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THE REACTION OF 1-METHYL-2-VINYLINDOLES WITH 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE

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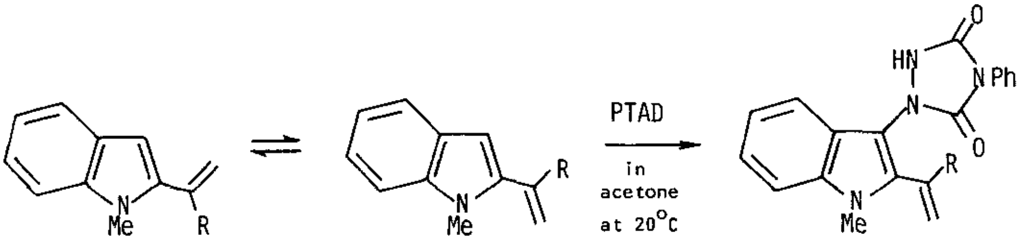
Abstract — 1-Methyl-2-vinylindoles ($1 \rightleftharpoons 2$) react readily with 4-phenyl-1,2,4-triazoline-3,5-dione at 20°C to yield the Michael-type 1:1 adducts (3). No evidence was found for the formation of any cycloadducts.

2-Vinylpyrroles react cleanly and in high yield at the free 5-position of the pyrrole ring with diethyl azodicarboxylate (DEAD) to yield Michael-type adducts[1] in a manner analogous to that reported for the corresponding reaction with simple 1-alkylpyrroles[2] or, when the 5-position is blocked or sterically hindered, they produce pyrrolo[3,2-*c*]pyridazine derivatives or dihydropyrrolyl-1,3,4-oxadiazines.[1] In contrast, the reactions of simple alkylindoles[3] and of 2- and 3-vinylindoles[4] with DEAD are extremely complex and produce many unstable products in low yield.

We now report that 1-methyl-2-vinylindoles ($1 \rightleftharpoons 2$) generally react readily at 20°C with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) to produce stable crystalline 1-(1-methyl-2-vinylindol-3-yl)-4-phenyl-1,2,4-triazolidine-3,5-diones (3) in high yield. However, the instability of 1-methyl-2-vinylindole[5] is such that only polymeric material was obtained from the reaction with PTAD, and the relatively low yield of (**3a**) from 2-(1-methylindol-2-yl)propene can be rationalised in terms of its susceptibility to dimerise readily at relatively low temperatures.[5] No evidence was found for the formation of $_{\pi}2 + _{\pi}4$ cycloadducts, which is in keeping with the reported Michael-type addition of 1-methyl-2-vinylindoles with dimethyl acetylenedicarboxylate and their failure to yield dihydrocarbazoles.[6] These observations are in accord with the analogous reaction of 1-methylindole with PTAD[7] and suggest that the "transoid" conformation for the diene system (2) predominates at ambient temperatures. Unfortunately, elevated temperatures, which should promote the conversion into the "cisoid" conformation, also promotes polymerisation of the vinylindoles ($1 \rightleftharpoons 2$) and of the Michael adducts (3).



(1) (2) (3)

(a) R = Me (b) R = Me_3C (c) R = Ph

The Michael adducts (3) were fully characterised by elemental analysis, mass spectral data, and by ^1H and ^{13}C n.m.r. spectroscopy. In all of the products, n.m.r. signals, characteristic of the vinyl group, were observed near 5.8 (d, J = ca. 2Hz), 5.5 (d, J = ca. 2Hz), and 121 p.p.m. (t).

EXPERIMENTAL

^1H and ^{13}C n.m.r. spectra were measured for ca. 40% solutions in $CDCl_3$ at 100 MHz and 25 MHz, respectively, using either a JEOL-JNM-100-FT or a Varian XL-100 spectrometer. All chemical shifts are given relative to the internal standard (Me_4Si).

General procedure for the reaction of the vinylindoles with PTAD:– The vinylindole (0.0064 mol) in acetone (10 ml) was added with stirring to PTAD, obtained by the addition of t-butyl hypochlorite (0.069 g, 0.0064 mol) to N-phenylurazole (0.115 g, 0.00064 mol) in acetone (10 ml) at -60°C. The red solution of the PTAD was immediately decolourised. Evaporation of the solvent under reduced pressure and purification of the crude product by chromatography from Merck silica gel 60, using hexane:diethyl ether (1:1) as the eluant, gave the 1:1 adducts.

2-(1-Methylindol-2-yl)propene[6] gave *1-(1-methyl-2-(propen-2-yl)indol-3-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione* (0.70 g, 50%), m p 125 - 128°C, Rf 0.12 (Found: C, 69.1; 5.2, N, 16.2 $C_{20}H_{18}N_4O_2$ requires C, 69.4, H, 5.2, N, 16.2%). δ_H 2.05 (3H, s), 3.60 (3H, s), 5.20 (1H, brs), 5.40 (1H, brs), and 7.10 - 7.40 (10H, m); δ_C 22.8 (q) 30.6 (q), 107.1 (s), 109.8 (d), 117.6 (d), 120.8 (d), 121.6 (t), 122.7 (d), 123.9 (s), 125.6 (d), 127.9 (d), 128.9 (d), 131.7 (s), 133.8 (s), 135.6 (s), 141.4 (s), 151.6 (s), and 153.1 (s).

3,3-Dimethyl-2-(1-methylindol-2-yl)but-1-ene[6] gave *1-(1-methyl-2-(3,3-dimethylbut-1-en-2-yl)indol-3-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione* (0.207 g, 82%), m p 104 - 107°C, Rf 0.12 (Found: C, 70.4; H, 6.2; N, 14.0, M^+ 388.1869 $C_{23}H_{24}N_4O_2$ requires C, 71.1; H, 6.2; N, 14.4%, M^+ 388.1898). δ_H 1.10 (9H, s), 3.50 (3H, s), 5.18 (1H, d, J = 1Hz), 5.54 (1H, d, J = 1Hz), and 7.00 - 7.55 (9H, m); δ_C 31.3 (q), 37.3 (s), 108.4 (s), 109.9 (d), 117.8 (s), 120.6 (t), 120.9 (d), 122.6 (d), 123.5 (s), 125.6 (d), 128.0 (d), 129.0 (d), 131.8 (s), 135.6 (s), 140.5 (s), 148.0 (s), 151.2 (s), and 153.2 (s).

1-(1-Methylindol-2-yl)-1-phenylethene[6] gave *1-(1-methyl-2-(1-phenylethen-1-yl)indol-3-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione* (0.236 g, 90%), m p 169 - 171°C, Rf 0.16 (Found: C, 73.1; H, 4.9; N, 13.5 $C_{25}H_{20}N_4O_2$ requires C, 73.5; H, 4.9; N, 13.7%). δ_H 3.23 (3H, s), 5.55 (1H, d, J = 1Hz), 5.83 (1H, d, J = 1Hz) and 7.00 - 7.50 (14H, m); δ_C 30.9 (q), 109.4 (s), 109.9 (d), 117.9 (d), 121.0 (d), 121.1 (t), 123.9 (s), 125.6 (d), 126.6 (d), 127.9 (d), 128.4 (d), 128.6 (d), 128.9 (d), 131.6 (s), 135.8 (s), 137.6 (s), 138.7 (s), 139.4 (s), 151.5 (s), and 153.1 (s).

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