A REVISION OF THE STRUCTURE OF "7-PHENYLOXINDOLE"; PHOTOCHEMICAL SYNTHESIS AND PYROLYTIC BEHAVIOUR OF AUTHENTIC 7-PHENYLOXINDOLE

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We required 7-phenyloxindole (I) for an extension of our work on the generation of aryl nitrenes by the high temperature pyrolysis of oxindoles.¹ The Stollé cyclization of the chloroacetyl derivative of 2-aminobiphenyl with aluminium chloride was reported^{2,3} to give 7-phenyl-oxindole, m.p. 231⁰.

A suspicion that this compound was <u>not</u> 7-phenyloxindole was roused by the following observations: (i) It was little decomposed on attempted decarbonylation in a flow system at $850^{\circ}/0.1$ mm. (ii) It failed to condense with methyl oxalate/sodium methoxide. (iii) It resisted oxidation with SeO₂ in refluxing glacial acetic acid. Oxindole itself reacted readily in all three cases. A survey of the literature showed that the m.p. of the supposed 7-phenyloxindole (231°) was nearly the same as that ($231-233^{\circ}$) of 5H-dibenz[b,d]azepin-6, (7H) one (II), the product of the alternative cyclization process, which had been prepared by an unambiguous route⁴ from 2'-nitrobiphenyl-2-acetic ester (III).

Direct comparison of the supposed "7-phenyloxindole" with a sample of dibenzazepinone (II) prepared from (III) showed that they were identical as judged by m.p.'s and mixed m.p.'s,t.l.c. behaviour, and the identity of the i.r. and u.v. spectra. It should be noted that a compound of rather similar m.p., 233-235°, which is erroneously shown as having structure II in <u>Chemical Abstracts</u>⁵, is actually the homologous dibenzazocinone.⁶



Because other conventional routes to authentic 7-phenyloxindole appeared to be either tedious or ambiguous, we resorted to photochemical phenylation of a pre-formed oxindole system by the method of Kharasch.⁷ o-Iodoaniline was converted via condensation with chloral and hydroxylamine to 7-iodoisatin,⁸ which was reduced <u>via</u> the hydrazone⁹ to <u>7-iodo-oxindole</u>(IV), m.p. 219-220⁰ (Found: C, 36.79; H, 2.38; I, 49.2. C_8H_6NOI requires C, 37.09; H, 2.34; I, 48.99%), v_{max} 1695 cm⁻¹. Mass spectrum: M⁺ 259 (base peak).

A degassed solution of 7-iodo-oxindole (1.0 g) in benzene (300 ml.) was irradiated through silica with a carousel array of 15 x 8 watt 254 nm lamps for 18 hours at room temperature. The resulting dark benzene solution was washed with aqueous bisulphite to remove iodine, dried, and evaporated. Recrystallization of the crude product from acetone/light petroleum gave 7-phenyloxindole as pale yellow needles, m. p. $170-3^{\circ}$ (375 mg., 46%). A sample was recrystallized from CHCl₃/petrol and sublimed at $150^{\circ}/0.1$ m. m. for analysis as a colourless solid, m. p. $172-3^{\circ}$. (Found: C, 80.59; H, 5.09; N, 6.53. $C_{14}H_{11}$ NO requires C, 80.36; H, 5.30; N, 6.69%), v_{max} 1695 cm⁻¹. NMR (CDCl₃): δ 3.58, s, 2H(CH₂); 7.0-7.4, m, 3H (aromatic);



The structure of 7-phenyloxindole produced by this photochemical route was confirmed by its behaviour on pyrolysis at $850^{\circ}/0.2$ m.m. in a flow system. The major products were 1-methyl carbazole(V) (43%) and carbazole (11%), the latter apparently formed by pyrolytic demethylation of the former. The formation of carbazoles¹⁰ lends strong support to the involvement of singlet nitrenes¹¹ as intermediates in the pyrolysis of oxindoles, and confirms the introduction of the phenyl group specifically at C-7.



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