

**3) Hydroxylic OH:** - oxidation or by dehydration to unsaturated compounds.

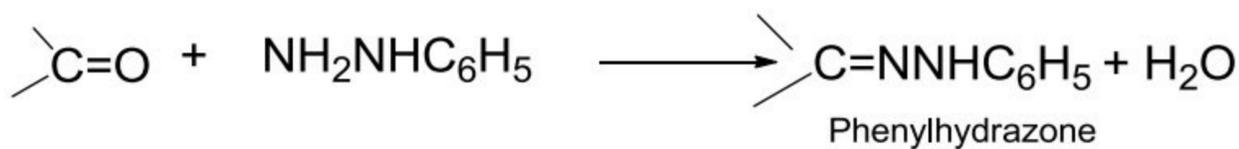
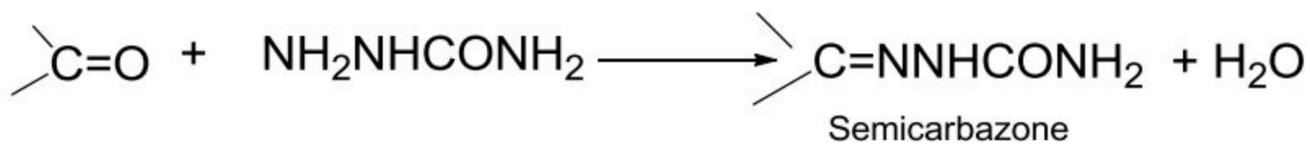
**4) Carboxylic acids:**

Solubility in aqueous sodium carbonate; ester on treatment with alcohol.

The number of carboxylic acids can be determined by titrating against Ba(OH)<sub>2</sub> or gravimetrically by silver salt method.

**5) Oxo Group:**

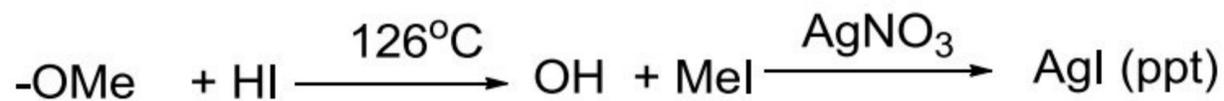
Carbonyl group: Reaction of the alkaloid with hydroxyl amine, semi carbazide, phenylhydrazine.



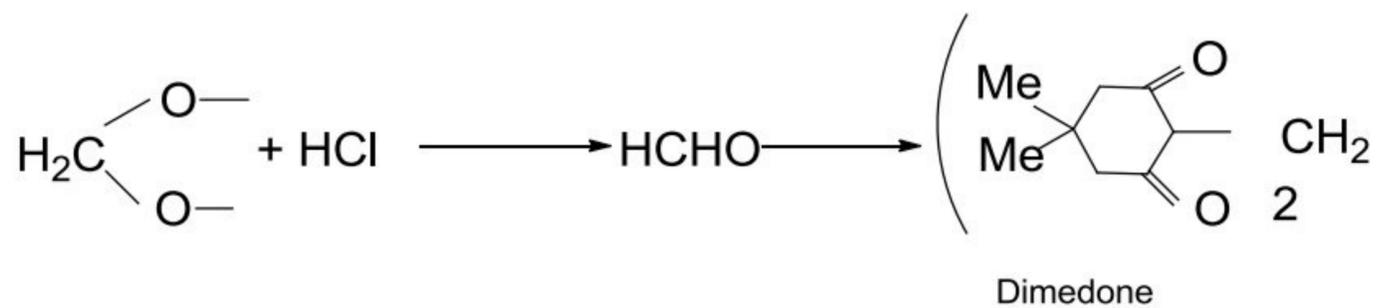
**6) Methoxyl group:**

a) Zeisel Method

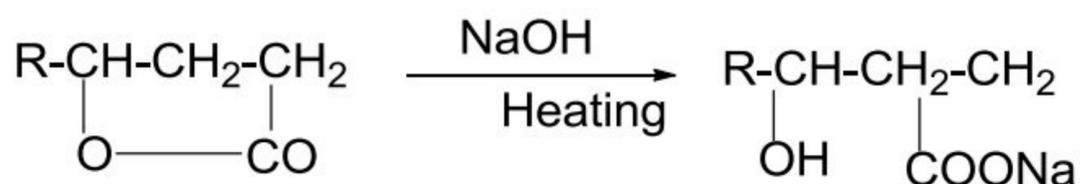
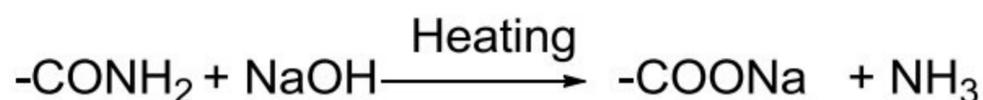
Alkaloid is heated with HI at 126°C and then precipitated as AgI.



**7) Methyleneedioxy group: (-OCH<sub>2</sub>OO-)**



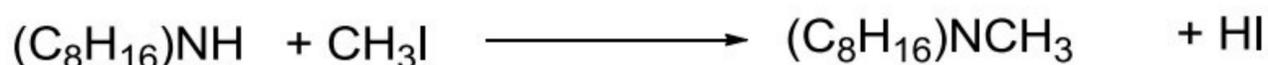
**8) Ester, amide, lactum or lactone:** These groups can be detected and estimated from the products of alkali or acid hydrolysis.



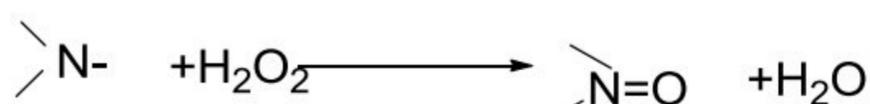
## b) Nature of Nitrogen:

It is present as a part of heterocyclic ring as secondary (NH) or tertiary (N).

Secondary nitrogen in the alkaloid is detected by reacting it with one molecule of methyl iodide to form N-methyl derivative.



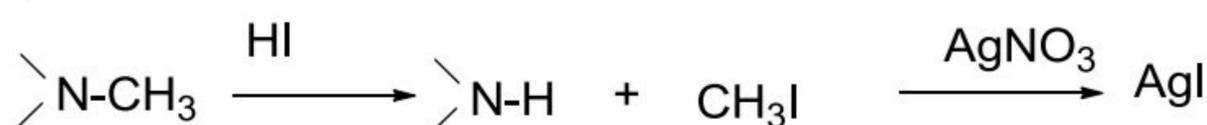
Tertiary nitrogen is treated with 30%  $\text{H}_2\text{O}_2$  where it is oxidised to amine oxide.



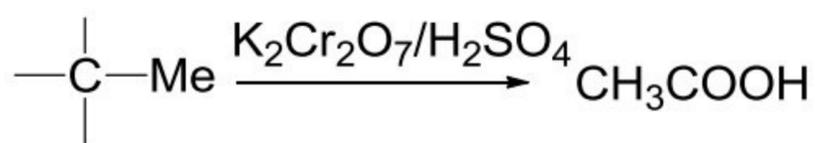
Presence of N-methyl amine is detected by distillation of alkaloid with soda-lime when methyl amine is obtained.



**Herzig-Meyer's method:** Cleaving N-methyl amine present in the alkaloid with HI at 150-300<sup>0</sup>C and estimating the methyl iodide formed by conversion to silver iodide with silver nitrate solution.



Estimation of C-methyl groups: Kuhn-Roth oxidation in which acetic acid formed is estimated.



## 1.9 DEGRADATION OF ALKALOID

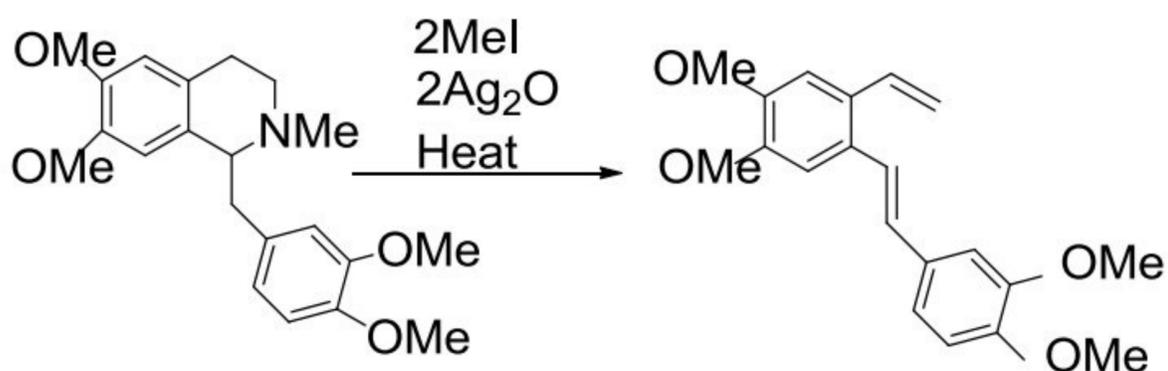
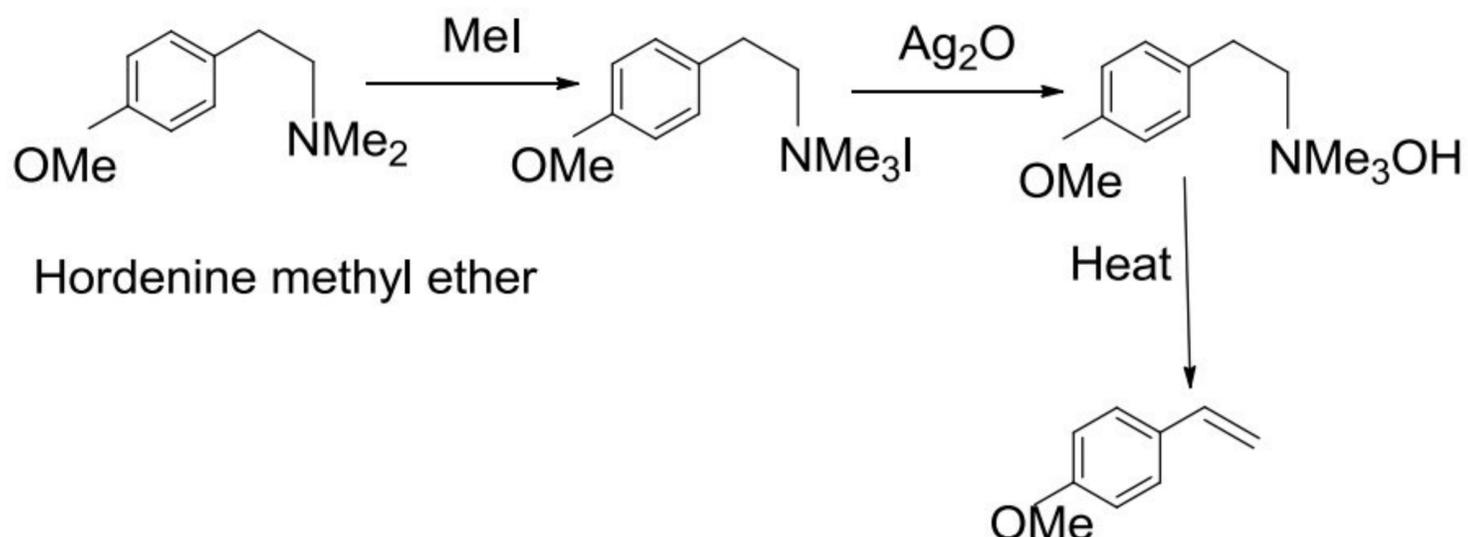
### 1.9.1 Hofmann Exhaustive methylation method:

The alkaloid amine is hydrogenated followed by its conversion to quaternary iodide, on excess methyl iodide. The salt is converted to hydroxide by reacting with moist  $\text{Ag}_2\text{O}$ . The hydroxide on heating at 200<sup>0</sup>c gives an olefin with the elimination of tertiary amine.



The reaction proceeds by E<sub>2</sub> mechanism in which the β hydrogen and quaternary nitrogen group are present in trans-anti-parallel configuration.

Reactions:



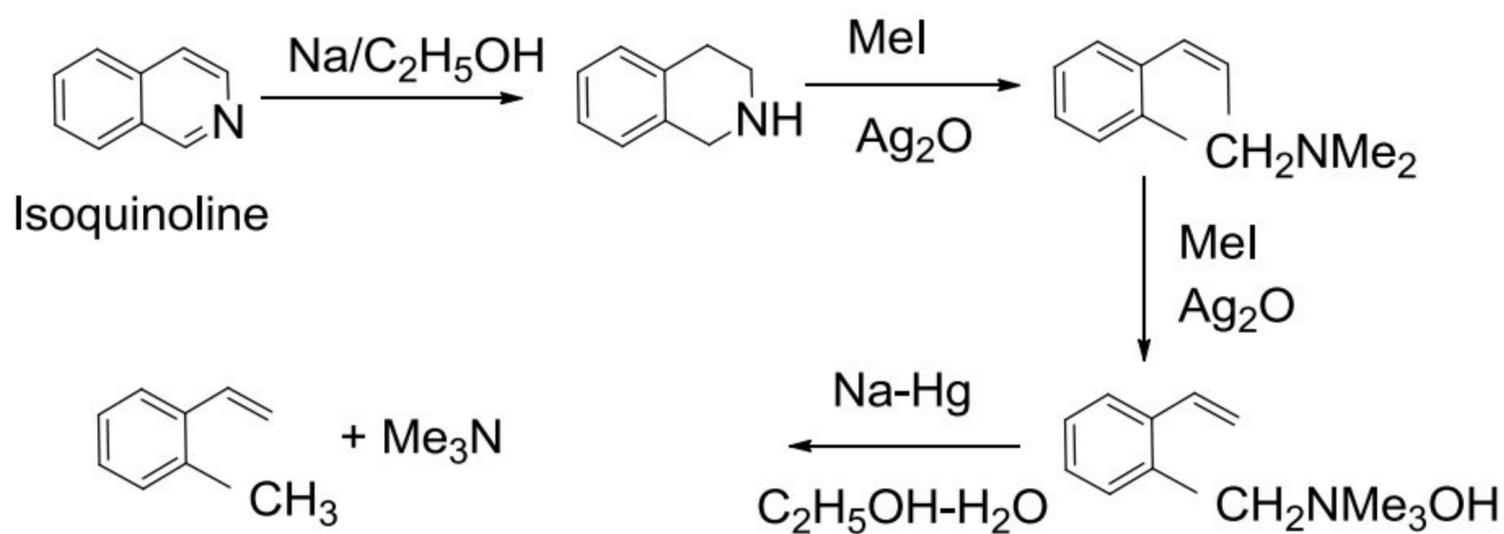
Hofmann's exhaustive methylation fails with unsaturated heterocyclic rings, when there is no  $\beta$ -hydrogen.

### 1.9.2 Emde's degradation:

The method involves the cleavage of quaternary ammonium salts with sodium amalgam or sodium in liquid ammonia or by catalytic hydrogenation.



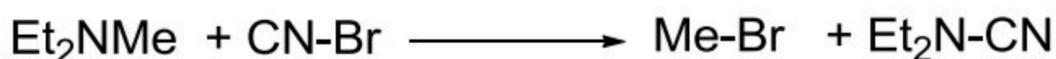
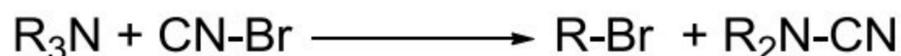
Reactions:



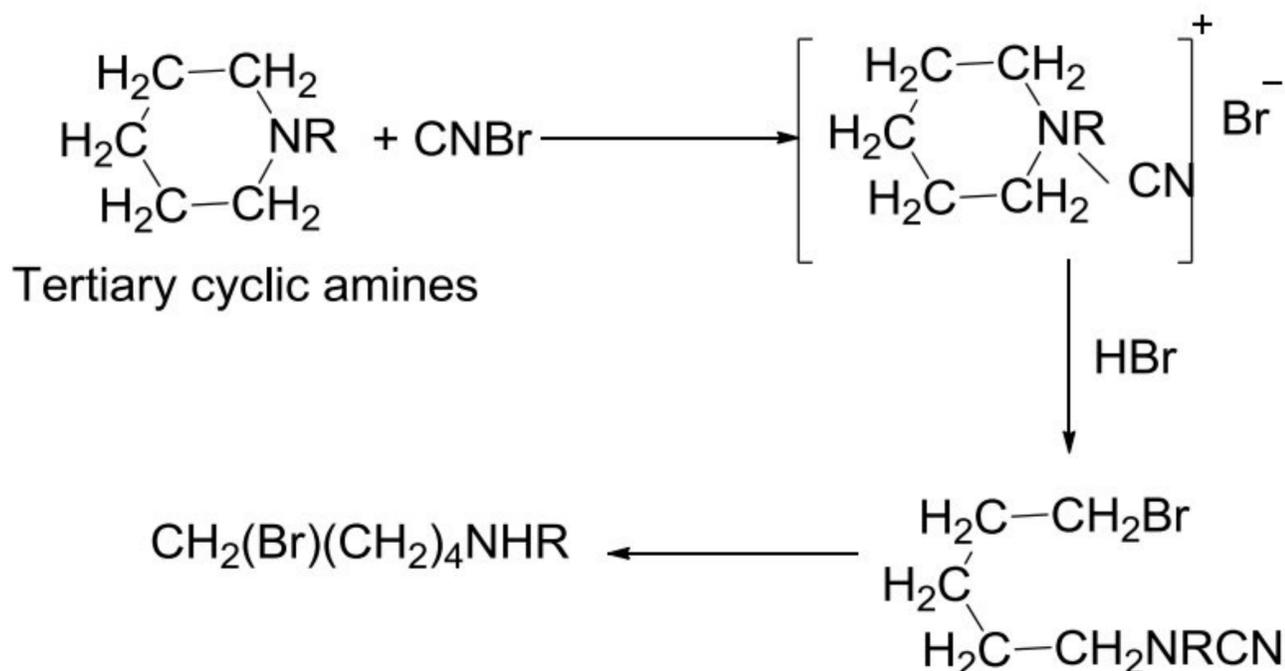
### 1.9.3 Van Braun's Method:

Tertiary amine containing alkyl substituent is treated with cyanogen bromide resulting in the cleavage of an alkyl-nitrogen bond to give alkyl halide and a substituted cyanamide.

This method can be applied to compounds which does not respond to Hoffman's method. Unsymmetrically substituted amines gives alkyl halide from the smallest alkyl substituent.



For Tertiary cyclic amines:



For secondary cyclic amines: The amine is treated with benzoyl chloride in the presence of NaOH which on treatment with Phosphorus followed by distillation under reduced pressure yields  $\alpha,\omega$ -dibromo derivative.

