

The Reaction of *o*-Phenylenediamine with 1,2-Dibenzoylethylene

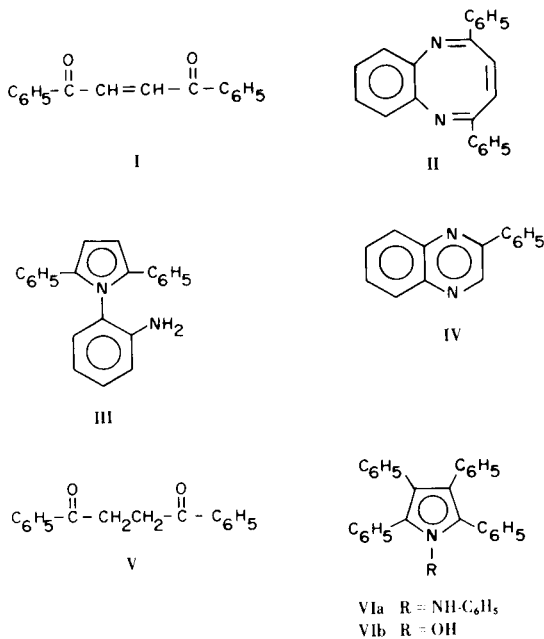
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Sir:

We recently reported (1) that the condensation of 1,2-dibenzoylethylene (I) with *o*-phenylenediamine gave several compounds, one of which was not the diazocine II, as had been previously claimed (2), but the triphenylpyrrole III. We now wish to report the isolation and characterization of the remaining reaction products.



As previously communicated, the reaction of 0.05 mole of I and *o*-phenylenediamine in refluxing acetic acid afforded 0.9 g. of pyrrole (III), plus 4.5 g. of a red-orange material shown to be heterogeneous by tlc. This mixture was chromatographed on neutral alumina, the eluent being changed gradually from carbon tetrachloride to benzene to chloroform. The compounds eluted were 2-phenylquinoxaline (IV, 0.8 g.) and 1,4-diphenyl-1,4-butanedione (V, 0.2 g.) (3). The structural assignments were based on physical and spectroscopic data and comparison of this data with that of authentic materials.

The nmr and ir spectra of V were identical to that reported in the literature (4). Compound IV was further

purified by sublimation.

The nmr spectrum of IV showed a singlet at  $\delta$  9.20 ppm [1H] and a pair of multiplets at  $\delta$  8.10 and 7.50 ppm [9H]. The mass spectrum showed a molecular ion at  $m/e$  206 plus peaks at  $m/e$  179, 152, 103 and 77.

The melting point, nmr, mass and infrared spectra were identical to that obtained from a sample prepared by the method of Figueras (5).

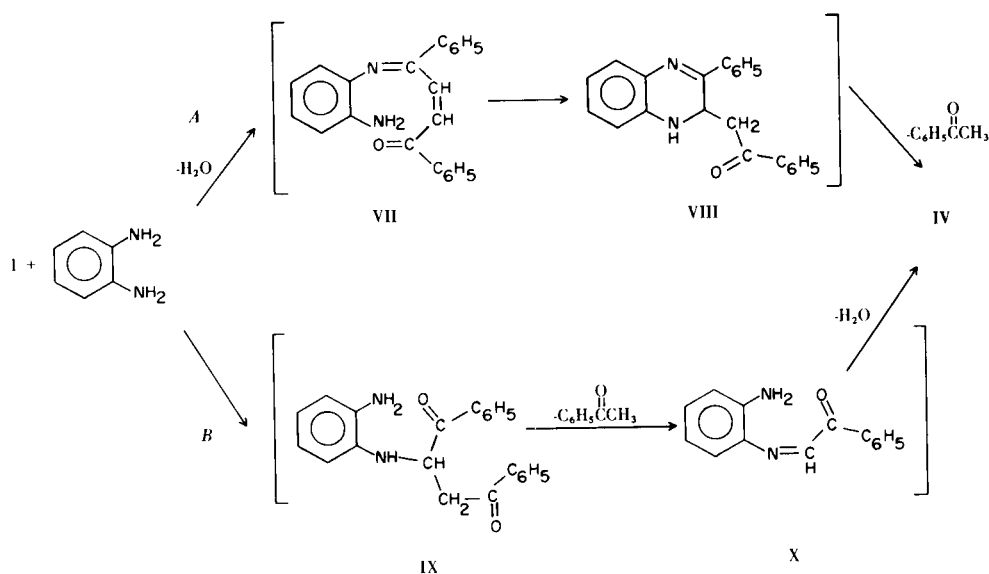
The presence of V, albeit in very small amounts, lends support to the idea that the pyrrole III is formed by Paal-Knorr condensation of *o*-phenylenediamine and V<sup>6</sup>, the latter being formed from I *via* oxidation-reduction, perhaps involving *o*-phenylenediamine. A similar reaction was recently reported by Ried and Lantzsch (7), who found that (*Z*)-dibenzoylstilbene condensed with phenylhydrazine and hydroxylamine in acetic acid to give pyrroles VIa and VIb, respectively.

The formation of 2-phenylquinoxaline was unexpected. For example, *o*-phenylenediamine was shown to react with dibenzoylstilbene to give a benzimidazole (7). Similar results have been found with analogous reactions (8). The presence of IV is rationalized by the sequences A and B.

Path A involves (a) formation of imine VII, (b) Michael-type addition to give the dihydroquinoxaline VIII, (c) retro-aldol reaction to give IV and acetophenone. Path B consists of (a) Michael-type addition to give diketodiamine IX, (b) retro-aldol reaction to give imine X plus acetophenone, (c) ring closure to give IV.

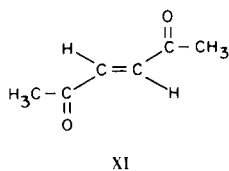
The following facts support these mechanisms: (1) acetophenone was found in the mother liquors obtained when the initial solid reaction product was filtered off. The amount of acetophenone was estimated by vpc, to be 2.1 g.; (2) vpc indicated the absence of any acetophenone or phenylglyoxal in the starting material I. The absence of phenylglyoxal is significant since it has been shown to condense with *o*-phenylenediamine to give IV (9); (3) Dibenzoylethylene alone under reaction conditions did not produce any acetophenone or phenylglyoxal.

The presence of acetophenone in much greater quantity than quinoxaline IV rules out path A as the exclusive



mechanism for formation of IV. Although IV was stable under reaction conditions, X would probably undergo intermolecular condensations, accounting for the relatively small amount of IV. The reaction therefore most likely either proceeds solely *via* path B or *via* both routes, path B being the predominant one.

Reactions of this type may occur in other related condensations (10, 11). Diacetone alcohol was detected as a byproduct in the reaction of hydrazine with (*E*)-1,2-diacetylene XI (11). We are currently seeking more details on the mechanism of formation of III and IV.



#### Acknowledgements.

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