Isoindole

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Summary Isoindole has been obtained as a white solid on a surface at *ca.* 77 K following pyrolysis of 2-(methoxycarbonyloxy)isoindoline in a silica tube at 500° and 0·01 mmHg; chemical reactions and spectroscopic data are reported: the solid decomposes rather rapidly at room temperature.

ALTHOUGH substituted isoindoles have become well known in recent years,[1] the parent (I) has remained elusive. The Communication[2] by Kreher and Seubert that it could be trapped in solution as a Diels-Alder adduct has been the one report of partial success during a long period of experimentation.[3,4] Preliminary experiments[5,6] in which 2-tosylisoindoline was treated with potassium t-butoxide in dimethyl sulphoxide gave low yields of a yellowish solid which was recognised as crude isoindole, and which rapidly resinified and blackened. In view of these difficulties we sought to avoid a wet method, and have developed a pyrolytic process which gives (I) accompanied by CO_2 and MeOH.

The isoindoline (II), prepared by treating 2-hydroxyisoindoline[6,7] with methyl *p*-nitrophenyl carbonate,[8] was sublimed from a Pyrex tube at 50—70° at *ca.* 0·01 mmHg through an empty silica tube (300 mm, 20 mm diam.) at 500° ± 20°. The products were collected in a depression on a cold finger (liquid N_2) 10 cm beyond the furnace. Isoindole formed a white deposit in the depression, in which reactions could be carried out. Alternatively, the system could be flushed with nitrogen, and the isoindole dissolved in an appropriate solvent.

At room temperature, solid isoindole rapidly darkened. It gave a red-purple colour (which gradually changed to blue) with Erhlich's reagent, and a deep red colour with ethanolic 1,3,5-trinitrobenzene. The i.r. spectrum (solid film, collected on a NaCl target at 77 K but measured at room temperature: some decomposition expected) showed no CO absorption (*i.e.* none of the precursor had survived) but included maxima at 3350, 3030, 2900, 2850, 1460, 1360, 1065, 1020, and 740 (s) cm^{-1}. The electronic spectrum (hexane; *in vacuo*; Thunberg tube), showed vibrational fine structure (λ_{max} 263·5, 268·5, 275, 286·5, 294 (i), 300, 306·5, 312·5, 320, 326·5, and 335 nm, Figure 1), and resembled the spectra of isobenzofuran[9] and 1,2,3,4,7-tetramethylisoindole.[10] The n.m.r. spectrum [$CO(CD_3)_2$; −40°] showed well resolved multiplets near τ 2·5 and 3·2 [H-4, 7 and H-5, 6, respectively) and a singlet at τ 2·72 ($W_{\frac{1}{2}}$ 3·5 Hz, H-1, 3) attributed to isoindole, in addition to signals due to methanol. Deuteriation (D_2O) at 0° considerably sharpened the singlet at τ 2·72 ($W_{\frac{1}{2}}$ 2 Hz) without affecting the remainder of the spectrum (Figure 2). The system is thus aromatic;[11] the chemical shifts on the benzenoid ring were assigned on the basis of recently calculated[12] charge-density distributions. Electronic and n.m.r. spectroscopy suggests that tautomer (Ia), rather than (Ib), predominates in these solvents, in accord with predictions.[4,13] The mass spectrum (also recorded by Smith[6]) showed M^+ 117·0576 as the base peak, and important fragments at *m/e* 90 $(M - HCN)^+$, 89 $(M - HCN - H)^+$, and 63 $(C_5H_3)^+$.

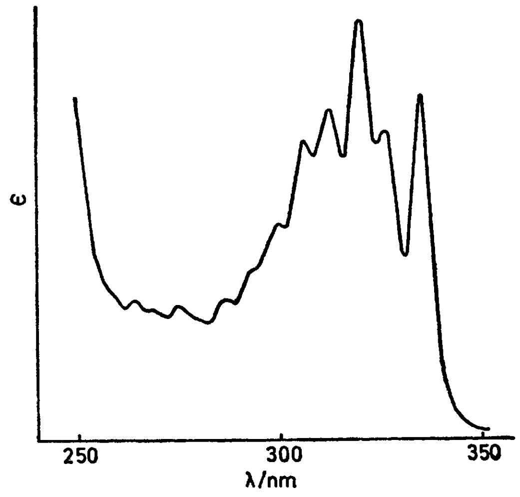


FIGURE 1. *Electronic spectrum for isoindole in degassed hexane (Thunberg cell).*

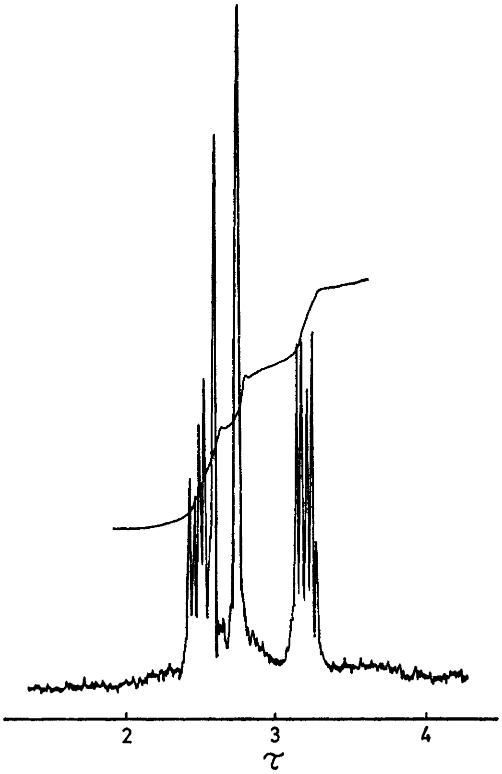
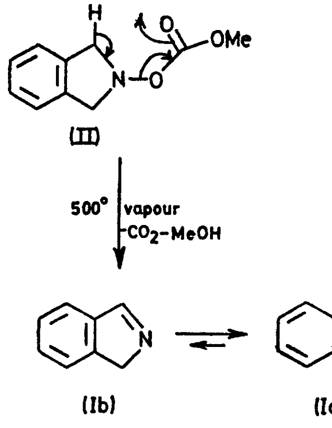
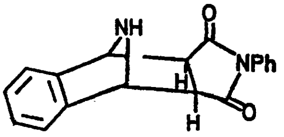


FIGURE 2. *N.m.r. spectrum (100 MHz) of isoindole in* $(CD_3)_2CO$ *containing* D_2O–Et_3N (trace) *at* 0°.



Decomposition of the carbonate (II) in boiling xylene in the presence of *N*-phenylmaleimide gave the *exo*-adduct [(III), m.p. 208—209° (decomp.)[2]] (78%). A film of iso-



(III)

indole was deposited on a layer of *N*-phenylmaleimide at 77 K, and methylene chloride was added; a crude adduct was obtained (75%), whose n.m.r. spectrum indicated a 3:2 mixture of the *exo*-adduct (III) and its *endo*-isomer. Crystallisation from ethanol gave the *exo*-isomer (III).

At room temperature isoindole is clearly very unstable as the solid, or in concentrated solution, probably because of autoxidation, and condensation between the tautomers (Ia) (π-excessive) and (Ib) (electron sink). However, our experiments suggest that this substance should be amenable to further study in dilute degassed solution, and in the gas phase.

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