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ORGANIC REDOX REACTIONS DURING THE INTERACTION OF o-PHENYLENEDIAMINE WITH BENZALDEHYDE

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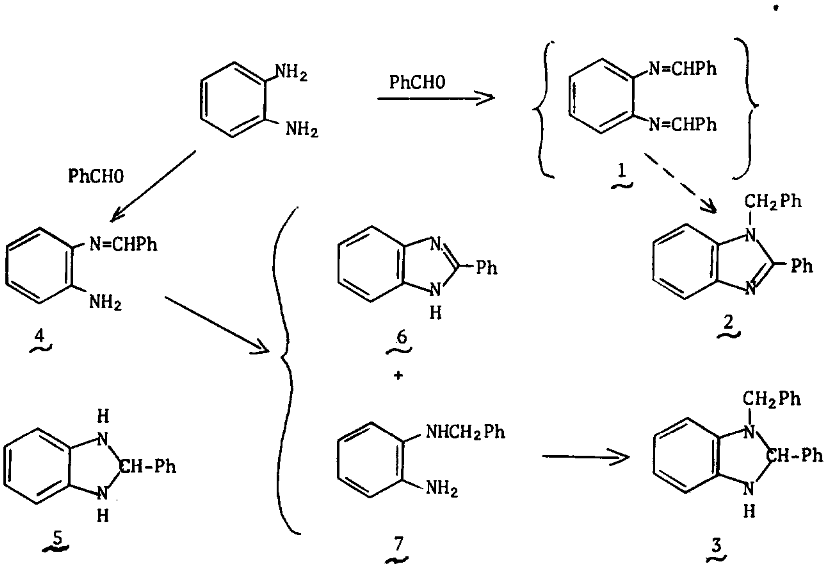
Our interest in the interaction of unsaturated nitrogen-containing compounds with alkali metals (1,2) has recently prompted us to prepare N,N'-dibenzal-o-phenylenediamine, **1**. Following the only reported preparation of **1** (3) provided the material (mp 112°) which has been accepted as **1**. However, its spectroscopic properties (4) clearly indicated that it cannot have this structure. The ir spectrum showed absorption due to an NH group and the nmr spectrum showed no signal characteristic of a methine proton but did show three distinct signals due to aliphatic protons.

Thin layer chromatography (5) showed that the substance consisted of two components. Separation of these by column chromatography (5) established that one component was 1-benzyl-2-phenylbenzimidazole, **2**, while the other, an oil, was assigned the structure 1-benzyl-2-phenylimidazoline, **3**. This assignement was based on the nmr spectrum (6) and on the rapid partial oxidation of **3** to **2** as indicated by the reversion of **3** to the 112° material on exposure to air. The original 112° material was then a 1:1 molecular complex of **2** and **3** (7) and, indeed, it could be produced by the reduction of **2** with lithium aluminium hydride.

Scheme 1 suggests a means whereby the complex can arise and is based on a number of observations made during attempts to obtain **1** by this reaction. Benzaldehyde and o-phenylenediamine reacted rapidly at -20° to produce N-benzal-o-phenylenediamine, **4**. This was indicated by the appearance of a methine signal at δ8.50 in the nmr spectrum of the reacting mixture and by the isolation of a 84% yield of **4**. Warming the mixture to room temperature resulted in the formation of a 19% yield of 2-phenylbenzimidazole, **6** (8) and the appearance of a second methine signal at δ8.42. After several days at room temperature, the reaction mixture contained **6** and the molecular complex of **2** and **3**.

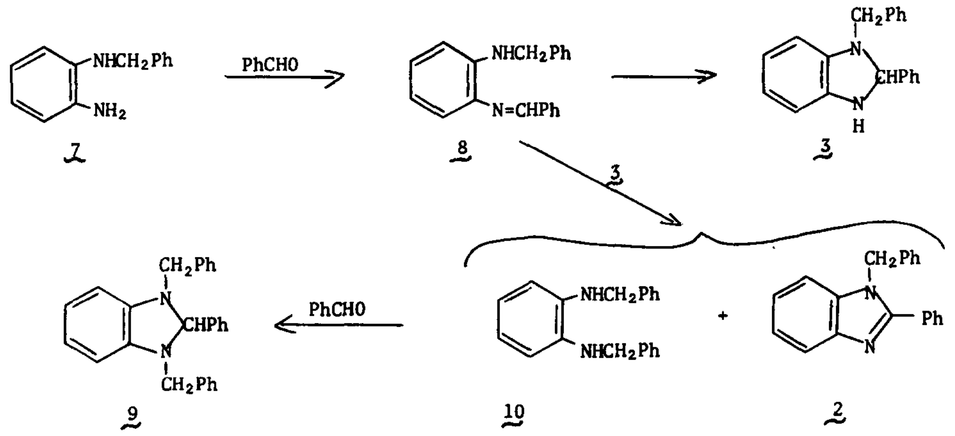


Scheme 1 Reaction of o-Phenylenediamine with Benzaldehyde

It is tempting to attribute the second methine proton signal at δ8.42 to the formation of 1. Indeed, this same signal is observed in the nmr spectrum of a reacting mixture of benzaldehyde and 4. However, from this last reaction only the complex of 2 and 3 could be isolated and it is equally probable that the signal could be due to N-benzal-N'-benzyl-o-phenylenediamine, 8 (vide infra).

The formation of 6 represents an oxidation of its precursor 4 (or more likely 5) and it is suggested that the compensating reduction is that of 4 to N-benzyl-o-phenylenediamine, 7. Further reaction of 7 with benzaldehyde probably via the N-benzal-N'-benzyl-o-phenylenediamine 8 provides 3. The observed 2 can come from two sources - either through the formation and cyclization of the dibenzal derivative 1 or through the imidazoline derivative 3 acting as a reducing agent to convert 4 to 7.

In support of this we have examined the reaction of 7 (9) with benzaldehyde (Scheme 2). The nmr spectrum of the reacting mixture showed the rapid formation of 8 (methine proton at δ8.42). Isolation of the products showed that the benzimidazoline derivative 3 was formed but again it was obtained as the molecular complex of 2 and 3. Accompanying this product was a 20% yield of 1,3-dibenzyl-2-phenylbenzimidazoline, 9. Since this last compound is known (10), to



Scheme 2. Reaction of Benzaldehyde and N-Benzyl-o-phenylenediamine

form rapidly from benzaldehyde and N,N'-dibenzyl-o-phenylenediamine, 10, it seems obvious that 9 was produced through reduction of the initially formed N-benzal-N'-benzyl derivative 8 by the product 3.

The superficially simple reaction of o-phenylenediamine and its derivatives with benzaldehyde is thus a complex sequence of competing reactions. In addition to the reactions resulting in imine formation, cyclizations of the imines to benzimidazolines occur and these can act as reducing agents towards the imines with concomitant oxidation to benzimidazoles. The N,N'-dibenzal-o-phenylenediamine, 1, if formed at all, appears to be a reactive transient species.

References

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4. ir (KBr) 3260 (NH), 1610 cm^{-1}(C=N): nmr (C_6D_6) δ, 3.91, 4.31 (q, J=15Hz, 3H, $PhCH_2$ of 3 + NH), 5.40 (S, 2H, $PhCH_2$ of 2), 5.80 (S, 1H, PhCH of 3), 6.5-8.0(m, 28H, aromatics); Anal. calcd for $C_{40}H_{34}N_4$: C,84.17; H,6.00; N,9.82. Found, C,84.37; H,6.01; N,9.68.
5. Thin-layer chromatography was carried out using Eastman Chromagram Sheet 6060 (silica gel with fluorescent indicator) with benzene as developing solvent. For column chromatography, silica gel (70-325 mesh A.S.T.M.) purchased from E. Merck (Germany) was utilized.

6. ir (film) 3400 cm^{-1} (NH); nmr (C_6D_6) δ, 3.91, 4.31 (q, J=15 Hz, 3H, Ph$\underline{CH_2}$ and NH), 5.80 (s, 1H, PhC$\underline{H}$<), 6.5-8.0 (m, 14H, aromatics).

7. We suggest a molecular complex rather than a eutectic composition since the latter would fail to explain the stability of **3** when associated with **2**. The ir spectrum of the complex showed a marked shift of the NH absorption which would support this suggestion.

8. The formation of **6** from o-phenylenediamine and benzaldehyde using more stringent reaction conditions has been reported by others. E. Mueller and R. Haller, Arzneim.-Forsch., **17**, 55 (1967). N. V. Subba Rao and C. V. Ratman, Proc. Indian Acad. Sci., **43A**, 173 (1956).

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