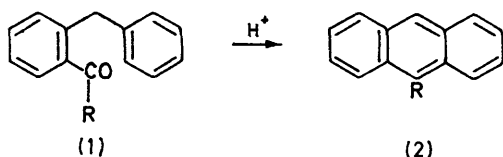


The Direct Bradsher Reaction.¹ Part I. Synthesis of Thiophen Analogues of Linear Polycyclic Hydrocarbons

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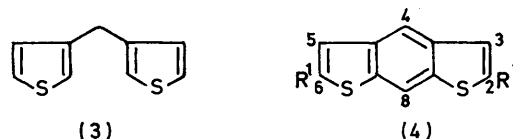
The action of dichloromethyl alkyl ethers and tin(IV) chloride on a variety of diarylmethanes (constructed such that electrophilic substitution occurs *ortho* to the methylene bridge) is shown to be an efficient means for the synthesis of polycyclic aromatic and heteroaromatic systems which are otherwise difficult to obtain.

THE Bradsher reaction, exemplified by the conversion of the 2-acyldiphenylmethane (1) into the anthracene (2), has been widely applied to the synthesis of specifically substituted anthracenes and related hydrocarbons.²



During acylation of thiophen derivatives, we observed products whose formation could best be rationalised by acylation of the heterocycle followed by a Bradsher-type cyclisation.³ The aim of the present work was to generalise this 'direct Bradsher reaction.' The necessary conditions would be: (i) a suitably reactive aromatic substrate that would direct the incoming acyl group *ortho* to the methylene bridge and (ii) a reagent that would both acylate the substrate and bring about the necessary acid-catalysed cyclisation. This type of reagent was to hand in the form of Vilsmeier complexes or Friedel-Crafts acylating systems. The first condition was particularly well met by the five-membered heterocycles and their benzo-derivatives, *e.g.* the thiophen (3). Electrophilic substitution of this system should occur predominantly at the 2-position. Thus treatment with dimethylformamide and phosphoryl chloride gave moderate yields of the relatively inaccessible benzodithio-

phen (4a) in one step. Since this and related systems are little known,⁴ this reaction was thoroughly explored in the thiophen series.



- a, R¹ = R² = H
 b, R¹ = H, R² = CHO
 c, R¹ = R² = CHO
 d, R¹ = H, R² = Me

The most effective syntheses by the direct Bradsher method were found to derive from use of Rieche reagents,⁵ a dichloromethyl alkyl ether and tin(IV) chloride in methylene chloride solution. The reaction frequently occurred below 0° and little charring or unwanted by-products were observed.

A series of diarylmethanes [(5)–(13)] was synthesised and treated with this reagent. The corresponding polycyclic aromatic products were obtained, frequently in high yield (Table 1). The only experiment conducted on a purely benzenoid system (6) was unsuccessful even when the more vigorous reagent polyphosphoric acid-acetic acid was employed. However, when only one of the aryl groups of the diarylmethane was benzenoid [*e.g.* (12) and (13)], cyclisation was successful. This simple, one-step reaction offers a convenient route to otherwise highly inaccessible systems, particularly

¹ Preliminary communication, M. Ahmed, J. Ashby, and O. Meth-Cohn, *Chem. Comm.*, 1970, 1094.

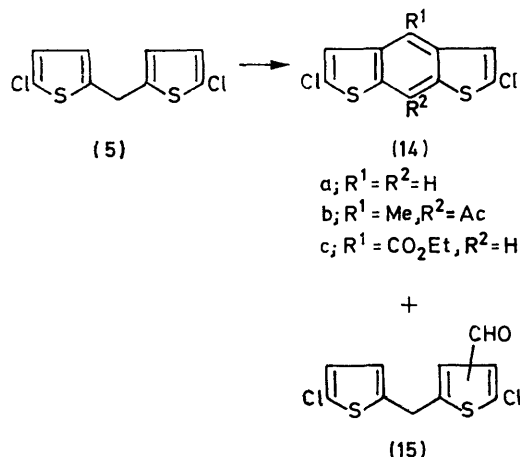
² C. K. Bradsher, *J. Amer. Chem. Soc.*, 1940, **62**, 486; see also C. K. Bradsher and F. A. Vingiello, *ibid.*, 1949, **71**, 1434; F. A. Vingiello and P. D. Henson, *J. Org. Chem.*, 1965, **30**, 2842; 1966, **31**, 1357; 1967, **32**, 3205; F. A. Vingiello and J. R. Thornton, *ibid.*, 1966, **31**, 659; F. A. Vingiello and A. Borkovec, *J. Amer. Chem. Soc.*, 1956, **78**, 3205; 1958, **80**, 1714; S. D. Saraf and F. A. Vingiello, *Chem. and Ind.*, 1967, 2145.

³ M. Ahmed and O. Meth-Cohn, *J. Chem. Soc. (C)*, 1971, 2104.

⁴ (a) D. S. Rao and B. D. Tilak, *J. Sci. Ind. Res., India*, 1954, **13**, 829; (b) H. Wynberg, J. de Wit, and H. J. M. Sinnige, *J. Org. Chem.*, 1970, **35**, 711.

⁵ A. Rieche, H. Gross, and E. Hoft, *Chem. Ber.*, 1960, **93**, 88; G. N. Taylor and K. B. Wiberg, *Org. Synth.*, 1967, **47**, 47.

since the parent system or a simply substituted derivative is obtained. In some cases by-products were obtained which were either uncyclised aldehyde derivatives of the diarylmethanes [*e.g.* (15) and (17)] or the further



formylated products [*e.g.* (9) + (10) + (11a) \rightarrow (19a) + (19b) + (20a) + (20b)]. In the latter case the aldehydes were separately synthesised by subjecting the heterocycle [(19) or (20); R = H] to the action of the Rieche reagent; high yields of the respective aldehydes (19b) and (20b) were isolated.

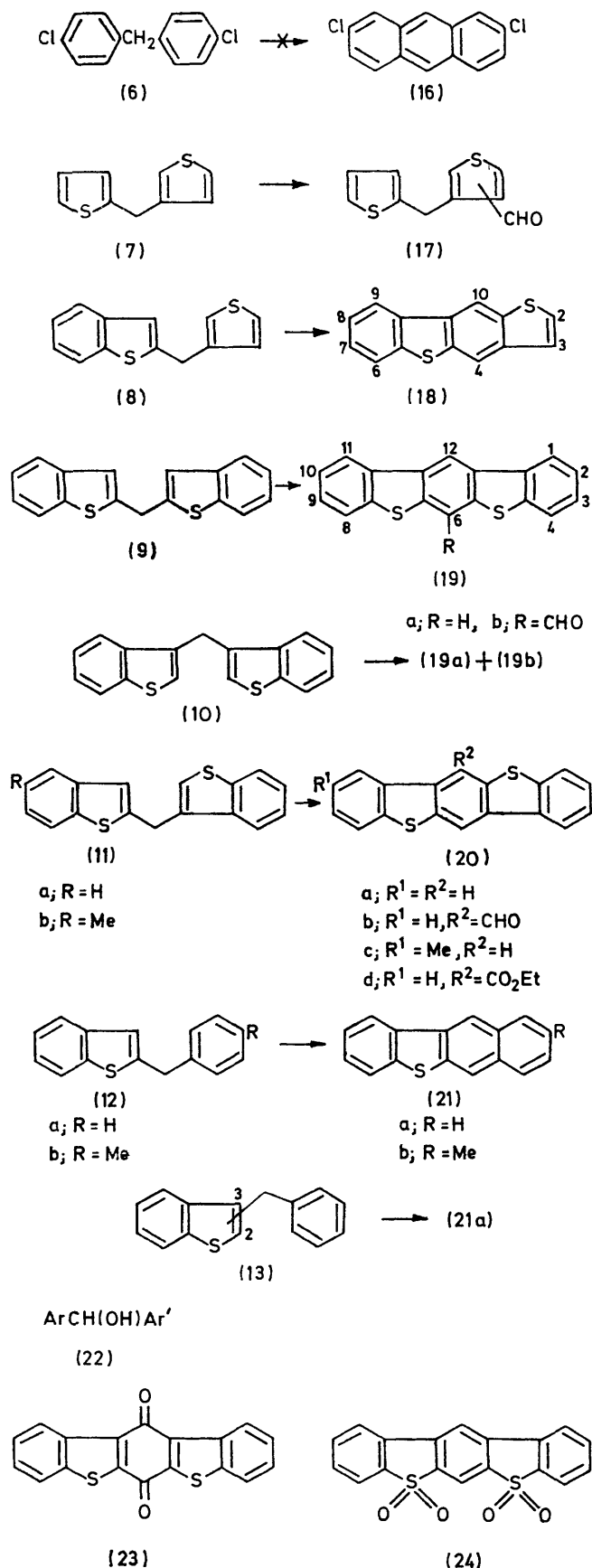
This method may be extended to the synthesis of specifically functionalised systems either by use of suitably substituted diarylmethanes (see Table 1) or by use of a substituted dichloromethyl methyl ether. Thus ethyl dichloro(ethoxy)acetate is readily prepared by the action of phosphorus pentachloride on ethyl oxalate.⁶ Benzo[*b*]thiophen was treated successively with tin(IV) chloride and then the reagent at 0°, and the 3-ethoxalylated product was obtained in 45% yield. 2,3'-Methylenebisbenzo[*b*]thiophen (11a) gave the pentacyclic ester (20d) in 25% yield and 2,2'-methylenebis-5-chlorothiophen (5) similarly produced the benzodithiophen ester (14c) in 30% yield, almost four times the yield obtained with dichloromethyl methyl ether.

In an attempt to convert the pentacyclic system (19a) into the known⁷ quinone (23), oxidation was attempted with chromium trioxide in acetic acid; although the red quinone formed to a small extent (4%), the major product was the disulphone (24) (72%). This surprising result probably arose because of the steric difficulty of attack at the mid-ring of the bow-shaped molecule.

Several derivatives of the benzodithiophen system (4) have been prepared. Metallation of compound (4a) with butyl-lithium in ether followed by addition of dimethylformamide gave a mixture of the mono-(4b) and di-formyl (4c) derivatives. The positions of substitution were indicated by the n.m.r. spectra (Table 2). Wolff-Kishner reduction of the mono-formyl derivative (4b) gave the corresponding methyl derivative in high yield.

⁶ R. G. Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 5168.

⁷ F. Mayer, A. Mombour, W. Lassmann, W. Werner, P. Landmann, and E. Schneider, *Annalen*, 1931, **488**, 259.



The required diarylmethane starting materials for the above syntheses were prepared by several different methods and they and their precursors are given in Tables 3 and 4 together with their properties.

EXPERIMENTAL

N.m.r. spectra were obtained on a Varian A60A or HA 100 spectrometer using deuteriochloroform solutions and tetramethylsilane as an internal standard. Mass spectra were

treated dropwise with an appropriate aldehyde (0.1 mol) in dry ether (100 ml). After 3—5 h at this temperature the mixture was allowed to warm to room temperature and was washed with water, dried, and evaporated. The products are given in Table 3.

Method (ii). 3-Thienyl-lithium (0.1 mol) was prepared as in method (i) and 2-benzo[*b*]thienyl-lithium was prepared by treatment of benzo[*b*]thiophen (13.4 g, 0.1 mol) in ether (200 ml) with butyl-lithium in hexane (0.1 mol) at

TABLE 1
Cyclisation of diarylmethanes by the direct Bradsher method with $\text{Cl}_2\text{CH}\cdot\text{OMe}-\text{SnCl}_4$

Starting material ArCH ₂ Ar'	Product	Yield (%)	M.p. (°C)	Purification method	Analysis					N.m.r. data (τ Values)
					Found (%)		Formula	Reqd. (%)		
					C	H			C	H
(3)	(4a)	33	184 ^a	EtOH						See Table 2
(5)	(14a)	8 ^b	199—200	Petroleum	46.2	1.5	C ₁₀ H ₄ Cl ₂ S ₂	46.4	1.6	See Table 2
(5)	(14b)	16	240	C ₆ H ₆	49.3	2.7	C ₁₃ H ₈ Cl ₂ OS ₂	49.6	2.6	See Table 2
(7)	(17)	24 ^d								
(8)	(18)	25	128—130	C ₆ H ₆	65.3	3.5	C ₁₄ H ₈ S ₂	65.1	3.4	1.54s (H-10); 1.92s (H-4); 1.9—3.1m 1.35s (H-12); 1.92m (H-1, H-11); 1.96s (H-6); 2.3m (H-4 H-8); 2.66m (H-2, H-3, H-9, H-10)
(9)	(19a)	64	216—218 ^e	C ₆ H ₆	73.8	3.6	C ₁₈ H ₁₀ S ₂	74.4	3.5	
(11a)	(20a)	24	313—315 ^f	Subl. at 0.1 mmHg	74.5	3.5	C ₁₈ H ₁₀ S ₂	74.55	3.5	
(11b)	(20c)	77	249—250	Subl. at 0.1 mmHg	74.6	4.1	C ₁₉ H ₁₂ S ₂	75.0	4.0	
(12a)	(21a)	15	160 ^g	EtOH						
(12b)	(21b)	50	185	EtOH	82.15	5.1	C ₁₇ H ₁₂ S	82.3	4.9	
(13)	(21a)	13	As above							

^a Lit.,^{4b} 187—188°. ^b Also isolated an aldehyde (15) (11%), ν_{max} (film) 1695 cm^{-1} . ^c Polyphosphoric acid and acetic acid (10:1) used. ^d Oil by chromatography, ν_{max} (liq.) 1670 cm^{-1} , M^+ , 208. ^e Lit.,¹⁴ 220°. ^f Lit.,¹⁵ 314°. ^g Lit.,¹⁶ 163°.

TABLE 2
N.m.r. spectra of the benzodithiophens (4) and (14)

Compound	Chemical shift (τ)						J/Hz
	H-2	H-3	H-4	H-5	H-6	H-8	
(4a) †	3.06	2.88	2.15	2.88	3.06	2.15	$J_{2,3} = J_{5,6} = 5.5$; $J_{3,8} = J_{5,8} \approx 1.0$
(4b) †	0.43	1.60	1.35 or 1.95	2.12	2.21	1.95 or 1.35	$J_{5,6} = 6.0$; $J_{5,8} \approx 1.0$
(4c) *	-0.19	1.43	1.13 or 1.20	1.43	-0.19	1.20 or 1.13	
(4d) †	7.87	3.34	2.25 or 2.27	2.87	3.09	2.27 or 2.25	$J_{5,6} = 5.5$; $J_{5,8} = 1.5$
(14b) ‡		‡	7.12	‡		7.22	

* In $(\text{CD}_3)_2\text{SO}$. † In CDCl_3 . ‡ In $\text{C}_5\text{D}_5\text{N}$: H-3 and -5 signals obscured by solvent peaks.

recorded on an A.E.I. MS12 or MS902 instrument. Thiophen-2-carbaldehyde,⁸ thiophen-3-carbaldehyde,⁹ benzo[*b*]thiophen-2-carbaldehyde,¹⁰ 5-methylbenzo[*b*]thiophen-2-carbaldehyde,¹¹ 3-bromothiophen,¹² and 3-bromobenzo[*b*]thiophen¹³ were made by literature methods.

Preparation of Diarylmethanols.—*Method (i).* 3-Bromothiophen or 3-bromobenzo[*b*]thiophen (0.1 mol) in dry ether (250 ml) at -70° was treated with butyl-lithium in hexane (Pfizer; 0.1 mol), and after 20 min at this tempera-

⁸ E. Campaigne and W. L. Archer, *J. Amer. Chem. Soc.*, 1953, **75**, 989.

⁹ S. Gronowitz, *Arkhiv Kemi*, 1955, **8**, 441.

¹⁰ V. P. Mamaev and O. P. Shkurko, *Zhur. obschei Khim.*, 1961, **31**, 3288 (*Chem. Abs.*, 1962, **57**, 4622).

¹¹ N. P. Buu-Hoi, A. Croisy, and P. Jacquignon, *J. Chem. Soc. (C)*, 1969, 339.

room temperature. To the above lithio-compound, ethyl formate (3.7 g, 0.05 mol) in ether (50 ml) was added dropwise with stirring. The mixture was stirred for a further 1 h and worked up as in method (i) to give the products in Table 3.

Preparation of Diarylmethanes.—(i) *Reduction of the corresponding diarylmethanol.* To a suspension of lithium aluminium hydride (1.9 g, 0.05 mol) in dry ether (100 ml) was added aluminium chloride (6.7 g, 0.05 mol) in dry ether

¹² S. Gronowitz and T. Raznikiewicz, *Org. Synth.*, 1964, **44**, 9.

¹³ B. Iddon and R. S. Dickinson, *J. Chem. Soc. (C)*, 1968, 2733.

¹⁴ L. J. Pandya, G. N. Pillai, and B. D. Tilak, *J. Sci. Ind. Res., India*, 1959, **18B**, 198.

¹⁵ D. S. Rao and B. D. Tilak, *J. Sci. Ind. Res., India*, 1958, **17B**, 260.

¹⁶ E. G. G. Werner, *Rec. Trav. chim.*, 1949, **68**, 520.

(50 ml). To this solution was added the appropriate alcohol (0.05 mol) in ether at such a rate as to maintain reflux, and then the mixture was refluxed for a further 1 h. The mixture was cooled and treated cautiously with moist ether and then poured into 2*N*-sulphuric acid (250 ml). The ether phase was washed successively with water, dilute aqueous alkali, and water, and was dried and evaporated. The residue was steam distilled and the steam distillate was ether extracted; the extracts were dried and evaporated to give the products recorded in Table 4.

(ii) *Chloromethylation in the presence of zinc chloride.* Hydrochloric acid (45 ml; *d* 1.19) was cooled to -10° with stirring, and zinc chloride (40.8 g, 0.3 mol) was added. To

After a further 0.5 h at this temperature the mixture was boiled for 4 h. The cooled mixture gave a small amount (0.7–1.0 g) of crystalline material identified as 2,2'-bi-benzo[*b*]thienyl, m.p. 262° (lit.,¹⁹ 262°). The ether phase was washed with water, dried, and evaporated to give the products in Table 4.

(iv) *The co-action of benzyl chloride and tin(IV) chloride on benzo[*b*]thiophen.* To a stirred solution of benzo[*b*]thiophen (26.8 g, 0.2 mol) in carbon disulphide (90 ml) at room temperature was added tin(IV) chloride (2.1 g) followed by benzyl chloride (12.6 g, 0.1 mol) in carbon disulphide (30 ml), added dropwise during 2 h. The solution was stirred overnight and poured into water, and the organic phase was

TABLE 3
Preparation and properties of diarylmethanols (22)

ArLi *	Other reactant *	Method (see Experimental section)	Product ArCH(OH)Ar'		Yield (%)	M.p. ($^\circ\text{C}$)	Found (%)		Formula	Reqd. (%)	
			Ar	Ar'			C	H		C	H
3-Th	3-Th-CHO	(i)	3-Th	3-Th	68	68 ^a					
3-Th	HCO ₂ Et	(ii)	3-Th	3-Th	72	68					
3-Th	2-Th-CHO	(i)	3-Th	2-Th	97 ^b						
3-Th	2-B-CHO	(i)	3-Th	2-B	11	53–55	63.8	4.3	C ₁₃ H ₁₀ OS ₂	63.5	4.1
2-B	HCO ₂ Et	(ii)	2-B	2-B	54	125	69.5	4.2	C ₁₇ H ₁₂ OS ₂	68.9	4.1
3-B	5-Me-2-B-CHO	(i)	3-B	5-Me-2-B	46 ^b	61–64					

* Th = thienyl; B = benzo[*b*]thienyl.

^a Lit.,¹⁷ 68–69°. ^b Used directly in next stage without purification.

TABLE 4
Preparation and properties of diarylmethanes

Reactants *	Method (see Experimental section)	Product	Yield (%)	M.p. ($^\circ\text{C}$) or b.p. ($^\circ\text{C}/\text{mmHg}$)	Found (%)		Formula	Reqd. (%)	
					C	H		C	H
(22; Ar = Ar' = 3-Th)	(ii)	(3)	80	31–32 ^a					
2-Cl-Thiophen	(ii)	(5)	51	148/3	43.5	2.6	C ₉ H ₆ Cl ₂ S ₂	43.2	2.4
(22; Ar = 2-Th, Ar' = 3-Th)	(i)	(7)	45	136–138/12	60.15	4.3	C ₉ H ₆ S ₂	60.1	4.5
(22; Ar = 2-B, Ar' = 3-Th)	(i)	(8)	97	50–52	68.3	4.6	C ₁₅ H ₁₀ S ₂	67.9	4.4
(22; Ar = Ar' = 2-B)	(i)	(9)	71	130–131	72.4	4.3	C ₁₇ H ₁₂ S ₂	72.8	4.3
Benzo[<i>b</i>]thiophen	(ii)	(9) + (10) + (11)	57	Oil ^b					
2-B-Li and 3-B-CH ₂ Cl	(iii)	(11; R = H)	12	Oil ^b					
(22; Ar = 3-B, Ar' = 5-Me-2-B)	(i)	(11; R = Me)	72	107–108	73.8	4.8	C ₁₈ H ₁₄ S ₂	73.55	4.8
2-B-Li and PhCH ₂ Cl	(iii)	(12; R = H)	27	86–87	80.0	5.5	C ₁₅ H ₁₀ S	80.3	5.4
2-B-Li and <i>p</i> -MeC ₆ H ₄ ·CH ₂ Cl	(iii)	(12; R = Me)	13	84–85	80.6	6.1	C ₁₆ H ₁₄ S	80.75	5.9
Benzo[<i>b</i>]thiophen and PhCH ₂ Cl	(iv)	(13)	20	220/3	80.2	5.55	C ₁₅ H ₁₂ S	80.4	5.4

^a Lit.,¹⁸ 31.5–32°. ^b Used without further purification.

* B = Benzo[*b*]thienyl; Th = thienyl.

this solution was added either 2-chlorothiophen (35.6 g, 0.3 mol) or benzo[*b*]thiophen (40.2 g, 0.3 mol) and the suspension was stirred well during dropwise addition of formaldehyde (9.0 g, 0.3 mol; as 40% aqueous solution) over 1.5 h at about 0° . The mixture was then stirred overnight at room temperature, and extracted with ether; the extract was washed successively with water, dilute sodium hydroxide solution, and water, and then dried and evaporated. The product from 2-chlorothiophen was distilled *in vacuo*; that from benzo[*b*]thiophen was chromatographed on alumina; light petroleum eluted some starting material (4.5 g), and light petroleum–benzene (2 : 1) gave a pale yellow oil (23 g). The products, 2,2'-methylenebis-5-chlorothiophen (5), and the mixture of bis(benzo[*b*]thienyl)methanes [(9) + (10) + (11)], are recorded in Table 4.

(iii) *Reaction of an aryl-lithium with an arylmethyl chloride.* 2-Benzo[*b*]thienyl-lithium (0.1 mol) prepared as above was treated dropwise with the appropriate arylmethyl chloride (0.1 mol) in dry ether (100 ml) at 0° .

washed with water and dried. Distillation *in vacuo* gave a small amount of unchanged benzo[*b*]thiophen followed by a mixture of 2- and 3-benzylbenzo[*b*]thiophen (13) as a yellow oil (4.44 g, 20%), b.p. 220° at 3 mmHg.

*The Action of Dichloromethyl Butyl Ether on the Mixed Bis(benzo[*b*]thienyl)methanes.*—Tin(IV) chloride (3 ml, 0.026 mol) was added to a stirred solution of the mixed bis(benzo[*b*]thienyl)methanes (4.8 g, 0.017 mol) in methylene chloride (40 ml) at 0° . To this solution was added dichloromethyl butyl ether (4.0 g, 0.026 mol) and the mixture was maintained at 0° for 1 h and then at room temperature overnight. The mixture was poured into water and the organic phase was washed with water, dried, and chromatographed on alumina. Elution with light petroleum–benzene (2 : 1) gave benzo[1,2-*b*:5,4-*b'*]bis[1]benzothiophen (19a) as a white solid (0.5 g, 10%). Further elution with the

¹⁷ S. Gronowitz and B. Eriksson, *Arkiv Kemi*, 1964, **21**, 335.

¹⁸ A. Kraak, A. K. Wiersema, P. Jordens, and H. Wynberg, *Tetrahedron*, 1968, **24**, 3381.

same solvent gave benzo[1,2-b:4,5-b']bis[1]benzothiophen (20a) (1.5 g, 30%). Both products were identical with the compounds reported in Table 1. Further elution with light petroleum-benzene (1:1) gave 6-formylbenzo[1,2-b:5,4-b']bis[1]benzothiophen (19b) (1.2 g, 20%) as yellow crystals, m.p. 233° (Found: C, 71.3; H, 3.3. $C_{19}H_{30}OS_2$ requires C, 71.8; H, 3.15%), ν_{max} (Nujol), 1670 cm^{-1} (CO), τ ($CDCl_3$ plus 6 drops Me_2SO) —0.74 (s, CHO), 0.97 (s, H-12), and 1.5—2.5 (m, ArH). Further elution with benzene gave 6-formylbenzo[1,2-b:4,5-b']bis[1]benzothiophen (20b) (0.9 g, 15%) as yellow crystals, m.p. 266—268° (Found: C, 71.5; H, 3.2. $C_{19}H_{30}OS_2$ requires C, 71.8; H, 3.15%), ν_{max} (Nujol) 1665 cm^{-1} (CO).

These two aldehydes were made from the appropriate parent system [(19a) or (20a)] in the following manner: the heterocycle (0.145 g, 0.0005 mol) in stirred methylene chloride (20 ml) at 0° was treated successively with tin(IV) chloride (0.26 g, 0.001 mol) and dichloromethyl butyl ether (0.08 g, 0.0005 mol) and the mixture was stirred at 0° for 30 min. After a further 30 min at room temperature the mixture was poured into water, and the organic phase was washed with water and dried. Evaporation gave the yellow formyl derivatives in almost quantitative yields, identical with the products reported above.

Similarly, treatment of the appropriate diarylmethane with tin(IV) chloride and dichloromethyl methyl ether gave the compounds recorded in Table 1. Purification was accomplished either by recrystallisation from the solvent indicated or by sublimation.

3-Ethoxalylbenzo[b]thiophen.—To benzo[b]thiophen (3.6 g, 0.268 mol) in methylene chloride (50 ml) at 0° was added tin(IV) chloride (3 ml, 0.0256 mol) followed by ethyl dichloro(ethoxy)acetate (6.03 g, 0.03 mol) dropwise with stirring. After 1 h at 0° the mixture was left overnight at room temperature and worked up in the usual manner. The residue was distilled to give first a pale yellow liquid, b.p. 52° at 1.2 mmHg (0.7 g), and then a yellow oil, b.p. 163—165° at 1.4 mmHg (2.65 g, 45%), identified as the title compound (Found: C, 61.8; H, 4.4. $C_{12}H_{10}O_3S$ requires C, 61.6; H, 4.3%), τ ($CDCl_3$) 8.62 (t, Me), 5.65 (d, CH_2), and 2.00—2.71 (m, ArH).

Ethyl 2,6-Dichlorobenzo[1,2-b:5,4-b']bis[1]benzothiophen-4-carboxylate (14c).—Tin(IV) chloride (0.75 ml, 0.0064 mol) was added to a solution of 2,2'-methylenebis(5-chlorothiophen) (1.3 g, 0.0052 mol) in methylene chloride (20 ml) at —20°. Ethyl dichloroethoxyacetate (1.1 g, 0.0054 mol) was added dropwise with stirring to the resultant yellow solution. After 15 min at this temperature the mixture was allowed to warm to room temperature and was set aside overnight. After the usual work-up the residue was chromatographed on alumina. Elution with light petroleum-benzene (4:1) gave the title compound (0.5 g, 30%), which crystallised from ethanol as white needles, m.p. 168—171° (Found: C, 47.3; H, 2.8. $C_{13}H_8Cl_2O_2S_2$ requires C, 47.2; H, 2.4%).

Ethyl Benzo[1,2-b:4,5-b']bis[1]benzothiophen-6-carboxylate (20d).—Ethyl dichloro(ethoxy)acetate (0.8 g, 0.0004 mol) was added to a stirred solution of 2,3'-methylenebisbenzo[b]thiophen (1.0 g, 0.0036 mol), tin(IV) chloride (1.3 g,

0.005 mol), and methylene chloride (20 ml) at 0°. After 1 h at 0° the solution was maintained at room temperature overnight and worked up in the usual manner, and the residue was chromatographed on alumina. Elution with light petroleum-benzene (2:1) gave the title compound (0.3 g, 23%) which crystallised from aqueous ethanol as needles, m.p. 127° (Found: C, 69.9; H, 4.1. $C_{21}H_{14}O_2S_2$ requires C, 69.7; H, 3.9%), ν_{max} (Nujol) 1740 cm^{-1} (CO).

Oxidation of Benzo[1,2-b:5,4-b']bis[1]benzothiophen (19a).—To the title compound (1.6 g, 0.0055 mol) in boiling acetic acid was added during 1 h a solution of chromium trioxide (2 g) in acetic acid (5 ml) and water (2 ml). After a further 15 min the mixture was cooled and poured into water (300 ml) with stirring. The orange precipitate was collected, washed with hot water, and dried (1.6 g). Vacuum sublimation of this solid gave a sublimate of the quinone (23) as red needles (0.07 g, 4%), m.p. 320° (lit.,⁷ 310°), ν_{max} (Nujol) 1668 cm^{-1} (CO), M^+ , 320. (Calc. for $C_{18}H_8O_2S_2$: M , 320). The remaining colourless residue crystallised from dimethyl sulphoxide to give the bis-dioxide (24) (1.41 g, 72%), m.p. 360° (Found: C, 62.1; H, 2.9%; M^+ , 354. $C_{18}H_{10}S_2O_4$ requires C, 61.7; H, 2.8%; M , 354).

Transformations of the Benzodithiophen (4a).—The benzodithiophen (1.90 g, 0.01 mol) in dry ether was treated with butyl-lithium (0.01 mol) at 20° and the mixture was stirred for 30 min. *NN*-Dimethylformamide (0.73 g, 0.01 mol) was added and after 30 min the mixture was refluxed for 30 min. The solution was poured into dilute aqueous hydrochloric acid and the organic phase was washed with water, dried, and evaporated. The residual solid (2.1 g) was chromatographed on alumina. Elution with benzene gave first starting material (0.48 g, 25%), followed by a yellow solid (0.75 g, 35%), as needles from ethanol, m.p. 171—173°, identified as 2-formylbenzo[1,2-b:5,4-b']dithiophen (4b), ν_{max} (Nujol) 1680 cm^{-1} (CO) (Found: C, 60.8; H, 2.8%, M^+ , 218. $C_{11}H_6S_2O$ requires C, 60.5; H, 2.8%; M^+ , 218). Elution with benzene-ethyl acetate (1:1) gave 2,5-diformylbenzo[1,2-b:5,4-b']dithiophen (4c) as a deep yellow solid (0.5 g, 21%) (yellow crystals from aqueous ethanol), m.p. 255—257°, ν_{max} (Nujol) 1680—1685 cm^{-1} (CO), M^+ , 246. (Calc. for $C_{12}H_6O_2S_2$: M^+ , 246).

The monoformyl derivative (4b) (0.26 g, 0.0012 mol) in diethylene glycol (7 ml) at 160° was treated with hydrazine hydrate (99%; 0.6 ml) and the mixture was maintained at 160° for 15 min. Sodium hydroxide (0.25 g) was added and the mixture warmed to 180°. After 2 h the solution was poured into water and the precipitate collected, washed with water, and recrystallised from ethanol to give 2-methylbenzo[1,2-b:5,4-b']dithiophen (4d) as plates (0.203 g, 80%), m.p. 170—171° (Found: C, 67.1; H, 3.8%; M^+ , 204. $C_{11}H_8S_2$ requires C, 67.4; H, 3.95%; M , 204).

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¹⁹ D. A. Shirley and M. D. Cameron, *J. Amer. Chem. Soc.*, 1952, **74**, 664.