

A Novel Synthesis of 2-Vinylindoles and their Utilization in the Diels-Alder Reaction for the Formation of new [c] Annellated Carbazole Derivatives

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A facile synthesis of 2-vinylindoles is detailed, starting from the corresponding indolecarbinols. The utility of the newly synthesized 2-vinylindoles in the preparation of novel [c] annellated carbazoles is demonstrated. 1-(1-Methyl-2-indolyl)-1-(*N*-methyl-2'-pyrrolyl)ethene (**3c**) has also a 2-vinylpyrrole partial structure. However, in the Diels-Alder reaction of **3c**, the exclusive formation of [c] annellated indoles was observed.

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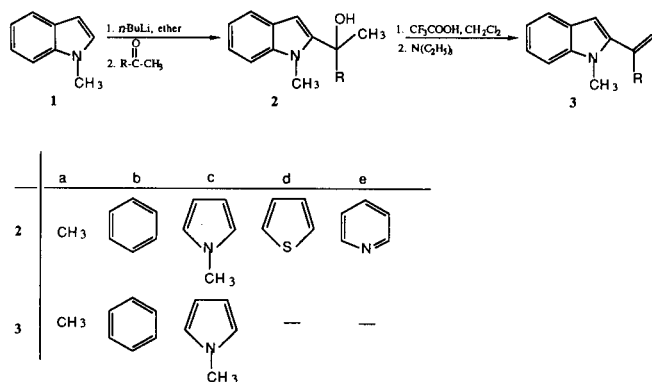
Introduction.

2-Vinylindoles are four carbon building blocks possessing high HOMO energy [1]. Therefore, they are often used as the diene component in the Diels-Alder reaction for the construction of the carbazole skeleton [2]. Many naturally occurring alkaloids containing this structural feature exhibit pronounced biological activities [3]. A variety of synthetic methods to produce 2-vinylindoles have been reported [2]. We wish now to detail a novel and convenient access toward this class of compounds *via* the aldol reaction of 2-lithioindoles followed by an elimination reaction of the resulting indole-carbinols to form the desired 2-vinylindoles in 40-80% overall yield. These newly synthesized 2-vinylindoles were also investigated in the Diels-Alder reaction with a variety of reactive dienophiles to produce novel [c] annellated carbazoles.

Results and Discussion.

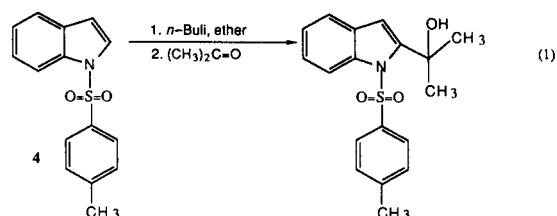
The 2-lithioindole of *N*-methylindole (**1**) was readily prepared by reaction with *n*-butyllithium in diethyl ether. Reaction of the lithiated *N*-methylindole (**1**) with a variety of methylketones (Scheme 1) produced the desired aldol products **2** in 40-80% yield.

Scheme 1

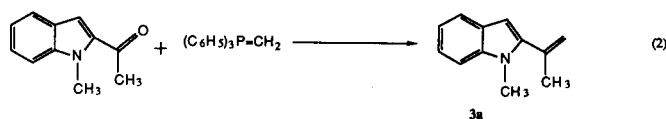


The methylketones investigated included acetone, acetophenone and heteroaromatic methylketones. The novel

indolecarbinols **2** were fully characterized and exhibited spectroscopic properties in agreement with their structures. We also investigated *N*-tosylindole (**4**) in this reaction (*e.g.* 1) and found that lithiated *N*-tosylindole reacted with acetone to form the desired 2-substituted indolecarbinol. However, the aromatic methylketones of Scheme 1 did not react with lithio *N*-tosylindole.



We expected that the subsequent elimination of water by means of trifluoroacetic acid and triethylamine in dichloromethane should produce the corresponding 2-vinylindoles **3b-3c** were accessible with this procedure. In the case of the indolecarbinols 1-(1-methyl-2-indolyl)-1-methylethanol (**2a**), 1-(1-methyl-2-indolyl)-1-(2'-thiophenyl)ethanol (**2d**) and 1-(1-methyl-2-indolyl)-1-(2'-pyridinyl)ethanol (**2e**), elimination did not occur under the same reaction conditions, and we recovered the starting material after workup of the reaction [5]. 1-(1-Methyl-2-indolyl)-1-phenylethene (**3b**), which had been synthesized before [6], exhibited spectroscopic properties identical to the reported data. The ¹H nmr spectrum of the new vinylindole, 1-(1-methyl-2-indolyl)-1-(*N*-methyl-2'-pyrrolyl)ethene (**3c**), displayed the following signals: δ = 3.16 (s, 3, *N*-CH₃), 3.3 (s, 3, *N*-CH₃), 5.41 (d, 1, Vinyl-H, ²J = 2.1 Hz), 5.48 (d, 1, Vinyl-H, ²J = 2.1 Hz), 6.1-7.6 (m, 8, Aromat-H). An alternate route was explored [6] for the synthesis of the vinylindole 2-(1-methyl-2-indolyl)propene (**3a**), namely a Wittig reaction of 2-acetyl-1-methylindole with methylenetriphenylphosphorane (equation 2).

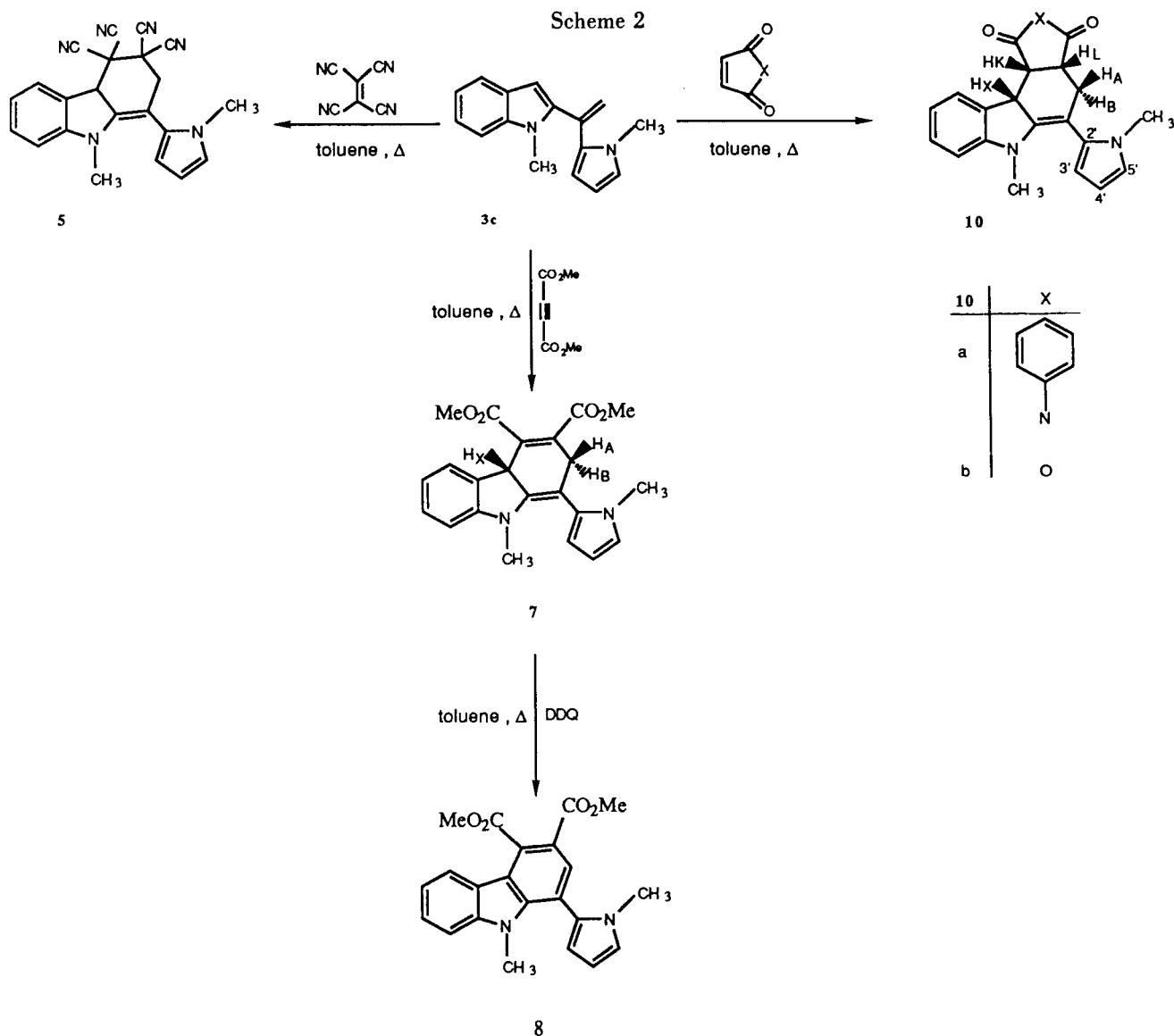


It is well known [7] that 2-vinylindoles of type **3** can be used as the diene in [4 + 2] π cycloaddition reactions for the synthesis of [c] annellated indoles and carbazole alkaloids. We therefore investigated 1-(1-methyl-2-indolyl)-1-(*N*-methyl-2'-pyrrolyl)ethene (**3c**) in the Diels-Alder reaction with reactive dienophiles (Scheme 2). An inspection of the structure of 1-(1-methyl-2-indolyl)-1-(*N*-methyl-2'-pyrrolyl)ethene (**3c**) suggests that the molecule could react in the cycloaddition reaction as a 2-vinylindole to give [c] annellated indoles or react as 2-vinylpyrrol to produce the corresponding [c] annellated pyrrols. We, however, found that the 2-vinylindoles gave only [c] annellated indoles.

Upon reaction with tetracyanoethylene, 1-(1-methyl-2-indolyl)-1-(*N*-methyl-2'-pyrrolyl)ethene (**3c**) formed a deep blue-black colored π -complex in toluene at room temperature [8]. After reaction for 12 hours at room temperature, 1,2,3,4,4 α ,9-hexahydro-1-(*N*-methyl-2'-pyrrolyl)-3,3,4,4-tetra-

tracyano-9-methylcarbazole (**5**) had precipitated in toluene and could be isolated by filtration. The ^1H nmr spectrum of the solid indicated that it contained no olefinic protons but three alicyclic protons. The signals for protons of two *N*-CH₃ groups were also present. The elemental analysis of the precipitate indicated that the compound had been formed by a [4 + 2] π addition reaction. The ^{13}C nmr spectrum displayed a triplet at 39.3 and a doublet at 47.5 ppm.

The Diels-Alder reaction of 1-(1-methyl-2-indolyl)-1-(*N*-methyl-2'-pyrrolyl)ethene (**3c**) with dimethylenedicarboxylate in refluxing toluene resulted in the formation of the cycloadduct dimethyl 2,4 α ,9-trihydro-9-methyl-1-(*N*-methyl-2'-pyrrolyl)carbazole-3,4-dicarboxylate (**7**). The spectral data, especially the ^1H nmr and ^{13}C nmr decoupling experiments, permitted the unequivocal characterization of dimethyl 2,4 α ,9-trihydro-9-methyl-1-(*N*-methyl-2'-pyrrolyl)-



carbazole-3,4-dicarboxylate (7).

The ^1H nmr spectra of **7** displays the methine proton as an X part of an ABX pattern at a relatively low field ($\delta_X = 4.45$, $J_{A,X} = 10$ Hz, $J_{B,X} = -6.5$ Hz) while the methylene protons appear as an AB system ($\delta_A = 3.06$, $\delta_B = 3.17$, $J_{A,B} = 2.6$ Hz). The structure of **7** was confirmed by selective decoupling experiments utilizing a computer simulation program (PANIC 853004, Bruker AG, AC 200). The coupling constants of the ABX system were determined and were found to be in agreement with the observed values. The protons of the pyrrole ring coupled to an AMX system. We analyzed as before ($\delta_X = 5.48$, $J_{A,X} = 3.10$ Hz, $\delta_M = 5.9$, $J_{M,X} = -1.71$ Hz, $\delta_A = 6.56$, $J_{A,M} = 2.6$ Hz). Dimethyl 2,4 α ,9-trihydro-9-methyl-1-(*N*-methyl-2'-pyrrolyl)-carbazole-3,4-dicarboxylate (**7**) was dehydrated [9] by DDQ to dimethyl 9-methyl-1-(*N*-methyl-2'-pyrrolyl)carbazole-3,4-dicarboxylate (**8**). The elemental analysis of **7-8** corresponded to a [4 + 2] π cycloaddition reaction. The ir spectra exhibited carbonyl absorptions for **7** at 1720 and 1700 cm^{-1} and for **8** at 1730 and 1710 cm^{-1} .

1-(1-Methyl-2-indolyl)-1-(*N*-methyl-2'-pyrrolyl)ethene (**3c**) reacts with *N*-phenylmaleimide giving moderate or good yields of the cycloadduct 1,1 α β ,2,3,3 α β ,4,6,10 β -octahydro-6-methyl-2-phenylpyrrolo[3,4-*c*]-5-[*N*-methyl-2'-pyrrolyl]carbazole-1,3-dione (**10a**) in refluxing toluene. In contrast to an analogous cycloaddition of 3-vinylindoles, the cycloaddition of 2-vinylindole **3c** was not successful in the presence of a Lewis acid (aluminum chloride). The elemental analysis of **10a** corresponded to a [4 + 2] π cycloaddition reaction. The ir spectra indicated carbonyl absorption at 1705 and 1700 cm^{-1} .

Since **10a** has three asymmetric centers, it was necessary to determine their relative stereochemistry by ^1H nmr spectroscopy and double resonance experiments. The ^1H nmr spectrum of **10a**, recorded in deuteriochloroform, displayed signals for the alicyclic protons at 2.33, 2.38 and 4.33 ppm which are coupled to an ABX system ($\delta_A = 2.33$, $\delta_B = 2.38$ and $\delta_X = 4.33$ ppm, $J_{A,B} = 5.88$ Hz, $J_{A,X} = -2.4$ Hz, $J_{B,X} = 7.19$ Hz). The signals at 3.21 and 4.23 ppm were due to H_K and H_L of **10a**. Of the two signals, the most deshielded proton at 4.23 ppm was coupled to a doublet ($J_{K,L} = 9.06$ Hz) which had no coupling to $C_{(10b)}$ -H. The signal at 4.23 ppm was then assigned to $C_{(1a)}$ -H because $C_{(1a)}$ -H and $C_{(10b)}$ -H were disposed *cis* and have, according to model structures, a torsional angle of almost 90°. Therefore, these protons do not show coupling to each other ($^3J_{vic} = 0$ at 90°). However, the signal at 3.21 ppm assigned to $C_{(3a)}$ -H showed coupling. The coupling constant of 9.06 Hz for $C_{(3a)}$ -H indicated that $C_{(1a)}$ -H and $C_{(3a)}$ -H were also *cis* disposed. $C_{(3a)}$ -H was coupled also with the $C_{(4)}$ -methylene protons to a triplet ($J_{3a,4} = 1.83$ Hz). Upon irradiation at 2.35 ppm ($C_{(4)}$ -H_AH_B), the $C_{(3a)}$ -H at 3.21 ppm became a doublet with a coupling constant of $J = 9.06$ Hz. This coupling experiment indicated that $C_{(3a)}$ -H and

$C_{(4)}$ -H_AH_B couple with each other.

We again confirmed the ^1H nmr spectrum by using the above mentioned Bruker simulation program. This underscored that **10a** was formed by *N*-phenylmaleimide addition to 2-vinylindole **3c** and that the addition itself was endo. The same high endo-preference was obtained when we used maleic anhydride as the dienophile. The stereochemistry of 1,1 α β ,2,3,3 α β ,4,6,10 β -octahydro-6-methyl-2-oxofurano[3,4-*c*]-5-(*N*-methylpyrrolyl)carbazole-1,3-dione (**10b**) was analyzed in a similar way. The signal at 4.34 ppm $C_{(1a)}$ -H had a coupling constant of 9.8 Hz, indicating that $C_{(1a)}$ -H and $C_{(3a)}$ -H were *cis* disposed. $C_{(1a)}$ -H shows no coupling to $C_{(10b)}$ -H. That means that $C_{(1a)}$ -H and $C_{(10b)}$ -H were also *cis* disposed and have a dihedral angle of about 90°. The $C_{(3a)}$ -H and $C_{(4)}$ -H_AH_B were again coupled to a triplet. The alicyclic protons at 2.22, 2.26 and 4.39 ppm were coupled to an ABX system ($J_{A,B} = 13.7$ Hz, $J_{A,X} = -0.45$ Hz, $J_{B,X} = 5.45$ Hz). The elemental analysis of **10b** corresponded also to a [4 + 2] π cycloaddition reaction. The ir spectrum indicated carbonyl absorption at 1700 and 1860 cm^{-1} .

The pronounced endo-selectivity of these reactions can be attributed to the energetically favorable interactions of a HOMO_{2-vinylindole}/LUMO_{dienophile} in the transition state. The intense secondary orbital interactions of both components contribute also to this endo-selectivity.

In conclusion, we have developed a novel synthesis for 2-vinylindoles and demonstrated their utility in the preparation of new [c] annellated indoles and carbazoles.

EXPERIMENTAL

The melting points were observed on a Buchi 510 apparatus (uncorrected). The ir spectra: were measured on a Perkin-Elmer 157 spectrophotometer; the ^1H nmr spectra on a Bruker AC 200 spectrometers with TMS as the internal standard unless otherwise stated. Likewise the ^{13}C nmr spectra were taken on a Bruker AC 200 spectrometers. Mass spectra were observed on a Varian CH-5 (The University of Kansas). The elemental analysis were obtained on Carlo Erba Strumentazione Model 1106 apparatus.

General Procedure for the Synthesis of Indolecarbinols **2**: 1-(1-Methyl-2-indolyl)-1-substituted Ethanol.

Nine ml (14 mmoles) of 1.55 molar *n*-butyllithium in hexane was added to 1-methylindole (**1**), 1.57 g (12 mmoles) in ether (10 ml). The reaction mixture was heated to reflux for 6 hours and then cooled to room temperature. The appropriate methyl ketone (12 mmoles) was added with stirring, and the mixture was heated to reflux for 2 hours and then cooled to room temperature. Water (20 ml) was added, and the organic layer separated. The aqueous phase was extracted with diethyl ether (3 x 15 ml), and the combined organic phases were washed with water (3 x 15 ml), dried (sodium sulfate), and evaporated to give carbinols **2** [10a].

1-(1-Methyl-2-indolyl)-1-methylethanol (**2a**).

This compound was obtained as a colorless powder, yield 1.81 g (80%), lit (78%) [11], mp 89-90°, lit 90-91° [11]; ir (potassium

bromide): ν 3500-3200 (s), 3050 (w), 2980 (m), 1470 (s), 1380 sh 1360 (s), 1160 (s), 950 (s), 780 (s), 760 (s) cm^{-1} ; ^1H nmr (deuteriochloroform): δ 1.52 (s, 6, 2 x CH_3), 3.71 (s, 3, $N\text{-CH}_3$), 6.09 (s, 1, OH), 6.80-7.80 (m, 4, aromat-H).

1-(1-Methyl-2-indolyl)-1-phenylethanol (2b).

This compound was obtained as a colorless powder, yield 2.32 g (77%), lit (62%) [6], mp 106-107°, lit 107° [6]; ir (potassium bromide): ν 3600-3100 (s), 3060 (w), 2960 (w), 1600 (w), 1460 (m), 1440 (m), 1350 (s), 1165 (s), 780 (s), 730 (s), 700 (s) cm^{-1} ; ^1H nmr (deuteriochloroform): δ 1.87 (s, 3, CH_3), 2.26 (s, 1, OH), 3.28 (s, 3, $N\text{-CH}_3$), 6.59-7.61 (m, 10, aromat-H); ^{13}C nmr (deuteriochloroform): δ 31.1 (q, CH_3), 33.1 (q, $N\text{-CH}_3$), 73.3 (s, quaternary-C), aromat-C, 100.4, 109, 119.4, 120.6, 121.8, 124.9, 126.4, 126.8, 128.1, 138.4, 143.6, 145.7.

1-(1-Methyl-2-indolyl)-1-(*N*-methyl-2'-pyrrolyl)ethanol (2c).

This compound was obtained as a colorless powder, yield 1.22 g (40%), mp 98-99°; ir (potassium bromide): ν 3480 (s), 3000 (w), 2950 (w), 1460 (s), 1310 (s), 1100 (s), 800 (m), 750 (s), 730 (s) cm^{-1} ; ^1H nmr (deuteriochloroform): δ 1.97 (s, 3, CH_3), 2.2 (s, 1, OH), 3.32 (s, 3, $N\text{-CH}_3$), 3.52 (s, 3, $N\text{-CH}_3$), 6.02-7.55 (m, 8, aromat-H); ^{13}C nmr (deuteriochloroform): δ 15.1 (q, CH_3), 30.6 (q, $N\text{-CH}_3$), 35.3 (q, $N\text{-CH}_3$), 70.1 (s, quaternary-C), aromat-C, 99.9, 106, 107.6, 109, 119.4, 120.5, 121.4, 124.3, 126.6, 135, 138.3.

Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}$ (254.3): C, 75.56; H, 7.13; N, 11.01. Found: C, 75.52; H, 7.40; N, 10.98.

1-(1-Methyl-2-indolyl)-1-(2'-thiophenyl)ethanol (2d).

This compound was obtained as a colorless powder, yield 1.20 g (39%), mp 86-87°; ir (potassium bromide): ν 3500 (s), 3100 (w), 2980 (w), 1470 (m), 1310 (m), 1140 (s), 750 (s) cm^{-1} ; ^1H nmr (deuteriochloroform): δ 2.0 (s, 3, CH_3), 2.48 (s, 1, OH), 3.49 (s, 3, CH_3), 3.54-7.6 (m, 8, aromat-H); ^{13}C nmr (deuteriochloroform): δ 31.3 (q, CH_3), 33.4 (q, $N\text{-CH}_3$), 72.2 (s, quaternary-C), aromat-C, 100, 109.1, 119.5, 120.7, 122, 122.4, 123.5, 126.4, 126.5, 138.5, 143, 150.7.

Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{NOS}$ (257.3): C, 70.00; H, 5.87; N, 5.44. Found: C, 70.40; H, 5.79; N, 5.42.

1-(1-Methyl-2-indolyl)-1-(2'-pyridinyl)ethanol (2e).

This compound was obtained as a colorless powder, yield 1.81 g (60%), mp 115-116°; ir (potassium bromide): ν 3600-3100 (s), 3070 (w), 2940 (w), 1580 (s), 1460 (s), 1430 (m), 1330 (s), 1160 (s), 790 (m), 750 (s) cm^{-1} ; ^1H nmr (deuteriochloroform): δ 1.92 (s, 3, CH_3), 3.34 (s, 3, $N\text{-CH}_3$), 6.05-8.47 (m, 9, aromat-H); ^{13}C nmr (deuteriochloroform): δ 30.6 (q, CH_3), 30.65 (q, $N\text{-CH}_3$), 72.6 (s, quaternary-C), aromat-C; 100, 108.6, 118.7, 119.6, 119.9, 121, 121.7, 126.3, 136.6, 137.6, 143.8, 147.6, 164.3.

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}$ (252.3): C, 76.16; H, 6.39; N, 11.10. Found: C, 76.23; H, 6.80; N, 10.90.

General Procedure for the Synthesis of 2-Vinylindoles 3.

The carbinols **2** 1.20 g (5 mmoles) and trifluoroacetic acid 0.57 g (5 mmoles) in chloroform (20 ml) were stirred at 20° for 2 minutes and triethylamine 1.0 g (6 mmoles) 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 over sodium sulfate and evaporated to give crude 2-vinylindoles **3**,

which were further purified [10b] by column chromatography on silica gel 60, utilizing ethyl acetate/*n*-hexanes as eluent.

2-(1-Methyl-2-indolyl)propene (3a).

This compound was obtained as a colorless liquid, yield 0.72 g (85%), lit (77%) [6], bp 96°/0.07 mm, lit 95°/0.07 mm [6]; ^1H nmr (deuteriochloroform): δ 2.15 (m, 3, CH_3), 3.7 (s, 3, $N\text{-CH}_3$), 5.13 (s (br), 1, =CH), 5.31 (m, 1, =CH), 6.45 (s, 1, $N\text{-H}$), 7.07-7.57 (m, 4, aromat-H).

1-(1-Methyl-2-indolyl)-1-phenylethene (3b).

This compound was obtained as a colorless powder, yield 0.7 g (60%), lit (77%) [6], mp 121-122°, lit 120° [6]; ^1H nmr (deuteriochloroform): δ 3.10 (s, 3, CH_3), 5.23 (d, 1, =CH, J = 2 Hz), 5.45 (d, 1, =CH, J = 2 Hz), 6.22-7.25 (m, 10, aromat-H).

1-(1-Methyl-2-indolyl)-1-(*N*-methyl-2'-pyrrolyl)ethene (3c).

This compound was obtained as an oil, yield 1.15 g (98%); ir (film): ν 3100 (m), 3050 (m), 2940 (s), 1705 (s), 1600 (m), 1460 (s), 1320 (s), 790 (s), 730 (s) cm^{-1} ; ^1H nmr (deuteriochloroform): δ 3.16 (s, 3, CH_3), 3.34 (s, 3, CH_3), 5.41 (d, 1, =CH, J = 2.1 Hz), 5.48 (d, 1, =CH, J = 2.1 Hz), 6.07-7.6 (m, 8, aromat-H); ^{13}C nmr (deuteriochloroform): δ 30.2 (q, $N\text{-CH}_3$), 34.7 (q, $N\text{-CH}_3$), vinyl-C, 102.4, 110.3, aromat-C, 107.6, 109.3, 116.9, 119.7, 120.5, 121.7, 124.3, 127.6, 132.6, 133, 138.2, 140.8.

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_2$ (236.3): C, 81.32; H, 6.82; N, 11.85. Found: C, 80.95; H, 6.54; N, 11.77.

1,2,3,4,4a,9-Hexahydro-1-(*N*-methyl-2'-pyrrolyl)-3,3,4,4-tetracyano-9-methylcarbazole (5).

To a solution of 2-vinylindole **3c** 707 mg (2.99 mmoles) in toluene (10 ml), a solution of 383 mg (2.99 mmoles) of tetracyanoethylene in toluene (10 ml) was added at room temperature. The mixture was stirred overnight at room temperature. The precipitate formed thereafter was filtered and washed with toluene (3 x 10 ml), resulting in 130 mg (12%) of **5** as a colorless solid, mp 141-142° dec; ir (potassium bromide): ν 3100 (w), 3060 (w), 2940 (m), 2250 (w, CN), 1660 (s), 1605 (s), 1485 sh 1470 (s), 1340 (s), 1100 (m), 750 (m), 730 (s) cm^{-1} ; ^1H nmr (deuteriochloroform): δ 2.63 (s, 2, CH_2), 3.47 (s (br), 6, 2 x $N\text{-CH}_3$), 4.86 (s, 1, CH), 6.17-7.67 (m, 7, aromat-H); ^{13}C nmr (deuteriochloroform): δ 34.0 (q, $N\text{-CH}_3$), 39.3 (t, CH_2), 47.5 (d, CH), aromat-C; 107.4, 108.6, 110.7, 111.4, 120.9, 122.6, 123.6, 131.2; ms: m/e 335, 299, 131, 76.

Anal. Calcd. for $\text{C}_{22}\text{H}_{16}\text{N}_6$ (364.4): C, 72.51; H, 4.42. Found: C, 72.27; H, 4.22.

Dimethyl 2,4a,9-Trihydro-9-methyl-1-(*N*-methyl-2'-pyrrolyl)carbazole-3,4-dicarboxylate (7).

2-Vinylindole **3c** (410 mg, 1.73 mmoles) and 246 mg (1.73 mmoles) of acetylenedimethyl ester were mixed in toluene (20 ml) and refluxed for 8 hours under a stream of nitrogen. The solvent was evaporated under reduced pressure. The residue was submitted to silica gel chromatography (ethyl acetate/*n*-hexanes), affording the corresponding cycloadduct. Final purification entailed recrystallization (ethanol), yield 200 mg (31%) as a colorless solid, mp 184-185°; ir (potassium bromide): ν 3040 (w), 2950 (m), 1720 (s, C=O), 1700 (s, C=O), 1600 (s), 1430 (s), 1270 sh 1260 (s), 1220 (s), 1200 (s), 1070 (s), 770 sh 760 (s), 750 (m), 720 (m) cm^{-1} ; ^1H nmr (deuteriochloroform): δ AB system ($\delta_A = 3.06$, $\delta_B = 3.17$, $J_{A,B} = 2.6$ Hz, 2, C(2)H), 3.44 (s, 3, $N\text{-CH}_3$), 3.67 (s, 3, $N\text{-CH}_3$), 3.71 (s, 3, OCH₃), 4.02 (s, 3, OCH₃), X system ($\delta_X = 4.45$, $J_{A,X} = 10.5$ Hz,

$J_{B,X} = -6.5$ Hz), AMX system ($\delta_X = 5.48$, $\delta_M = 5.9$, $\delta_A = 6.56$, $J_{A,X} = 3.10$ Hz, $J_{M,X} = -1.71$ Hz, $J_{A,M} = 2.6$ Hz, 3, C(3'-H), C(4'-H), C(5'-H), 7.1-7.51 (m, 4, arom-H); ^{13}C nmr (deuteriochloroform): δ 29.7 (q, *N*-CH₃), 31.0 (t, C-2), 33.9 (d, C-4a), 51.8 (q, OCH₃), 52.4 (q, OCH₃), arom-C + vinyl-C: 107.1, 107.9, 108.3, 109.7, 112.4, 118.5, 121.4, 122.3, 122.7, 123.5, 129.5, 138, 138.4, 138.5, 141.6, carbonyl-C, 166.6, 169.5, pyrrole-C, 108.3 (C-4'), 121.4 (C-3'), 129.5 (C-5'), 141.6 (C-2).

Anal. Calcd. for C₂₂H₂₂N₂O₄ (378.4): C, 69.82; H, 5.85; N, 7.40. Found: C, 69.94; H, 6.09, N, 6.95.

Dimethyl 9-Methyl-1-(*N*-methyl-2'-pyrrolyl)carbazole-3,4-dicarboxylate (**8**).

Eighty-seven mg (0.23 mmole) of **7** and 52 mg (0.23 mmole) of DDQ in toluene (10 ml) were refluxed for 4 hours. The hydroquinone formed was filtered, and the solvent was evaporated. The residue was recrystallized from ethyl acetate/*n*-hexanes (1:2), yield 50 mg (58%) as a colorless solid, mp 151-152°; ir (potassium bromide): ν 3060 (w), 3000 (w), 2950 (m), 1730 (s, C=O), 1710 (s, C=O), 1560 (m), 1440 (m), 1330 (m), 1260 (s), 1225 (s), 1095 (m), 800 (w), 730 sh 720 (m) cm⁻¹; ^1H nmr (deuteriochloroform): δ 3.32, 3.33 (s, 6, 2 x *N*-CH₃), 3.92 (s, 3, OCH₃), 4.18 (s, 3, OCH₃), 6.28-8.08 (m, 8, arom-H); ^{13}C nmr (deuteriochloroform): δ 30.0 (q, *N*-CH₃), 34.2 (q, *N*-CH₃), 52.2 (q, OCH₃), 53.0 (q, OCH₃), arom-C, 108.1, 109.3, 110.8, 120.8, 121.4, 122.1, 127.1, 131.4; ms: (m/e) 376 (M⁺), 345.

Anal. Calcd. for C₂₂H₂₀N₂O₄ (376.4): C, 70.20; H, 5.35; N, 7.44. Found: C, 69.80; H, 5.37; N, 7.13.

1,1 α ,2,3,3 α ,4,6,10 β -Octahydro-6-methyl-2-phenylpyrrolo[3,4-*c*]-5-[*N*-methyl-2'-pyrrolyl]carbazole-1,3-dione (**10a**).

2-Vinylindole **3c** (241 mg, 1.0 mmole) and 175 mg of *N*-phenylmaleimide in toluene (30 ml) were refluxed for 24 hours. Then the reaction mixture was cooled. The solvent was evaporated under reduced pressure. The residue was submitted to column chromatography (silica gel 60, Fluka AG, ethyl acetate/*n*-hexanes), affording the corresponding cycloadduct, yield 125 mg (31%), mp 218-220°; ir (potassium bromide): ν 3060 (w), 2930 (m), 1705 (s, C=O), 1500 (s), 1380 (s), 1180 (s), 790 (m), 750 (s), 740 (s), 690 (s) cm⁻¹; ^1H nmr (deuteriochloroform): δ ABX system ($\delta_A = 2.38$, $\delta_B = 2.33$, $\delta_X = 4.33$, $J_{A,B} = 5.88$ Hz, $J_{A,X} = -2.4$ Hz, $J_{B,X} = 7.19$ Hz, 3, 4-H, C(10 β -H), 3.21 (m, 1, C(3 α -H), 3.36 (s, 3, *N*-CH₃), 3.88 (s, 3, *N*-CH₃), 4.23 (m, 1, C(1 α -H), 5.33 (s, 1, C(4'-H), 6 (d, $J_{3,2'} = 2.81$ Hz, 1, C(3'-H), 6.61 (d, $J_{2,3'} = 2.81$ Hz, 1, C(2'-H), 7.0-7.3 (m, 9, arom-H) [13]; ^{13}C nmr (deuteriochloroform): δ 27.4 (q, *N*-CH₃), 28.9 (q, *N*-CH₃), 30.1 (t, C-4), 32.8 (s, C-10 β), 37.9 (d, C-3 α), 39.3 (d, C-1 α), arom-C + vinyl-C, 101.8, 106.6, 109.1, 119.5, 120.1, 121.5, 122.4, 126.1, 127.8, 128.4, 140, carbonyl-C, 176.0, 176.9; ms: (m/e) 409 (M⁺), 261, 131, 77, 64.

Anal. Calcd. for C₂₆H₂₃N₃O₂ (409.5): C, 76.26; H, 5.66; N, 10.26. Found: C, 76.53; H, 5.59; N, 10.34.

1-1 α ,2,3,3 α ,4,6,10 β -Octahydro-6-methyl-2-oxofurano[3,4-*c*]-5-(*N*-methyl-2'-pyrrolyl)carbazole-1,3-dione (**10b**).

Compound **10b** was synthesized from 730 mg (3.08 mmoles) of 2-vinylindole **3c** and 300 mg (3.08 mmoles) of maleic anhydride as described for **10a**, yield 200 mg (19%), mp 118° dec; ir (potassium bromide): ν 3050 (w), 2940 (m), 1860 (s, C=O), 1780 (s, C=O), 1460 (m), 920 (s), 780 (m), 750 (m) cm⁻¹; ^1H nmr (deuteriochloroform): δ ABX system ($\delta_A = 2.22$, $\delta_B = 2.26$, $\delta_X = 4.39$, $J_{A,B} = 13.7$ Hz, $J_{A,X} = -0.45$ Hz, $J_{B,X} = 5.45$ Hz, 3, 4-H, C(10 β -H),

2.85 (m, 1, C(3 α -H), 3.34 (s, 3, *N*-CH₃), 3.81 (s, 3, *N*-CH₃), 4.34 (m, 1, C(1 α -H), 5.37 (s, 1, C(4'-H), 6.37 (d, $J_{3,2'} = 3.69$ Hz, 1, C(3'-H), 6.69 (d, $J_{2,3'} = 3.69$ Hz, 1, C(2'-H), 7.0-7.4 (m, 4, arom-H); ^{13}C nmr (deuteriochloroform): δ 27.1 (q, *N*-CH₃), 28.5 (q, *N*-CH₃), 29.9 (t, C-4), 32.8 (d, C-10 β), 38.0 (d, C-3 α), 39.5 (d, C-1 α), arom-C + vinyl-C, 102.3, 106.0, 108.7, 109.9, 119.5, 120.5, 121.6, 122.9, 126.9, 127.7, 138.2, 138.5, carbonyl-C, 171.9, 172.2; ms: (m/e) 334 (M⁺), 262, 131, 77, 63.

Anal. Calcd. for C₂₀H₁₈N₂O₃ (334.4): C, 71.84; H, 5.42; N, 8.37. Found: C, 71.83; H, 5.34; N, 8.52.

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REFERENCES AND NOTES

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[1] I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", John Wiley, New York, 1976.

[2] E. Akgün and U. Pindur, *Chimia*, **39**, 266 (1985), and references therein.

[3a] P. Bhattacharyya, S. S. Jash and B. K. Chowdhury, *Chem. Ind. (London)*, 246 (1986); [b] B. K. Chowdhury, S. K. Hirani, A. Mustapha and P. Bhattacharyya, *Chem. Ind. (London)*, 128 (1987); [c] T. Martin and C. J. Moody, *J. Chem. Soc., Perkin Trans., 1*, 235 (1988); [d] T. Martin and C. J. Moody, *J. Chem. Soc., Perkin Trans., 1*, 241 (1988); [e] C. May and C. J. Moody, *J. Chem. Soc., Perkin Trans., 1*, 247 (1988); [f] S. Coffey, in "Rodd's Chemistry of Carbon Compounds" 2nd Ed, Vol IV, part A, Elsevier, Amsterdam, London, New York, 1973; [g] S. W. Pelletier, in "Chemistry of the Alkaloids", Van Nostrand Reinhold Company, New York, Cincinnati, Toronto, London, Melbourne, 1970.

[4a] V. O. Illi, *Synthesis*, 136 (1979); [b] D. Dhanek and C. B. Reese, *J. Chem. Soc., Perkin Trans. 1*, 2181 (1986); [c] I. Hasan, E. R. Marinelli, L. C. C. Liu, F. W. Fowler and A. B. Levy, *J. Org. Chem.*, **46**, 157 (1981).

[5] The elimination reaction from **2** to **3** is under continuing investigation.

[6a] R. A. Jones, P. M. Fresneda, T. A. Saliente and J. S. Arques, *Tetrahedron*, **40**, 4837 (1984); [b] U. Pindur and M. H. Kim, *Chem. Ztg.*, **112**, 113 (1988).

[7a] J. Bergman and A. Pelcman, *Tetrahedron Letters*, **26**, 6389 (1985); [b] N. S. Narasimhan and R. S. Kusurkar, *Indian J. Chem.*, **22(B)**, 846, (1983); [c] N. S. Narasimhan, R. S. Kusurkar and D. D. Dhavale, *Indian J. Chem.*, **22(B)**, 1004 (1983).

[8a] R. E. Merrifield and W. D. Philipps, *J. Am. Chem. Soc.*, **80**, 2778 (1958); [b] W. E. Noland, W. C. Kuryle and R. L. Lange, *J. Am. Chem. Soc.*, **81**, 6010 (1959).

[9a] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol XIII, John Wiley and Sons, Inc., New York, London, Sydney, 1987, p 215; [b] M. Zander and C. Grundman, "Methoden der Organischen Chemie, Houben-Weyl", Vol V/2b, Georg Thieme Verlag, Stuttgart, New York, 1981, p 124.

[10a] The percent yields of the products, the elemental data and spectroscopic data are given after each compound; [b] The percent yields of the products, the elemental data and the spectroscopic data are given after each compound.

[11] F. E. Ziegler, E. B. Spitzner and C. K. Wilkins, *J. Org. Chem.*, **36**, 1759 (1971).

[12] Compound **3a** was synthesized according to the procedure in reference [6].

[13] H. Friebolin, "NMR-Spektroskopie", Verlag Chemie, Physik Verlag, 1973, p 132.