

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PA.]

Derivatives of Thiacyclobutene (Thiete) and Thiacyclobutane (Thietane). I.¹⁻³

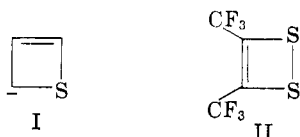
Reactions of Thiete Sulfone

BY DONALD C. DITTMER AND MARCIA E. CHRISTY⁴

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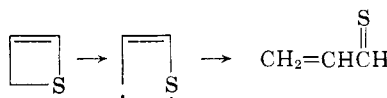
Some reactions of derivatives of thiete (thiacyclobutene) and thietane were investigated in attempts to prepare thiete itself or its anion. Thiete sulfone (thiacyclobutene-1,1-dioxide) is reduced by lithium aluminum hydride to *n*-propyl mercaptan and by sodium borohydride to thietane sulfone (thiacyclobutane-1,1-dioxide). Addition of ethanol, ammonia, dimethylamine, thiophenol and hydrogen sulfide occurs readily across the carbon-carbon double bond to give 3-substituted thietane sulfones. The 3-*N*, *N*-dimethylamino derivative can be reduced to the corresponding sulfide. Dimethyl sulfone is formed on treatment of thiete sulfone with aqueous sodium hydroxide. The anthracene adduct of thiete has been prepared by reduction of the sulfone adduct. Cracking the anthracene adduct of thiete yields anthracene but no volatile products.

The anion (I) of thiete may be considered to be isoelectronic with the anion of cyclopentadiene and may possess some of the stability and properties of the latter. For example, it may be possible to trap I as a metallocene derivative.⁵



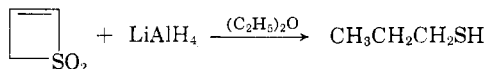
The ability of sulfur to participate in conjugated systems, where it may act as either an electron donor or acceptor, is well known.⁶ The sulfur atom in a conjugated system often has been compared formally to a carbon-carbon double bond. For example, there are sulfur-containing analogs of benzene (thiophene and II⁷), tropylium cation,⁸ tropone,⁹ tropolone,¹⁰ azulene,¹¹ heptafulvene¹² and cyclooctatetraene.¹³ There are no unsaturated sulfur analogs of ring systems containing less than six carbons. Thiete, the analog of cyclo-

pentadiene, may be rather unstable since the allylic C-S bond may be disposed to break.



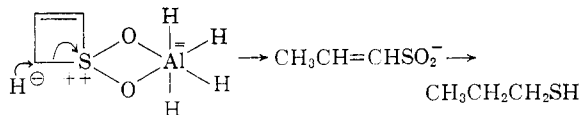
The results of some attempts to synthesize thiete and its anion (which may be more stable) from thiete sulfone are reported in this paper.

Reduction of Thiete Sulfone.—The synthesis of thiete sulfone (thiete-1,1-dioxide) has been reported recently.¹⁴ Thietane sulfone is reduced in good yield to thietane by excess lithium aluminum hydride in refluxing ether.¹⁵ When thiete sulfone was reduced under the same conditions, the only product isolated was *n*-propyl mercaptan (36%). Thietane, itself, was not affected by the same treatment. Therefore, it would seem that thietane sulfone and thietane could not be intermediates in the reduction.



Sodium borohydride in aqueous methanol or in 1,2-dimethoxyethane reduced only the double bond of thiete sulfone to give thietane sulfone.¹⁶ Double bonds are not usually reduced by sodium borohydride, but there are some examples.¹⁷ No cases of the reduction of sulfones by sodium borohydride have been reported.

A rationalization of the course of the reduction with lithium aluminum hydride involves a displacement by hydride ion on a chelate of the sulfone and aluminum which is facilitated by both the electron-withdrawing double bond and sulfone group. Diaryl sulfones complex with aluminum



(14) D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961) (thiete sulfone appears to have some vesicant activity).

(15) F. G. Bordwell and W. H. McKellin, *J. Am. Chem. Soc.*, **73**, 2251 (1951).

(16) Bordwell and McKellin (ref. 15) have shown that both the double bond and sulfone group of benzothiophene-1,1-dioxide are reduced by lithium aluminum hydride. The product is 2,3-dihydrobenzothiophene.

(17) See those cited by N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p. 964.

(1) Presented in part at the 137th Meeting, American Chemical Society, Cleveland, Ohio, April, 1960. Brief reports of this work have appeared in *Science*, **132**, 1490 (1960), and in *Angew. Chem.*, **72**, 533 (1960).

(2) Taken from the Ph.D. Thesis of M. E. Christy, University of Pennsylvania, 1961.

(3) An alternative name for thiete is thiacyclobutene. Alternative names for thietane are thiacyclobutane and trimethylene sulfide. The nomenclature used in this report is that recommended in the Rules for Nomenclature, *J. Am. Chem. Soc.*, **82**, 5545 (1960).

(4) University Fellow, 1958-1960.

(5) Thiophene chromium(0) tricarbonyl is an example of a metal derivative of a sulfur-containing heterocycle; E. O. Fischer and K. Öfele, *Chem. Ber.*, **91**, 2395 (1958).

(6) The conjugative ability of sulfur has been reviewed recently: G. Cilento, *Chem. Revs.*, **60**, 147 (1960).

(7) C. G. Krespan, B. C. McKusick and T. L. Cairns, *J. Am. Chem. Soc.*, **82**, 1515 (1960).

(8) V. Hanus and V. Cermak, *Coll. Czech. Chem. Commun.*, **24**, 1602 (1959); R. Pettit, *Tetrahedron Letters*, No. **23**, 11 (1960); A. Lüttringhaus and N. Engelhard, *Angew. Chem.*, **73**, 218 (1961); U. Schmidt, *Chem. Ber.*, **92**, 1171 (1959); D. Leaver and W. A. H. Robertson, *Proc. Chem. Soc.*, 252 (1960); E. Klingsberg, *Chemistry & Industry*, 1568 (1960).

(9) F. Arndt and N. Bekir, *Ber.*, **63**, 2393 (1930).

(10) V. Horak and N. Kucharczyk, *Chemistry & Industry*, 694 (1960).

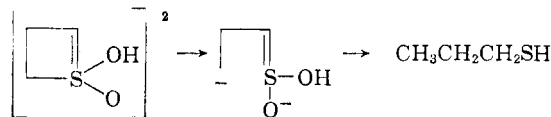
(11) A. G. Anderson, Jr., W. F. Harrison, R. G. Anderson and A. G. Osborne, *J. Am. Chem. Soc.*, **81**, 1255 (1959); R. Mayer and U. Weise, *Naturwissenschaften*, **45**, 312 (1958); R. Mayer, J. Franke, V. Horak, I. Hanker and R. Zahradnik, *Tetrahedron Letters*, No. **9**, 289 (1961).

(12) W. Kirmse and L. Horner, *Ann.*, **614**, 4 (1958); H. G. Herz, G. Traverso and W. Walter, *ibid.*, **625**, 43 (1959).

(13) W. E. Parham, H. Wynberg and F. L. Ramp, *J. Am. Chem. Soc.*, **75**, 2065 (1953); F. Arndt, *Chem. Ber.*, **89**, 730 (1956); A. A. Bothner-By and G. Traverso, *ibid.*, **90**, 453 (1957); F. Arndt and G. Traverso, *ibid.*, **89**, 124 (1956).

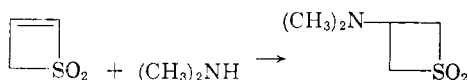
chloride,¹⁸ and antimony(V) chloride is reported to form an adduct with sulfones.¹⁹ Sulfinic acids are reduced by lithium aluminum hydride to disulfides²⁰ and disulfides are reduced to mercaptans.²¹

It is possible also that addition of two hydride ions could occur at the 3- and 1-positions to yield an ion which could be reduced eventually to *n*-propyl mercaptan.

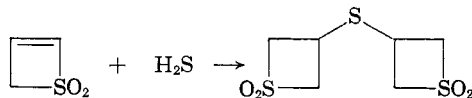


When the reduction of thiete sulfone with lithium aluminum hydride was done at 5–10°, eight components (in addition to solvents) were found in the reaction mixture by gas chromatography. The main component was *n*-propyl mercaptan (49%). The other products were present in traces and have not been identified.

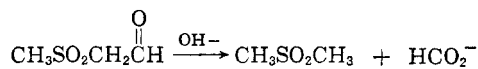
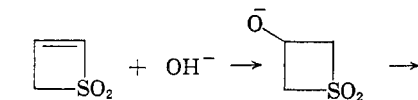
Addition of Nucleophilic Reagents to the Double Bond.—The 3-ethoxy, 3-amino, 3-*N,N*-dimethylamino and 3-phenylmercapto derivatives of thietane sulfone were obtained by respective additions of ethoxide, ammonia, dimethylamine and thiophenol to thiete sulfone.



A sulfide was obtained by addition of hydrogen sulfide.



Dimethyl sulfone was the major product obtained when either thiete sulfone or 3-hydroxythietane-1,1-dioxide (3-thietanol sulfone) were treated with aqueous hydroxide ions. This ring cleavage may be analogous to a reverse aldol condensation.²² The base-catalyzed cleavages of



β -hydroxysulfones to methyl sulfones and aldehydes or ketones have been reported.²³

(18) S. C. J. Olivier, *Rec. trav. chim.*, **35**, 91, 109 (1915).

(19) F. Klages and E. Muhlauer, *Angew. Chem.*, **68**, 704 (1956).

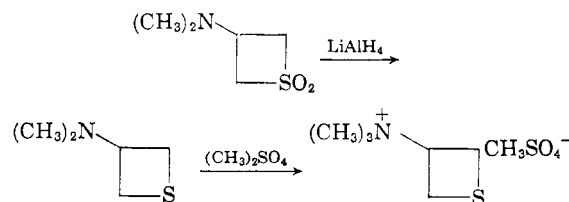
(20) J. Strating and H. J. Backer, *Rec. trav. chim.*, **69**, 838 (1950).

(21) R. C. Arnold, A. P. Lien and R. M. Alm, *J. Am. Chem. Soc.*, **72**, 731 (1950).

(22) Mr. Robert Shandies in our laboratory has observed an acidic substance with an odor resembling formic acid in the work-up of a reaction of thiete sulfone with hydroxide ion. A qualitative test for formic acid was positive (F. Feigl, "Spot Tests in Organic Analysis," Elsevier Publishing Co., Inc., New York, N. Y., 6th English Ed., 1960, p. 368). The formic acid has been identified as its phenylhydrazine derivative, m.p. 143–145° [G. H. Stemple, Jr., and G. S. Schaffel, *J. Am. Chem. Soc.*, **64**, 470 (1942)]. A mixed melting point with an authentic sample showed no depression.

(23) E. Rothstein, *J. Chem. Soc.*, 684 (1934); G. J. De Jong, Dissertation, Groningen University, P. Harte, Bergen Op Zoom, 1949, p. 48.

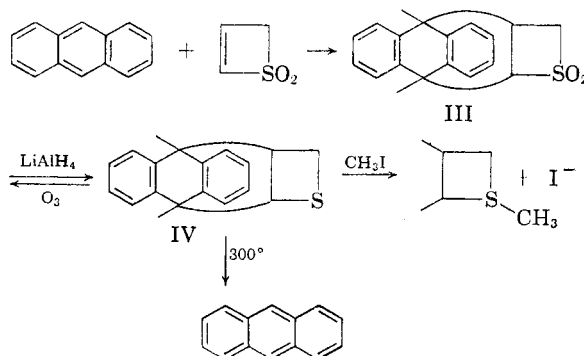
Reduction of 3-*N,N*-dimethylaminothietane-1,1-dioxide by lithium aluminum hydride gave the thietane derivative. Treatment of this compound with dimethyl sulfate in benzene caused the precipitation of a hygroscopic salt almost immediately. The proton magnetic resonance spectrum of this salt showed only two methyl proton signals in the ratio 3:1 [$\text{N}(\text{CH}_3)_3$ and CH_3SO_4^-] which shows that the compound is probably a quaternary ammonium salt rather than a sulfonium salt. The elemental analysis agrees with the given structure. The quaternary hydroxide was pre-



pared from the methosulfate and was pyrolyzed at 300°. Gas chromatography of the distillate indicated the presence of seven components, none of which have been identified. A tar remained in the distilling flask. None of the products was especially volatile.

Reduction of the thiophenol adduct of thiete sulfone by lithium aluminum hydride gave thiophenol and a non-volatile oil which was not identified. The elimination of mercaptides by *n*-butyllithium has been observed.²⁴

Diels-Alder Adduct of Thiete.—When thiete sulfone was treated with anthracene at 147° for five days, the adduct III was formed in 55% yield. Reduction of III by lithium aluminum hydride gave the Diels-Alder adduct IV of thiete (69% yield).²⁵ Adduct IV was stable to potassium *t*-butoxide in refluxing *t*-butyl alcohol and to sodium in refluxing benzene; it could be reoxidized to III. Compound IV gave no isolable complex with mercuric chloride but added one mole of methyl iodide to yield, presumably, the sulfonium iodide, a sample of which gave an immediate precipitate with alcoholic silver nitrate.²⁶



(24) W. E. Parham and P. L. Stright, *J. Am. Chem. Soc.*, **78**, 4783 (1956); W. E. Parham and R. F. Motter, *ibid.*, **81**, 2146 (1959); W. E. Parham, R. F. Motter and G. L. O. Mayo, *ibid.*, **81**, 3386 (1959).

(25) Diels-Alder adducts of α,β -unsaturated sulfides are known. For examples see K. Alder, H. Rieckert and E. Windemuth, *Ber.*, **71**, 2456 (1938); M. Janczewski and M. Wotjas, *Roczniki Chem.*, **33**, 865 (1959); C. A., **54**, 3343 (1960).

(26) It may be recalled that thietane and 3-hydroxythietane add two moles of methyl iodide with cleavage of the ring; ref. 14 and G. M. Bennett and A. L. Hock, *J. Chem. Soc.*, 2498 (1927).

Pyrolysis of IV at 300° gave anthracene and a non-volatile oil which was a mixture of at least six components. Compound IV could not be decomposed at lower temperatures.

Experimental²⁷

Thiete sulfone (thiete-1,1-dioxide) was prepared as previously described.¹⁴

Reduction of Thiete Sulfone. A. With Lithium Aluminum Hydride.—Dry *n*-butyl ether, 150 ml., was added to a solution of 7.6 g. (0.2 mole) of lithium aluminum hydride in 200 ml. of absolute ethyl ether and ethyl ether was distilled until the boiling point reached 45° and 100 ml. of distillate had been collected. After cooling to room temperature, and with stirring, a solution of 2.08 g. (0.02 mole) of thiete sulfone in 250 ml. of dry *n*-butyl ether was added dropwise during 45 minutes. After being stirred at 40° for 45 minutes, the mixture was cooled in ice and excess lithium aluminum hydride was destroyed by the cautious dropwise addition of 20 ml. of water. The precipitated salts were dissolved by the rapid dropwise addition of 250 ml. of 5 *N* hydrochloric acid. After re-extraction of the aqueous layer with three 50-ml. portions of butyl ether, the combined and dried ethereal extracts were distilled through a 25-cm. Hempel column packed with glass helices. The fraction distilling at 38–140° consisted of 6 ml. of colorless liquid and was shown by gas chromatography on alkaline Carbowax at 100° to contain only one component in addition to the two solvents. This component was identical in retention time (flow rate, 80 ml. He/min.) and infrared spectrum to *n*-propyl mercaptan. The concentration was calculated from peak areas to be 11% of the distillate or approximately 550 mg. (36% yield).

An aliquot of the distillate afforded a 2,4-dinitrophenyl thioether derivative identical in melting point, 84–86° (lit.²⁸ m.p. 81°), mixture melting point, 84–86°, and infrared spectrum with an authentic sample prepared from *n*-propyl mercaptan.

When the reduction was conducted at 5–10°, the distillate, b.p. 57–137°, was shown by gas chromatography on alkaline Carbowax at 100° to consist of an eight-component mixture of products in addition to the solvents. Of the product mixture, *n*-propyl mercaptan was the major component (49% by calculation from peak areas), but the mixture of products amounted to only 1.25% of the distillate. None of the other components, all of which were present in trace amounts, was identified.

B. With Sodium Borohydride.—A solution of 1.9 g. (0.05 mole) of sodium borohydride in 5 ml. of 0.2% aqueous sodium hydroxide was added dropwise, cooling when necessary, to a stirred solution of 2.08 g. (0.02 mole) of thiete sulfone in 20 ml. of methanol at 20–25°. After stirring at 25° for another 20 minutes, the solution was cooled in ice and acidified with 1 *N* sulfuric acid. The aqueous solution was evaporated to dryness and the residual solid extracted with 150 ml. of refluxing ethyl acetate and filtered hot. Evaporation of the filtrate gave 1.3 g. (61%) of colorless needles, identical in melting point, 73–75° (lit.²⁹ m.p. 75.5–76°), mixture melting point, 74–76°, and infrared spectrum with an authentic sample of trimethylene sulfone prepared by oxidation of trimethylene sulfide by hydrogen peroxide.

When the reduction of 0.01 mole of thiete sulfone was carried out by means of a suspension of 0.05 mole of sodium borohydride in 1,2-dimethoxyethane, 47% of trimethylene sulfone was obtained.

3-Ethoxythietane-1,1-dioxide.—A solution of 0.416 g. (0.004 mole) of thiete sulfone in 4 ml. of 0.1 *M* sodium ethoxide in absolute ethanol was refluxed for 35 minutes. After the reaction mixture was neutralized with glacial acetic acid and evaporated to dryness, the residual solid was extracted with ethyl acetate. Evaporation of the extract to dryness gave 0.409 g. (68%) of colorless crystals, m.p. 50–53°. Crystallization from ether-petroleum ether afforded colorless plates, m.p. 50–52°.

(27) All melting points are uncorrected. Microanalyses by Galbraith Laboratories, Knoxville, Tenn.

(28) R. W. Bost, J. O. Turner and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1985 (1932).

(29) E. Grishkevich-Trokhimovskii, *J. Russ. Phys. Chem. Soc.*, **48**, 880 (1916); *Chem. Zentr.*, **94**, III, 773 (1923).

Anal. Calcd. for $C_6H_{10}O_2S$: C, 39.98; H, 6.71; S, 21.35. Found: C, 39.80; H, 6.59; S, 21.41.

3-Aminothietane-1,1-dioxide.—A solution of 0.416 g. (0.004 mole) of thiete sulfone in 10 ml. of saturated alcoholic ammonia solution was allowed to stand at room temperature for 5 days. Upon evaporation of the ammonia, colorless needles separated from the cold alcohol solution; yield 0.236 g. (48%), m.p. 93–96°. The melting point did not change on crystallization from ethyl acetate.

Anal. Calcd. for $C_3H_7O_2NS$: C, 29.74; H, 5.82; N, 11.56. Found: C, 29.99; H, 5.88; N, 11.38.

3-*N,N*-Dimethylaminothietane-1,1-dioxide.—A solution of 2.08 g. (0.02 mole) of thiete sulfone in 25 ml. of dry benzene was cooled in ice and approximately 2 g. (0.04 mole) of dimethylamine was distilled into the solution. After 6 days at room temperature, the solution was evaporated to dryness to obtain 2.95 g. (99%) of a pale yellow oil which solidified on cooling in ice, but liquified upon removal from the ice-bath.

The picrate was obtained as yellow needles, m.p. 177–178° dec., from absolute ethanol.

Anal. Calcd. for $C_{11}H_{14}O_6N_4S$: C, 34.92; H, 3.73; N, 14.81. Found: C, 34.89; H, 3.75; N, 14.38.

The methiodide crystallized in colorless flakes, m.p. 188–190° dec., from 95% ethanol.

Anal. Calcd. for $C_6H_{14}O_2NIS$: C, 24.75; H, 4.85; N, 4.81. Found: C, 24.54; H, 4.70; N, 4.88.

3-Phenylmercaptothietane-1,1-dioxide.—A solution of 5.2 g. (0.05 mole) of thiete sulfone and 5.5 g. (0.05 mole) of thiophenol in 50 ml. of absolute ethanol containing 1 ml. of triethylamine was refluxed for 1.5 hours. Evaporation of the solution to dryness and crystallization of the residual solid from isopropyl alcohol afforded 9.9 g. (92.5%) of colorless flakes, m.p. 72–74°. An analytical sample melted at 72–73°.

Anal. Calcd. for $C_9H_{10}O_2S_2$: C, 50.44; H, 4.70; S, 29.93. Found: C, 50.24; H, 4.80; S, 30.12.

Reduction of 4.28 g. (0.02 mole) of this adduct with lithium aluminum hydride (0.2 mole) in absolute ether gave 1.2 g. (55%) of thiophenol, identified by gas chromatography and preparation of the 2,4-dinitrophenyl thioether derivative, m.p. and mixture m.p. 120–121° (lit.²⁸ m.p. 121°). The only other product isolated consisted of 0.3 g. of a colorless, high-boiling oil which was not identified.

Bis-(3-thietanyl-1,1-dioxide) Sulfide.—A 0.1 *M* aqueous solution of barium hydroxide, 40 ml., was saturated with hydrogen sulfide at room temperature. Thiete sulfone 0.416 g. (0.004 mole), was added and the solution stirred at 50° with continued passage of hydrogen sulfide for 30 minutes. During this period, a colorless solid precipitated. Crystallization from glacial acetic acid gave 0.313 g. (64%) of colorless needles, m.p. 226–227°.

Anal. Calcd. for $C_6H_{10}O_4S_3$: C, 29.74; H, 4.16; S, 39.70. Found: C, 29.90; H, 4.25; S, 39.93.

Reaction of Thiete Sulfone with Aqueous Barium Hydroxide.—A solution of 0.416 g. (0.004 mole) of thiete sulfone in 40 ml. of 0.1 *M* barium hydroxide was refluxed for 30 minutes. Carbon dioxide was passed through the solution until the precipitation of barium carbonate was complete. After filtration and evaporation of the filtrate to dryness, crystallization of the residue from benzene-petroleum ether gave 0.204 g. (54%) of colorless needles, m.p. 107–110°. Recrystallization from absolute ethanol afforded dimethylsulfone, identical in melting point, 109–111° (lit.³⁰ m.p. 109°), mixture melting point, 109–111°, and infrared spectrum with an authentic sample prepared by oxidation of dimethyl sulfide by hydrogen peroxide.

Under the same conditions, 3-thietanol sulfone afforded a 62% yield of dimethyl sulfone.

3-*N,N*-Dimethylaminothietane.—A solution of 2.95 g. (0.02 mole) of the amino sulfone in 50 ml. of absolute ether was added dropwise over 30 minutes to a stirred solution of 7.6 g. (0.2 mole) of lithium aluminum hydride in 300 ml. of absolute ether at room temperature. After being stirred at reflux for 30 minutes, the mixture was cooled in ice and hydrolyzed by the successive dropwise addition of 8 ml. of water, 6 ml. of 20% aqueous sodium hydroxide and 28 ml. of water. The crystalline precipitate of salts was collected and

(30) E. Baumann and G. Walter, *Ber.*, **26**, 1131 (1893).

washed on the filter with three 50-ml. portions of ether. Ether was distilled from the dried filtrate at atmospheric pressure through a 30-cm. Vigreux column to obtain 0.680 g. (30%) of a pale yellow liquid.

The hydrochloride was obtained as colorless needles, m.p. 180.5–182.5°, from absolute ethanol–ether.

Anal. Calcd. for $C_8H_{12}NClS$: C, 39.08; H, 7.87; N, 9.12. Found: C, 39.06; H, 8.07; N, 8.96.

The picrate crystallized in yellow needles, m.p. 210–212° dec., from absolute ethanol.

Anal. Calcd. for $C_{11}H_{14}O_7N_4S$: C, 38.15; H, 4.08; N, 16.18. Found: C, 38.11; H, 4.14; N, 15.90.

3-Trimethylammoniumthietane Methosulfate.—A solution of 0.275 g. (0.00235 mole) of 3-N,N-dimethylaminothietane in 5 ml. of dry benzene was treated with a solution of 0.325 g. (0.00258 mole) of dimethyl sulfate in 3 ml. of dry benzene at room temperature. Colorless crystals started to separate immediately and the mixture soon set to a semi-solid mass. After refrigeration overnight, the product was collected and crystallized from isopropyl alcohol–absolute ether to obtain 0.485 g. (85%) of hygroscopic needles, m.p. 162–173°. Repeated crystallizations from acetone gave an analytical sample, m.p. 166–170° (evacuated and sealed tube).

Anal. Calcd. for $C_7H_{17}O_2NS_2$: C, 34.55; H, 7.04; N, 5.76. Found: C, 34.64; H, 7.05; N, 5.63.

The proton magnetic resonance spectrum in D_2O at 60 Mc. with tetramethylsilane as an internal standard showed only two signals for methyl protons at 212 and 253 c.p.s. with the relative intensities of 3 to 1. The spectrum was obtained by Varian Associates.

Pyrolysis of 3-Trimethylammoniumthietane Hydroxide.—A solution of 3.05 g. (0.0125 mole) of 3-trimethylammoniumthietane methosulfate in 35 ml. of water was stirred with 3.0 g. of Amberlite IR-45 (hydroxide form, Rohm and Haas Co.) for 30 min., filtered, and the filtrate and washings allowed to stand overnight with 15 g. of Amberlite IR-45. After the resin was stirred for 3 hours it was collected and washed with water until the washings were neutral. The combined filtrate and washings were concentrated *in vacuo* at 40–50° to a volume of approximately 5 ml. The concentrated aqueous solution of the quaternary base was dropped into a small Claisen flask heated to 300° and connected by a short water-cooled condenser to a series of three traps, cooled in ice, Dry Ice–acetone and liquid nitrogen, respectively. The system was flushed with dry nitrogen. The distillate which collected entirely in the first trap consisted of water and a yellow oil. There was a tar which remained in the distilling flask. The oil was extracted into ether and the dried and concentrated extract was gas chromatographed on Carbowax at 200°. The product consisted of a mixture of seven components: four of these appeared as two pairs which were incompletely separated on the column and three were of almost equal concentration.

Reduction of 3-Phenylmercaptothietane Sulfone.—Reduction of 3-phenylmercaptothietane sulfone (4.28 g., 0.02 mole) by lithium aluminum hydride (0.2 mole) in absolute ether gave 1.2 g. (55%) of thiophenol, identified by gas chromatography and by preparation of the 2,4-dinitrophenyl thioether, m.p. and mixed m.p. 120–121° (lit.²⁸ m.p. 121°). The only other product isolated was 0.3 g. of a colorless, high-boiling oil which was not identified.

9,10-Dihydroanthracene-9,10-(2',3'-thietano-1,1-dioxide) (III).—A mixture of 4.16 g. (0.04 mole) of thiete sulfone and

7.5 g. (0.042 mole) of anthracene suspended in 20 ml. of dry toluene was heated in a sealed tube at 147° for 5 days. The solid product was collected, digested with 100 ml. of isopropyl alcohol on a steam-bath, filtered hot, and then crystallized from glacial acetic acid with decolorization by Norite. The adduct (6.3 g., 55%) was obtained as colorless needles, m.p. 266–267.5°.

Anal. Calcd. for $C_{17}H_{14}O_2S$: C, 72.31; H, 5.00; S, 11.36. Found: C, 72.43; H, 5.05; S, 11.61.

9,10-Dihydro-9,10-(2',3'-thietano)anthracene (IV).—A solution of 2.2 g. (0.0075 mole) of III in 450 ml. of dry benzene was added dropwise over 80 minutes to a stirred solution of 2.86 g. (0.075 mole) of lithium aluminum hydride in 175 ml. of absolute ether at room temperature. After stirring at reflux for 40 minutes, the mixture was cooled in ice and excess hydride was destroyed by cautious dropwise addition of 50 ml. of water. The precipitated salts were dissolved in dilute hydrochloric acid. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. After the solvents were removed, crystallization of the residual solid from isopropyl alcohol afforded 1.3 g. (69%) of colorless needles, m.p. 172–175°. Repeated crystallizations from isopropyl alcohol gave an analytical sample m.p. 175–175.5°.

Anal. Calcd. for $C_{17}H_{14}S$: C, 81.55; H, 5.64; S, 12.81. Found: C, 81.35; H, 5.71; S, 12.62.

Rast molecular weight determination (camphor) gave an average value of 255 (calcd. molecular weight, 250). Oxidation of the adduct in cold ethyl acetate solution with excess ozone gave the parent sulfone III, m.p. and mixture m.p. 265–267°. The proton magnetic resonance spectrum of IV (at 60 Mc. in CCl_4 with tetramethylsilane as internal standard) showed signals at 431 c.p.s. (8 aromatic hydrogens), 256 and 244 c.p.s. (a pair of doublets for the 9- and 10-hydrogens) and a complicated group of signals centered at 207, 174 and 134 c.p.s. (corresponding to the four hydrogens of the thietane ring).

9,10-Dihydroanthracene-9,10-(2',3'-trimethylene-1-methylsulfonium iodide).—A solution of 0.294 g. (0.00118 mole) of IV in 10 ml. of dry benzene was heated to refluxing with 1 ml. of methyl iodide for 8 hours. Evaporation to dryness and crystallization of the oily residue from cold ethanol–acetone–water gave 0.339 g. (75%) of colorless crystals, m.p. 117–124°. Repeated crystallizations from cold acetone–water afforded an analytical sample, m.p. 125.5–127.5°.

Anal. Calcd. for $C_{18}H_{17}IS$: C, 55.11; H, 4.37; I, 32.35. Found: C, 55.34; H, 4.46; I, 32.25.

Pyrolysis of IV.—A 6-inch side-arm test-tube fitted with a capillary inlet was connected to two traps in series, cooled in Dry Ice–acetone and in liquid nitrogen, respectively, and was flushed with dry nitrogen. The tube was charged with 0.5 g. (0.002 mole) of IV and heated at 295–300° for 1.5 hours. During this time colorless plates with a yellow oil adhering to them sublimed into the cooler part of the tube. Nothing was collected in the traps. The contents of the tube were extracted with ether, leaving a residue of 0.2 g. of a brittle, black glassy resin. The ether solution was concentrated and diluted with petroleum ether (b.p. 30–60°) to obtain 0.1 g. (30%) of anthracene, m.p. and mixed m.p. 212–214°. Chromatography of the mother liquor on acid-washed alumina gave six fractions of oily solids or oils. The total material recovered from the column was 0.153 g.