certainties in the use of proteins containing artificially introduced groups already have been indicated. In studies of the cross reaction of artificial carbohydrate protein antigens containing glucuronic, cellobiuronic and gentiobiuronic acids with certain antipneumococcal sera and their inhibition by glycosides of these sugars,[25,26] Goebel was able to establish certain specificity relationships, but no data on the relative effectiveness of oligosaccharides of various sizes were obtained.

It is evident for two kinds of antidextran, one having 1 → 6 and the other 1 → 4 specificity, that the homologous trisaccharide is enormously more effective as an inhibitor than the corresponding disaccharide and that each system is specific for the 1 → 6 or 1 → 4 repeating structure, respectively. These findings are uncomplicated by the possibility of albumin binding since Dr. M. E. Carsten in this Laboratory has shown that such binding does not occur with these oligosaccharides. That panose in each instance is no more effective than the homologous disaccharide (allowing in antiserum 9D$_{-2}$ for the presence of some 1 → 6 antibody) suggests that the place of attachment of the third pyranose ring is also of crucial importance. These observations immediately place a lower limit on the size of the antibody combining site as being complementary to a unit of two α-glycosidic linkages and three pyranose rings.

In defining further the dimensions of the antibody combining site, the data at this time do not permit a definitive answer, but suggest that a homologous tetrasaccharide might fit more closely than the homologous trisaccharide. In the case of the 1 → 6 antibody, 4α-isomaltotriosyl-D-glucose is only about one-third as effective as an inhibitor as isomaltotriose. This would suggest that the attachment of the fourth pyranose ring through a maltose linkage at carbon 4 interferes with the approach of this oligosaccharide to the antibody combining site. Since this antibody has formed to a long string of 1 → 6 linked glucopyranosides, one would expect that, if the antibody combining site were complementary only to a trisaccharide, the fourth unit would not interfere The finding of interference might therefore suggest that a unit larger than a trisaccharide, perhaps a tetrasaccharide, would be most complementary to the antibody grouping. Further suggestive but not conclusive evidence is obtained from the results with antibody from which, correcting for the 35% splitting of maltotetraose by the amylase in serum, the tetrasaccharide would be more effective as an inhibitor than the trisaccharide.

A more precise answer to this question must await the availability of isomaltotetraose for inhibition studies in the 1 → 6 system or the preparation of antidextran of 1 → 4 specificity free from amylase. Further studies along these lines are in progress. A more precise expression of these data in actual dimensions will require analysis from three dimensional models. In view of the known heterogeneity of antibodies even to a single antigen, it may be that these data should be considered representing a statistical average of the dimensions of the combining sites of all of the antibody groupings present.

NEW YORK N. Y.

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[25] (a) W. F. Goebel, *J. Exp. Med.*, **64**, 29 (1936); (b) W. F. Goebel and R. D. Hotchkiss, *ibid.*, **66**, 191 (1937).

[26] W. F. Goebel, *ibid.*, **72**, 33 (1940).

[CONTRIBUTION FROM GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY]

The Preparation and Properties of Some Organosilicon Sulfides and Sulfones

BY GLENN D. COOPER

RECEIVED FEBRUARY 18, 1954

Organosilicon sulfides of the type $\equiv SiCH_2SR$ were obtained by the reaction of the corresponding chlorosubstituted silane or siloxane with sodium mercaptides. The corresponding sulfones may be prepared by oxidizing the sulfides with hydrogen peroxide in acetic acid, if siloxane bonds are not present; the sulfone derivatives of the siloxanes were obtained when monoperphthalic acid in ether is used as the oxidizing agent. The sulfones underwent silicon–carbon cleavage very readily when treated with bases, but were much more resistant than the corresponding ketones, esters, and nitriles to cleavage by acids. The siloxanes were much more susceptible to silicon–carbon cleavage than the silanes.

As part of a program of study of the properties of organosilicon compounds having functional groups attached to carbon, a number of types of compounds having sulfur attached to a carbon atom α to silicon have been prepared, in most cases by the displacement of chlorine from a chloromethylsilane or -siloxane by a sulfur-containing compound or ion, such as thiourea, sulfide ion, mercaptide ion, thiocyanate ion or hydrosulfide ion. Nucleophilic reagents may attack organosilicon compounds having halogen on a carbon atom α to silicon either at the silicon atom, resulting in silicon–carbon cleavage, or at the carbon atom, resulting in the normal displacement reaction.[1] In addition, if siloxane bonds are present, extensive siloxane rearrangement may occur.[2] The sulfur compounds, presumably because of their high reactivity as nucleophilic reagents and relatively low basicity, gave in each case good yields of the normal products, without excessive silicon–carbon cleavage or siloxane rearrangement. The thiocyanates[3] and mercaptans[4] have been previously described; in this paper the preparation and properties of some organosilicon sulfides, sulfones and sulfonium iodides having sulfur attached to the α-carbon atom are reported. Since this work was completed,

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[1] C. R. Hauser and C. R. Hance, THIS JOURNAL, **74**, 5091 (1952), and references cited therein.

[2] J. L. Speier, B. F. Daubert and R. R. McGregor, *ibid.*, **71**, 1474 (1949).

[3] G. D. Cooper, *ibid.*, **76**, 2500 (1954).

[4] G. D. Cooper, *ibid.*, **76**, 2499 (1954).

TABLE I

ORGANOSILICON SULFIDES

Compound	Yield, %	B.p. °C.	B.p. Mm.	n^{20}_D	d^{20}_4	MR_D[a] Calcd.	MR_D[a] Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
$\mathrm{[(CH_3)_3SiCH_2]_2S}$	71	129	95	1.4570	0.8000	66.28	66.53	46.6	46.8	10.7	10.9	15.5	15.8
$\mathrm{(CH_3)_3SiCH_2SC_6H_5}$	67	158.5	52	1.5380	.9671	62.52	63.52	61.3	61.5	8.2	8.5	16.3	16.4
$\mathrm{(CH_3)_3SiOSi(CH_3)_2CH_2SC_6H_5}$	62	170.5	37	1.5014	.9705	81.16	82.19	53.3	53.0	8.1	7.6	11.9	12.1
$\overline{\mathrm{O[Si(CH_3)_2O]_3Si}}\mathrm{(CH_3)CH_2SC_6H_5}$	47	178	12	1.4807	1.0664	106.80	107.97	41.7	41.7	6.9	7.1	7.9	8.3
$\mathrm{(CH_3)_3SiCH_2SCH_3}$	67	70	93	1.4505	0.8399	42.76	43.02	44.9	45.4	10.4	10.8	23.9	24.1
$\mathrm{(CH_3)_3SiOSi(CH_3)_2CH_2SCH_3}$	40	114	96	1.4342	....	....	....	40.3	40.2	9.6	9.9	15.4	15.0
$\overline{\mathrm{O[Si(CH_3)_2O]_3Si}}\mathrm{(CH_3)CH_2SCH_3}$	45	110	11	1.4318	1.0203	87.04	87.09	31.6	31.4	7.6	7.7	9.4	9.7
$\mathrm{CH_3SCH_2Si(CH_3)_2OSi(CH_3)_2CH_2SCH_3}$	21	87	2	1.4742	....	....	....	37.8	37.4	8.7	8.5	25.2	25.0

[a] Calculated from the bond refraction values of E. L. Warrick, THIS JOURNAL, 68, 2455 (1946).

TABLE II

SULFONIUM IODIDES AND SULFONES

Compound	Yield, %	M.p. or b.p. (mm.) °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
$\mathrm{(CH_3)_3SiCH_2\overset{+}{S}(CH_3)_2I^-}$	96	106	26.1	26.2	6.1	6.1	11.6	11.3
$\overline{\mathrm{O[Si(CH_3)_2O]_3Si}}\mathrm{(CH_3)CH_2\overset{+}{S}(CH_3)_2I^-}$	98	129–130	24.8	24.5	6.0	5.8	6.6	6.2
$\mathrm{(CH_3)_3SiCH_2SO_2CH_3}$	30[a]	78–79	36.1	35.6	8.5	8.5	19.3	19.1
$\mathrm{[(CH_3)_3SiCH_2]_2SO_2}$	59[a]	47–48	40.3	40.5	9.3	9.2	13.4	13.1
$\mathrm{(CH_3)_3SiCH_2SO_2C_6H_5}$[d]	65[b]	160(6)	52.6	52.2	7.0	7.1	14.0	13.9
$\mathrm{(CH_3)_3SiOSi(CH_3)_2CH_2SO_2CH_3}$[e]	69[b]	91(1)	35.0	35.3	8.3	8.1	13.3	13.3
$\overline{\mathrm{O[Si(CH_3)_3O]_2Si}}\mathrm{(CH_3)CH_2SO_2CH_3}$	84[b]	61–62.5	28.9	29.2	7.0	7.3	9.7	9.4
$\mathrm{CH_3SO_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2SO_2CH_3}$	78[c]	71–72	30.2	30.1	6.9	7.1	20.1	19.9

[a] Oxidizing agent was hydrogen peroxide in acetic acid. [b] Oxidizing agent was monoperphthalic acid in ether. [c] Prepared by equilibrating $\mathrm{(CH_3)_3SiOSi(CH_3)_2CH_2SO_2CH_3}$ with sulfuric acid. [d] n^{20}_D 1.5250. [e] n^{20}_D 1.4432.

Post[5] has reported the preparation of a series of alkylthiomethylsilanes by the reaction of sodium mercaptides with bromomethyltrimethylsilane, and Gilman[6] has reported the preparation of some (arylthiomethyl)- and (arylsulfonylmethyl)-silanes by the reaction of arylthiomethyllithium and arylsulfonylmethyllithium with chloro- and alkoxysilanes. Siloxanes having sulfur attached to the α-carbon atom have not previously been reported.

Preparation.—Methyl and phenyl sulfides were prepared by treating the chloro compounds with sodium methyl mercaptide in absolute ethanol, or with sodium phenyl mercaptide in aqueous ethanol. Bis-(trimethylsilylmethyl) sulfide, $\mathrm{[(CH_3)_3SiCH_2]_2S}$, was prepared by the reaction of chloromethyltrimethylsilane with sodium sulfide. The yields and physical properties of the sulfides are listed in Table I.

The trimethyl-(methanesulfonylmethyl)-silane, $\mathrm{(CH_3)_3SiCH_2SO_2CH_3}$, and bis-(trimethylsilylmethyl)-sulfone, $\mathrm{[(CH_3)_3SiCH_2]_2SO_2}$, were prepared by oxidation of the corresponding sulfides with hydrogen peroxide in acetic acid. This procedure was unsuccessful with compounds containing siloxane bonds; silicon–carbon cleavage apparently occurred. Sulfone derivatives of the siloxanes were obtained in high yields, however, when monoperphthalic acid in diethyl ether was used as the oxidizing agent. The yields and physical properties of the sulfones are listed in Table II.

The alkyl sulfides readily formed sulfonium iodides when treated with methyl iodide; the phenyl alkyl sulfides gave no reaction. The sulfonium iodides which were purified and analyzed are included in Table II.

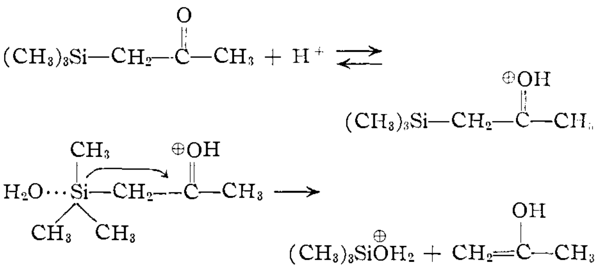
Stability Toward Acids and Bases.—All of the sulfones were very easily cleaved by bases.

$$\equiv\mathrm{SiCH_2SO_2R} \xrightarrow[\mathrm{H_2O}]{\mathrm{OH}^\ominus} \equiv\mathrm{SiOSi}\equiv + \mathrm{RSO_2CH_3}$$

A quantitative yield of hexamethyldisiloxane was obtained in one minute when trimethyl-(methanesulfonylmethyl)-silane was shaken with 5% sodium hydroxide solution.

Organosilicon compounds containing an α sulfonyl group are much more stable toward silicon–carbon cleavage by acids than are the corresponding ketones, esters and nitriles. Ethyl (trimethylsilyl)-acetate, $\mathrm{(CH_3)_3SiCH_2CO_2C_2H_5}$,[7] trimethylsilylacetone, $\mathrm{(CH_3)_3SiCH_2COCH_3}$,[1] and trimethylsilylacetonitrile, $\mathrm{(CH_3)_3SiCH_2CN}$,[8] were almost completely cleaved by refluxing for 20 hours with 5% hydrochloric acid. Trimethyl-(methanesulfonylmethyl)-silane, $\mathrm{(CH_3)_3SiCH_2SO_2CH_3}$, did not undergo cleavage under these conditions.

The facile cleavage of ketones, esters and nitriles by acids is probably due to the ease with which a relatively stable enol can be displaced[7]



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[5] D. C. Noller and H. W. Post, *J. Org. Chem.*, **17**, 1393 (1952).

[6] H. Gilman, L. F. Cason and H. G. Brooks, Jr., THIS JOURNAL, **75**, 3760 (1953).

[7] J. R. Gold, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 2874 (1948).

[8] Personal communication from Dr. Maurice Prober.

The relative stability of the sulfone group toward acids may be explained by the fact that the sulfonyl group has little or no tendency to participate in such enolization.[9]

The presence of siloxane bonds makes the sulfones much more susceptible to silicon–carbon cleavage. When heptamethyl-(methane sulfonylmethyl)-cyclotetrasiloxane, $\overline{\mathrm{O[Si(CH_3)_2O]_3Si}}\mathrm{(CH_3)CH_2SO_2CH_3}$, was refluxed for 20 hours with 5% hydrochloric acid, almost complete cleavage occurred. The organosilicon polymer obtained had a silicon: sulfur ratio of 16:1 as compared with 3.5:1 for the starting material; 38% of the theoretical amount of dimethyl sulfone was isolated. The reaction is probably not acid-catalyzed, since refluxing with water also brings about extensive cleavage; 90% of the theoretical amount of dimethyl sulfone was obtained upon refluxing for 20 hours with water. The reaction probably is a simple displacement of the sulfone anion by a water molecule.

The effect of silicon–oxygen bonds in facilitating silicon–carbon cleavage appears to be general. Roedel[10] found that methyl chloride was displaced much more readily by alkaline reagents from chloromethylpentamethyldisiloxane than from chloromethyltrimethylsilane. Trimethylsilylmethylamine, $\mathrm{(CH_3)_3SiCH_2NH_2}$, is much more resistant to silicon–carbon cleavage than is pentamethyldisiloxanylmethylamine, $\mathrm{(CH_3)_3SiOSi(CH_3)_2CH_2NH_2}$.[11]

Dimethyl-(trimethylsilylmethyl)-sulfonium iodide was cleaved very rapidly by 5% sodium hydroxide solution

$$\mathrm{(CH_3)_3SiCH_2S^{\oplus}(CH_3)_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{OH^{\ominus}}} \mathrm{(CH_3)_3SiOSi(CH_3)_3 + (CH_3)_3S^{\oplus}}$$

It was cleaved slowly by water alone; 80% of the theoretical amount of hexamethyldisiloxane was obtained when an aqueous solution of the sulfonium iodide was allowed to stand at room temperature for one week.

Sommer[12] has found that a number of organofunctional silanes evolve methane upon heating with sulfuric acid

$$\mathrm{(CH_3)_3SiCH_2CH_2CO_2H + H_2SO_4} \longrightarrow \mathrm{HO_2CCH_2CH_2Si(CH_3)_2OSO_3H + CH_4}$$

$$\mathrm{HO_2CCH_2CH_2Si(CH_3)_2OSO_3H} \xrightarrow{\mathrm{H_2O}} \mathrm{HO_2CCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2CO_2H}$$

When a solution of trimethyl-(methanesulfonylmethyl)-silane in 96% sulfuric acid was heated for 30 minutes at 90° one mole of methane was evolved for each mole of sulfone. The only product isolated upon dilution with water, however, was a 52% yield of dimethyl sulfone.

Polymerization.—Both heptamethyl-(methanethiomethyl)-cyclotetrasiloxane and heptamethyl-(benzenethiomethyl)-cyclotetrasiloxane yielded high molecular weight silicone oils containing $\mathrm{-CH_2SR}$ group when they were equilibrated with hexamethyldisiloxane using sulfuric acid as the catalyst according to the procedure of Patnode and Wilcock.[13] When heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane was similarly treated the product consisted of two mutually immiscible oils, one containing very little sulfur and the other with a much higher sulfur content than the starting material. Similarly, when pentamethyl-(methanesulfonylmethyl)-disiloxane, $\mathrm{(CH_3)_3SiOSi(CH_3)_2CH_2SO_2CH_3}$, was shaken with sulfuric acid, considerably more than the statistically predicted amount of the rearranged products, hexamethyldisiloxane and 1,3-bis-(methanesulfonylmethyl)-tetramethyldisiloxane, $\mathrm{CH_3SO_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2SO_2CH_3}$, was obtained

$$\mathrm{2(CH_3)_3SiOSi(CH_3)_2CH_2SO_2CH_3} \overset{\mathrm{H_2SO_4}}{\rightleftarrows} \mathrm{(CH_3)_3SiOSi(CH_3)_3 + CH_3SO_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2SO_2CH_3}$$

Experimental[14]

Trimethyl-(benzenethiomethyl) Sulfide.—A solution of 24.4 g. (0.2 mole) of chloromethyltrimethylsilane was added to a solution of 22 g. (0.2 mole) of thiophenol in 80 ml. of 10% sodium hydroxide solution. The mixture was stirred and heated under reflux for four hours. The mixture was cooled and 300 ml. of water was added. The organic layer was separated, washed with 10% sodium hydroxide solution, then with water and dried over anhydrous calcium chloride. The desired sulfide was obtained by fractional distillation through a two-foot column packed with glass helices.

Heptamethyl-(methanethiomethyl)-cyclotetrasiloxane.—Three hundred and thirty grams (1.0 mole) of chloromethylheptamethylcyclotetrasiloxane was added to a cold solution of one mole of sodium methyl mercaptide in 500 ml. of absolute ethanol. The solution was cooled in an ice-bath and stirred for four hours. Two liters of water was added. The organic layer was separated, washed with water, and dried over anhydrous calcium chloride. Fractional distillation yielded 153 g. (47%) of the desired sulfide. Some of the chloro compound was recovered; the yield, based on unrecovered starting material, was 57%.

Trimethyl-(methanesulfonylmethyl)-silane.—A solution of 57 g. (0.425 mole) of trimethyl-(methanethiomethyl)-silane in 200 ml. of acetic acid was placed in a flask equipped with a reflux condenser. The solution was cooled in an ice-bath and 125 ml. (1.2 moles) of 30% hydrogen peroxide was added in small portions through the top of the condenser. The mixture was allowed to stand overnight at room temperature. One liter of water was added and the solution was evaporated to approximately 200 ml. under vacuum. On cooling there was obtained 21 g. (30%) of trimethyl-(methanesulfonylmethyl)-silane, m.p. 75–76°. Recrystallization from benzene–hexane raised the melting point to 78–79°.

Heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane.—A solution of 0.118 mole of monoperphthalic acid in 200 ml. of ether was cooled in an ice-bath and 20.4 g. (0.059 mole) of heptamethyl-(methanethiomethyl)-cyclotetrasiloxane was added dropwise. After the initial vigorous reaction had subsided the mixture was allowed to stand at room temperature for 24 hours. The precipitate of phthalic acid was filtered off and the filtrate was evaporated to dryness. The residue was extracted with pentane and the pentane solution was evaporated to dryness. Recrystallization of the residue from pentane at −80° yielded 18.5 g. (84%) of heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane, m.p. 61–62.5°. The melting point was not raised by further recrystallization.

Cleavage of Sulfones by Bases.—Trimethyl-(benzenesulfonylmethyl)-silane (0.7 g., 0.003 mole) was dissolved in 10 ml. of 5% ammonia in 75% ethanol. The solution was allowed to stand for one hour at room temperature and then evaporated to dryness at reduced pressure. There

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(9) F. Arndt and C. Martius, *Ann.*, **499**, 228 (1932).

(10) G. F. Roedel, THIS JOURNAL, **71**, 269 (1949).

(11) Personal communication from Dr. P. D. George.

(12) L. H. Sommer, W. P. Barie and J. R. Gould, THIS JOURNAL, **75**, 3765 (1953).

(13) W. Patnode and D. F. Wilcock, *ibid.*, **68**, 358 (1946).

(14) Microanalyses were performed by L. B. Bronk, Mrs. Joan Martin and Miss M. J. Ferguson.

was obtained 0.48 g. (100%) of methyl phenyl sulfone, m.p. 87–88°; the melting point of a mixture with authentic methyl phenyl sulfone (m.p. 88°) was undepressed.

Similar results were obtained with bis-(trimethylsilylmethyl) sulfone and heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane.

Three grams (0.018 mole) of trimethyl-(methanesulfonylmethyl)-silane was placed in a tube with a narrow graduated top. Ten milliliters of 5% sodium hydroxide solution was added. The mixture became very hot. It was shaken for 30 seconds and quickly cooled to room temperature under running water. The upper phase (2.0 ml., 100%) had n^{20}_{D} 1.3774; hexamethyldisiloxane has n^{20}_{D} 1.3772.[15]

Cleavage of Sulfones by Acids.—Three grams of trimethyl-(methanesulfonylmethyl)-silane was heated under reflux for 24 hours with 15 ml. of 5% hydrochloric acid. The sulfone was completely soluble in the hot solution. On cooling there was obtained 2.05 g. (68%) of trimethyl-(methanesulfonylmethyl)-silane of unchanged melting point. No hexamethyldisiloxane was observed.

Six grams (0.016 mole) of heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane was heated under reflux for 24 hours with 100 ml. of 5% hydrochloric acid. The product was a soft gel. The gel was separated, washed thoroughly with boiling water, and dried for three days at room temperature and a pressure of 10 μ. It contained 2.2% sulfur and 35.3% silicon; the starting material contained 8.6% sulfur and 30% silicon.

The filtrate was evaporated to dryness under reduced pressure and the residue was recrystallized from benzene, yielding 0.56 g. (38%) of dimethyl sulfone, m.p. and m.m.p. 87–88°.

Three and two-tenths grams (0.0086 mole) of heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane was heated under reflux for 20 hours with 20 ml. of water. The mixture was filtered and the filtrate was extracted several times with pentane. The aqueous phase was evaporated to dryness, yielding 0.72 g. (90%) of dimethyl sulfone, m.p. and m.m.p. 87–88°.

Four grams (0.024 mole) of trimethyl-(methanesulfonylmethyl)-silane was dissolved in 15 ml. of 96% sulfuric acid. The solution was stirred and heated at 85–90° for 30 minutes. The evolved gas was collected in a gas buret; it measured 560 ml. (94%) at 24° and 750 mm. and was shown to be pure methane by mass spectrometric analysis.

The sulfuric acid solution was poured over ice and neutralized with barium carbonate. The mixture was filtered and the filtrate was evaporated to dryness. The residue was extracted with chloroform and the chloroform solution was evaporated to dryness. Recrystallization of the residue from benzene yielded 1.2 g. (52%) of dimethyl sulfone, m.p. and m.m.p. 87–88°.

Preparation of Silicone Oils Containing the $-CH_2SCH_3$ Group.—Thirty-four and two-tenths grams (0.1 mole) of heptamethyl-(methanethiomethyl)-cyclotetrasiloxane, 0.65 g. (0.004 mole) of hexamethyldisiloxane and 1.3 ml. of 96% sulfuric acid were shaken together for 23 hours. Ten milliliters of water was added and the mixture was shaken for another hour. The oil was drawn off, shaken with anhydrous calcium chloride and precipitated calcium carbonate and filtered. It was devolatilized by heating for one hour at 100° and 0.5 mm. The resulting oil contained 9.2% sulfur (calculated 9.4% sulfur) and had a viscosity of 111 centistokes at 100°F.

Attempted Equilibration of Heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane with Octamethylcyclotetrasiloxane and Hexamethyldisiloxane.—A mixture of 11.2 g. (0.03 mole) of heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane, 8.88 g. (0.03 mole) of octamethylcyclotetrasiloxane and 1.62 g. (0.01 mole) of hexamethyldisiloxane was shaken with 1.0 ml. of 96% sulfuric acid for 40 hours. The product consisted of two phases, a slightly yellow, extremely viscous lower layer and a colorless, less viscous, upper layer. The phases were separated and washed and dried as described above. The upper layer, 15.3 g., contained 0.5% sulfur; the lower layer, 4.5 g., contained 14.4% sulfur. Similar results were obtained when heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane was equilibrated with hexamethyldisiloxane alone, using sulfuric acid as the catalyst.

Reaction of Pentamethyl-(methanesulfonylmethyl)-disiloxane with Sulfuric Acid.—Twenty-one and seven-tenths grams (0.09 mole) of pentamethyl-(methanesulfonylmethyl)-disiloxane was shaken for 24 hours with 1.0 ml. of 96% sulfuric acid. The mixture was distilled at room temperature and a pressure of one mm. The volatile material consisted of 5.7 g. (0.035 mole) of hexamethyldisiloxane, n^{20}_{D} 1.3771.

The residue was extracted with pentane and the insoluble material was washed with water and dried, yielding 11.3 g. (0.035 mole) of 1,3-bis-(methanesulfonylmethyl)-tetramethyldisiloxane, m.p. 68–71°. Recrystallization from toluene–heptane raised the m.p. to 71–72°.

Acknowledgment.—The author wishes to thank Dr. J. R. Ladd for the preparation of the chloromethyl compounds, and Mr. E. M. Hadsell and Mrs. J. R. Ladd for fractional distillation of the sulfides.

SCHENECTADY, NEW YORK

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[15] R. O. Sauer, THIS JOURNAL, **66**, 1707 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Stability of Tetrabutylammonium Tetrachloroiodide[1]

BY ROBERT E. BUCKLES AND JACK F. MILLS

RECEIVED JULY 20, 1953

Tetrabutylammonium tetrachloroiodide on illumination either in solution or as a solid lost hydrogen chloride and yielded (1-chlorobutyl)-tributylammonium ion which was isolated as the tetrachloroiodide. No analogous reaction was observed with tetramethylammonium tetrachloroiodide. The dissociation of tetrabutylammonium tetrachloroiodide into the dichloroiodide and chlorine was measured spectrophotometrically. At 25° in acetonitrile the pK of dissociation was 3.8 and in ethylene chloride 3.7. Dissociation in trifluoroacetic acid was quantitative. The absorption spectra of the tetrachloroiodides in either acetonitrile or ethylene chloride were found to change appreciably when the dissociation was suppressed since the absorption characteristic of the dichloroiodide was no longer observed.

Earlier preparative and analytical work on both metal and substituted ammonium tetrachloroiodides has been well outlined by Sidgwick.[2] In most cases the compounds were found to decompose slowly to give the more stable dichloroiodide and molecular chlorine. This instability in the case of trimethylsulfonium tetrachloroiodide has been recently investigated spectrophotometrically in acetonitrile.[3] The equilibrium between the tetrachloroiodide and the dichloroiodide and chlorine was presumably set up, but the extent of dissocia-

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[1] Work carried out under Contract No. AT(11-1)-72, Project No. 7 with the U. S. Atomic Energy Commission. Abstracted from the Ph.D. Thesis of Jack F. Mills. Presented before the Division of Organic Chemistry of the American Chemical Society, Kansas City, Mo., March, 1954.

[2] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, London, 1950, pp. 1198–1200.

[3] A. I. Popov and J. N. Jessup, THIS JOURNAL, **74**, 6127 (1952).