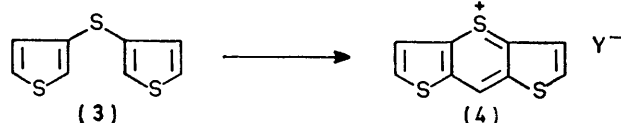
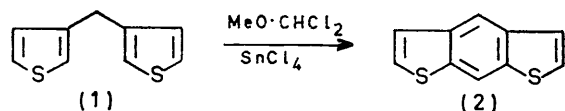


## The Direct Bradsher Reaction. Part II.<sup>1</sup> Synthesis of Pirylium and Thiopyrylium Salts<sup>2</sup>

By John Ashby, Mehdi Ayad, and Otto Meth-Cohn,\* Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, Lancs.

The action of dichloromethyl methyl ether and tin(IV) chloride on a variety of diaryl sulphides and diaryl ethers (designed so that electrophilic substitution occurs *ortho* to the bridge atom) gives the corresponding pyrylium and thiopyrylium salts, often in high yield.

WE have recently demonstrated<sup>1</sup> that suitable diaryl-methanes [*e.g.* (1)] are readily converted into the corresponding fused aromatic systems [*e.g.* (2)] by the action of dichloromethyl methyl ether and tin(IV) stannic chloride, a process which we have termed the direct Bradsher reaction. A reasonable extension of this work would involve the reactions of compounds in which



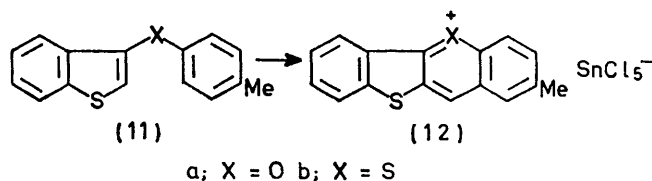
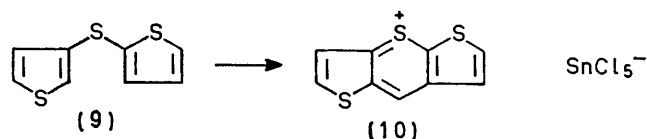
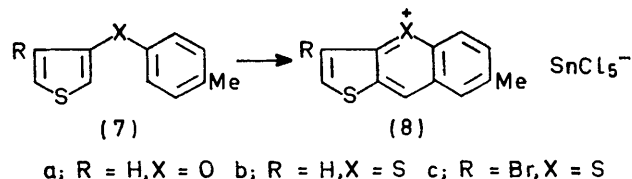
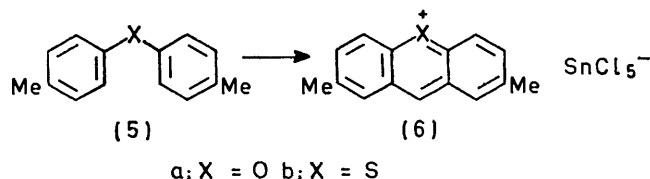
the bridge methylene group had been replaced by a heteroatom [*e.g.* as in (3)], which, by analogy, should give the corresponding salt (4). As fused thienopyrylium and -thiopyrylium salts are little known, the products would be of considerable interest. These expectations were realised and a series of pyrylium and thiopyrylium salts have now been synthesised by this method, generally in high yield (Table 1). The salts were readily isolated by filtration from the reaction mixture, but were highly insoluble and attempts to purify them by recrystallisation (*e.g.* from acetic acid, perchloric acid, aqueous sulphuric acid, or trifluoroacetic acid) inevitably resulted in some anion exchange and further reaction as described later. Hence analytical results were not very accurate. However, mass spectral data and subsequent chemical reactions served to confirm the structures. In one case [(21)  $\longrightarrow$  (22)] a bis-thiopyrylium salt was formed.

The salts all gave mass spectra in which the fragmentation pattern of the organic system was superimposed upon that of cations derived from the chlorostannyl group. The latter gave groups of peaks corresponding to SnCl<sub>5</sub><sup>+</sup>, SnCl<sub>4</sub><sup>+</sup>, SnCl<sub>3</sub><sup>+</sup>, SnCl<sub>2</sub><sup>+</sup>, SnCl<sup>+</sup>, and Sn<sup>+</sup> which were highly characteristic and served as useful markers to aid counting the spectrum. The base peak of the organic ions was invariably the molecular ion. In the case of the bispyrylium salt (22) the product was

<sup>1</sup> Part I, M. Ahmed, J. Ashby, M. Ayad, and O. Meth-Cohn, preceding paper.

<sup>2</sup> Preliminary communication: M. Ahmed, J. Ashby, and O. Meth-Cohn, *Chem. Comm.*, 1970, 1094.

insufficiently volatile to give a mass spectrum. Study of the dithienothiopyrylium salts (4) and (10) revealed a time-dependent formation of dimers in their mass spectra, presumably of thermal origin. Attempts to



isolate similar dimers either by heating the monomers in a solvent or by sublimation under high vacuum led only to charred products. The electrophilic alkylation of a thiophen ring by the bridge-carbon of a second molecule of the thiopyrylium salt, leading to structures such as (23), probably accounts for this observation. Thus xanthylum salts are known to alkylate aniline in the *para*-position.<sup>3</sup>

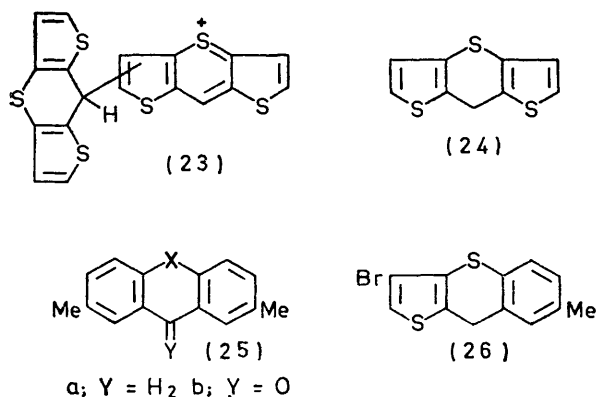
In accord with the known properties of xanthylum and thioxanthylum salts, the salts reacted readily with hot water thereby losing their colour. Thus the salts (6a and b) gave the products (25; X = S or O, respectively), produced presumably by disproportionation of the intermediate alcohol.<sup>4</sup>

The reduction of the salts to their corresponding fused

<sup>3</sup> F. Ullmann and G. Engi, *Ber.*, 1904, **37**, 2367.

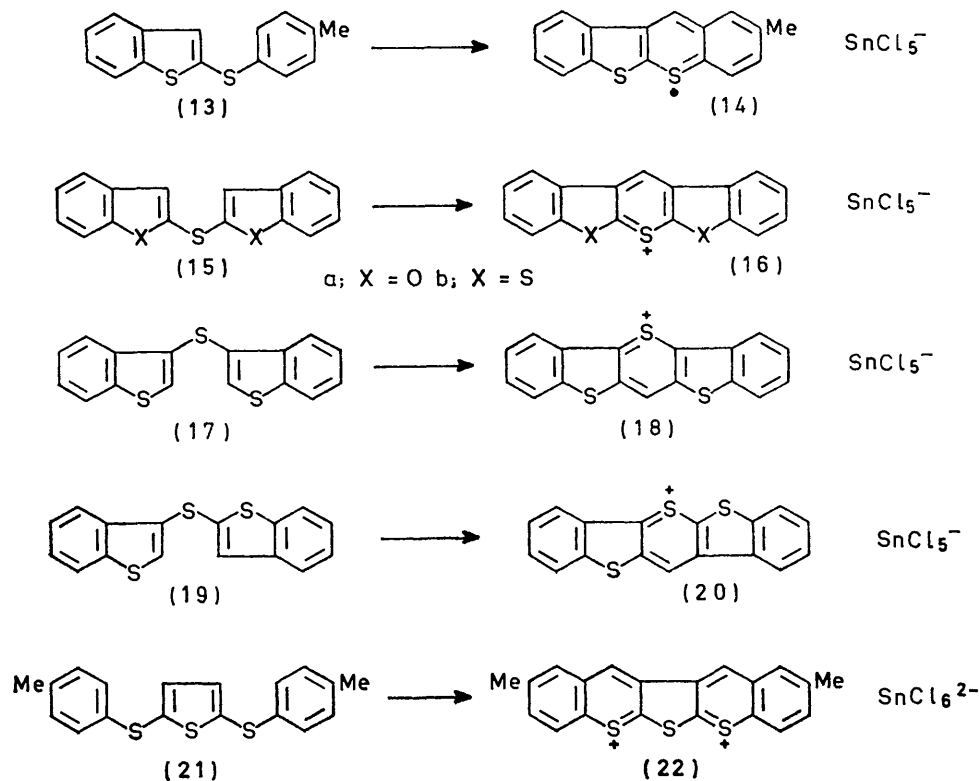
<sup>4</sup> D. S. Tarbell in R. C. Elderfield, 'Heterocyclic Compounds,' Wiley, New York, 1951, vol. 2, p. 546.

pyran and thiopyran derivatives proceeded exothermically and generally in good yield with ethanolic sodium



borohydride. The products were highly crystalline and gave good analytical and spectral data (Table 2). The mass spectra revealed the molecular ion and the  $M - 1$

The starting materials required (diaryl ethers and diaryl sulphides) were made by application of standard methods through the interaction of aryl bromides with suitable hydroxy- or mercapto-compounds or by the action of sulphur dichloride on lithium aryls in ether. The products are recorded in Table 3. The attempt to condense 3,4-dibromothiophen with *p*-thiocresol give solely the monosubstituted sulphide (7c), despite the successful disubstitution of 2,5-dibromothiophen with the same reagent. No substitution was observed at all when benzothiophen-2-thiol was treated with 3,4-dibromothiophen; the sole product was the oxidative dimer (31) of the thiol, as evidenced by accurate mass measurement of the molecular ion, confirming the formula C<sub>16</sub>H<sub>8</sub>S<sub>4</sub>. Production of the base peak in the mass spectrum of this molecule involved loss of sulphur from this ion to give, presumably, (32). These results are in contrast to the known<sup>5</sup> successful conversion of 3,4-dibromothiophen into the corresponding bis-sulphide with thiophen-2- or -3-thiol in good yield.



ion as the strongest peaks, the latter generally being the base peak and being indicative of the rearomatisation of the pyran or thiopyran ring. The action of triphenylmethyl perchlorate on one of these reduced products (24) gave an immediate and quantitative precipitate of the corresponding thiopyrylium perchlorate (4; Y = ClO<sub>4</sub>), thus allowing the conversion of the chlorostannates into the more useful perchlorates for the purpose of purification, analysis, and further study.

<sup>5</sup> E. Jones and I. M. Moodie, *J. Chem. Soc.*, 1965, 7018.

#### EXPERIMENTAL

The spectra were taken as described in the previous paper; experimental conditions are also as recorded therein.<sup>1</sup>

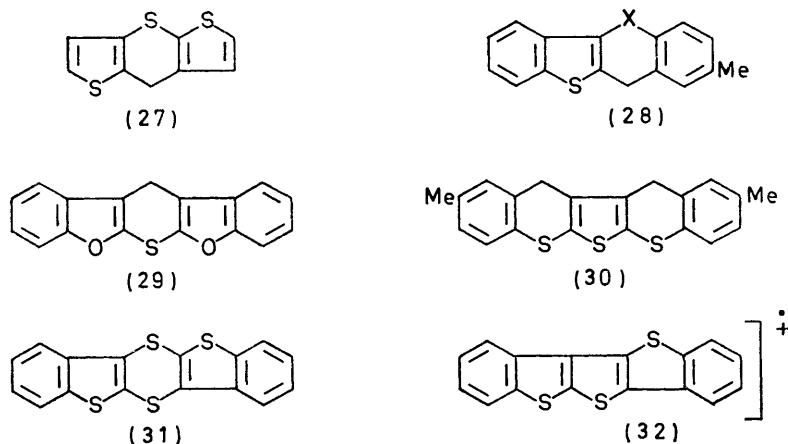
*Preparation of Diaryl Sulphides and Ethers.—Method A.* A suitable arenethiol or phenol (0.1 mol), an aryl bromide (0.1 mol), copper(I) oxide (7.15 g, 0.05 mol), potassium hydroxide (5.6 g, 0.1 mol), and dimethylformamide (100 ml) were mixed and heated at 130–140° under nitrogen with stirring for an appropriate time, after which the mixture was cooled and poured into 6*N*-hydrochloric acid and ice. The product was extracted with benzene and the extract

washed well with water, dried, and evaporated. The residue was either distilled or chromatographed and, if it was a solid, further recrystallised. Details are recorded in Table 3.

*Method B.* A solution of an aryl-lithium (0.1 mol) was made by either (i) treatment of benzothiophen or benzofuran (0.1 mol) in dry ether (200 ml) at  $-5^{\circ}$  under nitrogen with butyl-lithium (0.1 mol) in hexane; or (ii) treatment

The oily distillate was extracted with ether; the extract was dried and distilled to give the compounds recorded in Table 3.

*Preparation of Pirylium and Thiopyrylium Salts.*—Tin(IV) chloride (5 g, 0.02 mol) was added to a solution of an appropriate diaryl ether or diaryl sulphide (0.01 mol) in methylene chloride (15 ml) at  $-5$  to  $0^{\circ}$ . To the resultant



of 3-bromothiophen or 3-bromobenzothiophen (0.1 mol) in ether (200 ml) at  $-70^{\circ}$  under nitrogen with butyl-lithium (0.1 mol) in hexane. After 30 min the aryl-lithium, maintained under the foregoing conditions, was treated slowly, dropwise, with freshly distilled sulphur dichloride (5.15 g, 0.05 mol) in ether (100 ml), and the mixture was stirred at

highly coloured solution was added dichloromethyl methyl ether (1.15 g, 0.01 mol) and the mixture was stirred at the same temperature for 1 h. The solution changed colour and precipitated a highly coloured solid, which was filtered off and washed thoroughly with methylene chloride to give the products recorded in Table 1.

TABLE 1  
Fused pyrylium and thiopyrylium salts

Product		Yield (%)	Colour	Found (%)		Formula	Required (%)		M.p. (decomp.) (°C)	M <sup>+</sup>	
ArXAr'	No.			C	H		C	H		Found	Required
(3)	(4) <sup>a</sup>	80	Yellow	21.9	1.5	C <sub>9</sub> H <sub>5</sub> Cl <sub>5</sub> S <sub>3</sub> Sn	21.4	1.0	> 250°	208.9564	208.9555
	(4) <sup>b,c</sup>	100	Yellow	35.2	1.7	C <sub>9</sub> H <sub>5</sub> ClO <sub>4</sub> S <sub>3</sub>	35.0	1.6	224—225		
(5a)	(6a)	50	Orange	34.7	2.8	C <sub>15</sub> H <sub>13</sub> Cl <sub>5</sub> O <sub>2</sub> Sn	35.7	2.6	168—170	209.0968	209.0966
(5b)	(6b)	61	Orange	33.35	2.8	C <sub>15</sub> H <sub>13</sub> Cl <sub>5</sub> SSn	34.6	2.5	178—180	225.0742	225.0738
(7a)	(8a)	36	Green	33.1	2.2	C <sub>12</sub> H <sub>9</sub> Cl <sub>5</sub> OSSn	29.1	1.8	205—206	201.0370	201.0374
(7b)	(8b)	5	Yellow	28.8	2.2	C <sub>12</sub> H <sub>9</sub> Cl <sub>5</sub> S <sub>2</sub> Sn	28.1	1.8	139—143		
(7c)	(8c)	22	Tan	24.7	1.8	C <sub>12</sub> H <sub>9</sub> BrCl <sub>5</sub> S <sub>2</sub> Sn	24.3	1.4	175—178	294.9255	294.9252
(9)	(10)	44	Green	21.9	1.5	C <sub>9</sub> H <sub>5</sub> Cl <sub>5</sub> S <sub>3</sub> Sn	21.4	1.0	> 300	208.9556	208.9554
(11a)	(12a)	77	Orange	34.8	2.7	C <sub>16</sub> H <sub>4</sub> Cl <sub>5</sub> OSSn	35.1	2.0	208—210		
(11b)	(12b)	89	Red	35.8	2.15	C <sub>16</sub> H <sub>11</sub> Cl <sub>5</sub> S <sub>2</sub> Sn	34.1	2.0	227—230		
(13)	(14)	40	Yellow	34.2	2.3	C <sub>16</sub> H <sub>11</sub> Cl <sub>5</sub> S <sub>2</sub> Sn	34.1	2.0	218—220		
(15a)	(16a)	70	Yellow	36.1	2.0	C <sub>17</sub> H <sub>9</sub> Cl <sub>5</sub> O <sub>2</sub> SSn	35.6	1.6	208—210	277.0314	277.0321
(15b)	(16b)	100	Orange	32.8	1.8	C <sub>17</sub> H <sub>9</sub> Cl <sub>5</sub> S <sub>3</sub> Sn	33.8	1.5	350	308.9868	308.9867
(17)	(18)	40	Purple	32.3	1.8	C <sub>17</sub> H <sub>9</sub> Cl <sub>5</sub> S <sub>3</sub> Sn	33.8	1.5	280—282	308.9828	308.9867
(19)	(20)	64	Purple	32.9	1.7	C <sub>17</sub> H <sub>9</sub> Cl <sub>5</sub> S <sub>3</sub> Sn	33.8	1.5	278—282	308.9872	308.9867
(21)	(22)	20	Yellow	30.6	2.15	C <sub>20</sub> H <sub>14</sub> Cl <sub>5</sub> S <sub>3</sub> Sn	35.2	2.1	270—275		

<sup>a</sup> Y = SnCl<sub>5</sub>. <sup>b</sup> Y = ClO<sub>4</sub>. <sup>c</sup> See text for preparation.

the same temperature for 3.5 h. It was then allowed to reach room temperature, washed with water, dried, and evaporated to give the appropriate sulphide, which was purified by distillation if it was a liquid and recrystallised from light petroleum in the case of a solid. Details are recorded in Table 3.

*Method C.* *p*-Cresol (10.8 g, 0.1 mol), an aryl bromide (0.1 mol), potassium carbonate (3.5 g), and copper-bronze (0.05 g) were mixed and heated on a sand-bath for an appropriate time at about 200°, after which aqueous alkali (100 ml) was added and the product was steam distilled.

*Action of Water on 2,7-Dimethylthioxanthylum Pentachlorostannate (6b).*—The salt (0.5 g) was boiled in water (10 ml) until it became colourless (1—2 min); the white solid was then filtered off and dried. Chromatography on alumina gave (with light petroleum) 2,7-dimethylthioxanthone (0.1 g, 50%), m.p. 168—170°.

Further elution, with light petroleum-benzene (1:1) afforded yellow crystals (0.11 g, 50%) of 2,7-di-methyl-thioxanthone, m.p. 127—129° (lit.,<sup>6</sup> 128—129°).

*Reduction of the Salts with Sodium Borohydride.*—The salt

<sup>6</sup> F. Kröllpfeiffer and A. Wissner, *Annalen*, 1951, **572**, 195.

(0.5 g) in ethanol (20 ml) was stirred during the addition of sodium borohydride (0.5 g) in small portions. The exothermic reaction caused precipitation of a grey solid; after 1 h water was added and the mixture was extracted with chloroform. The extract was dried and evaporated, and

0.0064 mol), copper(I) oxide (1.0 g, 0.007 mol), potassium hydroxide (1.0 g, 0.0178 mol), and dimethylformamide (30 ml). The mixture was heated under nitrogen for 27 h at 140–150°, cooled, poured onto ice, acidified with hydrochloric acid, and extracted with ether. The dried extracts

TABLE 2  
Reduction products of the pyrylium and thiopyrylium salts

Product		Yield (%)	M.p. (°C)	Found (%)			Required (%)	
No.	X			C	H	Formula	C	H
(24)		100	112–113	51.2	3.0	C <sub>9</sub> H <sub>6</sub> S <sub>3</sub>	51.5	2.9
(25a)	O	95	143.5–144.5 <sup>a</sup>					
(25a)	S	80	168–170	79.2	6.0	C <sub>15</sub> H <sub>14</sub> S	79.6	6.2
(26)		40	93	48.8	3.0	C <sub>12</sub> H <sub>9</sub> BrS <sub>2</sub>	48.5	3.1
(27)		57	91–93	51.5	3.0	C <sub>9</sub> H <sub>6</sub> S <sub>3</sub>	51.5	2.9
(28)	O	64	83–84	76.1	5.5	C <sub>16</sub> H <sub>12</sub> OS	76.3	5.5
(28)	S	63	117–117.5	71.7	5.0	C <sub>16</sub> H <sub>12</sub> S <sub>2</sub>	71.7	4.5
(29)		72	136–138	73.1	3.4	C <sub>17</sub> H <sub>10</sub> O <sub>2</sub> S	73.45	3.6
(30)		50	179–182	68.1	4.6	C <sub>20</sub> H <sub>16</sub> S <sub>3</sub>	68.25	4.6

<sup>a</sup> Lit. m.p. 143° (T. Sengoku, *J. Pharm. Soc. Japan*, 1933, **53**, 962).

TABLE 3  
Diaryl ethers and diaryl sulphides and their properties

Reactants *		Conditions		Product	Yield (%)	M.p. (°C) [B.p. (°C)/mmHg]	Found (%)		Formula	Required (%)	
		Method	Time (h)				C	H		C	H
3-BrTh		B		(3)	57	(126/0.7) <sup>a</sup>					
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> Br	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ·OH	C	4	(5a)	26	{(282–285) <sup>b</sup> 50					
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> Br	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ·SH	A	48	(5b)	37	56.5 <sup>c</sup>					
3-BrTh	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ·OH	C	3.5	(7a)	17	(80.3)	69.7	5.6	C <sub>11</sub> H <sub>10</sub> OS	69.5	5.3
3-BrTh	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ·SH	A	24	(7b)	50	(113–114/0.4)	64.5	4.8	C <sub>11</sub> H <sub>10</sub> S <sub>2</sub>	64.1	4.9
3,4-Br <sub>2</sub> Th	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ·SH	A	25	(7c)	84	(165–168/1.5)					
3-BrTh	Th-2-SH	A	25	(9)	40	(110–112/1.0) <sup>d</sup>					
3-BrBT	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ·OH	A	8	(11a)	22	Oil <sup>e</sup>	(M <sup>+</sup> , 240.0603)		C <sub>15</sub> H <sub>12</sub> OS	(M, 240.0609)	
3-BrBT	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ·SH	A	28	(11b)	78	Oil <sup>f</sup>	70.7	4.7	C <sub>15</sub> H <sub>12</sub> S <sub>2</sub>	70.4	4.7
2-BrBT	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ·SH	A	24	(13)	50	69–70	70.65	4.8	C <sub>15</sub> H <sub>12</sub> S <sub>2</sub>	70.4	4.7
BF		B		(15a)	31	120–122	72.3	3.9	C <sub>16</sub> H <sub>10</sub> O <sub>2</sub> S	72.25	3.8
BT		B		(15b)	47	111	64.05	3.4	C <sub>6</sub> H <sub>10</sub> S <sub>2</sub>	64.4	3.4
3-BrBT		B		(17)	47	64.5	64.2	3.2	C <sub>16</sub> H <sub>10</sub> S <sub>3</sub>	64.4	3.4
3-BrBT	BT-2-SH	A	30	(19)	47	74.5 <sup>g</sup>	64.2	3.5	C <sub>16</sub> H <sub>10</sub> S <sub>3</sub>	64.4	3.4
2,5-Br <sub>2</sub> Th	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ·SH	A	72	(21)	76	59–60	65.2	5.0	C <sub>18</sub> H <sub>16</sub> S <sub>3</sub>	65.5	4.9

\* BF = benzofuran; BT = benzothiophen; Th = thiophen.

<sup>a</sup> Lit. b.p. 115° at 0.4 mmHg (E. Jones and I. M. Moodie, *Tetrahedron*, 1965, **21**, 2413). <sup>b</sup> Lit. m.p. 50° (P. Sabatier and A. Maihie, *Compt. rend.*, 1910, **151**, 493). <sup>c</sup> Lit. m.p. 57° (V. H. Hauptmann and B. Ladislaw, *Annalen*, 1952, **576**, 45). <sup>d</sup> Lit. b.p. 118° at 1.5 mmHg and 100° at 0.6 mmHg (ref. in footnote a). <sup>e</sup> Chromatographed: alumina; eluant light petroleum–benzene (1:1). <sup>f</sup> Chromatographed: alumina; eluant light petroleum. <sup>g</sup> Lit. m.p. 61.5° [R. P. Dickinson and B. Iddon, *J. Chem. Soc. (C)*, 1968, 2733].

the residue recrystallised from ethanol to give the products recorded in Table 2.

*Dithieno*[3,2-b:2',3'-e]*thiopyrylium Perchlorate* (4; Y = ClO<sub>4</sub>).—To the dithienothiopyran (24) (0.5 g) in methylene chloride (20 ml) was added freshly prepared triphenylmethyl perchlorate (1 g) in methylene chloride (50 ml). The resulting orange precipitate was filtered off, washed with methylene chloride, and recrystallised from acetic acid as yellow-orange needles (see Table 1).

*Reaction of Benzo*[b]*thiophen-3-thiol with 3,4-Dibromothiophen*.—Benzo[b]thiophen-3-thiol (2.15 g, 0.0128 mol) was added to a stirred mixture of 3,4-dibromothiophen (1.55 g,

were chromatographed on alumina. Elution with light petroleum gave some 3,4-dibromothiophen; light petroleum–benzene (3:1) gave *p*-dithiino[2,3-b:6,5-b']bis[1]-benzothiophen (31) (0.42 g, 20%) as white needles (from ethanol), m.p. 153–155° (Found: C, 58.0; H, 2.55%; M<sup>+</sup>, 327.9506. C<sub>16</sub>H<sub>8</sub>S<sub>4</sub> requires C, 58.6; H, 2.45%; M, 327.9510). Further elution, with benzene, gave some benzothiophen-3-thiol.

We thank the Libyan Government for a grant (to M. A.)

[3/051 Received, 10th January, 1973]