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Synthesis and Characterization of 3, Phenyl-1,4-Dihydroazacinnolines

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Abstract:

The condensation fabricated from 2-hydrazinopyridine and phenacyl bromide in presence of anhydrous aluminium chloride undergoes interamolecular Friedel Crafts response to end result 3-phenyl-1, four-dihydroazacinnolines. those outcomes have been showed via an alternative approach, i.e., NBS bromination of the condensation product of acetophenone and pyridylhydrazine and then cyclising in the presence of cyclizing agent.The observe of the spectral datas of 3-phenyl-1, four-dihydroazacinnolines turned into recorded and as compared which showed that three-phenyl-1, 4-dihydroazacinnolines received in both cases are same.

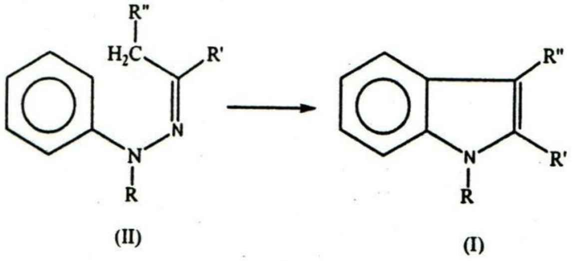
Key Words **-Interamolecular,Friedel Craftsreaction,3-phenyl-1,4-dihydrazacinnolines.**

INTRODUCTION

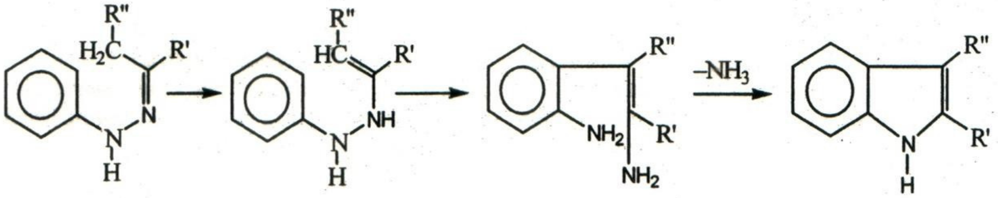
Pyridyl hydrazones (Pyridine-2-hydrazones) obtained from condensing pyridylhydrazines with carbonylcompoundsareusuallycrystallinecompoundswithwell-definedmeltingpoints.Theseare frequentlyemployedforidentificationofcarbonylcompoundslikephenylhydrazine.Sincethehydrazonesderivedhavebettercrystallizingproperties andhighermeltingpoints.

Hydrazones find many other uses in synthetic organic compounds. They may be used to prepare varioustypes of heterocyclic ring systems. If a carbonyl compound contains a second substitutents which can reactwith hydrazine the hydrazone may react further to undergo ring closures resulting in the formation of five orsixmemberedheterocyclicringcompounds1.

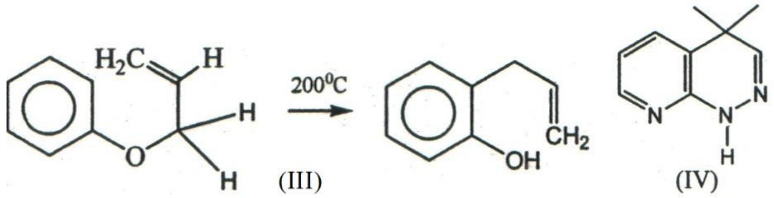
It is well known that cyclisation reaction undergone by phenylhydrazone is its conversion into indole,whichisknown asFischer indole synthesisanditinvolveseliminationof ammonia fromthe phenylhydroazone or substiued phenyl hydrazones of a variety of carbonyl compounds, e.g., the formation of indolederivatives(i)fromthephenylhydrazones (II).



The reaction requires an acid catalyst such as $ZnCl_2$ethanolic hydrogen chloride, dilute sulphuric acid,glacialaceticacidorPPAandheatingusuallytoabove150°C.

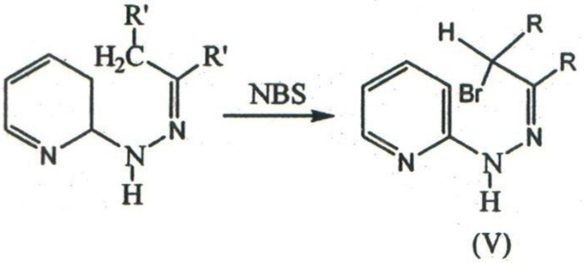


ThestepisconsideredtobeelectrocyclicincharacterandthusanalogoustotheClaisenRearrangementinphnyl allyl ethers (III). This prompted to explore the possibility of cyclising pyridyl hydrazones by closing the ring and result would then be an azacinnoline (iv)derivative.



The result can be characterized by spectral evidences as well as by further analytical proof. The structurecan further be explained by an alternative method of synthesis in which β-carbon of pyridyl hydra zone 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.



I. EXPERIMENTAL

Preparationofpyridylhydrazoneofphenacylbromide

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 ofphenacyl bromide prepared above. The mixture solution was shaken vigorously for ten minutes until itbecame warm for another ten minutes by dipping in warm water. The solution was then cooled when lightbrowncrystalsseparated.Thesewerecollectedatthepump,washedwithdiluteaceticacidseveraltimesandcrystallizedfromethanol,foundbrowncrystals (1.65g)m.p.134°C.

Analysis

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

Preparationof3-phenyl-1,4-dihydrazacinnoline

(ByintramolecularFriedelCraftsreactionofabovepreparedpyridylhydrazone)

In a small flask, anhydrous aluminium chloride (0.59) and carbon disulphide (10ml) were placed.

Theflask was cooled to about 10°C by immersing it in cold water. A solution of above prepared pyridylhydrazone of phenacyl bromide (1.5g) in dry carbon disulphide (10ml) was then added drop-wise withstirring continuously till the evolution of hydrogen chloride gas in ceased off. The reaction mixture wasallowed to stand at room temperature for two hours and then poured into a mixture of ice (20g) and conc.Hydrochloride acid (1ml). The solution was then extracted and washed with water and dried over calciumchloride. Removal of solvent by distillation gave a gummy residue, which crystallized on trituration withbenzeneandlightpetroleumether.Recrystallisationfrombenzenegavepure3-phenyl-1,4-dihydroazacinnoline(0.54g)asyellowbrowncrystals,m.p.-182°C.

PreparationofNBSbrominationofacetophenonepyridylhydrazone:

Acetophenoune pyridyl hydrazone (2.5g) in dry carbon tetrachloride (30ml) were added in N.B.S. (1.75g)andcatalyticamountofbenzylperoxide.Thereactionmixturewasheatedunderrefluxfornearlythreehours.Cooled and precipitated. Succinimide was filtered off. The filtrate was distilled to remove solvent and lightpetroleum ether added to the residue when orange solid separated. This was collected by filtration andrecrystallisedfromethanoltofurnishthepurebromocompoundaslightbrowncrystals(0.75g)m.p.134°C.

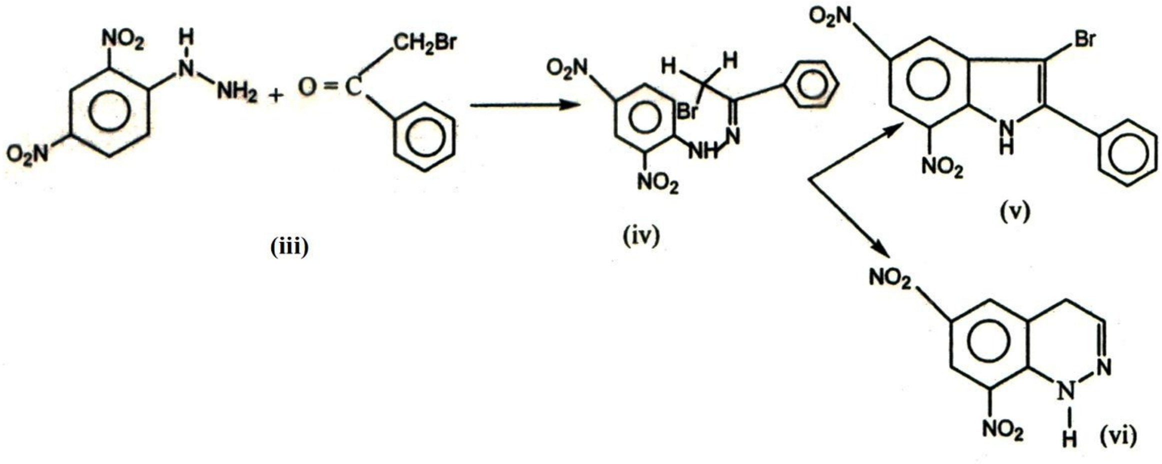
Analysis

Found	N-14.55%
CalculatedforC$_{13}$H$_{12}$N$_3$Br	N-14.48%

II. RESULTSANDDISCUSSION

Aryl hydrazones of simple carbonyl compound, cyclised under the influence of an acid catalyst and hightemperatureto giveindole(i).

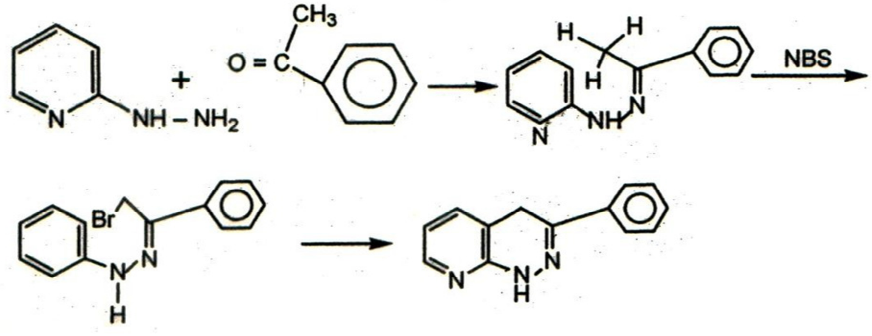
Primarily,rearrangementoccursinhydrazonesmoleculeinwhichtheorthocarbonofthearomaticringformsa carbon-carbon bond with the carbon atom situated in the β-carbon with respect to the aliphatic nitrogenfollowedbyexpulsionofammonia.



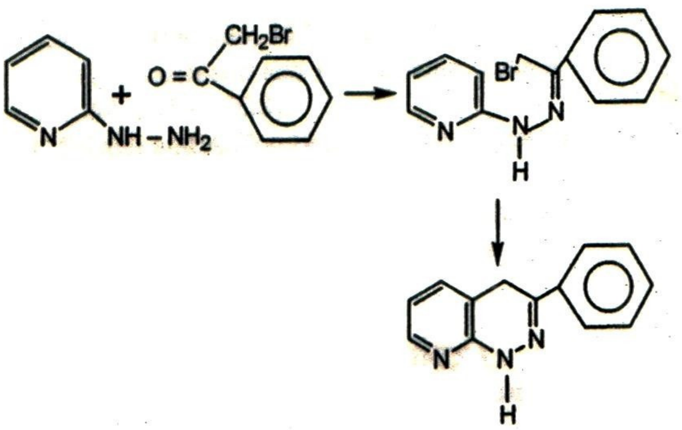
The transformation of 2, 4-dinitrophenyl bydrazone of α-halo carboxylcompound (II) in neutral solventsuchascarbondisulphideundersufficientlymildconditionto1,4-dihydrocinnolinederivativewasproposedbyintramolecularFriedelCraftsalkylationreactionandtherecouldbenopossibilityofIndolisalion.

Accordingly,phenacylbromide(iii)tocarryoutthissynthesis.

All the above discussion, it was then suggested the path for preparation of 1, 4-dihydroazacinnoline byintramolecular Friedel Crafts cyclisation reaction from acetophhenonoe pyridyl bydrazone as mentionedbelow:



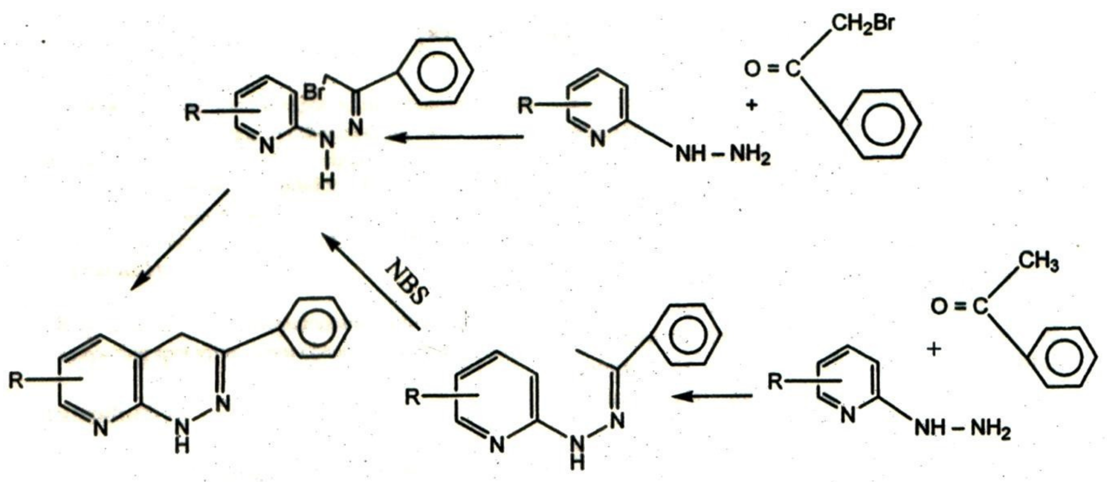
Another,1,4-dihydroazacinnolinemaybesynthesisebycyclisingthecondensationproductofpyridylhydrazineandphenacylbromideusingmildacedicconditionasgivenbelow.



A steady evolution of hydrogen bromide during the reaction showed that it was occurring in the expectedmanner.TLCexaminationwascarriedoutfromtimetotimetomonitortheprogressofreaction.Theproductfrom this reaction was a pure crystalline compound which was free from bromine (Beilstentest) whereasindolisationshouldgiveindolederivativecontainingbromine.

Further proof of the structure was adduced by spectrum of the compound has absorption at 1599cm^{-1} forC=N stretching 1620cm^{-1} for substituted benzene ring 1485cm^{-1} for substituted pyridine ring 2925cm^{-1} forC-Hstretching(showingthepresenceof–CH_2-grouping)and3250cm^{-1}forN-Hstretching.

Thenmrspectrumofthecompoundhadabsorptionforfoursetsofprotons.Thefivearomaticprotonshadresonance (multiplet) at δ7.2 three protons of pyridine ring had resonance at δ4.6 a singlet corresponding totwo protons at δ2.7 due to pyridylmethyl (-CH_2-) group and a singlet for one proton at δ4.3 for the N=Hgroup.



Theproductsobtainedinboththeaboverouteswerefoundidenticalcomparingtheirm.p.andthustheproductintheabovecyclisationreactionwas3-phenyl-1,4-dihydroazacinnoline.

Thissynthesismaybeextendedtoitssubstitutedpyridylhydrazonesofthetype.Spectraldatasstructurallyitwas3-phenyl-1, 4-dihydrazacinnoline:

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