1,3-Benzodithiolylium Salts. Synthesis and Reactions with Nucleophilic Reagents

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(Received March 15, 1976)

Various salts of 1,3-benzodithiolylium ion were prepared in excellent yields on treatment of 2-alkoxy- and 2-alkylthio-1,3-benzodithioles with acids in acetic anhydride. The reactions of 1,3-benzodithiolylium tetrafluoroborate (**1a**) with a wide variety of nucleophilic reagents (alcohols, water, thiols, hydrogen sulfide, primary, secondary, and tertiary amines, ammonia, *N,N*-dimethylformamide, electron-rich aromatic compounds, active methylene compounds, tropilidene, and sodium borohydride) were studied. In all cases examined, **1a** reacted with nucleophilic reagents at the 2-position to give the corresponding 1,3-benzodithioles in good yields, excepting the reactions with tertiary amines and *N,N*-dimethylformamide which resulted in the formation of dibenzotetrathiafulvalene. Salt **1a** was also prepared from 1,3-benzodithiole and trityl tetrafluoroborate.

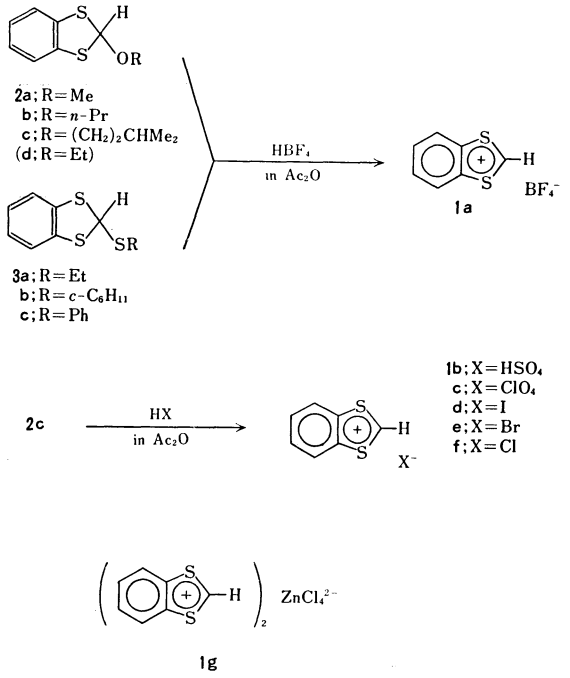
Like 1,2-dithiolylium ion, 1,3-dithiolylium ion possesses a potential aromatic sextet, its aromaticity being the subject of controversy. Recently the synthesis, reactivity, and spectral properties of 1,3-dithiolylium compounds have been intensively studied in efforts to find relationships between their structure and thier chemical and physical properties.[1-3] In a preliminary report we briefly described a convenient synthesis of 1,3-benzodithiolylium tetrafluoroborate (**1a**).[4] We now report the synthesis of various salts of 1,3-benzodithiolylium ion and the reactions of the fluoroborate salt **1a** with a wide variety of nucleophilic reagents.

Results and Discussion

Synthesis of 1,3-Benzodithiolylium Salts. We recently reported a one-step synthesis of 2-alkoxy-1,3-benzodithioles (**2**) on a preparative scale which involves addition of alcohols to the carbene (1,3-benzodithiol-2-ylidene) produced from carbon disulfide and benzyne generated by aprotic diazotization of anthranilic acid.[5] Treatment of a solution of 2-isopentyloxy-1,3-benzodithiole (**2c**) in acetic anhydride with tetrafluoroboric acid at 0 °C gave 1,3-benzodithiolylium tetrafluoroborate (**1a**) in 96% yield. The structure of **1a** was determined on the basis of spectral data and elemental analysis. Benzodithioles **2a** and **2b** gave the fluoroborate salt **1a** in 94 and 88% yields, respectively. Other slats of 1,3-benzodithiolylium ion could also be prepared in a similar way; sulfuric, perchloric, hydriodic, and hydrobromic acids reacted with the benzodithiole **2c** in acetic anhydride to give the hydrogen sulfate **1b** (81%), perchlorate **1c** (94%), iodide **1d** (81%), and bromide **1e** (95%), respectively. The chloride salt **1f**, soluble in the reaction medium when prepared from **2c** and concentrated hydrochloric acid in acetic anhydride, could not be isolated, but its zinc chloride double salt **1g** was obtained in 96% yield by treating the mixture with zinc chloride.

2-Alkylthio-1,3-benzodithioles (**3**) have been easily synthesized in good yields by treatment of the benzodithiole **2c** with thiols in acetic acid.[6] Treatment of compounds **3a**—**c** with tetrafluoroboric acid also yielded the fluoroborate salt **1a** in a respective yield of 86, 90, and 92%.

The only synthetic method for preparing 1,3-benzodithiolylium salts involves the condensation of 1,2-benzenedithiol with formic acid or triethyl orthoformate in the presence of acids.[7] However, the synthesis of 1,2-benzenedithiol is laborious.[8] The present reaction provides the most straightforward synthetic method of salts **1** since the starting material can be obtained on a preparative scale by one-step synthesis. The formation of 1,3-dithiolylium salts from 2-methoxy- and 2-methylthio-1,3-dithioles has been reported.[3b,9]



Scheme 1.

The fluoroborate salt **1a** is stable at room temperature and soluble in polar solvents; it was used to investigate the reactivity of 1,3-benzodithiolylium ion toward a wide variety of nucleophilic reagents.

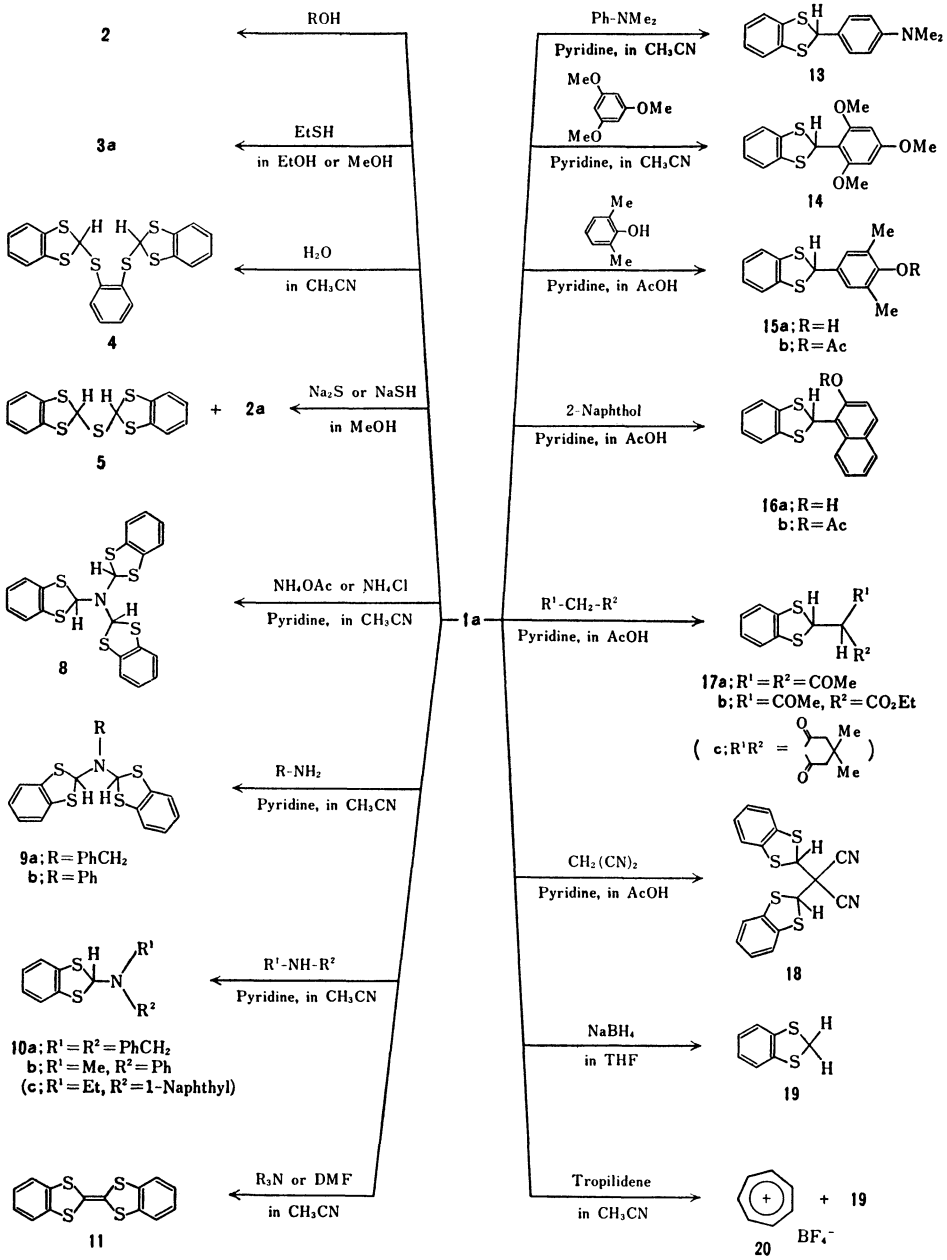
*Reactions of 1,3-Benzodithiolylium Tetrafluoroborate (**1a**) with Nucleophilic Reagents.* Standing the fluoroborate salt **1a** in methanol for 1 h at room temperature gave rise to 2-methoxy-1,3-benzodithiole (**2a**) in 87% yield. Similar treatment of **1a** with ethanol and 1-propanol gave benzodithioles **2d** (75%) and **2b** (94%), respectively. The formation of 2-alkoxy-1,3-dithioles from 1,3-dithiolylium perchlorates and alcohols

in the presence of base has been reported.[3b,7e,10]

Buza *et al.* reported that the perchlorate salt **1c**, on treatment with triethylamine in an aqueous acetonitrile or *N,N*-dimethylformamide, gives compound **4** by partial hydrolysis.[7c] The fluoroborate salt **1a**, when allowed to stand in an aqueous acetonitrile at room temperature for a long period, gave compound **4** in 88% yield. The mechanism of the formation of **4** probably involves the tautomerization of the 2-hydroxy compound **6** to the open chain compound **7** as an initial process as postulated. A similar reaction has been observed with the benzodithiole **2c** in acetic acid.[11]

A solution of the salt **1a** in ethanol was allowed to stand at room temperature for 1 h and then 4 molar amounts of ethanethiol was added. Standing the resulting mixture for another 1 h gave rise to 2-ethylthio-1,3-benzodithiole (**3a**) in 81% yield. This suggests that in ethanol the equilibrium between 1,3-benzodithiolylium ion and 2-ethoxy-1,3-benzodithiole (**2d**), which lies far to **2d**, takes place and that **2d** is converted into the final product **3a** *via* 1,3-benzodithiolylium ion on addition of ethanethiol. Thus, upon standing **1a** in ethanol containing 4 molar amounts of ethanethiol, compound **3a** was obtained in 80% yield; ^{1}H NMR analysis indicated no formation of **2d**. Similarly, **1a** and ethanethiol in methanol gave **3a** in 81% yield.

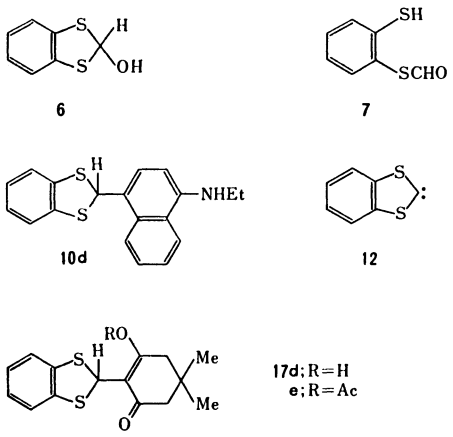
Sodium sulfide reacted with the salt **1a** in methanol to give the sulfide **5** (15%) and the benzodithiole **2a** (69%). The reaction of sodium hydrogensulfide with **1a** in methanol also yielded compounds **5** (33%)



Scheme 2.

and **2a** (54%). The tropylium ion reacts in a similar way with hydrogen sulfide to give ditropyl sulfide.[12] It is of interest that the reaction of 2,4,5-triphenyl-1,3-dithiolylium perchlorate with sodium hydrogensulfide in methanol gives 2,4,5-triphenyl-1,3-dithiole in good yield.[10] In our case no such reduction product was formed.

The reactions of some 1,3-dithiolylium salts with ammonia have been examined,[10,13] a 2-aminodithiole adduct being isolated in one instance.[10] The reaction of ammonium acetate with 3 molar amounts of the salt **1a** in the presence of pyridine in acetonitrile at room temperature gave tris(1,3-benzodithiol-2-yl)amine (**8**) in 86% yield. Neither (1,3-benzodithiol-2-yl)-amine nor bis(1,3-benzodithiol-2-yl)amine was isolated. The strongest support for structure of **8** was provided by ^{1}H NMR spectrum: δ (CS_2) 6.30 (3H, s, methine) and 6.90—7.25 (12H, A_2B_2m, aromatic). Under the same conditions, ammonium chloride and 3 molar amounts of **1a** also gave the amine **8** in 50% yield.



Scheme 3.

Benzylamine reacted with 2 molar amounts of the salt **1a** in the presence of pyridine in acetonitrile at room temperature to give *N*,*N*-bis(1,3-benzodithiol-2-yl)benzylamine (**9a**) in 86% yield. Similarly, aniline and **1a** gave the amine **9b** in 79% yield. Thus, evidently all the amino hydrogens of ammonia and primary amines are replaceable by 1,3-benzodithiol-2-yl groups by **1a**, whereas the reactions of 2-methylthio-1,3-dithiolylium salts with primary amines give either 2-imino-1,3-dithioles or 2-amino-1,3-dithiolylium salts with evolution of methanethiol, depending upon the number of moles of amines employed.[13a,14]

Secondary amines such as dibenzylamine and *N*-methylaniline reacted with the salt **1a** in the presence of pyridine in acetonitrile to give compounds **1a** (90%) and **10b** (92%), products of *N*-alkylation, respectively. With *N*-ethyl-1-naphthylamine, unexpectedly, 4-(1,3-benzodithiol-2-yl)-*N*-ethyl-1-naphthylamine (**10d**) was obtained nearly quantitatively. The formation of **10d** can be explained either by direct electrophilic attack of **1a** on the 4-position of the naphthalene ring of the substrate or by the rearrangement of the primary product **10c** under the conditions employed. In either case, the steric hindrance caused by the *peri*-hydrogen may be responsible for the formation of the product.[15] In this connection it is of interest that the reaction of 2-methylthio-4-phenyl-1,3-dithiolylium perchlorate with *N*-methylaniline gives 2-(*N*-methylanilino)-4-phenyl-1,3-dithiolylium perchlorate with loss of methanethiol, whereas the reaction with diphenylamine yields 2-(*p*-anilinophenyl)-4-phenyl-1,3-dithiolylium perchlorate.[16]

Treatment of the salt **1a** with triethylamine in acetonitrile gave dibenzotetrathiafulvalene **11** in 81% yield in accord with the findings with the perchlorate salt **1c**.[7c-e] Treatment of **1a** with tripropylamine also gave **11** in 84% yield. The formation of **11** can be readily explained by base-catalyzed deprotonation of **1a** and subsequent reaction of the resulting carbene **12** with **1a** followed by deprotonation. Standing **1a** in *N*,*N*-dimethylformamide for 1.5 h at room temperature resulted in the formation of **11** in 80% yield. In connection with the recent discovery of the highly conducting charge transfer salts of tetrathiafulvalenes with 7,7,8,8-tetracyanoquinonedimethane,[17] many derivatives of tetrathiafulvalene have been prepared by treatment of 1,3-dithiolylium salts with base. We believe that *N*,*N*-dimethylformamide serves as a useful base for this conversion, although only tertiary amines have been so far employed.[3b,7c-e,9,18]

Like other 1,3-dithiolylium ions,[16,19] 1,3-benzodithiolylium ion undergoes electrophilic substitution with electron-rich aromatic compounds; *N*,*N*-dimethylaniline and 1,3,5-trimethoxybenzene reacted with the salt **1a** to give compounds **13** (89%) and **14** (98%), respectively. Although the reaction of **1a** with phenol in the presence of pyridine in acetic acid at 60—70 °C for 3 h gave unidentified oils and intractable tars, 2,6-dimethylphenol and 2-naphthol reacted with **1a** to give **15b** (68%) and **16b** (97%), respectively. In these cases, primary products **15a** and **16a** must be acetylated under the conditions employed to give the final products **15b** and **16b**, respectivley.

Reaction of 1,3-dithiolylium salts with active methylene compounds leading to 1,3-dithiol-2-ylidene derivatives have been extensively studied.[3e,14,19c,20] The reaction of **1a** with acetylacetone and ethyl acetoacetate in the presence of pyridine in acetic acid afforded **17a** (92%) and **17b** (89%), respectively. Under the same conditions, dimedone and **1a** gave the acetate **17e** in 76% yield; the primary product **17c**, which exists in the enol form **17d**[21] must be acetylated to give **17e** as observed with 2,6-dimethylphenol and 2-naphthol. The reaction of **1a** with malononitrile, in striking contrast to the foregoing results, gave bis-(1,3-benzodithiol-2-yl)malononitrile (**18**) in 86% yield, although a slight excess of malononitrile was employed. Similar reactions have been observed with benzodithioles **2** and active methylene compounds in acetic acid.[21]

Reduction of the salt **1a** with sodium borohydride in tetrahydrofuran afforded 1,3-benzodithiole (**19**) in 81% yield. The reaction of **1a** with a slight excess of tropilidene in acetonitrile at 0 °C gave tropylium tetrafluoroborate (**20**) and the benzodithiole **19** in a respective yield of 90 and 65%. Hirai has reported

that the reaction of 4-phenyl-1,3-dithiolylium perchlorate with a slight excess of tropilidene in acetic acid at 80 °C gives a mixture of tropylium perchlorate and the starting perchlorate.[3d] These results lead to the conclusion that 1,3-benzodithiolylium ion surpasses 4-phenyl-1,3-dithiolylium ion in ability to accept a hydride, thus suggesting that the positive charge of the former ion is more localized on the 2-position as compared with that of the parent 1,3-dithiolylium ion by the influence of the fused benzene ring.

The benzodithiole **19**, when allowed to react with trityl tetrafluoroborate in acetonitrile, gave rise to the salt **1a** (75%) and triphenylmethane (75%). The reaction provides another new synthetic way to **1a** since **19** can be also synthesized by the literature method.[22]

$$\mathbf{19} + Ph_3C^+BF_4^- \longrightarrow \mathbf{1a} + Ph_3CH$$

Scheme 4.

Finally, it is concluded that 1,3-benzodithiolylium ion reacts exclusively at the 2-position with nucleophilic reagents in agreement with the results by molecular orbital calculations.[23]

Experimental

2-Alkoxy- and 2-alkylthio-1,3-benzodithioles (**2** and **3**) were prepared by the methods described.[5,6] Acetic acid and acetonitrile were distilled over phosphorus pentoxide before use. Other commercial materials were used without further purification, unless otherwise stated. ^1H NMR spectra were determined at 100 MHz with tetramethylsilane as internal reference. IR spectra of solids were taken for Nujol mulls, and those of liquids for films. All melting points are uncorrected.

*1,3-Benzodithiolylium Salts (**1**) from 2-Alkoxy-1,3-benzodithioles (**2**). a) 1,3-Benzodithiolylium Tetrafluoroborate (**1a**)*: To a stirred and ice-cooled solution of 2-isopentyloxy-1,3-benzodithiole (**2c**) (24.0 g, 0.1 mol) in acetic anhydride (300 ml) was added dropwise 42% tetrafluoroboric acid (42 g, 0.2 mol) over a period of 0.5 h. After 0.5 h of stirring at 0 °C, ether (400 ml) was added to precipitate the product completely. Filtration and washing with anhydrous ether (150 ml) gave **1a** as near-white crystals, 23.0 g (96%), mp 149—150 °C (dec). The salt thus obtained gave satisfactory result of elemental analysis and was used for investigation of the reactions with nucleophilic reagents. Recrystallization from anhydrous acetic acid gives a more pure specimen, mp 150—150.5 °C (dec).

ν_{max} 1000—1120 cm^{-1} (BF_4^-); δ (CF_3CO_2D) 8.06—8.26 and 8.66—8.86 (4H, m, aromatic) and 11.50 (1H, s, methine).

Found: C, 35.25; H, 2.11%. Calcd for $C_7H_5BF_4S_2$: C, 35.02; H, 2.10%.

In a similar way, **1a** was prepared from **2a** and **2b** in a respective yield of 94 and 88%.

*b) 1,3-Benzodithiolylium Hydrogen Sulfate (**1b**)*: This salt was prepared from **2c** (0.72 g, 3 mmol) and concentrated sulfuric acid (1.2 g, 12 mmol) in acetic anhydride (15 ml) in 81% yield (0.61 g) as white crystals. It showed no difinite melting point and decomposed gradually from 130 °C. It turned violet even when kept in refrigerator.

Found: C, 33.29; H, 2.46; S, 37.62%. Calcd for $C_7H_6O_4S_3$: C, 33.59; H, 2.42; S, 38.43%.

*c) 1,3-Benzodithiolium Perchlorate (**1c**)*: This salt was prepared from **2c** (0.72 g, 3 mmol) and 60% perchloric acid (1.0 g, 6 mmol) in acetic anhydride (15 ml) in 94% yield (0.71 g) as white crystals. It exploded violetly at 185 °C in agreement with the findings of the previous workers.[7c-e]

*d) 1,3-Benzodithiolylium Iodide (**1d**)*: This salt was prepared from **2c** (0.72 g, 3 mmol) and 57% hydriodic acid (1.35 g, 6 mmol) in acetic anhydride (15 ml) in 81% yield (0.68 g) as orange crystals, mp 101—103 °C (dec).

Found: C, 29.93; H, 1.79; I, 45.25; S, 22.84%. Calcd for $C_7H_5IS_2$: C, 30.00; H, 1.80; I, 45.30; S, 22.89%.

*e) 1,3-Benzodithiolylium Bromide (**1e**)*: This salt was prepared from **2c** (0.72 g, 3 mmol) and 47% hydrobromic acid (1.03 g, 6 mmol) in acetic anhydride (15 ml) in 95% yield (0.66 g) as white crystals, mp 169—170 °C (dec).

Found: C, 36.04; H, 2.14; Br, 34.14; S, 27.51%. Calcd for $C_7H_5BrS_2$: C, 36.06; H, 2.16; Br, 34.28; S, 27.51%.

*f) Bis(1,3-benzodithiolylium) Zinc Tetrachloride (**1g**)*: To a stirred and ice-cooled solution of **2c** (0.72 g, 3 mmol) in acetic anhydride (15 ml) was slowly added concentrated hydrochloric acid (0.61 g, 6 mmol) at 0 °C. After being stirred for 0.5 h, zinc chloride (0.20 g, 1.5 mmol) was added and the mixture was stirred at 0 °C for another 0.5 h. The resulting precipitate was collected and washed with acetonitrile (10 ml) to give 0.74 g (96%) of **1g**. Hurtley and Smiles[7a] reported this salt as orange needles with a red tint of varying depth. However, our product freshly prepared was a white solid, scarcely soluble in organic solvents, darkening from 180 °C and melting at 201—202°C accompanied by decomposition. Its IR spectrum was essentially the same as those of **1a—e**.

Found: C, 32.68; H, 1.96; S, 25.06%. Calcd for $C_{14}H_{10}Cl_4S_4Zn$: C, 32.73; H, 1.96; S, 24.97%.

*Fluoroborate Salt **1a** from 2-Alkylthio-1,3-benzodithioles (**3**).* **1a** was prepared from benzodithioles **3a**, **3b**, and **3c** in a respective yield of 86, 90, and 92% by treatment with tetrafluoroboric acid in the manner described above except that the reaction with **3b** (insoluble in acetic anhydride) was carried out in a mixture of ether and acetic anhydride.

*Reaction of the Salt **1a** with Alcohols.* **1a** (3.60 g, 15 mmol) was dissolved in alcohols (50 ml) and left to stand at room temperature for 1 h. The mixture was poured into water (150 ml) and extracted with ether (150 ml). The ether extract was washed with water, dried over sodium sulfate, and evaporated. The oily residue was purified by distillation.

2-Methoxy-1,3-benzodithiole (**2a**), 87%, colorless oil (solidified in a refrigerator), bp 80 °C/0.5 Torr (lit,[5b] bp 105—106 °C/2 Torr).

2-Ethoxy-1,3-benzodithiole (**2d**), 75%, colorless oil, bp 92—93 °C/1.5 Torr, ν_{max} 1050 cm^{-1} (C–O), δ (CCl_4) 1.12 (3H, t, methyl), 3.43 (2H, q, methylene), 6.80 (1H, s, methine), and 6.9—7.5 (4H, m, aromatic).

Found: C, 54.63; H, 5.14; S, 32.19%. Calcd for $C_9H_{10}OS_2$: C, 54.54; H, 5.09; S, 32.29%.

2-Propoxy-1,3-benzodithiole (**2b**), 94%, colorless oil, bp 86—88 °C/0.5 Torr (lit,[5a] bp 104—105 °C/0.1 Torr).

*Reaction of **1a** with Water.* **1a** (1.20 g, 5 mmol) was dissolved in 4:1 acetonitrile-water (25 ml) and left to stand at room temperature. After several hours colorless needles began to precipitate. The mixture was allowed to stand at room temperature until the needles no longer precipitated (one week). Filtration and wahsing with methanol (10 ml) gave 2,2′-(*o*-phenylenedithio)bis(1,3-benzodithiole), (**4**), 0.66 g (88%), mp 129—131 °C, undepressed on admixture with the authentic specimen.[11]

*Reaction of **1a** with Ethanethiol.* A solution of **1a** (1.20 g, 5 mmol) in ethanol (25 ml) was left at room temperature for 1 h, and then ethanethiol (1.24 g, 20 mmol) was added. After

being left to stand 1 h at room temperature, the mixture was poured into water and extracted with ether. The extract was washed successively with water, 2 M sodium hydroxide, and water, and dried over sodium slfate. The ether was evaporated and the crystalline residue was washed with cold methanol to give 2-ethylthio-1,3-benzodithiole (**3a**), 0.87 g (81%), mp 49—51 °C, undepressed on admixture with the authentic specimen.[6]

When **1a** (1.20 g, 5 mmol) was dissolved in a mixture of ethanethiol (1.24 g, 20 mmol) and ethanol (25 ml) and left to stand at room temperature for 1 h, **3a**, mp 51—51.5 °C, was obtained in 80% yield. ^{1}H NMR analysis of the crude product indicated no formation of **2d**.

*Reaction of **1a** with Sodium Sulfide and Sodium Hydrogensulfide.* **1a** (1.20 g, 5 mmol) was added to a stirred solution of sodium sulfide nonahydrate (1.20 g, 5 mmol) in methanol (15 ml) at room temperature and the mixture was stirred for 0.5 h. The crystalline precipitate was collected and washed with water (30 ml) and then with ethanol (10 ml) to give bis(1,3-benzodithiol-2-yl) sulfide (**5**), 0.13 g (15%), mp 145—147 °C (from $CHCl_3$/hexane), undepressed on admixture with the authentic specimen.[6] The filtrate was poured into water (50 ml) and extracted with ether (100 ml). The ether extract was washed with water, dried over sodium sulfate, and evaporated. The oily residue was distillated to give 2-methoxy-1,3-benzodithiole (**2a**), 0.63 g (69%), bp 130 °C (bath temperature) at 2 Torr.

1a (1.20 g, 5 mmol) was added with stirring to a solution of sodium hydrogensulfide (0.28 g, 5 mmol) in methanol (15 ml) at room temperature. The mixture was stirred for 2 h and worked up as described for the reaction with sodium sulfide to give the sulfide **5**, 0.28 g (33%), mp 145—147 °C and the benzodithiole **2a**, 0.49 g (54%), bp 110 °C (bath temperature) at 0.5 Torr.

*Reaction of **1a** with Ammonium Salts.* To a stirred mixture of ammonium acetate (154 mg, 2 mmol) and pyridine (0.2 ml) in acetonitrile (15 ml) was added in portions **1a** (1.44 g, 6 mmol) and the mixture was stirred at room temperature for 6 h. The crystalline precipitate was collected and washed with ethanol (10 ml) to give tris(1,3-benzodithiol-2-yl)amine (**8**), 0.81 g (86%), mp 247—248 °C (dec) (from benzene, colorless granules).

Found: C, 53.24; H, 3.33; N, 3.19; S, 40.05%. Calcd for $C_{21}H_{15}NS_6$: C, 53.28, H, 3.19; N, 2.96; S, 40.56%.

The reaction of **1a** (1.44 g 6 mmol) with ammonium chloride (105 mg, 2 mmol) in the presence of pyridine (0.2 ml) in acetonitrile (15 ml) at room temperature for 6 h gave compound **8** in 50% yield in addition to a small amount of dibenzotetrathiafulvalene **11**.

*Reaction of **1a** with Primary Amines.* To a stirred mixture of amines (2.5 mmol) and pyridine (0.5 ml) in acetonitrile (10 ml) was added dropwise a solution of **1a** (1.20 g, 5 mmol) in acetonitrile (15 ml) over a period of 5 min. After being stirred for 0.5 h at room temperature, ice water (15 ml) was added to precipitate the products. The precipitate was collected and washed with cold methanol (15 ml).

N,N-Bis(1,3-benzodithiol-2-yl)benzylamine (**9a**), 0.88 g (86%), mp 128—129 °C (from cyclohexane, colorless needles), δ ($CDCl_3$) 3.89 (2H, s, methylene), 6.37 (2H, s, methine), and 6.9—7.4 (13H, m, aromatic).

Found: C, 61.30; H, 4.26; N, 3.36; S, 30.65%. Calcd for $C_{21}H_{17}NS_4$: C, 61.31; H, 4.17; N, 3.41; S, 31.12%.

N,N-Bis(1,3-benzodithiol-2-yl)aniline (**9b**), 0.78 g (79%), mp 134—138 °C (from cyclohexane, colorless granules), δ ($CDCl_3$) 6.71 (2H, s, methine) and 6.8—7.5 (13H, m, aromatic).

Found: C, 60.43; H, 3.96; N, 3.35; S, 32.03%. Calcd for $C_{20}H_{15}NS_4$: C, 60.45; H, 3.81; N, 3.53; S, 32.22%.

*Reaction of **1a** with Secondary Amines.* **1a** (0.48 g, 2 mmol) was added in portions to a stirred mixture of amines (2 mmol) and pyridine (0.2 ml) in acetonitrile (10 ml). After 0.5 h of stirring at room temperature, ice water was added to precipitate the products completely. The precipitate was collected and washed with methanol (10 ml).

N,N-Dibenzyl-1,3-benzodithiol-2-ylamine (**10a**), 0.63 g (90%), mp 94—95 °C (from methanol, colorless needles), δ ($CDCl_3$) 3.63 (4H, methylene), 6.30 (1H, s, methine), and 6.9—7.5 (14H, m, aromatic).

Found: C, 72.14; H, 5.53; N, 4.00; S, 18.20%. Calcd for $C_{21}H_{19}NS_2$: C, 72.19; H, 5.48; N, 4.01; S, 18.32%.

N-Methyl-*N*-(1,3-benzodithiol-2-yl)aniline (**10b**), 0.48 g (92%), mp 120—121 °C (from hexane, colorless needles), δ ($CDCl_3$) 2.71 (3H, s, methyl), 7.13 (1H, s, methine), and 6.95—7.45 (9H, m, aromatic).

Found: C, 64.90; H, 5.10; N, 5.40; S, 24.70%. Calcd for $C_{14}H_{13}NS_2$: C, 64.86; H, 5.05; N, 5.40; S, 24.69%.

4-(1,3-Benzodithiol-2-yl)-*N*-ethyl-1-naphthylamine (**10d**), 0.64 g (99%), mp 97—99 °C (from cyclohexane, needles with a pink tinge), ν_{max} 3350 cm^{-1} (N–H), δ ($CDCl_3$) 1.33 (3H, t, methyl), 3.26 (2H, q, methylene), 4.34 (1H, broad s, N–H), 6.52 (1H, d, aromatic), 7.00 (1H, s, methine), 6.95—7.35 (4H, m, aromatic), *ca.* 7.5 (2H, m, aromatic), *ca.* 7.8 (1H, d/d, aromatic), 7.94 (1H, d, aromatic), and *ca.* 8.1 (1H, d/d, aromatic).

Found: C, 70.51; H, 5.33; N, 4.29; S, 19.81%. Calcd for $C_{19}H_{17}NS_2$: C, 70.57; H, 5.30; N, 4.33; S, 19.79%.

*Reaction of **1a** with Triethylamine.* To a stirred solution of **1a** (2.40 g, 10 mmol) in acetonitrile (10 ml) was added dropwise a solution of triethylamine (3 ml) in acetonitrile (15 ml) over a period of 15 min at room temperature. After being stirred for 0.5 h, the precipitate was collected and washed with benzene (15 ml) to give 1.24 g (81%) of dibenzotetrathiafulvalene **11** as yellow crystals, mp 235—237 °C, undepressed on admixture with the authentic specimen.[24]

*Reaction of **1a** with N,N-Dimethylformamide.* **1a** (2.40 g, 10 mmol) was dissolved in 20 ml of anhydrous *N,N*-dimethylformamide and left at room temperature for 1.5 h. The precipitate was collected and washed with benzene (10 ml) to give 1.21 g (80%) of **11**, mp 235—237 °C.

*Reaction of **1a** with Aromatic Compounds.* *a) With N,N-dimethylaniline and 1,3,5-Trimethoxybenzene*: To a stirred mixture of *N,N*-dimethylaniline (194 mg, 1.6 mmol) and pyridine (0.2 ml) in acetic acid (15 ml) was added **1a** (0.36 g, 1.5 mmol). After 0.5 h, the mixture was diluted with water (10 ml). Filtration of the precipitate and washing with methanol (5 ml) gave 2-[*p*-(dimethylamino)-phenyl]-1,3-benzodithiole (**13**), 0.37 g (89%), mp 119 °C (from ethanol), undepressed on admixture with the authentic specimen.[11]

The reaction of **1a** with 1,3,5-trimethoxybenzen carried out in a similar way gave 0.47 g (98%) of 2-(2,4,6-trimethoxyphenyl)-1,3-benzodithiole (**14**), mp 140—141 °C (from ethanol), undepressed on admixture with the authentic specimen.[11]

b) With 2,6-Dimethylphenol and 2-Naphthol: **1a** (0.36 g, 1.5 mmol) was added in portions to a stirred mixture of 2,6-dimethylphenol (1.6 mmol) and pyridine (0.2 ml) in acetic acid (15 ml). The mixture was heated at 60—70 °C for 3 h and cooled. Ice water (15 ml) was added to precipitate the products. The precipitate was collected and washed with ethanol (10 ml).

2-(4-Acetoxy-3,5-dimethylphenyl)-1,3-benzodithiole (**15b**), 0.32 g (68%), mp 136—137 °C (from ethanol, colorless granules), ν_{max} 1730 cm^{-1} (C=O), δ ($CDCl_3$) 2.10 (6H, s, methyl),

2.30 (3H, s, methyl), 6.18 (1H, s, methine), 6.95—7.30 (4H, m, aromatic), and 7.26 (2H, s, aromatic).

Found: C, 64.24; H, 5.11; S, 20.05%. Calcd for $C_{17}H_{16}O_2S_2$: C, 64.55; H, 5.10; S, 20.23%.

1-(1,3-Benzodithiol-2-yl)-2-acetoxynaphthalene (**16b**), 0.49 g (97%), mp 218—129 °C (from benzene, colorless needles), ν_{max} 1750 cm^{-1} (C=O), δ (DMSO-d_6, at 100 °C) 2.14 (3H, s, methyl), 7.05—7.40 (5H, m, aromatic), 7.48 (1H, s, methine), 7.5—7.6 (2H, m, aromatic), 7.9—8.1 (2H, m, aromatic), and 8.75 (1H, m, aromatic).

Found: C, 67.44; H, 3.88; S, 18.62%. Calcd for $C_{19}H_{14}O_2S_2$: C, 67.45; H, 4.17; S 18.92%.

Reaction of ***1a*** *with Active Methylene Compounds.* To a stirred mixture of active methylene compounds (1.5 mmol) and pyridine (0.2 ml) in acetic acid (10 ml) was added **1a** (0.36 g, 1.5 mmol). After being stirred for 3 h at room temperature, the mixture was diluted with ice water (10 ml). The precipitate was collected and washed with methanol (5 ml). In the reaction with malononitrile, colorless needles separated without addition of water.

3-(1,3-Benzodithiol-2-yl)-2,4-pentanedione (**17a**), 0.35 g (92%), mp 129 °C (from ethanol), undepressed on admixture with the authentic specimen.[21]

Ethyl 2-(1,3-benzodithiol-2-yl)acetoacetate (**17b**), 0.38 g (90%), mp 59—60 °C (from aqueous ethanol), undepressed on admixture with the authentic specimen.[21]

2-(1,3-Benzodithiol-2-yl)-3-acetoxy-5,5-dimethyl-2-cyclohexen-1-one (**17e**), 0.38 g (76%), mp 117—118 °C (from ethanol, colorless needles), ν_{max} 1760, 1658, and 1635 cm^{-1}, δ ($CDCl_3$) 1.07 (6H, s, methyl), 1.54 (3H, s, methyl), 2.34 (2H, s, methylene), 2.55 (2H, s, methylene), 6.38 (1H, s, methine), and 6.9—7.2 (4H, m, aromatic).

Found: C, 60.70; H, 5.20; S, 19.17%. Calcd for $C_{17}H_{18}O_3S_2$: C, 61.07; H, 5.43; S, 19.14%.

Bis(1,3-benzodithiol-2-yl)malononitrile (**18**), 0.24 g (86%), mp 220—221 °C (dec), undepressed on admixture with the authentic specimen.[21]

Reduction of ***1a*** *with Sodium Borohydride.* To a stirred mixture of sodium borohydride (0.40 g, 10 mmol) in anhydrous tetrahydrofuran (30 ml) was added in portions **1a** (2.40 g, 10 mmol) at room temperature. After being stirred for 2 h, the mixture was poured into ice water (200 ml) and extracted with ether (200 ml). The ether extract was washed with water, dried over sodium sulfate, and evaporated. The oily residue was distillated to give 1.24 g (81%) of 1,3-benzodithiole (**19**), bp 103—104 °C/3 Torr (lit,[22] bp 88 °C/0.6 Torr).

Reaction of ***1a*** *with Tropilidene.* To a stirred and ice-cooled solution of tropilidene (1.56 g, 17 mmol) in acetonitrile (10 ml) was added dropwise a solution of **1a** (3.60 g, 15 mmol) in acetonitrile (15 ml) during 20 min. After stirring for 0.5 h at 0 °C, anhydrous ether (40 ml) was added to precipitate the product. Filtration and washing with anhydrous ether (10 ml) gave tropylium tetrafluoroborate (**20**) as white crystals, 2.40 g (90%), mp>210 °C (dec) [lit,[25] mp>210 °C (dec)]. The filtrate and washings combined were washed with water and dried. The ether was evaporated and the residual oil was distillated to give the benzodithiole **19**, 1.50 g (65%), bp 83—85 °C/0.5 Torr.

Fluoroborate Salt ***1a*** *from 1,3-Benzodithiole.* To a stirred and ice-cooled solution of **19** (1.07 g, 7 mmol) in acetonitrile (10 ml) was added dropwise a solution of trityl tetrafluoroborate[25] (2.31 g, 7 mmol) in acetonitrile (15 ml) over a period of 20 min. After stirring for 20 min at 0 °C, anhydrous ether (50 ml) was added to the mixture. The resulting crystalline precipitate was collected and washed with anhydrous ether (10 ml) to give **1a**, 1.26 g (75%), mp 148—150 °C (dec). The filtrate and washings combined were washed with water, dried, and evaporated. The crystalline residue was washed with methanol (10 ml) to give triphenylmethane as white crystals, 1.29 g (75%), mp 93 °C.

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