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N-BENZOYLINDOLE-2,3-QUINODIMETHANE: DIELS-ALDER REACTIVITY AND SYNTHETIC APPLICATIONS FOR [b]ANNELLATED INDOLES

Manfred Haber and **Ulf Pindur***

Department of Chemistry and Pharmacy, University of Mainz, Saarstrasse 21, D-6500 Mainz 1, Federal Republic of Germany

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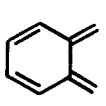
Abstract: The Diels-Alder reactivity of *in situ* generated N-benzoylindole-2,3-quinodimethane has been expanded considerably to include reactions with carbon- and hetero-dienophiles which furnish a variety of [b]annellated indoles as well as functionalized and annellated carbazoles. The frontier molecular orbital theory was found to be a useful model for the prediction of the experimental results under consideration of reactivity aspects.

INTRODUCTION

The utilization of *ortho*-quinodimethane intermediates (e.g. **1**) for the annellation of aromatic systems has now acquired practical importance and has been exploited in efficient syntheses of alkaloids, steroids, and terpenes.[1] An extension of the Diels-Alder methodology to heteroaromatic systems would be highly desirable[2] since, for example, many polycyclic heteroarenes containing the indole nucleus exhibit important pharmacological properties and thus constitute synthetically interesting target molecules.[3] Accordingly, the development of the *ortho*-quinodimethane concepts for the syntheses of polycyclic indoles is anticipated to provide a new access to this class of compounds. In addition to the above-mentioned high synthetic utility of both stable and *in situ* generated indole-2,3-quinodimethanes of the types **2** and **3**, a recent review article has emphasized the generally interesting Diels-Alder applications of these compounds including also the intramolecular processes.[4]



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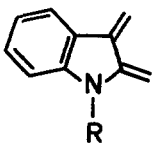

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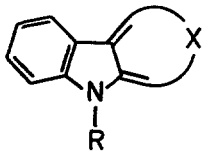

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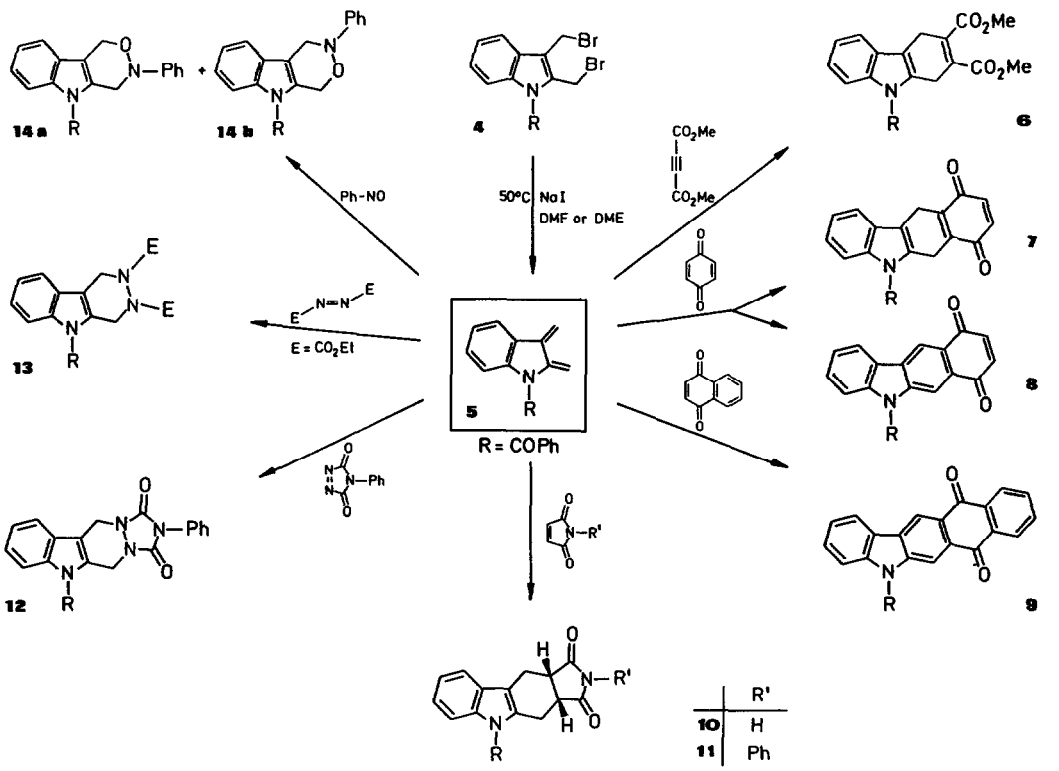
In continuation of our synthetic investigations in the field of pericyclic reactions with indole derivatives,[4,5] we report the full experimental details of some new results and further preparative developments of the transient N-benzoylindole-2,3-quinodimethane (5, R = PhCO) and its subsequent [4 + 2]cycloaddition reactions with a variety of CC- and hetero-dienophiles. Although this strategy was first described in Ref.[6a] and recently continued in another preliminary communication without experimental details,[6b] we have realized further novel synthetic developments, thus considerably extending the scope of its chemistry and, in addition, have observed some changes and variations in the product spectra obtained which are in contrast to the results of Ref.[6a].

PREPARATIVE RESULTS AND DISCUSSION OF DIELS-ALDER REACTIVITY

The crucial N-benzoylindole-2,3-quinodimethane (5) was readily generated from the corresponding 2,3-bis(bromomethyl)indole 4, probably by way of the 2,3-bis(iodomethyl) analog, according to the reported procedure.[6a] The lifetime of 5 is too short for it to be detectable by ^{1}H-NMR spectroscopy. However, the participation of 5 was unequivocally established by its subsequent trapping reactions with a variety of dienophiles (Scheme 1 and Table 1). Thus,

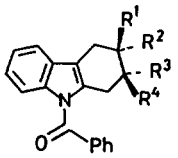


Scheme 1

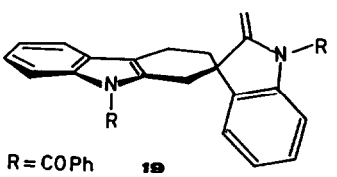
reaction of **5** with dimethyl acetylenedicarboxylate gave rise to the stable 1,4-dihydrocarbazole **6** as the main product. This result is in contrast to Ref.[6a] where the fully aromatized product was reported; we have only detected the latter product in trace amounts (< 2%) in the crude reaction mixture. The indole-2,3-quinodimethane **5** was also captured by [4 + 2]cycloaddition reactions with 1,4- benzoquinone and 1,4-naphthoquinone to furnish the annellated carbazoles **7**,[6a] **8**, and **9**, compounds of interest as potential DNA intercalators.[7] Maleimide and its N-phenyl analog (NPMI) reacted with **5** to give the [b]pyrrolo-annellated carbazoles **10** and **11**.[6a] Similarly, Diels-Alder reactions of **5** with the hetero-dienophiles 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), diethyl azodicarboxylate (DEAD), and nitrosobenzene yielded the cycloadducts **12**, **13**, and **14a/14b**, respectively.

Like nitrosobenzene, 1,1-bis(phenylsulfonyl)ethene also reacted with **5** to produce a regioisomeric mixture of the cycloadducts **15a/15b**. It was not possible to separate the mixtures of the constitutional isomers of **14** and **15** even by MPLC since decomposition occurred. However, in some cases with some less reactive CC-dienophiles, Diels-Alder reactions with **5** did occur in the presence of highly activated molecular sieves (4 Å). Thus, diethyl fumarate was able to trap *in situ* generated **5** to furnish exclusively, and hence stereospecifically, the *trans*-product **16**.

In the same way, reaction with phenyl vinyl sulfone gave rise to the functionalized tetrahydrocarbazoles **17a/17b** (2:1 mixture of unseparable constitutional isomers) while reaction with methyl vinyl ketone yielded the acetylcarbazoles **18a/18b** (4:1 mixture of unseparable isomers).



	R^1	R^2	R^3	R^4
15a	SO_2Ph	SO_2Ph	H	H
15b	H	H	SO_2Ph	SO_2Ph
16	CO_2Et	H	CO_2Et	H
17a	SO_2Ph	H	H	H
17b	H	H	SO_2Ph	H
18a	Ac	H	H	H
18b	H	H	Ac	H



R = COPh **19**

On the other hand, the trapping reactions of **5** with the, in these types of reaction, generally less reactive CC-dienophiles such as acrolein, propynoates, or diethyl maleate were not successful in spite of variations of the reactions conditions (temperature, solvent, catalyst). In these reactions with less reactive alkenes and alkynes, dimerization of the *in situ* generated **5** took place more rapidly than the cycloaddition process and the dimeric [4 + 2] product **19** having a regioselective orientation of two molecules of **5** was

formed exclusively as a consequence of the preferred reaction of the diene structure of **5** with the 3-methylene moiety of another molecule serving as a 2π-system. (Table 1). The spiro constitution is in full accord with an analogous dimeric product cited in Ref.[6b].

Table 1: Diels-Alder Reactions of **5** with dienophiles.

Product	Yield [%]	mp (solvent) [°C]	Product	Yield [%]	mp (solvent) [°C]
6	57	188 (EtOAc)	**12**	55	230 (EtOAc)
7	55	230 (EtOAc)	**13**	56	100 (EtOAc)
		(Ref.[6]: 212-214)	**14a,14b**[a]	77	128 (EtOAc)
8	22	248 (EtOAc)	**15a,15b**[b]	67	106 (EtOAc)
9	32	290 (EtOAc/40-60 °C petroleum ether)	**16**	63	108 (EtOAc)
			17a,17b[c]	4	188 (EtOAc)
10	98	196 (THF)	**18a,18b**[d]	59	105 (EtOAc)
11	95	168 (EtOH)	**19**	30-60	183 (EtOAc)

[a] 4:1 mixture. [c] 2:1 mixture.
[b] 1:1 mixture. [d] 4:1 mixture.

According to π-SCF-MO calculations[10] for the analysis of π-MO eigen values and eigen vectors, we generally predict a HOMO(diene)-LUMO(dienophile) interaction in the transition state of the $[_4\pi_s + _2\pi_s]$ electronic process in the Diels-Alder reactions of **5** with the tested dienophiles (Fig. 1, HOMO of **5**; E(LUMO) = -2.10 eV).[10] The HOMO/LUMO energy gap is less than 7 eV in the reactions with the sufficiently reactive dienophiles such as, for example, N-phenylmaleimide, 1,4-benzoquinone, PTAD, DEAD, and 1,1-bis(phenylsulfonyl)-ethene investigated so far [for example, E(LUMO) in eV: NPMI = -3.35, 1,4-benzoquinone = -4.05, PTAD = -4.45][10] and the Diels-Alder reactions occurred without any problems in the absence of a catalyst. The significantly lower reactivity of, in particular, the above-mentioned mono-acceptor substituted alkenes and alkynes in the absence of a catalyst can be explained by the higher lying LUMO energy level [e.g. E(LUMO) of methyl acrylate = 1.69 eV].[10] However, in the presence of molecular sieves, the reactivity of the dienophile is increased and this is reflected, for example, in the formation of the carbazoles **16-18**. In the Diels-Alder reactions with the tested unsymmetrical dienophiles, only a low degree of regioselectivity was observed. This phenomenon can be attributed to the small differences in the HOMO coefficients (Δc = 0.07) of the terminal carbon atoms in the 2-aminobutadiene unit of **5** (Fig. 1).

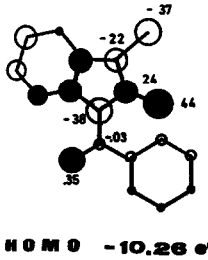


Fig. 1: HOMO of **5** according to π-SCF-MO calculations.[10]

The constitutions and/or relative configurations of the products were elucidated by high resolution ^{1}H-NMR and, in some cases, additionally by ^{13}C-NMR spectroscopy. For example, the trans-stereochemistry in compound **16** was clarified unambiguously by decoupling experiments of the aliphatic ring protons, by a qualitatively good agreement with a simulated (LAOCOON III)[12] ^{1}H-NMR spectrum, and by the absence of an NOE of the trans-ethyl ester group (Fig. 2). The proposed constitution of the dimeric spiro compound **19** was deduced from the characteristic spin pattern of the spiro protons in the ^{1}H-NMR spectrum, the ^{13}C-NMR chemical shifts of the carbon atoms, and ^{1}H,^{1}H-NOE measurements (see experimental section and Fig. 2).

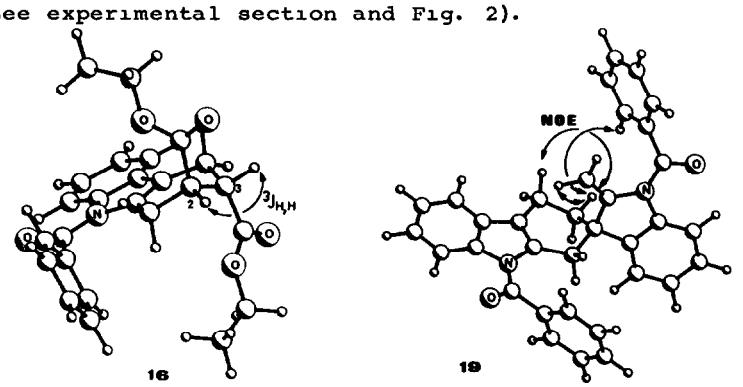


Fig. 2: Energy minimized (local) conformations of **16** and **19** according to MMX force field calculations.[11] The diagnostically relevant ^{3}J coupling constant for C-2H,C-3H of **16** (dihedral angle 58°) is about 3 Hz (calculated value for the compound is 2.86 Hz according to the Altona equation[13]). For compound **19** the diagnostically important NOE's are shown.

In summary, we have considerably expanded the reactivity pattern in indole-2,3-quinodimethane cycloaddition chemistry for the synthesis of new [b]-annellated carbazoles which are not so easily accessible by other more conventional routes. The first application of the FMO theory in this class of compounds appears to be very useful for predicting the experimental results.

EXPERIMENTAL SECTION

Melting points were determined on a Buchi SMP-20 apparatus and are uncorrected. Mass spectra were recorded on a Varian MAT CH 7 spectrometer at an ionization

voltage of 70 eV. ^{1}H- and ^{13}C-NMR spectra (400 and 100.6 MHz) were obtained on a Bruker WM 400 spectrometer (δ, ppm scale, TMS as internal standard). Additionally, for the analysis of the ^{13}C-NMR spectra of the products, a ^{13}C-NMR simulator program from the VISPER series[14] was employed. C,H,N-Analyses were performed with a Carlo-Erba Strumentazione 1164 apparatus. For flash chromatography, Merck silica gel 60 (grain size: 0.040-0.063 mm) was used; for column chromatography, Merck silica gel 60 (grain size 0.063-0.200 mm) was used. All reactions were performed in highly pure, anhydrous solvents under an inert gas atmosphere. In those reactions in which racemic products are formed the nomenclature and structures of only one of the enantiomers are given.

General Procedure for Compounds **6, 13, 14a, 14b, 15a, and 15b.**

The dienophile (2 mmol) was dissolved in 30 ml dimethoxyethane (DME) and heated to 50-55 °C. A solution of **4** (820 mg, 2 mmol) in 10 ml DME together with 10 mg powdered sodium iodide were added and the mixture was stirred at the same temperature for 1.5-2 h. Unreacted NaI was filtered off, the filtrate was concentrated under vacuum, and the residue was purified by column chromatography (40-60 °C petroleum ether/ethyl acetate).

General Procedure for Compounds **7-12.**

Compound **4** (100 mg, 0.25 mmol) and the respective dienophile (0.25 mmol) were dissolved in 50 ml DMF and then heated to 50-55 °C. Powdered sodium iodide (10 mg) was added to the mixture which was then stirred at 50 °C for 1.5-3 h. The solvent was subsequently evaporated under vacuum and the crude product was treated with aqueous sodium thiosulfate solution. The residue was dried, purified by flash chromatography (40-60 °C petroleum ether/ethyl acetate), and recrystallized from an appropriate solvent (Table 1).

General Procedure for Compounds **16, 17, and 18.**

Compounds **16-18** were prepared as described above from 10 mmol dienophile in 30 ml DME and 2 mmol **4** in 10 ml DME but with addition of 7 g highly activated molecular sieves (4 Å) and refluxing of the mixture for 1.5-3 h. The products were worked up by flash chromatography (40-60 °C petroleum ether/ethyl acetate).

1-Benzoyl-2,3-bis(bromomethyl)indole (**4**).

Preparation according to Ref.[6a]; yield: 1.22-1.42 g (60-70%); mp: 148-152 °C (Ref.[6a]) (CCl_4/40-60 °C petroleum ether). Anal. calcd. for $C_{17}H_{13}Br_2NO$ (406.92): C 50.16, H 3.22, N 3.44; found: C 49.93, H 3.31, N 3.21. MS (m/e): 407 ($M^{+\cdot}$, 9%), 105 (100%). ^{1}H-NMR ($CDCl_3$): 4.75 (s, 2H, C3-CH_2), 5.01 (s, 2H, C2-CH_2), 6.63 (d, ^{3}J = 8.45 Hz, 1H, C7-H), 7.08 (dd, ^{3}J = 7.40 Hz, 8.26 Hz, 1H, C5-H), 7.23 (dd, ^{3}J = 7.54

Hz, 7.41 Hz, 1H, C6-H), 7.50 (dd, ^3J = 7.73 Hz, 7.75 Hz, 2H, aromatic), 7.67 (m_c, 2H, aromatic), 7.78 (d, ^3J = 7.24 Hz, 2H, aromatic).

Dimethyl 9-Benzoyl-1,4-dihydro-9H-carbazole-2,3-dicarboxylate (6).

Prepared from 200 mg (0.5 mmol) **4** and dimethyl acetylenedicarboxylate (71 mg, 0.5 mmol). Anal. calcd. for $C_{23}H_{19}NO_5$ (389.41): C 70.94, H 4.92, N 3.60; found: C 70.40, H 4.77, N 3.55. MS (m/e): 389 ($M^{+\cdot}$, 14%), 105 (100%). ^{1}H-NMR (DMSO-d_6): 3.70 (s, 3H, C2-CO_2CH_3 or C3-CO_2CH_3), 3.74 (2, 4H, C1-H_2 and C4-H_2), 3.77 (s, 3H, C3-CO_2CH_3 or C2-CO_2CH_3), 6.83 (d, ^3J = 8.22 Hz, 1H, C8-H), 7.11 (dd, ^3J = 7.89 Hz, 7.90 Hz, 1H, C6-H or C7-H), 7.20 (dd, ^3J = 7.39 Hz, 7.50 Hz, 1H, C7-H or C6-H), 7.60 (m_c, 3H, aromatic), 7.70 (m_c, 3H, aromatic).

6-Benzoyl-5,11-dihydro-6H-benzo[b]carbazol-1,4-dione (7).

Prepared from 325 mg (0.8 mmol) **4** and 1,4-benzoquinone (86 mg, 0.8 mmol). Anal. calcd. for $C_{23}H_{15}NO_3$ (353.09): C 78.16, H 4.25, N 3.97; found: C 77.81, H 4.31, N 4.03. MS (m/e): 353 ($M^{+\cdot}$, 32%), 105 (100%). ^{1}H-NMR (DMSO-d_6): 3.72 (br. s, 2H, C5-H_2 or C11-H_2), 3.82 (br. s, 2H, C11-H_2 or C5-H_2), 6.53 (d, ^3J = 10.76 Hz, 1H, C2-H or C3-H), 6.56 (d, ^3J = 10.69 Hz, 1H, C3-H or C2-H), 6.91 (m_c, 2H, aromatic), 7.17 (dd, ^3J = 7.49 Hz, 7.71 Hz, 1H, C8-H or C9-H), 7.52 (m_c, 3H, aromatic), 7.71 (m_c, 3H, aromatic).

6-Benzoyl-6H-benzo[b]carbazole-1,4-dione (8).

Prepared from 325 mg (0.8 mmol) **4** and 1,4-benzoquinone (86 mg, 0.8 mmol). Anal. calcd. for $C_{23}H_{13}NO_3$ (351.09): C 78.61, H 3.73, N 3.99; found: C 78.45, H 3.81, N 4.03. MS (m/e): 351 ($M^{+\cdot}$, 10%), 105 (100%). ^{1}H-NMR (DMSO-d_6): 7.06 (d, ^3J = 10.27 Hz, 1H, C2-H or C3-H), 7.10 (d, ^3J = 10.23 Hz, 1H, C3-H or C2-H), 7.34 (d, ^3J = 8.64 Hz, 1H, C7-H), 7.48 (m_c, 2H, aromatic), 7.63 (dd, ^3J = 7.66 Hz, 7.81 Hz, 2H, aromatic), 7.78 (m_c, 3H, aromatic), 7.99 (s, 1H, C5-H), 8.50 (d, ^3J = 6.97 Hz, 1H, aromatic), 8.84 (s, 1H, C11-H). ^{13}C-NMR (DMSO-d_6): 112.9, 115.3, 119.0, 121.9, 124.2, 124.3, 127.3, 128.9, 129.1, 129.3, 129.9, 133.1, 134.5, 139.0, 140.2, 140.95, 168.9 (benzoyl-CO), 184.2 (C1 or C4), 184.3 (C4 or C1).

7-Benzoyl-7H-naphtho[2,3-b]carbazole-5,13-dione (9).

Prepared from 400 mg (1 mmol) **4** and 1,4-naphthoquinone (158 mg, 1 mmol). Anal. calcd. for $C_{27}H_{15}NO_3$ (401.1): C 80.80, H 3.74, N 3.49; found: C 80.61, H 3.83, N 3.34. MS (m/e): 401 ($M^{+\cdot}$, 17%), 105 (100%). ^{1}H-NMR (DMSO-d_6): 7.44 (d, ^3J = 8.10 Hz, 1H, C8-H), 7.52 (m_c, 2H, aromatic), 7.65 (dd, ^3J = 7.91 Hz, 7.72 Hz, 2H, aromatic), 7.81 (dd, ^3J = 8.12 Hz, 8.89 Hz, 3 H, aromatic), 7.93 (m_c, 2H, aromatic), 8.20 (dd, ^3J = 8.17 Hz, 8.17 Hz, 1H, aromatic), 8.22 (s, 1H, C6-H), 8.27 (d, ^3J = 8.50 Hz, 1H, aromatic), 8.58 (d, ^3J = 8.02 Hz, 1H, aromatic), 9.10 (s, 1H, C12-H).

5-Benzoyl-3aβ,4,10,10aβ-tetrahydro-2H,5H-pyrrolo[3,4-b]carbazole-1,3-dione (10).

Prepared from 100 mg (0.25 mmol) **4** and maleimide (25 mg, 0.25 mmol). Anal. calcd. for $C_{21}H_{16}N_2O_3$ (344.37): C 73.24, H 4.68, N 8.13; found: C 72.82, H 4.70, N 7.91. MS (m/e): 344 ($M^{+\cdot}$, 15%), 105 (100%). ^{1}H-NMR (DMSO-d_6): 2.76 (m_c, 2H, aliphatic), 2.86 (dd, J = 16.03 Hz, 7.42 Hz, 8.57 Hz, 1H, aliphatic), 3.15 (dd, J = 15.53 Hz, 2.02 Hz, 2.24 Hz, 1H, aliphatic), 3.45 (m_c, 2H, aliphatic), 7.15 (dd, ^{3}J = 7.25 Hz, 7.73 Hz, 1H, aromatic), 7.21 (dd, ^{3}J = 7.36 Hz, 7.14 Hz, 1H, aromatic), 7.37 (d, ^{3}J = 8.09 Hz, 1H, aromatic H), 7.58 (m_c, 3H, aromatic H), 7.64 (d, ^{3}J = 7.12 Hz, 2H, aromatic), 7.72 (dd, ^{3}J = 7.25 Hz, 7.22 Hz, 1H, aromatic), 11.12 (s, 1H, NH).

5-Benzoyl-2-phenyl-3aβ,4,10,10aβ-tetrahydro-2H,5H-pyrrolo[3,4-b]carbazole-1,3-dione (11).

Prepared from 410 mg (1 mmol) **4** and N-phenylmaleimide (174 mg, 1 mmol). Anal. calcd. for $C_{27}H_{20}N_2O_3$ (420.47): C 77.13, H 4.79, N 6.66; found: C 76.91, H 4.75, N 6.51. MS (m/e): 420 ($M^{+\cdot}$, 28%), 105 (100%). ^{1}H-NMR ($CDCl_3$): 3.08 (m_c, 2H, CH_2), 3.34 (dd, J = 2.61 Hz, 2.71 Hz, 17.14 Hz, 1H, CH), 3.41 (dd, J = 3.10 Hz, 2.73 Hz, 16.51 Hz, 1H, CH), 3.46 (ddd, J = 2.73 Hz, 2.76 Hz, 3.06 Hz, 8.05 Hz, 9.22 Hz, 1H, CH), 3.53 (ddd, J = 3.13 Hz, 3.49 Hz, 3.31 Hz, 8.55 Hz, 8.64 Hz, 1H, CH), 7.10 (d, ^{3}J = 7.36 Hz, 1H, C6-H), 7.12 (m_c, 2H, aromatic), 7.21 (dd, ^{3}J = 7.48 Hz, 7.52 Hz, 1H, aromatic), 7.27 (d, ^{3}J = 8.28 Hz, 1H, aromatic), 7.31 (dd, ^{3}J = 7.17 Hz, 7.48 Hz, 1H, aromatic), 7.38 (dd, ^{3}J = 7.01 Hz, 7.81 Hz, 2H, aromatic), 7.49 (m_c, 3H, aromatic), 7.63 (dd, ^{3}J = 7.50 Hz, 1H, aromatic), 7.67 (d, ^{3}J = 7.10 Hz, 2H, aromatic). ^{13}C-NMR ($CDCl_3$): 20.8 (C4), 23.72 (C10), 39.2 (C3a or C10a), 40.12 (C10a or C3a), 114.83 (CH), 115.41 ($C_{quart.}$), 117.9 (CH), 123.1 (CH), 124.0 (CH), 126.2 (2 CH), 128.4 ($C_{quart.}$), 128.5 (CH), 128.9 (2 CH), 129.1 (2 CH), 129.5 (2 CH), 131.8 ($C_{quart.}$), 132.9 (CH), 133.4 ($C_{quart.}$), 135.4 ($C_{quart.}$), 136.8 ($C_{quart.}$), 168.8 (benzoyl-CO), 177.8 (C1 or C3), 178.4 (C3 or C1).

6-Benzoyl-2-phenyl-5,11-dihydro-2H,6H-[1,2,4]triazolo[1,2-a]pyridazo[4,5-b]indol-1,3-dione (12).

Prepared from 100 mg (0.25 mmol) **4** and PTAD (132 mg, 0.75 mmol). Anal. calcd. for $C_{25}H_{18}N_4O_3$ (422.44): C 71.08, H 4.29, N 13.26; found: C 70.37, H 4.27, N 13.11. MS (m/e): 422 ($M^{+\cdot}$, 23%), 105 (100%). ^{1}H-NMR (DMSO-d_6): 4.87 (s, 2H, C5-H_2 or C11-H_2), 4.90 (s, 2H, C11-H_2 or C5-H_2), 6.79 (d, ^{3}J = 8.40 Hz, 1H, C7-H), 7.15 (dd, ^{3}J = 7.37 Hz, 8.23 Hz, 1H, C8-H or C9-H), 7.25 (dd, ^{3}J = 7.49 Hz, 7.51 Hz, 1H, C9-H or C8-H), 7.44 (m_c, 1H, aromatic), 7.53 (m_c, 4H, aromatic), 7.61 (dd, ^{3}J = 8.19 Hz, 7.19 Hz, 2H, aromatic), 7.70 (d, ^{3}J = 7.78 Hz, 1H, aromatic), 7.73 (d, ^{3}J = 7.39 Hz, 2H, aromatic), 7.74 (dd, ^{3}J = 7.39 Hz, 7.19 Hz, 1H, aromatic).

Diethyl 5-Benzoyl-1,2,3,4-tetrahydro-5H-pyridazino[4,5-b]indol-2,3-dicarboxylate (13).

Prepared from 820 mg (2 mmol) **4** and diethyl azodicarboxylate (348 mg, 2 mmol). Anal. calcd. for $C_{23}H_{23}N_3O_5$ (421.45): C 65.55, H 5.50, N 9.97; found: C 65.20, H 5.56, N 9.77. MS (m/e): 421 ($M^{+\bullet}$, 3%), 105 (100%). ^{1}H-NMR (DMSO-d_6): 1.17 (t, ^3J = 7.05 Hz, 6H, 2 $CH_2\underline{CH_3}$), 4.12 (m_c, 4H, 2 $\underline{CH_2}CH_3$), 4.32 (d, ^2J = 16.83 Hz, 1H, C1-H), 4.41 (d, ^2J = 16.66 Hz, 1H, C1-H), 4.96 (m_c, 1H, C4-H), 5.11 (m_c, 1H, C4-H), 6.90 (d, ^3J = 8.35 Hz, 1H, C6-H), 7.13 (dd, ^3J = 7.74 Hz, 7.85 Hz, 1H, C7-H or C8-H), 7.22 (dd, ^3J = 7.33 Hz, 7.36 Hz, 1H, C8-H or C7-H), 7.60 (m_c, 3H, aromatic), 7.72 (m_c, 3H, aromatic).

5-Benzoyl-2-phenyl-1,4-dihydro-2H,5H-1,2-oxazino[4,5-b]indole (14a) and 5-Benzoyl-3-phenyl-1,4-dihydro-3H,5H-1,2-oxazino[5,4-b]indole (14b).

Prepared from 820 mg (2 mmol) **4** and nitrosobenzene (214 mg, 2 mmol). A 4:1 mixture of isomers was obtained which could not be separated by chromatographic methods without decomposition of the products. Hence, analytical data for the mixture are given below. Anal. calcd. for $C_{23}H_{18}N_2O_2$ (354.41): C 77.95, H 5.12, N 7.90; found: C 77.77, H 5.04, N 8.15. MS (m/e): 354 ($M^{+\bullet}$, 6%), 247 (20%), 105 (100%). ^{1}H-NMR (DMSO-d_6): 4.37 (br. s, 2H, C1-H_2 or C4-H_2, minor isomer), 4.60 (br. s, 2H, C1-H_2 or C4-H_2, major isomer), 4.78 (br. s, 2H, C4-H_2 or C1-H_2, major isomer), 5.21 (br. s, 2H, C4-H_2 or C1-H_2, minor isomer), 7.02 (m_c, 2H, aromatic, both isomers), 7.12 (m_c, 4H, aromatic, both isomers), 7.33 (m_c, 10H, aromatic, both isomers), 7.53 (d, ^3J = 7.60 Hz, 1H, aromatic, minor isomer), 7.59 (m_c, 5H, aromatic, both isomers), 7.73 (m_c, 6H, aromatic, both isomers). ^{13}C-NMR (DMSO-d_6): 49.3 (C1 or C4, major isomer), 52.0 (C1 or C4, minor isomer), 65.9 (C4 or C1, minor isomer), 67.8 (C4 or C1, major isomer), 114.6 (CH, major isomer), 114.7 (CH, minor isomer), 114.8 ($C_{quart.}$, major isomer), 115.9 (CH, both isomers), 115.9 (CH, both isomers), 116.4 ($C_{quart.}$, minor isomer), 118.5 (CH, both isomers), 118.6 (CH, both isomers), 122.3 (CH, both isomers), 122.4 (CH, both isomers), 123.1 (CH, both isomers), 123.2 (CH, both isomers), 123.8 (CH, both isomers), 126.2 ($C_{quart.}$, minor isomer), 127.4 ($C_{quart.}$, major isomer), 128.5 (CH, both isomers), 128.7 (CH, both isomers), 128.8 (CH, both isomers), 131.9 ($C_{quart.}$, minor isomer), 132.5 (CH, both isomers), 133.6 ($C_{quart.}$, major isomer), 134.7 ($C_{quart.}$, major isomer), 134.8 ($C_{quart.}$, minor isomer), 135.7 ($C_{quart.}$, major isomer), 135.9 ($C_{quart.}$, minor isomer), 149.9 ($C_{quart.}$, both isomers), 167.9 (benzoyl-CO, major isomer), 168.1 (benzoyl-CO, minor isomer).

9-Benzoyl-3,3-bis(phenylsulfonyl)-1,2,3,4-tetrahydro-9H-carbazole (15a) and 9-Benzoyl-2,2-bis(phenylsulfonyl)-1,2,3,4-tetrahydro-9H-carbazole (15b).

Prepared from 1.23 g (3 mmol) **4** and 1,1-bis(phenylsulfonyl)ethene (0.62 g, 2 mmol). A 1:1 mixture of isomers was obtained which could not be separated by chroma-

tographic methods. Hence analytical data for the mixture are given below: Anal. calcd. for $C_{31}H_{25}NO_5S_2$ (555.68): C 67.01, H 4.53, N 2.52, S 11.54; found: C 66.92, H 4.65, N 2.51, S 11.34. MS (m/e): 555 ($M^{+\cdot}$, 0.5%), 413 (14%), 105 (100%). ^{1}H-NMR (DMSO-d_6): 2.52 (dd, J = 7.24 Hz, 6.15 Hz, 2H, C1-H_2 or C2-H_2), 2.64 (dd, J = 6.52 Hz, 6.37 Hz, 2H, C1-H_2 or C2-H_2), 2.78 (dd, J = 6.16 Hz, 6.08 Hz, 2H, C2-H_2 or C1-H_2), 2.95 (dd, J = 6.23 Hz, 6.13 Hz, 2H, C2-H_2 or C1-H_2), 3.36 (br. s, 2H, C4-CH_2), 3.60 (br. s, 2H, C4-CH_2), 6.98 (d, ^{3}J = 8.26 Hz, 1H, C8-H), 7.11 (m_c, 3H, aromatic), 7.18 (m_c, 2H, aromatic), 7.40 (d, ^{3}J = 7.38 Hz, 1H, aromatic), 7.59 (m_c, 16H, aromatic), 7.74 (m_c, 11H, aromatic), 7.97 (dd, ^{3}J = 8.41 Hz, 8.40 Hz, 4H, aromatic). ^{13}C-NMR (DMSO-d_6): 17.5 (CH_2), 21.8 (CH_2), 23.2 (CH_2), 23.2 (CH_2), 24.9 (CH_2), 27.2 (CH_2), 86.5 (C3 or C2 of one isomer), 87.60 (C3 or C2 of one isomer), 111.9 ($C_{quart.}$), 113.9 (CH), 114.2 (CH), 116.7 ($C_{quart.}$), 118.2 (CH), 118.3 (CH), 122.6 (CH), 122.9 (CH), 123.6 (CH), 124.0 (CH), 127.9 ($C_{quart.}$), 128.0 ($C_{quart.}$), 128.8 (6 CH), 128.9 (6 CH), 129.0 (6 CH), 130.2 (4 CH), 130.5 (4 CH), 132.6 (CH), 132.8 (CH), 133.7 ($C_{quart.}$), 134.8 (4 CH), 134.9 ($C_{quart.}$), 135.0 ($C_{quart.}$), 135.8 ($C_{quart.}$), 136.1 (2 $C_{quart.}$), 136.4 (2 $C_{quart.}$), 168.1 (benzoyl-CO), 168.3 (benzoyl- CO).

Diethyl 9-Benzoyl-1,2,3,4-tetrahydro-9H-carbazole-2α,3β-dicarboxylate (16).

Prepared from 814 mg (2 mmol) **4** and 344 mg (2 mmol) diethyl fumarate. Anal. calcd. for $C_{25}H_{25}NO_5$ (419.48): C 71.58, H 6.01, N 3.34; found: C 71.49, H 5.99, N 3.26. MS (m/e): 419 ($M^{+\cdot}$, 37%), 105 (100%). ^{1}H-NMR (DMSO-d_6): 1.11 (t, ^{3}J = 7.08 Hz, 3H, CH_2CH_3), 1.20 (t, ^{3}J = 7.08 Hz, 3H, CH_2CH_3), 2.63 (m_c, 2H, CH), 2.90 (dd, J = 4.32 Hz, 4.91 Hz, 16.66 Hz, 1H, CH), 3.03 (m_c, 3H, CH), 4.05 (m_c, 2H, CH_2CH_3), 4.11 (q with further weak coupling, ^{3}J = 7.07 Hz, 2H, CH_2CH_3), 7.00 (d, ^{3}J = 8.24 Hz, 1H, C8-H), 7.09 (dd, ^{3}J = 7.44 Hz, 7.87 Hz, 1H, C6-H or C7-H), 7.18 (dd, ^{3}J = 7.37 Hz, 7.43 Hz, 1H, C7-H or C6-H), 7.50 (d, ^{3}J = 7.68 Hz, 1H, aromatic), 7.56 (dd, ^{3}J = 7.62 Hz, 7.62 Hz, 2H, aromatic), 7.68 (m_c, 3H, aromatic).

9-Benzoyl-3-phenylsulfonyl-1,2,3,4-tetrahydro-9H-carbazole (17a) and 9-Benzoyl-2-phenylsulfonyl-1,2,3,4-tetrahydro-9H-carbazole (17b).

Prepared from 820 mg (2 mmol) **4** and phenyl vinyl sulfone (1.25 g, 7.4 mmol). A 2:1 mixture of regioisomers was obtained which could not be separated without decomposition of the products. Anal. calcd. for $C_{25}H_{21}NO_3S$ (415.12): C 72.27, H 5.10, N 3.37; found: C 72.01, H 5.11, N 3.41. MS (m/e): 415 ($M^{+\cdot}$, 7%), 105 (100%). ^{1}H-NMR (DMSO-d_6): 1.70 (m_c, 2H, both isomers), 2.17 (m_c, J = 12.47 Hz, 1H, minor isomer), 2.35 (m_c, J = 12.6 Hz, 2.61 Hz, 1H, major isomer), 2.63 (m_c, 4H, both isomers), 2.79 (dd, J = 16.27 Hz, 10.70 Hz, 2H, minor isomer), 2.91 (dd, J = 16.56 Hz, 3.60 Hz, 1H, major isomer), 2.98 (dd, J = 16.49 Hz, 5.12 Hz, 5.73 Hz, 1H, major isomer), 3.67 (m_c, 1H major isomer), 3.83 (m_c, 1H, minor isomer), 7.13 (m_c, 6H, aromatic, both isomers), 7.47 (m_c, 2H, aromatic, both isomers), 7.58 (m_c, 8H, aromatic, both iso-

mers), 7.73 (m_c, 10H, aromatic, both isomers), 7.86 (d, ^3J = 7.83 Hz, 1H, aromatic, minor isomer), 7.95 (d, ^3J = 7.95 Hz, 1H, aromatic, major isomer).

3-Acetyl-9-benzoyl-1,2,3,4-tetrahydro-9H-carbazole (18a) and 2-Acetyl-9-benzoyl-1,2,3,4-tetrahydro-9H-carbazole (18b).

Prepared from 814 mg (2 mmol) **4** and methyl vinyl ketone (140 mg, 2 mmol). A 4:1 mixture of regioisomers was obtained which could not be separated without decomposition of the products. Anal. calcd. for $C_{21}H_{19}NO_2$ (317.14): C 79.46, H 6.04, N 4.42; found: C 78.99, H 6.02, N 4.38. MS (m/e): 317 ($M^{+\bullet}$, 54%), 105 (100%). ^{1}H-NMR (DMSO-d_6): 1.81 (m_c, 2H, CH, both isomers), 2.16 (s, 3H, CH_3, major isomer), 2.25 (s, 3H, CH_3, minor isomer), 2.27 (m_c, 2H, CH both isomers), 2.71 (m_c, 6H, CH, both isomers), 2.89 (m_c, 4H, CH, both isomers), 7.10 (m_c, 2H, aromatic, both isomers), 7.22 (m_c, 4H, aromatic, both isomers), 7.47 (d, ^3J = 8.23 Hz, 1H, aromatic, major isomer), 7.50 (d, ^3J = 8.10 Hz, 1H, aromatic, minor isomer), 7.57 (m_c, 4H, aromatic, both isomers), 7.70 (dd, ^3J = 7.05 Hz, 8.04 Hz, 6H, aromatic, both isomers).

9-Benzoyl-1,2,3,4-tetrahydro-9H-carbazole-2-spiro-3'-[1'-benzoyl-2'-methylene-indoline] (19).

Prepared from 200 or 400 mg (0.5 or 1.0 mmol) **4** in reactions with less reactive dienophiles or in the absence of a dienophile and worked up by flash chromatography (40–60 °C petroleum ether/ethyl acetate, 1:1). Anal. calcd. for $C_{34}H_{26}N_2O_2$ (494.20): C 82.56, H 5.26, N 5.67; found: C 82.14, H 5.30, N 5.58. MS (m/e): 494 ($M^{+\bullet}$, 12%), 105 (100%). ^{1}H-NMR (DMSO-d_6): 2.10 (dd, J = 6.10 Hz, 5.90 Hz, 2H, C3-H_2), 2.85 (dd, J = 5.58 Hz, 5.90 Hz, 2H, C4-H_2), 2.89 (d, ^2J = 17.71 Hz, 1H, C1-H), 3.05 (d, ^2J = 17.65 Hz, 1H, C1-H), 4.50 (d, ^2J = 2.03 Hz, 1H, C=CH_2), 4.53 (d, ^2J = 2.06 Hz, 1H, C=CH_2), 7.02 (dd, ^3J = 7.46 Hz, 7.46 Hz, 1H, aromatic), 7.07 (dd, ^3J = 8.24 Hz, 7.20 Hz, 1H, aromatic), 7.13 (m_c, 2H, aromatic), 7.15 (dd, ^3J = 7.53 Hz, 8.00 Hz, 1H, aromatic), 7.23 (dd, ^3J = 7.34 Hz, 7.47 Hz, 1H, aromatic), 7.40 (d, ^3J = 8.02 Hz, 1H, aromatic), 7.51 (m_c, 8H, aromatic), 7.63 (m_c, 3H, aromatic). ^{13}C-NMR (DMSO-d_6): 17.8 (C3), 33.0 (C1 or C4), 35.2 (C4 or C1), 46.7 (C2-spiro carbon), 95.8 (C=CH_2), 114.2 (C8 or C7'), 114.8 (C7' or C8), 116.6 (C4a), 118.4 (CH), 122.8 (CH), 122.8 (CH), 123.5(CH), 124.1 (CH), 127.7 (CH), 127.9 2 CH), 128.6 (CH), 128.7 (2 CH), 128.9 (2 CH), 131.2 (CH), 132.6 (CH), 133.9 ($C_{quart.}$), 135.1 ($C_{quart.}$), 135.7 ($C_{quart.}$), 136.1 (2 $C_{quart.}$), 136.93 ($C_{quart.}$), 141.0 ($C_{quart.}$), 153.9 (C2'), 168.4 (benzoyl-CO), 168.6 (benzoyl-CO).

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