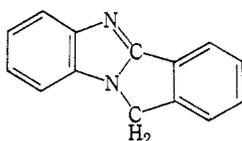


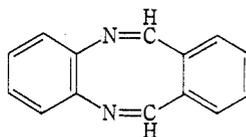
***o*-BENZYLENE-2,1-BENZIMIDAZOLE: THE CONDENSATION PRODUCT OF *o*-PHENYLENEDIAMINE AND *o*-PHTHALALDEHYDE\***

By D. AMOS† and R. G. GILLIS†

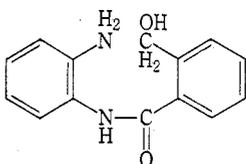
*o*-Phenylenediamine and *o*-phthalaldehyde were first condensed by Thiele and Falk<sup>1</sup> who obtained a substance (A), C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>. They assigned to it structure (I),‡ rather than the isomeric double Schiff's base structure (II). This assignment was supported by the synthesis of (A) by Bistrzycki and Schmutz<sup>2</sup> by fusion of phthalide



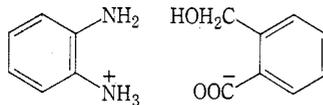
(I)



(II)



(III)



(IV)

with *o*-phenylenediamine hydrochloride. Apparently unaware of the work of Bistrzycki and Schmutz, Betrabet and Chakravarti<sup>3</sup> claimed to have prepared the amide (III) from phthalide and phenylenediamine, and from the salt (IV) of phenylenediamine and *o*-hydroxymethylbenzoic acid, and to have dehydrated (III) to a compound (B) C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>. They concluded that (B) had structure (I) and that Thiele and Falk's compound (A) must have structure (II).

We have been unable to repeat the work of Betrabet and Chakravarti. Phenylenediamine and phthalide gave only starting materials when shaken or refluxed in ethanol, alone or with acid or base catalyst. On refluxing the salt (III), only phenylenediamine and phthalide were isolated.

However, we have repeated the condensation of phenylenediamine and phthalaldehyde, and obtained compound (A). Its ultraviolet and proton magnetic resonance spectra leave no doubt that it has structure (I) in agreement with the

\* Manuscript received July 13, 1964.

† Defence Standards Laboratories, Department of Supply, Maribyrnong, Vic.

‡ Revised Ring Index No. 4174, 11*H*-isoindolo[2,1-*a*]benzimidazole, *o*-benzylene-2,1-benzimidazole.

<sup>1</sup> Thiele, J., and Falk, K. G., *Liebigs Ann.*, 1906, **347**, 112.

<sup>2</sup> Bistrzycki, A., and Schmutz, W., *Liebigs Ann.*, 1918, **415**, 1.

<sup>3</sup> Betrabet, M. V., and Chakravarti, G. C., *J. Indian Chem. Soc.*, 1930, **7**, 495.

assignment of Thiele and Falk, and of Bistrzycki and Schmutz on chemical grounds. In its ultraviolet spectrum, maxima were found at 208, 244, 252, and 309  $m\mu$  ( $\epsilon$  75,600, 16,400, 15,600, and 25,600). The spectrum was very similar to that of 1-benzyl-2-phenylbenzimidazole in which maxima occurred at 205, 240, and 297  $m\mu$  ( $\epsilon$  59,500, 13,700, and 17,100) and unlike that of benzylideneaniline in which there are maxima at 200 and 258  $m\mu$  ( $\epsilon$  34,700 and 12,400).

The proton magnetic resonance spectrum of (A) showed a complex absorption centred at  $\tau$  2.0 equivalent to two (aromatic) protons, another complex band at  $\tau$  2.6 equivalent to six (aromatic) protons and a single absorption at  $\tau$  5.15 equivalent to two (aliphatic) protons. The methylene protons in 1-benzyl-2-phenylbenzimidazole absorb at  $\tau$  4.55 and the azomethine proton in benzylideneaniline absorbs at  $\tau$  1.53. The p.m.r. spectrum of (A) is therefore compatible with structure (I) but not with structure (II), for which the azomethine protons might be expected to have a  $\tau$  value between 1 and 2.

Betrabet and Chakravarti began their investigation because they were unable to envisage a mechanism by which (I) is formed from phthalaldehyde. This reaction is simply a special case of Ladenberg's "aldehydine" synthesis.<sup>4</sup> It incorporates a hydrogen transfer, and a different example involving an azomethine system<sup>5</sup> has already been recognized.<sup>6</sup>

Our failure to repeat the work of Betrabet and Chakravarti (together with the conditions under which Bistrzycki and Schmutz found that phthalide and phenylenediamine gave (I)) indicates that phthalide is not an intermediate in the formation of (I) from phenylenediamine and phthalaldehyde.

### Experimental

Microanalyses were performed by the Australian Microanalytical Service, Melbourne. Infrared spectra were determined with a Beckman IR8 spectrophotometer, proton magnetic resonance spectra were determined in deuteriochloroform solution with a Varian A60 instrument. Melting points were uncorrected. Recovered starting materials were identified by melting point and mixed melting point.

Phthalide and *o*-phenylenediamine were B.D.H. reagent grade and phthalaldehyde was from Light & Co. Ltd.

*o*-Hydroxymethylbenzoic acid was prepared from phthalide by refluxing for 3 hr with one equivalent of aqueous sodium hydroxide solution. The reaction mixture was cooled and added slowly with stirring to an excess of ice-cold hydrochloric acid. The precipitated acid was collected by filtration, washed with water, and vacuum-dried at room temperature; m.p. 116–117° (lit.<sup>7</sup> 120.5–121.5°).

### 1-Benzyl-2-phenylbenzimidazole

This compound was prepared according to Ladenburg and Engelbrecht.<sup>8</sup> It was crystallized from aqueous ethanol and formed colourless needles; m.p. 132–133°.

<sup>4</sup> Hofmann, K., "Imidazole and its Derivatives." Part I, pp. 267–70. (Interscience: New York 1953.)

<sup>5</sup> Angyal, S. J., and Rassack, R. C., *J. Chem. Soc.*, 1949, 2700.

<sup>6</sup> Jackman, L. M., *Adv. Org. Chem.*, 1960, **2**, 329.

<sup>7</sup> Gilman, H., Brown, G. E., Webb, F. J., and Spatz, S. M., *J. Amer. Chem. Soc.*, 1940, **62**, 977.

<sup>8</sup> Ladenburg, A., and Engelbrecht, T., *Ber. dt. chem. Ges.*, 1878, **11**, 1653.

*o-Benzylene-2,1-benzimidazole*

This compound was prepared according to Thiele and Falk.<sup>1</sup> Crystallization from aqueous ethanol gave colourless crystals of *o*-benzylene-2,1-benzimidazole (I), m.p. 215° (lit.<sup>1</sup> m.p. 210°) (Found: C, 81.25; H, 4.8; N, 13.3%. Calc. for (C<sub>7</sub>H<sub>5</sub>N)<sub>n</sub>: C, 81.5; H, 4.9; N, 13.6%). Mol. wt. by mass spectrometer, 206.

*Preparation of Compound (IV)*

*o*-Phenylenediamine (10.8 g, 0.1 mole) and *o*-hydroxymethylbenzoic acid (15.2 g, 0.1 mole) were gently agitated in absolute ethanol (250 ml) at room temperature. After several hours the clear solution was reduced to half its volume in a rotary evaporator and was finally chilled. The precipitated salt was collected by filtration; yield 13.9 g (53%). An analytical sample recrystallized from a minimum amount of ethanol had m.p. 101–103° (Betrabet and Chakravarti<sup>3</sup> report m.p. 103–104°) (Found: C, 64.6; H, 6.1; N, 10.8%. Calc. for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: C, 64.6; H, 6.2; N, 11.0%).

The infrared spectrum (Nujol mull) showed a strong band at 1350 cm<sup>-1</sup> and a strong doublet at 1580 and 1590 cm<sup>-1</sup> which can be assigned to the symmetric and asymmetric stretching of the carboxylate ion. There was no indication of free carboxylic acid in the mull, but the spectrum of a melt showed a very strong band at 1470 cm<sup>-1</sup>. The salt was very soluble in water.

*Attempted Preparation of Compound (III)*

Phthalide (0.01 mole) and *o*-phenylenediamine (0.01 mole) were refluxed in ethanol (5 ml) for 3 hr, (i) without catalyst, (ii) with the addition of concentrated hydrochloric acid (0.1 ml), and (iii) with the addition of tributylamine (1 ml). The same quantities were also shaken for 8 hr at room temperature. In each case only starting material was recovered.

*o*-Hydroxymethylbenzoic acid (0.01 mole) and phenylenediamine (0.01 mole) when refluxed in ethanol (7 ml) for 3 hr gave phthalide and *o*-phenylenediamine. Under the same conditions, the salt (IV) also gave these products.

*Acknowledgments*

The authors are indebted to Dr. D. H. S. Horn for the p.m.r. spectra, and to Professor L. M. Jackman for helpful discussion.

This paper is published with the permission of the Chief Scientist, Australian Defence Scientific Service, Department of Supply, Melbourne.