

EXCHANGE OF SUBSTITUENTS BETWEEN THE DIMETHYLSILICON AND THE DIMETHYLGERMANIUM MOIETIES

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From a recent review¹ of scrambling reactions it appears that, prior to the work reported here and in two companion papers², there have been no quantitative studies of the equilibrium resulting from exchange of two kinds of substituents between a pair of different central moieties. This is probably due in great part to the mathematical complexity of such systems and the lack, prior to the last decade, of adequate analytical methods for the molecular assay of complex mixtures. We became interested in this problem because of its pertinence to the understanding of molecular structures to be obtained in equilibrated families of compounds exhibiting mixed-atom molecular backbones. If the scrambling of, say, a halogen atom and a methoxy group between two different central moieties is highly nonrandom, a similar situation may be expected in the scrambling of the halogen with bridging oxygens so that the moiety having the greatest affinity for the halogen will thus be forced into *meso* molecules (those structures based on a single central moiety) and into terminal positions in the larger molecules.

The scrambling of several kinds of groups between different central moieties involves the concomitant loss of one type of bond and formation of another; e.g., in the reaction $QZ_v + MT_\mu \rightarrow QZ_{v-i}T_i + MZ_iT_{\mu-i}$, there is a loss of i Q-Z and i M-T bonds accompanied by a gain of i Q-T and i M-Z bonds. Thus, this type of scrambling reaction cannot be classed as "thermoneutral"³ and, in general, a reasonably large heat of reaction is expected. The work described in this paper is a prelude to the study of families of molecules exhibiting mixed backbones and is necessary to the proper understanding of such systems.

EXPERIMENTAL

Reagents

Dimethyldichlorogermane, dimethyldibromogermane and dimethyldiiodogermane were prepared by an improved version⁴ of the direct synthesis⁵ from germanium powder and the respective methyl halide. Bis(methylthio)dimethylsilane⁶, and dimethoxydimethylgermane⁷ were prepared as reported previously. Bis(methylthio)dimethylgermane was prepared from dimethyldichlorogermane and lead methylmercaptide, in 65% yield, b.p. 42°/1 mm. Dimethoxydimethylsilane was purchased from the Anderson Chemical Company and redistilled.

Equilibration

Equilibrium was achieved by maintaining the chosen proportions of the starting materials, the dimethylgermanium compound and the dimethylsilicon compound, in

sealed 5 mm O.D. precision nuclear-magnetic-resonance (NMR) tubes at the desired reaction temperature. The time required for reaching equilibrium at this temperature was estimated on the basis of test runs at several different ratios of starting materials evaluated after various time intervals until the proton NMR spectra did not exhibit any further change. To assure that the equilibria correspond to the reported temperature, the samples were cooled by quenching and the NMR spectra were run immediately thereafter. Even with this precaution, the systems involving exchange of halogens with methoxyl groups react so rapidly that the reported data must correspond to equilibria at a lower temperature than the one cited.

It was found that equilibria in the systems $(\text{CH}_3)_2\text{SiT}_2$ vs. $(\text{CH}_3)_2\text{GeZ}_2$ were reached in periods less than the ones given below, with the times at which the data were obtained being given in parentheses. For $\text{T} = \text{OCH}_3$ and $\text{Z} = \text{Cl}$: 1 h at 25° (120 h at 120°); for $\text{T} = \text{OCH}_3$ and $\text{Z} = \text{Br}$: 1 h at 25° (24 h at 120°); for $\text{T} = \text{OCH}_3$ and $\text{Z} = \text{I}$: 1 h at 25° (26 h at 120°); for $\text{T} = \text{SCH}_3$ and $\text{Z} = \text{Cl}$: 108 h at 120° (154 h at 120°); for $\text{T} = \text{SCH}_3$ and $\text{Z} = \text{Br}$: 67 h at 120° (209 h at 120°); for $\text{T} = \text{SCH}_3$ and $\text{Z} = \text{I}$: 70 h at 25° (24 h at 120°); for $\text{T} = \text{SCH}_3$ and $\text{Z} = \text{OCH}_3$: 8 h at 120° (74 h at 120°).

NMR measurements

Proton NMR spectra were obtained on a Varian Model A-60 spectrometer as previously described^{1,5}, with measurements being carried out on the neat liquids at 35° . Proton NMR chemical shifts of the dimethylgermanium and dimethylsilicon moieties in the species present at equilibrium are reported in Table I. Peak areas were determined by electronic integration or - in cases of overlapping signals - by cutting out and weighing Xerox copies of the spectra⁹.

TABLE I

PROTON NMR CHEMICAL SHIFTS REPRESENTING THE DIMETHYLSILICON AND DIMETHYLGERMANIUM MOIETIES OBSERVED IN EQUILIBRATED SAMPLES OF EQUIMOLAR AMOUNTS OF $(\text{CH}_3)_2\text{SiT}_2$ vs. $(\text{CH}_3)_2\text{GeZ}_2$, IN PPM RELATIVE TO TMS AS INTERNAL STANDARD IN THE NEAT LIQUIDS

Z	T	$(\text{CH}_3)_2\text{GeZ}_2$	$(\text{CH}_3)_2\text{GeTZ}$	$(\text{CH}_3)_2\text{GeT}_2$	$(\text{CH}_3)_2\text{SiZ}_2$	$(\text{CH}_3)_2\text{SiTZ}$	$(\text{CH}_3)_2\text{SiT}_2$
Cl	OCH_3^a	-1.115	-0.737	-0.562	-0.761	-0.411	-0.041
Br	OCH_3^b	-1.438	-0.935	-0.428	-1.703	-0.552	-0.032
I	OCH_3^c	-1.962	-1.186	-0.410	-1.605	-0.820	-0.035
Cl	SCH_3	-1.187	-0.953 ^d	-0.709 ^e	-0.785	-0.643 ^f	-0.476 ^g
Br	SCH_3	-1.458	-1.092 ^h	-0.700 ⁱ	-1.092	-0.792 ^j	-0.475 ^k
I	SCH_3	-1.960	-1.279 ^l	-0.703 ^m	-1.605	-1.000 ⁿ	-0.475 ^o
OCH_3	SCH_3	-0.433 ^p	-0.583 ^q	-0.700 ^r	-0.033 ^s	-0.288 ^t	-0.475 ^u

^a Only one OCH_3 resonance observed at -3.418 ppm. ^b Only one OCH_3 resonance observed at -3.418 ppm. ^c Only one OCH_3 resonance observed at -3.482 ppm. ^d SCH_3 resonance seen at -2.157 ppm. ^e SCH_3 resonance seen at -2.037 ppm. ^f SCH_3 resonance seen at -2.067 ppm. ^g SCH_3 resonance seen at -1.982 ppm. ^h SCH_3 resonance seen at -2.143 ppm. ⁱ SCH_3 resonance seen at -2.030 ppm. ^j SCH_3 resonance seen at -2.065 ppm. ^k SCH_3 resonance seen at -1.969 ppm. ^l SCH_3 resonance seen at -2.100 ppm. ^m SCH_3 resonance seen at -2.010 ppm. ⁿ SCH_3 resonance seen at -2.042 ppm. ^o SCH_3 resonance seen at -1.960 ppm. ^p OCH_3 resonance at -3.472 ppm. ^q OCH_3 resonance at -3.438 ppm. ^r SCH_3 resonance at -2.022 ppm. ^s SCH_3 resonance at -2.030 ppm. ^t OCH_3 resonance at -3.405 ppm. ^u OCH_3 resonance at -3.422 ppm. ^v SCH_3 resonance at -1.933 ppm. ^w SCH_3 resonance at -1.968 ppm.

DATA REDUCTION

When the Z substituents of the compound QZ_ν are scrambled with the T substituents of the compound MT_μ , a total of $(\mu + \nu + 2)$ molecular species are formed. Letting the symbol Ξ_i stand for the compound $QZ_iT_{\nu-i}$ and Ξ'_i for $MZ_iT_{\mu-i}$, we see that there are $(\mu + 1)$ compounds of the type Ξ'_i where $i = 0, 1, \dots, \mu$. As previously pointed out¹⁰, a minimum of $(\nu - 1)$ equilibrium constants are needed to represent scrambling of Z and T substituents between molecules of the type Ξ_i and $(\mu - 1)$ for molecules of the type Ξ'_i . For the most precise treatment of experimental data, these $(\nu + \mu - 2)$ constants are chosen to be of the following form:

$$K_{Qi} = \frac{[\Xi_{i-1}][\Xi_{i+1}][\Xi_i]^2}{[\Xi_i]^4} \quad (1)$$

$$K_{Mi} = \frac{[\Xi'_{i-1}][\Xi'_{i+1}][\Xi'_i]^2}{[\Xi'_i]^4} \quad (2)$$

In addition, there is one other necessary equilibrium constant to relate the system of Ξ_i molecules with that of the Ξ'_i molecules. Although this constant, K_I , may be written in a number of different ways¹¹, we have chosen the following format for this constant since this is the form which is most readily evaluated from existing compilations of thermodynamic data:

$$K_I = \frac{[\Xi_0]^\mu [\Xi'_\mu]^x}{([\Xi_\nu]^\mu [\Xi'_0]^x)^{1-x}} \quad (3)$$

where $x = 1$; unless $\mu = \nu$, when $x = \mu = \nu$.

Evaluation of K_I

Due to the nonrandom character of the distribution of Z and T substituents on the two different central moieties, often one or more of the end members of the series (Ξ_0, Ξ_ν, Ξ'_0 , or Ξ'_μ) is present in undetectable amounts. It is therefore not possible to obtain an accurate value of K_I by direct substitution of analytical data into eqn. (3). However, it is feasible to calculate the missing data from the $(\nu - 1)$ K_{Qi} and the $(\mu - 1)$ K_{Mi} equilibrium constants which in turn can be evaluated and their statistical errors determined from the experimental data by use of a previously described computer program¹⁰. The resulting weighted-average equilibrium constants may then be employed to calculate the theoretical composition for any given R value in either system. These R values are obtained from the experimental data; since for the compounds based on the central atom Q, $R_Q = \frac{\sum_i (\nu - i) \Xi_i}{\sum_i \Xi_i}$, and for the system based on the central atom M, $R_M = \frac{\sum_i (\mu - i) \Xi'_i}{\sum_i \Xi'_i}$.

By this means, a value of K_I is obtained for each experiment. The deviation of the average of these values is obtained by taking the square root of the sum of the squares of the deviation of the individual values from the average. The overall composition of a mixture is characterized by two parameters: One to determine the relative amounts of Z and T in the mixture,

$$R = \frac{[T]}{[Q] + [M]} = \frac{\sum_i (\nu - i) \Xi_i + \sum_i (\mu - i) \Xi'_i}{\sum_i \Xi_i + \sum_i \Xi'_i} \quad (4)$$

and one to determine the relative amounts of Q and M,

$$R' = \frac{[Q]}{[Q] + [M]} = \frac{\sum_i \Xi_i}{\sum_i \Xi_i + \sum_i \Xi'_i} \quad (5)$$

Since there has been no previous quantitative treatment of this type of equilibrium, it is desirable to show the kind of composition diagrams to be found in various typical cases. This has been done in Fig. 1 for $\nu = \mu = 2$ in a system obtained by reorganizing various mixtures of Ξ_0 and Ξ'_μ . This situation corresponds to exchanging

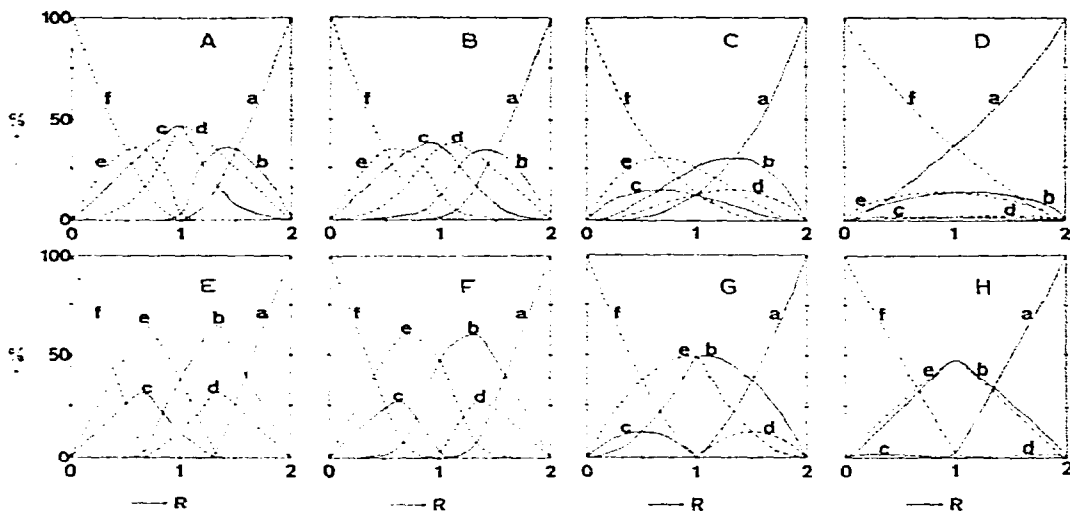


Fig. 1. Concentration of the six possible molecules obtained by equilibrating QT_2 with MZ_2 , as calculated for various sets of equilibrium constants, plotted against the over-all composition parameter $R = \frac{[T]}{[Q] + [M]}$. For Graphs A-D the constants $K_Q = K_M = 0.25$ (ideal randomness) with $K_I = 10^{-6}$ for A, 10^{-3} for B, 1.0 for C (ideal randomness) and 10^{-3} for D. For Graphs E-H the constants $K_Q = K_M = 10^{-4}$ with $K_I = 10^{-6}$ for E, 10^{-3} for F, 1.0 for G (ideal randomness) and 10^{-3} for H. The symbols in the graphs represent: a = $\Xi_0 = QT_2$, b = $\Xi_1 = QZT$, c = $\Xi_2 = QZ_2$, d = $\Xi'_0 = MT_2$, e = $\Xi'_1 = MZT$ and f = $\Xi'_2 = MZ_2$.

Z and T in mixtures made up from various combinations of QT_2 and MZ_2 , where Q stands for the $(CH_3)_2Si$ moiety and M for $(CH_3)_2Ge$ for instance. In this case, $R' = R/2$ because of the use of only QT_2 and MZ_2 as reagents. Graphs A through D of Fig. 1 corresponds to the random scrambling ($K_{Q1} = K_{M1} = 0.25$) of the T and Z substituents on both difunctional moieties, with the intersystem constant, K_I , having two small values (10^{-6} , 10^{-3}), the random value (1.0) and a large value (10^{-3}). As the order of magnitude of K_I is increased above the value of 10^{-3} shown in Graph D, the mixed species are found to decrease to nothing so that in the limiting case (say $K_I = 10^{-25}$), one obtains only the pair of compounds Ξ_0 and Ξ'_2 . Alternatively, for very small values of K_I (say, 10^{-25}), Ξ'_2 drops linearly to zero at $R = 0.5$ and Ξ_0 increases linearly from zero at $R = 1.5$.

A wide range of values for K_I is discussed since, as stated in the INTRODUCTION of this paper, a large plus or minus value for the enthalpy corresponding to the

TABLE 2
EQUILIBRIUM CONSTANTS a IN THE SYSTEMS QZ_4 vs. MT_2 , $[QZ_4] / [QZ_2] = [MT_2] / [MT_4]$ AND $M_{12} = (CH_3)_2C=Ce$

Z	T	K_{QZ_4}	$\frac{[QZ_4][QZ_4]}{[QZ_2]^2}$	K_{MT_2}	$\frac{[MT_2][MT_2]}{[MT_4]^2}$	$K_{M_{12}}$	$\frac{[QZ_4][MT_2]}{[QZ_2][MT_4]}$
Cl	OCH ₃		$(1.00 \times 10^{-2})^{b,c}$		$(1.09 \times 10^{-2})^{b,d}$		$4.5 \times 10^{13} \pm 1.6 \times 10^{11}$
Br	OCH ₃		$(6.4 \times 10^{-3})^e$		$(1.05 \times 10^{-2})^d$		$9.2 \times 10^{12} \pm 5.4 \times 10^{10}$
I	OCH ₃				$(5.37 \times 10^{-2})^d$		$1.14 \times 10^{10} \pm 0.21 \times 10^{10}$
Cl	SCH ₃	0.158 ^f	$(0.178)^g$	3.49×10^{-2}	$(5.49 \times 10^{-2})^g$		$1.02 \times 10^{-3} \pm 0.27 \times 10^{-3}$
Br	SCH ₃	4.06×10^{-2}	$(4.94 \times 10^{-2})^g$	1.92×10^{-2}	$(2.49 \times 10^{-2})^g$		4.45 ± 0.51
I	SCH ₃	1.26×10^{-2}		1.12×10^{-2}	$(1.23 \times 10^{-2})^g$		$3.47 \times 10^{14} \pm 0.53 \times 10^{14}$
OCH ₃	SCH ₃	5.17	$(2.02)^g$	1.99	$(2.66)^g$		$2.56 \times 10^{-4} \pm 0.42 \times 10^{-4}$

^a Calculated from the experimental data obtained from samples held at 120° and quenched to room temperature. ^b Data in parentheses are obtained from the systems QZ_4 vs. QT_4 or MZ_2 vs. MT_4 respectively. ^c Ref. 8, ^d Ref. 8, ^e Ref. 7, ^f From Table 11, ^g Data not in parentheses were obtained from the NMR data in the system QZ_4 vs. MT_4 , ^h Ref. 9.

equilibrium reaction of eqn. (3) is to be expected, even though the scrambling of the two substituents on one or the other of the difunctional moieties may have zero enthalpy.

Graphs E through H of Fig. 1 correspond to a like variation of K_I for the situation where the mixed species is preferred in the scrambling of two substituents on each of the difunctional moieties taken individually, *i.e.*, $K_{Q1} = K_{M1} = 10^{-4}$. The third case in which K_{Q1} and K_{M1} are both large, *e.g.* 10^{+2} or 10^{+4} is not shown in Fig. 1 since for all values of K_I the graphs are dominated by Ξ_0 and Ξ'_2 , somewhat similarly to Graph D.

Calculation of theoretical compositions

In the case of scrambling of two kinds of substituents on a given central atom or moiety, the calculation of the amounts of the various mixed species for a given over-all composition (R value) is sufficiently difficult to warrant use of a computer program¹⁰. The problem is more complex when two kinds of substituents are scrambled between two different central atoms, as described in this manuscript. This latter problem has now been programmed in Fortran IV for an IBM-7040 computer using an iterative procedure similar to that previously employed¹⁰.

In this program, the formerly used parameter, $G = [\Xi_0]/[\Xi'_2]$, is employed for the distribution of the substituents on the central moiety Q. A similar parameter $G' = [\Xi'_0]/[\Xi'_2]$ can then be obtained for the central moiety M from

$$G' = \sqrt{G \cdot K_I} \quad (9)$$

Thus a set of concentrations is obtained for each of the two central moieties, using eqn. (20) of ref. 10. Since R' gives the proportion in which these central moieties are present in the whole mixture, one can combine both sets accordingly and the R value can be calculated. Another iteration can then be made by properly correcting the parameter G . Iterations are stopped when the calculated R value is sufficiently close to the desired R value.

RESULTS AND CONCLUSIONS

Equilibrium constants and data

The equilibrium constants found for the seven systems studied in this investigation are presented in Table 2. The numbers given in parentheses in this table are the values obtained in our previous studies⁷⁻⁹ or those described in the Appendix of this paper for the scrambling of this pair of substituents on either the dimethyl-silicon or the dimethylgermanium moiety taken by itself. The supporting data from which the equilibrium constants of Table 2 were obtained are individually presented for each of the seven systems in Tables 3-9. In these latter tables, the values in parentheses were calculated according to a scheme presented earlier under the heading "Calculation of theoretical compositions" using the equilibrium constants of Table 2. In Table 5, a value for K_Q was assumed to be 1×10^{-3} by extrapolation of the data obtained for the chlorine and bromine analogs.

Inspection of Tables 3 through 9 shows generally good agreement between the experimentally measured concentrations and the values calculated from the equi-

TABLE 3

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA^d IN MOLE PERCENT IN THE SYSTEM $(\text{CH}_3)_2\text{GeCl}_2$ vs. $(\text{CH}_3)_3\text{Si}(\text{OC}_2\text{H}_5)_2$

$R = \text{CH}(\text{Si} + \text{Ge})$	$R' = \text{Si}(\text{Si} + \text{Ge})$	$(\text{CH}_3)_2\text{GeCl}_2$	$(\text{CH}_3)_2\text{GeCl}(\text{OC}_2\text{H}_5)$	$(\text{CH}_3)_2\text{Ge}(\text{OC}_2\text{H}_5)_2$	$(\text{CH}_3)_3\text{SiCl}_2$	$(\text{CH}_3)_3\text{Si}(\text{OC}_2\text{H}_5)$	$(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$
0.299 ^b	0.851 ^b	16.9	0.1	0.1	83.0
(0.333) ^c	(0.831) ^c	(14.8) ^d	(0.1)	(0.0)	(0.0)	(0.1)	(85.0)
0.577	0.712	31.5	0.1	0.1	68.3
(0.611)	(0.684)	(28.7)	(0.1)	(0.0)	(0.0)	(0.1)	(71.0)
0.847	0.577	45.8	0.3	0.1	53.8
(0.941)	(0.539)	(42.2)	(0.1)	(0.0)	(0.0)	(0.1)	(57.3)
1.113	0.443	58.6	0.3	41.1
(1.202)	(0.411)	(55.5)	(0.2)	(0.0)	(0.0)	(0.1)	(44.2)
1.360	0.320	71.2	0.3	28.5
(1.446)	(0.285)	(67.9)	(0.1)	(0.0)	(0.0)	(0.0)	(31.9)
1.589	0.206	81.4	0.2	18.4
(1.649)	(0.184)	(79.3)	(0.1)	(0.0)	(0.0)	(0.2)	(20.4)
1.837	0.082	94.8	0.1	7.1
(1.870)	(0.071)	(91.8)	(0.0)	(0.0)	(0.0)	(0.1)	(8.1)

^a Data were obtained within 1-2 h after quenching to room temperature. ^b From the ingredients. ^c Values in parentheses are calculated from the NMR data. ^d Values in parentheses are calculated from the equilibrium constants K_Q , K_M and K_1 in Table 2.

TABLE 4
EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA^a IN MOLE PERCENT IN THE SYSTEM $(CH_3)_2GeBr_2$ vs. $(CH_3)_2Si(OCH_3)_2$

$R_{Si} = Br/(Si + Ge)$	$R_{Ge} = Si/(Si + Ge)$	$(CH_3)_2GeBr_2$	$(CH_3)_2GeBr(OCH_3)$	$(CH_3)_2Ge(OCH_3)_2$	$(CH_3)_2SiBr_2$	$(CH_3)_2SiBr(OCH_3)$	$(CH_3)_2Si(OCH_3)_2$
0.234 ^b (0.216) ^c	0.883 ^b (0.900) ^c	10.7 (11.3) ^d	0.1 (0.1)	0.1 (0.4)	89.1 (87.9)
0.471 (0.474)	0.764 (0.764)	23.3 (23.0)	0.4 (0.6)	0.4 (0.5)	76.0 (75.9)
0.715 (0.715)	0.643 (0.643)	35.5 (35.1)	0.2 (0.6)	0.3 (0.6)	64.0 (63.6)
0.934 (0.936)	0.533 (0.537)	46.3 (46.0)	0.1 (0.7)	...	0.3 (0.0)	0.3 (0.7)	53.1 (52.6)
1.175 (1.169)	0.413 (0.420)	57.8 (58.1)	0.2 (0.6)	...	0.3 (0.0)	0.5 (0.7)	41.2 (40.6)
1.382 (1.345)	0.309 (0.317)	68.1 (68.5)	0.3 (0.6)	...	0.3 (0.0)	0.4 (0.6)	31.0 (30.3)
1.603 (1.589)	0.198 (0.205)	78.8 (79.6)	0.8 (0.5)	0.5 (0.5)	20.0 (19.3)

^a Data were obtained within 1-2 h after quenching to room temperature. ^b From the integrations. ^c Values in parentheses are calculated from the NMR data. ^d Values in parentheses are calculated from the equilibrium constants K_9 , K_M and K_I in Table 2.

TABLE 5

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA^a IN MOLE PERCENT IN THE SYSTEM $(\text{CH}_3)_2\text{GeI}_2$ vs. $(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$

$\text{Re} = \text{I}(\text{Si} + \text{Ge})$	$K^c = \text{Si}/(\text{Si} + \text{Ge})$	$(\text{CH}_3)_2\text{GeI}_2$	$(\text{CH}_3)_2\text{GeI}(\text{OCH}_3)$	$(\text{CH}_3)_2\text{Ge}(\text{OCH}_3)_2$	$(\text{CH}_3)_2\text{SiI}_2$	$(\text{CH}_3)_2\text{Si}(\text{OCH}_3)$	$(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$
0.233 ^b	0.883 ^b	10.9	0.7	88.3
(0.225) ^c	(0.883) ^c	(10.6) ^d	(1.1)	(0.0)	(0.0)	(1.1)	(87.3)
0.459	0.771	21.5	1.3	0.2	77.1
(0.445)	(0.773)	(21.5)	(1.4)	(0.0)	(0.0)	(1.5)	(75.6)
0.725	0.637	36.8	2.2	0.4	60.7
(0.762)	(0.611)	(34.6)	(1.7)	(0.0)	(0.0)	(1.7)	(62.1)
0.937	0.532	44.8	2.5	0.3	52.4
(0.924)	(0.527)	(45.1)	(1.7)	(0.0)	(0.0)	(1.7)	(51.4)
1.152	0.424	55.6	2.9	0.4	41.2
(1.145)	(0.416)	(55.9)	(1.7)	(0.0)	(0.0)	(1.7)	(40.7)
1.368	0.316	65.1	2.8	0.4	31.7
(1.334)	(0.321)	(66.8)	(1.6)	(0.0)	(0.0)	(1.6)	(30.0)
1.628	0.186	78.4	2.7	0.8	18.2
(1.603)	(0.190)	(80.1)	(1.3)	(0.0)	(0.0)	(1.3)	(17.3)

^a Data were obtained within 1-2 h after quenching to room temperature. ^b From the ingredients. ^c Values in parentheses are calculated from the NMR data. ^d Values in parentheses are calculated from the equilibrium constants K^c , K^M and K^I in Table 2.

TABLE 6

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA^a IN MOLE PERCENT IN THE SYSTEM $(CH_3)_2GeCl_2$ vs. $(CH_3)_2Si(SiCH_3)_2$

$R = Cl/Si + Ge$	$R^{100}Si/Si + Ge$	$(CH_3)_2GeCl_2$	$(CH_3)_2GeCl(SiCH_3)$	$(CH_3)_2Ge(SiCH_3)_2$	$(CH_3)_2SiCl_2$	$(CH_3)_2SiCl(SiCH_3)$	$(CH_3)_2Si(SiCH_3)_2$
0.255 ^b (0.244) ^c	0.872 ^b (0.839) ^c	---	0.3 (0.3)	15.7 (12.5)	0.9 (1.3)	22.3 (22.6)	60.7 (63.3)
0.492 (0.499)	0.754 (0.753)	---	1.1 (1.7)	23.0 (22.9)	6.2 (5.9)	35.9 (35.7)	33.2 (33.8)
0.759 (0.762)	0.620 (0.634)	---	8.0 (6.9)	28.6 (31.0)	16.6 (17.4)	35.0 (34.1)	11.8 (10.5)
1.015 (1.032)	0.493 (0.499)	0.8 (0.6)	24.6 (22.0)	24.7 (28.1)	28.7 (30.6)	19.6 (17.1)	1.6 (1.5)
1.274 (1.273)	0.367 (0.364)	6.5 (6.0)	46.4 (45.5)	10.7 (11.6)	31.7 (33.1)	4.5 (3.7)	0.2 (0.1)
1.510 (1.513)	0.245 (0.237)	31.8 (29.3)	41.1 (44.0)	2.6 (2.2)	22.9 (24.0)	0.8 (0.5)	— (0.0)
1.749 (1.749)	0.125 (0.118)	63.9 (62.8)	23.7 (24.4)	0.6 (0.3)	11.6 (12.5)	0.2 (0.1)	— (0.0)

^a The rate of equilibration at room temperature is sufficiently slow so that quenched samples represent the equilibrium at 120°. ^b From the ingredients. ^c Values in parentheses are calculated from the NMR data. ^d Values in parentheses are calculated from the equilibrium constants K_Q , K_M and K_I in Table 2.

TABLE 7

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA^a IN MOLE PERCENT IN THE SYSTEM $(\text{CH}_3)_3\text{GeBr}_2$ vs. $(\text{CH}_3)_2\text{Si}(\text{SCH}_3)_2$

$R_{\text{Si}} \text{Br} / (\text{Si} + \text{Ge})$	$R_{\text{Si}} / (\text{Si} + \text{Ge})$	$(\text{CH}_3)_2\text{GeBr}_2$	$(\text{CH}_3)_2\text{Ge}(\text{SCH}_3)$	$(\text{CH}_3)_2\text{Ge}(\text{SCH}_3)_2$	$(\text{CH}_3)_2\text{SiBr}_2$	$(\text{CH}_3)_2\text{Si}(\text{SCH}_3)$	$(\text{CH}_3)_2\text{Si}(\text{SCH}_3)_2$
0.238 ^b	0.881 ^b	0.5	4.6	6.8	0.7	19.4	68.0
(0.264) ^c	(0.881) ^d	(0.1) ^d	(5.2)	(6.6)	(0.2)	(18.0)	(69.9)
0.548	0.726	1.2	17.7	8.2	1.7	32.8	38.4
(0.563)	(0.729)	(0.9)	(18.9)	(7.6)	(1.1)	(32.0)	(39.5)
0.799	0.600	4.2	30.5	6.3	2.1	36.2	20.5
(0.795)	(0.588)	(3.3)	(31.1)	(5.6)	(2.7)	(36.9)	(20.5)
1.023	0.489	9.0	39.6	2.7	5.4	33.9	9.5
(1.023)	(0.488)	(8.9)	(39.0)	(3.3)	(5.5)	(34.5)	(8.9)
1.315	0.343	24.8	41.0	0.7	9.0	22.6	1.9
(1.311)	(0.335)	(25.0)	(39.5)	(1.2)	(9.8)	(22.4)	(2.1)
1.565	0.217	47.8	32.0	0.3	9.6	9.8	0.5
(1.566)	(0.199)	(46.5)	(31.3)	(0.4)	(10.8)	(10.5)	(0.4)
1.742	0.129	70.5	20.9	---	5.6	3.0	---
(1.760)	(0.086)	(65.7)	(21.3)	(0.1)	(8.7)	(4.1)	(0.1)

^aThe rate of equilibration at room temperature is sufficiently slow so that quenched samples represent the equilibrium at 120°. ^bFrom the ingredients. ^cValues in parentheses are calculated from the NMR data. ^dValues in parentheses are calculated from the equilibrium constants K_0 , K_1 and K_2 in Table 2.

TABLE 8

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA^a IN MOLE PERCENT IN THE SYSTEM $(CH_3)_2GeI_2$ vs. $(CH_3)_2Si(Si(CH_3)_2)_2$

$R_{Si} = I/(Si + Ge)$	$(CH_3)_2GeI_2$	$(CH_3)_2GeI(SiCH_3)$	$(CH_3)_2Ge(SiCH_3)_2$	$(CH_3)_2SiI_4$	$(CH_3)_2Si(SiCH_3)_2$	$(CH_3)_2Si(SiCH_3)_3$
0.266 ^b	3.2	10.3	0.4	0.2	10.8	75.2
(0.278) ^c	(3.0) ^d	(9.9)	(0.4)	(0.0)	(10.6)	(76.1)
0.553	10.4	17.2	0.3	0.2	16.7	55.3
(0.569)	(11.0)	(16.4)	(0.3)	(0.1)	(16.8)	(55.5)
0.759	19.6	19.2	---	0.3	18.7	42.3
(0.775)	(18.8)	(19.0)	(0.2)	(0.1)	(19.2)	(42.8)
0.882	24.9	20.6	---	0.4	19.7	34.4
(0.908)	(24.2)	(19.8)	(0.2)	(0.1)	(19.9)	(35.9)
1.356	52.9	17.0	---	0.4	15.3	14.3
(1.390)	(49.6)	(18.1)	(0.1)	(0.3)	(17.7)	(14.2)
1.556	64.5	13.5	---	0.3	15.8	5.9
(1.599)	(61.9)	(9.5)	(0.0)	(0.8)	(20.7)	(7.1)
1.808	83.0	7.7	---	0.4	6.8	2.1
(1.844)	(82.0)	(8.3)	(0.0)	(0.4)	(7.5)	(1.7)

^aThe rate of equilibration at room temperature is sufficiently slow so that quenched samples represent the equilibrium at 120°. ^bFrom the ingredients. ^cValues in parentheses are calculated from the NMR data. ^dValues in parentheses are calculated from the equilibrium constants K_q , K_M and K_1 in Table 2.

TABLE 9

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA^a IN MOLE PERCENT IN THE SYSTEM $(\text{CH}_3)_3\text{Ge}(\text{OCH}_3)_3$ vs. $(\text{CH}_3)_3\text{Si}(\text{SCH}_3)_3$

$R_{\text{Si}} = \frac{\text{SCH}_3}{\text{Si} + \text{Ge}}$	$R_{\text{Ge}} = \frac{\text{SCH}_3}{\text{Si} + \text{Ge}}$	$(\text{CH}_3)_3\text{Ge}(\text{SCH}_3)_3$	$(\text{CH}_3)_3\text{Ge}(\text{SCH}_3)(\text{OCH}_3)_2$	$(\text{CH}_3)_2\text{Ge}(\text{SCH}_3)_2$	$(\text{CH}_3)_2\text{Ge}(\text{SCH}_3)(\text{OCH}_3)$	$(\text{CH}_3)_2\text{Si}(\text{SCH}_3)_2$	$(\text{CH}_3)_2\text{Si}(\text{SCH}_3)(\text{OCH}_3)$	$(\text{CH}_3)_3\text{Si}(\text{OCH}_3)_3$
0.352 ^b	0.176 ^d	9.8	16.6	56.5	17.2
(0.364) ^b	(0.172) ^b	(9.4) ^c	(16.3)	(56.6)	(0.0)	(0.1)	(0.1)	(17.6)
0.589	0.294	20.6	17.9	33.0	28.5
(0.591)	(0.285)	(20.3)	(18.1)	(32.2)	(0.0)	(0.2)	(0.2)	(29.3)
0.828	0.414	34.9	13.9	9.9	40.7
(0.843)	(0.413)	(34.3)	(13.6)	(10.7)	(0.0)	(0.5)	(0.5)	(40.9)
1.066	0.533	47.1	46.8
(1.049)	(0.529)	(45.0)	(1.6)	(0.1)	3.7	2.4	2.4	(42.8)
1.286	0.643	55.5	(4.4)	(6.1)	(6.1)	...
(1.307)	(0.644)	(55.2)	(0.5)	(0.0)	24.2	11.3	11.3	28.9
1.522	0.761	64.4	(23.1)	(11.5)	(11.5)	(29.7)
(1.519)	(0.756)	(63.7)	(0.2)	(0.0)	45.7	11.7	11.7	18.2
1.767	0.883	72.0	(46.0)	(12.5)	(12.5)	(17.6)
(1.750)	(0.881)	(71.6)	(0.0)	(0.0)	70.0	11.0	11.0	7.1
					(71.8)	(9.7)	(9.7)	(6.8)

^a The rate of equilibration at room temperature is sufficiently slow so that quenched samples represent the equilibrium at 120°. ^b From the ingredients. ^c Values in parentheses are calculated from the NMR data. ^d Values in parentheses are calculated from the equilibrium constants K_Q , K_M and K_T in Table 2.

librium constants. In no case did there seem to be a systematic trend with the over-all composition (R and R' values shown in the table) so that there appears to be no need to use activity coefficients to make the thermodynamic concept of equilibria fit the data to within the experimental error. It should be noted that the experimental error in NMR measurements of the type reported in Tables 3-9 are, for each peak measured, about 1% of the total hydrogen in all peaks. Thus, the first experimental figure in the left-hand corner of Table 3 should read as 16.9 with an absolute error of *ca.* ± 1 . Although very small values [0.1% of the total (Si + Ge)] may be detected and quantitatively estimated, such values still carry an error of *ca.* 1 percentage point.

DISCUSSION

The agreement between the values for the equilibrium constants K_Q and K_M previously measured on the dimethylsilicon and dimethylgermanium systems taken independently and the values obtained in this study of the mixed systems is most gratifying. The poorest agreement was found in the system where $Z = \text{OCH}_3$ and $T = \text{SCH}_3$ where the disagreement was nearly twofold. In the case of K_Q for this system, the error is probably attributable to the fact that aluminum chloride had to be used as a catalyst (see Table 10) and it induced the formation of byproducts which probably caused K_Q to be somewhat inaccurate.

The extremely large values for the equilibrium constants where the dihalodimethylgermane is mixed with the dimethyldimethoxysilane indicates that the reverse reaction in which the dihalodimethylsilane is mixed with dimethyldimethoxygermane should give essentially complete transfer of the methoxyl from the germanium to the silicon, accompanied by noticeable evolution of heat. This was observed in a series of test experiments.

The approximate time to reach equilibrium in the exchange of a pair of substituents between dimethylsilicon and dimethylgermanium was found in this study to be intermediate between the approximate times for exchange of the same pair of substituents on either dimethylsilicon or dimethylgermanium when each system was studied individually. Thus, exchange of halogens with methoxyl groups on dimethylgermanium is rapid and is completed in less than a few seconds at room temperature; whereas, in the dimethylsilicon system⁸, several hours at 120° are needed. In the mixed dimethylsilicon/dimethylgermanium systems studied here, the rates were too fast to be measured by changes in concentration with time but slower than in the dimethylgermanium system. Similar relationships were found for the slower exchange of halogens with the methylthio group and the similarly slower exchange of methoxyl with methylthio groups.

Whereas the equilibrium in the case of exchange of halogens with methoxyl groups is such that the halogen strongly gravitates towards the germanium, there is continuous change when going from Cl to Br to I in the exchange of a halogen with methylthio groups. In the latter case, the chlorine gravitates to the silicon and the iodine to the germanium, with the bromine and methylthio groups being almost randomly distributed between the dimethylsilicon and the dimethylgermanium moieties. In the exchange of methoxyl with methylthio groups, the methoxyl group goes primarily with the dimethylsilicon and the methylthio with the dimethyl-

TABLE 10

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA FOR SOME SYSTEMS QZ_2 vs. QT_2 AND MZ_2 vs. MT_2 FOR $Q = (CH_3)_2Si$ AND $M = (CH_3)_2Ge$ AND VARIOUS T'S AND Z'S*The System^a $(CH_3)_2SiBr_2$ vs. $(CH_3)_2Si(OCH_3)_2$*

$R \equiv Br/Si$	$(CH_3)_2SiBr_2$	$(CH_3)_2SiBr(OCH_3)$	$(CH_3)_2Si(OCH_3)_2$
0.319 ^b (0.359) ^c	0.4 (0.1) ^d	32.6 (31.7)	67.0 (68.2)
0.652 (0.649)	0.6 (0.7)	62.4 (63.7)	37.0 (35.6)
1.015 ^e (1.027)	7.5 (7.7)	86.2 (86.1)	6.3 (6.2)
1.272 (1.293)	27.9 (28.3)	70.9 (70.6)	1.1 (1.1)
1.557 (1.507)	55.4 (55.9)	44.2 (43.9)	0.4 (0.2)

The System^f $(CH_3)_2SiCl_2$ vs. $(CH_3)_2Si(SCH_3)_2$

$R \equiv Cl/Si$	$(CH_3)_2SiCl_2$	$(CH_3)_2SiCl(SCH_3)$	$(CH_3)_2Si(SCH_3)_2$
0.382 ^b (0.368) ^c	2.0 (2.9) ^d	32.8 (32.4)	65.2 (64.7)
0.617 (0.634)	7.9 (8.0)	47.6 (45.6)	44.5 (46.3)
0.935 ^e (0.895)	17.4 (19.7)	54.7 (54.0)	27.9 (26.3)
1.323 (1.324)	44.9 (42.1)	42.6 (43.1)	12.6 (9.8)
1.653 (1.643)	68.1 (67.6)	28.6 (30.0)	3.3 (2.4)

The System^h $(CH_3)_2SiBr_2$ vs. $(CH_3)_2Si(SCH_3)_2$

$R \equiv Br/Si$	$(CH_3)_2SiBr_2$	$(CH_3)_2SiBr(SCH_3)$	$(CH_3)_2Si(SCH_3)_2$
0.361 ^b (0.371) ^c	1.0 (0.9) ^d	35.1 (34.3)	63.9 (64.8)
0.711 (0.724)	5.7 (5.3)	61.0 (60.5)	33.3 (34.2)
1.053 ⁱ (1.072)	19.2 (18.2)	68.8 (68.9)	12.1 (12.9)
1.357 (1.351)	41.6 (39.7)	54.9 (55.4)	3.5 (4.0)
1.724 (1.744)	74.9 (72.9)	24.6 (26.6)	0.4 (0.5)

Continued on p. 435

TABLE 10 (continued)

The Systemⁱ $(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$ vs. $(\text{CH}_3)_2\text{Si}(\text{SCH}_3)_2$

$R \equiv \text{SCH}_3/\text{Si}$	$(\text{CH}_3)_2\text{Si}(\text{SCH}_3)_2$	$(\text{CH}_3)_2\text{Si}(\text{SCH}_3)(\text{OCH}_3)$	$(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$
0.407 ^b (0.431) ^c	12.7 (11.8) ^d	17.7 (17.0)	69.6 (71.2)
0.722 (0.731)	25.8 (25.3)	21.5 (21.5)	52.7 (53.2)
1.049 ^k (1.108)	44.3 (41.1)	22.2 (22.6)	33.5 (36.3)
1.353 (1.396)	59.4 (57.3)	20.8 (20.8)	19.8 (22.0)
1.686 (1.734)	80.6 (76.9)	12.2 (14.8)	7.2 (8.3)

The System^l $(\text{CH}_3)_2\text{Ge}(\text{SCH}_3)_2$ vs. $(\text{CH}_3)_2\text{Ge}(\text{OCH}_3)_2$

$R \equiv \text{OCH}_3/\text{Ge}$	$(\text{CH}_3)_2\text{Ge}(\text{SCH}_3)_2$	$(\text{CH}_3)_2\text{Ge}(\text{SCH}_3)(\text{OCH}_3)$	$(\text{CH}_3)_2\text{Ge}(\text{OCH}_3)_2$
0.410 ^b (0.398) ^c	71.8 (70.6) ^d	16.6 (17.8)	11.6 (11.6)
0.650 (0.699)	54.0 (53.0)	22.1 (22.4)	23.9 (24.6)
1.001 ^m (1.010)	37.8 (37.7)	23.4 (23.7)	38.8 (38.7)
1.390 (1.388)	19.9 (19.9)	21.6 (21.2)	58.6 (58.9)
1.684 (1.693)	7.3 (8.1)	16.1 (15.4)	76.6 (76.5)

^a Equilibrium reached in less than 0.5 h at 25°, data corresponds to 6 h at 25°. ^b Values calculated from the ingredients. ^c Values in parentheses calculated from the NMR data. ^d Values in parentheses calculated from the equilibrium constants in Table 11. ^e A neat liquid sample of this composition showed signals having the following NMR shifts: $(\text{CH}_3)_2\text{SiBr}_2$, -1.063; $(\text{CH}_3)_2\text{SiBr}(\text{OCH}_3)$, -0.542, -3.467; $(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$, -0.022, -3.417 ppm. ^f Equilibrium reached in less than 100 h at 120°, data corresponds to 154 h at 120°. ^g A neat liquid sample of this composition showed signals having the following NMR shifts: $(\text{CH}_3)_2\text{SiCl}_2$, -0.750; $(\text{CH}_3)_2\text{SiCl}(\text{SCH}_3)$, -0.621, -2.037; $(\text{CH}_3)_2\text{Si}(\text{SCH}_3)_2$, -0.448, -1.947 ppm. ^h Equilibrium reached in less than 46 h at 120°; data correspond to 145 h at 120°. ⁱ A neat liquid sample of this composition showed signals having the following NMR shifts: $(\text{CH}_3)_2\text{SiBr}_2$, -1.060; $(\text{CH}_3)_2\text{SiBr}(\text{SCH}_3)$, -0.767, -2.047; $(\text{CH}_3)_2\text{Si}(\text{SCH}_3)_2$, -0.440, -1.950 ppm. ^j Equilibrium reached in less than 24 h at 120° with AlCl_3 as catalyst, data corresponds to 48 h at 120°. No reaction is observed in the absence of a catalyst at 120° and 150°. ^k A neat liquid sample of this composition showed signals having the following NMR shifts: $(\text{CH}_3)_2\text{Si}(\text{SCH}_3)_2$, -0.483, -2.033; $(\text{CH}_3)_2\text{Si}(\text{SCH}_3)(\text{OCH}_3)$, -0.297, -1.983, -3.500; $(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$, -0.025, -3.500 ppm. ^l Equilibrium reached in less than 46 h at 120°; data corresponds to 92 h at 120°. ^m A neat liquid sample of this composition showed signals having the following NMR shifts: $(\text{CH}_3)_2\text{Ge}(\text{SCH}_3)_2$, -0.717, -2.042; $(\text{CH}_3)_2\text{Ge}(\text{SCH}_3)(\text{OCH}_3)$, -0.596, -2.033, -3.441; $(\text{CH}_3)_2\text{Ge}(\text{OCH}_3)_2$, -0.445, -3.467 ppm.

TABLE II
EQUILIBRIUM CONSTANTS IN THE SYSTEMS QZ_2 vs. QT_2 AT 120°

Q	Z	T	K^a	s^b
$(CH_3)_2Si^c$	Br	OCH ₃	0.0064	0.0011
$(CH_3)_2Si$	Ci	SCH ₃	0.178	0.017
$(CH_3)_2Si$	Br	SCH ₃	0.0494	0.0062
$(CH_3)_2Si$	OCH ₃	SCH ₃	2.92	0.51
$(CH_3)_2Ge$	OCH ₃	SCH ₃	2.60	0.11

^a $K = [QZ_2][QT_2]/[QZT]^2$. ^b s = standard error. ^c At 25°.

germanium at equilibrium. These findings cannot be simply interpreted² in terms of ionic character of σ bonds using the defining equation for Pauling-type electronegativities. At present, we are ascribing much of the large deviation from randomness ($K_I = 1$) of the intersystem equilibrium constant, K_I , to differences in π bonding occurring as a result of the reaction described by eqn. (3). Theoretical work on this problem is underway in our laboratory.

APPENDIX

The equilibrium constants K_Q and K_M shown in Table 2 have been determined from the data in Tables 3-9, *i.e.*, from the QZ_2 vs. MT_2 systems at equilibrium. In order to check the reliability of the constants we redetermined them for the case where there was one kind of central moiety only, *i.e.*, in the systems QZ_2 vs. QT_2 and MZ_2 vs. MT_2 . The experimental data gathered on these latter systems are reported in Table 10. The data of Table 10 were employed to calculate¹⁰ the weighted-average equilibrium constants and standard errors listed in Table II. The constants in Table II were then used to calculate¹⁰ the theoretical values listed in parentheses in Table 10.

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SUMMARY

Equilibria in the scrambling between dimethylsilicon and dimethylgermanium of chlorine, bromine, or iodine with either methoxyl or methylthio groups have been studied by proton nuclear magnetic resonance. The scrambling of methoxyl with the methylthio group is also reported. As expected, most of these equilibria deviate greatly from the values corresponding to random sorting of the substituents. The mathematical treatment of the scrambling of two kinds of substituents between two different central moieties (including atoms) is discussed and typical examples are presented for the variation with over-all composition of the six molecular species resulting from such scrambling on a pair of bifunctional moieties.

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