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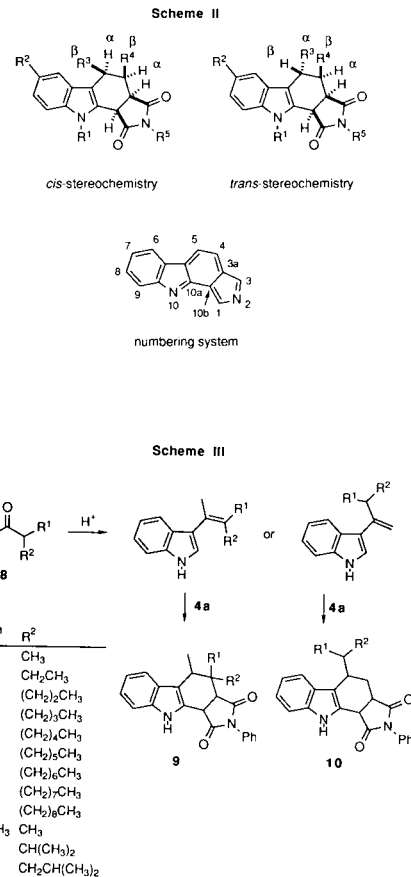
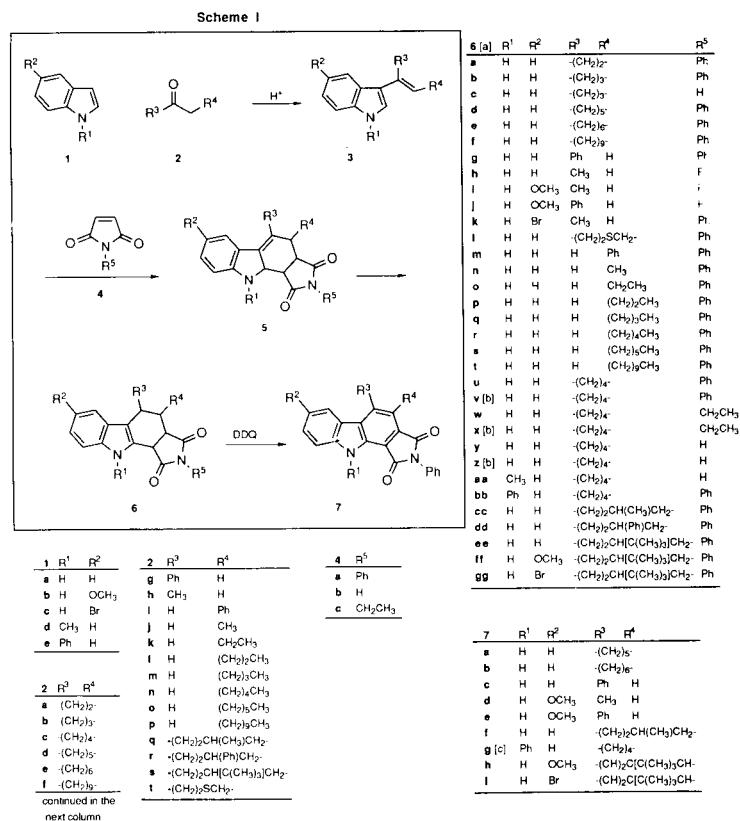
Tetrahydrocarbazoles have been prepared in one-flask syntheses from indoles, ketones or aldehydes, and maleimides, with acid catalysis. The reactions involve a condensation of the indole with the ketone or aldehyde, followed by an *in situ* trapping of the vinylindole in a Diels-Alder addition with a maleimide. Isomerization of the double bond into the indole nucleus gave the tetrahydrocarbazoles which were isolated (**6**, **9**, and **10**). Variation of the indole, carbonyl compound, and maleimide has been explored. The predominant stereochemistry of the tetrahydro ring in the products is all-*cis*, although a second stereoisomer has been isolated. Two regioisomers were generated from all unsymmetrical 2-alkanones, except 2-butanone, which gave the single isomer **9a**. Aromatization of tetrahydrocarbazoles **6** to carbazoles **7** was accomplished with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

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Discussion.

The use of Diels-Alder reactions of vinylindoles to produce carbazoles was first developed in our laboratory a number of years ago [2]. Recently, this methodology has

been exploited by a number of other researchers [3]. The "in situ vinylindole synthesis of carbazoles", also developed our laboratory, combines the synthesis of the vinylindole and the subsequent Diels-Alder reaction in one flask to produce a variety of substituted and annulated tetrahy-



[a] *cis* Stereochemistry (see Scheme II), unless noted otherwise.

[b] *trans* Stereochemistry (see Scheme II).

[c] Isolated directly from the "in situ vinylindole synthesis of carbazoles" as a minor product.

drocarbazoles. Thus, we have reported producing 1,2,3,4-tetrahydrocarbazole-2-carboxylic acids from indoles **1**, a methyl or methylene ketone **2**, and maleic acid [4]. In this reaction sequence, it is postulated that condensation of the indole with the ketone gives a vinylindole which undergoes cycloaddition with maleic acid, followed by double bond isomerization and regioselective decarboxylation.

The "in situ" vinylindole synthesis of carbazoles" is a simple one-flask synthesis with convenient workup that provides fair to good yields of tetrahydrocarbazoles without isolating the reactive vinylindole intermediates. In the present paper, we describe our results with maleimides as the dienophiles in this synthesis.

Table I
Yields of Tetrahydrocarbazoles **6a-6t** and Physical Data [a]

Indole Ketone	Maleimide Ketone	6	Yield %	Mp °C	Emperical Formula	Anal. Calcd.			Found			
						C	H	N	C	H	N	
1a	2a	4a	a	3	290-292	C ₂₂ H ₁₈ N ₂ O ₂	342.1364 [b]			342.1365 [b]		
1a	2b	4a	b	76	310-315	C ₂₃ H ₂₀ N ₂ O ₂	77.50	5.67	7.86	77.50	5.73	7.71
1a	2b	4b	c	55	306-310	C ₁₇ H ₁₆ N ₂ O ₂	72.83	5.76	9.99	72.73	5.75	9.99
1a	2d	4a	d	66	303-306	C ₂₅ H ₂₄ N ₂ O ₂	78.09	6.30	7.28	78.17	6.46	7.19
1a	2e	4a	e	57	294-300	C ₂₆ H ₂₆ N ₂ O ₂	78.35	6.59	7.03	78.19	6.49	7.02
1a	2f	4a	f	22	280-285	C ₂₉ H ₃₂ N ₂ O ₂	79.05	7.34	6.35	79.26	7.11	6.09
1a	2g	4a	g	46	297-298.5	C ₂₆ H ₂₀ N ₂ O ₂	392.1520 [b]			392.1508 [b]		
1a	2h	4a	h	17	268-269	C ₂₁ H ₁₈ N ₂ O ₂	76.34	5.50	8.47	76.44	5.74	8.50
1b	2h	4a	i	26	238.5-239.5	C ₂₂ H ₂₀ N ₂ O ₃	73.32	5.59	7.77	73.53	5.49	7.78
1b	2g	4a	j	44	309-310	C ₂₇ H ₂₂ N ₂ O ₃	76.76	5.25	6.63	76.65	5.40	6.51
1c	2h	4a	k	29	267-269	C ₂₁ H ₁₇ BrN ₂ O ₂	61.63	4.19	6.84	61.50	4.34	6.62
1a	2t	4a	l	19	346-350	C ₂₃ H ₂₀ N ₂ O ₂ S	71.11	5.19	7.21 [c]	71.00	5.19	7.03 [c]
1a	2i	4a	m	18	243-243.5	C ₂₆ H ₂₀ N ₂ O ₂	79.56	5.15	7.13	79.57	5.12	7.13
1a	2j	4a	n	14	265-266	C ₂₁ H ₁₈ N ₂ O ₂	76.34	5.50	8.47	76.27	5.34	8.41
1a	2k	4a	o	9	241.5-242	C ₂₂ H ₂₀ N ₂ O ₂	76.71	5.86	8.13	76.82	5.98	8.12
1a	2l	4a	p	20	226-227.5	C ₂₃ H ₂₂ N ₂ O ₂	77.06	6.20	7.81	76.95	5.99	7.84
1a	2m	4a	q	39	229.5-230.5	C ₂₄ H ₂₄ N ₂ O ₂	77.38	6.51	7.52	77.27	6.57	7.43
1a	2n	4a	r	11	234-235	C ₂₅ H ₂₆ N ₂ O ₂	77.68	6.79	7.24	77.78	6.81	7.24
1a	2o	4a	s	15	227-228	C ₂₆ H ₂₈ N ₂ O ₂	77.96	7.06	6.99	78.10	7.21	6.94
1a	2p	4a	t	24	198-199.5	C ₃₀ H ₃₆ N ₂ O ₂	78.90	7.96	6.13	79.12	8.01	6.05

[a] R¹ = H. All products were white to off-white in color and had the *cis*-stereochemistry illustrated in Scheme II. [b] Used hrms. [c] Anal. Calcd.: S, 8.25. Found: S, 8.41.

Table II
Yields of Tetrahydrocarbazoles **6u-6gg** and Physical Data [a]

Indole Ketone	Maleimide Ketone	6	Stereo- chemistry	Yield %	Mp °C	Emperical Formula	Anal. Calcd.			Found			
							C	H	N	C	H	N	
1a	2c	4a	u	<i>cis</i>	32, 33	305-307	C ₂₄ H ₂₂ N ₂ O ₂	77.81	6.00	7.56	77.78	5.86	7.42
			v	<i>trans</i>	40, 35	214-215	C ₂₄ H ₂₂ N ₂ O ₂	77.81	6.00	7.56	77.87	6.03	7.56
1a	2c	4c	w	<i>cis</i>	34	202-204	C ₂₀ H ₂₂ N ₂ O ₂	74.50	6.89	8.68	74.63	6.87	8.64
			x	<i>trans</i>	34	218-222.5	C ₂₀ H ₂₂ N ₂ O ₂	74.50	6.89	8.68	74.71	6.99	8.60
1a	2c	4b	y	<i>cis</i>	26	328-330	C ₁₈ H ₁₈ N ₂ O ₂	73.45	6.16	9.52	73.46	6.16	9.35
			z	<i>trans</i>	20	276-278	C ₁₈ H ₁₈ N ₂ O ₂	294.1364 [b]			294.1365 [b]		
1d	2c	4b	aa	<i>cis</i>	31	285-287	C ₁₉ H ₂₀ N ₂ O ₂	73.99	6.55	9.08	74.16	6.52	8.98
1e	2c	4a	bb	<i>cis</i>	13 [c]	213-215	C ₃₀ H ₂₆ N ₂ O ₂	80.69	5.87	6.27	80.70	5.89	6.18
1a	2q	4a	cc	<i>cis</i>	52	303-305	C ₂₅ H ₂₄ N ₂ O ₂	78.09	6.30	7.28	77.98	6.18	7.23
1a	2r	4a	dd	<i>cis</i>	27	310-315	C ₃₀ H ₂₆ N ₂ O ₂	80.68	5.88	6.27	80.87	6.00	6.11
1a	2s	4a	ee	<i>cis</i>	50	266-268	C ₂₈ H ₃₀ N ₂ O ₂	78.83	7.10	6.56	78.60	6.90	6.54
1b	2s	4a	ff	<i>cis</i>	83	291.5-292.5	C ₂₉ H ₃₂ N ₂ O ₃	76.29	7.06	6.14	76.47	7.23	6.21
1c	2s	4a	gg	<i>cis</i>	43	299-302	C ₂₈ H ₂₉ BrN ₂ O ₂	66.54	5.78	5.54	66.74	5.67	5.44

[a] All products listed were white to off-white. [b] Used hrms. [c] Carbazole **7g** (2%) was also isolated (Table VII).

Table III
Spectral Data for Tetrahydrocarbazoles **6a-6t**

6	¹ H NMR Data [a], J in Hertz				Other	IR C=O cm ⁻¹	MS (M ⁺⁺ , relative intensity)
	10b	3a	4	5			
a	4.60 d J = 6.7 1 H	3.41 m [b]	3.40 m [b]	3.62 p t 1 H	11.26 (s, 1 H), 7.55-7.41 (m), 7.38 (d, J = 7.7), 7.26 (d, J = 7.8 area for 7.55-7.26 is 7 H), 7.11 (t, J = 7.0, 1 H), 6.99 (t, J = 7.4, 1 H), 2.41 (m, 1 H), 1.91 (m, 1 H), 1.72 (m, 1 H), 1.52 (pt, 1 H)	1690	342 (14)
b	4.50 dd J = 8.2, 1.8 1 H	3.66 dd J = 8.2, 5.9 1 H	2.76 6-line m 1 H	3.45 p t 1 H	11.14 (s, 1 H), 7.56-7.51 (m), 7.47 (d, J = 7.2, area for 7.56-7.47 was 4 H), 7.39 (d, J = 7.9, 1 H), 7.28 (dd, J = 7.8, 1.4, 2 H), 7.06 (t, J = 7.0, 1 H), 6.96 (t, J = 7.0, 1 H), 2.35 (m, 1 H), 2.10 (m, 1 H), 1.61 (m, 2 H), 1.48 (5-line m, 1 H), 1.34 (m, 1 H)	1690	356 (100)
c	4.26 dd J = 8.3, 1.8 1 H	3.43 dd J = 8.3, 6.0 ~2 H [c]	2.61 6-line m 1 H	3.34 p t 1 H	11.37 (s, 1 H), 11.06 (s, 1 H), 7.52 (d, J = 7.6 1 H), 7.38 (d, J = 7.7, 1 H), 7.06 (dt, J = 7.5, 1.0, 1 H), 6.95 (dt, J = 7.4, 1.2, 1 H), 2.28 (m, 1 H), 2.07 (m, 1 H), 1.60-1.34 (m, 3 H), 1.20 (m, 1 H)	1695	280 (100)
d	4.35 d J = 8.0 1 H	3.65 dd 1 H	2.52 m ~8 H [d]	3.27 m ~15 H [c]	10.98 (s, 1 H), 7.52-7.38 (m, 4 H), 7.37 (d, J = 7.5, 1 H), 7.16 (d, J = 8.1, 2 H), 7.06 (t, J = 7.5, 1 H), 6.97 (t, J = 7.5, 1 H), 2.02-1.79 (m, 6 H), 1.64-1.34 (m, 4 H)	1690	384 (92)
e	4.41 d J = 8.5 1 H	3.63 dd J = 8.6, 5.2, 1 H	2.30 m 1 H	3.46 m 1 H	11.04 (s, 1 H), 7.48-7.40 (m, 4 H), 7.36 (d, J = 8.4, 1 H), 7.15 (d, J = 7.2, 2 H), 7.06 (t, J = 7.5, 1 H), 6.98 (t, J = 7.4, 1 H), 2.02-1.60 (m, 8 H), 1.47 (m, 4 H)	1690	398 (98)
f	4.41 d J = 8.8 1 H	3.58 dd J = 8.7, 5.5, 1 H	2.09 m 1 H	3.34 m ~12 H [c]	11.18 (s, 1 H), 7.56-7.37 (m, 4 H), 7.35 (d, J = 7.9, 1 H), 7.16 (d, J = 7.4, 2 H), 7.06 (t, J = 7.9, 1 H), 6.98 (t, J = 7.7, 1 H), 1.83 (m), 1.59 (m), 1.36 (m), 1.15 (m, area for 1.83-1.15 was 18 H)	1690	440 (92)
g	4.55 d J = 8.6 1 H	3.63 dd J = 8.4, 6.5, 1 H	2.44 m 2 H	4.42 t J = 5.4 1 H	11.41 (s, 1 H), 7.42 (m, 4 H), 7.21 (m, 3 H), 7.08 (m, 5 H), 6.79 (m, 2 H)	1694	392 (86)
h	4.42 d J = 8.5 1 H	3.60 dd J = 8.6, 5.6, 1 H	2.43 pq 1 H	3.18 pq 1 H	11.12 (s, 1 H), 7.51-7.41 (m, 4 H), 7.37 (d, J = 8.0, 1 H), 7.19 (d, J = 7.1, 2 H), 7.06 (t, J = 7.0, 1 H), 6.96 (t, J = 7.0, 1 H), 1.34 (m, 3 H), 1.23 (d, J = 6.7, 3 H)	1690	344 (41)
i	4.42 d J = 8.5 1 H	3.64 m 1 H	2.15 m 2 H	3.28 m 1 H	11.00 (s, 1 H), 7.52-7.42 (m, 3 H), 7.29-7.23 (m, 3 H), 7.01 (s, 1 H), 6.73 (d, J = 8.7, 1 H), 3.77 (s, 3 H), 1.26 (d, 6.9, 3 H)	1694	360 (82)
j	4.52 d J = 8.6 1 H	3.62 m 1 H	2.47 m 2 H	4.39 m 1 H	11.22 (s, 1 H), 7.45-7.19 (m), 7.10 (t, J = 8.4, area for 7.45-7.10 was 11 H), 6.70 (dd, J = 8.8, 2.4, 1 H), 6.23 (d, J = 2.3, 1 H), 3.64 (s, 3 H)	1695	422 (100)
k	4.46 d J = 8.6 1 H	3.62 dd J = 14.6, 6.1, 1 H	2.13 m 2 H	3.23 m 1 H	11.44 (s, 1 H), 7.72 (d, J = 1.8, 1 H), 7.55-7.43 (m, 3 H), 7.46 (d, J = 8.6, 1 H), 7.28-7.17 (m, 3 H), 1.26 (d, J = 7.0, 3 H)	1692	410 (47) 408 (49)
l	4.52 d J = 8.8 1 H	3.69 dd J = 8.5, 5.3, 1 H	2.76 m 1 H	3.52 m 1 H	11.32 (s, 1 H), 7.63-7.43 (m, 5 H), 7.35 (d, J = 7.3, 2 H), 7.12 (t, J = 7.2, 1 H), 7.01 (t, J = 7.3, 1 H), 2.61-2.43 (m, 4 H), 2.18-2.04 (m, 2 H)	1680	388 (100)

[a] In dimethyl sulfoxide-d₆, unless otherwise noted; pt = *pseudo* triplet. See Scheme II for the numbering system. [b] The area for 3.41-3.40 was 2 H. [c] Includes water. [d] Includes dimethyl sulfoxide.

The acid-catalyzed condensations of 3-unsubstituted indoles with ketones have been postulated to proceed through 3-vinylindole intermediates **3** [4,5]. Intermediates **3** have been isolated, in many instances, when the vinylindoles were sufficiently stable under the reaction conditions [5]. We did not attempt, in this study, to isolate the vinylindole intermediates. Instead, the intermediates were trapped in Diels-Alder additions with maleimides and the resulting tetrahydrocarbazoles **5** underwent double-bond isomerization to give the tetrahydrocarbazoles **6** (Scheme

I). Yields varied considerably in these reactions from 3% for **6a** to 83% for **6ff**. Physical and spectral data for **6** are provided in Tables I-V. Tetrahydrocarbazoles **6** were aromatized [4,6] with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in good yields, typically greater than 90%, to give carbazoles **7** (Table VI). Tetrahydrocarbazole **6cc** was selectively aromatized, by using 2 equivalents of DDQ, to the carbazole **7f** in 88% yield. Physical and spectral data for **7** are provided in Tables VII and VIII.

Table IV
More Spectral Data for Tetrahydrocarbazoles **6**

6	¹ H NMR Data [a], J in Hertz					Other	IR C=O cm ⁻¹	MS (M ⁺ , relative intensity)
	10b	3a	4	5α	5β			
m [b]	4.66 d J = 7.9 1 H	4.10 dd J = 7.9, 5.3, 1 H [c]	3.66 m	3.11 dd J = 15.6, 7.3 [c]	3.23 dd J = 15.3, 4.5 [c]	11.32 (s, 1 H), 7.52 (d, J = 7.7), 7.46 (d, J = 8.0), 7.36-7.23 (m), 7.13 (t, J = 7.5), 7.02 (t, J = 7.4), 6.79 (d, area for 7.52-6.79 was 14 H)	1710	392 (100)
n	4.29 d J = 8.1 1 H	3.55 dd J = 8.1, 4.6	2.56 m	2.68 ddd J = 15.4, 10.2, 1.7	2.94 ddd J = 15.4, 4.2, 1.9	8.45 (s, 1 H), 7.51 (d, J = 7.9, 1 H), 7.45-7.37 (m, 3 H), 7.35 (dd, J = 8.2, 2.2, 1 H), 7.25-7.17 (m), 7.12 (t, area for 7.25-7.12 was ~ 15 H [e]), 1.42 (d, J = 6.9, 3 H)	1675	330.1366 (100) [d]
o	4.31 d J = 7.9 1 H	3.63 dd J = 7.9, 4.6, 1 H	2.16 m	2.62 dd J = 15.7, 10.2, 1 H	2.97 dd J = 15.7, 4.3, 1 H	8.42 (s, 1 H), 7.53 (d, J = 7.7, 1 H), 7.43-7.36 (m), 7.33 (d, J = 8.2, area for 7.43-7.33 was 4 H), 7.22- 7.09 (m, 4 H), 2.00 (m, 2 H), 1.09 (d, J = 7.3, 3 H)	1690	344 (100)
p	4.30 d J = 7.9 1 H	3.60 dd J = 7.9, 4.4	2.26 m	2.61 ddd J = 15.7, 10.4, 2.0	2.95 dd J = 15.7, 4.3	8.43 (s, 1 H), 7.52 (d, J = 7.7, 1 H), 7.43-7.35 (m, 3 H), 7.32 (d, J = 8.4, 1 H), 7.22-7.10 (m, 4 H), 1.93 (m, 2 H), 1.51 (m, 2 H), 0.98 (t, J = 7.3, 3 H)	1690	358 (100)
q	4.29 d J = 7.9 1 H	3.60 dd J = 7.9, 4.4	2.22 m	2.62 ddd J = 15.7, 10.4, 1.9	2.96 dd J = 15.7, 4.4	8.54 (s, 1 H), 7.54 (d, J = 7.5, 1 H), 7.44-7.32 (m, 3 H), 7.28 (dd, J = 7.5, 1.0, 1 H), 7.22-7.18 (m, 3 H), 7.13 (dt, J = 7.4, 1.1, 1 H), 1.97 (m, 2 H), 1.42 (m, 4 H), 0.95 (t, J = 7.1, 3 H)	1690	372.1817 (100) [f]
r	4.31 d J = 7.9 1 H	3.62 dd J = 7.9, 4.4	2.24 m	2.61 ddd J = 10.5	2.95 dd J = 15.7, 4.4	8.43 (s, 1 H), 7.52 (d, J = 7.7, 1 H), 7.43-7.36 (m), 7.32 (d), 7.20-7.18 (m), 7.12 (t, area for 7.43-7.12 was ~ 11 H [e]), 1.97 (m, 2 H), 1.56-1.28 (m, ~ 7 H [g]), 0.90 (t, J = 6.6, 3 H)	1695	386 (100)
s	4.30 d J = 7.9 1 H	3.60 dd J = 7.9, 4.4	2.24 m	2.62 ddd J = 15.7, 10.4, 1.9	2.96 dd J = 15.7, 4.4	8.42 (s, 1 H), 7.53 (d, J = 7.5, 1 H), 7.44-7.10 (m, 8 H), 1.97 (m, 2 H), 1.48 (m, 2 H), 1.33 (m, 6 H), 0.90 (t, J = 7.1, 3 H)	1680	400 (83)
t	4.31 d J = 7.9 1 H	3.61 dd J = 7.9, 4.4	2.23 m	2.62 ddd J = 10.5	2.95 dd J = 15.7, 4.2	8.43 (s, 1 H), 7.52 (d, J = 7.7, 1 H), 7.43-7.34 (m, 3 H), 7.32 (d, J = 8.1, 1 H), 7.20-7.10 (m, 4 H), 1.95 (m, 2 H), 1.48 (m, 2 H), 1.27 (m, 14 H), 0.88 (t, J 6.6, 3 H)	1690	456.2778 (100) [h]

[a] In deuteriochloroform, unless otherwise noted. See Scheme II for the numbering system. [b] In dimethyl sulfoxide-d₆. [c] The area for 3.66-3.11 was 3 H. [d] Used hrms. Calcd.: 330.1364. [e] Includes chloroform. [f] Used hrms. Calcd.: 372.1832. [g] Includes water. [h] Used hrms. Calcd.: 456.2768.

Table V
Spectral Data for Tetrahydrocarbazoles **6u-6gg**

6	¹ H NMR Data [a], J in Hertz					IR C=O cm ⁻¹	MS (M ⁺ , relative intensity)
	10b	3a	4	5	Others		
u [b]	4.15 dd J = 8.9, 2.3 1 H	3.56 dd J = 8.9, 5.7 1 H	2.62 m 1 H	3.39 m 1 H	8.75 (s, 1 H), 7.72 (d, J = 8.0, 1 H), 7.51-7.39 (m, 5 H), 7.27 (dd, J = 8.5, 1.5, 2 H), 7.18 (t, J = 7.6, 1 H), 7.10 (t, J = 7.5, 1 H), 2.92 (pd, J = 13.8, 1 H), 1.79 (m, 1 H), 1.68-1.48 (m, 2 H), 1.42-1.20 (m, 4 H)	1700	370 (100)
v [b]	4.31 dd J = 7.9, 1.9 1 H	3.40 dd J = 7.8, 4.1 1 H	1.84 pt [c]	2.88 pt 1 H	8.56 (s, 1 H), 7.75 (d, J = 7.9, 1 H), 7.42-7.34 (m, 3 H), 7.25 (d, J = 7.9, 1 H), 7.17-7.13 (m, 3 H), 7.07 (t, J = 7.4, 1 H), 2.98 (pd, J = 12.8, 1 H), 2.47 (dq, J = 12.8, 3.1, 1 H), 1.94 (m [c]), 1.57 (pq, 1 H), 1.44-1.32 (m, 2 H)	1710	370 (100)
v	4.41 d J = 7.9 1 H	3.65 dd J = 7.7, 4.1 1 H	1.74 pt 1 H	2.73 pt 1 H	11.13 (s, 1 H), 7.65 (d, J = 7.8, 1 H), 7.43-7.36 (m, 4 H), 7.13 (d, J = 7.7, 2 H), 7.04 (t, J = 7.5, 1 H), 6.93 (t, J = 7.4, 1 H), 2.95 (pd, J = 11.4, 1 H), 2.34 (pq, 1 H), 1.88 (m, 3 H), 1.48 (pt, 1 H), 1.31 (m, 3 H)		
w	4.23 d J = 8.5 1 H	3.40 dd J = 8.3, 5.6 1 H	2.35 m 1 H	3.27 m 1 H	11.16 (s, 1 H), 7.59 (d, J = 7.9, 1 H), 7.44 (d, 8.0, 1 H), 7.05 (t, J = 7.8, 1 H), 6.94 (t, J = 8.0, 1 H), 3.49 (q, J = 7.2, 2 H), 2.81 (pd, J = 13.5, 1 H), 1.69 (pt, 1 H), 1.46 (m, 2 H), 1.22 (m, 2 H), 1.09 (t, J = 7.1), 1.05 (m, area for 1.09-1.05 was 5 H)	1675	322 (100)
x	4.23 dd J = 7.9, 1.7 1 H	3.41 dd J = 7.9, 4.3 1 H	1.64 pt 1 H	2.51 pt 1 H	11.10 (s, 1 H), 7.59 (d, J = 8.0, 1 H), 7.33 (d, J = 8.0, 1 H), 7.02 (t, J = 7.4, 1 H), 6.89 (t, J = 7.5, 1 H), 3.31 (m, 2 H), 2.89 (pd, J = 10.1, 1 H), 2.31 (pq, 1 H), 1.82 (m, 3 H), 1.44 (pq, 1 H), 1.24 (m, 2 H), 0.96 (t, J = 7.1, 3 H)	1685	322 (100)
y	4.24 d J = 8.5 1 H	3.33 dd J = 8.5, 5.4 1 H	2.26 m 1 H	3.24 m 1 H	11.37 (s, 1 H), 11.01 (s, 1 H), 7.59 (d, J = 7.9, 1 H), 7.41 (d, J = 7.9, 1 H), 7.04 (t, J = 7.0, 1 H), 6.94 (dt, J = 7.5, 1.2, 1 H), 2.80 (pd, J = 13.7, 1 H), 1.68 (pt, 1 H), 1.49 (m, 2 H), 1.25-1.02 (m, 4 H)	1705	294 (79)
z	4.15 dd J = 7.9, 1.6 1 H	3.36 dd J = 7.8, 4.2 1 H	1.60 pt 1 H	2.59 pt 1 H	11.10 (s, 1 H), 11.02 (s, 1 H), 7.61 (d, J = 8.0, 1 H), 7.34 (d, J = 8.0, 1 H), 7.02 (t, J = 7.5, 1 H), 6.90 (t, J = 7.3, 1 H), 2.86 (pd, J = 10.6, 1 H), 2.25 (pt, 1 H), 1.83 (m, 3 H), 1.47-1.03 (m, 3 H)	1705	294 (91)
aa	4.49 d J = 7.9 1 H	3.29 dd J = 8.0, 5.0 [d]	2.28 m 1 H	3.26 m [d]	11.39 (s, 1 H), 7.65 (d, J = 8.0, 1 H), 7.43 (d, J = 8.1, 1 H), 7.14 (t, J = 7.3, 1 H), 7.00 (t, J = 7.1, 1 H), 3.84 (s, 3 H), 2.83 (pd, J = 13.0, 1 H), 1.69 (pt, 1 H), 1.55 (pd, J = 11.7, 1 H), 1.45 (pd, J = 12.8, 1 H), 1.21 (m, 2 H), 1.08 (m, 2 H)	1695	308 (85)
bb [b]	4.53 dd J = 8.5, 1.7 1 H	3.42 dd J = 8.5, 4.6 1 H	2.39 m 1 H	3.09 m 1 H	7.85 (dd, J = 8.5, 2.1, 1 H), 7.54-7.06 (m, 16 H [e]), 2.94 (m, 1 H), 1.93 (m, 4 H), 1.53-1.25 (m, 4 H [f])	1710	446 (4)
cc [b]	4.16 d J = 8.7 1 H	3.58 dd J = 8.7, 5.9 1 H	2.81 m 1 H	3.30 m 1 H	8.67 (s, 1 H), 7.69 (d, J = 8.0, 1 H), 7.50-7.37 (m, 4 H), 7.26 (d, J = 6.2, 2 H), 7.18 (t, J = 7.0, 1 H), 7.10 (t, J = 7.0, 1 H), 2.45-2.25 (m, 1 H), 2.11-2.03 (m, 2 H), 1.70-1.55 (m, 2 H), 1.30 (m, 1 H), 1.25 (m, 1 H), 1.03 (d, J = 7.1, 3 H)	1695	384 (100)
dd	4.50 d J = 8.2 1 H	3.72 m 1 H	2.68 m 1 H	3.25 m 1 H	11.15 (s, 1 H), 7.60-7.41 (m, 5 H), 7.33-7.19 (m, 7 H), 7.09 (t, J = 7.1, 1 H), 6.99 (t, J = 7.0, 1 H), 2.35-1.60 (m, 7 H)	1690	446 (100)
ee	4.42 d J = 8.3 1 H	3.70 m 1 H	2.60 m 1 H	2.96 m 1 H	11.01 (s, 1 H), 7.50-7.41 (m, 4 H), 7.36 (d, J = 8.0, 1 H), 7.17 (d, J = 7.0, 2 H), 7.05 (t, J = 7.5, 1 H), 6.96 (t, J = 7.4, 1 H), 2.21-2.03 (m, 3 H), 1.78 (pd, 1 H), 1.64 (6-line m, 1 H), 1.26 (pq, 1 H), 1.06 (m, 1 H), 0.90 (s, 9 H)	1690	426 (100)
ee [b]	4.31 d J = 8.1 1 H	3.52 dd J = 8.1, 5.9, 1 H	2.70 m 1 H	3.01 m 1 H	8.41 (s, 1 H), 7.55 (d, J = 7.7, 1 H), 7.45-7.36 (m, 3 H), 7.33 (d, J = 8.0, 1 H), 7.21-7.08 (m, 4 H), 2.35-2.16 (m, 3 H), 1.86 (pd, 1 H), 1.74 (6-line m, 1 H), 1.30-1.16 (6-line m, 2 H), 0.93 (s, 9 H)		
ff	4.41 d J = 8.4 1 H	3.70 m 1 H	2.59 m 1 H	2.91 m 1 H	10.86 (s, 1 H), 7.55-7.40 (m, 3 H), 7.25 (d, J = 8.7, 1 H), 7.18 (d, J = 8.1, 2 H), 6.97 (s, 1 H), 6.72 (d, J = 8.8, 1 H), 3.76 (s, 3 H), 2.12-2.02 (m, 3 H), 1.78-1.61 (m, 2 H), 1.30-1.00 (m, 2 H), 0.90 (s, 9 H)	1695	456 (80)
gg	4.46 d J = 8.4 1 H	3.71 pt 1 H	2.58 m 1 H	2.94 m 1 H	11.27 (s, 1 H), 7.68 (s, 1 H), 7.52-7.42 (m, 3 H), 7.33 (d, J = 8.6, 1 H), 7.18 (pd, 3 H), 2.24-1.90 (m, 3 H), 1.75 (pd, 1 H), 1.60 (m, 1 H), 1.28 (m, 1 H), 1.02 (m, 1 H), 0.89 (s, 9 H)	1690	506 (100) 504 (100)

[a] In dimethyl sulfoxide-d₆, unless otherwise noted; *pd* = pseudo doublet, *pt* = pseudo triplet, *pq* = pseudo quartet. See Scheme II for the numbering system. [b] In deuteriochloroform. [c] The area for 1.94-1.84 was 4 H. [d] The area for 3.29-3.26 was 2 H. [e] Includes chloroform. [f] Includes water.

Table VI

Aromatization of Tetrahydrocarbazoles **6** with DDQ to Give Carbazoles **7**

Tetrahydrocarbazole	Product	Yield %
6d	7a	90
6e	7b	48
6g	7c	95
6i	7d	64
6j	7e	95
6cc	7f	88
6ff	7h	96
6gg	7i	92

Table VII

Data for Carbazoles **7** [a]

Carbazole	Mp °C	Empirical Formula	HRMS Calcd.	(M ⁺) Found
7a	310-311	C ₂₅ H ₂₀ N ₂ O ₂	380.1520	380.1493
7b	333-335	C ₂₆ H ₂₂ N ₂ O ₂	394.1676	394.1657
7c	310-311	C ₂₆ H ₁₆ N ₂ O ₂	388.1208	388.1223
7d	299-300	C ₂₂ H ₁₆ N ₂ O ₃	[b]	[b]
7e	281-282	C ₂₇ H ₁₈ N ₂ O ₃	418.1313	418.1292
7f	304-308	C ₂₅ H ₂₀ N ₂ O ₂	380.1520	380.1512
7g	260-263	C ₃₀ H ₂₂ N ₂ O ₂	[c]	[c]
7h	338 dec	C ₂₉ H ₂₄ N ₂ O ₃	448.1781	448.1769
7i	378-380	C ₂₈ H ₂₁ BrN ₂ O ₂	469.0781	496.0788

[a] Compounds **7a-g** were obtained as yellow crystals. Compounds **7h-7i** were obtained as orange crystals. [b] *Anal.* Calcd.: C, 74.15; H, 4.53; N, 7.86. Found: C, 73.98; H, 4.67; N, 7.65. For ms, M⁺ (relative intensity): 456 (100). [c] *Anal.* Calcd.: C, 81.43; H 5.01; N, 6.33. Found: C, 81.49; H, 5.05; N, 6.23. For ms, M⁺ (relative intensity): 442 (76).

The predominant stereoisomer of the carbazoles **6** has all of the hydrogens of the tetrahydro ring *cis* to each other, although a second isomer was isolated which had the *trans*-5*H* stereochemistry illustrated in Scheme II. Both stereoisomers result from *endo* addition in the Diels-Alder step, which determines the 10*b*-H, 3*a*-H, and 4-H as all *cis* (see Scheme II for numbering). This is followed by double-bond isomerization of intermediate **5** (Scheme I), and, if protonation at the 5-position occurred on the less hindered face of the molecule (followed by deprotonation at the 10*a*-position), this would give the *cis*-stereochemistry of the predominant product. If the protonation occurred on the more hindered face of **5**, then the minor *trans* stereoisomer would be formed.

The stereochemistry was determined by nmr studies and other evidence. It would be expected that the 10*b*-H and 3*a*-H would be *cis* due to the nature of the Diels-Alder reaction. When an acidic solution of 1-methylindole, acetone, and maleimide was refluxed, a bridged carbazole derivative was formed that resulted from an oxidation of the tetrahydrocarbazole **5** to a dihydrocarbazole, followed by a second Diels-Alder reaction with maleimide [7]. An X-ray crystal structure determination of this product showed that the hydrogens α to the carbonyls are *cis*. In the tetrahydrocarbazoles **5**, the relatively low coupling constants, J_{10*b*,3*a*} of 7.9-9.0 Hertz, are consistent with the *cis* assignment. Epimerization of the 10*b*-H or 3*a*-H didn't occur under the acidic (possibly equilibrating) conditions, possibly due to ring strain. Models indicate that there is considerably more strain in a *trans* 6:5 ring-fusion in this system than in a *cis* 6:5 ring-fusion. Coupling constants, J_{3*a*,4} of 4.1 to 6.0 Hertz established that the 3*a*-H and 4-H

Table VIII

Spectral Data for Carbazoles **7**

Carbazole	¹ H NMR Data [a], J in Hertz	IR, C=O cm ⁻¹
7a	11.99 (s, 1 H), 8.35 (d, J = 8.1, 1 H), 7.70 (d, J = 8.2, 1 H), 7.58-7.43 (m, 6 H), 7.27 (t, J = 7.6, 1 H), 3.58 (m, 4 H), 1.89 (m, 2 H), 1.79 (m, 2 H), 1.66 (m, 2 H)	1687
7b	12.04 (s, 1 H), 8.23 (d, J = 8.0, 1 H), 7.71 (d, J = 8.2, 1 H), 7.59-7.45 (m, 6 H), 7.31 (t, J = 7.6, 1 H), 3.50 (m, 4 H), 1.92 (m, 2 H), 1.74 (m, 2 H), 1.38 (m, 4 H)	1688
7c	12.41 (s, 1 H), 7.72 (d, J = 8.1, 1 H), 7.65-7.47 (m, 12 H), 7.30 (d, J = 8.0, 1 H), 7.06 (t, J = 7.9, 1 H)	1702, 1761
7d	12.04 (s, 1 H), 7.65 (dd, J = 7.9, 2.3, 1 H), 7.61-7.42 (m, 7 H), 7.21 (dd, J = 8.8, 2.4, 1 H), 3.89 (s, 3 H), 2.97 (s, 3H)	1701
7e	12.27 (s, 1 H), 7.66-7.47 (m, 12 H), 7.17 (dd, J = 8.9, 2.5, 1 H), 6.73 (d, J = 2.4, 1 H), 3.55 (s, 3 H)	1701
7f	12.03 (s, 1 H), 8.19 (d, J = 7.9, 1 H), 7.69 (d, J = 8.0, 1 H), 7.60-7.42 (m, 6 H), 7.28 (t, J = 7.3, 1 H), 3.60-3.30 (m, 8 H [b]), 2.60 (m, 1 H), 2.00 (m, 1 H), 1.95 (m, 1 H), 1.57 (m, 1 H), 1.14 (d, J = 6.4, 3 H)	1691
7g [c]	8.31 (d, J = 7.7, 1 H), 7.56 (m, 4 H), 7.48-7.26 (m, 8 H), 7.17 (d, J = 8.3, 1 H), 3.55 (t, J = 6.4, 2 H), 3.45 (t, J = 5.9, 2 H), 2.18-1.99 (m, 4 H)	1707
7h	12.26 (s, 1 H), 9.08 (d, J = 2.0, 1 H), 8.90 (d, J = 9.1, 1 H), 8.08-8.02 (m, 2 H), 7.77 (d, J = 8.9, 1 H), 7.61-7.49 (m, 5 H), 7.26 (dd, J = 9.0, 2.3, 1 H), 4.00 (s, 3 H), 1.48 (s, 9H)	1702
7i	12.55 (s, 1 H), 9.06 (d, J = 1.9, 1 H), 8.86-8.79 (m, 2 H), 8.01 (d, J = 9.0, 1 H), 7.75 (t, J = 8.7, 1 H), 7.69 (d, J = 8.8, 1 H), 7.61-7.48 (m, 5 H), 1.46 (s, 9 H)	1698

[a] In dimethyl sulfoxide-d₆, unless otherwise noted. [b] Includes water. [c] In deuteriochloroform.

are *cis* and that, therefore, the cycloadditions were *endo* for all reactions studied. The stereochemistry of the 5-H for most of the compounds was assigned by comparison of nmr and other physical data to those of **6y** and **6z**. Tetrahydrocarbazoles **6y** and **6z** are stereoisomers which were separated by fractional crystallization. Tetrahydrocarbazole **6y** had a lower solubility in ethanol and a significantly lower melting point, by approximately 90°, than **6z**. Establishment of the stereochemistry of 10b-H, 3a-H, and 4-H as all *cis* left only 5-C as a possible epimeric center. HETCOR, COSY, and DEPT experiments were used to assign the ¹H nmr peaks. It was found that the 5-H in **6y** gave a narrow multiplet ($w_{1/2} = \sim 11$ Hertz) at 3.23 ppm while the 5-H in **6z** gave a *pseudo* triplet ($w_{1/2} = \sim 25$ Hertz) at 2.61 ppm. The narrow multiplet fits the *cis* assignment in this system, since the 5-H would have two equatorial-axial (*ea*) and one equatorial-equatorial (*ee*) relationships with neighboring hydrogens. All of these couplings would be small and could lead to the narrow multiplet for the 5-H. In contrast, models show that the *trans* system forces the 5-H to have one *ea* and two axial-

axial (*aa*) relationships with neighboring hydrogens. It could be postulated that the coupling constant for the *ea* interaction is close to zero and the coupling constants for the two *aa* interactions are similar to each other. This could account for the *pseudo* triplet observed for **6z**. Two other pairs of isomers, **6u/6v** and **6w/6x**, were isolated. Their stereochemistry was assigned by comparison with **6y/6z**. The ¹H nmr chemical shifts for the 5-H of the *cis* isomers ranged from 3.24 to 3.39 ppm, while those for the *trans* isomers ranged from 2.51 to 2.88 ppm. The chemical shifts for the 4-H of the *cis* isomers ranged from 2.26 to 2.62, while those for the *trans* isomers ranged from 1.60 to 1.84 ppm. These differences were used for assigning the stereochemistry of the other tetrahydrocarbazoles. The assignment of stereochemistry of **6a** was also based partially on ring strain for the *cis* vs. *trans* 6:4 ring fusion. Although *trans* 6:4 fused ring systems are known [8], they are more highly strained than *cis* 6:4 systems. In addition, **6a** has the additional constraints of a double bond and a *cis*-fused succinimide ring, so a *trans* fusion is unlikely in **6a**.

Table IX
Yields of Tetrahydrocarbazoles **9** and **10** and Physical Data

Ketone	Product [a]	Yield %	Mp, °C	Empirical Formula	Anal. Calcd.			Found		
					C	H	N	C	H	N
8a	9a	46	266-267	C ₂₂ H ₂₀ N ₂ O ₂	76.71	5.86	8.13	76.75	6.00	8.16
8b	9b	37	189-190	C ₂₃ H ₂₂ N ₂ O ₂	77.06	6.20	7.81	76.86	6.28	7.75
	10b	5	210-212	C ₂₃ H ₂₂ N ₂ O ₂	358.1676 [b]			358.1646 [b]		
8c	9c	59	112-114	C ₂₄ H ₂₄ N ₂ O ₂	372.1832 [b]			372.1842 [b]		
	10c	8	238-240	C ₂₄ H ₂₄ N ₂ O ₂	77.38	6.51	7.52	77.33	6.30	7.51
8d	9d	50	163-164	C ₂₅ H ₂₆ N ₂ O ₂	77.68	6.79	7.24	77.70	6.74	7.27
	10d	15	240-241	C ₂₅ H ₂₆ N ₂ O ₂	77.68	6.79	7.24	77.69	6.61	7.19
8e	9e	60	206-207	C ₂₆ H ₂₈ N ₂ O ₂	77.96	7.06	6.99	77.79	7.01	7.04
	10e	17	230-231	C ₂₆ H ₂₈ N ₂ O ₂	77.96	7.06	6.99	77.79	6.82	6.88
8f	9f	41	169-171	C ₂₇ H ₃₀ N ₂ O ₂	414.2300 [b]			414.2315 [b]		
	10f	10	209-210	C ₂₇ H ₃₀ N ₂ O ₂	78.22	7.31	6.75	78.00	7.17	6.67
8g	9g	43	131-133	C ₂₈ H ₃₂ N ₂ O ₂	78.46	7.54	6.53	78.51	7.54	6.60
	10g	12	171-173	C ₂₈ H ₃₂ N ₂ O ₂	78.46	7.54	6.53	78.48	7.56	6.61
8h	9h	53	111-113	C ₂₉ H ₃₄ N ₂ O ₂	78.69	7.76	6.33	78.82	7.71	6.18
	10h	18	175-176	C ₂₉ H ₃₄ N ₂ O ₂	78.69	7.76	6.33	78.90	7.88	6.51
8i	9i	43	113-115	C ₃₀ H ₃₆ N ₂ O ₂	78.90	7.96	6.13	78.86	7.99	6.16
	10i	12	167-170	C ₃₀ H ₃₆ N ₂ O ₂	456.2768 [b]			456.2752 [b]		
8j	9j	<1 [c]		C ₂₃ H ₂₂ N ₂ O ₂	358.1676 [b]			358.1689 [b,d]		
	10j	7 [c]		C ₂₃ H ₂₂ N ₂ O ₂						
8k	9k	7 [d]		C ₂₄ H ₂₄ N ₂ O ₂						
	10k	35 [a,e]	228-229	C ₂₄ H ₂₄ N ₂ O ₂	77.39	6.51	7.52	77.23	6.53	7.44
8l	9l	20 [f]	153-154	C ₂₅ H ₂₆ N ₂ O ₂						
	10l	12 [f]		C ₂₅ H ₂₆ N ₂ O ₂						

[a] Each of the products, except **10k**, was obtained as single isomer and assigned the *cis*-stereochemistry illustrated in Scheme II. Compound **10k** was a mixture of isomers with the major isomer having the *cis*-stereochemistry and the minor isomer having the *trans*-stereochemistry. [b] Used hrs. [c] Compounds **9j** and **10j** were inseparable. The ratio was determined by ¹H nmr. [d] Pure **9k** was not obtained. The amount of **9k** in the mixture of **9k** and **10k** was determined by ¹H nmr. [e] Pure **10k** (29%) and a mixture of **9k** and **10k** were obtained. The ratio of the products in the mixture was determined by ¹H nmr. [f] Pure **9l** and a mixture of **9l** and **10l** were obtained. The ratio of the products in the mixture was determined by ¹H nmr.

Is the isomerization of the double bond kinetically or thermodynamically controlled? A ^1H nmr study was used to follow the progress of the reaction of indole with cyclohexanone and maleimide in ethanol catalyzed by dilute hydrochloric acid. Aliquots were taken at selected times. An initial spectrum obtained 1 minute after adding the acid to the reaction mixture at 19° showed the appearance of a vinyl multiplet at 6.17 ppm and a new NH peak at 11.05 ppm, which were probably due to the formation of the vinylindole. Six minutes after heat was applied (total: 7 minutes), the temperature had reached 35° . At this point, a second spectrum showed the appearance of **6y** and **6z** along with the starting compounds and the vinylindole. Several spectra over the next 27 minutes (total: 33 minutes, 48° at the end of this time) showed that **6y** and **6z** increased while indole and maleimide decreased. The vinylindole peaks initially increased and then decreased until

they disappeared by the end of 33 minutes. After a total of 33 minutes, the only further change noted was the appearance and buildup of a peak at 5.35 ppm. During the entire reaction, both tetrahydrocarbazole isomers appeared to be forming simultaneously in a constant ratio. This supports a mechanism of kinetic control.

Unsymmetrical ketones have the potential to give two different 3-vinylindoles, and, thus, two different regioisomeric tetrahydrocarbazoles (see Scheme III). In addition, there is the possibility of (*E*)- and (*Z*)-vinylindole intermediates, which could give different stereoisomers, although the (*Z*)-vinylindole would have been expected to have an unfavorable steric interaction between the 2-H of the indole and the β -substituent of the vinyl group. Thus, the (*Z*)-vinylindole would not have been able to adopt easily the *s-cis* conformation needed for the Diels-Alder reaction. The (*E*)- and (*Z*)-vinylindole intermediates could be in

Table X
Spectral Data for Tetrahydrocarbazoles **9**

9	^1H NMR Data [a], J in Hertz					IR C=O cm^{-1}	MS (M^{++} , relative intensity)
	10b	3a	4	5	Other		
b	4.29 d J = 8.6 1 H	3.50 dd J = 8.6, 4.8, 1 H	2.23 m 3 H [b]	3.33 dq J = 7.1 2.8, 1 H	8.59 (s, 1 H), 7.54 (d, J = 7.6, 1 H), 7.45-7.35 (m, 3 H), 7.30 (d, J = 7.8, 1 H), 7.21-7.12 (m, 4 H), 1.29-1.13 (m, 6 H)	1700	358 (66)
c	4.26 d J = 8.6 1 H	3.45 dd J = 8.4, 5.3, 1 H	2.29 m 1 H	3.30 dq J = 6.9, 4.6, 1 H	8.70 (s, 1 H), 7.55 (d, J = 7.4, 1 H), 7.45-7.34 (m, 3 H), 7.25 (d, J = 7.6, 1 H), 7.20-7.10 (m, 4 H), 2.19 (m, 1 H), 2.09 (m, 1 H), 1.58 (6 line m, 2 H), 1.22 (d, J = 7.1, 3 H), 1.07 (t, J = 7.2, 3 H)	1695	372 (64)
d	4.26 d J = 8.5 1 H	3.46 dd J = 8.5, 5.0, 1 H	2.27 m [c]	3.32 dq J = 6.9, 3.7, 1 H	8.86 (s, 1 H), 7.56 (d, J = 7.3, 1 H), 7.46-7.34 (m, 3 H), 7.27-7.11 (m, 5 H), 2.23 (m [c]), 2.11 (m, 1 H), 1.52 (m, 4 H), 1.22 (d, J = 7.1, 3 H), 1.02 (t, J = 6.9, 3 H)	1700	386 (68)
e	4.29 d J = 8.6 1 H	3.49 dd J = 8.5, 5.1, 1 H	2.28 m [c]	3.31 dq J = 6.9, 4.4, 1 H	8.70 (s, 1 H), 7.58 (d, J = 7.0, 1 H), 7.45-7.35 (m, 3 H), 7.28-7.11 (m, 5 H), 2.22 (m [c]), 2.10 (m, 1 H), 1.55 (m, 2 H), 1.43 (m, 4 H), 1.22 (d, J = 7.1, 3 H), 0.96 (t, J = 6.3, 3 H)	1700	400 (94)
f	4.28 d J = 8.5 1 H	3.48 dd J = 8.5, 5.1, 1 H	2.27 m [c]	3.31 dq J = 7.1, 3.6, 1 H	8.66 (s, 1 H), 7.56 (m), 7.46-7.37 (m), 7.25-7.11 (m, area for 7.56-7.11 was 10 H [d]), 2.22 (m [c]), 2.11 (m), 1.54 (m), 1.39 (m, area for 1.54-1.39 was 10 H [e]), 1.22 (d, J = 7.1, 3 H), 0.95 (t, J = 6.6, 3 H)	1695	
g	4.28 d J = 8.5 1 H	3.48 dd J = 8.5, 5.1, 1 H	2.28 m [c]	3.31 dq J = 6.7, 4.3, 1 H	8.55 (s, 1 H), 7.55 (d, J = 7.1, 1 H), 7.45-7.36 (m, 3 H), 7.28 (d, J = 7.5, 1 H), 7.20-7.12 (m, 4 H), 2.21 (m [c]), 2.11 (m, 1 H), 1.55 (m, 2 H), 1.45-1.24 (m, 8 H), 1.21 (d, J = 7.1, 3 H), 0.92 (t, J = 6.7, 3 H)	1705	428 (100)
h	4.29 d J = 8.5 1 H	3.49 dd J = 8.5, 5.1, 1 H	2.29 m 1 H	3.30 dq J = 6.9, 4.4, 1 H	8.53 (s, 1 H), 7.54 (d, J = 7.7, 1 H), 7.44-7.35 (m, 3 H), 7.29 (d, J = 7.9, 1 H), 7.20-7.14 (m, 3 H), 7.12 (t, J = 7.2, 1 H), 2.21 (m, 1 H), 2.09 (m, 1 H), 1.54 (m, 2 H), 1.45-1.34 (m, 10 H), 1.20 (d, J = 7.1, 3 H), 0.91 (t, J = 6.6, 3 H)	1705	442 (94)
i	4.28 d J = 8.5 1 H	3.48 dd J = 8.5, 5.1, 1 H	2.28 m 1 H	3.30 dq 1 H	8.58 (s, 1 H), 7.55 (d, J = 8.1, 1 H), 7.45-7.36 (m, 3 H), 7.28 (d, J = 8.0, 1 H), 7.19-7.15 (m, 3 H), 7.13 (t, J = 7.0, 1 H), 2.21 (m, 1 H), 2.10 (m, 1 H), 1.53 (m, 2 H), 1.45-1.23 (m, 12 H), 1.21 (d, J = 7.1, 3 H), 0.91 (t, J = 6.5, 3 H)	1700	456 (26)
l	4.32 d J = 8.5 1 H	3.45 dd J = 8.6, 5.4, 1 H	2.42 m 1 H	3.25 dq J = 6.6, 5.1, 1 H	8.49 (s, 1 H), 7.53 (d, J = 7.7, 1 H), 7.44-7.35 (m, 3 H), 7.31 (d, J = 7.8, 1 H), 7.21-7.09 (m, 4 H), 2.09 (m, 1 H), 1.96 (m, 2 H), 1.94 (m, 1 H), 1.20 (d, J = 7.1, 3 H), 0.89 (d, J = 8.4), 0.87 (d, J = 6.3, area for 0.89-0.87 was 6 H)	1716	386 (74)

[a] In deuteriochloroform, unless otherwise noted; pq = *pseudo* quartet. See Scheme II for the numbering system. [b] Includes a methylene. [c] The area for 2.28-2.22 was 2 H. [d] Includes chloroform. [e] Includes water.

equilibrium in the acidic reaction medium. Then, if one of the vinylindole stereoisomers reacts much faster than the other, it could drain the other away. The product ratio, ac-

cording to the Curtin-Hammett principle [9], may not represent the relative stabilities of the intermediate vinylindoles. These possibilities were explored with a series of

Table XI
Spectral Data for Tetrahydrocarbazoles **10**

10	¹ H NMR Data [a], J in Hertz						Other	IR	MS
	10b	3a	4α	4β	5	C=O cm ⁻¹		(M ⁺ , relative intensity)	
a [b]	4.44 d J = 8.4 1 H	3.62 dt J = 8.5, 6.2, 1 H	2.15 m 2 H		3.25 pq 1 H	11.17 (s, 1 H), 7.55-7.42 (m), 7.39 (d, J = 8.0, area for 7.55-7.39 was 5 H), 7.25 (d, J = 7.1, 2 H), 7.08 (t, J = 7.1, 1 H), 6.98 (t, J = 7.0, 1 H), 1.29 (d, J = 7.0, 3 H)	1690	330 (38)	
b	4.28 d J = 8.9 1 H	3.49 8-line m 1 H	2.60 dt J = 14.1, 3.6, 1 H	2.15 dt J = 14.1, 6.2, 1 H	3.17 m 1 H	8.58 (s, 1 H), 7.56 (d, J = 7.8), 7.48-7.35 (m, area for 7.56-7.35 was 4 H), 7.31 (d, J = 7.9, 1 H), 7.22 (d, J = 7.4), 7.17 (t, J = 7.3), 7.10 (t, J = 7.3, area for 7.31-7.10 was 4 H), 1.65 (m, 2 H), 1.47 (m, 1 H), 1.29-1.11 (m, 1 H), 0.93 (t, J = 6.5, 3 H)	1690	358 (17)	
c	4.30 d J = 8.9 1 H	3.51 8-line m 1 H	2.59 dt J = 14.1, 3.6, 1 H	2.16 dt J = 14.1, 6.0, 1 H	3.17 m 1 H	8.45 (s, 1 H), 7.56 (d, J = 7.8, 1 H), 7.47-7.33 (m, 4 H), 7.21-7.18 (m, 3 H), 7.10 (t, J = 7.4, 1 H), 1.74 (m, 1 H), 1.57 (m, ~ 2 H [c]), 1.41 (m, 2 H), 1.33 (m, 2 H), 0.88 (t, J = 7.1, 3 H)	1690	372 (22)	
d	4.30 d J = 8.9 1 H	3.51 8-line m 1 H	2.59 dt J = 14.0, 3.6, 1 H	2.18 dt J = 14.0, 6.0, 1 H	3.17 m 1 H	8.53 (s, 1 H), 7.56 (d, J = 8.0, 1 H), 7.47-7.38 (m, 3 H), 7.36 (d, J = 8.8, 1 H), 7.25-7.16 (m, 3 H), 7.11 (t, J = 7.4, 1 H), 1.80-1.22 (m, ~ 10 H [c]), 0.87 (t, J = 6.8, 3 H)	1695	386 (17)	
e	4.31 dd J = 8.9, 1.1, 1 H	3.52 8-line m 1 H	2.59 dt J = 14.3, 3.7, 1 H	2.16 dt J = 14.3, 6.5, 1 H	3.16 m 1 H	8.46 (s, 1 H), 7.56 (d, J = 7.9, 1 H), 7.47-7.39 (m), 7.36 (d, area for 7.47-7.36 was 4 H), 7.22-7.16 (m, 3 H), 7.11 (t, J = 7.3, 1 H), 1.71 (m, 1 H), 1.57 (m, ~ 3 H [c]), 1.42 (m, 2 H), 1.26 (m, 6 H), 0.85 (t, J = 6.7, 3 H)	1690	400 (16)	
f	4.30 dd J = 8.9, 1.0, 1 H	3.51 8-line m 1 H	2.59 dt J = 14.1, 3.6, 1 H	2.14 dt J = 14.1, 6.0, 1 H	3.17 m 1 H	8.51 (s, 1 H), 7.56 (d, J = 7.7, 1 H), 7.47-7.37 (m, 3 H), 7.34 (d, J = 8.4, 1 H), 7.23-7.16 (m, 3 H), 7.11 (t, J = 7.5, 1 H), 1.73 (m, 3 H), 1.62 (m), 1.43 (m), 1.35-1.21 (m, area for 1.62-1.21 was ~ 15 H [c]), 0.85 (d, J = 6.8, 3 H)	1690	414 (16)	
g	4.29 d J = 8.9 1 H	3.51 8-line m 1 H	2.59 dt J = 14.0, 3.6, 1 H	2.15 dt 1 H	3.18 m 1 H	8.58 (s, 1 H), 7.57 (d, J = 7.8, 1 H), 7.47-7.30 (m, 3 H), 7.33 (d, J = 8.1, 1 H), 7.25-7.19 (m, 3 H), 7.11 (dt, J = 7.9, 1.1, 1 H), 1.73 (m, 2 H), 1.43 (m), 1.38-1.19 (m, area for 1.43-1.19 was 12 H), 0.86 (t, J = 6.7, 3 H)	1690	428 (11)	
h	4.29 d J = 8.2 1 H	3.50 8-line m 1 H	2.59 dt J = 14.1, 3.6, 1 H	2.16 dt J = 14.1, 5.6, 1 H	3.17 m 1 H	8.47 (s, 1 H), 7.56 (d, J = 7.8, 1 H), 7.47-7.37 (m, 3 H), 7.34 (d, J = 7.8, 1 H), 7.23-7.15 (m, 3 H), 7.10 (t, J = 6.9, 1 H), 1.71 (m, 1 H), 1.62 (m, ~ 2 H [c]), 1.42 (m, 2 H), 1.23 (m, 12 H), 0.86 (t, J = 6.7, 3 H)	1695	442 (16)	
i	4.28 d J = 8.9 1 H	3.50 8-line m 1 H	2.59 dt J = 14.1, 3.6, 1 H	2.15 dt J = 14.1, 5.5, 1 H	3.16 m 1 H	8.53 (s, 1 H), 7.56 (d, J = 7.8, 1 H), 7.48-7.37 (m, 3 H), 7.31 (d, J = 7.9, 1 H), 7.24-7.18 (m, 3 H), 7.13 (dt, J = 8.0, 1.8, 1 H), 1.69 (m, 1 H), 1.59 (m, 1 H), 1.49 (m, 2 H), 1.24 (m, 14 H), 0.88 (t, J = 6.7, 3 H)	1690		
k	4.29 d J = 8.9 1 H	3.49 8-line m 1 H	2.62 dt J = 14.1, 3.1, 1 H	2.13 dt J = 14.1, 6.1, 1 H	3.29 m 1 H	8.56 (s, 1 H), 7.54 (d, J = 7.8, 1 H), 7.47-7.34 (m, 3 H), 7.31 (d, J = 7.8, 1 H), 7.23-7.17 (m, 3 H), 7.10 (dt, J = 7.9, 1.3, 1 H), 1.92 (m, 1 H), 1.55 (m, 1 H), 1.28 (m, 1 H), 1.00 (d, J = 6.5, 3 H), 0.98 (d, J = 6.5, 3 H)	1690	372 (19)	
[d]									

[a] In deuteriochloroform, unless otherwise noted; pq = *psuedo* quartet. See Scheme II for the numbering system. [b] In dimethyl sulfoxide-*d*₆. [c] Includes water. [d] Major isomer.

methyl ketones. Branchless methyl ketones gave, as the major products **9**, those derived from the vinylindole having the most-substituted double bond. In all cases where the ketone was unsymmetrical, except with 2-butanone, a minor product **10**, which was derived from the vinylindole with the least-substituted double bond, was also detected (Table IX). 2-Butanone gave only **9a**, from a Diels-Alder reaction of the vinylindole with the most-substituted double bond. The ratio of **9:10** dropped slowly with increasing length of R² from about 7:1 for R² = Et to about 3.5:1 for R² = *n*-decyl. Branching on the ketone decreased the amount of **9** relative to **10**, with the smallest ratios corresponding to branching closet to the carbonyl. Thus, while 2-butanone gave exclusively **9a**, 3-methyl-2-butanone gave a 1:9 mixture of **9j** to **10j**. Apparently, steric hindrance caused by branching slows down the Diels-Alder reaction of the more-substituted vinylindole enough so that, through an equilibrium, some is converted to the least-substituted vinylindole, which undergoes the Diels-Alder reaction more rapidly and irreversibly. If the branching is far enough from the carbonyl, however, steric hindrance is less and the ketone gives ratios of products that start to resemble ratios of products from branchless methyl ketones. Each of the regioisomers, except for **10k**, was obtained as a single stereoisomer and, by comparison of the nmr data to those of **6y** and **6z**, including coupling constants, was assigned the all-*cis*-stereochemistry consistent with the tetrahydrocarbazoles derived from cyclic ketones. Physical and spectral data for **9** and **10** are provided in Tables IX-XI.

We have also used aldehydes in place of ketones (Table I, entries **n-u**). Regioisomers are not possible and stereoisomers are not possible at C-5. Only one stereoisomer was obtained from each aldehyde, and the ¹H nmr data indicated that these tetrahydrocarbazoles had the all-*cis*-stereochemistry illustrated in Scheme II. Coupling constants, J_{3,4} of 4.3-4.6 Hertz were indicative of a *cis* relationship. The yields, in general, were lower with aldehydes than with ketones, ranging from 9% for **6o** to 39% for **6q**.

EXPERIMENTAL

General Information.

Melting points were determined with a Thomas-Hoover Unimelt apparatus and are uncorrected. The nmr spectra were obtained on Bruker AC-200 and Bruker AC-300 FT NMR spectrometers and were referenced to the solvent. Infrared spectra were obtained using potassium bromide pellets. Electron-impact ms were obtained with a Kratos/AEI MS-30. Microanalyses were performed by MHW Laboratories, Phoenix, AZ.

General Procedure for the "In Situ Vinylindole Synthesis of Tetrahydrocarbazoles."

The indole (10.0 mmoles) and the maleimide (10.0 mmoles) were dissolved in the ketone (10.0 ml), or added to ethanol (10.0 ml) along with the ketone (10.0 mmoles). Hydrochloric acid (12 M, 0.20 mmole) was added, and the solution was heated to reflux or until the solution became too thick with precipitate to reflux properly. The refluxing solutions were monitored by thin-layer chromatography (silica gel) until the indole could no longer be detected. Then the solution was cooled and the resulting precipitate was filtered and washed with cold solvent. The filtrate was cooled further in the freezer to give additional crops which, in some cases, included a second isomer. The precipitates were recrystallized from ethanol to give pure tetrahydrocarbazoles.

General Procedure for Aromatization of Tetrahydrocarbazoles.

The tetrahydrocarbazole (0.50 mmole) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.0-3.0 mmoles) were dissolved in 1,4-dioxane. The resulting olive-green solution was refluxed until the tetrahydrocarbazole could no longer be detected by thin-layer chromatography (usually 30-90 minutes). The solution was cooled and filtered and the resulting precipitate was rinsed with methylene chloride. The filtrate and rinses were combined and washed once with saturated sodium bicarbonate solution (15 ml) and several times with water (20 ml each). The organic layer was dried over anhydrous magnesium sulfate and then the solvent was evaporated to give carbazoles **7**.

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