

The Nitrobenzo[*b*]thiophenes

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Syntheses, and infrared and nuclear magnetic resonance spectral data for the six mono-nitrobenzo[*b*]thiophenes are described. Sulfonation of benzo[*b*]thiophene has been demonstrated to produce the 2- and 3-isomers.

Of the six isomeric nitrobenzo[*b*]thiophenes, only the 3-(I), 4-(II), and 5-(III) isomers have been described in the literature and quantitative aspects of their syntheses are lacking. Thus, I has been reported (2) as a major isomer from the nitration of benzo[*b*]thiophene (IV), but no characterization of other products has been made.

We have identified three mono-nitration products when IV was nitrated in acetic acid at 10°. Quantitative desulfurization of the nitration product by Raney nickel, using the Schwenk-Papa technique (3), yielded  $\alpha$ -aminoethylbenzene, *o*-ethylaniline, and *p*-ethylaniline. These results substantiated that the original nitration products were I (47%), II (43%), and 6-nitrobenzo[*b*]thiophene, V (9%). Raney nickel reductions of pure nitrobenzo[*b*]thiophene isomers and with nitroethylbenzenes demonstrated that no rearrangement occurred during reductive desulfurization. Also, the pure isomers, *o*-ethylaniline, *p*-ethylaniline, and  $\alpha$ -aminoethylbenzene, were recovered unchanged on treatment with Raney nickel under desulfurization conditions.

Zahradnik (4) has reported I, III, and 2-nitrobenzo[*b*]thiophene (VI) from nitration of IV in acetic acid. However using their procedure we have been unable to detect III by vapor phase chromatography, by infrared, or by Raney nickel reduction studies. Nitration at 60° has been reported to yield a mixture of 10-15% of VI, 60-65% of I, and 20-30% of II (5). Using these reaction conditions, which convert essentially all of IV to nitration product, we found somewhat less of VI and I, and, in addition, about 7% of V.

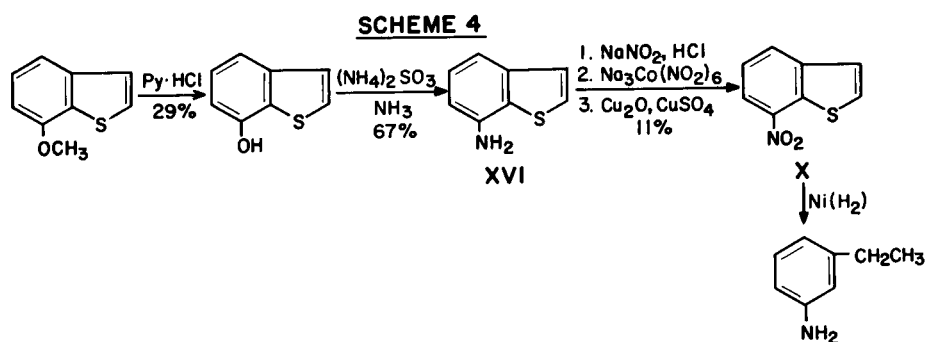
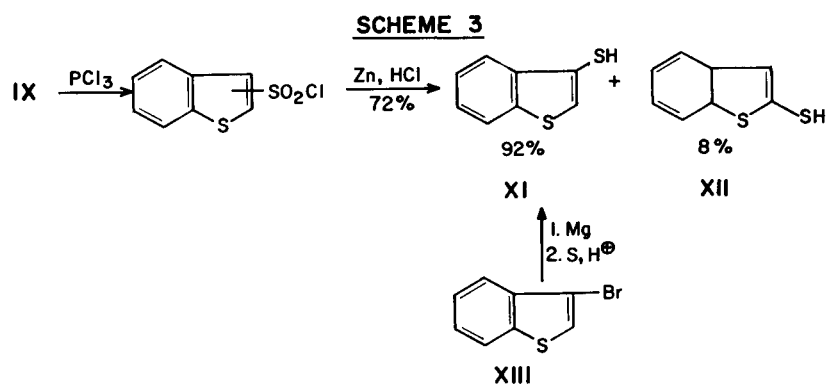
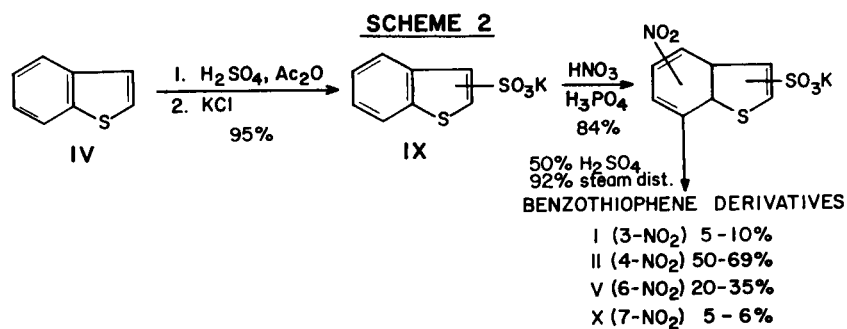
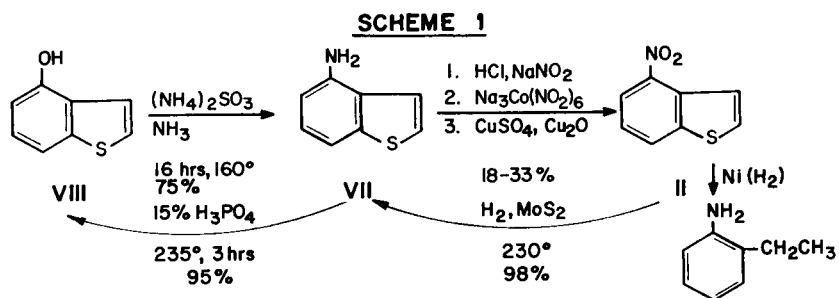
4-Nitrobenzo[*b*]thiophene (II) has been reported as the major product from removal of a nitro group from 3,4-dinitrobenzo[*b*]thiophene (6,7). 3,4-Dinitrobenzo[*b*]thiophene was obtained by fractional recrystallization from a mixture of the three dinitro isomers obtained by the nitration of I. In our hands, the denitration using alcoholic ammonium sulfide gave predominantly reduction products with only traces of the desired 4-nitrobenzo[*b*]thiophene (II).

Yields of 18-33% of II were obtained from the readily accessible 4-aminobenzo[*b*]thiophene (VII) by diazotization, conversion to the cobaltinitrite salt, and hydrolysis using copper sulfate catalyst. This replacement of amino by nitro with retention of orientation has been reported in the benzene and naphthalene ring systems (8) and was substantiated in this case by reduction of the nitro compound to VII. Proof of structure of II results from a two-step conversion to 4-hydroxybenzo[*b*]thiophene (VIII) and by Raney nickel desulfurization to *o*-ethylaniline. The interconversions are described in Scheme 1.

Compound II can also be obtained as a major isomer from IV in the sequence of reactions involving sulfonation, nitration, and desulfonation (see Scheme 2). Yields of the various isomers vary with nitration temperatures and medium.

The intermediate sulfonic acid salt (IX) has been described in the literature as the 3-isomer (9). Nuclear magnetic resonance data supports substitution in the thiophene ring (H-2, 8.46 ppm, singlet; H-4, 8.19 ppm; H-5, H-6, 7.56 ppm; H-7, 7.87 ppm). Conversion of the salt to a sulfonyl chloride followed by reduction with zinc dust and hydrochloric acid gave a mixture of two mercaptans in the ratio 11.5 to 1. The same isomeric mixture was obtained when the reaction was carried to only 10% conversion. The major isomer was characterized as 3-mercaptobenzo[*b*]thiophene (XI) by independent synthesis from 3-bromobenzo[*b*]thiophene (XII). These reactions are described in Scheme 3.

The SH protons in XI and XII had chemical shifts of 2.98 and 3.38 ppm (TMS reference), respectively, and the proton in each case was coupled to the adjacent thiophene ring proton to the extent of 1.3 cps. A second smaller coupling of 0.3 cps was also observed and was assigned to the 2,6- and 3,7-couplings. In benzenoid mercaptans, including 4-mercaptobenzo[*b*]thiophene, mercaptobenzene, and *o*-ethylmercaptobenzene, the SH-*ortho* H coupling was unresolved or ~0.2 cps. In 2-mercaptothio-



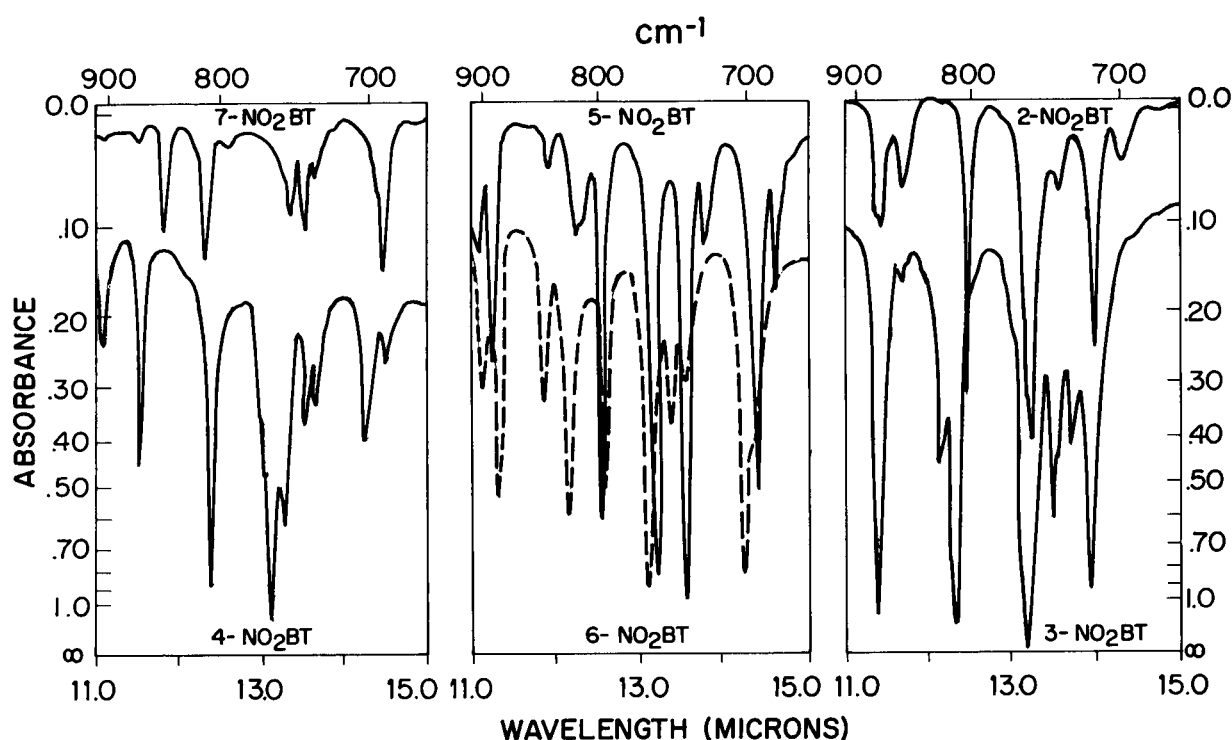


FIGURE 1

phene, the 2-SH-3H coupling was 1.4 cps, in accord with the values for XI and XII. It was logical to assign the 2-SH position as the minor isomer and to relate these findings to the presence of about 8% of benzo[*b*]thiophene-2-sulfonic acid and 92% benzo[*b*]thiophene-3-sulfonic acid in the sulfonation product (IX). Thus, throughout this paper, reference to compound IX implies a mixture of about 8% benzo[*b*]thiophene-2-, and 92% benzo[*b*]thiophene-3-sulfonic acids.

5-Nitrobenzo[*b*]thiophene (III) was prepared by the method of Bordwell and Stange (10) and was characterized by desulfurization to *m*-ethylaniline.

2-Nitrobenzo[*b*]thiophene (VI) can be obtained via nitration of 3-bromobenzo[*b*]thiophene (XIII). Two isomers, 3-bromo-2-nitrobenzo[*b*]thiophene, XIV, and 3-bromo-4-nitrobenzo[*b*]thiophene, XV, predominated from such nitration. The higher melting isomer, XIV, was easily separated from the mixture by virtue of its poor solubility in organic solvents. Orientation of groups in the two isomers was established by Raney nickel desulfurization, XIV yielding  $\beta$ -aminoethylbenzene and XV yielding *o*-ethylaniline. Loss of bromine during Raney nickel desulfurization is well known (11) and occurs rapidly, for example, with XIII. Debromination of XIV to 2-nitrobenzo[*b*]thiophene (VI) was accomplished in 60-70% yield by heating with copper bronze and benzoic acid (12).

An alternative procedure, involving intermediate formation of 2-nitrobenzo[*b*]thiophene-3-carboxylic acid, provided low yields of VI on decarboxylation with copper-quinoline. Orientation of the nitro group was established by reductive hydrolysis to 2-hydroxybenzo[*b*]thiophene (and its tautomer) and by desulfurization to  $\beta$ -aminoethylbenzene.

6-Nitrobenzo[*b*]thiophene (V) was obtained as the major isomer in the nitration of IX in sulfuric acid at 50-90°, followed by desulfonation at 150°. While isomer distributions varied with nitration and desulfonation temperatures, typical results at 80-90° yields provided 60% of V, 25% of I, and 15% of II. Compound V was readily separated from I and II by preparative vapor phase chromatography. The structure of V was verified by conversion to a sulfone identical to that obtained from nitration of benzo[*b*]thiophene-1,1-dioxide (13). Oxidation of V with basic potassium permanganate gave the known 4-nitro-2-sulfobenzoic acid (14).

Desulfurization of V by Raney nickel yielded *m*-ethylaniline.

7-Nitrobenzo[*b*]thiophene (X) was obtained in low yield from 7-methoxybenzo[*b*]thiophene (15) by hydrolysis to the corresponding hydroxy derivative, conversion to 7-aminobenzo[*b*]thiophene (XVI) using the Bucherer reaction, and by subsequent hydrolysis of the diazonium

TABLE I

Chemical Shifts (W) and Coupling Constants (J) for the Nitrobenzo[*b*]thiophene Protons (a)

Solvent	W(2)	W(3)	W(4)	W(5)	W(6)	W(7)	J(2,3)	J(2,6)	J(3,7)	J(4,5)	J(4,6)	J(4,7)	J(5,6)	J(5,7)	J(6,7)
3-NO <sub>2</sub> - (CD <sub>3</sub> ) <sub>2</sub> CO	8.47	--	8.05	7.18	7.11	7.60	--	0.36	--	8.47	1.15	0.77	7.24	1.06	8.33
2-NO <sub>2</sub> - (CD <sub>3</sub> ) <sub>2</sub> CO	--	7.87	7.63	7.22	7.12	7.50	--	--	0.38	8.49	1.13	0.82	7.21	1.05	8.31
4-NO <sub>2</sub> - C <sub>6</sub> D <sub>6</sub>	7.14	8.03	--	8.01	6.81	7.48	5.81	0.50	0.94	--	--	--	8.07	0.86	8.03
5-NO <sub>2</sub> - C <sub>6</sub> D <sub>6</sub>	7.83	7.69	8.31	--	7.45	7.19	2.55	0.15	0.20	--	1.71	1.30	--	--	6.33
6-NO <sub>2</sub> - C <sub>6</sub> D <sub>6</sub>	7.24	6.94	7.34	7.95	--	8.37	5.55	--	0.74	9.07	--	0.62	--	2.16	--
7-NO <sub>2</sub> - C <sub>6</sub> D <sub>6</sub>	7.49	6.64	7.33	7.07	7.22	--	2.20	0.45	--	7.97	1.08	--	7.83	--	--

(a) W in ppm; J in cps.

cobaltinitrite salt of XVI. Desulfurization of X gave *m*-ethylaniline. This sequence is described in Scheme 4.

The infrared spectra (910-666  $\text{cm}^{-1}$  region) of the six isomeric nitrobenzo[*b*]thiophenes are presented in Figure 1. There were definitive bands for distinguishing each of the isomers although the presence of less than 3% of any of the isomers in a mixture could not be detected. Similar problems were noted by Mamaev and Shkurko with nitration products of 2-substituted benzo[*b*]thiophenes (16). The definitive bands for the various isomers include 2-NO<sub>2</sub>-(VI), 803, 714; 3-NO<sub>2</sub>-(I), 611, 812, 718; 4-NO<sub>2</sub>-(II), 870, 807; 5-NO<sub>2</sub>-(III), 891, 799, 694; 6-NO<sub>2</sub>-(V), 885, 700; 7-NO<sub>2</sub>-(X), 855, 693  $\text{cm}^{-1}$ .

NMR data for the six isomers are given in Table I. Substitution of the nitro group into the benzene ring of the heterocyclic molecules yielded an easily resolved ABX spectrum with a superimposed long range 2,6- and/or 3,7-coupling of 0.3 to 0.9 cps. This long range coupling between the 2,6-protons and between the 3,7-protons in benzo[*b*]thiophene derivatives is well documented (17,18). The unsymmetrical 2- and 3-substituted benzo[*b*]thiophenes had an ABXY pattern more difficult to unravel because of long range couplings. In these two examples, the long range 2,6- and 3,7-couplings facilitate analysis since it allowed pinpointing the 6- and 7-protons.

In general, the *ortho* coupling in the thiophene ring of the benzo[*b*]thiophene derivatives was about 5 cps while *ortho* coupling in the benzenoid ring of the same derivative was 8 cps. Other observed couplings in this system were similar to those observed in benzene derivatives. As in nitrobenzene derivatives, the presence of the nitro group shifted the adjacent *ortho* hydrogen downfield and this shift was useful in making proton assignments.

## EXPERIMENTAL

Melting points were determined on a Fisher-John block and are corrected. Boiling points are uncorrected. Infrared spectra were taken as liquid films or as 0.5% solutions in potassium bromide on a Perkin-Elmer Model 137 Infrared Spectrophotometer. Nuclear magnetic resonance spectra were determined as solutions in deuteriochloroform on a Varian Associates Model A-60 using tetramethylsilane as an internal reference.

### 3-Bromo-2-nitrobenzo[*b*]thiophene (XIV).

To a stirred solution of 154 g. (0.72 mole) of XIII (6) in 525 ml. of acetic acid at 15-20°, there was added, during 0.75 hours, 214 ml. of 90% nitric acid in 150 ml. of acetic acid. The resultant solution was stirred an additional 6 hours at 15°, then refrigerated overnight. The cooled slurry was poured into 350 ml. of water and filtered with suction. The solid was crystallized from 4 l. of alcohol to yield 62 g. (33%) of XIV, m.p. 162.0-162.8° (lit. m.p. 160-161° (19)).

*Anal.* Calcd. for C<sub>8</sub>H<sub>4</sub>BrNO<sub>2</sub>S: C, 37.24; H, 1.56. Found: C, 37.02; H, 1.57.

Major infrared bands: 712, 728, 742, 765, 868, 918, 1060, 1120, 1140, 1170, 1245, 1308, 1320, 1335, 1425, 1455, 1480, 1520, 1555, and 1595  $\text{cm}^{-1}$ .

The alcoholic filtrate (above) was concentrated to one-half its volume, chilled and filtered to give 19 g. of a solid which was recrystallized twice from alcohol to yield 12.9 g. of a material melting at 115-117°. This substance was established as 3-bromo-4-nitrobenzo[*b*]thiophene (XV) through its desulfurization to *o*-ethylaniline (see below).

### Desulfurization of XV.

A vigorously stirred solution of 0.8 g. (0.0031 mole) of XV in 40 ml. of methanol and 50 ml. of water containing 8.1 g. of sodium hydroxide was treated portionwise, at 55-60°, with 8.1 g. of Raney Alloy during 0.25 hours. The mixture was refluxed for one hour, cooled, and filtered. The catalyst was washed with ether and water, the filtrate extracted with ether, and the combined ethereal solutions dried over magnesium sulfate. Removal of the ether left 0.36 g. of product. Vapor phase chromatographic and infrared analyses of the product gave 85.0% of *o*-ethylaniline, 6.4% of  $\beta$ -phenylethylamine, and 8.6% of *o*-toluidine. The two *ortho*-substituted compounds arose from substitution at the 4-position in the original benzo[*b*]thiophene, establishing XV as about 94% purity.

### 2-Nitrobenzo[*b*]thiophene (VI).

A mixture of 14 g. of benzoic acid and 8.6 g. (0.033 mole) of XIV was melted and hand stirred under a blanket of nitrogen at 140-150° while adding 10 g. of copper bronze. The addition required five minutes after which the reaction mass was allowed to cool. This procedure was repeated five times. The combined solids were crushed and added to 250 ml. of 20% sodium bicarbonate solution. Steam distillation gave 20.5 g. (70%) of VI as yellow needles, m.p. 113-117°. Crystallization from ethanol gave an analytical sample, m.p. 117.5-118.5°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>5</sub>NO<sub>2</sub>S: C, 53.62; H, 2.81; N, 7.81; S, 17.89. Found: C, 53.35; H, 3.28; N, 7.89; S, 17.8.

Major infrared bands: 716, 758, 806, 1085, 1190, 1323, 1351, 1466, 1497, 1520  $\text{cm}^{-1}$ .

Attempts to prepare a sulfone derivative by conventional techniques led to ring opening and formation of a water-soluble sulfonic acid.

### Desulfurization of VI.

The procedure for this desulfurization was entirely similar to that for XV (above). From 0.4 g. (0.0022 mole) of VI and proportional amounts of the other ingredients, there was obtained 0.15 g. of a yellow oil, analyzed by vapor phase chromatography as one component having the same retention time as  $\beta$ -phenylethylamine. Infrared analysis, of a sample trapped by preparative vapor phase chromatography, established it as  $\beta$ -phenylethylamine,  $n_D^{20}$  1.5401.

### 2-Keto-2,3-dihydrobenzo[*b*]thiophene.

One and eight-tenths g. (0.01 mole) of VI was refluxed for five hours with 20 ml. of 30% aqueous ammonium sulfide and 50 ml. of ethanol. The solution was poured into 100 ml. of water and extracted with 100 ml. of ether. The ether solution was extracted with 100 ml. of 6 *N* hydrochloric acid; the separated acid layer was mixed with 50 ml. of tetrahydrofuran and refluxed for three days, cooled, extracted with chloroform and the chloroform solution dried over magnesium sulfate. Evaporation of the chloroform left 0.15 g. (10%) of a tan solid which when crystallized from pentane gave m.p. 43-45°. The product showed a thiolactone stretching frequency at 1700  $\text{cm}^{-1}$  and was identical

to that reported by Stacy, *et al.*, (20).

### 3-Nitrobenzo[*b*]thiophene (I).

The nitration procedure of Fries and Hemmecke (2a) gave a red oil (80%) which slowly crystallized to a solid. Fractional crystallization of this solid from ethanol gave a 20% yield of pure I. Desulfurization, entirely similar to that for XV, above, gave a 72% yield of  $\alpha$ -phenylethylamine, b.p. 189-191°. Infrared analysis and desulfurization (as above) of the original red oil indicated it to be a mixture of 47% of I, 43% of II, and 9% of V. Major infrared bands: 712, 719, 758, 318, 885, 1010, 1149, 1266, 1333, 1351, 1361, 1425, 1453, 1488, 1527  $\text{cm}^{-1}$ .

### 3-Nitrobenzo[*b*]thiophene-1,1-dioxide.

Five-tenths g. (0.0028 mole) of I was oxidized with 20 ml. of 30% peracetic acid at 70° for ten hours. After pouring on ice, filtering, and drying, there was obtained 0.58 g. of solid, crystallized from hexane to m.p. 144-145°. The infrared spectrum showed the characteristic strong sulfone bands at 1390 and 1160  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_8\text{H}_5\text{NO}_4\text{S}$ : C, 45.50; H, 2.37. Found: C, 45.33; H, 2.50.

### 3-Aminobenzo[*b*]thiophene.

Reduction of 0.4 g. of I with 10 ml. of 30% alcoholic ammonium sulfide for eight hours at 80° gave 0.32 g. of oil which vapor phase chromatography showed to be a mixture of starting material (24%) and a second component (75%) of lower retention time. The second component was trapped and identified as a primary amine, presumably 3-aminobenzo[*b*]thiophene, m.p. 37-38°, infrared bands for  $\text{NH}_2$  at 3430, 3370  $\text{cm}^{-1}$ ; NMR, 20% in deuteriochloroform, TMS ref: 2 protons (3- $\text{NH}_2$ ), 3.54 ppm; one proton (2-H), 6.15 ppm; four protons (Ar-H), 6.75 ppm.

### 4-Aminobenzo[*b*]thiophene (VII).

Twenty g. (0.133 mole) of VIII (21), 68 ml. of concentrated ammonium hydroxide, 13 g. of sulfur dioxide, and 64 ml. of water were heated in a stirred autoclave at 160° for 24 hours. An oil layer was separated and the aqueous layer extracted with 400 ml. of ether. The ether extract was combined with the oil and washed thoroughly with water. Addition of 50 ml. of 30% hydrochloric acid partially precipitated the amine hydrochloride and the combined acid solution and precipitate was treated with excess 10% sodium hydroxide, cooled to 10°, and filtered. Yield of solid VII was 18.9 g. (95%), m.p. 48-49.5°, b.p. 98-101° at 0.4 mm. Recrystallization from hexane gave m.p. 50-51° (lit. m.p. 51-53° (13)) acetamide derivative, m.p. 134°. Major infrared bands: 3460, 3380, 1620, 1570, 1465, 1355, 1290, 927, 866, 790, 782, 748, 686  $\text{cm}^{-1}$ .

### 4-Nitrobenzo[*b*]thiophene (II).

Fourteen and nine-tenths g. (0.10 mole) of VII was dissolved in 150 ml. of 30% sulfuric acid by heating to 90°. The solution was cooled to 0° (producing fine crystals), 7.0 g. of sodium nitrite added, and the mixture stirred for two hours. The solution was neutralized with calcium carbonate, filtered cold, and the filtrate treated with 15.0 g. of powdered sodium cobaltinitrite. After standing overnight the precipitated cobaltinitrite salt was separated by filtration and air dried. Ten g. of the salt was added portionwise to a well-stirred mixture of 10 g. of sodium nitrite and 10 g. of hydrated copper sulfate in 60 ml. of water containing 4 g. of suspended cuprous oxide. The mixture was heated for 7 hours at 60° and then steam distilled at 100-150°. The yellow solid in the

distillate was separated by vacuum filtration, dried on the filter, and crystallized from hexane yielding 1.6 g. (41%) of II, m.p. 84-85° (lit. m.p. 80-82° (7) 88° (9)).

*Anal.* Calcd. for  $\text{C}_8\text{H}_5\text{NO}_2\text{S}$ : C, 53.62; H, 2.81. Found: C, 53.95; H, 2.70.

Major infrared bands: 699, 752, 758, 806, 869, 901, 1089, 1200, 1217, 1316, 1348, 1511, 1538  $\text{cm}^{-1}$ .

Reduction of II by the method of Fries (7) or by using aluminum amalgam also gave VII.

### 4-Nitrobenzo[*b*]thiophene-1,1-dioxide.

One g. of II was oxidized at 80° for 2 hours using 5 ml. of 30% hydrogen peroxide and 10 ml. of acetic. After pouring on ice, filtering, and drying, there was obtained 1.1 g. of sulfone, recrystallized from petroleum ether to m.p. 179-180°. The infrared spectrum showed strong sulfone bands at 1355, 1305, and 1160  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_8\text{H}_5\text{NO}_4\text{S}$ : C, 45.50; H, 2.37. Found: C, 45.53; H, 2.55.

### Potassium 4-nitro-3-benzo[*b*]thiophene Sulfonate.

To a stirred solution of 2.9 g. (0.016 mole) of II in 6 g. of acetic anhydride at 10°, there was added 2.4 g. of concentrated sulfuric acid. The solution was stirred 2 hours at 10°, an additional 3 hours at room temperature, and poured onto ice. The aqueous solution was extracted three times with ether, concentrated to 15 ml. on the hot plate, 6 g. of potassium chloride was added, and the solution was cooled. The precipitate was filtered and extracted with boiling ethanol. The extract was filtered hot, then cooled, and a yellow-brown precipitate which formed was filtered and dried *in vacuo* at 100°, yield 0.41 g. (8.6%) of potassium 4-nitro-3-benzo[*b*]thiophene sulfonate. Infrared spectrum:  $\nu_{\text{as}}\text{SO}_2$ , 1210  $\text{cm}^{-1}$ ;  $\nu_{\text{s}}\text{SO}_2$ , 1075  $\text{cm}^{-1}$ ;  $\nu_{\text{SO}}$ , 642,  $\text{cm}^{-1}$ . NMR, 10% in DMSO, TMS ref.: H-2, singlet, 8.17 ppm; H-5, quartet, 8.59 ppm; H-7 quartet, 8.24 ppm; H-6, triplet, 7.80 ppm.

*Anal.* Calcd. for  $\text{C}_8\text{H}_4\text{KNO}_5\text{S}_2$ : N, 4.71. Found: N, 4.68.

### 5-Nitrobenzo[*b*]thiophene (III).

The procedure of Bordwell (22) was used except that the decarboxylation of 5-nitro-2-benzo[*b*]thiophene carboxylic acid was carried out at 180-190° under 100 mm vacuum and III was separated and purified by distillation with super-heated steam at 170°, m.p. 149-150° (lit. m.p. 149-150° (22)). Major infrared bands: 697, 738, 758, 800, 893, 932, 1053, 1086, 1316, 1342, 1437, 1515  $\text{cm}^{-1}$ .

### 3-Mercaptobenzo[*b*]thiophene (XI) (Method A).

To 125 ml. of anhydrous ether and 1.6 g. of magnesium turnings at 30° there was added, with stirring, a mixture of 7.03 g. (0.033 mole) of XIII and 3.60 g. of ethylbromide. The mixture was warmed, refluxed for 2 hours, cooled to 5°, and 2.14 g. of sulfur added. The new mixture was refluxed for 2 hours, cooled to 10°, and then treated with 3.4 g. of reagent sulfuric acid in 50 ml. of water. The ether solution was separated and combined with an ether extract of the acidic layer. The ethereal solutions were washed with water and dried over magnesium sulfate, and the solvent evaporated to give 6.4 g. of an oil. A portion of the oil, 2.2 g. was distilled to give 1.8 g. (32.7%) of XI, b.p. 77-80°/0.2 mm. NMR, TMS ref.: 3-SH, quartet, 2.98 ppm; Ar-H, multiplet, 7.50 ppm. Infrared:  $\nu_{\text{SH}}$ , 2535  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_8\text{H}_6\text{S}_2$ : C, 57.80; H, 3.64. Found: C, 58.17; H, 3.70.

## Method B.

Benzo[*b*]thiophene-3-sulfonyl chloride, m.p. 90-91°, was prepared in 88% yield (9). The sulfonyl chloride (7 g., 0.03 mole) was added to 24 g. of concentrated sulfuric acid on 72 g. of crushed ice. Zinc dust (12 g.) was added, and the cold mixture stirred for 4 hours and then refluxed for 12 hours. The oily layer was separated and combined with an ether extract of the acidic phase and the resulting solution washed with water, dried over magnesium sulfate and the ether removed by evaporation. The residue was distilled yielding 3.6 g. (72%) of distillate boiling at 87-91°/0.5 mm. Vapor phase chromatography showed the presence of two components. The major peak, 92%, was trapped and identified by comparison of its infrared spectrum with that of the product from Method A above. The minor constituent (8%) was the isomeric 2-mercaptobenzo[*b*]thiophene. This assignment was based on infrared analysis,  $\nu$ -SH, 2525  $\text{cm}^{-1}$  and the NMR spectrum: one proton, 2-SH 3.38 ppm, quartet; five protons, Ar-H, 7.46 ppm, multiplet.

6-Nitrobenzo[*b*]thiophene (V).

To 10 g. of 80% sulfuric acid stirred at 5° there was added 5 g. (0.02 mole) of IX. The pasty solution was heated to 80°, and a solution of 1.8 g. of 90% nitric acid and 2 g. of sulfuric acid was added at a rate so that a temperature of 70-80° was maintained. After the addition, the brown solution was stirred 2 hours at 50°, poured into 50 ml. of water, and steam distilled with super-heated steam at 150-180° to give 2.9 g. (83%) of yellow crystals, m.p. 60-85°, demonstrated by vapor phase chromatography and infrared spectroscopy to be a mixture of isomeric nitrobenzo[*b*]thiophenes in the quantities of 60%, 25%, and 15%. Quantitative desulfurization established the isomers as V, II, and I, respectively. The major fraction was separated by preparative vapor phase chromatography, m.p. 95-97°.

*Anal.* Calcd. for  $\text{C}_8\text{H}_5\text{NO}_2\text{S}$ : C, 53.62; H, 2.81. Found: C, 54.03; H, 2.91.

Major infrared bands: 703, 768, 643, 826, 847, 890, 1075, 1134, 1337, 1475, 1511  $\text{cm}^{-1}$ .

6-Nitrobenzo[*b*]thiophene-1,1-dioxide.

Two-tenths g. of V was oxidized with 10 ml. of 30% peracetic acid for 2 hours at 80°. After pouring on ice, filtering, and drying, light yellow crystals of the sulfone were obtained, m.p. 183-185°. Recrystallization from benzene gave 0.19 g. of pure sulfone, m.p. 188°. A mixture melting point, obtained with a sample prepared from the nitration of benzo[*b*]thiophene-1,1-dioxide (13), gave m.p. 187-188°. Infrared spectra of the two samples were identical.

7-Aminobenzo[*b*]thiophene (XVI).

A mixture of 0.75 g. (0.005 mole) of 7-hydroxybenzo[*b*]thiophene (15), 4 ml. of concentrated ammonium hydroxide, 4 ml. of water, and 1.0 g. of absorbed sulfur dioxide was sealed in a pyrex Carius tube. The tube was submerged and rotated in a pre-heated oil bath at 160° for 30 hours. The crude product mixture was diluted with 20 ml. of water and extracted with chloroform. The chloroform extract was washed with 10% sodium carbonate and water, treated with charcoal, filtered and dried, and the solvent removed, leaving 0.5 g. (67%) of XVI, b.p. 125°/4 mm. Infrared spectrum:  $\nu$ -NH<sub>2</sub> at 3435, 3370  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_8\text{H}_7\text{NS}$ : C, 64.39; H, 4.73; N, 9.39. Found: C, 64.00; H, 4.75; N, 9.09.

7-Nitrobenzo[*b*]thiophene (X).

Three-tenths g. of XVI was diazotized using 10 ml. of 20%

hydrochloric acid and 0.3 g. of sodium nitrite. The diazonium solution was neutralized with calcium carbonate, filtered, and 0.3 g. of sodium cobaltinitrite stirred into the filtrate. The precipitated diazonium cobaltinitrite salt was filtered, air dried, and added to a well-stirred mixture of 0.2 g. of sodium nitrite and 0.2 g. of copper sulfate in 5 ml. of water containing 0.1 g. of suspended cuprous oxide. After stirring overnight, the mixture was steam distilled, and the distillate was filtered, giving X as yellow needles, 0.06 g. (15.4%), m.p. 88-91°. Recrystallization from hexane gave m.p. 92-93°.

*Anal.* Calcd. for  $\text{C}_8\text{H}_5\text{NO}_2\text{S}$ : C, 53.62; H, 2.81. Found: C, 53.61; H, 2.99.

Major infrared bands: 693, 738, 812, 848, 971, 1087, 1121, 1224, 1316, 1348, 1497, 1520  $\text{cm}^{-1}$ .

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