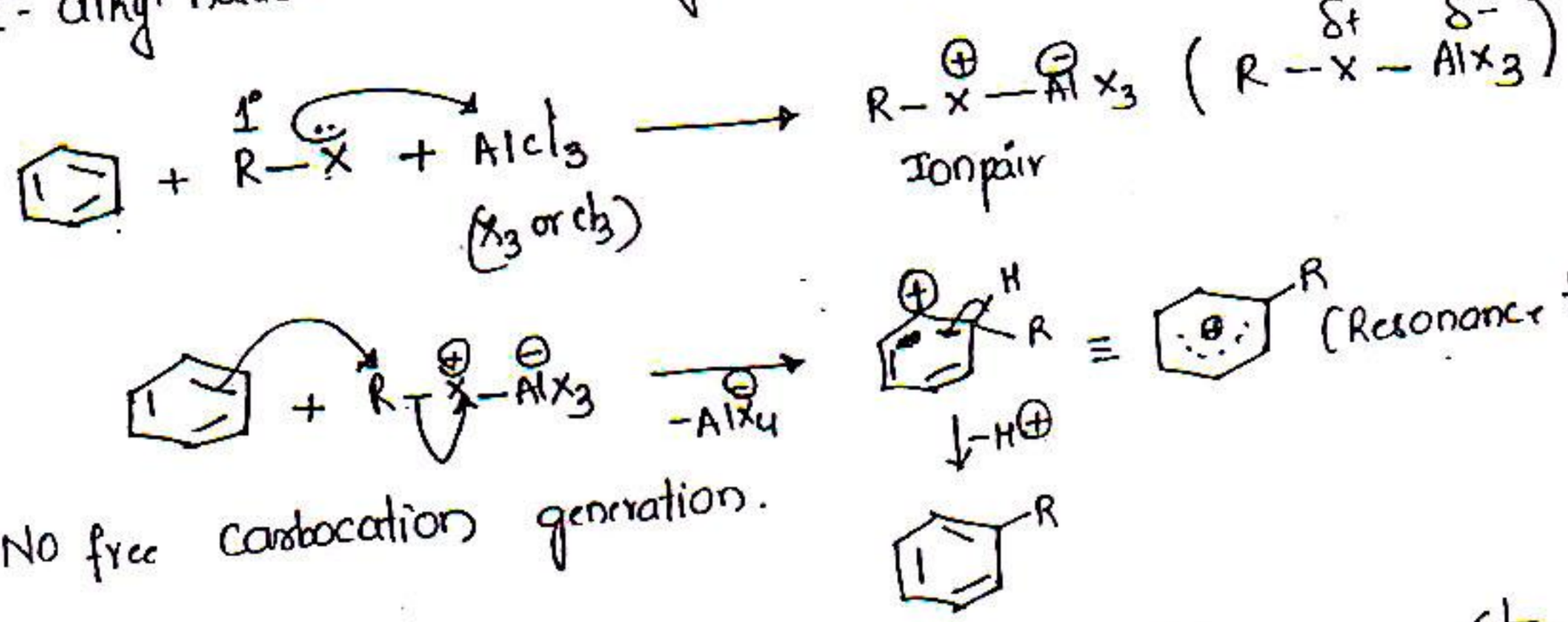


Reactivity : R-F > R-Cl > R-Br > R-I
w.r.t -Halide

Reactivity w.r.t alkyl : 3° alkyl halide > 2° alkyl halide > 1° alkyl halide

→ Mechanism depends on Nature of alkyl halide

→ 1° alkyl halides friedel craft's alkylation, by generation of ion pair.

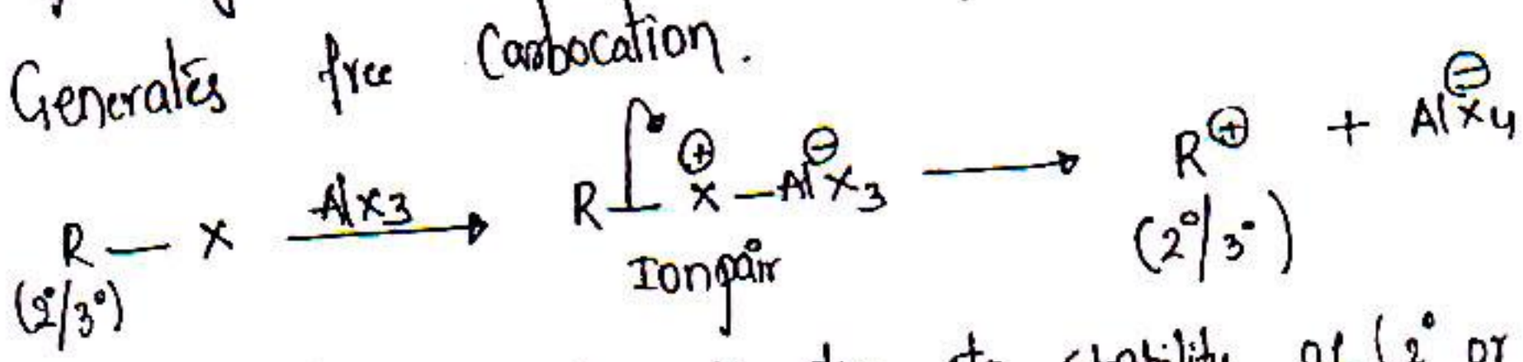


No free carbocation generation.

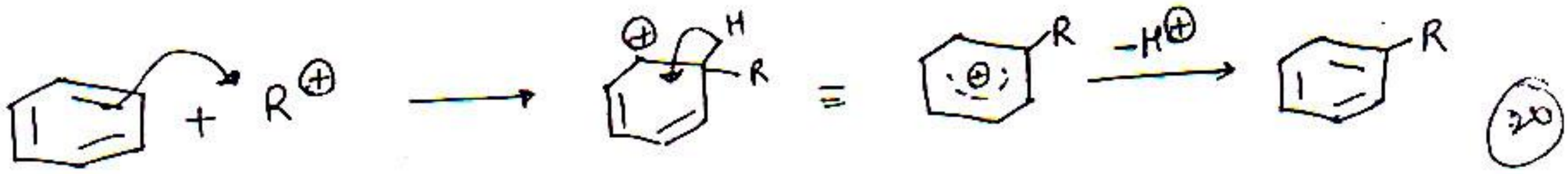
→ Attacking of Electrophile is the Rate determining step

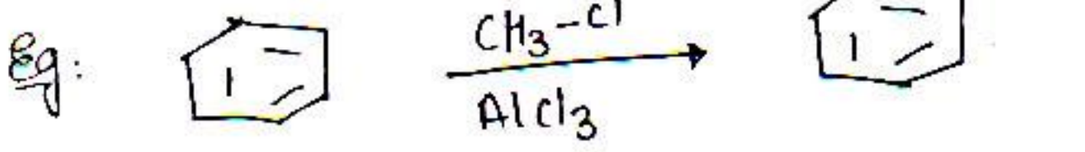
→ 3°/2° Alkyl halides.

Generates free Carbocation.



Free carbocation formation is due to stability of (2° or 3°) alkyl gp's

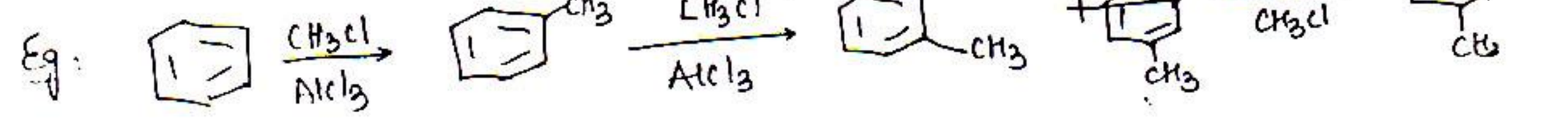




LIMITATIONS:

→ polyactylation: In friedel craft alkylations, initially produced mono-alkylated product is more reactive than corresponding reactant. ∴ further alkylation takes place on mono-alkylated product, Resulting New products are poly alkylated product.

→ ∴ It is difficult to produce mono-alkylated products.



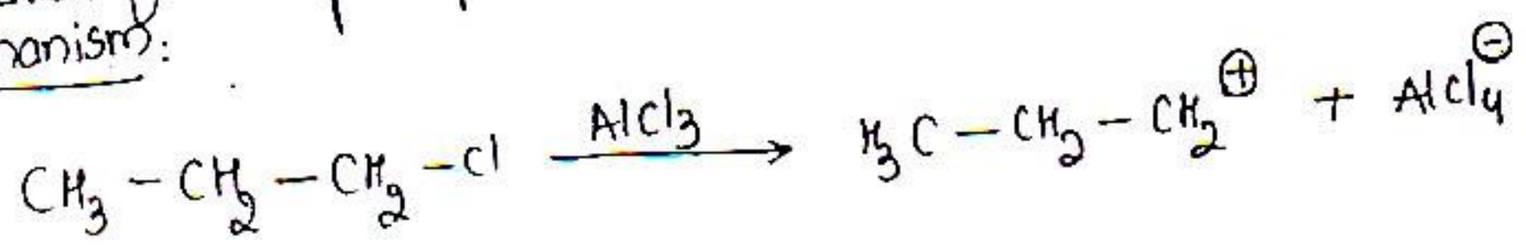
→

(expected product)

(unexpected product)

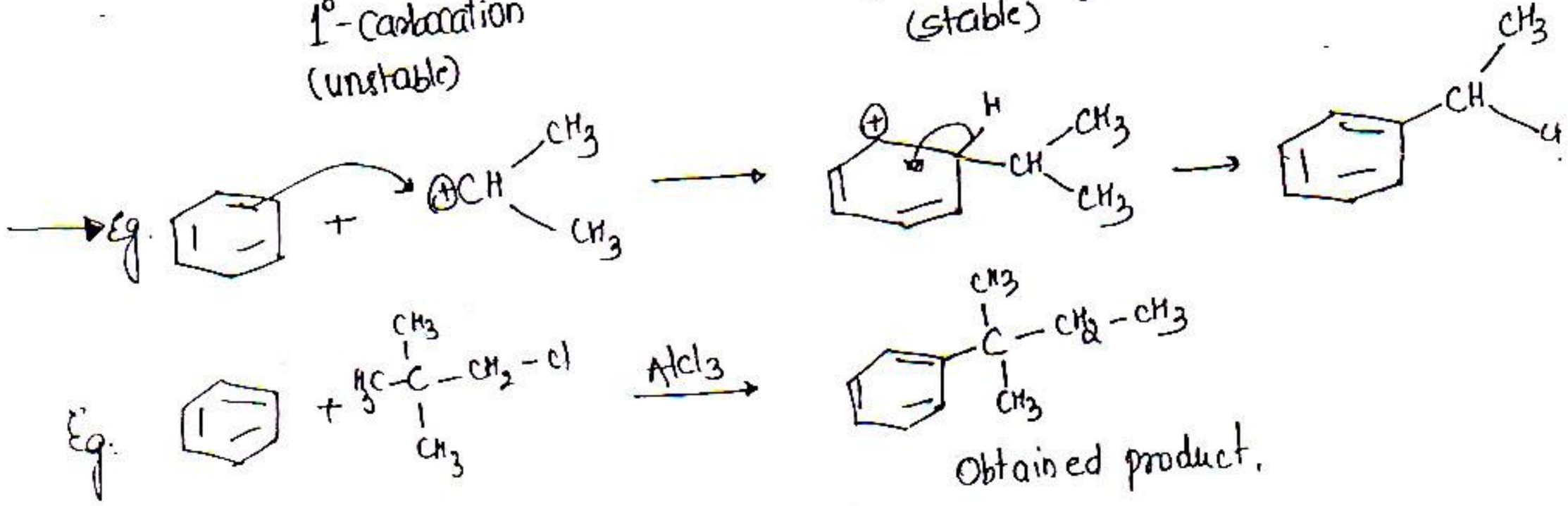
Explaination for unexpected product.

Mechanism:

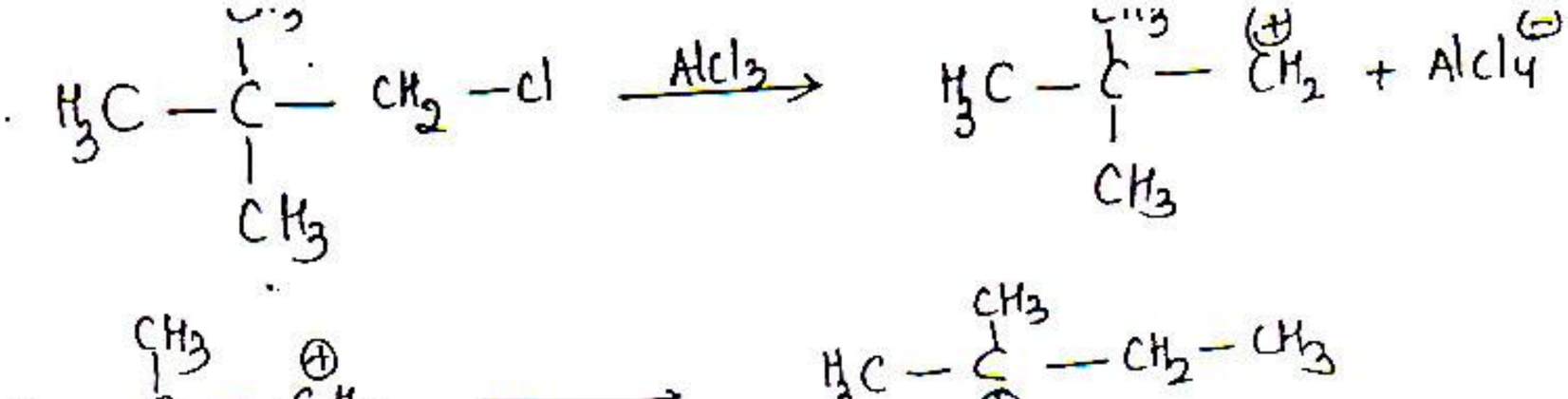


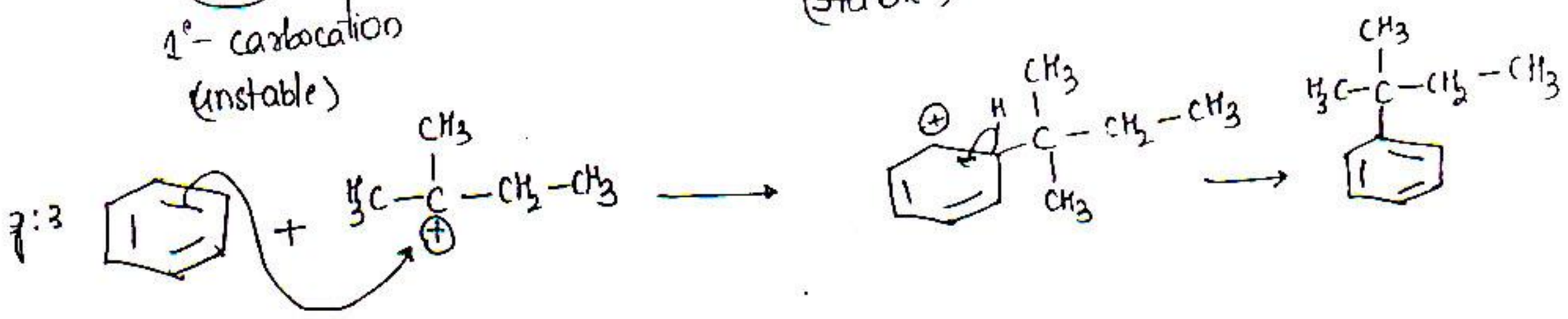
1°-carbocation (unstable)

2°-carbocation (stable)

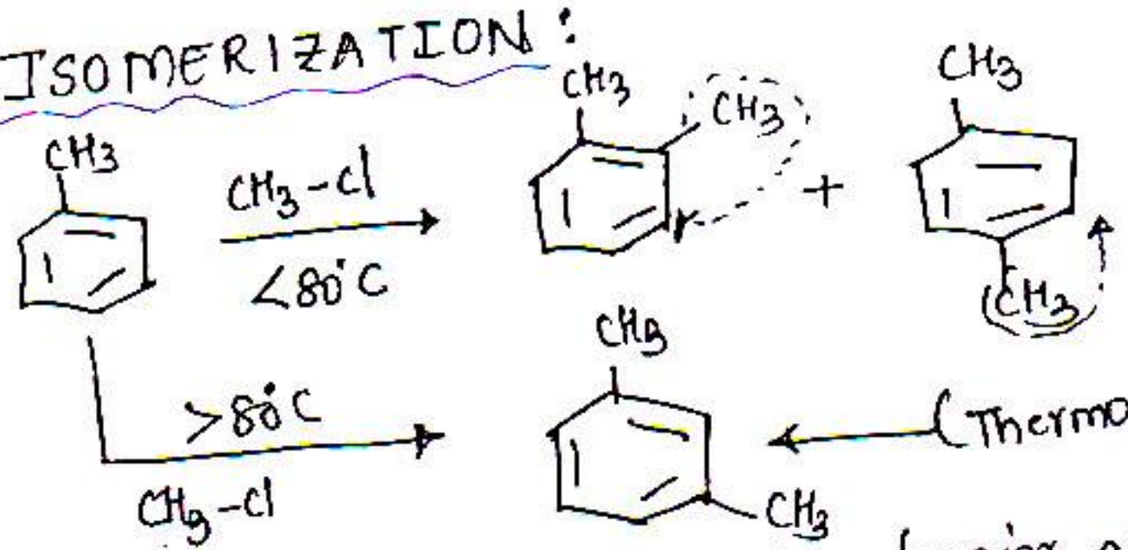


Obtained product.

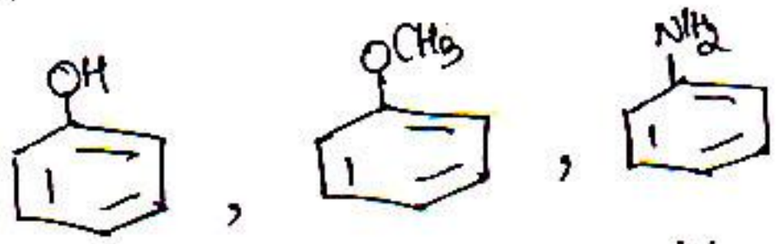




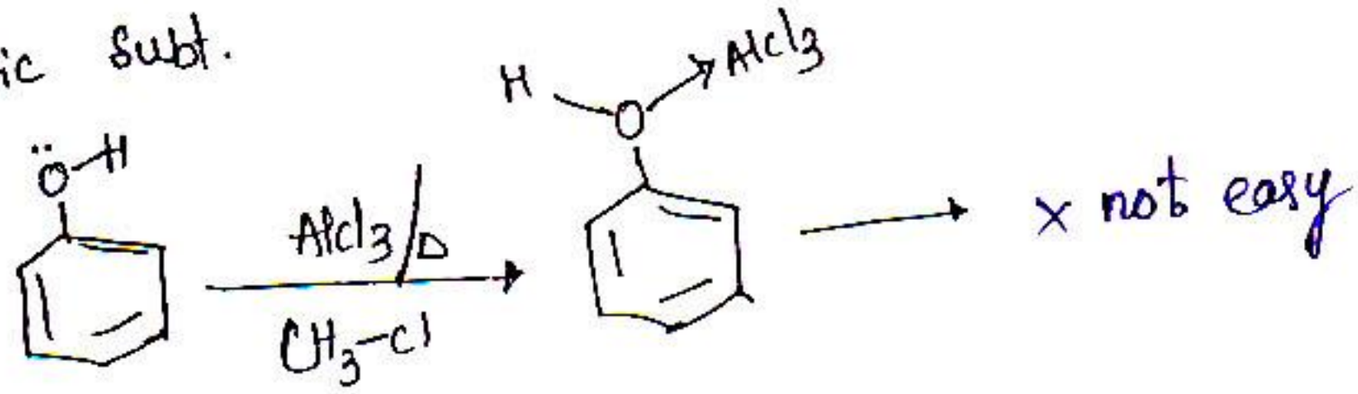
ISOMERIZATION :

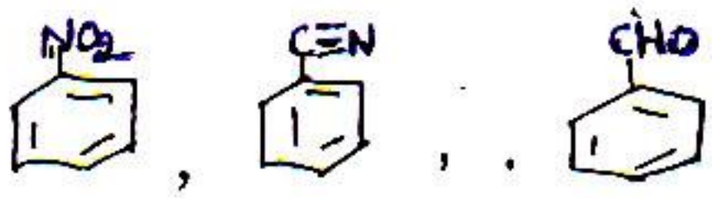


→ probably at high temperature migration of group from ortho-para position to meta-position.

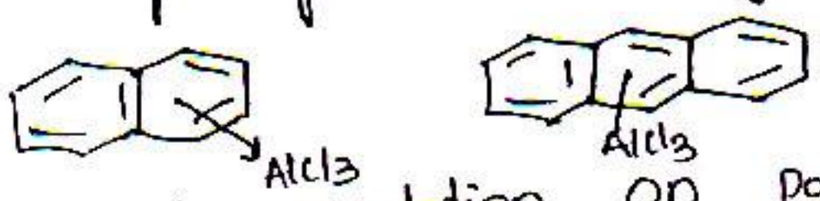
eg: (1) 

These compounds will does not undergo friedel crafts alkylation because Lewis acids (or) co-ordination with substituents make benzene less reactive towards Electrophilic Subt.



(2).  these also do not undergo friedal crafts alkylation.

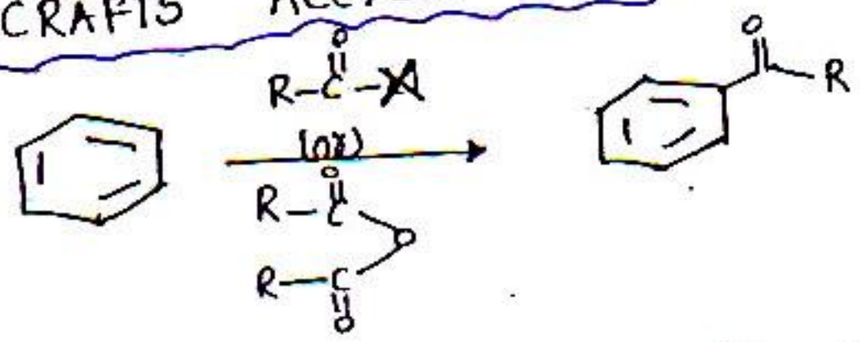
Because the substituents are electron withdrawing groups, ∴ make benzene very very electron deficient.



(3). → Frieldel crafts alkylation on polycyclic aromatic skeleton is difficult due to coordn of lewis acid with these aromatic polycyclic hydro-carbon

Excess π-system makes co-ordn with lewis acid.

FRIEDEL CRAFTS ACCYLATIONS :—



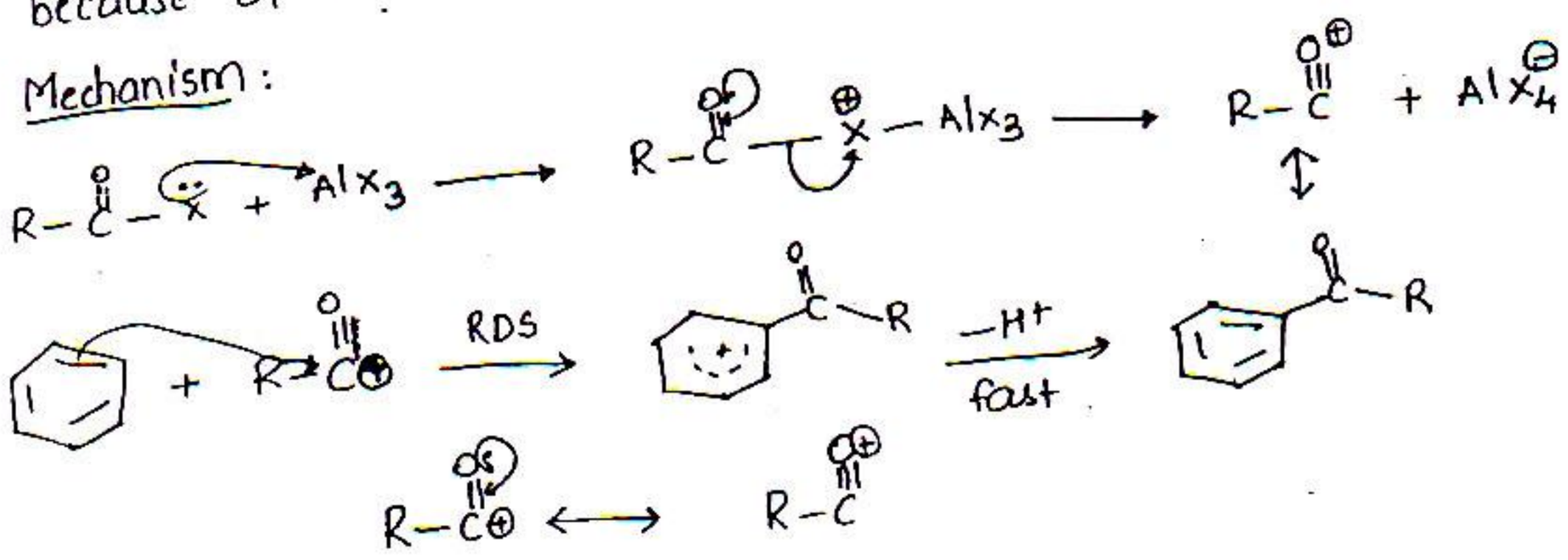
→ Best method to convert aromatic compound to ketones

$R-\overset{O}{\overset{\|}{C}}-$ Acyl group, $H_3C-\overset{O}{\overset{\|}{C}}-$ Acetyl.

→ In friedel crafts alkylations aromatic hydrocarbon are converted into active compounds where as in friedel crafts acylation, the resulting product is less reactive than the reactant

→ acyl carbocation is attacking electrophile in friedel crafts acylation, these rxn's will not involve in any kind of rearrangement irrespective of R-group, because the carbocation formed is stabilised because of resonance. It doesn't involve in rearrangement.

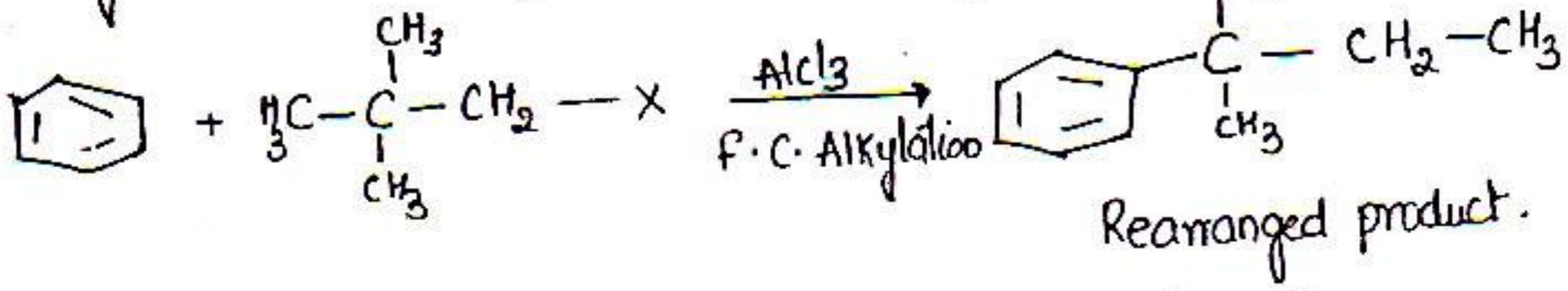
Mechanism :



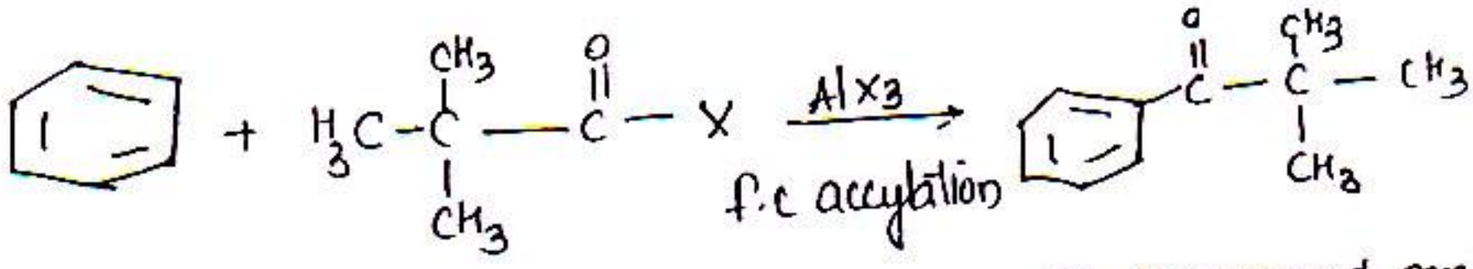
Advantages :-

→ No poly acylations

→ No possibility of re-arranged products formation.



Rearranged product.



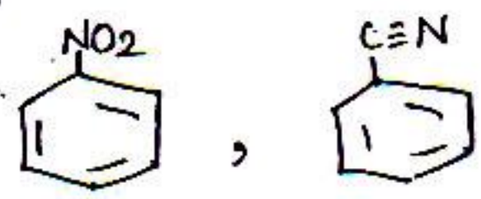
No- rearranged product

→ NO isomerisations.

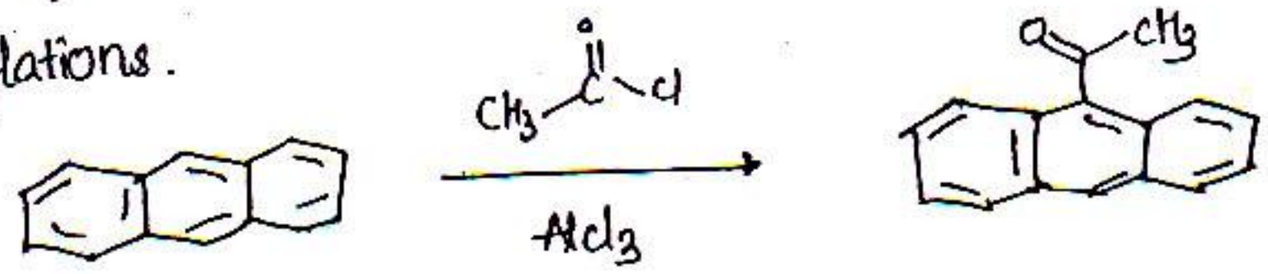
Limitations :-

→ It is not possible to do F.C. acylation on 

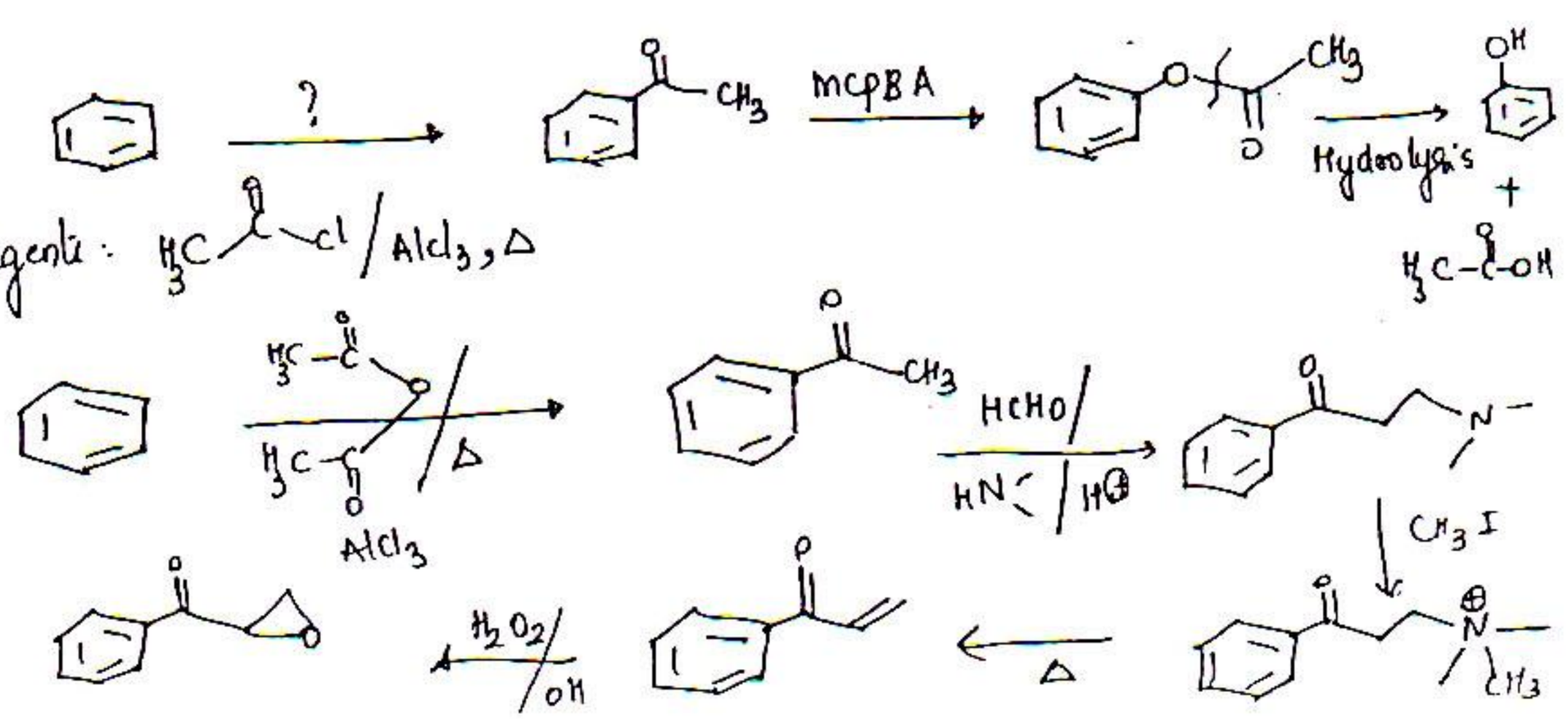
because lewis acid co-ordinates with -OH, $-NH_2$ gp's and deactivates benzene nucleus.

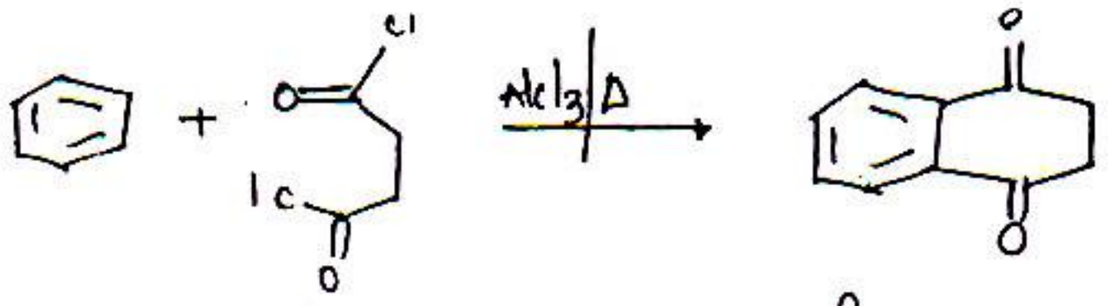
→ Withdrawing groups attached aromatic Skeletons also will not under go f.c acylations 

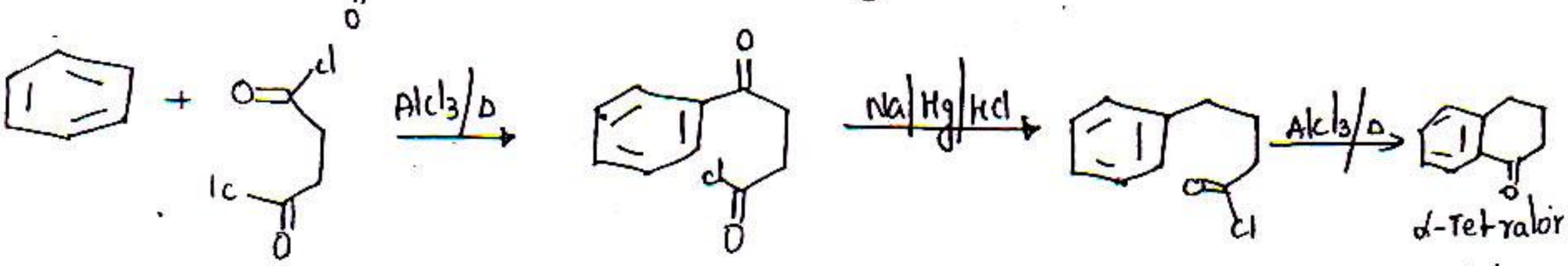
→ If Specific conditions maintained polycyclic aromatic Skeleton's undergo f.c acylations.



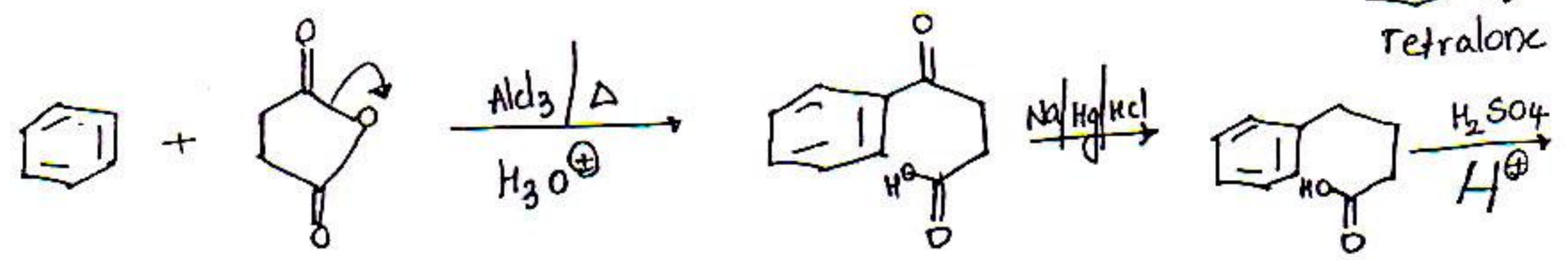
eg:

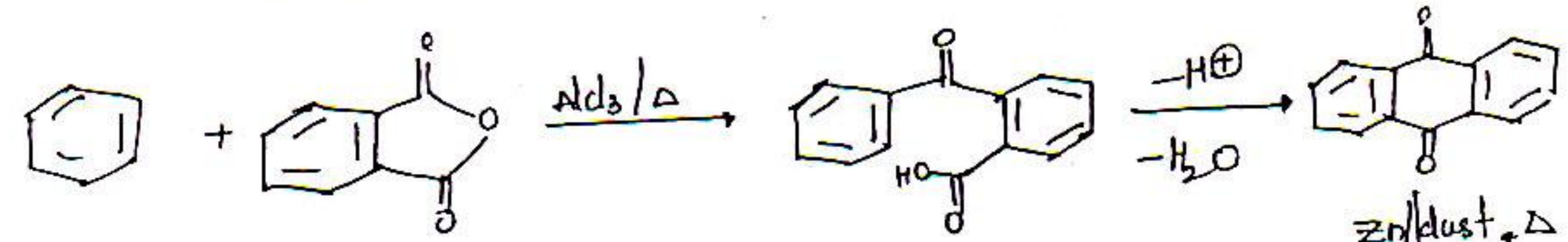


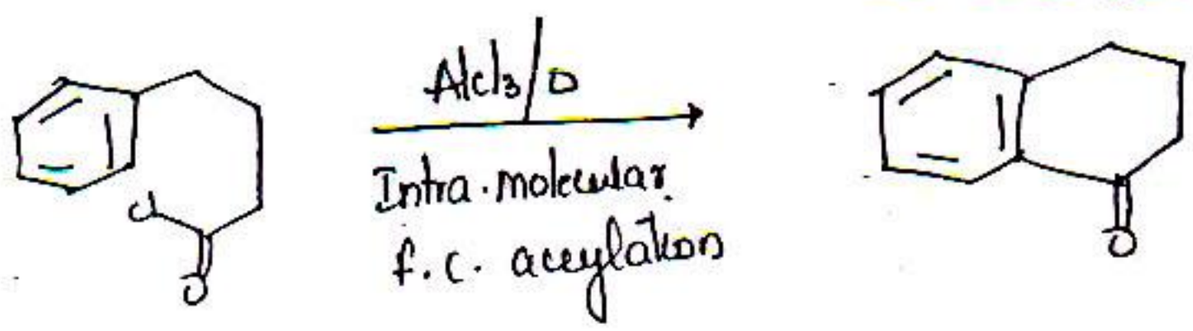
eg: 

Eg: 

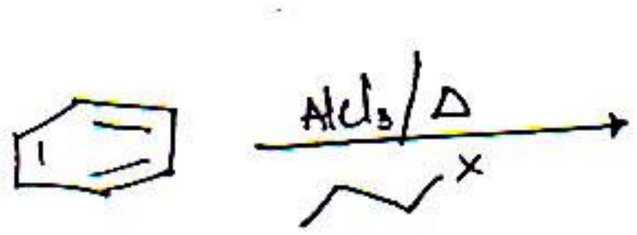

Tetralone

Eg: 

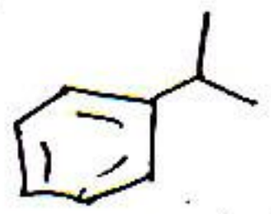
Eg: 

Eg: 

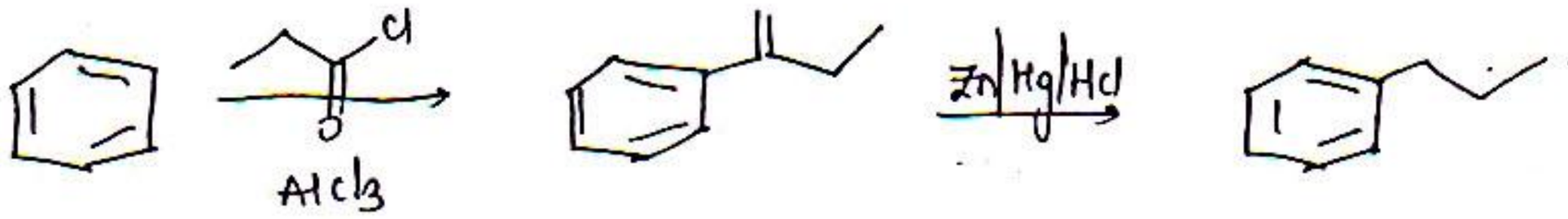
Intra molecular
f.c. acrylation

Eg: 

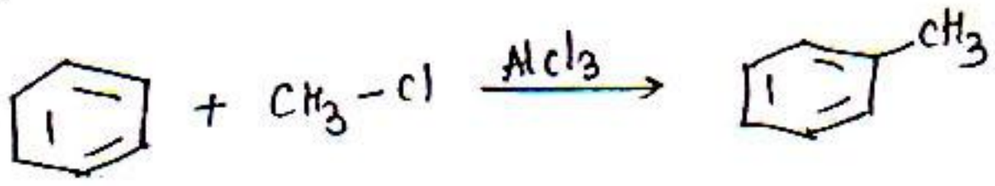
Expected product

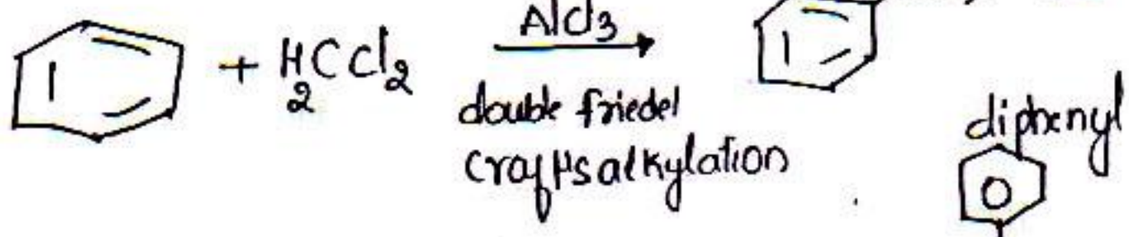
But 
obtained product.

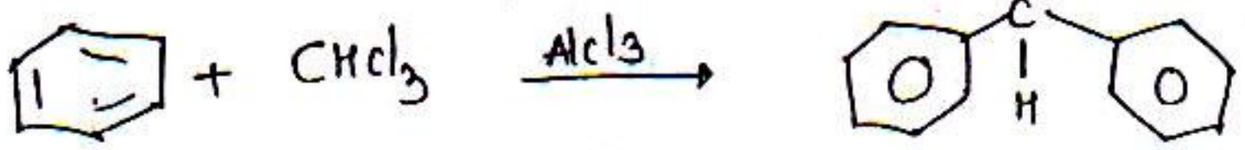
∴ To prepare n-propyl benzene F.C. acrylation is proper method than F.C alkylation because in f.c alkylation instead of expected product, rearranged product is obtained.

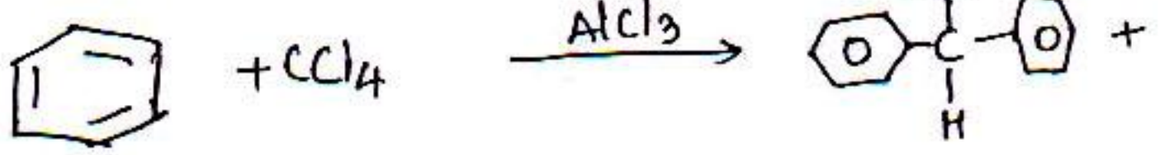
∴ 

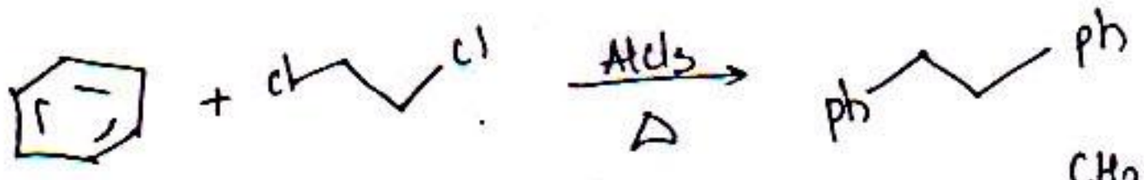
Eg. for friedel Crafts alkylation.

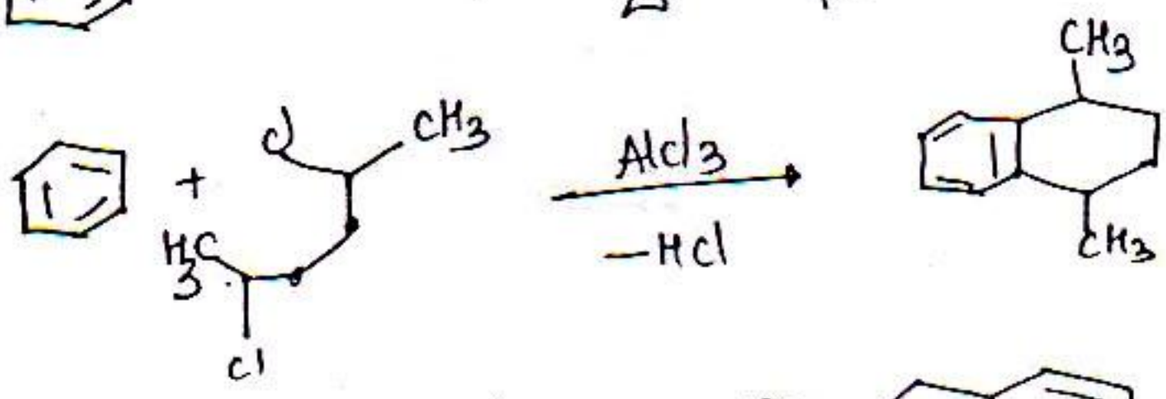
1) 

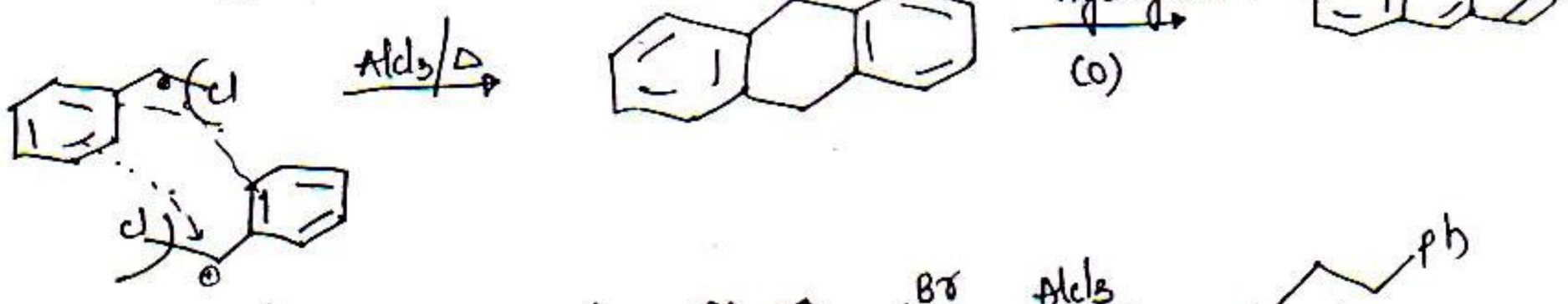
2) 

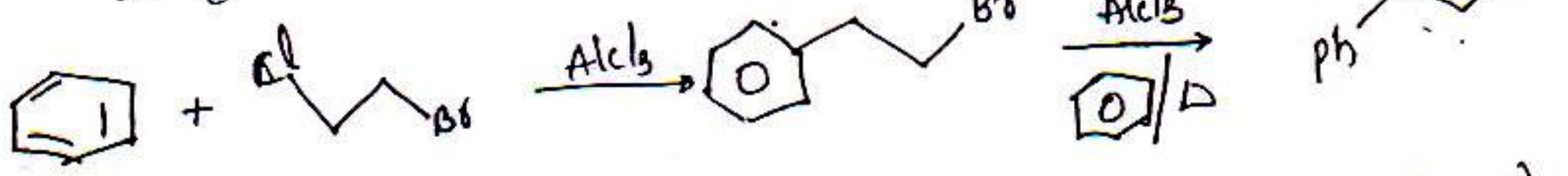
3) 

4) 

5) 

6) 

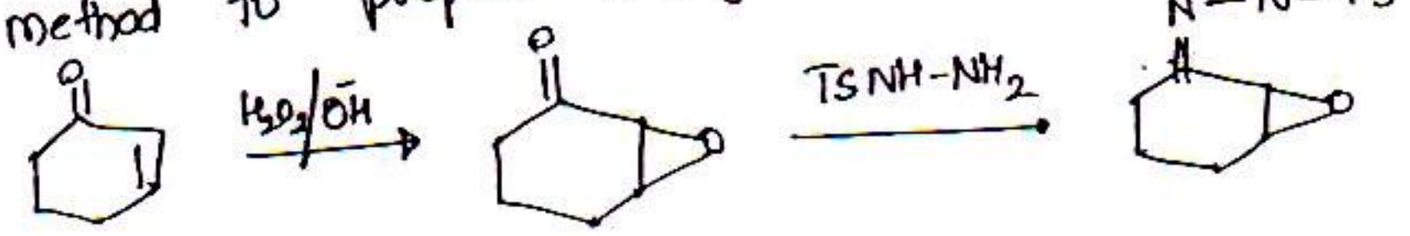
7) 

8) 

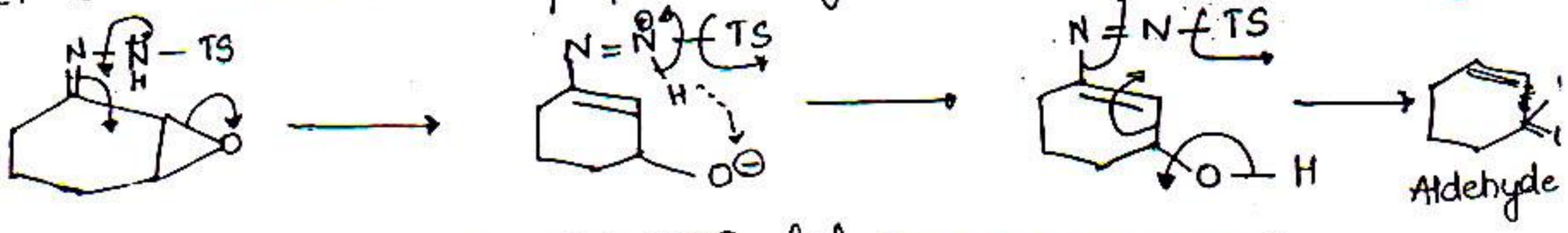
ESCHENMOSER : REARRANGEMENTS (FRAGMENTATION)

→ close to Shapro reactions

→ Best method to prepare alkenyl ketones.

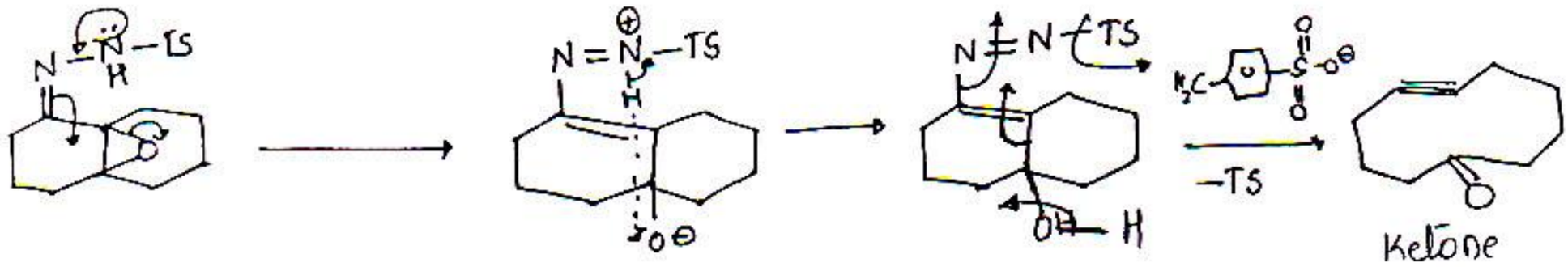


It is the method to prepare alkenyl Ketones.



ESCHENMOSER R.A

Eg:



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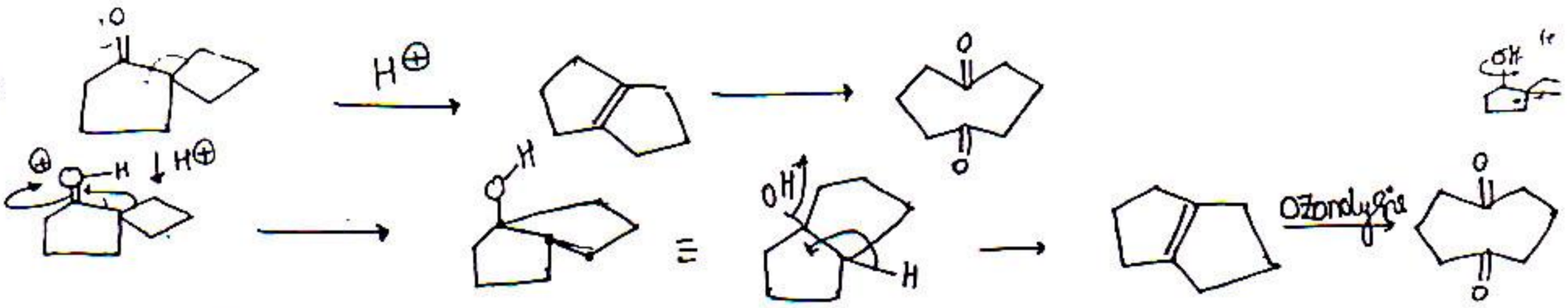
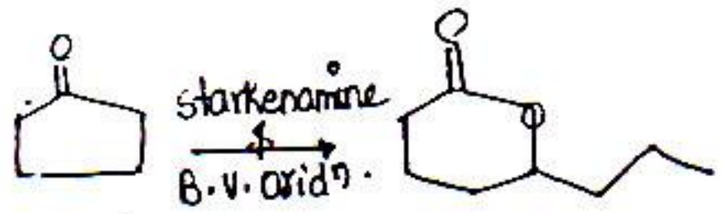


Eg)



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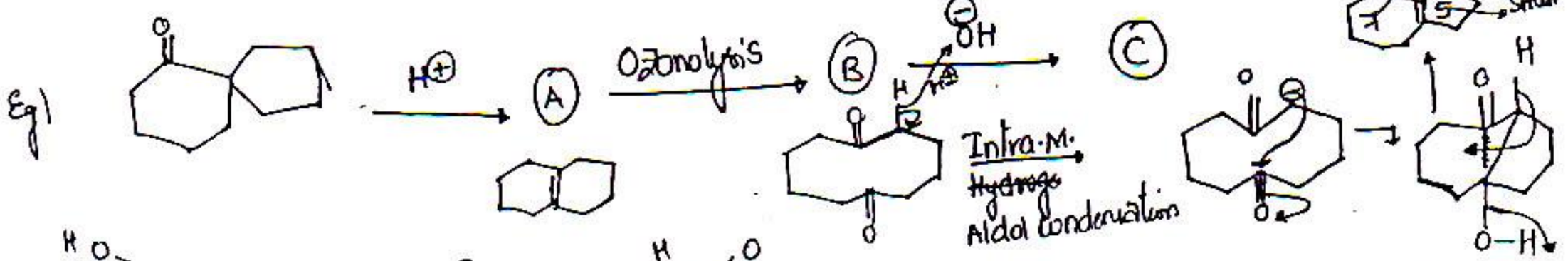

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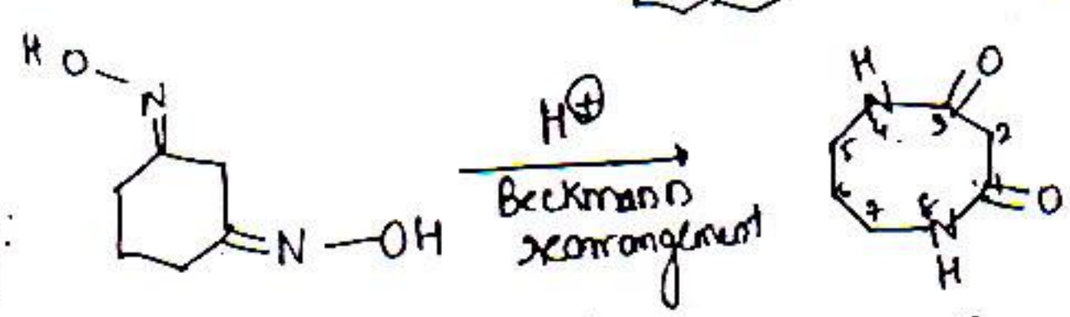
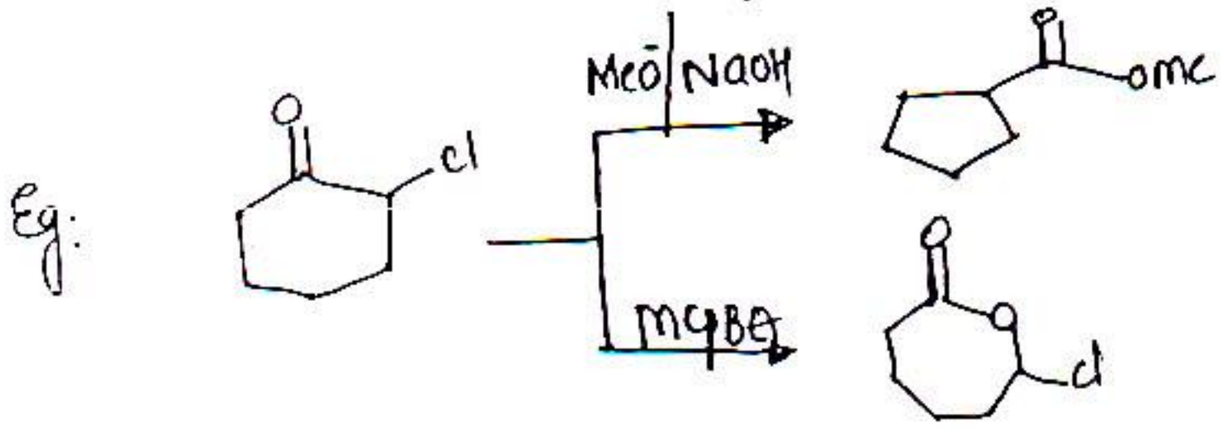


Eg:



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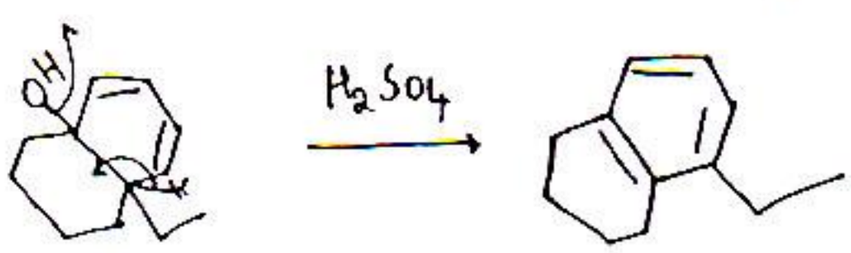

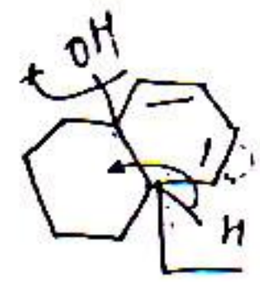

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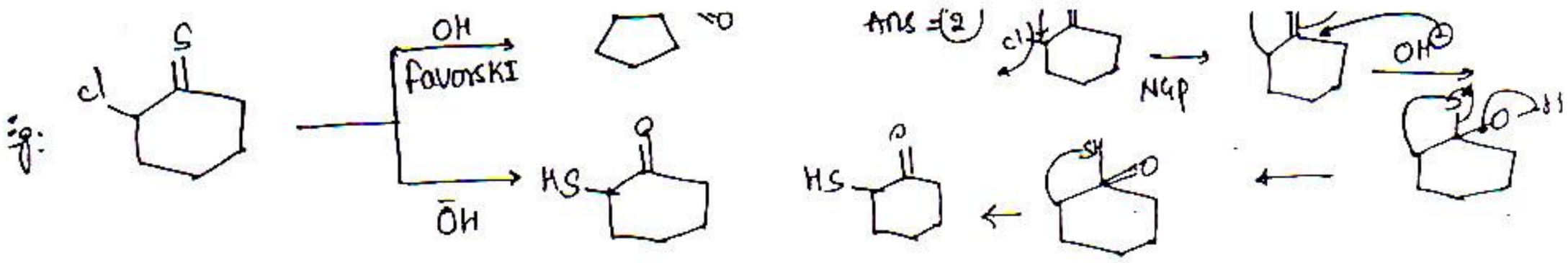

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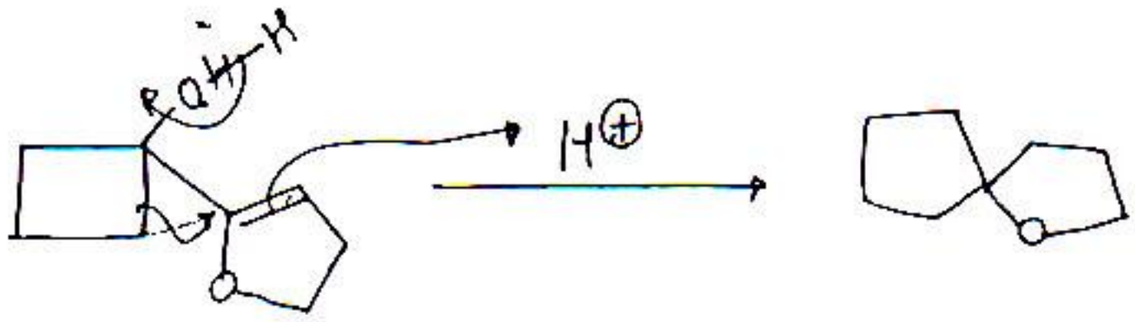

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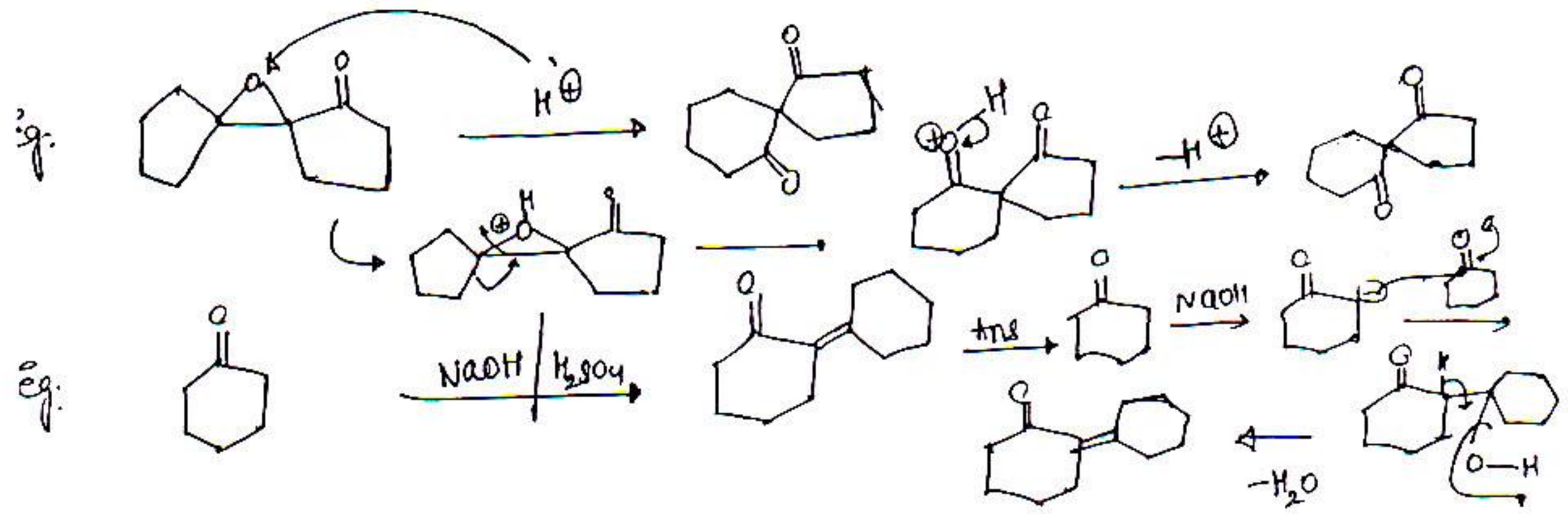

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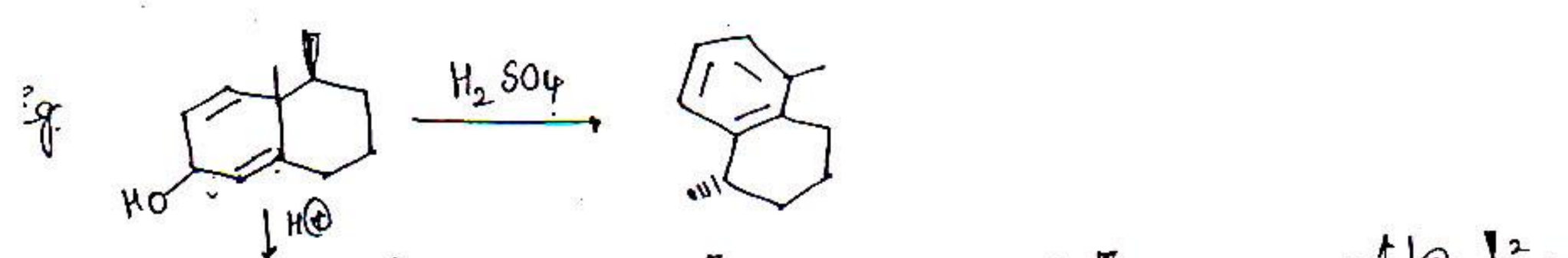

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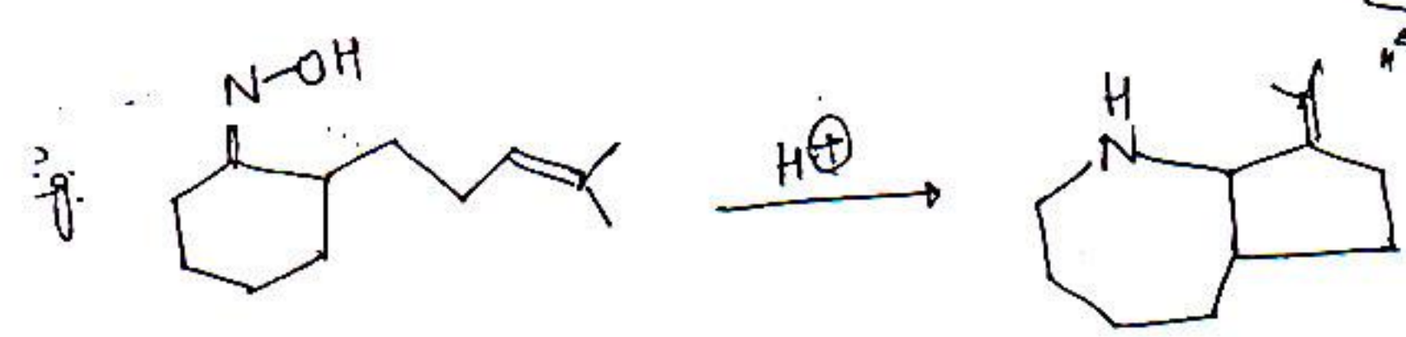

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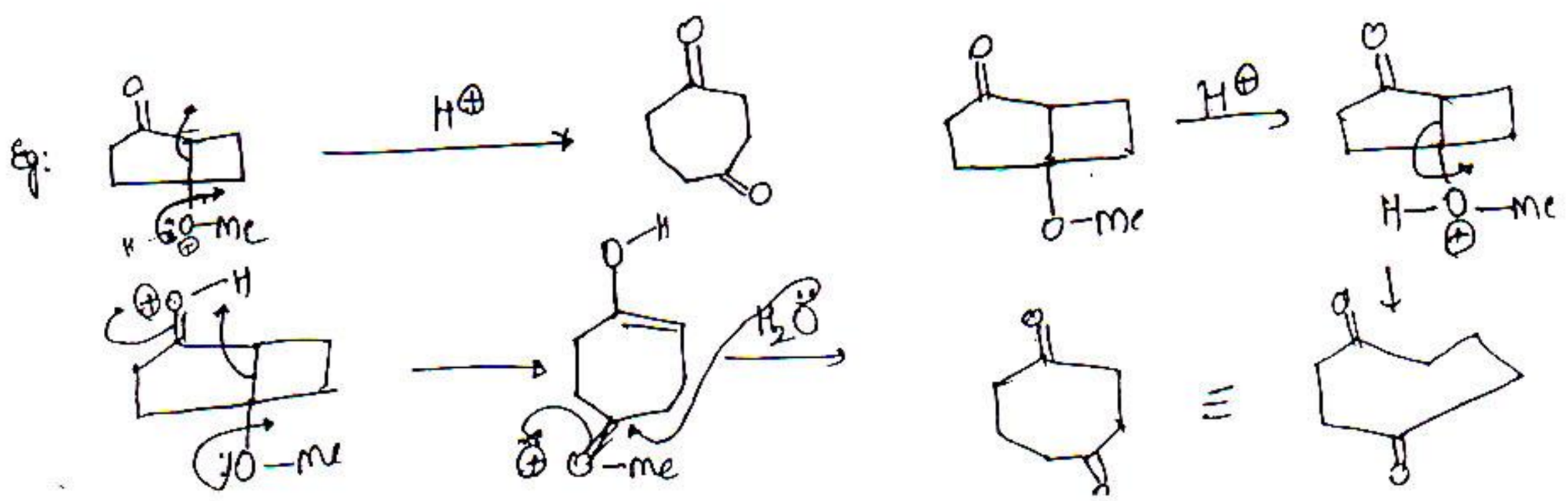

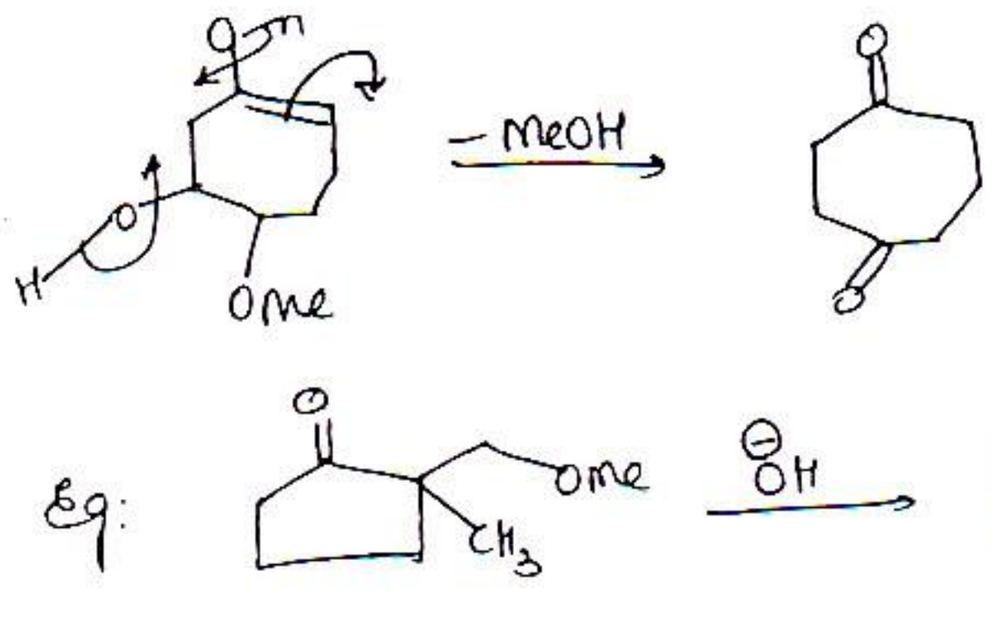

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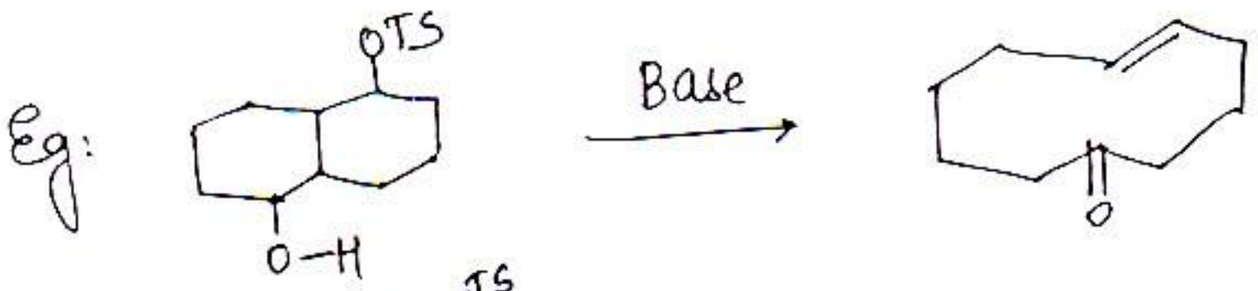

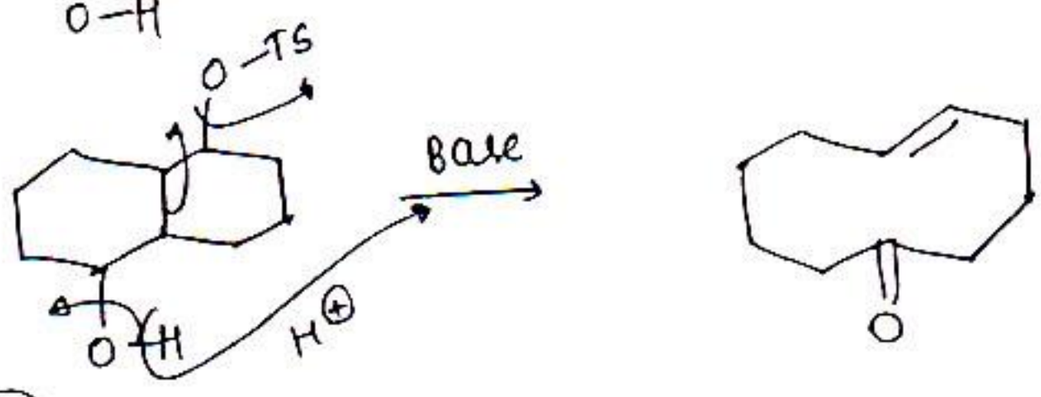

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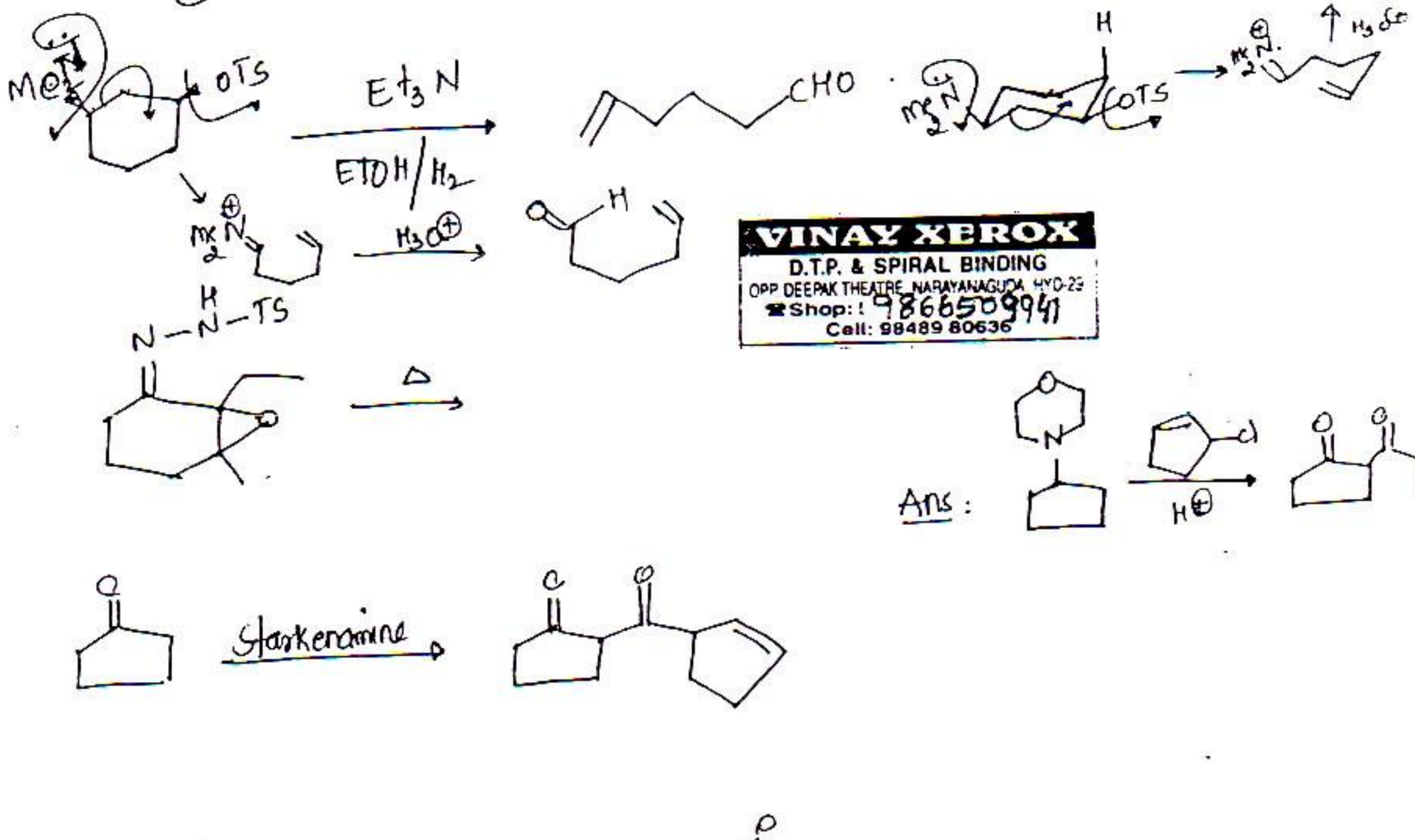

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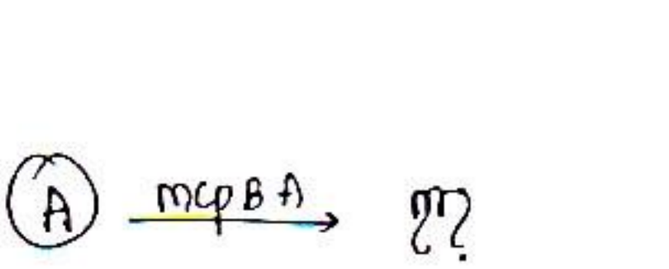

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