Condensed Thiophen Ring Systems. Part XVII.[1] A New Synthesis of 10*H*-Indeno[1,2-*b*][1]benzothiophen

By **Brian Iddon,* Hans Suschitzky, and David S. Taylor,** The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT

2-Phenylbenzo[*b*]thiophen-3-carbaldehyde *p*-tolylsulphonylhydrazone (7) reacted with sodium methoxide in hot bis-(2-methoxyethyl) ether to give the title compound (2) (30%), together with *NN'*-bis-(2-phenylbenzo[*b*]-thiophen-3-ylidene)hydrazine (15) (<5%), 2-phenyl-3-*p*-tolylsulphonylmethylbenzo[*b*]thiophen (8) (10·5%), and tar. By contrast, 3-phenylbenzo[*b*]thiophen-2-carbaldehyde *p*-tolylsulphonylhydrazone (13) gave a complex mixture of products which contained 2-hydroxymethyl-3-phenylbenzo[*b*]thiophen (14) (18%).

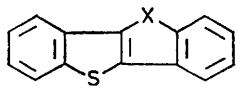
PREVIOUSLY [2] we prepared 10*H*-[1]benzothieno[3,2-*b*]-indole (1) from 3-nitro-2-phenylbenzo[*b*]thiophen (5) and triethyl phosphite as well as by thermolysis of 3-azido-2-phenylbenzo[*b*]thiophen (6) in bis-(2-methoxyethyl) ether. With triethyl phosphite, 2-nitro-3-phenylbenzo-[*b*]thiophen (10) gives small amounts of the phosphoramidate (11) and the amine (12).[2] The failure of the nitro-compound (10) to yield a cyclised product, isomeric with compound (1), was attributed to *peri*-interaction between the 4-proton and the phenyl ring, which causes the latter to be twisted out of the plane of the benzo[*b*]-thiophen ring. This prevents the nitrene from adopting a conformation suitable for insertion to occur (see also refs. 1 and 3). We now report the results of a parallel study in which the *p*-tolylsulphonylhydrazones (7) and

[1] Part XVI, B. Iddon, H. Suschitzky, D. S. Taylor, and K. E. Chippendale, preceding paper.

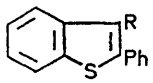
[2] K. E. Chippendale, B. Iddon, and H. Suschitzky, *J.C.S. Perkin I*, 1972, 2023; *Chem. Comm.*, 1971, 203.

[3] Part XV, K. E. Chippendale, B. Iddon, H. Suschitzky, and D. S. Taylor, *J.C.S. Perkin I*, 1974, 1168.

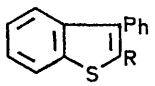
(13) were submitted to the Bamford–Stevens reaction.[1,3-8]



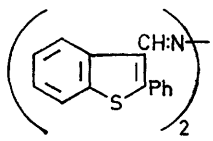
(1) X = NH
(2) X = CH_2
(3) X = CO
(4) X = C:CClPh



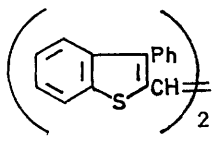
(5) R = NO_2
(6) R = N_3
(7) R = CH:N·NH·SO_2·C_6H_4Me – *p*
(8) R = CH_2·SO_2·C_6H_4Me – *p*
(9) R = CHN_2



(10) R = NO_2
(11) R = NH·P(:O)$(OEt)_2$
(12) R = NEt_2
(13) R = CH:N·NH·SO_2·C_6H_4Me – *p*
(14) R = CH_2·OH



(15)



(16)

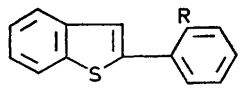
The *p*-tolylsulphonylhydrazone (7) reacted with sodium methoxide in hot bis-(2-methoxyethyl) ether to give a complex mixture of products from which 10*H*-indeno[1,2-*b*][1]benzothiophen (2), 2-phenyl-3-*p*-tolylsulphonylmethylbenzo[*b*]thiophen (8), and a small amount of the azine (15) were isolated. Our sample of compound (2) was identical with one prepared[9] by reduction of indeno[1,2-*b*][1]benzothiophen-10-one (3), obtained by Friedel–Crafts cyclisation of 2-phenylbenzo[*b*]thiophen-3-carboxylic acid.[10] Barton *et al.*[11] prepared 10*H*-indeno[1,2-*b*][1]benzothiophen (2) by reaction of compound (4) with potassium hydroxide in hot triethylene glycol. Compound (4) is obtained in high yield when 1,2-bis(phenethynyl)benzene is treated with sulphur dichloride.[11]

The synthetic utility of the Bamford–Stevens reaction depends on the extent to which side reactions occur. The intermediate diazoalkanes are known to give rise to azines, sulphones, and alkenes by carbenic as well as cationic mechanisms.[4,7,12,13] Attempts were made to prepare the diazoalkane (9) by Farnum's modification[14] of the Bamford–Stevens reaction. The *p*-tolylsulphonylhydrazone (7) did not react, however, with sodium methoxide in pyridine at 40° and it yielded a complex mixture of products at 60° from which the azine (15) and 2-phenylbenzo[*b*]thiophen-3-carbaldehyde were isolated. Formation of aldehydes during a Bamford–Stevens reaction is known.[15]

In a Bamford–Stevens reaction 3-phenylbenzo[*b*]-thiophen-2-carbaldehyde *p*-tolylsulphonylhydrazone (13) also gave a complex mixture of products from which we isolated only 2-hydroxymethyl-3-phenylbenzo[*b*]-thiophen (14) and a trace of the alkene (16). Failure to isolate the insertion product isomeric with compound (2) parallels the failure to cyclise 2-nitro-3-phenylbenzo[*b*]thiophen (10) and may be explained similarly (see before). Hydrolysis of sulphinate esters formed by decomposition of diazoalkenes is known to produce alcohols.[4,12,15]

It is noteworthy that Denney and Klemchuk[16] obtained a deuteriofluorene by irradiation of 2-(2-deuteriophenyl)phenyldiazomethane.

By analogy with the improved preparation of 10*H*-[1]benzothieno[3,2-*b*]indole (1) from 2-(2-benzo[*b*]thienyl)nitrobenzene (19) and triethyl phosphite or by the action of heat on 2-(2-benzo[*b*]thienyl)phenyl azide (20)[2] we planned to submit the *p*-tolylsulphonylhydrazone of 2-(2-benzo[*b*]thienyl)benzaldehyde (21) to the Bamford–Stevens reaction. An attempt to prepare the aldehyde (21) by selective oxidation of the methyl group in 2-(2-benzo[*b*]thienyl)toluene (17) with selenium dioxide failed. The starting material (17) was prepared (see Experimental section) from 2-benzo[*b*]thienyllithium and 2-methylcyclohexanone by a procedure similar to that described[17] for the synthesis of 3-phenylbenzo[*b*]thiophen.



(17) R = Me
(18) R = NH_2
(19) R = NO_2
(20) R = N_3
(21) R = CHO
(22) R = Br

[4] W. Kirmse, in 'Carbene Chemistry,' Academic Press, New York, 2nd edn., 1971, ch. 1, p. 29, and references cited therein.
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[7] G. V. Garner, D. B. Mobbs, H. Suschitzky, and J. S. Millership, *J. Chem. Soc.* (*C*), 1971, 3693.
[8] T. Takada, S. Kunugi, and S. Ohki, *Chem. and Pharm. Bull.* (*Japan*), 1971, **19**, 982.
[9] F. Sauter, personal communication.
[10] F. Sauter and A. Dzerovicz, *Monatsh.*, 1969, **100**, 913.
[11] T. J. Barton, A. J. Nelson, and J. Clardy, *J. Org. Chem.*, 1971, **36**, 3995.
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[14] D. G. Farnum, *J. Org. Chem.*, 1963, **28**, 870.
[15] J. W. Wilt, C. A. Schneider, H. F. Dabek, J. F. Kraemer, and W. J. Wagner, *J. Org. Chem.*, 1966, **31**, 1543, and references contained therein.
[16] D. B. Denney and P. P. Klemchuk, *J. Amer. Chem. Soc.*, 1958, **80**, 3289.
[17] D. S. Rao and B. D. Tilak, *J. Sci. Ind. Res.* (*India*), 1959, **18B**, 77.

Next, the possibility was examined of preparing the aldehyde (21) by successive treatment of 2-(2-benzo[*b*]thienyl)bromobenzene (22) with n-butyl-lithium, dimethylformamide, and acid. However, several attempts to prepare the bromo-compound failed. A Gattermann reaction starting with 2-(2-benzo[*b*]thienyl)aniline (18) [2] gave only a bromo[1]benzothieno[3,2-*c*]cinnoline of unknown orientation. This was not unexpected in the light of earlier results.[18] 2-Benzo[*b*]thienyl-lithium reacted with 2-bromochlorobenzene in the presence of piperidine [2] to give, after addition of water to the reaction mixture, benzo[*b*]thiophen (39% yield), 2-phenylbenzo[*b*]thiophen (7%), and a compound which appears to be 1,2-bis-(2-benzo[*b*]thienyl)benzene (10%). Finally, 2-bromophenacyl phenyl sulphide was cyclised in polyphosphoric acid in the hope that a mixture of 2-(2- and 3-benzo[*b*]thienyl)bromobenzene would result.[19] However, in agreement with the results of Benati *et al.*,[20] this gave only the 3-isomer of the required compound (22).

EXPERIMENTAL

General comments are as given previously.[1]

3-Phenylbenzo[*b*]thiophen-2-carbaldehyde (49%), m.p. 87—89° (lit.,[21] 87—89°) [p-*tolylsulphonylhydrazone* (13), m.p. 152—153° (from acetic acid), $\nu_{max.}$ (Nujol) 3185 cm^{-1} (NH) (Found: C, 64·9; H, 4·6; N, 6·9. $C_{22}H_{18}N_2O_2S_2$ requires C, 65·0; H, 4·5; N, 6·9%)], and 2-phenylbenzo[*b*]thiophen-3-carbaldehyde [22] (48%), b.p. 102—105° at 0·1 mmHg [p-*tolylsulphonylhydrazone* (7), m.p. 188—190° (from acetic acid), $\nu_{max.}$ (Nujol) 3185 cm^{-1} (NH) (Found: C, 64·8; H, 4·5; N, 7·0%)] were prepared by literature procedures.

Decomposition of 2-*Phenylbenzo*[b]*thiophen*-3-*carbaldehyde* p-*Tolylsulphonylhydrazone* (7).—A solution of the tosylhydrazone (1·0 g, 2·5 mmol) in bis-(2-methoxyethyl) ether (10 ml) was added dropwise to a stirred suspension of sodium methoxide (0·25 g, 4·6 mmol) in bis-(2-methoxyethyl) ether (50 ml) heated under reflux, and the mixture was heated under reflux for a further 15 min. The solvent was distilled off under reduced pressure and the residue was extracted with benzene. This yielded a product which was chromatographed on alumina. Elution with light petroleum gave 10*H*-indeno[1,2-*b*][1]benzothiophen (2) (0·17 g, 30%), m.p. 205—206° (from benzene) (lit.,[11] 201—202°), τ ($CDCl_3$) 2·00—2·75 (8H, m, aromatic) and 6·15 (2H, s, CH_2) (Found: C, 81·2; H, 4·4%; M^+, 222. $C_{15}H_{10}S$ requires C, 81·0; H, 4·5%; *M*, 222). Elution with benzene gave a mixture of products which left a residue of NN′-*bis*-(2-*phenylbenzo*[b]*thiophen*-3-*ylidene*)*hydrazine* (15) (10 mg, <5%) when washed with acetone, m.p. 266—268°, *m/e* 471·1057 (M^+, 1%. $C_{30}H_{20}N_2S$ requires 472·1067) and 236·0529 (base peak, arising by N–N cleavage. $C_{15}H_{10}NS$ requires 236·0534). The azine (15) was insufficiently soluble in all useful n.m.r. solvents. Consequently, its identification is based on its mass spectrum only. Elution with chloroform gave a solution which deposited 2-*phenyl*-3-p-*tolylsulphonylmethylbenzo*[b]*thiophen* (8) (0·1 g, 10·5%), m.p. 155—156° (from ethanol), τ ($CDCl_3$) 1·90—2·95 (13H, m, aromatic), 5·25 (2H, s, CH_2), and 7·60 (3H, s, CH_3) (Found: C, 69·7; H, 4·6%; M^+, 378. $C_{22}H_{18}O_2S_2$ requires C, 69·8; H, 4·8%; *M*, 378).

Decomposition of 3-*Phenylbenzo*[b]*thiophen*-2-*carbaldehyde* p-*Tolylsulphonylhydrazone* (13).—Similar decomposition of this tosylhydrazone (1·0 g, 2·5 mmol) gave a product which was chromatographed on alumina. Elution with light petroleum and chloroform gave two fractions, (A) and (B) respectively, which were shown by t.l.c. to be mixtures. Each of these fractions was chromatographed on several 20 × 20 cm glass plates covered with a 1·0 mm layer of silica. Elution of fraction (A) with light petroleum (b.p. 30—40°) gave several bands, one of which appeared to contain 1,2-*bis*-(3-*phenyl*-2-*benzo*[b]*thienyl*)*ethylene* (16) (2 mg, <5%). The molecular ion (*m/e* 444) for this compound was detected with an A.E.I. MS12 but not with an A.E.I. MS902S instrument. Fragmentation across the alkene double bond occurs extremely readily to give a fragment ion at *m/e* 222·0498 (90%. $C_{15}H_{10}S$ requires 222·0503) and is followed by loss of hydrogen, to give the base peak at *m/e* 221·0427 ($C_{15}H_9S$ requires 221·0425). Lack of material prevented us from carrying out further studies. Elution of fraction (B) with ether–ethyl acetate (1 : 3) gave 2-*hydroxymethyl*-3-*phenylbenzo*[b]*thiophen* (14) (0·1 g, 18%), b.p. 169—171° at 0·4 mmHg, $\nu_{max.}$ (film) 3400br cm^{-1} (OH), τ (CCl_4) 2·15—2·95 (9H, m, aromatic), 5·28 (2H, s, CH_2), and 7·50br (1H, s, exchangeable, OH) (Found: C, 74·8; H, 4·7%; M^+, 240. $C_{15}H_{12}OS$ requires C, 75·0; H, 5·0%; *M*, 240).

Attempted Synthesis of 3-*Diazomethyl*-2-*phenylbenzo*[b]-*thiophen* (9).—A mixture of 2-phenylbenzo[*b*]thiophen-3-carbaldehyde *p*-tolylsulphonylhydrazone (7) (0·5 g, 1·25 mmol), sodium methoxide (0·13 g, 2·4 mmol), and pyridine (7 ml) was heated at 60° for 15 min. The solvent was distilled off under reduced pressure, the residue was extracted with benzene, and the combined extracts were chromatographed on alumina. Elution with light petroleum–benzene (3 : 1) gave *NN′*-bis-(2-phenylbenzo[*b*]thiophen-3-ylidene)hydrazine (15) (0·05 g, 17%), m.p. 263—264°, identical (i.r. spectrum) with the sample prepared as described before. Elution with benzene gave 2-phenylbenzo[*b*]thiophen-3-carbaldehyde (0·06 g, 20%), identical (m.p. and i.r. spectrum) with an authentic sample.

1-(2-*Benzo*[b]*thienyl*)-2-*methylcyclohexanol*.—A solution of n-butyl-lithium (149·0 mmol) in hexane (52·5 ml) was added dropwise to a stirred solution of benzo[*b*]thiophen (20·0 g, 149·0 mmol) in anhydrous ether (150 ml) at 0°, and the resulting mixture was stirred for 1 h at 0°. Freshly distilled 2-methylcyclohexanone (16·7 g, 149·0 mmol) in ether (25 ml) was added and the mixture was stirred at 0° for a further 1 h. Water (150 ml) was added and the mixture was kept at 20° for 18 h. The organic layer was separated and dried ($MgSO_4$); distillation left a residue which was chromatographed on alumina. Light petroleum eluted benzo[*b*]thiophen (10·0 g, 50% recovery) and ether eluted 1-(2-*benzo*[b]*thienyl*)-2-*methylcyclohexanol* (15·2 g, 83% based on benzo[*b*]thiophen consumed), m.p. 118—119° (from light petroleum), $\nu_{max.}$ 3280br cm^{-1} (OH), τ ($CDCl_3$) 2·10—2·80 (4H, m, aromatic), 2·75 (1H, s, 3-H), 7·92br (1H, s, exchangeable, OH), 7·50—8·60 (9H, m, cyclohexane

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[20] L. Benati, G. Martelli, P. Spagnolo, and M. Tiacco, *J. Chem. Soc.* (*B*), 1969, 472.

[21] R. P. Dickinson, B. Iddon, and R. G. Sommerville, *Internat. J. Sulfur Chem.*, 1973, **8**, 233.

[22] R. P. Dickinson and B. Iddon, *J. Chem. Soc.* (*C*), 1970, 2592.

ring), and 9·06 (3H, d, *J* 5·0 Hz, CH_3) (Found: C, 73·1; H, 7·3. $C_{15}H_{18}OS$ requires C, 73·2; H, 7·4%).

1-(2-*Benzo*[b]*thienyl*)-2-*methylcyclohexene*.—A solution of 1-(2-benzo[*b*]thienyl)-2-methylcyclohexanol (2·0 g, 8·0 mmol) in toluene (50 ml) was heated under reflux for 6 h with azeotropic removal of water (Dean–Stark apparatus). The solvent was distilled off under reduced pressure and the residue was crystallised from light petroleum, to give 1-(2-*benzo*[b]*thienyl*)-2-*methylcyclohexene* (1·75 g, 96%), m.p. 89·5—91°, τ ($CDCl_3$) 2·20—2·85 (4H, m, aromatic), 2·94 (1H, s, 3-H), 7·40—8·50 (8H, m, 4 × CH_2), and 9·01 (3H, s, CH_3) (Found: C, 79·2; H, 6·9. $C_{15}H_{16}S$ requires C, 78·9; H, 7·1%).

2-(2-*Benzo*[b]*thienyl*)*toluene* (17).—A mixture of the cyclohexene derivative (15·0 g, 66·0 mmol), chloranil (32·5 g, 132·0 mmol), and toluene (250 ml) was heated under reflux for 20 h, then cooled, diluted with benzene, and filtered. The filtrate was washed successively with 2M-sodium hydroxide and water, and dried ($MgSO_4$). Distillation under reduced pressure left a residue which was chromatographed on alumina. Light petroleum eluted benzo[*b*]thiophen (3·0 g, 34%), and 2-(2-*benzo*[b]*thienyl*)-*toluene* (17) (4·5 g, 30%), m.p. 92—94° (from light petroleum), τ (CCl_4) 2·10—2·90 (9H, m, aromatic) and 7·58 (3H, s, CH_3) (Found: C, 80·7; H, 5·6%; M^+, 224. $C_{15}H_{12}S$ requires C, 80·3; H, 5·4%; *M*, 224).

Diazotisation of 2-(2-*Benzo*[b]*thienyl*)*aniline* (18).—A cold (0°) solution of sodium nitrite (0·28 g, 4·1 mmol) in water (1 ml) was added dropwise to a stirred solution of 2-(2-benzo[*b*]thienyl)aniline (18) hydrochloride [2] (1·0 g, 3·85 mmol) in a mixture of water (10 ml) and 48% hydrobromic acid (25 ml) at 0°, and the mixture was stirred for 10 min at 0°. Copper powder (0·05 g) was added and the mixture was stirred for a further 1·5 h at 0°, then heated on a water-bath for 1 h. The resulting mixture was diluted with water (50 ml) and extracted with chloroform, to give a product which was chromatographed on alumina. Chloroform eluted a bromo[1]benzothieno[3,2-*c*]cinnoline (0·25 g, 21%), m.p. 216—218° (Found: C, 53·1; H, 2·0; N, 9·3%; M^+, 315. Calc. for $C_{14}H_7BrN_2S$: C, 53·3; H, 2·2; N, 8·9%; *M*, 315).

Reaction of 2-*Benzo*[b]*thienyl-lithium with* 2-*Bromochlorobenzene*.—A solution of 2-bromochlorobenzene (3·75 g, 19·5 mmol) and freshly distilled piperidine (0·9 g, 11·0 mmol) in ether (25 ml) was added dropwise to a stirred solution of 2-benzo[*b*]thienyl-lithium (37·5 mmol) in ether (50 ml) at 0°, and the resulting mixture was heated under reflux for 7 h. It was then kept at ambient temperature for 18 h, the solvent was distilled off, and the residue was chromatographed on alumina. Light petroleum eluted benzo[*b*]thiophen (1·95 g, 39% recovery) and 2-phenylbenzo[*b*]thiophen (0·35 g, 7%), identical (m.p. and i.r. spectrum) with authentic samples. Ether eluted 1,2-*bis*-(2-*benzo*[b]*thienyl*)*benzene* (0·4 g, 10%), m.p. 235—236° [from light petroleum–benzene (1 : 1)] (Found: C, 76·9; H, 4·0%; M^+, 342. $C_{22}H_{14}S_2$ requires C, 77·0; H, 4·1%; *M*, 342).

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