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Chemistry

SUB. CODE- BSCC2402

For B.Sc. 4th Semester

(Alkaloids) **Module-V**

Alkaloids: General structure elucidation

By

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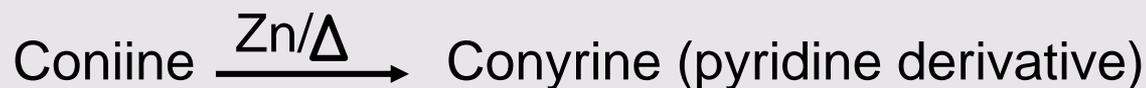


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General structure elucidation

- Molecular formula is determined by elemental analysis and molecular weight determination.
- Functional group analysis: Classical methods of organic analysis and spectroscopic methods are used to know the nature of the groups.
- Presence of unsaturation (C=C) detected by bromine addition.
- Catalytic hydrogenation estimates the number of carbon-carbon double bonds.
- Nature of carbon skeleton: Catalytic dehydrogenation and Zinc dust distillation can be used to know the carbon framework of the molecule.





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General structure elucidation

- Nature of nitrogen: N-atom can be part of the ring or can be present as $-NR_2$, $-NO_2$, $-CONH_2$ etc.
- Nature of amine (1° , 2° or 3°) can be determined by using Ac_2O , $PhCOCl$, H_2O_2 , HNO_2 , CH_3I etc.
- Presence of amide group can be confirmed by testing for acid and amine groups.
- N-Methyl groups, if present, will react with KOH to give CH_3NH_2 , $(CH_3)_2NH$, or $(CH_3)_3N$ depending on the number of $-CH_3$ groups present.
- Herzig-Meyer method for estimation of $-NMe$ groups: Heating of HI salt of alkaloid at $200-300^\circ C$. Released CH_3I is estimated by converting into AgI_2 .

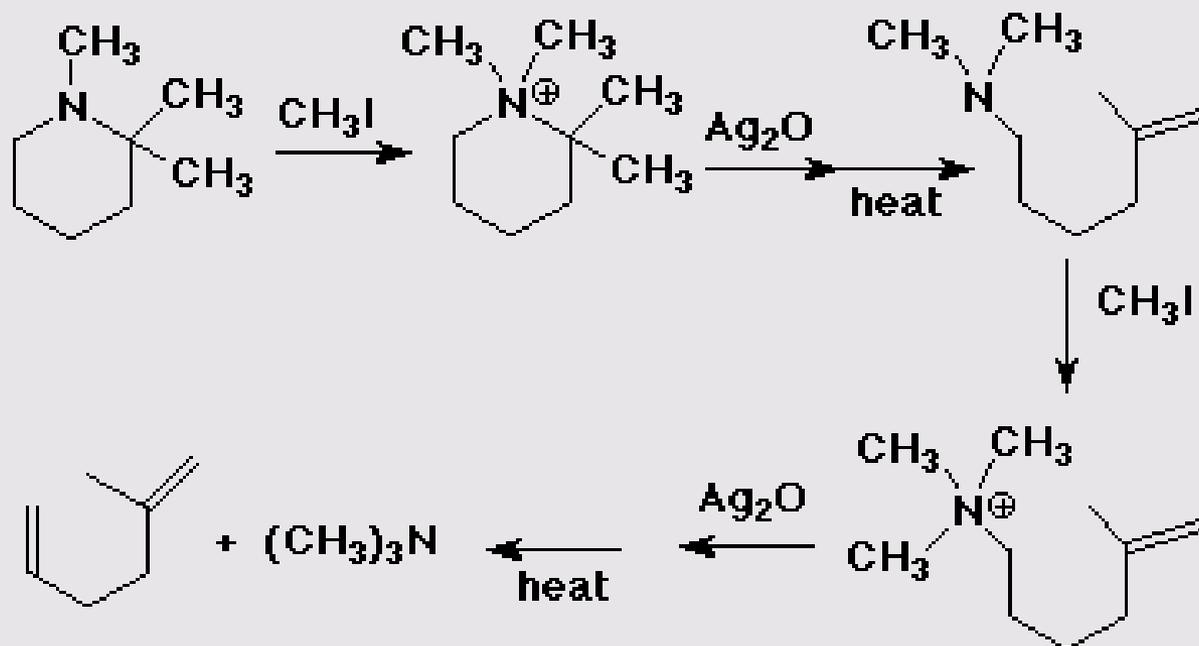


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General structure elucidation

- **Hofmann elimination** (exhaustive methylation): tertiary amine reacts to create a quaternary ammonium and an alkene by treatment with excess methyl iodide followed by treatment with silver oxide, water, and heat.

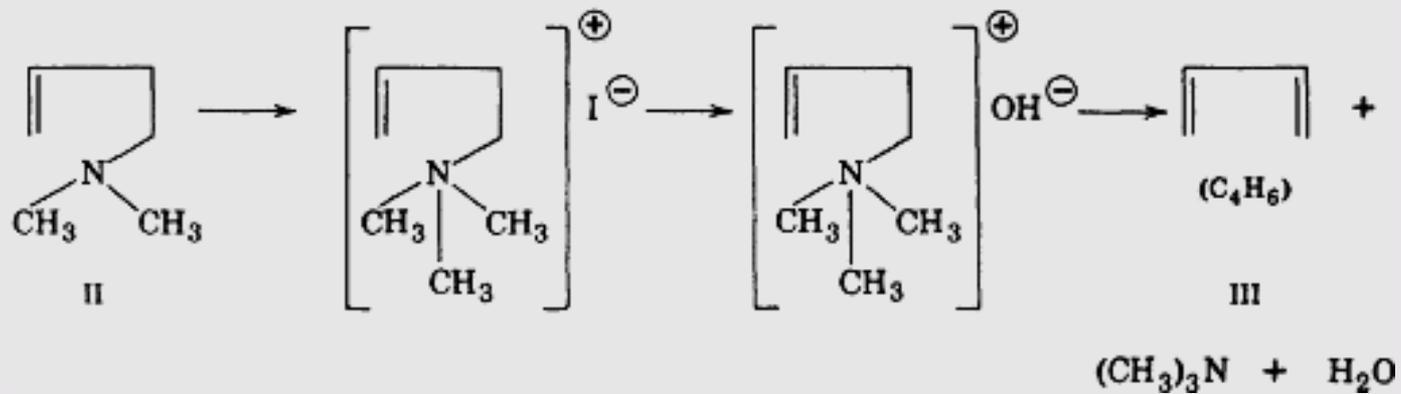
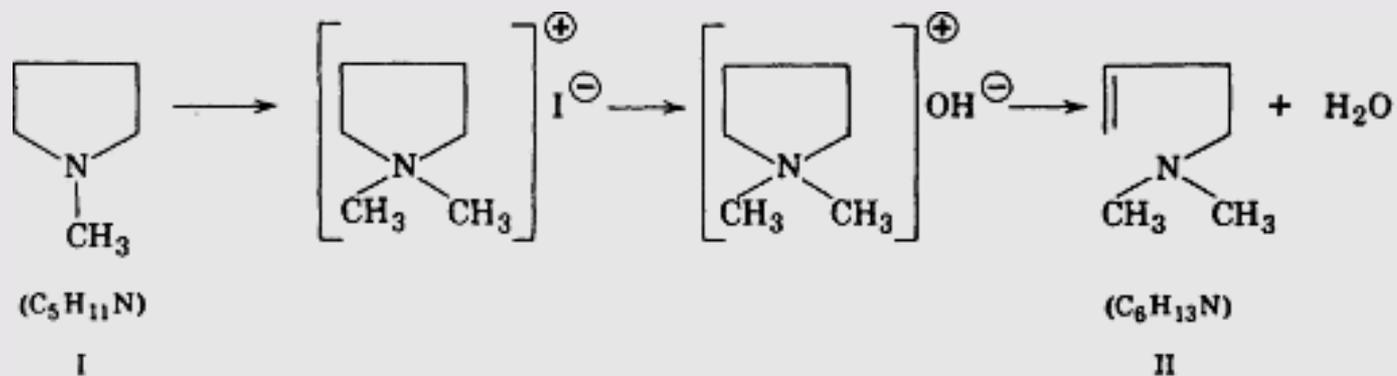




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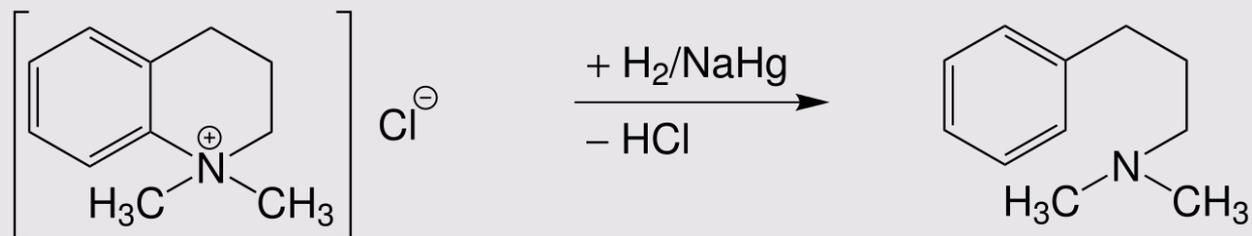




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The reductive cleavage of quaternary ammonium salt of nitrogen-containing compounds (especially in heterocyclic forms) by treatment with an excess of sodium amalgam in an alcoholic or aqueous solution is known as **Emde degradation**.



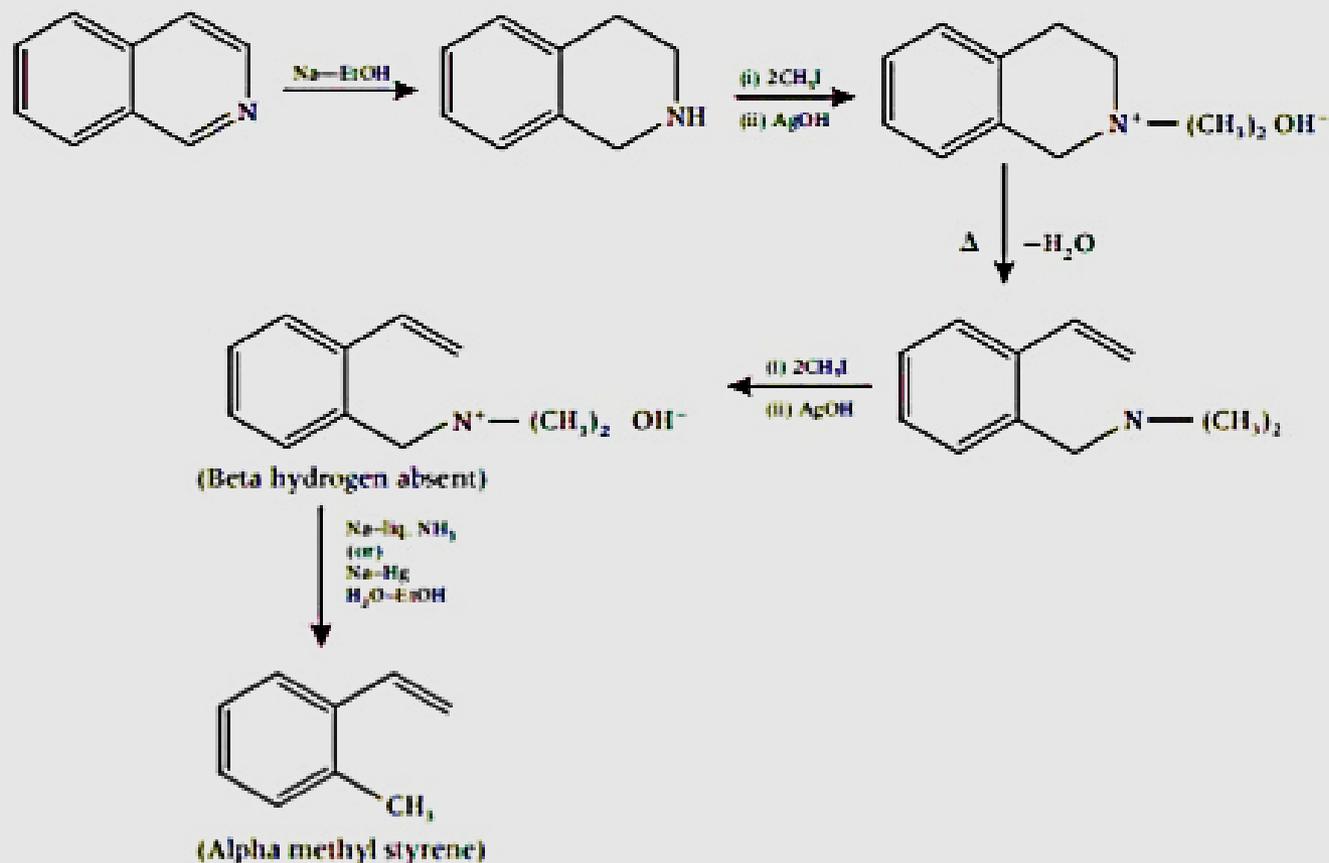


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Emde degradation of Isoquinoline





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- **Nature of oxygen:** O-atom can be present as phenolic or alcoholic $-\text{OH}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{OR}$ or $-\text{C}=\text{O}$ etc.
- Phenolic $-\text{OH}$ (3°) can be determined by using Ac_2O , PhCOCl , H_2O_2 , HNO_2 , CH_3I etc.
- Presence of amide group can be confirmed by testing for acid and amine groups.
- N-Methyl groups, if present, will react with KOH to give CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, or $(\text{CH}_3)_3\text{N}$ depending on the number of $-\text{CH}_3$ groups present.
- Herzig-Meyer method for estimation of $-\text{NMe}$ groups: Heating of HI salt of alkaloid at $200\text{-}300\text{ }^\circ\text{C}$. Released CH_3I is estimated by converting into AgI .
- Degradation studies: Alkaloids are degraded into simpler fragments, which are characterized. From combined data the structure of alkaloid is interpreted.
Degradation techniques are:
Hydrolysis and oxidation
- Synthesis: Synthesis of the molecule resolves the structural problems by comparing data with isolated ones.



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References

1. K.D Sharma and Y. R. Sharma, Kalyani Publishers, Unit-III page-310;
2. University Chemistry, Vol-IV, Dr. U. N. Dash, Dr. KK. Ojha, Himalaya Publishing house, Unit V, page-399