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# Condensed Thiophen Ring Systems. Part V.<sup>1</sup> Synthesis, Reactions, and Stability of 2-Methyl- and 2-Methylthio-3-benzo[b]thienyl-lithium and Related Compounds

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5-Chlorobenzo[b]thiophen on metallation with n-butyl-lithium gave 5-chloro-2-benzo[b]thienyl-lithium, which reacted with carbon dioxide, dimethyl sulphate, and dimethyl disulphide to give, after hydrolysis, the corresponding acid, methyl-, and methylthio-derivatives, respectively. 2,5-Dimethylbenzo[b]thiophen, 2-methylthiobenzo-[b]thiophen, and 5-methyl-2-methylthiobenzo[b]thiophen were similarly prepared from 5-methyl-2-benzo[b]thienyl-lithium or 2-benzo[b]thienyl-lithium. 2-Methyl- and 2-methylthio-benzo[b]thiophen and their 5-methyland 5-chloro-derivatives were brominated, and each of the resulting 3-bromo-derivatives was treated with n-butyllithium in ether at -70° to give the corresponding 3-lithium compound. These were treated with NN-dimethylformamide and carbon dioxide to give the corresponding 3-carbaldehyde or 3-carboxylic acid, respectively. 2-Methyl-3-benzo[b]thienyl-lithium and its derivatives undergo ring-opening reactions in ether at temperatures much in excess of  $-70^\circ$ .

PREVIOUSLY<sup>1</sup> we have described the synthesis and some reactions of 3-benzo[b]thienyl-lithium and several related compounds. We now report the preparation and some reactions of the six lithium compounds (1)—(6).

2-Methylbenzo[b]thiophen was prepared by treating 2-benzo[b]thienyl-lithium with dimethyl sulphate  $^2$  and 2,5-dimethyl- and 5-chloro-2-methyl-benzo[b]thiophen were similarly prepared. 5-Chloro-2-benzo[b]thienyllithium was also characterised by its reaction with carbon dioxide, which gave 5-chlorobenzo[b]thiophen-2-carboxylic acid.<sup>3</sup> 2-Methylthiobenzo[b]thiophen and its 5-methyl- and 5-chloro-derivatives were prepared by treating the appropriate 2-benzo[b]thienyl-lithium compound with dimethyl disulphide.



Bromination of 2-methyl- and 2-methylthio-benzo[b]thiophen and their 5-methyl- and 5-chloro-derivatives by a previously described procedure<sup>1</sup> gave the corresponding 3-bromo-compounds (see Tables 1 and 2). However, 3-bromo-5-methyl-2-methylthiobenzo[b]thiophen (38%) was obtained together with starting material and a considerable amount of the 3,6-dibromo-compound (7) (20%) on bromination of 5-methyl-2-methylthiobenzo[b]thiophen under these conditions. In addition to two singlets for the methyl protons, the n.m.r. spectrum of (7) in deuteriochloroform showed two singlets at  $\tau 2.47$  and 2.12 which we have assigned to H-4 and H-7, respectively, by comparison with the spectrum of 3-bromo-5-methyl-2-methylthiobenzo[b]thiophen. Dibromination of 5-methyl-2-methylthiobenzo[b] thiophen to give (7) is obviously made easy by conjugation of the 6-position with the 2-methylthio group, as shown (8), and with the adjacent methyl group. It is noteworthy that, whereas benzo[b]thiophen and many of its derivatives undergo electrophilic substitution predominantly at the 3-position, an alkoxygroup at the 6-position directs substitution to the 2-position.<sup>4</sup> The activation discussed above is the reverse of this effect. Monobromination of 5-methyl-2methylthiobenzo[b]thiophen was achieved by the slow addition of a very dilute solution of bromine in chloroform.

Treatment of each of the 3-bromo-compounds with n-butyl-lithium in ether at  $-70^{\circ}$  gave the corresponding lithium compounds, (1)—(6). On treatment with NNdimethylformamide or carbon dioxide each of these gave the corresponding aldehvde or acid, respectively. In general, the yields of products obtained were high (Table 3) and contrast markedly with some of the yields of products recorded previously,1 which lends further support to the suggestion that, in the latter case, the low yields were due to steric requirements. A noteworthy feature of the n.m.r. spectra of benzo[b]thiophen-3-carbaldehydes (Table 4) (cf. also ref. 1) is the large downfield shift of the H-4 signals attributed to the diamagnetic anisotropic deshielding effect of the pericarbonyl group. The potential of the lithium compounds (1)—(6) as synthetic intermediates is indicated

<sup>&</sup>lt;sup>1</sup> Part IV, R. P. Dickinson and B. Iddon, J. Chem. Soc. (C),

<sup>1970, 2592,</sup> and preceding papers in this Series. <sup>2</sup> E. N. Karaulova, D. Sh. Meilanova, and D. G. Gal'pern, Doklady. Akad. Nauk. SSSR, 1958, **99**, 123 (Chem. Abs., 1959, **53**, 5229).

<sup>&</sup>lt;sup>3</sup> N. B. Chapman, K. Clarke, and S. D. Saraf, J. Chem. Soc. (C), 1967, 731. 4 B. Iddon and R. M. Scrowston, Adv. Heterocyclic. Chem.,

<sup>1970, 11, 244.</sup> 

by the reactions of 3-benzo[b]thienyl-lithium which we have already reported.5-7

We have already reported the ring-opening reactions of 3-benzo[b]thienyl-lithium<sup>8</sup> and of several 2-phenyl-3-benzo[b]thienyl-lithium compounds.<sup>1</sup> When we allowed an ethereal suspension of 2-methyl-3-benzo[b]thienyl-lithium (prepared from 3-bromo-2-methylbenzo-[b]thiophen at  $-70^{\circ}$  as described before) to stir for 18 hr. at room temperature before hydrolysing the product, a mixture of starting material (1 mole %), 2-methylbenzo[b]thiophen (39 mole %), and the acetylene (9) (60 mole %) was obtained. An ethereal suspension of 2,5-dimethyl-3-benzo[b]thienyl-lithium similarly gave a mixture of starting material (*i.e.*, the bromo-compound) (3 mole %), 2,5-dimethylbenzo[b]thiophen (31 mole %), and the acetylene (10); likewise an ethereal suspension 5-chloro-2-methyl-3-benzo[b]thienyl-lithium of gave starting material (10 mole %), 5-chloro-2-methylbenzo[b]thiophen (47 mole %), and the acetylene (11). These results are consistent with those already reported <sup>1,8</sup> and can be similarly rationalised.

## EXPERIMENTAL

N.m.r. spectra were recorded with a Varian A60 spectrometer; tetramethylsilane was used as an internal standard and the recorded signals are singlets, unless stated otherwise. I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer and g.l.c. was carried out with a Pye 104 Chromatograph fitted with a flame-ionisation detector and 5 ft.  $\times$  5.0 mm columns.

n-Butyl-lithium was purchased as a 20% (w/w) solution in hexane: consequently, all later references to solutions of n-butyl-lithium in ether imply the presence of small amounts of hexane. Reactions with n-butyl-lithium were carried out under dry, oxygen-free nitrogen, and the solvents and other reagents used were dried by standard procedures.

2,5-Dimethylbenzo[b]thiophen.-A solution of n-butyllithium (84.5 mmoles) in ether (25 ml.) was added dropwise during 5 min. to a stirred solution of 5-methylbenzo[b]thiophen <sup>9</sup> (12.5 g., 84.5 mmoles) in ether (127 ml.) at  $0^{\circ}$ , and the resulting mixture was stirred at 0° for 1 hr. A solution of dimethyl sulphate (10.7 g., 84.5 mmoles) in ether (20 ml.) was added during 5 min. at 0° and the resulting mixture was stirred at room temperature for a further 1 hr. A solution of sodium (2.3 g., 0.1 g.-atoms) in ethanol (25 ml.) was then added and the mixture was stirred and heated under reflux for 1 hr.; it was then cooled, diluted with water, and the organic layer was separated. The aqueous layer was extracted with ether and the organic layer and ethereal extracts were combined, washed with water, and dried (MgSO<sub>4</sub>). Distillation gave 2,5-dimethylbenzo[b]thiophen (11.60 g., 85%), b.p. 129-133°/15 mm., m.p. 50-51° (from aqueous methanol) (lit.,<sup>10</sup> m.p. 52-52.5°),  $\tau$  (CCl<sub>4</sub>) 3.22 (q, 3-H), 2.65 (d, 4-H, J 1.7 Hz), 2.47 (d, 7-H, J 8.5 Hz), 3.01 (dd, 6-H), 7.47 (d, 2-CH<sub>3</sub>, J 1.2 Hz), and 7.59 (5-CH<sub>3</sub>).

<sup>5</sup> R. P. Dickinson and B. Iddon, J. Chem. Soc. (C), 1968, 2733.

<sup>6</sup> R. P. Dickinson and B. Iddon, J. Chem. Soc. (C), 1970, 1926.
<sup>7</sup> B. Iddon, C. K. Thadani, B. Northover, and R. G. Somerville, Chim. Therap., 1970, 5, 149.

5-Chloro-2-methylbenzo[b]thiophen (96%) was similarly prepared, b.p. 146-150°/13 mm., m.p. 82-83° [from light petroleum (b.p. 60-80°)], τ (CDCl<sub>3</sub>) 3·10 (q, 3-H), 2·35 (d, 4-H, J 1.8 Hz), 2.35 (d, 7-H, J 8.6 Hz), 2.78 (dd, 6-H), and 7.43 (d, 2-CH<sub>3</sub>, J 1.2 Hz) (Found: C, 59.5; H, 3.9. C<sub>9</sub>H<sub>7</sub>ClS requires C, 59.2; H, 3.9%).

2-Methylthiobenzo[b]thiophen.—A solution of dimethyl disulphide (11.3 g., 120.0 mmoles) in ether (10 ml.) was added during 5 min. to a stirred solution of 2-benzo[b]thienyl-lithium (100.0 mmoles) (prepared as described before for 5-methyl-2-benzo[b]thienyl-lithium) in ether (150 ml.) at 0°, and the resulting mixture was stirred at room temperature for 2 hr. An excess of 2n-hydrochloric acid was then added and work-up gave 2-methylthiobenzo[b]thiophen (15.7 g., 87%), b.p. 153-154°/9 mm., m.p. 28-29°,  $\tau$  (CCl<sub>4</sub>) 2.96 (3-H), 2.30-2.60 (m, 4-H and 7-H), 2.70-3.00 (m, 5-H and 6-H), and 7.58 (SCH<sub>3</sub>) (Found: C, 59.8; H, 4.5. C<sub>9</sub>H<sub>8</sub>S<sub>2</sub> requires C, 59.95; H, 4.5%).

The following compounds were prepared similarly: 5-methyl-2-methylthiobenzo[b]thiophen (91%), b.p. 177-179°/10 mm., m.p. 52-52.5° [from light petroleum (b.p. 40-60°)], τ (CCl<sub>4</sub>) 2·97 (3-H), 2·70 (d, 4-H, J 2·0 Hz), 2·51 (d, 7-H, 8.0 Hz), 3.03 (dd, 6-H), 7.52 (SCH<sub>3</sub>), and 7.62 (CH<sub>3</sub>) (Found: C, 61.7; H, 5.1; S, 33.0. C10H10S2 requires C, 61.8; H, 5.2; S, 33.0%): and 5-chloro-2-methylthiobenzo[b]thiophen (82%), b.p.  $193-194^{\circ}/10$  mm., m.p.  $72-73\cdot5^{\circ}$ [from light petroleum (b.p. 40—60°)],  $\tau$  (CCl<sub>4</sub>) 3.03 (3-H), 2.50 (d, 4-H, J 2.2 Hz), 2.48 (d, 7-H, J 8.5 Hz), 2.85 (dd, 6-H), and 7.47 (SCH<sub>3</sub>) (Found: C, 50.6; H, 3.5. C<sub>9</sub>H<sub>7</sub>ClS<sub>2</sub> requires C, 50.35; H, 3.3%).

5-Chlorobenzo[b]thiophen-2-carboxylic Acid.—An excess of crushed solid carbon dioxide was added in small amounts to a suspension of 5-chloro-2-benzo[b] thienyl-lithium (10.0)mmoles) (prepared as described before) in ether (50 ml.). When no solid carbon dioxide remained, the mixture was acidified with 2n-hydrochloric acid and the organic layer was separated; the aqueous layer was extracted with ether and the organic layer and ethereal extracts were combined. Extraction of the product with 2n-sodium hydroxide and acidification of the combined alkaline extracts gave 5chlorobenzo[b]thiophen-2-carboxylic acid (1.76 g., 83%), m.p. 255-257° (from ethyl acetate) (lit.,<sup>3</sup> m.p. 240-242°) (Found: C, 51.2; H, 2.5; S, 15.35. Calc. for C<sub>9</sub>H<sub>5</sub>ClO<sub>2</sub>S: C, 50.9; H, 2.4; S, 15.1%).

3-Bromo-2-methyland 3-Bromo-2-methylthio-benzo[b]thiophens.-2-Methylbenzo[b]thiophen and its 5-methyl- and 5-chloro-derivatives and 2-methylthiobenzo[b]thiophen and its 5-chloro- derivative were brominated in the manner described previously.<sup>1</sup> The solution of bromine in chloroform was usually added at  $0^{\circ}$  and the mixtures were then stirred for varying times at 0° and/or room temperature, depending upon the reactivity of the starting material. Data for new compounds are given in Tables 1 and 2.

When a solution of bromine (8.0 g., 50.0 mmoles) in chloroform (10 ml.) was added during 20 min. to a stirred solution of 5-methyl-2-methylthiobenzo[b]thiophen (9.70 g., 50.0 mmoles) in chloroform (25 ml.) at  $0^{\circ}$  and the resulting mixture was stirred at room temperature for 3 hr., a product

J. Chem. Soc. (C), 1968, 514.

<sup>10</sup> M. Pailer and E. Romberger, Monatsh., 1960, 91, 1070.

<sup>8</sup> R. P. Dickinson and B. Iddon, Abstracts of the Cork Mechanisms Conferences, Structure and Mechanism in Sulphur Chemistry, Cork, Sept. 29th to October 3rd, 1969, paper L-8; R. P. Dickinson and B. Iddon, Tetrahedron Letters, 1970, 975.
<sup>9</sup> N. B. Chapman, K. Clarke, B. Gore, and S. N. Sawhney,

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was obtained which, on distillation, gave 3-bromo-5-methyl-2-methylthiobenzo[b]thiophen (5.0 g., 38%) (details of the product are given in Tables 1 and 2) and 3,6-dibromo-5-methyl-2-methylthiobenzo[b]thiophen (3.51 g., 20%), b.p. 173-178°/0.7 mm., m.p. 102-103° [from light petroleum (b.p. 40-60°)],  $\tau$  (CDCl<sub>3</sub>) 2.47 (4-H), 2.12 (7-H), 7.41 (SCH<sub>3</sub>), and 7.49 (CH<sub>3</sub>) (Found: C, 34.4; H, 2.5; Br, 45.2. C<sub>10</sub>H<sub>8</sub>Br<sub>2</sub>S<sub>2</sub> requires C, 34.1; H, 2.3; Br, 45.4%).

Monobromination of 5-methyl-2-methylthiobenzo[b]thiophen (81%) was achieved by adding a solution of bromine

dried (MgSO<sub>4</sub>). Evaporation of the solvent gave the crude aldehyde which was purified by one of the following procedures: (a) through formation of the bisulphite addition compound; <sup>5</sup> (b) by chromatography on silica with light petroleum (b.p.  $60-80^{\circ}$ ) to elute the starting material and debrominated starting material, and benzene to elute the aldehyde; or (c) by trituration with light petroleum (b.p.  $40-60^{\circ}$ ) followed by filtration. Details of the products are given in Tables 3 and 4.

2-Methyl- and 2-Methylthio-benzo[b]thiophen-3-carboxylic

# TABLE 1





					-				
				Yield	Found	đ (%)		Requir	ed (%)
$\mathbb{R}^1$	$\mathbb{R}^2$	M.p. "	B.p. °C/mmHg	(%)	С	$\mathbf{H}$	Formula	С	$\mathbf{H}$
Me	$\mathbf{Me}$	$44 - 47^{\circ}$	165 - 166/12	79	50.2	<b>4</b> ·0	C <sub>10</sub> H <sub>9</sub> BrS	49.8	3.75
Me	Cl	98 - 101	174 - 176 / 9	86	41.4	$2 \cdot 4$	C,H,BrClS	41.3	$2 \cdot 3$
SMe	н		183—193/9	84	42.1	$2 \cdot 5$	$C_{9}H_{7}BrS_{2}$	41.7	2.7
SMe	Me	51 - 52	125 - 128 / 0.4	81	44.3	3.5	$C_{10}H_9BrS_2$	43.95	$3 \cdot 3$
SMe	Cl	$73 - 73 \cdot 5$	155 - 158 / 0.7	91	37.2	$2 \cdot 2$	$C_9H_6BrClS_2$	$36 \cdot 8$	$2 \cdot 1$

<sup>a</sup> Recrystallised from light petroleum (b.p.  $40-60^{\circ}$ ).

### TABLE 2

### <sup>1</sup>H N.m.r. data for 3-bromobenzo[b]thiophens

				R <sup>2</sup>	Br R <sup>1</sup>					
					Chemical s	shifts (τ)				
R <sup>1</sup> Me Me SMe	R <sup>2</sup> Me <sup>a</sup> Cl <sup>b</sup> H b	4-H 2·48(d) 2·39(d)	5-H	6-H 2·85(dd) 2·78(dd) 3·10	7-H 2·42(d) 2·47(d)	R <sup>1</sup> 7·48 7·47 7·65	or	R² 7·53 ℃	$J_{4,6} (Hz) \\ \frac{1 \cdot 7}{2 \cdot 0}$	J <sub>6.7</sub> (Hz) 8·2 8·2 8·2
SMe SMe	Me <sup>a</sup> Cl <sup>b</sup>	$2 \cdot 49(d) \\ 2 \cdot 46(d)$	2.01-	2.87(dd) 2.85(dd)	$2 \cdot 44(d)$ $2 \cdot 56(d)$	7.47 7.47		7.55	$1.7 \\ 2.0$	$8 \cdot 2 \\ 8 \cdot 2$

" Solvent CDCl<sub>a</sub>. <sup>b</sup> Solvent CCl<sub>4</sub>. <sup>c</sup> Assignment not made.

4.54 g., 28.2 mmoles) in chloroform (40 ml.) during 80 min. to a vigorously stirred solution of the benzo[b]thiophen (5.50 g., 28.2 mmoles) in chloroform (100 ml.) at 0°. The resulting solution was stirred for 3 hr. at 0° and was then worked up.<sup>1</sup>

2-Methyl- and 2-Methylthio-benzo[b]thiophen-3-carbaldehydes.—A solution of the 3-bromo-2-methyl- or 3-bromo-2-methylthio-benzo[b]thiophen (10.0 mmoles) in ether (5 ml.) was added during 5 min. to a stirred solution of n-butyl-lithium (10.0 mmoles) in ether (50 ml.) at  $-70^{\circ}$ , and the resulting mixture was stirred at  $-70^{\circ}$  for 30 min. NN-Dimethylformamide (0.88 g., 12.0 mmoles) in ether (5 ml.) was added at  $-70^{\circ}$  and the resulting mixture was stirred at  $-70^{\circ}$  for a further 4 hr. It was then allowed to warm up slowly to  $-5^{\circ}$  and was stirred at  $-5^{\circ}$  for 15 min. An excess of 2N-hydrochloric acid was then added to the stirred mixture after which the organic layer was separated, the aqueous layer was extracted with ether, and the organic layer and ethereal extracts were combined and Acids.—A suspension of the 3-benzo[b]thienyl-lithium compound (60.0 mmoles) in ether (200 ml.) was prepared at  $-70^{\circ}$  as described before. An excess of crushed solid carbon dioxide was added and the mixture was worked up as described before for the preparation of 5-chlorobenzo-[b]thiophen-2-carboxylic acid. Details of the products are given in Table 3.

Ring-Opening Reactions of 2-Methyl-3-benzo[b]thienyllithium Compounds.—The reactions were carried out as described previously.<sup>1</sup> In this way 2-methyl-3-benzo[b]thienyl-lithium gave a mixture (g.l.c., with a 10% polyethylene glycol adipate on Celite column at 180°) of starting material (*i.e.*, 3-bromo-2-methylbenzo[b]thiophen) (1 mole %), 2-methylbenzo[b]thiophen (39 mole %), and methylo-(n-butylthio)-phenylacetylene (60 mole %). The product was chromatographed on silica with light petroleum (b.p.  $40-60^{\circ}$ ) to elute starting material and 2-methylbenzo[b]thiophen, and carbon tetrachloride to elute the acetylene, which was purified further by chromatography and dis-

TABLE 3 Benzo[b]thiophen-3-carbaldehydes and -3-carboxylic acids



				Solvent of	Yield 4	Yield d Found (%)			Required (%)	
R1	$\mathbb{R}^2$	$\mathbb{R}^3$	M.p.	crystallisation "	(%)	С	$\mathbf{H}$	Formula	С	н
н	Me	н	91—93°	C	85(a)	68.0	<b>4</b> ·6	C <sub>10</sub> H <sub>8</sub> OS	68.2	$4 \cdot 6$
$\mathbf{H}$	$\mathbf{Me}$	Me	8081	в	68(b)	69.4	$5 \cdot 3$	C <sub>11</sub> H <sub>10</sub> OS	69.4	5.3
H	$\mathbf{Me}$	Cl	140 - 141	E	67(b)	56.8	3.05	C <sub>10</sub> H <sub>7</sub> ClOS	57.0	3.35
H	SMe	н	$53 - 54 \cdot 5$	в	82(c)	57.9	$4 \cdot 2$	$C_{10}H_8O_2S_2$	57.65	$3 \cdot 9$
н	SMe	Me	96 - 97	в	76(b)	59.4	<b>4</b> ·7	$C_{11}H_{10}OS_{2}$	59.4	4.5
$\mathbf{H}$	SMe	Cl	$108 \cdot 5 - 110 \cdot 5$	С	70(b)	49.6	$3 \cdot 2$	C <sub>10</sub> H <sub>7</sub> ClOS <sub>2</sub>	49.5	$2 \cdot 9$
OH	Me	$\mathbf{H}$	193194 <i><sup>b</sup></i>	A	80`´					
OH	Me	Me	208—209 °	Α	80	63.6	4.9	$C_{11}H_{10}O_{2}S$	64·0	<b>4</b> ·9
OH	Me	Cl	240 - 242	D	75	53.05	3.05	C <sub>10</sub> H <sub>7</sub> ClO <sub>2</sub> S	53.0	3.1
OH	SMe	$\mathbf{H}$	222 - 223	A	80	53.8	$3 \cdot 4$	$C_{10}H_8O_2S_2$	53.55	3.6
OH	SMe	Me	$251 \cdot 5 - 253 \cdot 5$	D	66	55.75	4.4	$C_{11}H_{10}O_2S_2$	$55 \cdot 4$	$4 \cdot 2$
OH	SMe	Cl	284 - 285	E	78	46.45	$3 \cdot 1$	$C_{10}H_7ClO_2S_2$	46.4	2.7

<sup>a</sup> A =  $C_6H_6$ , B = light petroleum (b.p. 40-60°), C = light petroleum (b.p. 60-80°), D = EtOAc, E = EtOH. <sup>b</sup> F. Sauter, L. Golser, and P. Stütz, Monatsh, 1967, 98, 2089, m.p. 194–195°. <sup>c</sup> Y. Matsuki and T. Kanda, Nippon Kagaku Zasshi, 1965, 86, 99 (Chem. Abs., 1965, 62, 16,172), m.p. 205–207°. <sup>a</sup> Letter in parentheses indicates work-up procedure (see text).

#### TABLE 4

<sup>1</sup>H N.m.r. data for benzo[b]thiophen-3-carbaldehydes



Chaminal shifts (-)

			Cher	mear sniits						
$\mathbb{R}^1$	$\mathbb{R}^2$	4-H	5-H	6-H	7-H	СНО	$\mathbb{R}^1$	$\mathbb{R}^2$	$J_{4,6}$ (Hz)	$J_{6.7}$ (Hz)
Me	Ηď	1.53(m) °	<b>←</b> 2·50-	-2.80	2·36(m) °	-0.18	7.25			
Me	Me <sup>b</sup>	1.57(d)		2.87(dd)	2.44(d)	-0.30	7.20	7.54	1.8	8.0
Me	C1 b	1.38(d)		2.70(dd)	2·38(d)	-0.28	7.12		2.0	8.5
SMe	H ª	1.53(m) °	<b>←</b> 2·50–	-2.80	2·37(m) °	-0.32	7.34			
SMe	Me <sup>b</sup>	1.75(d)		2·82(dd)	2·39(d)	-0.42	7.33	7.52	1.8	8.0
SMe	Clo	1.59(d)		2.73(dd)	$2 \cdot 42(d)$	-0.04	7.20		$2 \cdot 0$	8.5
		a Calman	+ CC1 1 5 -1	mant CDCI	· Timuna aliana	. :				

Solvent CCl<sub>4</sub>.
Solvent CDCl<sub>3</sub>.
Figure given is for approximate centre.

tillation, b.p. 155—157°/7 mm.,  $\nu_{max.}$  (liq. film) 2205, 2230, and 2255 cm.^-1 (C:C),  $\tau$  (CCl<sub>4</sub>) 2.60—3.20 (m, Ar), 7.13 \*

(a),  $8 \cdot 10 - 8 \cdot 90$  ( $\beta$  and  $\gamma$ ),  $9 \cdot 09 *$  ( $\delta$ ) (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), and 7 \cdot 92 (Me) (Found: C, 76 \cdot 8; H, 8 \cdot 3. C<sub>13</sub>H<sub>16</sub>S requires C, 76 \cdot 4; H, 7 \cdot 9%).

2,5-Dimethyl-3-benzo[b]thienyl-lithium (prepared in the usual way <sup>1</sup> from 3-bromo-2,5-dimethylbenzo[b]thiophen) similarly gave a mixture of starting material (3 mole %), 2,5-dimethylbenzo[b]thiophen (31 mole %), and methyl-2-n-butylthio-5-methylphenylacetylene (66 mole %), b.p. 170°/10 mm. (Kugelrohr apparatus),  $v_{max}$ . (liq. film) 2235 cm.<sup>-1</sup> (C:C),  $\tau$  (CCl<sub>4</sub>) 2.85 (d, 6-H, J 2.0 Hz), 2.90 (d, 3-H, J 8.5 Hz), 3.04 (dd, 4-H), 7.14 \* ( $\alpha$ ), 8.20—8.90 ( $\beta$  and  $\gamma$ ),  $\alpha \beta \gamma \delta$ 9.06 \* ( $\delta$ ) (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 7.73 (5-Me), and 7.88 (:CMe) (Found: C, 76.8; H, 8.5. C<sub>14</sub>H<sub>18</sub>S requires C, 77.0; H, 8.3%); and 5-chloro-2-methyl-3-benzo[b]thienyl-lithium gave starting material (10 mole %), 5-chloro-2-methylbenzo[b]thiophen (47 mole %), and methyl-2-n-butylthio-5-chlorophenylacetylene (43 mole %), b.p. 185°/14 mm. (Kugelrohr apparatus),  $v_{max}$  (liq. film) 2225 and 2255 cm.<sup>-1</sup> CiC);  $\tau$  (CCl<sub>4</sub>) 2.60—2.90 (m, Ar), 7.13 \* ( $\alpha$ ), 8.15—8.80 ( $\beta$  and  $\gamma$ ), and 9.05 \* ( $\delta$ ) (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), and 7.87 (CH<sub>3</sub>) (Found: C, 65.7; H, 6.2. C<sub>13</sub>H<sub>15</sub>ClS requires C, 65.4; H, 6.3%).

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\* Distorted triplet; figure given is for approximate centre.