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Diels–Alder Reactions of 1,5-Dihydropyrano[3,4-*b*]pyrrol-5(1*H*)-ones, Pyrrole-2,3-quinodimethane Analogues; a New Synthesis of Indoles†

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Dedicated with respect and affection to Charles W. Rees, FRS, Hofmann Professor of Organic Chemistry at Imperial College, London, on the occasion of his sixty-fifth birthday.

Abstract: The pyrano[3,4-*b*]pyrrol-5(1*H*)-ones **7** are stable cyclic analogues of pyrrole-2,3-quinodimethane, and undergo Diels–Alder reaction with a range of acetylenes (dimethyl acetylenedicarboxylate, ethyl propiolate, ethyl trimethylsilylpropynoate, benzyne and the acetylene equivalent, phenyl vinyl sulfoxide), to give, after loss of carbon dioxide, indoles. The Diels–Alder reaction can be extended to the intramolecular variant to give cycloalka-[*e*]- and [*g*]-indoles.

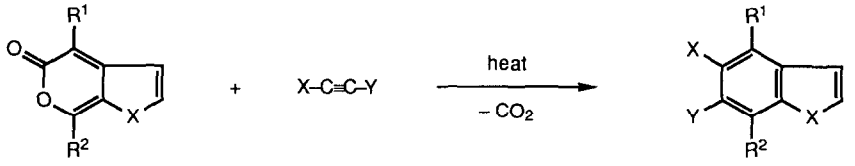
In the 120 years since Baeyer's first synthesis of indole,[1] this heteroaromatic compound has attracted much attention, not least because of the wide-ranging and potent biological activity of indoles, both synthetic and naturally occurring. Research in indole chemistry continues apace with many groups devoting considerable effort to developing new methods for the synthesis of, and functionalisation of, the indole ring system.[2] In continuation of our own interest in this area, we now report the details of a new synthesis of indoles based on the Diels–Alder reaction of pyrrole-2,3-quinodimethanes **1**.[3]

Although indole-2,3-quinodimethanes and stable cyclic analogues thereof are now quite well described,[4] little is known about the corresponding pyrroles **1**, although thiophene-2,3-quinodimethane **2** has been widely studied of late.[5] Therefore, based on our previous work with other heterocyclic analogues of orthoquinodimethane,[6] we chose to prepare the pyrrole fused α-pyrone system, 1,5-dihydropyrano[3,4-*b*]pyrrol-5(1*H*)-one, **3**, which by analogy with its thiophene analogue **4**, readily converted into benzothiophenes (Scheme 1, X = S),[7] would be expected to undergo Diels–Alder reaction with acetylenes to give, after loss of carbon dioxide, indoles. Although, indoles have been prepared from pyrroles before by a variety of routes, including cobalt mediated [2+2+2]-cycloadditions to the pyrrole 2,3-double bond,[8] intramolecular Friedel–Crafts reactions,[9–12] and Diels–Alder reactions involving 1-tosyl-2-vinylpyrrole as diene[13] and the 2,3-bond of 3-nitro-1-phenylsulfonylpyrrole as dienophile,[14] the present Diels–Alder route (Scheme 1, X = NSO_2Ph) is novel.

† *The initial part of this work was carried out in the Department of Chemistry, Imperial College, London SW7 2AY, U.K.*

1 X = NR
2 X = S

3 X = NSO_2Ph
4 X = S



Scheme 1

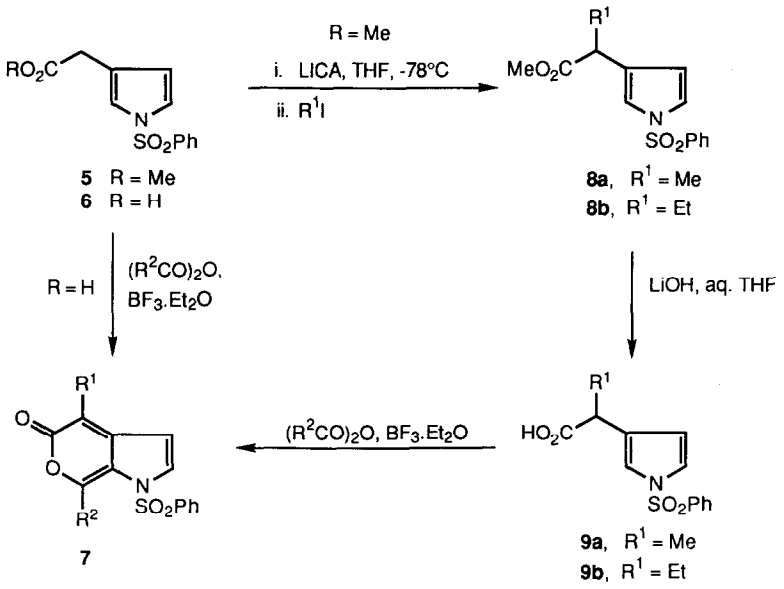
RESULTS AND DISCUSSION

Preparation of 1,5-Dihydropyrano[3,4-b]pyrrol-5(1H)-ones

Interestingly, highly substituted derivatives of the 1,5-dihydropyrano[3,4-*b*]pyrrol-5(1*H*)-one ring system have been prepared previously in poor yield by a multi-step sequence, although no Diels–Alder reactions were reported.[15] We found that the pyranopyrrolones **7b-g** could be prepared in modest yield simply by treating 1-phenylsulfonylpyrrole-3-acetic acid[16] **6** or its α-substituted derivatives **9** with the appropriate carboxylic acid anhydride in the presence of boron trifluoride diethyl ether. Thus, reaction of 1-phenylsulfonylpyrrol-3-ylacetic acid **6** with acetic anhydride in the presence of BF_3•Et_2O afforded 7-methyl-1-phenylsulfonylpyrano[3,4-*b*]pyrrol-5(1*H*)-one **7b** in 43% yield (Scheme 2). Similarly, treatment of the same acid with propionic anhydride, hexanoic anhydride, or isobutyric anhydride in the presence of BF_3•Et_2O gave the 7-ethyl **7c**, the 7-pentyl **7d**, and the 7-isopropyl **7e** substituted pyranopyrrolones in 36%, 33%, and 19% yield respectively.

The 4,7-disubstituted pyranopyrrolones **7f** and **7g** were prepared in a similar fashion. Alkylation of methyl 1-phenylsulfonylpyrrol-3-ylacetate **5** using lithium isopropylcyclohexylamide (LICA) as base, followed by quenching with methyl iodide or ethyl iodide gave the α-substituted esters **8a** and **8b** in 93% and 83% yield respectively. The esters were hydrolysed, with the 1-phenylsulfonyl group remaining intact, using lithium hydroxide hydrate, to give the α-substituted acids **9** in excellent yield. Treatment of the acids **9** with acetic anhydride in the presence of BF_3•Et_2O gave the 4,7-dimethyl substituted pyranopyrrolone **7f** in 25% yield and the 4-ethyl-7-methyl substituted pyranopyrrolone **7g** in 30% yield (Scheme 2).

The parent pyranopyrrolone **7a** was prepared by a slightly different route. Formylation of methyl 1-phenylsulfonylpyrrol-3-ylacetate **5**, using dichloromethyl methyl ether and tin(IV) chloride in dichloromethane, gave the 2-formyl compound along with its 5-substituted isomer as a 1:1 mixture in 92% yield. Since separation was not possible at this stage, hydrolysis of the mixture, using lithium hydroxide in aqueous THF, gave a 1:1 mixture of the corresponding carboxylic acids in 80% yield, followed by cyclodehydration, using isobutyl chloroformate and triethylamine in dry THF, and purification gave 1-phenylsulfonylpyrano[3,4-*b*]pyrrol-5(1*H*)-one **7a** in 21% yield (out of a maximum of 50% since it is based on the starting 1:1 mixture of acids).



7	R^1	R^2	
a	H	H	(prepared differently; see text)
b	H	Me	
c	H	Et	
d	H	Pentyl	
e	H	Pr^i	
f	Me	Me	
g	Et	Me	

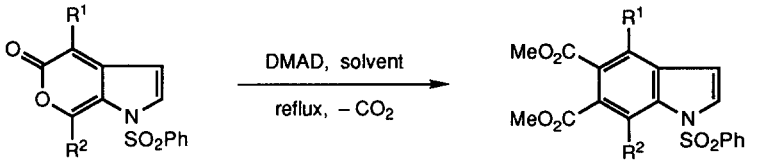
Scheme 2

Intermolecular Diels–Alder Reactions

On heating with the electron deficient acetylene, dimethyl acetylenedicarboxylate (DMAD), the pyranopyrrolones **7** underwent Diels–Alder reaction to give, after loss of carbon dioxide, the indole-5,6-diesters **10** (Table 1).

For the Diels-Alder reactions of the analogous benzothienopyranones[6g] and the thienopyranones,[7] bromobenzene had been the solvent of choice, its high boiling point offering fast reaction. However, with the pyranopyrrolones **7** decomposition competed with Diels-Alder reaction when the reactions were carried out in bromobenzene. The 7-methyl substituted pyranopyrrolone **7b** reacted with DMAD in good yield, at much lower temperature, in refluxing acetonitrile, although the same pyranopyrrolone reacted only very sluggishly with other dienophiles in this solvent, and therefore eventually, chlorobenzene was settled upon as the solvent of choice, its moderately high boiling point permitted reasonably fast reaction, while giving rise to less decomposition than the reaction in bromobenzene.

Table 1. *Diels–Alder reactions of pyranopyrrolones 7 with dimethyl acetylenedicarboxylate.*

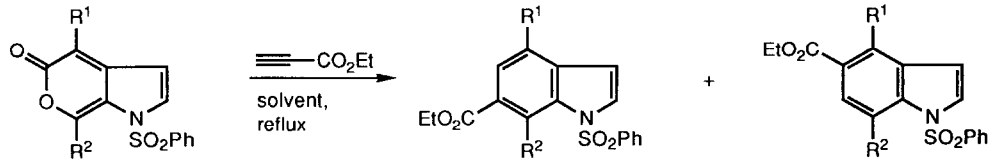


7 **10**

Compound	R^1	R^2	*Solvent*	*Time (h)*	*Product*	*Yield (%)*
7a	H	H	PhCl	4	**10a**	58
7b	H	Me	PhBr	24	**10b**	60
7b	H	Me	MeCN	15	**10b**	70
7d	H	Pentyl	PhBr	18	**10c**	51
7e	H	Pr^i	PhCl	30	**10d**	59
7f	Me	Me	PhCl	12	**10e**	71

As expected, the unsymmetrical acetylene, ethyl propiolate (EP), was generally not regioselective in its Diels-Alder reactions and gave inseparable mixtures of the indole-5-esters **12** and indole-6-esters **11** (Table 2). The reaction of the pyranopyrrolone **7b** with EP showed a slight preference for the formation of the 6-ester **11b**. The two isomers could be readily distinguished by NMR. The resonance occurring furthest downfield at δ8.11 was attributed to 4-H of the 5-ester **12b**. The resonances 4-H and 5-H of the 6-ester **11b** were obscured by other peaks, but both are expected to be doublets. Also the 7-Me group of the 6-ester **11b** resonates downfield at δ2.73 relative to that of the 5-ester **12b** (at δ2.56). The reaction of the pyranopyrrolone **7e** with EP gave predominantly the 5-ester **12d**, presumably as a result of the steric effect of the bulky isopropyl group. Again, the two isomers were distinguished by NMR; 4-H of the 5-ester **12d** was observed as a doublet (J 1.6 Hz) at δ8.08, whereas 4-H and 5-H of the 6-ester **11d** were observed as doublets (J 8 Hz) at δ7.30 and δ7.38 respectively.

Table 2. *Diels–Alder reactions of pyranopyrrolones 7 with ethyl propiolate.*



7 **11** **12**

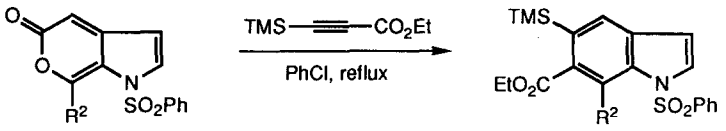
Compound	R^1	R^2	*Solvent*	*Time (h)*	*Product*	*Yield (%)*	*Ratio*
7a	H	H	PhCl	5	**11/12a**	61	1:1
7b	H	Me	PhBr	60	**11/12b**	56	1.6:1
7d	H	Pentyl	PhBr	24	**11/12c**	59	1:1
7e	H	Pr^i	PhCl	48	**11/12d**	49	1:5
7f	Me	Me	PhCl	12	**11/12e**	80	1:1

Ethyl 3-trimethylsilylpropynoate (ETMSP), however, underwent regioselective Diels-Alder reaction and gave the 5-trimethylsilylindole-6-esters **13** as the major products (Table 3). In the case of the unsubstituted pyranopyrrolone **7a** the 5-trimethylsilylindole-6-ester **13a** was the major product (2.5:1). The two isomers were distinguished by the resonances of 4-H and 7-H in their NMR spectrum; 7-H of the 6-ester **13a**, which is situated between two strongly electron withdrawing groups, resonated furthest downfield at δ8.67, and the 4-H occurred at δ7.84. In contrast, 4-H and 7-H of the minor 6-trimethylsilylindole-5-ester isomer coincided as a singlet at δ8.25.

The 7-alkyl substituted pyranopyrrolones **7b** and **7d** gave only a single isomer by 270 MHz NMR. These were assigned as the 5-trimethylsilylindole-6-esters **13b** and **13c** due to the resonance of 4-H, which in the case of the 7-methyl compound **13b** occurred at δ7.61 and in the case of the 7-pentyl compound **13c** occurred at δ7.59. Confirmation of the structure **13b** was obtained by protodesilylation which gave ethyl 7-methyl-1-phenylsulfonylindole-6-carboxylate **11b**, identical to the major isomer from Diels-Alder reaction of pyranopyrrolone **7b** with ethyl propiolate (Table 2).

Hence, the regiochemistry of the Diels-Alder reaction of 1-phenylsulfonylpyrano[3,4-*b*]pyrrol-5(1*H*)-ones **7** with unsymmetrical acetylenes, leads, in the absence of steric effects, to indoles with the electron withdrawing group at the 6-position, as expected for a cycloaddition which is 'controlled' by the pyrone ring oxygen, the pyrrolic nitrogen having no electronic effect because it bears a phenylsulfonyl group.

Table 3. *Diels–Alder reactions of pyranopyrrolones 7 with ethyl 3-trimethylsilylpropynoate.*



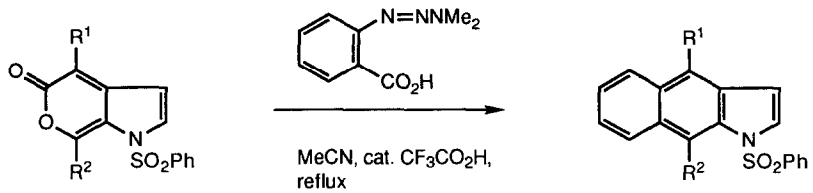
7 **13**

Compound	*R²*	*Time (h)*	*Product.*	*Yield (%)*
7a	H	24	**13a**	40*
7b	Me	96	**13b**	53
7d	Pentyl	120	**13c**	12

**Product is a 2.5:1 mixture of ethyl 1-phenylsulfonyl-5-trimethylsilylindole-6-carboxylate 13a and the isomeric ethyl 1-phenylsulfonyl-6-trimethylsilylindole-5-carboxylate*

The pyranopyrrolones **7** also reacted with benzyne, generated from 2-(3,3-dimethyltriazen-1-yl)benzoic acid,[17] to give benz[*f*]indoles **14** in good yield (Table 4), and with the acetylene equivalent, phenyl vinyl sulfoxide,[18] to give the 5,6-unsubstituted indoles **15** (Table 5).

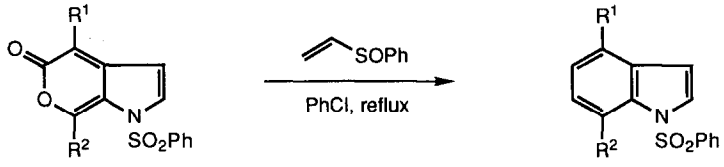
Table 4. *Diels–Alder reactions of pyranopyrrolones 7 with benzyne.*



7 14

Compound	R^1	R^2	*Time (h)*	*Product*	*Yield (%)*
7a	H	H	4	**14a**	49
7b	H	Me	5	**14b**	65
7d	H	Pentyl	12	**14c**	77
7f	Me	Me	12	**14d**	60

Table 5. *Diels–Alder reactions of pyranopyrrolones 7 with phenyl vinyl sulfoxide.*

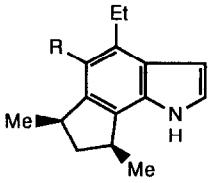


7 15

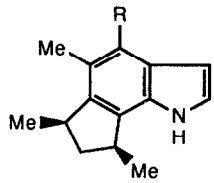
Compound	R^1	R^2	*Time (h)*	*Product*	*Yield (%)*
7b	H	Me	48	**15a**	60
7d	H	Pentyl	72	**15b**	44
7e	H	Pr^i	144	**15c**	20
7g	Et	Me	48	**15d**	60

Intramolecular Diels–Alder Reactions

In continuation of our interest in the intramolecular Diels–Alder (IMDA) reaction,[7,19] we also studied the IMDA reaction of 1-phenylsulfonylpyrano[3,4-*b*]pyrrol-5(1*H*)-ones as a route to cycloalkaindoles. The tetrahydrocyclopenta[*g*]indole ring system is present in a closely related series of natural products, namely the trikentrins **16**[20] and herbindoles **17**.[21] These compounds are of interest due to their unique structural characteristics and antimicrobial activity, the result of which is that a number of syntheses of trikentrins have been published recently.[22]

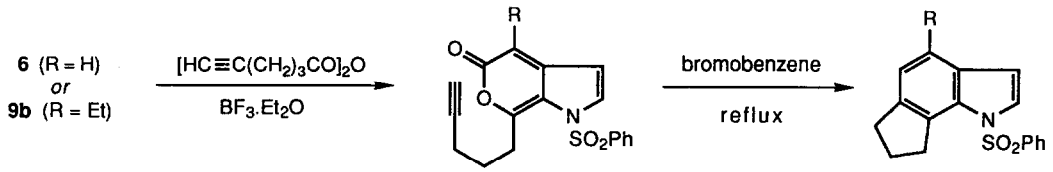


16
cis-trikentrin A, R = H
cis-trikentrin B, R = (E)-CH=CHEt



17
herbindole A, R = H
herbindole B, R = Et
herbindole C, R = (E)-CH=CHEt

Treatment of 1-phenylsulfonylpyrrol-3-ylacetic acid **6** with hex-5-ynoic anhydride[19] in the presence of BF_3•Et_2O gave the pyranopyrrolone **18a** as an unstable oil in 15% yield. On heating in bromobenzene, the pyranopyrrolone **18a** underwent smooth intramolecular Diels–Alder reaction to give, after loss of carbon dioxide, 1-phenylsulfonyl-1,6,7,8-tetrahydrocyclopenta[*g*]indole **19a** in 65% yield (Scheme 3). When a similar sequence of reactions was attempted on the ethyl substituted acid **9b**, isolation of the pyranopyrrolone **18b** proved difficult. However, heating the crude reaction mixture in acetic anhydride, followed by column chromatography, enabled 4-ethyl-1-phenylsulfonyl-1,6,7,8-tetrahydrocyclopenta[*g*]indole **19b** to be isolated, albeit in only 9% yield. Hence although the methodology leads to cycloalka[*g*]indoles, due to the low yielding pyranopyrrolone formation step, it was not progressed as a route to the trikentrins.

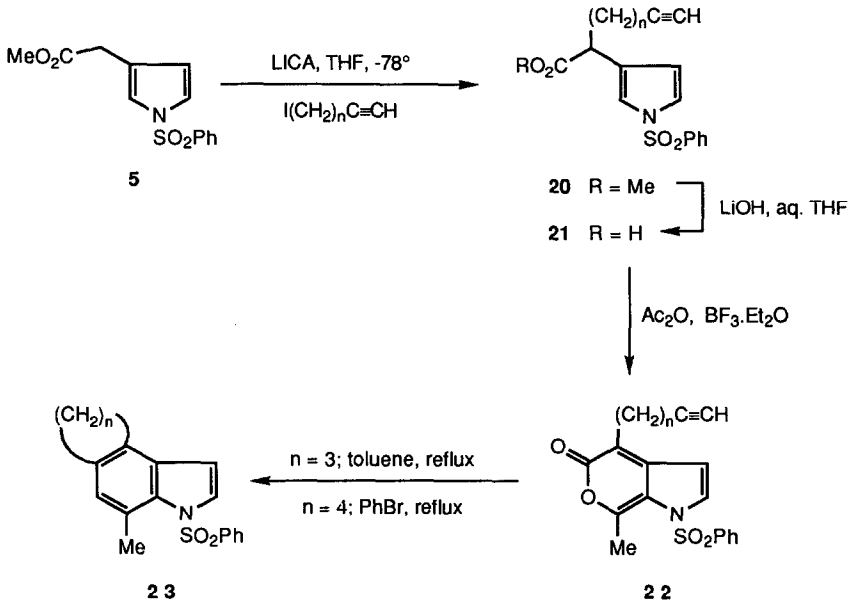


18a R = H
18b R = Et

19a R = H
19b R = Et

Scheme 3

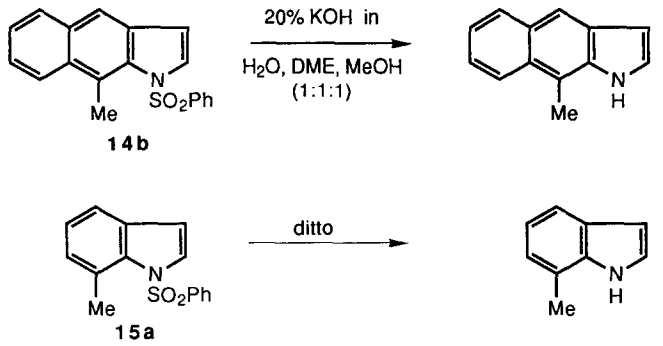
The preparation of cycloalka[*e*]indoles requires the 4-substituted pyranopyrrolones **22**, and these were synthesised using the same methodology developed in the thiophene series. Thus alkylation of methyl 1-phenylsulfonylpyrrol-3-ylacetate **5** with 5-iodopentyne[7] or 6-iodohexyne,[7] using LICA as base, gave the α-substituted esters **20a** and **20b** in 69% and 70% yield respectively. Hydrolysis of the esters **20**, using lithium hydroxide hydrate in aqueous THF, gave the α-substituted acids **21** in good yield. Treatment of the acid **21a** with acetic anhydride in the presence of BF_3•Et_2O gave the pyranopyrrolone **22a**, as an unstable oil, in 19% yield, which on refluxing in toluene underwent intramolecular cycloaddition to give, after loss of carbon dioxide, 8-methyl-1-phenylsulfonyl-1,4,5,6-tetrahydrocyclopenta[*e*]indole **23a** in 68% yield (Scheme 4). Similarly, treatment of the acid **21b** with acetic anhydride in the presence of BF_3•Et_2O gave the pyranopyrrolone **22b** as a stable crystalline solid in 16% yield. On heating in bromobenzene, the pyranopyrrolone **22b** underwent intramolecular cycloaddition to give, after loss of carbon dioxide, 9-methyl-1-phenylsulfonyl-4,5,6,7-tetrahydrobenz[*e*]indole **23b** in 78% yield.

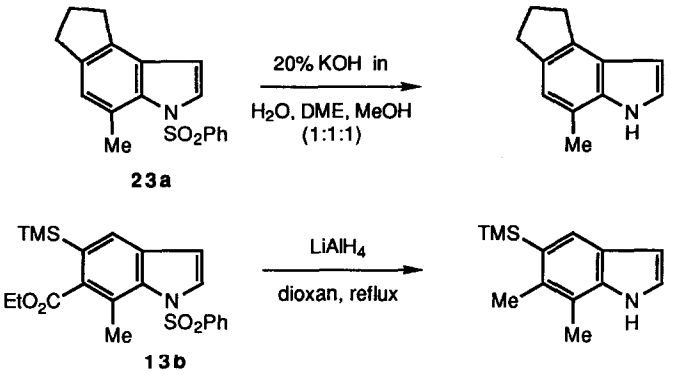


Scheme 4 (**a**, n = 3; **b**, n = 4)

Removal of the 1-Phenylsulfonyl Group

Since we were interested in developing this chemistry as a new route to indoles, it was necessary at some stage to remove the 1-phenylsulfonyl group. This could be accomplished by alkaline hydrolysis, using potassium hydroxide in a 1:1:1 mixture of methanol, 1,2-dimethoxyethane (DME) and water. Hence the *N*-phenylsulfonyl derivatives **14b**, **15a** and **23a** were converted into the corresponding indoles in 69%, 75%, and 97% yield respectively. The spectroscopic data of 7-methylindole so obtained showed good agreement with those reported in the literature.[23] Alternatively, the 1-phenylsulfonyl group could be reductively removed by reaction with lithium aluminium hydride in refluxing dioxan. This procedure also resulted in the reduction of an ester functionality to a methyl group. Hence, compound **13b** was reduced to the 6,7-dimethyl-5-trimethylsilylindole in 74% yield.





EXPERIMENTAL

For general experimental details see reference 6c.

Preparation of 1-Phenylsulfonylpyrano[3,4-*b*]pyrrol-5(1*H*)-ones

1-*Phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7a**

To a solution of the ester **5** (2.212 g, 7.92 mmol) and tin(IV) chloride (4.6 ml, 39.60 mmol) in dry dichloromethane (50 ml) at 0°C under nitrogen was added dichloromethyl methyl ether (0.93 ml, 10.3 mmol) dropwise with stirring. The mixture was allowed to warm to room temperature and stirred overnight. Dilute hydrochloric acid was added and the mixture extracted with ether. The combined extracts were washed with water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed [ether-light petroleum (4:1)] to give a mixture of *methyl* 2-*formyl*-1-*phenylsulfonylpyrrol*-3-*ylacetate* and *methyl* 2-*formyl*-1-*phenylsulfonylpyrrol*-4-*ylacetate* (2.239 g, 92%) in the ratio 1 to 1 as a yellow oil (Found: C, 54.75; H, 4.15; N, 4.6. $C_{14}H_{13}NO_5S$ requires C, 54.7; H, 4.3; N, 4.6%); ν_{max}(film) 1 740, 1 670, 1 376, and 1 176 cm^{-1}; δ (270 MHz; $CDCl_3$) 10.23 (1 H, s, CHO), 9.93 (1 H, s, CHO), 7.95-7.84 (m), 7.69-7.51 (m), 7.12 (1 H, d, *J* 2 Hz, 3-H, 2,4-isomer), 6.44 (1 H, d, *J* 3.2 Hz, 4-H, 2,3-isomer), 3.87 (2 H, s, CH_2CO_2Me, 2,3-isomer), 3.72 (3 H, s, CO_2Me), 3.68 (3 H, s, CO_2Me), and 3.51 (2 H, s, CH_2CO_2Me, 2,4-isomer); *m/z* 307 (M^+, 10%), 279 (15), 275 (2), 248 (7), 220 (9), 184 (9), 166 (21), 141 (27), and 77 (100).

A mixture of the above esters (2.078 g, 6.76 mmol) and lithium hydroxide monohydrate (1.42 g, 33.8 mmol) in tetrahydrofuran (30 ml) and water (30 ml) was stirred at 0°C for 1 h. Water (100 ml) was added, the mixture extracted with ethyl acetate and the ethyl acetate layer discarded. The aqueous layer was acidified and extracted with ethyl acetate. The combined extracts were washed with water, brine, and dried ($MgSO_4$). The solvent was evaporated to give 2-*formyl*-1-*phenylsulfonylpyrrol*-3-*ylacetic acid* and 2-*formyl*-1-*phenylsulfonylpyrrol*-4-*ylacetic acid* (1.586 g, 80%) in the ratio 1 to 1 as a yellow oil (Found: M^+, 293.0358. $C_{13}H_{11}NO_5S$ requires *M*, 293.0358); ν_{max}(film) 3 200-2 400, 1 714, 1 669, 1 376, and 1 178 cm^{-1}; δ[270 MHz; $(CD_3)_2CO$] 10.18 (1 H, s, CHO), 9.94 (1 H, s, CHO), 8.07-8.02 (m), 7.79-7.65 (m), 7.21 (1 H, d, *J* 2 Hz, 3-H, 2,4-isomer), 6.57 (1 H, d, *J* 3.2 Hz, 4-H, 2,3-isomer), 3.84 (2 H, s, CH_2CO_2H, 2,3-isomer), and 3.57 (2 H, s, CH_2CO_2H, 2,4-isomer); *m/z* 293 (M^+, 5%), 275 (1), 249 (9), 153 (21), 141 (16), 108 (63), and 77 (100).

Triethylamine (2.15 ml, 15.33 mmol) was added to a solution of the above acids (1.50 g, 5.11 mmol) in tetrahydrofuran (100 ml) at 0°C. Isobutyl chloroformate (1.46 ml, 11.24 mmol) in tetrahydrofuran (10 ml) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into brine, extracted with ethyl acetate, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed (ether) to give the *title compound* **7a** (294 mg, 21%), m.p. 129-135°C (decomp.) (Found: C, 56.5; H, 3.3; N, 5.1. $C_{13}H_9NO_4S$ requires C, 56.7; H, 3.3; N, 5.1%); $\nu_{max}(CH_2Cl_2)$ 1 718 cm^{-1}; λ_{max}(EtOH) 215 (ε 19 500), 261 (5 300), and 380 nm (7 000); δ[270 MHz; $(CD_3)_2SO$]

8.52 (1 H, dd, *J* 1.4, 0.7 Hz, 7-H), 8.02 (2 H, d, *J* 8 Hz), 7.99 (1 H, d, *J* 3.5 Hz, 2-H), 7.77 (1 H, t, *J* 8 Hz), 7.65 (2 H, t, *J* 8 Hz), 6.05 (1 H, d, *J* 3.5 Hz, 3-H), and 6.15 (1 H, d, *J* 1.2 Hz, 4-H); *m/z* 275 (M^+, 84%), 247 (5), 141 (37), 134 (100), and 77 (86).

7-Methyl-1-phenylsulfonylpyrano[3,4-b]*pyrrol-5*(1H)*-one* **7b**

Boron trifluoride diethyl ether (0.2 ml) was added dropwise to a stirred, ice-cooled mixture of 1-phenylsulfonylpyrrol-3-ylacetic acid **6** (360 mg, 1.35 mmol) and acetic anhydride (0.5 ml) in ether (3 ml). The mixture was stirred at room temperature for 6 h, diluted with ether, and filtered. The solid was washed with ether, sodium hydrogen carbonate solution, water, and dried under vacuum to give the *title compound* **7b** (168 mg, 43%), m.p. 157-162°C (Found: C, 58.1; H, 3.8; N, 4.8. $C_{14}H_{11}NO_4S$ requires C, 58.1; H, 3.8; N, 4.8%); ν_{max}(Nujol) 1 704 cm^{-1}; δ[270 MHz; $(CD_3)_2CO$] 7.84 (2 H, d, *J* 7 Hz), 7.79 (1 H, d, *J* 3.9 Hz, 2-H), 7.72 (1 H, t, *J* 7.5 Hz), 7.62 (2 H, t, *J* 7.5 Hz), 6.50 (1 H, d, *J* 3.7 Hz, 3-H), 5.83 (1 H, s, 4-H), and 2.66 (3 H, s, 7-Me); *m/z* 289 (M^+, 18%), 148 (100), 77 (30) and 43 (39).

7-Ethyl-1-phenylsulfonylpyrano[3,4-b]*pyrrol-5*(1H)*-one* **7c**

Boron trifluoride diethyl ether (1.05 ml, 8.5 mmol) was added dropwise to a stirred, ice-cooled mixture of 1-phenylsulfonylpyrrol-3-ylacetic acid **6** (1.50 g, 5.65 mmol) and propionic anhydride (1.8 ml, 14.1 mmol) in ether (12 ml). The mixture was stirred at room temperature for 48 h, partitioned between water and ethyl acetate, and the aqueous phase extracted with ethyl acetate. The combined extracts were washed with sodium hydrogen carbonate solution, water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed (ether) to give the *title compound* **7c** (609 mg, 36%), m.p. 92-95°C (Found: C, 59.15; H, 4.3; N, 4.6. $C_{15}H_{13}NO_4S$ requires C, 59.4; H, 4.3; N, 4.6%); ν_{max}($CHCl_3$) 1 702, 1 570, 1 378, and 1 176 cm^{-1}; δ (250 MHz; $CDCl_3$) 7.65-7.47 (6 H, m), 6.28 (1 H, d, *J* 3.9 Hz, 3-H), 5.89 (1 H, s, 4-H), 3.07 (2 H, q, *J* 7.4 Hz, CH_2CH_3), and 1.26 (3 H, t, *J* 7.4 Hz, CH_2CH_3); *m/z* 303 (M^+, 15%), 162 (97), and 77 (100).

7-Pentyl-1-phenylsulfonylpyrano[3,4-b]*pyrrol-5*(1H)*-one* **7d**

Boron trifluoride diethyl ether (0.15 ml) was added dropwise to a solution of the acid **6** (200 mg, 0.76 mmol) in hexanoic anhydride (0.35 ml) and ether (2 ml) at room temperature and the resulting mixture was stirred for 24 h. Water was added and the mixture extracted with ether. The combined extracts were washed with saturated sodium hydrogen carbonate solution, water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed (ether) to give the *title compound* **7d** (85 mg, 33%), m.p. 79-82°C (Found: C, 62.6; H, 5.5; N, 4.15. $C_{18}H_{19}NO_4S$ requires C, 62.6; H, 5.5; N, 4.1%); ν_{max}($CHCl_3$) 1 708, 1 381, and 1 177 cm^{-1}; λ_{max}(EtOH) 209 (ε 21 400), 211 (21 800), and 376 nm (9 980); δ (270 MHz; $CDCl_3$) 7.68-7.61 (3 H, m), 7.60 (1 H, d, *J* 3.9 Hz, 2-H), 7.53-7.48 (2 H, m), 6.27 (1 H, d, *J* 3.9 Hz, 3-H), 5.88 (1 H, s, 4-H), 3.02 (2 H, t, *J* 7.8 Hz, allylic CH_2), 1.65 (2 H, m), 1.30 (4 H, m), and 0.89 (3 H, t, *J* 7 Hz, pentyl CH_3); *m/z* 345 (M^+, 53%), 204 (33), 192 (38), 176 (19), 148 (100), and 77 (80).

7-Isopropyl-1-phenylsulfonylpyrano[3,4-b]*pyrrol-5*(1H)*-one* **7e**

Boron trifluoride diethyl ether (0.6 ml, 4.7 mmol) was added dropwise to a solution of the acid **6** (624 mg, 2.35 mmol) in isobutyric anhydride (1.2 ml, 7.1 mmol) and ether (2 ml) at 0°C. The mixture was allowed to warm to room temperature and stirred for 20 h. Water was added and the mixture extracted with ethyl acetate. The combined extracts were washed with saturated sodium hydrogen carbonate solution, water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed (ether) to give the *title compound* **7e** (144 mg, 19%), m.p. 136-142°C (Found: C, 60.2; H, 4.7; N, 4.3. $C_{16}H_{15}NO_4S$ requires C, 60.55; H, 4.8; N, 4.4%); ν_{max}($CHCl_3$) 1 708, 1 568, 1 380, 1 172, and 1 130 cm^{-1}; λ_{max}(EtOH) 376 (ε 9 830) nm; δ (250 MHz; $CDCl_3$) 7.66-7.62 (4 H, m), 7.55-7.49 (2 H, m), 6.29 (1 H, d, *J* 3.9 Hz, 3-H), 5.90 (1 H, s, 4-H), 3.84 (1 H, heptet, *J* 6.7 Hz, isopropyl CH), and 1.22 (6 H, d, *J* 6.7 Hz, isopropyl CH_3); *m/z* 317 (M^+, 36%), 176 (56), 77 (93), and 69 (100).

Methyl 2-(1-*Phenylsulfonylpyrrol-3-yl*)*propanoate* **8a**

n-Butyllithium (1.5 M, 1.67 ml) was added dropwise to a solution of *N*-isopropylcyclohexylamine (0.41 ml, 2.51 mmol) in dry tetrahydrofuran (15 ml) at -78°C under nitrogen. The mixture was warmed to 0°C, stirred for 5 min, and recooled to -78°C. A solution of the ester **5** (637 mg, 2.28 mmol) in dry tetrahydrofuran (5 ml) was added dropwise and the resulting solution stirred at -78°C for 2 h. Methyl iodide (2 ml) was added, the mixture allowed to warm to room temperature, and stirred

overnight. Water (50 ml) was added and the mixture extracted with ether. The combined ether extracts were washed with water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed [ether-light petroleum (1:1)] to give the *title compound* **8a** (620 mg, 93%) as a colourless oil (Found: C, 57.2; H, 5.4; N, 4.65. $C_{14}H_{15}NO_4S$ requires C, 57.3; H, 5.15; N, 4.8%); ν_{max}(film) 3 140, 1 738, 1 371, 1 176, 1 063 and 729 cm^{-1}; δ (270 MHz; $CDCl_3$) 7.85 (2 H, d, *J* 8 Hz), 7.58 (1 H, t, *J* 7 Hz), 7.50 (2 H, t, *J* 7 Hz), 7.12-7.05 (2 H, m, 2-H + 5-H), 6.28 (1 H, dd, *J* 3.2, 1.7 Hz, 4-H), 3.66 (3 H, s, CO_2Me), 3.59 (1 H, q, *J* 7 Hz, $CHCO_2Me$), and 1.41 (3 H, d, *J* 7 Hz, CH_3CH); *m/z* 293 (M^+, 26%), 234 (100), 141 (20), and 77 (51).

2-(1-*Phenylsulfonylpyrrol*-3-*yl*)*propionic Acid* **9a**

A mixture of the ester **8a** (530 mg, 1.81 mmol) and lithium hydroxide hydrate (380 mg, 9.03 mmol) in tetrahydrofuran (5 ml) and water (5 ml) was stirred at room temperature for 20 h. Water (20 ml) was added, the mixture extracted with ethyl acetate, and this extract discarded. The aqueous layer was acidified and extracted with ethyl acetate. The combined extracts were washed with water, brine, and dried ($MgSO_4$). The solvent was evaporated to give the *title compound* **9a** (489 mg, 97%), m.p. 100-104°C (Found: M^+, 279.0565. $C_{13}H_{13}NO_4S$ requires *M*, 279.0565); ν_{max}(Nujol) 3 200-2 400, 1 713, 1 371, 1 176, 1 110, 1 064, and 729 cm^{-1}; δ (270 MHz; $CDCl_3$) 7.87-7.83 (2 H, m), 7.63-7.57 (1 H, m), 7.54-7.47 (2 H, m), 7.12-7.08 (2 H, m, 2-H + 5-H), 6.31 (1 H, dd, *J* 4.2, 2.0 Hz, 4-H), 3.61(1 H, q, *J* 7.3 Hz, $CHCO_2H$), and 1.44 (3 H, d, *J* 7.3 Hz, CH_3CH); *m/z* 279 (M^+, 40%), 234 (100), 141 (26), 94 (28), and 77 (77).

4,7-*Dimethyl*-1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7f**

Boron trifluoride diethyl ether (0.41 ml, 3.3 mmol) was added dropwise to a stirred solution of the acid **9a** (467 mg, 1.67 mmol) in acetic anhydride (0.63 ml, 6.7 mmol) and ether (2 ml) at 0°C. The mixture was allowed to warm to room temperature and stirred for 15 h. Water (30 ml) was added and the mixture extracted with ethyl acetate. The combined extracts were washed with saturated aqueous sodium hydrogen carbonate solution, water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed (ether) to give the *title compound* **7f** (129 mg, 25%), m.p. 193-196 °C (Found: C, 59.2; H, 4.2; N, 4.5. $C_{15}H_{13}NO_4S$ requires C, 59.4; H, 4.3; N, 4.6%); ν_{max}(Nujol) 1 690, 1 379, and 1 182 cm^{-1}; λ_{max}(EtOH) 214 (ε 21 780), 325 (3 110), 369 (9 400), and 377 nm (8 550); δ (270 MHz; $CDCl_3$) 7.68-7.60 (3 H, m), 7.56 (1 H, d, *J* 3.9 Hz, 2-H) 7.53-7.50 (2 H, m), 6.32 (1 H, d, *J* 3.9 Hz, 3-H), 2.65 (3 H, d, *J* 0.7 Hz, 7-Me), and 2.04 (3 H, s, 4-Me); *m/z* 303 (M^+, 14%), 162 (100), 92 (31), 77 (25), and 43 (39).

Methyl 2-(1-*Phenylsulfonylpyrrol*-3-*yl*)*butanoate* **8b**

n-Butyllithium (1.45 M, 7.20 ml) was added to a solution of *N*-isopropylcyclohexylamine (1.47 g, 10.44 mmol) in dry tetrahydrofuran (50 ml) under nitrogen at -78°C. The mixture was allowed to warm to 0°C, stirred for 5 min, and recooled to -78°C. The ester **5** (2.65 g, 9.49 mmol) in dry tetrahydrofuran (20 ml) was added dropwise and the mixture stirred for 2 h. Ethyl iodide (5 ml) was added and the mixture allowed to warm to room temperature. After stirring overnight, the mixture was poured into brine and extracted with ethyl acetate. The combined organic extracts were washed with water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed [ether-light petroleum (1:1)] to give the *title compound* **8b** (2.425 g, 83%) as a colourless oil (Found: C, 58.7; H, 5.6; N, 4.3. $C_{15}H_{17}NO_4S$ requires C, 58.6; H, 5.6; N, 4.6%); ν_{max}(film) 3 140, 1 734, 1 370, 1 178, and 1 064 cm^{-1}; δ (250 MHz; $CDCl_3$) 7.86-7.82 (2 H, m), 7.60-7.57 (1 H, m), 7.53-7.47 (2 H, m), 7.11-7.06 (2 H, m, 2-H + 5-H), 6.28 (1 H, dd, *J* 3.2, 1.7 Hz, 4-H), 3.65 (3 H, s, CO_2Me), 3.35 (1 H, t, *J* 7.5 Hz, $CHCO_2Me$), 1.96-1.88 (1 H, m), 1.75-1.64 (1 H, m), and 0.85 (3 H, t, *J* 7.4 Hz, CH_2CH_3); *m/z* 307 (M^+, 26%), 278 (9), 248 (100), 141 (22), 106 (14), and 77 (68).

2-(1-*Phenylsulfonylpyrrol*-3-*yl*)*butanoic Acid* **9b**

A mixture of the ester **8b** (2.217 g, 7.21 mmol) and lithium hydroxide hydrate (1.51 g, 36.06 mmol) in tetrahydrofuran (10 ml) and water (10 ml) was stirred at room temperature for 24 h. Water was added, the mixture extracted with ethyl acetate, and this extract discarded. The aqueous phase was acidified with dilute hydrochloric acid and extracted with ethyl acetate. The combined extracts were washed with water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue triturated with light petroleum to give the *title compound* **9b** (1.736 g, 82%), m.p. 80°C (Found: C, 57.1; H, 5.1; N, 4.7. $C_{14}H_{15}NO_4S$ requires C, 57.3; H, 5.15; N, 4.8%); ν_{max}(film) 1 700, 1 462, 1 374, 1 170, and 1 064 cm^{-1}; δ (250 MHz; $CDCl_3$) 7.85-7.82 (2 H, m), 7.60 (1 H, t, *J* 7 Hz), 7.49 (2 H, t, *J* 7.5 Hz), 7.10 (2 H, m, 2-H + 5-H), 6.29 (1 H, t, *J* 2.4 Hz, 4-H), 3.35 (1 H, t, *J*

7.5 Hz, $CHCO_2H$), 2.01-1.90 (1 H, m), 1.77-1.66 (1 H, m), and 0.87 (3 H, t, *J* 7.4 Hz, CH_2CH_3); *m/z* 293 (M^+, 43%), 264 (14), 248 (93), 220 (7), 141 (34), and 77 (100).

4-Ethyl-7-methyl-1-phenylsulfonylpyrano[3,4-b]pyrrol-5(1H)-one **7g**

Boron trifluoride diethyl ether (0.16 ml, 1.34 mmol) was added dropwise to a solution of the acid **9b** (196 mg, 0.67 mmol) in acetic anhydride (0.25 ml, 2.67 mmol) and ether (1 ml) at 0°C. The mixture was allowed to warm to room temperature and stirred overnight. Water was added and the mixture extracted with ethyl acetate. The combined extracts were washed with saturated sodium hydrogen carbonate solution, water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed (ether) to give a yellow oil, trituration of which with ether-light petroleum gave the *title compound* **7g** (63 mg, 30%), m.p. 178-181°C (Found: M^+, 317.0706. $C_{16}H_{15}NO_4S$ requires *M*, 317.0722); ν_{max}(Nujol) 1 686, 1 652, 1 582, 1 374, 1 176, and 1 132 cm^{-1}; λ_{max}(EtOH) 377 (ε 9 110) nm; δ (250 MHz; $CDCl_3$) 7.69-7.60 (3 H, m), 7.57 (1 H, d, *J* 4.1 Hz, 2-H), 7.54-7.47 (2 H, m), 6.34 (1 H, d, *J* 3.8 Hz, 3-H), 2.65 (3 H, s, 7-Me), 2.47 (2 H, q, *J* 7.5 Hz, CH_2CH_3), and 1.08 (3 H, t, *J* 7.5 Hz, CH_2CH_3); *m/z* 317 (M^+, 20%), 176 (100), 77 (37), and 43 (35).

Intermolecular Diels–Alder Reactions of 1-Phenylsulfonylpyrano[3,4-*b*]pyrrol-5(1*H*)-ones 7

1. Dimethyl acetylenedicarboxylate (DMAD)

With 1-phenylsulfonylpyrano[3,4-b]pyrrol-5(1H)-one **7a**

A mixture of the pyranopyrrolone **7a** (41 mg, 0.15 mmol) and DMAD (42 mg, 0.30 mmol) in chlorobenzene (5 ml) was refluxed for 4 h. The solvent was evaporated and the residue chromatographed [ether-light petroleum (4:1)] to give *dimethyl 1-phenylsulfonylindole-5,6-dicarboxylate* **10a** (32 mg, 58%), m.p. 129-130°C (Found: C, 57.65; H, 4.0; N, 3.8. $C_{18}H_{15}NO_6S$ requires C, 57.9; H, 4.05; N, 3.75%); ν_{max}($CHCl_3$) 1 724, 1 307, and 1 118 cm^{-1}; δ (270 MHz; $CDCl_3$) 8.40 (1 H, s, 7-H), 7.91-7.87 (3 H, m), 7.72 (1 H, d, *J* 3.7 Hz, 2-H), 7.59-7.56 (1 H, m), 7.50-7.45 (2 H, m), 6.74 (1 H, d, *J* 3.7 Hz, 3-H), 3.95 (3 H, s, CO_2Me), and 3.90 (3 H, s, CO_2Me); *m/z* 373 (M^+, 100%), 342 (61), 201 (77), 141 (15), and 77 (45).

With 7-methyl-1-phenylsulfonylpyrano[3,4-b]pyrrol-5(1H)-one **7b**

(a) Similarly the pyranopyrrolone **7b** (66 mg, 0.23 mmol), and DMAD (65 mg, 0.46 mmol) in bromobenzene (10 ml) gave *dimethyl 7-methyl-1-phenylsulfonylindole-5,6-dicarboxylate* **10b** (53 mg, 60%), m.p. 108-112°C, (Found: C, 58.8; H, 4.4; N, 3.5. $C_{19}H_{17}NO_6S$ requires C, 58.9; H, 4.4; N, 3.6%); ν_{max}(Nujol) 1 729, 1 278, and 1 188 cm^{-1}; δ (270 MHz; $CDCl_3$) 8.11 (1 H, s, 4-H), 7.92 (1 H, d, *J* 3.4 Hz, 2-H), 7.66 (2 H, d, *J* 8 Hz), 7.57 (1 H, t, *J* 7.5 Hz), 7.47 (2 H, t, *J* 7.5 Hz), 6.76 (1 H, d, *J* 3.4 Hz, 3-H), 3.92 (3 H, s, CO_2Me), 3.88 (3 H, s, CO_2Me), and 2.49 (3 H, s, 7-Me); *m/z* 387 (M^+, 34%), 356 (14), and 77 (100).

(b) A mixture of the pyranopyrrolone **7b** (16 mg, 0.055 mmol), and DMAD (15 mg, 0.11 mmol) in acetonitrile (2 ml) gave *dimethyl 7-methyl-1-phenylsulfonylindole-5,6-dicarboxylate* **10b** (15 mg, 70%), data given above.

With 7-pentyl-1-phenylsulfonylpyrano[3,4-b]pyrrol-5(1H)-one **7d**

Similarly the pyranopyrrolone **7d** (44 mg, 0.13 mmol) and DMAD (36 mg, 0.25 mmol) in bromobenzene (5 ml) gave *dimethyl 7-pentyl-1-phenylsulfonylindole-5,6-dicarboxylate* **10c** (29 mg, 51%), m.p. 103-106°C (Found: M^+, 443.1404. $C_{23}H_{25}NO_6S$ requires *M*, 443.1403); ν_{max}($CHCl_3$) 1 724, 1 297, and 1 190 cm^{-1}; δ (270 MHz; $CDCl_3$) 8.07 (1 H, s, 4-H), 7.93 (1 H, d, *J* 3.9 Hz, 2-H), 7.64-7.55 (3 H, m), 7.47-7.41 (2 H, m), 6.76 (1 H, d, *J* 3.7 Hz, 3-H), 3.91 (3 H, s, CO_2Me), 3.87 (3 H, s, CO_2Me), 2.99 (2 H, m, benzylic CH_2), 1.6 (2 H, m), 1.2 (4 H, m), and 0.85 (3 H, m, pentyl CH_3); *m/z* 443 (M^+, 20%), 412 (31), 411 (28), 368 (66), 270 (40), 149 (100), and 77 (40).

With 7-isopropyl-1-phenylsulfonylpyrano[3,4-b]pyrrol-5(1H)-one **7e**

Similarly the pyranopyrrolone **7e** (57 mg, 0.18 mmol) and DMAD (51 mg, 0.36 mmol) in chlorobenzene (5 ml) gave *dimethyl 7-isopropyl-1-phenylsulfonylindole-5,6-dicarboxylate* **10d** (44 mg, 59%), m.p. 109-113°C (Found: C, 60.5; H, 5.1; N, 3.3. $C_{21}H_{21}NO_6S$ requires C, 60.7; H, 5.1; N, 3.4%); ν_{max}(Nujol) 3 164, 1 730, 1 450, 1 376, 1 298, and 1 266

cm^{-1}; δ (250 MHz; $CDCl_3$) 8.08 (1 H, s, 4-H), 7.93 (1 H, d, *J* 3.8 Hz, 2-H), 7.66 (2 H, d, *J* 7.3 Hz), 7.60 (1 H, t, *J* 7.3 Hz), 7.49 (2 H, t, *J* 7.4 Hz), 6.73 (1 H, d, *J* 3.8 Hz, 3-H), 4.01 (1 H, heptet, *J* 7.1 Hz, isopropyl CH), 3.88 (6 H, s, CO_2Me), and 1.09 (6 H, d, *J* 7.1 Hz, isopropyl CH_3); *m/z* 415 (M^+, 14%), 384 (13), 242 (100), 183 (18), and 77 (37).

With 4,7-*dimethyl*-1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7f**

Similarly the pyranopyrrolone **7f** (30 mg, 0.10 mmol) and DMAD (28 mg, 0.20 mmol) in chlorobenzene (5 ml) gave *dimethyl* 4,7-*dimethyl*-1-*phenylsulfonylindole*-5,6-*dicarboxylate* **10e** (28 mg, 71%) as a colourless oil (Found: M^+, 401.0933. $C_{20}H_{19}NO_6S$ requires *M*, 401.0933); ν_{max}($CHCl_3$) 1 729, 1 372, and 1 175 cm^{-1}; δ (270 MHz; $CDCl_3$) 7.91 (1 H, d, *J* 3.9 Hz, 2-H), 7.67-7.63 (2 H, m), 7.61-7.55 (1 H, m), 7.49-7.43 (2 H, m), 6.80 (1 H, d, *J* 3.9 Hz, 3-H), 3.86 (3 H, s, CO_2Me), 3.84 (3 H, s, CO_2Me), 2.53 (3 H, s, ArMe), and 2.50 (3 H, s, ArMe); *m/z* 401 (M^+, 23%), 370 (17), 369 (14), 304 (21), 228 (100), and 77 (25).

2. Ethyl propiolate (EP)

With 1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7a**

A mixture of the pyranopyrrolone **7a** (45 mg, 0.16 mmol) and EP (80 mg, 0.80 mmol) in chlorobenzene (5 ml) was refluxed for 5 h. The solvent was evaporated and the residue chromatographed [ether-light petroleum (2:1)] to give a mixture of *ethyl* 1-*phenylsulfonylindole*-5-*carboxylate* **12a** and *ethyl* 1-*phenylsulfonylindole*-6-*carboxylate* **11a** (33 mg, 61%) in the ratio 1 to 1, m.p. 98-105 °C (Found: C, 62.0; H, 4.55; N, 4.15. $C_{17}H_{15}NO_4S$ requires C, 62.0; H, 4.6; N, 4.25%); ν_{max}(Nujol) 3 142, 1 713, 1 376, 1 289, and 1 175 cm^{-1}; δ (270 MHz; $CDCl_3$) 8.69 (1 H, s, 7-H, 6-ester), 8.27 (1 H, s, 4-H, 5-ester), 8.02 (2 H, s), 7.95-7.87 (m, both isomers), 7.71 (1 H, d, *J* 3.7 Hz, 2-H), 7.63 (1 H, d, *J* 3.7 Hz, 2-H), 7.57-7.42 (m, both isomers), 6.73 (1 H, d, *J* 3.7 Hz, 3-H), 6.70 (1 H, dd, *J* 3.7, 1.0 Hz, 3-H), 4.42 (2 H, q, *J* 7.1 Hz, ester CH_2), 4.38 (2 H, q, *J* 7.1 Hz, ester CH_2), 1.43 (3 H, t, *J* 7.1 Hz, ester CH_3), and 1.39 (3 H, t, *J* 7.1 Hz, ester CH_3); *m/z* 329 (M^+, 100%), 284 (29), 188 (19), and 77 (57).

With 7-*methyl*-1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7b**

Similarly the pyranopyrrolone **7b** (42 mg, 0.15 mmol) and EP (71 mg, 0.73 mmol) in bromobenzene (10 ml) gave a mixture of *ethyl* 7-*methyl*-1-*phenylsulfonylindole*-6-*carboxylate* **11b** and *ethyl* 7-*methyl*-1-*phenylsulfonylindole*-5-*carboxylate* **12b** (28 mg, 56%) in the ratio 1.6 to 1 as a yellow oil (Found: C, 63.2; H, 5.1; N, 4.4. $C_{18}H_{17}NO_4S$ requires C, 63.0; H, 5.0; N, 4.1%); ν_{max}(film) 1 714, 1 367, 1 294, 1 174, and 1 130 cm^{-1}; δ (270 MHz; $CDCl_3$) 8.11 (1 H, s, 4-H, minor), 7.86-7.83 (m), 7.71-7.64 (m), 7.57-7.34 (m), 6.77 (1 H, d, *J* 4 Hz, 3-H, minor), 6.67 (1 H, d, *J* 3.9 Hz, 3-H, major), 4.38-4.31 (m, ester CH_2, both isomers), 2.73 (3 H, s, 7-Me, major), 2.56 (3 H, s, 7-Me, minor), 1.41-1.33 (m, ester CH_3, both isomers); *m/z* 343 (M^+, 100%), 298 (15), and 202 (54).

With 7-*pentyl*-1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7d**

Similarly the pyranopyrrolone **7d** (34 mg, 0.10 mmol) and EP (48 mg, 0.49 mmol) in bromobenzene (3 ml) gave a mixture of *ethyl* 7-*pentyl*-1-*phenylsulfonylindole*-5-*carboxylate* **12c** and *ethyl* 7-*pentyl*-1-*phenylsulfonylindole*-6-*carboxylate* **11c** (23 mg, 59%) in the ratio 1 to 1 (Found: M^+, 399.1504. $C_{22}H_{25}NO_4S$ requires *M*, 399.1504); ν_{max}($CHCl_3$) 1 713, 1 369, and 1 174 cm^{-1}; δ (270 MHz; $CDCl_3$) 8.07 (1 H, d, *J* 1.7 Hz, 4-H, 5-ester), 7.86 (1 H, d, *J* 3.7 Hz, 2-H), 7.84 (1 H, d, *J* 3.9 Hz, 2-H), 7.77 (1 H, d, *J* 1.7 Hz, 6-H, 5-ester), 7.65-7.52 (m, both isomers), 7.46-7.39 (m, both isomers), 7.34 (1 H, d, *J* 8 Hz, 6-ester), 6.76 (1 H, d, *J* 3.7 Hz, 3-H), 6.68 (1 H, d, *J* 3.9 Hz, 3-H), 4.41-4.30 (m, ester CH_2, both isomers), 3.32 (2 H, t, *J* 8 Hz, benzylic CH_2, 6-ester), 2.98 (2 H, t, *J* 8 Hz, benzylic CH_2, 5-ester), 1.54-1.11 (m, both isomers), and 0.90-0.78 (m, pentyl CH_3, both isomers); *m/z* 399 (M^+, 100%), 354 (44), 202 (43), 174 (45), and 77 (36).

With 7-*isopropyl*-1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7e**

Simiarly the pyranopyrrolone **7e** (57 mg, 0.18 mmol) and EP (88 mg, 0.90 mmol) in chlorobenzene (10 ml) gave a mixture of *ethyl* 7-*isopropyl*-1-*phenylsulfonylindole*-5-*carboxylate* **12d** and *ethyl* 7-*isopropyl*-1-*phenylsulfonylindole*-6-*carboxylate* **11d** (33 mg, 49%) in the ratio 5 to 1. Recrystallisation from light petroleum gave pure *ethyl* 7-*isopropyl*-1-*phenylsulfonylindole*-5-*carboxylate* **12d**, m.p. 106-111°C (Found: C, 64.5; H, 5.7; N, 3.75. $C_{20}H_{21}NO_4S$ requires C, 64.7; H, 5.7; N, 3.8%); ν_{max}(Nujol) 1 712, 1 376, and 1 176 cm^{-1}; δ (250 MHz; $CDCl_3$) 8.08 (1 H, d, *J* 1.6 Hz, 4-H),

7.90-7.88 (2 H, m), 7.65-7.62 (2 H, m), 7.57-7.55 (1 H, m), 7.49-7.44 (2 H, m), 6.77 (1 H, d, *J* 3.7 Hz, 3-H), 4.38 (2 H, q, *J* 7.1 Hz, ester CH_2), 3.89 (1 H, heptet, *J* 6.7 Hz, isopropyl CH), 1.40 (3 H, t, *J* 7.1 Hz, ester CH_3), and 1.03 (6 H, d, *J* 6.8 Hz, isopropyl CH_3); *m/z* 371 (M^+, 100%), 229 (35), 184 (54), 157 (44), and 77 (70).

With 4,7-*dimethyl*-1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7f**

Similarly the pyranopyrrolone **7f** (34 mg, 0.11 mmol) and EP (55 mg, 0.56 mmol) in chlorobenzene (5 ml) gave a mixture of *ethyl* 4,7-*dimethyl*-1-*phenylsulfonylindole*-5-*carboxylate* **12e** and *ethyl* 4,7-*dimethyl*-1-*phenylsulfonylindole*-6-*carboxylate* **11e** (32 mg, 80%) in the ratio 1 to 1 as a colourless oil (Found: C, 63.9; H, 5.5; N, 3.95. $C_{19}H_{19}NO_4S$ requires C, 63.85; H, 5.4; N, 3.9%); ν_{max}($CHCl_3$) 1 709, 1 371, and 1 175 cm^{-1}; δ (270 MHz; $CDCl_3$) 7.85 (1 H, d, *J* 3.9 Hz, 2-H), 7.84 (1 H, d, *J* 3.9 Hz, 2-H), 7.68-7.63 (m, both isomers), 7.59-7.52 (m, both isomers), 7.48-7.40 (m, both isomers), 6.87 (1 H, d, *J* 3.9 Hz, 3-H), 6.71 (1 H, d, *J* 3.9 Hz, 3-H), 4.35 (2 H, q, *J* 7 Hz, ester CH_2), 4.34 (2 H, q, *J* 7 Hz, ester CH_2), 2.71 (3 H, s, ArMe), 2.66 (3 H, s, ArMe), 2.50 (3 H, s, ArMe), 2.44 (3 H, s, ArMe), 1.38 (3 H, t, *J* 7 Hz, ester CH_3), and 1.37 (3 H, t, *J* 7 Hz, ester CH_3); *m/z* 357 (M^+, 100%), 312 (17), 216 (89), 188 (26), 170 (73), and 77 (32).

3. Ethyl 3-trimethylsilylpropynoate (ETMSP)

With 1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7a**

A mixture of the pyranopyrrolone **7a** (102 mg, 0.37 mmol) and ETMSP (189 mg, 1.11 mmol) in chlorobenzene (10 ml) was refluxed for 24 h. The solvent was evaporated and the residue chromatographed [ether-light petroleum (1:1)] to give a mixture of *ethyl* 1-*phenylsulfonyl*-5-*trimethylsilylindole*-6-*carboxylate* **13a** and *ethyl* 1-*phenylsulfonyl*-6-*trimethylsilylindole*-5-*carboxylate* (59 mg, 40%) in the ratio 2.5 to 1 (Found: M^+, 401.1117. $C_{20}H_{23}NO_4SSi$ requires *M*, 401.1117); ν_{max}(Nujol) 3 142, 3 068, 1 718, 1 377, 1 283, 1 174, and 1 142 cm^{-1}; δ (270 MHz; $CDCl_3$) 8.67 (1 H, s, 7-H, major), 7.94-7.88 (m, both isomers), 7.84 (1 H, s, 4-H, major), 7.67 (1 H, d, *J* 3.7 Hz, 2-H, major), 7.65 (1 H, d, *J* 3.9 Hz, 2-H, minor), 7.57-7.44 (m, both isomers), 6.71 (1 H, d, *J* 3.7 Hz, 3-H, minor), 6.70 (1 H, dd, *J* 3.7, 0.7 Hz, 3-H, major), 4.43 (2 H, q, *J* 7.1 Hz, ester CH_2, major), 4.37 (2 H, q, *J* 7.1 Hz, ester CH_2, minor), 1.46 (3 H, t, *J* 7.1 Hz, ester CH_3, major), 1.39 (3 H, t, *J* 7.1 Hz, ester CH_3, minor), 0.37 (9 H, s, Me_3Si, minor), and 0.33 (9 H, s, Me_3Si, major); *m/z* 401 (M^+, 2%), 386 (100), 358 (40), 217 (43), and 77 (13).

With 7-*methyl*-1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7b**

Similarly the pyranopyrrolone **7b** (216 mg, 0.75 mmol) and ETMSP (510 mg, 3.00 mmol) in chlorobenzene (20 ml) gave *ethyl* 7-*methyl*-1-*phenylsulfonyl*-5-*trimethylsilylindole*-6-*carboxylate* **13b** (165 mg, 53%), m.p. 122-127°C (Found: C, 60.7; H, 6.1; N, 3.2. $C_{21}H_{25}NO_4SSi$ requires C, 60.7; H, 6.1; N, 3.4%); ν_{max}($CHCl_3$) 1 718, 1 368, and 1 174 cm^{-1}; δ (270 MHz; $CDCl_3$) 7.83 (1 H, d, *J* 3.9 Hz, 2-H), 7.67 (2 H, d, *J* 8 Hz), 7.61 (1 H, s, 4-H), 7.56 (1 H, t, *J* 8 Hz), 7.46 (2 H, t, *J* 8 Hz), 6.68 (1 H, d, *J* 3.4 Hz, 3-H), 4.34 (2 H, q, *J* 7 Hz, ester CH_2), 2.48 (3 H, s, 7-Me), 1.36 (3 H, t, *J* 7 Hz, ester CH_3), and 0.28 (9 H, s, Me_3Si); *m/z* 415 (M^+, 7%), 400 (100), 372 (10), 259 (34), 231 (35), and 77 (16).

Protodesilylation of ethyl 7-*methyl*-1-*phenylsulfonyl*-5-*trimethylsilylindole*-6-*carboxylate* **13b**

A solution of the 5-trimethylsilylindole **13b** (19 mg, 0.046 mmol) in trifluoroacetic acid (2 ml) and water (1 ml) was heated at 70 °C for 2 h. The mixture was diluted with water (30 ml) and extracted with ether. The combined ether extracts were washed with saturated aqueous sodium hydrogen carbonate solution (until the washings remained basic), water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed [ether-light petroleum (2:1)] to give *ethyl* 7-*methyl*-1-*phenylsulfonylindole*-6-*carboxylate* **11b** (11 mg, 70%) as a colourless oil, ν_{max}(film) 1 713, 1 366, 1 173 cm^{-1}; δ (270 MHz; $CDCl_3$) 7.84 (1 H, d, *J* 3.9 Hz, 2-H), 7.67-7.63 (3 H, m), 7.55 (1 H, t, *J* 7 Hz), 7.45-7.34 (3 H, m), 6.67 (1 H, d, *J* 3.7 Hz, 3-H), 4.34 (2 H, q, *J* 7 Hz, ester CH_2), 2.73 (3 H, s, 7-Me), and 1.38 (3 H, t, *J* 7 Hz, ester CH_3); *m/z* 343 (M^+, 100%), 298 (21), 202 (62), 174 (29), 156 (42), 141 (15), 77 (41).

With 7-*pentyl*-1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7d**

Similarly the pyranopyrrolone **7d** (60 mg, 0.17 mmol) and ETMSP (88 mg, 0.52 mmol) in chlorobenzene (15 ml) gave *ethyl* 7-*pentyl*-1-*phenylsulfonyl*-5-*trimethylsilylindole*-6-*carboxylate* **13c** (10 mg, 12%) as a colourless oil (Found: M^+,

471.1900. $C_{25}H_{33}NO_4SSi$ requires *M*, 471.1900); $\nu_{max}(CCl_4)$ 1 726, 1 374, 1 265, and 1 177 cm^{-1}; δ (270 MHz; $CDCl_3$) 7.84 (1 H, d, *J* 3.9 Hz, 2-H), 7.66-7.62 (2 H, m), 7.59 (1 H, s, 4-H), 7.55-7.53 (1 H, m), 7.47-7.44 (2 H, m), 6.68 (1 H, d, *J* 3.8 Hz, 3-H), 4.34 (2 H, q, *J* 7 Hz, ester CH_2), 2.99 (2 H, t, *J* 8 Hz, benzylic CH_2), 1.40 (2 H, m), 1.37 (3 H, t, *J* 7 Hz, ester CH_3), 1.20 (4 H, m), 0.86 (3 H, t, *J* 7 Hz, pentyl CH_3), and 0.27 (9 H, s, Me_3Si); *m/z* 471 (M^+, 5%), 456 (100), 259 (17), 230 (14), and 77 (11).

4. Benzyne

With 1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7a**

A mixture of the pyranopyrrolone **7a** (53 mg, 0.19 mmol), 2-(3,3-dimethyltriazen-1-yl)benzoic acid (74 mg, 0.39 mmol), and trifluoroacetic acid (1 drop) in acetonitrile (10 ml) was refluxed for 4 h. The solvent was evaporated and the residue chromatographed [ether-light petroleum (1:1)] to give 1-*phenylsulfonylbenz*[f]*indole* **14a** (29 mg, 49%), m.p. 127-129 °C (Found: C, 70.4; H, 4.2; N, 4.5. $C_{18}H_{13}NO_2S$ requires C, 70.3; H, 4.3; N, 4.6%); ν_{max}(Nujol) 3 128, 1 372, 1 175, and 1 099 cm^{-1}; δ (270 MHz; $CDCl_3$) 8.46 (1 H, s, 9-H), 8.01-7.97 (2 H, m), 7.92-7.88 (3 H, m), 7.68 (1 H, d, *J* 3.7 Hz, 2-H), 7.50-7.37 (5 H, m), and 6.79 (1 H, d, *J* 3.9 Hz, 3-H); *m/z* 307 (M^+, 48%), 166 (100), and 139 (25).

With 7-*methyl*-1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7b**

Similarly the pyranopyrrolone **7b** (58 mg, 0.2 mmol), the triazene (116 mg, 0.6 mmol), and trifluoroacetic acid (1 drop) in acetonitrile (10 ml) gave 9-*methyl*-1-*phenylsulfonylbenz*[f]*indole***14b** (42 mg, 65%), (Found: C, 71.1; H, 4.7; N, 4.3. $C_{19}H_{15}NO_2S$ requires C, 71.0; H, 4.7; N, 4.4%); ν_{max}(film) 3 070, 1 583, 1 447, 1 364, 1 186, and 726 cm^{-1}; δ (270 MHz; $CDCl_3$) 8.16 (1 H, d, *J* 8 Hz), 7.84 (1 H, d, *J* 8 Hz), 7.73 (1 H, s, 4-H), 7.66 (1 H, d, *J* 3.9 Hz, 2-H), 7.57-7.40 (5 H, m), 7.31-7.25 (2 H, m), 6.71 (1 H, d, *J* 3.9 Hz, 3-H), and 3.05 (3 H, s, 9-Me); *m/z* 321 (M^+, 18%) and 180 (100).

With 7-*pentyl*-1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7d**

Similarly the pyranopyrrolone **7d** (64 mg, 0.19 mmol), the triazene (72 mg, 0.37 mmol), and trifluoroacetic acid (1 drop) in acetonitrile (10 ml) gave 9-*pentyl*-1-*phenylsulfonyl*-*benz*[f]*indole* **14c** (54 mg, 77%), m.p. 80-82°C (Found: C, 73.4; H, 6.2; N, 3.7. $C_{23}H_{23}NO_2S$ requires C, 73.2; H, 6.1; N, 3.7%); ν_{max}(Nujol) 1 448, 1 364, 1 175, and 1 092 cm^{-1} ; δ (270 MHz; $CDCl_3$) 8.14 (1 H, d, *J* 8 Hz), 7.86 (1 H, d, *J* 7 Hz), 7.79 (1 H, d, *J* 3.9 Hz, 2-H), 7.78 (1 H, s, 4-H), 7.63-7.60 (2 H, m), 7.51-7.31 (5 H, m), 6.74 (1 H, d, *J* 3.9 Hz, 3-H), 3.54 (2 H, t, *J* 8 Hz, benzylic CH_2), 1.56-1.50 (2 H, m), 1.35-1.25 (4 H, m), and 0.88 (3 H, t, *J* 7 Hz, pentyl CH_3); *m/z* 377 (M^+, 25%), and 180 (100).

With 4,7-*dimethyl*-1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7f**

Similarly the pyranopyrrolone **7f** (36 mg, 0.12 mmol), the triazene (46 mg, 0.24 mmol), and trifluoroacetic acid (1 drop) in acetonitrile (10 ml) gave 4,9-*dimethyl*-1-*phenylsulfonylbenz*[f]*indole* **14d** (24 mg, 60%), m.p. 154-156°C (Found: C, 71.4; H, 5.0; N, 4.05. $C_{20}H_{17}NO_2S$ requires C, 71.6; H, 5.1 N, 4.1%); ν_{max}(Nujol) 1 367 and 1 176 cm^{-1}; δ (270 MHz; $CDCl_3$) 8.21-8.17 (1 H, m), 8.07-8.03 (1 H, m), 7.65 (1 H, d, *J* 3.9 Hz, 2-H), 7.56-7.51 (3 H, m), 7.40 (1 H, t, *J* 7.3 Hz), 7.31-7.27 (3 H, m), 6.83 (1 H, d, *J* 3.6 Hz, 3-H), 3.02 (3 H, s, ArMe), and 2.70 (3 H, s, ArMe); *m/z* 335 (M^+, 22%) and 194 (100).

5. Phenyl vinyl sulfoxide

With 7-*methyl*-1-*phenylsulfonylpyrano*[3,4-b]*pyrrol*-5(1H)-*one* **7b**

A mixture of the pyranopyrrolone **7b** (90 mg, 0.31 mmol) and phenyl vinyl sulfoxide (142 mg, 0.93 mmol) in chlorobenzene (5 ml) was heated under reflux for 48 h. The solvent was evaporated and the residue chromatographed [ether-light petroleum (1:1)] to give 7-*methyl*-1-*phenylsulfonylindole* **15a** (51 mg, 60%) as a colourless oil (Found: C, 66.4; H, 4.9; N, 5.0. $C_{15}H_{13}NO_2S$ requires C, 66.4; H, 4.8; N, 5.2%); $\nu_{max}(CHCl_3)$ 1 586, 1 446, 1 364, and 1 166 cm^{-1}; δ (250 MHz; $CDCl_3$) 7.79 (1 H, d, *J* 3.8 Hz, 2-H), 7.68-7.64 (2 H, m), 7.54-7.51 (1 H, m), 7.46-7.38 (3 H, m), 7.12 (1 H, t, *J* 7.8 Hz, 5-H), 7.01 (1 H, d, *J* 6.8 Hz, 6-H), 6.70 (1 H, d, *J* 3.7 Hz, 3-H), and 2.52 (3 H, s, 3-Me); *m/z* 271 (M^+, 32%), 130 (100), and 77 (39).

With 7-pentyl-1-phenylsulfonylpyrano[3,4-b]pyrrol-5(1H)-one **7d**

Similarly the pyranopyrrolone **7d** (84 mg, 0.24 mmol) and phenyl vinyl sulfoxide (111 mg, 0.73 mmol) in chlorobenzene (5 ml) gave *7-pentyl-1-phenylsulfonylindole* **15b** (35 mg, 44%), m.p. 60-61°C (Found: C, 69.6; H, 6.4; N, 4.3. $C_{19}H_{21}NO_2S$ requires C, 69.7; H, 6.5; N, 4.3%); ν_{max}($CHCl_3$) 3 156, 1 446, 1 370, and 1 168 cm^{-1}; δ (250 MHz; $CDCl_3$) 7.77 (1 H, d, *J* 3.8 Hz, 2-H), 7.66-7.62 (2 H, m), 7.54-7.51 (1 H, m), 7.45-7.35 (3 H, m), 7.16 (1 H, t, *J* 7.4 Hz, 5-H), 7.08 (1 H, d, *J* 7.3 Hz, 6-H), 6.69 (1 H, d, *J* 3.8 Hz, 3-H), 2.96 (2 H, t, *J* 7.9 Hz, benzylic CH_2), 1.50-1.44 (2 H, m), 1.26-1.21 (4 H, m), and 0.86 (3 H, t, *J* 6.6 Hz, pentyl CH_3); *m/z* 327 (M^+, 33%), 130 (100), and 77 (21).

With 7-isopropyl-1-phenylsulfonylpyrano[3,4-b]pyrrol-5(1H)-one **7e**

Similarly the pyranopyrrolone **7e** (90 mg, 0.28 mmol) and phenyl vinyl sulfoxide (130 mg, 0.85 mmol) in chlorobenzene (5 ml) gave *7-isopropyl-1-phenylsulfonylindole* **15c** (17 mg, 20%), m.p. 49-50°C (Found: M^+, 299.0988. $C_{17}H_{17}NO_2S$ requires *M*, 299.0980); ν_{max}($CHCl_3$) 1 446, 1 374, 1 354, 1 168, 1 122, and 1 104 cm^{-1}; δ (250 MHz; $CDCl_3$) 7.79 (1 H, d, *J* 3.8 Hz, 2-H), 7.65-7.61 (2 H, m), 7.57-7.51 (1 H, m), 7.47-7.41 (2 H, m), 7.40-7.35 (1 H, m, 4-H), 7.23-7.19 (2 H, m, 5-H + 6-H), 6.69 (1 H, d, *J* 3.9 Hz, 3-H), 3.89 (1 H, heptet, *J* 6.7 Hz, isopropyl CH), and 1.02 (6 H, d, *J* 6.7 Hz, isopropyl CH_3); *m/z* 299 (M^+, 71%), 284 (13), 158 (100), 143 (28), 130 (21), 118 (39), and 77 (38).

With 4-ethyl-7-methyl-1-phenylsulfonylpyrano[3,4-b]-pyrrol-5(1H)-one **7g**

Similarly the pyranopyrrolone **7g** (63 mg, 0.20 mmol) and phenyl vinyl sulfoxide (121 mg, 0.79 mmol) in chlorobenzene (5 ml) gave *4-ethyl-7-methyl-1-phenylsulfonylindole* **15d** (36 mg, 60%) as a yellow oil (Found: C, 68.3; H, 5.8; N, 4.7. $C_{17}H_{17}NO_2S$ requires C, 68.2; H, 5.7; N, 4.7%); ν_{max}(film) 1 446, 1 364, 1 176, and 1 120 cm^{-1}; δ (250 MHz; $CDCl_3$) 7.80 (1 H, d, *J* 4.0 Hz, 2-H), 7.69-7.65 (2 H, m), 7.55-7.52 (1 H, m), 7.48-7.40 (2 H, m), 6.95 (2 H, s, 5-H + 6-H), 6.77 (1 H, d, *J* 3.8 Hz, 3-H), 2.83 (2 H, q, *J* 7.6 Hz, CH_2CH_3), 2.47 (3 H, s, 7-Me), and 1.28 (3 H, t, *J* 7.5 Hz, CH_2CH_3); *m/z* 299 (M^+, 30%), 158 (100), 143 (19), and 77 (15).

Intramolecular Diels–Alder Reactions

7-(Pent-1-yn-5-yl)-1-phenylsulfonylpyrano[3,4-b]pyrrol-5(1H)-one **18a**

Boron trifluoride diethyl ether (0.15 ml) was added dropwise to a solution of the acid **6** (193 mg, 0.73 mmol) in hex-5-ynoic anhydride (174 mg, 0.84 mmol) and ether (2 ml) at room temperature. The mixture was stirred for 24 h. Water was added and the mixture extracted with ethyl acetate. The combined extracts were washed with saturated sodium hydrogen carbonate solution, water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed (ether) to give the *title compound* **18a** (38 mg, 15%) as a yellow oil, ν_{max}($CHCl_3$) 3 308, 1 709, 1 574, 1 381, and 1 177 cm^{-1}; λ_{max}(EtOH) 215 (ε 18 500) and 374 nm (3 070); δ (270 MHz; $CDCl_3$) 7.70-7.62 (3 H, m), 7.60 (1 H, d, *J* 3.9 Hz, 2-H), 7.54-7.48 (2 H, m), 6.27 (1 H, d, *J* 3.7 Hz, 3-H), 5.90 (1 H, s, 4-H), 3.17 (2 H, t, *J* 7.5 Hz, allylic CH_2), 2.28 (2 H, td, *J* 7, 1.5 Hz, propargylic CH_2), 1.98 (1 H, t, *J* 1.5 Hz, acetylenic CH), and 1.95 (2 H, m, $C{\equiv}CCH_2CH_2$); *m/z* 341 (M^+, 0.2%), 297 (65), 156 (100), and 77 (32).

1-Phenylsulfonyl-1,6,7,8-tetrahydrocyclopenta[g]indole **19a**

A solution of the pyranopyrrolone **18a** (30 mg, 0.09 mmol) in bromobenzene was refluxed for 5 h. The solvent was evaporated and the residue chromatographed [ether-light petroleum (1:1)] to give the *title compound* **19a** (17 mg, 65%), m.p. 128-131°C (lit.,[10] 133-134°C) (Found: C, 69.0; H, 5.3; N, 4.55. Calc for $C_{17}H_{15}NO_2S$ C, 68.7; H, 5.1; N, 4.7%); ν_{max}($CHCl_3$) 1 377, 1 361, 1 173, and 728 cm^{-1}; δ (270 MHz; $CDCl_3$) 7.73-7.68 (2 H, m), 7.66 (1 H, d, *J* 3.9 Hz, 2-H), 7.53-7.50 (1 H, m), 7.48-7.40 (2 H, m), 7.34 (1 H, d, *J* 8 Hz, 4-H), 7.14 (1 H, d, *J* 8 Hz, 5-H), 6.68 (1 H, d, *J* 3.9 Hz, 3-H), 3.19 (2 H, t, *J* 7.3 Hz, benzylic CH_2), 2.93 (2 H, t, *J* 7.3 Hz, benzylic CH_2), and 2.02 (2 H, quintet, *J* 7.4 Hz, $CH_2CH_2CH_2$); *m/z* 297 (M^+, 80%), 156 (100), and 77 (21).

4-Ethyl-1-phenylsulfonyl-1,6,7,8-tetrahydrocyclopenta[g]indole **19b**

Boron trifluoride diethyl ether (0.25 ml, 2.03 mmol) was added dropwise to a solution of the acid **9b** (295 mg, 1.01 mmol) in hex-5-ynoic anhydride (309 mg, 1.50 mmol) and ether (1 ml) at 0°C. The mixture was allowed to warm to room temperature and stirred for 12 h. Water was added and the mixture extracted with ethyl acetate. The combined extracts were washed with

water, brine, and dried ($MgSO_4$). Evaporation of the solvent gave the crude pyranopyrrolone **18b** which was dissolved in acetic anhydride (30 ml) and refluxed for 2 h. The solvent was evaporated and the residue chromatographed [ether-light petroleum (1:1)] to give the *title compound* **19b** (29 mg, 9%), m.p. 92-94°C (Found: C, 70.0; H, 5.9; N, 4.25. $C_{19}H_{19}NO_2S$ requires C, 70.1; H, 5.9; N, 4.3%); $\nu_{max}(CHCl_3)$ 1 445, 1 360, 1 175, and 1 130 cm^{-1}; δ (250 MHz; $CDCl_3$) 7.72-7.67 (3 H, m), 7.52 (1 H, t, *J* 7.5 Hz), 7.42 (2 H, t, *J* 7.8 Hz), 7.00 (1 H, s, 5-H), 6.74 (1 H, t, *J* 3.7 Hz, 3-H), 3.14 (2 H, t, *J* 7.3 Hz, benzylic CH_2), 2.91 (2 H, t, *J* 7.5 Hz, benzylic CH_2), 2.83 (2 H, q, *J* 7.6 Hz, CH_3CH_2), 2.00 (2 H, quintet, *J* 7.4 Hz, $CH_2CH_2CH_2$), and 1.27 (3 H, t, *J* 7.5 Hz, CH_3CH_2); *m/z* 325 (M^+, 43%), 184 (100), 155 (25), and 77 (35).

Methyl 2-(1-*Phenylsulfonylpyrrol*-3-*yl*)*hept*-6-*ynoate* **20a**

n-Butyllithium (1.5 M, 0.80 ml) was added dropwise to a solution of *N*-isopropylcyclohexylamine (170 mg, 1.20 mmol) in dry tetrahydrofuran (10 ml) at -78°C under nitrogen. The mixture was warmed to 0°C, stirred for 5 min and recooled to -78°C. A solution of the ester **5** (305 mg, 1.09 mmol) in dry tetrahydrofuran (5 ml) was added dropwise, and the resulting solution stirred at -78°C for 2 h. 5-Iodopent-1-yne (434 mg, 2.24 mmol) in dry tetrahydrofuran (5 ml) was added, the mixture allowed to warm to room temperature, and stirred overnight. Water (30 ml) was added and the mixture extracted with ether. The combined ether extracts were washed with water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed [ether-light petroleum (1:2)] to give the *title compound* **20a** (261 mg, 69%) as a colourless oil. (Found: C, 62.85; H, 5.7; N, 4.0. $C_{18}H_{19}NO_4S$ requires C, 62.6; H, 5.5; N, 4.1%); ν_{max}(film) 3 295, 2 952, 2 117, 1 734, 1 372, 1 176, and 1 064 cm^{-1}; δ (270 MHz; $CDCl_3$) 7.85 (2 H, d, *J* 7 Hz), 7.60 (1 H, t, *J* 7.2 Hz), 7.50 (2 H, t, *J* 7.4 Hz), 7.10-7.08 (2 H, m, 2-H + 5-H), 6.28 (1 H, m, 4-H), 3.65 (3 H, s, CO_2Me), 3.46 (1 H, t, *J* 7.6 Hz, $CHCO_2Me$), 2.16 (2 H, td, *J* 7.1, 2.7 Hz, propargylic CH_2), 2.05-1.97 (1 H, m), 1.94 (1 H, t, *J* 2.7 Hz, acetylenic CH), 1.84-1.76 (1 H, m), and 1.44 (2 H, quintet, *J* 7.3 Hz, $C{\equiv}CCH_2CH_2$); *m/z* 345 (M^+, 1%), 204 (72), and 77 (100).

2-(1-*Phenylsulfonylpyrrol*-3-*yl*)*hept*-6-*ynoic Acid* **21a**

A mixture of the ester **20a** (822 mg, 2.38 mmol) and lithium hydroxide hydrate (500 mg, 11.90 mmol) in tetrahydrofuran (2.5 ml) and water (2.5 ml) was stirred at room temperature for 24 h. Water (30 ml) was added, the mixture extracted with ethyl acetate, and this extract discarded. The aqueous layer was acidified and extracted with ethyl acetate. The combined extracts were washed with water, brine, and dried ($MgSO_4$). The solvent was evaporated to give the *title compound* **21a** (536 mg, 68%) as a colourless oil (Found: M^+, 331.0878. $C_{17}H_{17}NO_4S$ requires *M*, 331.0878); ν_{max}(film) 3 296, 3 200-2 400, 2 117, 1 708, 1 371, 1 176, 1 104, and 1 065 cm^{-1}; δ (270 MHz; $CDCl_3$) 7.86-7.83 (2 H, m), 7.61-7.58 (1 H, m), 7.53-7.48 (2 H, m), 7.11 (2 H, d, *J* 2.4 Hz, 2-H + 5-H), 6.30 (1 H, t, *J* 2.4 Hz, 4-H), 3.47 (1 H, t, *J* 7.6 Hz, $CHCO_2H$), 2.17 (2 H, td, *J* 7, 2.7 Hz, propargylic CH_2), 2.07-2.02 (1 H, m), 1.94 (1 H, t, *J* 2.7 Hz, acetylenic CH), 1.84-1.81 (1 H, m), and 1.50-1.44 (2 H, m, $C{\equiv}CCH_2CH_2$); *m/z* 331 (M^+, 1%), 286 (5), 190 (100), and 77 (92).

7-*Methyl*-4-(*pent*-1-*yn*-5-*yl*)-1-*phenylsulfonylpyrano*[3,4-b]-*pyrrol*-5(1H)-*one* **22a**

Boron trifluoride diethyl ether (0.33 ml, 2.7 mmol) was added dropwise to a stirred solution of the acid **21a** (440 mg, 1.33 mmol) in acetic anhydride (0.50 ml, 5.3 mmol) and ether (1 ml) at 0°C. The mixture was stirred at 0°C for 1 h and then at room temperature for 4 h. Water (30 ml) was added and the mixture extracted with ethyl acetate. The combined extracts were washed with saturated aqueous sodium hydrogen carbonate solution, water , brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed (ether) to give the *title compound* **22a** (89 mg, 19%) as a yellow oil; ν_{max}(film) 3 296, 2 933, 1 699, 1 584, 1 374, 1 176, and 1 083 cm^{-1}; λ_{max}(EtOH) 216 (ε 16 740), 325 (1 520), 369 (5 840), and 378 nm (5 670); δ (270 MHz; $CDCl_3$) 7.69-7.61 (3 H, m), 7.56 (1 H, d, *J* 3.9 Hz, 2-H) 7.53-7.47 (2 H, m), 6.44 (1 H, d, *J* 3.9 Hz, 3-H), 2.65 (3 H, s, 7-Me), 2.59 (2 H, t, *J* 7 Hz, allylic CH_2), 2.07 (2 H, td, *J* 6.8, 2.7 Hz, propargylic CH_2), 1.94 (1 H, t, *J* 2.7 Hz, acetylenic CH), and 1.78-1.68 (2 H, m, $C{\equiv}CCH_2CH_2$); *m/z* 311 (33), 170 (100), 155 (17), and 77 (9).

8-*Methyl*-1-*phenylsulfonyl*-1,4,5,6-*tetrahydrocyclopenta*[e]*indole* **23a**

A solution of the pyranopyrrolone **22a** (72 mg, 0.20 mmol) in toluene (20 ml) was refluxed for 1 h. The solvent was evaporated and the residue chromatographed [ether-light petroleum (1:1)]to give the *title compound* **23a** (43 mg, 68%), m.p. 108-110°C (Found: C, 69.45; H, 5.4; N, 4.4. $C_{18}H_{17}NO_2S$ requires C, 69.4; H, 5.5; N, 4.5%); ν_{max}(Nujol) 1 350, 1 171, and 1 127 cm^{-1}; δ (270 MHz; $CDCl_3$) 7.78 (1 H, d, *J* 3.7 Hz, 2-H), 7.68-7.64 (2 H, m), 7.56-7.50 (1 H, m), 7.46-7.39 (2 H, m), 6.90 (1 H, s, 7-H), 6.62 (1 H, d, *J* 3.9 Hz, 3-H), 3.01 (2 H, t, *J* 7.4 Hz, benzylic CH_2), 2.92 (2 H, t, *J* 7.3 Hz, benzylic

CH_2), 2.49 (3 H, s, 8-Me), and 2.15 (2 H, quintet, *J* 7 Hz, $CH_2CH_2CH_2$); *m/z* 311 (M^+, 34%), 170 (100), 155 (18), and 77 (12).

Methyl 2-(1-*Phenylsulfonylpyrrol*-3-*yl*)*oct*-7-*ynoate* **20b**

n-Butyllithium (1.5 M, 0.60 ml) was added dropwise to a solution of *N*-isopropylcyclohexylamine (127 mg, 0.90 mmol) in dry tetrahydrofuran (10 ml) at -78°C under nitrogen. The mixture was warmed to 0°C, stirred for 5 min, and recooled to -78°C. A solution of the ester **5** (229 mg, 0.82 mmol) in dry tetrahydrofuran (5 ml) was added dropwise and the resulting solution stirred at -78°C for 2 h. 6-Iodohex-1-yne (343 mg, 1.65 mmol) in dry tetrahydrofuran (5 ml) was added, the mixture allowed to warm to room temperature, and stirred overnight. Water (50 ml) was added and the mixture extracted with ether. The combined ether extracts were washed with water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed [ether-light petroleum (1:2)] to give the *title compound* **20b** (205 mg, 70%) as a colourless oil (Found: C, 63.3; H, 5.9; N, 3.9. $C_{19}H_{21}NO_4S$ requires C, 63.5; H, 5.9; N, 3.9%); ν_{max}(film) 3 295, 2 948, 2 116, 1 735, 1 372, 1 176, and 1 063 cm^{-1}; δ (270 MHz; $CDCl_3$) 7.86-7.82 (2 H, m), 7.63-7.57 (1 H, m), 7.53-7.47 (2 H, m), 7.10-7.05 (2 H, m, 2-H + 5-H), 6.27 (1 H, dd, *J* 3.2, 1.7 Hz, 4-H), 3.64 (3 H, s, CO_2Me), 3.44 (1 H, t, *J* 7.6 Hz, $CHCO_2Me$), 2.13 (2 H, td, *J* 6.8, 2.7 Hz, propargylic CH_2), 1.96-1.85 (1 H, m), 1.91 (1 H, t, *J* 2.7 Hz, acetylenic CH), 1.71-1.63 (1 H, m), 1.52-1.44 (2 H, m), and 1.37-1.25 (2 H, m); *m/z* 359 (M^+, 4%), 300 (26), 279 (16), 218 (100), 158 (28), 141 (32), and 77 (96).

2-(1-*Phenylsulfonylpyrrol*-3-*yl*)*oct*-7-*ynoic Acid* **21b**

A mixture of the ester **20b** (725 mg, 2.02 mmol) and lithium hydroxide hydrate (423 mg, 10.08 mmol) in tetrahydrofuran (2.5 ml) and water (2.5 ml) was stirred at room temperature for 24 h. Water (20 ml) was added, the mixture extracted with ethyl acetate, and this extract discarded. The aqueous layer was acidified and extracted with ethyl acetate. The combined extracts were washed with water, brine, and dried ($MgSO_4$). The solvent was evaporated to give the *title compound* **21b** (450 mg, 64%), m.p. 94-97°C (Found: C, 62.4; H, 5.5; N, 4.0. $C_{18}H_{19}NO_4S$ requires C, 62.6; H, 5.5; N, 4.1%); ν_{max}(Nujol) 3 297, 3 200-2 400, 2 116, 1 708, 1 372, 1 176, 1 104, and 1 063 cm^{-1}; δ (270 MHz; $CDCl_3$) 7.85 (2 H, d, *J* 7.3 Hz), 7.60 (1 H, t, *J* 7.3 Hz), 7.50 (2 H, t, *J* 7.4 Hz), 7.11-7.09 (2 H, m, 2-H + 5-H), 6.28 (1 H, m, 4-H), 3.44 (1 H, t, *J* 7 Hz, $CHCO_2H$), 2.13 (2 H, td, *J* 6.8, 2.7 Hz, propargylic CH_2), 1.94-1.88 (1 H, m), 1.90 (1 H, t, *J* 2.7 Hz, acetylenic CH), 1.70-1.65 (1 H, m), 1.53-1.45 (2 H, m), and 1.40-1.28 (2 H, m); *m/z* 345 (M^+, 3%), 300 (14), 265 (17), 220 (15), 204 (100), 141 (30), and 77 (99).

4-(*Hex*-1-*yn*-6-*yl*)-7-*methyl*-1-*phenylsulfonylpyrano*[3,4-b]-*pyrrol*-5(1H)-*one* **22b**

Boron trifluoride diethyl ether (0.27 ml, 2.2 mmol) was added dropwise to a stirred solution of the acid **21b** (384 mg, 1.11 mmol) in acetic anhydride (0.42 ml, 4.45 mmol) and ether (1 ml) at 0°C. The mixture was stirred at 0°C for 1 h and then at room temperature for 4 h. Water (30 ml) was added and the mixture extracted with ethyl acetate. The combined extracts were washed with saturated aqueous sodium hydrogen carbonate solution, water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed (ether) to give the *title compound* **22b** (66 mg, 16%), m.p. 105-108°C (Found: C, 65.0; H, 5.2; N, 3.7. $C_{20}H_{19}NO_4S$ requires C, 65.0; H, 5.2; N, 3.8%); ν_{max}(Nujol) 3 296, 2 116, 1 698, 1 586, 1 373, and 1 185 cm^{-1}; λ_{max}(EtOH) 215 (ε 15 460), 217 (15 490), 370 (8 365), and 377 nm (8 650); δ (270 MHz; $CDCl_3$) 7.68-7.60 (3 H, m), 7.56 (1 H, d, *J* 3.9 Hz, 2-H) 7.50 (2 H, t, *J* 7.4 Hz), 6.34 (1 H, d, *J* 3.9 Hz, 3-H), 2.65 (3 H, s, 7-Me), 2.46 (2 H, t, *J* 7.3 Hz, allylic CH_2), 2.16 (2 H, td, *J* 7, 2.7 Hz, propargylic CH_2), 1.92 (1 H, t, *J* 2.7 Hz, acetylenic CH), 1.60-1.55 (2 H, m), and 1.47-1.41 (2 H, m); *m/z* 369 (M^+, 15%), 325 (11), 200 (27), 184 (45), 158 (77), 77 (55), and 43 (100).

9-*Methyl*-1-*phenylsulfonyl*-4,5,6,7-*tetrahydrobenz*[*e*]*indole* **23b**

A solution of the pyranopyrrolone **22b** (55 mg, 0.15 mmol) in bromobenzene (15 ml) was refluxed for 12 h. The solvent was evaporated and the residue chromatographed [ether-light petroleum (1:1)] to give the *title compound* **23b** (38 mg, 78%), m.p. 80-82°C (Found: C, 69.9; H, 5.9; N, 4.2. $C_{19}H_{19}NO_2S$ requires C, 70.1; H, 5.9; N, 4.3%); ν_{max}(Nujol) 1 485, 1 358, and 1 175 cm^{-1}; δ (270 MHz; $CDCl_3$) 7.76 (1 H, d, *J* 3.9 Hz, 2-H), 7.66 (2 H, dd, *J* 7.2, 1.6 Hz), 7.51 (1 H, t, *J* 7.3 Hz), 7.45 (2 H, t, *J* 7.5 Hz), 6.73 (1 H, s, 8-H), 6.68 (1 H, d, *J* 3.7 Hz, 3-H), 2.85 (2 H, t, *J* 6 Hz, benzylic CH_2), 2.73 (2 H, t, *J* 6 Hz, benzylic CH_2), 2.44 (3 H, s, 9-Me), and 1.86-1.78 (4 H, m, $CH_2CH_2CH_2CH_2$); *m/z* 325 (M^+, 40%), 184 (100), 169 (13), and 77 (9).

Removal of the 1-Phenylsulfonyl Group

9-Methylbenz[f]*indole*

A mixture of the *N*-phenylsulfonylindole **14b** (23 mg, 0.07 mmol) and potassium hydroxide (1.2 g, 21.4 mmol) in 1,2-dimethoxyethane (2 ml), methanol (2 ml), and water (2 ml) was refluxed under nitrogen for 24 h. The mixture was allowed to cool to room temperature, diluted with water, and extracted with ether. The combined ether extracts were washed with water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed [ether-light petroleum (1:1)] to give the *title compound* (9 mg, 69%), m.p. 53-55°C (Found: M^+, 181.0891. $C_{13}H_{11}N$ requires M, 181.0891); $\nu_{max}(CHCl_3)$ 3 484, and 1 412 cm^{-1}; δ (250 MHz; $CDCl_3$) 8.08 (1 H, d, *J* 8.5 Hz), 8.04 (1 H, s, 4-H), 7.95 (1 H, d, *J* 8.0 Hz), 8.1-7.9 (1 H, br, NH), 7.43-7.34 (3 H, m), 6.67 (1 H, dd, *J* 3.3, 1.9 Hz, 3-H), and 2.82 (3 H, s, 9-Me); *m/z* 181 (M^+, 100%), 180 (87), 152 (21), 91 (11), and 77 (15).

7-Methylindole

A mixture of the *N*-phenylsulfonylindole **15a** (40 mg, 0.15 mmol) and potassium hydroxide (1.2 g, 21.4 mmol) in 1,2-dimethoxyethane (2 ml), methanol (2 ml), and water (2 ml) was refluxed under nitrogen for 24 h. The mixture was allowed to cool to room temperature, diluted with water, and extracted with ether. The combined ether extracts were washed with water, brine, and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed [ether-light petroleum (1:1)] to give the *title compound* (14.5 mg, 75%), m.p. 81-83°C (lit.,[23] 82°C), $\nu_{max}(CHCl_3)$ 3 480, 1 426, and 1 338 cm^{-1}; δ (250 MHz; $CDCl_3$) 8.05 (1 H, br, NH), 7.51 (1 H, d, *J* 7.5 Hz, 4-H), 7.20 (1 H, t, *J* 2.8 Hz, 2-H), 7.05-7.01 (2 H, m, 5-H + 6-H), 6.56 (1 H, dd, *J* 3.1, 2.0 Hz, 3-H), and 2.50 (3 H, s, 7-Me); *m/z* 131 (M^+, 78%), 130 (100), 103 (12), and 77 (24).

8-Methyl-1,4,5,6-tetrahydrocyclopenta[e]*indole*

A mixture of the *N*-phenylsulfonylindole **23a** (28 mg, 0.09 mmol) and potassium hydroxide (0.6 g, 10.7 mmol) in 1,2-dimethoxyethane (1 ml), methanol (1 ml), and water (1 ml) was refluxed for 15 h. The mixture was allowed to cool to room temperature, diluted with water, and extracted with ethyl acetate. The combined organic extracts were washed with water, brine, and dried ($MgSO_4$). The solvent was evaporated to give the *title compound* (15 mg, 97%), m.p. 143-146°C (Found: M^+, 171.1048. $C_{12}H_{13}N$ requires M, 171.1048); $\nu_{max}(CHCl_3)$ 3 480 cm^{-1}; δ (250 MHz; $CDCl_3$) 8.07 (1 H, br, NH), 7.21 (1 H, t, *J* 2.8 Hz, 2-H), 6.93 (1 H, s, 7-H), 6.47 (1 H, dd, *J* 3.1, 2.1 Hz, 3-H), 3.08 (2 H, t, *J* 7.4 Hz, benzylic CH_2), 2.99 (2 H, t, *J* 7.3 Hz, benzylic CH_2), 2.48 (3 H, s, 8-Me), and 2.17 (2 H, quintet, *J* 7.3 Hz, $CH_2CH_2CH_2$); *m/z* 171 (M^+, 100%), 156 (67), 142 (10), 128 (10), 115 (8), 84 (11), and 77 (12).

6,7-Dimethyl-5-trimethylsilylindole

The ester **13b** (49 mg, 0.12 mmol) was added to a suspension of lithium aluminium hydride (45 mg, 1.2 mmol) in dry dioxane (5 ml) and the mixture refluxed under nitrogen for 24 h. The excess lithium aluminium hydride was destroyed by careful addition of water (0.5 ml) followed by solid sodium hydrogen carbonate until a white granular precipitate resulted. The mixture was diluted with ether (50 ml), filtered through Celite, and the filtrate dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed [ether-light petroleum (1:2)] to give the *title compound* (19 mg, 74%), m.p. 65-72°C (Found: M^+, 217.1270. $C_{13}H_{19}NSi$ requires M, 217.1287); ν_{max}(Nujol) 3 412 and 838 cm^{-1}; δ (250 MHz; $CDCl_3$) 7.98 (1 H, br, NH), 7.67 (1 H, s, 4-H), 7.13 (1 H, t, *J* 2.8 Hz, 2-H), 6.51 (1 H, dd, *J* 3.1, 2.0 Hz, 3-H), 2.50 (3 H, s, ArMe), 2.40 (3 H, s, ArMe), and 0.36 (9 H, s, Me_3Si); *m/z* 217 (M^+, 45%), 202 (100), and 144 (11).

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REFERENCES

1. Baeyer, A. *Annalen* **1866**, *140*, 295.
2. For representative recent examples, see Wender, P. A.; Cooper, C. B. *Tetrahedron Lett.* **1987**, *28*, 6125; Fürstner, A.; Jumbam, D. N.; Weidmann, H. *ibid.* **1991**, *32*, 6695; Macor, J. E.; Wehner, J. M. *ibid.* **1991**, *32*, 7195; Smith, A. B.; Haseltine, J. N.; Visnick, M. *Tetrahedron* **1989**, *45*, 2431; Harrington, P. J.; Hegedus, L. S.; McDaniel, K.F. *ibid.* **1987**, *109*, 4335; Larock, R. C.; Yum, E. K. *ibid.* **1991**, *113*, 6689; Moyer, M. P.; Shiurba, J. F.; Rapoport, H. *J. Org. Chem.* **1986**, *51*, 5106; Hegedus, L. S.; Sestrick, M. R.; Michaelson, E. T.; Harrington, P. J. *ibid.* **1989**, *54*, 4141; Kraus, G. A.; Bougie, D.; Jacobson, R. A.; Su, Y. *ibid.* **1989**, *54*, 2425; Bauta, W. E.; Wulff, W. D.; Pavkovic, S. F.; Zaluzec, E. J. *ibid.* **1989**, *54*, 3249; Mewshaw, R. E. ; Taylor, M. D.; Smith, A. B. *ibid.* **1989**, *54*, 3449; Gharpure, M.; Stoller, A.; Bellamy, F.; Firnau, G.; Snieckus, V. *Synthesis* **1991**, 1079.
3. Preliminary communication, Jackson, P. M.; Moody, C. J. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2156.
4. For a review, see: Pindur, U.; Erfanian-Abdoust, H. *Chem. Rev.* **1989**, *89*, 1681.
5. Chauhan, P. M. S.; Jenkins, G.; Walker, S. M.; Storr, R. C. *Tetrahedron Lett.* **1988**, *29*, 117; Crew, A. P. A.; Jenkins, G.; Storr, R. C.; Yelland, M. *ibid.* **1990**, *31*, 1491; Münzel, N.; Schweig, A. *Chem. Ber.* **1988**, *121*, 791; Chadwick, D. J.; Plant, A. *Tetrahedron Lett.* **1987**, *28*, 6085; Plant, A.; Chadwick, D. J. *Synthesis* **1990**, 915; van Leusen, A. M.; van den Berg, K. J. *Tetrahedron Lett.* **1988**, *29*, 2689; de Jong, J. C.; van den Berg, K. J.; van Leusen, A. M.; Feringa, B. L. *ibid.* **1991**, *32*, 7751; Friederichsen, W.; Schöning, A. *Heterocycles* **1986**, *24*, 307; Schöning, A.; Friederichsen, W. *Tetrahedron Lett.* **1988**, *29*, 1137; *Liebigs Ann. Chem.* **1989**, 405; Tamura, Y.; Kirihara, M.; Sekihachi, J.; Okunaka, R.; Mohri, S.; Tsugoshi, T.; Akai, S.; Sasho, M.; Kita, Y. *Tetrahedron Lett.* **1987**, *28*, 3971; Kita, Y.; Okunaka, R.; Sasho, M.; Taniguchi, M.; Honda, T.; Tamura, Y. *ibid.* **1988**, *29*, 5943; Kuroda, T.; Takahashi, M.; Ogiku, T.; Ohmizu, H.; Kondo, K.; Iwasaki, T. *J. Chem. Soc., Chem. Commun.* **1991**, 1635.
6. (a) Moody, C. J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2505; (b) May, C.; Moody, C. J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 247; (c) Moody, C. J.; Shah, P. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1407; (d) Moody, C. J. Shah, P. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2463; (e) Moody, C. J.; Shah, P. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2463; (f) Moody, C. J.; Rahimtoola, K. F. *J. Chem. Soc., Perkin Trans. 1* **1990**, 673; (g) Jackson, P. M. Moody, C. J. *J. Chem. Soc., Perkin Trans. 1* **1990**, 681; (h) Moody, C. J.; Rahimtoola, K. F. *J. Chem. Soc. Chem. Commun.* **1990**, 1667; (i) Jackson, P. M.; Moody, C. J.; Mortimer, R. J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2941.
7. Jackson, P. M.; Moody, C. J.; Shah, P. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2909.
8. Sheppard, G. S.; Vollhardt, K. P. C. *J. Org. Chem.* **1986**, *51*, 5496.
9. Natsume, M.; Muratake, H. *Tetrahedron Lett.* **1979**, 3477.
10. Muratake, H.; Natsume, M. *Heterocycles* **1989**, *29*, 771.
11. Muratake, H.; Natsume, M. *Heterocycles* **1990**, *30*, 691.
12. Kozikowski, A. P.; Shum, P. W.; Basu, A.; Lazo, J. S. *J. Med. Chem.* **1991**, *34*, 2420.
13. Keil, J.-M.; Kämpchen, T.; Seitz, G. *Tetrahedron Lett.* **1990**, *31*, 4581.
14. Wenkert, E.; Moeller, P. D. R.; Piettre, S. R. *J. Am. Chem. Soc.* **1988**, *110*, 7188.
15. Stoll, G.; Frank, J.; Musso, H.; Henki, H.; Herrendorf, W. *Liebigs Ann. Chem.* **1986**, 1968.
16. Kakushima, M.; Hamel, P.; Frenette, R.; Rokach, J. *J. Org. Chem.* **1983**, *48*, 3214.
17. Nakayama, J.; Simamura, O.; Yoshida, M. *J. Chem. Soc., Chem. Commun.* **1970**, 1222.
18. For a review on acetylene equivalents, see De Lucchi, O.; Modena, G. *Tetrahedron* **1984**, *40*, 2585.
19. Moody, C. J.; Shah, P.; Knowles, P. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3249.
20. Capon, R. J.; MacLeod, J. K.; Scammels, P. J. *Tetrahedron* **1986**, *42*, 6545.
21. Herb, R.; Carroll, A. R.; Yoshida, W. Y.; Scheuer, P. J.; Paul, V. J. *Tetrahedron* **1990**, *46*, 3089.
22. MacLeod, J. K.; Monahan, L. C. *Tetrahedron Lett.* **1988**, *29*, 391; *Aust. J. Chem.* **1990**, *43*, 329; Yasukouchi T.; Kanematsu, K. *Tetrahedron Lett.* **1989**, *30*, 6559; Yasukouchi, T.; Kanematsu, K. *J. Chem. Soc., Chem. Commun.* **1989**, 953; Muratake, H.; Natsume, M. *Tetrahedron Lett.* **1989**, *30*, 5771; Muratake, H.; Watanabe, M. Goto, K.; Natsume, M. *Tetrahedron* **1990**, *46*, 4179; Boger, D. L.; Zhang, M. *J. Am. Chem. Soc.* **1991**, *113* 4230.
23. McNab, H. *J. Chem. Soc., Perkin Trans. 1* **1984**, 377.