The Analysis of *t*-Butyl Sulfides[1]

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t-Butyl sulfides, like trityl sulfides but unlike other alkyl sulfides, consume 6 equiv. of bromine when titrated by the Siggia–Edsberg procedure. This behavior is attributed to solvolysis of intermediate bromosulfonium ions to yield *t*-butyl carbonium ions and sulfenyl bromides, the latter materials being oxidized subsequently to sulfonyl bromides. The results obtained indicate that the Siggia–Edsberg procedure may be used for the quantitative analysis of tertiary sulfides.

Organic sulfides generally are determined by bromimetric or bromometric procedures in which the sulfide becomes oxidized to a sulfoxide.[2] In such analyses, the sulfide usually consumes 2 equiv. of bromine, but care must be taken to prevent subsequent oxidation of the sulfoxide to sulfone, particularly when alkyl sulfides are being analyzed. Thus, bromometric procedures are suitable for the analysis of aryl and heterocyclic sulfides,[3] but only bromimetric methods can be utilized for the analysis of strictly aliphatic sulfides. Of the available bromimetric procedures, the method of Siggia and Edsberg[4] seems the most attractive from the standpoint of reagent stability, convenience, and reliability. In this procedure, an acidic solution of the sulfide is titrated with a standard potassium bromide–potassium bromate solution. Bromine is liberated *in situ* and the end point of the titration is signaled by the appearance of a permanent bromine color.

$$\mathrm{BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O}$$

$$\mathrm{R_2S + Br_2 \xrightarrow{H_2O} R_2SO + 2HBr}$$

Although many sulfides have been analyzed satisfactorily by the Siggia–Edsberg and other procedures, the limitations of such bromination techniques have not been defined and one must be cautious in the application of such techniques to the characterization of new sulfides. For example, Gregg and Blood[5] noted that triphenylmethyl (trityl) sulfides consume 6 equiv. of bromine when analyzed by the Siggia–Edsberg procedure. Primary and secondary alkyl sulfides have been analyzed satisfactorily by bromimetric procedures, but no studies have been reported on the determination of tertiary alkyl sulfides.

Results

In the course of other studies, we had occasion to analyze a number of *t*-butyl sulfides by the Siggia–Edsberg procedure. As is shown in Table I, these sulfides consumed three times as much reagent (6 equiv. of reagent per sulfur atom) as would be expected on the basis of the titration behavior of primary and secondary alkyl sulfides. A study of analysis conditions did not lead to any significant change in the results obtained. The water content of the titration mixtures did not influence the results, provided the mixtures were homogeneous. Titrations conducted at elevated temperatures gave better results than those conducted at room temperature, but the general stoichiometry of the titrations was not affected by temperature. The use of sulfuric or nitric acid instead of hydrochloric acid in these analyses caused premature oxidation of the samples.

TABLE I

TITRATION OF ALKYL SULFIDES BY THE SIGGIA–EDSBERG PROCEDURE

Sulfide	Equiv. of bromine consumed per sulfur atom
$(\mathrm{CH_3})_2\mathrm{S}$	1.93
$(n\text{-}\mathrm{C_3H_7})_2\mathrm{S}$	1.98
$(n\text{-}\mathrm{C_4H_9})_2\mathrm{S}$	1.98
$t\text{-}\mathrm{BuSCH_2CH_2S}(t\text{-}\mathrm{Bu})$	5.93
$t\text{-}\mathrm{BuSCH_2CH_2OH}$	5.85
$t\text{-}\mathrm{BuSCH_2CH_2Cl}$	5.87
$t\text{-}\mathrm{BuSCH_2CH_2CH_2CH_3}$	5.67
$(t\text{-}\mathrm{Bu})_2\mathrm{S}$	7.31
$t\text{-}\mathrm{BuSC_6H_5}$	5.64
$t\text{-}\mathrm{BuSCH_2C_6H_5}$	5.84

The similar stoichiometry noted for the bromination of *t*-butyl sulfides and for trityl sulfides[5] suggested that the brominations might have yielded similar products. Since Gregg and Blood reported that trityl aryl sulfides yield arenesulfonyl bromides and triphenylcarbinol on bromination, attempts were made to identify similar products from the *t*-butyl sulfide brominations.

In a study of products formed in the bromimetric titration of 1,2-bis(*t*-butylthio)ethane, 1,2-ethanedisulfonic acid was isolated in 53% yield. The acid was identified through its aniline and S-benzylisothiouronium salts. In addition, vapor phase chromatography (v.p.c.) established that *t*-butyl alcohol was formed during the titration in at least 20% yield.

The products formed in the bromimetric titration of *t*-butyl phenyl sulfide also were investigated. In this study, the oxidation was conducted stepwise. Reaction of the sulfide with 1 equiv. of oxidizing agent produced diphenyl disulfide in 73% yield; subsequent oxidation of the disulfide with 5 equiv. of bromide–bromate reagent per sulfur atom led to the formation of benzenesulfonyl bromide. This latter product was characterized by conversion to the corresponding amide, the derivative being isolated in 62% yield, based on the starting disulfide. The identity of the amide was established by melting point and by comparing its infrared spectrum with that of authentic benzenesulfonamide. Vapor phase chromatography established that *t*-butyl alcohol was present in the reaction mixture, in about 20% yield, after 2 equiv. of

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(1) (a) Abstracted from M.S. theses submitted by C. R. Strauss, 1963, and H. G. Guay, 1961, to the University of Akron; (b) presented before the Division of Analytical Chemistry at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1951.

(3) W. H. Houff and R. D. Scheutz, *Anal. Chem.*, **25**, 1258 (1953).

(4) S. Siggia and R. L. Edsberg, *ibid.*, **20**, 938 (1948).

(5) D. C. Gregg and C. A. Blood, Jr., *J. Org. Chem.*, **16**, 1255 (1951).

the bromide-bromate reagent had reacted with the sulfide.

In addition, the products from the titration of di(*t*-butyl) sulfide consumed nearly 8 equiv. of bromide–bromate reagent. Sulfuric acid was found to be a major product in this case. The sulfuric acid was converted to barium sulfate, and the latter product was identified by X-ray diffraction. Based on the starting sulfide, barium sulfate was obtained in 68.8% yield.

Discussion

The results obtained in this study indicate the bromination of *t*-butyl sulfides proceeds similarly to that of trityl sulfides according to the following reactions.

$$2t\text{-BuSR} + \mathrm{Br_2} \longrightarrow \mathrm{RS{-}SR} + (2t\text{-BuBr})$$

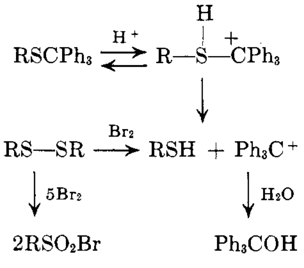
$$\mathrm{RS{-}SR} + 5\mathrm{Br_2} + 4\mathrm{H_2O} \longrightarrow 2\mathrm{RSO_2Br} + 8\mathrm{HBr}$$

$$\mathrm{RSO_2Br} + \mathrm{H_2O} \longrightarrow \mathrm{RSO_3H} + \mathrm{HBr}$$

Although aryl *t*-butyl sulfides yield arenesulfonyl bromides and alkyl *t*-butyl sulfides yield alkanesulfonic acids when brominated under the conditions of the Siggia–Edsberg procedure, this difference in behavior is probably not a result of the bromination reaction. Instead, it is believed that alkanesulfonyl bromides are intermediates in the formation of the sulfonic acids. Whether sulfonyl bromides or sulfonic acids are isolated from the bromination experiments would, of course, depend on the stability of the sulfonyl bromide. Since Johnson and Sprague[6] already have commented on the limited stability of alkanesulfonyl bromides in water, it is not surprising that an alkanesulfonic acid was obtained from the alkyl *t*-butyl sulfide experiment.

The inclination of *t*-butyl and trityl sulfides to consume 6 equiv. of bromine in the Siggia–Edsberg procedure, yielding sulfonyl bromides or sulfonic acids, is attributed to the tendency of *t*-butyl and trityl groups to form relatively stable carbonium ions in ionizing solvents. Thus, if solvolytic forces can facilitate the formation of such ions during the bromimetric titration of tertiary sulfides, then the remaining sulfur fragment is free to undergo advanced oxidation.

Gregg and Blood concluded that aryl trityl sulfides were not stable to the conditions of the Siggia–Edsberg procedure; their conjugate acids solvolyzed in dilute acetic acid, yielding mercaptans and triphenylcarbinol. Subsequent oxidation of the mercaptan to sulfonyl bromide required 6 equiv. of bromine. The instability of tertiary sulfides in acid media has been reported by Harnish and Tarbell[7,8] and one is tempted to assume that the oxidation of *t*-butyl sulfides proceeds by the same path as that of trityl sulfides. However, considerable evidence is available to indicate that *t*-butyl sulfides are more stable to acid than are trityl sulfides. Thus, the cleavage of *t*-butyl phenyl sulfide with aluminum bromide in chlorobenzene, while observable, is still considerably slower than that of trityl phenyl sulfide; *t*-butyl phenyl sulfide does not react with iodine under conditions in which trityl phenyl sulfide is rapidly converted to diphenyl disulfide; and all attempts[9,10] to prepare trityl sulfoxides or sulfones have failed, whereas *t*-butyl sulfones are easily prepared from corresponding sulfides by reaction with hydrogen peroxide.[11]

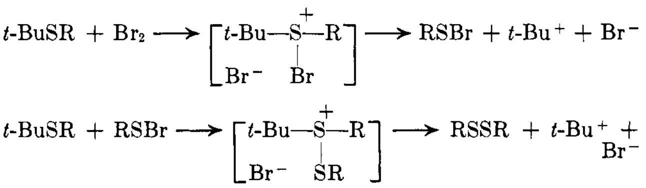


$$\begin{array}{ccc} & & \mathrm{H} \\ & & | \\ \mathrm{RSCPh_3} & \overset{\mathrm{H^+}}{\rightleftarrows} & \mathrm{R{-}\overset{+}{S}{-}CPh_3} \\ & & \downarrow \\ \mathrm{RS{-}SR} & \xrightarrow{\mathrm{Br_2}} & \mathrm{RSH} + \mathrm{Ph_3C^+} \\ \downarrow{\scriptstyle 5\mathrm{Br_2}} & & \downarrow{\scriptstyle \mathrm{H_2O}} \\ 2\mathrm{RSO_2Br} & & \mathrm{Ph_3COH} \end{array}$$

In addition, results obtained in our own work and that of others[12] indicate that *t*-butyl sulfides do not solvolyze fast enough in acetic acid–hydrogen chloride solutions to account for the results obtained in the bromimetric titration. For example, the concentration of *t*-butyl alcohol in the titration mixtures is considerably greater at the end of a bromimetric titration than it is at the beginning, regardless of how long the mixture has been allowed to stand prior to titration. Also, 1,2-bis(*t*-butylthio)ethane has been oxidized to the corresponding disulfone in about 60% yield using hydrogen peroxide in either acetic acid solution or in acetic acid containing a small amount of hydrogen chloride. Had the disulfide solvolyzed in the presence of strong acid, the yield of disulfone would have been considerably different in the two cases.

$$t\text{-}\mathrm{BuSCH_2CH_2S}(t\text{-Bu}) \xrightarrow[\mathrm{HOAc}]{\mathrm{H_2O_2}} t\text{-}\mathrm{BuSO_2CH_2CH_2SO_2}(t\text{-Bu})$$

It therefore seems most reasonable to assume that the solvolysis process occurring in the *t*-butyl sulfide titrations involves bromosulfonium ions, as is illustrated in the following scheme.



$$t\text{-BuSR} + \mathrm{Br_2} \longrightarrow \left[\begin{array}{ll} t\text{-Bu}{-}\overset{+}{\mathrm{S}}{-}\mathrm{R} \\ \mathrm{Br^-} \quad \;\; | \\ \qquad\quad \mathrm{Br} \end{array}\right] \longrightarrow \mathrm{RSBr} + t\text{-Bu}^+ + \mathrm{Br^-}$$

$$t\text{-BuSR} + \mathrm{RSBr} \longrightarrow \left[\begin{array}{ll} t\text{-Bu}{-}\overset{+}{\mathrm{S}}{-}\mathrm{R} \\ \mathrm{Br^-} \quad \;\; | \\ \qquad\quad \mathrm{SR} \end{array}\right] \longrightarrow \mathrm{RSSR} + t\text{-Bu}^+ + \mathrm{Br^-}$$

Bromosulfonium bromides are considered to be intermediates in the bromination of sulfides[13] and similar intermediates are known to be unstable when tertiary alkyl groups are bonded to sulfur.[14] Furthermore, a number of reactions related to those proposed have been reviewed by Tarbell and Harnish.[15] Most interesting of these are studies on the chlorination of aryl alkyl sulfides, in which chlorosulfonium chlorides are obtained in nonpolar solvents, but in which arenesulfonyl chlorides are obtained in ionizing solvents.[16,17] In certain cases, the chlorosulfonium chlorides were observed to decompose to alkyl chlorides and arene-

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[6] T. B. Johnson and J. M. Sprague, *J. Am. Chem. Soc.*, **58**, 1348 (1936).

[7] D. P. Harnish and D. S. Tarbell, *Anal. Chem.*, **21**, 968 (1949).

[8] D. S. Tarbell and D. P. Harnish, *J. Am. Chem. Soc.*, **74**, 1862 (1952).

[9] D. C. Gregg, K. Hazelton, and T. F. McKeon, Jr., *J. Org. Chem.*, **18**, 36 (1953).

[10] K. C. Schreiber and V. P. Fernandez, *ibid.*, **26**, 2478 (1961).

[11] F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, **77**, 572 (1955).

[12] M. E. Cain, M. B. Evans, and D. F. Lee, *J. Chem. Soc.*, 1694 (1962).

[13] R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 576.

[14] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 424.

[15] D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, **49**, 31 (1951).

[16] R. H. Baker, R. M. Dodson, and B. Riegel, *J. Am. Chem. Soc.*, **68**, 2636 (1946).

[17] T. Zincke and H. Rose, *Ann.*, **406**, 127 (1914).

sulfenyl chlorides. The chlorosulfonium chlorides also were demonstrated to be intermediates in the conversion of sulfides to sulfonyl chlorides in ionizing media.

Although tertiary sulfides do not behave like primary and secondary sulfides in the Siggia–Edsberg procedure, their reactions with bromine are rapid and they seem to involve rather exact stoichiometry. With the exception of di(*t*-butyl) sulfide, all the tertiary sulfides listed in Table I consumed approximately 6 equiv. of bromine per atom of sulfur. Assuming the titration of *t*-alkyl sulfides to require 6 equiv. of reagent per atom of sulfur, the determinations summarized in Table I accounted for 97–99% of the sulfide analyzed in most cases. Di(*t*-butyl) sulfide, a a compound containing two *t*-butyl groups, might have been expected to consume 8 equiv. of reagent, yielding sulfuric acid as a final product. The amount of sulfuric acid formed in this titration correlated very nicely with the amount of bromine consumed.

In conclusion, two types of behavior are observed in the bromimetric determination of sulfides. Primary and secondary sulfides are oxidized to the corresponding sulfoxides through the consumption of 2 equiv. of bromine; tertiary alkyl sulfides are oxidized to sulfonyl bromides through the consumption of 6 equiv. of bromine. Thus far, the sulfides studied have cleanly followed only one course of reaction and their analysis by bromimetric procedures has been possible. However, it is certainly possible that sulfides will eventually be encountered which undergo both oxidations simultaneously. The analysis of such sulfides will be very sensitive to experimental conditions and will most likely be unsuccessful by this particular procedure.

Experimental

Materials.—Dimethyl sulfide, di-*n*-propyl sulfide, di-*n*-butyl sulfide, and di-*t*-butyl sulfide were obtained from commercial sources and were used as received. Benzyl *t*-butyl sulfide, *t*-butyl phenyl sulfide, *t*-butyl β-chloroethyl sulfide, and *t*-butyl β-hydroxyethyl sulfide were prepared by literature procedures. The properties of the purified materials are summarized: *t*-BuS–$CH_2C_6H_5$, b.p. 81–83° (1.5 mm.), n^{20}_{D} 1.5305 [lit.[11] b.p., 129–131° (21 mm.)]; *t*-BuS–C_6H_5, b.p. 69–72° (5 mm.), n^{20}_{D} 1.5218 [lit.[18] b.p. 73° (5 mm.), n^{20}_{D} 1.5335]; *t*-BuS–CH_2CH_2Cl, b.p. 82.0–83.0° (30 mm.), n^{20}_{D} 1.4822 [lit.[19] b.p. 81–82° (30 mm.)]; *t*-BuS–CH_2CH_2OH, b.p. 101.5°–102.5° (27 mm.), n^{20}_{D} 1.4748 [lit.[9] b.p. 111–114° (45 mm.), n^{24}_{D} 1.4742].

In addition, the following sulfides, which were synthesized by conventional Williamson procedures, were characterized before being studied further: *t*-BuS–CH_2CH_2S–(*t*-Bu), b.p. 133–135° (30 mm.), n^{20}_{D} 1.4698, d^{20}_4 0.9247 [*Anal.* Calcd. for $C_{10}H_{22}S_2$: C, 58.16; H, 10.75; S, 31.08. Found: C, 58.92; H, 10.74; S, 30.61.]; *t*-BuS–$CH_2CH_2CH_2CH_3$, b.p. 96.5–98.0°, n^{20}_{D} 1.4483 [*Anal.* Calcd. for $C_8H_{18}S$: C, 65.67; H, 12.39; S, 21.91. Found: C, 65.46; H, 12.61; S, 22.61.].

Analytical Procedure.—A sample containing 1–2 mmoles of sulfide was weighed into a 250 ml. erlenmeyer flask and dissolved in a mixture of glacial acetic acid (40 ml.) and water (10 ml.). After being acidified by the addition of 3 ml. of concentrated hydrochloric acid, the solution was titrated with standard bromide–bromate reagent until a stable bromine color, lasting at least 5–10 sec. was noted. A solvent blank was determined to correct for the amount of reagent required to give a visible bromine color.

A study of titration variables showed that the best results were obtained when the titration was conducted at elevated temperatures and when hydrochloric acid was used as the acidifying agent. The water content of the titration medium did not influence the results provided it was not high enough to make the titration mixture heterogeneous. The results of these studies are summarized in Tables II–IV.

TABLE II

EFFECT OF WATER CONTENT ON THE TITRATION OF 1,2-BIS(*t*-BUTYLTHIO)ETHANE WITH BROMATE–BROMIDE REAGENT

Ml. of water/g. of sulfide	Equiv. of bromine consumed per sulfur atom
38.8[a]	0.81
15.2	6.08
4.4	6.19
0.0	6.12

[a] Corresponds to the titration conditions recommended by Siggia and Edsberg.

TABLE III

EFFECT OF MINERAL ACIDS ON THE TITRATION OF 1,2-BIS(*t*-BUTYLTHIO)ETHANE WITH BROMIDE–BORATE REAGENT

Acid used	Ml. of water/g. of sulfide	Equiv. of bromine per sulfur atom
HCl	4.4	6.19
H_2SO_4	2.2	0.21
HNO_3	3.2	0.28

TABLE IV

EFFECT OF TEMPERATURE ON THE TITRATION OF *t*-BUTYL SULFIDES

Sulfide	Temp., °C.	Equiv. of bromine consumed per sulfur atom
(*t*-$BuSCH_2$)$_2$	25	6.19
	60	6.00
t-$BuSCH_2CH_2OH$	25	6.15
	80	5.86
	80	5.82
t-$BuSCH_2CH_2Cl$	80	5.85
(*n*-Bu)$_2$S	25	2.11
	80	1.98

Reaction of 1,2-Bis(*t*-butylthio)ethane with Bromide–Bromate Reagent.—A solution of 1,2-bis(*t*-butylthio)ethane (3.00 g., 14.5 mmoles) in a mixture of glacial acetic acid (150 ml.), water (5 ml.), and concentrated hydrochloric acid (5 ml.) was titrated at 80° with 1.00 *N* bromide–bromate reagent until a bromine color lasting 10 sec. was noted. This macrotitration required 174.5 ml. of the reagent, and this corresponded to the consumption of 12.0 equiv. of bromine per mole of the disulfide. The reaction mixture was concentrated to about 100 ml. and then passed through a Dowex 50 ion-exchange bed to remove inorganic salts. The solution was then concentrated further to yield 1.7 g. (53%) of 1,2-ethanedisulfonic acid in the form of white crystals. The crystals were sensitive to air and were best stored in a moist condition. The acid was identified through its aniline salt (m.p. 270–280° dec., lit.[20] m.p. 270° dec.) and S-benzylisothiouronium salt (m.p. 196–199°, lit.[21] m.p. 199–202°) derivatives. The infrared spectrum of the aniline salt was identical with that of authentic material and a mixture melting point of the S-benzylisothiouronium salt with authentic material was undepressed.

In another experiment, the titration mixture was made alkaline and extracted with ether. Examination of the ether extract *via* v.p.c. indicated the presence of *t*-butyl alcohol in approximately 20% of the theoretical amount.

Reaction of *t*-Butyl Phenyl Sulfide with Bromide–Bromate Reagent.—A solution of *t*-butyl phenyl sulfide (2.82 g., 0.169 mmole) in a mixture of glacial acetic acid (200 ml.), water (12 ml.), and concentrated hydrochloric acid (12 ml.) was treated with 2 equiv. of bromide–bromate reagent at 60° during 5 min. The reaction mixture was poured into 800 ml. of distilled water and

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(18) V. N. Ipatieff, H. Pines, and B. S. Friedman, *J. Am. Chem. Soc.*, **60**, 73 (1939).

(19) C. D. Hurd and K. Wilkenson, *ibid.*, **71**, 3429 (1949).

(20) J. J. Blanksma, *Rec. trav. chim.*, **65**, 311 (1946); *Chem. Abstr.*, **40**, 1755.

(21) W. E. Truce and M. M. Boudakian, *J. Am. Chem. Soc.*, **78**, 2755 (1956).

the resulting solution was cooled in ice. White crystals of diphenyl disulfide separated almost immediately. These were washed with dilute alkali, filtered, and dried in a desiccator. The yield was 1.35 g. (73%), m.p. 60.4–60.9°, lit.[22] m.p. 61.5°. A mixture melting point was undepressed. In another experiment, the titration mixture was made alkaline and extracted with ether. Examination of the ether extract *via* v.p.c. indicated the presence of *t*-butyl alcohol in about 20% of the theoretical amount.

Reaction of Diphenyl Disulfide with Bromide–Bromate Reagent.—Diphenyl disulfide (0.3 g., 1.37 mmoles) was dissolved in a mixture of glacial acetic acid (50 ml.) and concentrated hydrochloric acid (2 ml.), and the solution was heated to 80°. With stirring, 13.8 ml. of 1.0 *N* bromide–bromate (13.8 mequiv.) was added to the hot solution. The reaction mixture was then quickly cooled to room temperature, diluted with 100 ml. of distilled water, and extracted twice with 20-ml. portions of benzene. Concentrated ammonia solution was then added to the benzene extract and the mixture was momentarily brought to reflux. After cooling, the aqueous phase was separated and allowed to evaporate at room temperature. Crystals of benzenesulfonamide (0.262 g. 61.6%) which separated overnight were filtered and dried in a desiccator, m.p. 151–152°, lit.[23] m.p. 150–151°. The infrared spectra of the product was identical with that of authentic benzenesulfonamide.

Reaction of Di(*t*-butyl) Sulfide with Bromide–Bromate Reagent.—A solution of di(*t*-butyl) sulfide (0.2390 g., 1.632 mmoles) in a mixture of glacial acetic acid (50 ml.) and concentrated hydrochloric acid (4 ml.) was treated with 116.5 ml. of 0.0995 *N* bromide–bromate reagent for 5 min. at room temperature. The pH of the reaction mixture was then adjusted to 6.5 with 25% sodium hydroxide solution.

An aqueous solution containing barium chloride (0.5 g.) was added to the reaction mixture and a white precipitate immediately appeared. The reaction mixture was digested for 0.5 hr. at about 60°. The precipitate was washed by decantation using distilled water. The precipitate was separated from the last traces of water by drying at 110°, after which it was heated to 1000° for 1 hr. in an open crucible suspended above a Fisher burner. The weight of the sample remained essentiallly constant during this latter treatment. The product, 0.2621 g. (1.12 mmoles), was identified as barium sulfate by its X-ray diffraction pattern.

Oxidation of 1,2-Bis(*t*-butylthio)ethane with Hydrogen Peroxide.—A solution of 1,2-bis(*t*-butylthio)ethane (1.006 g., 4.39 mmoles) in glacial acetic acid (50 ml.) was allowed to stand for 24 hr. The solution was then heated to 60° and a 10% excess of 30% hydrogen peroxide (2.5 ml.) was added dropwise. After the addition was complete, the mixture was heated an additional 0.5 hr. at 60°. The solution was then carefully evaporated to dryness at 40–60° and the residue was recrystallized from 95% ethanol to yield white crystals of 1,2-bis(*t*-butylsulfonyl)ethane, 0.8485 g. (64.6%), m.p. 228–230°, lit.[24] m.p. 230–231°.

Anal. Calcd. for $C_{10}H_{22}O_4S_2$: C, 44.42; H, 8.21; S, 23.70. Found: C, 44.72; H, 7.82; S, 22.96.

When this experiment was repeated in the presence of concentrated hydrochloric acid (6 ml.), the yield of recrystallized sulfone was 54.7%.

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[22] W. Steinkopf, I. Schubart, and S. Schmidt, *Ber.*, **61**, 680 (1928).

[23] H. F. Whalen and L. W. Jones, *J. Am. Chem. Soc.*, **47**, 1356 (1925).

[24] H. J. Backer, J. Strating, and J. F. A. Hazenberg, *Rec. trav. chim.*, **72**, 838 (1953).

The Reduction of Sulfur-Containing Functional Groups with Triphenyltin Hydride

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The reducing action of triphenyltin hydride on a variety of sulfur-containing functional groups has been studied. Aryl disulfides are cleaved at the S–S bond to give triphenyltin aryl sulfide, $(C_6H_5)_3SnSAr$. The allyl C–S bond in $(C_6H_5CH_2)_2S$, dibenzyl sulfide, and $(C_6H_5CH_2S)_2$, benzyl disulfide, is cleaved to give toluene. Thiophenols and methyl mercaptan evolve hydrogen and give the mixed sulfides. Thiobenzophenone is decolorized in the cold and on heating produces diphenylmethane. Benzenesulfonic acid gives hydrogen and triphenyltin benzenesulfonate. Benzenesulfinic acid and benzenesulfonyl chloride both give triphenyltin benzenesulfinate, hydrogen, and triphenyltin chloride, respectively. The aryl C–S bond is not reduced (Ph_2S, thianthrene) and diphenyl sulfone and diphenyl sulfoxide are not reduced. Catalytic effects of 2,2′-azobis(2-methylpropionitrile) and of triphenylborine were studied.

The purpose of this investigation is to report on the use of triphenyltin hydride as a reducing agent for sulfur functions. Only three previous reports in this area have been made: J. G. Noltes and G. J. M. van der Kerk have reported that allyl mercaptan is converted to propylene while triphenyltin hydride is converted to bis(triphenyltin) sulfide[5] and also that vinyl sulfone and sulfoxide[6] are reduced; Lorenz and Becker have reported that 1-naphthyl and phenyl isothiocyanates are converted to the corresponding aryl isocyanide and N-methylarylamine.[7] The reductions attempted here include aromatic and aliphatic mercaptans and related compounds, a sulfone and a sulfoxide, a sulfinic acid and a sulfonic acid and certain of their derivatives, and carbon disulfide and hydrogen sulfide.

The Aromatic C–S Bond.—No aromatic C–S bond was cleaved by triphenyltin hydride. Thus, neither diphenyl sulfide nor thianthrene reacted. Phenyl disulfide did react, but only to give triphenyltin phenyl sulfide, reduction having taken place only at the S–S bond (eq. 1). Thiophenol and 2-thionaphthol reacted,

$$C_6H_5SSC_6H_5 + 2(C_6H_5)_3SnH \longrightarrow 2(C_6H_5)_3SnSC_6H_5 + H_2 \quad (1)$$

but only at the S–H bond, producing the corresponding triphenyltin aryl sulfide and hydrogen (eq. 2).

$$ArSH + (C_6H_5)_3SnH \longrightarrow ArSSn(C_6H_5)_3 + H_2 \quad (2)$$

$$Ar = C_6H_5,\ \text{2-naphthyl}$$

Benzenesulfenyl chloride reacted spontaneously to give triphenyltin phenyl sulfide in yields as high as 95% (eq. 3).

$$C_6H_5SCl + 2(C_6H_5)_3SnH \longrightarrow (C_6H_5)_3SnCl + (C_6H_5)_3SnSC_6H_5 + H_2 \quad (3)$$

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[1] Presented at the Third Annual Metropolitan Regional Meeting, Jan. 27, 1964, New York, N. Y.

[2] Taken from a portion of the dissertation submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1964.

[3] Supported by the Army Research Office (Durham) under Contract No. DA-31-124-AROD-29. This support is gratefully acknowledged.

[4] To whom inquiries should be directed.

[5] Reports of Tin Research Institute, "Functionally Substituted Organotin Compounds," 1958, pp. 73, 115.

[6] J. G. Noltes and G. J. M. van der Kerk, *Chem. Ind.* (London), 294 (1959). In this report the products of the reduction were not established.

[7] D. H. Lorenz and E. I. Becker, *J. Org. Chem.*, **28**, 1707 (1963).