NEW REGIO- AND STEREOCONTROLLED REACTIONS OF 2-VINYLINDOLES WITH CC-DIENOPHILES: DIELS-ALDER REACTIONS, ENE REACTIONS, AND MICHAEL ADDITIONS[1]

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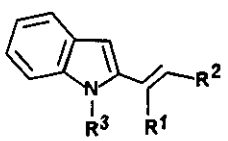
Abstract —— The reactions of selectively functionalized 2-vinylindoles with some acyclic and cyclic CC-dienophiles yield Diels-Alder adducts, Diels-Alder ene products, and Michael adducts, respectively, with very high regio- and/or stereoselectivities. This methodology provides a convenient access to functionalized indoles, carbazoles, and [c]pyrroloannellated carbazoles with substitution patterns that are not so easily accessible by other routes.

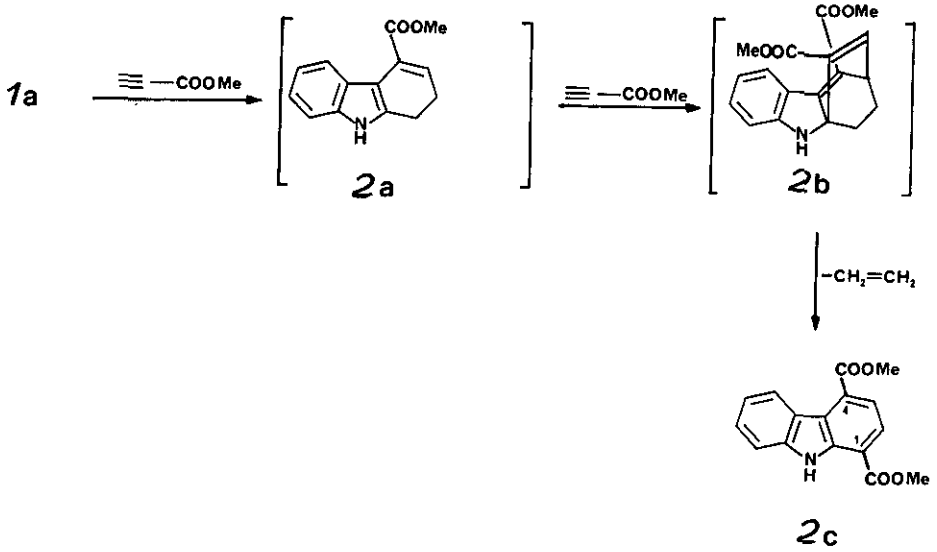
Diels-Alder reactions of vinylindoles have been found by others[1,4] and by us[1,2-5] to represent a synthetically very attractive concept for the preparation of novel [b]annellated indoles to serve as lead substances and as building blocks for alkaloids. However, the synthetic potential and limitations of the concept, as well as the analytical methodology required by the alternative reaction pathways, especially when 2-vinylindoles are used, have not yet been sufficiently delineated to allow use of the concept in the planning of syntheses of condensed heterocycles[4-8]. Thus, in continuation of our synthetic investigations on vinylheterocycles, we now report on some new and interesting reactions of selected, principally donor- and acceptor-substituted, 2-vinylindoles 1 with acyclic and cyclic CC-dienophiles and, *at the same time, illustrate the competing reaction pattern of* "Diels-Alder reaction, Diels-Alder ene reaction, and Michael addition"[6,7]. This pattern is markedly less frequently found in such a state of completeness in the 3-vinylindole series[4].

In the present communication on the reactions of **1a-i** with methyl propynoate, methyl acrylate, N-phenylmaleimide, 1-penten-3-one, and p-benzoquinone, only those combinations of reactants are discussed which, in our studies, produced a clear and structural-analytically perceivable reaction result.



1	R^1	R^2	R^3
a	H	H	H
b	H	Me	H
c	Me	H	H
d	COMe	Me	H
e	H	OMe	Me
f	Me	Me	H
g	H	Ph	H
h	COMe	Ph	H
i	H	COOMe	H

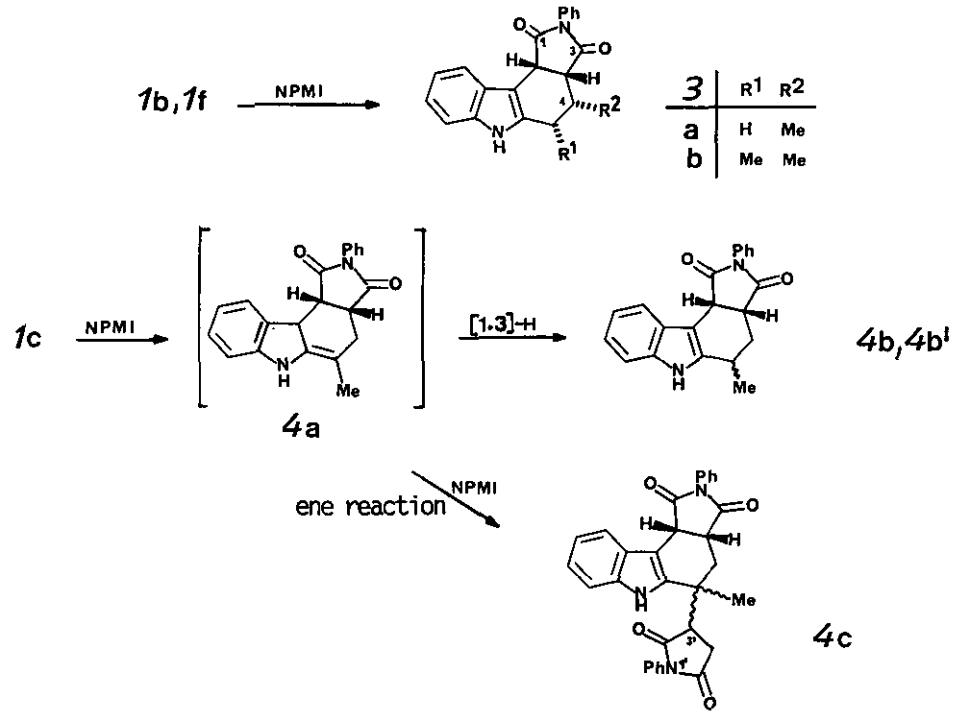
The parent compound 2-vinylindole[1] **1a**, first prepared by us, reacts with methyl propynoate via **2a** and **2b** in a double Diels-Alder reaction with subsequent extrusion of ethene[9] from **2b** to give dimethyl carbazole-1,4-dicarboxylate **2c** regioselectively (tlc control and 400 MHz ^{1}H-nmr analysis of the crude reaction mixture). In addition, the formation of a relatively large amount of polymers was observed with this combination of reactants. Further new results on cycloadditions of the parent compound **1a** with cyclic CC-dienophiles have been described by us[1].



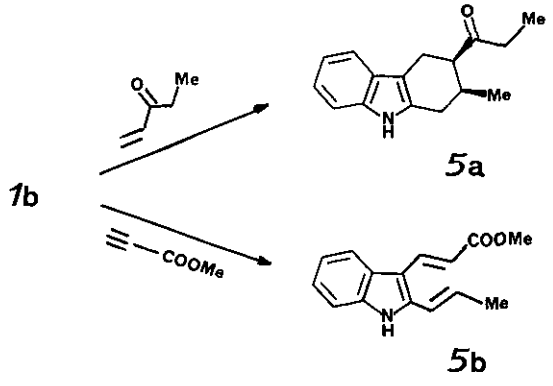
In dependence on the substitution patterns of the diene/dienophile reactant pairs, the reaction sequences of the 2-vinylindoles are considerably extended as a result of steric and/or electronic effects. This is illustrated by the following results (for reaction conditions and yields, see Table 1 with typical procedures).

The methylated (E)-2-vinylindoles **1b** and **1f** react stereoselectively with N-phenylmaleimide (NPMI) in satisfactory to good yields (Table 1) to form the cycloadducts **3a** and **3b**. In contrast, NPMI reacts with **1c**, which is regioisomeric with **1b**, to form **4b** and **4b'** (two epimers separated by tlc) as well as **4c**. The stereoselectively formed [c]pyrroloannellated carbazole **4c** (the relative configuration at C5 has

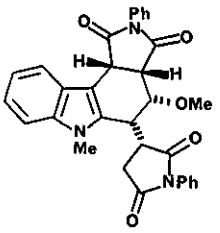
not yet been elucidated) represents the trapped product formed by an ene reaction of the not isolable primary cycloadduct **4a**.



Whereas (E)-2-propenylindole **1b** undergoes regio- and stereoselective cycloaddition with 1-penten-3-one via an endo-transition state to form the cis-substituted 1,2,3,4-tetrahydrocarbazole **5a**, the reaction of **1b** with methyl propynoate results exclusively in the formation of the Michael-type addition product **5b**[6] (both are mild reactions catalyzed by solid silica gel).



Similar to **1c**, the donor-activated methoxy-substituted (E)-2-vinylindole **1e** reacts stereoselectively with NPMI to form also the Diels-Alder ene product **6**.



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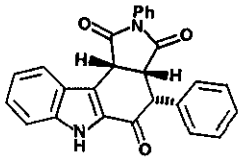

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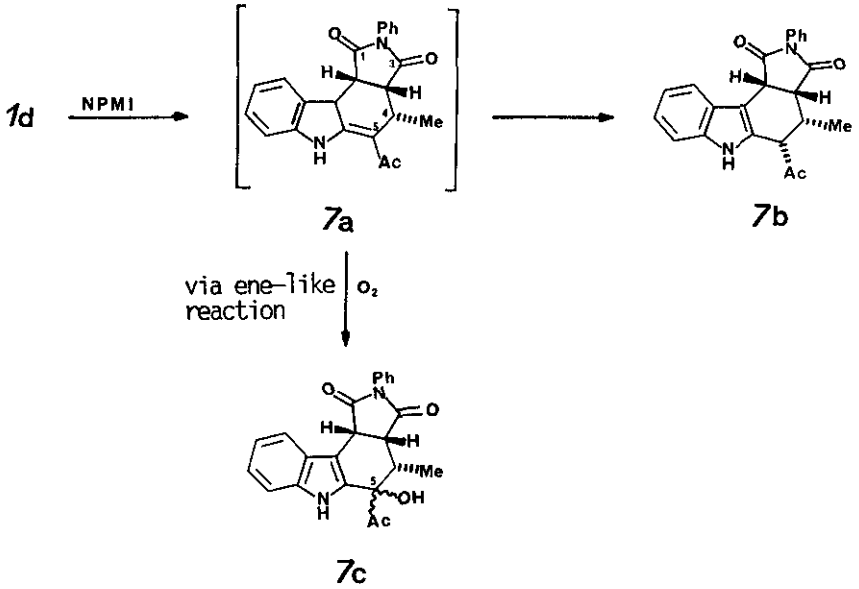
Interesting product distributions were observed in the reactions of the 1'-acetyl-2-vinylindoles **1d** and **1h** with NPMI. The reaction of **1d** with this dienophile gave rise to **7b** in low yield (Table 1) and to the autoxidation product **7c**. Compound **7c** should be a subsequent product of an autoxidation of the primary, not isolable cycloadduct **7a** with the oxygen present in the reaction medium. This route should proceed through a C5-hydroperoxide which could be formed directly from **7a** and O_2 by way of an ene-like reaction[10] at the allylic structural moiety of **7a**. A complete cleavage reaction of the hydroperoxide to form the stable **7c** takes place already in the reaction mixture (tlc monitoring)[11]. When the reaction is performed under an inert gas atmosphere, the formation of **7c** from **1d** does not occur.



The indole **1h** reacts analogously with NPMI to form the not isolable primary [4 + 2]-cycloadduct which is also trapped by O_2 in an ene-like reaction. The thus formed primary hydroperoxide should also be cleaved[11] to yield the isolated 1,3,5-trioxocarbazole derivative **8**. In contrast, the 2-vinylindole **1g** undergoes a "normal" reaction with NPMI to form the [4 + 2]-cycloadduct **9a** and under additional $AlCl_3$-catalysis to form the charge-controlled Michael adduct **9b**.

The reactions of **1g** with p-benzoquinone and methyl acrylate, respectively, yield exclusively the Diels-Alder adduct **10** (dehydrogenative [4 + 2]-cycloaddition)[1] and the carbazole derivative **11** regio- and stereoselectively. The [c]annellated carbazole **12** is the sole reaction product from the cycloaddition of methyl 2-indolylacrylate **1i** with NPMI; this reaction is also stereoselective.

Table 1. Reaction conditions for the syntheses of the new compounds and yield and mp data for analytically pure products.

Compound[a]	Reaction Conditions[b]; Reaction Time	Yield [%][c]	Mp [°C]
2c	B; 5 d	8	122
3a	B; 40 h	73	245
3b	B; 8 h	47	226
4b	B; 7 h	16	265
4b'	B; 7 h	12	241
4c	A; 8 h	29	216
5a	C; 8 h	46	182-184
5b	C; 3 d	34	169
6	B; 16 h	16	299
7b	A; 3 d	2	134
7c	A; 3 d	8	246
8	B; 3 d	22	268
9a	B; 36 h	21	226
9b	B (with 1 mmol of $AlCl_3$); 36 h	17	164
10	B; 21 d	49	182
11	A; 24 h	17	264
12	B; 14 h	32	226

a) For all products satisfactory elemental analyses were obtained and appropriate molecular ion peaks were observed in the 70 eV mass spectra. The nmr spectra (^1H and ^{13}C) were in agreement with the proposed structures; for ^1H-nmr data, see Table 2.

b) **Procedure for the reactions of 1 with CC-dienophiles:** 1 mmol of 2-vinylindole[13] **1** and 1.1 mmol of dienophile were dissolved in 5-10 ml of toluene and, after addition of 2 g of anhydrous (activated) 4 Å molecular sieve, the mixture was stirred at 20 °C (Method A) or under reflux (Method B) for 8 h to 21 d. The formation of the products was monitored by tlc. The products were finally separated by column chromatography [Merck silica gel 60, grain size 0.063-0.200 mm; elution with petroleum ether (bp 40-60 °C)/ethyl acetate (3/1, v/v)]. Method C: 1 mmol of 2-vinylindole **1** was dissolved in 1.5 mmol of the liquid dienophile, treated with a twentyfold amount by weight of the silica gel 60 used for the column chromatography, and allowed to stand at 20 °C.

c) In some cases the yields of the crude products were considerably higher (tlc monitoring, ^1H-nmr) than the values given here for the pure compounds subjected to structural analysis. Incomplete reactions were accompanied by the formation of polymers. The high regio- and stereoselectivities were confirmed by ^1H-nmr spectroscopy and tlc analyses of the crude product mixtures.

Table 2. 400 MHz ^{1}H-nmr data of the new compounds*).

Compound	Solvent	δ [ppm]
2c	acetone-d_6	4.02 (s, 3H, CH_3), 4.07 (s, 3H, CH_3), 7.26 (p-hept, 1H, J = 7.7 and 1.0 Hz, C6- or C7-H), 7.51 (p-hept, 1H, J = 7.7 and 1.2 Hz, C7- or C6-H), 7.78 (d, 1H, J = 8.2 Hz, C8-H), 7.80 (d, 1H, J = 7.9 Hz, C2- or C3-H), 8.12 (d, 1H, J = 8.1 Hz, C3- or C2-H), 8.74 (dd, 1H, J = 8.2 and 0.9 Hz, C5-H), 11.14 (brs, 1H, NH).
3a	acetone-d_6	1.49 (d, 3H, J = 7.1 Hz, CH_3), 2.40-2.48 (m, 1H, C4-H), 2.71 (dq, 1H, J = 16.1, 10.2, and 1.6/1.7 Hz, C5-H A or B), 2.91 (dd, 1H, J = 16.0 and 4.7 Hz, C5-H B or A), 3.70 (dd, 1H, J = 7.7 and 4.0 Hz, C3a-H), 4.43 (dt, 1H, J = 7.7 and 1.5 Hz, C10c-H), 6.99-7.41 (m, 8H, aryl-H and C7- to C9-H), 7.86 (d, 1H, J = 7.6 Hz, C10-H), 10.15 (brs, 1H, NH).
3b	acetone-d_6	1.21 (brs, dynamic process, 3H, CH_3 at C4), 1.36 (d, 3H, J = 7.0 Hz, CH_3 at C5), 2.69 (m, 1H, C4-H), 3.24 (m, 1H, C5-H), 3.60 (dd, 1H, J =8.4 and 5.2 Hz, C3a-H), 4.45 (dd, 1H, J = 8.4 and 1.5 Hz, C10c-H), 6.99-7.47 (m, 8H, aryl-H and C7- to C9-H), 7.93 (d, 1H, J = 7.85 Hz, C10-H), 10.2 (brs, 1H, NH).
4b (5-methyl group trans to succinimide ring)	acetone-d_6	1.42 (d, 3H, J = 6.8 Hz, CH_3), 1.71 (oct, 1H, J = 14.6, 9.5, and 5.0 Hz, C4-H A or B), 2.60 (p-sext, 1H, J = 14.5, 5.0, and 4.0 Hz, C4-H B or A), 3.00 (m, 1H, J = 10.7 and 5.0 Hz, C5-H), 3.78 (p-sext, 1H, J = 8.2, 4.5, and 3.8 Hz, C3a-H), 4.47 (dd, 1H, J = 8.1 and 1.5 Hz, C10c-H), 7.00-7.47 (m, 8H, aryl-H and C7- to C9-H), 7.87 (d, 1H, J = 7.6 Hz, C10-H).
4b' (5-methyl group cis to succinimdie ring)	CD_2Cl_2	1.34 (d, 3H, J = 7.0 Hz, CH_3), 2.03 (p-quint, 1H, J = 13.5, 8.0, and 4.0 Hz, C4-H A or B), 2.41 (p-quint, 1H, J = 13.5, 5.5, and 5.2 Hz, C4-H B or A), 3.10 (m, 1H, J = 7.0, 5.4, and 3.8 Hz, C5-H), 3.44 (p-sext, 1H, J = 8.4, 7.5, and 5.8 Hz, C3a-H), 4.40 (dd, 1H, J = 8.3 and 1.4 Hz, C10c-H), 7.12-7.49 (m, 8H, aryl-H and C7- to C9-H), 8.22 (brs, 1H, NH).
4c	CD_3NO_2	1.56 (s, 3H, CH_3), 2.24 (dd, 1H, J = 13.8 and 6.4 Hz, C4-H A or B), 2.49 (dd, 1H, J = 13.9 and 5.7 Hz, C4-H B or A), 2.84 (dd, 1H, J = 18.5 and 5.7 Hz, C4'-H A or B), 3.15 (dd, 1H, J = 18.4 and 9.3 Hz, C4'-H B or A), 3.64 (dd, 1H, J = 9.2 and 5.8 Hz, C3'-H), 3.72 (p-sext, 1H, J = 8.5, 6.1, and 6.0 Hz, C3a-H), 4.59 (d, 1H, J = 8.6 Hz, C10c-H), 7.10-7.59 (m, 13H, aryl-H and C7- to C9-H), 7.98 (d, 1H, J = 7.8 Hz, C10-H), 9.89 (s, 1H, NH).
5a	benzene-d_6	0.89 (d, 3H, J = 6.9 Hz, CH_3), 0.98 (t, 3H, J = 7.2 Hz, CH_3, X_3 part of ABX_3 system), 1.96-2.10 (m, 2H, CH_2, AB part of ABX_3 system), 2.13 (dd, 1H, J = 15.8 and 2.4 Hz, C1-H A), 2.30-2.38 (m, 2H, C2- and C3-H), 2.51 (dd, 1H, J = 16.0 and 5.5 Hz, C1-H B), 2.73 (dd, 1H, J = 15.6 and 4.9 Hz, C4-H A), 2.93 (dd, 1H, J = 15.0 and

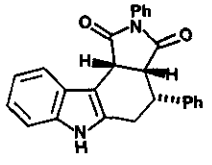
Table 2. (*Continued*).

Compound	Solvent	δ [ppm]
		10.0 Hz, C4-H B), 6.40 (brs, 1H, NH), 7.08 (dd, 1H, J = 6.1 and 2.8 Hz, C5- or C8-H), 7.20-7.26 (m, 2H, C6- and C7-H), 7.56 (dd, 1H, J = 5.9 and 2.8 Hz, C8- or C5-H).
5b	acetone-d_6	1.98 (dd, 3H, J = 6.7 and 1.7 Hz, CH_3), 3.73 (s, 3H, OCH_3), 6.41 (d, 1H, J = 15.9 Hz, C3'- or C4'-H), 6.50 (dd, 1H, J = 15.8 and 6.7 Hz, C2'-H), 6.87 (dd, 1H, J = 15.9 and 1.7 Hz, C1'-H), 7.14-7.24 (m, 2H, C5- and C6-H), 7.38 (t, 1H, J = 7.5 and 1.2 Hz, C7-H), 7.87 (d, 1H, J = 7.1 Hz, C4-H), 8.04 (d, 1H, J = 15.8 Hz, C4'- or C3'-H), 10.87 (brs, 1H, NH).
6	DMSO-d_6	2.15 (dd, 1H, J = 17.9 and 5.6 Hz, C4'-H A or B), 2.97 (dd, 1H, J = 17.9 and 9.5 Hz, C4'-H B or A), 3.32 (s, 3H, OCH_3), 3.52 (p-quint, 1H, J = 5.4 and 2.8 Hz, C3'-H), 3.58 (dd, 1H, J = 9.0 and 3.5 Hz, C3a-H), 3.60 (s, 3H, NCH_3), 4.17 (p-t, 1H, J = 2.7 and 2.7 Hz, C5-H), 4.49 (p-t, 1H, J = 3.0 and 3.0 Hz, C4-H), 4.62 (d, 1H, J = 8.7 Hz, C10c-H), 7.04-7.53 (m, 13H, aryl-H and C7- to C9-H), 7.90 (d, 1H, J = 7.9 Hz, C10-H).
7b	acetone-d_6	1.19 (d, 3H, J = 7.1 Hz, CH_3), 2.27 (s, 3H, acetyl-CH_3), 3.00 (p-sext, 1H, J = 7.1, 5.0, and 4.9 Hz, C4-H), 3.75 (dd, 1H, J = 8.1 and 5.0 Hz, C3a-H), 3.95 (d, 1H, J = 4.8 Hz, C5-H), 4.53 (dd, 1H, J = 8.2 and 0.7 Hz, C10c-H), 7.03-7.47 (m, 8H, aryl-H and C7- to C9-H), 7.98 (d, 1H, J = 7.7 Hz, C10-H), 10.2 (brs, 1H, NH).
7c	acetone-d_6	1.49 (d, 3H, J = 7.3 Hz, CH_3), 2.64 (p-quint, 1H, J = 7.1 and 7.3 Hz, C4-H), 3.78 (dd, 1H, J = 8.7 and 6.9 Hz, C3a-H), 4.59 (d, 1H, J = 8.7 Hz, C10c-H), 5.36 (s, 1H, OH, exchangeable with D_2O), 7.03 (p-sext, 1H, J = 7.9 and 0.9 Hz, C9-H), 7.11 (p-sept, 1H, J = 7.5 and 1.1 Hz, C8-H), 7.32-7.45 (m, 6H, aryl-H and C7-H), 7.96 (d, 1H, J = 7.9 Hz, C10-H), 10.2 (brs, 1H, NH).
8	acetone-d_6	4.38 (dd, 1H, J = 7.5 and 1.7 Hz, C3a-H), 4.66 (d, 1H, J = 1.7 Hz, C4-H), 5.15 (d, 1H, J = 7.5 Hz, C10c-H), 7.19-7.57 (m, 8H, aryl-H and C7- to C9-H), 8.22 (d, 1H, J = 8.2 Hz, C10-H), 11.1 (brs, 1H, NH).
9a	DMSO-d_6	3.12 (dd, 1H, J = 16.2 and 5.8 Hz, C5-H A or B), 3.23 (dd, 1H, J = 16.2 and 4.9 Hz, C5-H B or A), 3.66 (p-sext, 1H, J = 5.1, 5.0, and 4.9 Hz, C4-H), 4.05 (dd, 1H, J = 7.7 and 5.0 Hz, C3a-H), 4.59 (d, 1H, J = 7.7 Hz, C10c-H), 6.74-7.53 (m, 13H, aryl-H and C7- to C9-H), 7.75 (d, 1H, J = 7.7 Hz, C10-H), 11.17 (s, 1H, NH).
9b	DMSO-d_6	2.99 (dd, 1H, J = 18.2 and 5.8 Hz, C10'-H A or B), 3.43 (dd, 1H, J = 18.2 and 9.8 Hz, C10'-H B or A), 4.99 (dd, 1H, J = 9.8 Hz and 5.8 Hz, C9'-H), 6.99-7.64 (m, 16H, aryl-H, C4- to C7-H, C1'-H, and C2'-H), 11.5 (brs, 1H, NH).

Table 2. (Continued)

Compound	Solvent	δ [ppm]
10	acetone-d_6	6.83 (d, 1H, J = 10.2 Hz, C4- or C5-H), 7.04 (d, 1H, J = 10.2 Hz, C5- or C4-H), 7.30-7.63 (m, 8H, aryl-H and C8- to C10-H), 7.34 (s, 1H, NH), 7.67 (s, 1H, C1-H), 9.38 (d, 1H, J = 8.3 Hz, C7-H).
11	DMSO-d_6	2.60 (dd, 1H, J = 15.9 and 9.3 Hz, C1-H A), 2.93 (dd, 1H, J = 16.4 and 5.3 Hz, C1-H B), 3.05 (dd, 1H, J = 16.8 and 3.6 Hz, C4-H A), 3.24 (p-quint, 1H, J = 8.8, 5.0, and 4.5 Hz, C2-H), 3.31 (dd, 1H, J = 17.0 and 6.4 Hz, C4-H B), 3.56 (s, 3H, CH_3), 3.73 (m, 1H, J = 5.8, 5.0, and 3.5 Hz, C3-H), 6.92-7.22 (m, 7H, aryl-H, C6-H, and C7-H), 7.28 (d, 1H, J = 8.0 Hz, C5- or C8-H), 7.37 (d, 1H, J = 7.7 Hz, C8- or C5-H), 10.83 (s, 1H, NH).
12	acetone-d_6	3.00 (oct, 1H, J = 16.5, 12.0, and 1.2 Hz, C5-H A), 3.17 (dd, 1H, J = 16.5 and 5.0 Hz, C5-H B), 3.25 (p-sext, 1H, J = 11.8, 4.8, and 4.7 Hz, C4-H), 3.76 (s, 3H, CH_3), 4.43 (dd, 1H, J = 7.4 and 4.5 Hz, C3a-H), 4.60 (brd, 1H, J = 7.9 Hz, C10c-H), 7.00-7.40 (m, 8H, aryl-H and C7- to C9-H), 7.86 (d, 1H, J = 7.9 Hz, C10-H), 10.35 (brs, 1H, NH).

*) A, B = geminal protons; p- = pseudo.



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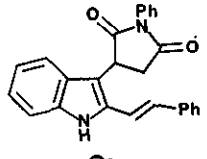

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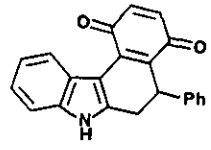

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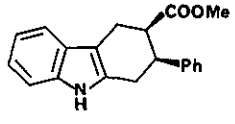

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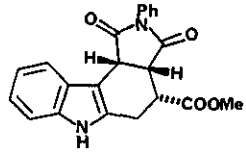

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As exemplarily shown by MNDO calculations performed by us on 2-vinylindoles[1], the Diels-Alder reactions mentioned here should represent $HOMO_{diene}$-$LUMO_{dienophile}$ controlled processes according to the FMO concept[12]. The regiochemistries found for the cycloadditions of 1 with methyl acrylate and 1-penten-3-one described here can also be predicted satisfactorily by a "large-large"-"small-small" interaction

of the frontier orbital coefficients[1,12]. However, in the unusual and mechanistically complex reaction of **1a** with methyl propynoate, a reversed direction of addition was deduced from an analysis of the product mixture and this contradicts the FMO concept.

The constitutions and relative configurations given for the new functionalized indole and carbazole derivatives have been confirmed by nmr spectroscopy (400 MHz, $^1H,^1H$-decoupling, 1D NOE experiments, 100.6 MHz J-modulated ^{13}C-nmr spin echo experiments; for ^1H-nmr data, see Table 2). However, in spite of application of these techniques, no final configurational analyses at C5 could be made for **4c** and **7c**. The stereochemistries of the products **3a**, **3b**, **5a**, **6**, **7b**, **9a**, **11**, and **12** provide convincing evidence for the assumption that they are formed in $[_\pi 4s + _\pi 2s]$-cycloaddition processes through (E)-endo-transition states. An (E/Z)-isomerization of the (E)-vinylindole used under the conditions of the cycloaddition has been excluded by the results of control experiments performed in the absence of the CC-dienophile. Considerations of Büchi-Dreiding models show - in accordance with the $^1H,^1H$ coupling constants on application of the Karplus relationship - that the cyclohexene rings of the tetrahydrocarbazoles take up a slightly distorted boat conformation (see for example Fig. 1: computer-simulated stereo drawing of **3a**).

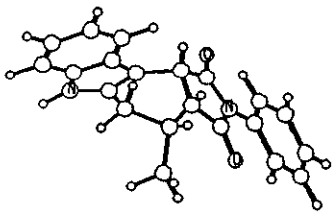

Fig. 1. Stereoview of **3a**. Computer simulation based on geometries and coordinates determined by us in an X-ray analysis of a related compound[14].

The described spectrum of products from 2-vinylindole chemistry demonstrates for the first time the significant dependence of the product distribution from the three mentioned competing reaction pathways on the structures of the reactants. The preparative results thus obtained are being used in our laboratory for, among others, the planning of syntheses of pharmacologically interesting lead structures and for the syntheses of alkaloids of the indole and carbazole series.

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