[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Sulfochlorination of Organosilicon Compounds

GLENN D. COOPER

Received May 14, 1956

A number of alkylsilanes, alkylchlorosilanes, and alkylsiloxanes have been sulfochlorinated by means of sulfuryl chloride. Those compounds having the chlorosulfonyl group on a carbon atom attached to silicon underwent silicon-carbon bond cleavage in acidic, basic, or neutral solution. Compounds having a sulfonamide group on the *alpha* carbon atom were readily cleaved in basic solution.

Sulfuryl chloride may react with hydrocarbons in either of two ways. In the presence of peroxides, chlorination occurs.[1]

$$\mathrm{RH + SO_2Cl_2 \longrightarrow RCl + HCl + SO_2}$$

Under strong illumination, in the presence of a trace of pyridine, hydrogen is replaced by the chlorosulfonyl group.[2]

$$\mathrm{RH + SO_2Cl_2 \longrightarrow RSO_2Cl + HCl}$$

The chlorination of organosilicon compounds by means of sulfuryl chloride has frequently been described,[3] but the sulfochlorination of organosilicon compounds has not previously been reported.

We have found that sulfonyl chlorides may be obtained from many alkyl silanes, alkylchlorosilanes, and alkylsiloxanes. The sulfochlorinations were carried out at room temperature by irradiating a mixture of sulfuryl chloride, the organosilicon compound, and a trace of pyridine. The yields ranged from 15 to 60 per cent. Some chlorination always accompanied the sulfochlorination. In some cases, it was difficult to distill the products without decomposition and the yields were low for this reason.

Tetramethylsilane reacted readily with sulfuryl chloride, yielding 53% of trimethylsilylmethanesulfonyl chloride. Trimethylchlorosilane also reacted, although less readily, and the yield of chlorodimethylsilylmethanesulfonyl chloride was only 17%. Dimethyldichlorosilane reacted very slowly and no sulfonyl chloride was obtained; a small amount of the monochlorinated compound was the only product isolated. Methyltrichlorosilane did not react at all under the conditions employed. This behavior is consistent with Speier's[4] observation that the photochemical chlorination of methylchlorosilanes becomes more difficult as the number of chlorine atoms attached to silicon is increased.

The reaction was also successful with methylsiloxanes. A 29% yield of heptamethylcyclotetrasiloxanylmethanesulfonyl chloride, $\overline{\mathrm{O[Si(CH_3)_2O]_3Si}}\mathrm{(CH_3)CH_2SO_2Cl}$, was obtained from octamethylcyclotetrasiloxane.

When a linear dimethylsilicone oil (chain-stopped by trimethylsiloxy groups) having an average molecular weight of 3000 was treated with sulfuryl chloride, an oil containing chlorosulfonyl groups was obtained. This oil, which contained about one chlorosulfonyl group for ten silicon atoms, slowly evolved hydrogen chloride on standing at room temperature. When a dimethylsilicone polymer having an average molecular weight of 2,000,000 was sulfochlorinated, cleavage of the siloxane bonds occurred, yielding low molecular weight oils.

In general, electron-withdrawing groups on a carbon atom attached to silicon render the silicon-carbon bond susceptible to cleavage, particularly in the presence of bases; the reaction is considered to occur by a displacement on silicon.[5] It is not surprising, therefore, that the silicon-carbon bond in trimethylsilylmethanesulfonyl chloride was cleaved very rapidly by five per cent sodium hydroxide solution.

$$\mathrm{(CH_3)_3SiCH_2SO_2Cl \xrightarrow[H_2O]{OH^{\ominus}} (CH_3)_3SiOSi(CH_3)_3 + Cl^{\ominus} + CH_3SO_3^{\ominus}}$$

Cleavage of the silicon-carbon bond also occurred in acid solution; an 80% yield of hexamethyldisiloxane was produced when the sulfonyl chloride was stirred with water for 12 hours. Even when the solution was kept neutral by means of precipitated calcium carbonate, the silicon-carbon bond was broken. The instability of the sulfonyl chloride (or the sulfonic acid) in neutral and acid solution is interesting since it has been shown[6] that the corresponding sulfone, $\mathrm{(CH_3)_3SiCH_2SO_2CH_3}$, is not affected by refluxing for 20 hours with five per cent

---

(1) Kharasch and Brown, *J. Am. Chem. Soc.*, **61**, 2142 (1939).

(2) Kharasch and Read, *J. Am. Chem. Soc.*, **61**, 3089 (1939).

(3) McBride and Beachell, *J. Am. Chem. Soc.*, **70**, 2532 (1948); Sommer and Whitmore, *J. Am. Chem. Soc.*, **68**, 485 (1946).

(4) Speier, *J. Am. Chem. Soc.*, **73**, 824 (1951).

(5) Krieble and Elliott, *J. Am. Chem. Soc.*, **68**, 2291 (1946); Gold, Sommer and Whitmore, *J. Am. Chem. Soc.*, **70**, 2874 (1948).

(6) Cooper, *J. Am. Chem. Soc.*, **76**, 3713 (1954).

hydrochloric acid.[7] Heptamethylcyclotetrasiloxanylmethanesulfonyl chloride reacted similarly, although at a slower rate, probably because of its lower solubility.

Trimethylsilylmethanesulfonyl chloride and heptamethylcyclotetrasiloxanylmethanesulfonyl chloride formed sulfonamides when treated with anhydrous ammonia in toluene. In the latter case, a small amount of methanesulfonamide was also isolated, presumably arising as a result of a displacement on silicon by an ammonia molecule, either on the sulfonamide or the sulfonyl chloride. Both sulfonamides underwent silicon-carbon cleavage in aqueous sodium hydroxide solution.

Although the sulfochlorination reaction was not successful with dimethyldichlorosilane and methyltrichlorosilane, sulfonyl chlorides were obtained from diethyldichlorosilane and ethyltrichlorosilane. The position of the chlorosulfonyl group has not been established. It has been shown that aliphatic sulfonyl chlorides can be converted to chlorides without rearrangement by heating for a short time at 200–220°.[8] When the sulfonyl chloride obtained from ethyltrichlorosilane was heated for two hours at 220°, some 2-chloroethyltrichlorosilane was obtained, but the amount was very small, only about 3%. None of the 1-chloro isomer was present. It is therefore believed that the sulfonyl chloride obtained from ethyltrichlorosilane is the 2-isomer, $Cl_3SiCH_2CH_2SO_2Cl$, but the identification must be regarded as only tentative.

EXPERIMENTAL[9]

Sulfochlorination. The procedure employed was essentially that of Kharasch and Read.[2] One mole of the organosilicon compound, 0.5 mole of sulfuryl chloride, and 0.5 ml. of pyridine were placed in a Pyrex flask equipped with a water-cooled reflux condenser surmounted by a reflux condenser cooled with Dry Ice. The flask was irradiated by means of a 1500 watt tungsten-filament lamp at a distance of about ten inches. A vigorous reaction usually began within 15 minutes. Irradiation was continued until hydrogen chloride was no longer evolved. The mixture then was fractionally distilled at reduced pressure. In addition to the sulfonyl chloride, 10–20% of monochlorinated material was always obtained as well as approximately 0.5 mole of unreacted organosilicon compound. Yields are based on sulfuryl chloride.

Trimethylsilylmethanesulfonyl chloride. From the reaction of 88 g. (1.0 mole) of tetramethylsilane and 67.5 g. (0.5 mole) of sulfuryl chloride, there was obtained 49.5 g. (53%) of trimethylsilylmethanesulfonyl chloride, b.p. 57°/1 mm.; n_D^{20} 1.4680.

Anal. Calc'd for $C_4H_{11}ClO_2SSi$: C, 25.8; H, 5.9; S, 17.2; Si, 15.0. Found: C, 25.9; H, 6.1; S, 17.2; Si, 15.1.

Trimethylsilylmethanesulfonamide. Dry ammonia was passed into a solution of 13 g. (0.07 mole) of trimethylsilylmethanesulfonyl chloride in 100 ml. of toluene until no further precipitate was formed. The mixture was warmed and filtered. The filtrate was evaporated to dryness and the residue was washed with water and then recrystallized from benzene-ethanol, yielding 3.6 g. (31%) of trimethylsilylmethanesulfonamide; large colorless plates, m.p. 122–123°.

Anal. Calc'd for $C_4H_{13}NO_2SSi$: C, 28.8; H, 7.7; S, 19.0. Found: C, 28.4; H, 7.7; S, 19.2.

Heptamethylcyclotetrasiloxanylmethanesulfonyl chloride. The reaction of 592 g. (2.0 moles) of octamethylcyclotetrasiloxane with 135 g. (1.0 mole) of sulfuryl chloride yielded 115 g. (29.2%) of heptamethylcyclotetrasiloxanylmethanesulfonyl chloride, b.p. 108–110°/1 mm.; n_D^{20} 1.4350.

Anal. Calc'd for $C_8H_{23}ClO_6SSi_4$: S, 8.1; Cl, 9.0. Found: S, 8.1; Cl, 9.3.

Heptamethylcyclotetrasiloxanylmethanesulfonamide. Dry ammonia was passed into a solution of 11.8 g. (0.03 mole of heptamethylcyclotetrasiloxanylmethane sulfonyl chloride in 75 ml. of benzene until no further precipitate was formed. The mixture was filtered and the filtrate was evaporated to dryness. The residue was recrystallized several times from *n*-pentane, yielding 4.7 g. (42%) of heptamethylcyclotetrasiloxanylmethanesulfonamide, m.p. 61–63°.

Anal. Calc'd for $C_8H_{25}NO_6SSi_4$: C, 25.6; H, 6.7; S, 8.5. Found: C, 25.3; H, 6.7; S, 8.7.

From a small amount of material which was insoluble in pentane, there was obtained 0.1 g. of methanesulfonamide, m.p. and mixture m.p. 89–90°.

Dimethylchlorosilanylmethanesulfonyl chloride. From the reaction of 180 g. (1.67 mole) of trimethylchlorosilane with 112 g. (0.83 mole) of sulfuryl chloride, there was obtained 29.6 g. (17.3%) of dimethylchlorosilanylmethanesulfonyl chloride, b.p. 70–73°/1 mm.; n_D^{20} 1.4780.

Anal. Calc'd for $C_3H_8Cl_2O_2SSi$: S, 15.4; Cl, 34.3. Found: S, 15.3; Cl, 34.5.

Sulfochlorination of diethyldichlorosilane. From 157 g. (1.0 mole) of diethyldichlorosilane and 67.5 g. (0.5 mole) of sulfuryl chloride, there was obtained 27.7 g. (21.8%) of a sulfonyl chloride having b.p. 85–87°/1 mm.; n_D^{20} 1.4928.

Anal. Calc'd for $C_4H_9Cl_3O_2SSi$: Cl, 41.8. Found: Cl, 42.1.

The sulfonyl chloride (11 g.) was added dropwise, with vigorous stirring, to 50 g. of cracked ice. The oil was extracted with ether, dried over sodium sulfate, and the ether was evaporated, leaving 7.1 g. (83%) of a viscous oil. The infrared spectrum showed the characteristic absorption of the sulfonyl group at 7.30 microns and 8.46 microns. A small amount of silanol was also indicated. Upon standing for a few hours at room temperature, the oil changed to a hard wax, which dissolved slowly in 10% sodium hydroxide solution.

Sulfochlorination of ethyltrichlorosilane. From the reaction of 337 g. (2.0 moles) of ethyltrichlorosilane with 135 g. (1.0 mole) of sulfuryl chloride, there was obtained 42.0 g. (16.2%) of the sulfonyl chloride, b.p. 69–70°/1.1 mm.; m.p. 29–30°.

Anal. Calc'd for $C_2H_4Cl_4O_2SSi$: Cl, 54.2; Si, 10.7. Found: Cl, 53.5; Si, 10.6.

The sulfonyl chloride (7 g.) was heated for two hours at 220° in a small glass-lined stainless steel bomb. The bomb was cooled to room temperature and the sulfur dioxide was allowed to escape slowly. The dark liquid residue weighed 3.5 g. and contained a large amount of black solid. It was distilled at 40 mm. pressure in a spinning-band column rated at 50 plates. A fraction weighing 0.16 g. and boiling at 55–60° was obtained. No other volatile material was obtained at a pot temperature of 210°. The infrared spectrum of the 55–60° fraction corresponded to the spectrum of

---

(7) This may indicate that it is the sulfonyl chloride rather than the sulfonate ion which is cleaved, at least in neutral solution, since the chlorosulfonyl group would be expected to have greater electron-withdrawing power than the methanesulfonyl group, whereas the sulfonate ion has less. Differences in solubility do not appear to account for the difference in stability; the sulfone is appreciably soluble in boiling water.

(8) Terent'ev and Gershenovich, *J. Gen. Chem.* (*U.S.S.R.*), **23**, 204 (1953).

(9) Microanalyses by the Analytical Unit of this laboratory.

2-chloroethyltrichlorosilane; no detectable amount of 1-chloroethyltrichlorosilane was present.

Sulfochlorination of methylsilicone oil. A mixture of 291 g. of methylsilicone oil (average molecular weight = 3000), 67.5 g. (0.5 mole) of sulfuryl chloride, and 0.5 ml. of pyridine was irradiated in the usual manner. After three hours, the mixture was filtered from a small amount of solid and heated for four hours in a stream of dry air at 50° and 1 mm. It was shaken with anhydrous sodium sulfate and precipitated calcium carbonate and filtered. Analysis showed 3.9% sulfur and 5.2% chlorine, indicating that approximately one chlorosulfonyl group was introduced for each ten silicon atoms, and that a small amount (approximately 25%) of chlorination accompanied the sulfochlorination reaction. The oil slowly evolved hydrogen chloride on standing; it was converted to a soft gel by heating with magnesium oxide or aniline.

Hydrolysis of trimethylsilylmethanesulfonyl chloride. Trimethylsilylmethanesulfonyl chloride (5 g.) was stirred for 12 hours with 25 ml. of water. The upper organic phase was drawn off and dried over calcium chloride; it weighed 1.79 g. (82%) and was identified by its refractive index as hexamethyldisiloxane.

The sulfonyl chloride (5 g.) was shaken for ten minutes with 25 ml. of 5% sodium hydroxide solution, yielding 1.75 g. (80%) of hexamethyldisiloxane.

The sulfonyl chloride (12 g.) was added dropwise to a rapidly stirred mixture of 10 g. of precipitated calcium carbonate in 25 ml. of water. Stirring was continued for 12 hours and the mixture was filtered. From the filtrate, there was obtained 3.3 g (45%) of calcium methanesulfonate.

Reaction of sulfonamides with sodium hydroxide solution. Trimethylsilylmethanesulfonamide (2 g.) was shaken with 10 ml. of 5% sodium hydroxide solution. The sulfonamide dissolved, but an oil phase began to appear almost immediately. The oil was identified by its refractive index as hexamethyldisiloxane.

Heptamethylcyclotetrasiloxanylmethanesulfonamide (5 g.) was dissolved in 40 ml. of 10% sodium hydroxide solution. An upper liquid phase began to appear almost immediately. After ten minutes, the mixture was extracted with pentane. The pentane solution was washed with water and dried over sodium sulfate. Evaporation of the pentane left 2.0 g. of a colorless oil having n_D^{20} 1.4093, d_4^{20} 1.040. The infrared spectrum showed considerable silanol but no trace of absorption due to the sulfone group. The material is believed to be principally the siloxane formed by the condensation of two molecules of heptamethylcyclotetrasiloxanol, with some uncondensed silanol present.

Anal. Calc'd for $C_{14}H_{42}O_9Si_8$: C, 29.0; H, 7.3; Molecular weight, 578. Found: C, 28.7; H, 7.6; Molecular weight 515.

SCHENECTADY, NEW YORK