THE REACTIVITY OF 2-VINYLINDOLES WITH DIMETHYL

ACETYLENEDICARBOXYLATE

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(Received in USA 7 August 1984)

Abstract - The overall rates of reaction of 1-substituted-1-(1-methyl-2-indolyl)ethenes with dimethyl acetylenedicarboxylate are considerably lower than those of the corresponding 2-vinylpyrroles. Steric interaction between the N-methyl group on the indole ring and the 1-substituent on the ethenyl group prevents the diene system adopting a coplanar <u>cisoid</u> configuration and, thereby, inhibits the $\pi^4 + \pi^2$ cycloaddition reaction of the system with dimethyl acetylenedicarboxylate. Under such conditions, the indolylethene preferentially undergoes a Michael addition reaction at the 3-position. The $\pi^4 + \pi^2$ cycloaddition reaction is promoted at elevated temperatures. No evidence was found for a Cope rearrangement of the Michael adducts to give the dihydrocarbazole.

Although the chemical reactivity of 3-vinylindoles have been examined in some detail,¹ there are relatively few reports relating to the reactivity of the 2-isomers. As a result of bond fixation within the indole system, the mesomeric interaction between the 2-vinyl group and the π -electron excessive heteroaromatic system is less than it is for the 3-vinylindoles. The few reported reactions of 1- and 2-substituted-1-(2-indolyl)ethenes have shown it to behave more generally as the dienophile in $\pi^4 + \pi^2$ cycloaddition reactions,² although in reactions with N-phenylmaleimide under vigorous conditions and with maleic anhydride the system has been reported to react as the 4π component in the cycloaddition reactions.³

As an extension to our studies of the chemical reactivity of 2-vinylpyrroles,⁴ we have synthesised a series of 1-substituted-1-(1-methyl-2-indolyl)ethenes (2) using either the standard Wittig reaction of the appropriate 2-acyl-1-methylindole (1) with methylenetriphenylphosphorane or via the reaction of 1-methyl-2-indolyl lithium with the appropriate methyl ketone and the subsequent elimination of a molecule of water from the so-formed carbinol (3).

By analogy with the corresponding 2-vinylpyrroles, the 2-vinylindoles would be expected to have two resonance stabilised conformations (22) and (2b). Steric interaction between the N-methyl group on the indole ring and the 1-substituent on the ethene bond destabilises the <u>cisoid</u> conformation of the diene system (2b) and would thereby be expected to inhibit the formation of 1,2-dihydrocarbazole--3,4-dicarboxylic esters (6) by the $_{\pi}4 + _{\pi}2$ cycloaddition of the vinylindoles with dimethyl acetylenedicarboxylate (DMAD). In contrast with the reaction of some 2-vinylpyrroles with DMAD,⁴ steric inhibition of the Michael addition reaction at the 3-position of the indole ring would not be expected to be significant. These expectations are borne out by the experimental observations presented in Table 1. It is noteworthy, however, that, by comparison with the corresponding reactions of DMAD with 2-vinylpyrroles, the vinylindoles are approximately 10 to 100 times less reactive.



E = COOMe

Indole (2) R		Reaction Temperature	Reaction Time	% Yield of Isolated Products			
) Solvent			(4)	(5)	(6)	Carbazole 3,4-diester
H	CHC13 CHC13	20 ⁰ C 62 ⁰ C	14 days 3 days			<u>a</u> b 80	<u></u>
Жe	CHC13 CHC13	20 ⁰ C 62 ⁰ C	11 days 3 days	7 6	9 8	< <u>2</u> <u>b</u> <u>d</u> < <u>2</u> <u>b</u> <u>d</u>	
^t Bu	CHC13 CHC13 MeOH MeOH	20 ⁰ C 62 ⁰ C 20 ⁰ C 65 ⁰ C	20 days 14 days 46 days 4 days	14	17 <u>b</u> 14 63 39	30	35
Ph	CHC1 MeOH ³	62 ⁰ C 65 ⁰ C	8 days 9 days			37 <u>b</u> 30	26 <u>°</u>

Table 1. Reactions of 1-Substituted-1-(1-methyl-2-indolyl)ethenes with DMAD

<u>a</u> no identifiable products isolated, only polymeric material formed. <u>b</u> polymeric material also formed. <u>c</u> 1-methoxy-1-(1-methyl-2-indolyl)-1-phenylethane (9%), dimethyl (Z)-2-methoxybut-2-ene-1,4-dioate (0.16 g), and dimethyl (E)-2-methoxy-but-2-ene-1,4-dioate (0.2 g) also isolated 5 Unchanged starting material (0.1 g) recovered. <u>d</u> product could not be purified sufficiently for full characterisation.

1-Methyl-2-vinylindole (2, R = H) and 2-(1-methyl-2-indolyl)propene (2, R = Me) are both extremely labile compounds and polymerised readily under the conditions used for the cycloaddition reactions. The high reactivities of 1- and 2-(1-methyl--2-indolyl)propenes have been reported previously,^{2,3} and it has been recorded that both compounds undergo Diels-Alder reactions in which one molecule behaves as the dienophile and a second molecule behaves as the diene to produce a dimeric system. The reaction is particularly facile with the ethene (2, R = H) and we found that prolonged reaction of the ethene at room temperature with DMAD failed to give either the dihydrocarbazole-3,4-diester (6, R = H) or the Michael adducts (4 and 5, R = H) and only dimeric/polymeric material was isolated. At 62°C the rate of the 4 + 2 cycloaddition reaction between the ethene and DMAD competed well with the dimerisation reaction and a low yield of $(\mathbf{G}, \mathbf{R} = \mathbf{H})$ was obtained. The propene (2, R = Me) was notably more stable and both the $\pi 4 + \pi 2$ cycloadduct and the Michael adducts were obtained from its reaction with DMAD at both 20° C and at 62° C. However. the overall conversion factor is low with the major reaction pathway leading to the dimeric/polymeric products and it is particularly noteworthy that, in contrast with the corresponding reaction of 2-(1-methyl-2-pyrrolyl)propene,⁴ the relative yields of the three addition products are comparable at both the high and the low temperatures. The course of the reactions of 3,3-dimethyl-2-(1-methyl-2--indolyl)but-1-ene (2, $R = {}^{t}Bu$) and of 1-(1-methyl-2-indolyl)-1-phenylethene (2, R = Ph) with DMAD are more in accord with the those of the corresponding pyrrole derivatives. At the lower temperature the transoid form of the tert-butyl compound (2a, R = ^tBu) is the more stable and only the Michael adducts were obtained, whilst, at the higher temperature, the energy barrier to form the less stable <u>cisoid</u> conformation is overcome and the $\pi^4 + \pi^2$ cycloadduct is formed preferentially. A similar pattern of reactivity was observed when the reaction was conducted in chloroform or methanol, although it is of interest to note that the reaction in methanol did not lead to the formation of polymeric products and that only the fumaric ester $(5, R = {}^{t}Bu)$ was isolated in high yield at the lower temperature, whilst at the higher temperature the initially formed dihydrocarbazole was rapidly converted into the fully aromatic compound. The 1-phenylethene (2, R = Ph) reacted extremely slowly at 20°C, possibly because the phenyl group of the preferred conformation (2g, R = Ph) hindered electrophilic attack at the 3-position of the indole ring. At the higher temperature, the ethene reacted in a manner analogous to that of the corresponding pyrrolylethene with the exclusive formation of the dihydrocarbazole-3,4-diester ($\underline{6}$, R =Ph) when the reaction was conducted in chloroform, whereas in methanol the rate of the reaction of DMAD and of the ethene with the solvent was comparable with that of the $\pi^4 + \pi^2$ cycloaddition reaction, which led to the formation of both the dihydrocarbazole diester and the fully aromatic compound together with the indolylmethyl methyl ether.

The overall lower reactivities of the 1-substituted-1-(1-methyl-2-indolyl)ethenes, compared with the corresponding pyrrolyl compounds, can be attributed to steric hindrance by the ethenyl substituent of both the $_{\pi}4 + _{\pi}2$ cycloaddition reaction and the electrophilic substitution reaction at the 3-position of the indole ring, although at the higher temperature it is apparent that, as with the pyrrole derivatives, the rate of the cycloaddition reaction was greater than that of the Michael addition reaction.

No evidence was obtained for a Cope rearrangement of the Michael adducts to give tricyclic products, which after a 1,5-sigmatropic shift of the 3-hydrogen atom would lead to the formation of the 1,2-dihydrocarbazole-3,4-diesters (6). All of the Michael adducts degenerated into polymeric material, when heated either in the presence or the absence of a solvent. The failure to effect the Cope rearrangement probably results from the high stabilities of the adducts (4) and (5) in which either one or both of the 2- and 3-vinyl groups adopt a transoid conformation. The severe steric interaction of the substituents presents a high energy barrier for the formation of the cisoid conformation required for the Cope rearrangement.

EXPERIMENTAL

¹H and ¹³C n.m.r. spectra were measured for <u>ca</u> 0.3 M solutions in CDCl₃ using a JEOL FX-100 spectrometer operating, respectively, at 100 and 25.05 MHz. All chemical shifts are reported downfield from the internal standard (Me₄Si) and the solvent provided the deuterium lock for the ⁻C n.m.r. spectra. IR spectra were measured as liquid films or as solutions in CHBr₃ using a Perkin-Elmer 287 spectrophotometer and the electronic spectra were recorded for <u>ca</u> 10⁻⁵ M solutions in EtOH using a Unicam SP 8-200 spectrophotometer. Unless otherwise stated, t.l.c. analyses and the preparative t.l.c. separation of the products were conducted on Merck silica gel 60 HF₂₅₄ using hexane:diethyl ether (4:3) as the eluant.

<u>1-Methyl-2-vinylindole.</u> 1-Methylindole (2.0 g, 0.015 mol) in diethyl ether (10 ml) was added to <u>n</u>-butyllithium in hexane (1.55 M, 11.4 ml, 0.017 mol) under nitrogen at 0°C. The reaction was heated under reflux for 6 h and then cooled to 15°C. Dimethylformamide (1.45 g, 0.015 mol) was added to the reaction mixture, which was then heated again under reflux for 2 h and then stirred at 20°C for 12 h. Water (20 ml) was added and the organic layer was separated. The aqueous phase was extracted with diethyl ether (3 x 15 ml). The combined organic solutions were washed with water (2 x 15 ml), dried (CaCl₂), and evaporated to give 2-formyl--1-methylindole (2.3 g, 94%) m.p. 84 - 85°C (lit., 'm.p. 83 - 85°C). The formylindole (0.5 g, 0.003 mol) in diethyl ether (10 ml) was added with stirring at 15°C to methylenetriphenylphosphorane, obtained from the addition of <u>n</u>-butyllithium in hexane (1.55 M, 2.75 ml, 0.0043 mol) to methyltriphenyl-phosphonium bromide (1.83 g, 0.0034 mol) in diethyl ether (20 ml). The reaction mixture was heated under reflux for 2 h and then cooled to 0°C. Saturated aqueous sodium sulphite (10 ml) was added and the organic layer was separated, washed with

The formylindole (0.5 g, 0.003 mol) in diethyl ether (10 ml) was added with stirring at 15 °C to methylenetriphenylphosphorane, obtained from the addition of n-butyllithium in hexane (1.55 M, 2.75 ml, 0.0043 mol) to methyltriphenyl-phosphonium bromide (1.83 g, 0.0034 mol) in diethyl ether (20 ml). The reaction mixture was heated under reflux for 2 h and then cooled to 0 °C. Saturated aqueous sodium sulphite (10 ml) was added and the organic layer was separated, washed with water (4 x 15 ml). dried (MgSO₄), and evaporated to give 1-methyl-2-vinylindole²⁴ (0.4 g, 82%), as a thermally unstable oil. $\delta_{\rm H}$ 3.70 (3H, s), 5.33 (1H, dd, J 11.2 and 1.6 Hz), 5.79 (1H, dd, J 17.5 and 1.6 Hz), 6.78 (1H, dd, 17.5 and 11.2 Hz) and 6.79 - 7.61 (5H, m); $\delta_{\rm C}$ 29.8 (NMe), 98.9 (C3), 109.1 (C7), 116.2 (CH=CH₂), 119.7 (C6), 120.4 (C4), 121.6 (C5), 125.8 (CH=CH₂), 127.7 (CSa), 137.8 (C2) and 138.3 (C7a)

<u>2-(1-Methyl-2-indolyl)propene</u>.- In a manner analogous to that described for the synthesis of 1-methyl-2-vinylindole, 2-acetyl-1-methylindole⁸ (1.23 g, 0.007 mol) was converted into the thermally labile 2-(1-methyl-2-indolyl)propene (0.92 g, 77%) b.p. 50 C (bath) at 10 mm (lit., 95 C at 0.07 mm). $\delta_{\rm L}$ 2.14 (3H, s), 3.69 (3H, s), 5.06 (1H, s), 5.22 (1H, s), 6.36 (1H, s), 6.84 - 7.64 H (4H, m).

 $\frac{1-(1-Methyl-2-indolyl)-1-phenylethene. - n-Butyllithium in hexane (1.55 M, 9.0 ml, 0.014 mol) was added to 1-methyllndole (1.57 g, 0.012 mol) in ether (10 ml). The reaction mixture was heated under reflux for 6 h and then cooled to 20°C. Acetophenone (1.44 g, 0.012 mol) was added with stirring and the mixture was heated under reflux for 2 h and then stirred at 20°C for a further 12 h. Water (20 ml) was added and the organic phase was separated. The aqueous phase was extracted with diethyl ether (3 x 15 ml) and the combined organic phases were washed with water (2 x 10 ml), dried (Na₂SO₄), and evaporated to give <math display="inline">1-(1-methyl-2-indolyl)--1-phenylethanol (1.87 g, 62%) (R, 0.47), m.p. 107°C (from hexane) (Found: C, 81.2; H, 6.7; N, 5.4 C, H, NO requires C, 81.2; H, 6.8; N, 5.6%). <math display="inline">\delta_{\rm H}$ 1.70 (3H, s), 2.35 (1H, s), 3.10 (3H, s); 6.35 (1H, s), 7.00 (8H, m), and 7.40 (1H, m); $\delta_{\rm C}$ 31.2 (CMe), 33.3 (NMe), 73.4 (COH), 100.5 (C3), 109.0 (C7), 119.4 (C6), 120.6 (C4), 121.8 (C5), 125.0 (phenyl C2,6), 126.5 (C3a), 126.9 (phenyl C4), 128.2 (phenyl C3,5), 138.4 (C2), 143.7 (C7a), and 145.8 (phenyl C1); λ 224 (log ϵ 3.77) and 263 nm (log ϵ 3.10). The phenylethanol (1.20 g, 0.005 mOl) and trifluoroacetic acid (0.57 g, 0.005 mOl) in chloroform (20 ml) was then added to the reaction mixture. All volatile material was removed under reduced pressure and water (5 ml) was added to the residue. The aqueous solution was extracted with diethyl ether (3 x 10 ml) and the ethereal extracts were dried (Na₂SO₄) and evaporated to give $\frac{1-(1-methyl-2-indolyl)-1-phenylethene (0.85 g, 77%) (R, 0.69)$ m.p. 120°C (from diethyl ether (3 x 10 ml) and the ethereal extracts were dried (Na_2SO₄) and evaporated to give $\frac{1-(1-methyl-2-indolyl)-1-phenylethene (0.85 g, 77%) (R, 0.69)$ m.p. 120°C (from diethyl ether: chloroform) (Found: C, 87.2; H, 6.45; N, 6.0 C, $\frac{1+5}{15}$ medures (C , 87.5; H, 6.65; N, 6.0%). $\delta_{\rm c}$ 3.10 (3H, s), 5.23 (1H, d), 2 H2), 5.45 (1H, d, 2 Hz), 6.22 (1H, s), 6.66 (1H, m), 6H90 (7H, m), and 7.

 $\begin{array}{l} 3,3-\underline{\text{Dimethyl-2-(1-methyl-2-indolyl)but-1-ene.}}_{\text{described for the synthesis of 1-(1-methyl-2-indolyl)-1-phenylethanol, 1-methyl-2-indolyl)-1-phenylethanol, 1-methyl-2-indolyl)thium, obtained from 1-methylindole (1.57 g, 0.012 mol), and 2,2-dimethyl-butan-3-one (1.20 g, 0.012 mol) gave 3,3-dimethyl-2-(1-methyl-2-indolyl)butan-2-ol (1.60 g, 59%) (R 0.47) m.p. 106°C (from hexane:cyclohexane) (Found: C, 78.0; H, 9.1; N, 6.1 C_{1}H_{2}NO requires C, 77.9; H, 9.15; N, 6.1%). <math>\delta_{\rm H}$ 1.03 (9H, s), 1.17 (1H, s), 1.65 (3H, 2), 3.90 (3H, s), 6.20 (1H, s), 7.10 (3H, m', and 7.45 (1H, m); $\delta_{\rm C}$ 26.1 (CMe₂), 27.5 (CMe), 33.4 (NMe), 39.3 (CMe₂), 79.2 (COH), 101.9 (C3), 109.1 (C7), 119.3 (C6), 119.8 (C4), 120.9 (C5), 126.8 (C3a), 138.0 (C2), and 143.1 (C7a); \\ \end{array}

 λ 255 (log ϵ 4.18) and 285 nm (log ϵ 3.56). The butan-2-ol (1.15 g, 0.005 mol) and trifluoroacetic acid (0.57 g, 0.005 mol) in chloroform (20 ml) were stirred at 20 C for 10 min and triethylamine (1.0 g, 0.006 mol) in chloroform (20 ml) was then added to the reaction mixture. The residue, obtained on evaporation of the reaction mixture, was dissolved in water (5 ml) and the aqueous solution was extracted with diethyl ether (3 x 10 ml) and the ethereal extracts were dried (Na_SO_4) and evaporated. The residual oil was purified by preparative t.l.c. to givé 3.3-dimethyl-2-(1-methyl-2-indolyl)but-1-ene (0.75 g, 66%) (R, 0.78) as a thermally unstable oil (Found: C, 85.05; H, 9.0; N, 6.5 C_{1}H_{10}N fequires C, 85.45; H, 9.0; N, 6.6%). $\delta_{\rm L}$ 1.16 (9H, s), 3.61 (3H, s), 5.00 (1H, d, 2Hz), 5.57 (1H, d, 2Hz), 6.31 (1H, s), 7.19 (3H, m), and 7.61 (1H, m); $\delta_{\rm L}$ 29.3 (CMe_3), 30.3 (CMe_3), 36.9 (NMe), 100.8 (C3), 109.3 (C7), 116.5 (C=CH_2); $\lambda_{\rm max}$ 224 (log ϵ 4.47) and 283 nm (log ϵ 3.88).

<u>General Procedures for the Reaction of the Vinylindoles with Dimethyl acetylene-</u> <u>dicarboxylate</u>. - Method A: Dimethyl acetylenedicarboxylate (0.56 g, 0.004 mol) was added to the vinylindole (0.004 mol) and hydroquinone (5 mg) in chloroform (2 ml) at 20° C and the reaction mixture stirred at the temperature indicated in Table 1. The solvent was removed under reduced pressure and the products isolated by preparative t.l.c.

Method B: Dimethyl acetylenedicarboxylate (0.56 g, 0.004 mol) was added to the vinylindole (0.004 mol) and hydroquinone (5 mg) in methanol (5 ml) at 20° C and the reaction mixture was stirred at the temperature indicated in Table 1. The solvent was removed under reduced pressure and the products isolated by preparative t.l.c.

Products of the Reaction of 1-Methyl-2-vinylindole

 $\begin{array}{c} \hline \textbf{Dimethyl 1,2-dihydro-9-methylcarbazole-3,4-dicarboxylate, m.p. 153.5 - 154.5^{O}C} \\ \hline \textbf{was recrystallised from chloroform:hexane (Found: C, 68.4; H, 5.6; N, 4.6 C_{17}H_{17}NO_{4} \\ requires C, 68.2; H, 5.7; N, 4.7\%). \\ \delta_{H} 2.82 (4H, s), 3.54 (3H, s), 3.77 (3H, s), \\ 4.01 (3H, s), and 7.00 - 7.47 (4H, m), \\ \delta_{L} 20.3 (-CH_{-}), 22.9 (-CH_{-}), 29.5 (NMe), \\ 51.8 (Ome), 52.4 (OMe), 106.9 (C4a), 109.6 (C8), 113.5 (C3), 117.8 (C7), 121.3 (C4), \\ 121.8 (C6), 123.6 (C5), 137.8 (C4b), 138.7 (C9a), 141.8 (C8a), 166.7 (C)), and \\ 169.6 (CO). \end{array}$

Products of the Reaction of 2-(1-Methyl-2-indolyl)propene

 $\begin{array}{c} \underline{\text{Dimethyl}} & (2-(2-\text{propenyl})-1-\text{methyl}-3-\text{indolyl})\text{fumarate}}_{\text{(R}} & (0.30) \text{ had m.p. } 190^{\text{O}}\text{C}\\ \hline \text{(Found: C, 68.6; H, 6.0; N, 4.3 C_{18}\text{H}_{19}\text{NO}_{4} \text{ requires C, } 69.0; H, 6.1; N, 4.5\%).}\\ \underline{\delta_{H}} & 2.14 & (3H, s), 3.51 & (3H, s), 3.76 & (3H, s), 3.78 & (3H_{2}s), 5.10 & (1H, m), 5.35 & (1H, m), 6.85 & (1H, s), \text{ and } 7.10 & (4H, m); \ \text{vC=O} & 1730 \ \text{cm}^{-1}; \lambda \\ 226 & (\log \epsilon \ 4.50), 281 & (\log \epsilon \ 4.22) \ \text{and } 363 \ \text{nm} (\log \epsilon \ 3.87). \end{array}$

 $\begin{array}{l} \underline{\text{Dimethyl }(2-(2-\text{propenyl})-1-\text{methyl}-3-\text{indolyl})\text{maleate }(\text{R},\ 0.26) \text{ was isolated as a} \\ \hline \text{thermally unstable oil (Found: C, 68.5; H, 6.0; N, 4.1%). } \\ \hline (3\text{H, s}),\ 3.70\ (3\text{H, s}),\ 3.92\ (3\text{H, s}),\ 5.07\ (1\text{H, s}),\ 5.30\ (1\text{H, m}),\ 6.60\ (1\text{H, m}),\ \text{and} \\ \hline 6.98\ -\ 7.06\ (4\text{H, m});\ \text{vC=O }1720\ \text{cm}^{-1};\ \lambda_{\max}\ 255\ (\log\ \epsilon\ 4.34)\ \text{and}\ 287\ \text{nm}\ (\log\ \epsilon\ 3.97). \end{array}$

<u>Products of the Reaction of 3,3-Dimethyl-2-(1-methyl-2-indolyl)but-1-ene</u>

 $\begin{array}{c} \hline \textbf{Dimethyl 1-tert-butyl-1,2-dihydro-9-methylcarbazole-3,4-dicarboxylate}{Product Markov Mar$

 $\begin{array}{c} \underline{\text{Dimethyl}} & (2-(3,3-\text{dimethyl-2-but-1-enyl})-1-\text{methyl-3-indolyl}) \text{fumarate}}_{\text{recrystallised from hexane and had m.p. 84°C (Found: C, 71.05; H, 7.1; N, 3.85 \\ C_{21}H_{25}NO_{4} \text{ requires C, 71.0; H, 7.1; N, 3.9\%)}, & \delta_{H} 1.20 (9H, s), 3.60 (3H, s), 3.70 (3H, S), 3.76 (3H_{15}s), 5.08 (1H, d, Hz), 5.72 (1H, d, Hz), and 6.70 - 7.40 (5H, m); vC=0 1720 cm⁻¹; <math>\lambda_{\text{max}} 224 (\log \epsilon 4.66) \text{ and } 282 \text{ nm} (\log \epsilon 3.97). \end{array}$

Dimethyl (2-(3,3-dimethyl-2-but-1-enyl)-1-methyl-3-indolyl)maleate (R, 0.35) rapidly isomerised to yield the fumarate. No pure sample of the maleate was obtained either for elemental analysis or for spectroscopic analysis.

Products of the Reaction of 1-(1-Methyl-2-indolyl)-1-phenylethene

 $\begin{array}{c} \underline{\text{Dimethyl 1,2-dihydro-9-methyl-1-phenylcarbazole-3,4-dicarboxylate}} (\text{R}, 0.25) \text{ was} \\ \underline{\text{recrystallised from diethyl ether:chloroform and had m.p. 204°C (Found: C, 73.45;} \\ \text{H}, 5.65; \text{N}, 3.8 & \underline{\text{C}_{23}\text{H}_{21}\text{NO}_4} \text{ requires C, 73.6; H, 5.6; N, 3.7\%). } \\ \underline{\text{S}_{3.36}} (3\text{H}, \text{s}), 3.56'(3\text{H}, \text{s}), 3.87'(3\text{H}, \text{s}), 4.12'(1\text{H}, \text{t}), \text{ and } 6.56^{\text{H}}\text{-} 7.03'(9\text{H}, \text{m});} \\ \underline{\text{S}_{C}} & \underline{\text{29.7}} (\text{NMe}), 32.8'(\text{S-CH}_2), 37.2'(1-\text{CH}), 51.7'(0\text{Me}), 52.4'(0\text{Me}), 107.8'(C4a), \\ 109.7'(\text{C8}), 112.4'(\text{C3}), 118.5'(\text{C7}), 121.5'(\text{C6}), 122.3'(\text{C5}), 123.5'(\text{C4}), 127.1' \\ \end{array}$

(phenyl C2,4,6), 128.9 (phenyl C3,5), 138.0 (C4b), 138.4 (C9a), 140.1 (phenyl C1), 142.7 (C8a), 166.6 (CO), and 169.5 (CO); ν C=O 1710 and 1680 cm⁻¹; λ max 231 (log ϵ 4.41), 263 (log ϵ 4.09), and 275 nm (log ϵ 4.06).

 $\begin{array}{c} \underline{\text{Dimethyl 9-methyl-1-phenylcarbazole-3,4-dicarboxylate}}_{\text{(Found: C, 74.1; H, 5.2; N, 3.7 C_2H_2NO_4 requires C, 74.0; H, 5.1; N, 3.75\%).}\\ \underline{\text{A}}_{\text{H}} & 3.30 \ (3\text{H, s}), 3.90 \ (3\text{H, s}), 4.22(3\text{H, s}), 7.15 \ (1\text{H, s}), 7.40 \ (8\text{H, m}), \text{ and}\\ 7.90 \ (2\text{H, m}); \ v\text{C=0} \ 1775 \ \text{and} \ 1750 \ \text{cm}^{-1}; \lambda \\ \underline{\text{max}} \ 234 \ (\log \ \epsilon \ 3.98) \ \text{and} \ 283 \ \text{nm} \ (\log \ \epsilon \ 4.25).} \end{array}$

 $\begin{array}{l} 1-\underline{\texttt{Methoxy-1-(1-methyl-2-indolyl)-1-phenylethane}}_{(Found: C, 82.1; H, 7.1; N, 5.2 C_{18}H_{19}NO \ requires^{1}C, 81.5; H, 7.2; N, 5.3\%).} \\ \delta_{L} & 1.86 \ (3H, \ s), 3.20 \ (3H, \ s), 3.34 \ (3H, \ s), 6.72 \ (1H, \ s), 7.15 \ (8H, \ m), \ and 7H_{60} \ (1H, \ m); \ \delta_{C} \ 27.0 \ (CMe), \ 30.7 \ (NMe), 50.6 \ (COMe), \ 78.5 \ (COMe), \ 103.7 \ (C3), 109.0 \ (C7), \ 119.3 \ (C6), \ 120.5 \ (C4), \ 121.7 \ (C5), \ 125.3 \ (phenyl \ C2,6), \ 126.7 \ (C3a), 126.8 \ (phenyl \ C4), \ 128.0 \ (phenyl \ C3,5), \ 138.5 \ (C2), \ 141.2 \ (C7a), \ and \ 146.5 \ (phenyl \ C1); \ \lambda_{max} \ 230 \ (\log \ \varepsilon \ 3.84), \ 275 \ (\log \ \varepsilon \ 3.84), \ and \ 285 \ nm \ (\log \ \varepsilon \ 3.81). \end{array}$

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<u>Acknowledgement:</u> Dr Pilar Martinez Fresneda thanks the University of Murcia, Spain for leave of absence to work in the School of Chemical Sciences at the University of East Anglia during the summer of 1983.