TABLE V

EQUILIBRIUM CONSTANTS[a] IN THE SYSTEMS YZ_3 *vs.* YT_3

Z	T	Y	$K_1 = \frac{[YT_3][YTZ_2]}{[YT_2Z]^2}$	$K_2 = \frac{[YT_2Z][YZ_3]}{[YTZ_2]^2}$
Cl	Br	CH_3Ge	0.41	0.42
			(0.03)[b]	(0.03)
Br	I	CH_3Ge	0.44	0.42
			(0.03)	(0.03)
Cl	I	CH_3Ge	0.72	0.79
			(0.06)	(0.07)
Cl	Br	CH_3Si	0.43	0.40
			(0.02)	(0.02)
Ideal randomness			0.333	0.333

[a] The samples were all heated at 120°, but, for the cases where Y = CH_3Ge, the equilibrium constants probably correspond to *ca.* 35°, the nmr probe temperature. The correct temperature for Y = CH_3Si is probably 120°, as the nmr measurements were made promptly after quenching the samples. Since the enthalpy of the exchange reaction is very small when the equilibria are close to random, the exact temperature to which the equilibria correspond is not significant. [b] Values in parentheses are the standard errors of the equilibrium constants.

CH_3GeBr_3, −2.083; CH_3GeBr_2Cl, −1.938; $CH_3GeBrCl_2$, −1.803; CH_3GeCl_3, −1.683. System CH_3GeBr_3 *vs.* CH_3GeI_3: CH_3GeI_3, −2.835; CH_3GeI_2Br, −2.565; CH_3GeIBr_2, −2.317; CH_3GeBr_3, −2.112. System CH_3GeCl_3 *vs.* CH_3GeI_3: CH_3GeI_3, −2.800; CH_3GeI_2Cl, −2.367; CH_3GeICl_2, −1.977; CH_3GeCl_3, −1.687. System CH_3SiCl_3 *vs.* CH_3SiBr_3: CH_3SiBr_3, −1.528; CH_3SiBr_2Cl, −1.368; $CH_3SiBrCl_2$, −1.220; CH_3SiCl_3, −1.083. The experimental data in Table IV were used to calculate[9] the weighted-average equilibrium constants and the standard errors presented in Table V.

The system CH_3SiCl_3 *vs.* CH_3SiBr_3 has been studied[12] by Kumada by distillative separation of the redistribution products. From his data, we calculated K_1 = 0.68 and K_2 = 0.38. Similarly, for the system $C_2H_5SiCl_3$ *vs.* $C_2H_5SiBr_3$, we calculated K_1 = 0.38 and K_2 = 0.28. In another study,[13] it has been found that $CH_3SiBrCl_2$ upon refluxing rearranges to give CH_3SiCl_3 and other methylbromochlorosilanes only in the presence of catalysts such as $AlCl_3$ or basic solvents (ethers or amines).

Acknowledgment.—We wish to thank Ray E. Miller for some of the nmr spectra and his assistance in the data reduction. Dr. Harold I. Weingarten gave helpful counsel concerning the kinetic data and its interpretation.

[12] M. Kumada, *J. Inst. Polytech. Osaka City Univ.*, **C2**, 131 (1952); *Chem. Abstr.* **48**, 11303 (1954).

[13] R. S. Feinberg and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **24**, 165 (1962).

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Tetra(alkylsilicon) Hexachalcogenides

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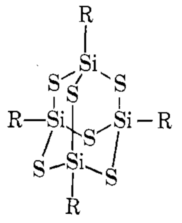
A new class of compounds with the adamantane structural unit has been prepared from alkylsilanes or alkylchlorosilanes and hydrogen sulfide or hydrogen selenide. These compounds have the composition $(RSi)_4S_6$ and $(RSi)_4Se_6$. The silicon atoms serve as the tertiary atoms, and the sulfur or selenium atoms serve as the secondary atoms in the adamantane skeleton.

The "adamantane" skeleton is a symmetrical array of four tertiary and six secondary atoms which have tetrahedral or quasi-tetrahedral coordination (see **1** below). This structure is found in some organic compounds, *e.g.*, adamantane and hexamethylenetetramine, and more extensively in inorganic species.[1] The latter are based mainly on oxygen, sulfur, and nitrogen derivatives with heavier group V elements, phosphorus through antimony. We wish to report in this article a new class which has silicon–sulfur (**1**) and silicon–selenium networks.



1

Methylsilane reacts with hydrogen sulfide and selenide at 200 and 400° to give $(CH_3Si)_4S_6$ and $(CH_3Si)_4Se_6$, respectively. Curiously, ethylsilane is unreactive toward these reagents up to 400°. However, ethyltrichlorosilane is readily thiolyzed to $(C_2H_5Si)_4S_6$ at 150° in the presence of aluminum metal. The selenide was prepared in a similar fashion. All of these sulfides and selenides are rapidly hydrolyzed in the atmosphere.

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[1] A representative sampling of adamantane chemistry may be found in the following reviews and articles: (a) R. R. Holmes and J. A. Forstner, *J. Am. Chem. Soc.*, **82**, 5509 (1960); (b) *Inorg. Chem.*, **2**, 377 (1963); (c) H. Nöth and H.-J. Vetter, *Naturwissenschaften*, **48**, 553 (1961); (d) D. Hass, *Z. Chem.*, **3**, 391 (1963); (e) E. Wiberg, M. van Ghemen, and G. Müller-Schiedmayer, *Angew. Chem.*, **75**, 814 (1963); (f) A. Fredga, *Svensk. Kem. Tidskr.*, **72**, 151 (1960); (g) H. Stetter, *Angew. Chem. Intern. Ed.*, **1**, 286 (1962); (h) R. C. Fort and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

These organosilicon sulfides and selenides are volatile and can be sublimed under vacuum without degradation. A unique determination of structure was not realized. However, the collective import of the analytical and spectroscopic data strongly implicates an adamantane skeleton of silicon and sulfur (or selenium) atoms. The composition and molecularity were rigorously established for all of these compounds, and the simplicity of the infrared spectrum, the spectroscopic equivalence of the alkylsilicon protons, and the fragmentation pattern obtained in the mass spectral analysis are fully consistent with an adamantane type of skeleton.

Alkyltrichlorostannanes react with aqueous solutions of sodium sulfide to give solids of the composition $(RSn)_2S_3$. The sulfides with methyl, butyl, or phenyl substituents are not volatile; they degraded under vacuum at temperatures around 200°. None of these compounds is sufficiently soluble in nonpolar solvents for a determination of molecular weight. Cryoscopic molecular weight determinations in dimethyl sulfoxide were rather anomalous in that the data were not consistent among the three sulfides, and none checked closely for an adamantane-type formulation, *i.e.*, $(RSn)_4S_6$. Possibly there was a significant interaction between the strongly basic dimethyl sulfoxide and these alkyltin sulfides. In any case, the available data do not establish molecularity, and we do not know whether these compounds are isostructural with the silicon compounds.

Experimental Section

Materials.—Methylsilane (Peninsular ChemResearch) and hydrogen sulfide (Matheson) were purchased in small cylinders and fractionated prior to use. Ethyltrichlorosilane (City Chemical Co.) was distilled under nitrogen, bp 97°. Methyltrichlorostannane[2] and hydrogen selenide[3] were prepared and purified by established methods.

Sodium sulfide enneahydrate (Baker crystal) was diluted with water, filtered, and used directly. Sodium selenide (City Chemical Co.) was pulverized in an agate mortar in an inert atmosphere. *n*-Butyltrichlorostannane (M and T Chemicals), phenyltrichlorostannane (Columbia Organic Chemicals), and anhydrous acetonitrile (Eastman Organic Chemicals) were used without purification. Aluminum granules (Baker, purified, 8–20 mesh) were used directly. Solution molecular weight determinations were made over a range of concentrations and extrapolated to infinite dilution.

$(CH_3Si)_4S_6$.—Methylsilane (1.9 g, 44 mmoles) and hydrogen sulfide (2.5 g, 74 mmoles) were condensed into a 100-ml stainless steel cylinder equipped with an aluminum gasket. The cylinder was degassed and heated at 200° for 12 hr under autogenous pressure. When the cylinder was opened, hydrogen and unreacted starting materials were recovered, as well as a mixture of clear crystals and black amorphous solids. The solids were extracted with pentane in a Soxhlet apparatus under a nitrogen atmosphere. The pentane solution was evaporated under vacuum to leave a white solid. The solid was triply sublimed under vacuum at 130° to give 1.0 g of a hygroscopic, white sublimate. *Anal.* Calcd for $C_4H_{12}Si_4S_6$: C, 13.2; H, 3.32; Si, 52.7; S, 30.8; mol wt, 365. Found: C, 13.9; H, 3.49, 3.52; Si, 51.8; S, 31.1; mol wt, 375 (benzene cryoscopic). Mass spectral data were obtained by admitting $(CH_3Si)_4S_6$ *via* an inlet system heated at 160°. The parent molecular peaks occurred at *m/e* 364 and 366.

$(CH_3Si)_4S_6$ is soluble in pentane, chloroform, and benzene and is moderately soluble in acetonitrile and alcohol. It melts at 272–275° in a sealed, evacuated capillary tube. The proton magnetic resonance spectrum (in deuterated chloroform) consists of a sharp singlet at −1.2 ppm (relative to external tetramethylsilane). The infrared spectrum (as a Nujol mull) shows absorptions at 1245 (s), 1010 (w), 890 (w), 790 (s), and 725 (s) cm^{-1}. Gas chromatographic analysis of a chloroform solution of $(CH_3Si)_4S_6$ at 280° showed only one peak other than that due to the solvent.

$(C_2H_5Si)_4S_6$.—Ethyltrichlorosilane (7.4 g, 45 mmoles) and hydrogen sulfide (2.5 g, 76 mmoles) were condensed into a stainless steel cylinder equipped with an aluminum gasket and heated under autogenous pressure at 150° for 3 hr. Unreacted starting material was recovered, as well as 1 g of black hygroscopic solid. The solid was washed out of the tube with acetonitrile, and the resultant mixture was evaporated to dryness and extracted with pentane in a Soxhlet apparatus. The extract was evaporated to a pasty solid which, upon vacuum sublimation at 105°, yielded 0.2 g of white solid.[4] *Anal.* Calcd for $C_8H_{20}Si_4S_6$: C, 22.8; H, 4.75. Found: C, 24.4; H, 5.05. The mass spectrum of $(C_2H_5Si)_4S_6$ was determined after admission of the sample through an inlet system held at 160°. Parent peaks appeared at 420 and 422 in agreement with the calculated molecular weight. The solid melts at 105–108° under vacuum and is very soluble in carbon tetrachloride and pentane. The infrared spectrum (as a Nujol mull) has peaks at 1260 (w), 1225 (w), 1060 (m, b), 1010 (s), 965 (m), and 700 (s, b) cm^{-1}.

Proton resonance measurements in carbon tetrachloride showed a broad singlet at −1.3 ppm (relative to tetramethylsilane), owing to the coincidence of methylene and methyl resonances. The ethyl group of ethyltrichlorosilane (neat) exhibits a multiplet centered at −1.3 ppm.

$(CH_3Si)_4Se_6$.—Methylsilane (3.87 mmoles) and 6.0 mmoles of hydrogen selenide were heated to 400° in a sealed Pyrex glass tube. After 40 min at 400°, a solid began to form. After 1 hr at 400°, the tube was allowed to cool; a white solid condensed on the walls of the tube. Unreacted starting material and 9.66 mmoles of hydrogen were recovered, as well as the white solid. The product was washed from the tube with chloroform, and the solution was evaporated to dryness under vacuum, yielding 2.4 g of product. Sublimation under vacuum at 250° yielded 0.3 g of white solid, mp 283–284°. *Anal.* Calcd for $(CH_3Si)_4Se_6$: C, 7.43; H, 1.87; Si, 17.4; mol wt, 646. Found: C, 7.88; H, 1.95; Si, 18.2; mol wt, 646 (mass spectral data).

The infrared spectrum of $(CH_3Si)_4Se_6$ is similar to that of $(CH_3Si)_4S_6$ and includes absorptions at 1240 (m), 1160 (w), 975 (w), 790 (s), and 715 (s) cm^{-1}. The proton resonance spectrum in deuterated chloroform consists of a very sharp singlet at −1.5 ppm (referred to external tetramethylsilane).

$(C_2H_5Si)_4Se_6$.—Ethyltrichlorosilane (4.9 g, 3.0 mmoles) and 1.0 g of aluminum granules were loaded into a stainless steel tube. Hydrogen selenide (4.0 g, 4.9 mmoles) was pressured into the tube which was heated at 150° for 3 hr. The volatile products were pumped off, leaving 6.0 g of gray solid. Two sublimations at 150° under vacuum yielded 0.25 g of white solid, mp 170–171° (under vacuum). *Anal.* Calcd for $C_8H_{20}Si_4Se_6$: C, 13.7; H, 2.88. Found: C, 13.8; H, 2.85.

$(C_2H_5Si)_4Se_6$ is soluble in carbon tetrachloride and moderately soluble in acetone. The infrared spectrum as a Nujol mull includes absorptions at 1220 (m), 1010 (s), 990 (m), 970 (w), 960 (m), and 690 (s) cm^{-1}. The proton resonance spectrum (in carbon tetrachloride) consists of a complex multiplet extending from −1.1 to −1.7 ppm, with a peak at −1.3 ppm.

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[2] A. D. Smith and E. G. Rochow, *J. Am. Chem. Soc.*, **75**, 4105 (1953).

[3] G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. 1, 2nd ed. Academic Press Inc , New York, N. Y., 1963, pp 418, 419.

[4] Aluminum apparently catalyzed the reaction between ethyltrichlorosilane and hydrogen sulfide. When the reactants were treated under identical conditions in the same stainless steel tube, fitted with a silver gasket in place of the aluminum gasket, the product was not formed. When rerun with the silver gasket and 0.5 g of aluminum granules, the reaction proceeded as with the aluminum gasket.

The mass spectrum of $(C_2H_5Si)_4Se_6$ was obtained by direct injection of a sample into an inlet system heated at just below 200°. Since the maximum observable *m/e* with our spectrometer is at about 675, the largest fragments observed were due to $(C_2H_5)_3Si_4Se_6$, the parent less an ethyl group. The most intense peaks were in the region of *m/e* 474–495, corresponding to $(C_2H_5Si)_3Se_4$.

$(CH_3Sn)_2S_3$.—Methyltrichlorostannane (4.4 g, 1.8 mmoles) was dissolved in 30 ml of acetone. A solution of 6.7 g (2.8 mmoles) of sodium sulfide enneahydrate in 12 ml of water was added dropwise, resulting in an exothermic reaction. After 0.5 hr, 50 ml of water was added, precipitating a white solid (1.6 g). After extraction with water for 2 hr to remove sodium sulfide, the water-insoluble product was vacuum dried over phosphoric anhydride for 4 days. *Anal.* Calcd for $C_2H_6Sn_2S_3$: C, 6.60; H, 1.65; S, 26.5; Sn, 65.3. Found: C, 6.96; H, 2.20; S, 26.6; Sn, 63.8.

$(CH_3Sn)_2S_3$ is a nonvolatile solid, which begins to decompose under vacuum at 200°. Cryoscopic molecular weight measurements in dimethyl sulfoxide yielded a value of 636 (calcd for $(CH_3Sn)_4S_6$, 727). The proton nmr spectrum [$(CD_3)_2SO$ solution] consists of a very sharp singlet at −1.0 ppm (referred to tetramethylsilane).

$(C_6H_5Sn)_2S_3$.—A solution of 10 g (33 mmoles) of phenyltrichlorostannane in 60 ml of acetone was added dropwise with stirring to a solution of 12 g (50 mmoles) of sodium sulfide enneahydrate in 18 ml of water. An exothermic reaction ensued with the production of a white precipitate. The mixture was stirred at room temperature for 3.5 hr, then filtered. The solid product was vacuum dried, then extracted with acetone in a Soxhlet apparatus. *Anal.* Calcd for $(C_6H_5Sn)_2S_3$: C, 29.5; H, 2.05; S, 19.7; Sn, 48.7. Found: C, 29.7, 29.0; H, 2.20, 2.15; S, 19.8, 19.4; Sn, 48.5, 47.8. Cryoscopic molecular weight measurements in dimethyl sulfoxide yielded 550 (calcd for $(C_6H_5Sn)_4S_6$, 731).

When heated under vacuum, $(C_6H_5Sn)_2S_3$ begins to decompose at 255°. The proton nmr spectrum in deuterated dimethyl sulfoxide consists of two broad peaks in the aromatic region, at −7.7 and −7.4 ppm (relative to tetramethylsilane) of relative intensity 2:3, respectively.

$(n\text{-}C_4H_9Sn)_2S_3$.—A solution of 28.2 g (100 mmoles) of *n*-butyltrichlorostannane in 50 ml of acetone was added slowly with stirring to a solution of 36.0 g (150 mmoles) of sodium sulfide enneahydrate in 75 ml of water. An exothermic reaction ensued with production of a white precipitate. The mixture was stirred at autogenous temperature for 2.5 hr and then filtered. The white solid was washed with three 25-ml portions of water, then dried over phosphoric anhydride under vacuum for 1 day, leaving 30 g of solid. The solid was extracted with acetone in a Soxhlet apparatus for 1 day, then dried further over phosphoric anhydride. *Anal.* Calcd for $(C_4H_9Sn)_2S_3$: C, 21.5; H, 4.05; Sn, 52.9; S, 21.5. Found: C, 21.7; H, 4.09; Sn, 50.7; S, 20.8. $(n\text{-}C_4H_9Sn)_2S_3$ melts with decomposition at 135–136° in an evacuated capillary tube and is soluble in dimethyl sulfoxide and slightly soluble in acetone. Cryoscopic molecular weight determination in dimethyl sulfoxide yielded 1070 (calcd for $(n\text{-}C_4H_9Sn)_4S_6$, 894).

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Lithium-7 Chemical Shifts of Lithium Perchlorate and Bromide in Various Solvents

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The Li^7 chemical shifts of dilute solutions of LiBr and $LiClO_4$ in water and eleven organic solvents were determined. The range of shifts observed (*ca.* 6 ppm) is nearly comparable to the total range reported for various compounds. These results do not appear to be dominated by any single solvent influence except possibly the effect of solvent anisotropy as determined by the geometry of the interaction between lithium ion and solvent molecules. Polar, dispersion, and coordination effects on the local shielding may also be important.

In spite of the rather promising characteristics of the Li^7 nucleus, high-resolution Li^7 magnetic resonance measurements have been limited in number. A few results have been reported on Li^7 chemical shifts of solutions of organolithium compounds,[1–4] lithium aluminum hydride,[3] and aqueous lithium chloride solutions.[5] Although the over-all range of shifts observed in previous work has been small, the prospect of probing the nature of lithium ion–solvent interactions by a study of Li^7 chemical shifts in several solvents appeared promising.

Experimental Section

Materials.—Lithium bromide was Reagent powder from Matheson Coleman and Bell, dried at 200–340° for 6 days at a pressure of 10^{-3} mm. Lithium perchlorate was anhydrous powder from G. Frederick Smith Chemical Co., Columbus, Ohio, dried at 190° for 6 days at a pressure of 10^{-3} mm. All of the solvents employed were Spectrograde materials from Matheson Coleman and Bell except dimethyl sulfoxide and triethylamine which were Reagent grade from the same company and were dried by passage through a column of molecular sieves (Linde 3A)

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