Condensed Thiophen Ring Systems. Part XIII.[1,2] Synthesis of Azidobenzo[*b*]thiophens and their Conversion into Thienobenzoxazoles

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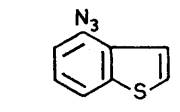
The preparation is reported of a series of azidobenzo[*b*]thiophens [(1)—(3). (5). (6). and (22)]. The 5-azides (2)—(5) gave the 2-methylthieno[2,3-*g*]benzoxazoles (7)—(10) (angular products) on thermolysis in a mixture of polyphosphoric and acetic acids. In contrast. similar treatment of 5-azidobenzo[*b*]thiophen 1,1-dioxide (6) gave the linear product. 2-methylthieno[3,2-*f*]benzoxazole 7,7-dioxide (11). 4-Azidobenzo[*b*]thiophen (1) underwent a Bamberger-type rearrangement under similar conditions. to give 4-acetamido-7-acetoxybenzo[*b*]-thiophen (17).

In continuation of our studies of azidobenzo[*b*]thiophens [3] we report the preparation of the azidobenzo[*b*]-thiophens (1)—(3), (5) and (6). A convenient synthesis of benzoxazoles [4,5] which involves thermolysis of an aryl azide in a mixture of polyphosphoric acid and an aliphatic carboxylic acid has been extended to the synthesis of the thienobenzoxazoles (7)—(11) from the azides (2)—(6), respectively.

Thermolysis of 4-acetamidobenzo[*b*]thiophen-5-ol is reported [6] to give 2-methylthieno[3,2-*e*]benzoxazole (12) which appears to be the only thienobenzoxazole reported to date. The isomeric compounds (13) and (14) may be prepared similarly.[6] Thieno[2,3-*g*][1,2]benzisoxazole (15) has been prepared recently.[7]

5-Azido-3-methylbenzo[*b*]thiophen (5) was prepared by successive treatment of the Grignard compound derived from 5-bromo-3-methylbenzo[*b*]thiophen with toluene-*p*-sulphonyl azide and sodium pyrophosphate; [8] the azides (1)—(3) and (6) were prepared from the corresponding amines *via* reaction of the derived diazonium compound with sodium azide. 4-Aminobenzo[*b*]thiophen was prepared in 34% yield from the oxime of 6,7-dihydrobenzo[*b*]thiophen-4(5*H*)-one (16) by treatment with acetic acid and acetic anhydride saturated with hydrogen chloride,[9] as well as by aromatisation of the cyclic ketone (16) with sulphur [10] followed by Bucherer reaction [11] of the product, benzo[*b*]thiophen-4-ol. The starting material (16) was prepared in the usual way: replacement of nitrobenzene [12] by dichloromethane [13] as the solvent for the condensation of



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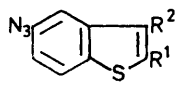
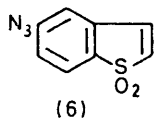


(2) $R^1 = R^2 = H$
(3) $R^1 = CO_2Et, R^2 = H$
(4) $R^1 = CO_2Me, R^2 = H$
(5) $R^1 = H, R^2 = Me$



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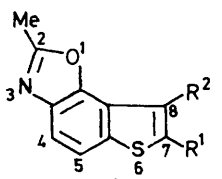
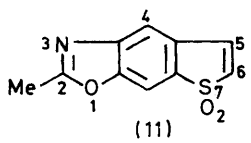


(7) $R^1 = R^2 = H$
(8) $R^1 = CO_2Et, R^2 = H$
(9) $R^1 = CO_2Me, R^2 = H$
(10) $R^1 = H, R^2 = Me$



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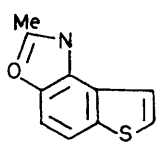

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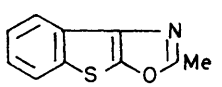

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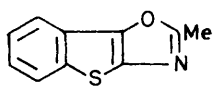

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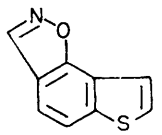

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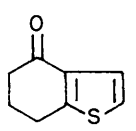

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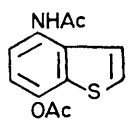

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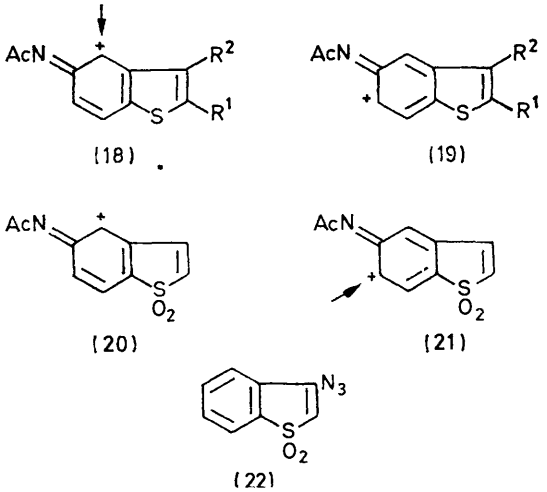
[12] L. F. Fieser and R. G. Kennelly, *J. Amer. Chem. Soc.*, 1935, **57**, 1611.
[13] Socony Mobil Oil Co., Inc., Neth. P. Appl. 6,511,447/1966 (*Chem. Abs.*, 1966, **65**, 7143).

thiophen with succinic anhydride increased the yield of β-(2-thenoyl)propionic acid from 45 to 83%, and Wolff–Kishner reduction of this compound to γ-(2-thienyl)-butyric acid gave a better yield than a Clemmensen reduction.[12] Cyclisation of γ-(2-thienyl)butyric acid to the cyclic ketone (16) was carried out according to the method of Nishimura *et al.*[14]

As expected by analogy with the behaviour of 1-azidonaphthalene,[5] thermolysis of 4-azidobenzo[*b*]thiophen (1) in a mixture of polyphosphoric and acetic acids gave a poor yield of 4-acetamido-7-acetoxybenzo[*b*]thiophen (17) by a Bamberger-type rearrangement. Similar treatment of the azides (2)—(5), however, gave the 2-methylthieno[2,3-*g*]benzoxazoles (7)—(10), respectively. The formation of angular products can be attributed to the greater stability of the intermediate carbonium ions (18) relative to those of the alternative species (19). 2-Azidonaphthalene behaves analogously.[5] Presumably, electronic effects overcome any *peri*-interaction that is present in these cases (see later). As in analogous cases,[4,5] the yields depended on electronic effects. Thus, the thiophen ring of the azide (2) is electron-donating towards the benzene ring. Consequently, the yield of the thienobenzoxazole (7) derived from this azide was only 37%. The presence of a methyl group on the thiophen ring in the azide (5) lowered the yield of the derived thienobenzoxazole (10) to 24%, whereas the presence of a strongly electron-withdrawing group in the azides (3) and (4) resulted in a nearly quantitative yield (Table 3) of the corresponding product, (8) or (9), respectively. Various attempts[4,5] to prepare 5-acetamido-4-acetoxybenzo[*b*]thiophen from 5-azidobenzo[*b*]-thiophen (2) failed.



The structures of thienobenzoxazoles (7)—(10) followed from their n.m.r. spectra. Compound (7), for example, showed two overlapping AB systems ($J_{4,5}$ 9·0, $J_{7,8}$ 5·0 Hz); the coupling constants agree with those obtained before for the 6,7- (8·0—9·0 Hz) and 2,3-couplings (5·0—6·0 Hz) in benzo[*b*]thiophen systems.[15] The assignment of the low field AB quartet in the spectrum of compound (7) to the 4- and 5-protons followed from the coupling constant and from the collapse of the high field AB quartet to a singlet on substitution of the thiophen ring by an ester function [*i.e.* in compounds (8) and (9)]: the 7-H signal of compound (10) was split by the adjacent methyl group, as expected.

In contrast to the formation of the angular systems (7)—(10) on thermolysis of the azides (2)—(5) in a mixture of polyphosphoric and acetic acids, similar treatment of 5-azidobenzo[*b*]thiophen 1,1-dioxide (6) gave a linear product, 2-methylthieno[3,2-*f*]benzoxazole 7,7-dioxide (11). The n.m.r. spectrum of this compound consisted of two pairs of doublets, $J_{4,8}$ 0·5, $J_{5,6}$ 7·0 Hz, in agreement with the values obtained before for the 4,7- (0·5—0·7 Hz) and 2,3-couplings (6·0—7·0 Hz) of benzo[*b*]thiophen 1,1-dioxides.[15] The formation of a linear product in this case may be explained in terms of the structures of the two possible intermediates, (20) and (21). These are expected to be of comparable stability in view of the fact that the sulphur atom is in a higher oxidation state. Nucleophilic attack by acetic acid (*cf.* refs. 4 and 5) occurs preferentially in the 6-position, presumably because the 4-position is subject to some steric hindrance (*peri*-interaction).

Confirmation of the structural assignment to compounds (7) and (11) was obtained by oxidation of the former to 2-methylthieno[2,3-*g*]benzoxazole 6,6-dioxide, which had physical characteristics different from those of its isomer (11).

Ethyl 2-methylthieno[2,3-*g*]benzoxazole-7-carboxylate (8) did not react with bromine in chloroform, and was oxidised to its 6,6-dioxide with bromine in acetic acid. Attempts to nitrate this compound failed.

An attempt to prepare the 8,8-dioxide of 2-methyl[1]-benzothieno[3,2-*d*]oxazole (13) by heating 3-azidobenzo-[*b*]thiophen 1,1-dioxide (22) in a mixture of polyphosphoric and acetic acids gave an unidentified product (see Experimental section). 3-Azidobenzo[*b*]thiophen 1,1-dioxide (22) was prepared from 3-bromobenzo[*b*]thiophen 1,1-dioxide and sodium azide.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded with a Varian A60 spectrometer (tetramethylsilane as internal standard); the recorded signals are singlets unless stated otherwise. Molecular weights were determined by mass spectrometry with an A.E.I. MS12 instrument. All new compounds gave mass spectra consistent with the proposed structures. I.r. spectra were recorded with a Perkin-Elmer 257 instrument.

Light petroleum refers to the fraction of b.p. 60—80° unless stated otherwise.

γ-(2-Thienyl)butyric Acid.—A mixture of β-(2-thenoyl)-propionic acid [12,13] (5·0 g, 27·0 mmol), hydrazine hydrate (1·5 g, 90%), and sodium hydroxide (1·5 g, 37·5 mmol) in

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[15] N. B. Chapman, D. F. Ewing, R. M. Scrowston, and R. Westwood, *J. Chem. Soc.* (*C*), 1968, 764.

diethylene glycol (30 ml) was heated at 100° for 1 h and then at 190° for 3 h. The resulting mixture was cooled, poured on crushed ice, and acidified with concentrated hydrochloric acid. Extraction with ether gave the product (3·7 g, 80%), b.p. 128—132° at 1·0 mmHg (lit.,[12] 130—134° at 1·5 mmHg).

6,7-Dihydrobenzo[*b*]thiophen-4(5*H*)-one (94%), prepared by the method of Nishimura *et al.*,[14] had m.p. 34—35°; oxime m.p. 130—131° (lit.,[14] 35—36·5 and 130—131°). Benzo[*b*]thiophen-4-ol (25%), prepared by the method of Kaufman *et al.*,[10] had m.p. 72—74° (lit.,[10] 74—78°; 65% yield). 4-Aminobenzo[*b*]thiophen (76%), prepared as described by Boswell *et al.*,[11] had m.p. 51—52° (lit.,[11] 50—51°; 95% yield).

Ethyl 5-nitrobenzo[*b*]thiophen-2-carboxylate, m.p. 164—165° (lit.,[16] 166°), was prepared by the method of Rossi and Trave.[16] The yield increased from 85 to 95% when anhydrous ethanol was used.

5-Nitrobenzo[b]*thiophen.*—A vigorously stirred mixture of 5-nitrobenzo[*b*]thiophen-2-carboxylic acid [16] (15·6 g, 70·0 mmol) and copper bronze (5·75 g) in quinoline (80 ml) was heated at 190° for 1 h under nitrogen. The resulting mixture was cooled, diluted with ether, washed with 4N-hydrochloric acid, and dried ($MgSO_4$). Distillation of the ether gave the product (8·4 g, 67%), m.p. 148—149° (lit.,[17] 149—150°).

5-Nitrobenzo[*b*]thiophen 1,1-dioxide (98%), prepared by the method reported [18] for the synthesis of 3-bromobenzo[*b*]thiophen 1,1-dioxide, had m.p. 164—165° (from ethanol) (lit.,[17] 166°). 5-Aminobenzo[*b*]thiophen (85%), prepared from 5-nitrobenzo[*b*]thiophen by reduction with Raney nickel and hydrazine hydrate,[19,20] had m.p. 70—71° (from benzene) (lit.,[21] 71°).

Ethyl 5-Aminobenzo[b]*thiophen-2-carboxylate.*—A solution of ammonium chloride (0·43 g, 8·0 mmol) in water (3 ml) was added to a vigorously stirred mixture of ethyl 5-nitrobenzo[*b*]thiophen-2-carboxylate (2·0 g, 8·0 mmol) and iron powder (1·7 g, 0·03 g atom) in ethanol (15 ml) heated under reflux, and the resulting mixture was heated under reflux for a further 4 h. The mixture was filtered hot and cooled; distillation left the product (1·77 g, 60%), m.p. 92—94° (from ethanol) (lit.,[22] 92—94°). 5-Aminobenzo[*b*]thiophen 1,1-dioxide (82%), m.p. 174—176° (from aqueous ethanol) (lit.,[17] 178°), was prepared similarly.

Azidobenzo[b]*thiophens.—General procedure.* A stirred mixture of the aminobenzo[*b*]thiophen (29·5 mmol), concentrated hydrochloric acid (7·5 ml), and water (7·5 ml) was treated dropwise at 0—5° with sodium nitrite (2·25 g, 32·5 mmol) in water (30 ml). The resulting solution was filtered into a stirred solution of sodium azide (2·25 g, 34·5 mmol) and sodium acetate (22·5 g, 275 mmol) in water (75 ml) kept at 0°. The mixture was stirred at 0° for a further 30 min and then worked up by one of the following procedures (see Table 1): (A) the product was extracted with ether, purified by distillation under reduced pressure and, in the case of solids, recrystallised from acetic acid; (B) the product was extracted with chloroform and recrystallised from ethanol. Data for the products are given in Tables 1 and 2.

5-Azido-3-methylbenzo[b]*thiophen* (5).—This was prepared from 5-bromo-3-methylbenzo[*b*]thiophen [23] by a procedure analogous to that used [8] for the synthesis of mesityl azide. The product was chromatographed on alumina; light petroleum–ether (1 : 1) eluted the azide (24%) as an extremely unstable oil, $\nu_{max.}$ (film) 2118 cm^{-1} (N_3), which was used immediately without further purification.

TABLE 1

Azidobenzo[*b*]thiophens [a]

Compound	Yield (%)	Work-up procedure	M.p. or b.p. (°C) [mmHg]	Decomp. temp. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N
(1)	56	(A)	66—70 [0·2]	128	54·4	3·0	23·8	$C_8H_5N_3S$	54·8	2·9	24·0
(2)	57	(A)	82—86 [0·3]	108	55·1	3·0	24·1	$C_8H_5N_3S$			
(3)	75	(B)	98—100	108	53·6	3·8	17·3	$C_{11}H_9N_3O_2S$	53·4	3·7	17·0
(6)	48	(A)		141	46·1	2·6	20·0	$C_8H_5N_3O_2S$	46·4	2·4	20·3

[a] The synthesis of the azide (4) is described elsewhere [D. S. Taylor, Ph.D. Thesis, University of Salford (1971)].

TABLE 2

Spectroscopic data for azidobenzo[*b*]thiophens

Compound	$\nu_{max.}$/cm^{-1} (N_3) [a]	Chemical shift (τ) 2-H	3-H	4-H	5-H	6-H	7-H	$J_{4,6}$/Hz	$J_{6,7}$/Hz
(1) [b]	2125	←		2·55—3·35 (m)	→				
(2) [c]	2120	2·90 (d) and	2·63 (d) [d]	2·69 (d)		3·12 (dd)	3·32 (d)	2·0	9·0
(3) [c,e]	2115		1·96	2·45 (d)		2·83 (dd)	2·11 (d)	2·0	8·5
(4) [c,f]	2135		2·04	2·52 (d)		2·90 (dd)	2·27 (d)	2·0	9·0
(6) [g]	2118	←		2·20—3·20 (m)	→				

[a] Nujol mulls except for compounds (1) and (2) which were liquid films. [b] N.m.r. solvent CCl_4. [c] N.m.r. solvent $CDCl_3$. [d] Precise assignments not made; $J_{2,3}$ 5·5 Hz. [e] $\nu_{max.}$(Nujol) 1710 cm^{-1} (C:O), τ 5·54 (q, *J* 7·0 Hz, CH_2) and 8·57 (t, *J* 7·0 Hz, CH_3). [f] τ 6·05 (Me). [g] N.m.r. solvent $CDCl_3$–$(CD_3)_2SO$.

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[17] F. G. Bordwell and C. J. Albisetti, *J. Amer. Chem. Soc.*, 1948, **70**, 1955.
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[22] E. I. du Pont de Nemours and Co., B.P. 695,164/1953 (*Chem. Abs.*, 1955, **49**, 755).
[23] R. P. Dickinson and B. Iddon, *J. Chem. Soc.* (*C*), 1968, 2733.

4-Acetamido-7-acetoxybenzo[b]*thiophen*.—A solution of 4-azidobenzo[*b*]thiophen (2·2 g, 12·6 mmol) in acetic acid (15 ml) was added dropwise during 20 min to a vigorously stirred mixture of polyphosphoric acid (22 g) and acetic acid (8 ml) at 70°. The temperature for the mixture was then raised to 80° and maintained at 80° for 2 h. The mixture was cooled, cold (0°) water (120 ml) was added, and extraction with chloroform gave a black tar which was extracted continuously (Soxhlet) for 24 h with light petroleum (b.p. 100—120°). The *product* (0·6 g, 19%) crystallised from the cooled solution; m.p. 148—149° [from light petroleum (b.p. 100—120°], $\nu_{max.}$ (Nujol) 3190 and 3215 (NH), 1550 and 1650 (amide C:O), and 1770 cm^{-1} (ester C:O), τ ($CDCl_3$) 2·10br (exchangeable, NH), 2·20 (1H, d, aromatic), 2·52—2·94 (3H, m, aromatic), 7·60 (ester Me), and 7·84 (amide Me); τ (aromatic region) [(CD_3)CO] [with Eu(fod)$_3$ added] 2·39 (d, *J* 9·0 Hz, H-5 or H-6), 2·95 (d, *J* 6·0 Hz, H-2 or H-3), 3·10 (d, *J* 6·0 Hz, H-2 or H-3), and 3·5 (d, *J* 9·0 Hz, H-5 or H-6) (Found: C, 57·8; H, 4·75; N, 5·4%; *M*, 249. $C_{12}H_{11}NO_3S$ requires C, 57·8; H, 4·45; N, 5·6%; *M*, 249).

Thieno[2,3-g]*benzoxazoles*.—*General procedure*. A mixture of the 5-azidobenzo[*b*]thiophen (1·0 g), polyphosphoric acid (50 g), and acetic acid (50 ml) was stirred and heated to 135° during 30 min and the mixture was stirred at this temperature for a further 2 h or for a further 15 min in the case of 5-azido- or 5-azido-3-methyl-benzo[*b*]thiophen. The resulting solution was cooled and poured into water, and the product was extracted with chloroform. Data for the products are given in Table 3.

With 0·1 and 5% solutions of 5-azidobenzo[*b*]thiophen in a mixture of polyphosphoric and acetic acids (1 : 1) the yields of 2-methylthieno[2,3-*g*]benzoxazole were 37 and 19%, respectively.

2-Methylthieno[3,2-f]*benzoxazole 7,7-dioxide* (11) (38%), m.p. 239—241° (sublimed at 135—140° and 0·1 mmHg), τ ($CDCl_3$) 2·03 and 2·31 (4-H and 8-H, $J_{4,8}$ *ca.* 0·5 Hz), 2·60 and 3·18 (H-5 and H-6, $J_{5,6}$ 7·0 Hz) (precise assignments not made), and 7·25 (CH_3) (Found: C, 54·2; H, 3·5; N, 6·2. $C_{10}H_7NO_3S$ requires C, 54·3; H, 3·2; N, 6·3%), was prepared similarly.

2-Methylthieno[2,3-g]*benzoxazole 6,6-Dioxide*.—A mixture of 2-methylthieno[2,3-*g*]benzoxazole (7) (0·1 g, 0·53 mmol), 30% hydrogen peroxide (0·6 ml), acetic acid (0·6 ml), and acetic anhydride (0·6 ml) was heated under reflux for 1 h, cooled, and poured into water. The *product* (0·05 g, 47%) was filtered off, m.p. 218—220° (sublimed at 200—204° and 2·0 mmHg) (Found: C, 54·0; H, 3·1; N, 6·1).

Reactions of Ethyl 2-Methylthieno[2,3-g]*benzoxazole-7-carboxylate* (8) *with Bromine in Acetic Acid*.—(i) A solution of bromine (0·64 g, 0·4 mmol) in acetic acid (1 ml) was added dropwise to a solution of the oxazole (0·1 g, 0·4 mmol) in acetic acid (5 ml) at room temperature and the mixture was stirred at this temperature for 24 h. The precipitate was filtered off to give *ethyl 2-methylthieno*[2,3-g]*benzoxazole-7-carboxylate 6,6-dioxide* (0·05 g, 42%), m.p. 258—261° (from acetic acid), $\nu_{max.}$ (Nujol) 1718 cm^{-1} (C:O) (Found: C, 53·0; H, 3·5; N, 4·4. $C_{13}H_{11}NO_5S$ requires C, 53·2; H, 3·8; N, 4·8%).

(ii) A similar reaction to that described in (i) was carried out but the mixture was heated under reflux for 4 h. The same product was obtained in the same yield.

3-Azidobenzo[b]*thiophen 1,1-Dioxide* (22).—A solution of sodium azide (2·56 g, 39·4 mmol) in 85% aqueous ethanol (30 ml) was added to a stirred solution of 3-bromobenzo[*b*]-thiophen 1,1-dioxide [18] (9·6 g, 39·2 mmol) in 85% aqueous ethanol (170 ml) heated under reflux, and the resulting mixture was heated under reflux for a further 20 min. The ethanol was distilled off under reduced pressure and the residue crystallised from ethanol to give the *product* (6·0 g, 75%), decomp. 132°, $\nu_{max.}$ (Nujol) 2155 cm^{-1} (N_3), τ ($CDCl_3$) 3·56 (2-H) and 2·15—2·50 (m, aromatic) (Found: C, 46·0; H, 2·4; N, 20·0. $C_8H_5N_3O_2S$ requires C, 46·4; H, 2·4; N, 20·3%).

Thermolysis of 3-Azidobenzo[b]*thiophen 1,1-Dioxide* (22) *in Polyphosphoric Acid–Acetic Acid*. A mixture of the azide (2·0 g, 9·7 mmol), polyphosphoric acid (20·0 g), and acetic acid (20 ml) was stirred and heated to 135° during 30 min. The mixture was heated at 135° for a further 2 h and then poured on ice. Extraction with chloroform gave a solid which was chromatographed on alumina. Elution with ethanol gave an unidentified compound (0·7 g), m.p. 211—212° (sublimed at 174—177° and 0·3 mmHg) (Found: C, 48·4; H, 3·6; N, 7·1%).

TABLE 3

Thieno[2,3-*g*]benzoxazoles

Compound	Yield (%)	M.p. or b.p. (°C) [mmHg]	Chemical shifts (τ) [a] 2-Me	4-H	5-H	7-H	8-H	$J_{4,5}$/Hz	$J_{7,8}$/Hz	Found (%) C	H	N	Formula	Required (%) C	H	N
(7)	37	70—75 [0·2] [b]	8·34	2·78 (d) and	3·12 (d) [c]	3·12 (d) and	3·48 (d) [c]	9·0	5·0	63·2	4·1	7·2	$C_{10}H_7NOS$	63·5	3·7	7·4
(8)	92	138—140 [d]	7·79	2·24 (d) and	2·87 (d) [c]		1·72 [e]	9·0		60·0	4·4	5·5	$C_{12}H_{11}NO_3S$	59·8	4·25	5·4
(9)	95	154—155 [f]	7·99	2·64 (d) and	2·97 (d) [c]		2·00 [g]	9·0		58·1	3·5	5·4	$C_{12}H_9NO_3S$	58·3	3·7	5·7
(10)	24	70—74 [0·1] [f]	7·50	←2·00—2·67 (m)→		2·92 (q) [h]				65·1	4·3	6·7	$C_{11}H_9NOS$	65·0	4·45	6·9

[a] In C_6D_6; compound (10) in CCl_4. [b] Chromatographed on alumina prior to distillation; CCl_4 eluted the product. [c] Precise assignments not made. [d] From benzene. [e] $\nu_{max.}$ (Nujol) 1708 cm^{-1} (C:O), τ(C_6D_6) 5·84 (q, *J* 7·5 Hz, CH_2) and 8·94 (t, *J* 7·5 Hz, CH_3). [f] Chromatographed on alumina prior to distillation or crystallisation from benzene; ether eluted the product. [g] $\nu_{max.}$(Nujol) 1712 cm^{-1} (C:O), τ(C_6D_6) 6·66 (CH_3). [h] Coupled to 8-CH_3 group at τ(CCl_4) 7·35 (d, *J* 1·5 Hz).

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