added. The product was extracted with ethyl acetate (3 × 30 mL), and the combined extracts were washed with dilute HCl, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried (Na_2SO_4), evaporated, and chromatographed (silica, hexane–ethyl acetate (2:1)) to give 0.29 g (44%) of **11** and starting amide **2** (43% recovery): mp 116.5–117 °C; $[\alpha]^{23}_D$ −37.9° (*c* 0.99, dioxane); IR (KBr) 3300, 2940, 1620, 1515, 755 cm^{-1}; ^1H NMR δ 0.81 (s, 3 H), 0.92 (s, 3 H), 1.09 (s, 3 H), 0.81–2.17 (m, 8 H), 3.10 (br s, 1 H), 3.74–4.21 (m, 6 H), 6.50 (d, *J* = 6.0 Hz, 1 H), 7.20–7.47 (m, 5 H).

(1*S*,5*R*)-3-Oxa-5-(phenylthio)bicyclo[3.1.0]heptan-2-one (12). To a solution of (1*S*,2*R*)-**11** (0.29 g, 0.77 mmol) in 1,4-dioxane (8 mL) was added 10% HCl (8 mL). The mixture was warmed to reflux for 1 h under argon and allowed to cool. The solvent was evaporated, and the residue was diluted with brine and extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated. The crude residue was chromatographed (silica, hexane–ethyl acetate (5:1)) to give 0.12 g (72%) of **12** as a colorless oil: bp 153 °C (0.7 mmHg); $[\alpha]^{23}_D$ +89.2° (*c* 1.00, dioxane); IR (thin film) 1780, 1480, 1185, 1030, 760, 705 cm^{-1}; ^1H NMR δ 1.45 (m, 1 H), 1.75 (m, 1 H), 2.37 (m, 1 H), 4.32 (d, *J* = 3.0 Hz, 2 H), 7.17–7.44 (m, 5 H); MS, *m/e* 206 (M^+).

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Supplementary Material Available: Model and tables of final atomic positional parameters and isotropic thermal parameters, bond distances, and bond angles for the crystal structure of (1*R*,2*S*)-**3**, and physical and spectral data for compounds **6**, **7**, **8a**, **8c**, **9**, **10**, **4**, **13**, and **14** (13 pages). Ordering information is given on any current masthead page.

Five-Membered Aromatic Heterocycles as Dienophiles in Diels–Alder Reactions. Furan, Pyrrole, and Indole

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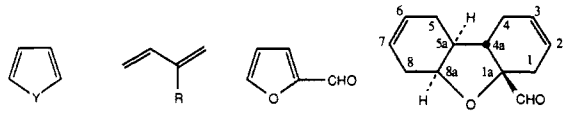
Abstract: Isoprene is shown to undergo high-yielding cycloaddition with β-acylfurans and N-benzenesulfonylated β-acylpyrroles and β-acylindoles and 1,3-butadiene with the latter. Except for the reactions catalyzed by aluminum trichloride they show poor regioselectivity. The Diels–Alder adducts of N-benzenesulfonylated β-nitropyrrole and β-nitroindole suffer from thermal nitrous acid extrusion and by *p*-quinone oxidation can be converted into indoles and carbazoles, respectively.

It has been known for some time, that aromatic heterocycles such as furan (**1a**), thiophene (**1b**), and pyrrole (**1c**) undergo Diels–Alder reactions despite their aromaticity and hence expected inertness. In view of their electron-rich constitution and elec-



1a, Y = O
b, Y = S
c, Y = NH

2a, R = Me
b, R = H

3

4

tron-donor properties they have been involved mostly as the diene component in the cycloaddition process. Thus, furans have been used efficiently in this capacity since the early days of the Diels–Alder reaction.[1] The much lower reactivity of the thiophenes has prevented their frequent use as Diels–Alder dienes.[2] Finally, whereas pyrroles initially were shunned as cycloaddition substrates in view of the formation of α-alkylpyrroles on their exposure to dienophiles,[3] they were shown later to be efficient Diels–Alder dienes when N-substituted by electron-withdrawing groups.[4]

There exists a limited number of examples of five-membered, aromatic heterocycles acting as dienophiles in Diels–Alder reactions, although in 8 of the 10 cases, a special driving force permits expression of such unusual heterocycle behavior—the cycloaddition requiring inverse electron demand (electron-poor diene reacting with an electron-rich dienophile)[5] or being constrained to an intramolecular, unidirectional process.[6] One of the two examples of an intermolecular Diels–Alder reaction (with normal electron demand) of an aromatic heterocycle of type **1** on record is the formation of 2:1 adduct **4** on thermal reaction of 1,3-butadiene (**2b**) with furfural (**3**).[7] Even this case is unusual, insofar as the reaction leads to something other than a 1:1 adduct and was carried out under specialized conditions intended to imitate the extractive distillation of unreacted butadiene with furfural solvent in industrial plants of synthetic rubber production. Nevertheless, this observation constitutes the first indication of the feasibility of normal Diels–Alder chemistry with five-membered, aromatic heterocycles, holding electron-withdrawing groups, as dienophiles. As the following discussion illustrates, this heterocycle reaction tendency could be translated into a new method of organochemical synthesis.

(1) (a) Diels, O.; Alder, K.; Naujoks, E. *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 554. (b) Diels, O.; Alder, K. *Justus Liebigs Ann. Chem.* **1931**, *490*, 243.
(2) (a) Rheinhoudt, D. N.; Kouwenhoven, C. G. *Tetrahedron* **1974**, *30*, 2093. (b) Rheinhoudt, D. N.; Trompenaars, W. P.; Geevers, J. *Tetrahedron Lett.* **1976**, 4777.
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(4) (a) Acheson, R. M.; Vernon, J. A. *J. Chem. Soc.* **1961**, 457. (b) Acheson, R. M.; Vernon, J. A. *Ibid.* **1963**, 1008.
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(6) Ghisalberti, E. L.; Jefferies, P. R.; Payne, T. G. *Tetrahedron* **1974**, *30*, 3099.
(7) (a) Hillyer, J. C.; Swadesh, S.; Leslie, M. L.; Dunlop, A. P. *Ind. Eng. Chem.* **1948**, *40*, 2216. (b) Hillyer, J. C.; Edmonds, J. T., Jr. *J. Org. Chem.* **1952**, *17*, 600. (c) Kraus, G. A.; Raggon, J. Abstracts of Papers, 193rd National Meeting of the American Chemical Society, Denver, CO; American Chemical Society: Washington, DC, 1987; Abstract ORGN 0030.

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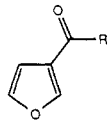
Furans as Dienophiles. Repetition of the industrial reaction, but under more standard Diels–Alder reaction conditions [heating of a 12:1 molar mixture of 1,3-butadiene (**2b**) and furfural (**3**) at 195 °C for 72 h], led to the reported product **4**.[7,8] The low reaction yield (10%) and the excessive diene involvement in the adduct formation suggested that the electron-withdrawing formyl group might have been positioned on the furan nucleus improperly for optimum effect on the cycloaddition process. For this reason, the diene addition was carried out next on β-acylfurans.

Heating a 12:1 mixture of isoprene (**2a**) and 3-furaldehyde (**5a**) at 195 °C for 72 h afforded a ca. 1:1 mixture (74%) of aldehydes **6a** and **6b**. Similar treatment of isoprene (**2a**) with methyl



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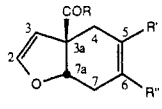
a, R = R' = H, R'' = Me
b, R = R'' = H, R' = Me
c, R = OMe, R' = H, R'' = Me
d, R = OMe, R' = Me, R'' = H



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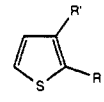
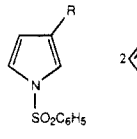


7a, R = CHO, R' = H
b, R = H, R' = CHO

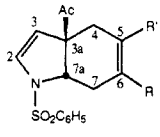
3-furoate (**5c**) gave a 2:1 mixture (64%) of esters **6d** and **6c**. The formation of 1:1 adducts in respectable yields showed the β-acylfurans to function as normal dienophiles.[9]

In analogy with their behavior as dienes, thiophenes proved to be poor dienophiles. 2-Thiophenecarboxaldehyde (**7a**) remained unchanged on being heated with 12 equiv of isoprene (**2a**) at 195 °C for 72 h, while 3-thiophenecarboxaldehyde (**7b**) underwent cycloaddition in less than 6% yield.[10]

Pyrroles as Dienophiles. On the assumption of stable pyrrole requiring more than one electron-withdrawing group to induce dienophile behavior, two such functions were placed on the pyrrole nucleus and 3-acetyl-1-(phenylsulfonyl)pyrrole (**8a**)[11] and 1-



8a, R = Ac
b, R = NO_2



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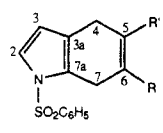
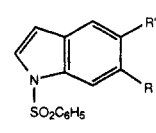


10

a, R = Me, R' = H; b, R = H, R' = Me



11

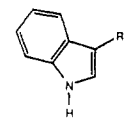
(phenylsulfonyl)-3-nitropyrrole (**8b**)[12] were chosen as Diels–Alder substrates. Reaction of pyrrole **8a** with isoprene (**2a**) under the aforementioned conditions produced a ca. 1:1 mixture (51%) of adducts **9a** and **9b**. The nitropyrrole **8b** proved to be more reactive, and its interaction (175 °C, 48 h) with isoprene (**2a**) led to a four-component, 6:2:3:1 mixture (49%) of dihydroindoles **10a** and **10b** and indoles **11a** and **11b**. Oxidation of the dihydroindoles (a 3:1 mixture of **10a** and **10b**) with *p*-quinone gave (91%) the indoles (a 3:1 mixture of **11a** and **11b**). Indole **11a** was identified by its preparation from 6-methylindole[13] and benzenesulfonyl chloride under base-induced phase-transfer conditions.[14] The ease of thermal extrusion of nitrous acid accompanying the Diels–Alder reaction of β-nitropyrroles and of the dehydrogenation of the resultant dihydroindoles makes this two-step reaction sequence a facile, new method of indole synthesis.[15]

Table I. Diels–Alder Reactions with 3-Substituted 1-(Phenylsulfonyl)indoles[a]

diene	dienophile	products	product ratio	product yield,[b] %
2a	**13a**	**14a, 15a**	3:1	95
2a	**13b**	**14b, 15b**	3:1	74[c]
2a	**13c**	**14c, 15c**	2:1	99
2a	**13d**	**14d, 15d**	2:1	99
2a	**13e**	**14e, 15e**	2:1	91
2b	**13a**	**17a**		92
2b	**13c**	**17b**		99
2b	**13d**	**17c**		99

[a] Reaction temperature 195 °C, reaction time 72 h. [b] Based on consumed starting indole. [c] Reduced yield because of ester hydrolysis on workup.

Indoles as Dienophiles. In order to test the efficacy of the new Diels–Alder reaction in the realm of indoles, the following compounds were used as substrates: *N,N*-diethyl-1-(phenylsulfonyl)-3-indoleglyoxylamide (**13a**), ethyl 1-(phenyl-



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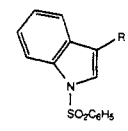

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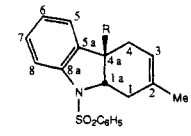

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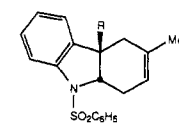
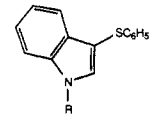
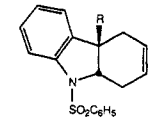


15

a, R = $COCONEt_2$; b, R = $COCO_2Et$; c, R = Ac; d, R = CHO;
e, R = CO_2Me; f, R = CN; g, R = $SO_2C_6H_5$; h, R = NO_2



16a, R = H
b, R = $SO_2C_6H_5$



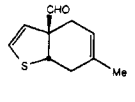
17a, R = $COCONEt_2$
b, R = Ac
c, R = CHO

sulfonyl)-3-indoleglyoxylate (**13b**), 3-acetyl-1-(phenylsulfonyl)-indole (**13c**),[17] 1-(phenylsulfonyl)-3-formylindole (**13d**),[18] methyl 1-(phenylsulfonyl)-3-indolecarboxylate (**13e**), 1-(phenylsulfonyl)-3-cyanoindole (**13f**),[17] 1,3-bis(phenylsulfonyl)indole (**13g**), and 1-(phenylsulfonyl)-3-nitroindole (**13h**). Indoles **13a**, **13d**, **13e**, and **13h** were prepared by N-benzenesulfonylation of their N-unsubstituted precursors **12a**,[19] **12d**, **12e**,[20] and **12h**,[21] respectively, under phase-transfer conditions. Treatment of keto

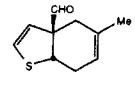
(8) Whereas the stereochemistry of tricycle **4** can be anticipated on grounds of the second cycloaddition following the path of least steric resistance, the configuration of aldehyde **4** rests on analogy with the structure of the adduct of isoprene (**2a**) and furfural (**3**). In the latter reaction, 2:1 adduct formation is followed by an intramolecular ene reaction (E. Wenkert and S. R. Piettre, unpublished observation), feasible only for a Diels–Alder product with a configuration of type **4**.

(9) It is noteworthy that the introduction of an α-methyl group on the β-ester (i.e., the use of ethyl 2-methyl-3-furoate) suppresses completely the Diels–Alder reaction with isoprene (**2a**) on the carbonyl side of the furan ring.

(10) The 1:1 adduct was a ca. 1:1 mixture of isomers i and ii: ^1H NMR, δ (one isomer) 1.70 (s, 3, Me), 1.9–2.7 (m, 4, methylenes), 4.10 (t, 1, J = 7



i



ii

Hz, H-7a), 5.30 (d, 1, J = 2 Hz, H-3), 5.50 (br s, 1, H-5 or H-6), 6.35 (d, 1, J = 2 Hz, H-2), 9.55 (s, 1, CHO); δ (other isomer) 1.70 (s, 3, Me), 1.9–2.7 (m, 4, methylenes), 4.20 (t, 1, J = 8 Hz, H-7a), 5.40 (d, 1, J = 2 Hz, H-3), 5.50 (br s, 1, H-6 or H-5), 6.40 (d, 1, J = 2 Hz, H-2), 9.55 (s, 1, CHO).

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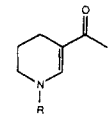
(15) In contrast to the behavior of ketone **8a**, compound iv, prepared by the sulfonylation of 3-acetyl-2-piperideine (iii)[16] (see Experimental Section), is inert to cycloaddition with isoprene (**2a**) under the same reaction conditions.



iii, R = H
iv, R = $SO_2C_6H_5$

(16) Freifelder, M. *J. Org. Chem.* **1964**, *29*, 2895.

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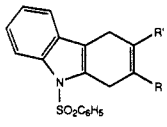
(21) Berti, G.; Da Settimo, A.; Nannipieri, E. *J. Chem. Soc. C* **1968**, 2145.

ester **12b**[22] with *n*-butyllithium and benzenesulfonyl chloride produced indole **13b**, while N-benzenesulfonylation of 3-(phenylthio)indole (**16a**)[23] under phase-transfer conditions, followed by *m*-chloroperbenzoic acid oxidation of the resultant disubstituted indole **16b**, led to sulfone **13g**.

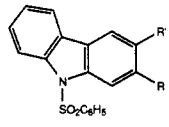
Exposure of indoles **13a–g** to isoprene (**2a**) under the conditions of the above pyrrole reactions yielded the results delineated in Table I. Indoles **13a–e** proved to be excellent dienophiles, their Diels–Alder reactions affording adducts **14a–e** and **15a–e**, whereas nitrile **13f**[24] and sulfone **13g** gave no cycloadducts. The Diels–Alder reactions of indoles **13a**, **c**, and **d** were studied also with 1,3-butadiene (**2b**), giving adducts **17a–c**, respectively (Table I). The product conversion in these cases was lower, presumably because of appreciable polymerization of the diene under the reaction conditions.

The nitroindole **13h** behaved in the Diels–Alder reaction like its pyrrole equivalent (**8b**), except for the reaction taking place under milder conditions (heating at 155 °C for 26 h). The cycloaddition with isoprene (**2a**) yielded (65%) a 16:3:5:1 mixture of dihydrocarbazoles **18a** and **18b** and carbazoles **19a** and **19b**.



18

a, R = Me, R' = H
b, R = H, R' = Me



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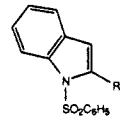


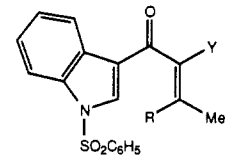
20a, R = CO_2Me
b, R = CN

Dehydrogenation of the dihydrocarbazoles (a 5:1 mixture of **18a** and **18b** with *p*-quinone gave (89%) the carbazoles (a 5:1 mixture of **19a** and **19b**).

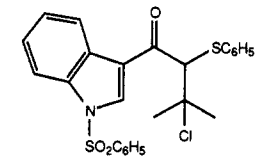
Two substances, possessing an electron-withdrawing group on the indole α-instead of β-carbon (ester **20a**[25] and nitrile **20b**[26]), were tested in the cycloaddition with isoprene (**2a**), but were found to be inert in this reaction.

Indoles with a Competing Dienophilic Center. As the above discussion indicates, N-sulfonylated 3-acylindoles had shown themselves to be efficient dienophiles toward isoprene (**2a**). It now became of interest to discover how they fared in competition with a neighboring Diels–Alder reaction site. Three acylindoles, **21a**,[27] **21b**,[14a] and **21c** [prepared from **21b** on treatment with benzenesulfenyl chloride and dehydrochlorination of the adduct (**22**) with sodium hydride], were chosen for this purpose. The cycloaddition of acylindole **21a** and isoprene (**2a**) under standard reaction conditions was complete in only 2 h and gave a 2:1 mixture (95%) of adducts **23a** and **23b**, indicative of the side chain being a better dienophile than the nucleus. The reaction of isoprene (**2a**) with acylindole **21b** yielded a complex mixture of products [89%; containing **23c**, **23d**, adduct pair **24a,b**, and 2:1 adduct **25b** (plus isomers) in ca. 2:1:4:1 ratio], showing that introduction of steric bulk into the side chain makes the nucleus competitively a better Diels–Alder reaction site. Finally, cycloaddition of acylindole **21c** with isoprene (**2a**) led to a 3:1 mixture (82%) of adducts **24c** and **24d**, illustrative of total suppression of side-chain reactivity by steric interference.[28]

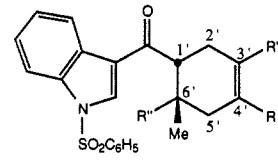
Indoles as Dienophiles in Acid-Catalyzed Reactions. It has been known for some time that Lewis acids, capable of complexing with dienophiles, enhance the rate and regioselectivity of the Diels–Alder reaction.[29] For this reason three of the above cycloadditions,

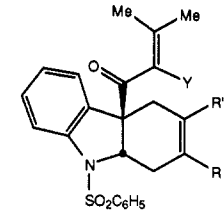


21a, R = Y = H
b, R = Me, Y = H
c, R = Me, Y = SC_6H_5



22

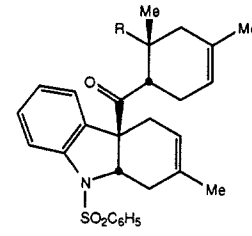




23

24

a, R = Me, R' = R'' = H, Y = H
b, R = R'' = H, R' = Me, Y = H
c, R = R'' = Me, R' = H, Y = SC_6H_5
d, R = H, R' = R'' = Me, Y = SC_6H_5



25a, R = H
b, R = Me

i.e., the reactions of indoles **13c**, **21a**, and **21b** with isoprene (**2a**), were repeated in the presence of aluminum trichloride. The reaction rates were dramatically different, as portrayed by the lowering of the uniform reaction temperature of 195 °C to 70 °C for the **13c–2a** reaction and to room temperature for the **21a–2a** and **21b–2a** reactions as well as by the decrease of the needed reaction time to 4, 6, and 24 h, respectively. The regioselectivity changed dramatically also, as illustrated by an increase of the uniform 2:1 regioisomer product ratio for the three reactions without catalysis. The **13c–2a** cycloaddition led to a 24:1 mixture (38%) of isomers **14c** and **15c**, the **21a–2a** reaction to a >9:1 mixture (79%) of isomers **23a** and **23b** and a >4:1 mixture (13%) of **25a** and its regioisomers, and the **21b–2a** reaction to a >9:1 mixture (15%) of **23c** and **23d**, a >9:1 mixture (13%) of **24a** and **24b**, and a >4:1 mixture (50%) of **25b** and its regioisomers.

Structure Analysis. ^1H and ^{13}C NMR spectroscopy aided in the determination of the configuration of the Diels–Alder adducts, two-dimensional ^1H–^1H COSY[30] and ^1H–^{13}C correlated[30] spectral analysis being especially helpful in this connection. The ^1H coupling characteristics could be interrelated with the two-dimensional ^1H–^{13}C correlation data, thereby permitting the differentiation of regioisomeric adducts. Thus, for example, the 2D COSY data for the major isomer of the **14a–15a** regioisomer pair showed coupling between H(1a) (5.21 ppm) and the C(1) hydrogens (2.5–2.7 ppm) and between H(3) (5.41 ppm) and the C(4) hydrogens (2.8–3.0 ppm), whereas the data for the minor isomer revealed coupling of H(1a) and H(2) only with the C(1) hydrogens. The regiochemical deductions were confirmed by carbon shift comparison of the isoprene (**2a**) adduct pairs **14a–15a**, **14c–15c** and **14d–15d** with the 1,3-butadiene (**2b**) adducts **17a**, **b**, and **c**, respectively. The important carbon shifts of all cycloadducts are listed in Table II.[31]

(22) Oddo, B.; Albanese, A. *Gazz. Chim. Ital.* **1927**, *57*, 827.
(23) Anzai, K. *J. Heterocycl. Chem.* **1979**, *16*, 567.
(24) Although 90% of the starting cyanide was recovered, the diene had undergone total decomposition.
(25) Reis, F.; Bannai, K.; Husson, H.-P. *Tetrahedron Lett.* **1976**, 1085.
(26) Indole **20b** was prepared from 2-cyanoindole (Doyle, F. P.; Ferrier, W.; Holland, D. O.; Mehta, M. D.; Nayler, J. H. C. *J. Chem. Soc.* **1956**, 2853) by N-benzenesulfonylation under phase-transfer conditions.
(27) Wenkert, E.; Moeller, P. D. R.; Piettre, S. R.; McPhail, A. T. *J. Org. Chem.* **1988**, *53*, 3170.
(28) The steric effect had overwhelmed the enhancement of dienophilicity of the α,β-unsaturated ketone by the α-thio group: Knapp, S.; Lis, R.; Miehna, P. *J. Org. Chem.* **1981**, *46*, 624.
(29) Inter alia: (a) Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436. (b) Angell, E. C.; Fringuelli, F.; Minuti, L.; Pizzo, F.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1986**, *51*, 5177.
(30) (a) Benn, R.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350. (b) Bax, A.; *Two-Dimensional Nuclear Magnetic Resonance in Liquids*; Delft University: Dordrecht, The Netherlands, 1984.

Table II. ^{13}C Chemical Shifts of the Cyclohexene Portion of the Hydrobenzofurans **6**, Hydroindoles **9**, and Hydrocarbazoles **14a–e**, **15a–e**, **17**, **24a**, **24c,d**, and **25**[a–c]

	C(3a)	C(4)	C(5)	C(6)	C(7)	C(7a)	C=O
6a	62.2	28.5	118.1	134.2	33.3	80.9	199.0
6b	62.2	32.1	135.9	119.3	27.5	80.7	199.3
6c[d]	56.6	31.5	118.4	135.5	33.5	82.5	175.3
6d[d]	57.4	36.1	135.5	119.1	28.8	82.9	175.3
9a[e]	65.6	30.5	120.1	135.4	34.3	60.9	206.6
6b[e]	66.0	34.9	135.4	118.8	29.6	60.7	206.6
	C(4a)	C(4)	C(3)	C(2)	C(1)	C(1a)	C=O
14a[f]	61.1	33.7	119.1	130.1	35.6	63.3	199.6
15a[f]	61.6	38.7	129.7	120.6	30.8	63.0	199.6
14b[g]	60.5	31.5	118.7	131.0	35.4	63.9	194.1
15b[g]	61.6	35.9	130.5	120.8	30.6	63.8	194.1
14c[e]	62.3	31.1	119.9	133.8	35.6	64.8	206.0
15c[e]	62.8	35.6	133.1	119.6	31.0	64.9	206.0
14d	60.3	28.7	118.9	131.2	35.4	62.0	195.9
15d	60.9	33.0	130.8	120.7	30.6	62.2	195.8
14e[d]	56.5	32.7	119.9	133.6	35.8	65.6	173.3
15e[d]	56.0	37.0	133.2	120.4	31.1	65.7	173.3
17a[f]	61.1	33.0	126.9	128.3	30.4	63.0	199.3
17b[e]	62.5	30.5	128.0	127.4	30.5	64.7	205.9
17c	60.5	28.1	126.8	128.5	30.2	62.7	195.7
24a[h]	61.8	31.6	120.4	134.6	35.7	65.5	197.6
24c[i]	62.2	34.3	119.8	133.2	35.8	65.8	203.0
24d[i]	62.5	38.6	132.8	120.6	31.2	65.8	203.0
25a	63.5	31.2	120.0	136.4	35.7	63.3	210.9
25b	63.6	31.4	118.9	136.9	35.7	62.8	209.9

[a] The δ values are in parts per million downfield from Me_4Si: $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. [b] The benzenesulfonyl carbon shifts are as follows: ipso-C, 137.4 ± 0.7; o-C, 127.2 ± 0.4; m-C, 128.8 ± 0.2; p-C, 133.0 ± 0.3 ppm. [c] Cyclohexene δ(Me) = 23.2 ± 0.3 ppm. [d] δ(OMe) = 52.1 ppm. [e] δ(Me) = 25.2 ppm. [f] δ(CON) = 165.6 ppm; δ(NCH) = 40.8, 38.1 ppm; δ(Me) = 12.9, 11.9 ppm. [g] $\delta(CO_2)$ = 162.3 ppm; $\delta(OCH_2)$ = 61.8 ppm; δ(Me) = 13.6 ppm. [h] δ(CH) = 119.5 ppm; δ(C) = 158.6 ppm; δ(E-Me) = 28.0 ppm; δ(Z-Me) = 21.0 ppm. [i] δ(CS) = 134.5 ppm; δ(C) = 148.4 or 147.7 ppm; δ(Me) = 21.9, 21.2 ppm; δ(ipso-C) = 147.7 or 148.4 ppm; δ(o-C) = 127.2 ppm; δ(m-C) = 128.5 ppm; δ(p-C) = 128.4 ppm.

Conclusion. It has been shown for the first time that furans, pyrroles, and indoles can act as dienophiles in reactions with nucleophilic dienes, when β-substituted with electron-withdrawing groups and, in the nitrogenous substrates, N-substituted with a powerful electron-withdrawing function. The high-yielding Diels–Alder reactions show poor regioselectivity, unless catalyzed by a Lewis acid. The new reaction can be expected to have a major impact on heterocycle as well as natural product synthesis and on medicinal chemistry.

Experimental Section

Melting points were observed on a Reichert microhotstage and are uncorrected. Infrared spectra of methylene chloride solutions and ultraviolet spectra of methanol solutions were measured on Perkin-Elmer 1330 and IBM 9400 spectrophotometers, respectively. ^1H and ^{13}C NMR spectra of deuteriochloroform solutions were recorded on a Nicolet QE-300 spectrometer operating at 300 and 75.5 MHz, respectively, in the Fourier transform mode. The carbon shifts are in parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. All reactions were carried out in a nitrogen atmosphere. On workup, all extracts were washed with brine and dried over magnesium sulfate. Column chromatography was executed on silica gel.

N-Benzenesulfonylation of Indoles (General Procedure). A 50% potassium hydroxide solution (1.0 mL) was added dropwise to a stirring mixture of 1.0 mmol of the requisite indole and 0.1 mmol of tetra-*n*-butylammonium bisulfate in 3.0 mL of benzene at room temperature and the stirring continued for 5 min. Benzenesulfonyl chloride (177 mg, 1.0 mmol) was added dropwise and the mixture stirred for 0.5 h. It was poured into 20 mL of water and extracted with 60 mL of methylene chloride. The extract was dried and evaporated and the residue chromatographed.

1-(Phenylsulfonyl)-6-methylindole (11a). Elution with 20:1 hexane–ethyl acetate yielded 240 mg (88%) of colorless, crystalline sulfonamide **11a**: mp 72–73 °C (Et_2O–hexane); UV, λ_{max} 212 nm (ϵ 23 400), 252 (11 100), 288 (1700); ^1H NMR, δ 2.47 (s, 3, Me), 6.58 (d, 1, J = 3.5 Hz, H-3), 7.03 (d, 1, J = 8.0 Hz, H-5), 7.39 (d, 1, J = 8.0 Hz, H-4), 7.3–7.5 (m, 2, m-Hs), 7.48 (m, 1, p-H), 7.49 (d, 1, J = 3.5 Hz, H-2), 7.81 (s, 1, H-7), 7.8–7.9 (m, 2, o-Hs); ^{13}C NMR, δ 21.8 (Me), 109.0 (C-3), 113.4 (C-7), 120.8 (C-4), 124.8 (C-5), 125.5 (C-2), 126.5 (o-C), 128.3 (C-6), 129.1 (m-C), 133.6 (p-C), 134.6 (C-3a or C-7a), 135.1 (C-7a or C-3a), 138.2 (ipso-C); MS, *m/e* 271 (M^+, 42), 130 (base), 77 (23); exact mass, *m/e* 271.0666, calcd for $C_{15}H_{13}NO_2S$ 271.0665.

***N,N*-Diethyl-1-(phenylsulfonyl)-3-indoleglyoxylamide (13a).** Elution with 3:2 hexane–ethyl acetate furnished 376 mg (98%) of colorless, gummy sulfonamide **13a**: UV, λ_{max} 209 nm (ϵ 25 600), 229 (16 900), 270 (5000), 279 (5800), 298 (8700); IR (CCl_4) (C=O) 1660 (s), 1637 (s), (SO_2) 1388 (s), 1179 (s) cm^{-1}; ^1H NMR, δ 1.21, 1.31 (t, 3 each, J = 7 Hz, methyls), 3.35, 3.57 (q, 2 each, J = 7 Hz, methylenes), 7.3–8.4 (m, 9, aromatic Hs), 8.34 (s, 1, indole α-H); MS, *m/e* 384 (M^+, 6), 284 (base), 141 (32), 100 (23), 77 (44); exact mass, *m/e* 384.1140, calcd for $C_{20}H_{20}N_2O_4S$ 384.1142.

1-(Phenylsulfonyl)-3-formylindole (13d). Elution with 9:1 hexane–ethyl acetate gave a solid, whose crystallization from dichloromethane–hexane afforded 253 mg (89%) of colorless, crystalline sulfonamide **13d**: mp 157–158 °C (lit.[18] mp 158–158.5 °C); IR and ^1H NMR spectrally identical with literature data.[18]

Methyl 1-(Phenylsulfonyl)-3-indolecarboxylate (13e). Elution with 4:1 hexane–ethyl acetate led to 284 mg (90%) of colorless, crystalline sulfonamide **13e**: mp 135–137 °C (CH_2Cl_2–C_6H_{14}); UV, λ_{max} 209 nm (ϵ 34 000), 264 (8600), 268 (8900), 273 (8500), 284 (7200); IR, (C=O) 1724 (s), (C=C) 1612 (w), 1588 (w), (SO_2) 1388 (s), 1179 (s) cm^{-1}; ^1H NMR, δ 3.93 (s, 3, OMe), 7.3–8.2 (m, 9, aromatic Hs), 8.28 (s, 1, indole α-H); MS, *m/e* 315 (M^+, 49), 146 (43), 143 (24), 141 (37), 77 (base), 51 (23); exact mass, *m/e* 315.0571, calcd for $C_{16}H_{13}NO_4S$ 315.0565.

1-(Phenylsulfonyl)-3-nitroindole (13h). Elution with 2:1 hexane–ethyl acetate yielded 260 mg (86%) of colorless, crystalline sulfonamide **13h**: mp 137–138 °C (CH_2Cl_2–C_6H_{14}); UV, λ_{max} 207 nm (ϵ 33 200), 235 (22 200), 270 (4200), 276 (3900), 325 (8100); IR, (C=C) 1588 (w), (NO_2) 1502 (s), (SO_2) 1386 (s), 1188 (s) cm^{-1}; ^1H NMR, δ 7.4–8.3 (m, 9, aromatic Hs), 8.57 (s, 1, indole α-H); MS, *m/e* 302 (M^+, base), 141 (9), 77 (13); exact mass, *m/e* 302.0375, calcd for $C_{14}H_{10}N_2O_4S$ 302.0359. Anal. Calcd for $C_{14}H_{10}N_2O_4S$: C, 55.62; H, 3.33; N, 9.27. Found: C, 56.09; H, 3.22; N, 9.30.

1-(Phenylsulfonyl)-3-(phenylthio)indole (16b). Elution with 2:1 hexane–ethyl acetate afforded 343 mg (94%) of colorless, crystalline sulfonamide **16b**: mp 73–74 °C (MeOH); UV, λ_{max} 208 nm (ϵ 38 700), 247 (18 100), 286 (6600), 293 (6900); IR, (SO_2) 1385 (s), 1178 (s) cm^{-1}; ^1H NMR, δ 7.0–8.1 (m, 14, aromatic Hs), 7.83 (s, 1, indole α-H); MS, *m/e* 365 (M^+, 46), 224 (base), 223 (43), 77 (22); exact mass, *m/e* 365.0535, calcd for $C_{20}H_{15}NO_2S_2$ 365.0543.

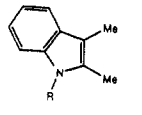
Methyl 1-(Phenylsulfonyl)-2-indolecarboxylate (20a). Elution with 9:1 hexane–ethyl acetate furnished 275 mg (87%) of colorless, crystalline sulfonamide **20a**: mp 127–128 °C (CH_2Cl_2–C_6H_{14}); IR, (C=O) 1738 (s), (C=C) 1610 (w), 1588 (w), (SO_2) 1378 (s), 1180 (s) cm^{-1}; ^1H NMR δ 3.93 (s, 3, OMe), 7.18 (s, 1, indole β-H), 7.2–8.2 (m, 9, aromatic Hs). For a previous, different preparation of **20a** see ref 25.

1-(Phenylsulfonyl)-2-cyanoindole (20b). Elution with 9:1 hexane–ethyl acetate gave 268 mg (95%) of colorless, crystalline sulfonamide **20b**: mp 126–127.5 °C (CH_2Cl_2–C_6H_{14}); IR, (C≡N) 2238 (s), (C=C) 1610 (w), 1587 (w), (SO_2) 1387 (s), 1179 (s) cm^{-1}; ^1H NMR, δ 7.37 (s, 1, indole β-H), 7.3–8.3 (m, 9, aromatic Hs). Anal. Calcd for $C_{15}H_{10}N_2O_2S$: C, 63.82; H, 3.57; N, 9.92. Found: C, 63.87; H, 3.52; N, 9.78.

3-Acetyl-1-(phenylsulfonyl)-1,4,5,6-tetrahydropyridine (iv).[15] Elution with 2:1 ethyl acetate–hexane produced 214 mg (81%) of colorless, gummy sulfonamide iv: UV λ_{max} 204 nm (ϵ 15 600), 216 (9200), 281 (23 300); IR, (C=O) 1658 (s), 1620 (s), (SO_2) 1370 (s), 1172 (s) cm^{-1}; ^1H NMR, δ 1.6–1.8 (m, 2, C-5 Hs), 2.1–2.3 (m, 2, C-4 Hs), 2.30 (s, 3, Me), 3.3–3.5 (m, 2, C-6 Hs), 7.5–7.9 (m, 5, aromatic Hs), 7.89 (s, 1, H-2); MS, *m/e* 265 (M^+, 41), 250 (48), 141 (20), 124 (base), 77 (52), 43 (39); exact mass, *m/e* 265.0773, calcd for $C_{13}H_{15}NO_3S$ 265.0773.

1-(Phenylsulfonyl)-2-methylskatole (vi).[31] Elution with 4:1 hexane–dichloromethane furnished 128 mg (42%) of colorless, crystalline sulfonamide vi: mp 132–134 °C (CH_2Cl_2–C_6H_{14}); UV, λ_{max} 209 nm (ϵ

(31) In order to aid in the methylene carbon shift assignment of compounds **18**, it was useful to obtain the $\Delta\delta$(Me) value for indole vi. For this reason the later substance was prepared from α-methylskatole (v)[32] by N-benzenesulfonylation under phase-transfer conditions (see Experimental Section).



v, R = H
vi, R = $SO_2C_6H_5$

(32) Buu-Hoï, N. P.; Jacquignon, P. *C. R. Hebd. Seances Acad. Sci.* **1960**, *251*, 1297.

21 300), 217 (20 500), 256 (12 400); IR, (SO_2) 1372 (s), 1178 (s) cm^{-1}; ^1H NMR, δ 2.11 (s, 3, β-Me), 2.51 (s, 3, α-Me), 7.2–8.2 (m, 9, aromatic Hs); ^{13}C NMR, δ 8.7 (β-Me), 12.6 (α-Me), 114.4 (C-7), 116.0 (C-3), 118.2 (C-4), 123.2 (C-6), 123.9 (C-5), 126.1 (C-2, o-C), 129.0 (m-C), 132.1 (C-3a), 133.3 (p-C), 136.1 (C-7a, ipso-C); MS, *m/e* 285 (M^+, 24), 144 (base), 77 (20); exact mass, *m/e* 285.0821, calcd for $C_{16}H_{15}NO_2S$ 285.0822.

Ethyl 1-(Phenylsulfonyl)-3-indoleglyoxylate (13b). A 1.50 M hexane solution of *n*-butyllithium (3.33 mL, 5.00 mmol) was added dropwise to a stirring suspension of 1.086 g (5.00 mmol) of ester **12b** in 20 mL of dry tetrahydrofuran at 0 °C, the stirring continued, and the mixture cooled to −78 °C. Benzenesulfonyl chloride (883 mg, 5.00 mmol) was added dropwise and stirring continued for 10 min. The solution was allowed to warm to room temperature and was stirred for 16 h. It then was poured into 100 mL of water and extracted with methylene chloride. The extract was dried and evaporated. Crystallization of the residue yielded 1.376 g (77%) of creamy, crystalline sulfonamide **13b**: mp 105–106 °C (CH_2Cl_2–C_6H_{14}); UV, λ_{max} 208 nm (ϵ 25 400), 235 (14 500), 268 (4100), 276 (4100), 308 (7100); IR, (C=O) 1733 (s), 1671 (s), (C=C) 1609 (w), 1586 (w), (SO_2) 1384 (s), 1178 (s) cm^{-1}; ^1H NMR, δ 1.45 (t, 3, J = 7 Hz, Me), 4.45 (q, 2, J = 7 Hz, OCH_2), 7.3–8.4 (m, 9, aromatic Hs), 8.87 (s, 1, indole α-H); ^{13}C NMR, δ 13.9 (Me), 62.5 (CH_2), 113.0 (C-7), 117.0 (C-3), 122.9 (C-4), 125.2 (C-5), 126.1 (C-6), 127.1 (o-C), 127.6 (C-3a), 129.6 (m-C), 134.4 (C-7a), 134.6 (p-C), 136.6 (C-2), 137.2 (ipso-C), 161.4 (CO_2), 178.6 (C=O); MS, *m/e* 357 (M^+, 7), 284 (base), 141 (44), 77 (67); exact mass, *m/e* 357.0656, calcd for $C_{18}H_{15}NO_5S$ 357.0668.

1,3-Bis(phenylsufonyl)indole (13g). A solution of 346 mg (2.0 mmol) of m-chloroperbenzoic acid in 5 mL of methylene chloride was added dropwise to a stirring solution of 365 mg (1.0 mmol) of sulfide **16b** in 5 mL of methylene chloride at room temperature and stirring continued up to completion of the reaction (by TLC analysis). The mixture was poured into 100 mL of 10% sodium sulfite solution and extracted with methylene chloride. The extract was dried and evaporated. Chromatography of the residue and elution with 4:1 hexane–ethyl acetate liberated 292 mg (74%) of colorless, crystalline sulfone **13g**: mp 202–203 °C (CH_2Cl_2–C_6H_{14}); UV, λ_{max} 208 nm (ϵ 34 900), 225 (20 700), 262 (11 100), 266 (11 200), 272 (9900), 283 (7900); IR, (SO_2) 1382 (s), 1180 (s) cm^{-1}; ^1H NMR, δ 7.2–8.1 (m, 14, aromatic Hs), 8.32 (s, 1, indole α-H); MS, *m/e* 397 (M^+, 55), 141 (39), 125 (61), 77 (base); exact mass, *m/e* 397.0438, calcd for $C_{20}H_{15}NO_4S_2$ 397.0440.

1-(Phenylsulfonyl)-3-[3-methyl-2-(phenylthio)-2-butenoyl]indole (21c). A solution of 145 mg (1.0 mmol) of benzenesulfenyl chloride[33] in 1 mL of acetonitrile was added dropwise to a stirring solution of 339 mg (1.0 mmol) of ketone **21b** in 4 mL of methylene chloride at room temperature and the stirring continued for 16 h. Evaporation of the solution and crystallization of the residue from dichloromethane–hexane gave 474 mg (98%) of colorless, crystalline 1-(phenylsulfonyl)-3-[3-chloro-3-methyl-2-(phenylthio)butanoyl]indole (**22**): mp 117–118 °C; UV, λ_{max} 206 nm (ϵ 35 000), 264 (8300), 272 (8600), 290 (10 100); IR (CCl_4) (C=O) 1671 (s), (C=C) 1609 (w), (SO_2) 1386 (s), 1178 (s) cm^{-1}; ^1H NMR, δ 1.91, 1.99 (s, 3 each, methyls), 4.55 (s, 1, CH), 7.2–8.4 (m, 14, aromatic Hs), 7.77 (s, 1, indole α-H); MS, *m/e* 483 (M^+, 1), 338 (15), 284 (65), 198 (22), 164 (base), 77 (23); exact mass, *m/e* 483.0737, calcd for $C_{25}H_{22}NO_3S_2Cl$ 483.0727.

A suspension of 24 mg (1.0 mmol) of sodium hydride and 483 mg (1.0 mmol) of chloride **22** in 10 mL of dry tetrahydrofuran was stirred at room temperature for 4 h. The mixture was poured into 50 mL of water and extracted with methylene chloride. The extract was dried and evaporated. Chromatography of the residue and elution with 4:1 hexane–ethyl acetate furnished 353 mg (79%) of colorless, crystalline sulfonamide **21c**: mp 131–132 °C (CH_2Cl_2–C_6H_{14}); UV, λ_{max} 207 nm (ϵ 38 900), 274 (10 000), 293 (9000); IR, (C=O) 1643 (s), (C=C) 1609 (m), (SO_2) 1382 (s), 1173 (s) cm^{-1}; ^1H NMR, δ 1.96, 2.23 (s, 3 each, methyls), 7.1–8.2 (m, 14, aromatic Hs), 8.14 (s, 1, indole α-H); MS, *m/e* 447 (M^+, 14), 292 (58), 183 (93), 119 (36), 105 (39), 93 (38), 91 (32), 82 (27), 80 (32), 77 (base). Anal. Calcd for $C_{25}H_{21}NO_3S_2$: C, 67.09; H, 4.73; H, 3.13. Found: C, 67.33; H, 4.88; N, 2.97.

Thermal Diels–Alder Reactions (General Procedure). An ampule containing a solution of 1.0 mmol of the requisite furan, pyrrole, or indole and 12.0 mmol of diene in 0.5 mL of dry benzene was cooled in liquid nitrogen, sealed, and then heated in a phosphoric acid bath at 195 °C for 72 h. It was cooled once more in liquid nitrogen and opened. The solution was evaporated and the residue chromatographed.

1aβ-Formyl-1a,1,4,4aβ,5aα,5,8,8aα-octahydrodibenzofuran (4). Elution with 9:1 hexane–ethyl acetate furnished 21 mg (10%) of colorless, liquid aldehyde **4**: bp 93–94 °C (0.5 Torr) [lit.[7a] bp 115 °C (1.1 Torr)]; IR, (CHO) 2709 (w), (C=O) 1734 (s) cm^{-1}; ^1H NMR, δ 1.9–2.5 (m, 8, methylenes), 4.40 (m, 1, OCH), 5.6–5.9 (m, 4, olefinic Hs), 9.55 (s, 1, CHO); ^{13}C NMR, δ 24.5 (C-4 or C-5), 25.2 (C-5 or C-4), 28.3 (C-8 or C-1), 28.8 (C-1 or C-8), 40.6 (C-5a), 42.3 (C-4a), 75.4 (C-8a), 84.9 (C-1a), 124.0 (C-3), 124.7 (C-6 or C-7), 125.0 (C-7 or C-6), 125.9 (C-2), 201 (C=O).

Aldehydes 6a and 6b. Elution with 20:1 hexane–ethyl acetate led to the recovery of 19 mg (19%) of starting aldehyde **5a**. Earlier fractions yielded 98 mg (60%) of a colorless, liquid, ca. 1:1 **6a–6b** mixture: IR, (CHO) 2710 (w), (C=O) 1723 (s), (C=C) 1613 (m) cm^{-1}; ^1H NMR, δ (**6a**) 1.76 (s, 3, Me), 2.03 (d, 1, J = 15.3 Hz, H-4), 2.2–2.5 (m, 3 H-4, C-7 Hs), 4.62 (d, 1, J = 2.7 Hz, H-3), 5.10 (t, 1, J = 4.9 Hz, H-7a), 5.55 (br t, 1, H-6), 6.43 (d, 1, J = 2.7 Hz, H-2), 9.57 (s, 1, CHO); δ (**6b**) 1.76 (s, 3, Me), 2.12 (dd, 1, J = 15.6, 5.8 Hz, H-4), 2.2–2.5 (m, 3, H-4, C-7 Hs), 4.60 (d, 1, J = 2.7 Hz, H-3), 5.03 (t, 1, J = 5.0 Hz, H-7a), 5.48 (br t, 1, H-5), 6.44 (d, 1, J = 2.7 Hz, H-2), 9.57 (s, 1, CHO); ^{13}C NMR, δ (**6a**) 101.1 (C-3), 148.9 (C-2); δ (**6b**) 100.5 (C-3), 149.1 (C-2).

A mixture of 82 mg (0.5 mmol) of aldehydes **6a** and **6b** and 100 mg (0.5 mmol) of 2,4-dinitrophenylhydrazine in 1 mL of diglyme and 4 mL of ethanol was refluxed for 1.5 h. The solution was evaporated and the residue chromatographed. Elution with 9:1 hexane–ethyl acetate afforded 80 mg (49%) of yellow solid whose crystallization from hexane–ether gave **6a–6b** 2,4-dinitrophenylhydrazones: UV, λ_{max} 206 nm (ϵ 15 900), 223 (12 400), 249 (10 000), 268 (8400), 359 (18 600); IR, (NH) 3301 (m), (C=N) 1611 (s), (NO_2) 1592 (s), 1333 (s) cm^{-1}; ^1H NMR, δ (**6a** hydrazone) 1.82 (s, 3, Me), 2.26 (dd, 1, J = 15.6, 6.0 Hz, H-4), 2.3–2.6 (m, 3, H-4, C-7 Hs), 4.73 (d, 1, J = 2.6 Hz, H-3), 5.02 (t, 1, J = 4.4 Hz, H-7a), 5.5–5.6 (m, 1, H-5), 6.40 (br s, 1, H-2), 7.55 (s, 1, CHN), 7.90 (dd, 1, J = 9.5, 2.4 Hz, aromatic H-5), 8.32 (dm, 1, J = 9.5 Hz, aromatic H-6), 9.13 (d, 1, J = 2.4 Hz, aromatic H-3); δ (**6b** hydrazone) 1.80 (s, 3, Me), 2.23 (d, 1, J = 15.1 Hz, H-4), 2.3–2.6 (m, 3, H-4, C-7 Hs), 4.71 (d, 1, J = 2.6 Hz, H-3), 4.94 (t, 1, J = 4.5 Hz, H-7a), 5.5–5.6 (m, 1, H-6), 6.40 (br s, 1, H-2), 7.55 (s, 1, CHN), 7.90 (dd, 1, J = 9.5, 2.4 Hz, aromatic H-5), 8.32 (dm, 1, J = 9.5 Hz, aromatic H-6), 9.13 (d, 1, J = 2.4 Hz, aromatic H-3); MS, *m/e* 344 (M^+, 16), 276 (base), 91 (19); exact mass, *m/e* 344.1131, calcd for $C_{16}H_{16}N_4O_5$ 344.1119.

A 1.0 M toluene solution of diisobutylaluminum hydride (0.2 mL) was added dropwise to a stirring solution of 39 mg (0.2 mmol) of a 2:1 mixture of esters **6d** and **6c** (vide infra) in 0.7 mL of dry tetrahydrofuran and 2 mL of dry toluene at −78 °C. Stirring was continued for 3 h, 1 mL of methanol added, and the mixture allowed to warm to room temperature. It was poured into water and extracted with methylene chloride. The extract was dried (K_2CO_3) and evaporated. Chromatography of the residue and elution with 20:1 hexane–ethyl acetate gave 16 mg (41%) of the starting ester mixture, followed by 13 mg (39%) of a 2:1 mixture of aldehydes **6b** and **6a**, the individual components being spectrally (IR, ^1H NMR, ^{13}C NMR) identical with the above aldehydes.

Esters 6c and 6d. Elution with 20:1 hexane–ethyl acetate caused recovery of 18 mg (14%) of starting ester **5c**. Earlier fractions afforded 107 mg (55%) of a colorless, liquid, ca. 2:1 **6d–6c** mixture: IR, (C=O) 1729 (s), (C=C) 1628 (m) cm^{-1}; ^1H NMR, δ (**6c**) 1.78 (s, 3, Me), 2.1–2.5 (m, 4, C-4 and C-7 Hs), 3.73 (s, 3, OMe), 4.78 (m, 1, H-3), 5.22 (t, 1, J = 4.1 Hz, H-7a), 5.53 (br s, 1, H-5), 6.30 (m, 1, H-2); δ (**6d**) 1.73 (s, 3, Me), 2.16 (d, 1, J = 14.9 Hz, H-4), 2.2–2.5 (m, 3, H-4, C-7 Hs), 3.74 (s, 3, OMe), 4.78 (d, 1, J = 2.6 Hz, H-3), 5.17 (t, 1, J = 4.0 Hz, H-7a), 5.53 (br, s, 1, H-6), 6.30 (d, 1, J = 2.6 Hz, H-2); ^{13}C NMR, δ (**6c**) 103.9 (C-3), 147.2 (C-2); δ (**6d**) 103.3 (C-3), 147.2 (C-2). The esters were converted immediately into aldehydes **6a** and **6b** (vide supra).

Ketones 9a and 9b. Elution with 4:1 hexane–ethyl acetate gave 168 mg (67%) of starting pyrrole **8a** and in previous fractions 53 mg (17%) of a ca. 1:1, colorless, oily mixture of ketones **9a** and **9b**: UV, λ_{max} 206 nm (ϵ 16 900), 254 (6300), 265 (5700), 273 (4700); IR, (C=O) 1709 (s), (C=C) 1617 (w), (SO_2) 1355 (s), 1173 (s) cm^{-1}; ^1H NMR, δ (**9a**) 1.76 (s, 3, COMe), 1.81 (s, 3, Me), 2.0–2.6 (m, 4, C-4 and C-7 Hs), 4.35 (t, 1, J = 4.6 Hz, H-7a), 4.93 (m, 1, H-3), 5.60 (br s, 1, H-5), 6.41 (d, 1, J = 4.1 Hz, H-2), 7.4–7.8 (m, 5, aromatic Hs); δ (**9b**) 1.70 (s, 6, methyls), 2.0–2.6 (m, 4, C-4 and C-7 Hs), 4.26 (t, 1, J = 4.8 Hz, H-7a), 4.93 (m, 1, H-3), 5.46 (br s, 1, H-6), 6.43 (d, 1, J = 4.1 Hz, H-2), 7.4–7.8 (m, 5, aromatic Hs); ^{13}C NMR, δ (**9a**) 114.3 (C-3), 132.8 (C-2); δ (**9b**) 113.7 (C-3), 132.8 (C-2); MS, *m/e* 274 (M^+ − Ac, base), 133 (26), 132 (54), 118 (20), 117 (19), 77 (55), 43 (18); exact mass (M − Ac), *m/e* 274.0899, calcd for $C_{15}H_{16}NO_2S$ 274.0901.

Dihydroindoles 10a and 10b and Indoles 11a and 11b. Elution with 9:1 hexane–ethyl acetate yielded 60 mg (22%) of a colorless, solid, ca. 3:1 mixture of dihydroindoles **10a** and **10b**: UV, λ_{max} 206 nm (ϵ 18 500), 265 (3800), 272 (2700); IR, (SO_2) 1373 (s), 1187 (s) cm^{-1}; ^1H NMR, δ (**10a**) 1.77 (s, 3, Me), 3.07 (br s, 2, C-4 Hs), 3.25 (t, 2, J = 7.0 Hz, C-7 Hs), 5.48 (br s, 1, H-5), 6.12 (d, 1, J = 3.3 Hz, H-3), 7.22 (d, 1, J = 3.3 Hz, H-2), 7.4–7.8 (m, 5, aromatic Hs); δ (**10b**) 1.74 (s, 3, Me),

(33) Hopkins, P. B.; Fuchs, P. L. *J. Org. Chem.* **1978**, *43*, 1208.

2.99 (t, 2, J = 7.0 Hz, C-4 Hs), 3.35 (br s, 2, C-7 Hs), 5.48 (br s, 1, H-5), 6.12 (d, 1, J = 3.3 Hz, H-3), 7.22 (d, 1, J = 3.3 Hz, H-2), 7.4–7.8 (m, 5, aromatic Hs); ^{13}C NMR, δ (**10a**) 23.3 (Me), 25.1 (C-4), 29.1 (C-7), 111.7 (C-3), 117.2 (C-3a), 118.3 (C-5), 121.0 (C-2), 126.5 (o-C), 126.7 (C-7a), 129.2 (m-C), 130.0 (C-6), 133.4 (p-C), 139.4 (ipso-C); MS, m/e 273 (M^+, 52), 132 (base), 131 (56), 130 (64), 117 (67), 77 (59), 51 (24); exact mass, m/e 273.0820, calcd for $C_{15}H_{15}NO_2S$ 273.0821.

Further elution gave 30 mg (11%) of a pale yellow, oily, ca. 3:1 mixture of indoles **11a** and **11b**: major component spectrally (UV, ^{1}H NMR, ^{13}C NMR) identical with the authentic sample (vide supra); ^{1}H NMR, δ (**11b**) 2.38 (s, 3, Me), 6.56 (d, 1, J = 3.8 Hz, H-3), 7.1–7.9 (m, 9, aromatic Hs); ^{13}C NMR, δ (**11b**) 21.1 (Me), 109.0 (C-3), 113.0 (C-7), 121.1 (C-2), 125.9 (C-4 or C-6), 126.3 (C-6 or C-4), 126.5 (o-C), 129.1 (m-C), 133.6 (p-C), 138.2 (ipso-C); MS, m/e 271 (M^+, 39), 130 (base), 77 (30); exact mass, m/e 271.0666, calcd for $C_{15}H_{13}NO_2S$ 271.0665.

More elution led to the recovery of 83 mg (33%) of starting pyrrole **8b**.

A chloroform solution of 27 mg (0.1 mmol) of a 3:1 mixture of dihydroindoles **10a** and **10b** and 22 mg (0.2 mmol) of *p*-benzoquinone was refluxed for 18 h and then evaporated. Chromatography of the residue and elution with 9:1 hexane–ethyl acetate furnished 25 mg (91%) of a 3:1, oily mixture of indoles **11a** and **11b**: spectrally identical with the above sample.

Glyoxamides 14a and 15a. Elution with 4:1 hexane–ethyl acetate gave 32 mg (8%) of starting indole **13a**. Earlier fractions yielded 394 mg (87%) of a colorless, solid, ca. 3:1 mixture of glyoxamides **14a** and **15a**: UV, λ_{max} 207 nm (ϵ 26 300), 260 (6800), 266 (6700), 272 (6200); IR, (C=O) 1702 (s), 1634 (s), (C=C) 1598 (w), (SO_2) 1360 (s), 1159 (s) cm^{-1}; ^{1}H NMR, δ (**14a**) 0.41, 1.01 (t, 3 each, J = 7.0 Hz, methyls), 1.79 (s, 3, 2-Me), 1.8–2.0 (m, 2, NCH_2), 2.6–2.7 (m, 2, C-1 Hs), 2.8–2.9 (m, 2, C-4 Hs), 3.0–3.1, 3.2–3.4 (m, 1 each, NCH_2), 5.21 (t, 1, J = 5.5 Hz, H-1a), 5.42 (br t, 1, H-3), 6.9–7.9 (m, 9, aromatic Hs); δ (**15a**) 0.39, 1.00 (t, 3 each, J = 7.0 Hz, methyls), 1.60 (s, 3, 3-Me), 1.8–2.0 (m, 2, NCH_2), 2.6–2.7 (m, 2, C-1 Hs), 2.8–2.9 (m, 2, C-4 Hs), 3.0–3.1, 3.2–3.4 (m, 1 each, NCH_2), 5.20 (t, 1, J = 5.6 Hz, H-1a), 5.63 (br t, 1, H-2), 6.9–7.9 (m, 9, aromatic Hs); ^{13}C NMR, δ (**14a**) 114.7 (C-8), 124.0 (C-6), 125.4 (C-5), 129.5 (C-7), 130.1 (C-5a), 142.1 (C-8a); δ (**15a**) 114.7 (C-8), 123.9 (C-6), 125.1 (C-5), 129.5 (C-7), 130.1 (C-5a), 142.1 (C-8a); MS, m/e 452 (M^+, 1), 325 (23), 324 (99), 311 (60), 183 (55), 182 (82), 100 (base). Anal. Calcd for $C_{25}H_{28}N_2O_4S$: C, 66.35; H, 6.24; N, 6.19. Found: C, 66.03; H, 6.43; N, 6.42.

Glyoxylates 14b and 15b. Elution with 4:1 hexane–ethyl acetate furnished 34 mg (9%) of starting indole **13b** and in previous fractions 288 mg (67%) of a colorless, gummy, ca. 3:1 mixture of glyoxylates **14b** and **15b**: UV, λ_{max} 212 nm (ϵ 16 400), 263 (4800), 267 (4800), 274 (4600); IR, (C=O) 1735 (s), (C=C) 1599 (w), (SO_2) 1358 (s), 1169 (s) cm^{-1}; ^{1}H NMR, δ (**14b**) 1.13 (t, 3, J = 7.1 Hz, 4a-Me), 1.76 (s, 3, 2-Me), 2.4–2.7 (m, 3, C-1 Hs, H-4), 2.76 (dd, 1, J = 15.2, 5.7 Hz, H-4), 4.0–4.2 (m, 2, OCH_2), 4.95 (t, 1, J = 5.9 Hz, H-1a), 5.40 (br t, 1, H-3), 7.0–7.8 (m, 9, aromatic Hs); δ (**15b**) 1.12 (t, 3, J = 7.1 Hz, 4a-Me), 1.63 (s, 3, 3-Me), 2.4–2.7 (m, 4, C-1 and C-4 Hs), 4.0–4.2 (m, 2, OCH_2), 4.91 (t, 1, J = 5.6 Hz, H-1a), 5.62 (m, 1, H-2), 7.0–7.8 (m, 9, aromatic Hs); ^{13}C NMR, δ (**14b**) 115.7 (C-8), 124.4 (C-6), 125.2 (C-5), 129.4 (C-7), 131.0 (C-5a), 142.4 (C-8a); δ (**15b**) 115.6 (C-8), 124.3 (C-6), 124.9 (C-5), 129.4 (C-7), 130.8 (C-5a), 142.5 (C-8a); MS, m/e 425 (M^+, 6), 325 (23), 324 (base), 284 (33), 183 (50), 182 (92), 168 (25), 167 (24), 141 (20), 77 (48); exact mass, m/e 425.1317, calcd for $C_{23}H_{23}NO_5S$ 425.1293.

Ketones 14c and 15c. Elution with 4:1 hexane–ethyl acetate led to the recovery of 110 mg (37%) of starting indole **13c**. Earlier fractions afforded 231 mg (63%) of a colorless, oily, ca. 2:1 mixture of ketones **14c** and **15c**: UV, λ_{max} 207 nm (ϵ 26 800), 258 (6300), 266 (6200), 273 (5700); IR, (C=O) 1657 (s), (C=C) 1598 (w), (SO_2) 1360 (s), 1171 (s) cm^{-1}; ^{1}H NMR, δ (**14c**) 1.47 (s, 3, COMe), 1.77 (s, 3, 2-Me), 2.27 (dd, 1, J = 13.8, 5.4 Hz, H-4), 2.5–2.6 (m, 3, C-1 Hs, H-4), 4.65 (t, 1, J = 5.5 Hz, H-1a), 5.44 (br t, 1, H-3), 7.0–7.8 (m, 9, aromatic Hs); δ (**15c**) 1.38 (s, 3, COMe), 1.63 (s, 3, 3-Me), 2.20 (d, 1, J = 13.5 Hz, H-4), 2.5–2.6 (m, 3, C-1 Hs, H-4), 4.53 (t, 1, J = 5.6 Hz, H-1a), 5.58 (m, 1, H-2), 7.0–7.8 (m, 9, aromatic Hs); ^{13}C NMR, δ (**14c**) 115.7 (C-8), 124.1 (C-6), 124.4 (C-5), 129.1 (C-7), 133.8 (C-5a), 142.4 (C-8a); δ (**15c**) 115.5 (C-8), 124.1 (C-6), 124.4 (C-5), 128.9 (C-7), 133.4 (C-5a), 142.5 (C-8a); MS, m/e 367 (M^+, 9), 325 (24), 324 (base), 183 (45), 182 (78), 168 (21), 167 (24), 77 (31); exact mass, m/e 367.1244, calcd for $C_{21}H_{21}NO_3S$ 367.1242.

Aldehydes 14d and 15d. Elution with 4:1 hexane–ethyl acetate liberated 108 mg (38%) of starting indole **13d** and in earlier fractions 216 mg (61%) of a colorless, solid, ca. 2:1 mixture of aldehydes **14d** and **15d**: UV, λ_{max} 206 nm (ϵ 19 600), 263 (3900), 267 (4000), 274 (3800); IR, (CHO) 2709 (w), (C=O) 1728 (s), (C=C) 1598 (w), (SO_2) 1371 (s), 1174 (s) cm^{-1}; ^{1}H NMR, δ (**14d**) 1.80 (s, 3, 2-Me), 2.24 (dd, 1, J = 15.3, 4.4 Hz, H-4), 2.50 (dd, 1, J = 14.8, 7.3 Hz, H-1), 2.5–2.7 (m, 1, H-4), 2.66 (dd, 1, J = 14.8, 6.1 Hz, H-1), 4.65 (dd, 1, J = 7.3, 6.1 Hz, H-1a), 5.45 (dd, 1, J = 5.4, 4.4 Hz, H-3), 7.0–7.8 (m, 9, aromatic Hs), 8.83 (s, 1, CHO); δ (**15d**) 1.66 (s, 3, 3-Me), 2.2–2.7 (m, 4, C-1, C-4 Hs), 4.54 (t, 1, J = 6.5 Hz, H-1a), 5.62 (br t, 1, H-2), 7.0–7.8 (m, 9, aromatic Hs), 8.73 (s, 1, CHO); ^{13}C NMR, δ (**14d**) 116.1 (C-8), 124.1 (C-6), 124.8 (C-5), 129.4 (C-7), 131.2 (C-5a), 142.0 (C-8a); δ (**15d**) 116.1 (C-8), 124.1 (C-6), 124.8 (C-5), 129.5 (C-7), 131.0 (C-5a), 142.3 (C-8a); MS, m/e 353 (M^+, 24), 325 (21), 324 (86), 285 (53), 183 (40), 182 (base), 168 (27), 167 (37), 141 (43), 77 (74); exact mass, m/e 353.1097, calcd for $C_{20}H_{19}NO_3S$ 353.1084.

Esters 14e and 15e. Elution with 4:1 hexane–ethyl acetate yielded 173 mg (55%) of starting indole **13e**. Previous fractions gave 157 mg of a colorless, oily, 2:1 mixture of esters **14e** and **15e**: UV, λ_{max} 206 nm (ϵ 25 200), 263 (5200), 267 (5200), 274 (4700); ^{1}H NMR, δ (**14e**) 1.79 (s, 3, 2-Me), 2.37 (dd, 1, J = 14.8, 5.4 Hz, H-4), 2.5–2.7 (m, 3, C-1 Hs, H-4), 3.29 (s, 3, OMe), 4.86 (t, 1, J = 5.5 Hz, H-1a), 5.44 (br t, 1, H-3), 7.0–7.8 (m, 9, aromatic Hs); δ (**15e**) 1.61 (s, 3, 3-Me), 2.34 (d, 1, J = 14.4 Hz, H-4), 2.5–2.7 (m, 3, C-1 Hs, H-4), 3.26 (s, 3, OMe), 4.76 (t, 1, J = 5.7 Hz, H-1a), 5.61 (br t, 1, H-2), 7.0–7.8 (m, 9, aromatic Hs); ^{13}C NMR, δ (**14e**) 115.4 (C-8), 124.3 (C-6), 124.6 (C-5), 128.9 (C-7), 133.6 (C-5a), 142.1 (C-8a); δ (**15e**) 115.3 (C-8), 124.2 (C-6), 124.4 (C-5), 129.0 (C-7), 133.0 (C-5a), 142.4 (C-8a); MS, m/e 383 (M^+, 17), 316 (21), 315 (base), 182 (21), 141 (20), 77 (31); exact mass, m/e 383.1194, calcd for $C_{21}H_{21}NO_4S$ 383.1190.

Glyoxamide 17a. Elution with 4:1 hexane–ethyl acetate afforded 200 mg (52%) of starting indole **13a**. Earlier fractions led to the isolation of colorless, crystalline glyoxamide **17a**: mp 138–140 °C (Et_2O–C_6H_{14}); UV, λ_{max} 206 nm (ϵ 22 700), 259 (4400), 264 (4400), 267 (4400), 273 (4100); IR, (C=O) 1713 (s), 1644 (s), (C=C) 1601 (w), (SO_2) 1364 (s), 1172 (s) cm^{-1}; ^{1}H NMR, δ 0.40, 1.00 (t, 3 each, J = 7.1 Hz, methyls), 1.7–2.0 (m, 2, NCH_2), 2.6–2.7 (m, 2, C-1 Hs), 2.8–3.1 (m, 2, C-4 Hs), 3.0–3.2, 3.2–3.4 (m, 1 each, NCH_2), 5.23 (t, 1, J = 5.6 Hz, H-1a), 5.7–5.9 (m, 1, H-3), 6.0–6.1 (m, 1, H-2), 7.0–7.9 (m, 9, aromatic Hs); ^{13}C NMR, δ 114.8 (C-8), 124.0 (C-6), 125.4 (C-5), 129.6 (C-7), 129.9 (C-5a), 142.2 (C-8a); MS, m/e 310 (M^+ – $COCONEt_2$, 78), 297 (30), 169 (29), 168 (base), 141 (18), 100 (74), 77 (33), 72 (23); exact mass (M – $COCONEt_2$), m/e 310.0895, calcd for $C_{18}H_{16}NO_2S$ 310.0899.

Ketone 17b. Elution with 4:1 hexane–ethyl acetate furnished 239 mg (80%) of starting indole **13c** and in earlier fractions 71 mg (20%) of colorless, crystalline ketone **17b**: mp 96–97 °C (Et_2O–C_6H_{14}); UV, λ_{max} 208 nm (ϵ 24 900), 263 (5000), 267 (5000), 274 (4600); IR, (C=O) 1715 (s), (C=C) 1602 (w), (SO_2) 1362 (s), 1174 (s) cm^{-1}; ^{1}H NMR, δ 1.44 (s, 3, Me), 2.25 (dd, 1, J = 15.1, 5.2 Hz, H-4), 2.6–2.7 (m, 3, C-1 Hs, H-4), 4.62 (t, 1, J = 5.7 Hz, H-1a), 5.8–5.9 (m, 1, H-3), 5.9–6.0 (m, 1, H-2), 7.0–7.8 (m, 9, aromatic Hs); ^{13}C NMR, δ 115.7 (C-8), 124.3 (C-6), 124.5 (C-5), 129.1 (C-7), 133.7 (C-5a), 142.4 (C-8a); MS, m/e 353 (m^+, 4), 310 (82), 169 (30), 168 (base), 167 (20), 77 (44); exact mass, m/e 353.1103, calcd for $C_{20}H_{19}NO_3S$ 353.1085.

Aldehyde 17c. Elution with 20:1 hexane–ethyl acetate liberated 226 mg (80%) of starting indole **13d**. Previous fractions gave 68 mg (20%) of colorless, crystalline aldehyde **17c**: mp 135–136 °C (Et_2O–C_6H_{14}); UV, λ_{max} 206 nm (ϵ 27 400), 261 (5600), 266 (5800), 273 (5500); IR, (CHO) 2711 (w), (C=O) 1732 (s), (C=C) 1602 (w), (SO_2) 1362 (s), 1174 (s) cm^{-1}; ^{1}H NMR, δ 2.2–2.3 (m, 1, H-4), 2.4–2.6 (m, 1, H-1), 2.6–2.8 (m, 2, H-1, H-4), 4.62 (dd, 1, J = 13.5, 6.5 Hz, H-1a), 5.8–5.9 (m, 1, H-3), 5.9–6.1 (m, 1, H-2), 7.0–7.8 (m, 9, aromatic Hs), 8.79 (s, 1, CHO); ^{13}C NMR, δ 116.3 (C-8), 124.2 (C-6), 124.9 (C-5), 129.6 (C-7), 131.1 (C-5a), 142.2 (C-8a); MS, m/e 339 (M^+, 15), 310 (80), 285 (27), 169 (28), 168 (base), 167 (22), 141 (29), 77 (58); exact mass, m/e 339.0917, calcd for $C_{19}H_{17}NO_3S$ 339.0926.

Dihydrocarbazoles 18a and 18b and Carbazoles 19a and 19b. Elution with 20:1 hexane–ethyl acetate furnished 197 mg (61%) of a colorless, oily, ca. 16:3:5:1 mixture of dihydrocarbazoles **18a** and **18b** and carbazoles **19a** and **19b**. Crystallization from acetone–hexane liberated a colorless, solid, ca. 5:1 mixture of dihydrocarbazoles **18a** and **18b**: UV, λ_{max} 210 nm (ϵ 21 300), 259 (10 700); IR, (C=C) 1610 (w), (SO_2) 1373 (s), 1176 (s) cm^{-1}; ^{1}H NMR, δ (**18a**) 1.88 (s, 3, 2-Me), 3.2–3.3 (m, 2, C-4 Hs), 3.57 (t, 1, J = 7.3 Hz, C-1 Hs), 5.62 (br s, 1, H-3), 7.2–8.2 (m, 9, aromatic Hs); δ (**18b**) 1.85 (s, 3, 3-Me), 3.1–3.2 (m, 2, C-4 Hs), 3.6–3.7 (m, 2, C-1 Hs), 5.62 (br s, 1, H-2), 7.1–8.3 (m, 9, aromatic Hs); ^{13}C NMR, δ (**18a**) 23.3 (Me), 23.4 (C-4), 30.7 (C-1), 114.2 (C-8), 115.8 (C-4a), 117.6 (C-3), 118.1 (C-5), 123.3 (C-7), 124.0 (C-6), 126.2 (o-C), 129.0 (C-5a), 129.1 (m-C), 129.8 (C-1a), 132.6 (C-2), 133.3 (p-C), 136.2 (ipso-C), 139.0 (C-8a).

Repeated crystallization (MeCOMe–hexane) of the mother liquor permitted the isolation of a colorless, solid, ca. 5:1 mixture of carbazoles **19a** and **19b**: UV, λ_{max} 224 nm (ϵ 37 800), 261 (14 400), 265 (14 300), 272 (12 300), 286 (10 700), 298 (6000), 309 (2800); IR, (C=C) 1625 (w), 1602 (w), (SO_2) 1372 (s), 1178 (s) cm^{-1}; ^{1}H NMR, δ (**19a**) 2.53

(s, 3, 2-Me), 7.15 (d, 1, J = 7.9 Hz, H-3), 7.2–7.4 (m, 3, H-6, m-C Hs), 7.3–7.5 (m, 3, H-7, p-H), 7.73 (d, 1, J = 7.9 Hz, H-4), 7.7–7.9 (m, 3, H-5, o-C Hs), 8.14 (s, 1, H-1), 8.28 (d, 1, J = 8.2 Hz, H-8); δ (**19b**) 2.45 (s, 3, 3-Me), 7.1–8.3 (m, 12, aromatic Hs); ^{13}C NMR, δ (**19a**) 22.1 (Me), 114.9 (C-8), 115.1 (C-1), 119.5 (C-4), 119.8 (C-5), 123.8 (C-6), 125.1 (C-3), 126.2 (o-C), 126.4 (C-5a), 126.7 (C-7), 128.3 (C-4a), 128.9 (m-C), 133.6 (p-C), 137.7 (C-1a, C-2, C-8a, or ipso-C), 137.8 (C-2, C-1a, C-8a, or ipso-C), 138.1 (C-8a, C-1a, C-2, or ipso-C), 138.6 (ipso-C, C-1a, C-2, or C-8a); MS, m/e 321 (M^+, 32), 180 (base); exact mass, m/e 321.0814, calcd for $C_{19}H_{15}NO_2S$ 321.0823.

More elution led to the recovery of 15 mg (5%) of starting indole **13b**.

A chloroform solution of 32 mg (0.1 mmol) of a 5:1 mixture of dihydrocarbazoles **18a** and **18b** and 22 mg (0.2 mmol) of *p*-benzoquinone was refluxed for 18 h and then evaporated. Chromatography of the residue and elution with 20:1 hexane–ethyl acetate yielded 28 mg (89%) of a solid, 5:1 mixture of carbazoles **19a** and **19b**, spectrally identical with the above sample.

Ketones 23a and 23b. Elution with 20:1 hexane–ethyl acetate produced 373 mg (95%) of a colorless, solid, ca. 2:1 mixture of ketones **23a** and **23b**: UV, λ_{max} 208 nm (ε 22 400), 223 (15 000), 268 (5000), 276 (6000), 290 (7000); IR, (C=O) 1661 (s), (C=C) 1605 (w), (SO_2) 1383 (s), 1171 (s) cm^{-1}; ^{1}H NMR, δ (**23a**) 0.92 (d, 3, J = 6.0 Hz, 6-Me), 1.71 (s, 3, 4′-Me), 1.7–1.9, 2.0–2.2 (m, 1 each, C-5′ Hs), 2.1–2.2 (m, 1, H-6′), 2.1–2.4 (m, 2, C-2′ Hs), 2.9–3.1 (m, 1, H-1′), 5.26 (br s, 1, H-3′), 7.3–8.4 (m, 9, aromatic Hs), 8.26 (s, 1, indole α-H); δ (**23b**) 0.90 (d, 3, J = 6.0 Hz, 6′-Me), 1.71 (s, 3, 3′-Me), 1.7–2.4 (m, 5, C-2′ and C-5′ Hs, H-6′), 3.1–3.2 (m, 1, H-1′), 5.26 (br s, 1, H-4′), 7.3–8.4 (m, 9, aromatic Hs), 8.28 (s, 1, indole α-H); ^{13}C NMR δ (**23a**) 19.8 (C-6′), 23.0 (C-4′), 30.2 (C-2′), 31.2 (C-6′), 38.5 (C-5′), 50.1 (C-1′), 112.8 (C-7), 119.1 (C-3′), 122.0 (C-3), 123.2 (C-4), 124.7 (C-5), 125.6 (C-6), 126.8 (o-C), 127.5 (C-3a), 129.4 (m-C), 131.6 (C-2), 133.4 (C-4′), 134.3 (p-C), 134.8 (C-7a), 137.2 (ipso-C), 200.4 (C=O); MS, m/e 393 (M^+, 12), 285 (24), 284 (base), 144 (36), 141 (34), 108 (25), 77 (55). Anal. Calcd for $C_{23}H_{23}NO_3S$: C, 70.20; H, 5.89; N, 3.56. Found: C, 70.60; H, 6.28; N, 3.42.

Ketones 23c, 23d, 24a, 24b, and 25b. Elution with 9:1 hexane–ethyl acetate gave 14 mg (3%) of a colorless, solid mixture of ketone **25b** and isomers: UV, λ_{max} 208 nm (ε 26 800), 262 (6200), 268 (6300), 274 (5800); IR, (C=O) 1702 (s), (C=C) 1598 (w), (SO_2) 1359 (s), 1172 (s) cm^{-1}; ^{1}H NMR, δ (**25b**) −0.09, 0.46 (s, 3 each, C-6′ methyls), 1.39 (d, 1, J = 17.3 Hz, H-5′), 1.49 (d, 1, J = 17.3 Hz, H-5′), 1.57 (s, 3, 2-Me), 1.74 (s, 3, 4′-Me), 1.81 (br d, 1, J = 18.2 Hz, H-2′), 1.96 (dd, 1, J = 18.2, 8.8 Hz, H-2′), 2.39 (dd, 1, J = 15.7, 4.4 Hz, H-4), 2.4–2.6 (m, 2, H-1, H-4), 2.60 (dd, 1, J = 15.0, 5.8 Hz, H-1), 2.76 (dd, 1, J = 8.8, 5.6 Hz, H-1′), 5.16 (br s, 1, H-3′), 5.23 (t, 1, J = 6.4 Hz, H-1a), 5.39 (br s, 1, H-3), 7.0–7.9 (m, 9, aromatic Hs); ^{13}C NMR δ (**25b**) 22.0 (ax 6′-Me), 23.4 (4′-Me), 27.5 (eq 6′-Me), 29.3 (C-2′), 32.6 (C-6′), 45.0 (C-5′), 47.0 (C-1′), 115.1 (C-8), 117.6 (C-3′), 123.4 (C-6), 125.5 (C-5), 129.1 (C-7), 132.9 (C-5a), 133.3 (C-4′), 142.1 (C-8a); MS, m/e 324 (M^+ − $C_9H_{15}CO$, base), 183 (37), 182 (67), 123 (34), 77 (23). Anal. Calcd for $C_{29}H_{33}NO_3S$: C, 73.22; H, 6.99; N, 2.94. Found: C, 73.48; H, 6.91; N, 3.02.

Further elution liberated 49 mg (13%) of a colorless, oily, ca. 2:1 mixture of ketones **23c** and **23d**: UV, λ_{max} 208 nm (ε 30 200), 268 (3700), 275 (4100), 290 (9000), (sh) 224 (20 400); IR, (C=O) 1661 (s), (C=C) 1609 (w), (SO_2) 1383 (s), 1181 (s) cm^{-1}; ^{1}H NMR, δ (**23c**) 0.96, 1.05 (s, 3 each, C-6′ methyls), 1.70 (s, 3, 4′-Me), 1.79, 2.05 (d, 1 each, J = 17.3 Hz, C-5′ Hs), 2.1–2.5 (m, 2, C-2′ Hs), 3.14 (dd, 1, J = 9.9, 5.2 Hz, H-1′), 5.41 (br s, 1, H-3′), 7.3–8.4 (m, 9, aromatic Hs), 8.24 (s, 1, indole α-H); δ (**23d**) 0.94, 1.02 (s, 3 each, C-6′ methyls), 1.70 (s, 3, 3′-Me), 1.6–2.5 (m, 4, C-2′ and C-5′ Hs), 3.24 (dd, 1, J = 10.0, 5.1 Hz, H-1′), 5.40 (br s, 1, H-4′), 7.3–8.4 (m, 9, aromatic Hs), 8.25 (s, 1, indole α-H); ^{13}C NMR, δ (**23c**) 21.9 (ax 6′-Me), 23.5 (4′-Me), 27.1 (C-2′), 29.7 (eq 6′-Me), 32.7 (C-6′), 46.0 (C-5′), 51.2 (C-1′), 112.9 (C-7), 118.4 (C-3′), 122.9 (C-3), 123.4 (C-4), 124.7 (C-5), 125.7 (C-6), 126.9 (o-C), 127.7 (C-3a), 129.4 (m-C), 131.5 (C-2), 132.8 (C-4′), 134.3 (p-C), 135.0 (C-7a), 137.5 (ipso-C), 199.5 (C=O); MS, m/e 407 (M^+, 35), 299 (27), 285 (22), 284 (base), 266 (23), 144 (29), 141 (22), 77 (51); exact mass, m/e 407.1556, calcd for $C_{24}H_{25}NO_3S$ 407.1555.

Next there was collected 72 mg (17%) of a colorless, solid mixture of ketones **24a** and **24b**: UV, λ_{max} 207 nm (ε 26 000), 245 (16 000); IR, (C=O) 1681 (s), (C=C) 1620 (w), (SO_2) 1362 (s), 1177 (s) cm^{-1}; ^{1}H NMR, δ (**24a**) 1.55, 1.91 (s, 3 each, acrylic methyls), 1.78 (2-Me), 2.24 (dd, 1, J = 14.9, 5.2 Hz, H-4), 2.5–2.7 (m, 3, C-1 Hs, H-4), 4.72 (t, 1, J = 5.5 Hz, H-1a), 5.43 (br s, 1, α-keto H), 5.48 (br s, 1, H-3), 7.0–7.8 (m, 9, aromatic Hs); δ (**24b**) 1.64, 1.93 (s, 3 each, acrylic methyls), 1.75 (s, 3, 3-Me), 2.17 (d, 1, J = 15.0 Hz, H-4), 2.5–2.7 (m, 3, C-1 Hs, H-4), 4.63 (t, 1, J = 5.6 Hz, H-1a), 5.38 (br s, 1, α-keto H), 5.58 (br s, 1, H-2), 7.0–7.8 (m, 9, aromatic Hs); ^{13}C NMR, δ (**24a**) 115.2 (C-8), 124.1 (C-5), 124.7 (C-6), 128.6 (C-7), 134.6 (C-5a), 142.4 (C-8a); MS, m/e 407 (M^+, 3), 325 (24), 324 (base), 183 (47), 182 (89), 168 (19), 167 (18), 83 (39), 77 (15). Anal. Calcd for $C_{24}H_{25}NO_3S$: C, 70.73; H, 6.18; N, 3.44. Found: C, 70.55; H, 6.26; N, 3.34.

Lastly, there appeared 213 mg (63%) of starting indole **21b**.

Ketones 24c and 24d. Elution with 4:1 hexane–ethyl acetate furnished 324 mg (72%) of starting indole **21c** and in previous fractions 121 mg (23%) of a yellowish, oily, ca 3:1 mixture of ketones **24c** and **24d**: UV, λ_{max} 210 nm (ε 32 800), 242 (13 100), 287 (5500); IR, (C=O) 1679 (s), (C=C) 1584 (w), (SO_2) 1355 (s), 1169 (s) cm^{-1}; ^{1}H NMR, δ (**24c**) 1.17, 1.84 (s, 3 each, acrylic methyls), 1.75 (2-Me), 2.4–2.6 (m, 2, C-4 Hs), 2.6–2.8 (m, 2, C-1 Hs), 4.96 (t, 1, J = 5.1 Hz, H-1a), 5.35 (br s, 1, H-3), 6.8–7.8 (m, 14, aromatic Hs); δ (**24d**) 1.26, 1.86 (s, 3 each, acrylic methyls), 1.52 (s, 3, 3-Me), 2.37 (d, 1, J = 14.4 Hz, H-4), 2.4–2.8 (m, 3, C-1 Hs, H-4), 4.92 (t, 1, J = 5.3 Hz, H-1a), 5.57 (br s, 1, H-2), 6.8–7.8 (m, 14, aromatic Hs); ^{13}C NMR δ (**24c**) 114.2 (C-8), 123.2 (C-5), 124.1 (C-6), 127.6 (C-7), 133.2 (C-5a), 142.1 (C-8a); MS, m/e 515 (M^+, 2), 325 (24), 324 (base), 323 (27), 183 (23), 182 (47), 163 (19), 77 (13); exact mass, m/e 515.1586, calcd for $C_{30}H_{29}NO_3S_2$ 515.1589.

Catalyzed Diels–Alder Reactions. A solution of 1.00 mmol of ketone **13c**, **21a**, or **21b** in 1 mL of dry benzene was added dropwise to a stirring suspension of 120 mg (0.90 mmol) of anhydrous aluminum chloride (only 40 mg for the **13c–2a** reaction) in 4 mL of dry benzene at room temperature (at 70 °C for the **13c–2a** reaction) and the stirring continued for 15 min (i.e., the period for the suspension to have changed into a clear, yellow solution). Then 820 mg (12.0 mmol) of isoprene (**2a**) was added and the solution stirred for 4, 6, or 24 h, respectively. It was poured into 100 mL of 5% sodium bicarbonate solution and extracted with methylene chloride. The extract was dried and evaporated. The residue was chromatographed.

Elution with 4:1 hexane–ethyl acetate afforded 106 mg (29%) of a colorless, oily, 24:1 mixture of adducts **14c** and **15c** (vide supra), 46 mg of material of unknown constitution, and 68 mg (23%) of starting indole **13c**.

Elution with 20:1 hexane–ethyl acetate gave 310 mg (79%) of colorless, solid, >9:1 mixture of indoles **23a** and **23b** (vide supra) and in earlier fractions 61 mg (13%) of a colorless, gummy, >4:1 mixture of ketone **25a** and isomers: UV, λ_{max} 208 nm (ε 27 800), 267 (5500), 273 (5300), 288 (3900); IR, (C=O) 1698 (s), (C=C) 1594 (w), (SO_2) 1358 (s), 1170 (s) cm^{-1}; ^{1}H NMR, δ (**25a**) −0.01 (d, 3, J = 6.7 Hz, 6′-Me), 1.55 (s, 3, 4′-Me), 1.5–1.9 (m, 4, C-2′ and C-5′ Hs), 1.70 (m, 1, H-6′), 1.75 (s, 3, 2-Me), 2.24 (dt, 1, J = 10.8, 4.8 Hz, H-1′), 2.33 (m, 1, H-4), 2.59 (m, 2, C-1 Hs), 2.64 (m, 1, H-4), 5.04 (t, 1, J = 6.0 Hz, H-9a), 5.10 (br s, 1, H-3′), 5.46 (br s, 1, H-3), 7.0–7.9 (m, 9, aromatic Hs); ^{13}C NMR, δ (**25a**) 19.0 (6′-Me), 22.9 (4′-Me), 31.6 (C-6′), 32.3 (C-2′), 38.0 (C-5′), 47.3 (C-1′), 115.1 (C-8), 119.0 (C-3′), 123.6 (C-6), 125.1 (C-5), 129.2 (C-7), 132.0 (C-4′), 132.7 (C-5a), 142.5 (C-8a); MS, m/e 461 (M^+, 2), 325 (24), 324 (base), 183 (33), 182 (68), 109 (19), 77 (19); exact mass, m/e 461.2053, calcd for $C_{28}H_{31}NO_3S$ 461.2024.

Elution with 10:1 hexane–ethyl acetate yielded 160 mg (39%) of a colorless, solid, >4:1 mixture of ketone **25b** and its isomers (vide supra), 56 mg (13%) of a colorless, solid, >9:1 mixture of indoles **23c** and **23d** (vide supra), 40 mg (10%) of a colorless, solid, >9:1 mixture of ketones **24a** and **24b** (vide supra), and 78 mg (23%) of starting indole **21b**.

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Note Added in Proof. The dienophilicity of β-acylindoles is reduced strongly by replacement of the *N*-phenylsulfonyl group by an *N*-acetyl unit, e.g., the reaction of 1-acetyl-**12a** with isoprene (**2a**) at 195 °C for 72 h leading to a ca. 2:1 mixture of the *N*-acetyl equivalents of **14a** and **15a** in 25% yield and to 66% recovery of starting indole (Wenkert, E.; Piettre, S. R., unpublished observation).