# Preferential Exchange of Bromines and Bridging Oxygens between Dimethylgermanium and Dimethylsilicon Moieties

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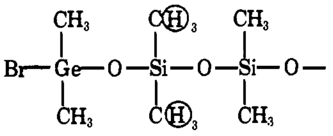
**Abstract:** The various molecules resulting from scrambling of the bridging oxygen with the monofunctional bromine atoms between dimethylgermanium and dimethylsilicon moieties are to be found in the equilibrated system $(CH_3)_2SiBr_2$–$(CH_3)_2GeBr_2$–$[(CH_3)_2SiO]$–$[(CH_3)_2GeO]$, which is the subject of the investigation reported here. Proton nuclear magnetic resonance of the methyl groups (nonexchangeable) bonded to the germanium and silicon atoms shows that there is a very strong preference for the bromine atoms to be on the dimethylgermanium and the bridging oxygens to be on the dimethylsilicon moiety. This causes the composition region bounded by $(CH_3)_2SiBr_2$, $(CH_3)_2GeBr_2$, and $(CH_3)_2SiO$ to consist of germanium-free siloxanes dissolved in dimethyldibromogermane. Germanosiloxanes, exhibiting preferential placement of the germanium at the ends of the chains, are found in the remaining region bounded by $(CH_3)_2GeBr_2$, $(CH_3)_2SiO$, and $(CH_3)_2GeO$. The nmr fine structure is interpreted, and the resulting experimental data are compared with the corresponding values calculated from the four equilibrium constants which are needed to describe the distribution of linear molecules resulting from equilibration of any stoichiometric composition in the system.

Although a great deal of work[1,2] has been done on what generally appears to be equilibrium-controlled oligomeric structures in which a number of different atoms can replace each other in the molecule, the question of a possible preferential arrangement of such atoms at equilibrium has not received attention. In most of the work in this area, it is either implied or stated that the replacement atoms will be found in an alternating sequence or more-or-less randomly scattered throughout the molecular structure. As will be shown below, one would not necessarily expect this to be the case.

This paper represents the first quantitative study of the structure-determining parameters for an example of the widely discussed[1] class of "polymetallosiloxanes." Before considering the system $(CH_3)_2SiBr_2$–$(CH_3)_2GeBr_2$–$[(CH_3)_2SiO]$–$[(CH_3)_2GeO]$ described herein (in which there are molecular structures based on dimethylgermanium and dimethylsilicon moieties separated by bridging oxygen atoms, with the chain molecules being terminated by bromine atoms), the reader is referred to two previous studies[3,4] describing the subsumed $(CH_3)_2SiBr_2$–$[(CH_3)_2SiO]$ system[3] and $(CH_3)_2GeBr_2$–$[(CH_3)_2GeO]$ system,[4] each of which represents a family of compounds.

## Experimental Section

The reagents, preparation of equilibrium mixtures, and use of proton nuclear magnetic resonance (nmr) for analysis are the same as previously described.[3,4] However, a new computer program[5] was set up to handle the statistical calculations underlying the evaluation from the equilibrium constants of the relative amounts of the various molecular fragments (graphs[6]) corresponding to the observed nmr peaks: the *neso*, *n*; end group, *e*; and middle group, *m*. The notation used here is the same as that previously employed in recent publications[3,4,6,7] from this laboratory, with the subscript 1 referring to silicon and 2 to germanium. Thus, for example, $e_1$ stands for $(CH_3)_2SiBr(O_{1/2}-)$ and $m_2$ for $(CH_3)_2Ge(O_{1/2}-)_2$. Also, following prior usage,[7] bold-face type is employed to indicate which group bears the pair of methyl groups causing the observed resonance, with the neighboring groups which affect the exact position of this resonance being shown in italics. For example, $e_2\mathbf{m}_1m_1$ indicates that the resonance is attributable to the encircled hydrogens in the following assemblage of atoms.



$$Br-\underset{CH_3}{\overset{CH_3}{Ge}}-O-\underset{C\textcircled{H}_3}{\overset{C\textcircled{H}_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-$$

Assignment of the various resonances observed in the nmr spectra was readily made by comparison with the spectra of the $(CH_3)_2SiBr_2$–$[(CH_3)_2SiO]$ system,[3] which showed a great deal of fine structure, and with the $(CH_3)_2GeBr_2$–$[(CH_3)_2GeO]$ system,[4] in which there was line broadening due to exchange. Also the chemical shifts observed in this study are not very different from those obtained[8] for the all-*neso* system resulting from substituting the bridging oxygen atoms by methoxyl groups. As shown in Figure 1, the proton shifts of the methyl groups vary linearly within the system of molecules $(CH_3)_2GeBr_2$, $(CH_3)_2GeBr(OCH_3)$, and $(CH_3)_2Ge(OCH_3)_2$, and this is also the case for their silicon analogs.[9]

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(1) K. A. Andrianov, "Metalorganic Polymers," Interscience Publishers, Inc., New York, N. Y., 1965; J. I. Jones, "Developments in Inorganic Polymer Chemistry," M. F. Lappert and G. J. Leigh, Ed., Elsevier Publishing Co., New York, N. Y., 1962, Chapters 7, 8, pp 162–255.

(2) D. N. Hunter, "Inorganic Polymers," John Wiley and Sons, Inc., New York, N. Y., 1963; E. L. Gefter, "Organophosphorus Monomers and Polymers," Associated Technical Services, Inc., Glenridge, N. J., 1962; F. R. Gimblett, "Inorganic Polymer Chemistry," Butterworth & Co., Ltd., London, 1963.

(3) K. Moedritzer and J. R. Van Wazer, manuscript in preparation.

(4) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **4**, 1753 (1965).

(5) Developed by L. C. D. Groenweghe of our laboratory.

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

(7) J. R. Van Wazer and K. Moedritzer, *Angew. Chem. Intern. Ed. Engl.*, **5**, 341 (1966).

(8) J. R. Van Wazer, K. Moedritzer, and L. C. D. Groenweghe, *J. Organometal. Chem.* (Amsterdam), **5**, 420 (1966).

(9) The fact that the shifts for these two series are displaced by about half of the distance between the resonances of a neighboring pair of molecules in the series of either silicon or germanium *neso* compounds would indicate that the resonances of the various kinds of molecules in the $(CH_3)_2SiBr_2$–$(CH_3)_2GeBr_3$–$[(CH_3)_2SiO]$–$[(CH_3)_2GeO]$ system would be rather well separated. This plus the fact that the constant $K_I$ of the related all-*neso* system[8] was very nonrandom formed the basis on which this particular study was selected for study.

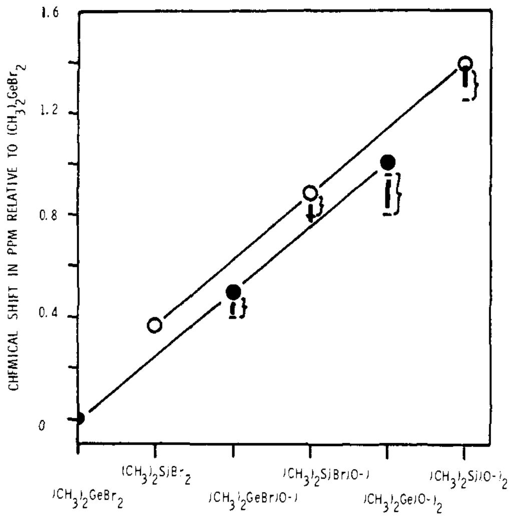

Figure 1. Change of proton chemical shift with molecular composition. The open circles represent compounds obtained by scrambling of bromine with methoxy groups on dimethylsilicon and the blackened circles the same scrambling on dimethylgermanium. The bracketed lines represent the ranges of chemical shifts reported[3,4] for the equivalent scrambling with bridging oxygens substituted for methoxyl groups, whereas the ranges observed in this study are depicted by the vertical black bars.

In many cases, the series of shifts in an all-*neso* system depart considerably from linearity,[10] and this may cause the fine structure within a given group (*e.g.*, end, middle, etc.) to appear in an unpredictable sequence in the nmr spectra of a related family of compounds. However, when the shifts are linear, as in the case studied here, the ordering of the resonances can be predicted accurately on the assumption that a given group having a resonance lying upfield (downfield) would as a nearest neighbor tend to move the particular resonance upfield (downfield). For example, since the resonances of this study lie in the order $e_2$, $e_1$, $m_2$, and $m_1$ in the upfield direction (see Figure 1), we predict that the $e_2m_1e_2$ resonance will be downfield of the $e_2m_1e_2$ resonance, which in turn will be somewhat downfield of $e_1m_1e_1$, etc. In this manner, the preliminary assignments of the various resonances shown in Table I were obtained. It should be noted that this kind of relationship had been found to hold for the $(CH_3)_2SiBr_2$–$[(CH_3)_2SiO]$ and $(CH_3)_2GeBr_2$–$[(CH_3)_2GeO]$ systems when studied independently.[3,4]

The stoichiometry of the over-all system bounded by the four compositions $(CH_3)_2SiBr_2$, $(CH_3)_2SiO$, $(CH_3)_2GeBr_2$, and $(CH_3)_2GeO$ may be represented in a number of ways. We have chosen for this representation the two mole-ratio parameters: $R \equiv Br/(Si + Ge)$ and $R' \equiv Si/(Si + Ge)$. The nmr assignments for the various groups ($n_2$, $n_1$, $e_2$, $e_1$, $m_2$, and $m_1$) were shown to be correct by material-balance calculations, as demonstrated by agreement between the values calculated from ingredient weights and from the relative nmr peak areas for both $R$ and $R'$ in Table I. It should be noted that the resonances for the silicon end groups overlap the resonance for two of the germanium middle groups, $e_2m_2e_2$ and $e_2m_2m_2$. However, this caused no practical problems since these dimethylsilicon and dimethylgermanium resonances never appear simultaneously.

Exchange of methyl groups will always result in the formation of monomethyl-plus trimethyl-substituted silicon or germanium. Although the trimethyl moieties are in the same region of the nmr spectrum covered by Figure 1, the monomethyl resonances appear downfield from this region so that they can readily be recognized and measured quantitatively. In the two preceding studies[3,4] as well as in this work, $CH_3Si<$ or $CH_3Ge<$ were not seen (except as trace amounts when the time of heating was carried far beyond that needed to reach equilibrium). These results are in accord with the literature[11] dealing with exchange of methyl groups and halogen atoms on silicon as well as germanium.

## Results and Interpretation

**Rates of Equilibration.** Since the prior work[8] on the scrambling of bromine atoms with methoxyl groups between dimethylsilicon and dimethylgermanium showed that there is a strong preference for the bromine atoms to be on the dimethylgermanium and the methoxyl groups on the dimethylsilicon, a pronounced reaction was expected when various proportions of dimethyldibromosilane were mixed with dimethylgermanium oxide, and this was indeed found to be the case. Thus, on mixing equimolar quantities of $(CH_3)_2SiBr_2$ with $[(CH_3)_2GeO]_n$, where $n = 3$, 4, or $\infty$, noticeable heat was evolved and the nmr pattern taken after 5 min gave evidence of thorough reaction. On the other hand, like mixtures of dimethyldibromogermane with dimethylsiloxane, $[(CH_3)_2SiO]_n$, showed no heat evolution and exhibited an nmr pattern consisting of little more than the unchanged reagents after several weeks at 150°, using 2% by weight of $AlBr_3$ as catalyst, or after several months of standing at room temperature. The rapid evolution of heat indicates that the exchange of bromine atoms with bridging oxygens occurs in a matter of minutes at room temperature. This does not mean, however, that the resulting molecules will represent an equilibrium distribution. Instead, full equilibration is expected to take a considerably longer time since it has generally been found[12] that the exchange of a halogen with an oxygen is very rapid as compared to the exchange of one oxygen for a differently substituted oxygen. Because of the slow exchange about the oxygen atoms, the equilibrium data at 120° were not measured until after 11 days for expt 1 to 7 in Table I, 6 days for expt 8 to 14, and 8 days for expt 15 to 21.

The nmr spectra generally show some line broadening due to exchange in the dimethylgermanium regions of the spectrum, with very sharp lines (and hence much higher resolution) in the dimethylsilicon regions. It is apparent from these spectra that, even at room temperature, there is considerable exchange of dimethylgermanium groups between chemically different sites. For those compositions where the equilibrium mixture consisted of all-siloxane molecules dissolved in either dimethyldibromogermane or mixtures of this with dimethyldibromosilane (expt 1–4, 13–14, and 19–21 in Table I), there was no noticeable line broadening. However, in the equilibrium mixture when there were appreciable amounts of end and middle groups based on germanium (expt 6–12), line broadening gave evidence for rapid exchange. The exchange was most rapid for expt 6 and 7, in which it appeared that the lifetime for exchange (calculated[13] on a pseudo-first-order basis) of the germanium end and middle groups was of the order of magnitude of hundredths of a second, while the germanium *neso* compound exchanged somewhat less rapidly, exhibiting a lifetime of *ca.* 0.1 sec. In expt 8, the calculated lifetime for the *neso* compound

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[10] *E.g.*, see Figure 9 in J. R. Van Wazer, *Am. Scientist*, **50**, 450 (1962); also see E. Fluck and J. R. Van Wazer, *Z. Anorg. Allgem. Chem.*, 307, 8 (1961).

[11] K. Moedritzer, *Organometal. Chem. Rev.*, **1**, 179 (1966).

[12] *E.g.*, see K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, 3, 268 (1964); J. R. Van Wazer and K. Moedritzer, *J. Inorg. Nucl. Chem.*, 26, 737 (1964).

[13] K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, 3, 139 (1964); see eq 3.

**Table I.** Relative Areas and Chemical Shifts[a] of the Nmr Resonances Observed in the System $(CH_3)_2SiBr_2$–$(CH_3)_2GeBr_2$–$[(CH_3)_2SiO]$–$[(CH_3)_2GeO]$

| | | Nmr shift = | 0.000 | 0.373 | 0.417 | 0.450 | 0.467 | 0.812 | 0.858 | 0.842 | 0.867 | 0.883 | 0.908 | 0.925 | 0.950 | 1.317 | 1.325 | 1.330 | 1.350 | 1.363 | 1.375 | 1.383 | 1.400 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R \equiv$ | $R' \equiv$ | | | | | | | | Germanium middles | | | | | | Silicon middles | | | | | | | |
| Expt | Br | Si | *neso* compd | | Germanium ends | | | Silicon | ends | | | | | $m_1$- | $m_1$- | $e_2$- | | | $e_2$- | $m_2$- | $e_1$- | | |
| no. | Si + Ge | Si + Ge | $\mathbf{n}_2$ | $\mathbf{n}_1$ | $\mathbf{e}_2e_2$ | $\mathbf{e}_2m_2$ | $\mathbf{e}_2m_1$ | $\mathbf{e}_1e_1$ | $\mathbf{e}_1m_1$ | $e_2\mathbf{m}_2e_2$ | $e_2\mathbf{m}_2m_2$ | $e_2\mathbf{m}_2m_1$ | $m_2\mathbf{m}_2m_2$ | $\mathbf{m}_2m_2$ | $\mathbf{m}_2m_1$ | $\mathbf{m}_1e_2$ | $e_2\mathbf{m}_1m_2$ | $e_1\mathbf{m}_1e_1$ | $\mathbf{m}_1m_1$ | $\mathbf{m}_1m_2$ | $\mathbf{m}_1m_1$ | $m_1\mathbf{m}_1m_2$ | $m_1\mathbf{m}_1m_1$ |
| 1 | 1.732[b] | 0.866[b] | 13.5[d] | 62.2 | | | | 16.1 | 5.7 | | | | | | | | | 2.1 | | | 0.5 | | 0.0 |
| | (1.732)[c] | (0.866)[c] | (13.4)[e] | (61.2) | | | | (21.5) | (2.5) | | | | | | | | | (1.1) | | | (0.3) | | (0.0) |
| 2 | 1.465 | 0.733 | 28.1 | 25.7 | | | | 23.4 | 15.0 | | | | | | | | | 5.3 | | | 2.4 | | 0.1 |
| | (1.460) | (0.719) | (26.7) | (27.6) | | | | (26.8) | (11.1) | | | | | | | | | (3.9) | | | (3.2) | | (0.7) |
| 3 | 1.135 | 0.568 | 41.9 | 0.9 | 0.0 | | 0.0 | 3.6 | 19.9 | | | | | | | | | 3.8 | 0.0 | | 15.2 | | 15.1 |
| | (1.091) | (0.585) | (43.2) | (2.4) | (0.0) | | (0.0) | (5.8) | (16.6) | | | | | | | | | (2.2) | (0.0) | | (12.3) | | (17.6) |
| 4 | 0.955 | 0.478 | 44.9 | 0.0 | 2.0 | 0.0 | 5.5 | 0.0 | 0.0 | | | ← 0.0 → | | | 0.0 | 0.0 | | 0.3 | 8.0 | | 0.0 | 0.0 | 39.3 |
| | (0.973) | (0.476) | (43.3) | (0.0) | (1.0) | (0.0) | (7.8) | (0.0) | (0.0) | | | (0.0) | | | (0.1) | (0.4) | | (0.0) | (6.9) | | (0.0) | (0.2) | (40.2) |
| 5 | 0.860 | 0.430 | 31.7 | | 10.5 | 0.0 | 12.8 | | | | | ← 0.0 → | | 0.0 | 0.7 | 2.0 | 0.0 | | 13.5 | | | 0.0 | 28.8 |
| | (0.867) | (0.443) | (30.0) | | (7.1) | (0.5) | (18.4) | | | | | (0.5) | | (0.0) | (0.5) | (2.5) | (0.4) | | (13.0) | | | (1.1) | (25.5) |
| 6 | 0.493 | 0.246 | 2.6 | | | ← 48.2 → | | | | | | ← 16.0 → | | 6.0 | 4.5 | | ← 9.2 → | | | | ← 10.3 → | | 3.3 |
| | (0.534) | (0.228) | (2.8) | | | (43.7) | | | | | | (19.3) | | (6.2) | (3.3) | | (11.2) | | | | (10.1) | | (3.5) |
| 7 | 0.251 | 0.126 | 0.2 | | ← 24.5 → | | 3.2 | | | ← 13.8 → | | ← 33.7 → | | 11.7 | 0.0 | 0.0 | 2.9 | | 0.0 | | ← 10.1 → | | 0.0 |
| | (0.281) | (0.130) | (0.4) | | (20.9) | | (3.3) | | | (13.8) | | (35.1) | | (11.8) | (1.6) | (0.2) | (2.4) | | (0.5) | | (9.4) | | (0.4) |
| 8 | 0.333 | 0.076 | 0.3 | | 5.1 | ← 28.6 → | | | | 4.2 | 17.7 | 0.0 | 21.9 | 14.7 | 0.0 | 0.4 | 0.0 | | 0.9 | 2.4 | | 1.8 | 1.2 |
| | (0.343) | (0.067) | (0.7) | | (6.1) | (25.7) | | | | (2.2) | (16.5) | (2.0) | (31.0) | (7.4) | (0.6) | (0.3) | 2.0 | | (0.3) | (3.8) | | (1.3) | (0.1) |
| 9 | 0.429 | 0.109 | 0.7 | | 8.7 | ← 35.0 → | | | | 6.5 | 16.7 | 5.2 | 10.5 | 5.9 | 0.0 | 1.5 | | ← 6.7 → | | | | 1.9 | 0.7 |
| | (0.451) | (0.110) | (1.4) | | (10.3) | (29.7) | | | | (3.1) | (14.9) | (3.2) | (17.8) | (7.3) | (1.1) | (0.7) | | (7.8) | | | | (2.2) | (0.3) |
| 10 | 0.578 | 0.146 | 2.9 | | 15.7 | ← 34.5 → | | | | 8.1 | 2.5 | 5.0 | 8.0 | 8.2 | 0.0 | 1.3 | 2.0 | | 4.1 | 2.1 | | 3.6 | 1.0 |
| | (0.560) | (0.141) | (3.6) | | (18.4) | (32.4) | | | | (4.1) | (10.0) | (4.4) | (6.2) | (5.0) | (1.5) | (1.8) | (4.4) | | (1.9) | 2.7) | | (3.0) | (0.9) |
| 11 | 0.806 | 0.192 | 13.0 | | 30.0 | 8.0 | 19.2 | | | 4.4 | 2.0 | 2.4 | 0.0 | 1.2 | 1.2 | 2.5 | 1.7 | | 2.6 | 2.4 | | 2.8 | 6.2 |
| | (0.832) | (0.182) | (11.7) | | (28.3) | (11.9) | (17.0) | | | (2.9) | (2.5) | (3.5) | (0.5) | (1.3) | (1.3) | (4.2) | (3.5) | | (5.0) | (0.7) | | (2.6) | (2.6) |
| 12 | 0.974 | 0.239 | 22.8 | | 32.3 | 3.3 | 13.2 | | | 0.0 | 0.0 | 1.9 | 0.0 | ← 1.3 → | | 2.4 | 2.0 | | 11.5 | 0.0 | | ← 9.2 → | |
| | (0.944) | (0.251) | (25.1) | | (23.3) | (3.8) | (20.1) | | | (0.9) | (0.3) | (1.6) | (0.0) | (1.1) | | (5.0) | (1.6) | | (8.6) | (0.1) | | (7.9) | |
| 13 | 1.283 | 0.332 | 62.3 | 0.0 | 0.3 | 0.0 | 3.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 | | 0.0 | 0.0 | 1.7 | 0.0 | 0.0 | 5.6 | 0.0 | 0.0 | 0.0 | 26.3 |
| | (1.284) | (0.336) | (61.5) | (0.0) | (0.5) | (0.0) | (4.8) | (0.0) | (0.0) | (0.0) | (0.0) | (0.0) | | (0.0) | (0.0) | (0.2) | (0.0) | (0.0) | (4.3) | (0.0) | (0.0) | (0.0) | (28.5) |
| 14 | 1.573 | 0.398 | 65.5 | 10.0 | 0.0 | | 0.0 | 2.9 | 9.6 | | | 0.0 | | | | 0.0 | | 4.9 | 0.0 | | 4.0 | | 3.1 |
| | (1.535) | (0.345) | (60.2) | (7.3) | (0.0) | | (0.0) | (11.6) | (10.6) | | | (0.0) | | | | (0.0) | | (2.8) | (0.0) | | (5.1) | | (2.3) |
| 15 | 0.161 | 0.175 | 0.1 | | 2.1 | ← 13.0 | | | | 1.4 | 10.9 | ← 32.4 → | | ← 23.6 → | | 0.0 | 7.8 | | 0.0 | 2.9 | | 3.5 | 2.2 |
| | (0.153) | (0.164 ) | (0.2) | | (1.4) | (14.3) | | | | (0.5) | (8.5) | (37.9) | | (19.2) | | (0.1) | (2.1) | | (0.5) | (8.8) | | (5.6) | (1.0) |
| 16 | 0.312 | 0.326 | 0.7 | | 6.1 | ← 24.2 → | | | | ← 4.7 → | | 11.8 | 7.5 | 10.4 | 3.9 | 0.5 | 10.6 | | ← 10.5 → | | | 7.2 | 2.0 |
| | (0.317) | (0.308) | (1.0) | | (5.3) | (23.9) | | | | (7.4) | | (4.8) | (8.0) | (10.7) | (5.8) | (0.9) | (4.8) | | (9.8) | | | (11.5) | (6.2) |
| 17 | 0.373 | 0.379 | 1.3 | | 8.1 | 14.8 | 12.6 | | | 0.0 | 3.9 | 4.4 | 5.2 | 8.0 | 4.4 | | ← 12.8 → | | | 2.9 | | 12.5 | 9.2 |
| | (0.381) | (0.374) | (1.8) | | (7.5) | (11.8) | (14.4) | | | (1.3) | (4.1) | (5.0) | (3.3) | (6.8) | (5.8) | | (12.7) | | | (4.0) | | (11.6) | (9.9) |
| 18 | 0.514 | 0.497 | 8.6 | | 16.7 | 4.4 | 13.4 | | | 2.5 | 1.3 | 2.8 | 1.2 | 0.4 | 0.3 | ← 6.4 → | | | 6.4 | | ← 35.7 → | | |
| | (0.517) | (0.485) | (7.9) | | (9.8) | (3.8) | (22.0) | | | (0.5) | (0.4) | (2.3) | (0.1) | (0.7) | (2.9) | (5.3) | | | (13.6) | | (30.3) | | |
| 19 | 0.604 | 0.615 | 21.9 | | 2.7 | 0.0 | 12.6 | 0.0 | 0.0 | 0.0 | 0.0 | | ← 1.3 → | | | ← 6.6 → | | | 12.0 | | 0.0 | 0.0 | 42.9 |
| | (0.591) | (0.615) | (22.4) | | (2.3) | (0.1) | (13.2) | (0.0) | (0.0) | (0.0) | (0.0) | | (0.5) | | | (1.1) | | | (11.2) | | (0.0) | (0.7) | (48.2) |
| 20 | 0.755 | 0.670 | 34.0 | 0.0 | 0.0 | | 0.0 | 0.5 | 6.5 | | | | | | | ← 0.0 → | | 0.0 | 0.0 | | 9.3 | | 49.8 |
| | (0.749) | (0.659) | (33.0) | (0.2) | (0.0) | | (0.0) | (0.7) | (8.4) | | | | | | | (0.0) | | (0.3) | (0.0) | | (7.8) | | (49.5) |
| 21 | 0.775 | 0.836 | 14.7 | 3.2 | | | | 8.4 | 26.6 | | | | | | | | | 6.1 | | | 20.5 | | 20.6 |
| | (0.708) | (0.854) | (16.4) | (4.4) | | | | (10.5) | (25.3) | | | | | | | | | (3.7) | | | (17.9) | | (21.7) |

[a] Referenced to dimethyldibromogermane (internal standard, having a shift of −1.46 ppm with respect to tetramethylsilane). [b] Values calculated from ingredient weights. [c] Values calculated from relative nmr peak areas. [d] Observed relative nmr peak areas. [e] Calculated values from $K_{Si} = 0.15$, $K_{Ge} = 0.043$, $K_O = 0.35$, and $K_I = 10^{10}$.

was 0.3 sec and, in expt 9–12, it was greater than *ca.* 5 sec (upper limit of detection). In expt 9, the width of the $e_2\mathbf{m}_2e_2$ peak corresponded to a lifetime of 0.1 sec, and, in expt 10, the same lifetime was observed for the $e_2e_2$ configuration. In expt 12, the width of the $e_2e_2$ peak corresponded to the much slower rate of exchange of *ca.* 0.8 sec. From these nmr line widths as well as from other related work,[3,4,14] one must conclude that the equilibrium data of Table I correspond to room temperature for the dimethylgermanium moieties and 120° for the dimethylsilicon moieties.

**Equilibrium Constants for the Linear Molecules.** In any complex system of molecules at equilibrium, such as the system studied here, a vast number of equilibrium constants relating the various different molecules are needed for a complete thermodynamic description. However, generally most of these constants have been shown to exhibit a statistically random value so that one need only to evaluate a small number of equilibrium constants *dealing with parts of molecules*[6] and then to invoke statistical sorting of these parts to obtain the equilibrium distribution of either the molecules or variously chosen molecular fragments (parts, graphs[6]). On the assumption that the thermodynamic properties of any given end or middle group in the system studied here are dependent only on its neighboring groups, an assumption demonstrated[3,4] to be applicable to both the $\mathrm{(CH_3)_2SiBr_2}$–$\mathrm{[(CH_3)_2SiO]}$ and $\mathrm{(CH_3)_2GeBr_2}$–$\mathrm{[(CH_3)_2GeO]}$ subsystems, it may be seen that only four equilibrium constants are needed to define the kinds, sizes, and amounts of the various noncyclic molecules in the entire system of molecules described herein. The first of these four equilibrium constants—the intersystem constant, $K_\mathrm{I}$—deals with the relative distribution of bromine *vs.* bridging oxygen atoms on dimethylsilicon as compared to dimethylgermanium (eq 1). Since this constant involves only the *neso* com-

$$K_\mathrm{I} = \mathrm{[(CH_3)_2Si(O_{1/2}-)_2][(CH_3)_2GeBr_2]/[(CH_3)_2SiBr_2]} \\ \mathrm{[(CH_3)_2GeO_{1/2}-)_2]} = m_1n_2/n_1m_2 \quad (1)$$

pounds and the total silicon as well as the total germanium middle groups, it can readily be evaluated from the areas of the various clumps of peaks in the nmr spectra without getting into the problem of making assignments of the fine structure making up these clumps. It was found that the best fit to the experimental data (see Table I) was obtained for $K_\mathrm{I} \geq (1.0 \pm 0.5) \times 10^{10}$. In the analogous all-*neso* system[8] in which bromine atoms were exchanged with methoxyl groups instead of bridging oxygen atoms between the dimethylsilicon and dimethylgermanium moieties, $K_\mathrm{I}$ was found to be equal or greater than $1 \times 10^{13}$.

The next two equilibrium constants to be evaluated, $K_\mathrm{Si}$ and $K_\mathrm{Ge}$, deal with the sorting of bromine and bridging oxygen atoms on dimethylsilicon and on dimethylgermanium, respectively (eq 2 and 3). The con-

$$K_\mathrm{Si} = \mathrm{[(CH_3)_2SiBr_2][(CH_3)_2Si(O_{1/2}-)_2\ in\ chains]/} \\ \mathrm{[(CH_3)_2SiBr(O_{1/2}-)]^2} = n_1m_1/e_1^{\,2} \quad (2)$$

$$K_\mathrm{Ge} = \mathrm{[(CH_3)_2GeBr_2][(CH_3)_2Ge(O_{1/2}-)_2\ in\ chains]/} \\ \mathrm{[(CH_3)_2GeBr(O_{1/2}-)]^2} = n_2m_2/e_2^{\,2} \quad (3)$$

stants $K_\mathrm{Si}$ and $K_\mathrm{Ge}$ were previously evaluated[3,4] to be 0.150 and 0.043, respectively, for the limiting cases of this system (the top and bottom lines of Figure 2). Since these values are expected to be applicable to the over-all system studied here, they were employed in the calculation of the values of the relative amounts of the various arrangements of end and middle groups corresponding to the observed nmr peaks.

The fourth equilibrium constant needed to describe the over-all system is the linkage constant, $K_\mathrm{O}$, which deals with the sorting of silicon and germanium atoms on the bridging oxygens (eq 4, where $\sigma$ stands for either

$$K_\mathrm{O} = \mathrm{[-\{(CH_3)_2Si\}_{1/2}O\{Si(CH_3)_2\}_{1/2}-]} \times \\ \mathrm{[-\{(CH_3)_2Ge\}_{1/2}O\{Ge(CH_3)_2\}_{1/2}-]/} \\ \mathrm{[-\{(CH_3)_2Si\}_{1/2}O\{Ge(CH_3)_2\}_{1/2}-]^2} \supset \\ (\sigma_1\sigma_1)(\sigma_2\sigma_2)/(\sigma_1\sigma_2)^2 \quad (4)$$

an *e* or an *m*). The constant $K_\mathrm{O}$ determines the sequence of germanium and silicon atoms in the molecular backbone; and, as will be shown elsewhere, $K_\mathrm{I}$ is truly constant only when $K_\mathrm{O}$ exhibits the random value. When $K_\mathrm{O}$ is very large, there will be no germanosiloxanes but only a mixture of pure siloxanes with pure germoxanes. When $K_\mathrm{O}$ exhibits the random value of 0.25, the sequence of germanium and silicon atoms in any molecule will be statistically random. On the other hand, when $K_\mathrm{O}$ is very small, the silicon and germanium atoms will alternate with each other. It was concluded from the data of Table I that the value of $K_\mathrm{O}$ for the system studied here is $0.35 \pm 0.20$. In other words, the data indicate that SiOSi and GeOGe sequences probably appear somewhat more often than random sorting of the silicon and germanium atoms would dictate.

For low values of the composition parameter $R$, cyclic molecules will be present[15] in the mixtures. The equilibrium constants are known for the cyclic siloxanes and cyclic germoxanes but no information has as yet been published concerning the cyclic germanosiloxanes. Several nmr spectra corresponding to $R = 0.0$ and $R' = 0.5$ were taken to investigate whether or not cyclic germanosiloxanes exist in the equilibrium mixtures. Rather sharp resonances of the type attributable to ring structures were observed, but we were unable to conclude from the experimental evidence whether or not mixed silicon–germanium rings were present and to what amount.

**Equilibrium Data.** Twenty-six different compositions were investigated in the course of the work reported here, of which 21 are presented in Table I. The various compositions corresponded to straight-line cuts across the system as depicted in Figure 2. Thus, expt 1–7 in Table I represent the equilibria resulting from mixing various proportions of $\mathrm{(CH_3)_2SiBr_2}$ with $\mathrm{[(CH_3)_2GeO]}$; expt 8–14 are likewise based on mixtures of $\mathrm{\{[(CH_3)_2SiBr_2]}$–$\mathrm{(CH_3)_2GeBr_2}$, equimolar$\}$ with [(C-

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[14] K. Moedritzer and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 802 (1964).

[15] See p 248 in K. Moedritzer, *Organometal. Chem. Rev.*, **1**, 179 (1966); also see p 236 of this reference or p 1758 of ref 4 for a definition of the ring-chain constants.

$H_3)_2GeO]$; and expt 15–21 are based on mixtures of $\{(CH_3)_2SiBr_2\text{–}[(CH_3)_2SiO]$, equimolar$\}$ with $[(CH_3)_2GeO]$. No data are presented in Table I for mixtures of $(CH_3)_2GeBr_2$ with $[(CH_3)_2SiO]$ since the equilibrium products were the same as the reagents plus, upon extended heating, a small proportion of products resulting from a slow accretion of methyl groups on silicon (predominantly $(CH_3)_3Si$ derivatives).

The experimental data in Table I are compared with equivalent values (in parentheses) calculated from the four equilibrium constants $K_I = 10^{10}$, $K_{Si} = 0.150$, $K_{Ge} = 0.043$, and $K_O = 0.35$, and it should be observed that the agreement between the experimental and calculated values is generally quite good. Since the exchange of bromine for bridging oxygens is rapid, we believe that the value of $K_I$ is an accurate one. Trust may also be placed in the values of $K_{Si}$ and $K_{Ge}$ since they were carefully evaluated for the limiting cases of the top and bottom boundaries of Figure 2. The value of $K_O$, however, is open to suspicion since we have not demonstrated that the observed relative positioning of the dimethylgermanium and dimethylsilicon groups within the backbone of a germanosiloxane molecule represents the equilibrium situation.

In order to conserve space, all of the separately determined resonances are not shown in Table I. For example, the resonance listed as $\mathbf{e}_1m_1$ was observed in expt 2, 3, 20, and 21 as three well-resolved peaks: $\mathbf{e}_1m_1e_1$, $\mathbf{e}_1m_1m_1e_1$, and $\mathbf{e}_1m_1m_1m_1$. Similarly, for these same experiments, $e_1\mathbf{m}_1m_1$ was seen as three peaks and, in expt 20 and 21, $m_1\mathbf{m}_1m_1$ was also resolved into as many as six to seven resonances, of which the first, $e_1m_1\mathbf{m}_1m_1e_1$, was reasonably separated. Proof that the assignments given for the nmr fine structure are correct is obtained from area ratios of related resonances. Thus the area of $\mathbf{e}me$ always is twice as great as the area of $e\mathbf{m}e$ having the same arrangement of subscripts. Further, these area relationships hold into the fine structure corresponding to extremely high resolution so that the area of $\mathbf{e}_1m_1m_1e_1$ was found to equal that of $e_1\mathbf{m}_1m_1e_1$ and a 2:1 area ratio was found for $e_1\mathbf{m}_1m_1m_1e_1$ and $e_1m_1\mathbf{m}_1m_1e_1$. An even more convincing proof that the assignments which were tentatively made on the basis discussed in the Experimental Section are correct comes from the fact that the resonances corresponding to single molecules stood out as the sharper peaks and that peaks of the type $e\mathbf{m}_1m$ were always less broad than those of the type $m\mathbf{m}_1m$.

In expt 6–9 and 15–17 of Table I, there should be an appreciable amount of cyclic molecules because of the low value of the parameter $R$. Assuming that the ring-chain equilibrium constants for the cyclic germanosiloxanes are in line with those observed for the cyclic siloxanes and germoxanes, we estimate that in Table I the largest proportion of cyclic molecules [*ca.* 17% of the total (Si + Ge)] will occur for expt 8. The presence of even this amount of cyclics does not greatly upset[16] the distribution of structure fragments of the type shown in Table I. Indeed the main effect should be to cause the $ee$ molecules to be present to a somewhat larger extent than theoretically estimated but, for expt 8, this is masked by the uncertainty in the nmr peak-area measurement caused by overlapping of $\mathbf{e}_2e_2$ and $\mathbf{e}_2m$ resonances.

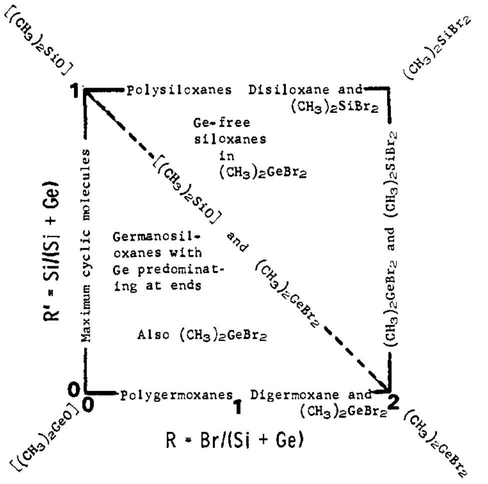

Figure 2. Schematic diagram indicating the molecular composition within the system $(CH_3)_2SiBr_2\text{–}(CH_3)_2GeBr_2\text{–}[(CH_3)_2SiO]\text{–}[(CH_3)_2GeO]$.

## Discussion

This study of the $\alpha,\omega$-dibromopolydimethylgermanosiloxanes illustrates several previously unrecognized important features of equilibrium families of compounds based on mixed backbones. As summarized in Figure 2, these are (1) the highly preferential placement of a given backbone atom either in the end groups or, alternatively, in the middle (or the branch) groups making up the molecules; and (2) the ability of a simple molecule (*neso* compound) to act as a "nonreactive" solvent while being in dynamic equilibrium with the dissolved species of higher molecular weight. This latter effect is exemplified by the upper right-hand half of Figure 2. Both of these effects, which are predicted to be of common occurrence in mixed-backbone families of compounds, follow from the fact that scrambling of substituents between two different central atoms involves the simultaneous gain and loss of particular chemical bonds; *i.e.*, a $\Delta H$ is expected for this kind of scrambling, even if the bond energies are additive. In many cases,[7,17] the resulting $\Delta H$ is large enough to force the equilibrium corresponding to the constant $K_I$ all the way toward either the reactants or products, thereby giving rise in families of compounds to the effects noted above.

Available thermodynamic data[18] have been used to evaluate equilibrium constants for the exchange of a

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(16) *E.g.*, see ref 14 where the cyclic molecules were included in with the linear ones.

(17) K. Moedritzer and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*, **28**, 957 (1966).

(18) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed, Prentice-Hall, Inc., New York, N. Y., 1952, supplied all but two of the values on which Figure 3 is based. Other sources considered were D. R. Stull, *et al.*, "JANAF Thermochemical Tables," U. S. Government P.B. Report 168 370, 1965; and F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standard Circular 500, U. S. Government Printing Office, Washington, D. C., 1952. In nearly all cases, the calculations were carried out for a crystalline and liquid reagent forming a liquid and a crystalline product. In the exceptions, the reagents and products were crystalline. In the two cases where data were available for all-liquid systems, it was found that the enthalpy of the exchange reaction was the same whether or not crystalline species were involved.

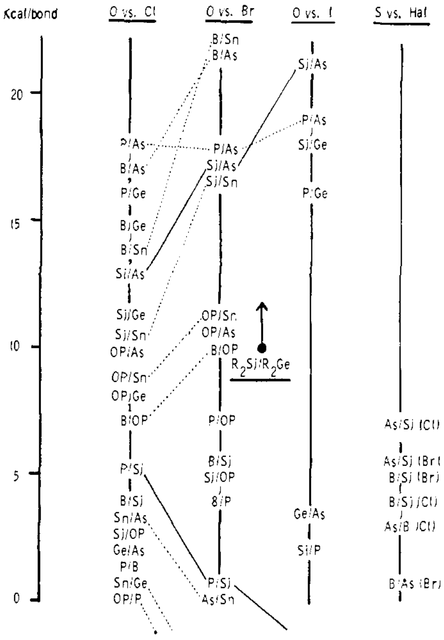

Figure 3. Values of the enthalpy or free energy per bond for exchange of bridging oxygen (or sulfur) *vs.* halogen atoms on pairs of different central moieties. These pairs (*e.g.*, B/Sn) are shown, with the moiety preferentially bonded to oxygen being given first.

bridging oxygen or sulfur with a halogen atom between two kinds of central moieties (similar to the constant $K_I$ of eq 1 but without blocking of exchangeable sites with methyl groups), and the results are shown in Figure 3.

Letting M and Q be central moieties of functionalities $\nu$ and $\mu$, respectively, we consider the exchange of difunctional Z with monofunctional T ligands according to the following equation

$$\mu MZ_\nu(c) + \nu QT_\mu(l) = \mu MT_\nu(l) + \nu QZ_\mu(c) \tag{5}$$

In order to put the data on a comparable basis, the calculations of $\Delta H°$ and $\Delta F°$ were carried out on a per-bond basis by dividing the value computed for eq 5 by $\nu\mu$. The value of either $\Delta H°$ or $\Delta F°$ per bond is shown on the vertical axis of Figure 3. The pairs of central moieties separated by a slash in this figure are arranged so that the moiety preceding the slash is preferentially associated with the bridging oxygen or sulfur and the one following the slash with the halogen. On a per-bond basis, the measured value of $K_I$ for the study reported here corresponds to the value of $\Delta F°$ in Figure 2 labeled as $R_2Si/R_2Ge$.

Since combinatorial analysis indicates that $\Delta S° = 0$ for the reaction of eq 5, the respective $\Delta F°$ should equal $\Delta H°$. Of the 46 equilibrium constants plotted in Figure 3, the thermodynamic tables gave both $\Delta F°$ and $\Delta H°$ values for 16. For all of these 16, the differences between the free energy and the enthalpy of the reaction as measured on a per-bond basis was in the range of 0–2 kcal and averaged less than 1 kcal.

All of the systems for which the value of $(\Delta F° = \Delta H°) >$ *ca.* 8 kcal/bond will exhibit the nonreactive-solvent effect and the extreme preferential placement observed in the study described here. Thus for the systems $SiHal_4$–$AsHal_3$–$SiO_2$–$As_2O_3$, we predict on the basis of Figure 3 that the arsenic trihalide will act as an inert solvent while being in equilibrium with arsenic-free chlorosiloxanes based on tetrafunctional silicon. In the composition region where the arsenic is forced into oxygen-bridged structures by the stoichiometry (*e.g.*, see Figure 2), the arsenic will preferentially be at end groups and, for high average degrees of polymerization, in middle-group positions—in contradistinction to the silicon which will preferentially act as branches.

From the available thermodynamic data (Figure 3), we may tentatively set up the following series for preferential bonding to oxygen as compared to halogen: $B\!<$, $({:}P\!<) > ({>}Si\!<) > (OP\!<) > ({>}Ge\!<), ({>}Sn\!<), ({:}As\!<)$. When halogen and bridging oxygens are exchanged between two different classes in this series, the preferential effects treated in this paper will be observed; whereas, for exchange within a given class, the sorting of these polyfunctional atoms within a molecular backbone approaches randomness. As indicated by the connecting lines in Figure 3, increasing the molecular weight of the halide generally causes an increase in the value of $\Delta F°$ for $\Delta F° >$ *ca.* 6 and a decrease for lower values. This decrease may lead to a reversal of the preference, as is seen in the case of Hal *vs.* O exchange between ${:}P\!<$ and ${>}Si\!<$ where at equilibrium (1) chlorine is preferentially located on the silicon, (2) there is little preference for the Br *vs.* O case, and (3) the iodine is preferentially situated on the phosphorus.

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