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Exchange of Halogens between the Methylsilicon and Methylgermanium Moieties

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Equilibria resulting from the exchange of pairs of different halogen atoms (Cl, Br, or I) between the trifunctional methylsilicon and methylgermanium moieties have been studied by proton nuclear magnetic resonance. The data have been evaluated in terms of five equilibrium constants—two for the scrambling of the two kinds of halogens on the methylsilicon moiety, two for scrambling on the methylgermanium moiety, and an intersystem equilibrium constant for the distribution of the two kinds of halogens between the methylsilicon and methylgermanium moieties. The kinetics of the scrambling of chlorine and bromine in an equimolar mixture of CH_3SiBr_3 and CH_3GeCl_3 is treated in terms of the predominant exchange-pair processes plus a continuous state of equilibrium between the various methylgermanium halides.

While this work was in progress, a review[1] of exchange reactions appeared in which it was pointed out that there have been no quantitative studies of equilibria resulting from the scrambling of two kinds of substituents between two kinds of central atoms or moieties. This paper represents such a study of exchange equilibria resulting from the scrambling of two types of monofunctional substituents—halogen atoms—on two kinds of trifunctional moieties, the methylsilicon and methylgermanium moieties. In two related communications[2,3] scrambling equilibria of two kinds of substituents between the dimethylsilicon and dimethylgermanium moieties have been described.

Experimental Section

Materials.—Methyltrichlorogermane, methyltribromogermane, and methyltriiodogermane were prepared by an improved version[4] of Rochow's direct synthesis[5] from germanium powder and the respective methyl halide. Methyltribromosilane has been prepared in a similar fashion, using 100 g of silicon powder (purchased from A. F. Mackay, New York, N. Y.) plus 40 g of copper powder and methylbromide at 400°. The crude reaction product (829 g) was shown by nmr to consist of 15.6 mole % CH_3Br, 71.0 mole % CH_3SiBr_3, 11.2 mole % $(CH_3)_2SiBr_2$, and 2.2 mole % $(CH_3)_3SiBr$. Methyltrichlorosilane, free of dimethyldichlorosilane, was obtained by treating $CH_3Si[N(CH_3)_2]_3$ with dry HCl in an inert solvent.

Equilibration.—Equilibrium was achieved by heating the desired proportions of the starting materials, the methylgermanium compound and the methylsilicon compound, in three-fourths filled, sealed, 5-mm o.d., precision, nuclear magnetic resonance (nmr) tubes at 120°. Nmr measurements were performed immediately after quenching of the samples to room temperature. The times required for reaching equilibrium at 120° were estimated on the basis of test runs at several different ratios of starting materials held for various time intervals until the proton nmr spectra did not exhibit any further change. The reported equilibrium values generally correspond to very much longer times.

Nmr Measurements.—Proton nmr spectra were obtained on a Varian Model A-60 spectrometer as previously described,[6] with measurements being carried out on the neat liquids at 35°. The proton nmr chemical shifts of the methylgermanium and methylsilicon moieties in the species present at equilibrium are reported in Table I. Peak areas were determined by electronic integration and—in cases of overlapping signals—by cutting out and weighing of Xerox copies of the spectra.[7] A typical set of spectra is shown (as Figure 1) in a review[8] of our recent nmr work. The referencing was carried out on only some of the samples by breaking open the nmr tubes and adding a drop of tetramethylsilane after the quantitative measurements had been completed.

Halogen Exchange between CH_3Si and CH_3Ge

A general approach to the treatment of data obtained from scrambling two kinds of monofunctional substituents on a pair of different multifunctional central moieties has been reported elsewhere.[3] The systems discussed here represent the special case for $\nu = \mu = 3$, where ν and μ are the respective functionalities of the two central moieties. As pointed out previously,[9] a minimum of two equilibrium constants is needed to represent scrambling of the substituents Z and T on a single trifunctional central moiety, Q. A suitable set of two such independent constants is

$$K_{Q1} = [QT_3][QZ_2T]/[QZT_2]^2 \tag{1}$$

$$K_{Q2} = [QZT_2][QZ_3]/[QZ_2T]^2 \tag{2}$$

Similarly, the two equilibrium constants

$$K_{M1} = [MT_3][MZ_2T]/[MZT_2]^2 \tag{3}$$

$$K_{M2} = [MZT_2][MZ_3]/[MZ_2T]^2 \tag{4}$$

properly describe the scrambling equilibria of Z and T on a second trifunctional central moiety, M. In addition, one other equilibrium constant is needed to define the over-all mixture. It is the intersystem constant K_I, which relates the molecules based on the central moiety Q with those of the central moiety M.

Although a constant relating the two systems may be written in a number of different ways, we have chosen the following format since this is the form which is most readily evaluated from existing compilations of thermodynamic data

$$K_I = [QT_3][MZ_3]/[QZ_3][MT_3] \tag{5}$$

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[1] J. C. Lockhart, *Chem. Rev.*, **65**, 131 (1965).

[2] K. Moedritzer and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*, in press.

[3] J. R. Van Wazer, K. Moedritzer, and L. C. D. Groenweghe, *J. Organometal. Chem.*, in press.

[4] K. Moedritzer, *ibid.*, in press.

[5] E. G. Rochow, *J. Am. Chem. Soc.*, **69**, 1729 (1947).

[6] K. Moedritzer and J. R. Van Wazer, *ibid.*, **86**, 802 (1964).

[7] K. Moedritzer and J. R. Van Wazer, *ibid.*, **87**, 2360 (1965).

[8] J. R. Van Wazer and L. C. D. Groenweghe, "NMR in Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapter 33, pp 283–298.

[9] L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, **36**, 303 (1964).

TABLE I

PROTON NMR CHEMICAL SHIFTS (IN PPM RELATIVE TO TMS[a]) OBSERVED IN NEAT SAMPLES OF EQUIMOLAR MIXTURES OF CH_3SiZ_3 AND CH_3GeT_3 AT EQUILIBRIUM

Z	T	CH_3GeT_3	CH_3GeT_2Z	CH_3GeTZ_2	CH_3GeZ_3	CH_3SiT_3	CH_3SiT_2Z	CH_3SiTZ_2	CH_3SiZ_3
Cl	Br	−2.017	−1.875	−1.742	−1.617	−1.530	−1.375	−1.227	−1.092
Br	I	−2.773	−2.500	−2.260	−2.037	−2.267	−2.070	−1.790	−1.548
Cl	I	−2.792	−2.317	. . .[b]	. . .[b]	. . .[b]	. . .[b]	−1.413	−1.083

[a] Tetramethylsilane, TMS, was added as internal reference after the samples had reached equilibrium. [b] Not observed.

TABLE II

EQUILIBRIUM CONSTANTS FOR QZ_3 *vs.* MT_3 SYSTEMS AT 120°, WHERE $Q = CH_3Si$, $M = CH_3Ge$, AND Z AND T ARE HALOGENS

Z	T	K_{M1}	K_{M2}	K_{Q1}	K_{Q2}	K_I
Cl	Br	0.37[a]	0.53	0.42	0.48	$(9.7 \pm 4.0) \times 10^{-6}$
		(0.41)[b]	(0.42)	(0.43)	(0.40)	
Br	I	0.42	0.81	1.43	0.52	$(4.2 \pm 0.9) \times 10^{-5}$
		(0.44)	(0.42)	. . .	. . .	
Cl	I	. . .[c]	. . .[c]	. . .[c]	. . .[c]	$(1.5 \pm 0.7) \times 10^{-12}$
		(0.72)	(0.79)	(0.33)[d]	(0.33)[d]	
Ideal randomness		0.333	0.333	0.333	0.333	1.00

[a] Constants not in parentheses were calculated from the experimental values in Table III. [b] Constants in parentheses are calculated from the system QZ_3 *vs.* QT_3 or MZ_3 *vs.* MT_3, respectively; see Table V. [c] Constants could not be determined owing to the presence of insufficient species at equilibrium. [d] See ref 10.

Calculation of K_I.—The equilibrium constants K_{Q1}, K_{Q2}, K_{M1}, and K_{M2} were evaluated from the experimental data, and their statistical errors were determined, using a computer program previously described.[9] The weighted-average values of these constants may then be employed to compute[9] the theoretical composition for any given over-all composition, expressed for either the Q or M system in terms of an R value. These composition parameters (R values) must be evaluated from the experimental data since, for the compounds based on the central atom Q, R_Q is defined as the T/Q mole ratio corresponding to the total amount of T associated with the Q moiety and, likewise, for the compounds of the central moiety M, $R_M \equiv T/M$, where the T is associated with the M. From the computed theoretical compositions for the respective composition parameters, R_Q and R_M, the amounts of QT_3, QZ_3, MT_3, and MZ_3 for the calculation of the intersystem constant K_I according to eq 5 are obtained.

By this means, each experimental run yields one value for K_I. The mean deviation of the average of these values is obtained by taking the square root of the squares of the deviation of the individual values from the average.

Results and Discussion

Equilibrium Constants.—The intersystem equilibrium constants determined for the mixtures studied are presented in Table II along with the pertinent equilibrium constants K_{Qi} and K_{Mi} where $i = 1$ or 2. The values of K_{Qi} and K_{Mi} given in parentheses in Table II are obtained from the scrambling of the same pair of substituents on either the methylsilicon or the methylgermanium moiety taken by itself. The experimental data from which the equilibrium constants in Table II were computed are reported in Table III. In this table, the numbers listed in parentheses were calculated[3] from the appropriate set of five equilibrium constants, K_{Qi}, K_{Mi}, and K_I, of Table II for the over-all composition (characterized by the parameters R and R') determined from the starting ingredients.

In the system CH_3SiCl_3 *vs.* CH_3GeI_3, the equilibrium constants K_{Qi} and K_{Mi} ($i = 1$ or 2) could not be calculated from the experimental data listed in Table III since only four species were seen by nmr at equilibrium at any composition, with the expected four additional species being present in concentrations too small to be detected. Therefore, the constants K_{M1} and K_{M2} listed in parentheses in Table II were used in calculating K_I. These constants were obtained from the study of the system CH_3GeCl_3 *vs.* CH_3GeI_3 described in Tables IV and V. Since K_{Q1} and K_{Q2} could also not be determined from the data listed in Table III and are needed to calculate K_I, it was assumed that the exchange of Cl and I atoms on the methylsilicon moiety is random, as previously reported by Anderson.[10] Thus, values of $K_{Q1} = K_{Q2} = 0.333$ were used for this system.

The kinetic measurements presented in the next section show that the various methylgermanium compounds reach equilibrium within the time of an nmr run at 35° (and hence probably at room temperature) so that the measured values of K_{Mi} should correspond closely to room temperature, reequilibration occurring during quenching and the subsequent nmr measurement. However, since these constants (see Table II) do not deviate greatly from the random value of 0.333, the reported room temperature values for K_{Mi} are expected to be nearly equal to those for 120° because ΔH is zero for an ideally random scrambling reaction. Furthermore, kinetic measurements show that the over-all set of exchange reactions are controlled by the release and acceptance of substituents on the methylsilicon moiety—a process which proceeds sufficiently slowly at room temperature so that the several minutes required for quenching and nmr analysis are negligible.

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(10) H. H. Anderson, *J. Am. Chem. Soc.*, **73**, 5804 (1951).

TABLE III

EQUILIBRIUM DATA IN MOLE PER CENT IN THE SYSTEMS $\mathrm{CH_3GeT_3}$ *vs.* $\mathrm{CH_3SiZ_3}$ AT 120°

SYSTEM[a] $\mathrm{CH_3GeCl_3}$ vs. $\mathrm{CH_3SiBr_3}$

$\underline{R} \equiv$ Cl/(Si+Ge)	$\underline{R}' \equiv$ Si/(Si+Ge)	$\mathrm{CH_3GeBr_3}$	$\mathrm{CH_3GeBr_2Cl}$	$\mathrm{CH_3GeBrCl_2}$	$\mathrm{CH_3GeCl_3}$	$\mathrm{CH_3SiBr_3}$	$\mathrm{CH_3SiBr_2Cl}$	$\mathrm{CH_3SiBrCl_2}$	$\mathrm{CH_3SiCl_3}$
0.438[b] (0.441)[c]	0.854[b] (0.855)[c]	14.5 (14.4)[d]	– (0.2)	– (0.0)	– (0.0)	50.2 (49.9)	27.5 (28.1)	6.8 (6.6)	1.0 (0.7)
0.938 (0.900)	0.687 (0.692)	29.8 (29.9)	0.9 (1.3)	– (0.0)	– (0.0)	14.7 (13.5)	27.0 (26.1)	20.4 (21.0)	7.1 (8.1)
1.219 (1.206)	0.594 (0.596)	37.2 (37.1)	3.0 (3.4)	– (0.1)	– (0.0)	3.1 (3.2)	14.3 (13.4)	23.6 (23.3)	18.7 (19.4)
1.439 (1.412)	0.520 (0.520)	38.1 (38.0)	8.8 (9.1)	1.2 (0.8)	– (0.0)	0.4 (0.3)	4.5 (3.4)	15.8 (15.3)	31.3 (33.0)
1.710 (1.694)	0.430 (0.432)	23.4 (22.8)	23.4 (23.4)	8.7 (8.9)	1.4 (1.8)	– (0.0)	– (0.2)	4.3 (4.2)	38.9 (38.6)
2.019 (1.980)	0.327 (0.340)	9.8 (8.9)	24.3 (23.5)	23.1 (23.0)	8.9 (11.9)	– (0.0)	– (0.0)	1.2 (1.3)	32.8 (31.3)
2.480 (2.440)	0.160 (0.164)	1.5 (1.2)	12.7 (9.7)	26.1 (28.7)	43.3 (44.4)	– (0.0)	– (0.0)	– (0.2)	16.4 (15.8)

SYSTEM[e] $\mathrm{CH_3GeI_3}$ vs. $\mathrm{CH_3SiBr_3}$

$\underline{R} \equiv$ I/(Si+Ge)	$\underline{R}' \equiv$ Si/(Si+Ge)	$\mathrm{CH_3GeI_3}$	$\mathrm{CH_3GeI_2Br}$	$\mathrm{CH_3GeIBr_2}$	$\mathrm{CH_3GeBr_3}$	$\mathrm{CH_3SiI_3}$	$\mathrm{CH_3SiI_2Br}$	$\mathrm{CH_3SiIBr_2}$	$\mathrm{CH_3SiBr_3}$
0.376 (0.362)	0.875 (0.869)	5.3 (6.4)	5.4 (3.1)	2.0 (2.2)	0.3 (0.8)	– (0.0)	0.2 (0.7)	6.9 (8.4)	79.8 (78.3)
0.902 (0.820)	0.733 (0.724)	16.1 (20.3)	8.9 (4.7)	1.9 (1.5)	0.6 (0.3)	0.4 (0.2)	1.1 (2.4)	10.5 (13.1)	60.4 (57.5)
0.979 (0.932)	0.674 (0.687)	19.9 (22.9)	9.2 (6.5)	1.8 (2.7)	0.5 (0.6)	0.2 (0.1)	1.2 (1.5)	10.5 (10.2)	56.8 (55.5)
1.244 (1.249)	0.585 (0.584)	29.3 (30.9)	10.4 (7.5)	1.6 (2.6)	0.3 (0.5)	0.3 (0.1)	1.5 (1.8)	10.8 (10.1)	45.8 (46.5)
1.503 (1.458)	0.499 (0.509)	36.1 (39.2)	11.1 (8.1)	1.5 (2.4)	0.4 (0.4)	0.5 (0.2)	1.4 (2.0)	9.5 (9.6)	39.5 (38.1)
1.826 (1.794)	0.391 (0.399)	47.3 (49.9)	11.2 (8.6)	1.6 (2.1)	0.2 (0.3)	0.2 (0.2)	1.7 (2.1)	9.7 (8.6)	28.3 (28.2)
2.296 (2.305)	0.235 (0.232)	65.9 (66.7)	10.3 (8.2)	0.6 (1.5)	0.0 (0.1)	0.5 (0.3)	1.5 (2.2)	7.2 (6.3)	14.0 (14.7)

SYSTEM[f] $\mathrm{CH_3GeI_3}$ vs. $\mathrm{CH_3SiCl_3}$

$\underline{R} \equiv$ Cl/(Si+Ge)	$\underline{R}' \equiv$ Si/(Si+Ge)	$\mathrm{CH_3GeI_3}$	$\mathrm{CH_3GeI_2Cl}$	$\mathrm{CH_3GeICl_2}$	$\mathrm{CH_3GeCl_3}$	$\mathrm{CH_3SiI_3}$	$\mathrm{CH_3SiI_2Cl}$	$\mathrm{CH_3SiICl_2}$	$\mathrm{CH_3SiCl_3}$
0.437[b] (0.456)[c]	0.146[b] (0.151)[c]	83.9 (84.7)[d]	1.1 (0.7)	– (0.0)	– (0.0)	– (0.0)	– (0.0)	0.8 (0.7)	14.3 (13.8)
0.755 (0.758)	0.252 (0.250)	73.3 (73.9)	1.7 (0.9)	– (0.0)	– (0.0)	– (0.0)	0.2 (0.0)	0.5 (0.9)	24.3 (24.3)
1.235 (1.240)	0.412 (0.411)	57.1 (57.8)	1.7 (1.0)	– (0.0)	– (0.0)	– (0.0)	0.3 (0.0)	0.4 (1.0)	40.4 (40.1)
1.440 (1.410)	0.480 (0.465)	51.4 (51.0)	2.1 (1.0)	– (0.0)	– (0.0)	– (0.0)	0.1 (0.0)	0.4 (1.1)	46.0 (46.9)
1.892 (1.900)	0.631 (0.629)	35.1 (35.9)	2.1 (1.0)	– (0.0)	– (0.0)	– (0.0)	0.4 (0.0)	– (1.0)	62.5 (62.1)
1.949 (1.980)	0.650 (0.657)	32.8 (34.0)	1.5 (1.0)	– (0.0)	– (0.0)	– (0.0)	0.3 (0.0)	– (1.0)	65.4 (64.0)
2.481 (2.503)	0.827 (0.834)	15.6 (16.5)	1.0 (0.8)	– (0.0)	– (0.0)	– (0.0)	– (0.0)	0.9 (0.8)	82.5 (81.9)

[a] Equilibrium reached in less than 22 hr. at 120°; data correspond to 151 hr. at 120° with the samples run immediately after quenching to room temperature

[b] From the ingredients

[c] Values in parentheses are calculated from the n.m.r. data

[d] Values in parentheses are calculated from the constants in Table II

[e] Equilibrium reached in less than 5 hr. at 120°; data correspond to 70 hr. at 120° with the samples run immediately after quenching to room temperature

[f] Equilibrium reached in less than 20 hr. at 120°; data correspond to 173 hr. at 120° with the samples run immediately after quenching to room temperature

Thus, the reported values for the equilibrium constants K_{Qt} and K_I must correspond closely to 120°.

Inspection of the data in Table III shows generally good agreement between the experimentally measured concentrations of the eight components present at equilibrium and the values calculated from the equilibrium constants. Because of this and the absence of systematic deviations with changing R value, there was no need to use activity coefficients to make the thermodynamic concept of equilibria fit the data within the experimental error. The experimental error of the data of Table III for each peak measured is about 1% of the total hydrogen in all peaks [*i.e.*, 1% of the total (Si + Ge)]. Furthermore, generally good agreement

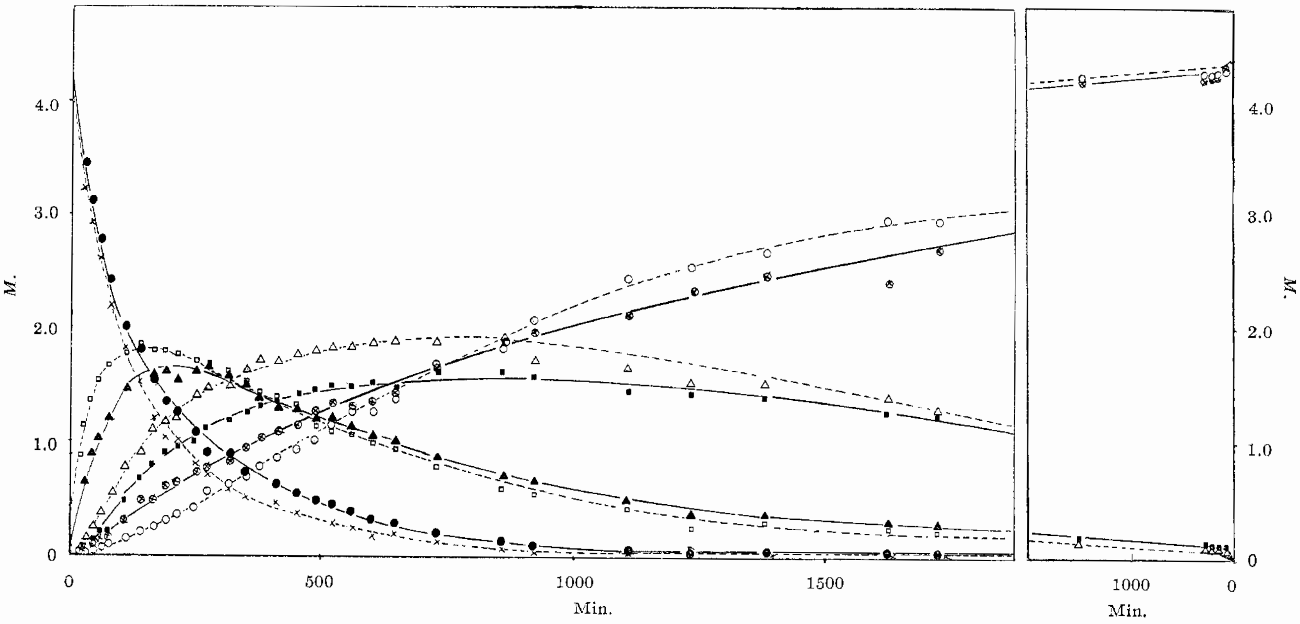

Figure 1.—Kinetics of the reaction of equimolar amounts of CH_3SiBr_3 and CH_3GeCl_3 (left-hand graph) and CH_3SiCl_3 and CH_3GeBr_3 (right-hand graph) in the neat liquid state at 35°. The solid lines represent the silicon compounds and the broken lines the germanium compounds: ●, CH_3SiBr_3; ▲, CH_3SiBr_2Cl; ■, $CH_3SiBrCl_2$; ⊗, CH_3SiCl_3; O, CH_3GeBr_3; △, CH_3GeBr_2Cl; □, $CH_3GeBrCl_2$; ×, CH_3GeCl_3.

was found between the values for the equilibrium constants K_{Qi} and K_{Mi} obtained from the data of Table III and measured on either the methylsilicon or the methylgermanium system independently.

The relatively small values of K_I as compared to the value of this constant for ideal random sorting of substituents, $(K_I)_{rand} = 1$, indicate that there is a pronounced preference of a given central moiety for one of the two substituents involved in the scrambling. It turns out that the methylsilicon moiety is always preferentially associated with the halogen which is located higher in the periodic table, thus leaving the halogen appearing lower in the table to the methylgermanium moiety. For the pair Cl and Br, the methylsilicon moiety is preferentially bonded to the Cl; for the pair Br and I, to the bromine; and, for the pair Cl and I, to the chlorine atoms. This tendency is about twice as strong for the latter case than for the first two cases. Similar preferences have also been observed for the scrambling equilibria of halogen atoms between the dimethylsilicon and dimethylgermanium moieties.[2]

Since there is no reason for a block of either three Z or three T substituents to be preferentially associated with either a Q or an M moiety, the value of K_I corresponding to statistically random sorting of the T and Z substituents must equal unity. By definition, a random system is completely entropy controlled so that $\Delta S_{rand} = -R \ln K_{rand}$. Because $(K_I)_{rand} = 1$, it is seen that $\Delta S_{rand} = 0$ for eq 5; and, since ΔS_{rand} should account for practically the entirety of the entropy of any nonrandom reaction, we see that $\Delta H \approx \Delta F° = -RT \ln K$ for eq 5. The values of ΔH thus estimated are compared as follows with values (in parentheses) calculated from the difference between the 120° data of Table III and remeasurements after standing for 1.0 year at 25°: for Z = Cl, T = Br, +9.0 kcal (+9.2 kcal); Z = Br, T = I, +7.9 (+12); and Z = Cl, T = I, +21.2 (+19). It should be noted that the experimentally determined values for the larger enthalpies are rather inaccurate since the differences (with temperature change) of the observed concentrations are small, being significant only in the composition region of equimolar reagent mixtures.

The σ-bond contribution to the enthalpy of the reaction of eq 5 may be estimated from the defining equation of Pauling bond energies which reduces to the following form in this case

$$\Delta H\ (\text{kcal}) = 138(\chi_Q - \chi_M)(\chi_Z - \chi_T)$$
$$= 14(\chi_Z - \chi_T),\ \text{for}\ (\chi_Q - \chi_M) = 0.1 \quad (6)$$

Assuming that the difference in electronegativity, χ, between the CH_3Si and CH_3Ge moieties is 0.1, the σ-bond enthalpies of eq 5 are: for Z = Cl, T = Br, +3 kcal; Z = Br, T = I, +4; and Z = Cl, T = I, +7. The differences between these values and the ones listed in the preceding paragraph are attributable to π bonding.

Kinetic Studies.—Upon mixing methyltribromosilane with an equimolar amount of methyltrichlorogermane as neat liquids at 35°, the resulting sequence of reactions may be followed by proton nmr to give the kinetic curves shown in the left-hand graph of Figure 1. The reverse reaction resulting from combining methyltrichlorosilane with an equimolar amount of methyltribromogermane is shown as the right-hand graph of the figure. The first reaction of the left-hand graph is obviously

$$CH_3SiBr_3 + CH_3GeCl_3 \longrightarrow CH_3SiClBr_2 + CH_3GeCl_2Br \quad (7)$$

The data for the scrambling of chlorine with bromine on the methylsilicon moiety show that substituent exchange between the various silicon halides is probably too slow to have much effect on the course of the reactions shown in Figure 1. On the other hand, scrambling of chlorine and bromine on the methylgermanium moiety is fast and should play a major role in the reactions of Figure 1. Indeed, once a small amount of the halogen from the methylsilicon starting compound has been transferred to the methylgermanium moiety, it is found that the methylgermanium halides come into equilibrium with each other and remain in a state of dynamic equilibrium throughout the entire course of the reaction. From all of the experimental points given in Figure 1, we calculate a value of $K_{Ge2} = [CH_3GeCl_3][CH_3GeClBr_2]/[CH_3GeCl_2Br]^2$ equal to 0.42 ± 0.03 and a $K_{GeI} = [CH_3GeCl_2Br][CH_3GeBr_3]/[CH_3GeClBr_2]^2$ of 0.40 ± 0.03. These values are within 1 standard error of the equivalent ones given in Table V.

The second major reaction for transferring a bromine from the methylsilicon to the methylgermanium moiety in the graph shown on the left of Figure 1 appears to be

$$CH_3SiClBr_2 + CH_3GeCl_2Br \longrightarrow CH_3SiCl_2Br + CH_3GeClBr_2 \quad (8)$$

since the maxima in the amounts of $CH_3SiClBr_2$ and CH_3GeCl_2Br appear at about the same time. Likewise, since the $CH_3SiBrCl_2$ and $CH_3GeClBr_2$ also maximize together, the third major reaction of the left-hand graph seems to be

$$CH_3SiCl_2Br + CH_3GeClBr_2 \longrightarrow CH_3SiCl_3 + CH_3GeBr_3 \quad (9)$$

The fact that the methylgermanium compound in the pairs of compounds $CH_3SiCl_iBr_{3-i}$ and $CH_3GeCl_{3-i}Br_i$ for *i* being either 1 or 2 is present in somewhat larger relative amounts at the maximum value than the methylsilicon compound shows the presence of more exchange-pair processes than those of eq 7–9.

Indeed, a detailed analysis of the situation[11] shows that there are six fast exchange-pair reactions (three forward and three their reverse) leading to equilibration between the various methylgermanium halides plus 18 (half forward, half reverse) which need be considered for interpreting the exchange of chlorine with bromine between the methylsilicon and methylgermanium moieties. In addition to the three major forward reactions out of the 18 (*i.e.*, the reactions of eq 7–9), it appears that a significant contribution of the reaction between CH_3GeCl_3 and $CH_3SiClBr_2$ is needed to explain the initially faster generation of CH_3GeCl_2Br than of $CH_3SiClBr_2$ in the first part of the left-hand graph of Figure 1.

TABLE IV

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA IN MOLE PER CENT FOR SUBSTITUENT INTERCHANGE ON THE METHYLGERMANIUM AND METHYLSILICON MOIETY[a]

The System[b] CH_3GeCl_3 vs. CH_3GeBr_3

R ≡ Cl/Ge	CH_3GeBr_3	CH_3Ge-Br_2Cl	CH_3Ge-$BrCl_2$
0.526[c]	57.7[d]	34.1	7.7
(0.513)[e]	(57.2)[f]	(33.7)	(8.2)
1.222	27.4	40.3	25.8
(1.117)	(26.9)	(40.8)	(25.7)
1.502	15.0	36.0	35.6
(1.477)	(14.6)	(35.3)	(35.5)
1.765	8.3	28.7	39.5
(1.785)	(8.7)	(28.8)	(39.8)
2.492	1.5	8.9	34.2
(2.438)	(0.8)	(7.7)	(33.1)

The System[h] CH_3GeI_3 vs. CH_3GeCl_3

R ≡ Cl/Ge	CH_3GeI_3	CH_3Ge-I_2Cl	CH_3Ge-ICl_2
0.688[c]	51.2[d]	30.8	13.2
(0.716)[e]	(52.4)[f]	(30.5)	(12.8)
0.838	43.9	32.1	17.0
(0.871)	(45.4)	(32.0)	(16.2)
1.688	15.7	25.7	29.9
(1.716)	(16.3)	(26.1)	(30.1)
1.974	9.5	19.9	31.5
(2.005)	(9.9)	(20.8)	(31.5)
2.471	2.1	8.5	26.9
(2.495)	(2.4)	(9.4)	(27.0)

The System[g] CH_3GeBr_3 vs. CH_3GeI_3

R ≡ I/Ge	CH_3GeI_3	CH_3Ge-I_2Br	CH_3Ge-IBr_2
0.408[c]	0.6[d]	5.4	28.8
(0.414)[e]	(0.4)[f]	(5.4)	(28.8)
0.754	2.4	14.2	38.8
(0.744)	(2.4)	(14.6)	(39.0)
1.233	8.4	27.9	39.9
(1.209)	(9.0)	(28.4)	(39.5)
1.652	18.8	36.6	32.4
(1.620)	(19.6)	(37.4)	(31.7)
2.171	38.4	39.9	18.2
(2.132)	(40.4)	(39.4)	(17.1)

The System[i] CH_3SiCl_3 vs. CH_3SiBr_3

R ≡ Cl/Si	CH_3SiBr_3	CH_3Si-Br_2Cl	CH_3Si-$BrCl_2$
0.400[c]	66.8[d]	27.7	5.1
(0.391)[e]	(66.0)[f]	(28.3)	(5.3)
0.878	38.7	40.2	18.0
(0.855)	(37.7)	(40.2)	(18.6)
1.407	17.6	36.7	33.5
(1.403)	(17.4)	(36.7)	(33.6)
1.939	5.7	23.8	41.3
(1.937)	(5.8)	(23.6)	(41.4)
2.460	1.2	8.2	34.5
(2.452)	(0.9)	(8.3)	(34.3)

[a] Percentages for the one compound not listed in each system are 100% minus sum of values for other compounds.
[b] Data obtained after 2 hr. at 120° but the rapid rate of equilibration probably means that the respective temperature is that of the n.m.r. probe, 33°.
[c] Values calculated from ingredients.
[d] Data obtained from n.m.r. peak areas.
[e] Values in parentheses are calculated from n.m.r. peak areas.
[f] Data in parentheses are calculated from the equilibrium constants in Table V.
[g] Data obtained after 70 hr. at 120° but probably correspond to 33°.
[h] Data obtained after 144 hr. at 25°.
[i] Equilibrium was reached in less than 20 hr. at 120°; data correspond to 40 hr. at 120°.

The right-hand graph of Figure 1 is considerably less complicated than the left-hand graph since the equilibrium is close to the starting composition and the reaction rate is slow. The main exchange-pair reaction is the reverse of the final major reaction (eq 9) used to explain the curves given in the left-hand graph. The equilibrium constant of eq 9 is equal to

$$\sqrt[3]{K_{Si1}K_{Si2}{}^2K_{Ge1}{}^2K_{Ge2}/K_I} = 9$$

a value which agrees to about one order of magnitude with the ratio of the forward and reverse rate constants, using reasonable assumptions in estimating these rate constants from the terminal portion of the curves on the left of Figure 1 and from the curves on the right.

Halogen Exchange on either CH_3Si or CH_3Ge

The experimental data for the determination of some of the equilibrium constants for the exchange of halogen atoms on either the methylsilicon or the methylgermanium moiety independently are listed in Table IV. The relative concentrations of the four species present in each system at equilibrium were determined by proton nmr. The following nmr chemical shifts (in ppm relative to TMS as internal standard) were observed in neat equilibrated samples of 1:1 mole ratios of the two components: System CH_3GeCl_3 *vs.* CH_3GeBr_3:

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[11] These exchange-pair processes may be symbolized in terms of the number of chlorine atoms per compound with the compound donating the chlorine to the other being listed first and a prime being used to identify the germanium species. Thus, in this short-form numerical notation, the exchange-pair reactions (regardless of the detailed mechanism) of eq 7–9 may be denoted as 3′0, 2′1, and 1′2, respectively. The full set of possible exchange-pair reactions for the case of both central moieties exhibiting three exchangeable substituents are given in this notation as follows. For interchanges between the methylgermanium and the methylsilicon moieties, 3′0 with the reverse reaction 12′, 2′0 with 11′, 3′1 with 22′, 2′1 with 21′, 3′2 with 32′, 1′0 with 10′, 1′2 with 30′, 2′2 with 31′, and 1′1 with 20′. For exchanges between the methylgermanium compounds themselves, there are three forward reactions—3′0′, 3′1′, 2′0′—and the three reverse ones—1′2′, 2′2′, and 1′1′, respectively. Likewise, there is yet another similar set of six exchange-pair reactions (but not primed) for the reactions between the methylsilicon compounds by themselves—reactions which are too slow to be of significance to the kinetic work reported in Figure 1.

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).

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Tetra(alkylsilicon) Hexachalcogenides

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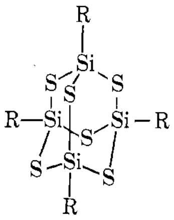
A new class of compounds with the adamantane structural unit has been prepared from alkylsilanes or alkylchlorosilanes and hydrogen sulfide or hydrogen selenide. These compounds have the composition $(RSi)_4S_6$ and $(RSi)_4Se_6$. The silicon atoms serve as the tertiary atoms, and the sulfur or selenium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



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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.

(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).