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SYNTHESIS OF SOME HETEROCYCLIC COMPOUNDS CONTAINING TWO NITROGEN ATOMS (FUSED RING SYSTEM WITH AROMATIC RING)

DR. ANIL PATHAK AND DR. SUGAM KUMAR

Department of Chemistry & Biology Inter Raj High School Darbrbanga

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In continuation of our previous work we are reporting here some heterocyclic compounds (fused ring system with aromatic ring) that is 3-hydroxy-1,4- dihydrocinnoline. o – substituted phenylacethydrazides could be cyclised to furnish the above mentioned six membered heterocyclic compound.

INTRODUCTION

Hydrazine and substituted hydrazines are easily available and have replaceable hydrogen atoms. Literatures are available to prepare various substituted hydrazines by simple methods. Hydrazine and substituted hydrazines have tendency to take part into substitution as well as condensation reaction. This activity provides a method to prepare alkyl, acyl hydrazide as well as condensation with suitable carbonyl compounds viz, substituted or unsubstituted aldehydes and ketones to give rise hydrazones. Standard methods are available in this regard for the said reactions. Substitution products as well as condensation products may be forced to cyclise under suitable conditions of reagents solvent, cyclising agents, temperatures and others. This may lead to the formation of two nitrogen atoms containing heterocyclic ring systems fused ring systems of cinnolinephthalaxine and quinoxaline derivatives. It has been found that these compounds have great antibacterial power as well as promoters of various organic reactions; these series of compounds are highly toxic and less curatives, so it is essential to explore their synthesis covering the simpler methods of preparation, less toxicity and high power of curative action by the replacement of substituents from one position to other. Substituted and unsubstituted carbonyl compound may help in this regard because it consists carbonyl group which possesses reaction activities in condensation reactions, as well as addition reactions, since α – position of carbonyl compound is reactive and if hydrogen atoms are available it may be replaced by suitable substituents. All the above evidences compelled to go through this plan to synthesize the two nitrogen atoms containing heterocyclic ring systems. It has also been shown by way of exploratory experiments that the o- substituted phenylacethydrazides could be cyclised to furnish the six membered heterocyclic compound (fused ring system with aromatic ring.) i,e 3- hydroxy – 1,4 – dihydrocinnoline.

EXPERIMENTAL, RESULT AND DISCESSION

Preparation of Ethyl o- Amino Phenyl Acetate

(This was done by the catalytic reduction of ethyl o- nitro phenyl acetate)

Following the method of Blatt a solution of ethyl o- nitro phenyl acetate (1-10. 1 mol) in 150 ml 95% alcohol was placed in the reaction bottle of the catalytic reduction apparatus and 0.2 gm of platinum oxide catalyst was added, the mixture was shaken well with passing hydrogen gas until three molecular equivalence had been absorbed. The platinum was filtered off and the alcohol was removed from the filtrate by distillation. The resultant amino compound i.e. Ethyl o-amino phenyl acetate was re-crystallised from 40ml of ether. The yield was (50-85%)

Preparation of o-Amino Phenylacethydrazide

Following the standard method of Vogel Ethyl o- Amino Phenyl acetate (10gm) in ethanol (30ml) was heated with hydrazine hydrate (5ml-90%) under reflux for three hours, when a homogenous mixture was obtained. The volume of the solution was reduced to half. On cooling this solution, yellowish white solid was separated which was collected by filtration. Re-crystallisation of the solid from methanol furnished pure o-Amino pnenylacethydrazide (9 gm) as a yellowish white crystals m.pt.-124°C

Analysis

Found	N-25.15%
Calculated for $C_8H_{11}N_3O$	N-25.45%

Preparation of 3-hydroxy-1, 4- dihydrocinnoline

(The condensation was done under the variety of conditions)

(A) DIRECT ON HEATING

O- Amino pnenylacethydrazide (0.5 gm) in methanol was heated under reflux for ten hour and then set aside at room temperature overnight. The yellow solid separated out from reaction mixture was triturated with dilHcl washed with sodium bicarbonate solution and then with water. The solid was then rectystallised from ethanol to furnish the pure 3- hydroxy- 1,4 dishydrocinnoline (0.35 gm) m.p. 149^0C.

Analysis

Found	N- 18.80%
Calculated for $C_8H_8N_2O$	N-18.91%

(B) WITH DRY HYDROGEN CHLORIDE GAS

O- Amino phenylacethydrazide (0.5 gm) in methanol (5 ml) were heated on a water bath. A steady current of dry Hydrogen Chloride gas was passed for nearly three hours when reaction was shown to be complete by T.L.C. examination. The reaction mixture was left at room temperature overnight. Next day the separated solid was triturated with Benzene and ethanol and then rectystallised from ethanol to furnished deep yellow crystal of the pure 3-hydroxy- 1,4, - dihydrocinnoline (0.75 gm) m.p. 149^0C

Analysis

Found	N-18.75%
Calculated for $C_8H_8N_20$	N-18.91%

I.R. STRETCHING FREQUENCIES

KBr	1580 cm^{-1} for C=N stretching frequency
V_{max}	1605 cm^{-1} for substituted Benzene ring
	3250 cm^{-1} for –NH- stretching frequency
	1420 cm^{-1} - C- OH grouping

N.M.R. Spectrum

The N.M.R. Specturm of the compound had adsorption for three sets of protons. The nine-aromatic protons had resonance (multiplet) at delta 7.3 singlet corresponding to two protons at delta 2.7 due to benzylic $–CH_2$- group and a singlet for one proton at delta 4.3 for the – NH-NH-grouping and at 7.8 for –C-OH group

(C) WITH PERCHLORIC ACID

A mixture of o- Amino phenylacethydrazide (0.5 gm) perchloric acid (1ml) and methanol (5 ml) were heated on water bath under reflux for six hours and then set aside at room temperature overnight. Yellow brown solid separating from the reaction mixture was triturated with aqueous sodium bicarbonate solution washed with ice cold water and then re-crystallised from ethanol to furnish pure 3- hydroxy – 1, 4- dihydrocinnoline (0.65 gm) m.p. and mixed m.p.- 149^0C

Analysis

Found	N-18.60%
Calculated for $C_8H_8N_2O$	N-18.91%

I.R. STRETCHING FREQUENCIES

KBr	1585 cm^{-1} for C=N stretching frequency
V_{max}	1605 cm^{-1} for substituted Benzene ring
	3240 cm^{-1} –NH- stretching frequency
	1420 cm^{-1} –C-OH grouping

N.M.R. Spectrum

The N.M.R. Spectrum of the compound had adsorption for three sets of protons. The nine aromatic protons had resonance (multiplet at delta 7.3 singlet corresponding to two protons at delta 2.7 due to benzylic –CH_2- group and a singlet for one proton at delta 4.3 for the –NH-NH-grouping and at delta 7.8 for –C-OH group

(D) WITH PHOSPHORUS PENTOXIDE

o- Amionphenylacethydrazide (0.5 gm) methanol (5 ml) and phosphorus pentoxide (0.02 gm) in carbon tetrachloride were heated on a water bath for nearly six hours, when reaction was shown to be complete by T.L.C. examination. The reaction mixture was left at room temperature overnight. The separated solid was triturated with Benzene and methanol and then recrystallised from ethanol to furnished yellow crystal of the pure 3- hydroxy – 1, 4 dihydrocinnoline (0.75 gm) m.p and mixed m.p 149 – 150^oC

Found	N-19.15%
Calculated for $C_8H_8N_2O$	**N-18.91%**

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