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DERIVATIVES OF 5-METHYL<u>ISO</u>INDOLO [1,2-<u>b</u>]-BENZIMIDAZOLE, A NEW AROMATIC SYSTEM

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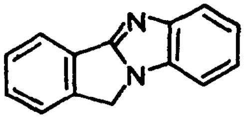
The readily accessible base (I) is a convenient starting material for the synthesis of derivatives of the hitherto unknown 5-methyl<u>iso</u>indolo-[1,2-b]benzimidazole (III), in which the two heterocyclic rings constitute a 10π - electron system. The nature of this 10π - electron system, however, is more closely analogous to azulene than to the pentalene dianion, aromatic azapentalenes[1] being compounds in which the distribution of charge is symmetrical. Since the hetero-atoms in this new system are not symmetrically disposed an asymmetrical charge distribution occurs within the molecule as represented by the structure (IIIb) reminiscent of the dipolar structure (VI) of azulene. This similarity to azulene is borne out by the properties of the compounds described below.

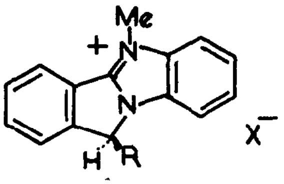
Reaction of <u>o</u>-phenylenediamine with <u>o</u>-phthalaldehyde gave the base (I)[2 3]. Quaternisation of this with methyl toluene-<u>p</u>-sulphonate and treatment of the resulting crude salt (IIa) with perchloric acid afforded in almost quantitative yield the perchlorate[4] (IIb), m.p. 300-310°, decomp; λ_{max} (MeCN) 244, 248, 306 and 319 mn (ϵ 13,730; 18,900; 19,540 and 16,400); ν_{max} (KBr) included 1620, 1603, 1595, 1578 (double bonds) and 1090 (ClO_4^-) cm^{-1}. The n.m.r. spectrum (CF_3COOH) showed a singlet δ 4.47 (3H) N.Me protons, a singlet δ 5.58 (2H) methylene protons and a complex pattern δ 7.6 - 8.5 (8H) aromatic protons.

Addition of acetic anhydride to a solution of this salt (IIb) in acetonitrile followed by triethylamine gave a green solution showing an intense blue fluorescence. Chromatography of the crude product over neutral alumina gave the ketone (IV), in <u>ca</u>. 75% yield, as bright yellow prisms m.p. 221-222° decomp; λ_{max} (95% EtOH) 268, 297sh, 305, 316sh, 328sh, 390sh, 407 and 427 mn (ϵ 23,700; 12,000; 13,200; 10,950; 5,550; 3,980; 8,100 and 9,900);(95% EtOH/1% $HClO_4$) 233, 251, 270, 300sh, 310, 323, 355sh, 375sh mn (ϵ 16,630; 13,500; 7,800; 13,000; 14,880; 12,020; 2,470 and 1,275); ν_{max} (KBr) included 1632, 1615, 1594, 1568 (double bonds) and 1531 (C=O) cm^{-1}. ν_{max} for the perchlorate (VII) derived from this ketone (see later) included 1730 (C=O), 1620, 1605, 1595 and 1580 (double bonds) cm^{-1}. The n.m.r. spectrum ($CDCl_3$) showed two singlets δ 2.60 and 3.93 (3H) CO.Me and N.Me protons respectively, a complex region δ 6.90 - 8.00 (7H) aromatic protons and a multiplet centred δ 9.45 (1H) 1-proton. The n.m.r. spectrum (CF_3CO_2H) showed two singlets δ 2.75 and 4.50 (3H) CO.Me and N.Me respectively, a singlet δ 6.69 (1H) 10-proton, and a complex region δ 7.70 - 8.60 (8H) aromatic protons. The mass spectrum showed a molecular ion at <u>m/e</u> 262.

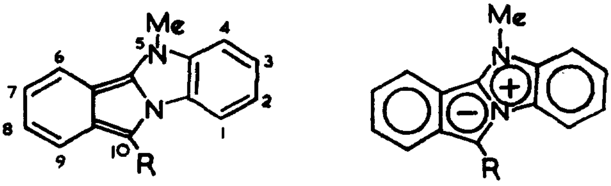
In a similar manner the reaction of methylchloroformate and triethylamine with the salt (IIb) gave in <u>ca</u>. 80% yield the ester (V) as feathery yellow needles m.p. 198-200°; λ_{max} (95% EtOH) 216, 240, 268, 296, 308, 387sh, 404 and 425 mn (ϵ 24,700; 16,100; 50,600; 16,350; 14,000; 7,000; 13,440 and 13,950); (95% EtOH/1% $HClO_4$) 236, 245, 251, 300sh, 311 and 323sh mn (ϵ 16,100; 12,950; 17,450; 17,700; 21,720 and 15,950); ν_{max} (KBr) included 1670 (C=O), 1628, 1595, 1575 and 1536 (double bonds) cm^{-1}. ν_{max} for the perchlorate (VIII) derived from this ester (see later) included 1756 (C=O), 1620, 1609, 1599, and 1584 (double bonds) cm^{-1}. The n.m.r. spectrum ($CDCl_3$) showed two singlets δ 3.95 and 4.03 (3H) N.Me and CO_2Me protons respectively, a complex region δ 6.80 - 8.30 (7H) aromatic protons and a multiplet centred at δ 9.20 (1H) 1-proton. The n.m.r. spectrum recorded in trifluoracetic acid showed two singlets δ 4.15 and 4.50 (3H)



I.

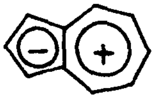


II. R=H; a,X=$C_7H_7SO_3$; b,X=ClO_4.
VII. R=COMe; X=ClO_4.
VIII. R=CO_2Me; X=ClO_4.

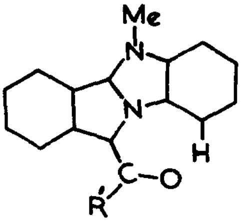


a. b.

III. R=H.
IV. R=COMe.
V. R=CO_2Me.



VI.



IX.

CO_2Me and N.Me protons respectively, a singlet δ 6.55 (1H) 10-proton, and a complex region δ 7.70-8.40 (8H) aromatic protons. The mass spectrum showed a molecular ion at m/e 278.

In the i.r. spectra of compounds (IV) and (V) the low frequency carbonyl absorptions (1531 and 1670 cm^{-1} respectively) indicate the groups to be considerably polarised. This suggests a negative charge on the pyrrole ring (and thus a positive charge on the imidazole ring). The electrostatic interaction of the negatively charged oxygen atom with the positively charged benzimidazole moiety leads to the geometry shown in partial structure (IX). The n.m.r. spectra of these compounds are consistent with this hypothesis, the low field resonance of the 1-proton (at δ 9.45 and 9.20 respectively) being due to deshielding by the appositely placed carbonyl group.

The ketone (IV) and ester (V) are sufficently basic to yield, on treatment with perchloric acid, stable crystalline perchlorates (VII) and (VIII) respectively, the i.r. spectra of which exhibit normal carbonyl stretching frequencies (1730 and 1756 cm^{-1}). Since conjugation of the carbonyl group with the aromatic system is thus broken, protonation at C-10 is suggested and this is adequately confirmed by the appearance of sharp singlets at δ 6.69 and 6.55 respectively in the n.m.r. spectra of compounds (IV) and (V) determined in trifluoracetic acid. Further confirmation for this site of protonation arises from the similarity which exists between the U.V. spectra of the compounds (IV) and (V) measured in acidic solution and the spectrum of the salt (IIb) in neutral solution.

The action of sodium carbonate on the salt (IIb) yields several products, the structures of which are being investigated.

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