BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2912—2913 (1973)

Electrochemistry of Organic Sulfur Compounds. IV.[1] Anodic Sulfonium Formation from Alkyl Phenyl Sulfides

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(Received March 19, 1973)

In recent years, various sulfonium salts and sulfonium ylides have been utilized as key intermediates for organic syntheses.[2] We have examined the electrochemical preparation of useful sulfonium salts which would provide sulfonium ylides. In a previous paper,[1] we described a novel anodic synthesis of a sulfonium salt from diphenyl sulfide and proposed a mechanism for the anodic process; sulfides (Ph–S–R) are oxidized in the anodic process to provide primarily a radical cation $[\text{Ph–S–R}]^{+\cdot}$, which undergoes either S–R bond cleavage to give thiyl radical and cation R^+, or electrophilic attack by water and/or sulfide to provide sulfoxide and/or sulfonium salt. The S–R cleavage is promoted by a substituent R such as benzyl and triphenylmethyl groups due to the stability of the cation R^+. Selection of the reaction pathway, either sulfoxidation or sulfonium salt formation, probably depends on the stability of the cation radical **2** and the presence of water in the reaction media.[3] This paper shows that anodic oxidation of alkyl phenyl sulfides **1** in general gives sulfonium salts **3** in anhydrous media and some chemical properties of **3**.

Alkyl phenyl sulfides **1** (2.5 mmol) dissolved in acetonitrile containing lithium perchlorate were electrolyzed at room temperature using platinum foils as electrodes without separation of the anodic compartment. Thus, 1.2 equivalent of constant current (200 mA) was applied with the terminal voltage kept at about 5.5 V. Products were separated by column chromatography on silica gel. The results are listed in Table 1.

TABLE 1. PRODUCTS OF ANODIC OXIDATION OF **1** IN ACETONITRILE

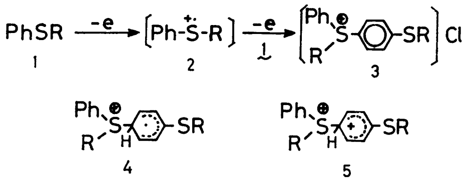
1 R	**3** (%)[a]	Sulfoxide (%)[a]	Recovered **1** (%)[b]
Methyl (**1a**)	60 (**3a**)	trace	19
3-Butenyl (**1b**)	67 (**3b**)	4	6
Cyclohexyl (**1c**)	57 (**3c**)	trace	20
Phenyl[1]	71	trace	19

a) The yield is calculated on the basis of **1**. b) *m*-Chlorothioanisole, diphenyl sulfide, and phenyl benzyl sulfide were employed for internal standards for glpc.

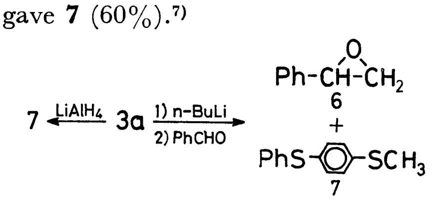
Alkyl phenyl sulfides **1** afforded the corresponding sulfonium perchlorates **3** in *ca.* 60—70% yields on the basis of **1**. This suggests that in the absence of water anodic oxidation of **1** takes place predominantly leading to the formation of the salts **3** in contrast to the results obtained with water–acetonitrile[3] or water–hydrogen chloride giving sulfoxides.[4]

Formation of **3b** from **1b** reveals that the divalent sulfide would be more reactive as compared with the double bond[5] of **1b**, since the phenyl group of **1** should undergo electrophilic attack by the cation radical of **2** rather than intramolecular attack of the double bond. No evidence of the S–R bond cleavage of **1** was observed during the course of electrolysis since no diphenyl disulfide was detected in glpc.[3]

Accordingly, the cation radical **2** would attack the *para*-position of the phenyl ring to give a cyclohexadienyl radical intermediate **4**, which would be readily oxidized to **5** followed by deprotonation to give **3**. Or, a dication formed incipiently from further oxidation of **2** would couple with the sulfide **1** leading to **5**.



The sulfonium salt **3a**, pale brownish crystals, could be purified by recrystallization from dichloromethane–ether. Its IR spectrum had a characteristic strong band at 1095 cm^{-1} due to the sulfonium group and its NMR spectrum showed a singlet (3H) at δ 3.62 corresponding to the methyl group attached to the trivalent sulfur atom of **3a**. Treatment of **3a** with *n*-butyllithium followed by benzaldehyde in tetrahydrofuran at −78 °C gave the epoxide **6** (50%) and the sulfide **7** (50%).[6] Reduction of **3a** with lithium aluminum hydride gave **7** (60%).[7]



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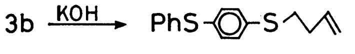
[4] F. Fichter, P. Sjostedt, W. Wenk, and F. Braun, *Chem. Ber.*, **47**, 1526 (1914).

[5] The halfwave potentials of the monosubstituted double bonds and phenyl sulfide group are about 2.7—2.8 V *vs.* Ag and 1.5 V *vs.* SCE, respectively. N. W. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968); C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, Inc., New York (1970).

[6] M.J. Bogdanowicz and B. M. Trost, *Tetrahedron Lett.*, **1972**, 887.

[7] Electrochemical reduction of sulfonium salts: See M. Finkelstein, R. C. Petersen, and S. D. Ross, *J. Electrochem. Soc.*, **110**, 422 (1963). Phosphonium salts are also reduced to the corresponding phosphines by lithium aluminum hydride: W.J. Bailey and S. A. Buckler, *J. Amer. Chem. Soc.*, **79**, 3567 (1957); S. T. D. Gough and S. Trippett, *J. Chem. Soc.*, **1961**, 4263.

The structure of the sulfonium salt **3b**,[8] a brown oil, was characterized by its IR and NMR spectra. Treatment of **3b** with potassium hydroxide in ethylene glycol at 80 °C provided **8** and butadiene, the latter being trapped in a bromine–carbon tetrachloride solution.



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Structural assignment of the salt **3c**,[8] a slightly brownish amorphous solid, was carried out by comparison of its IR and NMR spectral data with those of the homologous compounds **3a** and **3b**.

Experimental

Preparation of Sulfides. Sulfides **1a** and **1c** were prepared from sodium thiophenoxide and the corresponding alkyl halides.[9] Sulfide **1b** was prepared as follows. Thiophenol (22.0 g) in 25 ml of dioxane was refluxed with 1,4-dibromobutane (50 g) and pyridine (18.0 g) with stirring for 12.5 hr. The mixture was poured onto ice and extracted with $CHCl_3$. Distillation of the extracts gave phenyl δ-bromobutyl sulfide (31%): bp 151—157 °C/8.0 mmHg. Refluxing of the sulfide with an equimolar amount of potassium *t*-butoxide in dry *t*-butanol for 1 hr provided sulfide **1b** (60%): bp 95—98 °C/6.0 mmHg; IR (Neat) 1640 (m, C=C), 1580 (m, Ph–S), 915, 740, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.00—7.40 (m, 5H, Ph), 5.40—6.20 (m, 1H, –CH=C), 4.80—5.30 (m, 2H, C=CH_2), 2.80—3.10 (m, 2H, CH_2–C=C), 2.40 (t, 2H, J=8 Hz, CH_2–S); Mass (*m/e*) 164 (M^+). Found: C, 73.00; H, 7.25%. Calcd for $C_{10}H_{12}S$: C, 73.13; H, 7.37%.

Electrolysis. Electrolysis of **1a** was carried out as follows: A solution of **1a** (310 mg) and $LiClO_4$ (500 mg) in 10 ml of dry CH_3CN in a 20 ml tall beaker was electrolyzed under N_2 at *ca.* 20 °C using two 3 cm^2 platinum foils without separation of the compartment. Constant current (200 mA, 1.2 equiv) was applied while the terminal voltage was about 5.5 V. Electrolyses of **1b** and **1c** were carried out in a similar manner to that for **1a**.

*Phenyl Methyl-*p*-methylthiophenyl-sulfonium Perchlorate (3a).* The reaction mixture combined with *m*-chlorothioanisole (79 mg, 0.5 mmol) as an internal standard for glpc was concentrated. The residue was taken up in $CHCl_3$, washed with water, dried (Na_2SO_4) and concentrated. The residue was developed on silica gel column with $CHCl_3$ and then acetone. The $CHCl_3$ eluent was subjected to glpc analysis (Diasolid L, 10% polyneopentyl glycol succinate (PNGS) coated column, 1 m long, 150 °C). The amount of recovered **1a** was calculated by comparison of the peak area with that of the internal standard. The acetone eluent was crude sulfonium salt **3a** (261 mg), which was solidified in a vacuum. Crystallization of the salt from CH_2Cl_2–ether (1 : 2) gave slightly brownish white crystals: mp 132.0—132.5 °C; IR (Nujol) 1580 (m), 1120—1070 (vs, sulfonium), 820, 760, 695 cm^{-1}; NMR ($CDCl_3$) δ 7.30—8.00 (m, 9H, Ph), 3.62 (s, 3H, =S^+–CH_3), 2.43 (s, 3H, S–CH_3). Found: C, 48.30; H, 4.28%. Calcd for $C_{14}H_{15}ClO_4S_2$: C, 48.48; H, 4.35%.

Reaction of 3a with n*-Butyllithium.* To a mixture of **3a** (347 mg) in 5 ml of dry THF under N_2 at −78 °C was added dropwise with stirring 0.9 ml of *n*-butyllithium in ether (1.64 M). The yellow solution was stirred for 45 min and to this was added 0.1 ml (*ca.* 1 mmol) of benzaldehyde in 3 ml of THF. The mixture was stirred for 1 hr at −78 °C, then the bath was removed. After tetralin (66 mg, 0.5 mmol) and phenyl benzyl sulfide (100 mg) had been added as internal standards for glpc, the reaction mixture was poured onto ice and extracted with ether. The extracts were washed, dried (Na_2SO_4), and distilled. The fraction, bp below 123 °C/13 mmHg, was analyzed by glpc (Diasolid L, 10% PNGS coated column, 2 m long, 100 °C) giving benzaldehyde (53 mg) and **6** (60 mg); their retention times in glpc were consistent with those of authentic samples, their spectral data supporting their structures. Continued distillation of the pot residue gave a fraction, bp below 120 °C/0.08 mmHg, which was analyzed by glpc (Diasolid L, 10% Silicone SE-30, 2 m long, 180—210 °C) giving **7** (147 mg) as a colorless oil: IR (neat) 1580 (m), 1480 (m), 810, 740, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.10—7.40 (9H, Ph), 2.45 (s, 3H, S–CH_3); Mass (*m/e*) 232 (M^+), 217, 185, 108. Found: C, 67.21; H, 5.30%. Calcd for $C_{13}H_{12}S_2$: C, 67.19; H, 5.21%.

*Phenyl-3-butenyl-*p*-(3-butenylthio)phenyl-sulfonium Perchlorate (3b).* Crude sulfonium salt **3b** was purified by passing through a short silica gel column with $CHCl_3$–acetone (1 : 1), followed by tlc on silica gel with ethyl acetate to afford a brown oily **3b**:[8] IR (neat) 1650, 1580, 1120—1070 (s), 930, 820, 750, 680 cm^{-1}; NMR ($CDCl_3$) δ 7.20—8.10 (m, 9H, Ph), 5.50—6.20 (m, 2H, –CH=C), 4.90—5.30 (m, 4H, –C=CH_2), 4.22 (t, 2H, J=8 Hz, =S^+–CH_2), 3.03 (t, 2H, J=7 Hz, S–CH_2), 2.30—2.80 (m, 4H, CH_2–C=C).

*Phenyl Cyclohexyl-*p*-cyclohexylthiophenyl-sulfonium Perchlorate (3c).* Isolation was carried out in a similar manner to that for **3a**. The sulfonium salt **3c**, a slightly brownish amorphous solid:[8] IR (Nujol) 1580, 1070—1110 (s), 820, 750, 685 cm^{-1}; NMR ($CDCl_3$) δ 7.20—8.40 (m, 9H, Ph), 4.50—5.20 (m, 1H, =S^+–CH), 2.90—3.60 (m, 1H, S–CH), 1.00—2.30 (m, 20H, CH_2).

Reduction of 3a by Lithium Aluminum Hydride. To a mixture of **3a** (347 mg) in 4 ml of dry THF under N_2 was added at once 57 mg of $LiAlH_4$. This was stirred at 5 °C for 1 hr and quenched by addition of 5 ml of saturated aqueous ammonium chloride. After phenyl benzyl sulfide (100 mg) had been added as an internal standard for glpc, the mixture was extracted with ether, washed and dried (Na_2SO_4). The residue was analyzed by glpc (Diasolid L, 10% Silicone SE-30, 2 m long, 180—210 °C) giving **7** (139 mg). The retention time of **7** in glpc and its spectral data support the structure.

Reaction of 3b with Potassium Hydroxide. A mixture of **3b** (580 mg) and KOH (120 mg) in 4 ml of ethylene glycol was heated at 80 °C for 1 hr in a 10 ml tall beaker equipped with N_2 bubbler. The N_2 gas was passed through a trap containing 5 ml solution of CCl_4 with bromine. The mixture was extracted with ether, washed and dried (Na_2SO_4). Separation of the concentrated extracts by tlc on silica gel with CH_2Cl_2 gave **8** (133 mg) as a major product: IR (neat) 1650, 1580, 920, 740, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.10—7.40 (broad s, 9H, Ph), 5.50—6.20 (m, 1H, –CH=C), 4.80—5.20 (m, 2H, C=CH_2), 2.70—3.10 (m, 2H, S–CH_2), 2.10—2.60 (m, 2H, –CH_2–C=C); Mass (*m/e*) 272 (M^+), 231, 218, 197. Found: C, 70.67; H, 6.03%. Calcd for $C_{16}H_{16}S_2$: C, 70.54; H, 5.96%.

From the CCl_4 solution white crystals were obtained and assigned to be 1,2,3,4-tetrabromobutane in comparison with its spectral data with that of authentic sample.

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8) Difficulties were encountered in the microanalyses of **1b** and **1c** because of their hygroscopic nature.

9) A. I. Vogel, *J. Chem. Soc.*, **1948**, 1820.