The Synthesis, Oxidation, and Electronic Spectra of Four Dithienothiophenes

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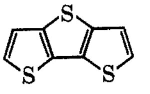
The dithienothiophenes (**2**-**4**) have been synthesized using oxidative ring closure of the appropriate dilithiodithienyl sulfides. The dilithio intermediates were obtained from α,α'-dibromodithienyl sulfides by halogen-metal interconversion. A new method is reported for the synthesis of symmetric dithienyl sulfides, consisting of the reaction of thienyllithium with bis(phenylsulfonyl) sulfide (**6**). Peracid oxidized the sulfur atom of the central ring exclusively. The ultraviolet spectra of the title compounds are in excellent agreement with those calculated by SCF-MO methods.

Synthesis.—Investigations of condensed thiophene systems have mainly been limited to the thienothiophene isomers.[1-3] Of the next higher homolog, dithienothiophenes, two of the six isomers (**1** and **2**) have been prepared,[4,5] but no spectroscopic data were reported. In view of the current interest in physical and chemical properties of condensed thiophene systems, a convenient synthesis of four dithienothiophenes (**1**-**4**), including two new ones, is described.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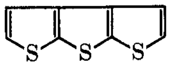
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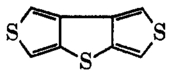
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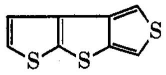
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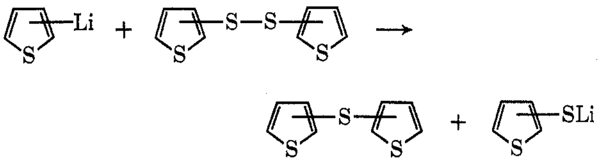
In the procedure used, α,α'-dibromodithienyl sulfides were key compounds for the ring closure. The synthesis of dithienyl sulfides from a thiophene thiol and a thienyl halide[6] cannot be used starting from bromo-substituted thiophene thiols, since treatment of 4-bromo-3-thiophene thiol with an equivalent amount of 3,4-dibromothiophene yielded only a dithieno-*p*-dithiin[7] rather than the expected 4,4′-dibromo-3,3′-dithienyl sulfide.

The reaction of thienyllithium with a dithienyl disulfide,[4,8] as represented by eq 1, was used for the synthesis of asymmetric dithienyl sulfides. We have made use of the strong thiophilicity[9] of thienyllithium to prepare symmetric dithienyl sulfides in a one-step procedure (eq 2). Substituent X must be a group of low thiophilicity. Attempts with SCl_2 or S_2Cl_2 (X = Cl) gave only low (10–25%) yields of dithienyl sulfides, thiophene thiol being the main product isolated. Much better results (60–70% yields) were obtained from the reaction of thienyllithium with bis(phenylsulfonyl) sulfide (**6**) ($X = C_6H_5SO_2$). Bis(phenylsulfonyl) sulfide is easily prepared by a modification of the literature procedure.[10]



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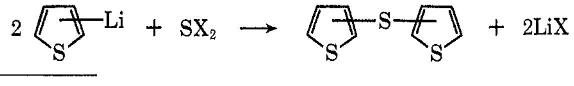

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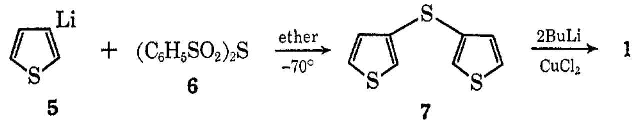
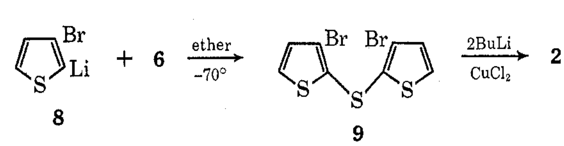
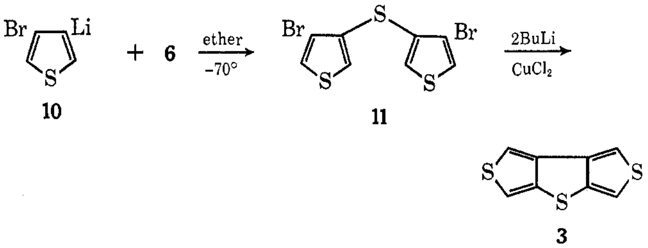
From 3-thienyllithium[11] (**5**) and bis(phenylsulfonyl) sulfide (**6**), 3,3′-dithienyl sulfide (**7**) was isolated in 68% yield. Dilithiation of **7** followed by oxidative ring closure by the method of Federov and Stoyanovich[4] afforded dithieno[3,2-*b*:2′,3′-*d*]thiophene (**1**) in 52% yield.



From 3-bromo-2-thienyllithium[11] (**8**), 3,3′-dibromo-2,2′-dithienyl sulfide (**9**) was obtained and converted to dithieno[2,3-*b*:3′,2′-*d*]thiophene (**2**) in 21% overall yield. This procedure is much easier to perform and gives greatly improved yields over those reported by Pandya and Tilak.[5] The previously unknown dithieno[3,4-*b*:3′4′-*d*]thiophene (**3**) was prepared in 20% overall yield from 4-bromo-3-thienyllithium[11] (**10**) *via* 4,4′-dibromo-3,3′-dithienyl sulfide (**11**). Alternatively, sulfide **11** could be obtained in 83% yield from the reaction of 4-bromo-3-thienyllithium (**10**) and 4,4′-dibromo-3,3′-dithienyl disulfide (**12**). The disulfide **12** was prepared by oxidation of 4-bromo-3-thiophene thiol[12] in aqueous $K_3Fe(CN)_6$ (90%).





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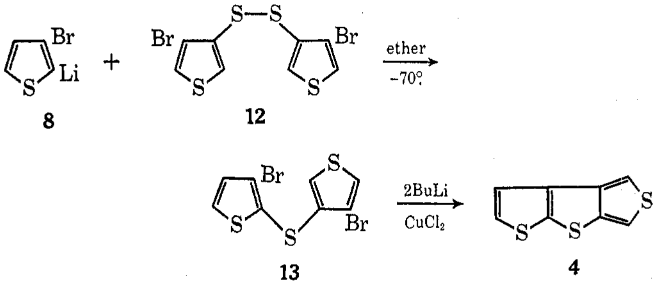
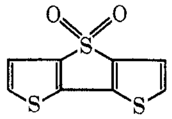
The sulfides **9** and **11** were characterized by elementary analysis, and the nmr spectra show the characteristic coupling constants for 2,3- and 2,5-substituted thiophenes.[13] The nmr spectrum of **3** in deuteriochloroform showed two doublets at δ 7.00 and 7.43 with J = 2.6 Hz. The unusually small value[14] of $J_{2,5}$ is probably due to geometrical deformation of the thiophene ring system caused by 3,4 anellation, since in systems like thieno[3,4-*b*]thiophene,[1] cyclopentadithiophenes,[15] and cyclopentadithiophenones[16] small values (1.9–2.2 Hz) for $J_{2,5}$ are also observed.

Finally, reaction of 3-bromo-2-thienyllithium[11] (**8**) and the disulfide **12** afforded 94% of 3,4′-dibromo-2,3′-dithienyl sulfide (**13**). On oxidative ring closure of the dilithio intermediate, sulfide **13** furnished dithieno[2,3-*b*:3′,4′-*d*]thiophene (**4**) in 29% yield. Its nmr spectrum shows one AB system with J = 5.5 Hz (2,3 coupling) and one with J = 2.6 Hz (2,5 coupling, but again smaller than usual).



The two remaining dithienothiophenes cannot be prepared by the same procedure, owing to the inaccessibility of 2-bromo-3-thienyllithium. An alternative synthesis is being studied.

Oxidation of the Dithienothiophenes.—In order to obtain information about the relative reactivity of the three sulfur atoms in each isomer, the dithienothiophenes were subjected to peracid oxidation. When the compounds **1** and **3** were treated in acetic acid solution by hydrogen peroxide, the corresponding sulfones **15** and **16** were obtained in good yield. The presence of the sulfone group was concluded from the ir spectra, showing the characteristic sulfone absorptions at 1130 and 1290 cm^{-1}. In addition, the nmr spectra show two different protons (two doublets with J = 5.0 Hz for **15** and J = 2.4 Hz for **16**), indicating that the sulfur atom of the central ring has been oxidized.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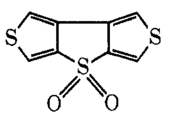
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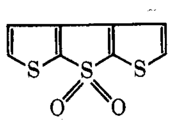
When the dithienothiophenes **2** and **4** were treated under the same conditions with hydrogen peroxide, low yields of impure sulfones **17** and **18** were obtained. However, the latter were obtained in good yield when **2** and **4** were oxidized by *m*-chloroperbenzoic acid in dichloromethane solution at −10°. The presence of the sulfone group was again based on the ir spectra (sulfonyl absorptions at 1150 and 1300 cm^{-1}). The nmr spectrum of **17** showed the correct symmetry (two doublets with J = 5.0 Hz) expected from oxidation of the central ring.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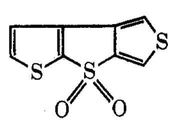
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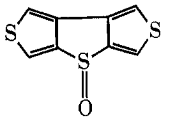
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The site of oxidation in **18** could be determined from its nmr spectrum showing two sets of doublets: δ 7.68, 8.15 with J = 2.4 Hz; and δ 7.80, 7.62 with J = 5.0 Hz. Formally, the structures obtained by oxidation of one of the terminal rings would give rise to a similar splitting pattern. However, no change in coupling constants is observed upon going from the starting dithienothiophene **4** to the oxidized product **18**, indicating that the aromaticity of the thiophene rings is not drastically changed.[17] From these considerations and by anology with the oxidation products of the other dithienothiophene isomers, structure **18** is assigned to this sulfone.

Although the presence of the intermediate sulfoxides could be demonstrated by tlc, only in the case of dithieno[3,4-*b*:3′,4′-*d*]thiophene (**3**) the sulfoxide **19** was isolated free from the sulfone. The structure of **19** was supported by its elementary analysis and its ir spectrum showing the characteristic sulfoxide absorption at 1030 cm^{-1}.

Electronic Spectra.—In order to correlate chemical and physical properties of the dithienothiophenes with their structures, we carried out LCI-SCF-MO calculations and checked the results with the electronic transition energies. The method of Pariser, Parr, and Pople[18,19] was used with an idealized model of the geometry (bond lengths and angles were taken from thiophene[20]). Standard parameters were used: for carbon, $I_C = 11.22$ eV, $\gamma_{CC} = 10.53$ eV, and $\beta_{CC} = -2.318$ eV; and for sulfur $I_S = 20.0$ eV, $\gamma_{SS} = 10.84$ eV, and $\beta_{CS} = -1.623$ eV.[21] Limited configuration interaction was included by taking 16 configurations resulting from excitation of one electron from each of the four highest occupied MO's to the four lowest vacant orbitals. The two-center integrals were evaluated according to Nishimoto and Mataga.[22] The observed and calculated electronic transitions are compiled in Table I.

The remarkable difference between the longest wavelength band of compound **2** (250 mμ) and the other compounds (around 300 mμ) is in accordance with the theoretical values. Compared with the bicyclic analogs, the thiophthenes,[23] no red shift is observed going from the bicyclic to the tricyclic systems. It also is remarkable that very little similarity exists between the spectra of the dithienothiophenes and the corresponding benzodithiophenes.[24,25]

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TABLE I

CALCULATED AND OBSERVED ELECTRONIC TRANSITIONS

Compd	λ_{max}, mμ Obsd (log ε)	 Calcd (f)
1	282 (4.28),[a] 290 (4.40), 298 (4.24)[a]	212 (0.08), 218 (0.003), 232 (0.02), 242 (0.02), 290 (0.40), 301 (0.90)
2	215 (4.52), 233 (4.16), 250 (4.21)	207 (0.57), 219 (0.29), 238 (0.54), 247 (0.56), 259 (0.28), 272 (0.0003)
3	255 (4.22), 278 (4.14), 290 (4.21), 310 (3.00)	207 (0.08), 214 (0.23), 231 (0.005), 248 (0.37), 267 (0.67), 281 (0.30), 310 (0.03)
4	223 (4.42), 271 (4.05), 298 (3.70)	218 (0.54), 226 (0.78), 238 (0.01), 261 (0.10), 267 (0.33), 305 (0.33)

[a] Inflection.

Experimental Section

All experiments in which lithio compounds are used were conducted in a dry N_2 atmosphere. Melting points are uncorrected. Nmr spectra were obtained using a Varian A-60 spectrometer with TMS (τ 10) as an internal standard. Uv spectra were determined with a Zeiss PMQ II and infrared spectra with an Unicam SP 200. The microanalyses were carried out in the analytical section of this department under direction of Mr. W. M. Hazenberg.

Bis(phenylsulfonyl) Sulfide (6).[10]—To a stirred suspension of 25 g (0.155 mol) of sodium sulfinate in 400 ml of dry benzene was added a solution of 7.8 g (0.075 mol) of sulfur dichloride in 25 ml of benzene. The mixture was stirred at room temperature for 2 hr, and after filtration and evaporation of the solvent left a crystalline residue, which on recrystallization from benzene yielded 19 g (80%) of **6**, mp 128–130° (lit.[10] mp 133°).

3,3′-Dithienyl Sulfide (7).—A solution of 3-thienyllithium was prepared at −70° from 16.3 g (0.1 mol) of 3-bromothiophene[26] in 100 ml of absolute ether and 65 ml of 1.52 *N* ethereal *n*-BuLi (0.098 mol). In small portions 15.6 g (0.049 mol) of **6** was added. After stirring at −70° during 2 hr, the reaction mixture was allowed to warm and at 0° 10 ml of water was added. The lithium sulfinate was filtered and washed with ether, the combined ether layers were extracted with water, dried ($MgSO_4$), and concentrated, and the residue was distilled yielding 6.70 g (68%) of the sulfide **7**, bp 98–100° (0.08 mm), $n^{20}\mathrm{D}$ 1.6720 [lit.[6] bp 115° (0.4 mm), $n^{25}\mathrm{D}$ 1.6671].

Dithieno[3,2-*b*:2′,3′-*d*]thiophene (1).—To a stirred solution of 17.2 g (0.088 mol) of 3,3′-dithienyl sulfide (**7**) in 150 ml of absolute ether, 100 ml of a 1.72 *N* ethereal *n*-BuLi was added and heated under reflux for 1 hr. The mixture was cooled to 0°, transferred to a dropping funnel, and slowly added to a stirred, ice-cold suspension of 26 g (0.19 mol) of anhydrous $CuCl_2$ in 100 ml of absolute ether. The mixture was stirred at room temperature overnight, 100 ml of water was added, and the ether layer separated after filtration. After drying ($MgSO_4$) and concentration to a small volume, this reddish residue was purified over an alumina column using ether–pentane 1:1 as the eluent. Evaporation of the solvent left a solid residue, which on recrystallization from methanol yielded 8.9 g (52%) of **1**: mp 66–67° (lit.[4] mp 66.5–67.5°); nmr (CD_3COCD_3) δ 7.57 (d, 2, *J* = 5.0 Hz), 7.40 (d, 2, *J* = 5.0 Hz).

3,3′-Dibromo-2,2′-dithienyl Sulfide (9).—Starting from 54.0 g (0.22 mol) of 2,3-dibromothiophene[27] and 34.0 g (0.107 mol) of **6**, the procedure described for the synthesis of **7** yielded 30 g of a crude oil, which on distillation and recrystallisation from ether-pentane 1:1 furnished 22–26 g (61–70%) of **9**: bp 170–173° (0.08 mm); mp 54–55; uv max (EtOH) 256 mμ (log ε 4.16); nmr (CD_3COCD_3) δ 7.63 (d, 2, *J* = 5.2 Hz), 7.10 (d, 2, *J* = 5.2 Hz).

Anal. Calcd for $C_8H_4S_3Br_2$: C, 26.98; H, 1.13; S, 27.01; Br, 44.88. Found: C, 27.01; H, 1.10; S, 26.75; Br, 45.08.

Dithieno[2,3-*b*:3′,2′-*d*]thiophene (2).—A solution of 3,3′-dilithio-2,2′-dithienyl sulfide was prepared at −70° from 12.5 g (0.035 mol) of **9** in 100 ml of absolute ether and 50 ml of a 1.4 *N* ethereal *n*-BuLi solution (0.070 mol). After stirring at −70° for 45 min, the mixture was transferred to an externally cooled (−70°) dropping funnel and slowly added to a vigorously stirred suspension of 13 g (0.08 mol) of anhydrous $CuCl_2$ in 200 ml of absolute ether cooled to −50°. The mixture was stirred at −50° for 1 hr and then at room temperature overnight. After addition of 100 ml of water, the gray Cu_2Cl_2 precipitate was filtered, and the ether layer separated, washed with 2 *N* HCl and water, and dried over $MgSO_4$. After the ethereal solution was concentrated to a small volume, an alumina column was used for purification (eluent petroleum ether, bp 40–60°). The white solid obtained afforded on recrystallization from methanol 2.2 g (32%) of **2**: mp 84–86° (lit.[5] mp 85–86°); nmr (CD_3COCD_3) δ 7.58 (d, 2, *J* = 5.3 Hz), 7.48 (d, 2, *J* = 5.3 Hz).

4,4′-Dibromo-3,3′-dithienyl Sulfide (11). A. From 4-Bromo-3-thienyllithium (10) and 4,4′-Dibromo-3,3′-dithienyl Disulfide (12).—A solution of **10** in absolute ether was prepared at −70° from 41.2 g (0.17 mol) of 3,4-dibromothiophene[28] and 100 ml of a 1.5 *N* ethereal *n*-BuLi solution. The mixture was transferred to an externally cooled (−70°) dropping funnel and added during 15 min to a stirred suspension of 58.0 g (0.15 mol) of **12** in 200 ml of absolute ether cooled to −70°. After stirring at −70° for 2 hr the disulfide **12** had disappeared and the mixture was allowed to warm up. At 0° 100 ml of water was added, and the ether layer was separated, extracted with 1 *N* NaOH, washed with water, and dried ($MgSO_4$). Evaporation of the ether and distillation yielded 44.3 g (83%) of **11** as a colorless oil: bp 164–165° (0.06 mm); $n^{25}\mathrm{D}$ 1.7100; uv max (EtOH) 260 mμ (log ε 3.78); nmr (CD_3COCD_3) δ 7.33 (d, 2, *J* = 3.4 Hz), 7.62 (d, 2, *J* = 3.4 Hz).

Anal. Calcd for $C_8H_4S_3Br_2$: C, 26.98; H, 1.13; S, 27.01; Br, 44.88. Found: C, 26.81; H, 1.05; S, 27.20; Br, 44.94.

The aqueous layers were oxidized using the method described for the preparation of **12**, by which 25 g (86%) of the disulfide **12** could be reobtained, mp 65–68°.

B. From 4-Bromo-3-thienyllithium (10) and 6.—Starting from 24.2 g (0.1 mol) of 3,4-dibromothiophene[28] and 15.9 g (0.05 mol) of **6**, the procedure described for the synthesis of **7** yielded 11.2 g (63%) of the sulfide **11**.

Dithieno[3,4-*b*:3′,4′-*d*]thiophene (3).—From 26 g (0.074 mol) of **11**, 100 ml of a 1.5 *N* ethereal *n*-BuLi solution, and 26 g (0.16 mol) of anhydrous $CuCl_2$, the procedure described for the synthesis of **2** afforded 14 g of crude material, which on distillation yielded a solid. On recrystallization from *n*-hexane–ether 3:1, 4.5 g (31%) of **3** was obtained as long white needles: bp 118–120° (0.1 mm); mp 87–87.5°; nmr (CD_3COCD_3) δ 7.00 (d, 2, *J* = 2.6 Hz), 7.43 (d, 2, *J* = 2.6 Hz).

Anal. Calcd for $C_8H_4S_3$: C, 48.95; H, 2.06; S, 48.99. Found: C, 49.04; H, 2.13; S, 48.54.

4,4′-Dibromo-3,3′-dithienyl Disulfide (12).—The preparation of 4-bromo-3-thienyl thiolate parallels the synthesis of the corresponding thiol.[12] A solution of 4-bromo-3-thienyllithium (**10**) was prepared from 260 g (1.075 mol) of 3,4-dibromothiophene[28] and 600 ml of a 1.72 *N* etheral *n*-BuLi solution at −70°. In the course of 5 min 33 g (1.03 mol) of dry sulfur was added and after stirring at −70° for 1.5 hr the mixture was allowed to warm up. At −30° 100 ml of water was added and the ether layer extracted twice with a 100-ml portion of 2 *N* NaOH. The combined aqueous layers were washed with ether and then slowly added to a stirred, ice-cold solution of 600 g of $K_3Fe(CN)_6$ in 2.5 l. of water. The precipitate was filtered, washed with water, dissolved in dichloromethane, and dried ($MgSO_4$). Evaporation of the solvent yielded 168 g of **12** (mp 64–67°), which on further recrystallization from ether–CH_2Cl_2 1:1 gave 155 g (78%) of **12** as colorless prisms: mp 68–69°; uv max (EtOH) 225 mμ (log ε 4.14), 258 (3.91); nmr (CD_3COCD_3) δ 7.63 (d, 2, *J* = 3.5 Hz), 7.70 (d, 2, *J* = 3.5 Hz).

Anal. Calcd for $C_8H_4S_4Br_2$: C, 24.74; H, 1.03; S, 33.05; Br, 41.18. Found: C, 24.88; H, 0.97; S, 33.10; Br, 41.22.

3,4′-Dibromo-2,3′-dithienyl Sulfide (13).—From the reaction of 3-bromo-2-thienyllithium (**8**) [prepared at −70° from 18 g (0.074 mol) of 2,3-dibromothiophene[31] and 50 ml of a 1.5 *N* etheral *n*-BuLi solution] and 28.5 g (0.074 mol) of the disulfide **12**, 25 g (94%) of **13** were obtained: bp 168–172° (0.15 mm); uv max (EtOH) 254 mμ (log ε 4.07); nmr (CD_3COCD_3) δ 7.35 (d, 2, *J* = 3.4 Hz), 7.70 (d, 2, *J* = 3.4 Hz), 7.15 (d, 2, *J* = 5.6 Hz), 7.63 (d, 2, *J* = 5.6 Hz).

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Anal. Calcd for $C_8H_4S_3Br_2$: C, 26.98; H, 1.13; S, 27.01; Br, 44.88. Found: C, 27.24; H, 1.22; S, 27.35; Br, 44.72.

On oxidation of the aqueous layers with 40 g of $K_3Fe(CN)_6$ as described for the synthesis of **12**, 12.2 g (85%) of the disulfide **12** could be reobtained, mp 66–68°.

Dithieno[2,3-*b*:3′,4′-*d*]thiophene (4).—Starting from 13.4 g (0.038 mol) of **13** and 50 ml of a 1.5 *N* ethereal *n*-BuLi solution, the dilithio derivative was prepared at −70°. The usual oxidative ring closure with 13 g (0.08 mol) of anhydrous $CuCl_2$ yielded a yellow oil, which on distillation furnished a solid, which was recrystallised from ether–pentane 1:3, giving 2.1 g (29%) of **4** as colorless needles: bp 114–116° (0.07 mm); mp 76–77°; nmr (CD_3COCD_3) δ 7.17 (d, 2, J = 5.5 Hz), 7.33 (d, 2, J = 5.5 Hz), 7.25 (d, 2, J = 2.6 Hz), 7.31 (d, 2, J = 2.6 Hz).

Anal. Calcd for $C_8H_4S_3$: C, 48.95; H, 2.06; S, 48.99. Found: C, 48.67; H, 2.14; S, 48.92.

Dithieno[3,2-*b*:2′,3′-*d*]thiophene 4,4-Dioxide[4] (15).—From 196 mg (1 mmol) of **1** dissolved in 15 ml of acetic acid and 3 ml of 30% H_2O_2, 130 mg (57%) of **15** was obtained after stirring for 30 hr at room temperature: mp 248–249° (lit.[4] mp 251.5–253°); uv max (EtOH) 236 mμ (log ϵ 4.06), 243 (4.06), 354 (3.78); nmr (CD_3COCD_3) δ 7.37 (d, 2, J = 5.0 Hz), 7.73 (d, 2, J = 5.0 Hz); ir (KBr) 1130, 1285 cm^{-1} (SO_2).

Dithieno[3,4-*b*:3′,4′-*d*]thiophene 4,4-Dioxide (16).—In 50 ml of dry dichloromethane 588 mg (3 mmol) of **3** and 1.20 g (7 mmol) of *m*-chloroperbenzoic acid were dissolved. The mixture was allowed to stand 14 hr at −10°, the solvent was evaporated, and the solid residue was washed with 10 ml of a saturated $NaHCO_3$ solution. After the residue was recrystallized from dioxane–water 1:1, 500 mg (70%) of **16** was obtained as long white needles: mp 239–240°; uv max (EtOH) 226 mμ (log ϵ 4.40), 234 (4.41), 243 (4.39), 271 (3.86), 294 (3.69); nmr (CD_3COCD_3) δ 7.77 (d, 2, J = 2.4 Hz), 8.13 (d, 2, J = 2.4 Hz); ir (KBr) 1130, 1290 cm^{-1} (SO_2).

Anal. Calcd for $C_8H_4S_3O_2$: C, 42.08; H, 1.76; S, 42.13. Found: C, 42.03; H, 1.84; S, 42.35.

Dithieno[2,3-*b*:3′,2′-*d*]thiophene 7,7-Dioxide (17).—From 588 mg (3 mmol) of **2** and 1.20 g (7 mmol) of *m*-chloroperbenzoic acid the procedure described for the preparation of **16** afforded 342 mg (50%) of the sulfone **17** as white needles from methanol: mp 193–195°; uv max (EtOH) 223 mμ (log ϵ 4.31), 285 (3.91), 335 (2.99); nmr (CD_3COCD_3) δ 7.38 (d, 2, J = 5.0 Hz), 8.00 (d, 2, J = 5.0 Hz); ir (KBr) 1150, 1305 cm^{-1} (SO_2).

Anal. Calcd for $C_8H_4S_3O_2$: C, 42.08; H, 1.76; S, 42.13. Found: C, 42.68; H, 2.00; S, 42.54.

Dithieno[2,3-*b*:3′,4′-*d*]thiophene 7,7-Dioxide (18).—By the method described for the preparation of **16**, from 500 mg (2.55 mmol) of **4** and 1.1 g (6.4 mmol) of *m*-chloroperbenzoic acid 370 mg (64%) of **18** was obtained as white needles from dioxane–water 1:1: mp 210–211°; uv max (EtOH) 236 mμ (log ϵ 4.24), 256 (4.00), 264 (4.16), 304 (3.08); nmr (CD_3COCD_3) δ 8.15 (d, 2, J = 2.4 Hz), 7.68 (d, 2, J = 2.4 Hz), 7.80 (d, 2, J = 5.0 Hz), 7.62 (d, 2, J = 5.0 Hz); ir (KBr) 1140, 1290 cm^{-1} (SO_2).

Anal. Calcd for $C_8H_4S_3O_2$: C, 42.08; H, 1.76; S, 42.13. Found: C, 42.07; H, 1.84; S, 42.08.

Dithieno[3,4-*b*:3′,4′-*d*]thiophene 4-Oxide (19).—To a solution of 196 mg (1 mmol) of **3** in 20 ml of acetic acid was added 2 ml of a 30% H_2O_2 solution. After the solution was stirred at room temperature for 5.5 hr, 40 ml of water was added, and the crystalline material was filtered and recrystallized from methanol yielding 160 mg (75%) of **19** as white needles: mp 203–204°; uv max (EtOH) 220 mμ (log ϵ 4.41), 242 (4.40), 248 (4.41), 268 (3.88), 278 (3.84), 298 (3.47); nmr (CD_3COCD_3) δ 7.71 (d, 2, J = 2.4 Hz), 8.18 (d, 2, J = 2.4 Hz); ir (KBr) 1030 cm^{-1} (S=O).

Anal. Calcd for $C_8H_4S_3O$: C, 45.26; H, 1.89; S, 45.31. Found: C, 45.08; H, 2.02; S, 44.87.

Registry No.—**1**, 3593-75-7; **2**, 236-63-5; **3**, 13090-49-8; **4**, 28504-79-2; **9**, 28504-80-5; **11**, 28504-81-6; **12**, 28504-82-7; **13**, 28504-83-8; **15**, 3807-53-2; **16**, 28504-85-0; **17**, 28504-86-1; **18**, 28504-87-2; **19**, 28504-88-3.

Solvolyses of 2α,5-Epithio-5α- and -Epoxy-5α-cholestane Derivatives. A Reactivity Factor of 10^{11} Due to Sulfur Participation in a 7-Thiabicyclo[2.2.1]heptane Derivative

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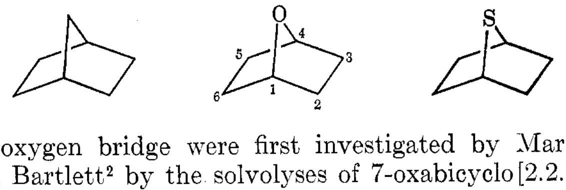
Solvolysis reactions of 2α,5-epithio-5α-cholestanes, a corresponding sulfoxide, and 2α,5-epoxy-5α-cholestanes bearing a bromo or methanesulfonyloxy group at the C-3 exo (α) or endo (β) reaction site were investigated in aqueous dioxane and compared with the solvolyses of *exo*- and *endo*-2-norbornyl methanesulfonates (**12** and **13**). Rates of exo derivatives of the epithiocholestane (**6**), the epoxycholestane (**9**), and 7-oxabicyclo[2.2.1]heptane (**1**) are of the same order of magnitude and about 10^3 times less than that of **12**. The products were those expected to result from Wagner–Meerwein rearrangement of the C(1)–C(2) bond, the hemithioacetal **14** (formed by cyclization of a *cis*-mercaptoaldehyde) from **6** and the *cis*-hydroxyaldehyde **16** from **9**. The small reactivities of **6** and **9** relative to **12** are considered to arise from the inductive effect of the oxygen or the sulfur bridge and the effects of bridging C-5 with C-10 (exo) by the B ring are indicated to be unimportant. The *endo*-epithiocholestane (**5**) solvolyzes with a very fast rate which is, in 70% dioxane, 1.1 × 10^{10} times the rate of *endo*-epoxycholestane (**8**) and 1.2 × 10^8 times that of **6**. A product of retention of configuration is exclusively formed from **5**. The results are interpreted in terms of participation of the sulfur atom, greatly enhanced by its geometric situation in the steroidal [2.2.1] system. Conversion of **5** to its sulfoxide **7** results in a disappearance of the sulfur participation. Whereas the *endo*-7-oxabicyclo[2.2.1]heptane (**2**) undergoes a Wagner–Meerwein rearrangement, **8** produces mainly a product of retention of configuration. This retention is discussed as being indicative of a small degree of participation of oxygen.

The ring system most extensively studied in connection with the interest in the role of neighboring group participation in carbonium ion reactions is the bicyclo[2.2.1]heptane system.[1] Effects of the replacement of the 1,4-methylene bridge in this system by an oxygen bridge were first investigated by Martin and Bartlett[2] by the solvolyses of 7-oxabicyclo[2.2.1]hept-2(*exo* and *endo*)-yl chlorides (and bromides).



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