the ions alone; effects of polarization on the additivity of the component group properties have been blamed for the irregular behavior of ions.[17]

In view of what has been said about the polarizability of $B_{20}H_{18}^{-2}$, it may seem strange that the magnetic susceptibility of the ion differs from that of two $B_{10}H_{10}^{-2}$ ions by an amount almost equivalent to the contribution from the two lost hydrogens. However, examination of a somewhat analogous case of benzene and biphenyl reveals that although the polarizability of biphenyl exceeds that of two C_6H_5 units joined by a C–C bond by about 6% the magnetic susceptibility of $C_{12}H_{10}$ is almost exactly double that of two phenyl groups, indicating that the two diamagnetic ring currents remain relatively independent of each other.[35] This explains the anomalous position of $B_{20}H_{18}^{-2}$ in Figure 2. The other hydrides and halides at the bottom of Figure 2 were included for comparison.

Conclusion

In developing the molecular orbital theory of polyhedral molecules Hoffman and Lipscomb have shown[36] that the calculations can be considerably simplified, without significantly altering the final results, by factoring out all the localized covalent bonds directed outward from the molecular center and treating them separately. Our results indicate that the dielectric and magnetic properties of polyhedral boranes and their derivatives can be treated in a somewhat analogous fashion. The total property of such ions or molecules can be expressed as a sum of two terms, one giving the contribution from the boron framework electrons, the other from the attached atoms or side groups. Thus for the polarizability of any of the astronomically large number[37] of possible substituted boranes we can write

$$\alpha_T = \alpha_C + \sum_i n_i \alpha_i \qquad (8)$$

and similarly for the magnetic susceptibility

$$\chi_T = \chi_C + \sum_i n_i \chi_i \qquad (9)$$

where α_T and χ_T are the total polarizability and susceptibility, respectively, of an ion or molecule; α_C and χ_C are the respective contributions from the delocalized cage electrons; n_i is the number of external localized covalent bonds of polarizability α_i or the number of atoms or radicals of magnetic susceptibility χ_i attached to the cage. α_C = 10, 11, and 26 Å.[3] at the Na D-line and $\chi_C = -106, -127$, and -212×10^{-6} cm.^{3}/mole for the $B_{10}X_{10}^{-2}$, $B_{12}X_{12}^{-2}$, and $B_{20}X_{18}^{-2}$ ions, respectively; for the χ_i of the halogens the aromatic Pascal constants should be used.[9]

The cage parameters are very satisfactory for the ionic hydrides and halides, but it remains to be seen whether any correction factors will be needed when hydrogen is replaced by ligands such as N_2^+, NH_3^+, and CO^+ which alter the charge of the cage[38] and for neutral carboranes, such as $B_{10}C_2H_{12}$.

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(35) P. W. Selwood, ref. 16, pp. 115–116.

(36) R. Hoffman and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962); see also W. N. Lipscomb, ref. 2, pp. 88, 112.

(37) The number of derivatives of the general composition $B_{12}H_aF_bCl_cBr_dI_e^{-2}$ that could in principle be synthesized from $B_{12}H_{12}^{-2}$ is 1820 (16!/4!12!), which does not even include the various possible isomers.

(38) W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 115 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND
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Organosilyl Sulfides and Organogermyl Sulfides

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The convenient preparation of compounds of the type $(CH_3)_nSi(SCH_3)_{4-n}$, n = 1, 2, 3, from the corresponding silyl halide and methylthiomagnesium iodide is described together with the applicability of this reaction to similar systems. Organogermyl sulfides are prepared more conveniently from the interaction of the germyl halide and the mercaptan in the presence of pyridine. Bis(trimethylsilyl) telluride is reported. Some properties and reactions of these compounds are discussed.

Introduction

Several methods for the preparation of organosilanes containing the silicon–sulfur link are described in the literature.[2] However, the only report of polysubstituted thiosilanes of the type $R_nSi(SR')_{4-n}$ was made by Schmeisser and Müller,[3] who prepared a series of ethyl compounds by redistribution reactions followed by reaction of the ethylthiochlorosilanes with ethylmagnesium bromide.

(1) Alfred P. Sloan Research Fellow.

(2) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, pp. 333–338.

(3) M. Schmeisser and H. Müller, *Angew. Chem.*, **69**, 781 (1957).

$$(4-n)(C_2H_5S)_4Si + nSiCl_4 \longrightarrow 4Cl_nSi(SC_2H_5)_{4-n} \xrightarrow{4nC_2H_5MgBr} 4(C_2H_5)_nSi(SC_2H_5)_{4-n} + 4nMgBrCl \quad n = 1, 2, 3$$

After early reports of compounds of the type $(RS)_4Ge$, $R = CH_3$, C_2H_5, n-C_3H_7,[4] and $R = C_6H_5$,[5] germanium–sulfur chemistry was mostly neglected until recently. Henry and co-workers[6] reported the preparation of what they describe as $(C_6H_5)_3GeSNa$ and $(C_6H_5)_2Ge(SNa)_2 \cdot 3H_2O$ from the interaction of sodium sulfide and the corresponding bromogermane. These sodium germanethiolates were used to prepare several tri(di)phenyl(di)alkylthiogermanes. Recently Wieber and Schmidt[7] have prepared a series of heterocyclic silicon and germanium sulfides by reaction of the metal halide with a thiol in the presence of a tertiary amine.

Discussion

During the course of another investigation the compounds trimethylmethylthiosilane (I, $(CH_3)_3SiSCH_3$), trimethylmethylthiogermane (II, $(CH_3)_3GeSCH_3$), and methylthiotriphenylgermane (III, $(C_6H_5)_3GeSCH_3$) were required. Many attempts were made to prepare the silane (I) by methods which have been employed previously to prepare similar compounds. Trimethylchlorosilane did not react with lead(II) methanethioate at atmospheric pressure and at the reflux point of the silane. Some reaction was observed on heating the reactants to 120° in a sealed tube but considerable decomposition of the lead(II) methanethiolate occurred. No reaction was observed between trimethylchlorosilane and methanethiol in the presence of pyridine at 70°. The reaction between trimethylchlorosilane and a suspension of sodium methanethiolate, which unavoidably contained some free metallic sodium, gave not trimethylmethylthiosilane but a moderate yield of hexamethyldisilthiane.

$$2(CH_3)_3SiCl + CH_3SNa \longrightarrow [(CH_3)_3Si]_2S$$

The addition of trimethylchlorosilane to a suspension of methylthiomagnesium iodide in ether resulted in an immediate, mildly exothermic reaction, and trimethylmethylthiosilane was isolated in high yield.

$$CH_3MgI + CH_3SH \longrightarrow CH_3SMgI + CH_4$$
$$CH_3SMgI \xrightarrow{(CH_3)_3SiCl} (CH_3)_3SiSCH_3 + MgClI$$

The corresponding reactions involving dimethyldichlorosilane and methyltrichlorosilane led to the formation of dimethyldimethylthiosilane and methyltrimethylthiosilane, respectively, in moderate yield.

$$2CH_3SMgI + (CH_3)_2SiCl_2 \longrightarrow (CH_3)_2Si(SCH_3)_2 + 2MgClI$$
$$3CH_3SMgI + CH_3SiCl_3 \longrightarrow CH_3Si(SCH_3)_3 + 3MgClI$$

Surprisingly, silicon(IV) chloride failed to yield isolable quantities of pure tetramethylthiosilane, $(CH_3S)_4Si$, although, in one case, a slightly impure product was obtained in which the main impurities appeared to be methylthiosilyl halides. Tetramethylthiosilane, which has been reported briefly,[3] was prepared, however, from the reaction between the silicon(IV) chloride–bis(pyridine) adduct and methanethiol in the presence of pyridine in moderate yield.

$$SiCl_4 \cdot 2C_5H_5N + 4CH_3SH + 2C_5H_5N \longrightarrow Si(SCH_3)_4 + 4C_5H_5N \cdot HCl$$

Tetramethylthiosilane is a colorless solid at room temperature (m.p. 30°), obviously a reflection of the high degree of symmetry. Distillation of tetramethylthiosilane is possible. Similarly, phenylthiomagnesium bromide gave trimethylphenylthiosilane on reaction with trimethylchlorosilane.

$$C_6H_5SMgBr + (CH_3)_3SiCl \longrightarrow (CH_3)_3SiSC_6H_5 + MgBrCl$$

Triphenylchlorosilane did not react with methylthiomagnesium bromide.

The applicability of this reaction toward the preparation of the as yet unknown selenium and tellurium analogs was examined. Phenylselenomagnesium bromide was treated with trimethylchlorosilane at room temperature. Magnesium halides were produced in the reaction, but the product isolated was not the expected trimethylphenylselenosilane, $(CH_3)_3SiSeC_6H_5$, but the symmetrical selenide, bis(trimethylsilyl) selenide. In an identical manner phenyltelluromagnesium bromide and trimethylchlorosilane gave, not trimethylphenyltellurosilane, but low yields of bis(trimethylsilyl) telluride. This is apparently the first organometallic compound to be prepared containing the silicon–tellurium bond. Both the selenide and the telluride, particularly the telluride, are extremely air-sensitive and decompose to the free "metal." The selenide has an odor of hydrogen selenide, and the telluride has a slightly musty odor and causes intense nasal irritation. The analytical data for the telluride were not good, probably due to the air-sensitivity of the compound. The mode of formation of the symmetrical selenide and telluride in these reactions is not proven but probably there is a simple disproportionation.

$$2(CH_3)_3SiMC_6H_5 \longrightarrow [(CH_3)_3Si]_2M + (C_6H_5)_2M \quad M = Se, Te$$

Organothiosilanes undergo a similar disproportionation at higher temperatures,[3] consistent with the temperature of disproportionation decreasing as the atomic weight of the group VI element increases.

The preparation of methylthiotriphenylgermane was attempted by the reported method.[6] This involves the reaction between sodium sulfide and triphenylbromogermane

$$Na_2S + (C_6H_5)_3GeBr \xrightarrow{C_2H_5OH} \underset{\text{IV}}{(C_6H_5)_3GeSNa} + NaBr$$

and treatment of the sodium salt IV with methyl iodide

$$(C_6H_5)_3GeSNa + CH_3I \longrightarrow (C_6H_5)_3GeSCH_3 + NaI$$

Initial attempts to prepare the sodium salt IV from anhydrous sodium sulfide met with failure, since ethanolysis of the triphenylbromogermane occurred to

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(4) H. J. Backer and F. Stienstra, *Rec. trav. chim.*, **52**, 1033 (1933); **54**, 607 (1935).

(5) R. Schwarz and W. Reinhardt, *Ber.*, **65**, 1743 (1932).

(6) M. C. Henry and W. E. Davidson, *J. Org. Chem.*, **27**, 2252 (1962); *Can. J. Chem.*, **41**, 1276 (1963).

(7) M. Wieber and M. Schmidt, *J. Organometal. Chem.*, **2**, 336 (1964).

yield ethoxytriphenylgermane and hexaphenyldigermoxane. However, from the reaction involving hydrated sodium sulfide, impure sodium triphenylgermylthioate was obtained.

Triphenylbromogermane reacted rapidly with methanethiol in the presence of pyridine, and methylthiotriphenylgermane was isolated in high yield.

$$(C_6H_5)_3GeBr + CH_3SH + C_5H_5N \longrightarrow (C_6H_5)_3GeSCH_3 + C_5H_5N\cdot HBr$$

The preparation of methylthiotriphenylgermane was carried out in benzene solution in which the pyridinium bromide was insoluble. Dimethylthiodiphenylgermane ($(C_6H_5)_2Ge(SCH_3)_2$), trimethylthiophenylgermane ($C_6H_5Ge(SCH_3)_3$), and trimethylmethylthiogermane (II) were prepared from the corresponding bromides in a like manner. Tetramethylthiogermane was prepared from the germanium(IV) chloride–bis(pyridine) adduct for spectral comparison. Benzenethiol also was allowed to react with triphenylbromogermane to give the expected triphenylphenylthiogermane, and the reaction appears to be generally applicable. The difference in behavior of the halogermanes on the one hand and trimethylchlorosilane on the other with respect to their reactions with methanethiol is striking, for hydrogen sulfide reacts with organohalosilanes, and, as recently reported,[8] dimethyldichlorosilane reacts with a variety of dithiols, for example 1,2-ethanedithiol, to yield the expected cyclic product.

Triphenylbromogermane underwent a rather slow reaction with methylthiomagnesium iodide, probably due to the exchange reaction

$$(C_6H_5)_3GeBr + CH_3SMgI \longrightarrow (C_6H_5)_3GeI + CH_3SMgBr$$

although some methylthiotriphenylgermane was isolated.

All the organothiosilanes prepared, with the exception of tetramethylthiosilane, were colorless liquids and all decomposed rapidly on exposure to the atmosphere; dimethyldimethylthiosilane and methyltrimethylthiosilane deposited a yellow solid and tetramethylthiosilane gave silicon(IV) oxide. The organothiogermanes, with the exception of methylthiotriphenylgermane and triphenylphenylthiogermane, were high-boiling liquids. All of the organothiogermanes were stable on exposure to the atmosphere. The sensitivity of the organothiosilanes was due to hydrolysis, as distinct from oxidation, as the reaction of trimethylmethylthiosilane with equivalent amounts of water, either in the presence or absence of solvent, was rapid.

$$\begin{array}{l} 2(CH_3)_3SiSCH_3 + 2H_2O \longrightarrow 2(CH_3)_3SiOH + 2CH_3SH \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad [(CH_3)_3Si]_2O + H_2O \end{array}$$

No reaction of trimethylmethylthiosilane with molecular oxygen in refluxing benzene was observed. Methylthiotriphenylgermane was readily oxidized at 0° by either hydrogen peroxide or nitrogen dioxide to give hexaphenyldigermoxane; no germyl sulfoxide or sulfone was obtained.

Methylthiotriphenylgermane underwent a rapid reaction with aqueous silver nitrate solution to yield hexaphenyldigermoxane and silver(I) methanethiolate. The reaction probably proceeds *via* the formation of triphenylgermyl nitrate which then undergoes hydrolysis.

$$2(C_6H_5)_3GeSCH_3 + 2AgNO_3 + H_2O \longrightarrow [(C_6H_5)_3Ge]_2O + 2AgSCH_3 + 2HNO_3$$

The germanium–sulfur bond in methylthiotriphenylgermane was readily cleaved by *n*-butyllithium in ether at 0° to give *n*-butyltriphenylgermane and lithium methanethiolate.

$$(C_6H_5)_3GeSCH_3 + n\text{-}C_4H_9Li \longrightarrow (C_6H_5)_3GeC_4H_9 + CH_3SLi$$

Bis (trimethylsilyl) selenide was stable in the presence of *n*-butyllithium in toluene up to 110°.

According to previous reports, *n*-butylthiotrimethylsilane is cleaved by *n*-butyl iodide at the reflux point to give trimethyliodosilane and tri-*n*-butylsulfonium iodide.[9] During the course of this work Abel and coworkers[10] reported the isolation of *n*-butylmethyltrimethylsilylsulfonium iodide from the interaction of *n*-butylthiotrimethylsilane and methyl iodide. The silyl–sulfonium salts are said to be intermediates in the above cleavage reactions.

$$(CH_3)_3SiSC_4H_9 + C_4H_9I \longrightarrow [(CH_3)_3SiS(C_4H_9)_2]^+I^-$$

$$[(CH_3)_3SiS(C_4H_9)_2]^+I^- \longrightarrow (CH_3)_3SiI + (C_4H_9)_2S$$

$$(C_4H_9)_2S + C_4H_9I \longrightarrow [(C_4H_9)_3S]^+I^-$$

However, the analytical data given fit the cleavage product, $[(CH_3)_2SC_4H_9]^+I^-$, somewhat better than the compound $[(CH_3)_3SiSCH_3(C_4H_9)]^+I^-$.

Considerable effort has been made in this work to prepare either a silyl- or germylsulfonium salt by reaction of the corresponding organothiosilane or -germane with methyl iodide at room temperature. However, in all cases the products isolated were those which would arise from scission of the metal–sulfur bond.

$$(CH_3)_3SiSCH_3 + 2CH_3I \longrightarrow (CH_3)_3SiI + [(CH_3)_3S]^+I^-$$

$$(CH_3)_3GeSCH_3 + 2CH_3I \longrightarrow (CH_3)_3GeI + [(CH_3)_3S]^+I^-$$

$$(C_6H_5)_3GeSCH_3 + 2CH_3I \longrightarrow (C_6H_5)_3GeI + [(CH_3)_3S]^+I^-$$

No bands due to either $(CH_3)_3Si$–, $(CH_3)_3Ge$–, or $(C_6H_5)_3Ge$– groups were observed. Similar reactions have been observed for germylphosphines[11] and stannylphosphines.[12]

No reaction was observed between dimethyl sulfide and trimethylchlorosilane under vigorous conditions (120° in a sealed tube).

$$(CH_3)_2S + (CH_3)_3SiCl \longrightarrow [(CH_3)_3SiS(CH_3)_2]^+Cl^-$$

Consideration of the above reaction involving methyl iodide prompted an attempted preparation of trimethylsilylmethyl sulfate, the trimethylsilyl ester of methylsulfuric acid, by the reaction between trimethylmethylthiosilane and dimethyl sulfate.

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[8] M. Wieber and M. Schmidt, *Z. Naturforsch.*, **18b**, 846 (1963).

[9] E. W. Abel, *J. Chem. Soc.*, 4406 (1960).

[10] E. W. Abel, D. A. Armitage, and R. P. Bush, *ibid.*, 2455 (1964).

[11] F. Glockling and K. A. Hooton, *Proc. Chem. Soc.*, 146 (1963).

[12] I. G. M. Campbell, G. W. A. Fowles, and L. A. Nixon, *J. Chem. Soc.*, 1389 (1964).

$$(CH_3)_3SiSCH_3 + 2(CH_3)_2SO_4 \longrightarrow (CH_3)_3SiOSO_2OCH_3 + [(CH_3)_3S]^+ + [CH_3SO_4]^-$$

Trimethylsulfonium methyl sulfate and a small yield of a colorless liquid, which fumed on exposure to the atmosphere, were isolated, and from the analysis and spectral data it appears to be trimethylsilylmethyl sulfate contaminated with dimethyl sulfate.

In contrast to the above reaction, the reaction between trimethylmethylthiogermane and dimethyl sulfate proceeded cleanly at 0° to give an almost quantitative yield of trimethylsulfonium methyl sulfate, together with a high yield of trimethylgermylmethyl sulfate.

$$(CH_3)_3GeSCH_3 + 2(CH_3O)_2SO_2 \longrightarrow (CH_3)_3GeOSO_2OCH_3 + [(CH_3)_3S]^+ + [CH_3SO_4]^-$$

Bis(trimethylsilyl) telluride underwent a rapid reaction at room temperature with silver(I) iodide to give a quantitative yield of trimethyliodosilane, which was removed by distillation.

$$[(CH_3)_3Si]_2Te + 2AgI \longrightarrow 2(CH_3)_3SiI + Ag_2Te$$

This metathesis places bis(trimethylsilyl) telluride to the left of trimethyliodosilane in the "conversion series" of silyl halides and similar compounds.[13]

$$[(CH_3)_3Si]_2Te > (CH_3)_3SiI > [(CH_3)_3Si]_2Se > [(CH_3)_3Si]_2S > (CH_3)_3SiBr$$

In this series, any compound can be converted to any on its right by reaction with the corresponding silver salt.

Infrared Spectra.—The infrared spectra of some of the described compounds are presented in Table I. A rather detailed infrared and Raman study has been made previously for hexamethyldisilthiane[14] and has been used as a basis for this work. Assignments have also been made for ethylthiotrimethylsilane.[9] The bands at 489 and 438 cm.$^{-1}$ in hexamethyldisilthiane agree well with those reported by Kriegsmann[14] and are ascribed to the asymmetric and symmetric modes of vibration, respectively, for the Si–S–Si grouping. As expected these bands are absent in the selenium and tellurium analogs as they also are in hexamethyldisiloxane. Trimethylmethylthiosilane shows a single absorption only in the range 400–600 cm.$^{-1}$, and this absorption at 461 cm.$^{-1}$ is tentatively assigned to an essentially stretching mode of Si–S. Substitution of a phenyl group for the methyl attached to the sulfur atom appears to have little effect on the position of this band; it appears at 459 cm.$^{-1}$ in $(CH_3)_3SiSC_6H_5$. The corresponding band in $(CH_3)_3SiSC_2H_5$ is at 486 cm.$^{-1}$.[9] As the methyl groups on the central silicon atom are replaced progressively by CH_3S– groups, to give $(CH_3)_2Si(SCH_3)_2$ and $CH_3Si(SCH_3)_3$, considerable variations in the position of the absorption bands due to the Si–S–C system occur. The former absorbs at 431 and 512 cm.$^{-1}$ and the latter at 522 and 540 cm.$^{-1}$. The spectrum of $(CH_3S)_4Si$ shows a broad, intense band in the region 500–600 cm.$^{-1}$ which is split into five components.

TABLE I[a]: INFRARED SPECTRA (CM.$^{-1}$) AND TENTATIVE ASSIGNMENTS

	$[(CH_3)_3Si]_2S$	$[(CH_3)_3Si]_2Se$	$[(CH_3)_3Si]_2Te$	$(CH_3)_3SiSCH_3$	$(CH_3)_2Si(SCH_3)_2$	$CH_3Si(SCH_3)_3$	$(CH_3)_3SiSC_6H_5$[b]	$(CH_3S)_4Si$	$(CH_3S)_4Ge$
[c]		415 w				416 w			409 s, 421 s, 439 s
ν_s Si–S–Si	438 m								
ν_{as} Si–S–Si	489 s							547 sh	
ν Si–S				461 s	431 s, 512 s	522 s, 540 s	459 s	531 s, 573 s	
								586 s, 599 s	
[c]					670 m				
ν_s SiC_3	625 s	625 s	623 s	629 s			632 s		
ν S–C, ν_{as} SiC_3	690 s	695 m	695 m	690 m			695 s, sh		
ν S–C, ν_s SiC_2					697 m	692 m		694 m	693 m
[c]			729 m						
ν_{as} SiC_2, ν SiC					777 s	724 m			
(Si)$(CH_3)_3$ rock	752 s, 828 vs 852 vs	756 m, 825 vs 845 vs	758 m, 825 vs 844 vs	749 m, 839 vs			761 s 845 s		
(Si)$(CH_3)_2$ rock					805 s, 832 s				
(Si)CH_3 rock						780 s			
(S)CH_3 rock				950 vw	956 w	958 w		964 m	963 m
(Si)CH_3 sym. def.	1250 s	1253 s	1252 s	1246 s	1249 s	1248 m	1250 s		
[c], (S)CH_3 sym. def.*	1401 m	1410 w	1405 w	1401 w	1400 w	1400 w	1405 w	1316 m*	1315 m*
(S, Si)CH_3 as. def.	1445 w	1443 w	1445 w	1436 w	1436 w	1430 m	1470 m	1431 m	1427 m
ν_s C–H	2905 m	2900 m	2891 m	2932 m	2923 m	2930 s	2895 m	2843 w	2830 w
ν_{as} C–H	2965 s	2958 s	2952 s	2965 m	2960 m	3000 w	2955 m	2928 s	2915 m

[a] All spectra were recorded on a Beckman I.R. 9 spectrometer as liquid contact films: v, very; w, weak; m, medium; s, strong; sh, shoulder. [b] C_6H_5 bands omitted. [c] Unassigned.

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(13) C. Eaborn, *J. Chem. Soc.*, 3077 (1950).

(14) H. Kriegsmann, *Z. Elektrochem.*, **61**, 1088 (1957).

A band at 416 cm.$^{-1}$ in the spectrum of $[(C_6H_5)_2GeS]_3$ has been attributed to the asymmetric Ge–S–Ge stretching frequency.[15] Of the methylthiogermanes prepared, the following showed absorption near 400 cm.$^{-1}$, the limit of the instrument: $(C_6H_5)_2Ge(SCH_3)_2$ at 410 cm.$^{-1}$, $C_6H_5Ge(SCH_3)_3$ at 410 and 420 cm.$^{-1}$, and $(CH_4S)_4Ge$ at the values given in Table I. An examination of the spectra of these compounds at lower frequencies should help to discern whether or not absorption in the region of 400 cm.$^{-1}$ is due to the Ge–S–C system.

Absorption at 690 cm.$^{-1}$ in hexamethyldisilthiane has been ascribed to the asymmetric $Si–C_3$ (methyl) stretching vibration,[14] and a band appears at this position for all the compounds which contain this grouping in Table I. Dimethyldimethylthiosilane shows a band at 697 cm.$^{-1}$ and this is ascribed to the symmetric mode of vibration of the $Si–C_2$ (methyl) grouping.[16] However, both $CH_3Si(SCH_3)_3$ and $(CH_3)_4Si$, as well as $(CH_3)_4Ge$, show absorption in this region and therefore some additional mode of vibration must be suggested. It is tentatively postulated that this absorption is due to sulfur–methyl stretching vibration since many sulfides containing the sulfur–methyl group absorb over the narrow range 685–705 cm.$^{-1}$, and this has been attributed to S–C stretch.[17]

All compounds shown in Table I which contain the CH_3S– group also show weak to medium absorption at approximately 955 cm.$^{-1}$. This band is also evident in the methylthiogermanes $(C_6H_5)_nGe(SCH_3)_{4-n}$, $n = 1$, 2, 3, and it is assigned to the rocking mode of the methyl group attached to sulfur.[18]

Bands in the range 750–850 cm.$^{-1}$ in the organosilanes are very characteristic of CH_3–Si groups and are ascribed to the rocking mode of the methyl groups for simplicity's sake, but it is very likely that there is some Si–C stretching vibration involved.[19] The other band characteristic of CH_3–Si groups occurs almost constantly at 1250 cm.$^{-1}$ and is accepted as due to the symmetric deformation mode of vibration of the C–H bonds in the methyl groups.[19]

Proton Magnetic Resonance Spectra.—The values of the chemical shifts for the described compounds are presented in Table II. The values for hexamethyldisiloxane and the sulfur and selenium analogs agree well with the values which were reported previously[20] and are included here for comparison with the telluride. The replacement of O by S and then by Se in these compounds causes a downfield shift of the methyl proton resonance frequency; the value obtained for the telluride is thus in accord with this trend. As has been reported[20] this trend is opposite to the behavior predicted by simple inductive effects. This behavior is similar to that of the trimethylsilyl halides and is probably due to anisotropy and/or dispersion effects of the ligands rather than to d_π–p_π bonding between silicon and the halogen or group VI element.[21,22]

TABLE II

PROTON MAGNETIC RESONANCE DATA[a]

Compound	δ (S–CH_3)	δ (Si–CH_3)
$(CH_3)_3SiSCH_3$	-115.9	-16.5
$(CH_3)_2Si(SCH_3)_2$	-120.2	-29.9
$CH_3Si(SCH_3)_3$	-124.7	-42.6
$Si(SCH_3)_4$	-129.6	
$(CH_3)_3SiSC_6H_5$		-14.5
$[(CH_3)_3Si]_2O$		-3.5
$[(CH_3)_3Si]_2S$		-19.4
$[(CH_3)_3Si]_2Se$		-25.1
$[(CH_3)_3Si]_2Te$		-36.0
$(C_6H_5)_3GeSCH_3$	-114.8	
$(C_6H_5)_2Ge(SCH_3)_2$	-120.0	
$C_6H_5Ge(SCH_3)_3$	-124.9	
$Ge(SCH_3)_4$	-132.6	
$(CH_3)_3GeSCH_3$	-118.0	

[a] All chemical shifts are given in c.p.s. and were recorded on a Varian A-60 spectrometer. Spectra were observed in CCl_4 solution (5% v./v.) with tetramethylsilane (1%) as the internal standard.

For the series of methylthio-substituted methylsilanes, increasing the number of CH_3S– groups causes a downfield shift for both the methyl–silicon and methyl–sulfur protons, with the shift more pronounced in the former.

A small downfield shift is observed in the value of δ for the methyl protons as we pass down the series $(C_6H_5)_3Ge(SCH_3)$ . . . . $Ge(SCH_3)_4$. It should be noted that the nature of the central metal atom has little effect upon the methyl–sulfur resonance: δ for $(CH_3)_3SiSCH_3$ is -115.9 c.p.s. and for $(CH_3)_3GeSCH_3$ it is -118.0 c.p.s.

Experimental

All reactions and manipulations involving air-sensitive compounds were carried out in an atmosphere of dry, oxygen-free nitrogen. Reactions involving methanethiol were carried out in a flask fitted with a sealed stirrer, a CO_2–acetone condenser, and a dropping funnel cooled with solid carbon dioxide.

Grignard reagents were filtered through a glass wool plug to remove the bulk of the unreacted magnesium. All organochlorosilanes were fractionated prior to use. Triphenylbromogermane and diphenyldibromogermane were prepared by the usual procedures. In the preparation of phenyltribromogermane equimolar amounts of phenylmagnesium bromide and germanium(IV) chloride were allowed to react at 0°, and the reaction mixture was treated with lithium aluminum hydride. After acid hydrolysis, phenylgermane was fractionated (b.p. 48° (23 mm.); 28% yield) and this was treated with bromine in chloroform at 0° to give phenyltribromogermane (b.p. 85° (0.1 mm.); 68% yield).[23] Trimethylbromogermane was prepared by the bromination of tetramethylgermane.[24]

Trimethylmethylthiosilane.—To methylmagnesium iodide, prepared from methyl iodide (142 g., 1.0 mole) and magnesium (27 g., 1.13 g.-atoms) in diethyl ether (900 ml.) was added dropwise methanethiol (50 g., 1.04 moles) at 0°. Immediate decomposition of the Grignard reagent occurred with the deposition of a heavy white precipitate of methylthiomagnesium iodide. After the complete addition of the methanethiol, the reaction mixture

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was allowed to warm to room temperature and trimethylchlorosilane (54.0 g., 0.5 mole) was added. A slightly exothermic reaction occurred and the reaction mixture was refluxed gently for 4 hr. All volatile material was then removed under high vacuum and condensed at −78°. Final traces were removed from the solid residue by slight warming of the reaction flask. Fractionation of the condensate through a column packed with glass helices gave trimethylmethylthiosilane, b.p. 110–111°; 78% yield.

Anal. Calcd. for $C_4H_{12}SiS$: C, 40.0; H, 10.1. Found: C, 40.05; H, 10.1.

The following two silanes were prepared by the same procedure.

Dimethyldimethylthiosilane was prepared from methylthiomagnesium iodide (0.5 mole) and dimethyldichlorosilane (21.2 g., 0.16 mole), b.p. 52–54° (7 mm.); 43% yield.

Anal. Calcd. for $C_4H_{12}SiS_2$: C, 31.55; H, 7.9. Found: C, 31.8; H, 7.7.

Methyltrimethylthiosilane was prepared from methylthiomagnesium iodide (0.5 mole) and methyltrichlorosilane (14.9 g., 0.1 mole), b.p. 45° (0.2 mm.); 41% yield.

Anal. Calcd. for $C_4H_{12}SiS_3$: C, 26.1; H, 6.6. Found: C, 25.8; H, 6.3.

Methylthiotriphenylgermane.—To a solution of triphenylbromogermane (10 g., 26.1 mmoles) in benzene (150 ml.) at room temperature was added pyridine (3.2 g., 39.1 mmoles). The reaction mixture was cooled to 0° and methanethiol (2.0 g., 42 mmoles) added dropwise. A precipitate of pyridinium bromide rapidly formed, and, after the reaction mixture had warmed to room temperature, was removed by filtration in an atmosphere of nitrogen (89% yield). The filtrate was evaporated under vacuum and the residue recrystallized from hexane to give cubic crystals, m.p. 85°; 81% yield.

Anal. Calcd. for $C_{19}H_{18}GeS$: C, 65.0; H, 5.2. Found: C, 64.7; H, 5.3.

The following germanes were prepared by a similar procedure.

Dimethylthiodiphenylgermane.—From diphenyldibromogermane (26.6 g., 68.7 mmoles) and methanethiol (13.1 g., 0.273 mole) in the presence of pyridine (11.9 g., 0.15 mole) was obtained pyridinium bromide in 92% yield. The dimethylthiodiphenylgermane was fractionated through a short column packed with glass helices, b.p. 132–135° (0.2 mm.); 85% yield.

Anal. Calcd. for $C_{14}H_{16}GeS_2$: C, 52.4; H, 5.0. Found: C, 52.3; H, 5.1.

Trimethylthiophenylgermane.—This compound was prepared from phenyltribromogermane (10.0 g., 25.7 mmoles) and methanethiol (4.3 g., 0.09 mole) in the presence of pyridine (6.1 g., 77.1 mmoles). A 91% yield of pyridinium bromide was separated and the trimethylthiophenylgermane was fractionated, b.p. 110° (0.2 mm.); 81% yield.

Anal. Calcd. for $C_9H_{14}GeS_3$: C, 37.2; H, 4.8. Found: C, 37.0; H, 4.7.

Trimethylmethylthiogermane.—From trimethylbromogermane (11.1 g., 56.1 mmoles) and methanethiol (2.8 g., 57 mmoles) in the presence of pyridine (4.5 g., 57 mmoles) in hexane (200 ml.) was obtained a 91% yield of pyridinium bromide. The trimethylmethylthiogermane was fractioned, b.p. 129–131°; 73% yield. Only two peaks were observed in the p.m.r. spectrum.

Anal. Calcd. for $C_4H_{12}GeS$: C, 29.2; H, 7.3. Found: C, 30.0; H, 7.5.

Triphenylphenylthiogermane.—The reaction between triphenylbromogermane (10.0 g., 26.1 mmoles) and benzenethiol (3.0 g., 26.8 mmoles) in the presence of pyridine (2.4 g., 30.4 mmoles) gave a 95% yield of pyridinium bromide. The benzene solution gave triphenylphenylthiogermane, which was recrystallized from hexane, m.p. 90.5–91.5°; 80% yield.

Anal. Calcd. for $C_{24}H_{20}GeS$: C, 69.8; H, 4.9. Found: C, 69.6; H, 5.1.

Tetramethylthiogermane.—This compound was prepared from germanium(IV) chloride (20.1 g., 93.8 mmoles) and methanethiol (27 g., 0.565 mole) in the presence of pyridine (31.6 g., 0.4 mole) in benzene (500 ml.). The germanium(IV) chloride–pyridine adduct which formed initially, and which was incompletely soluble in the quantity of benzene employed, was slowly converted to pyridinium chloride. The reaction mixture was stirred at room temperature for 24 hr. and the pyridinium chloride (92%) removed by filtration. Fractionation of the filtrate gave tetramethylthiogermane, b.p. 85° (0.4 mm.); 73% yield.

Anal. Calcd. for $C_4H_{12}S_4Ge$: C, 18.4; H, 4.6. Found: C, 18.6; H, 4.7.

Reaction between Triphenylbromogermane and Methylthiomagnesium Iodide.—To a suspension of methylthiomagnesium iodide (0.1 mole) in ether (100 ml.) was added a solution of triphenylbromogermane (10 g., 26.1 mmoles) in benzene (50 ml.). The reaction mixture was refluxed overnight and then evaporated to dryness under vacuum. The residue was extracted with two 100-ml. portions of boiling benzene. From the benzene solution was obtained, on evaporation, a white solid which was fractionally recrystallized from hexane to yield methylthiotriphenylgermane (m.p. 84–85°; 32% yield) and triphenyliodogermane (m.p. 154–156°; 55% yield).

Trimethylphenylthiosilane.—To phenylmagnesium bromide (0.2 mole) in diethyl ether (200 ml.) was added benzenethiol (22.0 g., 0.2 mole). The reaction mixture was refluxed gently for 2 hr., and to the resulting suspension of phenylthiomagnesium bromide was added trimethylchlorosilane (10.9 g., 0.1 mole). A mildly exothermic reaction occurred and completion was achieved by refluxing for 3 hr. All volatile material was removed under vacuum and condensed at −78°. Fractionation of the condensate gave trimethylphenylthiosilane, b.p. 40° (0.3 mm.); 34% yield.

Anal. Calcd. for $C_9H_{14}SiS$: C, 59.3; H, 7.7. Found: C, 59.8; H, 7.6.

Tetramethylthiosilane.—To silicon(IV) chloride (16.8 g., 0.1 mole) in pentane (200 ml.) at 0° was added pyridine (31.6 g., 0.4 mole) and a precipitate of $SiCl_4 \cdot 2C_5H_5N$ was formed immediately. Methanethiol (40.0 g., 0.835 mole) was then added and the reaction mixture allowed to warm to room temperature and stirred overnight. Filtration under nitrogen gave a residue consisting of unreacted $SiCl_4 \cdot 2C_5H_5N$ and pyridinium chloride. The clear filtrate was fractionated to give pentane, pyridine, and tetramethylthiosilane, b.p. 66° (0.3 mm.), m.p. 30°; 34% yield.

Anal. Calcd. for $C_4H_{12}S_4Si$: C, 22.2; H, 5.6. Found: C, 22.4; H, 5.6.

Reaction between Trimethylchlorosilane and Phenylselenomagnesium Bromide.—An ethereal solution of phenylmagnesium bromide (0.2 mole) was filtered through a sintered glass disk onto a stirred suspension of selenium powder (0.2 g.-atom) in ether at room temperature. The reaction mixture was stirred overnight, and the resulting reaction mixture consisted of two liquid layers, the lower deep brown in color and the upper orange-brown. Trimethylchlorosilane (22.0 g., 0.2 mole) was added and the reaction mixture was stirred at room temperature for 24 hr., during which time a white precipitate slowly formed. All volatile material was removed under vacuum and condensed at −78°. The condensate was fractionated to yield bis(trimethylsilyl) selenide, b.p. 39° (4 mm.); 39% yield. A single peak was observed in the p.m.r. spectrum.

Anal. Calcd. for $C_6H_{18}Si_2Se$: C, 32.0; H, 8.1. Found: C, 33.3; H, 8.3.

Reaction between Trimethylchlorosilane and Phenyltelluromagnesium Bromide.—An ethereal solution of phenylmagnesium bromide (0.2 mole) was filtered through a sintered glass disk onto a stirred suspension of finely divided tellurium metal (25.4 g., 0.2 g.-atom) in ether (50 ml.). After complete addition, the reaction mixture was refluxed gently for 3 hr. and then trimethylchlorosilane (22.0 g., 0.2 mole) was added. Refluxing the reaction mixture for 2 hr. led to the production of a copious, white, gelatinous precipitate and a considerable quantity of tellurium metal. All volatile material was removed under vacuum with cautious warming and condensed at −78°. The condensate was fractionated to yield bis(trimethylsilyl) telluride, b.p. 40–42° (0.25 mm.); 15% yield. Only one peak appeared in the p.m.r. spectrum.

Anal. Calcd. for $C_6H_{18}Si_2Te$: C, 26.3; H, 6.6. Found: C, 28.7; H, 7.2.

Reactions of the Organosilyl and Organogermyl Sulfides. (1) **Hydrolysis.** (a) **Trimethylmethylthiosilane.**—To trimethylmethylthiosilane (6.3 g., 52.5 mmoles) in tetrahydrofuran (50 ml.) was added water (1.4 g., 78.5 mmoles). A slow stream of nitrogen was passed over the solution, and the emergent gases were led into an aqueous solution of silver nitrate (20%). Rapid precipitation of the yellow silver(I) methanethiolate occurred. Precipitation was complete after 3 hr. (87% yield). The tetrahydrofuran solution was dried with anhydrous magnesium sulfate and fractionated, with difficulty, to give hexamethyldisiloxane (b.p. 95–100°; 45% yield). Characterization was by infrared and p.m.r. spectra. No evidence for the presence of trimethylsilanol was obtained. An identical reaction was observed in the complete absence of solvent.

(b) **Methylthiotriphenylgermane.**—To methylthiotriphenylgermane (1.0 g., 2.85 mmoles) in tetrahydrofuran (50 ml.) was added water (0.5 g.) and a slow stream of nitrogen was passed first over the solution and then into a solution of silver nitrate. After 3 hr. at room temperature no silver(I) methanethiolate had been formed. Methylthiotriphenylgermane was recovered (90%) unchanged from the tetrahydrofuran.

(c) **Trimethylmethylthiogermane.**—Equal volumes of water and trimethylmethylthiogermane were mixed and left in contact overnight. The water was then removed and the residue examined. No hexamethyldigermoxane was detected.

(2) **Ethanolysis.**—To methylthiotriphenylgermane (1.0 g., 2.85 mmoles) was added dry ethanol (25 ml.), and the clear solution was refluxed under nitrogen overnight. The ethanol was evaporated under vacuum and the white residue fractionally recrystallized from pentane to give a small amount of the soluble ethoxytriphenylgermane (m.p. 83–85°). The infrared spectrum showed bands at 911 and 1060 cm.$^{-1}$ due to the Ge–O–C_2H_5 system.[25] The portion insoluble in pentane was recrystallized from heptane to give hexaphenyldigermoxane (m.p. 183–184°).

(3) **Oxidation.** (a) **Trimethylmethylthiosilane.**—Through a solution of trimethylmethylthiosilane (3.0 g., 2.5 mmoles) in benzene (60 ml.) at its reflux point was passed dry oxygen for 24 hr. Fractionation gave only benzene and unchanged trimethylmethylthiosilane (b.p. 108–111°; 60% yield).

(b) **Methylthiotriphenylgermane.**—To methylthiotriphenylgermane (3.5 g., 10.0 mmoles) in acetone (50 ml.) was added hydrogen peroxide (20.0 mmoles), and the reaction mixture was kept at 0° for 12 hr. The solvent was removed under vacuum and the white residue recrystallized from heptane to give hexaphenyldigermoxane (m.p. 182–184°; 70% yield).

A similar low temperature oxidation using nitrogen dioxide also gave hexaphenyldigermoxane as the only isolable product.

(4) **Reaction with Aqueous Silver Nitrate Solution.**—To methylthiotriphenylgermane (1.0 g., 2.85 mmoles) in tetrahydrofuran (20 ml.) was added silver nitrate (0.54 g., 3.0 mmoles), in water (1.5 ml.). An immediate yellow precipitate formed and was removed by filtration after 1 hr. The filtrate gave, on evaporation, hexaphenyldigermoxane which was recrystallized from heptane (m.p. 183–184°; 90% yield).

(5) **Reaction with *n*-Butyllithium.**—To methylthiotriphenylgermane (1.0 g, 2.85 mmoles) dissolved in diethyl ether (50 ml.) at 0° in a Schlenk tube was added *n*-butyllithium (2.9 mmoles). A white precipitate rapidly formed and after 3 hr. was removed by filtration and washed with ether. The filtrate was evaporated to dryness and the residue recrystallized from aqueous alcohol to give *n*-butyltriphenylgermane (m.p. 79–80°; 81% yield).

Anal. Calcd. for $C_{22}H_{24}Ge$: C, 73.2; H, 6.7. Found: C, 72.8; H, 6.7.

The original white precipitate was dried under vacuum, dissolved in water, and titrated with standard acid. The solution contained 2.51 equivalents of base (88%).

(6) **Reaction with Methyl Iodide.** (a) **Trimethylmethylthiosilane.**—To trimethylmethylthiosilane (1.6 g., 13.4 mmoles) was added methyl iodide (3.8 g., 26.8 mmoles) at room temperature. A white solid separated slowly and was removed by filtration in a Schlenk tube, then washed with pentane. The microcrystalline material was trimethylsulfonium iodide (m.p. 210° (sealed tube); 25% yield). The infrared spectrum was identical with that of the authentic material prepared from methyl iodide and dimethyl sulfide. The following bands were observed in the infrared spectrum (Nujol mull): 646 (w), 728 (s), 937 (m), 946 (m), 1040 (s), and 1061 (m) cm.$^{-1}$.

(b) **Methylthiotriphenylgermane.**—Methylthiotriphenylgermane (1.0 g., 2.85 mmoles) was dissolved completely in methyl iodide (5 ml.). After 1 week the white precipitate, which had separated slowly, was removed and washed with hexane. The infrared spectrum of the precipitate corresponded to that of trimethylsulfonium iodide (72% yield). The filtrate was evaporated under vacuum, and the white residue was recrystallized from hexane to give triphenyliodogermane (m.p. 155–156°; 65% yield) together with a small amount of unchanged methylthiotriphenylgermane.

(c) **Trimethylmethylthiogermane.**—In an identical experiment trimethylmethylthiogermane gave a 67% yield of trimethylsulfonium iodide after 1 week at room temperature.

The trimethylsulfonium iodide prepared in these experiments rapidly became yellow on exposure to the atmosphere.

(7) **Reaction with Dimethyl Sulfate.** (a) **Trimethylmethylthiosilane.**—To trimethylmethylthiosilane (8.6 g., 72.0 mmoles) in a Schlenk tube was added dimethyl sulfate (22.6 g., 179 mmoles) at room temperature. A white turbidity developed approximately 15 min. after mixing and a white crystalline material precipitated rapidly thereafter. The reaction was exothermic and external cooling was necessary to maintain the temperature at, or slightly above, room temperature. A light brown color then slowly developed and was accompanied by the formation of two liquid layers, the upper being clear and colorless. After the reaction mixture had stood overnight the other limb of the Schlenk tube was cooled in liquid nitrogen. The internal pressure was reduced to approximately 5 mm. and the upper liquid layer evaporated and condensed over. The condensate was removed and fractionated to give hexamethyldisiloxane (b.p. 97–101°; 62% yield), which was characterized by its infrared and p.m.r. spectra. A strong odor of sulfur dioxide was noted. All volatile material was then removed from the crystalline solid in the Schlenk tube at 0.1 mm. pressure and temperatures up to 50°. This condensate was fractionated through a short column packed with glass helices to give unchanged dimethyl sulfate (11.6 g., b.p. 43–45° (3 mm.), 51% yield) and a small amount of higher boiling material (b.p. 55–60° (3 mm.), 1.4 g.). The p.m.r. spectrum of this second fraction (pure liquid, external tetramethylsilane standard) showed peaks at −43.9 and −254.5 c.p.s.; the integrated areas were in the ratio of approximately 3:1. An additional peak at −256.0 c.p.s., due to dimethyl sulfate, was also evident. The infrared spectrum was very similar to that of dimethyl sulfate, except for the supplementary bands at 800 (m) and 1259 (m) cm.$^{-1}$; the latter band is probably due to the symmetric deformation vibration of methyl groups attached to silicon. Broadening of the existing bands at 830 cm.$^{-1}$ ((Si)CH_3 rock) and 1000 cm.$^{-1}$ (Si–O stretch) was also observed.

Anal. Calcd. for $C_4H_{12}SiO_4S$: C, 26.1; H, 6.6. Found: C, 22.2; H, 5.6.

Further purification of this material could not be effected. A sample was hydrolyzed with water and then extracted with carbon tetrachloride. The p.m.r. spectrum of this extract showed the single peak at −3.5 c.p.s. (tetramethylsilane internal standard) due to hexamethyldisiloxane.

The crystalline material produced in the initial reaction was washed with two 20-ml. portions of benzene and dried under vacuum. The infrared spectrum was identical with that of trimethylsulfonium methyl sulfate which was prepared from dimethyl sulfate and dimethyl sulfide (51% yield). The p.m.r. spectrum of an aqueous solution showed two peaks, at −257 c.p.s. (CH_3–O protons) and −207 c.p.s. (CH_3–S protons), relative to an external tetramethylsilane standard; integrated areas were in the ratio 1:2.7. No band due to methanol, which would

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[25] O. H. Johnson and H. E. Fritz, *J. Am. Chem. Soc.*, **75**, 718 (1953).

arise from hydrolysis of the trimethylsulfonium methyl sulfate, was observed.

The initial crystalline material was isolated by the following procedure. To trimethylmethylthiosilane (6.3 g., 52.5 mmoles) in a Schlenk tube was added dimethyl sulfate (13.2 g., 105 mmoles). After the first signs of precipitation were observed, the reaction mixture was cooled to 0° and left overnight. The crystalline precipitate was filtered off, and the filtrate was transferred to a two-neck flask and returned to a cold bath. The colorless crystals were washed with two 20-ml. portions of benzene and dried under vacuum (1.5 g.). The infrared spectrum was identical with that of authentic trimethylsulfonium methyl sulfate.

After 1 week at 0° the mother liquors had deposited a further quantity (1.7 g.) of trimethylsulfonium methyl sulfate and two liquid layers had formed. The upper was characterized as hexamethyldisiloxane and the lower consisted essentially of dimethyl sulfate. A strong odor of sulfur dioxide was also detected during the work-up procedure.

(b) **Trimethylmethylthiogermane.**—To trimethylmethylthiogermane (9.1 g., 55.1 mmoles) in a two-neck flask was added dimethyl sulfate (14.0 g., 111 mmoles) at room temperature, and then the reaction mixture was cooled to 0°. After 3 days the total reaction mixture was transferred, as an ether slurry, to a Schlenk tube, and the white crystalline material was removed by filtration (9.7 g.; 93% yield). The infrared spectrum was identical with that of authentic trimethylsulfonium methyl sulfate. The ether solution was fractionated to give trimethylgermylmethyl sulfate (b.p. 55–57° (0.2 mm.); 70% yield). The p.m.r. spectrum showed two peaks, −77.5 c.p.s. (CH_3Ge–) and −259.6 c.p.s. (CH_3O–), relative to an external tetramethylsilane standard. The integrated areas were in the ratio 3:1. Bands characteristic of $(CH_3)_3Ge$– were observed in the infrared spectrum at 635 (ν_{as} Ge–C_3), 785 (CH_3–Ge rock), and 1250 cm.$^{-1}$ (symmetric deformation of CH_3– (Ge)). A strong band was also observed at 970 cm.$^{-1}$ which could be due to a stretching mode of vibration of the Ge–O–S system.

Anal. Calcd. for $C_4H_{12}GeSO_4$: C, 21.0; H, 5.3. Found: C, 21.3; H, 5.3.

(8) **Reaction with Silver(I) Iodide.**—To silver(I) iodide (5.5 g., 23.5 mmoles) in a small distilling apparatus was added bis-(trimethylsilyl) telluride (2.3 g., 9.1 mmoles). Immediate reaction was indicated by the silver(I) iodide turning black. The temperature of the reaction mixture was raised slowly to 120° and the trimethyliodosilane distilled off (99%). Characterization was by infrared and p.m.r. spectroscopy (CH_3–Si protons at −47.3 c.p.s. from internal tetramethylsilane). The presence of iodine in the distillate was confirmed qualitatively.

Preparation of Sodium Triphenylgermanethiolate.[6]—Triphenylbromogermane (7.2 g., 18.8 mmoles) in benzene (60 ml.) was added dropwise to a suspension of *anhydrous* sodium sulfide (7.2 g., 93 mmoles) in dry ethanol (110 ml.). After 30 min. the reaction mixture was filtered under nitrogen and the clear filtrate evaporated under vacuum to give a white residue. This residue was extracted with benzene in a Schlenk tube and the benzene filtrate evaporated to dryness. The residue contained no sodium and was extracted with hexane to give ethoxytriphenylgermane (2.5 g., 38% yield, m.p. 86–87°). The infrared spectrum showed bands at 911 and 1060 cm.$^{-1}$ due to the Ge–O–C system.

Anal. Calcd. for $C_{20}H_{20}GeO$: C, 68.8; H, 5.8. Found: C, 69.2; H, 5.5.

The hexane-insoluble material gave hexaphenyldigermoxane (2.5 g., 43% yield, m.p. 183–184°). The infrared spectrum showed absorption at 861 cm.$^{-1}$ due to the Ge–O–Ge group.

The procedure was repeated except for the use of sodium sulfide·$x$hydrate purified by recrystallization from an aqueous solution (1.5 *M*) of sodium hydroxide, two recrystallizations from anhydrous ethanol, and then drying for 3 hr. at 65° and 10^{-2} mm. pressure. The white crystalline product, sodium triphenylgermanethiolate, melted in the range of 180–197°, was water soluble, and decomposed as previously described.[6]

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA

N-Perfluoroalkyl S-Perfluoroisopropyl Iminosulfur Monofluorides[1]

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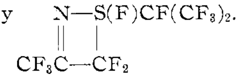
The new class of fluorocarbon compounds, named for the first time in the title, involving a –C—N═S—C– bonding arrangement is prepared by reaction of the analogous fluorocarbon iminosulfur difluorides with perfluoropropene over solid powdered CsF at 80–90° in a closed vessel. The reaction appears to proceed slowly *via* the formation of a perfluoroisopropyl carbanion, which as a Lewis base complexes with the acidic sulfur by using its d-orbitals while essentially simultaneously the less basic F^- ion is eliminated to a neighboring defect site. When the reaction was studied with $C_3F_7N{=}SF_2$, one of the by-products that was also isolated and identified was a rather unique compound for which it is impossible, as yet, to account, *viz.*, $C_6F_{13}NS$, probably



$$\begin{array}{ll} \text{N}\!-\!\text{S(F)CF(CF}_3)_2. \\ \| \quad | \\ \text{CF}_3\text{C}\!-\!\text{CF}_2 \end{array}$$

Introduction

Although there are many examples of negative ion Lewis bases as attacking species in the general field of fluorine chemistry, the number of examples is more limited in the case of perfluoroalkyl carbanions.[2–6]

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[1] This work was supported by the Advanced Research Projects Agency through the Army Research Office at Durham, N. C. This support is gratefully acknowledged.

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