***endo*-3-Bromobicyclo[2.2.1]heptan-2-*exo*-ol (18).**—*exo*-3-Mercurichloridebicyclo[2.2.1]heptan-2-*exo*-ol (**19**)[22] (86 g, 0.25 mol) was dissolved in carbon tetrachloride (2 l.) and, with stirring, bromine (40 g, 0.5 mol) in CCl_4 (500 ml) was added through a pressure-equilibrated dropping funnel. The reaction was permitted to stir overnight at room temperature and the precipitate which formed was removed with suction filtration. The CCl_4 filtrate was washed with water and 10% sodium carbonate, and dried over magnesium sulfate. Removal of the solvent at reduced pressure yielded a dark oil (30.7 g) a portion of which (9.50 g) was chromatographed (3.5 cm i.d., 1000 g), 250-ml fractions being taken. Fractions 12–15 (0.965 g) consisted of nearly pure **14** (pmr). Fractions 17–21 (1.524 g) consisted of **16** while fractions 24–35 (1.625 g) were a new compound which crystallized on standing and was identified as **18**, mp 80–81°, by (a) elemental analysis (*Anal.* Calcd for $C_7H_{11}OBr$: C, 43.98; H, 5.75; Br, 41.88. Found: C, 43.88; H, 5.76; Br, 41.26); (b) spectra [ir –OH 2.78 (sharp) and 2.90 μ (broad); pmr δ 3.91 (1 H) complex multiplet ($W_{1/2}$ = 9.0 Hz), 3.76 (1 H), t, $J_{2,3,\mathrm{trans}} = J_{2,7\text{-anti}} = 2.1$ Hz].

Attempted Isomerization of Products in DMSO in the Presence of NBS.—The product (1.5 g) was dissolved in DMSO (25 ml). Water (0.5 ml) was added and this was followed by NBS (2.0 g). The mixture was heated to 60° and allowed to cool and stir for 0.5 hr. The work-up then paralleled that of the original reaction mixture. The resulting product (1.35–1.45 g) was examined by pmr and tlc. No evidence for rearrangement, within the limits of detectability (*ca.* 2–3%), by comparison to known mixtures, was found.

Registry No.—**1**, 498-66-8; **3**, 32819-60-6; **4**, 695-02-3; **5**, 32784-96-6; **5** *p*-nitrobenzoate, 32819-61-7-**6**, 32819-62-8; **7**, 7176-91-2; **8**, 32819-64-0; **9**, 7242-94-6; **10**, 2843-52-9; **11**, 32346-69-3; **12**, 7242-95-7; **14**, 1073-25-2; **14** 2,4-DNP, 32784-98-8; **15**, 1073-24-1; **15** 2,4-DNP, 32819-68-4; **16**, 4321-51-1; **17**, 32819-70-8; **18**, 4321-52-2; dimethyl sulfoxide, 67-68-5; NBS, 128-08-5.

A Novel Anodic Synthesis of Sulfonium Salt from Diphenyl Sulfide[1]

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Diphenyl sulfide (1), dissolved in acetonitrile containing $LiClO_4$, was electrolyzed at 30° to give diphenyl *p*-(phenylthio)phenyl sulfonium perchlorate (3), diphenyl sulfoxide (4), and 1,4-bisphenylthiobenzene (5). Sulfonium salt 3 predominated in the absence of water, while 4 increased as the concentration of water was raised.

The anodic oxidation of organic sulfides examined by Fichter, *et al.*,[2] gave corresponding sulfoxides, sulfones, and sulfonic acids in the mixed media of water and protic solvents such as methanol and acetic acid, but the reaction in aprotic media has received little attention except for some polarographic studies.[3,4] In the previous paper,[1] we reported an anodic oxidation of some phenyl sulfides in acetonitrile in which substrates competitively undergo either sulfoxidation or S–R bond cleavage to thiyl radical PhS· and cation R^+ through electron deficient divalent sulfide of the type $Ph\overset{+\cdot}{S}R$ and that the reaction pathways are controlled by the stability of the cation R^+. As an extention of the work, this paper describes a novel anodic synthesis of a sulfonium salt from diphenyl sulfide **1**.

Diphenyl sulfide **1** (465 mg, 2.5 × 10^{-3} mol) dissolved in 10 ml of acetonitrile containing 500 mg of $LiClO_4$ was electrolyzed at 30° using 3 cm^2 platinum foils as electrodes without separation of the anodic compartment from the cathodic. One equivalent of constant current (200 mA) was applied while terminal voltage range was 6–10 V.

Products were diphenyl *p*-(phenylthio)phenyl sulfonium perchlorate (**3**), diphenyl sulfoxide (**4**), and 1,4-bisphenylthiobenzene (**5**). No diphenyl disulfide was detected by vpc. Sulfonium salt **3** predominated in the absence of water, while sulfoxide **4** increased as the concentration of water was raised (Table I).

TABLE I

PRODUCTS OF ANODIC OXIDATION OF 1 IN ACETONITRILE

$[H_2O]^a$	1^b	3^c	4^c	5^c
0	19	71	1	4
0.1	25	63	4	3
1.0	27	46	25	2

[a] Milliliters of water in 10 ml of acetonitrile solution. [b] Recovered phenyl sulfide **1**. [c] Per cent on the basis of starting material **1**.

Sulfonium salt **3**, a slightly brown colored amorphous solid, showed a positive Beilstein test and was soluble in chloroform and acetone and insoluble in ether, benzene, and *n*-hexane. Its ir spectrum showed a strong band at 1090 cm^{-1} corresponding to sulfonium perchlorate and the nmr revealed a singlet (10 H) at τ 2.30 in $CDCl_3$ which is consistent with that of triphenyl sulfonium perchlorate.[5]

Oxidation of **3** with hydrogen peroxide in acetic acid afforded sulfone **6** (Scheme I). The sulfone **6** was subjected to nucleophilic substitution with sodium ethoxide in ethanol–tetrahydrofuran at room temperature to afford **1** (50%), *p*-ethoxyphenyl phenyl sulfone (**7**, 62%), and phenyl *p*-(phenylsulfonyl)phenyl sulfide (**8**, 2%) and phenetole **9** (2%). Treatment of **6** with benzenethiol in pyridine provided **1** (62%) and **8** (68%). Thus, sodium ethoxide and benzenethiol preferentially attack the *p*-phenylsulfonylphenyl ring to split out **1**.[6] The structures of **4**, **5**, **7**, and **8** were assigned by comparing their spectrum data with those of authentic samples prepared by the routes as described in the Experimental Section.

It was previously proposed that anodic oxidation of

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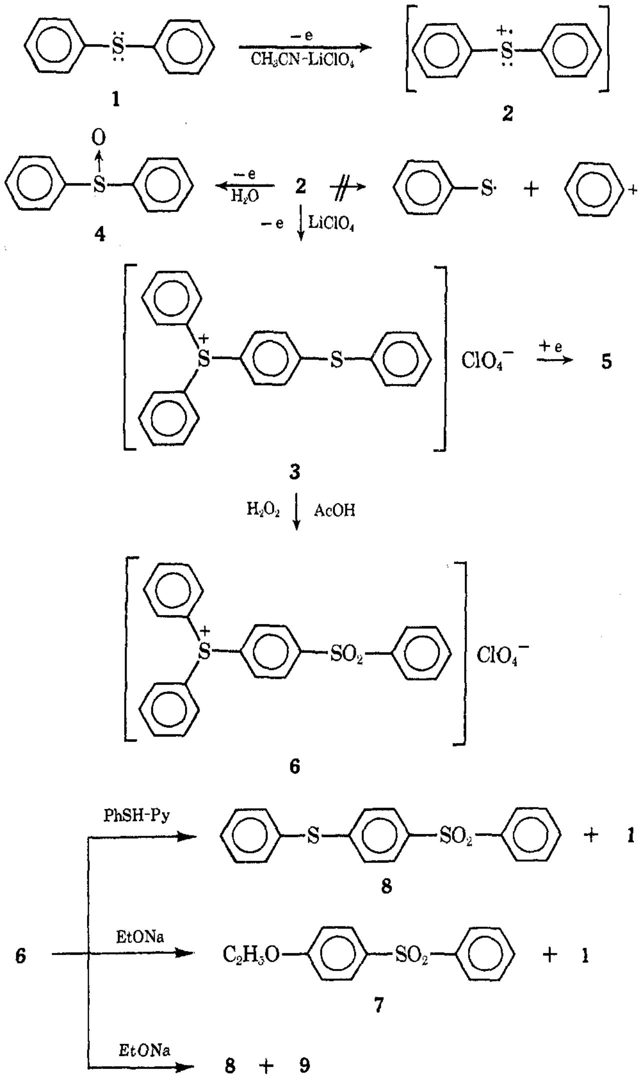
some phenyl sulfides affords electron-deficient intermediates of the type $\mathrm{Ph\overset{+\cdot}{S}R}$ which undergo either sulfoxidation or S–R bond cleavage depending on the stability of cation R^+. Thus, phenyl triphenylmethyl sulfide afforded diphenyl disulfide and triphenylcarbinol while phenyl methyl sulfide gave the corresponding sulfoxide as a main product. Since phenyl cation is too unstable to leave from **2**, intermediate **2** would undergo electrophilic attack instead of S–Ph bond cleavage. Therefore, **2** would suffer either hydrolysis to sulfoxide **4** after disproportionation to dication and **1**, or nucleophilic attack by water at the same time as further one-electron oxidation, while in the absence of water **2** or its dication would attack preferentially the para position of the phenyl ring of **1** to afford sulfonium salt **3**.

Vpc analysis of the electrolysis products revealed absence of 4-(phenylthio)phenol (**10**) and 4-(phenylthio)acetanilide (**11**). This fact suggests that the cation center of **2** predominantly localizes on the sulfur atom. Formation of **5** would result from cathodic reduction of **3** as similarly as proposed in the reduction of phosphonium[7] and sulfonium salts[8] since **5** was not actually produced in the electrolysis in which the anodic compartment was separated from the cathodic with a glass filter.

The good current yield of **3** has prompted us to use the anodic reaction for a synthesis of other sulfonium salts.

SCHEME I



Experimental Section

Materials.—Diphenyl sulfide (**1**)[9], phenyl sulfoxide (**4**),[10] benzyl phenyl sulfide,[11] 4-(phenylthio)acetanilide (**11**),[12] 4-(phenylthio)phenol (**10**),[13] 4-(phenylthio)aniline (**12**),[13] and 4-chlorophenyl phenyl sulfide (**13**)[14] were prepared as described in the literature.

1,4-Bisphenylthiobenzene (5).—The diazonium salt obtained from 1 g of **12** in a sulfuric acid solution was decomposed at 50° for 2 hr in aqueous sodium thiophenoxide (4 g of thiophenol). The neutral ether extract was dried (Na_2SO_4) and concentrated. The resulting oil was subjected to an elution column chromatography on silica gel using *n*-hexane to afford a slightly red-brown oil. The oil was fractionated by preparative vpc (SE-30, 70 cm column, 200°) to give **5** as crystals, mp 79–80.5° (lit.[15] mp 81.5°).

4-Ethoxyphenyl Phenyl Sulfone (7).—The phenol **10** (0.15 g) was stirred with 1 g of ethyl bromide in 10 ml of 1 *M* sodium ethoxide–ethanol solution for 15 hr at room temperature. The reaction mixture was poured onto ice and extracted with ether. The extract was treated as an usual manner to provide a yellow oil. Then, without purification, the oil was dissolved in 2 ml of acetic acid and stirred with 0.5 g of 30% aqueous hydrogen peroxide at room temperature for 2 hr and at 60° for 1 hr. The reaction mixture was poured on ice water and extracted with ether. The extract was concentrated to afford an oily product which was kept under suction to solidify. The solid was recrystallized twice from *n*-hexane–benzene to give 0.12 g of colorless crystals: mp 113–114°; ir (Nujol) 1595 (m), 1300–1315 and 1153 (s, $-SO_2-$), 1108 (m), and 809 cm^{-1} (w); nmr ($CDCl_3$) τ 8.63 (t, 3, $-OCH_2\mathbf{CH_3}$), 5.96 (q, 2, $-O\mathbf{CH_2}CH_3$), 3.10 (d, 2, ortho to ethoxy, $J = 9$ Hz), 2.17 (d, 2, meta to ethoxy, $J = 9$ Hz), 2.4–2.7 (m, 3), 2.0–2.3 (m, 2).

Anal. Calcd for $C_{14}H_{14}O_3S$: C, 64.10; H, 5.38. Found: C, 64.35; H, 5.36.

Phenyl *p*-(phenylsulfonyl)phenyl Sulfide (8).—The sulfide **13** (1.2 g, 5 × 10^{-3} mol) was stirred with 30% aqueous hydrogen peroxide (0.9 g, 1.5 × 10^{-2} mol) in 5 ml of acetic acid at 30° for 2 hr and 50° for 30 min. The reaction mixture was evaporated under suction and the residual oil was extracted with chloroform. The extract was washed with water, 10% aqueous sodium hydroxide and finally twice with water, dried (Na_2SO_4), and concentrated to afford crystalline product. The crude crystals, without purification, were dissolved in 10 ml of ethanol–tetrahydrofuran (1:2 mixture) containing 5 × 10^{-3} mol of sodium thiophenoxide and warmed with stirring at 70° for 10 hr. After evaporating the solvent, the resulting oil was combined with 100 ml of chloroform and 50 ml of water. The extract was washed with 10% aqueous sodium hydroxide and then water twice, dried (Na_2SO_4), and concentrated to give crude crystals, which were recrystallized from *n*-hexane–benzene to afford **8** as colorless crystals: mp 97–98°; ir (Nujol) 1580 (m, SPh), 1320–1310 and 1157 (s, $-SO_2-$), 820 cm^{-1} (w); nmr ($CDCl_3$) τ 2.58 (s, 5, –SPh), 2.84 (d, 2, ortho to SPh, $J = 9$ Hz), 2.24 (d, 2, meta to SPh, $J = 9$ Hz), 2.4–2.7 (m, 3), 2.0–2.2 (m, 2).

Anal. Calcd for $C_{18}H_{14}O_2S_2$: C, 66.24; H, 4.32. Found: C, 66.45; H, 4.44.

Electrolysis.—A typical run of the electrolyses was as follows. Diphenyl sulfide (0.465 g, 2.5 × 10^{-3} mol) was dissolved in 10 ml of acetonitrile containing 0.5 g of lithium perchlorate in a 20-

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ml tall beaker. The solution was electrolyzed at 30° using 3-cm^2 platinum foils without separation of an anodic compartment from a cathodic. One equivalent of constant current (200 mA) was applied while the terminal voltage was 6–10 V. An electrolysis in which an anodic compartment was separated from a cathodic was done using a cell described previously[1].

Product Analysis and Assignment.—The reaction mixture was combined with 0.100 g (5×10^{-4} mol) of benzyl phenyl sulfide as an internal standard for vpc and evaporated by suction. The resulting oily materials were extracted with chloroform. The extract was washed with water, dried (Na$_2$SO$_4$), and concentrated. The residual oil was dissolved in 50 ml of ether and stirred for 30 min. Ether was removed by decantation. The ether-insoluble product was washed twice again with each 50 ml of ether and dried under vacuum, giving 0.41 g of a slightly brown colored amorphous solid. The solid, diphenyl *p*-(phenylthio)phenyl sulfonium perchlorate (**3**), showed a positive Beilstein test: ir (Nujol) 1573 (m, SPh), 1080–1100 (s, broad, sulfonium), 815 (w), 745 (s), 683 cm^{-1} (m); nmr (CDCl$_3$) τ 2.30 (s, 10), 2.53 (s, 5), 2.41 (d, 2, J = 9 Hz), and 2.74 (d, 2, J = 9 Hz).

The ether layer was dried (Na$_2$SO$_4$) and concentrated, giving an oily material. The oil was then subjected to vpc analysis (SE-30, 1-m column, 170°) showing the existence of products, **1**, **4**, and **5**. Yields of sulfoxide **4** and sulfides **1** and **5** were obtained by calculating each peak area as compared with that of the internal standard.

To the sulfonium salt **3** (0.30 g) dissolved in 10 ml of acetic acid, 0.2 g of 30% aqueous hydrogen peroxide was added dropwise. The mixture was stirred at room temperature for 1 hr and at 50° for 1 hr and evacuated by suction to remove acetic acid. The resulting oil was dissolved in 50 ml of chloroform. The extract was washed with 5% aqueous sodium hydroxide and twice with water, dried (Na$_2$SO$_4$), and concentrated. After the resulting product was washed twice with each 50 ml of ether, the ether-insoluble product was dried and solidified under vacuum, giving diphenyl *p*-(phenylsulfonyl)phenyl sulfonium perchlorate (**6**) as an almost colorless amorphous solid (0.28 g): ir (Nujol) 1590 (w), 1330 and 1160 (s, –SO$_2$–), 1090–1100 (vs, sulfonium), 830 (w), 750 cm^{-1} (vs); nmr (CDCl$_3$) τ 2.28 (s, 10, Ph$_2$S$^+$–), 1.75–2.55 (m, 9).

Anal. Calcd for C$_{24}$H$_{19}$O$_6$S$_2$Cl: C, 57.30; H, 3.81. Found: C, 56.94; H, 3.95.

Reaction of 6 with Sodium Ethoxide.—Sulfonium salt **6** (0.3 g, 6×10^{-4} mol) was dissolved in 5 ml of tetrahydrofuran and 2 ml of ethanol containing 50 mg of sodium metal. The reaction mixture was stirred at room temperature for 1 day and at 70° for 20 min and then combined with 50 mg (2.5×10^{-4} mol) of benzyl phenyl sulfide as an internal standard for vpc analysis and suctioned out to remove solvent. The resulting products were washed with water and extracted with chloroform. The extract was concentrated to give oily products, which were analyzed by vpc (SE-30, 80-cm column, at 120–190°, scan rate 4°/min) giving **1** (50%), **7** (62%), **8** (2%), and **9** (2%). The product mixture was kept at room temperature overnight to crystallize in part. The crude crystals were collected and recrystallized from *n*-hexane–benzene to give colorless crystals whose ir spectrum and melting point are consistent with those of the authentic sample **7**.

Reaction of 6 with Thiophenol.—Sulfonium salt **6** (0.32 g) was stirred with 1 g of thiophenol and 1.5 g of pyridine at room temperature for 2 days. Products were analyzed by vpc as similarly as described above giving **1** (62%) and **8** (68%). Crystals obtained from the product mixture were recrystallized from *n*-hexane–benzene and were identified by comparing with authentic sample **8**.

Registry No.–**1**, 139-66-2; **3**, 32958-90-0; **6**, 32958-91-1; **7**, 14193-13-6; **8**, 32846-68-7.

The Alkaline Decomposition of Organic Disulfides. VI. Further Examples of Elimination Reactions (1,2-Dithiolanecarboxylic Acids) and of Nucleophilic Substitution

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In aqueous, alkaline solution 1,2-dithiolane-4-carboxylic acid (**1**) appears to undergo a β elimination, the primary product of which decomposes to yield α-(mercaptomethyl)acrylic acid, which has been isolated as its *S*-ethyl derivative, and hydrogen sulfide. The corresponding polymeric disulfide, (–SCH$_2$CH(COOH)CH$_2$S–)$_n$, depolymerizes to **1** instantly in alkaline solution and at measurable rates at pH values as low as 4.2. The profile of pH *vs.* rate suggests that the carboxylate ion participates in this depolymerization, a conclusion which is confirmed by the stability of the methyl ester of the polymer. In aqueous, alkaline solution both *rac*- and *meso*-1,2-dithiolane-3,5-dicarboxylic acids decompose at the same rate to yield 2-mercapto-2-pentenedioic acid by a process which is probably an α elimination initially. Dithiobis(methylcyclopropane-1-carboxylic acid) decomposes very slowly by direct nucleophilic attack of hydroxide ion on disulfide sulfur.

It has been amply demonstrated experimentally that the alkaline decomposition of organic disulfides takes place by one of three alternative pathways, as determined by secondary features of their molecular structures:[2] α elimination,[3,4] β elimination,[5] or direct nucleophilic displacement of sulfur from sulfur by hydroxide ion.[5–7] Several more disulfides have now been found to decompose *via* the pathways predictable from their structures. However, those of this group which undergo an initial elimination gave unstable intermediates which decompose further to unsaturated compounds which were not anticipated.

Jansen[8] isolated from asparagus a crude disulfide which he could not crystallize but which he successfully reduced to 2-mercaptomethyl-3-mercaptopropionic acid. Schotte and Ström[9] found that the 1,2-dithiolane-4-carboxylic acid (**1**) which they obtained by the aerial oxidation of the dithiol was appreciably contaminated by the isomeric polymeric disulfide **2**. Pure **1** was obtained by recrystallization from benzene, in which **2** is insoluble. Schotte and Ström conjectured that **1** exists in the asparagus plant and that some of it had undergone polymerization during Jansen's recovery procedure. Analogously, we recently suggested that "...

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