

A Reinvestigation of the Reaction Between Dibenzoylethylene and Orthophenylenediamine

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The synthesis of compounds containing 1,4-diazocine ring I has been an elusive goal of many researchers (1,2). Most attempts, involving the condensation of 1,4-dicarbonyl compounds and 1,2-diamines, have resulted instead in formation of imidazoles, *via* phenyl or hydrogen shifts (3). For example, Ried and Lantzsch's recently reported reaction of the *cis*-dibenzoylstilbene II with *o*-phenylenediamine afforded the benzimidazole IV and not benzodiazocine V (4).

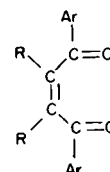
Shevchuk, Tolochko, and Dombrovskii recently investigated the condensation of *trans*-dibenzoyl ethylenes with *o*-phenylenediamine and reported the formation of benzodiazocines VI, presumably *via* the *cis*-dibenzoyl ethylenes (5). In a typical reaction, the *trans*-isomer of III reacted with diamine to give a pale yellow fluorescing solid that was assigned structure VII. A partial ir spectrum, a uv spectrum and percent nitrogen was reported.

Because of the well-documented inaccessibility of 1,4-diazocines (*vide supra*), the reported synthesis of VII was viewed with interest, and the reaction was repeated. A solution of *trans*-dibenzoyl ethylene and *o*-phenylenediamine in glacial acetic acid was refluxed for 10-15 minutes. The cooled dark solution was diluted with water, whereupon a red-orange solid precipitated. Thin-layer chromatography (tlc) of this material showed the presence of several components. Elution with benzene on a silica gel column separated the crude product into two fractions. The first, a pale-yellow fluorescing solid (*A*), was shown to be homogeneous by tlc. The second, a red-orange material (*B*), gave several spots on tlc. Compound *A* was further purified by recrystallization from absolute ethanol. The melting point (204-205°) and uv spectrum, λ_{max} (ethanol) 301 nm, were virtually identical to that reported for VII. However, further examination of *A* led to the conclusion that the assignment of structure VII for this compound was incorrect. The ir spectrum for VII was reported only in the range 700-1600 cm^{-1} . In this region, the spectrum (potassium bromide) of compound *A* was identical to that of VII. The spectrum of *A* evinced, in addition, two bands at *ca.* 3400 cm^{-1} , a finding clearly inconsistent with VII. No nmr spectrum was reported for VII. The spectrum of *A* (60 MHz, dms O-d_6) dis-

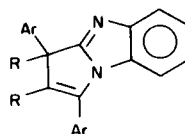
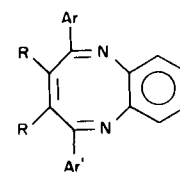
played a multiplet at δ 6.60-7.42 ppm (14H), a singlet at δ 6.55 ppm (2H), and a singlet at δ 4.61 ppm (2H), the latter resonance collapsing upon shaking the sample with deuterium oxide. The nmr spectrum is also at variance with the benzodiazocine structure VII. The mass spectrum of *A* showed a molecular ion at *m/e* 310, not 308, as expected for VII.



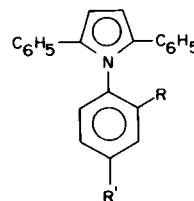
I



II R = C₆H₅, Ar = C₆H₄-OCH₃ (p)
III R = H, Ar = C₆H₅

IV R = C₆H₅, Ar = C₆H₄-OCH₃ (p)

V R = C₆H₅, Ar = Ar' = C₆H₄-OCH₃ (p)
VI R = H, Ar = C₆H₅, Ar' = C₆H₄-G (p)
(G = CH₃, OCH₃, Cl, Br, C₁₀H₇)
VII Ar = Ar' = C₆H₅, R = H



VIII R = NH₂, R' = H
IX R = R' = H
X R = H, R' = NH₂

In light of the above observations, Shevchuk, Tolochko, and Dombrovskii's assignment of structure VII for the condensation product of the *trans*-isomer of dibenzoyl-ethylene III and *o*-phenylenediamine is rejected in favor of 1-(2-aminophenyl)-2,5-diphenylpyrrole (VIII). This seems reasonable on chemical and spectroscopic grounds. The Paal-Knorr synthesis of substituted pyrroles from 1,4-diketones and primary amines is well known (6). Phenylated pyrroles such as IX and similar compounds are known to fluoresce. For example, X finds use as an optical brightener (7). The uv λ max of VIII is virtually identical to that of IX (8). The protons in VIII have an nmr chemical shift in the same range as those in other pyrroles (9). The mass spectral fragmentation is also consistent with VIII, showing, in addition to the molecular ion m/e 310, significant peaks at m/e 233, 206, 116, 115, and 65.

The fact that the compound obtained by Shevchuk and co-workers is not benzodiazocine VII is certainly consistent with previous experience (1,3,4). However, VIII comprises only a fraction of the isolable reaction product. The separation and analysis of the other products (*B*) is currently under investigation.

EXPERIMENTAL

1-(2-Aminophenyl)-2,5-diphenylpyrrole (VIII).

A solution of 11.80 g. (0.05 mole) of *trans*-dibenzoyl-ethylene (Aldrich Chemical Co.) and 5.40 g. (0.05 mole) of *o*-phenylenediamine in 100 ml. of glacial acetic acid was refluxed for 15 minutes (5). The resulting dark red reaction mixture was cooled and diluted with water, whereupon 4.50 g. of red-orange solid precipitated. The crude product showed several spots on silica gel

tlc, including one of relatively high R_f and several overlapping spots of lower R_f . The mixture was chromatographed on a silica gel column. Elution with benzene afforded two fractions, *A* and *B*. The first (*A*) yielded 0.90 g. of pale yellow fluorescing solid, shown to be homogeneous by tlc. An analytical sample of colorless product, prepared by recrystallization from absolute ethanol, melted at 204-205°. The spectroscopic data (*vide supra*) was consistent with the assignment of 1-(2-aminophenyl)-2,5-diphenylpyrrole (VIII) as the structure of compound *A*. Fraction *B* showed at least three overlapping spots on tlc. Attempts to separate this material have so far been unsuccessful.

Anal. Calcd. for $C_{22}H_{18}N_2$: C, 85.13; H, 5.84; N, 9.02. Found: C, 84.84; H, 5.89; N, 8.94.

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