A Stable Analogue of Indole-2,3-quinodimethane: Synthesis and Diels–Alder Reaction of 2-Methoxycarbonyl-4-[(p-methoxyphenyl)sulphonyl]-2,4-dihydropyrrolo-[3,4-b]indole

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The preparation of stable analogues of the indole-2,3-quinodimethane system (1) is of current interest, and a number of cyclic derivatives (2), (3), (4), and (5) have been synthesized. However, these cyclic analogues, except the 4H-furo[3,4-b]indole (2), do not show marked diene character. In particular the pyrrolo[3,4-b]indole derivative (5), the only compound prepared containing this ring system, was not found to undergo Diels–Alder reactions.

We now report the synthesis of the new compounds (6) and (7), which also contain the pyrrolo[3,4-b]indole ring system, by a novel route, namely via the intramolecular 1,3-dipolar cycloaddition of the azide (11) followed by 1,3-dipolar...
The triazoline (12). Treatment of the triazoline (12) with a catalytic amount of toluene-p-sulphonic acid in tetrahydrofuran at room temperature gave diethyl diazomalonate (14) (92%) and a more polar product (82%), which was characterized spectroscopically as the 2,4-dihydropyrrolo[3,4-b]-indole (6).† m.p. 122–124 °C. We reasoned that acid-catalysed 1,3-dipolar cycloreversion of the triazoline (12) would give diethyl diazomalonate (14) and compound (13) which tautomerized to give the more stable (6), which is stable under nitrogen.

Attempted Diels–Alder reactions of (6) by prolonged heating with N-phenylmaleimide and benzene in toluene led only to unchanged (6). On the basis of the reactivity of pyrrole derivatives as diene systems, we concluded that N-substituted derivatives of (6) should undergo Diels–Alder reactions. Thus, compound (6) was treated with potassium hydride and methyl chloroformate in tetrahydrofuran to give the methoxy carbonyl derivative (7),† m.p. 145–147 °C (95%). Compound (7) was then heated with N-phenylmaleimide in refluxing tetrahydrofuran, and the Diels–Alder reaction proceeded smoothly to give the endo- (15) (57%) and exo-adducts (16) (19%) (Scheme 2). Similarly, the Diels–Alder reaction of (7) with benzene, generated from benzenediazonium-2-carboxylate, in refluxing tetrahydrofuran gave the adduct (17) (75%) in 1 h. The difference between (7) and (6) in their reactivity as dienes is in good accord with the reactivity of N-substituted pyrrole derivatives. It is interesting that (7) is stable even in the air. Owing to their stability and reactivity as diene systems, derivatives of the 2,4-dihydropyrrolo[3,4-b]indole ring systems, such as (7), have potential for use as the synthetic equivalent of indole-2,3-quinodimethanes.

† Compounds (6) and (7) were characterized by $^1$H and $^{13}$C n.m.r., i.r., and mass spectroscopy, and also gave satisfactory elemental analyses: e.g. (6): $^1$H n.m.r. (CDCl$_3$): δ 3.68 (s, 3H), 6.65 (d, 2H, $J_{AB}$ 9 Hz), 6.83–6.88 (m, 5H, 1H), 7.11–7.24 (m, 2H), 7.44–7.56 (m, 1H), 7.67 (d, 2H, $J_{AB}$ 9 Hz), 7.92–8.04 (m, 1H), and 8.34 (br. s, 1H); $^{13}$C n.m.r. (CDCl$_3$+CD$_3$SOCD$_3$) 54.28(q), 98.85(d), 104.94(d), 112.67(d), 115.47(s), 119.12(d), 122.52(d), 124.10(s), 127.15(s), 127.44(d), 129.78(s), 141.03(s), and 162.07(s); $m/z$ (CHCl$_3$): 1590 and 1500 cm$^{-1}$; $m/z 326 (M^+ 37%)$, 155 (100), and 128 (28).
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References