Condensed Thiophen Ring Systems. Part VIII.[1] Intramolecular Cyclisation of Azido- and Nitro-substituted 2-Arylbenzo[*b*]thiophens; New Routes to 10*H*-[1]Benzothieno[3,2-*b*]indoles

By **K. E. Chippendale, B. Iddon,* and H. Suschitzky,** Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, Lancs.

10*H*-[1]Benzothieno[3,2-*b*]indole (1) and some of its derivatives have been prepared by reductive cyclisation of a 2-(2-nitroaryl)- or a 2-aryl-3-nitro-benzo[*b*]thiophen with triethyl phosphite. The parent compound (1) has been prepared also by thermolysis of either 3-azido-2-phenyl- or 2-(*o*-azidophenyl)-benzo[*b*]thiophen in bis-(2-methoxyethyl) ether. 2-(*o*-Nitrophenyl)benzo[*b*]thiophen and its 5-methyl derivative have been prepared by reaction of the corresponding 2-benzo[*b*]thienyl-lithium compounds with *o*-nitrofluorobenzene. The scope of the reaction of benzo[*b*]thienyl-lithium compounds with other fluoroaromatic compounds has been studied, and the preparations of starting materials are also reported. Bromination of compound (1) gave the 2-bromo-derivative.

We have briefly reported various preparations of 10*H*-[1]benzothieno[3,2-*b*]indole (1) and some of its derivatives [2] and now give details of this work.

10*H*-[1]Benzothieno[3,2-*b*]indoles may be prepared by condensation of benzo[*b*]thiophen-3(2*H*)-one or one of its derivatives with a phenylhydrazine under the conditions of the Fischer indole synthesis.[3-5] This method is limited, however, by the availability and instability of the benzothiophenone, and cyclisation is moreover inhibited by 4-substitution in the benzothiophenone as well as by *ortho*-substitution in the phenylhydrazine. Mixtures of products are likely to arise with *m*-substituted phenylhydrazines. In general, the limitations of the previous method are avoided by the use of our procedures.

The nitro-compounds (6)—(9) were prepared by nitration of the corresponding 2-arylbenzo[*b*]thiophens with fuming nitric acid in acetic acid. 2-Phenyl- and 2-*p*-tolyl-benzo[*b*]thiophen reacted at 5—10° to give mainly compounds (6) and (7), respectively. Small amounts of isomers of (6) and (7) may have been formed also but no attempts were made to isolate these. Nitration of 2-phenylbenzo[*b*]thiophen also gave a dinitro-derivative of compound (10) (17% yield); this reaction is analogous to the formation of compound (11) during nitration of benzo[*b*]thiophen.[6] 2-(*p*-Chloro- and *p*-bromo-phenyl)benzo[*b*]thiophen could not be nitrated at 5—10° but at 65° gave good yields of compounds (8) and (9), respectively, together with a small amount (10—16% yield) of an unidentified dinitro-compound in each case.

The 2-arylbenzo[*b*]thiophens required as starting materials for the synthesis of compounds (6)—(9)

[1] Part VII, R. P. Dickinson and B. Iddon, *J. Chem. Soc.* (*C*), 1971, 3447.

[2] K. E. Chippendale, B. Iddon, and H. Suschitzky, *Chem. Comm.*, 1971, 203.

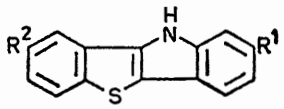
[3] H. D. Hartough and S. L. Meisel, in 'Compounds with Condensed Thiophene Rings,' ed. A. Weissberger, Interscience, New York, 1954, p. 412.

[4] L. H. Werner, D. C. Schroeder, and S. Ricca, *J. Amer. Chem. Soc.*, 1957, **79**, 1675; Ciba Ltd., B.P. 830,223/1960; L. H. Werner, U.S.P. 3,024,248/1962.

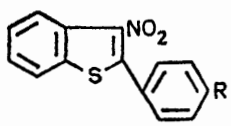
[5] C. E. Dalgliesh and F. G. Mann, *J. Chem. Soc.*, 1947, 653.

[6] G. Van Zyl, C. J. Bredeweg, R. H. Rynbrandt, and D. C. Neckers, *Canad. J. Chem.*, 1966, **44**, 2283.

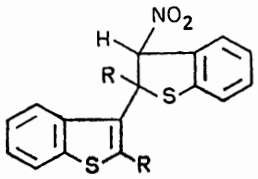
were prepared by literature procedures. For example, 2-phenylbenzo[*b*]thiophen was prepared by cyclisation of phenacyl phenyl sulphide [7,8] as well as by the reaction of 2-benzo[*b*]thienyl-lithium with chlorobenzene in the presence of piperidine,[9] for which the authors of ref. 9



(1) $R^1 = R^2 = H$
(2) R^1 = Me, $R^2 = H$
(3) R^1 = Cl, $R^2 = H$
(4) R^1 = Br, $R^2 = H$
(5) $R^1 = H$, R^2 = Me

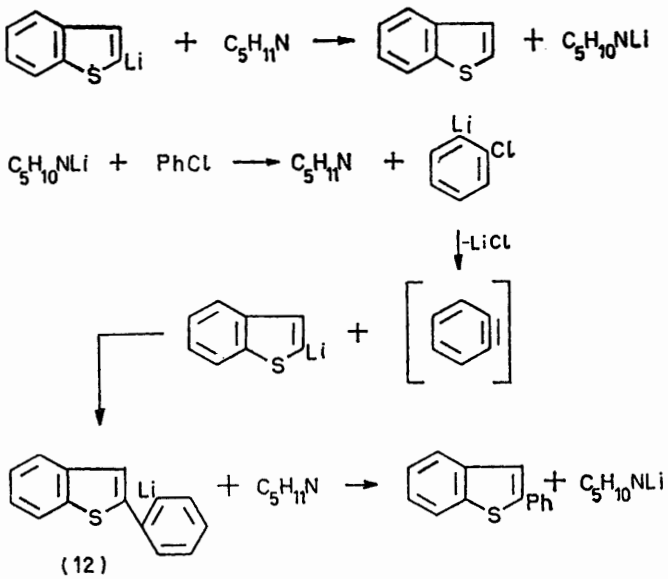


(6) R = H
(7) R = Me
(8) R = Cl
(9) R = Br



(10) R = Ph
(11) R = H

have suggested [10] an aryne mechanism (see Scheme) (*cf.* ref. 11). The yield (41% based on chlorobenzene) of 2-phenylbenzo[*b*]thiophen obtained by the latter procedure was the same whether the molar ratio of 2-benzo[*b*]thienyl-lithium to chlorobenzene was 1·0 : 0·5 or 1·0 : 1·0. Attempts to trap the intermediate (12) (Scheme) with carbon dioxide or dimethyl sulphate [1]



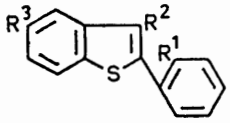
(12)

SCHEME

failed, presumably because it reacts rapidly with the piperidine. We hoped to demonstrate an aryne mechanism by isolating a mixture of 2-*m*- and 2-*p*-tolyl-benzo[*b*]thiophen from the similar reaction of 2-benzo[*b*]thienyl-lithium with *p*-chlorotoluene. However, only 2-*p*-tolylbenzo[*b*]thiophen (22% yield based on *p*-chlorotoluene), together with starting materials, was obtained.

2-Benzo[*b*]thienyl-lithium is reported [8,12] to react with fluorobenzene to give 2-phenylbenzo[*b*]thiophen. In our laboratories this reaction has proved abortive; starting material was recovered quantitatively (commercial n-butyl-lithium was used). We have shown, however, that the lithium compound and fluorobenzene can react in the presence of piperidine but to give only a low yield of 2-phenylbenzo[*b*]thiophen, together with much tar. This reaction probably proceeds *via* an aryne mechanism (Scheme).[11] We decided at this point to study the reactions of 2-benzo[*b*]thienyl-lithium with other aromatic fluorine compounds.

An ethereal solution of 2-benzo[*b*]thienyl-lithium was added to a solution of *o*-nitrofluorobenzene in ether at −70° (in the absence of piperidine) in order to avoid oxidation of the lithium compound by the nitro-group.[13] After 4 h the mixture was allowed to warm slowly to room temperature. This gave a 58% yield of 2-(*o*-nitrophenyl)benzo[*b*]thiophen (13) together with a



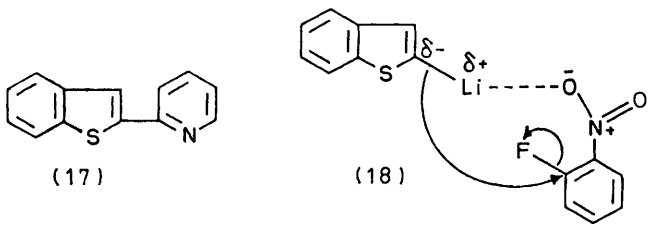
(13) $R^1 = NO_2$, $R^2 = R^3 = H$
(14) $R^1 = NO_2$, $R^2 = H$, R^3 = Me
(15) $R^1 = N_3$, $R^2 = R^3 = H$
(16) $R^1 = R^3 = H$, $R^2 = N_3$

small amount (10%) of 2,2′-bibenzo[*b*]thienyl, the coupling product of the lithium compound.[14] 5-Methyl-2-benzo[*b*]thienyl-lithium [15] reacted similarly with *o*-nitrofluorobenzene to give 5-methyl-2-(*o*-nitrophenyl)-benzo[*b*]thiophen (14). In contrast, an analogous reaction between 2-benzo[*b*]thienyl-lithium and *o*-chloronitrobenzene gave only 2,2′-bibenzo[*b*]thienyl (45% yield) and tar.

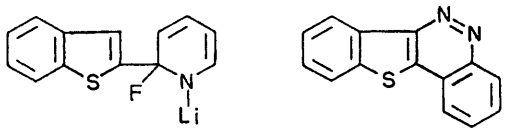
When an ethereal solution of pentafluoropyridine was added to 2-benzo[*b*]thienyl-lithium in ether at 0°, a mixture of 2,4,6-tris-(2-benzo[*b*]thienyl)difluoropyridine (82% yield) and 2-(tetrafluoro-4-pyridyl)benzo[*b*]thiophen (14%) was obtained. A similar reaction with hexafluorobenzene gave mainly 2-(pentafluorophenyl)-benzo[*b*]thiophen (40%), together with 1,4-bis-(2-benzo[*b*]thienyl)tetrafluorobenzene (16%). In these reactions the fluorine compound was added to the lithium compound (*cf.* before) in a deliberate attempt to assess qualitatively the reactivity of the latter. The formation of a high yield of the tri-substituted pyridine under these conditions suggests that 2-benzo[*b*]thienyl-lithium is highly reactive. It also reacted with 2-fluoropyridine, but under more vigorous conditions, to give 2-(2-pyridyl)-

[7] O. Dann and B. Kokorudz, *Chem. Ber.*, 1958, **91**, 172.
[8] J. E. Banfield, W. Davies, N. W. Gamble, and S. Middleton, *J. Chem. Soc.*, 1956, 4791.
[9] A. W. Chow, N. M. Hall, J. R. E. Hoover, M. M. Dolan, and R. J. Ferlauto, *J. Medicin. Chem.*, 1966, **9**, 551.
[10] Personal communication.
[11] L. Friedman and J. F. Chlebowski, *J. Amer. Chem. Soc.*, 1969, **91**, 4864.
[12] S. Middleton, *Austral. J. Chem.*, 1959, **12**, 218.
[13] G. Köbrich and P. Buck, *Chem. Ber.*, 1970, **103**, 1412.
[14] B. Iddon and R. M. Scrowston, *Adv. Heterocyclic Chem.*, 1970, **11**, p. 260; Y. Matsuki and F. Shoji, *Nippon Kagaku Zasshi*, 1965, **86**, 1067 (*Chem. Abs.*, 1966, **65**, 13638).
[15] R. P. Dickinson and B. Iddon, *J. Chem. Soc.* (*C*), 1971, 182.

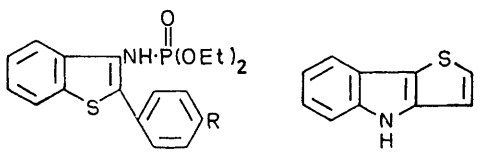
benzo[*b*]thiophen (17) (44%). An attempt to nitrate compound (17) failed. Since the completion of our studies, Kauffmann *et al.*[16] have reported an analogous synthesis of 2-(2-pyridyl)thiophen.



(17) (18)



(19) (20)



(21) (22)

Encouraged by these results, we treated 2-benzo[*b*]-thienyl-lithium with *p*-nitro- and 2,4-dinitro-fluorobenzene. Unfortunately, these reactions gave mainly tars, from which small amounts of 2,2'-bibenzo[*b*]-thienyl were isolated.

3-Benzo[*b*]thienyl-lithium is unstable in ether at temperatures much in excess of −70°.[1,17] At −70°, it reacted with *o*-nitrofluorobenzene to give an intractable product, but with pentafluoropyridine it gave exclusively 3-(tetrafluoro-4-pyridyl)benzo[*b*]thiophen, and with hexafluorobenzene it gave mainly 3-(pentafluorophenyl)-benzo[*b*]thiophen, together with a small amount of 1,4-bis-(3-benzo[*b*]thienyl)tetrafluorobenzene.

From the evidence at present available, it seems likely that the reactions of 2- and 3-benzo[*b*]thienyl-lithium with aromatic fluorine compounds proceed *via* a mechanism different from that already discussed for the reaction of 2-benzo[*b*]thienyl-lithium with chlorobenzene, which requires a higher reaction temperature and the presence of piperidine. We suggest that the lithium compounds behave as nucleophiles in these reactions. The fact that 2-benzo[*b*]thienyl-lithium reacts with *o*-nitrofluorobenzene to give (13) and with *p*-nitro- and 2,4-dinitro-fluorobenzene to give mainly tars is in accordance with the recent observations of Köbrich and Buck[13] that a nitro-group *para* to a halogen substituent will oxidise a lithium compound, hence causing tar formation. We suggest that 2-benzo[*b*]-thienyl-lithium complexes initially with the nitro-group of *o*-nitrofluorobenzene, as shown in (18). This holds the lithium compound close to the fluorine atom and simultaneously enhances its nucleophilicity. In the case of *p*-nitro- or 2,4-dinitro-fluorobenzene, complex formation with the *p*-nitro-group hinders nucleophilic displacement of the fluorine atom and oxidation of the lithium compound by the nitro-group occurs instead.[13]

With 2-fluoropyridine, addition of the lithium compound across the 1,2-double bond, as shown in (19), followed by elimination of lithium fluoride, is more likely to occur than complex formation with the ring nitrogen atom followed by displacement of fluoride ion.[16] Pentafluoropyridine and hexafluorobenzene are known to undergo ready nucleophilic displacement of fluorine by organolithium reagents;[18] fluorobenzene is unreactive probably because the fluorine atom is not activated towards nucleophilic attack.

The azides (15) and (16) were obtained from the nitro-compounds (13) and (6), respectively, by reduction with iron and ammonium chloride followed by diazotisation and treatment of the resulting diazonium compound with sodium azide. [1]Benzothieno[3,2-*c*]cinnoline (20)[19] was obtained as a by-product during the conversion of 2-(*o*-aminophenyl)benzo[*b*]thiophen into the corresponding azide.

When 2-(*o*-nitrophenyl)benzo[*b*]thiophen (13) is heated in triethyl phosphite (TEP), it gives 10*H*-[1]benzothieno-[3,2-*b*]indole (1) (60% yield), together with a small amount of 10-ethyl[1]benzothieno[3,2-*b*]indole (11%). The *N*-ethyl compound undoubtedly arises from alkylation of the parent heterocycle (1) by the TEP. 8-Methyl-10*H*-[1]benzothieno[3,2-*b*]indole (5) was prepared similarly from compound (14). Similar treatment of the 2-aryl-3-nitrobenzo[*b*]thiophens (6)—(9) gave the corresponding 10*H*-[1]benzothieno[3,2-*b*]indoles (1)—(4), usually together with the corresponding phosphoramidates (21; R = H, Cl, or Br) (see Table 1).

We have also prepared 10*H*-[1]benzothieno[3,2-*b*]-indole (1) in about 60% yield in each case by heating the azides (15) and (16) in bis-(2-methoxyethyl) ether. 4*H*-Thieno[3,2-*b*]indole (22) has been prepared similarly from 2-(*o*-azidophenyl)thiophen.[20]

The formation of indoles from azides is believed to be a nitrene insertion reaction;[21] however the mechanism of reductive cyclisation of nitro-compounds with TEP is not clear.[22,23] Thus, ring-closure of the

[16] T. Kauffmann, E. Wienhöfer, and A. Woltermann, *Angew. Chem. Internat. Edn.*, 1971, **10**, 741; T. Kauffmann, J. Jackisch, H.-J. Streitberger, and E. Wienhöfer, *ibid.*, p. 744.

[17] R. P. Dickinson and B. Iddon, *J. Chem. Soc.* (*C*), 1968, 2733.

[18] R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave, *J. Chem. Soc.*, 1964, 3736; R. E. Banks, J. E. Burgess, W. M. Cheng, and R. N. Haszeldine, *ibid.*, 1965, 575; R. D. Chambers, B. Iddon, W. K. R. Musgrave, and L. Chadwick, *Tetrahedron*, 1968, **24**, 877.

[19] Part IX, K. E. Chippendale, B. Iddon, and H. Suschitzky, following paper.

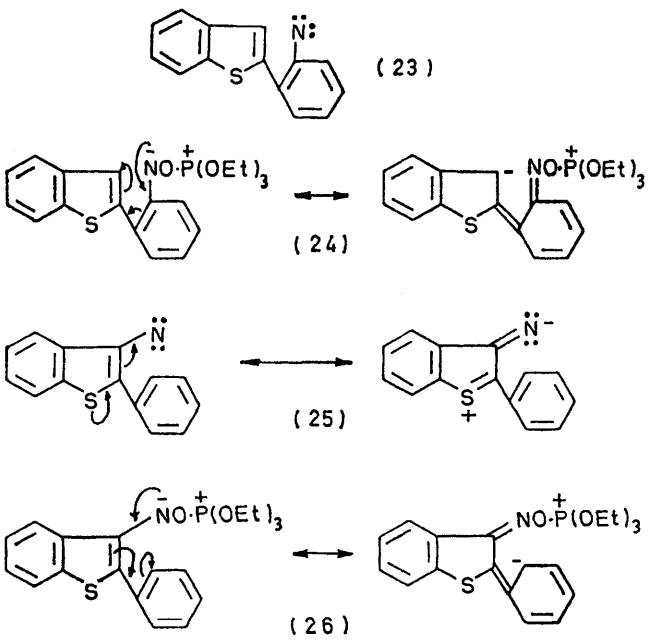
[20] P. A. S. Smith and J. H. Boyer, *J. Amer. Chem. Soc.*, 1951, **73**, 2626.

[21] P. A. S. Smith, in ' Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970, ch. 4; T. L. Gilchrist and C. W. Rees, ' Carbenes, Nitrenes, and Arynes,' Nelson, London, 1969.

[22] J. I. G. Cadogan and A. Cooper, *J. Chem. Soc.* (*B*), 1969, 883.

[23] J. I. G. Cadogan and M. Cameron-Wood, *Proc. Chem. Soc.*, 1962, 361.

nitro-compound (13) with TEP could involve intermediate (23) or (24) and that of the nitro-compound (6), intermediate (25) or (26). In the former case, each



of the intermediates (23) and (24) would be expected to give a high yield of product (1), since cyclisation occurs into an electron-rich thiophen ring. In the latter case, however, cyclisation would be expected to be more difficult. These expectations are confirmed by our yields (see Table 1). It is not possible to say which intermediate [(23) or (24)] is involved in the cyclisation of (13), but there is some evidence for the involvement of a nitrene at some stage in the cyclisation of the nitro-compounds (6)—(9) with TEP. Phosphoramidates, which arise *via* the corresponding phosphorimidates, the usual coupling products of a nitrene with the phosphorus reagent, were isolated in these cases. Moreover, considerably more phosphoramidate (21; R = Cl or Br) was isolated from the product of cyclisation of (8) or (9), respectively (Table 1). Halogen substituents presumably deactivate the aryl ring, thereby inhibiting cyclisation and causing the nitrene to be trapped by the TEP. Isolation of the same product (1) from cyclisation of compounds (6), (13), (15), and (16) further supports the suggestion of nitrene intermediates in these reactions.

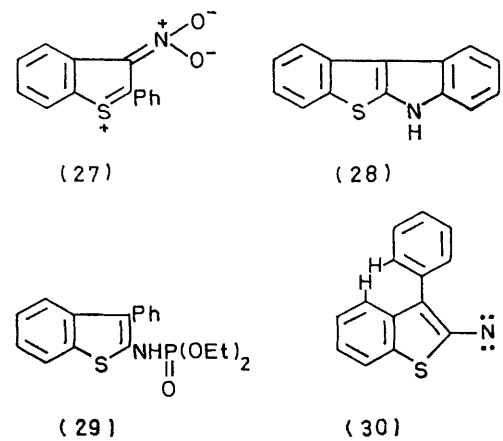
Both of the intermediates (25) and (26) are resonance-stabilised. However, whereas the ring sulphur atom is involved in stabilisation in the former case, resonance stabilisation of (26) opposes the usual release of electrons by the ring sulphur atom. Consequently, the nitrene intermediate (25) is predicted to be more stable than the alternative (26). In fact, stabilisation of (25) is similar to stabilisation of *p*-(dimethylamino)phenylnitrene relative to phenylnitrene.[24]

The considerable difference in reactivity between 3-nitro-2-phenyl- (6) and 2-(*o*-nitrophenyl)-benzo[*b*]thiophen (13) may be attributed to mesomeric stabilisation of the former, as shown in (27) (*cf.* ref. 24). From the products of cyclisation of the former compound (6) starting material was recovered, even after long reaction times (Table 1).

We also prepared 2-nitro-3-phenyl[*b*]thiophen by nitration of 3-phenylbenzo[*b*]thiophen with fuming nitric acid in acetic acid and heated it in TEP in an attempt to prepare 5*H*-[1]benzothieno[2,3-*b*]indole (28). Work-up gave small amounts of the phosphoramidate (29) and 2-(diethylamino)-3-phenylbenzo[*b*]thiophen, together with an intractable tar. 5-Bromo-2-nitro-3-phenylbenzo[*b*]thiophen gave only intractable material on treatment with TEP.

An attempt to prepare the benzothienoindole (28) from the phenylhydrazone of benzo[*b*]thiophen-2(3*H*)-one under conditions reported[3,5] for the similar preparation of (1) was unsuccessful. This result is in agreement with that of Dalgliesh and Mann.[5]

The failure of 2-nitro-3-phenylbenzo[*b*]thiophen to give compound (28) is in striking contrast to the successful synthesis of compound (1) from 3-nitro-2-phenylbenzo[*b*]thiophen (6). We attribute this difference to *peri*-interaction between H-4 and the 3-phenyl ring, which prevents an intermediate, such as the nitrene (30), from adopting a suitable conformation for cyclisation. The u.v. spectrum of 3-phenylbenzo[*b*]thiophen



is similar to that of benzo[*b*]thiophen because the former system is prevented from coplanarity by similar *peri*-interaction,[12,25] whilst the u.v. spectrum of 2-phenylbenzo[*b*]thiophen is consistent with a coplanar structure.[12] A comparison of the u.v. spectra of 2-nitro-3-phenyl- and 3-nitro-2-phenyl-benzo[*b*]thiophen with each other and with those of benzo[*b*]thiophen and its 2- and 3-phenyl derivatives suggests that neither of the nitro-compounds achieves coplanarity. Presumably, however, when the 3-nitro-2-phenyl isomer reacts with TEP, it generates an intermediate which can adopt a satisfactory conformation for cyclisation, whereas the 2-nitro-3-phenyl isomer cannot.

[24] J. I. G. Cadogan, *Quart. Rev.*, 1968, **22**, 222; P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, 1963, 42.

[25] D. S. Rao and B. D. Tilak, *J. Sci. Res.* (*India*), 1959, **18***B*, 77.

Bromination of 10*H*-[1]benzothieno[3,2-*b*]indole gave a monobromo-derivative identical with the 2-bromo-10*H*-[1]benzothieno[3,2-*b*]indole (4) obtained by cyclisation of 2-(*p*-bromophenyl)-3-nitrobenzo[*b*]thiophen (9). Our sample of 2-methyl-10*H*-[1]benzothieno[3,2-*b*]indole (2) appears to be identical with the product from the cyclisation of the *m*-tolylhydrazone of benzo[*b*]thiophen-3(2*H*)-one described previously [3,5] as either the 2- or the 4-methyl derivative.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded with a Varian A60 spectrometer (tetramethylsilane as internal standard) and ^{19}F n.m.r. spectra with a Varian HA-100 spectrometer (trichlorofluoromethane as internal standard); the recorded signals are singlets unless stated otherwise. Molecular weights were determined by mass spectrometry with an A.E.I. MS12 instrument.

n-Butyl-lithium was purchased from Pfizer Ltd (Sandwich, Kent) as a 20% w/w solution in hexane; consequently, all references to solutions of this reagent in ether imply the presence of small amounts of hexane. Reactions with n-butyl-lithium and triethyl phosphite (TEP) were carried out under dry, oxygen-free nitrogen, and the solvents and other reagents used were dried by standard procedures. Light petroleum refers to the fraction of b.p. 60—80° unless stated otherwise.

Ethereal solutions of 2-benzo[*b*]thienyl-lithium were prepared by the method of Shirley and Cameron [26] and ethereal solutions of 3-benzo[*b*]thienyl-lithium by the method of Dickinson and Iddon.[17]

2-(*p*-Chlorophenyl)benzo[*b*]thiophen (50%), m.p. 191—191·5° (from benzene) (lit.,[27] 197—198°) (Found: C, 68·7; H, 4·0%; *M*, 244. $C_{14}H_9ClS$ requires C, 68·7; H, 3·7%; *M*, 244), and 2-(*p*-bromophenyl)benzo[*b*]thiophen (30%), m.p. 210—213° (from benzene) (lit.,[28] 211—213°) were prepared in the usual way.[8,29] We made no attempts to isolate the 3-aryl isomers.[29]

Reactions of 2-*Benzo*[b]*thienyl-lithium.*—(a) *With chlorobenzene.* A reaction carried out according to the procedure of Chow *et al.*[9] gave 2-phenylbenzo[*b*]thiophen (41% based on chlorobenzene), m.p. 174—175° (from benzene) (lit.,[9] 171—173°).

(b) *With* p-*chlorotoluene.* 2-*p*-Tolylbenzo[*b*]thiophen (22%), prepared similarly, had m.p. 169—171° (from light petroleum after initial chromatography on alumina; light petroleum was used to elute starting material and product) (lit.,[30] 170—172°); *M*, 224; τ (CCl_4) 2·12—2·98 (m, aromatic) and 7·66 (CH_3).

(c) *With* o-*nitrofluorobenzene.* A solution of the lithium compound (15·0 mmol) in ether (20 ml) was added dropwise during 15 min to a stirred solution of *o*-nitrofluorobenzene (2·1 g, 15·0 mmol) in ether (20 ml) at −70°, and the resulting mixture was stirred at −70° for a further 4 h. It was then allowed to warm slowly to room temperature and an excess of water was added with stirring. The mixture was diluted with a large excess of ether and the organic and aqueous layers were separated. The aqueous layer was extracted with several portions of ether; the organic layer and ethereal extracts were combined, washed with water, and dried ($MgSO_4$). Removal of the solvent by distillation gave 2-(o-*nitrophenyl*)*benzo*[b]*thiophen* (2·21 g, 58%), m.p. 86—88° (from methanol); τ (CCl_4) 2·15—2·90 (m, aromatic) (Found: C, 65·5; H, 3·5; N, 5·4%; *M*, 255. $C_{14}H_9NO_2S$ requires C, 65·9; H, 3·6; N, 5·5%; *M*, 255). Extraction of the residual gelatinous aqueous layer with chloroform gave 2,2′-bibenzo[*b*]thienyl (0·2 g, 10%), m.p. 260—262° (from toluene) (lit.,[26] 260—261°).

(d) *With* o-*chloronitrobenzene.* A solution of the lithium compound (7·46 mmol) in ether (30 ml) was added dropwise during 15 min to a solution of *o*-chloronitrobenzene (1·18 g, 7·50 mmol) in ether (30 ml) at −70°, and the resulting mixture was stirred at −70° for a further 30 min. It was then worked up as described in (c) to give a product which was chromatographed on alumina. Light petroleum eluted a mixture (0·80 g) of benzo[*b*]thiophen and 2,2′-bibenzo[*b*]thienyl. Crystallisation of this mixture from toluene gave 2,2′-bibenzo[*b*]thienyl (0·45 g, 45%), m.p. 260—262° (lit.,[26] 260—261°). More polar solvents eluted only intractable tars.

(e) *With* 2-*fluoropyridine.* A solution of 2-fluoropyridine (1·5 g, 15·5 mmol) in ether (15 ml) was added dropwise to a stirred solution of 2-benzo[*b*]thienyl-lithium (15·0 mmol) in ether (20 ml) at room temperature, and the resulting mixture was then heated under reflux for 2 h. It was cooled, an excess of water was added, and extraction with chloroform gave a tar which was chromatographed on alumina. Light petroleum eluted benzo[*b*]thiophen (0·2 g, 10%) followed by a mixture of 2-fluoropyridine and another component. Crystallisation of the latter fraction from ethanol gave 2-(2-*pyridyl*)*benzo*[b]*thiophen* (1·4 g, 44%), m.p. 124—126°; τ (CCl_4) 1·30—1·47 (m, assigned to α-H of pyridine ring) and 2·10—3·00 (m, aromatic) (Found: C, 73·5; H, 4·4; N, 6·5%; *M*, 211. $C_{13}H_9NS$ requires C, 73·9; H, 4·3; N, 6·6%; *M*, 211).

(f) *With pentafluoropyridine.* A solution of pentafluoropyridine (2·54 g, 15·0 mmol) in ether (25 ml) was added dropwise to a stirred solution of the lithium compound (15·0 mmol) in ether (20 ml) at 0°. The resulting mixture was stirred at room temperature for 3 h and then an excess of water was added. Work-up as described in (e) gave a product which was chromatographed on alumina. Ether eluted 4-(2-*benzo*[b]*thienyl*)*tetrafluoropyridine* (0·6 g, 14%), m.p. 146—148° (sublimed, 115° at 0·3 mmHg); ^{19}F n.m.r. δ ($CHCl_3$) 83·7 (2- and 6-F) and 140·7 p.p.m. (3- and 5-F) (Found: C, 55·6; H, 2·0; N, 4·9%; *M*, 283. $C_{13}H_5F_4NS$ requires C, 55·1; H, 1·8; N, 4·95%; *M*, 283). Chloroform eluted 2,4,6-*tris*-(2-*benzo*[b]*thienyl*)-*difluoropyridine* (2·1 g, 82%), m.p. 224—226° (from benzene) (Found: C, 68·2; H, 3·2; N, 2·6%; *M*, 511. $C_{29}H_{15}F_2NS_3$ requires C, 68·2; H, 3·0; N, 2·7%; *M*, 511). This compound was insufficiently soluble in most of the common solvents to enable us to record its ^{19}F n.m.r. spectrum.

(g) *With hexafluorobenzene.* A solution of hexafluorobenzene (2·79 g, 15·0 mmol) in ether (25 ml) was added dropwise to a solution of the lithium compound (15·0 mmol) in ether (20 ml) at 0°, and the mixture was then heated under reflux for 1 h. An excess of water was added, and extraction of the mixture with chloroform gave a product which was chromatographed on alumina. Light petroleum eluted a small amount of benzo[*b*]thiophen and

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2-(*pentafluorophenyl*)*benzo*[b]*thiophen* (1·8 g, 40%), m.p. 182—184° (from light petroleum); ^{19}F n.m.r. δ ($CHCl_3$) 138·7 (2- and 6-F), 154·0 (4-F), and 161·9 p.p.m. (3- and 5-F) (Found: C, 55·9; H, 1·8%; *M*, 300. $C_{14}H_5F_5S$ requires C, 56·0; H, 1·7%; *M*, 300). Ether eluted 1,4-*bis*-(2-*benzo*[b]*thienyl*)*tetrafluorobenzene* (0·5 g, 16%), m.p. 284—286° (from chloroform); ^{19}F n.m.r. δ ($CHCl_3$) 139·0 p.p.m. (Found: C, 63·45; H, 2·6%; *M*, 414. $C_{22}H_{10}F_4S_2$ requires C, 63·75; H, 2·4%; *M*, 414).

Reactions of 3-*Benzo*[b]*thienyl-lithium*.—(a) *With pentafluoropyridine*. A solution of pentafluoropyridine (2·54 g, 15·0 mmol) in ether (10 ml) was added dropwise to a stirred suspension of the lithium compound (15·0 mmol) in ether (10 ml) at −70°. The resulting mixture was stirred at −70° for a further 2 h and was then allowed to warm slowly to room temperature. Work-up in the usual way gave 4-(3-*benzo*[b]*thienyl*)*tetrafluoropyridine* (2·1 g, 50%), m.p. 116—118° (from light petroleum); ^{19}F n.m.r. δ (CCl_4) 90·9 (2- and 6-F) and 141·3 p.p.m. (3- and 5-F) (Found: C, 55·45; H, 1·9; N, 4·9%; *M*, 283).

(b) *With hexafluorobenzene*. A solution of hexafluorobenzene (2·79 g, 15·0 mmol) in ether (25 ml) was added dropwise to a stirred suspension of the lithium compound (15·0 mmol) in ether (30 ml) at −70°. The mixture was stirred at −70° for a further 5 h and was then allowed to warm slowly to room temperature. Work-up in the usual way gave a product which was chromatographed on alumina. Light petroleum eluted benzo[*b*]thiophen and 3-(*pentafluorophenyl*)*benzo*[b]*thiophen* (1·1 g, 24·5%), m.p. 164—166° (from light petroleum); ^{19}F n.m.r. δ ($CHCl_3$) 138·4 (2- and 6-F), 149·8 (4-F), and 161·2 p.p.m. (3- and 5-F) (Found: C, 55·7; H, 1·9%; *M*, 300). Ether eluted 1,4-*bis*-(3-*benzo*[b]*thienyl*)*tetrafluorobenzene* (0·4 g, 13%), m.p. 266—268° (from chloroform); ^{19}F n.m.r. δ ($CHCl_3$) 139·1 p.p.m. (Found: C, 63·4; H, 2·6%; *M*, 414).

5-*Methyl*-2-(o-*nitrophenyl*)*benzo*[b]*thiophen*.—A solution of 5-methyl-2-benzo[*b*]thienyl-lithium (27·0 mmol) in ether (40 ml) was prepared in the usual way;[15] its reaction with *o*-nitrofluorobenzene (3·8 g, 27·0 mmol) was performed in a manner similar to that previously described for the synthesis of 2-(*o*-nitrophenyl)benzo[*b*]thiophen to give 5-*methyl*-2-(o-*nitrophenyl*)*benzo*[b]*thiophen* (3·5 g, 48%), m.p. 84—86° (from methanol); τ (CCl_4) 2·15—3·10 (m, aromatic) and 7·52 (CH_3) (Found: C, 66·5; H, 3·9; N, 5·1%; *M*, 269. $C_{15}H_{11}NO_2S$ requires C, 66·9; H, 4·1; N, 5·2%; *M*, 269).

3-*Nitro*-2-*phenylbenzo*[b]*thiophen*.—A mixture of fuming nitric acid (13 ml) and acetic acid (13 ml) was added dropwise to a suspension of 2-phenylbenzo[*b*]thiophen (6·5 g, 30·9 mmol) in acetic acid (26 ml) at 0—5° at such a rate that the temperature did not exceed 10°. The resulting mixture was stirred at 5—10° for a further 4 h and then poured into water. Extraction with chloroform gave a two-component mixture which was chromatographed on alumina. Ether–light petroleum (1 : 4) eluted 3-*nitro*-2-*phenylbenzo*[b]*thiophen* (4·1 g, 52%), m.p. 90—92° (from ethanol); τ (CCl_4) 1·65 (q, J_o 7·0, J_m 2·0 Hz, 4-H) and 2·10—2·68 (m, aromatic) (Found: C, 66·3; H, 3·7; N, 5·5%; *M*, 255. $C_{14}H_9NO_2S$ requires C, 65·9; H, 3·55; N, 5·5%; *M*, 255). Ether eluted the second component (1·43 g, 17%), m.p. 199—201° (from ethanol) (Found: C, 60·65; H, 3·2; N, 7·7. Calc. for $C_{28}H_{17}N_3O_6S_2$: C, 60·55; H, 3·1; N, 7·6%) (see Discussion section for assignment of structure).

3-*Nitro*-2-p-*tolylbenzo*[b]*thiophen* (56%), prepared similarly, had m.p. 98—100° (from ethanol); τ (CCl_4) 1·64 (q, J_o 7·0, J_m 2·5 Hz, 4-H), 2·10—2·80 (m, aromatic), and 7·65 (CH_3) (Found: C, 66·8; H, 4·2; N, 5·0%; *M*, 269. $C_{15}H_{11}NO_2S$ requires C, 66·9; H, 4·1; N, 5·2%; *M*, 269.)

2-(p-*Chlorophenyl*)-3-*nitrobenzo*[b]*thiophen*.—A mixture of fuming nitric acid (7·5 ml) and acetic acid (7·5 ml) was added dropwise to a suspension of 2-(*p*-chlorophenyl)benzo[*b*]-thiophen (2·5 g, 10·2 mmol) in acetic acid (35 ml) at 60—70°, and the resulting mixture was stirred at 60—70° for a further 4 h. It was then cooled and poured into water. Extraction with chloroform gave a two-component mixture which was chromatographed on alumina. Ether–light petroleum (1 : 5) eluted 2-(p-*chlorophenyl*)-3-*nitrobenzo*[b]-*thiophen* (2·0 g, 67%), m.p. 145—147° (from ethanol); τ ($CDCl_3$) 1·62 (q, J_o 6·5, J_m 2·0 Hz, 4-H) and 2·00—2·72 (m, aromatic) [Found: C, 58·35; H, 2·8; N, 4·8%; *M*, 289; *M* + 2, 291 (ratio 3 : 1). $C_{14}H_8ClNO_2S$ requires C, 58·0; H, 2·8; N, 4·8%; *M*, 289; *M* + 2, 291 (ratio 3 : 1)]. Ether eluted a dinitro-derivative (0·62 g, 16%), m.p. 186—188° (from ethanol) [Found: C, 49·9; H, 2·1; N, 8·4%; *M*, 334; *M* + 2, 336 (ratio 3 : 1). Calc. for $C_{14}H_7ClN_2O_4S$: C, 50·25; H, 2·1; N, 8·4%; *M*, 334; *M* + 2, 336 (ratio 3 : 1)].

2-(p-*Bromophenyl*)-3-*nitrobenzo*[b]*thiophen* (58%), prepared similarly, had m.p. 155—157° (from ethanol); τ ($CDCl_3$) 1·57 (q, J_o 7·5, J_m 2·5 Hz, 4-H) and 2·05—2·78 (m, aromatic) [Found: C, 50·7; H, 2·5; N, 4·1%; *M*, 333; *M* + 2, 335 (ratio 1 : 1). $C_{14}H_8BrNO_2S$ requires C, 50·3; H, 2·4; N, 4·2%; *M*, 333; *M* + 2, 335 (ratio 1 : 1)]. A dinitro-compound (10%) was isolated also, in the manner described in the preceding experiment. It had m.p. 176—178° (from ethanol) [Found: C, 44·1; H, 2·2; N, 7·4%; *M*, 378; *M* + 2, 380 (ratio 1 : 1). Calc. for $C_{14}H_7BrN_2O_4S$: C, 44·35; H, 1·9; N, 7·4%; *M*, 378; *M* + 2, 380 (ratio 1 : 1)].

2-(o-*Aminophenyl*)*benzo*[b]*thiophen*.—A slurry of 2-(*o*-nitrophenyl)benzo[*b*]thiophen (4·0 g, 15·7 mmol) in ethanol (40 ml) was added slowly to a well stirred mixture of iron dust (2·8 g, 0·05 g atom), ammonium chloride (2·68 g, 50·0 mmol), and water (30 ml) heated under reflux, and the resulting mixture was heated under reflux with vigorous stirring for a further 3 h. It was then cooled; extraction with ether gave 2-(o-*aminophenyl*)*benzo*[b]*thiophen* (1·3 g, 37%), m.p. 136—138° (from ethanol); τ (CCl_4) 2·10—3·50 (m, aromatic) and 6·00br (exchangeable, NH_2); $\nu_{max.}$ (Nujol) 3460w and 3375w cm^{-1} (NH_2) (Found: C, 74·3; H, 5·0; N, 6·2%; *M*, 225. $C_{14}H_{11}NS$ requires C, 74·6; H, 4·9; N, 6·2%; *M*, 225); *hydrochloride*, m.p. 206—208° (from ethanol); $\nu_{max.}$ (Nujol) 2560br cm^{-1} ($\overset{+}{N}H_3$) (Found: C, 63·8; H, 4·6; N, 5·7. $C_{14}H_{12}ClNS$ requires C, 64·2; H, 4·6; N, 5·4%).

2-(o-*Aminophenyl*)-5-*methylbenzo*[b]*thiophen hydrochloride* (68%), m.p. 209—211° (from ethanol); τ (Me_2SO) 1·90—2·95 (m, aromatic), 4·30br (exchangeable, $\overset{+}{N}H_3$), and 7·60 (CH_3); $\nu_{max.}$ (Nujol) 2560br cm^{-1} ($\overset{+}{N}H_3$) (Found: C, 65·5; H, 5·1; N, 5·0. $C_{15}H_{14}ClNS$ requires C, 65·3; H, 5·1; N, 5·1%); and 3-*amino*-2-*phenylbenzo*[b]*thiophen hydrochloride* (64%), m.p. 204—206° (from ethanol–ether); τ (Me_2SO) 1·73—2·60 (m, aromatic) and 3·35br (exchangeable, $\overset{+}{N}H_3$); $\nu_{max.}$ (Nujol) 2515 cm^{-1} ($\overset{+}{N}H_3$) (Found: C, 63·9; H, 4·7; N, 5·3. $C_{14}H_{12}ClNS$ requires C, 64·2; H, 4·6; N, 5·35%), were prepared similarly.

2-(o-*Azidophenyl*)*benzo*[b]*thiophen*.—A solution of sodium

nitrite (0·28 g, 4·05 mmol) in water (2 ml) was added to a stirred mixture of 2-(*o*-aminophenyl)benzo[*b*]thiophen hydrochloride (1·0 g, 3·85 mmol), concentrated hydrochloric acid (7·5 ml), and water (5 ml) at 0°, and the resulting mixture was stirred at 0° for a further 30 min. This solution was then added dropwise to a solution of sodium azide (0·3 g, 4·6 mmol) and sodium acetate (3·6 g, 43·9 mmol) in water (12 ml) at 0°, and the resulting mixture was stirred at 0° for a further 45 min. The precipitate was filtered off, dried by suction on the filter pad, and chromatographed on alumina. Ether eluted 2-(*o-azidophenyl*)*benzo*[b]*thiophen* (0·5 g, 50%), m.p. 75—77° (decomp.); $\nu_{max.}$ (Nujol) 2110s and 2090s cm^{-1} (N_3). The azide rapidly darkened on exposure to air and was used immediately as described later. Ether–chloroform (4 : 1) (2 : 1) eluted 10*H*-[1]benzothieno[3,2-*b*]indole (2·1 g, 60%), m.p. 250—252° (from benzene) (lit.,[3,4] 252—253°), $\nu_{max.}$ (Nujol) 3400s cm^{-1} (NH).

(b) *From 3-nitro-2-phenylbenzo*[b]*thiophen.* A mixture of the nitro-compound (2·0 g, 7·85 mmol) and triethyl phosphite (2·85 g, 17·2 mmol) was heated under reflux for 24 h. The mixture was then worked up as described in (a) to give a product which was chromatographed on alumina. Ether–light petroleum (1 : 2) eluted starting material (0·7 g 35%), ether–chloroform (1 : 2) eluted 10*H*-[1]benzothieno-[3,2-*b*]indole (0·6 g, 34%), m.p. 250—252° (from benzene), and chloroform eluted *diethyl* N-(*2-phenyl-3-benzo*[b]*thienyl*)*phosphoramidate* (0·16 g, 6%), m.p. 174—176° (from benzene); τ ($CDCl_3$) 1·85—2·70 (m, aromatic), 5·95—6·35 (q, CH_2 coupled to P), 8·30br (exchangeable, NH),

TABLE 1

Cyclisation of nitro-substituted 2-arylbenzo[*b*]thiophens to 10*H*-[1]benzothieno[3,2-*b*]indoles

		Products [a]						
			10*H*-[1]Benzothieno[3,2-*b*]indole			Phosphoramidate (21)		
Starting material	Reaction time (h)	Starting material Yield (%)	Compound	M.p. (°C)	Yield (%)	R	M.p. (°C)	Yield (%)
(13)	8	10	(1)	250—252	60 [b]			
(14)	8	0	(5)	222—224	53			
(6)	10	45	(1)	250—252	23	H	174—176	5
(6)	24	35	(1)	250—252	34	H	174—176	6
(7)	24	20	(2) [c]	250—252 [d]	45	Me		0
(8)	24	12	(3) [c]	258—260 [e]	27	Cl [f]	181—183 [g]	25
(9)	24	10	(4) [c]	256—258 [h]	34	Br [f]	183—185 [g]	31

[a] Yields based on total starting material (*i.e.* not on that consumed). [b] The *N*-ethyl compound (11%) was also isolated. [c] Eluted from an alumina column with ether–light petroleum [1 : 2 for (2) and 1 : 4 for (4)] or ether [for (3)]. [d] From benzene (lit.,[3,5] 256°); picrate, m.p. 181—183° (decomp.) (from ethanol) [lit.,[3,5] 185° (decomp.)]. [e] From benzene (lit.,[4] 258—260°). [f] Eluted from the same column with chloroform. [g] From benzene–light petroleum. [h] From benzene.

TABLE 2

Analytical data for compounds (2)—(4) and (21; R = Cl or Br)

	10*H*-[1]Benzothieno[3,2-*b*]indoles								Phosphoramidates (21)								
		Found (%)				Required (%)					Found (%)				Required (%)		
Compd.	$\nu_{max.}$/cm^{-1} (NH) [a]	C	H	N	Formula	C	H	N	R	$\nu_{max.}$/cm^{-1} (NH) [a]	C	H	N	Formula	C	H	N
(2)	3400	76·0	4·75	5·9	$C_{15}H_{11}NS$	75·9	4·7	5·9									
(3)	3420								Cl	3090 [b]	54·3	4·6	3·6	$C_{18}H_{19}ClNO_3PS$	54·6	4·8	3·5
(4)	3415	55·3	2·7	4·55	$C_{14}H_8BrNS$	55·6	2·7	4·6	Br	3090 [c]	48·9	4·2	3·2	$C_{18}H_{19}BrNO_3PS$	49·1	4·35	3·2

[a] Nujol mulls. [b] τ ($CDCl_3$) 1·85—2·70 (m, aromatic), 5·00br (exchangeable, NH), 5·90—6·40 (q, CH_2 coupled to P), and 8·88 (t, CH_3). [c] τ ($CDCl_3$) 1·85—2·73 (m, aromatic), 4·85br (exchangeable, NH), 5·85—6·32 (q, CH_2 coupled to P), and 8·89 (t, CH_3).

eluted [1]*benzothieno*[3,2-c]*cinnoline* (0·2 g, 22%), m.p. 212—214° (from ethanol) (Found: C, 71·2; H, 3·6; N, 11·8%; *M*, 236. $C_{14}H_8N_2S$ requires C, 71·2; H, 3·4; N, 11·85%; *M*, 236).

3-Azido-2-phenylbenzo[b]*thiophen* (53%), prepared similarly, was an oil, $\nu_{max.}$ (film) 2100s cm^{-1} (N_3), which decomposed in air. It was used immediately following its preparation, as described later.

10H-[1]*Benzothieno*[3,2-b]*indole.*—(a) *From* 2-(o-*nitrophenyl*)*benzo*[b]*thiophen.* A mixture of the nitro-compound (4·0 g, 15·70 mmol) and triethyl phosphite (5·70 g, 34·4 mmol) was heated under reflux for 8 h. The excess of triethyl phosphite and the triethyl phosphate were distilled off at 0·1 mmHg and the residue was chromatographed on alumina. Light petroleum eluted starting material (0·4 g, 10%) and light petroleum–ether (1 : 1) eluted 10-*ethyl*-10H-[1]*benzothieno*[3,2-b]*indole* (0·4 g, 11%), m.p. 118—120° (from ethanol); τ (CCl_4) 2·05—3·00 (m, aromatic), 5·5 (q, *J* 7·0 Hz, CH_2), and 7·52 (t, *J* 7·0 Hz, CH_3) (Found: C, 76·1; H, 5·2; N, 5·3%; *M*, 251. $C_{16}H_{13}NS$ requires C, 76·45; H, 5·2; N, 5·6%; *M*, 251). Chloroform–ether and 8·75—9·05 (t, CH_3); $\nu_{max.}$ (Nujol) 3100br cm^{-1} (NH) (Found: C, 59·8; H, 5·6; N, 3·8%; *M*, 361. $C_{18}H_{20}NO_3PS$ requires C, 59·8; H, 5·6; N, 3·9%; *M*, 361).

The other 2-aryl-3-nitrobenzo[*b*]thiophens were treated similarly with triethyl phosphite. Details of the products are given in Tables 1 and 2.

(c) *From* 2-(o-*azidophenyl*)*benzo*[b]*thiophen.* A solution of the azide (0·3 g, 1·19 mmol) in bis-(2-methoxyethyl) ether (2 ml) was added dropwise to bis-(2-methoxyethyl) ether (3 ml) heated under reflux, and the resulting solution was heated under reflux for a further 1 h. The solvent was distilled off under reduced pressure, the residue was dissolved in chloroform (50 ml), and the chloroform solution was washed with water (4 × 50 ml) and dried ($MgSO_4$). Removal of the solvent by distillation gave 10*H*-[1]-benzothieno[3,2-*b*]indole (0·16 g, 60%), m.p. 250—252° (from benzene).

(d) *From 3-azido-2-phenylbenzo*[b]*thiophen.* A solution of the azide (0·5 g, 2·0 mmol) in bis-(2-methoxyethyl) ether (2 ml) was added dropwise to bis-(2-methoxyethyl) ether (8 ml) heated under reflux, and the resulting mixture

was heated under reflux for a further 1 h. It was then worked up as described in (c) to give 10*H*-[1]benzothieno-[3,2-*b*]indole (0·25 g, 56%), identical with the other samples.

8-*Methyl*-10H-[1]*benzothieno*[3,2-b]*indole* (53%), prepared from 5-methyl-2-(*o*-nitrophenyl)benzo[*b*]thiophen in a manner similar to that described in (a) for the parent system, had m.p. 222—224° (from benzene) (lit.,[4] 222—224°); τ [$(CD_3)_2CO$] 2·10—2·92 (m, aromatic) and 7·50 (CH_3); $\nu_{max.}$ (Nujol) 3420s cm^{-1} (NH).

Bromination of 10H-[1]*benzothieno*[3,2-b]*indole*.—A solution of bromine (0·89 g, 5·56 mmol) in chloroform (10 ml) was added slowly to a stirred mixture of 10*H*-[1]benzothieno[3,2-*b*]indole (1·25 g, 5·6 mmol) and chloroform (30 ml) at room temperature, and the resulting mixture was stirred at room temperature for a further 48 h. Sufficient chloroform was then added to dissolve the precipitate, and the resulting solution was washed with aqueous sodium hydrogen carbonate (10%; 3 × 50 ml) and dried ($MgSO_4$). Removal of the solvent by distillation and crystallisation of the residue twice from benzene gave 2-*bromo*-10H-[1]*benzothieno*[3,2-b]*indole* (0·95 g, 57%), m.p. 256—258°, identical (i.r.; mixed m.p.) with the sample prepared by treating 2-(*p*-bromophenyl)-3-nitrobenzo[*b*]-thiophen with triethyl phosphite (see Table 1).

2-*Nitro*-3-*phenylbenzo*[b]*thiophen*.— 3-Phenylbenzo[*b*]-thiophen [7] was nitrated in a manner similar to that for the nitration of the 2-phenyl isomer. The *product* (53%) had m.p. 136—138° (from ethanol); τ ($CDCl_3$) 2·05—2·70 (m, aromatic) (Found: C, 65·7; H, 3·7; N, 5·4%; *M*, 255).

5-*Bromo*-2-*nitro*-3-*phenylbenzo*[b]*thiophen* (83%), prepared similarly, had m.p. 130—132° (from ethanol); τ ($CDCl_3$) 2·10—2·70 (m, aromatic) [Found: C, 50·6; H, 2·5; N, 4·0%; *M*, 333; *M* + 2, 335 (ratio 1 : 1). $C_{14}H_8BrNO_2S$ requires C, 50·3; H, 2·4; N, 4·2%; *M*, 333; *M* + 2, 335 (ratio 1 : 1)].

Reaction of 2-*Nitro*-3-*phenylbenzo*[b]*thiophen with Triethyl Phosphite*.—A mixture of the nitro-compound (3·0 g, 11·8 mmol) and triethyl phosphite (4·03 g, 24·3 mmol) was heated under reflux for 8 h. The excess of reagent and the triethyl phosphate were distilled off at 0·1 mmHg and the residue was chromatographed on alumina. Light petroleum eluted 2-(*diethylamino*)-3-*phenylbenzo*[b]*thiophen* (0·3 g, 9%), b.p. 110—114° at 3 mmHg (Kugelrohr apparatus); τ (CCl_4) 2·20—2·92 (m, aromatic), 7·00 (q, *J* 7·0 Hz, CH_2), and 9·00 (t, *J* 7·0 Hz, CH_3) (Found: C, 76·6; H, 6·7; N, 5·0%; *M*, 281. $C_{18}H_{19}NS$ requires C, 76·8; H, 6·5; N, 5·0%; *M*, 281). Chloroform eluted *diethyl* N-(3-*phenyl*-2-*benzo*[b]*thienyl*)*phosphoramidate* (0·38 g, 9%), m.p. 84—86° (from light petroleum); τ ($CDCl_3$) 2·15—2·81 (m, aromatic), 4·39br (exchangeable, NH), 5·50—6·10 (q, CH_2 coupled to P), and 8·62 (t, CH_3); $\nu_{max.}$ (Nujol) 3080br cm^{-1} (NH) (Found: C, 59·45; H, 5·3; N, 3·9%; *M*, 361).

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