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Received May 15, 1992

The Diels-Alder reactions of 1-substituted-3-(2-nitrovinyl)indoles **3** with quinones and acetylenes give aromatized 1:1 adducts (- nitrous acid) (**1**) or (- nitrous acid, -2 hydrogens) **2,5**. Likewise, dimerization (-2 nitrous acids) of **3** gives aromatized 2-(3-indolyl)carbazoles **4**. In contrast, **3** reacts with maleimides **6** to give 1:2 adducts (- nitrous acid or -2 hydrogens) **10** and **11**, respectively, along with smaller amounts of 1:1 adducts (- nitrous acid, -2 hydrogens; or -4 hydrogens) **12** and **13**, respectively. A mechanism for formation of the nitro products **11** and **13** is discussed. A 1:2 adduct (-2 hydrogens) **19** was also obtained from a Diels-Alder reaction between maleimide and the vinylindole produced *in situ* by condensing 1-methylindole with acetone. The stereochemistry of this 1:2 adduct has been determined by X-ray crystallography.

J. Heterocyclic Chem., **30**, 183 (1993).

Introduction.

There is considerable interest in synthesizing carbazole derivatives due to the great diversity of biological activity shown by this class of natural and synthetic alkaloids. We first published the synthesis of carbazoles through Diels-Alder reactions of vinylindoles in 1959 [1a] and 1963 [1b]. In recent years, other researchers have found utility for and have expanded upon this methodology [2,3]. The products of these reactions have the potential for being precursors for other, more complicated carbazole derivatives [4].

From the reactions of most vinylindoles, the major products that have been isolated are tetrahydrocarbazoles, although these often aromatize *in situ* to a small extent [1a,5,6]. With nitrovinylindoles, however, the initial adducts eliminate nitrous acid and then subsequently aromatize [3b,7]. The elimination of methanol has been reported [5] when 3-(2-methoxyvinyl)-1-phenylsulfonylindole undergoes cycloaddition with *N*-phenylmaleimide (**6a**). The intermediate adduct then undergoes a second cycloaddition with **6a** to produce a 1:2 adduct (- methanol) (Scheme II, compound **14**). Two other examples of bridged carbazoles being formed through Diels-Alder reactions have been found in the literature [3d,8].

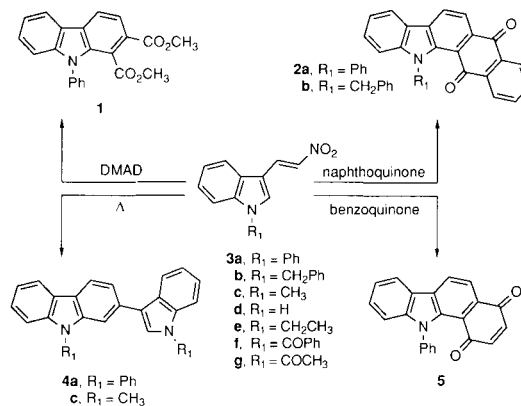
In this paper, we report a number of bridged carbazoles that are formed by the trapping of intermediates of the reactions of nitrovinylindoles with maleimides and we also report some related results involving other Diels-Alder reactions of vinylindoles.

Results and Discussion.

When 3-(2-nitrovinyl)-1-phenylindole (**3a**) reacted in re-

fluxing xylene in the presence of three equivalents of benzoquinone, a 1:1 adduct (- nitrous acid, -2 hydrogens) **5** was obtained as the sole crystalline product (Scheme I). Likewise, **3a** and also 3-(2-nitrovinyl)-1-benzylindole (**3b**) with naphthoquinone gave only the 1:1 adducts (- nitrous acid, -2 hydrogens) **2a** and **2b**, respectively. With dimethyl acetylenedicarboxylate (DMAD), **3a** also gave a 1:1 adduct (- nitrous acid) **1**. These results are analogous to what has previously been reported with nitrovinylindoles [3b,7].

Scheme I

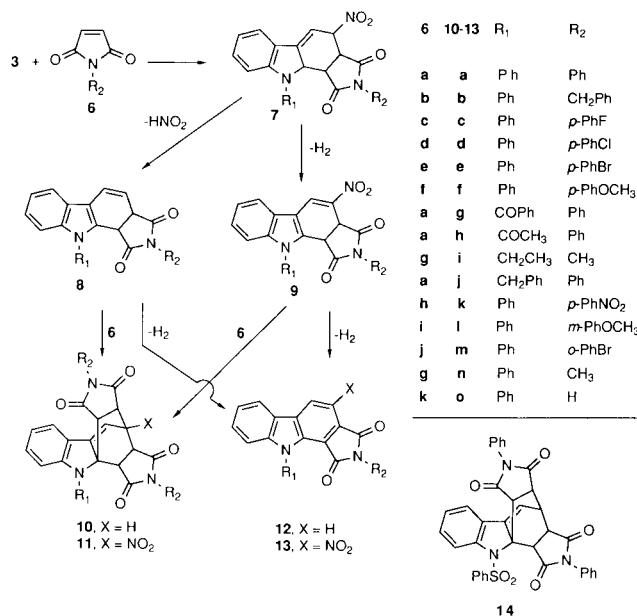


At higher temperatures (180-200°), **3a** dimerized and eliminated 2 nitrous acids to form the indolylcarbazole **4a**. In this reaction, one equivalent of **3a** was the diene and the other was the dienophile. We were not able to rigorously assign the indolyl moiety to the 1- or 2-position of the carbazole, but favor the 2-position because of the orientation of the polarity of the dienophile in the Diels-Alder reaction [9]. In addition, with the dimerized product

(-2 nitrous acids) **4c** from 1-methyl-3-(2-nitrovinyl)indole (**3c**), two singlets were seen in the ^1H nmr spectrum at 7.63 and 7.81 which are assigned to the 2'-indolyl and 1-carbazolyl protons. 3-(2-Nitrovinyl)indole (**3d**) gave only tar when heated under the same conditions.

When **3a** was refluxed in benzene or xylene with one or two equivalents of maleimide **6a**, the 1:2 adduct (- nitrous acid) **10a** was obtained as the major product, while the 1:1 adduct (- nitrous acid, -2 hydrogens) **12a** was isolated in less than 1% yield. While **3a** reacted with **6a** to give **10a** as the only 1:2 adduct, **3a** reacted with other maleimides to give 1:2 nitro adducts (-2 hydrogens) of structure **11**, as well as adducts of structure **10**. In addition, higher yields (2-57%) of carbazoles **12** were isolated in many of these reactions in refluxing benzene or xylene. The results of the Diels-Alder reactions of vinylindoles **3** with maleimides **6** are summarized in Table I. Physical and spectral data for carbazoles **10-13** are given in Tables III-IV.

Scheme II



The proposed mechanistic pathways for formation of **10-13** are shown in Scheme II. After the initial cycloaddition, intermediate **7** can either eliminate nitrous acid or be oxidized with loss of 2 hydrogens. This divergence leads to 1:2 adducts **10** or **11** after a second cycloaddition or to 1:1 adducts **12** or **13** if aromatization occurs instead. We had initially not isolated nitrocarbazoles such as **13**, so we had speculated that bridged carbazoles **10** were being nitrated by nitrogen oxides from decomposition of the byproduct nitrous acid. Since then, we have isolated and characterized carbazole **13i** from the reaction of 1-ethyl-3-(2-nitrovinyl)indole (**3e**) with *N*-methylmaleimide (**6g**). In addition, we detected (by ^1H nmr and ms of crude samples), but

Table I
Diels-Alder-Derived Products of Nitrovinylindoles **3**
and Maleimides **6** [a]

Vinylindole	Maleimide	Products, % yield		
3 R ₁	6 R ₂	10	11	12
a Ph	a Ph	a 45	0	0
"	b CH ₂ Ph	b 22 [b]	14 [b]	0
"	c <i>p</i> -PhF	c 42 [b]	21 [b]	12
"	d <i>p</i> -PhCl	d 0	0	57
"	e <i>p</i> -PhBr	e trace [c]	22	0
"	f <i>p</i> -PhOCH ₃	f 19	0	0
f COPh	a Ph	g 0	29	0
a Ph	a Ph	a 47	0	0.7
"	e <i>p</i> -PhF	e 34 [b]	19 [b]	0
"	d <i>p</i> -PhCl	d 35 [b]	9 [b]	17
"	e <i>p</i> -PhBr	e 48 [b]	7 [b]	2
g COCH ₃	a Ph	h 38	25	0
e CH ₂ CH ₃	g CH ₃	i 28	0	14 [d]
a Ph	a Ph	a 0	0	71
b CH ₂ Ph	a Ph	j 0	0	46

[a] The solvent for the first 7 entries was benzene. The solvent for the next 6 entries was xylene. The solvent for the last 2 entries was acetic acid. [b] Products **10** and **11** were not separated. The ratio of each was determined by ^1H nmr. [c] Product **10e** was not isolated in this reaction; it could, however, be seen by ^1H nmr as a minor impurity in **11e**. [d] Product **13i** (4%) was also isolated.

Table II

Diels-Alder-Derived Products of Nitrovinylindoles and Maleimides
When the Reaction Mixture Was Flushed with Nitrogen [a]

Vinylindole	Maleimide	Products
3 R ¹	6 R ²	10 % yield
a Ph	b CH ₂ Ph	b 39 [b]
"	c <i>p</i> -PhF	c 60
"	d <i>p</i> -PhCl	d 50
"	e <i>p</i> -PhBr	e 46
"	h <i>p</i> -PhNO ₂	k 42 [c]
"	i <i>m</i> -PhOCH ₃	l 63
"	j <i>o</i> -PhBr	m 19
"	g CH ₃	n 44
"	k H	o 59
g COCH ₃	a Ph	h 37

[a] The solvent was xylene in all cases. [b] The reaction also produced **11b** (17% by ^1H nmr); compounds **10b** and **11b** were not separated. [c] Compound **12k** (6%) was also isolated.

not isolated, traces of nitrocarbazoles **13** in the products from other reactions. Other evidence also indicates that the nitro group must be retained throughout the reaction. We were unable to nitrate **10** with nitrous acid. If nitrogen

Table III
¹H NMR Spectral Data for Bridged Carbazoles **10** [a]

10	H _a d, 2H	H _b dd, 2H	H _c m, 1H	H _d d, 1H	other
a	3.42 J = 8.3	3.10 J = 8.2, 2.7	4.16	6.21 J = 6.2	6.77 (m, 2 H), 6.92 (dd, J = 8.0, 1.5, 4 H), 7.14 (t, J = 8.1, 1 H), 7.25-7.50 (m, 10 H), 8.03 (d, J = 7.7, 2 H)
c	3.55 J = 9.0	3.21 J = 8.4, 3.0	4.23	6.23 J = 6.2	6.71- 7.51 (m, ~16 H, includes chloroform), 8.04 (d, J = 7.4, 2 H)
d	3.56 J = 8.3	3.23 J = 8.4, 3.0	4.25	6.22 J = 6.2	6.72 (d, J = 7.4), 6.81 (d, J = 8.2), 6.89-6.93 (m, area for 6.72-6.93 is 6 H), 7.12-7.38 (m), 7.44 (t, J = 8.1, area for 7.12-7.44 is ~12 H, includes chloroform), 8.04 (d, J = 7.4, 2 H)
e	3.53 J = 8.4	3.19 J = 8.3, 3.0	4.22	6.20 J = 6.2	6.70-6.85 (m, 7 H), 7.15 (t, J = 7.7, 1 H), 7.28-7.49 (m, 7 H), 8.03 (d, J = 7.7, 2 H)
f	3.46 J = 8.3	3.14 J = 8.3, 2.8	4.20	6.21 J = 6.2	3.73 (s, 6 H), 6.70-7.00 (m), 7.13 (t, 7.6), 7.29 (t, J = 7.3), 7.37 (d, J = 7.6), 7.45 (t, J = 7.6, area for 6.70-7.45 is ~18 H, includes chloroform)
h	4.54 J = 8.6	3.32 J = 8.6, 3.1	4.20	6.38 J = 6.2	2.68 (s, 3 H), 6.89 (dd, J = 8.1, 1.9, 4 H), 7.06 (t, J = 7.5, 1 H), 7.25-7.40 (m, 8 H), 7.47 (d, J = 7.5, 1 H)
i	3.25 J = 8.3	3.02 J = 8.3, 3.1	4.07	5.89 J = 6.3	1.59 (t, J = 7.3, 3 H), 2.73 (s, 6 H), 3.75 (q, J = 7.3, 2 H), 6.57 (t, J = 7.6, 1 H), 6.68 (d, J = 7.9), 7.17 (d, J = 7.5, 1 H), 7.21 (t, J = 7.3, 1 H)
k [b]	3.98 J = 8.4	3.67 J = 8.3, 3.0	4.11	6.51 J = 6.2	6.71 (t, J = 7.5, 1 H), 6.78 (d, J = 8.2, 1 H), 7.14 (t, J = 7.2, 1 H), 7.35 (d, J = 9.0, 4 H), 7.53 (m, 3 H), 8.10 (d, J = 8.4, 2 H), 8.26 (d, J = 9.1, 4 H)
l	3.53 J = 8.3	3.20	4.24	6.25 J = 6.3	3.67 (s, 6 H), 6.42 (s, 2 H), 6.55 (d, J = 7.7, 2 H), 6.70 (t, J = 7.4, 1 H), 6.79 (d, J = 7.1, 1 H), 6.84 (d, J = 8.4, 2 H), 7.13 (t, J = 7.8, 1 H), 7.22-7.32 (m, ~5 H, includes chloroform), 7.38 (d, J = 7.6, 1 H), 7.46 (t, J = 7.7, 2 H), 8.06 (d, J = 8.2, 2 H)
m [c]	3.77 J = 8.3	3.52	3.91	6.57 J = 6.2	6.64 (d, J = 7.5, 2 H), 7.04 (t, J = 7.7, 1 H), 7.28-7.51 (m, 8 H), 7.65 (d, J = 7.9, 2 H), 7.89 (d, J = 8.2, 2 H)
n	3.33 J = 8.3	2.97 J = 8.2, 2.9	4.07	6.01 J = 6.2	2.77 (s, 6 H), 6.67 (t, J = 7.5, 1 H), 6.77 (d, J = 7.5, 1 H), 7.12 (t, J = 7.4, 1 H), 7.25 (t, J = 7.5, 1 H), 7.31 (d, J = 7.4, 1 H), 7.48 (t, J = 7.7, 2 H), 8.04 (d, J = 7.9, 2 H)
o	3.58 J = 8.4	3.27 J = 8.4, 3.0	3.82	6.29 J = 6.2	6.65 (d, J = 7.4, 1 H), 6.70 (d, J = 8.2, 1 H), 7.10 (dt, 7.2, 1.3, 1 H), 7.30 (t, J = 7.3, 1 H), 7.45 (t, J = 8.0, 2 H), 7.49 (t, J = 7.4, 1 H), 8.08 (dd J = 7.4, 1.3, 2 H), 9.98 (br s, 1 H)

[a] See Figure II. Chemical shifts are given in δ ppm. Coupling constants are given in hertz. The solvent was deuteriochloroform unless otherwise noted. [b] In acetone- d_6 . [c] In dimethyl sulfoxide- d_6 .

Table IV
 Data for Bridged Carbazoles **11**

11	Mp, °C	Appearance	¹ H NMR Data δ ppm, J in Hertz	Molecular Formula	Analysis		
					Calcd./Found C	H	N
e	244-245	yellow powder	3.88 (d, J = 8.6, 2 H), 4.16 (d, J = 8.6, 2 H), 6.66-6.90 (m, 8 H), 7.25-7.43 (m, 8 H), 7.92 (d, J = 7.8, 2 H)	C ₃₆ H ₂₂ Br ₂ N ₄ O ₆	56.42 56.23	2.89 3.04	7.31 7.41
g	349-359.5	white flakes	4.20 (d, J = 9.0, 2 H), 4.94 (d, J = 8.9, 2 H), 5.90 (m, 1 H), 6.90 (m, 4 H), 7.01 (m, 2 H), 7.18 (s, 1 H), 7.25-7.36 (m, 5 H), 7.45-7.60 (m, 5 H), 7.79 (d, J = 6.9, 2 H)	C ₃₇ H ₂₄ N ₄ O ₇	69.81 70.02	3.80 4.00	8.80 8.64
h	305-307	white flakes	2.60 (s, 3 H), 4.41 (d, J = 8.7, 2 H), 4.68 (d, J = 8.5, 2 H), 6.86 (dd, J = 8.0, 1.8, 4 H), 7.17 (t, J = 7.5, 1 H), 7.32-7.44 (m, 7 H), 7.47 (s, 1 H), 7.53 (d, J = 8.5, 1 H), 7.98 (d, J = 7.6, 1 H)	C ₃₂ H ₂₂ N ₄ O ₇	66.90 66.76	3.86 4.00	9.75 9.58

was bubbled through the reaction mixture, only 1:2 adducts **10** were obtained in most of the reactions (Table II). By itself, this does not differentiate between the two mechanisms since the nitrogen flushes out not only nitrogen ox-

ides but also oxygen from the air. When air was bubbled through the reaction mixture, however, an increased proportion of **11c** compared to **10c** was produced. This is most easily explained if oxygen from the air is oxidizing

Table V
More Spectral Data for Bridged Carbazoles **10** and **11**

Compound	¹³ C NMR Data [a] δ ppm, J in Hertz	IR [b] C=O	MS [c] method	Found (relative intensity)
10a	35.4, 41.1, 43.7, 70.5, 108.0, 109.1, 118.7, 120.4, 121.2, 126.3, 126.4, 128.1 128.8, 129.1, 129.3, 131.3, 131.7, 139.0, 143.0, 153.9, 172.2, 174.8	1714	A	564 (M ^{•+} + 1, 41) 391 (100)
e	35.5, 41.2, 43.8, 70.6, 108.0, 109.4, 116.3 (d, J = 23), 118.8, 120.3, 121.3, 126.6, 127.2, 127.3, 128.3 (d, J = 4), 129.5, 132.0, 138.9, 143.2, 154.1, 162.3 (d, J = 248), 172.1, 174.8	1719	B	599 (M ^{•-} , 0.22) 406 (60)
d	35.7, 41.4, 43.9, 70.4, 108.1, 108.9, 119.0, 120.1, 121.5, 126.8, 127.7, 128.3, 129.6, 129.6, 129.9, 132.1, 134.9, 139.0, 142.4, 153.3, 172.0, 174.6	1719	C	631 (M ^{•+}) 424
e	35.5, 41.2, 43.8, 70.5, 107.9, 109.4, 118.8, 120.3, 121.3, 122.8, 126.6, 127.8, 128.1, 129.4, 130.2, 131.9, 132.4, 138.8, 143.2, 154.2, 171.7, 174.4	1719	C	721 (M ^{•+})
f	35.5, 41.2, 43.7, 55.5, 70.6, 108.0, 109.3, 114.5, 118.6, 121.2, 123.9, 126.4, 127.5, 128.3, 129.3, 131.7, 139.1, 143.2, 153.8, 159.6, 165.1, 172.4, 175.1	1715	A	624 (M ^{•+} + 1, 1) 421 (96)
h	26.6, 35.1, 41.3, 42.4, 68.7, 111.6, 115.2, 121.6, 123.7, 124.0, 126.2, 128.8, 129.2, 131.3, 131.6, 139.9, 146.2, 170.4, 172.8, 175.3	1712	A	530 (M ^{•+} + 1, 3) 357 (11)
i	14.2, 24.9, 34.4, 38.8, 41.3, 43.5, 68.8, 106.8, 108.0, 116.7, 119.9, 121.6, 131.7, 142.3, 154.1, 172.8, 176.0	1701	D	Calcd. 391.1527 Found 391.1528
k [d]	36.8, 42.2, 45.0, 71.6, 109.5, 110.3, 119.1, 122.0, 122.4, 124.9, 126.8, 128.2, 128.7, 129.9, 131.8, 138.6, 140.3, 143.7, 147.9, 154.7, 173.1, 175.7	1722	C	653 (M ^{•+}) 435
l	35.5, 41.1, 43.7, 55.4, 70.6, 108.3, 109.3, 112.0, 114.9, 118.4, 118.6, 120.5, 121.2 126.4, 128.1, 129.3, 129.9, 131.7, 132.4, 139.3, 143.2, 154.1, 160.0, 172.3, 174.6	1717	A	623 (M ^{•+} , 100)
m	24.9, 34.8, 41.3, 43.9, 70.1, 108.0, 108.8, 118.3, 120.8, 121.7, 126.4, 128.2, 129.4, 131.4, 139.5, 142.6, 153.9, 173.1, 175.8	1700	A	440 (M ^{•+} + 1, 100) 328 (67)
o [e]	34.3, 41.9, 44.8, 69.8, 108.1, 110.1, 117.6, 121.3, 121.9, 125.3, 127.0, 128.9, 130.3, 139.3, 141.2, 152.7, 175.3, 178.0	1732 1687	A	412 (M ^{•+} +1, 13) 315 (100)
11e		1723	C	766 (M ^{•+}) 516
g [e]	42.0, 46.1, 68.4, 86.3, 108.6, 114.6, 122.6, 123.0, 126.3, 126.3, 126.5, 128.8, 129.0, 129.2, 131.0, 131.2, 136.3, 138.7, 146.2, 168.1, 171.9, 172.5	1721	A	637 (M ^{•+} +1, 1) 432 (68)
h [e]	26.3, 41.8, 46.1, 68.3, 86.3, 108.1, 115.0, 122.6, 123.1, 123.8, 126.5, 128.9, 129.1 131.2, 132.2, 139.1, 146.1, 169.6, 171.7, 172.5	1718	E	574 (M ^{•+} , 2)

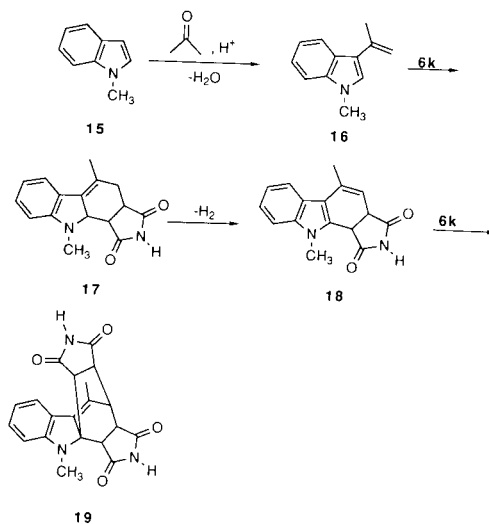
[a] The solvent was deuteriochloroform unless otherwise noted. [b] In cm⁻¹. The ir C=O band for **10m** is at 1717. [c] Methods A: chemical impact ms (ammonia, positive ion). B: chemical impact ms (ammonia, negative ion). C: fast-atom bombardment ms. D: hrms. E: electron impact ms. [d] In acetone-d₆. [e] dimethyl sulfoxide-d₆.

intermediate **7** to intermediate **9**, since the nitrogen oxides are being flushed out of the reaction system by air just as with nitrogen.

One interesting and potentially useful result apparent from Table I is that, if glacial acetic acid is used as the solvent, the major product is the aromatized carbazole **12**. Other solvents such as dimethyl sulfoxide, pyridine, and ethanol gave the 1:2 adducts **10** and **11** as the major products; even hydrochloric acid in ethanol gave **10** and **11** as the major products. Hence, the role of the acetic acid in bringing about the aromatization of **12** is still unknown.

It is possible that carbazoles **12** and **13** could be formed from bridged carbazoles **10** and **11** through a retro Diels-Alder step [10]. Fragmentation patterns of the ms of bridged carbazoles **10**, **11**, and **19** indicate that these molecules do undergo retro Diels-Alder reactions in the mass spectrometer. An attempt to produce carbazole **12a**, however, by refluxing a solution of bridged carbazole **10a**

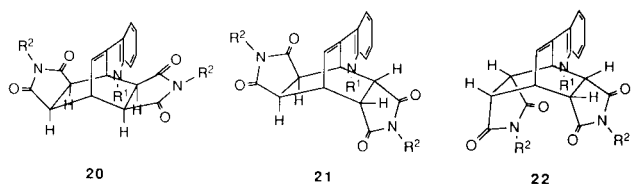
Scheme III



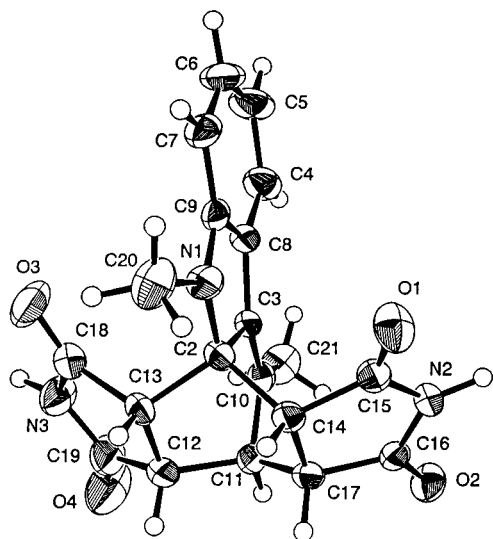
in acetic acid gave, after 24 hours, only the starting material **10a** without any detectable carbazole **12a**.

The *in situ* vinylindole synthesis of carbazoles [11] provided a compound **19** structurally similar to **10** from the reaction of 1-methylindole (**15**) with maleimide **6k** in refluxing acetone with maleic acid as the catalyst. The proposed mechanism involves a condensation of **15** with acetone to produce the vinylindole **16** which undergoes an *in situ* Diels-Alder reaction. Adduct **17** dehydrogenates to form dihydrocarbazole **18**, which subsequently undergoes a second Diels-Alder reaction to give the bridged carbazole **19** (Scheme III). The proposed intermediate **18** is structurally similar to intermediates **8** and **9** proposed by us for bridged carbazoles **10** and **11** and the dihydrocarbazole intermediate proposed by Pfeuffer and Pindur [5]. Therefore, the stereochemistry is expected to be and appears to be the same for all of the bridged carbazoles.

Scheme IV



An examination of Table V shows good consistency for the ^{13}C nmr values of the carbazoles **10** in deuteriochloroform. An examination of Table III shows some consistencies and some variability for the ^1H nmr values of the carbazoles **10** in deuteriochloroform. The signals for H_b , H_c , and H_d (Figure 2) are fairly consistent for all of the bridged carbazoles **10** and the bridged carbazole reported by Pfeuffer and Pindur [5], regardless of the nature of R^1 or R^2 . The

Figure 1. ORTEP plot of compound **19**.Table VI
More Data for Bridged Carbazoles **10**

10	Mp, °C	Appearance	Molecular Formula	Analysis		
				Calcd./Found C	H	N
a	273-276	white	$\text{C}_{36}\text{H}_{25}\text{N}_3\text{O}_4$	76.72	4.47	7.63
		flakes		76.86	4.40	7.63
c	194-196	white	$\text{C}_{36}\text{H}_{23}\text{F}_2\text{N}_3\text{O}_4$	72.12	3.87	7.01
		flakes		71.93	4.00	6.97
d	206-207	white	$\text{C}_{36}\text{H}_{23}\text{Cl}_2\text{N}_3\text{O}_4$	68.36	3.67	6.64
		flakes		68.16	3.66	6.66
e	260.5-261.0	white	$\text{C}_{36}\text{H}_{23}\text{Br}_2\text{N}_3\text{O}_4$	59.94	3.21	5.82
		flakes		60.08	3.22	5.89
f	230.5-231	white	$\text{C}_{38}\text{H}_{29}\text{N}_3\text{O}_6$	73.18	4.69	6.74
		flakes		73.00	4.69	6.71
h	260-262	white	$\text{C}_{32}\text{H}_{23}\text{N}_3\text{O}_5$	72.58	4.38	7.94
		flakes		72.72	4.31	8.01
i	250-252.5	white	$\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_4$	[a]		
		flakes				
k	237-238	yellow	$\text{C}_{36}\text{H}_{23}\text{N}_5\text{O}_8$	66.16	3.55	10.71
		needles		65.98	3.78	10.46
l	270-271	white	$\text{C}_{38}\text{H}_{29}\text{N}_3\text{O}_6$	73.18	4.69	6.74
		flakes		72.94	4.89	6.64
m	299-302	white	$\text{C}_{36}\text{H}_{23}\text{Br}_2\text{N}_3\text{O}_4$	[b]		
		powder				
n	271-272.5	tan	$\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}_4$	71.06	4.82	9.56
		flakes		71.16	4.75	9.71
o	299-302	white	$\text{C}_{24}\text{H}_{17}\text{N}_3\text{O}_4$	70.07	4.16	10.21
		powder		69.88	4.33	10.12

[a] With hrms. Calcd. for M^{++} : 391.1527. Found: 391.1528. [b] With hrms. Calcd. for M^{++} with 2 ^{79}Br isotopes: 719.0049. Found: 719.0038.

chemical shift for H_a varied considerably depending on R^1 . Pfeuffer and Pindur [5] described three possible stereochemical configurations for the bridged carbazoles (Scheme IV). Stereoisomer **21** was eliminated [5] because its lack of symmetry should have produced more ^1H nmr signals than were observed. Pfeuffer and Pindur [5] did not find a ^1H - ^1H nuclear Overhauser effect between the *o*-phenyl protons on the succinimide rings and the bridging vinyl proton. Therefore, on the basis of this negative evidence, they eliminated stereoisomer **20** and proposed that **22** was the correct stereoisomer. An X-ray crystal

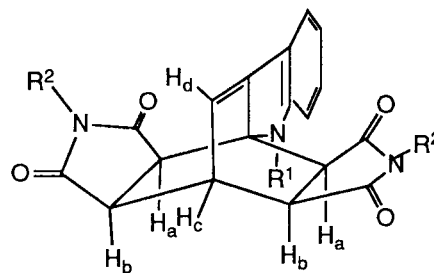


Figure 2. Hydrogen assignments for Table III.

Table VII
Data for Carbazoles **12** and **13**

Compound	Appearance	Mp, °C	¹ H NMR Data in Deuteriochloroform δ ppm, J in Hertz	IR cm ⁻¹ (C=O)	MS [a] M ⁺⁺ (Relative intensity)	Analysis		
						Calcd./Found C	H	N
12a	yellow powder	288-290	7.15-7.56 (m, ~19 H, includes chloroform), 7.88 (d, J = 7.6, 1 H), 8.20 (d, J = 7.3, 1 H), 8.5 (d, J = 7.8, 1 H)	1711	hrms	388.1208 388.1228		
e	yellow powder	301-303	7.05-7.60 (m, ~17 H, includes chloroform), 7.88 (d, J = 7.7, 1 H), 8.21 (d, J = 7.5, 1 H), 8.51 (d, J = 7.8, 1 H)	1706	406 (100)	76.84	3.72	6.89
d [b]	yellow powder	260-262	7.18 (d, J = 8.1, 1 H), 7.25-7.60 (m, ~14 H, includes chloroform), 7.88 (d, J = 7.3, 1 H), 8.20 (d, J = 7.7, 1 H), 8.50 (d, J = 7.7, 1 H)	1712	424 (37) 422 (100)	73.85	3.58	6.62
e	yellow powder	220-222	7.16-7.58 (m, ~15 H, includes chloroform), 7.88 (d, J = 7.7, 1 H), 8.21 (d, J = 7.2, 1 H), 8.52 (d, J = 7.8, 1 H)	1713	hrms	466.0313 [c] 466.0330		
i	yellow needles	251-251.5	1.47 (t, J = 7.1, 3 H), 3.22 (s, 3 H), 5.02 (q, J = 7.1, 2 H), 7.33 (t, J = 7.8, 1 H), 7.51 (4-line m, 2 H), 7.69 (d, J = 7.8, 1 H), 8.12 (d, J = 7.7, 1 H), 8.34 (d, J = 7.7, 1 H)	1700	hrms	278.1052 278.1029		
j [d]	yellow needles	211-211.5	6.32 (s, 2 H), 7.06-7.52 (m, 13 H), 7.83 (d, J = 7.7, 1 H), 8.16 (d, J = 7.8, 1 H), 8.43 (d, J = 7.7, 1 H)	1703	402 (17)	80.58	4.51	6.96
k	dark yellow flakes	283-284	7.18 (d, J = 8.1, 1 H), 7.36-7.64 (m, 9 H), 7.90 (d, J = 7.8, 1 H), 8.22 (d, J = 9.2), 8.27 (d, J = 9.2, area for 8.22-8.27 is 3 H), 8.55 (d, J = 7.8, 1 H)	1716	433 (100)	72.05	3.49	9.69
13i	dark yellow powder	290-291	1.52 (t, J = 7.1, 3 H), 3.26 (s, 3 H), 5.11 (q, J = 7.2, 2 H), 7.44 (dt, J = 7.6, 1.2, 1 H), 7.59 (d, J = 7.7, 1 H), 7.82 (dt, J = 7.7, 1.2, 1 H), 8.16 (d, J = 7.8, 1 H), 8.73 (s, 1 H)	1702	hrms	323.0903 323.0900		

[a] Electron impact. [b] **12d** had the following ¹³C nmr: 111.2, 112.6, 114.9, 120.6, 120.7, 121.6, 122.0, 122.3, 126.0, 128.1, 128.4, 128.5, 129.1, 129.4, 130.4, 130.5, 131.2, 133.4, 138.6, 144.6, 165.2, 167.7. [c] With ⁷⁹Br. [d] **12j** had the following ¹³C nmr: 50.1, 110.9, 113.1, 114.4, 120.9, 121.2, 122.6, 126.0, 126.3, 127.0, 127.3, 128.0, 128.5, 128.7, 129.1, 130.6, 130.8, 132.0, 137.0, 137.8, 142.8, 167.4, 167.9. [e] Also nitro bands at 1527, 1466 cm⁻¹.

Table VIII
Crystal and Experimental Data for Compound **19**

Space Group and Cell Dimensions Orthorhombic P2₁2₁2₁
a 8.220(3) b 13.484(4) c 14.449(4)
Volume 1601.5(9)Å³
Empirical formula: C₂₉H₁₇N₃O₄
Cell dimensions were obtained from 25 reflections with 2θ angle in the range 22.00-25.00 degrees.
Crystal dimensions: 0.25 x 0.30 x 0.40 mm
Fw = 363.37 Z = 4 F(000) = 760
Dcalc 1.507 Mg.m-3, μ 0.10 mm⁻¹, λ 0.70930Å, 2θ (max) 45°
The intensity data were collected on a Nonius diffractometer, using the θ/2θ scan mode.
The h,k,l ranges are :- 0 8, 0 14, -15 15
No. of reflections measured 2448
No. of unique reflections 2043
No. of reflections with I_{net} > 2.0 σ (I_{net}) 1868
No correction was made for absorption
The last least squares cycle was calculated with 44 atoms, 245 parameters and 1868 out of 2043 reflections.
Weights based on counting-statistics were used.
The weight modifier K in KFo**2 is 0.001000
The residuals are as follows :-
For significant reflections, RF 0.034, R_w 0.047 GoF 1.26
For all reflections, RF 0.034, R_w 0.047.
where RF = Sum(Fo-Fc)/Sum(Fo),
R_w = Sqrt[Sum(w(Fo-Fc)**2)/Sum(wFo**2)] and
GoF = Sqrt[Sum(w(Fo-Fc)**2)/(No. of reflections - No. of parameters)]
The maximum shift/sigma ratio was 0.001.
The last map type is not given. D-Map is assumed
In the last D-map, the deepest hole was -0.200e/Å**3, and the highest peak 0.150e/Å**3.

Table IX
Atomic Coordinates and Thermal Parameters
and their E. S. Ds. [a]

	x	y	z	Uequiv [b]
O1	0.6339 (3)	0.01878(15)	0.63836(15)	3.91(9)
O2	0.34705(24)	0.26852(15)	0.50587(14)	3.34(9)
O3	0.0837 (3)	-0.00371(18)	0.91676(16)	4.80(11)
O4	-0.2032 (3)	0.20835(24)	0.73840(18)	6.31(14)
N1	0.4008 (3)	0.00206(16)	0.80645(15)	2.62(9)
N2	0.52241(25)	0.15630(15)	0.57059(15)	2.30(10)
N3	-0.0824 (3)	0.10533(21)	0.84215(17)	3.83(11)
C2	0.2964 (3)	0.05454(19)	0.74379(18)	2.20(10)
C3	0.3120 (3)	0.16302(19)	0.77280(17)	1.94(10)
C4	0.4790 (4)	0.23966(22)	0.90867(20)	3.27(12)
C5	0.5789 (4)	0.2151 (3)	0.98318(21)	4.27(16)
C6	0.6174 (4)	0.1182 (3)	1.00104(21)	4.32(16)
C7	0.5616 (4)	0.04161(25)	0.94686(20)	3.39(13)
C8	0.4197 (3)	0.16413(19)	0.85323(18)	2.27(11)
C9	0.4634 (3)	0.06509(20)	0.87190(18)	2.40(11)
C10	0.2214 (3)	0.22641(20)	0.72509(17)	2.25(11)
C11	0.1267 (3)	0.17754(20)	0.64848(17)	2.53(11)
C12	0.0135 (3)	0.09826(24)	0.69015(19)	3.13(13)
C13	0.1125 (3)	0.02624(19)	0.75011(18)	2.65(11)
C14	0.3405 (3)	0.04457(19)	0.63935(17)	2.32(10)
C15	0.5165 (3)	0.06676(19)	0.61848(18)	2.44(11)
C16	0.3728 (3)	0.19166(21)	0.54769(17)	2.32(12)
C17	0.2451 (3)	0.12239(20)	0.58447(18)	2.46(11)
C18	0.0429 (4)	0.03826(22)	0.84741(21)	3.18(13)
C19	-0.1054 (4)	0.1448 (3)	0.75662(23)	3.97(15)
C20	0.3928 (4)	-0.10509(22)	0.81563(21)	3.90(14)
C21	0.2000 (4)	0.33540(22)	0.74175(22)	3.85(14)
H4	0.449	0.307	0.897	4.0
H5	0.623	0.264	1.024	5.0
H6	0.682	0.103	1.054	5.2
H7	0.590	-0.025	0.961	4.1
H11	0.065	0.225	0.615	3.3
H12	-0.042	0.062	0.643	3.9
H3	-0.147	0.124	0.894	4.6
H13	0.096	-0.040	0.729	3.4
H14	0.314	-0.020	0.619	3.1
H2	0.621	0.189	0.556	3.1
H17	0.189	0.091	0.535	3.2
H20A	0.293	-0.124	0.844	4.7
H20B	0.478	-0.127	0.855	4.7
H20C	0.404	-0.131	0.755	4.7
H21A	0.216	0.370	0.685	4.6
H21B	0.282	0.357	0.783	4.6
H21C	0.094	0.344	0.766	4.6

[a] The estimated standard deviations given in the parentheses are for the last digit of the parameters printed. [b] For atoms refined anisotropically, Uequiv is the mean of the principal values of the thermal ellipsoid. For hydrogen atoms it is Biso, the isotropic thermal parameter.

structure determination of our compound **19** (Figure 1) shows that it is stereoisomer **20**, which results from the expected *endo*-addition of the maleimide to the less sterically-hindered side of intermediate **18**, rather than stereoisomer **22** which would result from *exo*-addition to

the more sterically-hindered side as implied by Pfeuffer and Pindur [5].

EXPERIMENTAL

General Information.

3-(2-Nitrovinyl)-1-phenylindole (**3a**) and *N*-methylmaleimide (**6g**) were purchased from the Aldrich Chemical Company. Maleimide **6k** was purchased from Schweizerhall, Inc. Other maleimides were synthesized by the method of Cava, Deanna, and Muth [12]. 1-Acetyl-3-(2-nitrovinyl)indole (**3g**) was synthesized by the method of Berlin [13]. Melting points were determined with a Thomas-Hoover Unimelt apparatus and are uncorrected. The ¹H and ¹³C nmr spectra were obtained on Bruker AC-200 and Bruker AC-300 FT nmr spectrometers and referenced to the solvent. Coupling constants are given in hertz. Infrared maxima are reported in cm⁻¹ and were obtained using potassium bromide pellets with a Perkin-Elmer 1600 Series FTIR spectrometer. Electron impact ms were obtained with a Kratos/AEI MS-30, chemical impact ms were obtained with a Finnigan 4000, and fast-atom bombardment ms were obtained with a VG 7070E-HF spec-

Table X
Anisotropic Parameters [a] U_(i,j) X 100 and their E.S.Ds. [b]

	u11 (U)	u22	u33	u12	u13	u23
O1	3.47(12)	4.65(12)	6.75(15)	1.24(10)	0.96(11)	1.40(11)
O2	3.80(11)	4.67(13)	4.21(11)	0.60(10)	0.19(9)	1.50(11)
O3	6.09(14)	8.05(16)	4.12(13)	0.57(14)	1.29(11)	2.42(12)
O4	5.43(16)	11.21(21)	7.34(18)	3.44(17)	2.03(14)	2.82(17)
N1	3.66(12)	2.64(12)	3.67(13)	0.14(11)	-0.38(11)	0.82(11)
N2	2.31(13)	3.15(12)	3.30(12)	-0.14(10)	0.32(10)	0.07(10)
N3	3.61(14)	7.10(17)	3.84(15)	0.90(15)	1.33(12)	0.71(14)
C2	2.47(13)	2.94(14)	2.93(15)	-0.37(12)	-0.04(11)	-0.16(12)
C3	2.00(13)	3.09(14)	2.29(13)	-0.11(11)	0.17(11)	-0.04(11)
C4	3.50(15)	5.07(18)	3.85(17)	-0.27(14)	-0.08(14)	-1.20(14)
C5	4.23(18)	8.5 (3)	3.50(18)	-0.52(19)	-0.76(15)	-2.30(17)
C6	3.46(17)	9.9 (3)	3.02(17)	0.63(20)	-0.83(15)	0.09(19)
C7	3.11(16)	6.48(21)	3.30(16)	1.04(15)	0.17(13)	1.32(16)
C8	2.29(13)	3.80(16)	2.53(14)	-0.21(12)	0.02(11)	-0.12(12)
C9	2.39(14)	4.34(16)	2.40(14)	0.21(12)	0.53(12)	0.42(12)
C10	2.20(14)	3.52(14)	2.84(15)	0.35(12)	0.59(11)	-0.10(12)
C11	2.21(14)	4.68(16)	2.72(14)	0.17(13)	0.00(12)	0.58(13)
C12	2.59(15)	6.26(20)	3.04(15)	-0.87(15)	-0.26(13)	-0.02(14)
C13	3.00(15)	3.72(14)	3.33(15)	-1.36(13)	0.16(13)	-0.29(12)
C14	3.04(15)	3.14(14)	2.65(14)	-0.33(12)	0.05(11)	-0.65(12)
C15	3.23(16)	3.11(14)	2.92(14)	-0.07(13)	0.27(12)	-0.41(12)
C16	2.84(16)	3.89(16)	2.10(14)	0.02(14)	0.11(11)	-0.09(13)
C17	2.50(14)	4.29(16)	2.55(14)	-0.41(13)	-0.24(12)	-0.38(12)
C18	3.54(17)	4.81(17)	3.73(17)	-1.01(15)	0.29(13)	0.29(16)
C19	2.85(17)	7.23(23)	5.00(20)	0.46(17)	0.57(16)	1.31(17)
C20	6.33(22)	3.56(17)	4.94(20)	0.78(18)	1.17(17)	0.98(14)
C21	5.32(20)	4.34(17)	4.96(20)	1.40(15)	0.47(16)	0.19(16)

[a] Anisotropic temperature factors are of the form: $\exp[-2\pi^2(h^2*U_{11}*(a^*)^2 + \dots + 2h*k*U_{12}*(a^*)(b^*) + \dots)]$. [b] The estimated standard deviations given in the parentheses are for the last digit of the parameters printed.

Table XI
Bond Distances and Angles

O(1)-C(15)	1.197(4)	C(4)-C(5)	1.394(5)
O(2)-C(16)	1.218(3)	C(4)-C(8)	1.384(4)
O(3)-C(18)	1.199(4)	C(5)-C(6)	1.370(6)
O(4)-C(19)	1.204(4)	C(6)-C(7)	1.374(5)
N(1)-C(2)	1.434(3)	C(7)-C(9)	1.387(4)
N(1)-C(9)	1.372(3)	C(8)-C(9)	1.409(4)
N(1)-C(20)	1.452(4)	C(10)-C(11)	1.505(4)
N(2)-C(15)	1.393(3)	C(10)-C(21)	1.499(4)
N(2)-C(16)	1.360(3)	C(11)-C(12)	1.540(4)
N(3)-C(18)	1.373(4)	C(11)-C(17)	1.535(4)
N(3)-C(19)	1.359(4)	C(12)-C(13)	1.535(4)
C(2)-C(3)	1.527(4)	C(12)-C(19)	1.507(4)
C(2)-C(13)	1.562(4)	C(13)-C(18)	1.526(4)
C(2)-C(14)	1.558(4)	C(14)-C(15)	1.508(4)
C(3)-C(8)	1.461(4)	C(14)-C(17)	1.531(4)
C(3)-C(10)	1.327(4)	C(16)-C(17)	1.502(4)
C(2)-N(1)-C(9)	110.75(21)	C(10)-C(11)-C(12)	109.20(20)
C(2)-N(1)-C(20)	121.44(23)	C(10)-C(11)-C(17)	109.11(20)
C(9)-N(1)-C(20)	124.76(23)	C(12)-C(11)-C(17)	106.40(23)
C(15)-N(2)-C(16)	113.15(21)	C(11)-C(12)-C(13)	109.87(21)
C(18)-N(3)-C(19)	114.39(25)	C(11)-C(12)-C(19)	110.6(3)
N(1)-C(2)-C(3)	104.42(20)	C(13)-C(12)-C(19)	104.33(23)
N(1)-C(2)-C(13)	114.95(21)	C(2)-C(13)-C(12)	108.99(20)
N(1)-C(2)-C(14)	115.44(21)	C(2)-C(13)-C(18)	112.98(22)
C(3)-C(2)-C(13)	107.43(20)	C(12)-C(13)-C(18)	104.73(23)
C(3)-C(2)-C(14)	109.20(20)	C(2)-C(14)-C(15)	113.58(21)
C(13)-C(2)-C(14)	105.13(20)	C(2)-C(14)-C(17)	108.86(20)
C(2)-C(3)-C(8)	106.21(21)	C(15)-C(14)-C(17)	104.58(21)
C(2)-C(3)-C(10)	115.29(22)	O(1)-C(15)-N(2)	124.02(25)
C(8)-C(3)-C(10)	138.32(24)	O(1)-C(15)-C(14)	128.22(25)
C(5)-C(4)-C(8)	118.7(3)	N(2)-C(15)-C(14)	107.76(23)
C(4)-C(5)-C(6)	120.6(3)	O(2)-C(16)-N(2)	125.16(24)
C(5)-C(6)-C(7)	122.2(3)	O(2)-C(16)-C(17)	125.69(25)
C(6)-C(7)-C(9)	117.9(3)	N(2)-C(16)-C(17)	109.13(23)
C(3)-C(8)-C(4)	132.9(3)	C(11)-C(17)-C(14)	110.16(21)
C(3)-C(8)-C(9)	107.29(22)	C(11)-C(17)-C(16)	110.79(22)
C(4)-C(8)-C(9)	119.79(25)	C(14)-C(17)-C(16)	104.58(21)
N(1)-C(9)-C(7)	128.0(3)	O(3)-C(18)-N(3)	124.6(3)
N(1)-C(9)-C(8)	111.07(22)	O(3)-C(18)-C(13)	128.0(3)
C(7)-C(9)-C(8)	120.9(3)	N(3)-C(18)-C(13)	107.45(25)
C(3)-C(10)-C(11)	112.97(23)	O(4)-C(19)-N(3)	124.8(3)
C(3)-C(10)-C(21)	127.9(3)	O(4)-C(19)-C(12)	126.2(3)
C(11)-C(10)-C(21)	119.12(24)	N(3)-C(19)-C(21)	109.0(3)

trometer. Microanalyses were performed by MHW Laboratories, Phoenix, AZ. Column chromatography was performed using silica gel (Baker, 60-200 Mesh) with the eluents described below. The X-ray crystal structure of **19** at room temperature was solved by direct methods. Non-H atoms were refined with anisotropic thermal parameters and the H-atoms were placed at the calculated positions with isotropic thermal parameters and were not refined. All of the calculations were carried out with the NRCVAX programs (NRCVAX - an interactive program system for structure analysis) [14]. Lists of observed and calculated structure factors are available from the authors upon request.

1-Benzoyl-3-(2-nitrovinyl)indole (**3f**).

Compound **3d** (3.00 g, 16 mmoles) was added to an ice-cold solution of crushed sodium hydroxide (2.0 g, 50 mmoles) and

tetrabutylammonium hydrogen sulfate (0.14 g, 0.4 mmole) in methylene chloride (25 ml). The solution was stirred for 5-10 minutes, during which the yellow solution turned orange. Benzoyl chloride (2.3 ml, 2.8 g, 20 mmoles) was added dropwise, over 10 minutes. The solution was stirred for 1 hour, then warmed to room temperature, and stirred for an additional 1 hour. The volume was reduced by evaporation and ethanol was added. After cooling, **3f** was collected as yellow needles (1.33 g), mp 184-185°. The mother liquor was evaporated and the resulting brown solid was chromatographed using petroleum ether (bp 60-70°)-methylene chloride, giving additional **3f** (0.26 g, total 1.59 g, 5.4 mmoles, 34%); ¹H nmr (deuteriochloroform): δ 7.40-7.80 (m, 10 H), 8.11 (d, J = 13.7, 1 H), 8.41 (d, J = 7.1, 1 H); ¹³C nmr (deuteriochloroform): δ 113.5, 117.0, 120.2, 125.3, 125.5, 126.6, 129.0, 129.4, 131.2, 133.0, 133.1, 133.4, 136.4, 137.3, (a signal was not observed for the carbonyl carbon, probably due to a long relaxation time for this carbon [15]); ir: 3078, 1660, 1609, 1481, 1347; electron impact ms: m/z (relative intensity) 292 (M⁺, 11), 140 (3), 105 (100), 77 (51), 51 (11).

Anal. Calcd. for C₁₇H₁₂N₂O₃: C, 69.86; H, 4.14; N, 9.58. Found: C, 69.78; H, 4.25; N, 9.44.

Dimethyl 9-Phenyl-9H-carbazole-1,2-dicarboxylate (**1**).

A solution of **3a** (1.0 g, 3.8 mmoles) and dimethyl acetylenedicarboxylate (DMAD) (0.55 g, 3.8 mmoles) in xylene (10 ml) was refluxed for 5 days. Then, additional DMAD (0.50 g) was added. After 2 days of additional refluxing, a third portion of DMAD (0.50 g, total 1.55 g, 10.8 mmoles) was added and the solution was refluxed for 8 hours (total time, 7 1/3 days). The solvent was evaporated off, the resulting tar was chromatographed using acetone-petroleum ether (bp 60-70°), and the fractions were evaporated, giving **1** (0.1607 g, 0.44 mmole, 12%) as yellow needles, mp 190-192°; ¹H nmr (deuteriochloroform): δ 3.27 (s, 3 H), 3.89 (s, 3 H), 7.04 (d, J = 8.1, 1 H), 7.25-7.59 (m, ~11 H, includes chloroform), 7.93 (d, J = 8.3, 1 H), 8.16 (d, J = 7.7, 1 H), 8.22 (d, J = 8.2, 1 H); ¹³C nmr (deuteriochloroform): δ 52.0, 52.5, 110.5, 119.6, 120.8, 121.2, 121.5, 125.4, 127.9, 128.3, 128.5, 128.7, 128.9, 129.5, 129.6, 136.6, 136.9, 144.3, 166.9, 167.5; ir: 2947, 1716; electron impact ms: m/z (relative intensity) 359 (M⁺, 100), 296 (60), 241 (57), 240 (36).

Anal. Calcd. for C₂₂H₁₇NO₄: C, 73.53; H, 4.77; N, 3.90. Found: C, 73.33; H, 4.78; N, 3.85.

12-Phenyl-12H-naphtho[2,3-a]carbazole-5,13-dione (**2a**).

A solution of **3a** (1.0 g, 3.8 mmoles) and 1,4-naphthoquinone (1.80 g, 3.8 mmoles) in xylene (20 ml) was refluxed for 24 hours under nitrogen. The solvent was evaporated and the solid was chromatographed using acetone-petroleum ether (bp 60-70°). Upon slow evaporation of the fractions, yellow needles and red prisms, mp 229-229.5°, separated, which gave identical mp and nmr spectra and were identified as **2a** (1.027 g, 2.7 mmoles, 73%); ¹H nmr (deuteriochloroform): δ 7.36-7.69 (m, 10 H), 7.80 (d, J = 5.2, 1 H), 8.16 (d, J = 7.6, 1 H), 8.23 (d, J = 7.2, 1 H), 8.32 (d, J = 8.0, 1 H), 8.46 (d, J = 8.0, 1 H); ¹³C nmr (deuteriochloroform): δ 111.7, 119.8, 120.8, 121.7, 122.1, 125.2, 126.0, 126.6, 126.7, 127.3, 128.4, 129.2, 131.7, 132.6, 133.0, 133.2, 133.8, 135.1, 138.7, 141.1, 145.5, 156.2, 182.5, 183.6; ir: 3056, 1663; electron impact ms: m/z (relative intensity) 373 (M⁺, 100), 356 (32), 315 (25), 158 (39).

Anal. Calcd. for C₂₆H₁₅NO₂: C, 83.63; H, 4.05; N, 3.75. Found: C, 83.41; H, 4.07; N, 3.55.

Table XII
Torsion Angles

C9	N1	C2	C3	4.9 (1)	C9	N1	C2	C13	-112.6 (3)
C9	N1	C2	C14	124.8 (3)	C20	N1	C2	C3	166.0 (3)
C20	N1	C2	C13	48.6 (2)	C20	N1	C2	C14	-74.1 (2)
C2	N1	C9	C7	176.2 (3)	C2	N1	C9	C8	-5.7 (1)
C20	N1	C9	C7	15.8 (2)	C20	N1	C9	C8	-166.0 (3)
C16	N2	C15	O1	173.5 (3)	C16	N2	C15	C14	-6.8 (1)
C15	N2	C16	O2	179.9 (3)	C15	N2	C16	C17	1.5 (2)
C19	N3	C18	O3	179.1 (4)	C19	N3	C18	C13	-2.7 (2)
C18	N3	C19	O4	-176.1 (4)	C18	N3	C19	C12	2.3 (2)
N1	C2	C3	C8	-2.4 (1)	N1	C2	C3	C10	-178.4 (3)
C13	C2	C3	C8	120.1(3)	C13	C2	C3	C10	-55.9 (2)
C14	C2	C3	C8	-126.4 (3)	C14	C2	C3	C10	57.6 (2)
N1	C2	C13	C12	171.7 (3)	N1	C2	C13	C18	55.8 (2)
C3	C2	C13	C12	56.0 (2)	C3	C2	C13	C18	-59.9 (2)
C14	C2	C13	C12	-60.2 (2)	C14	C2	C13	C18	-176.2 (3)
N1	C2	C14	C15	-50.9 (2)	N1	C2	C14	C17	-167.0 (3)
C3	C2	C14	C15	66.3 (2)	C3	C2	C14	C17	-49.7 (2)
C13	C2	C14	C15	-178.7 (3)	C13	C2	C14	C17	65.3 (2)
C2	C3	C8	C4	179.6 (3)	C2	C3	C8	C9	-0.7 (1)
C10	C3	C8	C4	-5.9 (2)	C10	C3	C8	C9	173.8 (3)
C2	C3	C10	C11	-2.6 (1)	C2	C3	C10	C21	174.7 (3)
C8	C3	C10	C11	-176.8(3)	C8	C3	C10	C21	0.5 (2)
C8	C4	C5	C6	0.0 (2)	C5	C4	C8	C3	178.5 (4)
C5	C4	C8	C9	-1.2 (2)	C4	C5	C6	C7	0.5 (2)
C5	C6	C7	C9	0.1 (2)	C6	C7	C9	N1	176.6 (4)
C6	C7	C9	C8	-1.3 (2)	C3	C8	C9	N1	3.9 (1)
C3	C8	C9	C7	-177.9 (3)	C4	C8	C9	N1	-176.4 (3)
C4	C8	C9	C7	1.9 (2)	C3	C10	C11	C12	59.6 (2)
C3	C10	C11	C17	-56.3 (2)	C21	C10	C11	C12	-118.0 (3)
C21	C10	C11	C17	126.1 (3)	C10	C11	C12	C13	-53.8 (2)
C10	C11	C12	C19	60.8 (2)	C17	C11	C12	C13	63.8(2)
C17	C11	C12	C19	178.4 (3)	C10	C11	C17	C14	58.9 (2)
C10	C11	C17	C16	-56.4 (2)	C12	C11	C17	C14	-58.8 (2)
C12	C11	C17	C16	-174.0 (3)	C11	C12	C13	C2	-3.2 (1)
C11	C12	C13	C18	118.0 (3)	C19	C12	C13	C2	-121.8 (3)
C19	C12	C13	C18	-0.6 (2)	C11	C12	C19	O4	59.5 (3)
C11	C12	C19	N3	-119.0 (3)	C13	C12	C19	O4	177.5 (4)
C13	C12	C19	N3	-0.9 (1)	C2	C13	C18	O3	-61.5 (2)
C2	C13	C18	N3	120.4 (3)	C12	C13	C18	O3	-180.0 (4)
C12	C13	C18	N3	1.9 (2)	C2	C14	C15	O1	70.1 (2)
C2	C14	C15	N2	-109.6 (3)	C17	C14	C15	O1	-171.4 (3)
C17	C14	C15	N2	9.0 (1)	C2	C14	C17	C11	-5.2 (1)
C2	C14	C17	C16	113.9 (3)	C15	C14	C17	C11	-127.0 (3)
C15	C14	C17	C16	-7.9 (1)	O2	C16	C17	C11	-55.5 (2)
O2	C16	C17	C14	-174.1 (3)	N2	C16	C17	C11	123.0 (3)
N2	C16	C17	C14	4.3 (1)					

12-(Phenylmethyl)-12*H*-naphtho[2,3-*a*]carbazole-5,13-dione (**2b**).

A solution of **3b** (0.800 g, 2.9 mmol) and 1,4-naphthoquinone (1.23 g, 7.8 mmol) in 1,4-dioxane (40 ml) was refluxed for 24 hours. The solvent was evaporated and the resulting solid was recrystallized from benzene twice, giving **2b** (0.118 g, 0.30 mmol, 11%) as orange needles, mp 230-232.5° (lit mp [16] 235.5-236.5°).

9-Phenyl-2-[3-(1-phenyl-1*H*-indolyl)]-9*H*-carbazole (**4a**).

Compound **3a** (1.0 g, 3.8 mmol) was heated in a test tube at 180-200° for 30 minutes under nitrogen. Brown fumes were evolved. After cooling, the resulting black solid was chromatographed using methylene chloride-petroleum ether (bp 60-70°), giving **4a** (0.1409 g, 0.32 mmol, 9%) as white needles, mp

123.5-124.5°; ¹H nmr (deuteriochloroform): δ 7.24-7.69 (m, 18 H), 7.70 (d, J = 2.4, 1 H), 8.01 (dd, J = 9.0, 2.4, 1 H), 8.17 (d, J = 7.5, 1 H), 8.23 (d, J = 7.9, 1 H); ¹³C nmr (deuteriochloroform): δ 108.5, 109.8, 110.9, 120.1, 120.1, 120.2, 120.2, 120.3, 120.7, 121.0, 121.9, 122.9, 123.3, 124.6, 125.7, 125.7, 126.7, 127.3, 127.4, 127.5, 129.6, 129.7, 130.0, 133.2, 136.8, 137.4, 139.6, 141.4; ir: 3058, 1596; electron impact ms: m/z (relative intensity) 434 (M⁺, 100), 330 (25), 253 (25), 77 (74).

Anal. Calcd. for C₃₂H₂₂N₂: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.19; H, 5.37; N, 6.22.

9-Methyl-2-[3-(1-methyl-1*H*-indolyl)]-9*H*-carbazole (**4c**).

The procedure and evolution of brown fumes were similar to those for **4a**, but with harsher conditions. Compound **3c** (1.0 g, 5.0 mmol) was heated at 200-230° for 1 hour, giving **4c** (0.2669

g, 0.86 mmole, 17%) as white needles, mp 157-157.5°; ¹H nmr (acetone-d₆): δ 3.92 (s, 3 H), 3.96 (s, 3 H), 7.17-7.22 (m, 3 H), 7.44-7.51 (m), 7.58 (d d, J = 8.0, 1.5, area for 7.44-7.58 is 4 H), 7.63 (s, 1 H), 7.81 (s, 1 H), 8.08 (d, J = 5.8), 8.09 (d, J = 6.9), 8.17 (d, J = 8.5, area for 8.08-8.17 is 3 H); ¹³C nmr (deuteriochloroform): δ 29.2, 32.9, 107.0, 108.5, 109.7, 117.8, 119.0, 119.2, 120.0, 120.2, 120.6, 121.0, 121.4, 122.1, 123.1, 125.4, 126.5, 126.7, 133.6, 137.7, 141.4, 141.9; ir: 3045, 2928, 1598; electron impact ms: m/z (relative intensity) 310 (M⁺, 100), 295 (11).

Anal. Calcd. for C₂₂H₁₈N₂: C, 85.13; H, 5.84; N, 9.03. Found: C, 85.13; H, 6.00; N, 9.17.

11-Phenyl-11H-benzo[a]carbazole-1,4-dione (5).

A solution of **3a** (1.0 g, 3.8 mmoles) and 1,4-benzoquinone (1.23 g, 11.4 mmoles) in xylene (20 ml) was refluxed for 22 hours under nitrogen. The solvent was evaporated and the resulting black solid was chromatographed (eluent: acetone-petroleum ether (bp 60-70°)) and the fractions were evaporated, giving **5** (0.7944 g, 2.5 mmoles, 65%) as orange needles, mp 221-221.5°; ¹H nmr (deuteriochloroform): δ 6.69 (d, J = 10.3, 1 H), 6.86 (d, J = 10.3, 1 H), 7.59-7.27 (m, 8 H), 8.13 (pseudo t, actually overlapping d, J = 8.1, 2 H), 8.44 (d, J = 8.0, 1 H); ¹³C nmr (deuteriochloroform): δ 111.8, 116.2, 119.3, 119.7, 120.7, 121.8, 125.1, 127.6, 128.5, 129.2, 131.1, 137.0, 139.5, 141.0, 145.8, 185.5; ir: 3224, 1654; electron impact ms: m/z (relative intensity) 323 (M⁺, 100), 241 (38), 240 (24).

Anal. Calcd. for C₂₂H₁₃NO₂: C, 81.72; H, 4.05; N, 4.33. Found: C, 81.87; H, 4.05; N, 4.29.

Typical Procedure for Diels-Alder Reactions with Maleimides.

A solution of **3** (5 mmoles) and **6** (10 mmoles) was refluxed in the solvents (10 ml) described in Tables I and II until **3** could no longer be detected by thin-layer chromatography (5-120 hours). Brown fumes were evolved in all of the reactions listed in Table I. The solvent was evaporated and the resulting solid was chromatographed by using an acetone-petroleum ether (bp 60-70°) mixed solvent gradient elution scheme. In the cases where nitrogen was bubbled through the solution, xylene (20 ml) was used as the solvent.

3a,4,10,10b-Tetrahydro-5,10-dimethyl-1H,11H-4,10a[3',4']-endopyrrolopyrrolo[3,4-a]carbazole-1,3,12,14(2H,13H,15H)-tetrone (19).

A solution of **15** (7.0 ml, 7.18 g, 55 mmoles), **6k** (21.1 g, 218 mmoles), and maleic acid (7.2 g, 62 mmoles) in acetone (100 ml) was refluxed for 20 hours. The yellow precipitate which separated during the reaction was filtered off and washed with ethanol, leaving off-white flakes, mp 303-305°. Additional product was obtained by evaporating the filtrate, leaving a residue which was dissolved in ether, washed with aqueous 5% sodium bicarbonate until neutral, and the ether evaporated. The residue dissolved upon warming in 95% ethanol (15 ml). Cooling of the solution in a freezer caused precipitation of additional **19** as a white powder, which was filtered off after 30 minutes, yield > 1 g (2.8 mmoles, 5%), mp > 300°; ¹H nmr (dimethyl sulfoxide-d₆): δ 1.96 (s, 3 H), 3.13-3.17 (m, 5 H), 3.22-3.40 (m, 3 H), 6.47 (t, 1 H), 6.51 (d, 1 H), 7.02 (t, 1 H), 7.29 (d, 1 H), 10.2 (broad s, 2 H); ¹³C nmr (dimethyl sulfoxide-d₆): δ 18.8, 27.7, 41.2, 41.3, 44.2, 69.3, 104.8, 115.0, 115.1, 122.7, 129.1, 129.3, 131.8, 153.7, 175.1, 177.9; ir: 3343, 3240, 1711; electron impact ms: m/z (relative intensity) 363 (M⁺, 30), 266 (M⁻ maleimide; the retro-Diels-Alder product, 100), 195 (M⁻ maleimide -CONHCO, 81); hrms Calcd. for C₂₀H₁₇N₃O₄ (M⁺):

363.1215. Found: 363.1235.

Acknowledgement.

MJK acknowledges the DuPont Company for 1988 and 1989 summer fellowships and the Wayland E. Noland Research Fellowship Fund for financial support. RDC acknowledges the University of Minnesota Undergraduate Research Opportunities Program (UROP) for grants during 1989 and 1990. DMP acknowledges the National Science Foundation for an NSF-REU 1988 Summer Fellowship (Grant NSF/CHE 8712736-01). We would also like to thank Mr. Joseph J. Dalluge, a 1990 Lando summer fellow, for providing a supply of **3e**, and the X-ray crystal structure reviewer of this paper for help with titles for Tables IX and X.

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