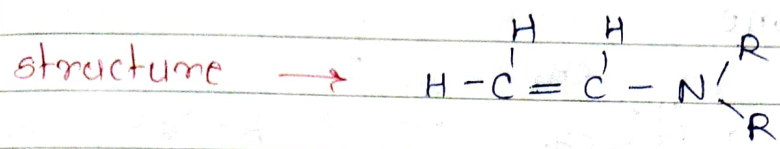
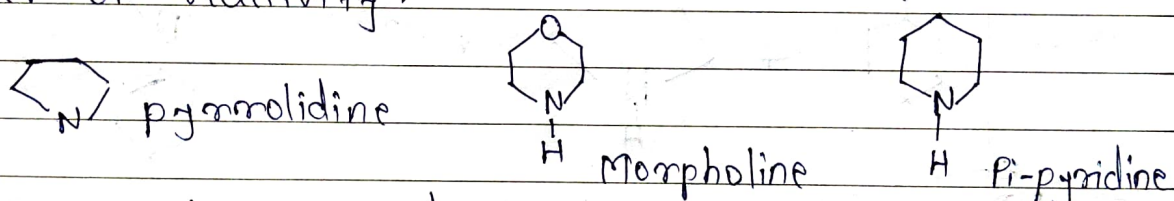


(B) Enamines



α - β unsaturated amine.

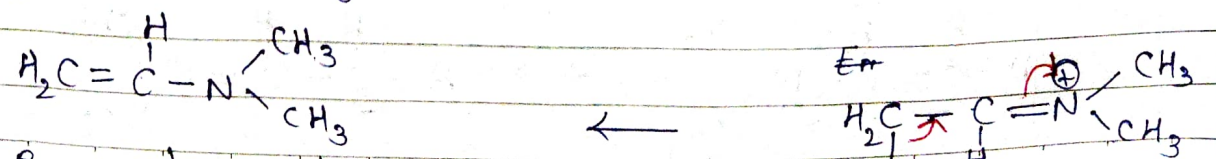
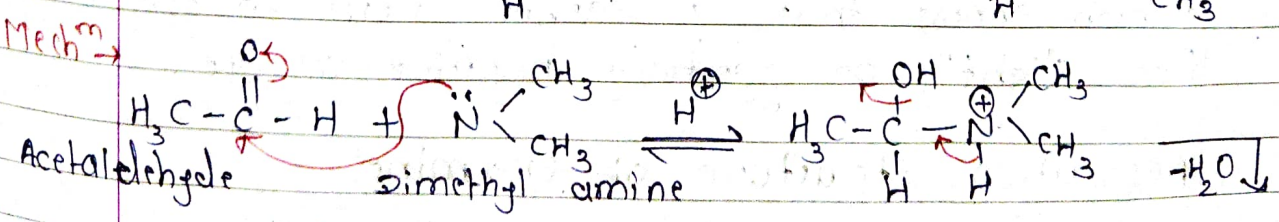
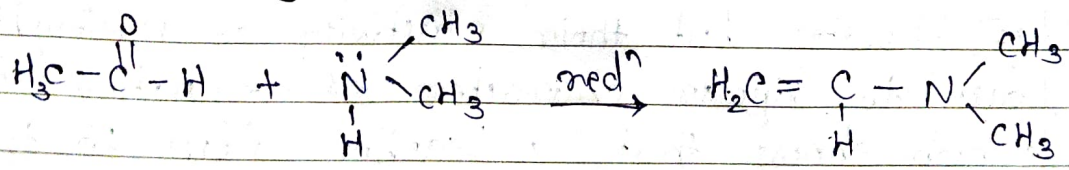
- i) Enamines are α - β unsaturated amine.
- ii) Enamines are obtained by the reaction of an carbonyl compound such as aldehyde or ketone with a secondary amine in presence of a suitable dehydrating agent such as potassium carbonate (K_2CO_3) or better reflux in benzene solution.
- iii) The secondary amines which are commonly used are pyrrolidine, morpholine & piperidine in descending order of reactivity.



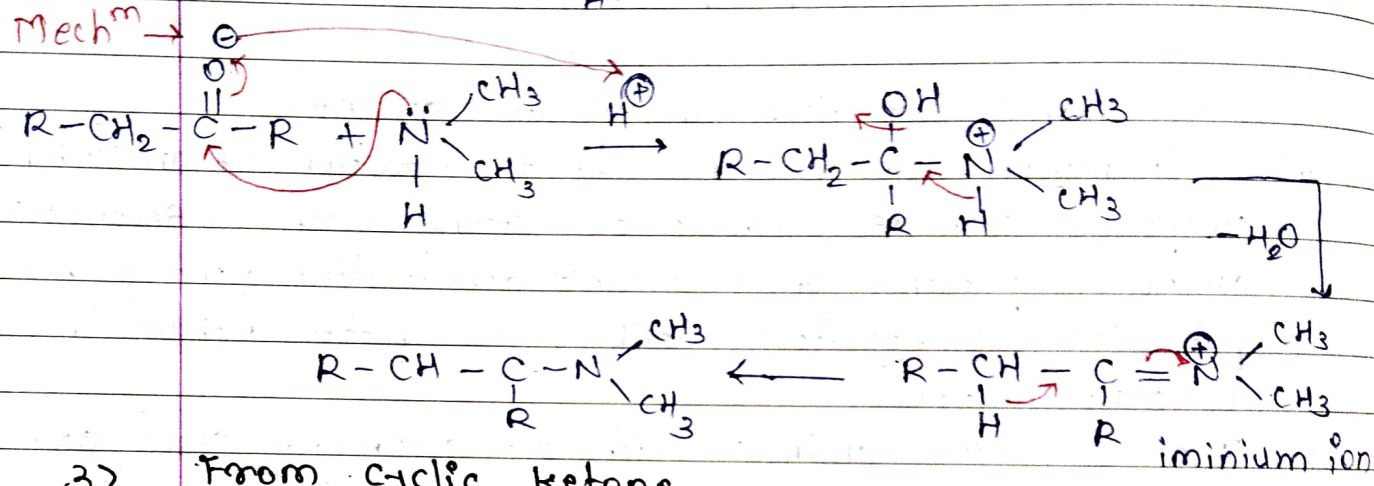
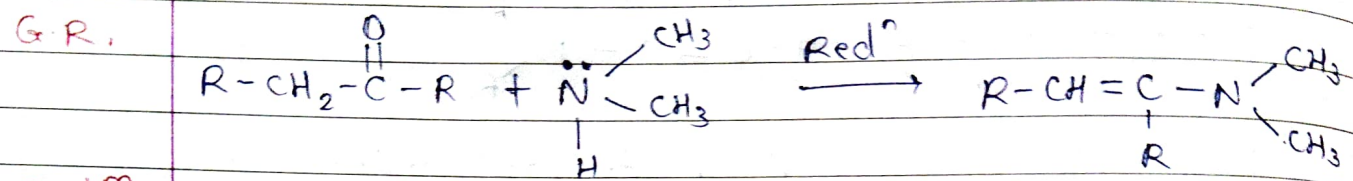
iv) The reaction proceeds through the intermediate of iminium ion which loses a proton from a carbon atom β to the nitrogen resulting in the formation of double bond between α & β -carbon atom.

* Preparation of Enamines \rightarrow

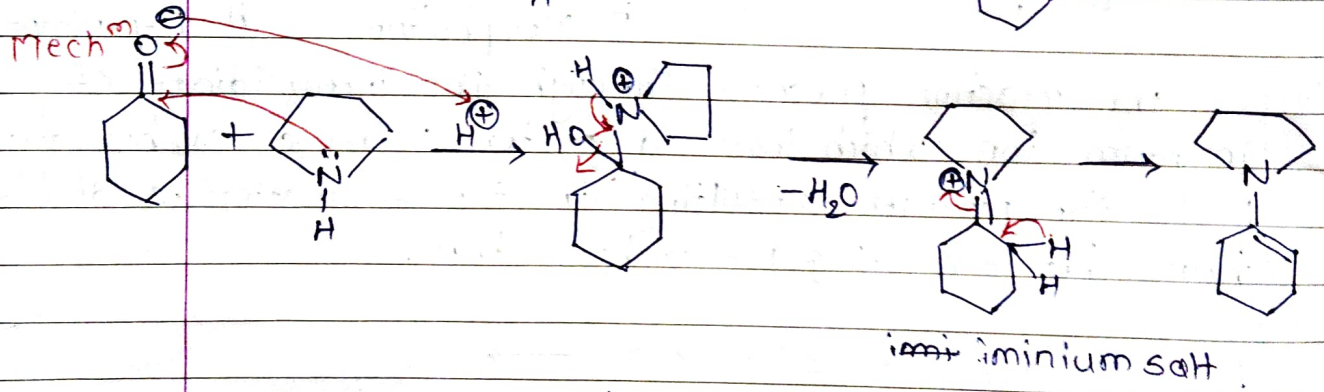
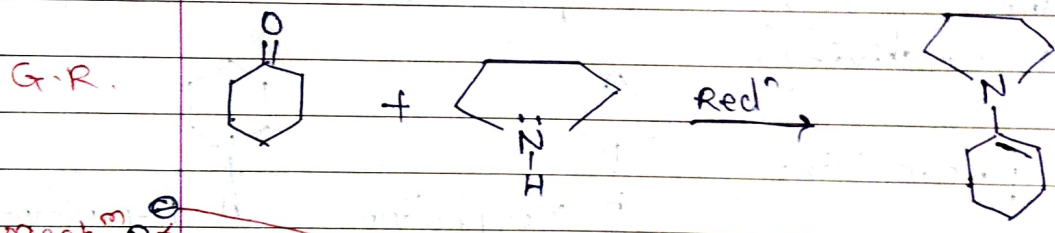
1) From aldehyde \rightarrow



2) From ketone



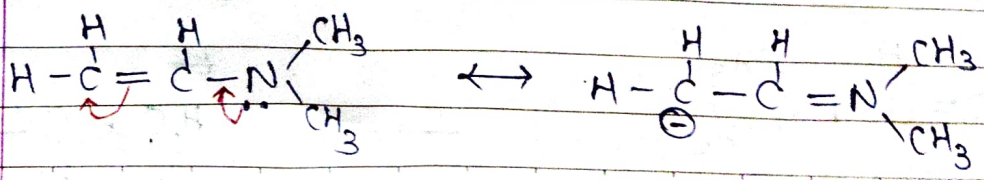
3) From cyclic ketone.



★

Enamines can be considered as nitrogen analogues of enolates but their reactivity as nucleophile is due to dipolar character of resonating structure which shows that β carbon atom to the nitrogen has slightly or partially negative charge.

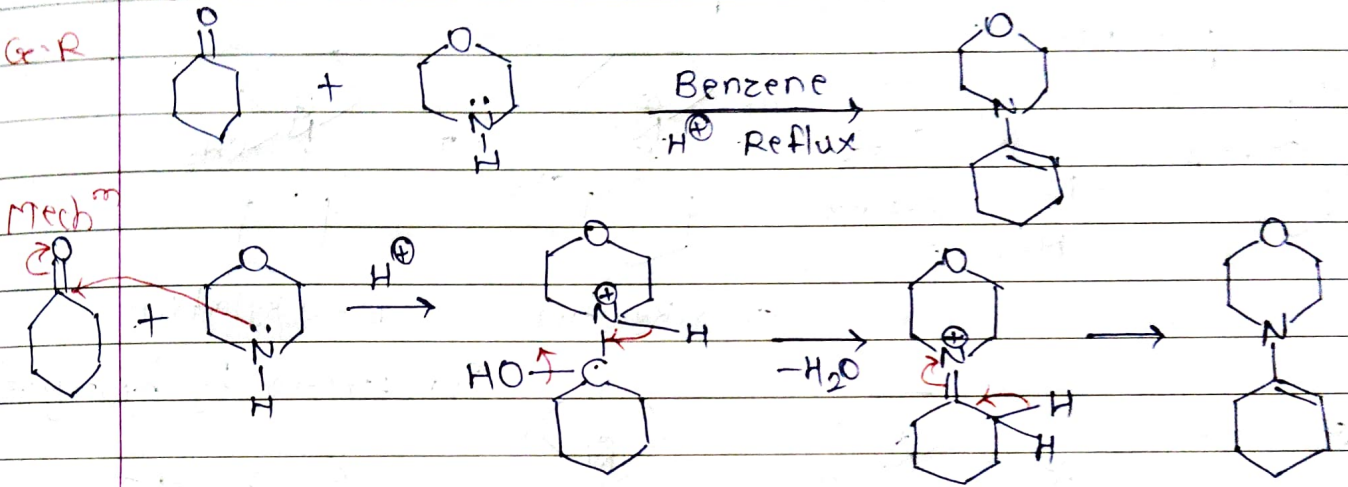
Resonating structure of enamines



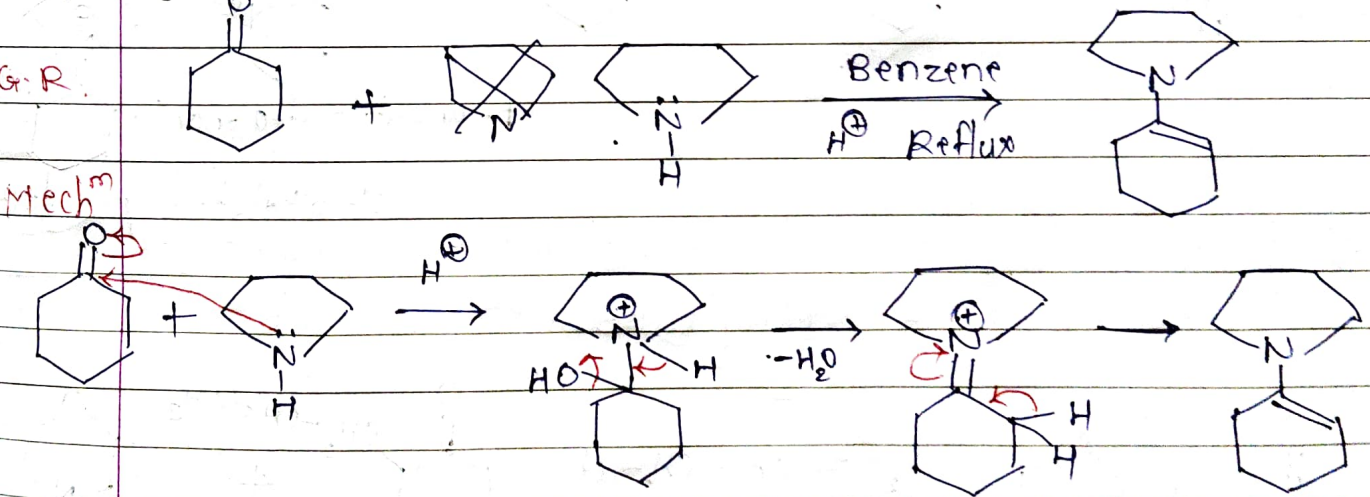
★ Generation of enamines

Enamines are generated from carbonyl compound & 2° amine.

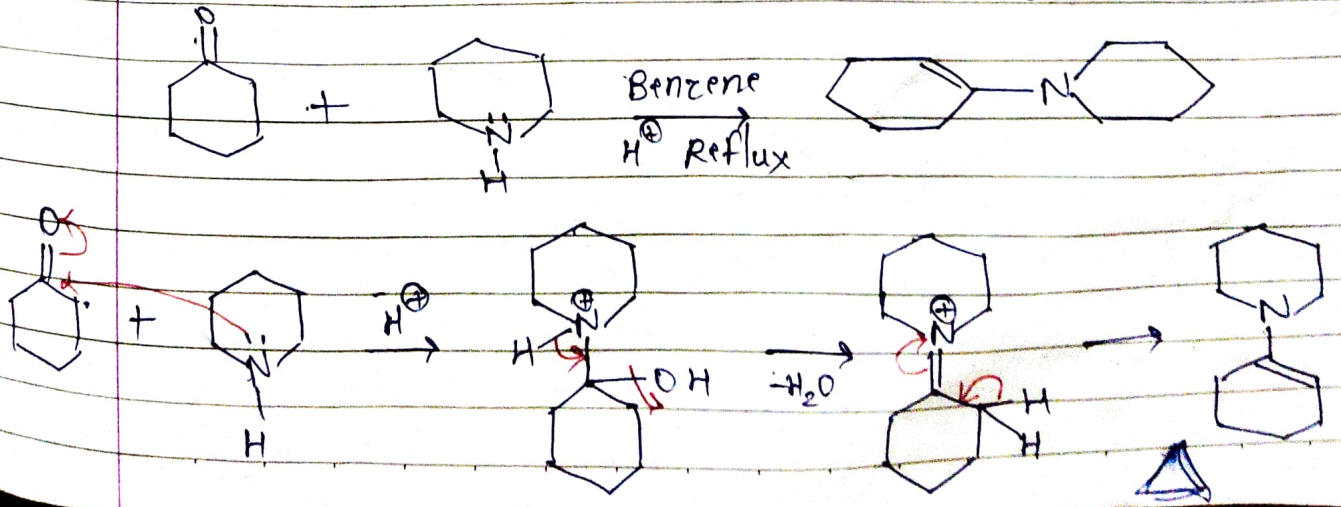
1) Synthesis of cyclohexanone - Morpholineamine



2) Synthesis of cyclohexanone pyrrolidine enamine



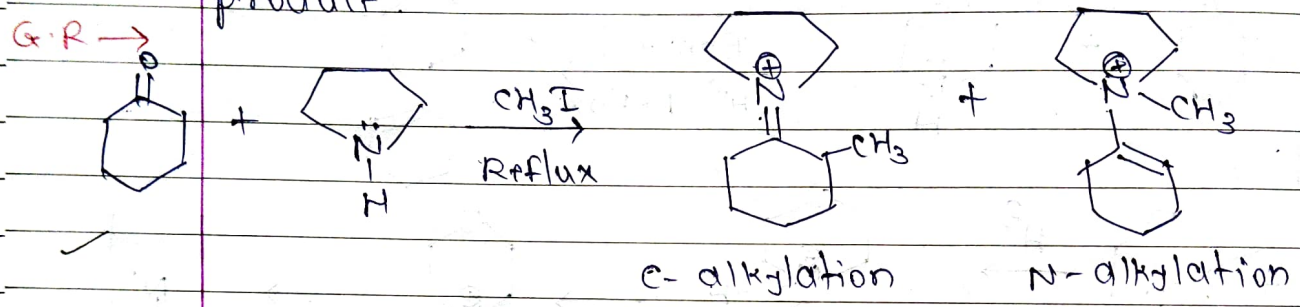
3) Synthesis of cyclohexanone Pi-Pyridine



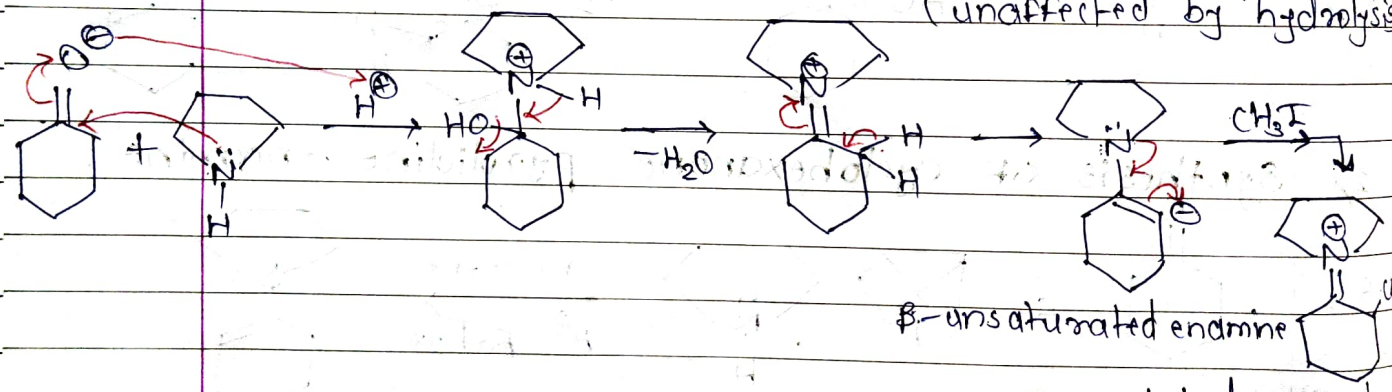
★ Reaction of Enamines

1) Alkylation of ketone. →

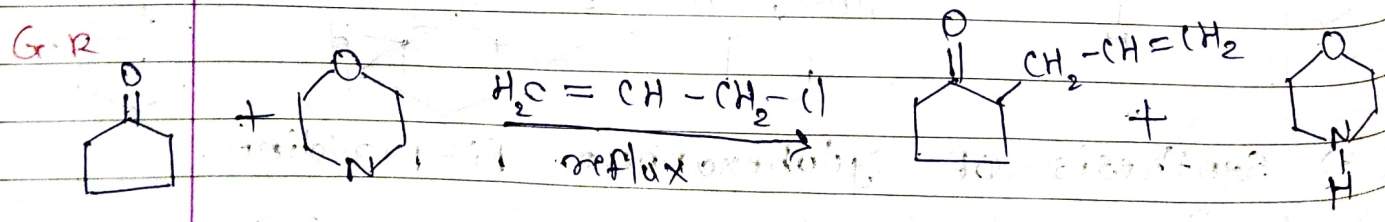
The reaction of enamine with alkyl halide initially forms C-alkylated product also form N-alkylated product.

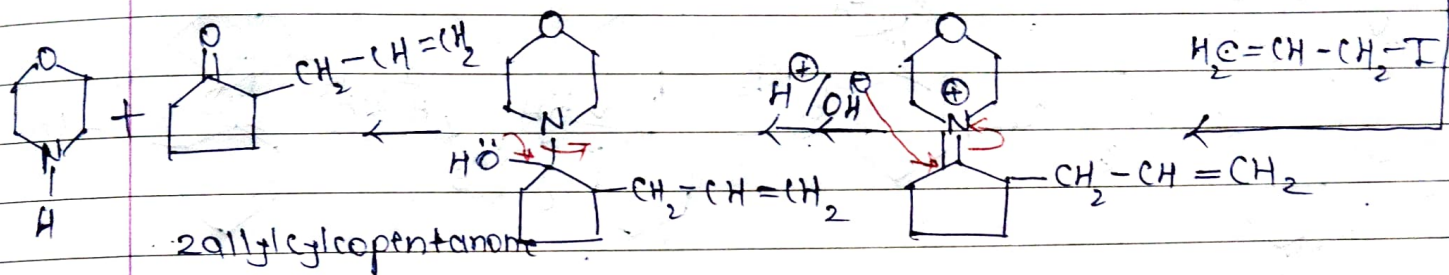
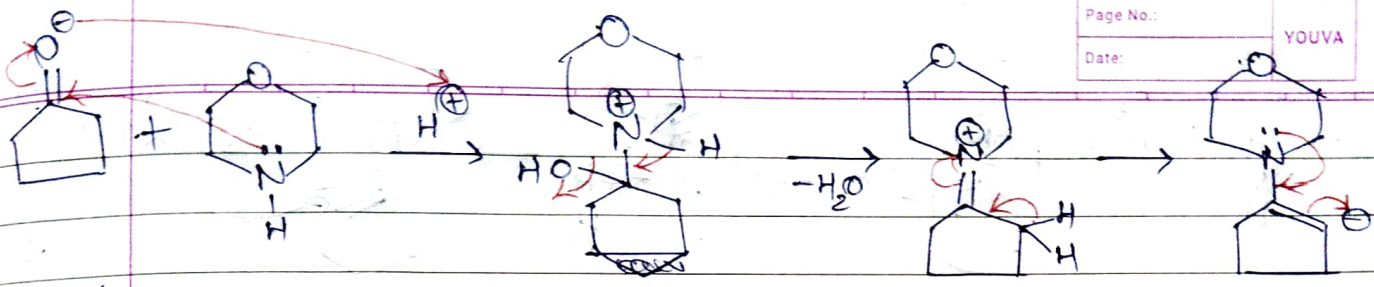


(unaffected by hydrolysis)



⇒ ii) Cyclopentanone is react with morpholine to give 2-cyclopentanone

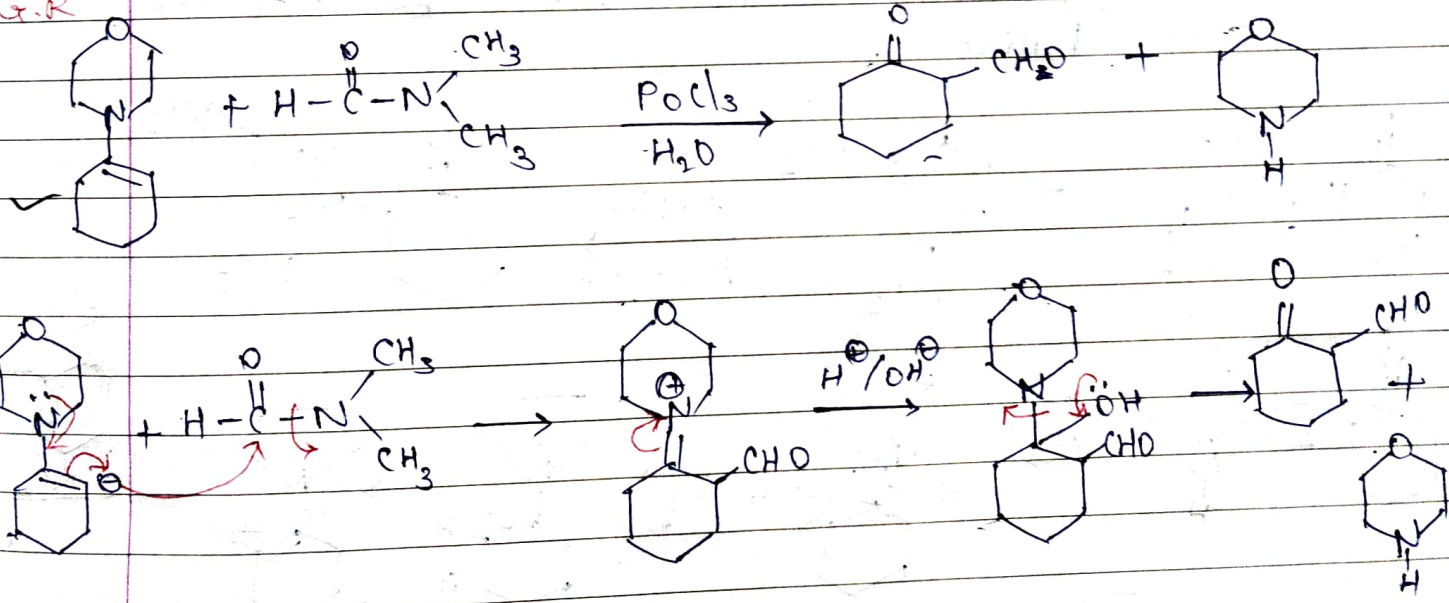




2) Formylation

Formylation can be achieved dimethyl formamide

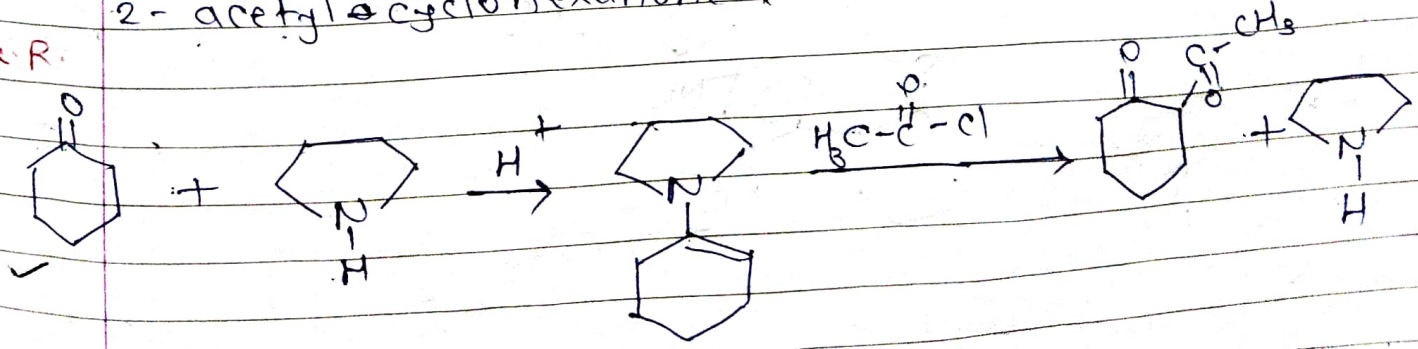
G.R.

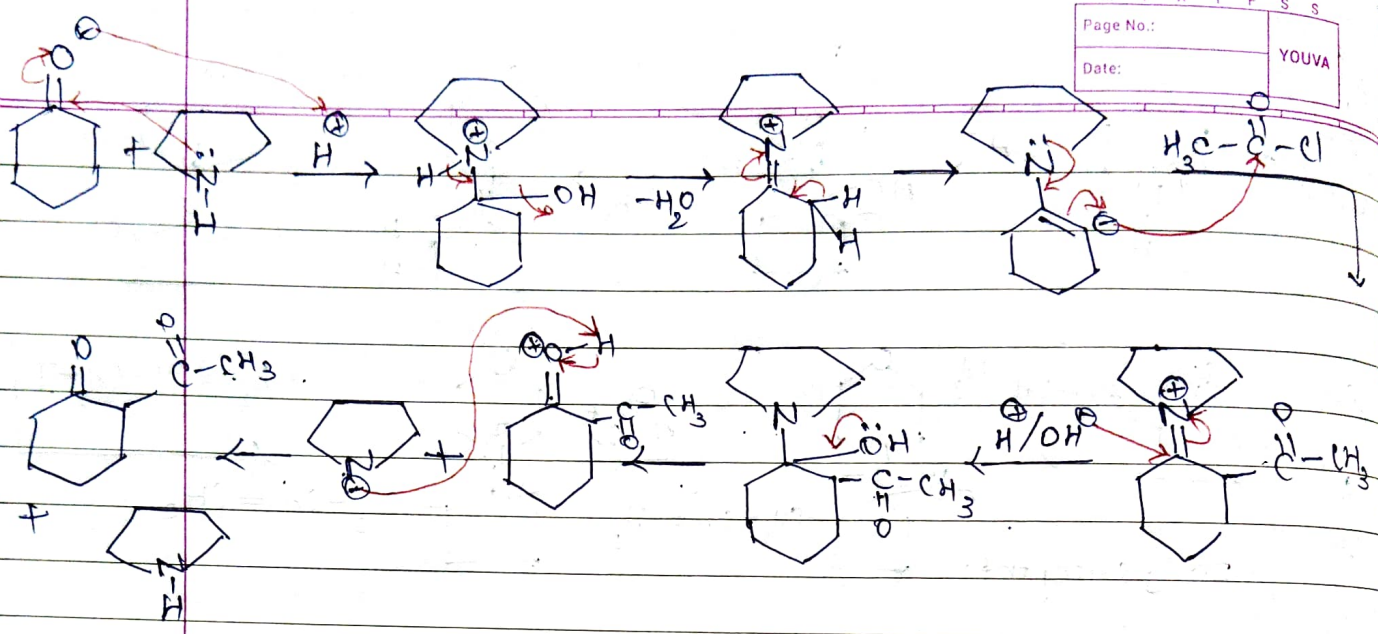


3) Acylation of ketone

This principle are used for synthesis of 2-acetylcyclohexanone.

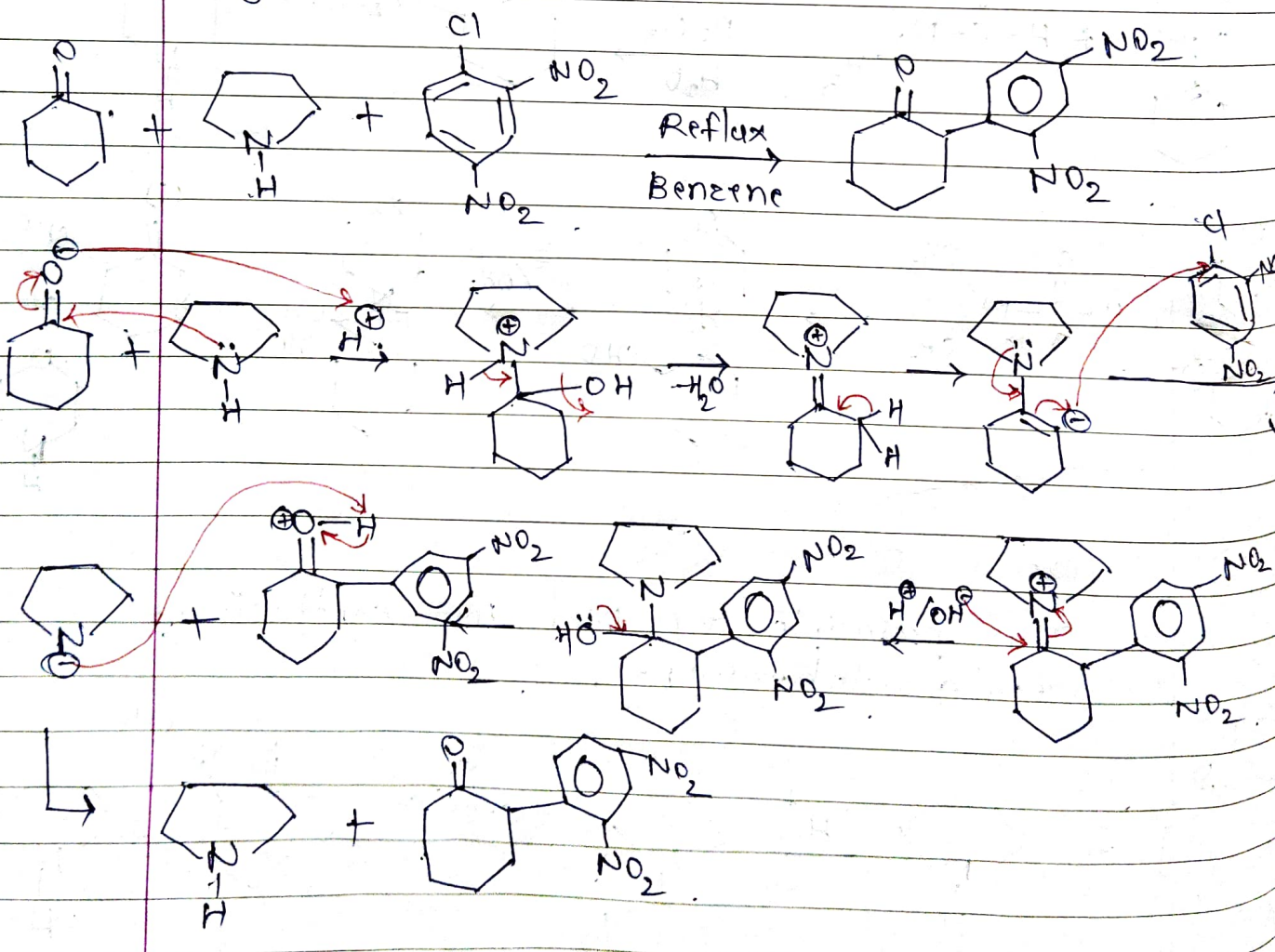
G.R.





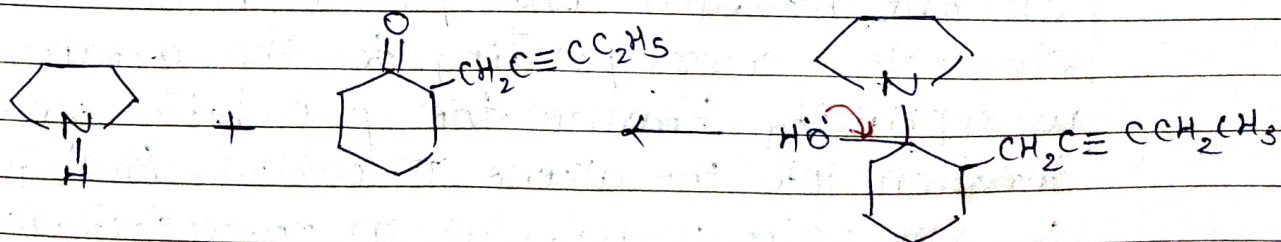
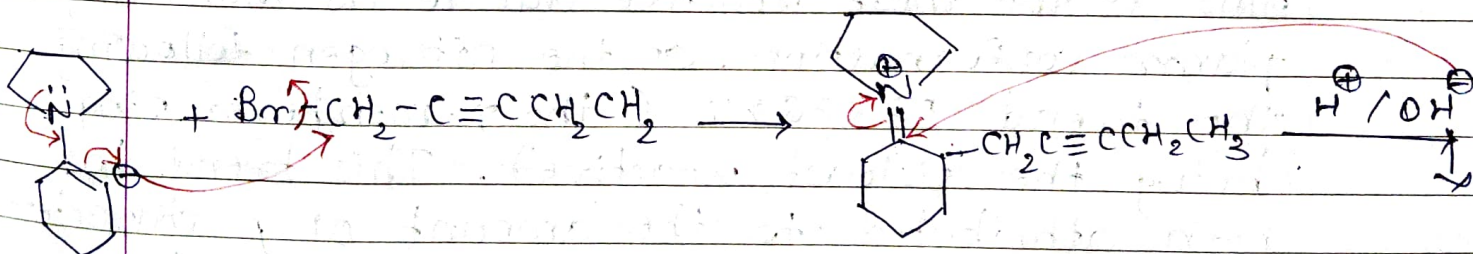
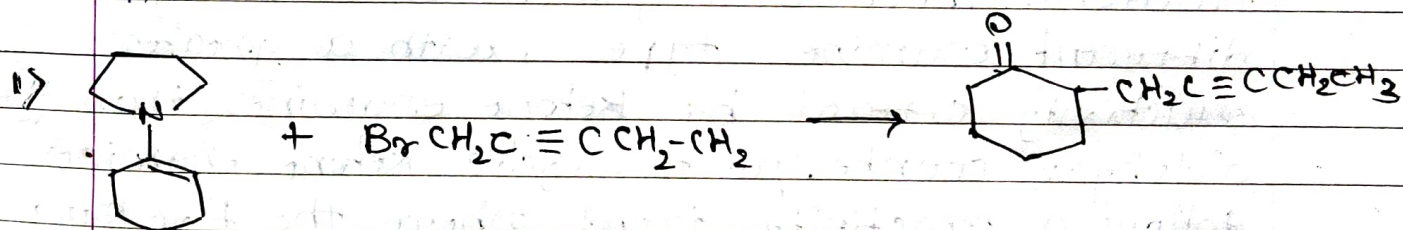
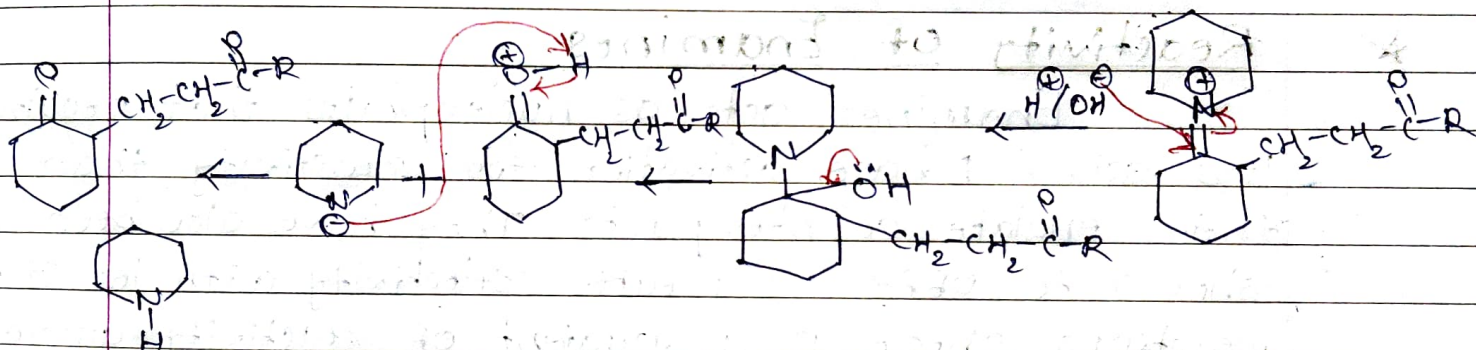
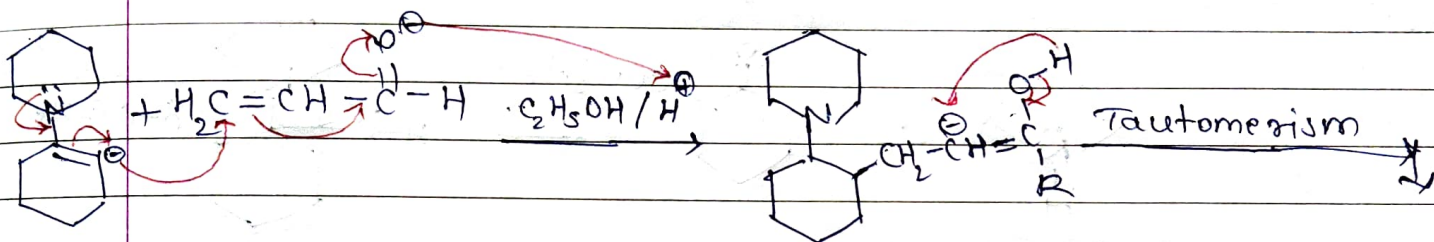
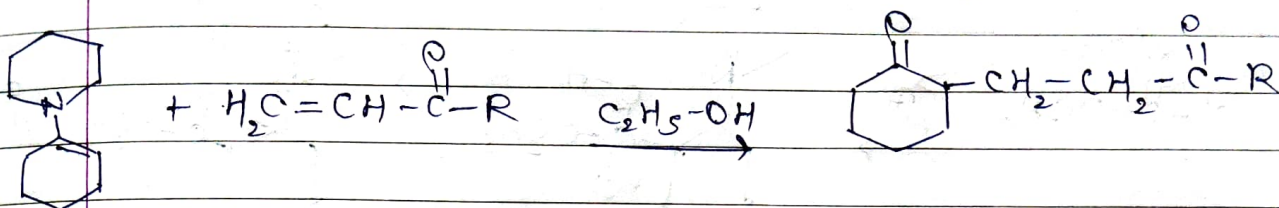
4) Alkylation of ketone

Alkylation can be achieved by activated aryl halide.

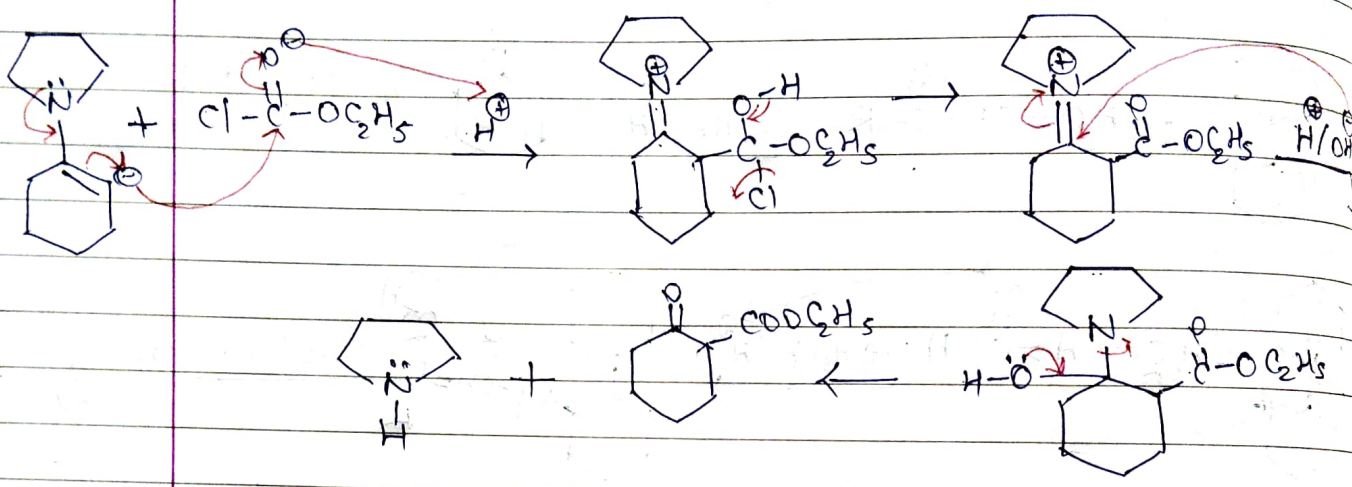
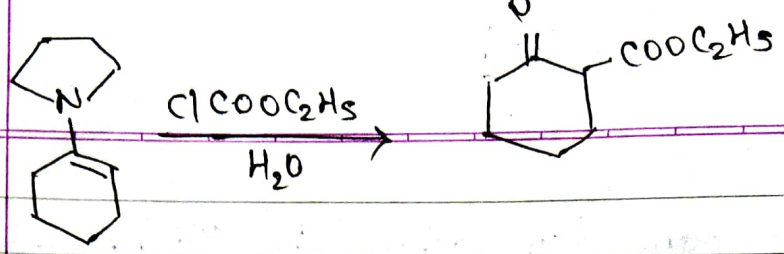


5) Michel addition

Enamines can also be achieved by Michel addⁿ.



2)



★ Reactivity of Enamines

Enamines acts as nucleophiles that requires less acid / base activation for reactivity than their enolate counterparts. They have also been shown to offer a greater selectivity with less side reactions. There is a gradient of reactivity among different enamines types, with a greater reactivity offered by ketone enamines than their aldehyde counterparts. Cyclic ketone enamines follow a reactivity trend where the five membered ring is the most reactive due to its maximally planar conformation, at the nitrogen following the trend $5 > 8 > 6 > 7$ (the 7 membered ring being the least reactive). This trend has been attributed to the amount of p-character on the nitrogen lone pair orbital - the higher p-character corresponding to the greater nucleophilicity because the p-orbital would allow for donation into the alkene π -orbital, Analogously, if the N lone pair participates in stereoelectronic interactions on the amine moiety the lone pair will pop out of the plane (will pyramidalize) & compromise the donation into the adjacent π C-C bond.