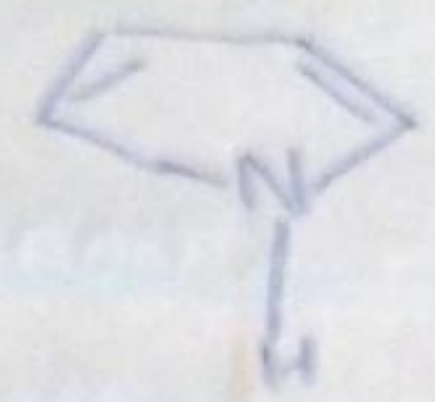
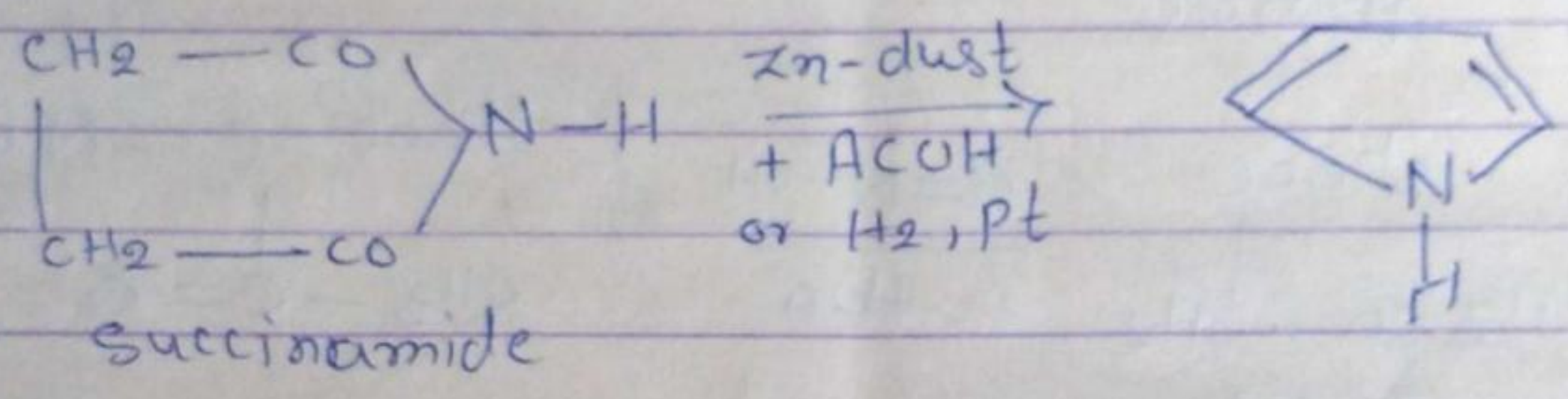
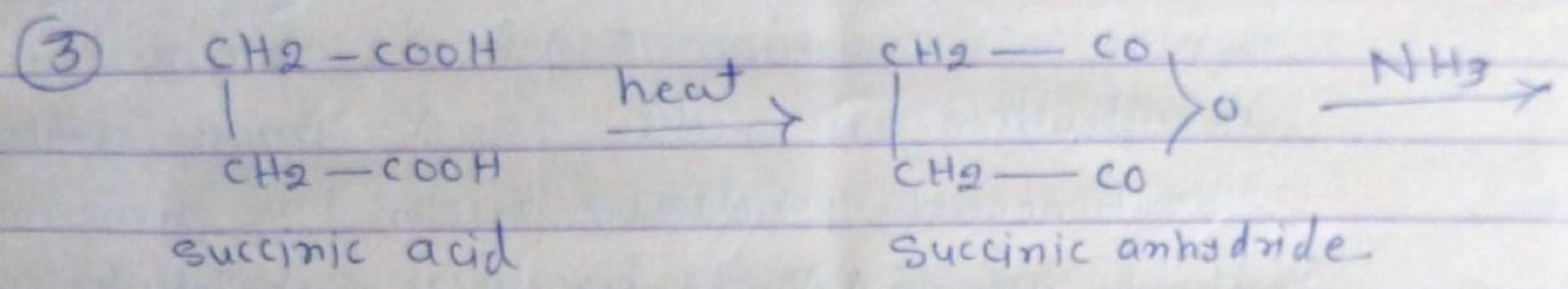
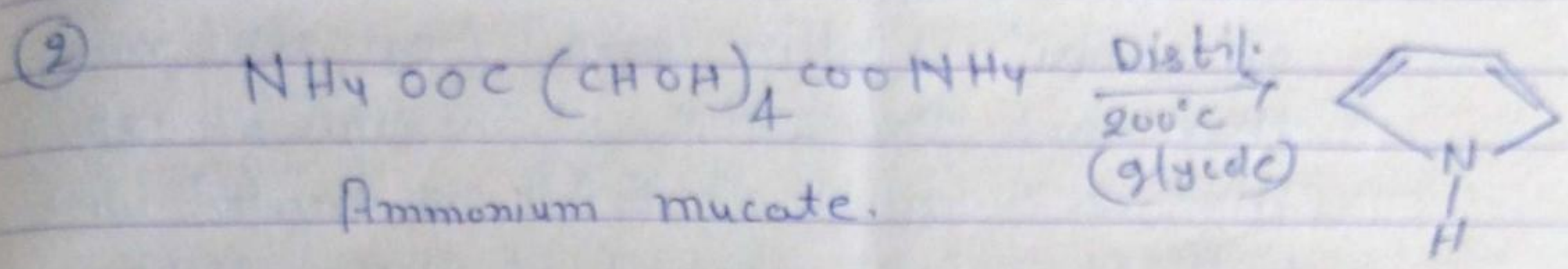
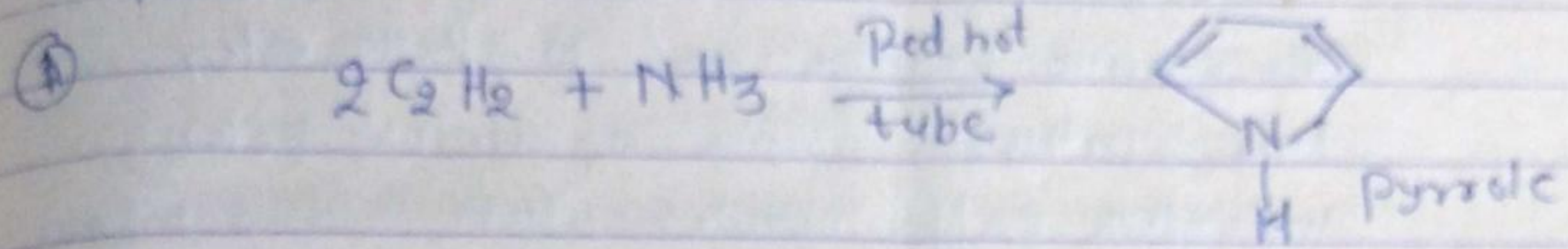


Unit V

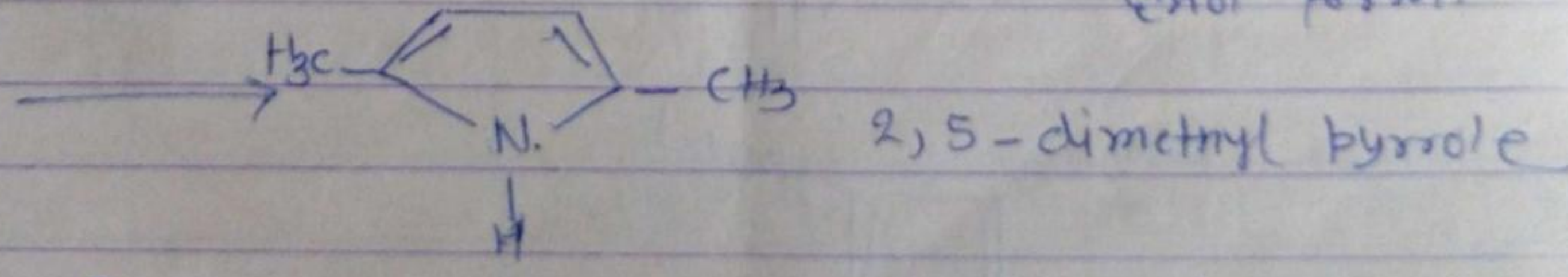
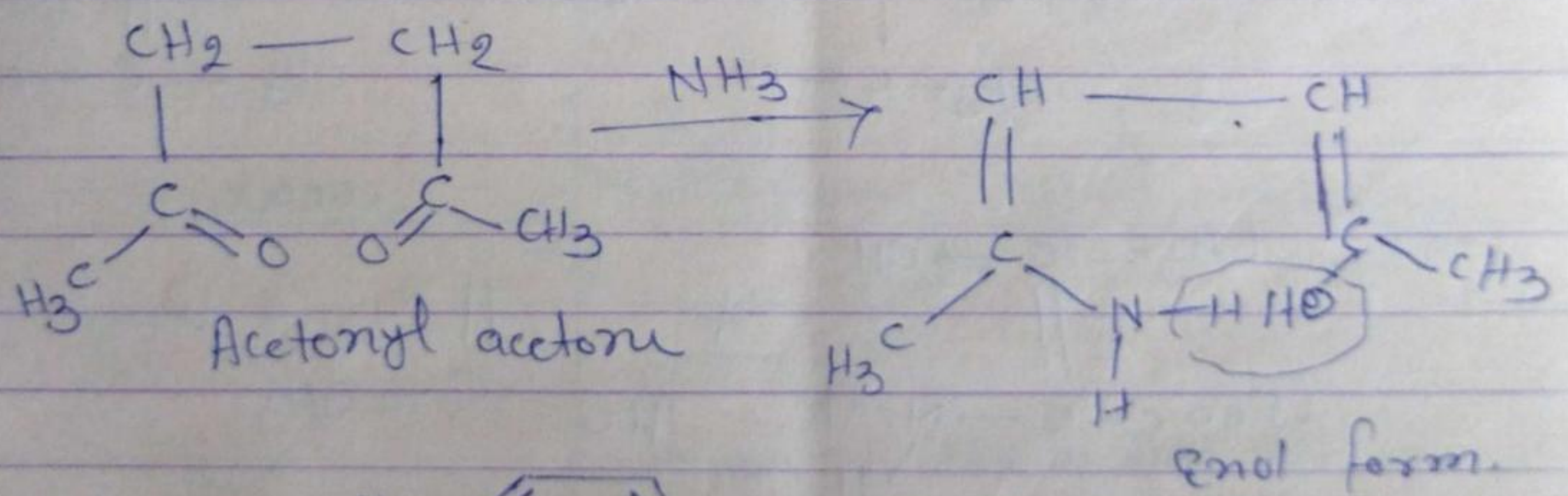
Pyrrrole



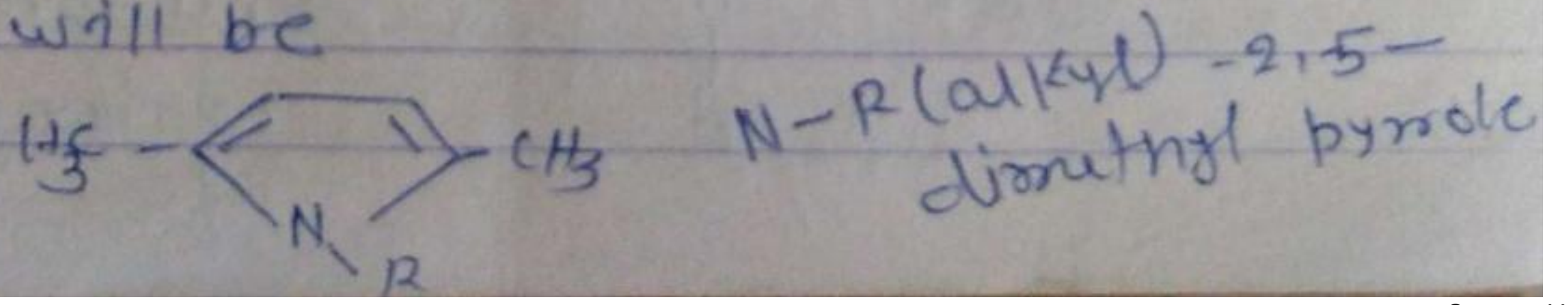
Preparation :->



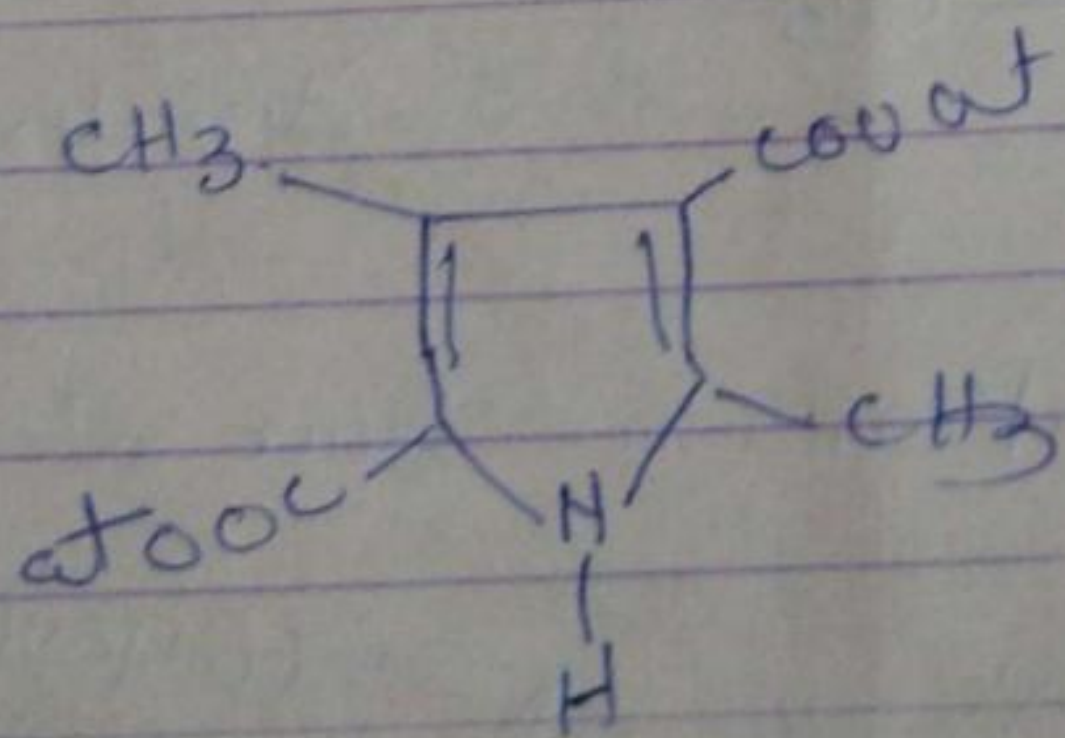
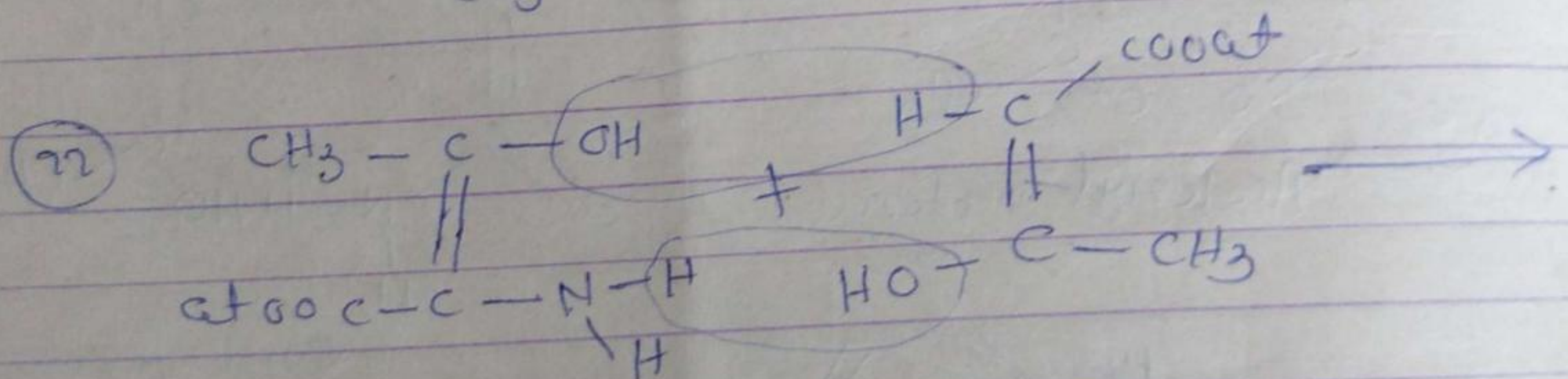
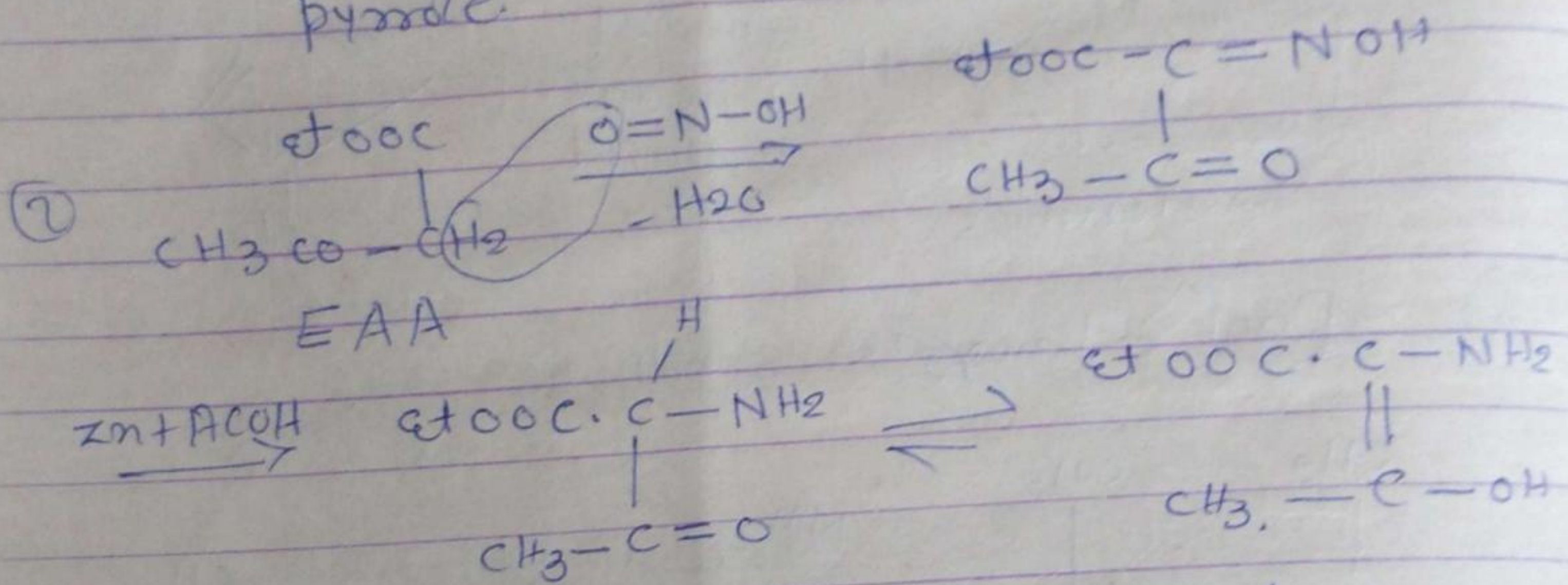
④ Paaf - Knorr's synthesis :->



if R-NH<sub>2</sub> is taken in place of NH<sub>3</sub>, product will be



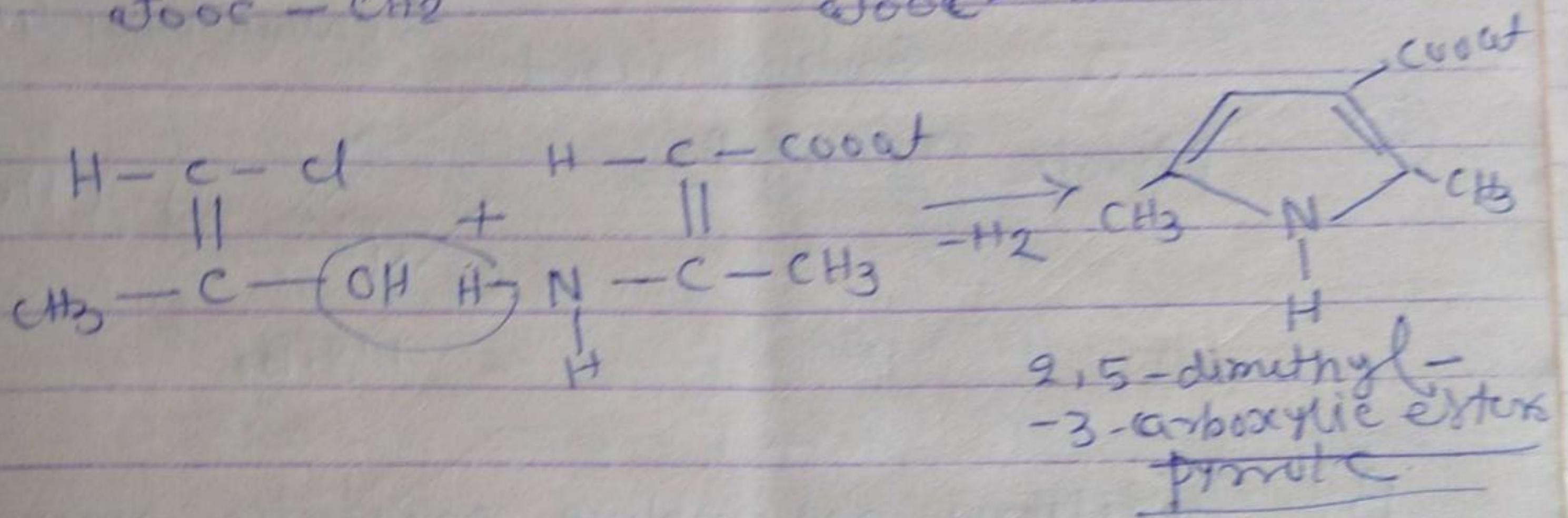
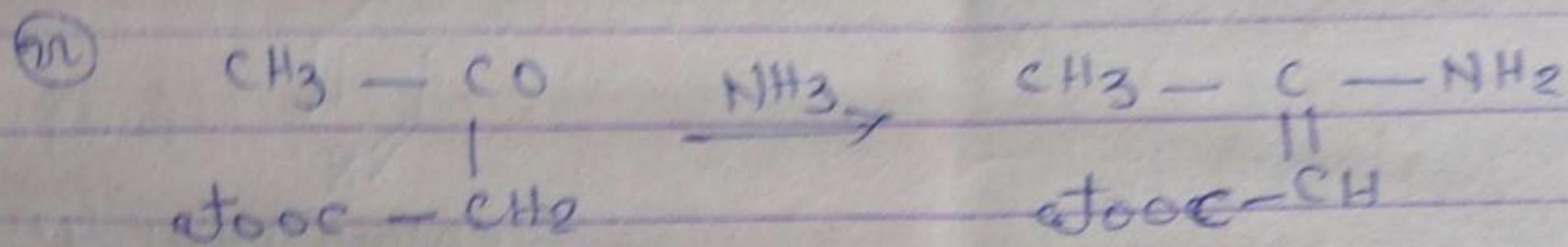
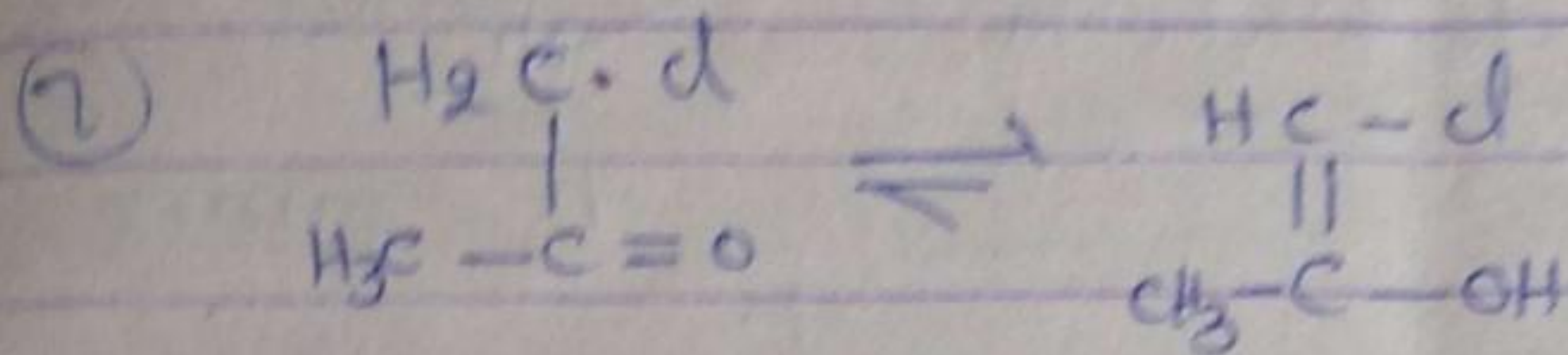
⑤ Knorr's Synthesis  $\rightarrow$   
 condensation has been affected between  $\alpha$ -amino ketone and  $\beta$ -keto ester in this synthesis. Since  $\alpha$ -amino ketone undergoes self condensation it is prepared "in situ" (Latin word) (on site means then and there i.e. at the time of exp.) Thus a quantity of EAA is treated with half equivalent amount of  $\text{HNO}_2$  -  $\text{HNO}_2$  when  $\alpha$ -oximino EAA is obtained. The latter on red<sup>n</sup> to  $\alpha$ -amino compound spontaneously condenses with the remaining half of EAA to produce substituted pyrrrole.



2,4-dimethyl-3,4-dicarboxyl ester pyrrrole

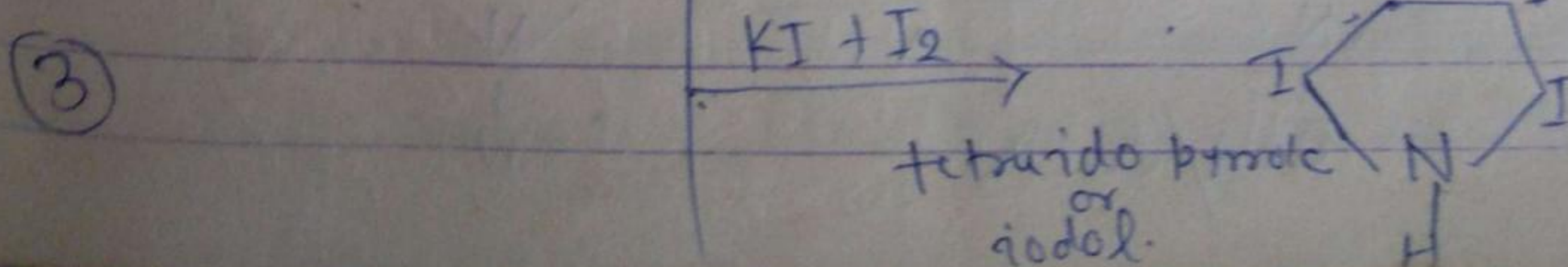
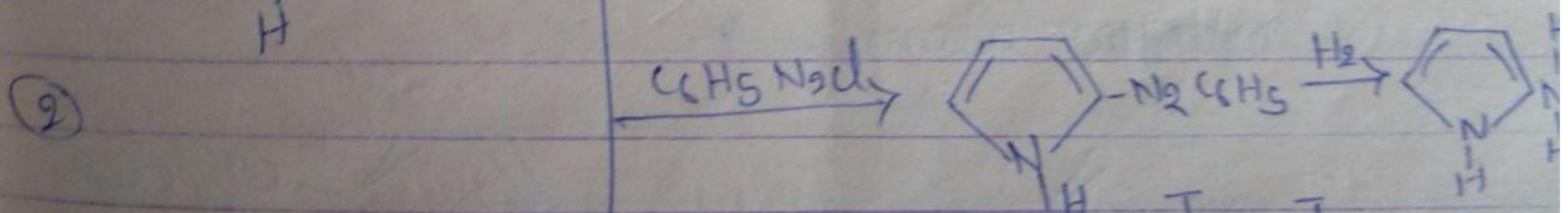
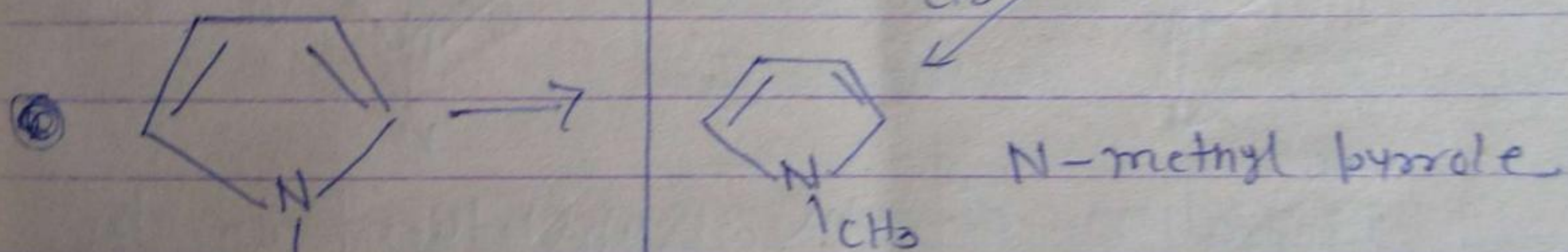
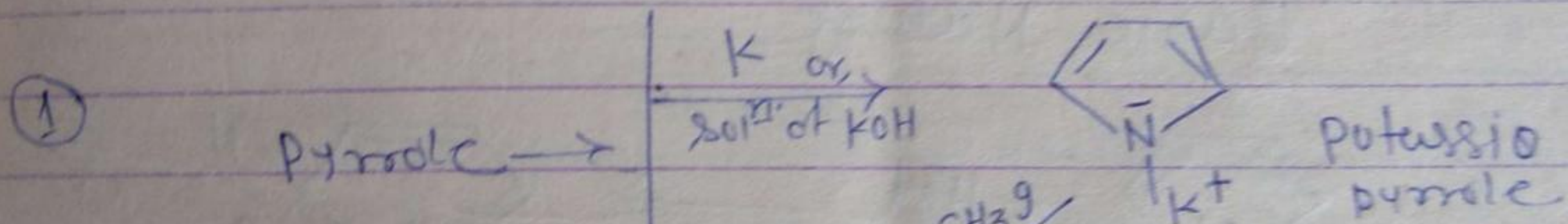
① Hantzsch's Synthesis :->

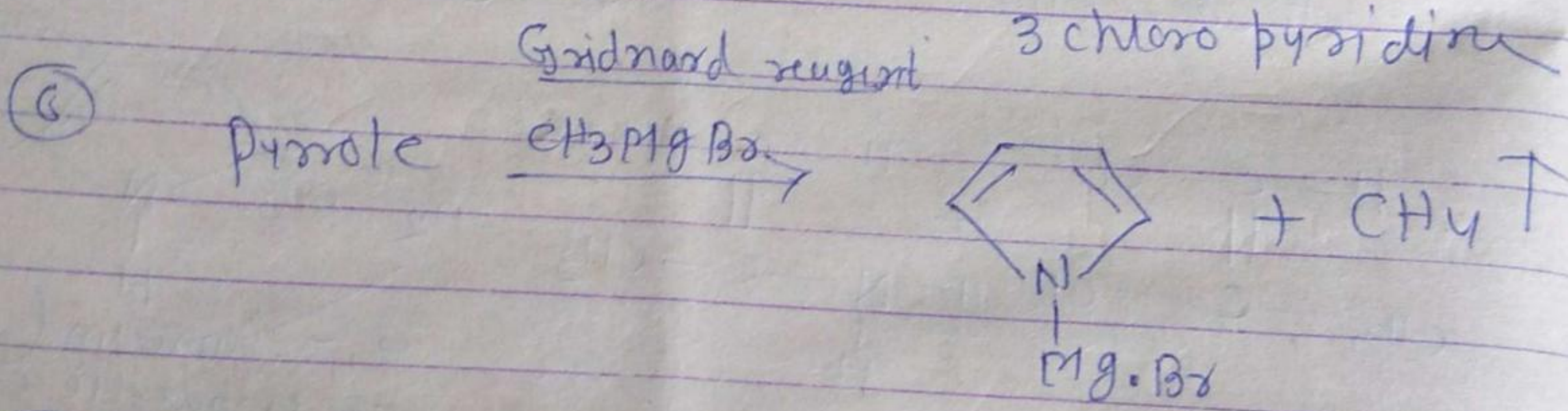
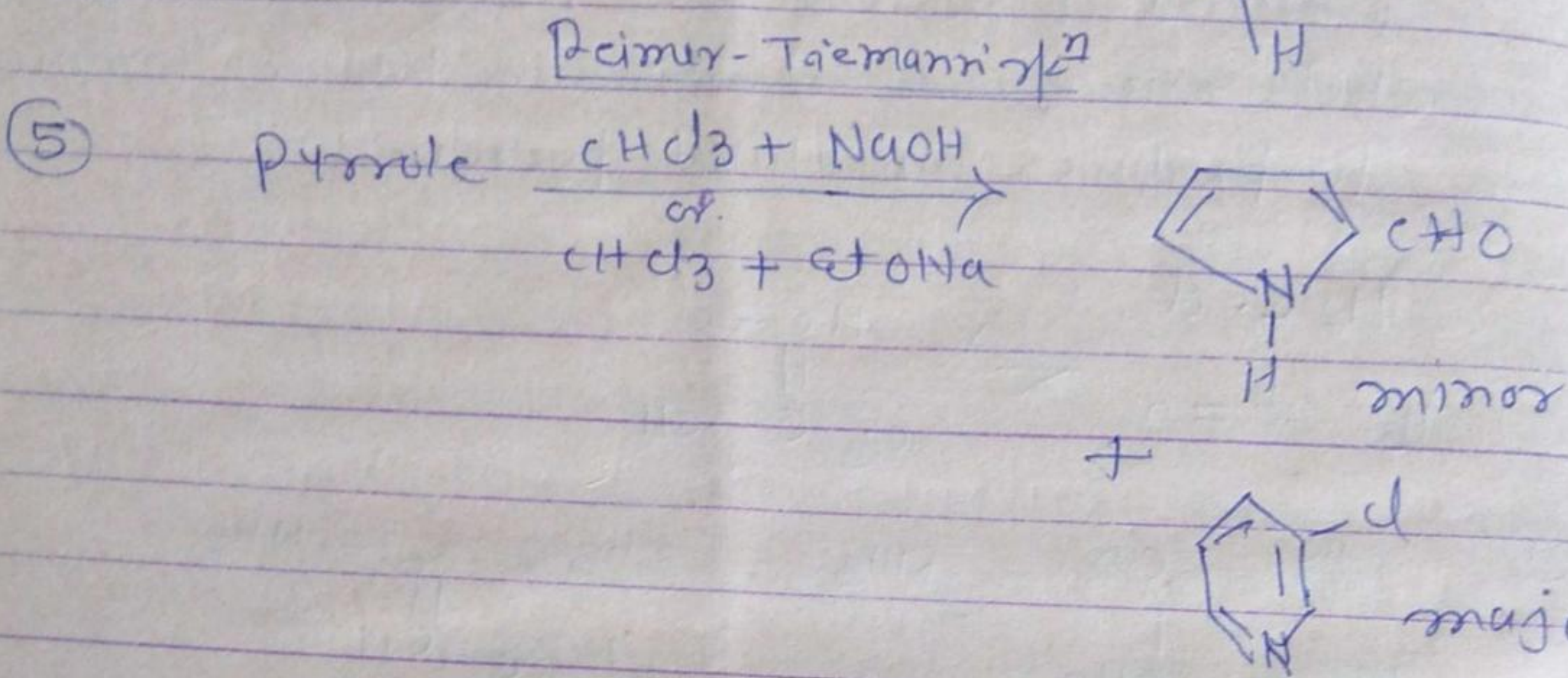
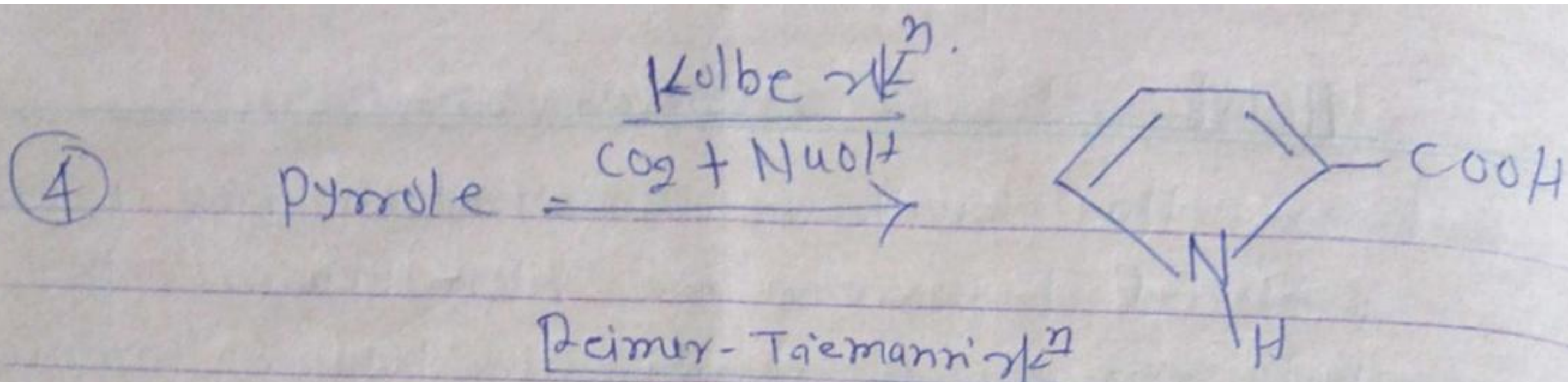
In this synthesis condensation has been effected between  $\alpha$ -chloro ketone,  $\beta$ -keto ester and ammonia or primary amine to produce substituted pyrrole.



Properties :->

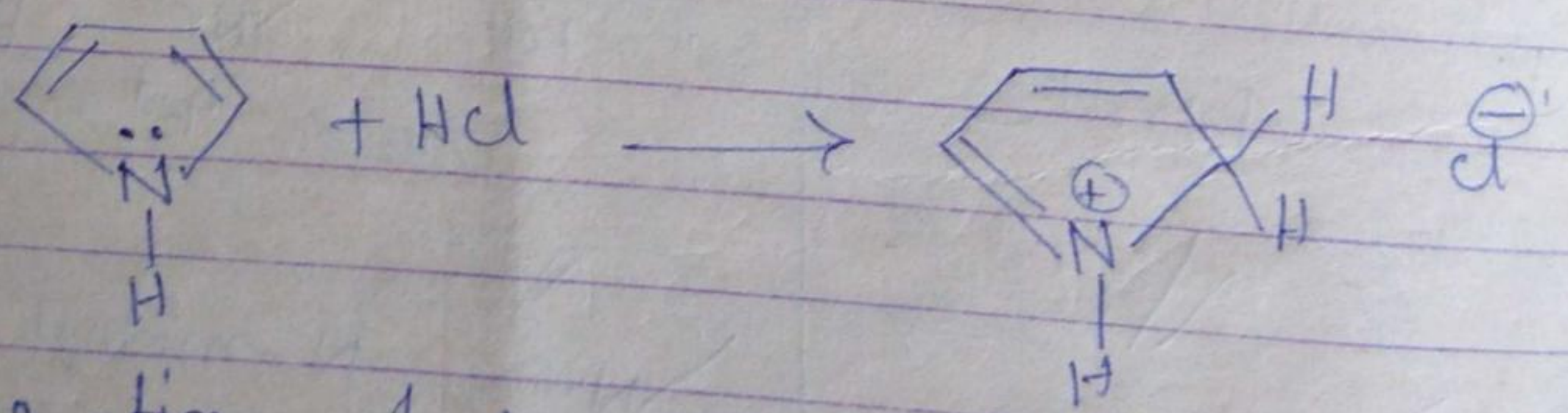
① Properties resembling Phosphorus :->



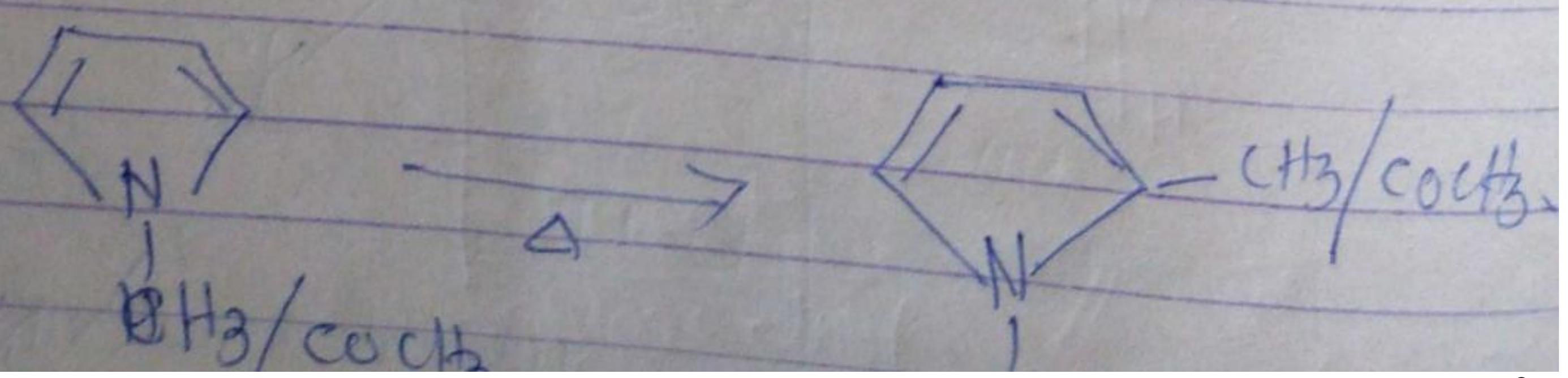


B) Reactions resembling aromatic amines →  
 Reactions ①, ②, ③ & ⑥ given above are same for aromatic amines

Basic Nature →

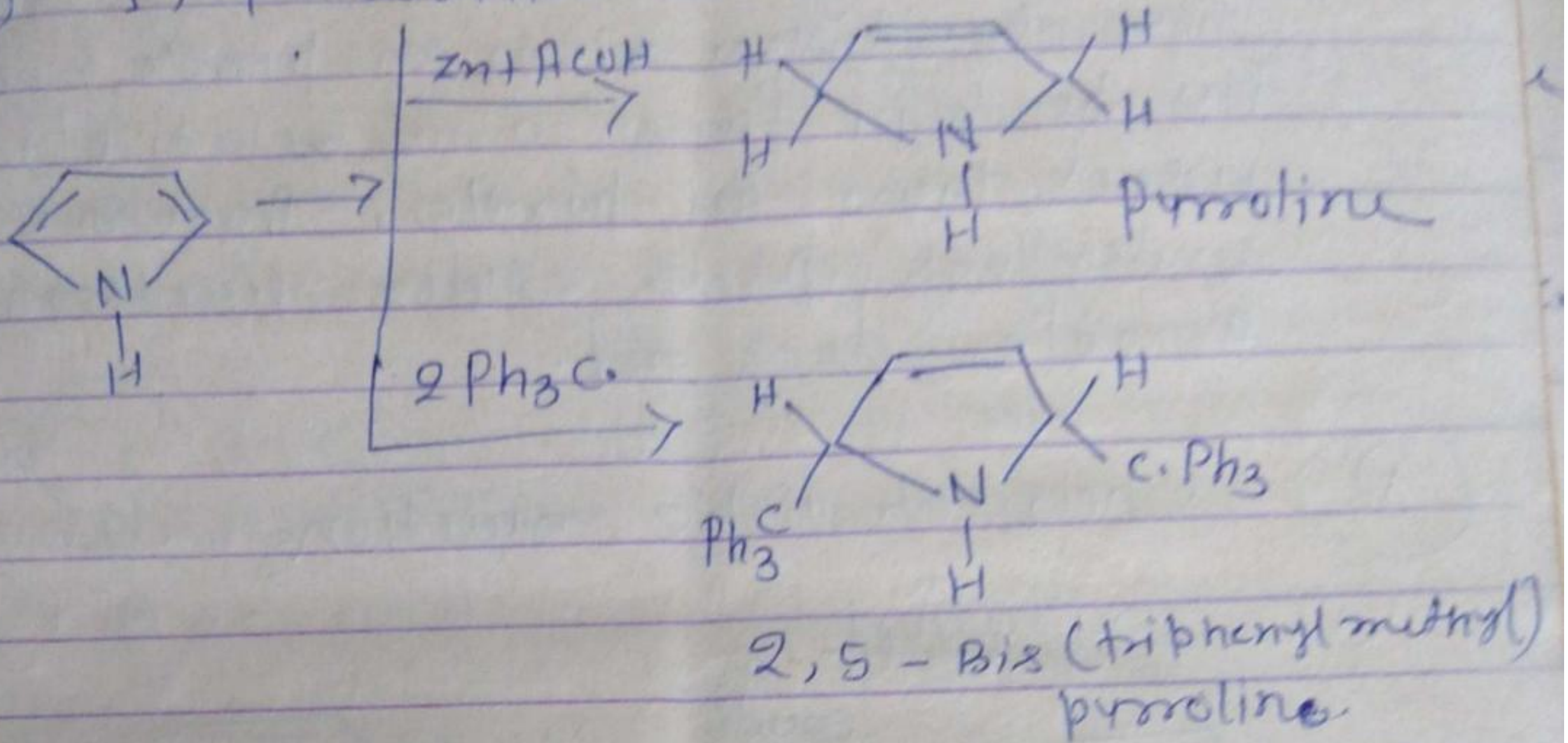


Migration of the substituent on the nitrogen atom. →

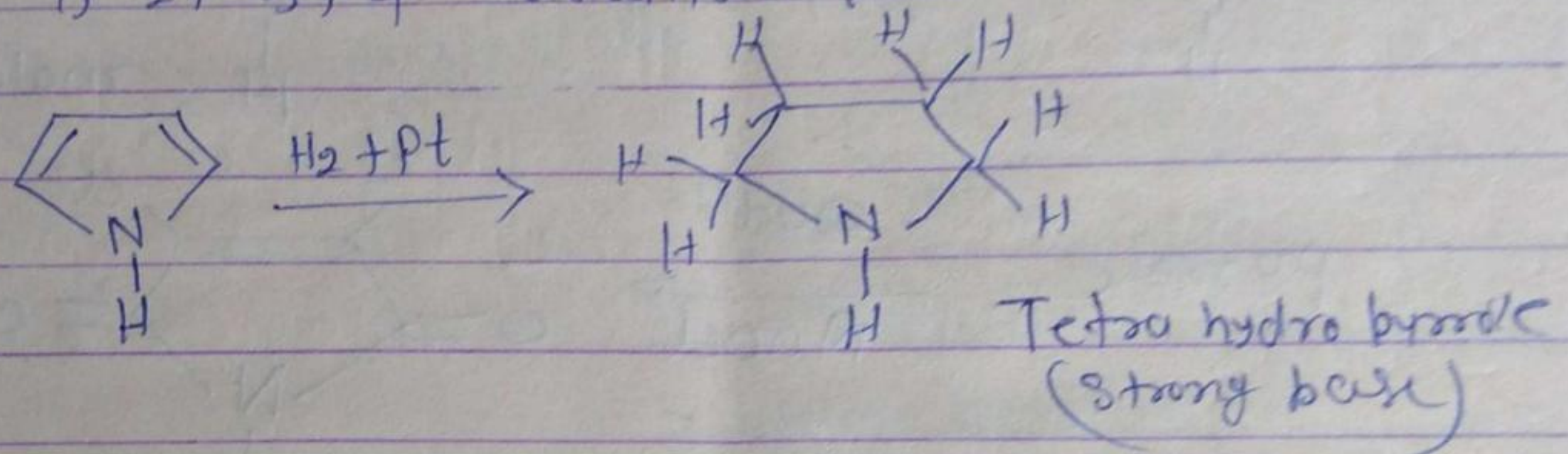


(c) Reactions resembling Diene  $\rightarrow$

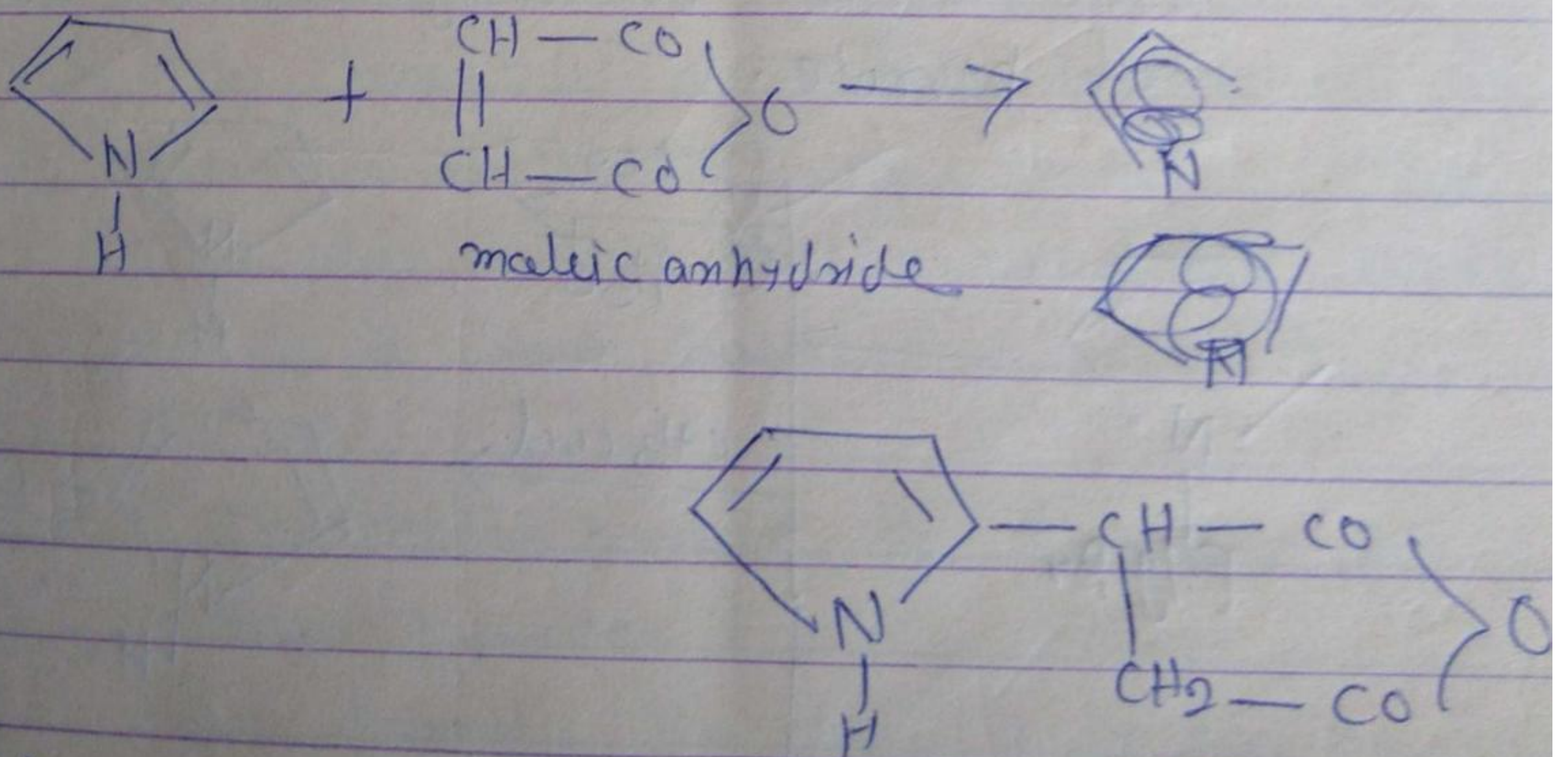
(a) 1, 4 - addition.



(b) 1, 2, 3, 4 addition  $\rightarrow$



With maleic anhydride it does not undergo Diels - Alder reaction. It forms 2-pyrrole succinic anhydride.

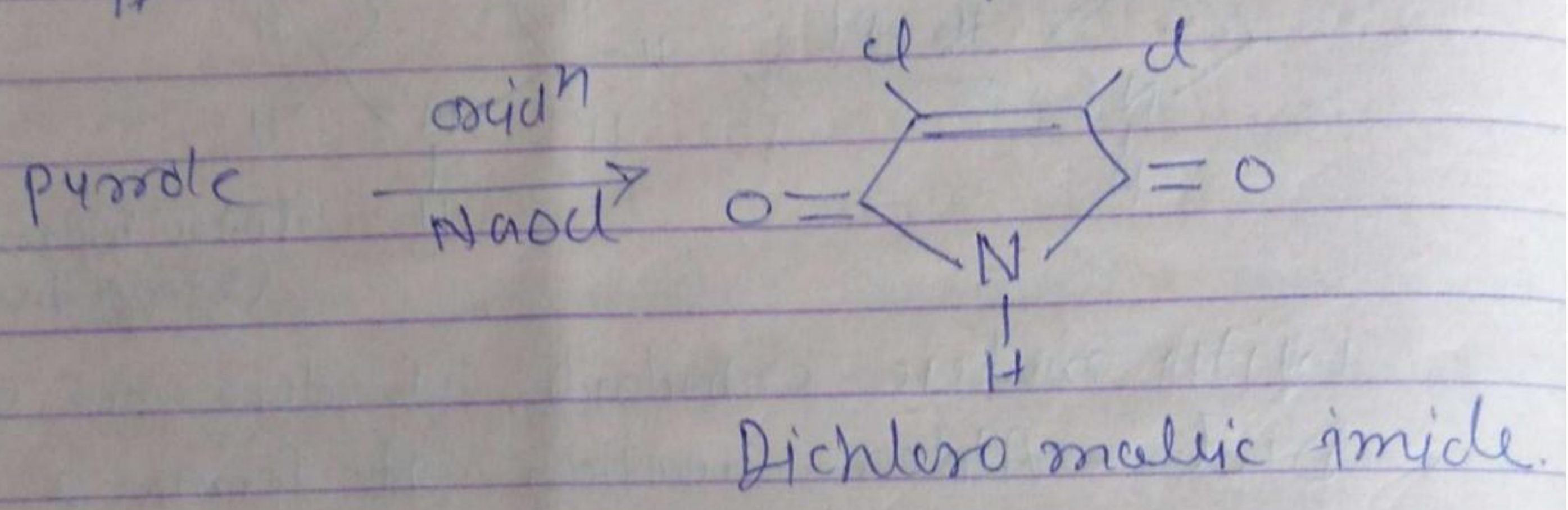
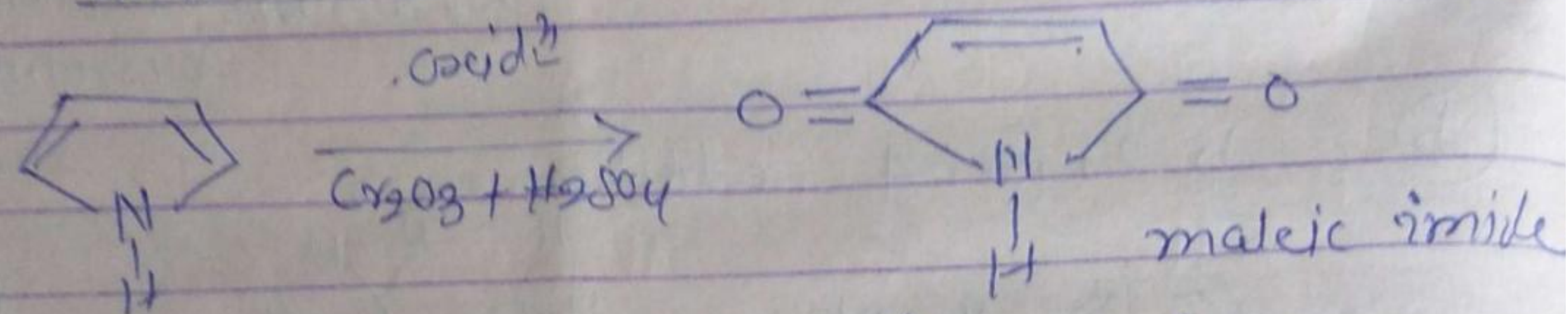


Since oxygen atom is more electronegative than nitrogen, the lone pair of the oxygen

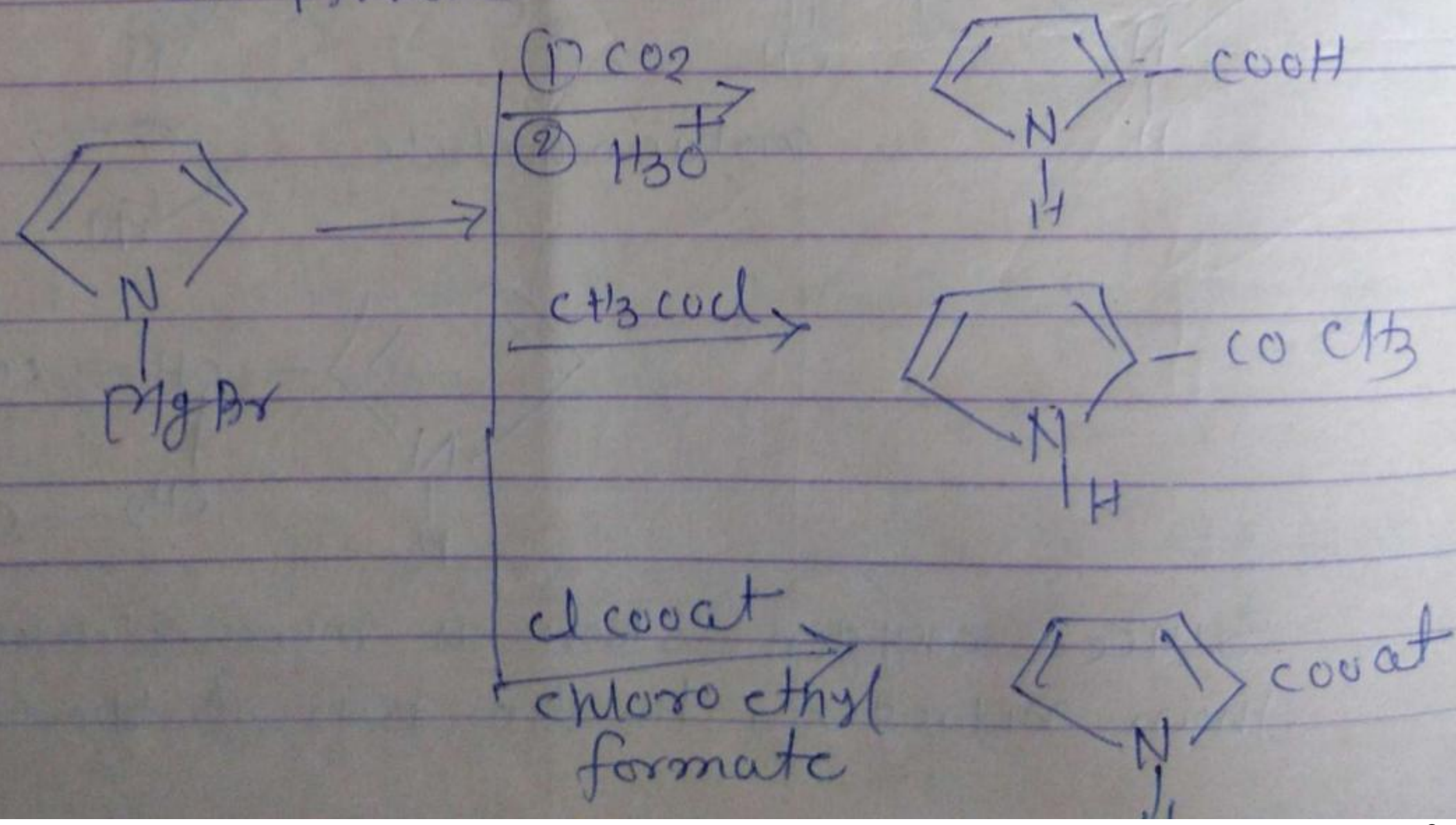
atom in furan is less available to the ring for delocalization than those of nitrogen atom in pyrrole, hence the bonds in furan are relatively more fixed than in pyrrole. Therefore furan undergoes Diels-Alder reaction while pyrrole does not.

(D) Characteristic reactions. ———

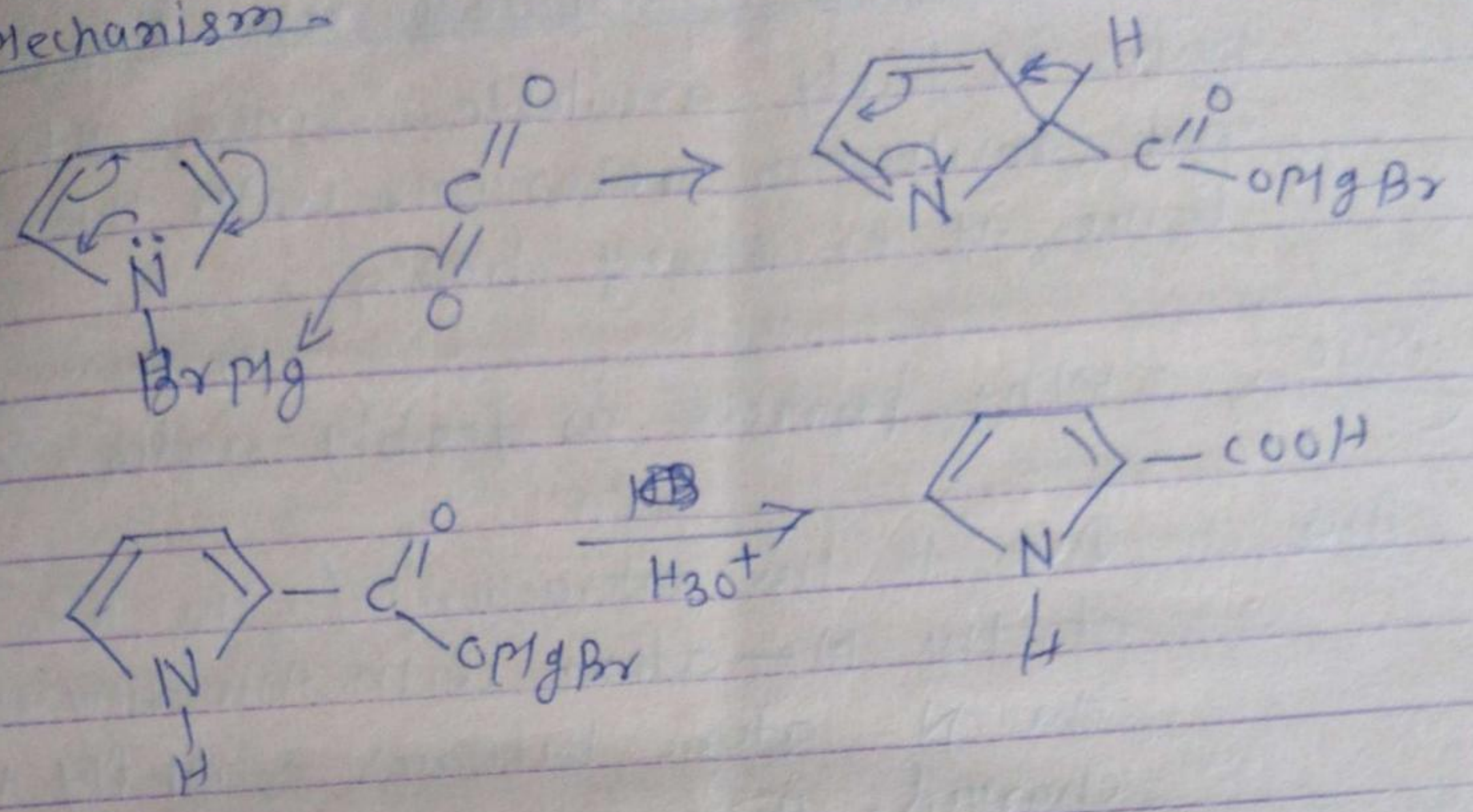
(a) Oxidation



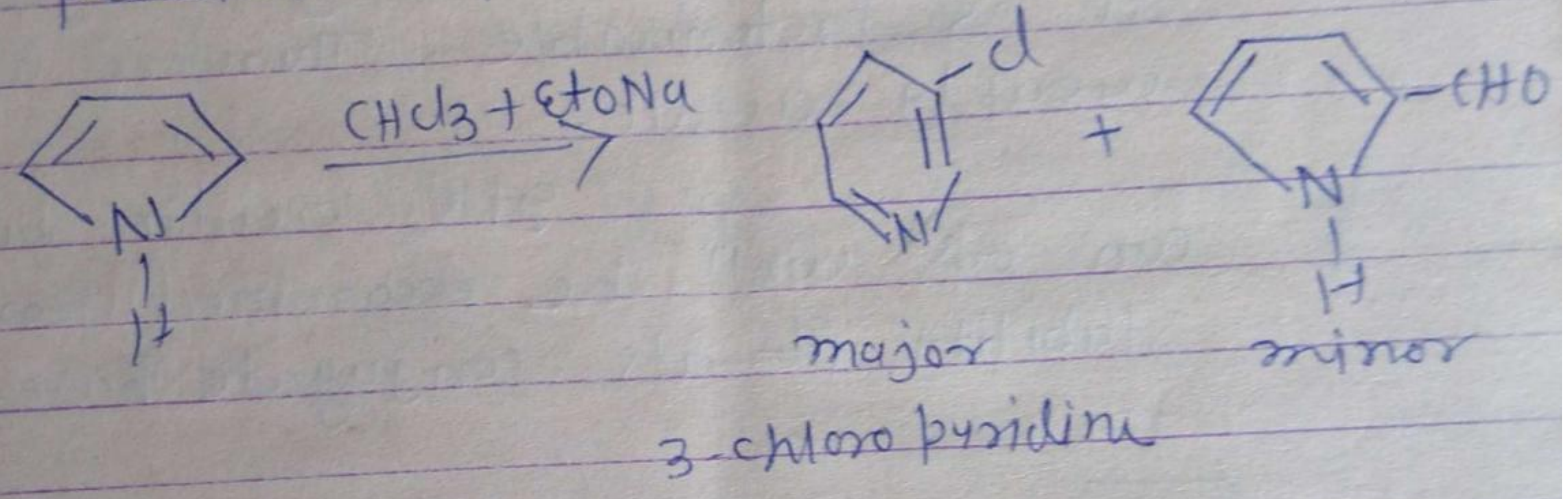
(b) Reaction of N-magnesium bromide of pyrrole.



Mechanism



(3) Reaction expansion  $\rightarrow$



Que  $\Rightarrow$  Why is pyrrole weakly basic?

Ans.  $\Rightarrow$  The lone pair in pyrrole is involved in resonance with the ring, therefore, the lone pair is not freely available hence it is a weak base.

Que  $\Rightarrow$  Tetrahydro pyrrole is stronger base than pyrrole?

Ans. In pyrrole the lone pair on the N-atom is involved in resonance with the ring. Hence it is a weak base.

in tetrahydropyrrole the lone pair is freely available, since, it is not involved in resonance with the ring. Hence it is strong base.

Que. Why pyrrole is feebly acidic?

Ans. Due to the interaction of the lone pair of the N-atom with the ring electrons, the N-atom becomes slightly freely charged. Hence, the H-atom attached to it is slightly freely charged, i.e. it is protonisable. Therefore it is weakly acidic.

Its acidic behaviour can as well be examined from the stability of its conjugate base.

