1159. *Synthesis of Methyl Derivatives of Naphtho*[2,1-b]*thiophen and* 11-*Thiabenzo*[a]*fluorene by Photocyclisation of Stilbene Isosters* *

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Methyl derivatives of naphtho[2,1-*b*]thiophen and of 11-thiabenzo[*a*]-fluorene are conveniently prepared by irradiation of appropriately substituted styrylthiophens and styrylbenzo[*b*]thiophens with ultraviolet light.

Stilbene and substituted stilbenes on irradiation with ultraviolet light in presence of a suitable oxidant form phenanthrenes in good yield.[1] The reaction is thought to proceed by cyclisation of the *cis*-stilbene in its lowest excited singlet state to a dihydrophenanthrene of type (I) which then undergoes hydrogen abstraction by the oxidants to give the phenanthrene.[1,2] Azo-compounds, similarly, when irradiated under strongly acidic

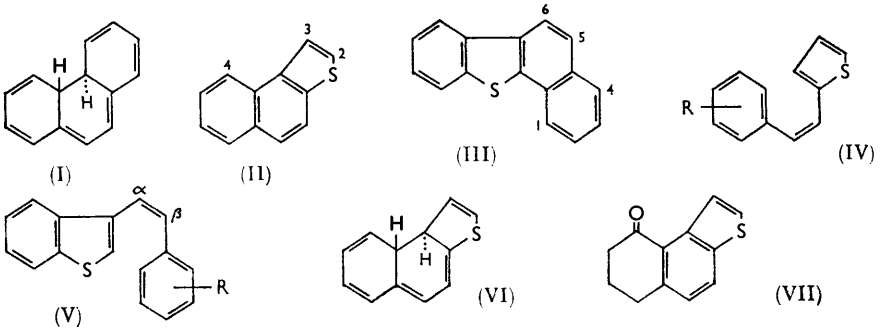
* A preliminary account of this work was published in *Tetrahedron Letters*, 1965, No. 5, p. 301.

[1] For leading references see F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, 1964, **86**, 3094; C. S. Wood and F. B. Mallory, *J. Org. Chem.*, 1964, **29**, 3373.

[2] H. Stegemeyer, *Z. Naturforsch.*, 1962, **17b**, 153; G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, 1964, **86**, 3187.

conditions give rise to benzo[*c*]cinnolines,[3] and benzylideneanilines are converted into phenanthridines.[4] We have obtained methyl derivatives of naphtho[2,1-*b*]thiophen (II) and 11-thiabenzo[*a*]fluorene (III) by photocyclisation of appropriately substituted styrylthiophens (IV) and styrylbenzo[*b*]thiophens (V), and the method offers a convenient route to some of these compounds.

Thus irradiation of a solution in hexane of 2-α-styrylthiophen (IV) in presence of 5 mole-% of iodine [1] gave naphtho[2,1-*b*]thiophen (II) in almost quantitative yield after 2 hr. Molecular oxygen could also be used as oxidant but, as in the case of stilbene,[1] was much less efficacious and gave only 25% conversion after 24 hr. Both the *cis*- and the *trans*-isomer of the styrylthiophen could be used; on irradiation an equilibrium mixture of the isomers was rapidly set up (displaced in favour of the *trans*-form by iodine—cf. ref. 1) and was followed more slowly by formation of the cyclised product (cf. Lewis [5]). Presumably a dihydro-compound (VI), analogous to (I), is an intermediary in the reaction.

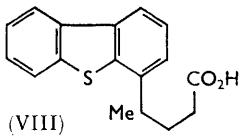


Irradiation of the *o*, *m*-, and *p*-methylstyrylthiophens (IV; R = Me) gave the methylnaphtho[2,1-*b*]thiophens. With the *para*-isomer the one possible cyclisation product, 5-methylnaphtho[2,1-*b*]thiophen, was obtained in high yield. In the case of the *o*-methyl compound cyclisation took place mainly into the available unsubstituted position to give 7-methylnaphthothiophen, but some methyl displacement also occurred, and gas–liquid chromatography showed that the unsubstituted parent compound (II) formed about 20% of the total product. Ejection of methyl substituents also occurred during photocyclisation of substituted azobenzenes [3] but was apparently not noticed in the stilbene series.[1] In *m*-methylstyrylthiophen (IV; R = *m*-Me) two modes of cyclisation are possible and a mixture of approximately equal amounts of 4- and 6-methylnaphthothiophen was produced. They were separated by preparative gas chromatography and were distinguished by a separate synthesis of the 4-methyl isomer from the ketone (VII) [6] by reaction with methylmagnesium iodide and dehydrogenation with sulphur.

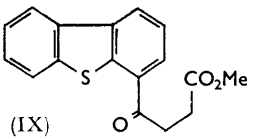
Similarly, by irradiation in presence of iodine, 3-α-styrylbenzo[*b*]thiophen (V) and a number of methyl derivatives were smoothly converted into 11-thiabenzo[*a*]fluorenes [as (III)]. Preparation of 7-, 8-, 9-, and 10-methyl-11-thiabenzo[*a*]fluorene, by Pschorr cyclisation of suitable aminonaphthyl tolyl sulphides, was described recently by Campbell and Keen.[7] We have obtained all the other isomers except the 1-methyl, which were required in connection with work on condensed thiophen derivatives in a petroleum fraction, by photocyclisation of suitably substituted styrylbenzo[*b*]thiophens [as (V)]. The α-, β-, and *p*-methylisomers cyclised without complication, and 6-, 5-, and 2-methylthiabenzo[*a*]fluorene were readily obtained pure in good yield by chromatography of the crude products on alumina. With the *o*-methyl derivative (V; R = *o*-Me) ejection of the methyl

[3] G. M. Badger, R. J. Drewer, and G. E. Lewis, *Austral. J. Chem.*, 1963, **16**, 1042; 1964, **17**, 1036.
[4] M. P. Cava and R. H. Schlessinger, *Tetrahedron Letters*, 1964, No. 31, 2109; G. M. Badger, C. P. Joshua, and G. E. Lewis, *ibid.*, No. 49, 3711.
[5] G. E. Lewis, *J. Org. Chem.*, 1960, **25**, 2193.
[6] W. Carruthers, A. G. Douglas, and J. Hill, *J.*, 1962, 704.
[7] A. D. Campbell and A. R. Keen, *J.*, 1964, 1637.

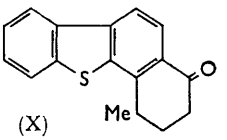
group again occurred and a mixture was produced, shown by gas-liquid chromatography (g.l.c.) to contain approximately equal amounts of 4-methylthiabenzofluorene and the unsubstituted parent compound. These were separated by fractional crystallisation and chromatography on alumina. The *m*-methyl compound (V; R = *m*-Me), as expected, gave a mixture of equal amounts of 1- and 3-methylthiabenzofluorenes (g.l.c.), but only the 3-methyl compound could be obtained pure by chromatography on alumina. The compounds were too high-boiling for convenient separation by preparative gas chromatography, although they were readily distinguished on an analytical scale. The difficulty in separating the products thus lessens the synthetic utility of the photocyclisation reaction with the *meta*-substituted compounds (V) (cf. ref. 1).



(VIII)



(IX)



(X)

1-Methyl-11-thiabenzo[*a*]fluorene was synthesised by another route. 1-Lithio-9-thiafluorene was condensed with menthyl lævulate [8] and the product dehydrated and hydrogenated to give the valeric acid (VIII). The bulky menthyl ester was used to direct attack of the lithium compound to the carbonyl group. In another approach the keto-ester (IX), prepared from 1-lithio-9-thiafluorene and succinic anhydride, was treated with methylmagnesium iodide, but only a poor yield of the required product was obtained and the route was abandoned in favour of the lævulic ester method. Cyclisation of the acid (VIII) be treatment of the acid chloride with stannic chloride gave the ketone (X) whence reduction by the Huang-Minlon procedure and dehydrogenation with sulphur afforded 1-methylthiabenzo[*a*]fluorene. An attempt to convert the ketone (X) directly into the thiabenzofluorene by fusion with a mixture of potassium and sodium hydroxides as described recently by Birch and White for another case,[9] gave a poor yield of an impure product which contained some of the parent compound produced by ejection of the methyl group. The g.l.c. retention time of the 1-methyl isomer prepared by this route was identical with that of the second component obtained in the photocyclisation of the *m*-tolyl derivative (V; R = *m*-Me).

All the styryl compounds used for the cyclisations, except α- and β-methylstyrylbenzo[*b*]-thiophens [as (V)], were prepared from thiophen-2-aldehyde or benzo[*b*]thiophen-3-aldehyde and the Grignard reagent or, better, the triphenylphosphonium ylid [10] derived from the appropriate methylbenzyl bromide. The α-methyl compound [as (V)] was obtained from 3-phenacetylbenzo[*b*]thiophen and methylmagnesium iodide or, better, 3-acetylbenzo [*b*], thiophen and benzylmagnesium bromide and the β-methyl isomer by reaction of the triphenylphosphonium ylid from 3-chloromethylbenzo[*b*]thiophen and acetophenone. In all cases mixtures of the *cis*- and *trans*-isomers were obtained, which could be separated by chromatography on alumina if required, but generally the mixture of isomers was used for cyclisation. 3-Phenacetylbenzo[*b*]thiophen was obtained, along with some of the 2-isomer, by reaction of phenacetyl chloride and benzo[*b*]thiophen in presence of stannic chloride. By reduction with lithium aluminium hydride and dehydration of the carbinol with potassium hydrogen sulphate *trans*-3-α-styrylbenzo[*b*]thiophen was formed.

Experimental

Melting points were determined on a Kofler hot-stage apparatus. U.v. spectra refer to solutions in 95% ethanol. Light petroleum is the fraction of b. p. 40—60° unless otherwise stated. Gas–liquid chromatographic analyses (g.l.c.) were made with a Pye " Argon " instrument, with 0·1%

[8] A. McKenzie, *J.*, 1906, 365.
[9] A. J. Birch and D. A. White, *J.*, 1964, 4086.
[10] Cf. S. Trippett in " Advances in Organic Chemistry. Methods and Results," eds. R. A. Raphael, E. C. Taylor, and H. Wynberg, Interscience, London, 1960, vol. 1, p. 83.

Apiezon L on glass beads as column packing, at 150° (naphthothiophen series) and 200° (thiabenzofluorene series). For the preparative-scale separation an Aerograph "Autoprep" instrument was used with a 20 ft. column packed with 30% silicone gum on chromosorb at 250° and helium as carrier gas.

Photocyclisations.—The light source was a 125 w Mazda mercury vapour lamp from which the outer glass envelope had been cut away, mounted externally to the solution contained in a quartz flask. A solution of the styryl compound [(IV or (V)] (200—500 mg.) and iodine (0·05 mol.) in hexane or light petroleum (150—200 ml.) was irradiated at reflux temperature until g.l.c. of a test sample showed no further increase in cyclised product (2—6 hr.). Further small amounts of iodine were added from time to time when necessary to maintain a purple colour in the solution. The solution was washed with dilute sodium hydroxide, and the crude product purified by chromatography on alumina and crystallisation from ethanol or ethanol–benzene. Yields were variable but in the best cases were almost quantitative and in other instances could probably be improved. Melting points, elemental analyses and the principal ultraviolet absorption maxima of new compounds are given in the Tables.

4-*Methylnaphtho*[2,1-b]*thiophen.*—A solution of 4,5,6,7-tetrahydro-4-oxonaphtho[2,1-*b*]-thiophen [6] (1 g.) in ether (10 ml.) was added to a solution prepared from methyl iodide (0·84 g.) and magnesium (0·15 g.) in ether (25 ml.). The mixture was stirred and boiled for 3 hr. and the recovered product was heated with sulphur (160 mg.) at 200—220° for 45 min. The product was extracted with benzene and after purification by chromatography and by crystallisation of the picrate [red needles (from ethanol), m. p. and mixed m. p. 157—159°], 4-methylnaphtho-[2,1-*b*]thiophen was obtained as colourless blades (from ethanol), m. p. 76—77°, not depressed when mixed with product, m. p. 76—77°, from irradiation of 2-α-(*m*-methylstyryl)thiophen.

γ-1-(9-*Thiafluorenyl*)*valeric Acid.*—A solution of 1-lithio-9-thiafluorene, prepared from 9-thiafluorene (5·5 g.) and n-propyl-lithium (N, 60 ml.) in ether,[11] was added dropwise under nitrogen to a stirred solution of menthyl lævulate [8] (14 g.) in ether (80 ml.) at 0°. The solution was stirred at 0° for 1 hr. and kept at −5° for 48 hr., then acidified with ice-cold sulphuric acid and extracted with ether. The product was hydrolysed with aqueous ethanolic potassium hydroxide and the recovered acid (3·4 g.) converted into its methyl ester with methanol and hydrogen chloride. *Methyl* γ-1-(9-*thiafluorenyl*)*pent*-3-*enoate* (1·5 g.) was obtained as an oil, b. p. 210°/0·4 mm. (Found: C, 73·0; H, 5·4; S, 10·5. $C_{18}H_{16}O_2S$ requires C, 73·0; H, 5·4; S, 10·8%). Hydrogenation of this ester (1·5 g.) with palladised charcoal in methanol gave *methyl* γ-1-(9-*thiafluorenyl*)*valerate*, b. p. 220°/0·5 mm. (Found: C, 72·4; H, 6·1; S, 10·5. $C_{18}H_{18}O_2S$ requires C, 72·5; H, 6·1; S, 10·7%). The *acid*, obtained by hydrolysis with aqueous ethanolic potassium hydroxide, had b. p. 230° (air bath)/0·5 mm. (Found: C, 72·3; H, 6·0. $C_{17}H_{16}O_2S$ requires C, 71·8; H, 5·7%).

1,2,3,4-*Tetrahydro*-1-*methyl*-4-*oxo*-9-*thiabenz*[a]*fluorene.*—The above acid (250 mg.) was converted into the acid chloride with phosphorus pentachloride (250 mg.) in benzene (10 ml.) for 1 hr. Stannic chloride (2 ml.) in benzene (10 ml.) was added at 0° and the solution kept at room temperature for 2 hr. Ice and hydrochloric acid were added and the *ketone* was obtained after chromatography on alumina as plates (180 mg.), m. p. 129° (from ethanol) (Found: C, 76·7; H, 5·3; S, 11·8. $C_{17}H_{14}OS$ requires C, 76·7; H, 5·3; S, 12·0%).

1-*Methyl*-11-*thiabenz*[a]*fluorene.*—The foregoing ketone (220 mg.) was heated with 90% hydrazine hydrate (0·7 ml.) and potassium hydroxide (300 mg.) in diethylene glycol (5 ml.) at 50° for 1 hr., and 180° for 4 hr. The crude product (200 mg.) and sulphur (60 mg.) were heated at 200—240° for 6 hr. The product, which contained some of the parent compound formed by ejection of the methyl group (g.l.c.), was purified by chromatography on alumina and by crystallisation of the picrate. 1-*Methyl*-11-*thiabenz*[a]*fluorene* (92 mg.) was obtained as needles, m. p. 108°. Elemental analyses and ultraviolet absorption maxima are recorded in the Tables.

γ-*Oxo*-γ-(9-*thiafluoren*-1-*yl*)*butyric Acid.*—A solution of 1-lithio-9-thiafluorene prepared [11] from 9-thiafluorene (16·5 g.) and n-propyl-lithium (1·06N, 175 ml.) was added dropwise under nitrogen to a stirred solution of succinic anhydride (20 g.) in tetrahydrofuran (200 ml.) at −70°. After 2 hr. the temperature was allowed to rise to −10° and water (20 ml.) was added.

[11] H. Gilman and A. J. Jacoby, *J. Org. Chem.*, 1938, **3**, 108. See also H. D. Hartough and S. L. Meisel in "The Chemistry of Heterocyclic Compounds. Compounds with Condensed Thiophen Rings," ed. A. Weissberger, Interscience, London, 1954, p. 279.

Tetrahydrofuran was distilled off and the residue was extracted with benzene and dilute sodium carbonate. The *acid* (7 g.) crystallised from ethanol as plates, m. p. 211—212° (Found: C, 67·8; H, 4·3; S, 11·0. $C_{16}H_{12}O_3S$ requires C, 67·6; H, 4·3; S, 11·2%). The *methyl ester*, prepared with methanol and hydrogen chloride, formed plates in methanol, m. p. 146° (Found: C, 68·6; H, 4·9; S, 10·6. $C_{17}H_{14}O_3S$ requires C, 68·5; H, 4·7; S, 10·7%).

Compound	M. p.	Found (%) C	H	N	S	Formula	Required (%) C	H	N	S
Naphtho[2,1-b]*thiophen*										
4-Methyl	76—77°	78·9	5·1		16·0	$C_{13}H_{10}S$	78·8	5·1		16·1
picrate (orange-red needles)	157	53·8	3·0	9·8		$C_{19}H_{13}N_3O_7S$	53·4	3·1	9·8	
5-Methyl	65—66	78·7	5·4		15·8					
picrate (orange-red needles)	135—136	53·9	3·1	10·1						
6-Methyl	97—98	78·7	5·5							
picrate (orange-red needles)	132—133	53·5	2·9	10·0						
7-Methyl	120—122	79·1	5·1		15·3					
picrate (orange needles)	140—142	53·4	2·8	10·1						
11-*Thiabenzo*[a]*fluorene*										
1-Methyl	108	81·9	5·2		12·9	$C_{17}H_{12}S$	82·2	4·9		12·9
picrate (red needles)	131	57·9	3·2	8·8		$C_{23}H_{15}N_3O_7S$	57·9	3·2	8·8	
2-Methyl	143	82·3	5·0		12·8					
picrate (red needles)	147	57·6	3·0	9·2						
3-Methyl	161	81·7	4·8		12·8					
picrate (red needles)	147	57·4	3·3	8·7						
4-Methyl	206	82·0	4·8		13·1					
2,4,7-trinitrofluorenone complex (deep red needles)	239	63·8	3·0			$C_{30}H_{17}N_3O_7S$	63·9	3·0		
5-Methyl	97	82·4	5·1		12·4	$C_{17}H_{12}S$	82·4	4·9		12·9
picrate (red needles)	161	57·9	3·2	9·3		$C_{23}H_{15}N_3O_7S$	57·9	3·2	8·8	
6-Methyl	96	82·2	4·8		12·8					
picrate (red needles)	144	57·9	3·4	8·8						

Ultraviolet absorption maxima of methylnaphtho[2,1-*b*]thiophens and methyl-11-thiabenzo[*a*]fluorenes (mμ), log ε in parentheses

Naphtho[2,1-b]*thiophen*

4-Methyl ..... infl. 235(4·62), 244(4·67), 257(4·46), infl. 290(3·92), 300(4·07), 313(4·02), infl. 333(2·73), 339(271)
5-Methyl ..... infl. 233(4·59), 246(4·75), 256(4·39), 286(3·92), 294(4·07), 306(4·01), 320(3·43), 327(3·26), 335(3·39)
6-Methyl ..... 225(4·28), 233(4·31), 247(4·51), 255(4·31), 296(3·95), 306(3·90), 322(3·42), 337(3·25)
7-Methyl ..... infl. 238(4·59), 248(4·63), 258(4·48), 289(3·98), 301(4·19), 313(4·11), 337(3·05)

11-*Thiabenzo*[a]*fluorene*

1-Methyl ..... infl. 250(4·82), 258(4·89), infl. 263(4·84), infl. 268(4·77), 278(4·74), 296(4·35), 307(4·50), infl. 321(3·89), 342(3·64), 360(3·80)
2-Methyl ..... 248(4·36), 256(4·40), infl. 270(4·19), 278(4·40), 294(3·99), 306(4·09), infl. 321(3·74), 337(3·22), 353(3·29)
3-Methyl ..... 248(4·71), 256(4·70), 270(4·41), 280(4·55), 294(4·17), 306(4·21), infl. 320(3·78), 337(3·29), 354(3·26)
4-Methyl ..... 250(4·56), 258(4·74), 270(4·39), 278(4·44), 296(4·06), 308(4·12), infl. 320(3·74), 337(3·32), 355(3·40)
5-Methyl ..... 248(4·90), 256(4·96), 263(4·79), 270(4·75), 280(4·89), 294(4·38), 306(4·47), infl. 321(4·06), 336(3·78), 356(3·79)
6-Methyl ..... 248(4·79), 256(4·79), 268(4·70), 278(4·78), 292(4·13), 303(4·19), infl. 321(3·73), 339(3·47), 356(3·53)

Addition of a solution prepared from magnesium (0·6 g.) and methyl iodide (2 g.) in ether (30 ml.) to a solution of the ester (4 g.) in benzene (150 ml.) and heating at 60° for 1½ hr. gave an acidic product (0·7 g.), the methyl ester of which, b. p. 250°/0·3 mm., had an infrared spectrum identical with that of methyl γ-(9-thiafluoren-1-yl)pent-3-enoate described above. The neutral fraction was a complex mixture.

2- and 3-*Phenacetylbenzo*[b]*thiophen*.—Stannic chloride (0·18 g.) was added to a stirred mixture of phenacetyl chloride (10 g.) and benzo[*b*]thiophen (9 g.) cooled in ice–water. After 1 hr. water was added and the product extracted with ether and distilled at 220°/2 mm. (7 g.). Chromatography on alumina with graded mixtures of benzene in light petroleum (b. p. 60—80°) gave 3-phenacetylbenzo[*b*]thiophen (3·1 g.) as needles, m. p. 76° (lit.,[12] 70°) (Found: C, 75·9; H, 4·9; S, 12·4. Calc. for $C_{16}H_{12}OS$: C, 76·2; H, 4·8; S, 12·7%); $\lambda_{max.}$ (240), 310 mμ (log ε 4·06, 3·90). The 3-carboxylic acid, m. p. and mixed m. p. 175—176°, was obtained by oxidation with sodium hypoiodite. Further elution afforded 2-*phenacetylbenzo*[b]*thiophen* (1·1 g.), needles, m. p. 136° (from ethanol) (Found: C, 75·8; H, 4·6; S, 13·0%); $\lambda_{max.}$ 235, 253, 310 mμ (log ε 4·26, 4·12, 4·35). Oxidation with hypoiodite gave the 2-carboxylic acid, m. p. 230—232° (lit.,[13] 236°).

3-α-*Styrylbenzo*[b]*thiophen*.—3-Phenacetylbenzo[*b*]thiophen (500 mg.) was reduced with lithium aluminium hydride (60 mg.) in ether and the crude alcohol (250 mg.) was distilled from fused potassium hydrogen sulphate (50 mg.) at 0·5 mm. Crystallisation from ethanol afforded trans-3-α-*styrylbenzo*[b]*thiophen* ($\nu_{max.}$ 950 cm.$^{-1}$) (200 mg.) as needles, m. p. 97° (Found: C, 81·4; H, 5·3; S, 13·4. $C_{16}H_{12}S$ requires C, 81·3; H, 5·1; S, 13·5%); $\lambda_{max.}$ 240, (263), 323 mμ [log ε 4·20, (4·02), 4·19].

3-α-(α-*Methylstyryl*)*benzo*[b]*thiophen*.—3-Acetylbenzo[*b*]thiophen [14] (2·3 g.) in ether (20 ml.) was added dropwise to a stirred solution prepared from benzyl bromide (2·8 g.) and magnesium (0·35 g.) in ether. The mixture was boiled for 2 hr. and decomposed with dilute sulphuric acid. The oily product (3·4 g.) was dehydrated with iodine in boiling xylene for 30 min. Distillation at 200—220°/0·5 mm., and chromatography on alumina with light petroleum (b. p. 60—80°) containing increasing proportions of benzene, gave cis-3-(α-*methylstyryl*)*benzo*[b]*thiophen* (0·11 g.), as an oil, b. p. 200°/0·5 mm. (Found: C, 81·6; H, 6·1. $C_{17}H_{14}S$ requires C, 81·6; H, 5·6%); $\lambda_{max.}$ 236, (256), 294, 303 mμ [log ε 4·48, (4·25), 3·96, 3·94]. Further elution gave the trans-*isomer* (0·85 g.), m. p. 69° (from ethanol) (Found: C, 81·7; H, 5·6; S, 13·1. $C_{17}H_{14}S$ requires C, 81·6; H, 5·6; S, 12·8%); $\lambda_{max.}$ 240, 282 mμ (log ε 4·31, 4·06).

3-(β-*Methylstyryl*)*benzo*[b]*thiophen*.—A solution of 3-chloromethylbenzo[*b*]thiophen (5 g.) and triphenylphosphine (7·5 g.) in nitromethane (30 ml.) was boiled for 24 hr. Benzene (100 ml.) was added and the crystalline solid was filtered off, washed with benzene, and dried at 150°. The salt (8·5 g.) was suspended in ether (30 ml.) and converted into the deep red phosphonium ylid by addition of the theoretical amount of ethereal n-butyl-lithium, under nitrogen. The mixture was stirred for 30 min. and then a solution of acetophenone (2·3 g.) in ether (10 ml.) was added and the mixture was boiled for 2 hr. The solution was filtered and evaporated, and the product (4 g.) was chromatographed on alumina. Elution with benzene–light petroleum (b. p. 60—80°) gave cis-3-(β-*methylstyryl*)*benzo*[b]*thiophen* (0·2 g.), b. p. 240° (air bath)/0·4 mm. (Found: C, 81·7; H, 5·6; S, 12·4. $C_{17}H_{14}S$ requires C, 81·6; H, 5·6; S, 12·8%). Continued elution with benzene afforded the trans-*isomer* (0·5 g.), m. p. 65° (Found: C, 81·2; H, 5·6; S, 13·1%); $\lambda_{max.}$ 240, 294, 311 mμ (log ε 4·38, 4·10, 4·13).

2-(o-, m-, *and* p-*Methylstyryl*)*thiophen and* 3-(o-, m-, *and* p-*methylstyryl*)*benzo*[b]*thiophen*.—Some of these were prepared from the appropriate methylbenzylmagnesium bromide and thiophen-2-aldehyde or benzo[*b*]thiophen-3-aldehyde, but yields were variable because of the formation of dibenzyls from the benzyl halides. Better results were obtained by reaction of the benzylidenetriphenylphosphonium ylids and the aldehyde, as described above for 3-(β-methylstyryl)benzo[*b*]thiophen. *cis*- and *trans*-Isomers were readily separated by chromatography on alumina. The *trans*-compound was invariably eluted after the *cis* both on alumina and on g.l.c. and was distinguished by the strong peak at about 970 cm.$^{-1}$ in the infrared spectrum. The *cis*- and *trans*-isomers also differed in their ultraviolet absorption. With the styrylthiophens, the long wavelength band of the *cis*-isomers was of lower intensity and occurred at shorter wavelengths than that of the *trans*-, as with stilbene derivatives.[15] With the styrylbenzo[*b*]thiophens the difference was not so noticeable, but in the *trans*-series the long- and short-wavelength absorption bands were much more clearly defined than in the *cis*. Melting points and elemental analyses of the *trans*-isomers are shown in the Table.

[12] Ng. Ph. Buu-Hoi and P. Cagnaint, *Rec. Trav. chim.*, 1948, **67**, 64.
[13] R. Weissgerber and O. Kruber, *Ber.*, 1920, *B***53**, 1551.
[14] M. W. Farrar and R. Levine, *J. Amer. Chem. Soc.*, 1950, **72**, 4433.
[15] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., London, 1962, p. 424.

Compound	M. p. or b. p.	Found (%) C	H	S		Required (%) C	H	S
o-Methylstyrylthiophen	120° (air bath)/ 0·5 mm.	77·8	6·1	16·0	$C_{13}H_{12}S$	78·0	6·0	16·0
m-Methyl-	80	78·3	6·4	15·8				
p-Methyl-	115—116	78·1	6·0	15·6				
o-Methylstyrylbenzo[*b*]thiophen	85	82·0	6·0	13·0	$C_{17}H_{14}S$	81·6	5·6	12·8
m-Methyl-	260 (air bath)/ 0·4 mm.	81·5	5·7	12·6				
p-Methyl-	110	81·5	5·8	12·9				

Ultraviolet absorption maxima of styrylthiophens and styrylbenzo[*b*]thiophens (mμ), log ε in parentheses

cis-o-Methylstyrylthiophen	238(3·79), 288(3·94)
trans-	237(3·78), infl. 254(3·16), 262(3·25), 329(4·30)
cis-m-Methyl-	236(3·85), 294(3·50)
trans-	238(4·01), infl. 244(3·91), 330(4·45)
trans-p-Methyl-	233(3·95), infl. 242(3·83), 333(4·37), infl. 345(4·17)
trans-3-α-Styrylbenzo[*b*]thiophen	240(4·20), infl. 263(4·02), 323(4·19)
cis-α-Methyl-	236(4·48), infl. 256(4·25), 294(3·96), 303(3·94)
trans-	240(4·31), 282(4·06)
trans-β-Methyl-	240(4·38), 294(4·10), 311(4·13)
trans-o-Methyl-	244(4·12), infl. 263(4·19), 330(4·31)
cis-m-Methyl-	242(4·47), infl. 263(4·23), 294(4·12), 323(4·12)
trans-	242(4·32), infl. 263(4·09), 323(4·30)
trans-p-Methyl-	245(4·42), infl. 260(4·26), 323(4·44)

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