

Results and Discussion

The O¹⁷ n.m.r. spectrum of XeO¹⁷F₄ appeared as a triplet with a strong central peak and two symmetrically disposed satellites. A similar picture was found by Brown, *et al.*,⁴ for the F¹⁹ n.m.r. spectrum of XeOF₄.

The O¹⁷ chemical shift using water as an external reference was -313 ± 2 p.p.m. The spacing between the two satellites was 692 ± 10 c.p.s., which apparently is the coupling constant between Xe¹²⁹ and O¹⁷. Indeed the ratio of the intensities of the main peak to each of the two satellites as determined from the ratio of the recorded area on the chart was found to be 5.6, as would be expected if the satellites are due to Xe¹²⁹ (spin $1/2$, natural abundance 26.2%) species and the main peak is due to all the other xenon isotopes. The failure to observe splitting due to coupling with Xe¹³¹ (spin $3/2$, abundance 21.2%) may be caused by fast relaxation due to the quadrupole moment of this nucleus in the asymmetric environment in the molecule. The large Xe¹²⁹-O¹⁷ spin-spin coupling observed in XeO¹⁷F₄ is of interest for the elucidation of the bonding in xenon compounds. This has recently

been discussed in connection with the calculation of chemical shifts where the magnitude of the coupling was found to lend support to the model involving d-orbital participation.⁸ It is of interest that the line width of the central peak is about 130 c.p.s. and that of the satellites about 110 c.p.s. It is apparent that the central peak which includes the Xe¹³¹ species is somewhat broader owing to incomplete averaging of the splitting.

The position of the O¹⁷ resonance line in XeOF₄ is to lower field than that of xenic acid³ which indicates greater double bond character of the xenon-oxygen bond in the former. However, it is still at a higher field than that of double-bonded oxygen (-500 to -600 p.p.m.) in most compounds⁹ which may in part be due to hydrogen bonding with the HF present.¹⁰

Acknowledgment. We (J. R. and D. S.) are grateful to Dr. Z. Luz for his comments on the manuscript.

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Exchange of Parts between Molecules at Equilibrium. VII. Scrambling of Sulfur with Halogens on Dimethylgermanium

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Exchange on the dimethylgermanium moiety of the monofunctional thiomethyl group or of bridging sulfur with either chlorine, bromine, or iodine atoms has been studied by proton nuclear magnetic resonance. The resulting equilibria were found to deviate considerably from the statistically random case. Equilibrium constants are presented for the systems (CH₃)₂GeX₂ vs. (CH₃)₂Ge(SCH₃)₂, where X = Cl, Br, or I. For the systems involving bridging sulfur, (CH₃)₂GeX₂ vs. [(CH₃)₂-GeS], it is shown that the resulting equilibrium compositions are mixtures of chain and ring molecules, with the trimeric ring compound [(CH₃)₂GeS]₃ being present in large amounts. Equilibrium constants are given for the distribution of structure-building units between the various sized chains and the trimeric ring.

In earlier studies from this laboratory, we have demonstrated that the equilibria resulting from exchange on the dimethylsilicon moiety of bridging sulfur with halogen atoms is shifted strongly toward the ring compounds,¹ with the trimer predominating over the dimer. The exchange of the same substituents on the dimethyltin moiety,² however, proceeded so fast that fine structure due to different types of build-

ing units could not be resolved by nuclear magnetic resonance (n.m.r.). It was therefore of interest to study the rate of equilibration and the resulting equilibria for exchange of bridging sulfur with halogen atoms on the dimethylgermanium moiety and to relate these data to the results reported earlier for the analogous silicon and tin compounds. In addition, the exchange on the dimethylgermanium moiety of halogen atoms with thiomethyl groups was investigated in order to compare the equilibrium constants for the *neso* compounds³ with those obtained for the related families of compounds based on Ge-S-Ge molecular backbones.

Experimental

Materials. Dimethyldichlorogermane and dimethyldibromogermane were prepared according to a modified version⁴ of Rochow's direct synthesis⁵ from metallic germanium (purchased from A. D. Mackay, Inc.) and methyl chloride and methyl bromide, respectively. Dimethyldiiodogermane was made by following the procedure worked out by Anderson⁶ for the corresponding *n*-propyl compound, b.p. 190° (760 mm.), as well as by the direct synthesis.⁴ Di-

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methylbis(thiomethyl)germane was obtained by stirring 80 g. (0.27 mole) of lead mercaptide with 53 g. (0.2 mole) of dimethyldibromogermane in 300 ml. of benzene for 48 hr. at room temperature, b.p. 42° (0.1 mm.), yield 25 g. (64%). Crystalline dimethylgermanium sulfide was prepared as described in the literature.⁷ Proton n.m.r. showed that the carefully purified materials were free of hydrogen-containing impurities (<0.2% of the total hydrogen in a given resonance).

Equilibration. Equilibrium was achieved by heating the desired proportions of starting materials in sealed 5-mm. o.d. precision n.m.r. tubes at 120°. The time required for reaching equilibrium was estimated on the basis of test runs at several different ratios of starting materials held for various time intervals until the proton n.m.r. spectra did not exhibit any further change.

The reported equilibrium values correspond to very much longer times. Thus, equilibria in the systems (CH₃)₂GeX₂ vs. (CH₃)₂Ge(SCH₃)₂ were measured after 12 hr. at 120° for X = Cl, 2 hr. at 120° for X = Br, and 1 hr. at 120° for X = I. Equilibria in the systems (CH₃)₂GeX₂ vs. [(CH₃)₂GeS] were measured after 3 hr. at 120° for X = Cl, 72 hr. for X = Br, and 130 hr. at this temperature for X = I. Methyl groups directly attached to Ge do not undergo exchange under the above conditions.⁸

Proton n.m.r. spectra were obtained on a Varian Model A-60 spectrometer as previously described,⁹ with measurements being carried out on the neat liquids except in those cases where solids precipitated at room temperature, where 1:1 or 1:3 solutions (v./v.) of the quenched samples in carbon tetrachloride were used. As is shown in the rate study of Figure 2, the rate of equilibration is sufficiently slow so that immediate dilution of quenched samples does not disturb the equilibria in the systems involving the dimethylgermanium sulfide families of compounds. Chemical shifts of the observed n.m.r. signals for these systems are reported in Tables III, IV, and V. Proton n.m.r. shifts, which vary somewhat with the over-all composition of the *neso* systems (CH₃)₂GeX₂ vs. (CH₃)₂Ge(SCH₃)₂ are reported only for neat liquids having the over-all composition $R = X/Ge \sim 1$. These shifts are given below in terms of p.p.m. from tetramethylsilane (internal standard). (CH₃)₂GeCl₂, -1.230; (CH₃)₂GeCl(SCH₃), -2.210 (CH₃S), -0.991 (CH₃Ge); (CH₃)₂Ge(SCH₃)₂, -2.086 (CH₃S), -0.734 (CH₃Ge); (CH₃)₂GeBr₂, -1.522; (CH₃)₂GeBr(SCH₃), -2.197 (CH₃S), -1.128 (CH₃Ge); (CH₃)₂Ge(SCH₃)₂, -2.078 (CH₃S), -0.737 (CH₃Ge); (CH₃)₂GeI₂, -1.892; (CH₃)₂GeI(SCH₃), -2.100 (CH₃S), -1.292 (CH₃Ge); (CH₃)₂Ge(SCH₃)₂, -2.017 (CH₃S), -0.725 (CH₃Ge). The variations in these values with changes in the over-all composition were of the order of 0.01 p.p.m.

Peak areas were determined by electronic integration and, in cases where there was considerable overlap, by cutting out and weighing Xerox copies of the spectra.

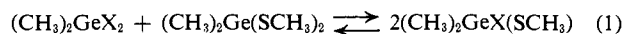
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Results and Discussion

Halogen-Thiomethyl Exchanges. The experimental data for the equilibria described by eq. 1 are presented



in Table I. These data were employed to calculate¹⁰

Table I. Experimental and Calculated Equilibrium Data (in Mole %) for the Substituent Interchange (X vs. SCH₃) in the Systems (CH₃)₂GeX₂ vs. (CH₃)₂Ge(SCH₃)₂ at 120°

X	R ≡ X/Ge	(CH ₃) ₂ GeX ₂	(CH ₃) ₂ -GeX-(SCH ₃)	(CH ₃) ₂ -Ge-(SCH ₃) ₂
Cl	0.368 ^a	1.1	35.2	63.7
	(0.374) ^b	(1.0) ^c	(34.7)	(64.2)
	0.802	8.1	64.4	27.4
	(0.807)	(8.1)	(64.0)	(27.9)
	1.131	24.2	65.7	10.1
	(1.141)	(23.4)	(66.3)	(10.3)
	1.401	45.3	51.8	3.0
	(1.423)	(43.6)	(52.9)	(3.5)
	1.703	72.3	27.4	0.4
	(1.719)	(70.9)	(28.4)	(0.6)
Br	0.458	0.9	43.1	56.0
	(0.449)	(0.9)	(44.0)	(55.1)
	0.752	3.8	68.4	27.8
	(0.761)	(3.9)	(67.3)	(28.7)
	1.070	16.6	74.6	8.8
	(1.077)	(15.9)	(75.3)	(8.9)
	1.376	43.3	55.7	0.9
	(1.424)	(39.7)	(58.2)	(2.1)
	1.674	73.5	26.2	0.2
	(1.733)	(67.8)	(31.9)	(0.4)
I	0.471	0.5	46.2	53.4
	(0.471)	(0.5)	(46.1)	(53.4)
	0.778	2.5	72.1	25.4
	(0.772)	(2.6)	(72.6)	(24.8)
	1.052	11.0	81.6	7.4
	(1.037)	(12.0)	(81.2)	(6.8)
	1.356	37.0	61.4	1.7
	(1.353)	(36.9)	(61.8)	(1.3)
	1.658	68.1	31.7	0.2
	(1.679)	(66.0)	(33.8)	(0.2)

^a Values calculated from ingredients. ^b Values in parentheses calculated from n.m.r. peak areas of the (CH₃)₂Ge region of the spectra. ^c Values in parentheses calculated from the equilibrium constants given in Table II.

the equilibrium constants for substituent interchange listed in Table II. In turn, the equilibrium constants

Table II. Equilibrium Constants for the Systems (CH₃)₂GeX₂ vs. (CH₃)₂Ge(SCH₃)₂ at 120°

X	K ^a	s ^b
Cl	0.055	0.005
Br	0.025	0.008
I	0.0123	0.0011
Ideal randomness	0.250	

^a $K = [(CH_3)_2GeX_2][(CH_3)_2Ge(SCH_3)_2]/[(CH_3)_2GeX(SCH_3)]^2$
^b s = standard error.

were used for calculating¹⁰ the values given in parentheses in Table I where the agreement of the experimental and calculated values is seen to be good. It is apparent from Table II that the exchange of halogen

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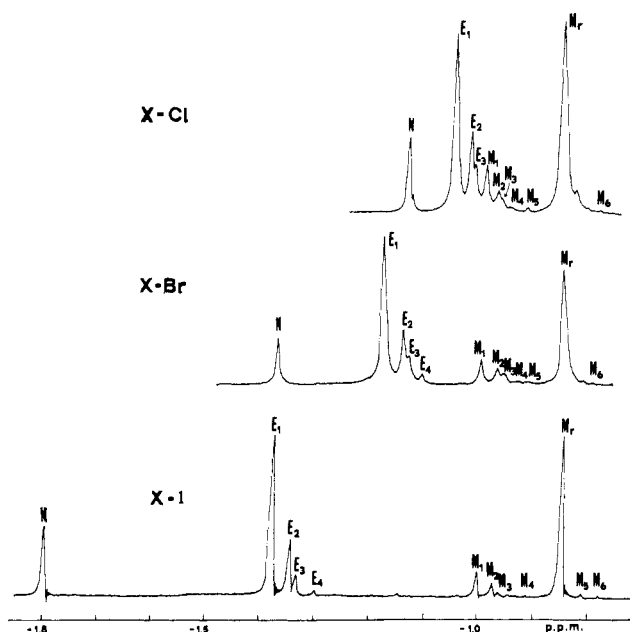
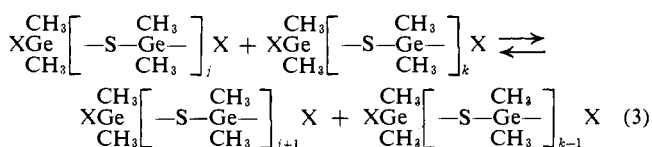
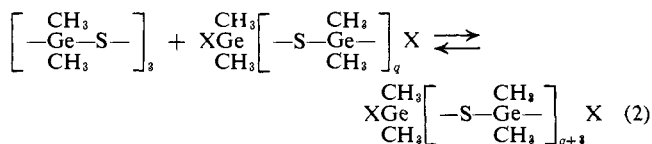


Figure 1.

atoms with the thiomethyl groups on the dimethylgermanium moiety is quite nonrandom (methyl groups directly attached to germanium did not exchange under the conditions of the equilibration), with the mixed species $(\text{CH}_3)_2\text{GeX}(\text{SCH}_3)$ being preferred. The equilibrium constants given in Table II decrease when going from $\text{X} = \text{Cl}$ to Br to I , indicating a greater degree of nonrandomness of the exchange equilibria in the order $\text{I} > \text{Br} > \text{Cl}$. Assuming that the entropy term in the reaction of eq. 1 is due entirely to the entropy of mixing,¹¹ we can estimate the enthalpy, ΔH , of formation of 1 mole of $(\text{CH}_3)_2\text{GeX}(\text{SCH}_3)$ from 0.5 mole of $(\text{CH}_3)_2\text{GeX}_2$ and 0.5 mole of $(\text{CH}_3)_2\text{Ge}(\text{SCH}_3)_3$. The values of ΔH thus calculated for 25° are -0.6 kcal. for $\text{X} = \text{Cl}$, -0.9 kcal. for $\text{X} = \text{Br}$, and -1.2 kcal. for $\text{X} = \text{I}$.

A qualitative study of the rate of exchange in the neat liquids indicates that the over-all process (eq. 1) appears to be fastest for $\text{X} = \text{I}$ with equilibrium being reached for all compositions in less than 2 hr. at room temperature. Less than 30 hr. at this temperature was required for the equilibration in the systems with $\text{X} = \text{Br}$ and more than 100 hr. for $\text{X} = \text{Cl}$.

Halogen vs. Bridging Sulfur Exchange. Proton n.m.r. spectra of equilibrated samples of dimethyldihalo-germanes and dimethylgermanium sulfide, as shown in Figure 1, are interpretable in terms of molecular equilibria of the type ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$)



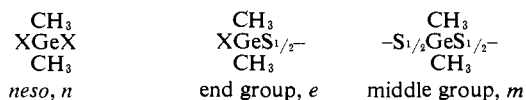
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Table III. Experimental and Calculated Percentage of Total Germanium in Various Building Units in the System $(\text{CH}_3)_2\text{GeCl}_2$ vs. $[(\text{CH}_3)_2\text{GeS}]$ at Equilibrium at 120°

R = Cl/Ge	Chemical shift, p.p.m.										
	-1.167	-1.092	-1.053	-1.045	-1.023	-1.003	-0.992	-0.947	-0.893	-0.855	
	Assignment										
	ee	eme	enm	eme	emr	emr	emr	emr	emr	emr	emr
0.197 ^a	2.4	4.3	1.4	1.9	1.9	1.0	1.9	1.4	74.1	0.4	
(0.196) ^b	(2.7) ^c	(3.6)	(3.4)	(1.8)	(1.7)	(1.6)	(0.4)	(0.8)	(76.4)	(0.8)	
0.370	4.7	7.9	2.1	2.8	1.7	2.8	2.1	1.7	57.1	1.4	
(0.351)	(5.4)	(6.0)	(5.0)	(3.0)	(2.7)	(2.2)	(0.6)	(1.0)	(60.2)	(1.0)	
0.604	8.9	11.2	3.1	4.5	1.6	2.9	1.9	1.2	38.3	1.0	
(0.574)	(10.1)	(8.9)	(5.8)	(4.4)	(1.4)	(2.3)	(0.7)	(0.9)	(40.5)	(0.9)	
0.804	14.7	12.3	3.2	6.4	2.0	2.0	1.2	0.8	22.3	0.6	
(0.795)	(16.4)	(10.5)	(5.4)	(5.2)	(3.6)	(1.8)	(0.6)	(0.6)	(24.9)	(0.6)	
1.003	23.8	11.1	2.2	4.7	1.7	3.3	13.7	0.7	
(0.992)	(23.7)	(10.5)	(4.2)	(5.3)	(3.0)	(1.2)	(0.4)	(0.3)	(14.2)	(0.3)	
1.199	33.1	8.9	2.9	4.3	1.0	2.4	6.8	(0.4)	
(1.175)	(32.4)	(9.2)	(2.7)	(4.6)	(2.1)	(0.6)	(0.2)	(0.1)	(7.2)	(0.1)	
1.393	46.3	5.6	2.0	3.1	1.3	1.3	3.0	0.5	
(1.372)	(44.5)	(6.6)	(1.3)	(3.3)	(1.1)	(0.2)	(0.1)	(0.0)	(2.6)	(0.0)	
1.597	62.5	2.6	1.3	1.6	1.6	2.5	0.1	
(1.567)	(59.5)	(3.5)	(0.4)	(1.7)	(0.4)	(0.0)	(0.0)	(0.0)	(0.7)	(0.0)	
1.798	80.6	1.6	...	1.0	1.0	0.3	
(1.782)	(78.7)	(0.9)	(0.0)	(1.1)	(0.0)	(0.0)	(0.0)	(0.0)	(0.1)	(0.0)	

^a From the ingredients. ^b Calculated from the n.m.r. data. ^c Calculated from $K_1 = 0.09$ and $K_3^\circ = 50$, using the R values from the n.m.r. data.

where $q \geq 0, j \geq 0$, and $k \geq i \geq 1$. Molecules present in the equilibrium mixture are made up of the three types of building units



N.m.r. Assignments. The dimethylgermanium sulfide as prepared⁷ or in reorganized mixtures showed a single sharp peak in the range of -0.89 to -0.83 p.p.m. depending on the halogen in the *neso* compound. This sharp resonance was seen in all three systems investigated, and n.m.r. measurements taken immediately after dissolution at room temperature of additional crystalline dimethylgermanium sulfide in various equilibrated mixtures showed that the presence of the newly added sulfide, which could not have reacted in that short time, only intensified this one sharp resonance and did not cause peak broadening or produce or intensify other resonances. Since cryoscopic and tensimetric measurements by Brown and Rochow⁷ gave strong support to a trimeric formulation for the crystalline sulfide, we assume in all following calculations that this resonance corresponds only to the trimeric ring compound.

For the system $(\text{CH}_3)_2\text{GeCl}_2$ vs. $[(\text{CH}_3)_2\text{GeS}]$, the *neso* resonance (N in Figure 1) was seen at -1.167 p.p.m. along with resonances at -1.092 (E_1), -1.053 (E_2), and -1.045 p.p.m. (E_3). From the fact that the latter three resonances formed a cluster and from the variation of the relative intensities of these resonances with the composition parameter $R \equiv \text{Cl/Ge}$, these signals were assigned to end groups in molecules of differing chain length. The peak E_1 was attributed to the *ee* molecule, E_2 to the *eme* molecule and E_3 to the *emm* configuration, the latter comprising all end groups in chains consisting of four or more germanium atoms. In this notation, the boldface letter refers to the group corresponding to the specific n.m.r. peak.

Further upfield from the end-group peaks, there are seen six resonances, M_1 to M_6 , in addition to the signal of the trimeric dimethylgermanium sulfide, M_7 , at -0.893 p.p.m. These six resonances are attributed to middle groups in chains, exhibiting different chemical shifts due to their linkage to other building units having differing shielding effects on the dimethylgermanium moiety. The resonance M_1 at -1.023 p.p.m. is readily assigned to the *eme* molecule because of its constant 1:2 intensity relationship with E_2 . The peak M_2 at -1.017 p.p.m. is attributed to the *emme* molecule, M_3 at -1.002 to middle groups in the arrangement *emmm*, M_4 at -0.992 to the *emmm* molecule, M_5 at -0.947 to *emmmm*, and M_6 at -0.855 to *mmmmm*. Material-balance calculations (as indicated by the good agreement of the R values computed from the ingredients with those obtained from the n.m.r. data) support the assignment of peaks E_1 to E_3 to end groups and M_1 to M_6 to middle groups.

Similar assignments were made in the system $(\text{CH}_3)_2\text{GeBr}_2$ vs. $[(\text{CH}_3)_2\text{GeS}]$. The *neso* compound, $(\text{CH}_3)_2\text{GeBr}_2$, is seen at -1.400 p.p.m.; the signal E_1 at -1.192 is assigned to the *ee* molecule, E_2 at -1.162 to *eme*, E_3 at -1.152 to *emme*, and E_4 at -1.128 to the *emmm* configuration. The signal E_4 was expected to

Table IV. Experimental and Calculated Percentage of Total Germanium in Various Building Units in the System $(\text{CH}_3)_2\text{GeBr}_2$ vs. $[(\text{CH}_3)_2\text{GeS}]$ at Equilibrium at 120°

$R \equiv \text{Br/Ge}$	Resonance, p.p.m.												
	Assignment						Impurities						
	<i>Neso</i>	<i>ee</i>	<i>eme</i>	<i>emmm</i>	<i>eme</i>	<i>emme</i>	<i>emmm</i>	<i>emme</i>	<i>emmm</i>	<i>emme</i>	<i>emmm</i>	<i>emme</i>	
0.254 ^a	1.7	10.9	6.4	0.6	2.2	2.8	1.3	1.1	0.7	68.4	0.7	0.7	0.7
(0.244) ^b	(2.6) ^c	(10.2)	(4.8)	(2.0)	(2.4)	(2.3)	(2.0)	(0.5)	(1.0)	(69.7)	(0.4)	(1.0)	(0.4)
0.406	3.6	18.7	7.4	1.2	4.7	3.4	2.2	1.0	1.0	54.0	0.7	1.0	0.7
(0.365)	(4.3)	(15.7)	(6.9)	(2.4)	(3.5)	(3.0)	(2.4)	(0.7)	(1.1)	(56.8)	(0.4)	(0.7)	(0.4)
0.695	8.4	33.5	11.4	2.3	5.3	3.8	1.7	1.1	0.8	28.0	0.2	0.8	0.2
(0.675)	(10.2)	(30.3)	(10.8)	(2.1)	(5.4)	(3.9)	(2.1)	(0.7)	(0.8)	(29.7)	(0.2)	(0.7)	(0.2)
0.971	19.5	41.7	11.1	2.4	5.1	2.2	2.3	0.9	0.6	10.8	...	0.6	...
(0.976)	(19.7)	(43.0)	(11.3)	(1.1)	(5.6)	(3.0)	(1.1)	(0.4)	(0.3)	(11.7)	(0.0)	(0.3)	(0.0)
1.216	31.0	45.2	7.9	2.3	4.0	1.0	2.6	0.2	0.4	3.0	...	0.4	...
(1.197)	(30.6)	(47.6)	(8.9)	(0.4)	(4.4)	(1.7)	(0.4)	(0.2)	(0.1)	(4.2)	(0.0)	(0.1)	(0.0)
1.471	50.9	37.6	4.3	1.8	1.5	0.5	1.3	0.4
(1.467)	(50.0)	(42.0)	(4.2)	(0.1)	(2.1)	(0.4)	(0.0)	(0.0)	(0.0)	(0.7)	(0.0)	(0.0)	(0.0)
1.733	72.4	23.4	1.4	0.8	0.4	...	0.9	0.4
(1.703)	(71.0)	(27.0)	(1.2)	(0.0)	(0.6)	(0.1)	(0.0)	(0.0)	(0.0)	(0.1)	(0.0)	(0.0)	(0.0)

^a From ingredients. ^b Calculated from the n.m.r. data. ^c Calculated from $K_1 = 0.06$ and $K_2 = 50$, using the R values from the n.m.r. data.

Table V. Experimental and Calculated Percentage of Total Germanium in Various Building Units in the System $(\text{CH}_3)_2\text{GeI}_2$ vs. $[(\text{CH}_3)_2\text{GeS}]$ at Equilibrium at 120° .

R - I/Ge	Resonance, p.p.m.														
	-1.800	-1.362	-1.332	-1.320	-1.303	-1.207	-1.128	-1.032	-0.973	-0.945	-0.935	-0.900	-0.827	-0.775	-0.700
	Assignment														
	<i>neso</i>	<i>ee</i>	<i>eme</i>	<i>emme</i>	<i>emmm</i>	Impurities	<i>eme</i>	<i>emnie</i>	<i>emmm</i>	<i>emmmie</i>	<i>emmmmm</i>	<i>emmmmm</i>	<i>emmmmm</i>	<i>emmmmm</i>	<i>emmmmm</i>
0.226 ^a	2.9	9.1	4.4	1.8	0.7	...	2.0	2.0	0.9	0.9	0.9	0.9	0.9	0.4	1.3
(0.217) ^b	(3.1) ^c	(8.1)	(3.9)	(1.9)	(1.7)	...	(1.9)	(1.9)	(1.7)	(1.7)	(1.7)	(1.7)	(1.7)	(0.8)	(0.4)
0.468	7.0	17.9	8.4	2.8	1.1	...	3.9	3.3	0.9	0.7	0.7	0.7	0.7	0.7	1.4
(0.442)	(7.2)	(17.1)	(7.2)	(3.1)	(2.3)	...	(3.6)	(3.1)	(2.2)	(0.7)	(0.7)	(0.7)	(0.7)	(1.0)	(0.4)
0.710	12.9	30.6	9.6	2.1	0.7	0.5	5.3	3.1	0.8	0.7	0.7	0.7	0.7	0.5	1.0
(0.687)	(13.4)	(26.9)	(9.8)	(3.5)	(2.0)	...	(4.9)	(3.5)	(2.0)	(0.6)	(0.6)	(0.6)	(0.6)	(0.7)	(0.2)
0.970	21.8	38.6	9.2	3.5	1.4	0.6	5.3	2.2	0.8	0.3	0.3	0.3	0.3	0.7	0.2
(0.962)	(22.7)	(36.2)	(10.4)	(3.0)	(1.2)	...	(5.2)	(3.0)	(1.2)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)	(0.1)
1.206	34.4	42.6	7.7	1.6	1.1	0.2	3.9	1.1	0.3	0.4	0.4	0.4	0.4	0.4	0.2
(1.217)	(35.0)	(40.9)	(8.6)	(1.8)	(0.5)	...	(4.3)	(1.8)	(0.5)	(0.2)	(0.2)	(0.2)	(0.2)	(0.1)	(0.0)
1.472	51.9	35.6	4.0	1.2	0.9	0.4	1.8	0.7	...	0.4	0.4	0.4	0.2	0.2	0.4
(1.455)	(50.7)	(38.2)	(5.2)	(0.7)	(0.1)	...	(2.6)	(0.7)	(0.1)	(0.1)	(0.1)	(0.1)	(0.1)	(0.0)	(0.0)
1.738	73.8	20.8	0.9	...	0.8	0.5	0.9	0.7
(1.701)	(71.3)	(25.8)	(1.7)	(0.1)	(0.0)	...	(0.8)	(0.1)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)

^a From the ingredients. ^b Calculated from the n.m.r. data. ^c Calculated from $K_1 = 0.09$ and $K_2 = 50$, using the R values from the n.m.r. data.

appear much closer to E_3 , since the distance between consecutive end-group peaks appears to decrease in upfield direction; e.g., $\Delta_{E_1E_2} = 0.030$, $\Delta_{E_2E_3} = 0.010$, as compared to $\Delta_{E_3E_4} = 0.024$ p.p.m. However, the assignment of E_4 as end group is supported by the material balances (i.e., the good agreement of the R values from ingredients and as calculated from the n.m.r. data) and by the fact that the intensity of E_4 maximizes with varying R in the manner expected for an end group.

The remaining peaks are attributed to middle groups or impurities: with M_1 at -1.000 p.p.m. being assigned to the *eme* molecule, M_2 at -0.975 to *emme*, M_3 at -0.958 to the *emmm* configuration, M_4 at -0.933 to the *emmmie* molecule, M_5 at -0.908 to *emmmmm*, the peaks at -0.883 and -0.867 to impurities or side products, M_r at -0.842 to the dimethylgermanium sulfide ring, and M_6 at -0.683 to the configuration *mmmmmm*.

It should be noted that the assignment gives an n.m.r. order of environment¹² for the middle groups which is smaller by one than that for the end groups (for which $\theta = 7$). Since the majority of middle groups are in rings, it is also possible to obtain a fit—but not as good a fit—of the M_1 to M_6 resonances to the same order of environment as used for the end groups. However, we think that the order of environment of the middle groups is truly one less than that of the end groups owing to lesser configurational restrictions¹³ on the end groups.

In the system $(\text{CH}_3)_2\text{GeI}_2$ vs. $[(\text{CH}_3)_2\text{GeS}]$, the signal at -1.800 p.p.m. was assigned to the *neso* compound, E_1 at -1.362 to the *ee* molecule, E_2 at -1.332 to *eme*, E_3 at -1.320 to *emme*, and E_4 at -1.303 to the *emmm* configuration. The argument concerning the peak E_4 (as well as that dealing with the order of environment) in the analogous bromine system applies here also. Impurities were found at -1.207 , -1.128 , and -1.032 p.p.m. The signals located further upfield are all middle groups, with M_1 at -0.973 being assigned to *eme*, M_2 at -0.945 to *emme*, M_3 at -0.935 to *emmm*, M_4 at -0.900 to *emmmie*, M_r at -0.827 to the trimeric ring compound $[(\text{CH}_3)_2\text{GeS}]_3$, M_5 at -0.75 to *emmmmm*, and M_6 at -0.700 to *mmmmmm*.

Inspection of the spectra presented in Figure 1 shows an increasing downfield shift of the signal of the *neso* compound when going from $X = \text{Cl}$ to Br and to I , which is in disagreement with a simple electronegativity effect upon the shielding of the methyl groups on germanium. Although the signals for the *neso* compound and the clusters of end groups and middle groups are spread farther apart in the order $\text{Cl} < \text{Br} < \text{I}$, there is little change in the distance between corresponding individual peaks in the respective clusters of signals. For example, the distances between E_1 and E_2 appear to be fairly constant in all three systems; also the distances M_1 to M_r change very little when comparing the chlorine, bromine, and iodine systems.

Calculation of Equilibrium Constants. The experimental data for these three systems are reported in Tables III, IV, and V, from which it is apparent that

(12) D. W. Matula, L. C. D. Groenweghe, and J. R. Van Wazer, *J. Chem. Phys.*, **41**, 3105 (1964).

(13) J. R. Van Wazer and D. Grant, *J. Am. Chem. Soc.*, **86**, 1450 (1964).

most of the middle groups are found in the trimeric ring compound. By arbitrarily deducting various amounts of middle groups ascribed to rings from the total number of middles, the *ee* and *eme* resonances were fitted,¹² using a computer program which simulates random sorting of the available building units into molecules (for the case¹² of $\rho = 1$). Thus a preliminary estimate was obtained for the distribution of total middles into rings and chains as a function of the over-all composition.

The preliminary estimated data were employed to calculate a pair of equilibrium constants: one relating the amount of *neso*, end, and middle groups *in chains*,^{2,12} and another relating the amount of middle groups in chains to those in rings.¹² The final set of equilibrium constants was then obtained by calculating the areas of the various observed n.m.r. peaks for a number of assumed values of the equilibrium constants in the immediate neighborhood of the values first estimated. The best over-all fit of the calculated to the experimental data was found for the equilibrium constants given in Table VI. Each system is completely described by only two constants. A comparison of the constants in Table VI shows that the ring-chain constant, K_3° , is the same for all three systems. The constants describing the sorting of building units into chains are identical for the chlorine and iodine systems with that for the bromine system being somewhat smaller.

Table VI. Equilibrium Constants for the System $(\text{CH}_3)_2\text{GeX}_2$ vs. $[(\text{CH}_3)_2\text{GeS}]$

X	K_1	K_3°
	Chains vs. chains ^a	Trimeric rings vs. chains ^b
Cl	0.09	50
Br	0.06	50
I	0.09	50

^a $K_1 = [\textit{neso}][\textit{chain middles}]/[\textit{ends}]^2$. ^b $K_3^\circ = [\textit{ring middles}]/[V_2 + (R/2)(V_0 - V_2)] \{([\textit{ends}] + 2[\textit{chain middles}])/2[\textit{chain middles}]\}^3$ where V_0 is the volume of the *neso* compound in l./mole and V_2 is the volume of the middle groups (estimated from the ring compound) in l./mole, using no dilution.

In the related *neso* system, $(\text{CH}_3)_2\text{GeX}_2$ vs. $(\text{CH}_3)_2\text{Ge}(\text{SCH}_3)_2$, the constants in each case are approximately twofold smaller than those for the corresponding families $(\text{CH}_3)_2\text{GeX}_2$ vs. $[(\text{CH}_3)_2\text{GeS}]$, thus indicating a greater degree of "nonrandomness" for the exchange of halogen with sulfur in the *neso* systems. This difference is probably due to a predominantly enthalpy change ($\Delta H = \text{ca. } 0.5 \text{ kcal.}$) when substituting on the dimethylgermanium moiety a group based on $-\text{SC}$ for one based on $-\text{SGe}$, i.e., to a change in the Ge-S bond related to the effective diminution of the group electronegativity of the sulfur by replacing a neighboring carbon atom by a germanium.

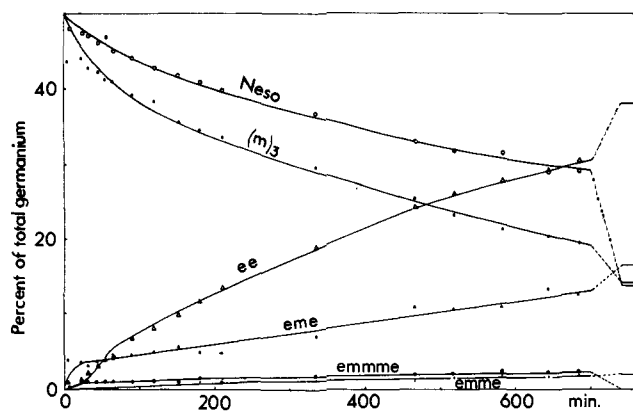


Figure 2.

Equilibration Kinetics. A pair of kinetic runs was carried out at 33.5° on a neat liquid mixture of $(\text{CH}_3)_3\text{GeCl}_2$ and $[(\text{CH}_3)_2\text{GeS}]_3$ which had an equal amount of germanium present as each reagent. The experimental data from one of these runs are plotted in Figure 2 in terms of percentage of total germanium (not concentration in moles/l.) The set of curves for each run were essentially the same except for a difference in the time scale (the run depicted in Figure 2 went about half as fast as the other one). This difference is probably attributable to catalysis by trace impurities, perhaps HCl.

Unlike the results from our other kinetic studies of scrambling reactions involving a ring compound interacting with a *neso*^{9,14} (or dichain¹⁵) molecule, none of the rate curves of Figure 2 was seen to exhibit a maximum. Furthermore, the opening of a trimeric ring by a single *neso* molecule should give the four-membered chain, *em₂e*; as the initial product, but yet this compound is seen to increase slowly and always remain in small proportions. The reaction product which initially builds up at the most rapid rate (on either a molecular or germanium-content basis) is the three-membered chain, which cannot be the major product from any reasonably simple interaction of the reagents. Therefore, we tentatively conclude that some kind of molecular fragmentation is probably involved in the kinetic process so that the mechanism might, for example, be based on the ionization of chlorines from the dichlorodimethylgermane molecules.

A comparison of the rates of interchange of chlorine with bridging sulfur shows that the reaction at the dimethylsilicon moiety¹ is roughly 10^6 times as fast and that the corresponding scrambling on the dimethyltin moiety² is about 10^4 times faster than the rates reported here for the dimethylgermanium system.

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(14) J. R. Van Wazer and K. Moedritzer, *J. Chem. Phys.*, **41**, 3122 (1964); see Figure 1.

(15) D. Grant and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 3012 (1964); see Figure 2.