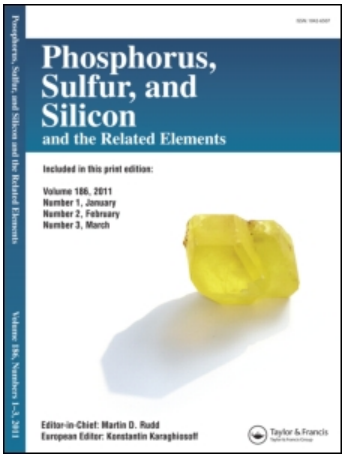

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THE REACTIONS OF SOME THIOPHENE SULFONYL DERIVATIVES

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THE REACTIONS OF SOME THIOPHENE SULFONYL DERIVATIVES

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Thiophene-2-sulfonyl chloride has been allowed to react with 7 amines, hydrazine and sodium azide. The hydrazide was converted into 21 hydrazones. The azide reacts with cyclohexene, norbornene and triphenylphosphine. The sulfonyl chloride with chlorosulfonic acid gave a mixture of the 2,4- and 2,5-bis-sulfonyl chlorides (2:1). These were not separated by conversion to amides, azides, hydrazides, or hydrazones. 2-Carboxythiophene with chlorosulfonic acid gave a mixture of the 4- and 5-sulfonyl chlorides (9:1), conversion to amides and recrystallization gave the 4-sulfonamides. Chlorosulfonation of 2-carboxamido- and 2-N,N-dimethylcarboxamidothiophene gave the 4-sulfonyl chlorides, characterized as amides, hydrazides and 18 hydrazones. Some N-arylthiophenesulfonamides were condensed with trichloromethylsulfonyl chloride. The i.r., n.m.r. and mass spectra of the various thiophenesulfonyl derivatives are discussed.

INTRODUCTION

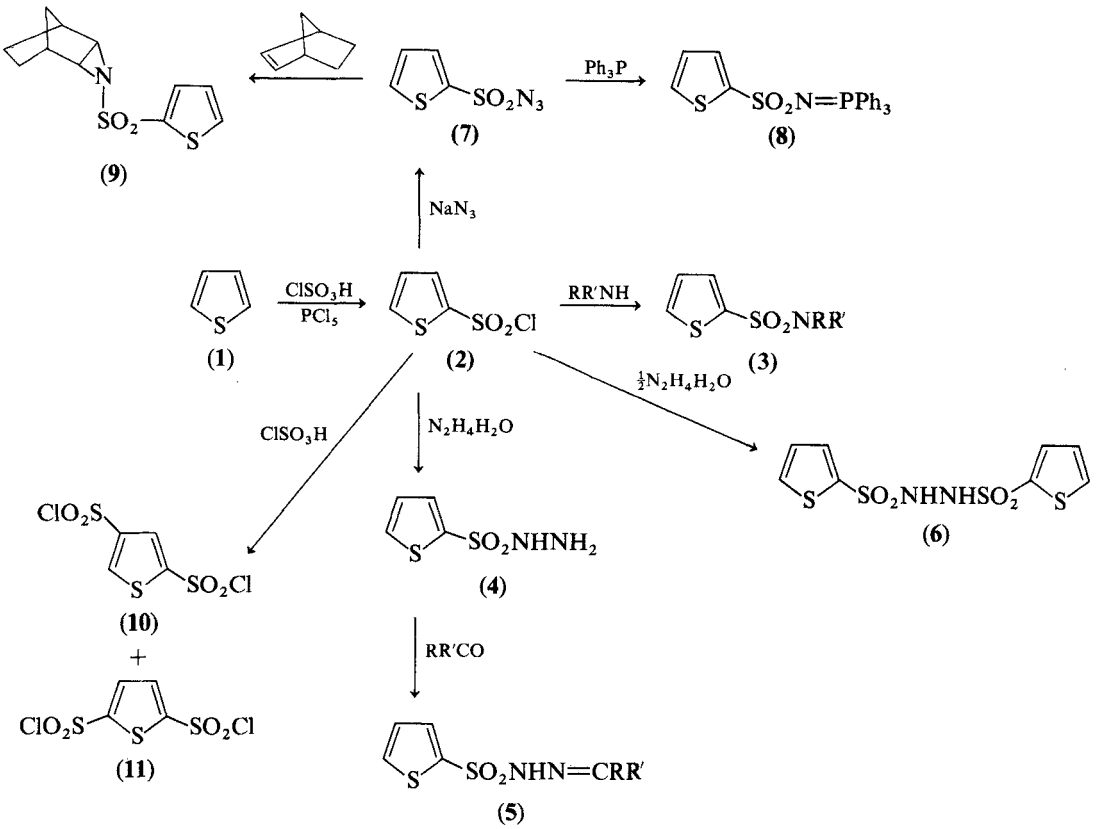
Many heterocyclic compounds have been developed as commercial pesticides,[1] in addition several sulfonyl derivatives, such as amides,[2] azides,[3] and hydrazides[4–6] have shown valuable biological activity as, for example, antibacterials, fungicides and nematicides. As part of our research into the synthesis of novel pesticides, it therefore seemed useful to examine the biological properties of a series of heterocyclic sulfonyl derivatives. This idea was supported by the reported[7] fungicidal activity exhibited by certain heterocyclic sulphonamides.

DISCUSSION

Sulfonation of thiophene (**1**) (Scheme 1) is known[8] to occur in the 2-position. Previous workers[9,10] reported that reaction with an excess of chlorosulfonic acid gave the 2-sulfonyl chloride (**2**) in poor yield (37%). However the yield was improved by the addition of phosphorus pentachloride[11] and by this procedure we converted thiophene (**1**) into the 2-sulfonyl chloride (**2**) in excellent yield (90%).

The sulfonyl chloride (**2**) was condensed with amines to give the sulphonamides (**3**) (Table 1). Several of the N-aryl amides (3; R=aryl, R′=H) were condensed with trichloromethylsulfenyl chloride giving the corresponding N-trichloromethylsulfenyl derivatives, but the condensation failed with thiophene-2-sulfonamide (3; R=R′=H). These derivatives are of interest since many compounds containing the N-trichloromethylsulfenyl group are important fungicides.[1] Thiophene-2-sulfonyl chloride (**2**) reacted with hydrazine hydrate to give the hydrazide (**4**),[12] and this was condensed with carbonyl compounds to give the corresponding hydrazones (**5**) (Table II).

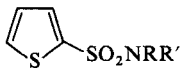
The melting points of several of the benzaldehyde hydrazones had substantially different melting points from those previously reported[13] (see Table II). Repetition of the literature method of preparation afforded products of identical melting points to those reported here. Although these hydrazones are capable of being produced as E- or Z-geometrical isomers, the former should be favoured on steric grounds. The n.m.r. spectra of the hydrazones (**5**) showed typical ABC patterns (δ7.98–7.00) which can be assigned to the ring protons.[14a] The benzylidene proton resonates at approximately δ8.0 due to the anisotropic deshielding of benzene ring. There is surprisingly little variation (0.25 ppm) in the chemical shift on altering substituents in view of the conjugation of the imino group with the benzene ring. This may be due to the predominance of long-range effects in the shielding of this proton. Attempts to obtain



SCHEME 1

TABLE I

Thiophene-2-sulfonamides



No.	R	R′	Yield (%)	m.p.	Formula	Found (%) C	H	N	Required (%) C	H	N
1	H	H	67	141–144°	(lit.[21] 142°)						
2	R = R′ = morpholino		63	104–105°	$C_8H_{11}NO_3S_2$	41.1	4.8	6.1	41.2	4.75	6.0
3	*p*-$MeC_6C_6H_4$	H	58	115°	(lit.[22] 115°)						
4	*m*-$NO_2C_6H_4$	H	40	163°	(lit.[23] 162–163°)						
5	*p*-ClC_6H_4	H	63	115–116°	(lit.[24] 115–116°)						
6	*p*-BrC_6H_4	H	70	107–109°	$C_{10}H_8BrNO_2S_2$	38.0	2.7	4.2	37.7	2.5	4.4
7	3,4-$Cl_2C_6H_3$	H	60	116–118°	$C_{10}H_7Cl_2NO_2S_2$	39.1	2.1	4.5	38.9	2.3	4.5
8	2,4-$Cl_2C_6H_3$	H	65	115	$C_{10}H_7Cl_2NO_2S_2$	38.8	2.2	4.6	38.9	2.3	4.5

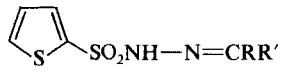
a direct correlation of the chemical shift of the benzylidene proton of the arylsulfonohydrazones (**5**) with the Hammett constant (σ) of the substituent were unsuccessful (Table II).

The i.r. spectra of the thiophenesulfonyl compounds showed sharp absorption bands in the 3120–2900 cm^{-1} region which are associated with the thiophene C—H stretching vibrations.[14b] The sulfonyl group showed two characteristic bands in the regions 1380–1320 and 1180–1165 cm^{-1}, while those compounds with amino groups showed the normal N—H stretching vibrations.

The mass spectra of the aromatic thiophene-2-sulfonohydrazones (**5**) showed the molecular ions

TABLE II

Thiophene-2-sulfonohydrazones



No.	R	R′	Yield (%)	m.p.	Formula	Found (%)			Required (%)			ArC*H* = N	
						C	H	N	C	H	N	(δ)	σ
1	C_6H_5	H	70	143–144°[a]	$C_{11}H_{10}N_2O_2S_2$	49.7	3.5	10.3	49.6	3.7	10.5	8.0	0
2	*p*-MeC_6H_4	H	80	148–149°[b]	$C_{12}H_{12}N_2O_2S_2$	51.6	4.5	10.1	51.4	4.3	10.0	7.98	−0.17
3	*p*-$HO\cdot C_6H_4$	H	68	163–164°[c]	$C_{11}H_{10}N_2O_3S_2$	47.0	3.6	10.0	46.8	3.6	9.9	7.89	−0.37
4	*m*-$HO\cdot C_6H_4$	H	70	93–95°	$C_{11}H_{10}N_2O_3S_2$	47.1	3.6	10.05	46.8	3.6	9.9	7.88	+0.121
5	*p*-$NO_2C_6H_4$	H	68	170–173°	$C_{11}H_9N_3O_5S_2$	40.6	2.9	12.1	40.4	2.75	12.05	8.10	+0.778
6	*p*-$Me_2NC_6H_4$	H	57	167–170°	$C_{13}H_{15}N_3O_2S_2$	56.1	5.6	15.0	56.3	5.4	15.2	7.85	−0.83
7	*p*-$MeOC_6H_4$	H	98	171–173°	(lit.[13] 170–171°)							7.90	−0.268
8	*p*-FC_6H_4	H	72	136–138°	$C_{11}H_9FN_2O_2S_2$	46.7	3.2	10.0	46.5	3.2	9.85	8.0	+0.062
9	*m*-FC_6H_4	H	82	147–149°	$C_{11}H_9FN_2O_2S_2$	46.3	3.0	10.0	46.5	3.2	9.85	7.92	+0.337
10	*p*-ClC_6H_4	H	92	142–143°	$C_{11}H_9ClN_2O_2S_2$	43.9	3.0	9.5	43.9	3.0	9.3	7.96	+0.227
11	*p*-BrC_6H_4	H	75	148–150°	$C_{11}H_9BrN_2O_2S_2$	38.5	2.4	8.0	38.2	2.5	8.1	7.95	+0.232
12	*m*-$NO_2C_6H_4$	H	45	196–198°	$C_{11}H_9N_3O_4S_2$	42.7	3.0	13.7	42.4	2.9	13.5	8.10	+0.778
13	3,4-$Cl_2C_6H_3$	H	67	177–179°	$C_{11}H_8Cl_2N_2O_2S_2$	39.4	2.6	8.2	39.4	2.4	8.4		
14	2,6-$Cl_2C_6H_3$	H	60	165–166°	$C_{11}H_8Cl_2N_2O_2S_2$	39.5	2.5	8.4	39.4	2.4	8.4		
15	2,4-$(HO)_2C_6H_3$	H	60	155–156°	$C_{11}H_{10}N_2O_4S_2$	44.2	3.5	9.3	44.3	3.35	9.4		
16	3,4-$(MeO)_2C_6H_3$	H	60	143–144°	$C_{13}H_{14}N_2O_4S_2$	47.8	4.3	8.4	47.8	4.3	8.6		
17	2-Thienyl	H	77	106–107°	$C_9H_8N_2O_2S_3$	39.6	3.0	10.1	39.7	3.0	10.3		
18	2-Furyl	H	90	106–108°	$C_9H_8N_2O_3S_2$	42.0	3.1	10.7	42.2	3.2	10.9		
19	Me	Me	80	120–122°	$C_7H_{10}N_2O_2S_2$	38.4	4.7	13.0	38.5	4.6	12.8		
20	R = R′ = cyclohexyl		66	134–135°	$C_{10}H_{14}N_2O_2S_2$	46.2	5.6	10.8	46.5	5.5	10.8		
21	$HOCH_2(CHOH)_4$	H	50	137–138°	$C_{10}H_{16}N_2O_7S_2$	33.8	5.2	7.7	33.5	5.1	7.8		

[a] lit.[13] 78°.
[b] lit.[13]. 84–85°.
[c] lit.[13] 90–91°.

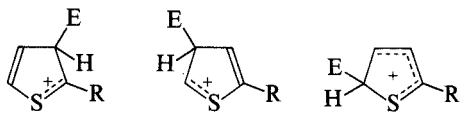
and subsequent fragmentation occurred at the sulfonyl group giving thiophenesulfinic acid which eliminates SO_2 to give thiophene; the results are in general agreement with those recently reported[14,15] for other thiophene-2-sulfonyl derivatives. The aromatic residue then undergoes the usual fragmentation pattern (cf. Ref. 16).

An attempt to condense acetone thiophene-2-sulfonohydrazone (5; R=R′=Me) with trichloromethylsulfenyl chloride-sodium hydroxide failed, as did a similar reaction using thiophene-sulfonohydrazide (**4**).

Thiophene-2-sulfonyl chloride (2) was condensed with isonicotinic acid hydrazide and semicarbazide to give the corresponding derivatives. When the chloride (**2**) (2 mols.) was reacted with hydrazine hydrate (1 mol.) in the presence of a tertiary base, the *bis*-sulfonohydrazide (**6**) was isolated.

With sodium azide, the chloride (**2**) gave the azide (**7**) which with triphenylphosphine and norbornene gave the phosphinimine (**8**) and the aziridine (**9**). In contrast, reaction with cyclohexene afforded a complex mixture of products which could not be separated. After this work was completed, a recent publication[15] has appeared claiming that this reaction yields thiophene-2-sulfonamide (cf. Ref. 3). Attempts to carry out a Wittig-type reaction by treatment of the azide (**7**) with boiling acetone (24h) or benzaldehyde failed; this contrasts with successful reactions using steroid phosphoroazides.[17]

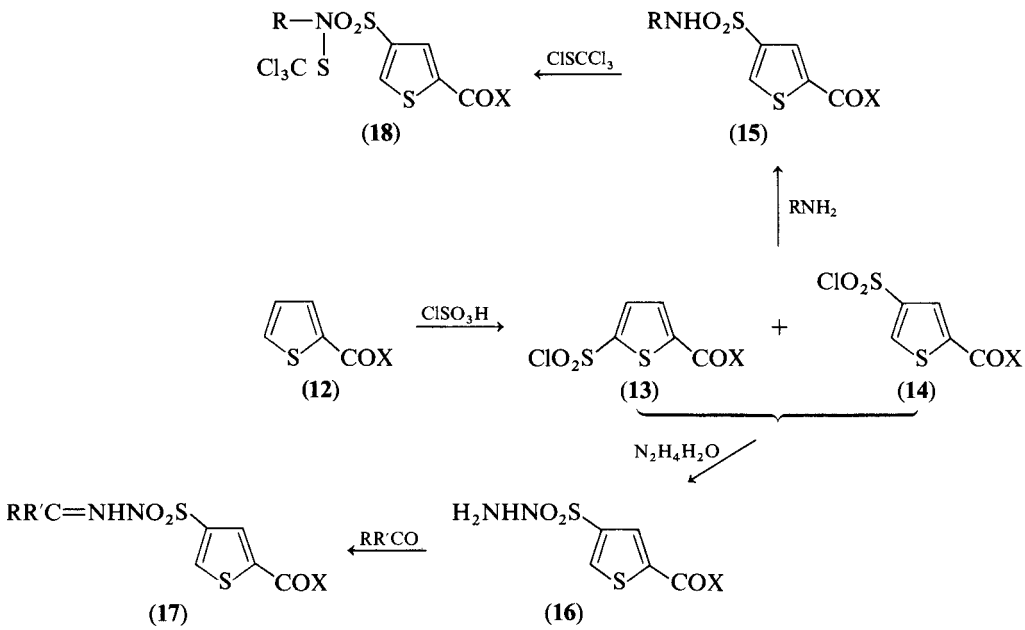
The presence of an electron-withdrawing substituent in the 2-position of thiophene deactivates the nucleus towards electrophilic substitution. On the other hand, the heterocyclic sulfur atom enhances electron density especially in the 2- and 5-positions. Competition between these electronic effects results in further electrophilic substitution occurring in the 4- and 5-positions as can be predicted on the basis of the relative stabilities of the respective Wheland intermediates:



(where E and R are electrophilic groups).

The σ-complex for 3-substitution is significantly destabilised by the electron-withdrawing effect of R, and, of the remaining positions, there is probably preference for 4-substitution.

Thiophene-2-sulfonyl chloride (**2**) with chlorosulfonic acid gave a mixture of the 2,4- and 2,5-*bis*-sulfonyl chlorides (**10**, **11**). This was confirmed by the n.m.r. spectrum of the mixture which showed an AB pattern (δ8.30, thiophene-3H; 7.89, thiophene-5H $J_{3,5}$ 1.2 Hz) (**10**) and a singlet (A_2) (δ7.70,



SCHEME 2

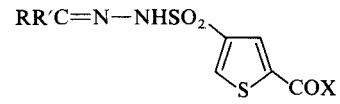
thiophene-3,4 H) (**11**) due to chemical shift equivalence, in an approximate ratio of 2:1. The results agree with those of Steinkopf and Höpner,[18] but contrast with the work of Buzas and Teste[10] who only obtained the 2,4-isomer (**10**). Thiophene-2-carboxylic acid (Scheme 2) (12; X=OH) with chlorosulfonic acid was claimed[19] to give the 5-sulfonyl chloride (13; X=OH), but we obtained a mixture of the 2,4- and 2,5-sulfonyl chlorides (**14**, **13**) in a ratio of 4:1. The n.m.r. spectrum showed an AB pattern (δ7.95, thiophene-3H; 7.80, thiophene-5H; $J_{3,5}$ 1.2 Hz) (**14**), together with an AB pattern (δ7.57, thiophene-4H; 7.28, thiophene-3H; $J_{3,4}$ 3.8 Hz) (**13**). Chlorosulfonation of thiophene-2-carboxamide (12; X=NH_2) similarly afforded a mixture of the 2,4- (14; X=NH_2) and 2,5- (13; X=NH_2) isomers in the ratio of 9:1. An identical result was obtained by chlorosulfonation of thiophene-2-(N,N-dimethylcarboxamide) (12; X=NMe_2). In both cases, recrystallization of the carboxamidesulfonyl chlorides (13, 14; X=NH_2 or NMe_2) afforded the pure 2,4-isomers (14; X=NH_2 or NMe_2).

Reaction of the mixture of thiophene-2,4- and 2,5-*bis*-sulfonylchlorides (**10**, **11**) with amines gave the corresponding amides in the ratio of 2:1, which could not be separated by crystallization. However when a mixture of the 2,4- and 2,5-dimorpholidates was heated with concentrated sulfuric acid, the pure 2,4-isomer was isolated, possibly due to migration of the sulfonyl group from the 5 to the 4 position. Such migrations are well-established with aryl sulfonic acids[20a] and have also been reported with sulfonamides.[20b] The product may also arise from selective destruction of the 2,5-isomer by the sulfuric acid. Condensation of the thiophene *bis*-sulfonyl chlorides (**10**, **11**) with sodium azide and hydrazine again gave a mixture of 2,4- and 2,5-*bis*-azides and hydrazides; the latter were converted to a number of hydrazones but n.m.r. studies showed that separation did not occur during hydrazone formation or subsequent recrystallization. In contrast, reaction of 2-carboxythiophenesulfonyl chlorides (14, 13; X=OH) with *p*-chloro- or 3,4-dichloro-aniline gave the corresponding sulfonamides which were separated by recrystallization to give the pure 2,4-sulfonamides (15; X=OH; R=*p*-ClC_6H_4 or 3,4-$Cl_2C_6H_3$).

The mixture of 2-carboxythiophenesulfonyl chlorides (13, 14; X=OH) with hydrazine afforded the 2-carboxy-4-sulfonohydrazide (16; X=OH). Similarly reaction with hydrazine gave the 2-carboxamido- and 2-(N,N-dimethylcarboxamido)

TABLE III

2-Carboxythiophene-4-sulfonohydrazones



No.	R	R′	X	Yield (%)	m.p.	Formula	Found (%) C	H	N	Required (%) C	H	N
1	Me	Me	OH	43	178°	$C_8H_{10}N_2O_4S_2$	36.6	3.8	10.8	36.6	3.8	10.7
2	*p*-$NO_2C_6H_4$	H	OH	60	214–216°	$C_{12}H_9N_3O_6S_2$	40.4	2.5	11.7	40.6	2.55	11.8
3	*p*-FC_6H_4	H	OH	65	166–167°	$C_{12}H_9FN_2O_4S_2$	41.6	3.2	8.1	41.7	3.1	8.0
4	*p*-ClC_6H_4	H	OH	65	128–131°	$C_{12}H_9ClN_2O_4S_2$	42.1	2.75	8.0	41.8	2.6	8.1
5	*p*-BrC_6H_4	H	OH	50	246–249°	$C_{12}H_9BrN_2O_4S_2$	37.2	2.4	7.0	37.0	2.3	7.2
6	*m*-ClC_6H_4	H	OH	57	254–256°	$C_{12}H_9ClN_2O_4S_2$	41.6	2.6	8.2	41.8	2.6	8.1
7	3,4$Cl_2C_6H_3$	H	OH	55	202–204°	$C_{12}H_8Cl_2N_2O_4S_2$	37.8	2.0	7.3	38.0	2.1	7.4
8	3,4$(MeO)_2C_6H_3$	H	OH	70	182–183°	$C_{14}H_{14}N_2O_6S_2$	45.2	3.9	7.5	45.4	3.8	7.6
9	Me	Me	NH_2	50	184–187°	$C_8H_{11}N_3O_3S_2$	36.8	4.2	15.8	36.8	4.2	16.1
10	*p*-$NO_2C_6H_4$	H	NH_2	77	214–217°	$C_{12}H_{10}N_4O_5S_2$	40.5	2.8	15.9	40.7	2.8	15.8
11	*p*-$Me_2NC_6H_4$	H	NH_2	70	198–201°	$C_{14}H_{16}N_4O_3S_2$	48.0	4.7	16.1	47.7	4.6	15.9
12	*p*-HOC_6H_4	H	NH_2	80	179–182°	$C_{12}H_{11}N_3O_4S_2$	44.5	3.2	13.1	44.3	3.4	12.9
13	*p*-BrC_6H_4	H	NH_2	70	207–208°	$C_{12}H_{10}BrN_3O_3S_2$	37.4	2.4	11.0	37.1	2.6	10.8
14	C_6H_5	H	NMe_2	81	163–165°	$C_{14}H_{15}N_3O_3S_2$	49.95	4.7	12.3	49.8	4.5	12.45
15	*p*-MeC_6H_4	H	NMe_2	76	139–141°	$C_{15}H_{17}N_3O_3S_2$	51.2	4.85	12.2	51.3	4.9	12.0
16	*p*-ClC_6H_4	H	NMe_2	60	171–173°	$C_{14}H_{14}ClN_3O_3S_2$	45.4	3.9	11.2	45.2	3.9	11.3
17	*p*-$Me_2NC_6H_4$	H	NMe_2	35	142–145°	$C_{16}H_{20}N_4O_3S_2$	50.1	5.1	14.5	50.5	5.3	14.7
18	*p*-$MeOC_6H_4$	H	NMe_2	70	164–165°	$C_{15}H_{17}N_3O_4S_2$	49.0	4.5	11.5	49.0	4.7	11.4

thiophene-4-sulfonohydrazides (16; X=NH_2, NMe_2). The hydrazides were characterized as hydrazones (**17**), (Table III).

EXPERIMENTAL

I.r. spectra were determined as Nujol mulls using a Perkin Elmer 237 spectrophotometer. N.m.r. spectra were measured with a Varian HA100 spectrometer using tetramethylsilane as internal standard. Mass spectra were determined with an AES MS10 spectrometer at 70 eV. Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. T.l.c. was carried out on silica gel G plates developed with iodine vapour. Microanalyses were carried out by the Butterworth Microanalytical Consultancy Ltd., Teddington, England.

Thiophene-2-sulfonyl chloride (**2**)

Thiophene (**1**) was reacted with chlorosulfonic acid–phosphorus pentachloride as previously described[11] to give the *chloride* (90%), m.p. 24–25° (lit.[11] 27–30°). ν_{max} 3090 (C-H), 1380, 1165 (SO_2) cm^{-1}.

N-Arylthiophene-2-sulfonamides (**3**) (Table 1)

Thiophene-2-sulfonyl chloride was reacted with a mixture of the amine (1 mol. equiv.) and sodium acetate (1 mol. equiv.) in ethanol for 24h. The products were purified by recrystallization from aqueous ethanol in the presence of activated charcoal.

Thiophene-2-sulfonohydrazide (**4**)

Thiophene-2-sulfonyl chloride (**2**) (18.2 g), was reacted with hydrazine hydrate (15 ml of 95%; 3 mol. equivs.) in tetrahydrofuran (25 ml) at room temperature for 12 h. Ice-water was added and the oil extracted with ethyl acetate (3 × 30 ml), the extract was dried ($MgSO_4$) and evaporated. Recrystallization (ethyl acetate-light petroleum (60–80°)) gave the *hydrazide* (4) (12.5 g, 70%), m.p. 67–68° (lit.[12] 68–69°). ν_{max} 3470, 3400, 3240 (NH), 3080 (CH), 1375, 1160 (SO_2) cm^{-1}. N.m.r. ($(CD_3)_2SO$) δ 8.2–8.1, m. 1H, thiophene-3H; 7.96–7.88, m, 1H, thiophene-5H; 7.42–7.32, m, 1H, thiophene-4H; 7.3, s br, 3H, $NHNH_2$. The signal at δ7.3 was removed by D_2O treatment.
The hydrazide (**4**) was converted into hydrazones (**5**) (Table II).

N,N¹-bis (Thiophene-2-sulfono)hydrazide (**6**)

Hydrazine hydrate (1 g; 1 mol. equiv.) was gradually added to a stirred solution of thiophene-2-sulfonyl chloride (2) (3.65 g; 1 mol. equiv.) in tetrahydrofuran (25 ml) and triethylamine (2 ml) at 0°. After 1 h at room temperature, the mixture was boiled under reflux for 24 h and evaporated. The residue was treated with water (20 ml), and the solid boiled in ethanol (20 ml) with activated charcoal, removal of the charcoal and recrystallization (toluene) gave the *hydrazide* (6) as needles (0.5 g, 35%), m.p. 232° (decomp.). (Found: C, 29.8; H, 2.5; N, 8.5. $C_8H_8N_2O_4S_4$ requires C, 29.6; H, 2.5; N, 8.6%). ν_{max} 3290, 3200 (NH), 1350, 1160 (SO_2) cm^{-1}.

N¹-(4-Pyridylcarbonyl)-N-(thiophene-2-sulfono) hydrazide

A solution of thiophene-2-sulfonyl chloride (**2**) (5 g; 1 mol. equiv.) in ethanol (15 ml) was gradually added to a stirred solution of isonicotinic acid hydrazide (3.5 g; 1 mol. equiv.) and sodium acetate (4 g; 1.1 mol. equiv.) in 50% aqueous ethanol (20 ml).

After 2 days at room temperature, ethanol was evaporated off (*in vacuo*) and the mixture was extracted with ethyl acetate (3 × 20 ml), dried ($MgSO_4$), and the solvent removed. Recrystallization (toluene) gave the *hydrazide* (6 g, 86%), m.p. 170–173° (decomp.). (Found: C, 42.1; H, 3.2; N, 14.7. $C_{10}H_9N_3O_3S_2$ requires C, 42.4; H, 3.2; N, 14.8%). ν_{max} 3320, 3140 (NH), 1685 (CO), 1350, 1165 (SO_2) cm^{-1}.

Thiophene-2-sulfonyl semicarbazide

Reaction of the chloride (**2**) with semicarbazide hydrochloride (1 mol. equiv.) and sodium acetate (2.5 mol. equivs.) in tetrahydrofuran (10 ml) and water (15 ml) for 12 h. gave the *semicarbazide* (64%), m.p. 214–217° (decomp.) from MeOH). (Found: C, 27.1; H, 3.1; N, 18.9. $C_5H_7N_3O_3S_2$ requires C, 27.1; H, 3.2; N, 19.0%). ν_{max} 3495, 3390 (NH), 3080 (thiophene CH), 1650 (CO), 1350, 1170 (SO_2) cm^{-1}. N.m.r. ($(CD_3)_2SO$) δ 9.54, d, 1H, NH; 8.12, s, 1H, NH; 7.98–7.89, m, 1H, thiophene-3H; 7.70–7.66, m, thiophene-5H; 7.24–7.13, m, thiophene-4H; 6.85, br s, 2H, NH_2. Signals at δ 9.54, 8.12, and 6.85 were removed by D_2O treatment.

Thiophene-2-sulfonyl azide (**7**)

A solution of thiophene-2-sulfonyl chloride (2) (4 g; 1 mol. equiv.) in acetone (15 ml) was reacted with sodium azide (3 g; 2 mol. equivs.) in water (10 ml) at 5°. After 1 h, acetone was removed under reduced pressure and the azide extracted with ether (3 × 20 ml), dried ($MgSO_4$) and evaporated. Vacuum distillation afforded the *azide* (7) (1.5 g, 35%), b.p. 64–66° 10.2 mm (lit.[15] m.p. 31–33°) (Found: C, 25.1; H, 1.8; N, 22.5. Calc. for $C_4H_3N_3O_2S_2$: C, 25.4; H, 1.6; N, 22.2%). ν_{max} 3105, 3095 (CH), 2120 (N_3), 1370, 1170 (SO_2) cm^{-1}.

Reactions of thiophene-2-sulfonyl azide (**2**)

(i) *With triphenylphosphine* The azide (**7**) (2 g) was boiled under reflux with triphenylphosphine (2.78 g; 1 mol. equiv.) in ether (20 ml) for 1 h, to give the *phosphinimine* (**8**) as flakes (ethyl acetate-light petroleum (60–80°)) (2.2 g, 55%), m.p. 160–162° (lit.[15] 152–153°) (Found: C, 62.4; H, 4.3; N, 3.5. Calc. for $C_{22}H_{18}NO_2PS_2$: C 62.4; H, 4.3; N, 3.3%). ν_{max} 3100 (thiophene C-H), 3060 (phenyl C-H), 1440 (N=P), 1160 (SO_2) cm^{-1}.

(ii) *With norbornene* The azide (**7**) (2.5 g) was boiled under reflux with norbornene (2.5 g; 2 mol. equivs.) in tetrahydrofuran (25 ml) for 1 h, to give the *aziridine* (**9**) as needles (ether-petroleum ether (40–60°)) (1.3 g, 39%), m.p. 69.5–70° (Found: C, 51.9; H, 5.2; N, 5.6.(lit.[15] 80–82°). Calc. for $C_{11}H_{13}NO_2S_2$: C, 51.8; H, 5.1; N, 5.5%). ν_{max}3080, 3070 (thiophene C-H), 1320, 1150 (SO_2) cm^{-1}. N.m.r. ($CDCl_3$) δ 8.08–7.95, m, 1H, thiophene-3H; 7.78–7.70, m, 1H, thiophene –5H; 7.38–7.19, m, 1H, thiophene-4H; 2.93, s, 2H, norbornyl-2,3 H; 2.44, s, 2H, norbornyl – H; 1.5–1,2, 0.82–0.72, m, 6H, norbornyl–1,4,5,6–H.

iii) *With cyclohexene* The azide (7) (1 g) was boiled under reflux with cyclohexene (20 ml) for 7 days, when the i.r. spectrum showed absence of the azide band. Evaporation under reduced pressure gave a brown gum. T.l.c. (EtOAc-light petroleum 1:1) showed 5 spots (R_F 0.15 (major), 0.35 (major), 0.4 (minor), 0.55

(major) and 0.7 (minor)). Recrystallization and column chromatography failed to separate the mixture.

Thiophene-2,4- and 2,5-bis-sulfonyl chlorides (**10**, **11**)

Thiophene-2-sulfonyl chloride (2) with chlorosulfonic acid (3 mol. equivs.) at 100° for 1½h, gave a mixture of the 2,4- and 2,5- *bis*-sulfonyl chlorides in the ratio of 2:1 (70%), m.p. 48–50° (lit.[10] 30°). ν_{max} 3100(CH), 1375, 1180(SO_2)cm^{-1}. N.m.r. ($CDCl_3$) δ 8.30, 1H, thiophene-3H; 7.89, 1H, thiophene-5H; $J_{3,5}$ 1.2 Hz; 7.70, s, thiophene-3,4H.

Thiophene-2,4- and 2,5-bis-sulfonamides

(45%), m.p. 203–205° (lit.[10,18] 218–219°, lit.[21] 211°). ν_{max} 3370, 3270 (NH_2), 3120 (CH), 1360, 1160 (SO_2) cm^{-1}. N.m.r. ($(CD_3)_2SO$): δ 8.3, d, $J_{3,5}$ 1.2 Hz, ⅔H thiophene-3H; 7.89, d, $J_{3,5}$ 1.2 Hz, ⅔H, thiophene-5H; 7.78, s br, 4H, 2 × NH_2; 7.60, s, ⅔H thiophene 3, 4–H. The signal at δ 7.78 was removed by D_2O treatment.The following N-substituted thiophene-2,4- and 2,5- *bis*-sulfonamides were obtained: *N-Phenyl* (42%), m.p. 122–123°. (Found: C, 48.5; H, 3.4; N, 7.4. $C_{16}H_{14}N_2O_4S_3$ requires C, 48.7; H, 3.6; N, 7.1. ν_{max} 3260 (NH), 3100 (thiophene CH), 1350, 1160 (SO_2) cm^{-1}. N.m.r. ($(CD_3)_2SO$) δ 10.6–9.6 s br, 2H (2 × NH), 8.31, d $J_{3,5}$ 2Hz, ⅔H, thiophene-3H; 7.7, d, $J_{3,5}$ 2Hz, ⅔H, thiophene-5H; 7.43, s, ⅔H, thiophene-3,4 H; 7.37–7.06, m, 10H, 2 × $C_6H_5 \cdot D_2O$ treatment removed the signal at δ 10.6–9.6.

N-p-chlorophenyl (60%), m.p. 168° (Found: C, 41.8; H, 2.6; N, 5.8. $C_{16}H_{12}Cl_2N_2O_4S_3$ requires C, 41.5; H, 2.6; N, 6.0%), ν_{max} 3310, 3260 (NH), 3120 (thiophene CH), 1340, 1170 (SO_2) cm^{-1}.

N-morpholino (50%), m.p. 168–170° (Found: C, 37.9; H, 5.0; N, 7.1. $C_{12}H_{18}N_2O_6S_3$ requires C, 37.7; H, 4.8; N, 7.3%). ν_{max} 3100 (thiophene CH), 1360, 1160 (SO_2) cm^{-1}. N.m.r. ($(CD_3)_2SO$-$CDCl_3$) δ 8.6, d, ½H, thiophene-3H; 7.78, d, ½H, thiophene-5H; 7.74, s, ½H, thiophene-3,4H; 3.82–3.70, 3.26–3.04, m, 16H, (morpholino H).

The action of sulfuric acid on a mixture of thiophene-2,4- and 2,5-bis-sulfonylmorpholidates

The mixture (1 g) was heated with conc. sulfuric acid (10 ml) at 120° for 2½h. The cold solution was poured onto ice-water (100 ml) and the precipitate collected, and washed with water to give *thiophene - 2,4 - bis - sulfonylmorpholidate* (0.5 g, 50%), m.p. 194–197°. ν_{max} 3100 (thiophene CH), 1360, 1160 (SO_2) cm^{-1}. N.m.r. ($(CD_3)_2SO$-$CDCl_3$) δ 8.60, d, 1H, thiophene-3H; 7.78, d, 1H, thiophene-5H; 3.82–3.70, 3.26–3.04, m, 16H (morpholino H).

Thiophene-2,4- and 2,5-bis-sulfonyl azides

Thiophene-2,4- and 2,5-*bis*-sulfonyl chlorides (2 g) were reacted with sodium azide (1 g; 2 mol. equivs.) in acetone (10 ml) and water (5 ml). After 3 h, acetone was removed *in vacuo* and the aqueous mixture extracted with ether (3 × 20 ml) to give the *2,4- and 2,5- bis azides* as a viscous oil (2 g, 95%). ν_{max} 3110, 3095 (thiophene CH), 2150 (N_3), 1380, 1170(SO_2) cm^{-1}. The azides (2 g) were characterized by treatment with norbornene (1.3 g, 1 mol. equiv.) in boiling tetrahydrofuran for 3 h to give the *2,4- and 2,5-bis-sulfonyl aziridines* (2.4 g, 83%), m.p. 196–198°. (Found: C, 50.9; H, 5.3; N, 6.3. $C_{18}H_{22}N_2O_4S_3$ requires C, 50.7; H, 5.2; N, 6.6%). N.m.r. ($CDCl_3$) δ 8.6, d, ⅔H, thiophene-3 H; 7.85, d, ⅔H, thiophene-5H; 7.67, s, ⅔H, thiophene-3,4H; 3.0, s, 4H, 2 × -CH-N-CH-; 2.42, s, 4H, norbornyl-7H; 1.55 – 1.15, 0.85–0.6, m, 12H, 2 × 1,4,5,6-aziridine H.

Thiophene-2,4-bis-sulfonyl semicarbazide

The mixture of thiophene-2,4- and 2,5-*bis*-sulfonyl chlorides (12, 13) (2 g) was reacted with semicarbazide hydrochloride (1.6 g; 2 mol. equivs.) and sodium acetate (2 g) in aqueous ethanol (20 ml of 50%). After 10 h at room temperature, the precipitate was collected and recrystallized (CH_3CN) to give the *bis-semicarbazide* (1.6 g, 63%), m.p. 235–236° (decomp.). (Found: C, 20.1; H, 2.9; N, 23.6. $C_6H_{10}N_6O_6S_3$ requires C, 20.1; H, 2.8; N, 23.45%). ν_{max} 3535, 3430, 3200 (NH), 3120 (thiophene CH), 1380, 1180(SO_2) cm^{-1}. N.m.r. ($(CD_3)_2SO$) δ 9.82, br s, 2 H, NH; 9.63, br s, 2 H, 2 × NH; 8.5, d, 1 H, thiophene-3 H; 7.67, d, 1 H, thiophene-5 H; 6.20, 4 H, 2 × NH_2. The signals at δ 9.82 and 9.63 were removed by D_2O treatment.

Thiophene-2,4- and 2,5-bis-sulfono N-phenylhydrazide

The mixture of sulfonyl chlorides (10, 11) (2 g) was reacted with phenylhydrazine (4.3 g; 4 mol. equivs.) in ether (20 ml) for 12 h. The precipitate, by recrystallization (toluene) afforded the *bis-phenylhydrazide* (1.8 g; 42%), m.p. 150–154 (decomp.). (Found: C, 45.1; H, 3.8; N, 13.3. $C_{16}H_{16}N_4O_4S_3$ requires C, 45.3; H, 3.8; N, 13.2%). ν_{max} 3340, 3220 (NH), 3100 (thiophene CH), 1385, 1150 (SO_2) cm^{-1}.

Thiophene 2,4- and 2,5-bis-sulfonohydrazides

The sulfonyl chlorides (10, 11) (7.5 g) with hydrazine hydrate (10.5 ml of 98%; 6 mol. equivs.) in tetrahydrofuran (15 ml) for 3 h, gave a mixture of the *2,4- and 2,5- bis-hydrazides* as an oil (5 g, 63%), ν_{max} 3380, 3250 (NH), 3080 (thiophene CH), 1350 1160 (SO_2) cm^{-1}. The hydrazides were characterized by the preparation of the following hydrazones:

p-Fluorobenzaldehyde (47%), m.p. 177–179°. (Found: C, 44.7; H, 3.0; N, 11.4. $C_{18}H_{14}F_2N_4O_4S_3$ requires C, 44.6; H, 2.9; N, 11.6%). ν_{max} 3220 (NH), 1380, 1170 (SO_2) cm^{-1}. N.m.r. ($CDCl_3$) δ 11.98, brs, ⅔ H, NH; 11.87, 11.68, 2 × s, 1⅓ H, NH; 8.69, d, ⅔ H, thiophene-3 H; 8.04, s, 2 H, 2 × N = CH; 7.98, d, ⅔H, thiophene-5H; 7.79–7.60, 7.38–7.08, m, 8⅔H, 2 × C_6H_4 and ⅔ H, thiophene–3,4 H. Signals at δ 11.98, 11.87 and 11.68 were removed by treatment with D_2O.

p-Chlorobenzaldehyde (25%), m.p. 176–177° (Found: C, 41.5; H, 3.0; N, 10.6. $C_{18}H_{14}Cl_2N_4O_4S_3$ requires C, 41.8; H, 2.7; N, 10.8%). N.m.r. ($CDCl_3$) δ 12.1, 11.98 and 11.79, 3 × brs, 2 H, 2 × NH; 8.72, d, ⅔H, thiophene–3 H; 8.04, s, 2 H, 2 × N = CH; 8.00, d, ⅔ H, thiophene–5 H; 7.80–7.25, m, 8⅓ H, 2 × C_6H_4 ⅓(C_4H_2S). The signals at δ 12.1, 11.98 and 11.79 disappeared after D_2O treatment.

3,4-Dichlorobenzaldehyde (25%), m.p. 185–187° (Found: C, 36.7; H, 2.2; N, 9.5. $C_{18}H_{12}Cl_4N_4O_4S_3$ requires C, 36.9; H, 2.1; N, 9.6%). N.m.r. ($CDCl_3$) δ 11.95, brs, 2 H, 2 × NH; 8.71, d, H, thiophene–3 H; 7.97, s, 2 H, 2 × N = CH, 7.94, d, H, thiophene–5 H; 7.78–7.0, 7.56–7.52, m, 6 H, 2 × C_6H_3. The signal at δ 11.95 was removed by D_2O treatment.

Thiophene-2-aldehyde (42%), m.p. 223–224°. (Found: C, 36.7; H, 2.7; N, 12.1. $C_{14}H_{12}N_4O_4S_5$ requires C, 36.5; H, 2.6; N, 12.2%). N.m.r. ($CDCl_3$) δ 11.9–11.4, m, 2 H, 2 × NH; 8.62, d, H, thiophene–3 H; 8.19, s, 2 H, 2 × N = CH; 7.87, d, 1 H, thiophene–5 H; 7.61–7.55, m, 2 H, thiophene–3 H; 7.40–7.35 m, 2 H, thiophene–5 H; 7.15–7.05, m, 2 H, thiophene–4 H.

2-Carboxythiophene-4-and 5-sulfonyl chlorides (14.13; X = OH) Thiophene-2-carboxylic acid (12; X = OH) was reacted with chlorosulfonic acid (5 mol. equivs.) at 100° for 1½ h to give the *sulfonyl chlorides* (14, 13) (70%), m.p. 135–139° (lit.[19] 132–133°). ν_{max} 3200 (br, OH), 1690 (CO), 1370, 1175 (SO_2) cm^{-1}.

2-Carboxamidothiophene-4-sulphonyl chloride (14; X = NH_2)

Thiophene-2-carboxyamide (12; X = NH_2) with chlorosulfonic acid (4 mol. equivs.) at 100° for 1½ h. have the *chloride* (14) (60%), m.p. 115–177°. (Found: C, 26.8; H, 2.0; N, 6.5. $C_5H_4ClNO_3S_2$ requires C, 26.5; H, 1.8; N, 6.2%). ν_{max} 3450, 3190 (NH_2), 3100 (CH), 1670 (CO), 1380, 1190 (SO_2) cm^{-1}.

2-(NN-Dimethylcarboxamido) thiophene-4-sulfonyl chloride (14; X = Me_2N) Thiophene-2-dimethylcarboxamide (14; X = N Me_2) with chlorosulfonic acid (3 mol. equivs.) at 100° for 4 h. gave the *chloride* (14) (65%), m.p. 31°. (Found: C, 33.4; H, 3.0; N, 5.4. $C_7H_8ClNO_3S_2$ requires C, 33.1; H, 3.15; N, 5.5%). ν_{max} 3100 (thiophene CH), 1630 (CO), 1340, 1150 (SO_2) cm^{-1}.

2-Carboxythiophene-4-sulfonamides (15; X = OH)

i) 2-Carboxythiophene-4-p-chlorobenzenesulfonamide (15; X = OH, R = *p*-Cl-C_6H_4) The mixture of 2-carboxythiophene-4- and 5-sulfonyl chlorides (13, 14; X = OH) (1.5 g) dissolved in ethanol (15 ml) was gradually added to a solution of *p*-chloroaniline (0.85 g; 1 mol. equiv.) and sodium acetate (1.8 g, 2 mol. equivs.) in ethanol (10 ml). After stirring for 1 h, the solution was evaporated *in vacuo* to give the *sulphonamides* (2 g, 95%). Four recrystallizations (toluene) gave the *4-p-chlorobenzenesulfonamide* (1.2 g; 53%), m.p. 183–185°. (Found: C, 41.9; H, 2.6; N, 4.2, $C_{11}H_8ClNO_4S_2$ requires C, 41.6; H, 2.5; N, 4.4%). ν_{max} 3250 (NH), 3100 (br OH), 1680 (CO), 1370, 1160 (SO_2) cm^{-1}. N.m.r. (NaOD–D_2O) δ 7.96–7.85, m, 2 H, thiophene H; 7.50, s, 4 H, C_6H_4. The mother liquors on evaporation gave a residue which by recrystallization (ethyl acetate-cyclohexane) afforded the *5-p-chlorobenzenesulfonamide* (0.2 g, 10%), m.p. 227–229°. ν_{max} 3245 (NH), 3150 (br OH), 1650 (CO), 1370, 1160 (SO_2) cm^{-1}. N.m.r. (NaOD–D_2O) δ 7.55, d. J 3.5 Hz), 1 H, thiophene–4 H; 7.25, d, J 3.5 Hz, 1 H, thiophene–3 H; 7.18, s, 4 H, C_6H_4.

ii) *3,4-Dichloroaniline* similarly gave the *4-amide* (15; X = OH, R = 3,4 $Cl_2C_6H_3$) (52% from aq EtOH), m.p. 196–199°. (Found: C, 37.4; H, 2.0; N, 3.9. $C_{11}H_7Cl_2NO_4S_2$ requires C, 37.5; H, 2.0; N, 3.95%). ν_{max} 3280 (NH), 3020 (br OH), 1685 (CO), 1380, 1160 (SO_2) cm^{-1}. N.m.r. (NaOD-D_2O) δ 8.1–7.95, m, 2H, thiophene H; 7.35–7.08, 3H, C_6H_3.

2-Carboxamidothiophene-4-sulfonamides (17; X = NH_2)

i) *N-morpholino* (45%), m.p. 202–204° (decomp.). (Found: C, 39.4; H, 4.5; N, 10.2. $C_9H_{12}N_2O_4S_2$ requires C, 39.1; H, 4.4; N, 10.1%). ν_{max} 3440, 3160 (NH_2), 3105 (thiophene CH), 1680 (CO), 1360, 1160 (SO_2) cm^{-1}. N.m.r. ($(CD_3)_2SO$) δ 8.4, 7.97, 2 × d, 2H, thiophene H; 8.16, 7.60, 2 × brs, 2H, NH_2; 3.71–2.81, m, 8H, morpholino H. Signals at δ 8.16, 7.60 disappeared slowly on D_2O treatment.

ii) *p-chlorophenyl* (17; X = NH_2, R = *p*-ClC_6H_4), (55%), m.p. 245–248°. (Found: C, 41.5; H, 3.0; N, 8.6. $C_{11}H_9ClN_2O_3S_2$ requires C, 41.7; H, 2.8; N, 8.8%).

2 - (N,N - Dimethylcarboxamido) thiophenesulphonamides (17; X = NMe_2)

i) *Amides* The sulfonyl chlorides (15, 16; X = NMe_2) with ammonia gave a mixture of the corresponding *amides* (40%), m.p. 195–196°. (Found: C, 35.8; H, 4.2; N, 11.9. $C_7H_{10}N_2O_3S_2$ requires C, 35.9; H, 4.3; N, 11.95%). ν_{max} 3300, 3180 (NH_2), 1600 (br, CO), 1345, 1165 (SO_2) cm^{-1}. N.m.r. ($(CD_3)_2SO$) δ 8.21, 7.76, 2 × d, ½H, thiophene 3, 5H; 7.73, brs, 2H, NH_2; 7.47, q, 1½H, thiophene-3, 4H; 3.30, 3.14, 2 × s, 6H, 2 × CH_3. The signal at δ 7.73 was removed by D_2O treatment.

ii) *Phenyl* (17; X = NMe_2, R = C_6H_5), (67%), m.p. 163–164° (Found: C, 50.3; H, 4.6; N, 9.3. $C_{13}H_{14}N_2O_3S_2$ requires C, 50.3; H, 4.55; N; 9.0%). ν_{max} 3100 (NH), 1600 (CO), 1345, 1160 (SO_2) cm^{-1}. N.m.r. ($(CD_3)_2SO$) δ 11.6, brs, 1H, NH; 8.23, 7.75, 2 × d, 2H, thiophene-3, 5H; 7.43, q, 4H, C_6H_4; 3.15, s, 6H, 2 × CH_3. The signal at δ 11.6 was removed after D_2O treatment.

2-Carboxythiophene-4-sulfonohydrazide (16: X = OH)

The mixture of the sulfonyl chlorides (13, 14) (15 g) was reacted with hydrazine hydrate (9.8 g, 3 mol equivs.) in toluene (30 ml) at 0° for 1 h. Dilution with water (40 ml) gave a precipitate which was extracted with ethyl acetate (3 × 30 ml). The extract was dried ($MgSO_4$) and evaporated *in vacuo* and the residue was recrystallized (ethyl acetate–light petroleum 60–80°) to give the *hydrazide* (16) (8 g; 55%), m.p. 148–150° (decomp.). (Found: C, 27.5; H, 2.9; N, 12.8. $C_5H_6N_2O_4S_2$ requires C, 27.0; H, 2.7; N, 12.6%). ν_{max} 3420, 3180 (NH), 1675 (CO), 1350, 1160 (SO_2) cm^{-1}. N.m.r. ($(CD_3)_2SO$) δ 8.8–7.0, 2 × brs, 5H, $NHNH_2$, $CONH_2$); 8.25, d, 1 H, thiophene–3 H; 8.0, d, 1 H, thiophene-5 H. The signals δ 8.8–7.0 were removed by D_2O treatment.

2-Carboxamidothiophene-4-sulfonohydrazide (16; X = NH_2)

Similarly prepared (55%), m.p. 148–150° (decomp.). (Found: C, 27.5; H, 3.3; N, 19.1. $C_5H_7N_3O_3S_2$ requires C, 27.1; H, 3.2; N, 19.0%). ν_{max} 3420, 3180, (NH), 1675 (CO), 1350, 1160 (SO_2) cm^{-1}. N.m.r. ($(CD_3)_2SO$) δ 8.8–7.0, 2 × brs, 5H, $NHNH_2$, $CONH_2$; 8.25, d, 1 H thiophene-3 H; 8.0, d, 1 H, thiophene–5 H. The signals at δ 8.8–7.0 were removed by D_2O treatment.

2 - (N,N - Dimethylcarboxamido) thiophene - 4 - sulfonohydrazide (16; X = N Me_2), (60%), m.p. 138°.

(Found: C, 33.7; H, 4.3; N, 16.7. $C_7H_{11}N_3O_3S_2$ requires C, 33.7; H, 4.45; N, 16.85%). ν_{max} 3380, 3230, 3170 (NH), 3100 (thiophene CH), 1620 (CO), 1330, 1160 (SO_2) cm^{-1}. N.m.r. $(CD_3)_2SO$ δ 8.32, d, 1 H, thiophene-3 H; 7.69, d, 1 H, thiophene −5 H; 8.20, brs, 1 H, NH; 4.08, brs, 2H, NH_2; 3.17, s, 6H, 2 × CH_3. The signals at δ 8.2, 4.08 were removed by D_2O treatment. The hydrazides (16; X = OH, NH_2, and NMe_2) were converted into the corresponding hydrazones (**17**) (Table III).

N-Trichloromethylsulfenyl N-phenylthiophene-2-sulfonamide

N-Phenylthiophene-2-sulfonamide (3; R = Ph, R^1 = H) (1.45 g) was boiled under reflux with trichloromethylsulfenyl chloride (1.13 g; 1 mol. equiv.) and aqueous sodium hydroxide (2.5 ml of 10%) in ether (25 ml) for 3h. Evaporation of the ether *in vacuo* gave a solid which was collected, washed with water, and recrystallized (toluene) to give the *trichloromethylsulphenyl derivative* as needles (1.1 g, 50%), m.p. 98°. (Found: C, 34.05; H, 2.1; N, 3.6. $C_{11}H_8Cl_3NO_2S_3$ requires C, 34.0; H, 2.1; N, 3.6%). ν_{max} 3100 (thiophene CH), 1360, 1160 (SO_2) cm^{-1}. The following N-substituted N-trichloromethylsulphenyl thiophene-2-sulfonamides were similarly prepared: *N-p-Tolyl* (45%), m.p. 119–120°. (Found: C, 35.7; H, 2.5; N, 3.5. $C_{12}H_{10}Cl_3NO_2S_3$ requires C, 35.8; H, 2.5; N, 3.5). ν_{max} 3110 (thiophene CH), 1370, 1170 (SO_2) cm^{-1}.

N-p-Chlorophenyl (52%), m.p. 143° (Found: C, 31.1; H, 1.6; N, 3.3. $C_{11}H_7Cl_4NO_2S_3$ requires C, 31.2; H, 1.7; N, 3.3%). ν_{max} 3100 (thiophene CH), 1360, 1170 (SO_2) cm^{-1}.

2 - (N^1N^1 - dimethylcarboxamido) - N - trichloromethylsulfenyl N - phenylthiophene - 4 - sulfonamide (18; X = N Me_2, R = Ph) (50%), m.p. 142–144°. (Found: C, 36.8; H, 2.8; N, 6.2. $C_{14}H_{13}Cl_3N_2O_3S_2$ requires C 36.6; H, 2.85; N, 6.1%). ν_{max} 3100 (thiophene CH), 1350, 1160 (SO_2) cm^{-1}.

REFERENCES

1. R. J. Cremlyn, *Pesticides: Preparation and Mode of Action* (Wiley, Chichester 1978).
2. L. Weinstein, *Sulfonamides* in *The Pharmacological Basis of Therapeutics*, L. S. Goodman and A. Goodman (Eds.) (Macmillan, New York 1975), 5th Ed. p. 113.
3. R. J. Cremlyn, *Int. J. Sulfur Chem.*, **8**(1), 133 (1973).
4. R. J. Cremlyn, *J. Chem. Soc.*, 1132 (1965).
5. R. J. Cremlyn, *J. Chem. Soc.* (C), 77 (1967).
6. R. J. Cremlyn, *J. Chem. Soc.* (C), 1341 (1969).
7. G. A. Carter, G. W. Dawson, and J. L. Garraway, *Pestic. Sci.*, **6**(1), 43 (1975).
8. *Rodd's Chemistry of Carbon Compounds* (Ed. S. Coffey) 2nd edn., Vol. IVA (Elsevier, London 1973), p. 245.
9. J. Cymerman-Craig, G. N. Vaughan, and W. K. Warburton, *J. Chem. Soc.*, 4114 (1956).
10. A. Buzas and J. Teste, *Bull. Soc. Chim. France*, 793 (1960).
11. W. Siedel and K. Strum, Ger. P. 1,088, 509/1958; *Chem. Abstr.*, **56**, 456f (1962).
12. E. Maccarone, G. Musumarra, and G. A. Tomaselli, *J. Org. Chem.*, **39** (22), 3286 (1974).
13. A. A. Munshi, N. M. Shah, and J. P. Trivadi, *Indian J. Chem.*, **1**, 318 (1963); *Chem. Abstr.*, **59**, 13919d (1963).
14. A. R. Katritzky, *Advances in Heterocyclic Chemistry*, Vol.1 (Academic Press, New York, 1963), (a) p. 9. (b) p. 12.
15. C. A. Obafemi, *Phosphorus and Sulfur*, **8**, 201 (1980).
16. S. F. Dyke, A. J. Floyd, M. Sainsbury, and R. S. Theobald, *Organic Spectroscopy—An Introduction*, (Penguin books, London, 1971), p. 190.
17. R. J. Cremlyn, B. B. Dewhurst, and I. Khattak, *Phosphorus and Sulfur*, **3**, 325 (1977).
18. W. Steinkopf and T. Höpner, *Liebigs Ann. Chem.*, **501**, 174 (1933); *Chem. Abstr.*, **27**, 2443 (1933).
19. M. Lora-Tamayo, R. Madronero, J. del Rio, and G. Alonso, *Anales Real Soc. Espan. Fis Quim.* (Madrid), *Ser.* B. **62** (2) (1966); *Chem. Abstr.*, **65**, 13636e (1966).
20. H. J. Shine, *Aromatic Rearrangements*, (Elsevier, London, 1967) (a) p. 257; (b) p. 262.
21. A. P. Terent'ev and G. M. Kadatskii, *Zhur. Obschchei Khim.*, **22**, 153 (1952); *Chem. Abstr.*, **46**, 11178b (1952).
22. A. Arcoria, E. Maccarone, G. Musumarra, and G. A. Tomaselli, *Spectrochim. Acta.*, PtA, **30A**, 611 (1974).
23. A. Arcoria, E. Maccarone, G. Musumarra, and G. A. Tomaselli, *J. Org. Chem.*, **38**, 2457 (1973).
24. D. D. Woods, *Brit. J. Exp. Pathol.*, **21**, 74 (1940).