A STUDY OF THE SUBSTITUTION REACTIONS OF BENZO[*b*]THIOPHENE AND ITS DERIVATIVES

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ABSTRACT

The nitration, halogenation, and amination reactions of benzo[*b*]thiophene and some of its derivatives are reported. Several new benzo[*b*]thiophenes have been prepared and directional influences of groups in the thiophene portion of the nucleus confirmed.

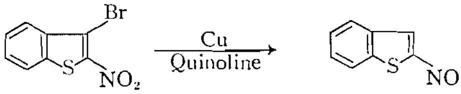
In a continuation of our interest in substitution reactions of benzo[*b*]thiophene and its derivatives, we have reinvestigated the isomer distribution in the nitration and halogenation of benzo[*b*]thiophene. It was of interest to study the orientation effects in reactions of electrophilic reagents with benzo[*b*]thiophene derivatives which were substituted on the thiophene portion of the benzo[*b*]thiophene ring system.

RESULTS AND DISCUSSION

Nitration of Benzo[b]thiophene

The nitration of benzo[*b*]thiophene (1–8) has been reported to give 3-nitrobenzo[*b*]thiophene. No other mononitro derivatives have been isolated. Recently, an infrared study (8) suggested that the nitration reaction mixture contained about 61% 3-nitrobenzo[*b*]thiophene and 16% 5-nitrobenzo[*b*]thiophene. The 2-nitro derivative was also assumed to be present in the nitration mixture (9, 10). Since 2-nitrobenzo[*b*]thiophene has not been characterized previously, its synthesis was necessary to establish its presence in the nitration mixture. 2-Nitrobenzo[*b*]thiophene was prepared by an unambiguous synthesis involving a copper–quinoline dehalogenation (11) of 3-bromo-2-nitrobenzo[*b*]thiophene (eq. [1]).

[1]

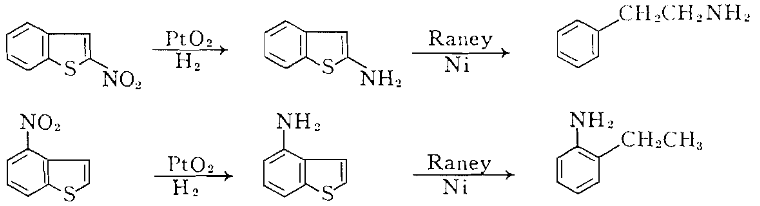


The nitration of benzo[*b*]thiophene with fuming nitric acid – acetic acid mixtures at 60–70° results in the formation of mononitrated benzo[*b*]thiophene (85% yield). The mixture was shown to contain 2-, 3-, and 4-nitrobenzo[*b*]thiophene. Infrared analysis of the reaction mixture indicated that the products included 10–15% 2-nitrobenzo[*b*]thiophene, 60–65% 3-nitrobenzo[*b*]thiophene, and 20–30% of other components, mainly 4-nitrobenzo[*b*]thiophene.

The presence of 4- and 2-nitrobenzo[*b*]thiophene in the nitration mixture was confirmed by chemical degradation. Thus, the nitration mixture was catalytically reduced over platinum oxide, followed by Raney nickel desulfurization, to give a mixture of aromatic amines including 2-phenylethylamine and *o*-aminoethylbenzene (eq. [2]).

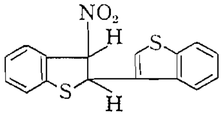
Although 3-nitrobenzo[*b*]thiophene is also known to be in the nitration mixture, none of the corresponding degradation product, α-phenylethylamine, was observed. The reduction product of 3-nitrobenzo[*b*]thiophene, 3-aminobenzo[*b*]thiophene, reportedly

[2]



cannot be distilled (2, 12), and is too unstable to be isolated in the pure form (3, 13, 14). No evidence was obtained for the presence of 5-nitrobenzo[*b*]thiophene or other isomers in the nitration mixture.

Optimum yields of the 3-nitrobenzo[*b*]thiophene were obtained when the nitration of benzo[*b*]thiophene was carried out above room temperature. At lower temperatures the formation of I, an unstable intermediate observed earlier by Komppa (3), was competitive with 3-nitrobenzo[*b*]thiophene formation.



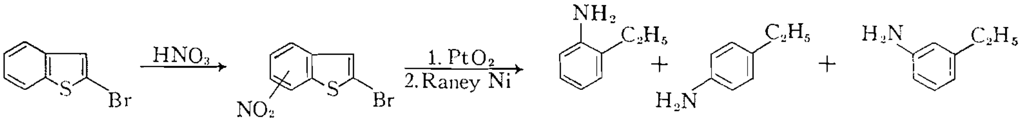
I

3-Nitrobenzo[*b*]thiophene undergoes no further nitration with fuming nitric acid and glacial acetic acid at 105°. Therefore, the possibility of the presence of dinitro products in the nitration mixture is doubtful. This is substantiated by the fact that no residue remained after the distillation of the mononitro products from the reaction mixture of nitric acid and benzo[*b*]thiophene at 60–70°.

Nitration of 2- and 3-Bromobenzo[b]thiophene

Although the nitration of 3-bromobenzo[*b*]thiophene occurs with preferential attack at the 2 position of the thiophene nucleus,[1] the nitration of 2-bromobenzo[*b*]thiophene yields several products. Vapor-phase chromatographic analysis, after dehalogenation, reduction, and desulfurization, confirmed the presence of *o*-aminoethylbenzene, *p*-aminoethylbenzene, and *m*-aminoethylbenzene. These products result from 4-nitro-2-bromobenzo[*b*]thiophene, 6-nitro-2-bromobenzo[*b*]thiophene, and 5(or 7)-nitro-2-bromobenzo[*b*]thiophene, respectively. Although no α-aminoethylbenzene was found, this does not prove that 3-nitro-2-bromobenzo[*b*]thiophene was not formed, because of the possible instability of the intermediate amino derivative mentioned previously (eq. [3]).

[3]



From the nitration mixture of 2-bromobenzo[*b*]thiophene, three distinct mononitro-2-bromobenzo[*b*]thiophenes were isolated. After debromination of the nitration mixture (11) one of the isolated compounds had a melting point corresponding to that of 4-nitrobenzo[*b*]thiophene. This fact further supports the postulate that 4-nitro-2-bromobenzo[*b*]thiophene was one of the original nitration products.

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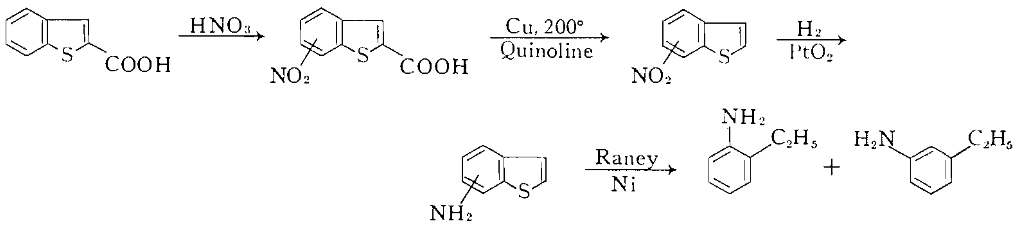
[1] *Reference 3 reports the 3-bromo-2-nitro derivative, but the 3-bromo derivative, which is a liquid, is incorrectly listed as a solid melting at 146–156°.*

Nitration of 2- and 3-Benzo[b]thiophenecarboxylic Acids

Nitration of benzo[*b*]thiophene-2-carboxylic acid also produced a mixture of products. Structural elucidation was effected by decarboxylation to the corresponding nitrobenzo[*b*]thiophenes followed by reduction and desulfurization as previously described (eq. [4]).

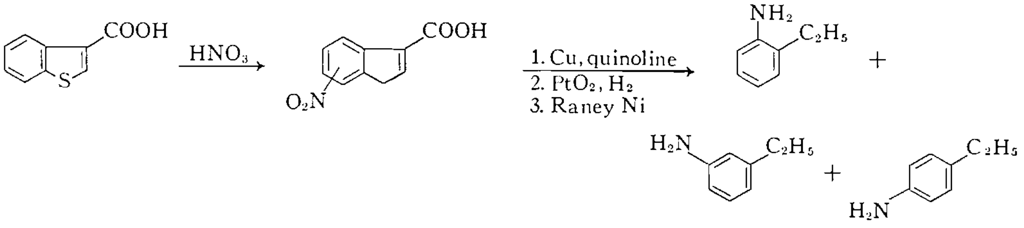
[4]



The *o*- and *m*-aminoethylbenzenes which were obtained correspond to 4-nitrobenzo[*b*]thiophene-2-carboxylic acid and either 5- or 7- (or a mixture of both) nitrobenzo[*b*]thiophene-2-carboxylic acid. No *p*-aminoethylbenzene was found. Again, the 3-nitrobenzo[*b*]thiophene-2-carboxylic acid cannot be eliminated, because of the unstable intermediate, 3-aminobenzo[*b*]thiophene.

Nitration of benzo[*b*]thiophene-3-carboxylic acid also led to a mixture of mononitro derivatives. By the decarboxylation, reduction, and desulfurization technique previously outlined, *o*-aminoethylbenzene was obtained as the major product. Minor quantities of *m*- and *p*-aminoethylbenzene, corresponding to 4-nitro-, 5- or 7-nitro-, and 6-nitrobenzo[*b*]thiophene-3-carboxylic acid, were also obtained (eq. [5]).

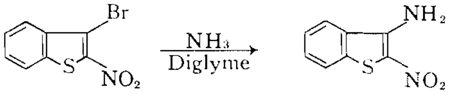
[5]



Preparation of Amino Derivatives of 2-Nitrobenzo[b]thiophene

Heating 3-bromo-2-nitrobenzo[*b*]thiophene in diglyme with anhydrous ammonia gives 3-amino-2-nitrobenzo[*b*]thiophene by a simple aromatic nucleophilic substitution reaction (eq. [6]).

[6]



3-Amino-2-nitrobenzo[*b*]thiophene was shown by its infrared spectrum to exist only in the tautomeric amino form. Recent reports indicate that 2-aminobenzo[*b*]thiophene also exists in the amino form (15). In addition to the known aminobenzo[*b*]thiophenes (16), 3-diethylamino and 3-phenylamino derivatives were also prepared by heating 3-bromo-2-nitrobenzo[*b*]thiophene with diethylamine and aniline, respectively.

Halogenation of Benzo[b]thiophene

Although the chlorination (3, 17, 18), bromination (3, 4, 19–22), and iodination (23–25) of benzo[*b*]thiophene have been reported, no isomer distributions are known. In the chlorination and bromination of benzo[*b*]thiophene, we observed the formation of small quantities of 2-substituted and disubstituted products. Substitution in the 3 position is predominant. In the iodination of benzo[*b*]thiophene, no evidence for any 2-substitution or disubstitution products was obtained. Table I lists the isomer distributions obtained upon halogenation of benzo[*b*]thiophene.

TABLE I

Halogenation distribution products of benzo[*b*]thiophene

Halogen	2-Substitution (%)	3-Substitution (%)	2,3-Disubstitution (%)
Chlorine	3	69	28
Bromine	3	87	10
Iodine	0	100	0

EXPERIMENTAL[2]

Preparation of Mononitrobenzo[b]thiophenes

To a heated (60–70°) solution of 50 ml acetic acid and 12 ml fuming nitric acid was added dropwise, with stirring, 15 g (0.11 mole) benzo[*b*]thiophene which had been diluted with an equal volume of acetic acid. After the addition of the nitric acid solution was complete, the reaction mixture was stirred for an additional 2 h at 60–70° and then poured into ice water. The oily layer was extracted with chloroform, neutralized with an aqueous solution of sodium bicarbonate, and dried over anhydrous magnesium sulfate. An 85% yield of yellow mononitrobenzo[*b*]thiophenes was obtained upon distillation at 105–110° and 0.1 mm.

Preparation of Aminobenzo[b]thiophenes

A solution of 17 g (0.09 mole) of the mononitration mixture in 150 ml of acetone was reduced with 0.2 g of platinum oxide as catalyst in a Parr hydrogenation apparatus for 1 h at 50 p.s.i. hydrogen pressure. The reaction mixture was filtered and concentrated under vacuum. Vacuum distillation of the residue gave a mixture of aminobenzo[*b*]thiophenes; yield 11.9 g (81%), b.p. 110–115° at 0.2 mm.

Preparation of Aminoethylbenzenes

A mixture of 12 g (0.08 mole) of the aminobenzo[*b*]thiophenes, 800 ml of methanol, and 150 g of Raney nickel was refluxed for 0.5 h. After the Raney nickel was removed by filtration, the resulting filtrate was distilled *in vacuo* to give a mixture of aminoethylbenzenes; b.p. 49–53° at 0.1 mm. The aminoethylbenzenes were shown to consist of a mixture of 2-phenylethylamine and *o*-aminoethylbenzene in a ratio of about 2:1, as determined by vapor-phase chromatography with a 2 m Carbowax column.

Preparation of Mononitro-2-bromobenzo[b]thiophenes

A mixture of 5 ml of fuming nitric acid and 5 ml of acetic acid was added dropwise to a cooled (5–10°) solution of 5 g (0.02 mole) of 2-bromobenzo[*b*]thiophene in 20 ml of acetic anhydride. The reaction mixture was stirred for 2 h at room temperature and the resulting yellow solution poured into an ice–water mixture. After the yellow precipitate was washed with water and sodium carbonate solutions, 6 g of solid yellow product was obtained. From column chromatography with activated alumina, three mononitro-2-bromobenzo[*b*]thiophenes were obtained. They possessed the following melting points: 124.5–125°, 148°, and 164.0–164.5°.

Anal. Calcd. for $C_8H_4NO_2BrS$: C, 37.27; H, 1.56; S, 12.43; N, 5.43; Br, 30.97. Found:

Melting point	C	H	S	N	Br
124.5–125°	37.63	1.78	12.05	5.32	31.13
148°	37.17	1.71	12.05	5.17	30.69
164.0–164.5°	37.33	1.75	12.60	5.31	31.03

Debromination of the Nitration Products of 2-Bromo[b]thiophene

A mixture of 10 g of the nitration product of 2-bromo-[*b*]thiophene, 3.3 g of copper bronze powder, and 55 ml of quinoline was heated to 135° under a nitrogen atmosphere for 30 min. After the reaction mixture was cooled, dilute hydrochloric acid and benzene were added. The benzene layer was evaporated and the residue distilled at 0.1 mm. The resulting solid yellow material was chromatographed on activated alumina. A fraction melting at 85–86° was obtained (lit. (7, 26, 27) m.p. 84–85° and 88° for 4-nitrobenzo[*b*]thiophene).

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[2] *All melting points are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory. Infrared spectra were obtained with a Perkin–Elmer model 137 Infracord. Vapor-phase chromatographic analyses were performed with a Burrell model K-2 chromatograph equipped with thermal conductivity detectors.*

Preparation of Aminoethylbenzenes from Mononitro-2-bromobenzo[b]thiophenes

Reduction and desulfurization of the mononitration products of 2-bromobenzo[*b*]thiophene were carried out under conditions similar to those used for the mononitration products of benzo[*b*]thiophene. Vapor-phase chromatographic analysis of the products indicated the presence of *o*-aminoethylbenzene, *p*-aminoethylbenzene, and *m*-aminoethylbenzene by comparison of their retention times with those of known samples. No α-aminoethylbenzene was observed.

Nitration of 3-Bromobenzo[b]thiophene

A solution of 23 ml of fuming nitric acid and 23 ml of acetic acid was added dropwise, with stirring, to a cooled (5–10°) mixture of 20 g (0.095 mole) of 3-bromobenzo[*b*]thiophene and 80 ml of acetic anhydride. The reaction mixture was stirred for 1 h and poured onto ice. The yellow solid was recrystallized from ethanol and sublimed, m.p. 164–165° (4).

When a mixture of 3-bromo-2-nitrobenzo[*b*]thiophene and 20% sodium hydroxide was refluxed, 3-hydroxy-2-nitrobenzo[*b*]thiophene was obtained, m.p. 104–105° (decomp.) (lit. (28) m.p. 104–105° (decomp.)).

Preparation of 2-Nitrobenzo[b]thiophene

A mixture of 6 g (0.02 mole) of 3-bromo-2-nitrobenzo[*b*]thiophene, 1.8 g of copper bronze powder, and 30 ml of quinoline was vigorously stirred under a nitrogen atmosphere, gradually heated to 150°, and maintained at that temperature for 45 min. The reaction mixture was then cooled, made acidic with dilute hydrochloric acid, and extracted with benzene. After the benzene was removed, the residue was distilled at 105° and 0.1 mm. After recrystallization from methanol and sublimation, the yellow crystals melted at 117°; yield 25%.

Anal. Calcd. for $C_8H_5NO_2S$: C, 53.62; H, 2.81; S, 17.89; N, 7.82. Found: C, 53.83; H, 2.98; S, 17.93; N, 7.85.

Preparation of Mononitrobenzo[b]thiophene-2-carboxylic Acids

To a cold (0–5°) solution of 10 g (0.055 mole) of benzo[*b*]thiophene-2-carboxylic acid (19, 29) in 75 ml of acetic anhydride was added 10 ml of fuming nitric acid in 10 ml of acetic acid. After the solution was stirred for 30 min at 0°, it was allowed to warm to room temperature; the stirring was continued for an additional $2\frac{1}{2}$ h. The mixture was poured into ice water, filtered, and washed. A 68% yield of a yellow mixture of mononitrocarboxylic acids, m.p. 230–240°, was obtained.

Anal. Calcd. for $C_9H_5NSO_4$: N, 6.28; S, 14.35. Found: N, 6.56; S, 14.35.

Decarboxylation of the Mixture of Mononitrobenzo[b]thiophene-2-carboxylic Acids

A mixture of 10 g (0.045 mole) of the mononitrobenzo[*b*]thiophene-2-carboxylic acids (30, 31) was decarboxylated with 2.5 g of copper bronze powder and 50 ml of quinoline by heating it at 190° for 30 min in a nitrogen atmosphere. At the end of this period, the reaction mixture was poured into a mixture of 250 g of ice and 50 ml of concentrated hydrochloric acid. The resulting yellow precipitate was filtered off, dried, and distilled *in vacuo* to give 4 g (50% yield) of mononitrobenzo[*b*]thiophenes, b.p. 105–110° at 0.1 mm, m.p. 50–70°.

Anal. Calcd. for $C_8H_5NSO_2$: N, 7.82; S, 17.90. Found: N, 7.89; S, 17.80.

Reduction and Desulfurization of the Mixture of the Decarboxylation Products from the Mononitrobenzo[b]thiophene-2-carboxylic Acids

The reduction and desulfurization procedure for the mononitrobenzo[*b*]thiophenes was the same as that described earlier.

Nitration of Benzo[b]thiophene-3-carboxylic Acid

The nitration procedure for benzo[*b*]thiophene-3-carboxylic acid was the same as that used for benzo[*b*]thiophene-2-carboxylic acid (32). A 75% overall yield of a mixture of mononitrobenzo[*b*]thiophene-3-carboxylic acids, m.p. 192–225°, was obtained.

Anal. Calcd. for $C_9H_5NSO_4$: N, 6.28; S, 14.35. Found: N, 6.38; S, 13.93.

Decarboxylation of the Nitration Products of Benzo[b]thiophene-2-carboxylic Acid

A 62% yield of a mixture of mononitrobenzo[*b*]thiophenes was obtained by a decarboxylation procedure analogous to that used for the nitration mixture of benzo[*b*]thiophene-2-carboxylic acid.

Anal. Calcd. for $C_8H_5NSO_2$: N, 7.82; S, 17.90. Found: N, 7.91; S, 18.00.

Reduction and Desulfurization of the Decarboxylation Products from the Mononitrobenzo[b]thiophene-3-carboxylic Acids

Catalytic reduction and Raney nickel desulfurization were carried out by the previously described techniques. A 60% yield of aminobenzo[*b*]thiophenes was obtained, b.p. 120–123° at 0.5–0.3 mm. A 52% yield of aminoethylbenzene resulted after desulfurization, b.p. 48–52° at 0.1 mm. The aminoethylbenzenes consisted of mostly *o*- and minor amounts of *m*- and *p*-aminoethylbenzenes.

Gas Chromatographic Analysis

A 2½ m glass column packed with 20% Carbowax 4000 on Chromosorb W was used in all cases. Identifications were made by comparison of peaks with those of authentic compounds under the same experimental conditions (150° and a helium flow rate of 90 ml/min). The compounds used for comparison, α-phenylethylamine, 2-phenylethylamine, *o*-aminoethylbenzene, and *p*-aminoethylbenzene, were commercially available. *m*-Aminoethylbenzene was prepared from *m*-nitroacetophenone.

3-Amino-2-nitrobenzo[b]thiophene

A mixture of 10 g (0.039 mole) of 3-bromo-2-nitrobenzo[*b*]thiophene and 100–150 ml of diglyme was heated to 120°, and dry ammonia was passed into the solution for 3 h. After the solution was added to ice water, the crude solid was filtered off and dried. The crude material, which melted near 200°, was chromatographed on grade 3 activated alumina, yielding yellowish-orange crystals, m.p. 218.0–218.5°.

Anal. Calcd. for $C_8H_6N_2O_2S$: C, 49.47; H, 3.11; N, 14.43; S, 16.51. Found: C, 49.53; H, 3.17; N, 14.70; S, 16.24.

3-Phenylamino-2-nitrobenzo[b]thiophene

A mixture of 1 g (3.9 mmoles) of 2-nitro-3-bromobenzo[*b*]thiophene and 1.8 g (19.4 mmoles) of aniline was heated for 15 min at 100°. Dilute hydrochloric acid was added and the resulting mixture was extracted with benzene. After the benzene was evaporated, the residue was recrystallized from a mixture of chloroform and ethanol, to give a quantitative yield of bright-orange needles, m.p. 210–211°.

Anal. Calcd. for $C_{14}H_{10}N_2O_2S$: C, 62.21; H, 3.73; S, 11.86; N, 10.35. Found: C, 62.11; H, 3.56; S, 11.90; N, 10.50.

3-Diethylamino-2-nitrobenzo[b]thiophene

The procedure was the same as that used for the preparation of 3-phenylamino-2-nitrobenzo[*b*]thiophene, except that diethylamine was used instead of aniline; yield quantitative, m.p. 54°.

Halogenation of Benzo[b]thiophene

Benzo[*b*]thiophene was chlorinated, brominated, and iodinated according to the procedures of Schlesinger and Mowry (17), Szmuszkovicz and Modest (21), and Gaertner (24), respectively. Vapor-phase chromatographic analysis of the reaction products was accomplished on a 7 ft column packed with 20% Carbowax 4000 on Chromosorb W. The retention times of the various halobenzo[*b*]thiophenes were determined with authentic samples, and these times were compared with those of the various components found in the halogenation mixture.

Preparation of 2-Chlorobenzo[b]thiophene

An ethereal solution of *n*-butyllithium was prepared by the gradual addition, with stirring, of 20.0 g (0.2 mole) of *n*-butyl chloride in 40 ml of anhydrous ether to 3.7 g (0.5 mole) of lithium ribbon suspended in 100 ml of anhydrous ether. One milliliter of *n*-butyl bromide was added as catalyst and the mixture was allowed to reflux for 1 h. The solution was then cooled to 0–5°, and 13.5 g (0.10 mole) of benzo[*b*]thiophene in 30 ml of ether was added with stirring. The mixture was kept at 0° for 1 h. Into the above solution was bubbled 7.1 g (0.10 mole) of chlorine gas, during which time the temperature was maintained between −30° and −20°. The ether solution was washed with 200 ml of water and dried, and the solvent was removed *in vacuo*. Distillation gave 5 g (30% conversion, 48% yield) of 2-chlorobenzo[*b*]thiophene, b.p. 60–70° at 0.1 mm, m.p. 34°.

Anal. Calcd. for C_8H_5SCl: C, 57.0; H, 2.97; S, 19.0; Cl, 21.0. Found: C, 56.7; H, 3.16; S, 18.2; Cl, 20.8.

The picrate melted at 97°. The 1-dioxide was prepared by hydrogen peroxide oxidation, m.p. 141–142° (lit. (17) m.p. 142–143°).

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