

Flash Vacuum Pyrolysis of 5-(Indol-2- and -3-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-diones

David W. M. Benzies, Pilar Martinez Fresneda, and R. Alan Jones*

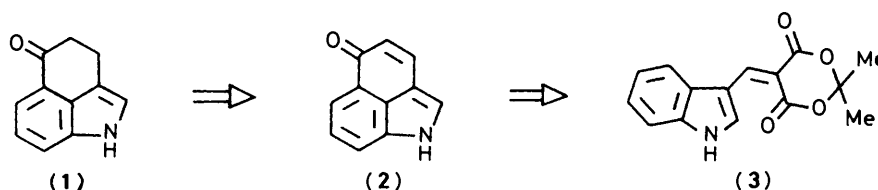
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

Hamish McNab

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Flash vacuum pyrolysis of 5-(indol-2- and -3-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-diones results in the initial formation of indolylmethyleneketenes, which generally either lose carbon monoxide to produce ethynylindoles or undergo [1,5]-sigmatropic shifts, followed by electrocyclic rearrangements, to yield carbazolols or benz[*c,d*]indol-5(1H)-one. 5-(Indol-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione and the 3-methylindol-2-yl derivative both yield 3*H*-pyrrolo[1,2-*a*]indol-3-ones *via* a [1,7]-sigmatropic rearrangement of the initially formed ketene.

The total synthesis of ergot alkaloids is a topic of importance and interest,^{1,2} with Uhle's ketone (1) remaining a key intermediate in many reaction sequences. Recent studies of the mechanism of the pyrolytic decomposition of 5-substituted 2,2-dimethyl-1,3-dioxane-4,6-diones^{3,4} prompted our examination of the possible formation of the tricyclic ketone by the route outlined by the retrosynthetic scheme (1) → (2) (Scheme 1).



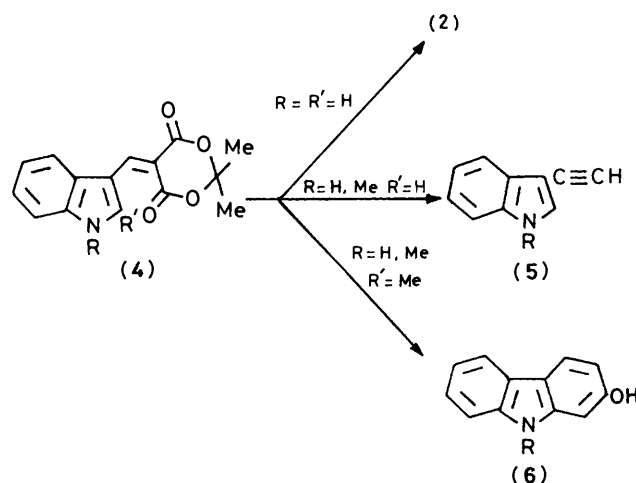
Scheme 1.

Although the pyrolysis of pyrrolyl analogues of (3) have been examined in some detail,^{5,6} the synthesis of only three indolyl derivatives has been recorded,⁶⁻⁸ with only one report of the pyrolytic decomposition of an indolyl compound, which showed that (4; R = H, R' = Me) gave 9-methylcarbazol-2-ol (6; R = Me).⁶ In view of this lack of experimental data, we have undertaken a full study of the flash vacuum pyrolysis of the indol-3- and -2-ylmethylene derivatives, (4) and (7), which were readily obtained in high yield by a Knoevenagel-type condensation reaction between the appropriate formylindoles and 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid).

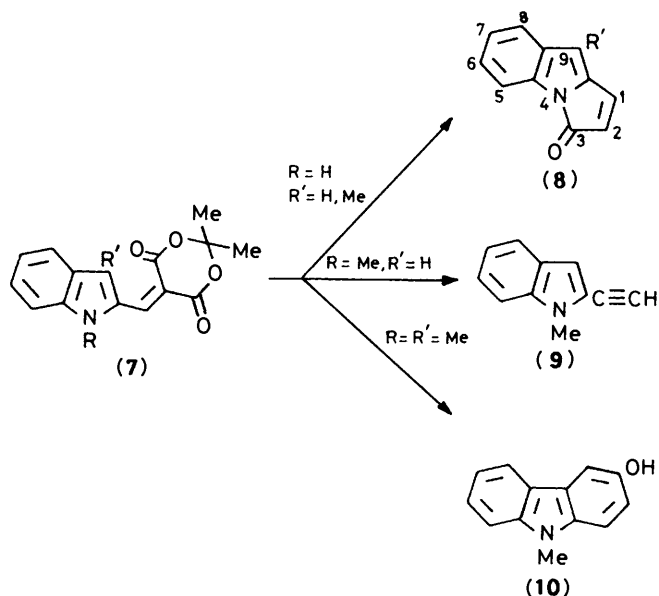
In general, the pyrolyses were conducted at 600 °C under a vacuum of between 10⁻² and 10⁻³ Torr. The formation of 9-methylcarbazol-2-ol (6; R = Me) (89%) from (4; R = H, R' = Me)⁶ was confirmed and it was shown that, with the one major exception of 2,2-dimethyl-5-(3-methylindol-2-ylmethylene)-1,3-dioxane-4,6-dione (7; R = H, R' = Me), the pyrolysis of all of the condensation adducts in which there was a methyl group on the indolyl ring at the carbon atom adjacent to the Meldrum's acid moiety (4; R = H, Me; R' = Me); (7; R = R' = Me) gave carbazole derivatives (6; R = H, Me) and (10). The yields were generally high (>90%), except for the formation of carbazol-2-ol (40%) from (4; R = H, R' = Me), where a competing reaction pathway is possible (Scheme 4). In the absence of the adjacent methyl group, the only identifiable products, with the exception of 3*H*-pyrrolo[1,2-*a*]indol-3-one (8; R' = H) obtained in 95% yield from (7; R = R' = H), were generally isolated in low yield (20%) and they were shown by ¹H and ¹³C

n.m.r. spectroscopic analysis to be the ethynylindoles (5; R = H, Me) and (9). In addition to the formation of 3-ethynylindole, the tricyclic ketone (2) was also obtained in low yield from (4; R = R' = H), whereas pyrolysis of the corresponding 1-methylindol-3-yl system (4; R = Me, R' = H) gave an unstable mixture of at least seven products from which only the ethynylindole (5; R = Me) could be isolated in an analytically

pure form. No unequivocal evidence was found for the formation of the *N*-methyl derivative of the tricyclic ketone (2). The 3*H*-pyrrolo[1,2-*a*]indol-3-ones (8; R' = H or Me) were isolated in high yield (>95%) from the Meldrum's acid adducts of indole- and of 3-methylindole-2-carbaldehyde (7; R = H, R' = H or Me). The pyrolyses of adducts (4) and (7) are shown in Schemes 2 and 3, respectively.



Scheme 2.

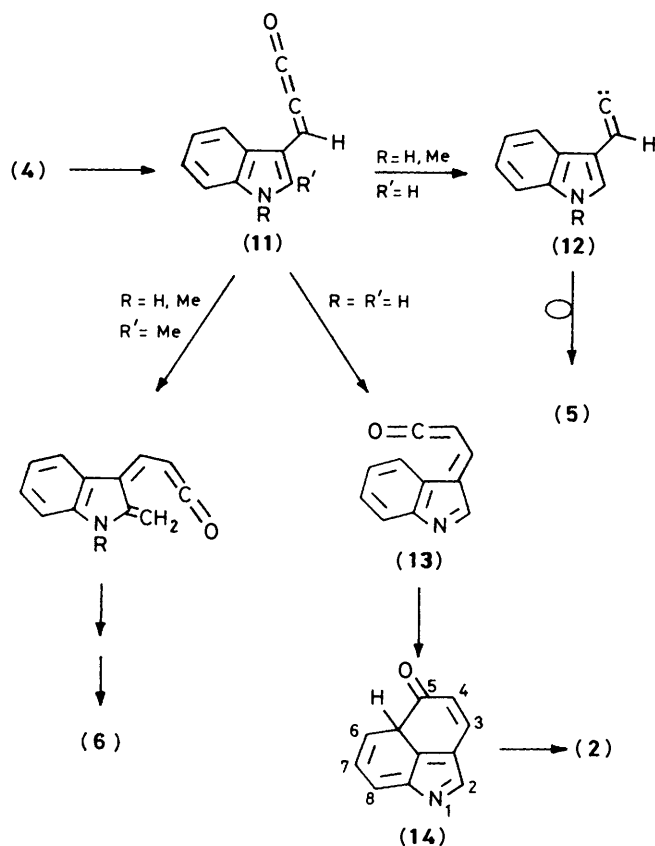


Scheme 3.

A mechanistic pathway, which accounts for the formation of all of the pyrolysis products, is similar in many respects to that postulated earlier for the pyrolysis of the aminomethylene and benzylidene derivatives of Meldrum's acid.^{3,4} Fragmentation of the 2,2-dimethyl-1,3-dioxane-4,6-dione ring produced the indolymethyleneketene [e.g., (4) \rightarrow (11)]. In the absence of an adjacent methyl group, decarbonylation of the ketene (11; $R' = H$) leads, *via* the carbene (12), to the ethyne (5). In contrast, a [1,5]-sigmatropic shift involving a hydrogen of the methyl group of the 2-methylindole derivatives and a subsequent electrocyclic ring closure, followed by a tautomeric shift, produces the carbazol-2-ols (6). Similar mechanistic sequences account for the formation of 2-ethynyl-1-methylindole (9) and 9-methylcarbazol-3-ol (10) from (7; $R = Me, R' = H$; and $R = R' = Me$, respectively).

The formation of the benz[*c,d*]indol-5-one system (2) from the intermediate ketene (13) requires an initial [1,5]-sigmatropic shift of the proton at the 1-position of the indole ring (11; $R = R' = H$) \rightarrow (13). The reaction pathway is completed by an electrocyclic ring closure onto the 4-position of the indole system to give the tricyclic ketone (14), and a prototropic shift. Evidence for this mechanism is provided by the observation that pyrolysis of the 1-deuterio compound (4; $R = D, R' = H$) yields 4-deuteriobenz[*c,d*]indol-5(1*H*)-one. In support of the proposed mechanism it is significant that the corresponding 1-methylbenz[*c,d*]indol-5(1*H*)-one does not appear to be formed during the pyrolysis of compound (4; $R = Me, R' = H$). It is noteworthy, however, that no evidence was found for the formation of 2-methylbenz[*c,d*]indol-5(1*H*)-one *via* a [1,5]-sigmatropic shift of the 1-proton during the pyrolysis of compound (4; $R = H, R' = Me$). Extensive polymerisation occurred during the pyrolysis and the only product isolated was carbazol-2-ol, resulting from a preferential [1,5]-sigmatropic rearrangement involving a hydrogen of the 2-methyl group.

The pyrrolo[1,2-*a*]indol-3-ones (8; $R' = H$ and Me) arise from a [1,7]-prototropic rearrangement of the initially formed methylene ketene (15), followed by ring closure (Scheme 5). It is notable that the yields of both pyrolysis products are high and that, in contrast with the pyrolysis of 2,2-dimethyl-5-(2-methylindol-3-ylmethylene)-1,3-dioxane-4,6-dione (4; $R = H, R' = Me$), it is the more acidic NH proton of the 3-methylindol-

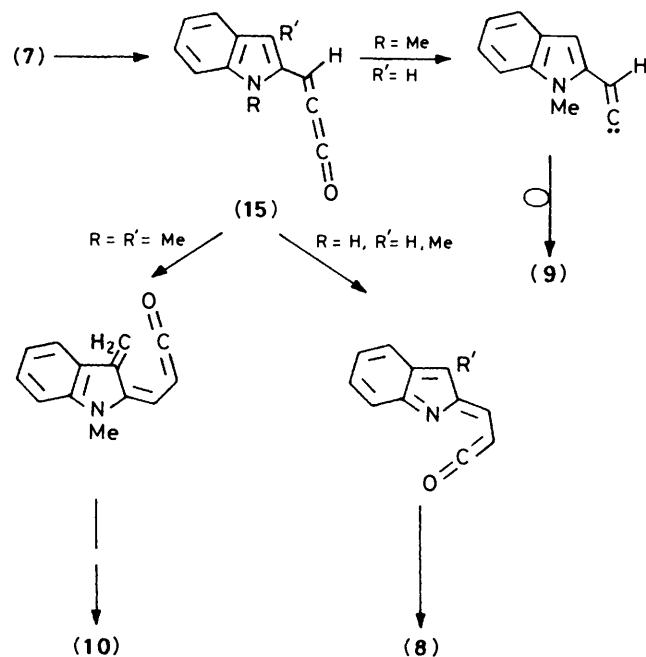


Scheme 4.

2-yl-methylene system which migrates in preference to a [1,5]-sigmatropic hydrogen shift from the 3-methyl group.

Experimental

I.r. spectra were measured for all compounds as mulls in Nujol using a Perkin-Elmer 298 spectrometer. A Pye-Unicam SP



Scheme 5.

8-200 spectrophotometer was used to measure the electronic spectra of *ca.* 10^{-5} M solutions of the compounds in ethanol. ^1H and ^{13}C n.m.r. spectra were measured for *ca.* 40% solutions in the solvents indicated at 100 or 200 MHz and at 25 or 50 MHz, respectively, using JEOL-JNM-100 FT and Bruker WP-200-SY spectrometer. All chemical shifts are given relative to the internal standard (SiMe_4). The ^2H n.m.r. spectrum was measured at 55.28 MHz using a Bruker WH-360 spectrometer. Light petroleum refers to the fraction boiling in the range 60–80 °C.

General Procedure for the Reaction of Formylindoles with 2,3-Dimethyl-1,3-dioxane-4,6-dione (Meldrum's Acid).—Acetic acid (0.1 ml) and piperidine (0.1 ml) were added to equimolar quantities (*ca.* 0.006 mol) of the formylindole and 2,2-dimethyl-1,3-dioxane-4,6-dione in benzene (20 ml) and the mixture was stirred at 20 °C for 24 h. Evaporation of the volatile material gave a solid, which was recrystallised to give the pure condensation product.

2-Formylindole (0.8 g, 0.0055 mol) was converted into 5-(indol-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**7**; $\text{R} = \text{R}' = \text{H}$) (1.3 g, 87%), m.p. 142 °C (from ethanol) (Found: C, 66.3; H, 4.7; N, 5.1. $\text{C}_{15}\text{H}_{13}\text{NO}_4$ requires C, 66.4; H, 4.8; N, 5.2%); ν_{max} 3 300, 1 700, and 1 580 cm^{-1} ; λ_{max} 206 (log ϵ 4.76), 255 (inf.) (4.14), and 417.5 nm (4.92); $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ 1.76 (6 H, s), 7.14 (1 H, t), 7.41 (1 H, t), 7.66 (1 H, s), 7.80 (2 H, m), 8.43 (1 H, s), and 11.79 (1 H, br s); $\delta_{\text{C}}[(\text{CD}_3)_2\text{SO}]$ 26.8 (q), 104.3 (q), 106.6 (2), 113.4 (d), 121.2 (3), 122.1 (d), 122.7 (d), 127.3 (s), 128.1 (d), 131.3 (s), 140.2 (s), 144.1 (d), 161.8 (s), and 162.7 (s).

2-Formyl-1-methylindole (1.0 g, 0.0063 mol) gave 2,2-dimethyl-5-(1-methylindol-2-ylmethylene)-1,3-dioxane-4,6-dione (**7**; $\text{R} = \text{Me}$, $\text{R}' = \text{H}$) (1.6 g, 90%), m.p. 175–176 °C (from dichloromethane–light petroleum) (Found: C, 67.4; H, 5.1; N, 4.7. $\text{C}_{16}\text{H}_{15}\text{NO}_4$ requires C, 67.4; H, 5.3; N, 4.9%); ν_{max} 1 715 and 1 570 cm^{-1} ; λ_{max} 210 (log δ 4.36), 259 (3.81), and 421 nm (4.45); $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ 1.75 (6 H, s), 3.96 (3 H, s), 7.14 (1 H, t), 7.43 (1 H, t), 7.59 (1 H, s), 7.74 (2 H, t), and 8.46 (1 H, s); $\delta_{\text{C}}[(\text{CD}_3)_2\text{SO}]$ 26.8 (q), 29.7 (q), 104.0 (s), 109.1 (s), 111.1 (d), 116.8 (d), 121.1 (d), 123.2 (d), 126.6 (s), 127.5 (d), 131.5 (s), 140.6 (s), 141.3 (d), 159.7 (s), and 163.2 (s).

2-Formyl-3-methylindole (0.7 g, 0.0044 mol) gave 2,2-dimethyl-5-(3-methylindol-2-ylmethylene)-1,3-dioxane-4,6-dione (**7**; $\text{R} = \text{H}$, $\text{R}' = \text{Me}$) (0.9 g, 72%), m.p. 200 °C (from ethanol) (lit.⁸ 196.1–196.6 °C) (Found: C, 67.4; H, 5.2; N, 4.9. Calc. for $\text{C}_{16}\text{H}_{15}\text{NO}_4$: C, 67.4; H, 5.3; N, 4.9%); ν_{max} 3 290, 1 725, 1 690, and 1 575 cm^{-1} ; λ_{max} 210 (log ϵ 4.35), 255.5 (3.72), and 425 nm (4.63); $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ 1.76 (6 H, s), 2.58 (3 H, s), 7.11 (1 H, t), 7.41 (1 H, t), 7.68 (2 H, t), 8.40 (1 H, s), and 11.60 (1 H, br s); $\delta_{\text{C}}[(\text{CD}_3)_2\text{SO}]$ 9.4 (q), 26.9 (q), 104.1 (s), 104.3 (s), 113.0 (d), 120.5 (d), 121.2 (d), 127.3 (s), 128.7 (s), 129.0 (d), 131.9 (s), 139.4 (s), 139.8 (d), 162.5 (s), and 162.7 (s).

2-Formyl-1,3-dimethylindole (1.0 g, 0.0056 mol) was converted into 5-(1,3-dimethylindol-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**7**; $\text{R} = \text{R}' = \text{Me}$) (1.6 g, 95%), m.p. 230–232 °C (from dichloromethane–light petroleum) (Found: C, 68.1; H, 5.5; N, 4.6. $\text{C}_{17}\text{H}_{17}\text{NO}_4$ requires C, 68.2; H, 5.7; N, 4.7%); ν_{max} 1 720 and 1 580 cm^{-1} ; λ_{max} 223 (log ϵ 4.45), 266 (3.96), and 427 nm (4.19); $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ 1.82 (6 H, s), 2.25 (3 H, s), 3.73 (3 H, s), 7.12 (1 H, t), 7.45 (2 H, m), 7.71 (1 H, d), and 8.50 (1 H, s); $\delta_{\text{C}}[(\text{CD}_3)_2\text{SO}]$ 12.0 (q), 27.1 (q), 31.2 (q), 104.1 (s), 110.5 (s), 111.8 (d), 120.0 (d), 120.6 (d), 123.5 (s), 126.5 (s), 127.1 (d), 131.4 (s), 140.0 (s), 142.8 (d), 159.2 (s), and 162.0 (s).

3-Formylindole (1.0 g, 0.0067 mol) gave 5-(indol-3-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**4**; $\text{R} = \text{R}' = \text{H}$) (1.8 g, 97%), m.p. 241 °C (from ethanol) (lit.⁷ 254–255 °C) (Found: C, 66.2; H, 4.8; N, 5.1. Calc. for $\text{C}_{15}\text{H}_{13}\text{NO}_4$: C, 66.4; H, 4.8; N, 5.2%); ν_{max} 3 150, 1 670, and 1 550 cm^{-1} ; λ_{max} 213 (log ϵ 4.58), 270 (4.20), and 411 nm (4.79); $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ 1.74 (6 H, s), 7.36

(2 H, m), 7.64 (1 H, dd), 7.92 (1 H, dd), 8.78 (1 H, s), 9.37 (1 H, s), and 11.79 (1 H, br s); $\delta_{\text{C}}[(\text{CD}_3)_2\text{SO}]$ 26.7 (q), 103.0 (s), 103.3 (s), 111.3 (s), 113.2 (d), 117.8 (d), 122.9 (d), 123.8 (s), 128.8 (s), 136.3 (s), 140.0 (d), 146.1 (d), 161.3 (s), and 163.9 (s).

3-Formyl-1-methylindole (1.0 g, 0.0063 mol) was converted into 2,2-dimethyl-5-(1-methylindol-3-ylmethylene)-1,3-dioxane-4,6-dione (**4**; $\text{R} = \text{Me}$, $\text{R}' = \text{H}$) (1.67 g, 93%), m.p. 215–217 °C (from ethanol) (Found: C, 67.1; H, 5.3; N, 4.7. $\text{C}_{16}\text{H}_{15}\text{NO}_4$ requires C, 67.4; H, 5.3; N, 4.9%); ν_{max} 1 695 and 1 550 cm^{-1} ; λ_{max} 217.5 (log ϵ 4.39), 244.5 (3.84), 275 (4.06), 281.5 (3.95), and 416 nm (4.54); $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ 1.71 (6 H, s), 4.02 (3 H, s), 7.44 (2 H, m), 7.65 (1 H, m), 7.90 (1 H, m), 8.69 (1 H, s), and 9.32 (1 H, s); $\delta_{\text{C}}[(\text{CD}_3)_2\text{SO}]$ 26.9 (q), 34.2 (q), 102.7 (s), 103.0 (s), 110.5 (d), 111.2 (s), 117.8 (d), 123.2 (d), 123.9 (d), 129.5 (s), 137.1 (s), 142.8 (d), 145.5 (d), 161.3 (s), and 164.0 (s).

3-Formyl-2-methylindole (1.0 g, 0.0063 mol) gave 2,2-dimethyl-5-(2-methylindol-3-ylmethylene)-1,3-dioxane-4,6-dione (**4**; $\text{R} = \text{H}$, $\text{R}' = \text{Me}$) (0.41 g, 23%), m.p. 225–228 °C (from ethanol) (Found: C, 67.1; H, 5.4; N, 4.8. $\text{C}_{16}\text{H}_{15}\text{NO}_4$ requires C, 67.4; H, 5.3; N, 4.9%); ν_{max} 3 200, 1 690, and 1 560 cm^{-1} ; λ_{max} 218 (inf.) (log ϵ 5.00), 260 (4.66), and 417 nm (4.66); $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ 1.78 (6 H, s), 2.63 (3 H, s), 7.19 (3 H, m), 7.45 (1 H, m), 8.55 (1 H, s), and 12.73 (1 H, br s); $\delta_{\text{C}}[(\text{CD}_3)_2\text{SO}]$ 12.9 (q), 26.6 (q), 102.6 (s), 103.1 (s), 111.8 (s), 112.0 (d), 122.0 (d), 123.0 (d), 123.2 (d), 125.5 (s), 136.7 (s), 147.3 (d), 153.5 (s), 160.9 (s), and 164.0 (s).

3-Formyl-1,2-dimethylindole (1.0 g, 0.0056 mol) gave 5-(1,2-dimethylindol-3-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**4**; $\text{R} = \text{R}' = \text{Me}$) (1.26 g, 75%), m.p. 204–207 °C (from ethanol) (lit.⁶ 194 °C) (Found: C, 68.2; H, 5.7; N, 4.5. Calc. for $\text{C}_{17}\text{H}_{17}\text{NO}_4$: C, 68.2; H, 5.7; N, 4.7%); ν_{max} 1 705 and 1 560 cm^{-1} ; λ_{max} 221.5 (log ϵ 4.19), 261 (3.74), 273 (3.67), 286 (inf.) (3.52), and 422 nm (4.45); $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$ 1.79 (6 H, s), 2.62 (3 H, s), 3.84 (3 H, s), 7.00–7.20 (1 H, m), 7.20–7.45 (2 H, m), 7.55–7.70 (1 H, m), and 8.57 (1 H, s); $\delta_{\text{C}}[(\text{CD}_3)_2\text{SO}]$ 11.9 (q), 26.7 (q), 30.7 (q), 102.6 (s), 102.9 (s), 110.8 (d), 111.4 (s), 122.2 (d), 122.8 (d), 122.9 (d), 124.9 (s), 138.1 (s), 147.0 (d), 153.4 (s), 159.9 (s), and 163.6 (s).

General Procedure for the Flash Pyrolysis of the 5-(Indolylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-diones.—The Meldrum's acid adducts were sublimed at 10^{-2} to 10^{-3} mmHg pressure into a horizontal silica tube (35 × 2.5 cm), which was maintained at a temperature of 600 °C unless otherwise stated. Inlet temperatures of 190–210 °C were required for sublimation to give a through-put rate of 0.0005–0.001 mol h⁻¹. The products were trapped in a U-tube, which was cooled to –196 °C. T.l.c. analyses of the pyrolysis mixture were carried out in Merck Kieselgel 60F₂₅₄ plates, and analytically pure samples of the products were obtained by preparative centrifugally accelerated radial t.l.c. using a Chromatotron model 7924T chromatograph using Merck Kieselgel 60PF₂₅₄ as the stationary phase.

5-(Indol-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**7**; $\text{R} = \text{R}' = \text{H}$) (0.192 g, 0.001 mol) gave 3H-pyrrolo[1,2-*a*]indol-3-one (**8**; $\text{R}' = \text{H}$) (0.115 g, 95%), R_F 0.96 (diethyl ether); m.p. 90–92 °C (lit.⁹ 94–95 °C) (Found: C, 77.85; H, 4.2; N, 8.2. Calc. for $\text{C}_{11}\text{H}_7\text{NO}$: C, 78.1; H, 4.2; N, 8.3%); ν_{max} 1 720 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 5.89 (1 H, d, J 6.0 Hz), 6.28 (1 H, s), 6.90–7.15 (2 H, m), 7.27 (2 H, t, J 7.3 Hz), 7.61 (1 H, d, J 7.3 Hz); $\delta_{\text{C}}(\text{CDCl}_3)$ 108.3 (d), 112.1 (d), 122.8 (d), 123.1 (d), 127.3 (d), 128.0 (s), 133.7 (s), 134.4 (d), 135.0 (d), 141.1 (s), and 164.7 (s).

Pyrolysis of 2,2-dimethyl-5-(1-methylindol-2-ylmethylene)-1,3-dioxane 4,6-dione (**7**; $\text{R} = \text{Me}$, $\text{R}' = \text{H}$) (0.417 g, 0.0015 mol) at 750 °C gave 2-ethynyl-1-methylindole (**9**) (0.013 g, 5.7%), R_F 0.67 (tetrachloromethane); m.p. 63–65 °C (lit.¹⁰ 70.5–72 °C) (Found: 84.9; H, 5.6; N, 8.9. Calc. for $\text{C}_{11}\text{H}_9\text{N}$: 85.1; H, 5.85; N, 9.0%); ν_{max} 3 255 and 2 110 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.51 (1 H, s), 3.83 (3 H, s), 6.89 (1 H, s), 7.10–7.35 (3 H, m), and

7.64 (1 H, d); $\delta_{\text{C}}(\text{CDCl}_3)$ 30.3 (q), 75.6 (s), 83.2 (d), 108.2 (d), 109.3 (d), 120.5 (d), 120.8 (s), 121.0 (d), 123.2 (d), 126.8 (s), and 137.1 (s).

2,2-Dimethyl-5-(3-methylindol-2-ylmethylene)-1,3-dioxane-4,6-dione (**7**; R = H, R' = Me) (0.828 g, 0.0029 mol) gave 9-methyl-3H-pyrrolo-[1,2-a]indol-3-one (**8**; R' = Me) (0.520 g, 98%), R_{F} 0.55 [hexane-ethyl acetate (1:1)]; m.p. 94–95 °C (Found: C, 78.4; H, 4.9; N, 7.5. $\text{C}_{12}\text{H}_9\text{NO}$ requires C, 78.7; H, 4.95; N, 7.65%); m/z 183; ν_{max} 1 715 and 1 612 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.16 (3 H, s), 5.81 (1 H, d), 7.02 (1 H, td), 7.08 (1 H, d), 7.20 (1 H, td), 7.24 (1 H, dt), and 7.57 (1 H, dt); $\delta_{\text{C}}(\text{CDCl}_3)$ 8.9 (q), 112.0 (d), 119.2 (d), 120.7 (d), 122.7 (d), 126.0 (d), 127.4 (d), 133.2 (d), 134.5 (s), 134.8 (s), 138.3 (s), and 164.6 (s); and a second, unidentified, component (0.009 g), R_{F} 0.41 [hexane-ethyl acetate (1:1)].

5-(1,3-Dimethylindol-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**7**; R = R' = Me) (0.234 g, 0.0008 mol) gave 9-methylcarbazol-3-ol (**10**) (0.127 g, 82%), R_{F} 0.48 [light petroleum-ethyl acetate (1:1)]; m.p. 146–147 °C (Found: C, 79.1; H, 5.6; N, 6.95. $\text{C}_{13}\text{H}_{11}\text{NO}$ requires C, 79.2; H, 5.6; N, 7.1%); ν_{max} 3 500 and 3 250 cm^{-1} ; $\delta_{\text{H}}([\text{}^2\text{H}_6\text{]acetone})$ 3.68 (3 H, s), 7.00–7.60 (5 H, m), 7.55 (1 H, dd), and 7.94 (1 H, dt); $\delta_{\text{C}}([\text{}^2\text{H}_6\text{]acetone})$ 29.0 (q), 105.7 (d), 108.7 (d), 109.3 (d), 115.2 (d), 118.3 (d), 120.4 (d), 122.8 (s), 123.6 (s), 125.8 (d), 136.0 (s), 141.8 (s), and 150.8 (s).

5-(Indol-3-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**4**; R = R' = H) (0.310 g, 0.0011 mol) gave 3-ethynylindole (**5**; R = H) (0.013 g, 8.06%), R_{F} 0.60 [light petroleum-ethyl acetate (1:1)]; m.p. 106–108 °C (lit.^{11,12} 102 °C) (Found: C, 84.7; H, 4.9; N, 9.6. Calc. for $\text{C}_{10}\text{H}_7\text{N}$: C, 85.1; H, 5.0; N, 9.9%); ν_{max} 3 410, 3 265, and 2 105 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.22 (1 H, s), 7.18–7.40 (3 H, m), 7.44 (1 H, d), 7.73–7.80 (1 H, m), and 8.15 (1 H, br s); $\delta_{\text{C}}(\text{CDCl}_3)$ 78.5 (d), 97.7 (s), 111.1 (d), 119.8 (d), 120.7 (d), 122.5 (s), 123.0 (d), 128.5 (d), 129.7 (s), and 135.0 (s); and benz[*c,d*]indol-5(1H)-one (**2**) (0.015 g, 8.1%), R_{F} 0.16 [light petroleum-ethyl acetate (1:1)]; m.p. 216–218 °C (lit.¹³ 215–220 °C) (Found: C, 77.9; H, 4.0; N, 8.3. Calc. for $\text{C}_{11}\text{H}_7\text{NO}$: C, 78.1; H, 4.2; N, 8.3%); ν_{max} 1 670, 1 630, and 1 580 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 6.45 (1 H, d), 7.55 (1 H, t), 7.95 (2 H, overlapping br t), 8.14 (1 H, s), and 12.26 (1 H, br s); $\delta_{\text{C}}(\text{CDCl}_3)$ 110.8 (s), 117.4 (d), 120.0 (d), 124.6 (d), 126.9 (d), 127.9 (s), 132.0 (d), 134.5 (d), 136.0 (s), 184.6 (s), and 206.6 (s).

Pyrolysis of 5-(1-deuterioindol-3-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**4**; R = D, R' = H) produced 4-deuterio-benz[*c,d*]indol-5(1H)-one, $\delta_{\text{D}}[(\text{CD}_3)_2\text{SO}]$ 6.32 (s).

2,2-Dimethyl-5-(1-methylindol-3-ylmethylene)-1,3-dioxane-4,6-dione (**4**; R = Me, R' = H) (0.514 g, 0.018 mol) gave 1-methyl-3-ethynylindole (**5**; R = Me) (0.059 g, 19.6%), R_{F} 0.59 [light petroleum-ethyl acetate (1:1)]; m.p. 76–78 °C (lit.¹⁰ 37–38 °C) (Found: C, 85.0; H, 5.7; N, 9.0. Calc. for $\text{C}_{11}\text{H}_9\text{N}$: C, 85.1; H, 5.85; N, 9.0%); ν_{max} 3 270 and 2 105 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.27 (1 H, s), 3.72 (3 H, s), 7.20–7.40 (3 H, m), 7.38 (1 H, d), and 7.77–7.83 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 32.8 (q), 78.5 (d), 95.8 (s), 109.5 (d), 119.9 (d), 120.3 (d), 121.4 (s), 122.6 (d), 129.3 (s), 133.0 (d), and 136.0 (s).

2,2-Dimethyl-5-(2-methylindol-3-ylmethylene)-1,3-dioxane-4,6-dione (**4**; R = H, R' = Me) (0.58 g, 0.002 mol) gave carbazol-2-ol (**6**; R = H) (0.149 g, 40%), R_{F} 0.67 [light petroleum-ethyl acetate (1:1)]; m.p. 262–264 °C (lit.^{14–16} 259–262, 274–275, and 277 °C) (Found: C, 78.3; H, 4.85; N, 7.4. Calc. for $\text{C}_{12}\text{H}_9\text{NO}$: C, 78.7; H, 4.95; N, 7.65%); ν_{max} 3 410 and 3 270 cm^{-1} ; $\delta_{\text{H}}([\text{}^2\text{H}_6\text{]acetone})$ 6.75 (1 H, dd), 6.97 (1 H, d), 7.00–7.50 (3 H, m), 7.92 (2 H, overlapping t), 8.33 (1 H, s), and 10.03 (1 H, br s); $\delta_{\text{C}}([\text{}^2\text{H}_6\text{]acetone})$ 97.3 (d), 109.2 (d), 111.1 (d), 117.0 (s), 119.4 (d), 121.4* (d), 124.3 (s), 124.6 (d), 140.8 (s), 142.0 (s), and 157.3 (s).

5-(1,2-Dimethylindol-3-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**4**; R = R' = Me) (0.520 g, 0.0017 mol) gave 9-methylcarbazol-2-ol (0.299 g, 89%), R_{F} 0.68 (ethyl acetate); m.p. 166–168 °C (lit.^{6,14,17} 164–165, 166–166.5, and 167–168 °C) (Found: C, 78.9; H, 5.6; N, 7.0. Calc. for $\text{C}_{13}\text{H}_{11}\text{NO}$: C, 79.2; H, 5.6; N, 7.1%); ν_{max} 3 420 and 3 350 cm^{-1} ; $\delta_{\text{H}}([\text{}^2\text{H}_6\text{]acetone})$ 3.78 (3 H, s), 6.77 (1 H, dd), 6.92 (1 H, d), 7.00–7.40 (3 H, m), 7.94 (2 H, overlapping t), and 8.44 (1 H, s); $\delta_{\text{C}}([\text{}^2\text{H}_6\text{]acetone})$ 29.1 (q), 95.5 (d), 109.1* (d), 116.5 (s), 119.5 (d), 119.7 (d), 121.6 (d), 124.0 (s), 124.8 (d), 142.0 (s), 143.6 (s), and 157.7 (s).

Acknowledgements

One of us (P. M. F.) thanks the University of Murcia, Spain, for leave of absence during the academic year 1984–1985, and the Comunidad Autonoma de Region Murcia for financial support.

References

- 1 D. C. Horwell, *Tetrahedron*, 1980, **36**, 3123.
- 2 A. P. Kozikowski, *Heterocycles*, 1981, **16**, 267.
- 3 H. J. Gordon, J. C. Martin, and H. McNab, *J. Chem. Soc., Chem. Commun.*, 1983, 957; *J. Chem. Soc., Perkin Trans. 1*, 1984, 2129.
- 4 H. Briehl, A. Lukosch, and C. Wentrup, *J. Org. Chem.*, 1984, **49**, 2772.
- 5 H. McNab, *J. Org. Chem.*, 1981, **46**, 2809.
- 6 G. Baxter, R. F. C. Brown, and C. L. McMullen, *Aust. J. Chem.*, 1974, **27**, 2605.
- 7 I. N. Khaimov, Yu. Dzhurakulov, and A. N. Kost, *Fiziol. Akt. Veshchestva*, 1978, **10**, 1070 (*Chem. Abstr.*, 1979, **90**, 22927).
- 8 R. M. Wilson and A. Hengge, *Tetrahedron Lett.*, 1985, **26**, 3673.
- 9 R. W. Franck and J. Auerbach, *J. Org. Chem.*, 1971, **36**, 31.
- 10 M. S. Shvartsberg, S. F. Vasilevskii, and T. A. Prikhodko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 2562 (*Chem. Abstr.*, 1983, **98**, 125812).
- 11 C. Wentrup and H. W. Winter, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 609.
- 12 N. N. Suvorov, A. B. Kamenski, Yu. I. Smushkevich, and A. Livshits, *Zh. Org. Khim.*, 1977, **13**, 197 (*Chem. Abstr.*, 1977, **86**, 139745).
- 13 C. A. Grob and B. Hofer, *Helv. Chim. Acta*, 1952, **35**, 2095.
- 14 Y. Oikawa and O. Youemitsu, *J. Org. Chem.*, 1976, **41**, 1118.
- 15 H. J. Teuber and D. Cornelius, *Justus Liebigs Ann. Chem.*, 1964, **671**, 127.
- 16 J. A. Cummins and M. L. Tomlinson, *J. Chem. Soc.*, 1955, 3475.
- 17 F. Muth, G.P. 553 409/1931 (*Chem. Abstr.*, 1932, **26**, 4612).

* Attributable to two carbon nuclei.