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Formation and Properties of Phenylthiomethyl Radical. Anodic Oxidation of Sodium Phenylthioacetate and Thermal Decomposition of *t*-Butyl Phenylthiooperacetate¹⁾

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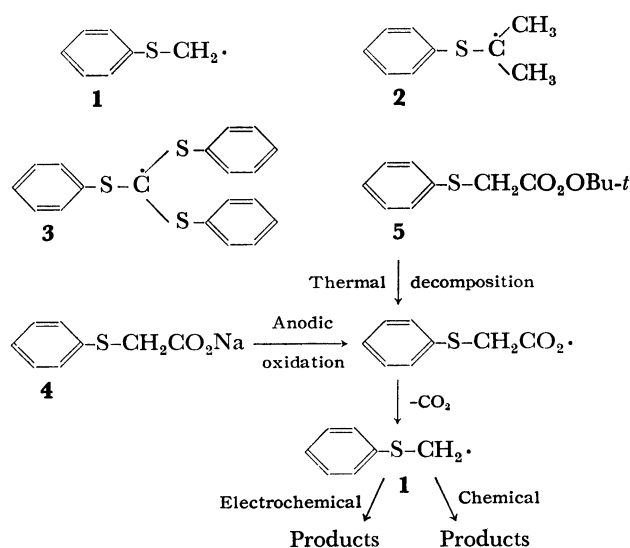
Phenylthiomethyl radical **1** was generated both from anodic oxidation of sodium phenylthioacetate **4** in sodium methoxide-methanol solution and from thermal decomposition of *t*-butyl phenylthiooperacetate **5** in benzene. Both reactions afforded a similar trend of product ratios, phenyl disulfide **7** in 31—32% yield as a major product and 1,2-diphenylthioethane **6**, the dimer of radical **1** in 1—2% yield. A chemical and electrochemical reaction process of **1** along with a plausible mechanism for α -elimination of **1** is discussed.

Investigation of stability and property of thiomethyl radicals is of interest. Kinetic studies of the formation of thiomethyl radicals reveal that the radical intermediates are stabilized by divalent sulfide group.²⁻⁶⁾ Chemical properties of these transient reactive intermediates have attracted attention recently. Thermal decomposition of azobis-(2-phenylthio-2-propane) afforded phenyl disulfide and propylene.⁷⁾ Homolytic

α -elimination of trisphenylthiomethyl radical **3** gave principally phenyl disulfide and tetrakisphenylthioethylene.⁸⁾ These results suggest that phenylthiomethyl radicals eliminate a thiophenoxy group to afford carbene intermediates. However, more data on the chemical properties of phenylthiomethyl radicals are required for a detailed discussion on the carbene mechanism. Studies on the electrochemical behavior of benzyl⁹⁾ and related radical intermediates¹⁰⁾ indicate that

1) Electrochemistry of organic sulfur compounds. I.

2) C. C. Price and J. Zomlefer, *J. Amer. Chem. Soc.*, **72**, 14 (1950); C. C. Price and T. C. Schman, *J. Polym. Sci.*, **16**, 577 (1955); C. E. Scott and C. C. Price, *J. Amer. Chem. Soc.*, **81**, 2670, 2672 (1959); K. Tsuda, S. Kobayashi, and T. Otsu, *J. Polym. Sci.*, **6**, 41 (1968); W. Tagaki, T. Tada, R. Nomura, and S. Oae, *This Bulletin*, **41**, 1696 (1968).3) H. J. Alkema and J. F. Arens, *Rec. Trav. Chim. Pays-Bas*, **79**, 1257 (1960) and literatures cited therein.4) K. Uneyama, H. Namba, and S. Oae, *This Bulletin*, **41**, 1928 (1968).5) R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963).6) C. Ruchardt, H. Bock, and I. Ruthardt, *Angew. Chem.*, **78**, 268 (1966).7) A. Ohno and Y. Onishi, *Tetrahedron Lett.*, **1969**, 4405.8) K. Uneyama, T. Sadakage, and S. Oae, *ibid.*, **1969**, 5193.9) a) L. Eberson and K. Nyberg, *J. Amer. Chem. Soc.*, **88**, 1686 (1966); L. Eberson and K. Nyberg, *Tetrahedron Lett.*, **1966**, 2389. b) S. D. Ross, M. Finkelstein, and R. C. Peterson, *J. Amer. Chem. Soc.*, **89**, 4088 (1967). c) V. D. Parker and B. E. Emgert, *Tetrahedron Lett.*, **1968**, 2411, 2415. d) N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968).10) a) E. J. Corey, N. L. Bould, R. T. Lalonde, J. Casanova, and E. T. Kaiser, *J. Amer. Chem. Soc.*, **82**, 2645 (1960). b) P. H. Reichenbacher, M. D. Morris, and P. S. Skell, *ibid.*, **90**, 3432 (1968); P. S. Skell and P. H. Reichenbacher, *ibid.*, **90**, 3436 (1968). c) J. G. Traynham and J. S. Dehn, *ibid.*, **89**, 2139 (1967).



benzylic radical is oxidized to the corresponding benzylic cation. Wladislaw¹¹⁾ showed an example of anodic oxidation of thiomethyl radical such as α,α -diphenyl- α -phenylthiomethyl radical. However, it is impossible to work out a theory on anodic oxidation process of thiomethyl radicals from the limited result. In order to get detailed information on the chemical and electrochemical behaviors of phenylthiomethyl radical **1** as a basic model for phenylthiomethyl radicals, we have examined anodic oxidation of sodium phenylthioacetate **4** and thermal decomposition of *t*-butyl phenylthioacetate **5**.

Results and Discussion

Phenylthioacetic acid was electrolyzed at 15–20°C in methanol-sodium methoxide at current density 30 mA/cm² and terminal voltage 25–30 volt with platinum plates. The reaction mixture in the anode compartment was handled in the usual way¹²⁾ and the product was fractionated by elution chromatography on silica gel. Current yield to the consumption of **4** was about 50%.

Phenyl disulfide **7** and phenyl methoxymethyl sulfide **9** were obtained as major products (Table 1). Phenyl-

TABLE 1. PRODUCTS FORMED FROM THE ELECTROLYSIS OF α -PHENYLTHIOACETIC ACID IN MeOH-MeONa

	Product	Yield (%) ^{a)}
6	Ph-S-CH ₂ -CH ₂ -S-Ph	1.5 ^{b)}
7	Ph-S-S-Ph	32 ^{b)}
8	Ph-S-CH ₂ -S-Ph	4.5
9	Ph-S-CH ₂ -OMe	34
10	Ph-S-CH ₂ -CO ₂ Me	3.2
11	Ph-S-CH ₃	trace

a) Yield based on reacted carboxylic acid

b) 2 × (Yield obtained from vpc)

11) B. Wladislaw, *Chem. Ind. (London)*, **1962**, 1868.

12) A. Takeda, S. Wada, S. Torii, and Y. Matsui, *This Bulletin*, **42**, 1047 (1969).

TABLE 2. PRODUCTS AND THEIR YIELDS IN THE THERMAL DECOMPOSITION OF *t*-BUTYL PHENYLTHIOPERACETATE IN BENZENE AT 70°C

	Product	Yield (%) ^{a)}
6	Ph-S-CH ₂ -CH ₂ -S-Ph	2.3 ^{b)}
7	Ph-S-S-Ph	31 ^{b)}
8	Ph-S-CH ₂ -S-Ph	6.5 ^{b)}
12	Ph-S-CH ₂ -O-Bu- <i>t</i>	19
10	Ph-S-CH ₂ -CO ₂ CH ₃	0
11	Ph-S-CH ₃	14
13	Ph-S-CH ₂ -Ph	2.5
14	CO ₂	90

a) Yield based on *t*-butyl phenylthioacetate

b) 2 × (yield obtained from vpc)

thioformal **8**, methyl phenylthioacetate **10** and 1,2-diphenylthioethane **6** were obtained as minor products. A trace of thioanisole **11** was also detected by vpc.

In the thermolysis of *t*-butyl phenylthioacetate **5** in benzene solution, dimer **6** was produced in only 2.3%, while disulfide **7** was obtained as a major product (Table 2). Formation of phenyl benzyl sulfide **13** indicates that phenylthiomethyl radical **1** which is undoubtedly formed as a transient intermediate attacks the solvent.

We see from the Tables that the ratios of Kolbe dimer **6** to the other principal products (**7**, **8**, **9**, and **12**) in both experiments are similar, which suggests that radical **1** would exist as an intermediate during the course of electrolysis. However, the yield of Kolbe dimer **6** was unexpectedly small as compared with the results obtained from the anodic oxidation of phenylacetic and phenoxyacetic acid.¹³⁾ One reason for this may be explained as follows, together with the mechanism of the formation of phenyl disulfide **7**. Radical **1** undergoes further electron oxidation to give phenylthiomethyl cation,¹⁴⁾ which undergoes solvolysis with methanol to provide the methyl ether **9** (Path A).¹⁷⁾ If the methanolysis of **9** took place successively in the electrolytic solution to provide thiophenol, it would readily be oxidized to thiophenoxy radical¹¹⁾ whose recombination may give phenyl disulfide **7** and diphenylthioformal **8**. However, the equilibrium process of **9** in

13) F. Fichter and H. Stenzl, *Helv. Chim. Acta*, **22**, 970 (1939).

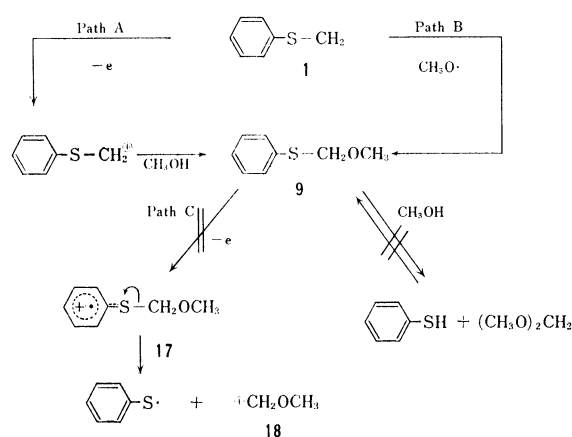
14) Benzyl radical is easily oxidized to benzyl cation.¹⁵⁾ The oxidation potential of phenylthiomethyl radical would be lower than that of benzyl radical since solvolysis of halomethyl sulfide proceeds much faster than benzyl halide.¹⁶⁾ (Ref. 8)

15) V. P. Parker and B. E. Emgert, *Tetrahedron Lett.*, **1968**, 2411, 2415.

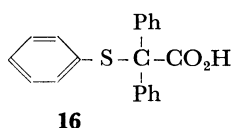
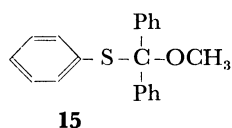
16) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York (1962); H. Böhme, H. Fischer, and R. Frank, *Ann. Chem.*, **563**, 54 (1949).

17) A recombination¹⁸⁾ of **1** with methoxy radical can not be necessarily excluded, but the carbonium ion process (Path A) would be more favorable than (Path B) on the basis of the analogy of easy oxidation of benzyl radical and easy formation of phenylthiomethyl cation is solvolytic reaction of phenyl chloromethyl sulfide.

18) T. Inoue, K. Koyama, and S. Tsutsumi, *This Bulletin*, **37**, 1597 (1964); K. Sasaki, H. Urata, K. Uneyama, and S. Nagaura, *Electrochim. Acta*, **12**, 137 (1967).



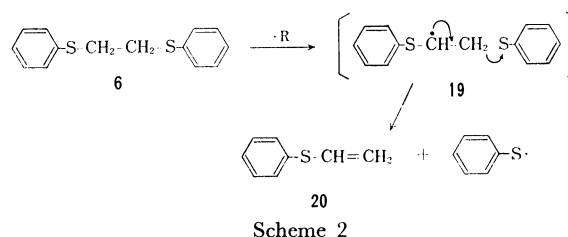
alkaline methanol medium requires further investigation. Methyl ether **9** obtained by treatment of phenyl chloromethyl sulfide with sodium methoxide in methanol was subjected to solvolysis in electrolytic condition, but neither disulfide **7** nor thiophenol was detected. The fact that anodic oxidation of **16** in methanol afforded disulfide **7** and benzophenone dimethylketal¹¹) suggests that an intermediate **15** is more reactive than **9** in alkaline methanol medium, due to *gem*-phenyl groups.



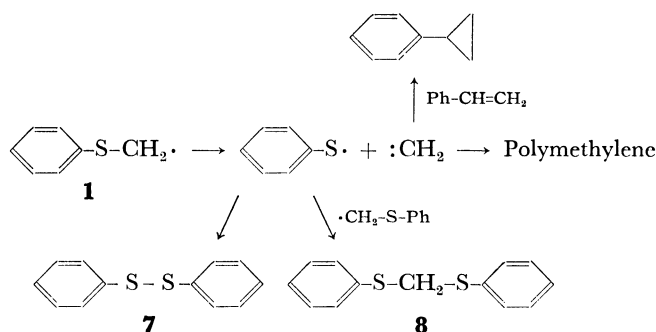
Another plausible mechanism on the thiophenoxy formation from **9** is one electron oxidation of **9** to cationic radical **17** followed by the elimination of thiophenoxy group to form methoxymethyl cation **18** as shown in Path C of Scheme 1. In order to examine the hypothesis, ether **9** was subjected to electrolysis in methanol-sodium methoxide solution as in the case of **4**, but no indication of the formation of **7** was observed. Thus, ether **9** is not a precursor for the thiophenoxy radical formation.

The second process is a homolytic 1,2-elimination of dimer **6** via intermediate **19** to produce thiophenoxy radical. Thus, 0.005 M methanol solution of **6** was electrolyzed under the condition for phenylthioacetic acid, but neither disulfide **7** nor phenyl vinyl sulfide **20** was detected by vpc. Thus, the homolytic 1,2-elimination is not plausible in our electrolysis of **4**^{19,20}) (Scheme 2).

The third process involves a homolytic α -elimination of the radical **1** into thiophenoxy radical and methylene carbene. In the case of phenylthioisopropyl **2** and trisphenylthiomethyl radical **3**, α -elimination has been reported.^{7,8}) In connection with a plausible carbene mechanism, decomposition of *t*-butyl phenylthio-



acetate **5** in benzene containing 0.06–0.013 M of styrene was studied. Vpc analysis revealed the formation of phenyl cyclopropane in 0.2–0.4% yield indicating that the α -elimination occurs during thermolysis (Scheme 3). In the electrolysis, however, attempts to trap methylene group have not been achieved even when **4** was electrolyzed in methanol-sodium methoxide containing *p*-chlorothiophenol. The major products were di-*p*-chlorophenyl, *p*-chlorophenyl phenyl and diphenyl disulfides. *p*-Chlorothiobenzene which might arise from the insertion of methylene group into the thiol was not confirmed by vpc. Radical **1** would split out methylene near the electrode surface which then would polymerize to afford hydrocarbons. Column chromatography of the product provided hydrocarbons. The fact that there is a similar trend of product ratios between the electrolysis and the thermolysis and the observation of hydrocarbon formation, suggests the carbene process of radical **1** in electrolysis.



In the present stage, we believe that radical **1** would undergo three chemical and electrochemical processes; (i) recombination with other radical, (ii) further one electron oxidation to phenylthiomethyl cation and (iii) α -elimination to thiophenoxy radical. The low yield of **6** in the electrolysis would be derived from the predominance of process (ii) and (iii) because of the low oxidation potential to phenylthiomethyl cation and the stable thiophenoxy radical formation from radical **1**. Extensive studies on the electrochemical fate of thiomethyl radicals having α -substituents other than hydrogen would provide more reliable information on the electrode process.

Experimental

Electrolysis of Sodium Phenylthioacetate 4. A typical run of the electrolyses is as follows. Phenylthioacetic acid (0.46 g) dissolved in 40 ml of carefully distilled methanol containing 200 mg of metallic sodium was electrolyzed at 30 mA/cm² for 1 hr at terminal voltage 25–30 V in a cell (Fig. 1). The temperature was kept at 10–15°C. After electrolysis, 70 mg

19) The second process would be practical in an intrinsic radical reaction as in the peroxide decomposition of sulfides.²⁰) Disulfide **7** and the vinyl sulfide **20** were confirmed by vpc on decomposing di-*t*-butylperoxide in 1M benzene solution of the sulfide **6**.

20) A. B. Terentev, R. P. Geer, A. J. Meskin, and R. M. D'Silva, *J. Amer. Chem. Soc.*, **88**, 1257 (1966); E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, **31**, 3366 (1966).

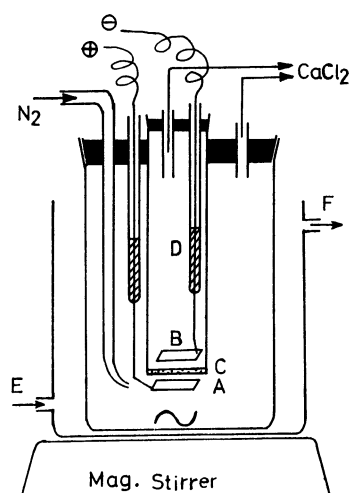


Fig. 1. Electrolysis cell.

- A) Anode Pt plate (3 cm²)
- B) Cathode Pt plate (3 cm²)
- C) Glass filter
- D) Hg pool
- E) Cooling Water inlet
- F) Cooling water outlet

of phenyl benzyl sulfide was added to the reaction mixture as an internal standard for vpc. After evaporation of the solvent and the usual work-up, 340 mg and 100 mg of neutral and acidic portions were obtained, respectively. The neutral portion was fractionated by elution chromatography on silica gel using *n*-hexane - benzene and each fraction was identified in comparing with authentic samples by IR, NMR, mp, vpc and tlc. Yields of the products were obtained by calculation of relative peak area of vpc (10% coated SE-30, 1 m, 150°C) using phenyl benzyl sulfide as an internal standard.

Thermal Decomposition of *t*-Butyl Phenylthioacetate **5 in Benzene.** Perester **5** was dissolved in dry benzene to prepare 0.01M solution. The reaction mixture was kept at 70°C for 3 hr under N₂ atmosphere. Carbon dioxide was absorbed in alkaline solution and the excess alkali was back-titrated.²¹⁾ After evaporation of benzene, residual oil was worked up as usual and the products were analyzed in a similar way to those in electrolysis. Yields of the products (Table 2) were obtained by the value of relative peak area of vpc (SE-30, 1 m, 150 and 190°C) using phenyl sulfide as an internal standard.

Thermal Decomposition of **5 in Benzene-Styrene Solution.** Perester **5** (0.39 g) and styrene (0.31 g for run 1, 0.16 g for run 2, and 0.07 g for run 3) were dissolved in 50 ml of dry benzene. The reaction mixture was subjected to thermolysis at 70°C

TABLE 3. YIELD OF PHENYLCYCLOPROPANE IN THE THERMOLYSIS OF THE PERESTER **5**

Run	1	2	3	4
Styrene (g)	0.31	0.16	0.07	0
Phenylcyclopropane(%) ^{a)}	0.4	0.2	0.2	0

a) Yield based on the perester **5**

21) K. Uneyama, W. Tagaki, I. Minamida, and S. Oae, *Tetrahedron*, **24**, 5271 (1968).

for 3 hr under N₂ atmosphere. After evaporation of the solvent, residual oil was analyzed by vpc (SE-30, 2 m, 110°C). The results are listed in Table 3.

Preparation of Starting Materials and Authentic Samples. *t*-Butyl Phenylthioacetate **5**: Into an ethereal solution of 6.3 g of *t* butyl hydroperoxide and 8 g of pyridine, 10.0 g of phenylthioacetyl chloride dissolved in 50 ml of dry ether was added dropwise for 20 min under cooling below -15°C. The reaction mixture was kept at -15°C for 7 hr with stirring. The mixture was then washed with 5% aqueous hydrogen chloride, then with ice water, with 5% aqueous sodium carbonate and finally with water. The ether layer was dried over anhydrous sodium sulfate for 30 min at 0°C and then ether was removed *in vacuo*. The residue was passed through an activated alumina column cooled by ice water to remove a trace of *t*-butyl hydroperoxide and acidic impurities using ether as an elute. The collected ether layer (100 ml) was washed with ice water and dried over sodium sulfate. After removing the solvent *in vacuo*, 6.0 g of slightly yellow colored oil was obtained. IR 1745 (C=O), 1574 (PhS-), 845 cm⁻¹ (-O-O-R); NMR (CCl₄, TMS), ppm, 1.18 (s, 9H), 3.52 (s, 2H), and 7.3 (m, 5H). Found: C, 60.13; H, 6.79%. Calcd for C₁₂H₁₆O₃S: C, 60.00; H, 6.71%.

Phenyl Methoxymethyl Sulfide (9**):** To a solution of 9 g of thioanisole dissolved in 30 ml *n*-hexane, 12 g of sulfonyl chloride was added dropwise, then the mixture was refluxed for 1 hr. After evaporation of the solvent, residual oil was subjected to distillation under reduced pressure to afford 8 g of colorless oil (bp 118-120°C/20 mmHg). The chloride (6.3 g) was refluxed in 30 ml of methanol containing 2 g of sodium metal for 1 hr. Into the residue obtained by evaporation of methanol by a suction pump, 50 ml of ice water was added and organic layer was extracted with ether. Usual work-up and fractional distillation gave 5.5 g of colorless oil, bp 108-110°C/20 mmHg; IR, 2790, 1090 (OCH₃), 1591 cm⁻¹ (PhS); NMR, (CCl₄, TMS), ppm, 3.38 (s, 3H), 4.90 (s, 2H), and 7.3 (m, 5H).

Found: C, 62.45; H, 6.55%. Calcd for C₈H₁₀OS: C, 62.33; H, 6.54%.

Phenyl *t*-Butoxymethyl Sulfide (12**):** This was synthesized similarly by treatment of phenyl chloromethyl sulfide with potassium *t*-butoxide in *t*-butanol. Sulfide **12** is colorless oil, bp 107-109°C/6 mmHg; IR, 2960, 2920 (CH₃), 1594 (PhS), 1057 cm⁻¹ (*t*-Bu-O); NMR, (CDCl₃, TMS), ppm, 1.26 (s, 9H), 5.01 (s, 2H) and 7.5 (m, 5H).

Found: C, 66.53; H, 8.14%. Calcd for C₁₁H₁₆OS: C, 67.03; H, 8.22%.

Other authentic samples and starting materials such as phenylthioacetic acid **6**, diphenylthioformal **8**,²¹⁾ 1,2-diphenylthioethane **6**,²²⁾ phenyl disulfide **7**,²³⁾ methylphenylthioacetate (**10**), benzyl phenyl sulfide (**13**),²⁴⁾ phenyl sulfide,²⁵⁾ phenyl vinyl sulfide **20**,²⁶⁾ *p*-chlorothioanisole,⁴⁾ phenylcyclopropane,²⁷⁾ and thioanisole were prepared as described in literatures.

22) T. Fromm, *Ann. Chem.*, **253**, 161 (1922).

23) P. Hubner and G. Alsberg, *ibid.*, **156**, 330 (1912).

24) R. L. Shriner, H. C. Struck, and W. J. Jorison, *J. Amer. Chem. Soc.*, **52**, 2066 (1930).

25) W. W. Hartman, L. A. Smith, and J. B. Dickey, "Organic Syntheses," Coll. Vol. II, p. 242 (1943).

26) K. Tsuda, S. Kobayashi, and T. Otsu, *J. Macromol. Sci.*, **A1** (6), 1025 (1969).

27) The authors thank Professor M. Ikeda, Wakayama University, for kindly supplying the authentic phenylcyclopropane.