

# Synthesis and characterization of 3-Phenyl-1, 4-dihydroazacinnolines

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**Abstract :** The condensation product of 2-hydrazinopyridine and phenacyl bromide in presence of anhydrous aluminium chloride undergoes intermolecular Friedel Crafts reaction to result 3-phenyl-1, 4-dihydroazacinnolines. These results were confirmed by an alternative method, i.e., NBS bromination of the condensation product of acetophenone and pyridylhydrazine and then cyclising in the presence of cyclising agent. The study of the spectral datas of 3-phenyl-1, 4-dihydroazacinnolines was recorded and compared which confirmed that 3-phenyl-1, 4-dihydroazacinnolines obtained in both cases are identical.

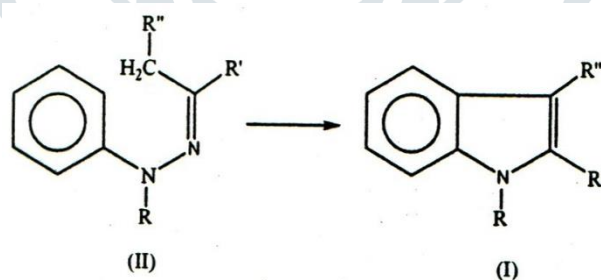
**Index Terms -** Interamolecular, Friedel Crafts reaction, 3-phenyl-1, 4-dihydroazacinnolines.

## I. INTRODUCTION

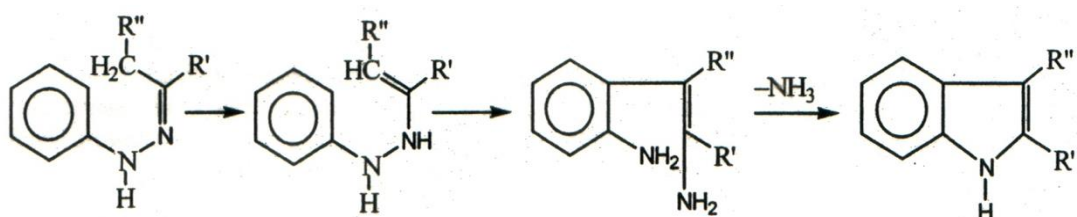
Pyridyl hydrazones (Pyridine-2-hydrazones) obtained from condensing pyridylhydrazines with carbonyl compounds are usually crystalline compounds with well defined melting points. These are frequently employed for identification of carbonyl compounds like phenyl hydrazine. Since the hydrazones derived have better crystallizing properties and higher melting points.

Hydrazones find many other uses in synthetic organic compounds. They may be used to prepare various types of heterocyclic ring systems. If a carbonyl compound contains a second substituent which can react with hydrazine the hydrazone may react further to undergo ring closures resulting in the formation of five or six membered heterocyclic ring compounds<sup>1</sup>.

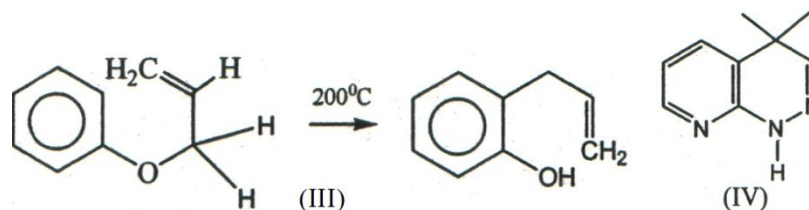
It is well known that cyclisation reaction undergone by phenylhydrazone is its conversion into indole, which is known as Fischer indole synthesis and it involves elimination of ammonia from the phenyl hydroazone or substituted phenyl hydrazones of a variety of carbonyl compounds, e.g. the formation of indole derivatives (i) from the phenyl hydrazones(II).



The reaction requires an acid catalyst such as  $\text{ZnCl}_2$  ethanolic hydrogen chloride, dilute sulphuric acid, glacial acetic acid or PPA and heating usually to above  $150^\circ\text{C}$ .

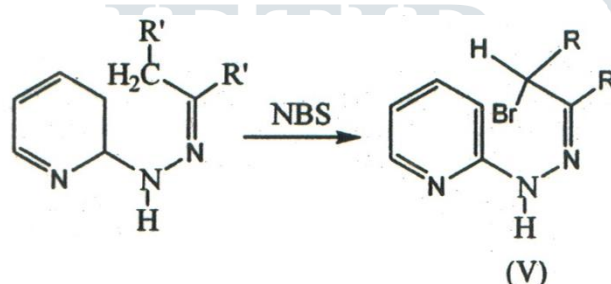


The step is considered to be electrocyclic in character and thus analogous to the Claisen Rearrangement in phenyl allyl ethers (III). This prompted to explore the possibility of cyclising pyridyl hydrazones by closing the ring and result would then be an azacinnoline(IV) derivative.



The result can be characterized by spectral evidences as well as by further analytical proof. The structure can further be explained by an alternative method of synthesis in which  $\beta$ -carbon of pyridyl hydrazone with respect to N-atom was brominated by NBS bromination and then cyclising the brominated product (V) by the use of specific conditions and acid catalyst.

The result obtained in both the cases were found identical by the comparison of spectral datas, melting point and mixed melting point determination.



## II. EXPERIMENTAL

### Preparation of pyridyl hydrazone of phenacyl bromide

Phenacyl bromide (0.01 Mol) was dissolved in glacial acetic acid (5ml). A solution of pyridyl hydrazine (2-hydrazinopyridine) (2ml) in glacial acetic acid (4ml) and water (5ml) was added to the solution of phenacyl bromide prepared above. The mixture solution was shaken vigorously for ten minutes until it became warm for another ten minutes by dipping in warm water. The solution was then cooled when light brown crystals separated. These were collected at the pump, washed with dilute acetic acid several times and crystallized from ethanol, found brown crystals (1.65 g) m.p. 134°C.

#### Analysis

Found	N-14.55%
Calculated for $C_{13}H_{12}N_3Br$	N-14.48%

### Preparation of 3-phenyl-1, 4-dihydroazacinnoline

(By intramolecular Friedel Crafts reaction of above prepared pyridyl hydrazone)

In a small flask, anhydrous aluminium chloride (0.59) and carbon disulphide (10ml) were placed. The flask was cooled to about 10°C by immersing it in cold water. A solution of above prepared pyridyl hydrazone of phenacyl bromide (1.5g) in dry carbon disulphide (10ml) was then added drop-wise with stirring continuously till the evolution of hydrogen chloride gas in ceased off. The reaction mixture was allowed to stand at room temperature for two hours and then poured into a mixture of ice (20g) and conc. Hydrochloric acid (1ml). The solution was then extracted and washed with water and dried over calcium chloride. Removal of solvent by distillation gave a gummy residue, which crystallized on trituration with benzene and light petroleum ether. Recrystallisation from benzene gave pure 3-phenyl-1, 4-dihydroazacinnoline (0.54g) as yellow brown crystals, m.p.-182°C.

### Preparation of NBS bromination of acetophenone pyridyl hydrazone:

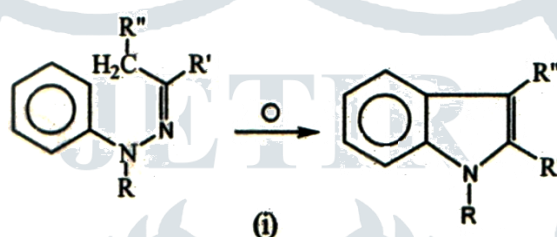
Acetophenone pyridyl hydrazone (2.5g) in dry carbon tetrachloride (30ml) were added in N.B.S.(1.75g) and catalytic amount of benzyl peroxide. The reaction mixture was heated under reflux for nearly three hours. Cooled and precipitated. Succinimide was filtered off. The filtrate was distilled to remove solvent and light petroleum ether added to the residue when orange solid separated. This was collected by filtration and recrystallised from ethanol to furnish the pure bromo compound as light brown crystals (0.75g) m.p. 134°C.

#### Analysis

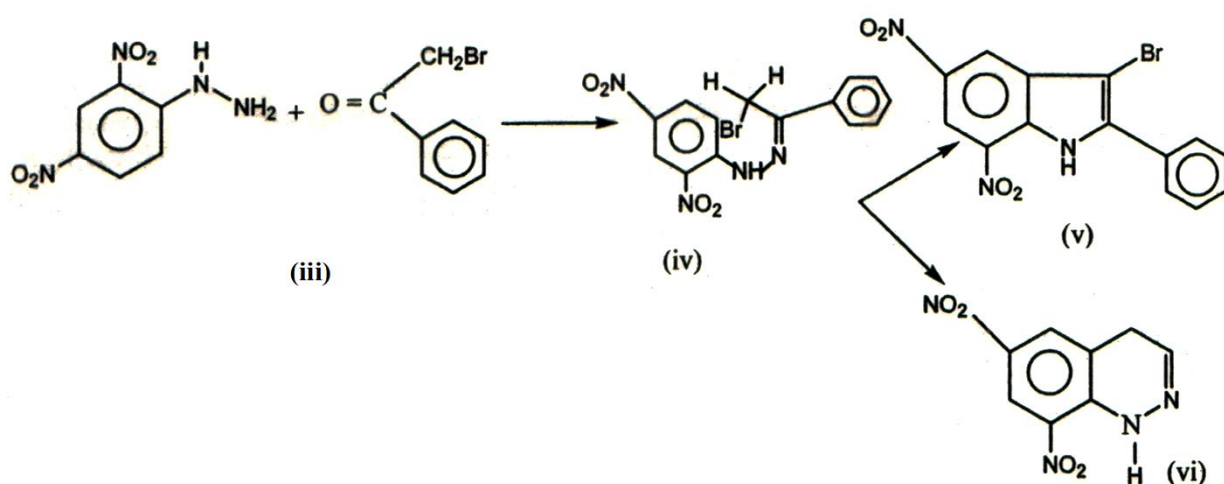
Found	N-14.55%
Calculated for $C_{13}H_{12}N_3Br$	N-14.48%

### III. RESULTS AND DISCUSSION

Aryl hydrazones of simple carbonyl compound, cyclised under the influence of an acid catalyst and high temperature to give indole (i).



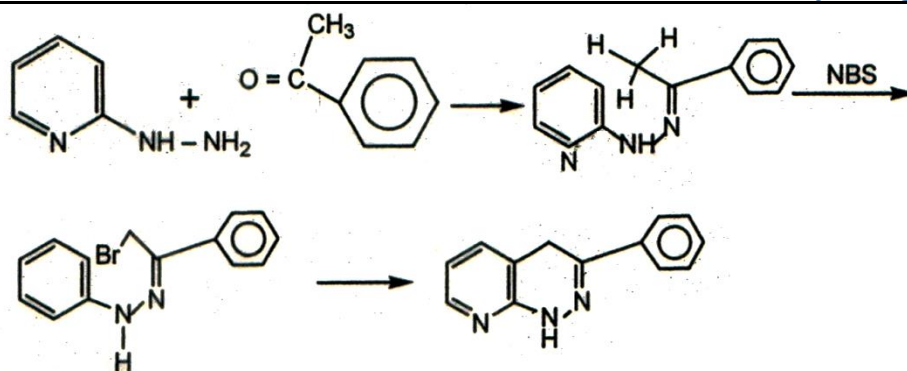
Firstly rearrangement occurs in hydrazones molecule in which the ortho carbon of the aromatic ring forms a carbon-carbon bond with the carbon atom situated in the  $\beta$ -carbon with respect to the aliphatic nitrogen followed by expulsion of ammonia.



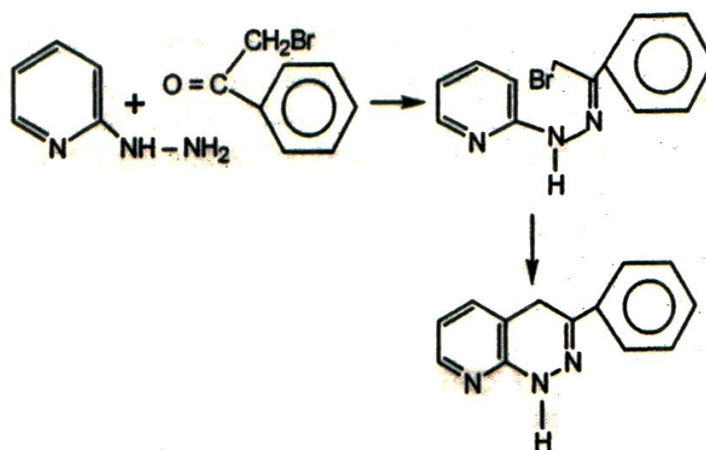
The transformation of 2, 4-dinitrophenyl hydrazone of  $\alpha$ -halo carboxyl compound (II) in neutral solvent such as carbon disulphide under sufficiently mild condition to 1, 4-dihydrocinnoline derivative was proposed by intramolecular Friedel Crafts alkylation reaction and there could be no possibility of Indolisation.

Accordingly, phenacyl bromide (iii) to carry out this synthesis.

All the above discussion, it was then suggested the path for preparation of 1, 4-dihydroazacinnoline by intramolecular Friedel Crafts cyclisation reaction from acetophenone pyridyl hydrazone as mentioned below:



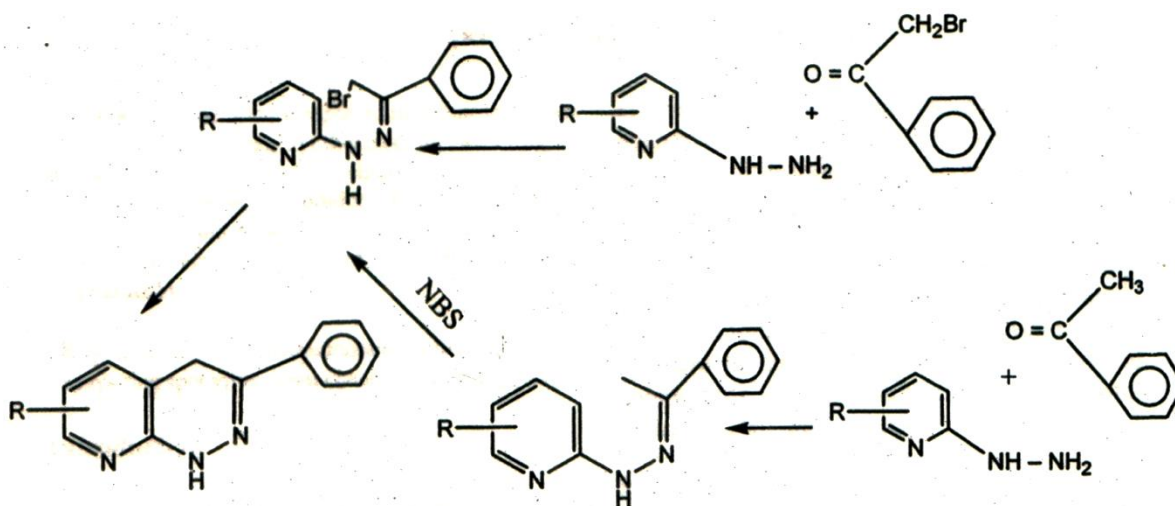
Alternatively 1, 4-dihydroazacinnoline may be synthesise by cyclising the condensation product of pyridyl hydrazine and phenacyl bromide using mild acedic condition as given below.



A steady evolution of hydrogen bromide during the reaction showed that it was occurring in the expected manner. TLC examination was carried out from time to time to monitor the progress of reaction. The product from this reaction was a pure crystalline compound which was free from bromine (Beilsten test ) whereas indolisation should give indole derivative containing bromine.

Further proof of the structure was adduced by spectrum of the compound has absorption at  $1599\text{cm}^{-1}$  for C=N stretching  $1620\text{cm}^{-1}$  for substituted benzene ring  $1485\text{cm}^{-1}$  for substituted pyridine ring  $2925\text{cm}^{-1}$  for C-H stretching (showing the presence of  $-\text{CH}_2-$  grouping) and  $3250\text{cm}^{-1}$  for N-H stretching.

The nmr spectrum of the compound had absorption for four sets of protons. The five aromatic protons had resonance (multiplet) at  $\delta 7.2$  three protons of pyridine ring had resonance at  $\delta 4.6$  a singlet corresponding to two protons at  $\delta 2.7$  due to pyridylmethyl ( $-\text{CH}_2-$ ) group and a singlet for one proton at  $\delta 4.3$  for the N=H group.



The products obtained in both the above routes were found identical comparing their m.p. and Thus the product in the above cyclisation reaction was 3-phenyl-1, 4-dihydroazacinnoline.

This synthesis may be extended to its substituted pyridyl hydrazones of the type. Spectral datas structurally it was 3-phenyl- 1, 4-dihydrazacinnoline:

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