

Condensed Thiophen Ring Systems. Part XVI.¹ Derivatives of 11H-[1]Benzothieno[2,3-*b*][1]benzothiopyran

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Deoxygenation of 2-(2-benzo[*b*]thienylthio)nitrobenzene (2) with triethyl phosphite and thermolysis of 2-(2-benzo[*b*]thienylthio)phenyl azide (3) gave 2-(2-benzo[*b*]thienylthio)-*NN*-diethylaniline (5) and 2-(2-benzo[*b*]thienylthio)aniline (4), respectively. In a Bamford–Stevens reaction the tosylhydrazone of the aldehyde (6) gave 2-nitro-11*H*-[1]benzothieno[2,3-*b*][1]benzothiopyran (10), which was prepared also by thermolysis of the diazomethane derivative (7) and by reduction of the thiopyrylium salt (24; X = Cl) with sodium borohydride. Reaction of the aldehyde (6) with phosphoryl chloride in toluene gave the salt (24; X = Cl) and Friedel–Crafts cyclisation of the acid chloride (9) gave 2-nitro[1]benzothieno[2,3-*b*][1]benzothiopyran-11-one (12). Various reactions of the ketone (12) are reported.

PHENOTHIAZINE is formed by thermolysis of 2-(phenylthio)phenyl azide or by deoxygenation of 2-(phenylthio)nitrobenzene.² By analogy, we attempted to prepare the heterocycle (1) by reaction of 2-(2-benzo[*b*]thienylthio)nitrobenzene (2) with triethyl phosphite. This gave mainly tar, together with starting material and 2-(2-benzo[*b*]thienylthio)-*NN*-diethylaniline (5). Compound (5) arises presumably by formation of 2-(2-benzo[*b*]thienylthio)aniline (4) and its alkylation by the excess of triethyl phosphite. The amine (4) was isolated, together with tar and starting material, when 2-(2-benzo[*b*]thienylthio)phenyl azide (3) was heated in xylene. Thermolysis of the azide (3) in bis-(2-methoxyethyl) ether gave only tar.

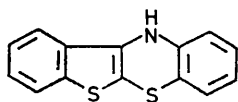
In contrast, although decomposition of the *p*-tolylsulphonylhydrazone of 2-(2-benzo[*b*]thienylthio)-5-nitrobenzaldehyde (6) with sodium methoxide in bis-(2-methoxyethyl) ether (Bamford–Stevens reaction^{3,4}) gave a complex mixture of products, the cyclised compound, namely 2-nitro-11*H*-[1]benzothieno[2,3-*b*][1]benzothiopyran (10), was isolated in 15% yield. In an attempt to improve the yield (*cf.* ref. 3) the diazomethane derivative (7) was prepared by Farnum's⁵ modification of the Bamford–Stevens reaction and heated in bis-(2-methoxyethyl) ether; this also gave a complex mixture of products. Partial chromatographic separation of this mixture yielded the heterocycle (10), but in only 10% yield, and a second compound to which we assign the structure (20) on the basis of its spectroscopic properties.

Thermolysis of a diazomethane derivative is believed⁶ to produce a singlet carbene which can lead to the formation of an alkene as set out in Scheme 1.^{3,7} Isolation of 1,2-bis-[2-(2-benzo[*b*]thienylthio)-5-nitrophenyl]ethylene (20) suggests that 2-nitro-11*H*-[1]benzothieno[2,3-*b*][1]benzothiopyran (10) may be formed by insertion of the carbene at the electron-rich 3-position of the thiophen ring, as shown in Scheme 2. The positive charge in the intermediate (23) is stabilised by the adjacent sulphur atoms. Denney and Klemchuk⁸ pro-

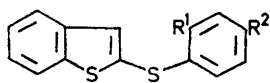
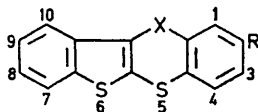
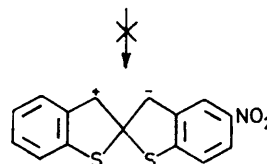
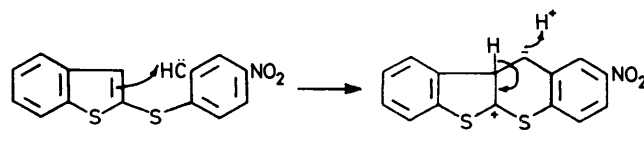
pyran (10), was isolated in 15% yield. In an attempt to improve the yield (*cf.* ref. 3) the diazomethane derivative (7) was prepared by Farnum's⁵ modification of the Bamford–Stevens reaction and heated in bis-(2-methoxyethyl) ether; this also gave a complex mixture of products. Partial chromatographic separation of this mixture yielded the heterocycle (10), but in only 10% yield, and a second compound to which we assign the structure (20) on the basis of its spectroscopic properties.

¹ Part XV, K. E. Chippendale, B. Iddon, H. Suschitzky, and D. S. Taylor, *J.C.S. Perkin I*, 1974, 1168.
² J. I. G. Cadogan, *Accounts Chem. Res.*, 1972, **5**, 303; R. M. Scowston, in *MIP International Review of Science, Organic Chemistry Series One*, vol. 4, Heterocyclic Compounds, ed. K. Schofield, Butterworths, London, 1973, ch. 9, p. 285; J. I. G. Cadogan and R. K. Mackie, *Chem. Soc. Rev.*, 1974, **3**, 87.
³ R. Garner, *Tetrahedron Letters*, 1968, 221.
⁴ W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 1952, 4735.
⁵ D. G. Farnum, *J. Org. Chem.*, 1963, **28**, 870.
⁶ R. A. Moss, *Chem. Eng. News*, June 16th, 1969, 60.
⁷ G. V. Garner, D. B. Mobbs, H. Suschitzky, and J. S. Miller-ship, *J. Chem. Soc. (C)*, 1971, 3693.
⁸ D. B. Denney and P. P. Klemchuk, *J. Amer. Chem. Soc.*, 1958, **80**, 3289.

posed a similar mechanism for the formation of a deuteriofluorene by irradiation of 2-(2-deuteriophenyl)phenyldiazomethane. These syntheses of the new heterocyclic



(1)

(2) R¹ = NO₂, R² = H(3) R¹ = N₃, R² = H(4) R¹ = NH₂, R² = H(5) R¹ = NEt₂, R² = H(6) R¹ = CHO, R² = NO₂(7) R¹ = CHN₂, R² = NO₂(8) R¹ = CO₂H, R² = NO₂(9) R¹ = COCl, R² = NO₂(10) R = NO₂, X = CH₂(11) R = NH₂, X = CH₂(12) R = NO₂, X = CO(13) R = NH₂, X = CO(14) R = NO₂, X = CH·OH

(22)

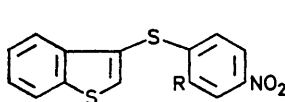
(23)

(10)

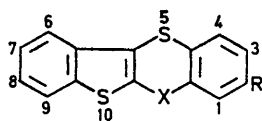
SCHEME 2

amounts in the complex mixture obtained by decomposition of 2-(3-benzo[*b*]thienylthio)-5-nitrophenyldiazomethane (16) in bis-(2-methoxyethyl) ether. A compound was isolated in small quantities from this reaction mixture which is thought to be *NN'*-bis-[2-(2-benzo[*b*]thienylthio)-5-nitrobenzylidene]hydrazine (21) on the basis of its spectroscopic properties. The only derivatives of 11*H*-[1]benzothieno[3,2-*b*][1]benzothiopyran reported previously are compounds (18) and (19), which are by-products in the synthesis of 2-(1,2-benzodithiol-3-ylidene)benzo[*b*]thiophen-3(2*H*)-one from 3-methylthio-1,2-benzodithiolium perchlorate and benzo[*b*]thiophen-3(2*H*)-one.¹⁰ If we assume that the mechanism shown in Scheme 2 operates, the failure to isolate a cyclised product [*i.e.* (17)] in significant quantities in this series may be due to the fact that cyclisation at the 2-position of the thiophene ring is less favoured because the electron density is lower than at the 3-position. Furthermore, the intermediate analogous to (23) would contain a positive charge adjacent to only one sulphur atom and therefore would be expected to be less stable than the intermediate (23).

The synthesis of phenothiazines mentioned before involves a molecular rearrangement.² In order to confirm its identity, 2-nitro-11*H*-[1]benzothieno[2,3-*b*][1]benzothiopyran (10) was prepared unambiguously by reduction with sodium borohydride of the thiopyrylium salt (24; X = Cl) formed in a Bradsher reaction from 2-(2-benzo[*b*]thienylthio)-5-nitrobenzaldehyde (6) and phosphoryl chloride in toluene. Thus, the carbene generated by decomposition of the *p*-tolylsulphonylhydrazone of the aldehyde (6) or the diazomethane derivative (7) does give this compound and no rearrangement *via* the dipolar species (22) (Scheme 2)

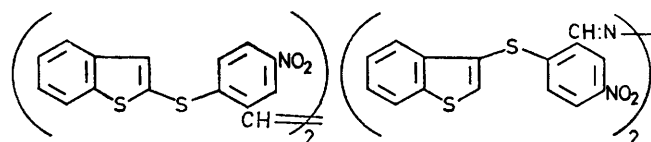


(15) R = CHO

(16) R = CHN₂(17) R = NO₂, X = CH₂

(18) R = H, X = CO

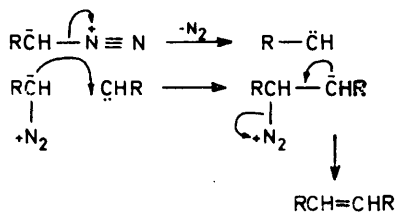
(19) R = H, X = CS



(20)

(21)

system (10) represent the first examples of carbene insertion from an *ortho*-side-chain into a benzo[*b*]thiophene ring. Previously⁹ we have prepared 10*H*-[1]benzothieno[3,2-*b*]indole from 2-(2-benzo[*b*]thienyl)nitrobenzene and triethyl phosphite as well as by thermolysis



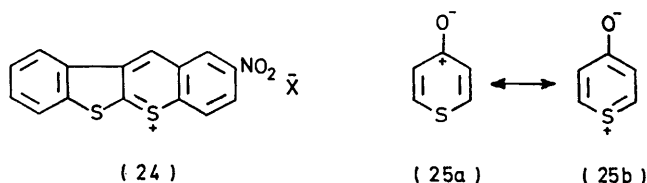
SCHEME 1

of 2-(2-benzo[*b*]thienyl)phenyl azide in bis-(2-methoxyethyl) ether.

⁹ K. E. Chippendale, B. Iddon, and H. Suschitzky, *J.C.S. Perkin I*, 1972, 2023; *Chem. Comm.*, 1971, 203.

¹⁰ D. B. J. Easton, D. Leaver, and D. M. McKinnon, *J. Chem. Soc. (C)*, 1968, 642.

occurs. The aldehyde (6) reacted successively with 48% aqueous hydrobromic acid and sodium borohydride to give a mixture of 2-nitro-11*H*-[1]benzothieno[2,3-*b*]-[1]benzothiopyran (10) (4% yield) and 2-nitro[1]benzothieno[2,3-*b*][1]benzothiopyran-11-one (12) (42% yield), presumably by reaction of the thiopyrylium salt (24; X = Br) with water followed by dismutation of the alcohol (14) produced.¹¹



In an alternative approach to the synthesis of the benzothienobenzothiopyran (10) 2-nitro[1]benzothieno[2,3-*b*][1]benzothiopyran-11-one (12) (56%) was prepared by a Friedel-Crafts cyclisation of 2-(2-benzo[*b*]thienylthio)-5-nitrobenzoyl chloride (9). Various attempts to reduce selectively the carbonyl group in compound (12) failed. Wolff-Kishner reduction surprisingly yielded only 2-amino[1]benzothieno[2,3-*b*][1]benzothiopyran-11-one (13) (28%), which was prepared also for confirmation purposes by reduction of compound (12) with iron and ammonium chloride. A modified Wolff-Kishner procedure reported¹² to reduce sterically hindered carbonyl groups gave an intractable tar. Reduction with tin and hydrochloric acid gave mainly starting material and tar, together with small amounts of the amine (13) and a second amine to which we assign the structure (11) on the basis of its spectroscopic properties. 2-Nitro[1]benzothieno[2,3-*b*][1]benzothiopyran-11-one (12) did not react with sodium borohydride or aluminium isopropoxide and it gave an intractable tar with lithium aluminium hydride. It failed to react also with hydroxylamine and hydrazine and gave only starting material (60% recovery) and tar with an equivalent amount of *n*-butyl-lithium. A molecular model of this compound shows that the carbonyl group is sterically hindered by the 1- and 10-protons. Its behaviour in the reactions described is reminiscent, however, of the behaviour of 4-pyrones and 1-thio-4-pyrones.^{13,14} 1-Thio-4-pyrones are characterised also by the absence of a carbonyl i.r. absorption in the 1660 cm⁻¹ region, which would be expected for a conjugated carbonyl group. This is attributed to contributions by the resonance forms (25a) and (25b).¹⁴ The i.r. spectrum of the benzothienobenzothiopyranone (12) shows an absorption at

1630 cm⁻¹ but this is of low intensity only, suggesting a similar lack of carbonyl structure.

2-(2-Benzo[*b*]thienylthio)nitrobenzene (2) was prepared by a literature procedure¹⁵ and converted into the azide (3) by reduction, diazotisation of the resulting amine (4), and reaction of the diazonium compound with sodium azide. Reduction of the nitro-compound (2) with tin and acid failed to give the amine (4) (*cf.* ref. 15) but reduction with sodium sulphide in methanol gave the amine in 48% yield. The use of titanous chloride in hydrochloric acid increased the yield to 77%. The sulphides (6), (15), and (8) were prepared by condensation of benzo[*b*]thiophen-2(or 3)-thiol with 2-chloro-5-nitrobenzaldehyde or 2-chloro-5-nitrobenzoic acid, respectively. The literature^{16,17} synthesis of benzo[*b*]thiophen-3-thiol involves iodination of benzo[*b*]thiophen, to give the 3-iodo-compound, followed by reaction of 3-benzo[*b*]thienylmagnesium iodide with sulphur. The low yields reported for these reactions prompted us to devise alternative procedures. Previously, we have described convenient syntheses of 3-bromo-¹⁸ and 3-chloro-benzo[*b*]thiophen¹⁹ which involve dihalogenation of benzo[*b*]thiophen followed by selective 2-dehalogenation of the 2,3-dihalogeno-compound by successive treatment with *n*-butyl-lithium and acid. Similar treatment of 2,3-di-iodobenzo[*b*]thiophen gives 3-iodobenzo[*b*]thiophen in good yield. An improved yield of benzo[*b*]thiophen-3-thiol is obtained when 3-benzo[*b*]thienylmagnesium iodide is treated with a large excess of sulphur. 3-Benzo[*b*]thienyl-lithium¹⁸ reacted with sulphur to give mainly 3-*n*-butylthiobenzo[*b*]thiophen by alkylation of the benzo[*b*]thiophen-3-thiolate ion with the *n*-butyl bromide present in the reaction mixture (*cf.* ref. 20). Since the completion of our work, Chapman *et al.*²¹ have prepared benzo[*b*]thiophen-3-thiol by chlorosulphonation of benzo[*b*]thiophen and reduction of the resulting 3-sulphonyl chloride.

EXPERIMENTAL

¹H N.m.r. spectra were recorded with a Varian A60 spectrometer (tetramethylsilane as internal standard); the recorded signals are singlets unless stated otherwise. I.r. spectra were recorded with a Perkin-Elmer 257 spectrometer, mass spectra with an A.E.I. MS12 or MS902S instrument, and u.v. spectra with a Unicam SP800 instrument.

n-Butyl-lithium was purchased as a 20% w/w solution in hexane. Reactions with *n*-butyl-lithium were carried out under dry, oxygen-free nitrogen and the solvents and reagents used were dried by standard procedures. Light petroleum refers to the fraction of b.p. 60–80° unless stated otherwise.

Benzo[*b*]thiophen-2-thiol (65%), b.p. 145–150° at 9.0

¹⁶ V. V. Ghaisas and B. D. Tilak, *J. Sci. Ind. Res. (India)*, 1957, **16B**, 345.

¹⁷ C. E. Hyde, Ph.D. Thesis, Michigan State University, 1957 (*Diss. Abs.*, 1960, **20**, 3490).

¹⁸ R. P. Dickinson and B. Iddon, *J. Chem. Soc. (C)*, 1968, 2733.

¹⁹ R. P. Dickinson, B. Iddon, and R. G. Sommerville, *Internat. J. Sulfur. Chem.*, 1973, **8**, 233.

²⁰ R. P. Dickinson and B. Iddon, *J. Chem. Soc. (C)*, 1971, 3447.

²¹ N. B. Chapman, C. G. Hughes, and R. M. Scowston, *J. Chem. Soc. (C)*, 1970, 2431.

¹¹ J. Ashby, M. Ayad, and O. Meth-Cohn, *J.C.S. Perkin I*, 1973, 1104; M. Ahmed, J. Ashby, and O. Meth-Cohn, *Chem. Comm.*, 1970, 1094.

¹² W. Nagata and H. Itazaki, *Chem. and Ind.*, 1964, 1194.

¹³ J. Fried, in 'Heterocyclic Compounds,' ed. R. C. Elderfield, Wiley, New York, 1950, vol. 1, pp. 370–376, 396.

¹⁴ D. S. Tarbell and P. Hoffman, *J. Amer. Chem. Soc.*, 1954, **76**, 2451.

¹⁵ R. B. Mitra, L. J. Pandya, and B. D. Tilak, *J. Sci. Ind. Res. (India)*, 1957, **16B**, 348.

mmHg, m.p. 42–44° (sublimed at 1.0 mmHg) (lit.,¹⁶ b.p. 106–110° at 2.0 mmHg; lit.,¹⁷ m.p. 42–44°), benzo[*b*]thiophen-3-thiol (44%), b.p. 140–144° at 7.0 mmHg (lit.,¹⁶ 100–105° at 1.5 mmHg; lit.,¹⁷ 116–117° at 3.0 mmHg), and 2-(2-benzo[*b*]thienylthio)nitrobenzene (2) (90%), m.p. 128–130° (from ethanol) (lit.,¹⁵ 129°), were prepared by literature procedures. In the thiol preparations a large excess of sulphur was used.

3-Iodobenzo[*b*]thiophen.—(a) Prepared (39% yield) by the method of Hyde¹⁷ this had b.p. 138–142° at 5.0 mmHg (lit.,²² 120–121° at 1.6 mmHg).

(b) A solution of *n*-butyl-lithium (2.59 mmol) in hexane (1.25 ml) was added dropwise to a stirred solution of 2,3-diiodobenzo[*b*]thiophen²³ (1.0 g, 2.59 mmol) in ether (25 ml) at 0° and the resulting mixture was stirred at 0° for a further 1 h. 2*M*-Hydrochloric acid (25 ml) was added and the organic layer was separated and dried (MgSO₄). Distillation gave 3-iodobenzo[*b*]thiophen (0.4 g, 60%), b.p. 128–132° at 2.0 mmHg.

Reaction of 3-Benzo[*b*]thienyl-lithium with Sulphur.—Dry powdered sulphur (3.0 g, 0.094 g atom) was added to a suspension of 3-benzo[*b*]thienyl-lithium (50 mmol) in ether (75 ml) at –70°, and the mixture was allowed to warm slowly to room temperature. It was heated under reflux for a further 1 h, then cooled, and an excess of 2*M*-hydrochloric acid was added. The organic layer was separated, washed successively with 2*M*-sodium hydroxide (50 ml) and water, and dried (MgSO₄). Distillation gave 3-*n*-butylthio-benzo[*b*]thiophen (9.7 g, 88%), b.p. 155–160° at 10 mmHg (Found: C, 64.6; H, 6.3. C₁₂H₄S₂ requires C, 64.8; H, 6.35%). Addition of 2*M*-hydrochloric acid to the alkaline washing, and extraction with ether followed by distillation, gave benzo[*b*]thiophen-3-thiol (0.3 g, 4%), b.p. 141–145° at 7.0 mmHg.

Reduction of 2-(2-Benzo[*b*]thienylthio)nitrobenzene (2).—(a) With titanium chloride. An aqueous 15% w/v solution of titanous chloride (60 ml) was added dropwise to a stirred mixture of 2-(2-benzo[*b*]thienylthio)nitrobenzene (2) (5.0 g, 17.4 mmol), concentrated hydrochloric acid (55 ml), and ethanol (100 ml) heated at 80° under nitrogen. The resulting mixture was heated at 80° for a further 1 h, cooled, and then made alkaline by addition of 4*M*-sodium hydroxide. Extraction with chloroform gave 2-(2-benzo[*b*]thienylthio)aniline (4) (3.4 g, 77%), m.p. 80–82° (from ethanol) (lit.,¹⁵ 82–83°), ν_{\max} (Nujol) 3480s and 3380s cm⁻¹ (NH₂).

(b) With sodium sulphide. A solution of sodium sulphide decahydrate (34.2 g, 13.25 mmol) and sodium hydrogen carbonate (4.25 g, 5.1 mmol) in water (42.5 ml) was added dropwise during 20 min to a vigorously stirred solution of 2-(2-benzo[*b*]thienylthio)nitrobenzene (2) (5.0 g, 17.4 mmol) in methanol (42.5 ml) heated under reflux, and the mixture was heated under reflux for a further 20 h. It was then cooled and the product (4) (2.1 g, 48%) was filtered off; m.p. 80–82° (from ethanol), identical (i.r.) with the sample prepared as described in (a).

2-(2-Benzo[*b*]thienylthio)phenyl Azide (3).—Sodium nitrite (0.5 g, 7.25 mmol) in water (2.5 ml) was added dropwise during 10 min to a stirred solution of 2-(2-benzo[*b*]thienylthio)aniline (4) (1.5 g, 5.8 mmol) in concentrated hydrochloric acid (7 ml) at 0°, and the mixture was stirred at 0° for a further 1 h. A solution of sodium azide (0.43 g, 6.6 mmol) in water (2.5 ml) was then added dropwise during 10 min and stirring was continued at 0° for 30 min. The crude product was filtered off and chromatographed on

alumina. Ether eluted the azide (3) (1.3 g, 79%), m.p. 76–78° (decomp.), ν_{\max} (Nujol) 2130s and 2095s cm⁻¹ (N₃) (Found: C, 58.8; H, 3.3; N, 14.5%; *M*⁺, 283. C₁₄H₉N₃S₂ requires C, 59.3; H, 3.2; N, 14.8%; *M*, 283).

Reaction of 2-(2-Benzo[*b*]thienylthio)nitrobenzene (2) with Triethyl Phosphite.—A mixture of the nitro-compound (5.0 g, 17.4 mmol) and triethyl phosphite (7.5 g, 45.0 mmol) was heated under reflux for 20 h under nitrogen. The excess of triethyl phosphite and the triethyl phosphate produced were distilled off at 0.1 mmHg and the residue was chromatographed on alumina. Light petroleum eluted a mixture of starting material and another compound. Recrystallisation of this mixture from ethanol gave 2-(2-benzo[*b*]thienylthio)-*NN*-diethylaniline (5) (0.42 g, 7%), m.p. 142–144°, τ (CCl₄) 2.10–3.15 (m, aromatic), 6.91 (q, *J* 7.0 Hz, CH₂), and 8.90 (t, *J* 7.0 Hz, Me) (Found: C, 68.7; H, 6.3; N, 4.3%; *M*⁺, 313. C₁₈H₁₉NS₂ requires C, 69.0; H, 6.1; N, 4.5%; *M*, 313).

Thermolysis of 2-(2-Benzo[*b*]thienylthio)phenyl Azide (3).—A solution of the azide (0.25 g, 0.88 mmol) in xylene (5 ml) was added with stirring to xylene (20 ml) heated under reflux under nitrogen, and the resulting solution was heated under reflux for a further 30 min. The solvent was distilled off under reduced pressure and the residue was chromatographed on silica. Light petroleum eluted starting material (0.17 g, 68% recovery). Chloroform eluted 2-(2-benzo[*b*]thienylthio)aniline (4) (0.05 g, 22%), identical (m.p. and i.r.) with the sample prepared as described before.

2-(2-Benzo[*b*]thienylthio)-5-nitrobenzaldehyde (6).—2-Chloro-5-nitrobenzaldehyde (1.2 g, 6.5 mmol) was dissolved in the minimum amount of hot ethanol and added to a stirred solution of benzo[*b*]thiophen-2-thiol (1.0 g, 6.0 mmol) in a mixture of ethanol (8.0 ml) and aqueous 10% sodium hydroxide (2.5 ml) heated under reflux. After 3 h the mixture was cooled and the product (1.8 g, 95%) was filtered off, m.p. 138–139° (from ethanol), ν_{\max} (Nujol) 1678 cm⁻¹ (C=O), λ_{\max} (EtOH) 342 (ϵ 10,760), τ (CDCl₃) –0.28 (CHO), 1.35 (d, *J*_m 3.0 Hz, 6-H), 1.87 (dd, *J*_o 9.0 Hz, *J*_m 3.0 Hz, 4-H), 2.03–2.75 (m, aromatic), and 2.83 (thiophen ring H) (Found: C, 57.1; H, 3.3; N, 4.7. C₁₅H₉NO₃S₂ requires C, 57.1; H, 2.9; N, 4.4%; thiosemicarbazone, m.p. 221–222° (from ethanol) (Found: C, 49.1; H, 3.3; N, 14.8; S, 25.1. C₁₆H₁₂N₄O₂S₃ requires C, 49.5; H, 3.1; N, 14.4; S, 24.8%); *p*-tolylsulphonylhydrazine, m.p. 179–180° (from ethanol) (Found: C, 54.9; H, 3.4; N, 9.0. C₂₂H₁₇N₃O₄S₃ requires C, 54.6; H, 3.5; N, 8.7%).

2-(3-Benzo[*b*]thienylthio)-5-nitrobenzaldehyde (15) (98%), m.p. 153–155° (from aqueous dimethylformamide), ν_{\max} (Nujol) 1685 cm⁻¹ (C=O), τ (CDCl₃) –0.40 (CHO), 1.30 (d, *J*_m 3.0 Hz), and 1.85–3.20 (m, aromatic) (Found: C, 57.35; H, 3.0; N, 4.6%); thiosemicarbazone, m.p. 223–225° (from acetic acid) (Found: C, 49.3; H, 3.2; N, 14.8%); *p*-tolylsulphonylhydrazine, m.p. 204–206° (from aqueous dimethylformamide) (Found: C, 54.8; H, 3.7; N, 8.95%); and 2-(2-benzo[*b*]thienylthio)-5-nitrobenzoic acid (8) (94%), m.p. 254–256° (from acetic acid), ν_{\max} (Nujol) 1680 cm⁻¹ (C=O), τ (sodium salt) [(CD₃)₂SO] 1.23 (d, *J*_m 3.0 Hz, 6-H) and 1.83–3.00 (m, aromatic) (Found: C, 54.0; H, 2.8; N, 3.9. C₁₅H₉NO₄S₂ requires C, 54.4; H, 2.7; N, 4.2%), were prepared similarly.

Decomposition of 2-(2-Benzo[*b*]thienylthio)-5-nitrobenzaldehyde (6) *p*-Tolylsulphonylhydrazine.—A solution of the

²² R. Gaertner, *J. Amer. Chem. Soc.*, 1952, **74**, 4950.

²³ B. Iddon, C. K. Thadani, B. Northover, and R. G. Somerville, *Chim. therap.*, 1970, **5**, 149.

p-tolylsulphonylhydrazone (1.0 g, 2.1 mmol) in bis-(2-methoxyethyl) ether (10 ml) was added during 15 min to a stirred suspension of sodium methoxide (0.25 g, 4.6 mmol) in bis-(2-methoxyethyl) ether (30 ml) heated under reflux, and the resulting mixture was heated under reflux for a further 15 min. The solvent was distilled off under reduced pressure; extraction of the residue with benzene gave a complex mixture (t.l.c.) of products which was chromatographed on several 20 × 20 cm glass plates covered with a 1.0 mm layer of silica. Light petroleum-benzene (1:1) eluted several bands. Only one band yielded a compound which was identified. This was 2-nitro-11*H*-[1]benzothieno[2,3-*b*][1]benzothiopyran (10) (0.1 g, 15%), m.p. 162–164° (from light petroleum-benzene), ν_{\max} (hexachlorobutadiene) 1340 and 1518 cm^{-1} (NO_2), τ (CDCl_3) 1.60–2.00 and 2.50–2.80 (m, aromatic) and 7.33 (CH_2) (Found: C, 59.9; H, 2.9; N, 4.2. $\text{C}_{15}\text{H}_9\text{NO}_2\text{S}_2$ requires C, 60.2; H, 3.0; N, 4.7%).

Similar decomposition of 2-(3-benzo[*b*]thienylthio)-5-nitrobenzaldehyde (15) *p*-tolylsulphonylhydrazone (1.0 g) also gave a complex mixture of products which was chromatographed on a 'dry' alumina column.²⁴ Light petroleum-benzene (1:1) eluted a number of fractions one of which yielded a small amount of a compound whose mass spectrum suggests that it is a 2-nitro-11*H*-[1]benzothieno[3,2-*b*][1]benzothiopyran (17): *m/e* 299 (M^+), 298 ($M - H$, base peak), 297 ($M - 2H$, 90%; m^* 296), and 252 ($M - H - \text{NO}_2$, 80%; m^* 213).

2-(2-Benzo[*b*]thienylthio)-5-nitrophenyldiazomethane (7).—Sodium methoxide (0.52 g, 9.6 mmol) was added to a stirred solution of 2-(2-benzo[*b*]thienylthio)-5-nitrobenzaldehyde (6) *p*-tolylsulphonylhydrazone (2.0 g, 4.15 mmol) in pyridine (28 ml) at 40°, and the mixture was stirred for 15 min at this temperature. Evaporation of the solvent under reduced pressure and extraction of the residue with benzene gave the product (0.75 g, 55%), ν_{\max} (in acetone) 2065 cm^{-1} (CH:N_2), which was unstable and therefore used without further purification as described later.*

A similar reaction carried out at 60° gave a mixture of the diazomethane (0.3 g, 22%) and 1,2-bis-[2-(2-benzo[*b*]thienylthio)-5-nitrophenyl]ethylene (20) (0.25 g, 20%), m.p. 234–236° (from benzene), ν_{\max} (Nujol) 1623 cm^{-1} (C:C), *m/e* 598-0154 (M^+ , weak). $\text{C}_{30}\text{H}_{18}\text{N}_2\text{O}_4\text{S}_4$ requires 598-0149), 299-0059 (cleavage across the alkene double bond, 44%. $\text{C}_{15}\text{H}_9\text{NO}_2\text{S}_2$ requires 299-0075), 297-9991 ($\text{C}_{15}\text{H}_9\text{NO}_2\text{S}_2 - H$, base peak. $\text{C}_{15}\text{H}_8\text{NO}_2\text{S}_2$ requires 297-9997), 252-0057 ($\text{C}_{15}\text{H}_9\text{NO}_2\text{S}_2 - H - \text{NO}_2$, 45%. $\text{C}_{15}\text{H}_8\text{S}_2$ requires 252-0068); m^* 297-0 and 213-3 accompanying the last two fragmentations. The low solubility of this compound in most useful n.m.r. solvents prevented us from recording its n.m.r. spectrum.

2-(3-Benzo[*b*]thienylthio)-5-nitrophenyldiazomethane (16) (45%), ν_{\max} (in acetone) 2060 cm^{-1} (CH:N_2), was prepared similarly. Because of its instability* it was used without further purification as described later.

Decomposition of 2-(2-Benzo[*b*]thienylthio)-5-nitrophenyldiazomethane (7).—A solution of the diazomethane derivative (0.5 g, 1.5 mmol) in bis-(2-methoxyethyl) ether (10 ml) was heated under reflux for 45 min. The solvent was distilled off under reduced pressure and the residue was extracted with benzene, to give a complex mixture of products which was chromatographed on several 20 × 20 cm glass plates

* These compounds decompose over a wide range on being heated.

²⁴ B. Loev and M. M. Goodman, *Chem. and Ind.*, 1967, 2026.

covered with a 1.0 mm layer of silica. Light petroleum-benzene (1:1) eluted several bands, two of which were shown to contain 2-nitro-11*H*-[1]benzothieno[2,3-*b*][1]benzothiopyran (10) (0.05 g, 10%) and 1,2-bis-[2-(2-benzo[*b*]thienylthio)-5-nitrophenyl]ethylene (20) (0.03 g, 5%), identical (m.p., t.l.c., and i.r. and mass spectra) with the samples prepared as described before.

Decomposition of 2-(3-Benzo[*b*]thienylthio)-5-nitrophenyldiazomethane (16).—Similar decomposition of this compound (0.1 g, 0.3 mmol) in bis-(2-methoxyethyl) ether (2 ml) also gave a complex mixture of products on work-up. The presence of a compound with the same R_F value as that obtained as described before and which we believe to be 2-nitro-11*H*-[1]benzothieno[3,2-*b*][1]benzothiopyran (17) was shown by t.l.c. Extraction of the mixture of products with acetone yielded a solution which was kept for 1 week. A precipitate formed (0.01 g, 10%) of a compound which we believe to be *NN'*-bis-[2-(2-benzo[*b*]thienylthio)-5-nitrobenzylidene]hydrazine (21), m.p. 245–246°, *m/e* 626 (M^+ ; too weak for mass measurement), 313-0110 ($N-N$ cleavage, 59%. $\text{C}_{15}\text{H}_9\text{N}_2\text{O}_2\text{S}_2$ requires 313-0106), and 297-9997 (further loss of NH , base peak. $\text{C}_{15}\text{H}_8\text{NO}_2\text{S}_2$ requires 297-9997).

2-Nitro-11*H*-[1]benzothieno[2,3-*b*][1]benzothiopyran (10).—(a) A mixture of 2-(2-benzo[*b*]thienylthio)-5-nitrobenzaldehyde (6) (2.0 g, 6.35 mmol), phosphoryl chloride (3 ml), and toluene (40 ml) was heated under reflux for 6 h. It was cooled and the precipitate (1.5 g) was filtered off and dried. A mixture of this compound and sodium borohydride (0.5 g, 13.2 mmol) in ethanol (20 ml) was stirred at room temperature for 30 min. The precipitate was filtered off and the filtrate evaporated to dryness under reduced pressure. The residue was combined with the precipitate and chromatographed on alumina. Ethyl acetate eluted 2-nitro-11*H*-[1]benzothieno[2,3-*b*][1]benzothiopyran (10) (0.4 g, 20%), identical (m.p. and i.r. and mass spectra) with the sample provided as described before.

(b) A mixture of 2-(2-benzo[*b*]thienylthio)-5-nitrobenzaldehyde (6) (1.2 g, 3.8 mmol) and aqueous 48% hydrobromic acid (10 ml) was heated under reflux for 2.5 h. It was evaporated to dryness and the residue was triturated with ethanol. A mixture of the solid which remained after trituration and sodium borohydride (0.2 g, 5.3 mmol) in ethanol (20 ml) was stirred at room temperature for 30 min. The resulting mixture was filtered and the filtrate was evaporated to dryness under reduced pressure to give a residue which was extracted several times with chloroform. The extracts were combined and distilled and the residue was chromatographed on alumina. Light petroleum-ether (4:1) eluted 2-nitro-11*H*-[1]benzothieno[2,3-*b*][1]benzothiopyran (10) (0.05 g, 4%), identical (m.p. and i.r. and mass spectra) with the samples prepared as described before. Ether-chloroform (1:1) eluted 2-nitro[1]benzothieno[2,3-*b*][1]benzothiopyran-11-one (12) (0.5 g, 42%), m.p. 301–304° (from anisole), ν_{\max} (Nujol) 1630 cm^{-1} (C:O) (Found: C, 57.75; H, 2.3; N, 4.0. $\text{C}_{15}\text{H}_7\text{NO}_3\text{S}_2$ requires C, 57.5; H, 2.25; N, 4.5%).

2-Nitro[1]benzothieno[2,3-*b*][1]benzothiopyran-11-one (12).—(a) A mixture of 2-(2-benzo[*b*]thienylthio)-5-nitrobenzoic acid (8) (4.5 g, 13.5 mmol) and thionyl chloride (10 ml) was heated under reflux for 1.5 h. The excess of thionyl chloride was distilled off under reduced pressure and the residue was extracted with benzene, to give 2-(2-benzo[*b*]thienylthio)-5-nitrobenzoyl chloride (9) (3.0 g, 65%) as a solid, ν_{\max} (Nujol) 1740 cm^{-1} (C:O), which was used without

purification in the following reaction. The residue after extraction with benzene was 2-nitro[1]benzothieno[2,3-*b*][1]benzothiopyran-11-one (12) (0.46 g, 11%), m.p. 307–308° (from anisole), identical (i.r. and mass spectra) with the samples prepared as described before and in (b).

(b) A mixture of the acid chloride (1.0 g, 2.9 mmol), aluminium chloride (0.42 g, 3.2 mmol), and 1,2-dichloroethane (18 ml) was heated under reflux until evolution of hydrogen chloride ceased. The mixture was poured onto crushed ice and acidified with 2M-hydrochloric acid, to give 2-nitro[1]benzothieno[2,3-*b*][1]benzothiopyran-11-one (12) (0.5 g, 56%), m.p. 307–308° (from anisole), identical (i.r. and mass spectra) with the samples prepared as described before.

*Reactions of 2-Nitro[1]benzothieno[2,3-*b*][1]benzothiopyran-11-one (12).*—(a) *Wolff-Kishner reduction.* A mixture of the benzothienobenzothiopyran (1.0 g, 3.3 mmol), hydrazine hydrate (0.5 ml; 85%), sodium hydroxide (0.5 g), and ethylene glycol (10 ml) was heated at 100° for 1.5 h and then at 190° for 3 h with removal of water by distillation. The mixture was poured on crushed ice; extraction with chloroform gave 2-amino[1]benzothieno[2,3-*b*][1]benzothiopyran-11-one (13) (0.25 g, 28%), m.p. 207–209° (from acetic acid), ν_{\max} (Nujol) 1620 (C=O) and 3320 and 3420 cm^{-1} (NH_2) (Found: C, 63.9; H, 3.5; N, 4.6. $\text{C}_{15}\text{H}_9\text{NOS}_2$ requires C, 63.6; H, 3.2; N, 4.9%).

(b) *Modified Wolff-Kishner reduction.* A mixture of the benzothienobenzothiopyran (12) (1.0 g, 3.3 mmol), hydrazine dihydrochloride (1.0 g), anhydrous hydrazine²⁵ (4.2 g), and triethylene glycol (75 g) was heated at 130° for 7 h. Potassium hydroxide (13 g) was added and the mixture was heated at 220° for 3 h, then poured on ice. Extraction with chloroform gave only an intractable tar.

(c) *Reduction with iron and ammonium chloride.* Ammonium chloride (0.4 g, 7.5 mmol) in water (10 ml) was added to a stirred suspension of the benzothienobenzothiopyran (12) (2.0 g, 6.6 mmol) and iron dust (2.7 g, 0.048 g atom) in ethanol (20 ml), and the resulting mixture was heated under reflux for 20 h. It was then filtered and the ethanol was distilled off. Extraction of the residue with ether gave 2-amino[1]benzothieno[2,3-*b*][1]benzothiopyran-11-one (13) (0.4 g, 23.5%), identical (m.p. and i.r. spectrum) with the sample prepared as described in (a).

(d) *Reduction with tin and acid.* A mixture of the benzothienobenzothiopyran (12) (1.0 g, 3.3 mmol), tin (0.75 g, 0.006 g atom), concentrated hydrochloric acid (10 ml), and ethanol (30 ml) was heated under reflux for 5 h. More tin (0.75 g) and acid (10 ml) were added after 1 and 2 h. The mixture was filtered, made strongly alkaline with 4M-sodium hydroxide, and filtered again. The residue was chromatographed on alumina. Ether eluted a trace (mass spectrometry) of a compound which we believe to be 2-amino-11*H*-[1]benzothieno[2,3-*b*][1]benzothiopyran (11), and chloroform eluted 2-amino[1]benzothieno[2,3-*b*][1]benzothiopyran-11-one (13) (0.05 g, 6%), identical (m.p. and i.r. and mass spectra) with the sample prepared as described before. Compound (11) showed *m/e* 269 (M^+ , 25%), 268 ($M - H$, base peak), 267 ($M - 2H$), and 236 ($M - H - S$, 30%; m^* 207.5).

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²⁵ K. Kusama, *J. Biochem.*, 1957, **44**, 375.