

## Reaction of 1,5-Disubstituted-indoline-2,3-dione with Aroylhydrazines

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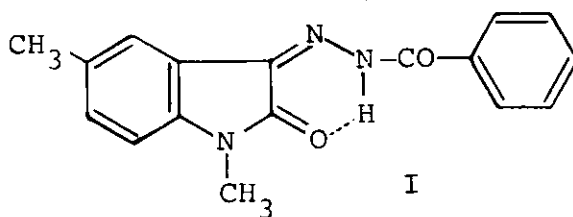
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**Summary:** 1,5-Dimethyl-indoline-2,3-dione when treated under various conditions with benzoyl hydrazine yields 1,5-dimethyl-3-(benzoylhydrazono)-indolin-2-one. Spectral data of hydrazone and its benzoyl/acetyl derivative indicate that there is an intramolecular hydrogen bonding in I between the imino proton of hydrazone residue and the C-2 carbonyl group.

El Ashry and co-workers have recently demonstrated<sup>1</sup> that camphoroquinone benzoyl hydrazine exhibits intramolecular hydrogen bonding between the imino proton of the hydrazone residue and the carbonyl group. This demonstration was in consistency with the earlier observation<sup>2</sup> that monoaryl hydrazones of  $\alpha$ -dicarbonyl compounds exhibit intramolecular hydrogen bonding between imino proton and carbonyl group. In this communication an extension of this work to further study the hydrogen bonding in different  $\alpha$ -dicarbonyl compounds. 1,5-dimethyl-3-(benzoylhydrazono)-indoline-2-One (I) is undertaken.

1,5-Dimethyl-3-(benzoyl hydrazono)-indoline-2-one was prepared by the reaction of 1,5-dimethyl-3-hydrazono-indoline-2-one with benzoyl chloride. Reaction of 1,5-dimethyl-indoline-2,3-dione with benzoylhydrazine, under normal condition for the preparation of bis (benzoylhydrazones), afforded the corresponding mono benzoylhydrazone and not the bis-hydrazone derivative. The spectral and elemental analyses proved the structure of indolinone hydrazone to be I.

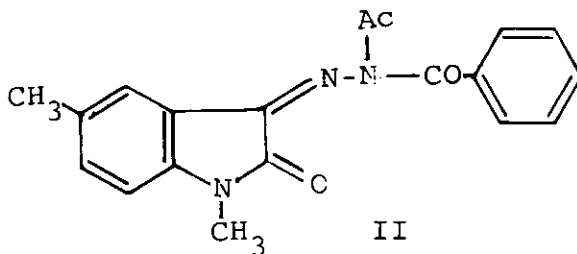
The C-2 carbonyl of 1,5-dimethyl indoline-2,3-dione is less reactive than the normal carbonyl compounds. Condensation of 1,5-dimethyl-3-(benzoyl hydrazono)-indoline-2-one with hydrazine hydrate proceeds, only in a high boiling protic solvent such as isopropyl alcohol containing a drop of conc.  $H_2SO_4$ , and may be attributed to the steric hinderance of the methyl group at C-1.



This is due to the hydrogen bonding expected in monohydrazones of 1,2-dicarbonyl compounds.

The PMR spectrum (chemical shift in  $\delta$  ppm) of 1,5-dimethyl-3-(benzoylhydrazono)-indoline-2-one showed two singlets of three protons intensity each at 2.35 and 3.09 due to the C-5-methyl group and N-methyl group is deshielded by the electron density of the nitrogen atom which is drifted towards the C-2 carbonyl group. The NH proton appeared at  $\delta$  11.80 (a higher value than expected for amide) due to its involvement in hydrogen bonding. The aromatic protons appeared as a multiplet at  $\delta$  6.84 – 7.42.

Benzoylation of I with benzoyl chloride in pyridine afforded the corresponding monobenzoyl derivative (II,  $R=C_6H_5CO$ ). Acetylation of I with acetic anhydride afforded similarly, the monoacetyl derivative (II,  $R=CH_3CO$ ). The IR spectrum of the



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acetyl derivative showed bands at 1640 (C=N), 1670 (OCH) and 1755  $\text{cm}^{-1}$  (CO). The  $\nu$  CO band appeared at a higher frequency in the acetylated derivative (II) than in monohydrazone (I), which is anticipated if hydrogen bonding is present in I.

The reactivity of compound I towards  $\text{Ac}_2\text{O}$  can be attributed to the hydrogen bonding of the imino proton which enhances the nucleophilicity of the nitrogen of the imino group involved in the hydrogen bonding. The hydrogen bonding would weaken the covalent N-H bond and render the nitrogen more nucleophilic. Furthermore, hydrogen bonding may stabilise an intermediate in the reaction.

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