Some Reactions of 7-Chloro-3-methylbenzo[*b*]thiophen

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3-Bromomethyl-7-chlorobenzo[*b*]thiophen has been converted into related amino-, guanidino-, and ureido-compounds, among others, by modifications of known methods. Nitration, bromination, and acetylation of 7-chloro-3-methylbenzo[*b*]thiophen gave mainly the 2-substituted compounds. 7-Hydroxy- and 7-mercapto-3-methylbenzo[*b*]thiophen resulted from the treatment of the Grignard reagent derived from 7-chloro-3-methylbenzo[*b*]thiophen with oxygen or with sulphur. Direct nucleophilic displacement of the 7-chloro-group also gave 7-hydroxy- or 7-amino-3-methylbenzo[*b*]thiophen in high yield.

7-CHLORO-3-METHYLBENZO[*b*]THIOPHEN [1] is readily prepared by the cyclisation of(2-chlorophenylthio)propanone with hot polyphosphoric acid and is probably the most accessible 7-substituted benzo[*b*]thiophen derivative. After having made a number of compounds for biological testing, we decided to broaden our study to include electrophilic substitution, and to investigate the possibility of using the nucleophilic replacement of the 7-chloro-group to provide a route to other more inaccessible 7-substituted benzo[*b*]thiophen derivatives, in particular 7-hydroxy-3-methylbenzo[*b*]thiophen.

An improved yield (95%) from the cyclisation of (2-chlorophenylthio)propanone with hot polyphosphoric acid was obtained (see Experimental section). Nuclear bromination of 7-chloro-3-methylbenzo[*b*]thiophen with bromine in dry boiling carbon tetrachloride gave the 2-bromo-derivative. Both 7-chloro-3-methylbenzo[*b*]-thiophen and the 2-bromo-derivative were treated with *N*-bromosuccinimide in boiling carbon tetrachloride [2] to give the corresponding 3-bromomethyl compound, which was condensed with a number of secondary amines to give the corresponding tertiary amines. 3-Bromomethyl-7-chlorobenzo[*b*]thiophen was converted into the corresponding primary amine by standard procedures (see Experimental section). Treatment of the bromomethyl derivative with sodium cyanide in (*a*) hot dimethyl sulphoxide [3] or (*b*) boiling 20% aqueous acetone gave respectively 45 and 83% yield of 7-chloro-3-cyanomethylbenzo[*b*]thiophen. Reduction [3] of this cyanide gave 2-(7-chloro-3-benzo[*b*]thienyl)ethylamine. Both the aminomethyl and the aminoethyl derivative readily gave the corresponding substituted urea,[3] and the aminoethyl compound was treated with *S*-methylthiouronium iodide in boiling ethanol [3] to give the corresponding guanidine derivative.

Hydrolysis of the cyanide as described in Part VII [3] gave 7-chloro-3-benzo[*b*]thienylacetic acid, which was converted *via* the acid chloride into the *N*-methyl or the *NN*-dimethylacetamide. Reduction [3] of these amides gave the corresponding *N*-substituted ethylamine derivatives.

Friedel–Crafts acetylation of 7-chloro-3-methylbenzo-[*b*]thiophen in nitrobenzene gave the 2-acetyl derivative (54%), whereas nitration with 70% nitric acid in glacial acetic acid at 50—60° gave the 2-nitro-derivative (36%) and a complex mixture of other products. Unchanged 7-chloro-3-methylbenzo[*b*]thiophen (21%) and 7-chloro-2,3-dihydro-3-hydroxy-3-methylbenzo[*b*]thiophen (14%) were isolated from among these products by preparative g.l.c. Spectroscopic evidence suggested the presence of 7-chloro-3-methylbenzo[*b*]thiophen-2(3*H*)-one and 7-chloro-3-nitromethylbenzo[*b*]thiophen in the mixture but these compounds could not be isolated in a pure state. However, such compounds are known to be formed in the nitration of 3-methylbenzo[*b*]thiophen.[4]

The Grignard reagent prepared from 7-chloro-3-methylbenzo[*b*]thiophen by the entrainment procedure involving cyclohexyl bromide [5] in tetrahydrofuran was treated with oxygen (2 h) or with air (16 h), and 7-hydroxy-3-methylbenzo[*b*]thiophen (50%) was obtained. The non-phenolic fraction contained unchanged starting material and 3-methylbenzo[*b*]thiophen. Similarly, 7-chlorobenzo[*b*]thiophen gave 7-hydroxybenzo[*b*]thiophen (19%) and a residue consisting mainly of starting material. The reaction with sulphur was less successful and a reaction in tetrahydrofuran involving methyl iodide as entraining agent gave only 11% of the expected 7-mercapto-3-methylbenzo[*b*]thiophen.

We decided therefore to investigate the direct nucleophilic displacement of the 7-chloro-group. Reaction of 7-chloro-3-methylbenzo[*b*]thiophen with aqueous ammonia (*d* 0·880) at 235° for 20 h (ref. 6) gave 7-amino-3-methylbenzo[*b*]thiophen (51%) and with aqueous 10% sodium hydroxide at 260—290° for 45 h gave 7-hydroxy-3-methylbenzo[*b*]thiophen (63%). The preparation of 7-hydroxy-3-methylbenzo[*b*]thiophen by either of the above methods is superior to any previously reported synthesis.

EXPERIMENTAL

^{1}H N.m.r. spectra (100 MHz) were obtained with a JNM-4H-100 spectrometer, for solutions in deuteriochloroform except where otherwise stated, with tetramethylsilane as internal standard. I.r. spectra were determined for potassium chloride discs with a Perkin-Elmer P.E. 457 spectrophotometer. Mass spectra were determined with an A.E.I. MS902 spectrometer.

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[2] N. B. Chapman, K. Clarke, and B. Iddon, *J. Chem. Soc.*, 1965, 774.
[3] N. B. Chapman, K. Clarke, A. J. Humphries, and S. U-D. Saraf, *J. Chem. Soc.* (*C*), 1969, 1612.
[4] J. Cooper, Ph.D. Thesis, University of Hull, 1970.
[5] M. S. Kharasch and W. B. Reynolds, *J. Amer. Chem. Soc.*, 1943, **65**, 501.
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7-Chloro-3-methylbenzo[*b*]thiophen (95%), b.p. 79—80° at 0·3 mmHg (lit.,[1] 114° at 2 mmHg) was prepared as described in Part V [1] except that the (2-chlorophenylthio)-acetone was heated with polyphosphoric acid at 115—120° for 4 h then at 80—100° for 1 h.

2-Bromo-7-chloro-3-methylbenzo[b]*thiophen.*— Bromine (1·55 ml, 0·031 mol) in dry carbon tetrachloride (2·5 ml) was added to a stirred solution of 7-chloro-3-methylbenzo[*b*]thiophen (5·64 g, 0·031 mol) in dry carbon tetrachloride (8 ml) during 30 min. The mixture was heated on a steam-bath until the colour of bromine was discharged (20 min), and was then diluted with benzene (100 ml) and washed with aqueous 5% sodium carbonate and with water, and dried ($MgSO_4$). Removal of the solvent gave *2-bromo-7-chloro-3-methylbenzo*[b]*thiophen* (6·46 g, 79%), m.p. 97—98° [needles from light petroleum (b.p. 60—80°)] (Found: C, 41·45; H, 2·5. C_9H_6BrClS requires C, 41·5; H, 2·3%), δ 7·6—7·2 (m, 4-H, 5-H, and 6-H) and 2·35 p.p.m. (s, 3-Me). 3-Bromomethyl-7-chlorobenzo[*b*]thiophen was prepared as previously described,[1] and under the same conditions 2-bromo-7-chloro-3-methylbenzo[*b*]thiophen gave the corresponding *3-bromomethyl derivative* (82%), m.p. 111—112° (Found: C, 31·8; H, 1·6. $C_9H_5Br_2ClS$ requires C, 31·9; H, 1·5%), δ 4·65 p.p.m. (s, CH_2Br).

Substituted 3-Aminomethylbenzo[b]*thiophen Hydrochlorides* (*Table* 1).—The 3-bromomethyl compounds were condensed with diethylamine, morpholine, piperidine, or pyrrolidine in boiling benzene.[2]

3-Aminomethyl-7-chlorobenzo[b]*thiophen Hydrochloride.*— (*a*) 3-Bromomethyl-7-chlorobenzo[*b*]thiophen was heated under reflux with the potassium salt of phthalimide.[3] The *phthalimido-compound* (100%) had m.p. 204° (from ethyl acetate) (Found: C, 62·1; H, 2·8; N, 4·1. $C_{17}H_{10}Cl_2NO_2S$ requires C, 62·3; H, 3·1; N, 4·3%). Treatment with 100% hydrazine hydrate in boiling ethanol gave the amine, which was characterised as its *hydrochloride* (60%), m.p. 260° (decomp.) (from ethanol–ether) (Found: C, 46·45; H, 3·7; N, 5·8. $C_9H_9Cl_2S$ requires C, 46·2; H, 3·9; N, 6·0%).

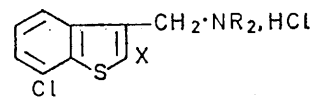
(*b*) 3-Bromomethyl-7-chlorobenzo[*b*]thiophen was boiled with a solution of hexamethylenetetramine in chloroform.[3] The resulting *salt* (94%), m.p. 179—181° (from ethanol) (Found: C, 44·9; H, 4·45; N, 13·9. $C_{15}H_{18}BrClN_4S$ requires C, 45·0; H, 4·5; N, 13·9%), on treatment with hot concentrated hydrochloric acid gave the same hydrochloride (72%) as before.

7-Chloro-3-benzo[b]*thienylacetonitrile.*—3-Bromomethyl-7-chlorobenzo[*b*]thiophen (25·5 g, 0·097 mol) was stirred overnight in a refluxing suspension of potassium cyanide (12·7 g, 0·2 mol) in acetone (125 ml) and water (410 ml). The mixture was cooled and poured into ice–water, and the resulting precipitate was collected and dissolved in ether. The solution was washed with water, with dilute hydrochloric acid, again with water, and dried ($MgSO_4$). Removal of the solvent gave a buff *solid* (16·8 g, 83%), m.p. 109—110° [from benzene–light petroleum (b.p. 60—80°)] (Found: C, 57·6; H, 2·9; N, 7·1. $C_{10}H_6ClNS$ requires C, 57·6; H, 2·9; N, 6·75%), $\nu_{max.}$ 2255 cm^{-1} (CN). In a similar reaction sodium cyanide in boiling dimethyl sulphoxide [3] gave a dark coloured product in only 45% yield.

2-(7-Chloro-3-benzo[b]*thienyl)ethylamine Hydrochloride.*—Reduction of 7-chloro-3-benzo[*b*]thienylacetonitrile with lithium aluminium hydride and aluminium chloride in dry ether [3] gave the *amine hydrochloride* (72%), m.p. 192° (from ethanol) (Found: C, 48·5; H, 4·4; N, 5·5. $C_{10}H_{11}Cl_2NS$ requires C, 48·4; H, 4·5; N, 5·65%), $\nu_{max.}$ 3450—3350 cm^{-1} (NH_3^+).

TABLE 1

7-Chloro-3-dialkylaminomethylbenzo[*b*]thiophen hydrochlorides



				Found (%)				Required (%)		
NR_2	X	Yield (%)	M.p. (°C) (decomp.)	C	H	N	Formula	C	H	N
Morpholino	H	75	213—214	51·3	5·0	4·7	$C_{13}H_{15}Cl_2NOS$	51·3	5·0	4·6
Piperidino	H	78	247—248	55·8	5·5	4·8	$C_{14}H_{17}Cl_2NS$	55·6	5·7	4·6
Diethylamino	H	69	179—180	53·5	5·9	5·0	$C_{13}H_{17}Cl_2NS$	53·8	5·9	4·8
Pyrrolidin-1-yl	H	63	225—226	54·2	5·3	4·9	$C_{13}H_{15}Cl_2NS$	54·2	5·2	4·9
Piperidino	Br	68	201—203	43·8	4·2	3·6	$C_{14}H_{16}BrCl_2NS$	44·1	4·2	3·7
Pyrrolidin-1-yl	Br	62	215—216	42·4	3·8	4·1	$C_{13}H_{14}BrCl_2NS$	42·5	3·8	4·1
Morpholino	Br	82	211—211·5	40·8	3·6	3·9	$C_{13}H_{14}BrCl_2NOS$	40·8	3·7	3·7

N-Substituted Ureas and Guanidines (*Table* 2).—These were prepared from the foregoing aminomethyl and aminoethyl derivatives as described in Part VII.[3]

7-Chloro-3-benzo[b]*thienylacetic Acid.*—7-Chloro-3-benzo[*b*]thienylacetonitrile, hydrolysed with aqueous sulphuric acid in boiling acetic acid,[3] gave the *substituted acetic acid* (79%), m.p. 131—132° (from propan-2-ol–hexane) (Found: C, 52·9; H, 3·1. $C_{10}H_7ClO_2S$ requires C, 52·9; H, 3·1%), $\nu_{max.}$ 3300—2500 (OH) and 1700—1690 cm^{-1} (C=O).

N-Methyl- and NN-Dimethyl-7-chloro-3-benzo[b]*thienylacetamide* (*Table* 2).—7-Chloro-3-benzo[*b*]thienylacetic acid in dry benzene was heated under reflux with an excess of pure thionyl chloride for 2 h. The excess of thionyl chloride and the solvent were removed under reduced pressure and the crude acid chloride was used directly in the next experiment as described in Part VII.[3] Reactions with methylamine and dimethylamine in acetone gave the corresponding substituted *N-methyl-* and *NN-dimethylacetamide*.

NN-Dimethyl-2-(7-chloro-3-benzo[b]*thienyl)ethylamine Hydrochloride.*—A solution of *NN*-dimethyl-7-chloro-3-benzo[*b*]thienylacetamide (1·27 g, 0·005 mol) in dry ether (50 ml) was added to a stirred suspension of lithium aluminium hydride (0·25 g, 0·006 mol) in dry ether (50 ml). The stirred mixture was heated under reflux for 2 h, then cooled, and the excess of reducing agent was decomposed by treatment with ethyl acetate, followed by moist ether and then 10N-sodium hydroxide. The ethereal layer was

separated and the aqueous phase was washed with more ether. The combined ethereal layers were washed with water and dried ($MgSO_4$). Addition of dry ethereal hydrogen chloride gave the *amine hydrochloride* (1·30 g, 94%), m.p. 202—203° (from ethanol) (Found: C, 52·4; H, 5·1; N, 5·4. $C_{12}H_{15}Cl_2NS$ requires C, 52·2; H, 5·5; N, 5·1%).

Nitration.—A solution of 70% nitric acid (2·65 ml, 0·04 mol) in glacial acetic acid (25 ml) was added dropwise during 1 h to a stirred solution of 7-chloro-3-methylbenzo[*b*]thiophen (7·3 g, 0·04 mol) in acetic acid (20 ml) at room temperature. The mixture was stirred at 50—60° for 18·5 h and cooled to give *7-chloro-3-methyl-2-nitrobenzo*[b]*thiophen* (1·95 g, 21%), m.p. 168·5—170° (from acetic acid) (Found: C, 47·6; H, 2·4; N, 6·2. $C_9H_6ClNO_2S$ requires C, 47·7; H, 2·65; N, 6·1%), $\nu_{max.}$ 1530 and 1340 (NO_2) cm^{-1}, δ 2·83 p.p.m. (3-Me). The mixture was shaken with chloroform, and the extract was washed, dried, and evaporated. G.l.c. of the residue showed that it contained more of the 2-nitro-derivative (total yield 36%), some unchanged 7-chloro-3-methylbenzo[*b*]thiophen (21%), and *7-chloro-3-hydroxy-3-methylbenzo*[b]*thiophen-2*(3H)*-one* (14%), m.p. 83—84° (from chloroform) (Found: *M*, 214. $C_9H_7{}^{35}ClO_2S$ requires *M*, 214), $\nu_{max.}$ 1720 (C=O) cm^{-1}, δ 2·8br (OH) and 1·6 p.p.m. (s, 3-Me). The i.r. spectrum was similar to that of an authentic sample of 3-hydroxy-3-methylbenzo[*b*]-thiophen-2(3*H*)-one.[4]

2-Acetyl-7-chloro-3-methylbenzo[b]*thiophen.*— Acetyl chloride (2·6 g, 2·3 ml) was added dropwise to a stirred solution of 7-chloro-3-methylbenzo[*b*]thiophen (5·42 g, 0·03 mol) in nitrobenzene (17·5 ml) at −5°. Aluminium chloride (4·41 g) was then added during 30 min and the mixture was stirred for 15 min and poured on to ice (500 g). The organic layer was separated and the aqueous layer was shaken with nitrobenzene (30 ml). The combined organic layers were washed with dilute hydrochloric acid and with water, and dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude product (5·7 g, 85%) was crystallised from light petroleum (b.p. 60—80°) to give the *2-acetyl derivative* (3·63 g, 54%), m.p. 101·5—102° (Found: C, 58·5; H, 4·3; N, 15·7. $C_{11}H_9ClOS$ requires C, 58·8; H, 4·0; N, 15·8%), $\nu_{max.}$ 1930, 1870, and 1808 (1,2,3-trisubstituted benzene) and 1640 (C=O) cm^{-1}, δ 7·80—7·65 (dd, 4-H or 6-H), 7·53—7·25 (m, 5-H and 6-H or 4-H), 2·70 (s, COMe), and 2·60 p.p.m. (s, 3-Me). The *oxime* had m.p. 154° (from benzene) (Found: C, 54·8; H, 4·2; N, 6·2. $C_{11}H_{10}ClNOS$ requires C, 55·1; H, 4·2; N, 5·8%).

3-Methylbenzo[b]*thiophen-7-ol.*—(*a*) Cyclohexyl bromide (32·6 g, 0·2 mol) and 7-chloro-3-methylbenzo[*b*]thiophen (18·25 g, 0·1 mol) in dry tetrahydrofuran (400 ml) were added during 10 min to a stirred suspension of magnesium turnings (7·30 g, 0·3 g atom) in dry tetrahydrofuran (100 ml) containing a crystal of iodine. After 20 min, the mixture became hot, and turned dark green, then blue, and finally grey. The mixture was stirred for 2 h, and then heated on a water-bath with stirring for a further 2 h. The rapidly stirred mixture was cooled to −5° and dry oxygen was bubbled in slowly; a buff precipitate formed. Oxygen could then be bubbled through rather more rapidly, for 2 h, with little increase in temperature. The mixture was stirred overnight at room temperature, the complex was decomposed with 2N-sulphuric acid (750 ml), and the mixture was shaken with benzene (3 × 200 ml). The benzene layer was shaken with aqueous 5% sodium hydroxide (200, 100, and 50 ml), and the aqueous layer, containing ice, was acidified with concentrated hydrochloric acid. The mixture was shaken with ether (200, 100, and 50 ml), and the ethereal layer was washed with water and dried ($MgSO_4$). The ether was removed, and the reddish-brown residue sublimed to give needle-like crystals (8·2 g, 50%), m.p. 95—96° (lit.,[7] 95·5°) (Found: C, 65·6; H, 5·0; S, 19·3. Calc. for C_9H_8OS: C, 65·8; H, 4·9; S, 19·5%), $\nu_{max.}$ (cyclohexanol) 226·2 (ε 27,740), 260·4 (2900), 269·5 (2300), 297·5 (2300), and 307·5 nm (3320), $\nu_{max.}$ 3400—3200 (OH) cm^{-1}, δ 7·43—7·23 (m, 4-H and 5-H), 7·05 (s, 2-H), 6·73 (dd, 6-H), 5·21 (s, OH), and 2·38 p.p.m. (s, 3-Me).

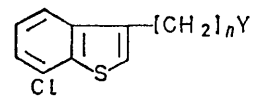
The benzene layer, containing non-phenolic material, was concentrated under reduced pressure and gave an oil containing (g.l.c.) 7-chloro-3-methylbenzo[*b*]thiophen (74%) and 3-methylbenzo[*b*]thiophen (15%).

When air instead of oxygen was passed through the reaction mixture overnight a similar yield was obtained. Experiments with hexamethylphosphoramide, *N*-methylmorpholine, or triethylamine as solvent for the Grignard reaction gave low yields.

Benzo[*b*]thiophen-7-ol (19%) was prepared as described in (*a*); the sublimed product had m.p. 63·5—66° (lit.,[8] 67—68°). However much unchanged 7-chlorobenzo[*b*]-thiophen (75%) was recovered from the reaction.

TABLE 2

Substituted ureas, guanidines, and acetamides derived from benzo[*b*]thiophen



Y	*n*	M.p. (°C)	Yield (%)	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
$NH{\cdot}CO{\cdot}NH_2$	1	192—193	94	49·7	4·1	11·6	$C_{10}H_9ClN_2OS$	49·9	3·75	11·6
$NH{\cdot}CO{\cdot}NH_2$	2	153—154	69	51·7	4·3	11·0	$C_{11}H_{11}ClN_2OS$	51·6	4·4	11·0
$NH{\cdot}C(:NH){\cdot}NH_2,HI$	2	191—194	90							
$NH{\cdot}C(:NH){\cdot}NH_2,HCl$ *	2	177—178	96	45·3	4·2	14·3	$C_{11}H_{13}Cl_2N_3S$	45·5	4·5	14·5
$CO{\cdot}NHMe$	1	169	75	55·0	4·3	6·0	$C_{11}H_{10}ClNOS$	55·1	4·2	5·85
$CO{\cdot}NMe_2$	1	61—62	90	57·0	4·9	5·4	$C_{12}H_{12}ClNOS$	56·8	4·8	5·5

* Prepared from the crude hydroiodide by use of an ion-exchange resin (Amberlite IRA 401).

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(*b*) A stirred mixture of 7-chloro-3-methylbenzo[*b*]-thiophen (18·25 g, 0·1 mol), aqueous 10% sodium hydroxide (400 ml), and copper(I) chloride (1·14 g) was heated at 260—290° (*ca.* 45 atm.) for 45 h under nitrogen. The cooled mixture was shaken thrice with 36% hydrochloric acid and with ether, and the ethereal layers were combined, washed with water, and dried ($MgSO_4$). The ether was removed, and the residue was sublimed to yield 3-methylbenzo[*b*]thiophen-7-ol (10·4 g, 63·5%). During this reaction serious pitting of the autoclave vessel may occur unless it is made of alkali-resistant stainless steel.

7-*Amino*-3-*methylbenzo*[b]*thiophen*.—A mixture of 7-chloro-3-methylbenzo[*b*]thiophen (18·2 g, 0·1 mol), aqueous ammonia (*d* 0·88; 110 ml), and copper(I) chloride (2 g) was stirred for 20 h at 235° and 52 atm. The cooled mixture was acidified with hydrochloric acid and the precipitated amine hydrochloride was collected. The filtrate was basified and shaken with ether, and the ethereal layer was separated. The amine hydrochloride was added to aqueous 5% sodium hydroxide (250 ml) with stirring, the free amine was extracted with ether, and the two ethereal layers were combined and dried ($MgSO_4$). The ether was removed to give a grey *solid* (8·44 g, 51·4%), m.p. 56° [needles from light petroleum (b.p. 60—80°)] (Found: C, 66·4; H, 5·6; N, 8·6. C_9H_9NS requires C, 66·4; H, 5·5; N, 8·5%), $\nu_{max.}$ 3410 (asym. free NH_2), 3310—3330 (sym. free, and asym. assoc. NH_2), 3210 (sym. assoc. NH_2), and 1290 (NH_2) cm^{-1}.

3-*Methylbenzo*[b]*thiophen*-7-*thiol*.—A solution of 7-chloro-3-methylbenzo[*b*]thiophen (36·1 g, 0·2 mol) and methyl iodide (56·8 g, 0·4 mol) in dry tetrahydrofuran (400 ml) was added dropwise during 1·5 h to a stirred suspension of magnesium turnings (14·6 g, 0·6 g atom) in dry tetrahydrofuran (100 ml) containing a crystal of iodine. The mixture was stirred at room temperature for 1·5 h to give a grey suspension, which was then heated under reflux for 3 h. Stirring was continued at room temperature overnight, and powdered sulphur (19·3 g, 0·6 g atom) was then added during 45 min. The mixture became warm, and was stirred at room temperature for 24 h. It was poured into 2N-sulphuric acid (1 l) and a stream of nitrogen was passed through the mixture to remove the methanethiol. The mixture was shaken with benzene (1·5 l) and the benzene layer was shaken with aqueous 4% sodium hydroxide. This alkaline solution was acidified with dilute hydrochloric acid to give a white emulsion, which turned yellow. The acidified mixture was shaken with ether (1 l), and the ethereal layer was dried ($MgSO_4$) and evaporated to give a residue (8·1 g), which was distilled to give a pale yellow oil (3·9 g, 11%), b.p. 94—95° at 1·5 mmHg, $\nu_{max.}$ 2540 (SH) cm^{-1}, δ 7·57 (dd, 4-H), 7·11 (s, 2-H), 3·48 (s, SH), and 2·30 p.p.m. (s, 3-Me). (The compound was not analysed since it slowly deposited a pale yellow solid, presumably the disulphide.)

A portion of the crude reaction residue was dissolved in benzene and passed down a column of magnesium carbonate. The first band eluted (toluene) gave pale yellow plates of *bis*-7-(3-*methylbenzo*[b]*thienyl*) *disulphide*, m.p. 100—101° [from benzene–light petroleum (b.p. 60—80°)] (Found: C, 60·5; H, 3·8; S, 36·1. $C_{18}H_{14}S_2$ requires C, 60·3; H, 4·0; S, 35·8%), $\nu_{max.}$ 1925, 1908; 1845br (poorly resolved); and 1795 and 1785 cm^{-1} (double bands) (dimer, 1,2,3-trisubstituted benzene), *m/e* 356 (M^+) and 178($M^+/2$).

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