Synthesis of Pyrrolo[2,1-*c*][1,4]benzothiazines by Annellation of 3-Alkoxycarbonylmethylene-4*H*-1,4-benzothiazines (β-Enamine Esters) with Dimethyl Acetylenedicarboxylate

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The annellation of the benzothiazines (**1a—c**) with DMAD affords the corresponding pyrrolo[2,1-*c*]-[1,4]benzothiazines (**5a—c**) rather than pyrido[2,1-*c*][1,4]benzothiazines. Such structural assignments are based on spectroscopic and *X*-ray evidence

As part of our continuing investigation of the chemistry of the 1,4-benzothiazine system,[1] which occurs in natural products as well as in biologically active compounds,[2] it appeared to be of interest to synthesize both pyrido- and pyrrolo-[2,1-*c*][1,4]-benzothiazines for biological evaluation. Furthermore, taking into account that the desired compounds (**3**)—(**6**) could in principle arise from appropriate configurational isomers of the dienamine (**2**), by 5-*exo-trig*- and 6-*exo-trig*-ring closure respectively, the synthesis of compounds such as (**2**) was attempted by reaction between β-enamino esters (**1**) and dimethyl acetylenedicarboxylate (DMAD).

In a recent communication[3] we reported that the 1,4-benzothiazine (**1a**) reacts with DMAD in refluxing toluene to give the Michael adduct (**2a**), together with a (**2a**)–CH_4O compound (**A**). Similarly, compound (**2b**) together with the (**2b**)–CH_4O compound (**B**), and (**2c**) together with the (**2c**)–CH_4O compounds (**C**) and the phenothiazine (**7**), were obtained starting from compounds (**1b**) and (**1c**) respectively. Moreover, the formation of compound (**7**) was suggested to occur *via* the intermediate *Z,Z*-(**2**): compounds (**A**), (**B**), and (**C**), which are also obtained by acid-catalysed cyclisation of the corresponding dienamine compounds (**2a—c**) in toluene at reflux, were tentatively assigned the pyrido-structures (**4a**), (**4b**), and (**6**), respectively, based on ^1H n.m.r. data. However, these data would not exclude structures (**3**), (**3'**) and (**5**).

In order to solve this structural ambiguity further experimental work has been carried out.

By running the above annellation reactions with toluene-*p*-sulphonic acid as catalyst, compounds (**A**), (**B**), and (**C**) are obtained in higher yield and shorter time.

In the proton-coupled ^{13}C n.m.r. spectra of these compounds (Table 1) the lactam carbonyl signal at δ 165.1 p.p.m. clearly appears as a triplet (*J* 4.7 Hz). This is consistent with structure (**5**) or (**6**), and not with (**4**), (**3**), and (**3'**). Furthermore, it has been found that in dimethylformamide (DMF) at reflux both compounds (**2a**) and (**A**) are unstable. The former yields (**A**) together with a (**A**)–$C_2H_2O_2$ compound (**8a**), and the latter give rise to (**8a**). Therefore, compound (**A**) must be an intermediate in the conversion of compound (**2a**) into (**8a**). Similarly, under the above conditions both compounds (**2b**) and (**B**) gave the pyrrolo compound (**8b**) with very similar ^1H and ^{13}C (proton-decoupled) n.m.r. and i.r. spectra to those of compound (**8a**).

The ^1H n.m.r. spectra of compounds (**8a**) and (**8b**) look very simple. They are characterised by a one-proton doublet of doublets centred at δ 9.16 and a three-proton singlet at δ 2.33, the upfield resonance indicating the presence of a methyl group linked to an sp^2 carbon and the downfield one a deshielded aromatic proton; this suggests that a lactam moiety is present. Moreover, taking into account that proton coupled ^{13}C n.m.r. spectra (Table 1) reveal the lactam carbonyl coupled to the protons of the methyl group, compounds (**8a**) and (**8b**) must be characterised as 3-alkoxycarbonyl-2-methylpyrrolo[21,-*c*]-benzothiazines.

The ^1H and ^{13}C n.m.r. spectra of compounds (**A**), (**B**), and (**C**) are very similar to those of compounds (**8a**) and (**8b**). Therefore, the following two conclusions can be drawn: (i) the pyrrolo[2,1-*c*][1,4]benzothiazine structures (**5a**), (**5b**), and (**5c**) are assigned to compounds (**A**), (**B**), and (**C**), respectively; and (ii) the dienamines (**2a—c**) should undergo a 5-*exo-trig*-ring closure *via* an appropriate intermediate [*i.e.* *E*/*E*- and/or *Z*/*E*-(**2**)]. Since our conclusions contrast with those reported for the cyclisation of similarly substituted dienamines, which afford pyrido derivatives,[4] an *X*-ray analysis of compound (**A**) has been carried out to confirm the pyrrolo structure (**5a**) and consequently the ring-closure mode of the compounds (**2a—c**). Details of this analysis are given in the Experimental section. The Figure depicts a general view of the molecular structure of compound (**A**).

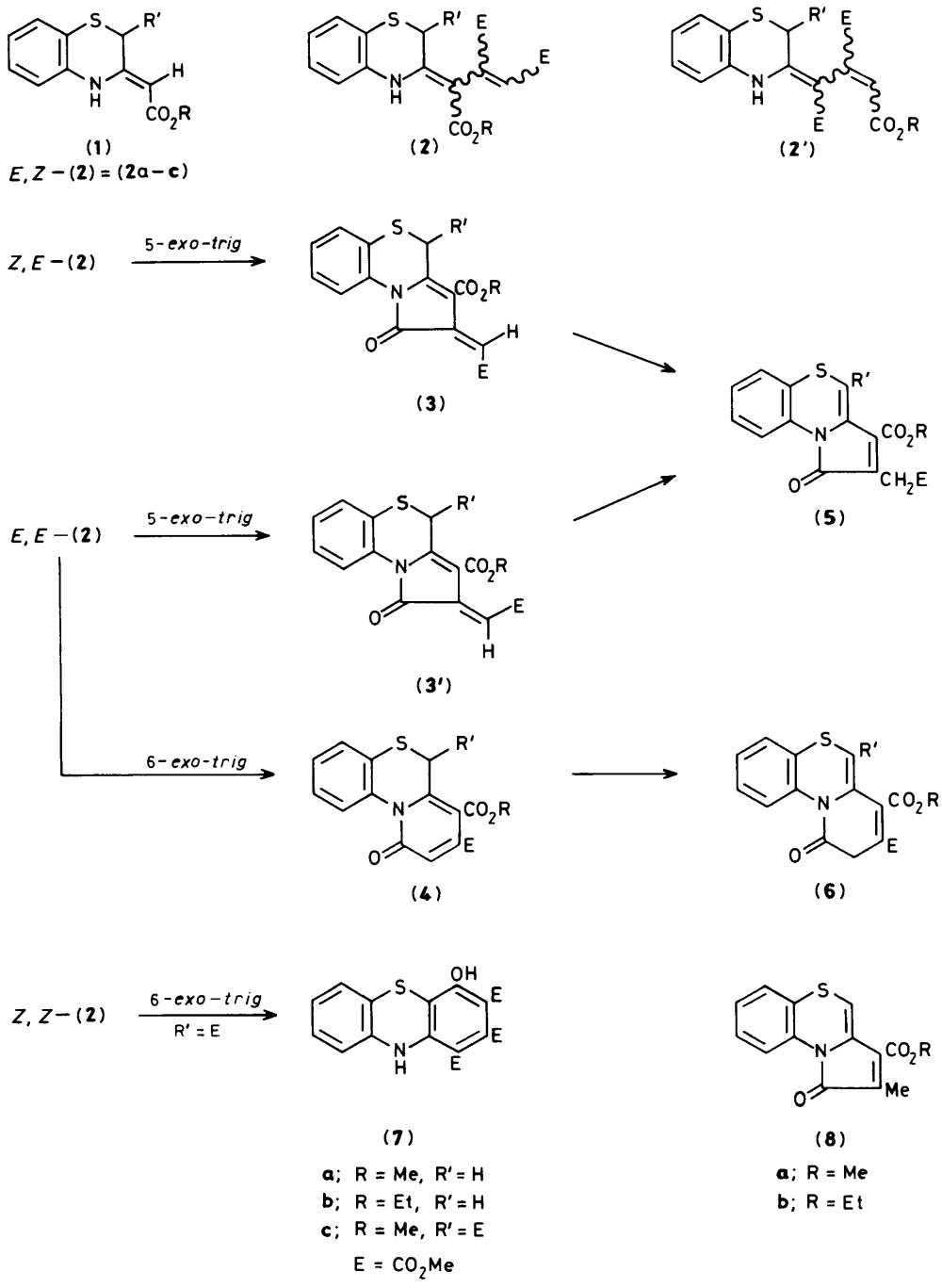
It is noteworthy that the (**2b**) ⟶ (**5b**) conversion constitutes chemical evidence in favour of the ethoxycarbonyl group being linked at the β-C of the dienamine (**2b**). This is supported also from the proton coupled ^{13}C n.m.r. spectrum of compound (**2b**) (Table 1), which shows the ethoxycarbonyl at δ 168.5 p.p.m. as a triplet and the two methoxycarbonyls at δ 167.6 and 165.3 p.p.m., each as a double quartet. As these data are consistent with the Michael adducts (**2b**) and not with the regioisomer (**2'b**), which in turn should arise from the ring opening of a cyclobutene adduct of compound (**1b**) with DMAD, the structures originally assigned to compounds (**2a—c**) are now confirmed.

These results clearly show that the annellation of the 1,4-benzothiazines (**1**) with DMAD proceeds through the Michael adduct (**2**) as an intermediate, and affords the pyrrolo[2,1-*c*]-[1,4]benzothiazines (**5**).

Experimental

M.p.s are uncorrected. I.r. spectra were taken on a Perkin–Elmer 257 instrument as Nujol mulls for solids or with KBr discs or as liquid films. Mass spectra were recorded on a Perkin–Elmer 270 low-resolution spectrometer. ^1H N.m.r. spectra†

† Once the structures of compounds (**5a—c**) were unequivocally established, certain previously made n.m.r. assignments had to be revised.



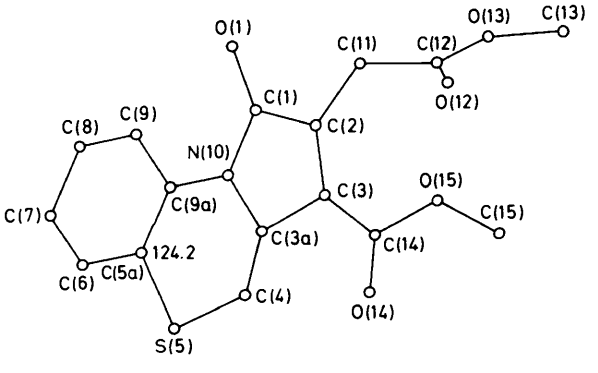


Figure.

were recorded on a Varian EM-390 instrument operating at 90 MHz, and ^{13}C n.m.r. spectra using a Varian XL-200 instrument for solutions in $CDCl_3$. Chemical shifts are given as δ values from tetramethylsilane as internal standard. Preparative t.l.c. on Carlo Erba SIF_{254} silica gel plates (2-mm thickness) and column chromatography on silica gel (Merck 70—325 mesh) were carried out using light petroleum (b.p. 40—70 °C)–ethyl acetate (8:2 v/v) as eluant unless otherwise stated. All the following reactions were carried out under nitrogen.

(Z)-3,4-*Dihydro*-3-*methoxycarbonylmethylene*[1,4]*benzothiazine* (**1a**).—To a solution of compound (**1c**)[5] (3.0 g, 10.8 mmol) in methanol (50 ml), KOH (300 mg, 5.36 mmol) in pellets was added. The mixture was heated at 60 °C for 4 h with stirring until t.l.c. indicated no further change. The solution was concentrated and acidified with 2.5M-aqueous hydrogen

Table 1. ^{13}C N.m.r. spectra for solutions in $CDCl_3$ and recorded as δ values (p.p.m.) from Me_4Si as internal standard. The multiplicities observed on off-resonance decoupling are noted

	(2a)	(2b)	(5a)	(5b)	(5c)	(8a)	(8b)
Ester CO	168.92s[a] 167.37s[b] 165.24s[c]	168.51s[d] 167.57s[e] 165.30s[f]	169.79s[g] 162.62s[h]	169.79s[g] 169.23s[i]	168.95s[g] 163.00s[h] 162.71s[h]	163.37s	162.98s
Amide CO			165.11s[i]	165.26s[i]	165.13s[i]	166.14s	166.23s
sp^2–C	149.87s 139.94s 136.11s 121.02s 90.90s	149.90s 140.20s 136.13s 121.04s 91.29s	133.04s 132.73s 129.52s 124.11s 117.01s	133.13s 132.46s 129.73s 124.44s 117.07s	132.93s 132.65s 132.24s 129.88s 117.48s 115.32s	137.88s 133.09s 129.73s 122.69s 117.33s	137.70s 133.15s 129.86s 122.95s 117.37s
sp^2–CH	129.54d 127.87d 127.03d 122.85d 118.09d	129.00d 127.86d 127.01d 122.80d 118.10d	128.25d 126.18d 125.42d 119.09d 112.57d	128.28d 126.23d 125.43d 119.15d 112.50d	128.36d 126.05d 125.92d 118.89d	128.02d 126.12d 125.25d 119.00d 109.61d	128.04d 126.13d 125.24d 119.00d 109.53d
OCH_2		60.00t		61.64t			61.34t
OCH_3	52.93q 52.04q 51.37q	52.84 52.02q	52.28q	52.22q	53.25q 52.48q	52.07q	
CH_2	26.71t	26.70t	30.63t	30.65t	29.85t		
CH_3		14.23q		14.05q		11.26q	14.21q 11.26q

The multiplicities and the main coupling constants observed in the proton-coupled spectra are as follows: [a] q $^3J_{CO.Me}$ 3.8 Hz; [b] dq $^3J_{CO.H}$ 6.7 Hz, $^3J_{CO.Me}$ 3.8 Hz; [c] dt $^3J_{CO.Me}$ 3.9 Hz, $^2J_{CO.H}$ 2.2 Hz; [d] t $^3J_{CO.Me}$ 3.3 Hz; [e] dq $^3J_{CO.H}$ 7.2 Hz, $^3J_{CO.Me}$ 3.9 Hz; [f] dq $^3J_{CO.Me}$ 3.9 Hz, $^2J_{CO.H}$ 2.1 m; [g] m; [h] q; [i] t.

chloride. The organic phase was extracted with $CHCl_3$, dried and evaporated. The residue was purified by column chromatography affording compound (**1a**) as a white solid (55% yield): m.p. 105 °C (Found: C, 59.85; H, 5.1; N, 6.3. Calc. for $C_{11}H_{11}NO_2S$: C, 59.7; H, 5.0; N, 6.3%); $\nu_{max.}$ 1 660, 1 630, cm^{-1}; δ($CDCl_3$) 10.58 (br s, 1 H, NH), 7.3—6.8 (m, 4 H, ArH), 4.70 (s, 1 H, vinyl H), 3.70 (s, 3 H, OCH_3), and 3.40 (s, 2 H, CH_2); *m/z* 221 (M^+/base) 189, 161.

By the same procedure compound (**1b**)[5] was obtained in 50% yield.

Reactions of 3-*Alkoxycarbonylmethylene*-3,4-*dihydro*-2H-1,4-*benzothiazine* (**1a—c**) *with DMAD. General Procedure.*—A solution of the [1,4]benzothiazine (**1**) (10 mmol) and DMAD (10.1 mmol) in toluene (50 ml) was refluxed until t.l.c. indicated no further change (*ca.* 10 h). The solvent was evaporated off, the resulting oil was chromatographed on silica gel and the following products were isolated in the order given. From compound (**1a**): (i) *methyl* (E,Z)-4-(3,4-*dihydro*-2H-1,4-*benzothiazin*-3-*ylidene*)-3,4-*dimethoxycarbonylbut*-2-*enoate* (**2a**) (44%), as a yellow oil (Found: C, 56.4; H, 4.65; N, 3.9. $C_{17}H_{17}NO_6S$ requires C, 56.2; H, 4.7; N, 3.9%); *m/z* 363 (M^+) (base), 331, 303, 272, 244, 212, and 105; (ii) 3-*methoxycarbonyl*-2-*methoxycarbonylmethyl*-1H-*pyrrolo*[2,1-c][1,4]*benzothiazin*-1-*one* (**5a**) (43%), as red crystals, m.p. 55 °C (from MeOH) (Found: C, 58.3; H, 4.2; N, 4.3. $C_{16}H_{13}NO_5S$ requires C, 58.0; H, 4.0; N, 4.2%); $\nu_{max.}$(Nujol) 1 740, 1 720, and 1 670 cm^{-1}; δ($CDCl_3$) 9.20 (dd, 1 H, *J* 9 and 1 Hz, ArH), 7.47 (s, 1 H, vinylic H), 7.0—7.4 (m, 3 H, ArH), 3.86 (s, 5 H, OCH_3 + CH_2CO), and 3.69 (s, 3 H, OCH_3); *m/z* 331 (M^+) (base), 299, 272, 244, 212, and 184. From compound (**1b**): (i) *methyl* (E,Z)-4-*ethoxycarbonyl*-3-*methoxycarbonyl*-4-(3,4-*dihydro*-2H-1,4-*benzothiazin*-3-*ylidene*)*but*-2-*enoate* (**2b**) (46%), as a yellow oil (Found: C, 57.1; H, 5.15; N, 3.9. $C_{18}H_{19}NO_6S$ requires C, 57.3; H, 5.1; N, 3.7%); *m/z* 377 (M^+) (base), 331, 303, 272, 244, and 212; (ii) 3-*Ethoxycarbonyl*-2-*methoxycarbonylmethyl*-1H-*pyrrolo*[2,1-c]-[1,4]*benzothiazin*-1-*one* (**5b**) (42%), as red crystals, m.p. 178 °C (Found: C, 59.3; H, 4.45; N, 4.2. $C_{17}H_{15}NO_5S$ requires C, 59.1; H, 4.4; N, 4.1%); $\nu_{max.}$(Nujol) 1 740, 1 720, and 1 670 cm^{-1}; δ($CDCl_3$) 9.16 (dd, 1 H, *J* 9 and 1 Hz, ArH), 7.47 (s, 1 H, vinylic H), 7.3—7.0 (m, 3 H, ArH), 4.35 (q, 2 H, OCH_2), 3.86 (s, 2 H, CH_2CO), 3.69 (s, 3 H, OCH_3) and 1.34 (t, 3 H, CH_2CH_3); *m/z* 345 (M^+) (base), 299, 285, 272, and 258. From (**1c**): (i) *methyl*(E,Z)-3,4-*dimethoxycarbonyl*-4-(2-*methoxycarbonyl*-3,4-*dihydro*-2H-1,4-*benzothiazin*-3-*ylidene*)*but*-2-*enoate*. (**2c**) (30%), as a yellow solid, m.p. 119 °C (Found: C, 54.3; H, 4.7; N, 3.4. $C_{19}H_{19}NO_8S$ requires C, 54.2; H, 4.55; N, 3.3%); (ii) 3,4-*methoxycarbonyl*-2-*methoxycarbonylmethyl*-1H-*pyrrolo*[2,1-c]-[1,4]*benzothiazin*-1-*one* (**5c**) (30%), as red crystals, m.p. 114 °C (from MeOH) (Found: C, 55.7; H, 3.8; N, 3.7. $C_{18}H_{15}NO_7S$ requires C, 55.5; H, 3.9; N, 3.6%); $\nu_{max.}$(Nujol) 1 740 and 1 695 cm^{-1}; δ($CDCl_3$) 8.96 (dd, 1 H, *J* 9 and 1 Hz, ArH), 7.3—7.0 (m, 3 H, ArH), 3.83 (s, 6 H, OCH_3), and 3.70 (s, 5 H, OCH_3 + CH_2CO_2Me); *m/z* 389 (M^+) (base) 357, 330, 298, 270, and 228; (iii) 4-*hydroxy*-1,2,3-*trimethoxycarbonyl*-10H-*phenothiazine* (**7**) (21%) as a yellow solid, m.p. 159 °C (Found: C, 55.2; H, 4.0; N, 3.8. $C_{18}H_{15}NO_7S$ requires C, 55.5; H, 3.9; N, 3.6%); $\nu_{max.}$(Nujol) 3 220, 1 750, 1 700, and 1 670 cm^{-1}; δ($CDCl_3$) 11.93 (s, 1 H, OH), 9.87 (br s, 1 H, NH), 7.0—6.6 (m, 3 H, ArH), 6.5—6.4 (m, 1 H, ArH), and 3.83, 3.80, and 3.78, (three s, 9 H, OCH_3); *m/z* 389 (M^+), 358, 357, and 325 (base). On carrying out the above reactions for 6 h only with a trace of toluene-*p*-sulphonic acid, the products (**2**) and (**5**) were obtained

Table 2. Fractional co-ordinates (× 10^4) of non-H atoms with e.s.d.s in parentheses

	x	*y*	*z*
S(5)	8 760(1)	1 905(2)	2 008(1)
N(10)	9 804(3)	2 477(4)	−1 919(4)
C(1)	1 390(3)	2 928(4)	−3 545(4)
C(3a)	10 350(3)	2 787(4)	−554(4)
C(3)	11 333(3)	3 391(4)	−1 399(4)
C(2)	11 360(3)	3 506(5)	−3 171(4)
C(4)	9 976(3)	2 569(5)	1 159(4)
O(1)	10 137(3)	2 860(4)	−4 997(3)
C(9)	8 441(4)	1 266(6)	−2 961(5)
C(8)	7 509(4)	560(6)	−2 647(7)
C(7)	6 943(4)	347(6)	−967(7)
C(6)	7 359(4)	786(6)	407(6)
C(5a)	8 305(3)	1 477(5)	114(5)
C(9a)	8 847(3)	1 762(5)	−1 598(5)
O(13)	14 110(3)	3 679(4)	−5 415(5)
C(14)	12 141(4)	3 798(5)	−393(5)
O(12)	13 421(3)	1 370(4)	−4 361(5)
O(14)	11 955(3)	4 082(5)	1 087(4)
C(12)	13 283(3)	2 861(5)	−4 758(5)
O(15)	13 127(3)	3 825(4)	−1 369(4)
C(11)	2 163(3)	4 118(5)	5 366(5)
C(15)	3 979(5)	4 226(8)	9 495(8)
C(13)	5 242(4)	2 560(8)	4 439(10)

in the following yields: (**2a**) 22%, (**2b**) 24%, (**2c**) 20%; (**5a**) 63%, (**5b**) 65%, (**5c**) 45%.

Conversion of the Dienamines (**2a**) *and* (**2b**) *into the* [1,4]*Benzothiazines* (**8a**) *and* (**8b**), *respectively. General procedure.*—A solution of the dienamine (**2**) (1.4 mmol) in DMF (30 ml) was refluxed for 6 h. The solvent was evaporated off and the resulting oil was purified by preparative chromatography on silica gel. 3-*Methoxycarbonyl*-2-*methyl*-1H-*pyrrolo*[2,1-c][1,4]-*benzothiazine*-1-*one* (**8a**) (21%), as a yellow solid, m.p. 162—165 °C (from MeOH) (Found: C, 61.9; H, 4.2; N, 5.2. $C_{14}H_{11}NO_3S$ requires C, 61.5; H, 4.1; N, 5.1%); $\nu_{max.}$(KBr) 1 715, 1 680, and 1 630 cm^{-1}; δ($CDCl_3$) 9.16 (dd, 1 H, *J* 9 and 1 Hz, ArH), 7.27 (s, 1 H, vinylic H), 7.2—7.0 (m, 3 H, ArH), 3.90 (s, 3 H, OMe), and 2.33 (s, 3 H, CH_3); *m/z* 273 (M^+) (base), and 186. 3-*Ethoxycarbonyl*-2-*methyl*-1H-*pyrrolo*[2,1-c][1,4]*benzothiazin*-1-*one* (**8b**) (18%), as a yellow solid, m.p. 123—124 °C (from EtOH) (Found: C, 62.85; H, 4.5; N, 4.8. $C_{15}H_{13}NO_3S$ requires C, 62.7; H, 4.6; N, 4.9%); $\nu_{max.}$(KBr) 1 715, 1 680, and 1 630 cm^{-1}; δ($CDCl_3$) 9.16 (dd, 1 H, *J* 9 and 1 Hz, ArH), 7.27 (s, 1 H, vinylic H), 7.2—7.0 (m, 3 H, ArH), 4.36 (q, 2 H, OCH_2), 2.33 (s, 3 H, CH_3), and 1.40 (t, 3 H, CH_3); *m/z* 287 (M^+) (base), 259, and 186.

Conversion of Compounds (**5a**) *and* (**5b**) *into* (**8a**) *and* (**8b**) *respectively.*—By refluxing a DMF (50 ml) solution of compound (**5a**) (2.2 mmol) or (**5b**) (2 mmol) for 6 h and working up as above, compounds (**8a**) (53%) and (**8b**) (48%) were obtained respectively.

Crystal Data.—$C_{16}H_{13}SNO_5$, M_r = 331.346. Triclinic, P$\bar{1}$, *a* = 12.326, *b* = 8.295, *c* = 7.769 Å, α = 79.17, β = 81.92, γ = 76.20°, V = 753.84 $Å^3$, *Z* = 2, D_x = 1.459 g cm^{-3}, λ(Mo-K_α) = 0.710 69 Å, *F*(000) = 172.0.

A ruby prismatic single crystal with dimension *ca.* 0.2 × 0.3 × 0.65 mm was used to measure the cell parameters and record the intensities of 4 434 independent reflections with a Nicolet R 3 four-circle diffractometer.

Mo-K_α radiation, graphite monochromator, θ/2θ scan, $2\theta_{max.}$ = 60°, LP correction, no absorption and secondary extinction correction. The structure was solved by direct methods using the SIR package[6] of computer programs, and refined by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms, using 3 162 independent reflections with $F_o > 3\sigma(F_o)$. The hydrogen atoms were located from a difference Fourier map, except for methyl type, CH_3, were placed in geometrically defined positions and refined as a rigid group with the constraint that all C–H = 1.08; temperature factors equal to the isotropic temperature factor of their carrier atoms. Convergence at *R* = 0.053.

Table 3. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses, and relevant torsion angles (°)

C(4)–S(5)	1.722(4)	C(5a)–S(5)	1.769(4)
N(10)–C(1)	1.397(4)	C(2)–C(1)	1.473(5)
O(1)–C(1)	1.227(4)	C(3a)–N(10)	1.424(4)
C(9a)–N(10)	1.415(5)	C(4)–C(3a)	1.339(5)
C(3)–C(3a)	1.447(5)	C(2)–C(3)	1.359(4)
C(14)–C(3)	1.482(5)	C(11)–C(2)	1.495(5)
C(8)–C(9)	1.383(6)	C(9a)–C(9)	1.397(5)
C(7)–C(8)	1.392(7)	C(6)–C(7)	1.387(7)
C(5a)–C(6)	1.391(6)	C(9a)–C(5a)	1.407(5)
C(12)–O(13)	1.347(5)	C(13)–O(13)	1.483(6)
O(14)–C(14)	1.197(5)	O(15)–C(14)	1.341(5)
C(12)–O(12)	1.139(5)	C(11)–C(12)	1.552(6)
C(14)–O(15)	1.341(5)	C(15)–O(15)	1.454(5)

C(5a)–S(5)–C(4)	102.0(2)	C(2)–C(1)–N(10)	106.6(3)
O(1)–C(1)–N(10)	126.4(4)	C(9a)–N(10)–C(1)	127.5(3)
O(1)–C(1)–C(2)	127.0(3)	C(9a)–N(10)–C(3a)	123.3(3)
C(3)–C(3a)–N(10)	106.6(3)	C(4)–C(3a)–N(10)	124.6(4)
C(2)–C(3)–C(3a)	109.2(3)	C(4)–C(3a)–C(3)	128.8(3)
C(14)–C(3)–C(3a)	122.6(3)	C(14)–C(3)–C(2)	128.3(4)
C(3)–C(2)–C(1)	108.4(3)	C(11)–C(2)–C(1)	120.9(3)
C(3a)–C(4)–S(5)	124.6(3)	C(11)–C(2)–C(3)	130.7(3)
C(9a)–C(9)–C(8)	120.9(4)	C(7)–C(8)–C(9)	120.7(4)
C(6)–C(7)–C(8)	118.9(4)	C(5a)–C(6)–C(7)	120.9(4)
C(6)–C(5a)–S(5)	115.6(3)	C(9a)–C(5a)–S(5)	124.2(3)
C(9)–C(9a)–N(10)	120.9(3)	C(9a)–C(5a)–C(6)	120.1(4)
C(5a)–C(9a)–N(10)	120.8(3)	C(5a)–C(9a)–C(9)	118.3(4)
C(13)–O(13)–C(12)	113.9(4)	O(14)–C(14)–C(3)	125.5(4)
O(15)–C(14)–C(3)	111.0(3)	O(15)–C(3)–O(14)	123.5(4)
O(12)–C(12)–O(13)	124.3(3)	C(11)–C(12)–O(13)	109.8(4)
C(15)–O(15)–C(14)	115.3(4)	C(11)–C(12)–O(12)	125.9(4)

C(4)–S(5)–C(5a)–C(9a)	−3.2(9)
C(4)–S(5)–C(5a)–C(6)	175.5(8)
C(5a)–S(5)–C(4)–C(3a)	4.6(9)
O(1)–C(1)–C(2)–C(3)	179.7(9)
C(2)–C(1)–N(10)–C(9a)	−176.3(9)
O(1)–C(1)–N(10)–C(9a)	4.02(9)
C(1)–N(10)–C(9a)–C(5a)	−175.8(9)
C(1)–N(10)–C(3a)–C(4)	176.6(8)

Crystal Structure Solution.—The first attempt *via* the usual tangent formula[7] was unsuccessful: the most promising figures of merit indicated Patterson-like solutions. The structure was solved by application of the so-called P10 formula.[6] *A posteriori* analysis of the phase relationships revealed some features which deserve to be noted because of their methodological implication: (i) the negative quartets, which usually give rise to an efficient figure of merit, proved completely unuseful. Indeed a very small fraction (0.086) of the quartets estimated negative were really negative; (ii) the first error in the triplet invariants estimated by Cochran's formula was unexpected for 93 in the list: 13 negative triplets occurred among the largest 800. That was probably the most important reason for the failure. Conversely when triplets were estimated *via* the P10 formula, the first error was at 573 in the list. Furthermore, 137 triplets

were estimated negative: they were estimated from the set of active triplets and used as a figure of merit. Unlike negative quartets negative triplets were estimated by P10 with sufficient accuracy. For example 30 of the 54 triplets estimated negative with largest *reliabilities* were really negative. Thus the use of the P10 formula, both *via* the active use of the positive estimated triplets and the positive use of the negative ones, allowed us to overcome the inefficiency of Cochran's formula and solve the structure.

Fractional atomic co-ordinates for non-hydrogen atoms are shown in Table 2, and bond lengths and angles in Table 3. Anisotropic thermal parameters and the hydrogen atom atomic co-ordinates are available on request from the Cambridge Crystallographic Data Centre.*

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* See Instructions for Authors (1987), para. 5.6.3, in *J. Chem. Soc., Perkin Trans. 1*, 1987, Issue 1.

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