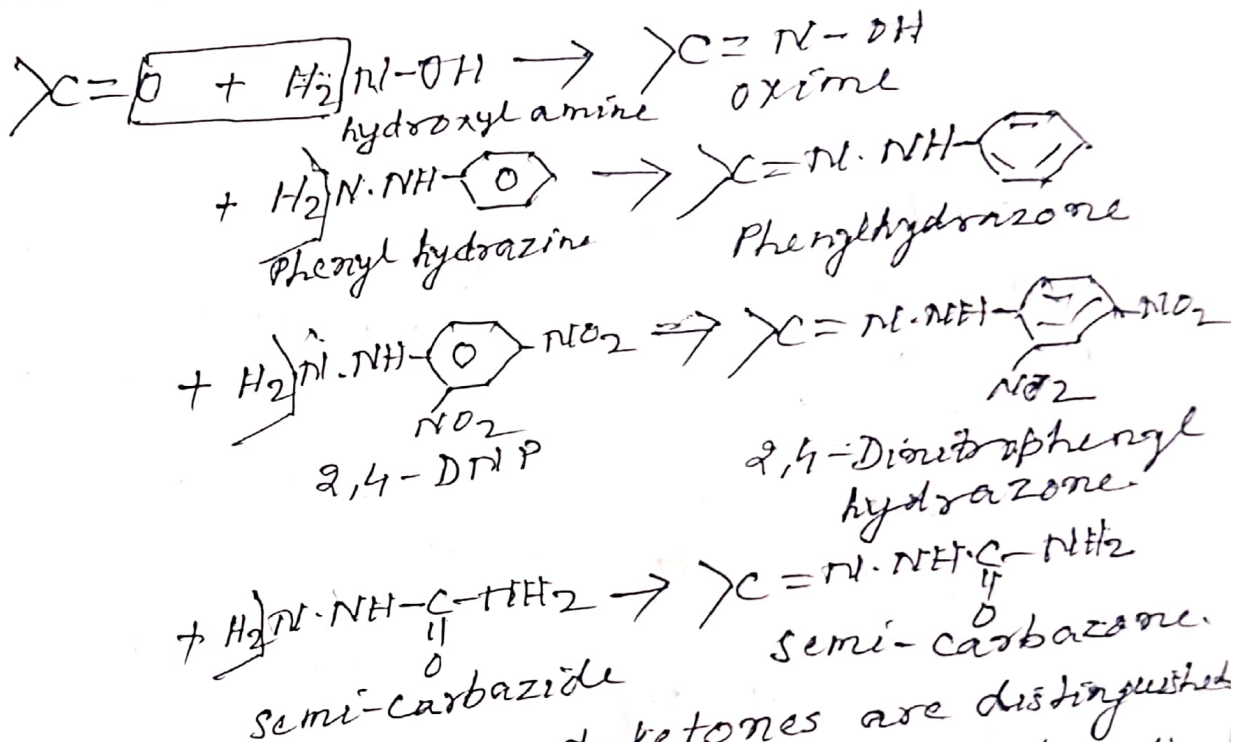


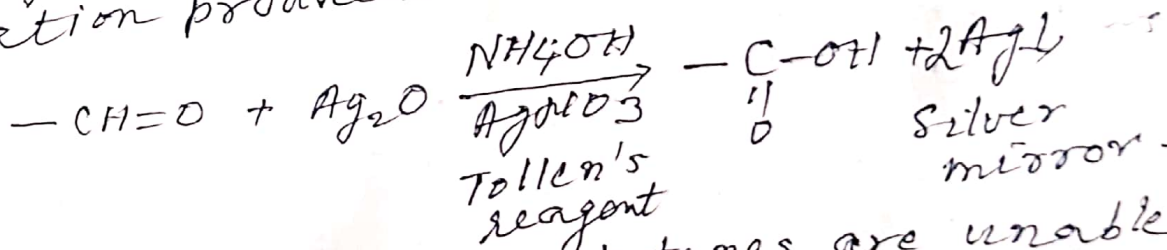
ALKALOIDS (continued)

ⓑ Oxo group ($C=O$ group)

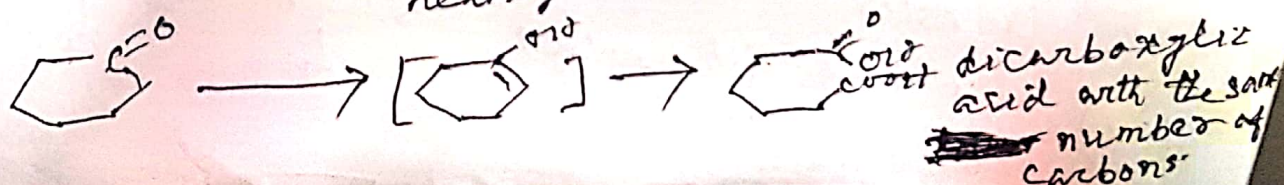
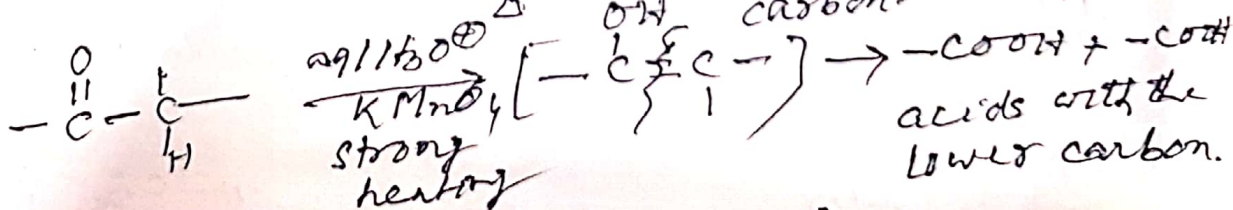
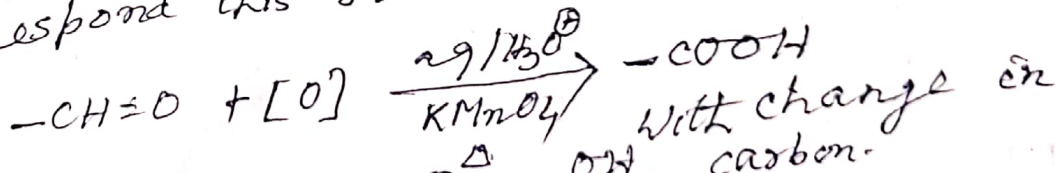
The presence of oxo group i.e. aldehydic or the ketonic group is detected with the help of phenyl hydrazine, 2,4-DNP, hydroxyl amine and semi-carbazide.



Finally the aldehydes and ketones are distinguished by using Tollen's test, Fehling's test and by the oxidation products.

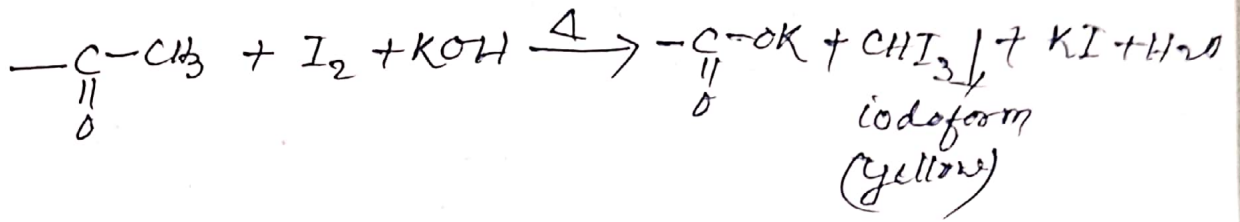


except α -hydroxy ketone, ketones are unable to respond this silver mirror test.

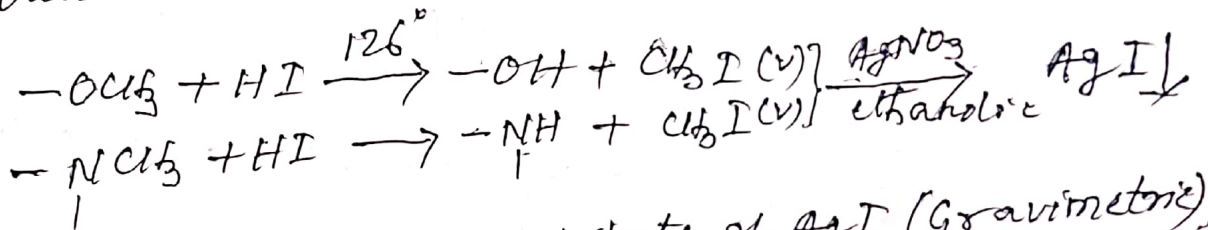


(C) Methylketones ($-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ unit)

This group is tested by the iodoform test.



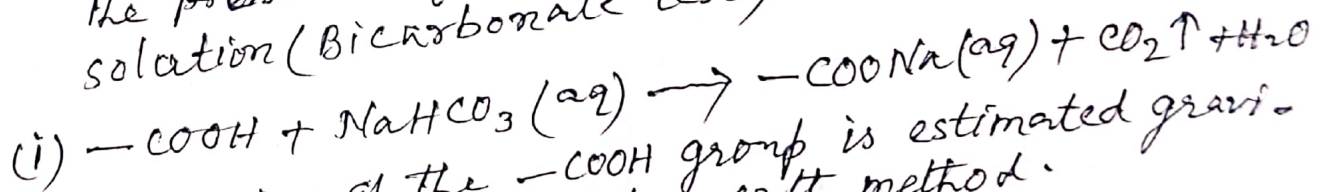
(D) Methoxy group ($-\text{OCH}_3$ group) or N-methyl group. In the Zeisel test (for the $-\text{OCH}_3$ group) and in the Herzog-Meyer test (for the $-\text{NCH}_3$ group), the compound is HI at its boiling point (126°C).



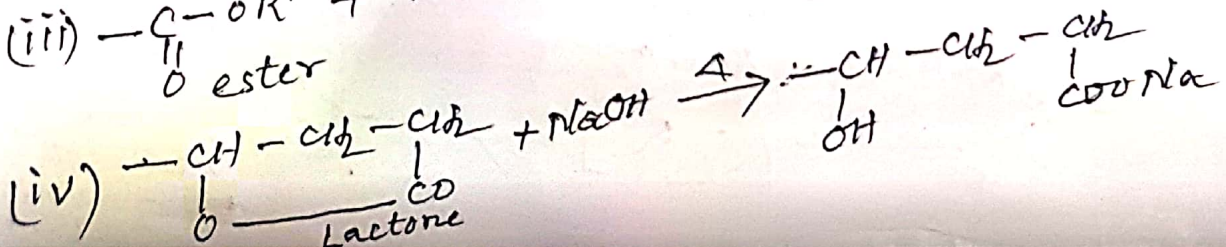
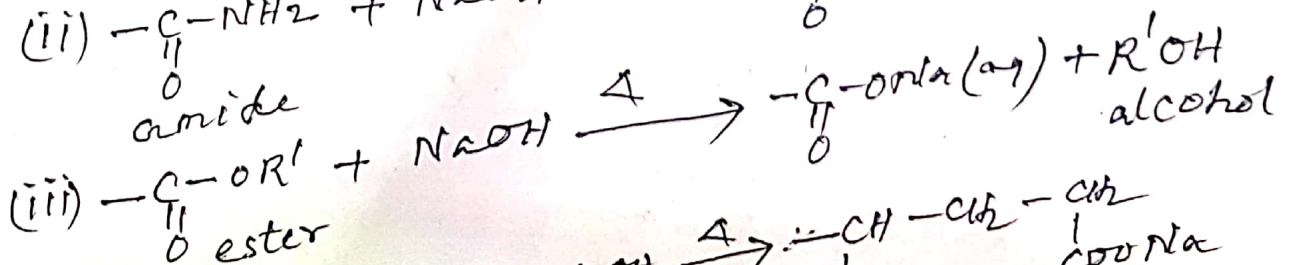
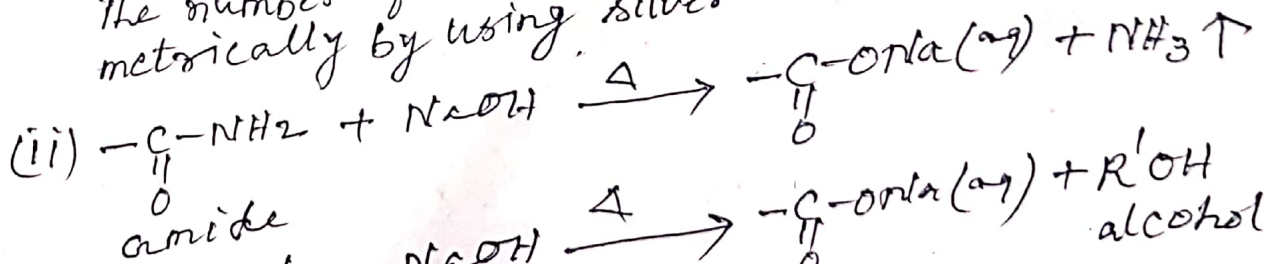
By using the dry precipitate of AgI (Gravimetric), the of $-\text{OCH}_3$ or $-\text{NCH}_3$ group is estimated.

(E) Carboxylic, amide, ester, lactone and lactam groups.

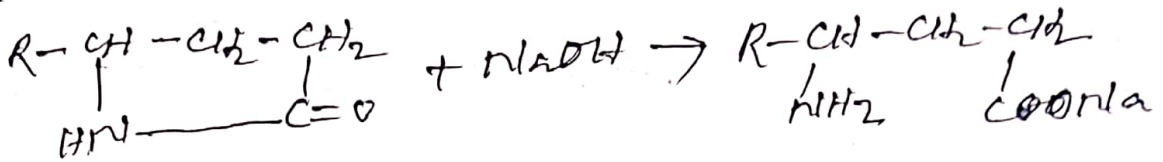
The presence of $-\text{COOH}$ is tested with the NaHCO_3 solution (Bicarbonate test)



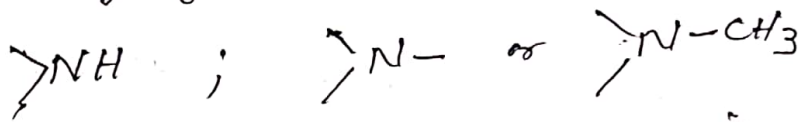
The number of the $-\text{COOH}$ group is estimated gravimetrically by using silver salt method.



(V) Lactam

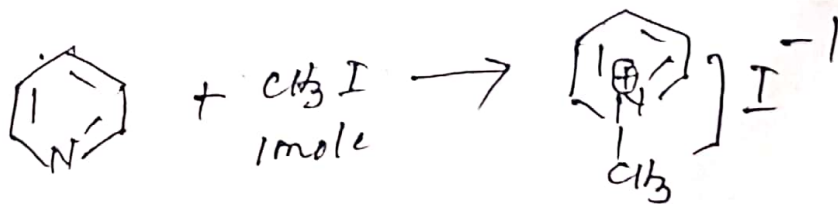
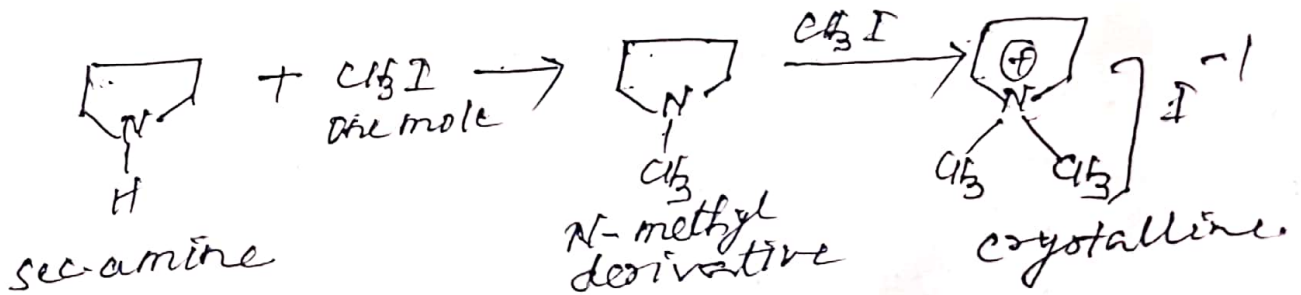


If nitrogen is present in the alkaloid (which is most common) in its heterocyclic ring, the following forms are possible:-

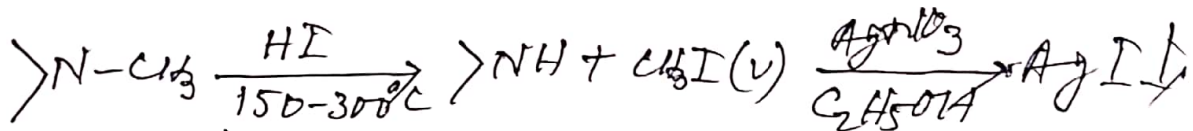


In some cases, the nitrogen is ~~not~~ the part of the heterocyclic ring and in that situation, the test for the primary amino group is performed.

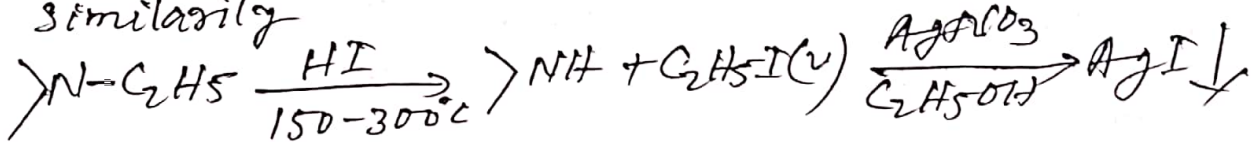
The nature of nitrogen is carefully observed by using methyl iodide (CH_3I). If the compound absorbs ~~two~~ moles of CH_3I to form quaternary ammonium salt (crystalline), it is secondary.



The presence of >N-CH_3 is detected by using Herzig-Meyer's method. In this method, the alkaloid is heated with hydroiodic acid at $150-300^\circ C$ and the vapours of CH_3I is passed into alcoholic $AgNO_3$ solution. By using the precipitate of AgI (Gravimetric) the amount of CH_3I and then the number of group is estimated.



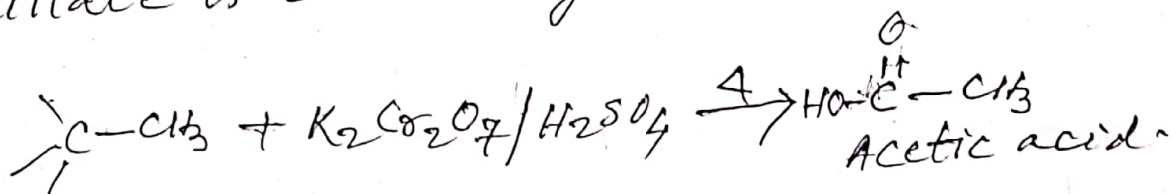
similarly



The NMR of the compound is used to make distinction between >N-CH_3 and $\text{>N-C}_2\text{H}_5$.

Estimation of >C-CH_3 in alkaloids.

The >C-CH_3 is estimated quantitatively by using Kuhn-Roth oxidation in which the acetic acid formed is distilled off and the distillate is titrated against standard NaOH.



Degradation of Alkaloids.

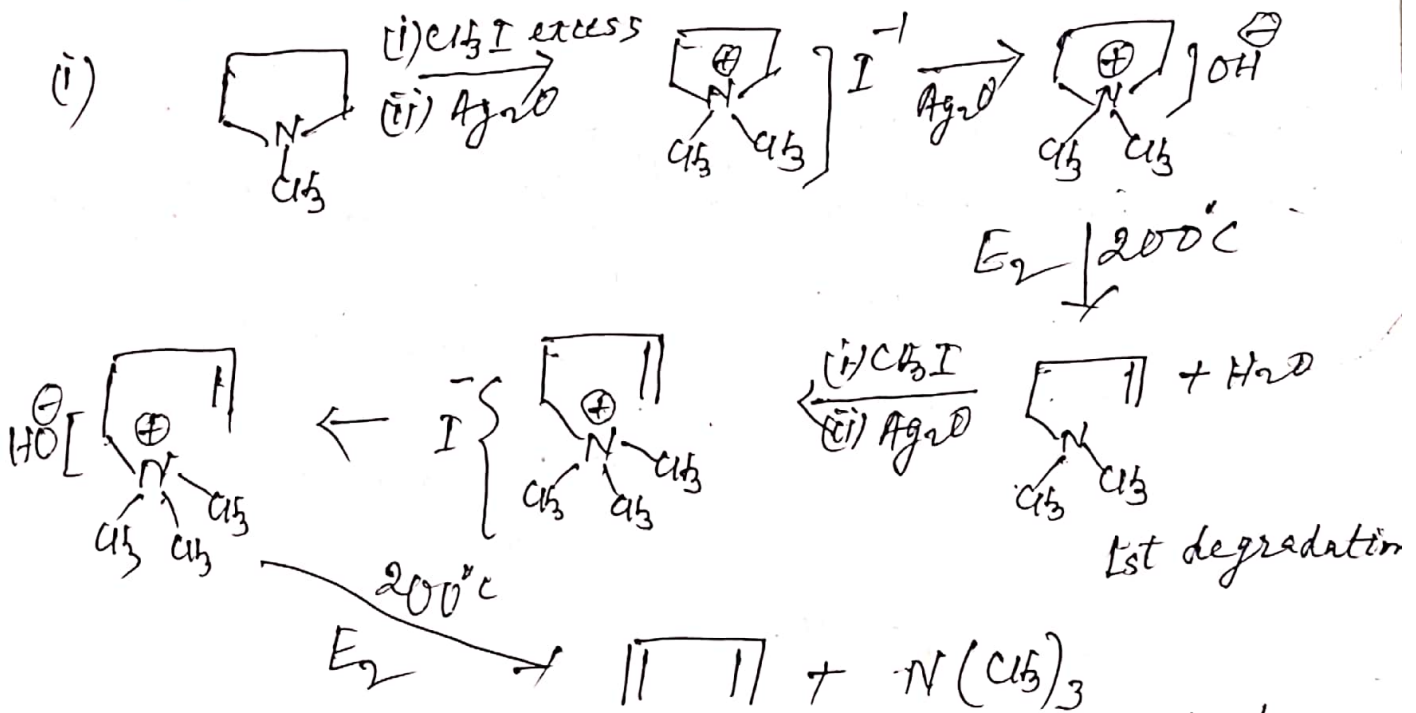
In order to discover the structural system of the compound, the alkaloids are degraded through the following methods :-

- (i) Hofmann's exhaustive methylation.
- (ii) Emde's degradation.
- (iii) Von Braun's method.
- (iv) Alkali fusion.
- (v) Oxidation.

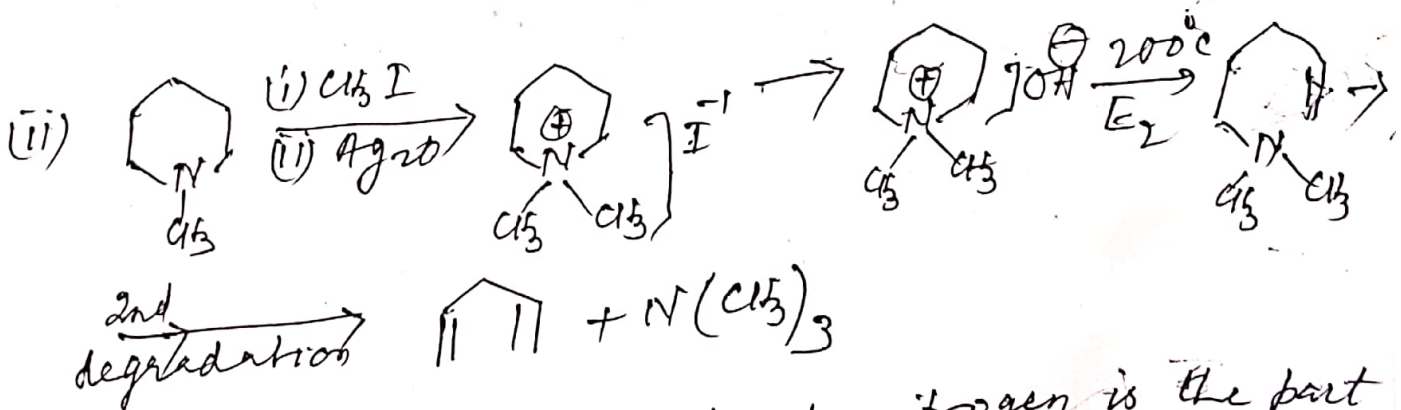
Hofmann's exhaustive methylation.

In this degradation, the compound is first converted into quaternary ammonium iodide

and then into quaternary ammonium hydroxide which on pyrolysis gives $>C=C<$ containing compounds.



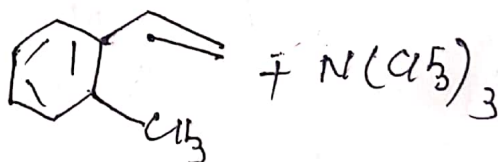
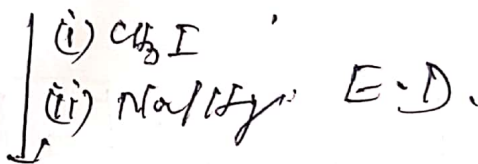
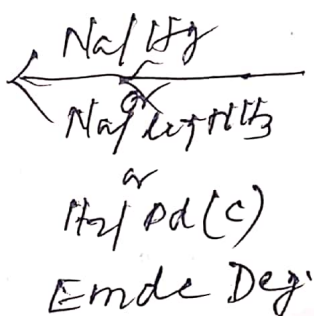
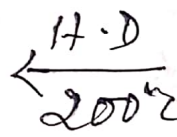
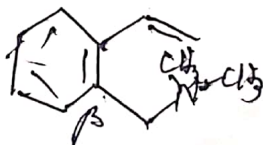
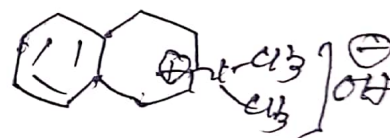
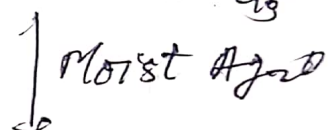
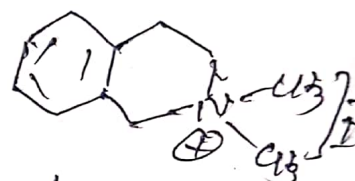
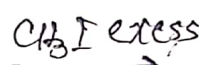
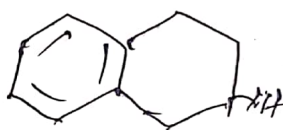
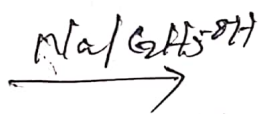
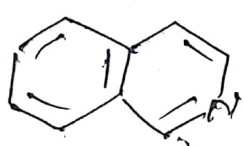
The identification of the unsaturated compound, indicates the position of nitrogen in the compound and the size of the nitrogen containing ring.



The degradation fails if nitrogen is the part of aromatic ring and after the hydrogen of ring, the process is possible. For this degradation, the presence of a β -hydrogen is essential near the nitrogen atom.

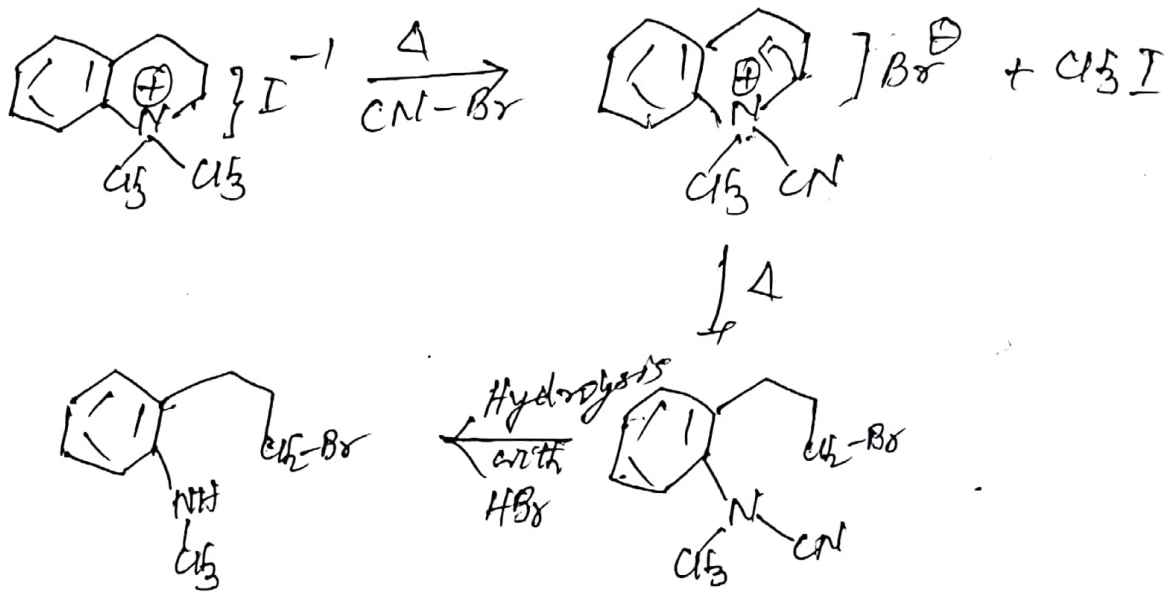
Emde Degradation

of β -hydrogen is absent, the quaternary ammonium salt is degraded as:



Van-Braun's Method

The degradation starts with the quaternary salt which is allowed to react with CN-Br .



Alkali fusion or oxidation or Reduction is sometimes used for the determination of the ring size.

In the next step, the position of the functional groups in the basic skeleton is fixed through various methods.

Finally the synthetic evidence is given for the compound.

* Students, this part is very important for your compulsory multiple choice question.