INORGANICA CHIMICA ACTA

Volume 2, Number 2 June 1968

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Multicomponent Redistributions of Exchangeable Substituents between Methylgermanium and Dimethylgermanium

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Received April 12, 1968

Equilibria in the scrambling of the exchangeable substituents Cl, Br, and I (System I) and Cl, Br, I, and OC_6H_5 *(System II) between the methylgermanium and dimethylgermanium moieties have been studied quantitatively by proton nuclear magnetic resonance. The experimental data have been evaluated in terms of sets of the minimum number of equilibrium constants, twelve for System I and twenty five for System II, which in turn have been used to compute theoretical equilibrium distributions. As a result of preferential affinities for methylgermanium* versus *dimethylgermanium, certain species at equilibrium appear in only small amounts or not at all.*

Introduction

Recent progress[1] in the study of redistribution equilibria has been aided greatly by the availability of sensitive instrumentation for the assaying of mixtures of compounds at equilibrium and of high-speed computers which facilitate the statistical and iterative calculations required in this field. The present study reports redistribution equilibria of three or four exchangeable substituents between the methyl- and dimethylgermanium moieties. These moieties remain intact under the conditions where facile exchange of substituents such as halogens or oxygen-bonded groups take place. In the more complicated system of this paper, the presence at equilibrium of a maximum of thirty compounds has been considered experimentally and theoretically in quantitative terms. The results reported herein are related to other studies of multicomponent equilibria from this laboratory.[2-4]

Experimental Section

Reagents. Methyltrihalo- and dimethyldihalogermanes were prepared as reported in the literature.[5] Dimethyldiphenoxygermane, b.p. 135°/0.6 mm, was prepared in benzene from dimethyldihalogermane, phenol, and triethylamine.

Sample Preparation and Data Acquisition. For System I of this paper, equilibrated samples were prepared by sealing various proportions of the four components $(CH_3)_2GeCl_2$, $(CH_3)_2GeI_2$, CH_3GeCl_3, and CH_3GeBr_3 in 5 mm o.d. nuclear magnetic resonance (nmr) tubes and holding these at room temperature. Proton nmr spectra obtained within 10 and 48 hr after sample preparation were identical. For System II, various proportions of the four components $(CH_3)_2Ge(OC_6H_5)_2$, $(CH_3)_2GeI_2$, CH_3GeCl_3, and CH_3GeBr_3 were reacted similarly. In the latter case, nmr spectra obtained 6 and 10 days after sample preparation were identical. Since it has been shown[3] that exchange of halogens with each other and with oxygen-bonded groups on germanium proceeds quite rapidly at room temperature, with half lives of *ca.* 1 sec, the measured equilibria should correspond to the nmr probe temperature of 33°.

The mole fractions of the various compounds present at equilibrium were determined by quantitatively evaluating the proton nmr spectra (Varian A-60) given by the methyl and dimethylgermanium moieties of the species participating in the equilibrium. From these data, weighted-average equilibrium constants were calculated using previously reported procedures.[6] Also the computation of theoretical equilibrium distributions[2] in the multicomponent systems from the chosen equilibrium constants was done by computer.

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(5) K. Moedritzer, *J. Organometal. Chem.* (Amsterdam), 6, 282 (1966).
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Results and Discussion

Two-Substituent Systems. It has been shown in previous studies[7] that, upon redistribution of a pair of exchangeable substituents between methylgermanium and dimethylgermanium moieties, a total of seven different compounds is formed. If the exchangeable substituents are halogens or oxygen-bonded groups and the samples are kept at or above room temperature, these seven species are in a rapid dynamic equilibrium with each other. Further it has been demonstrated that for a given pair of substituents, Z and T, a set of four equilibrium constants derived from the equilibria presented below gives a complete mathematical description of the sytsem at equilibrium.

$$2(CH_3)_2GeZT \rightleftarrows (CH_3)_2GeZ_2 + (CH_3)_2GeT_2 \qquad (1)$$

$$2CH_3GeZ_2T \rightleftarrows CH_3GeZ_3 + CH_3GeZT_2 \qquad (2)$$

$$2CH_3GeZT_2 \rightleftarrows CH_3GeT_3 + CH_3GeZ_2T \qquad (3)$$

$$2CH_3GeZ_3 + 3(CH_3)_2GeT_2 \rightleftarrows 2CH_3GeT_3 + 3(CH_3)_2GeZ_2 \qquad (4)$$

Assuming that, for example, Z=Cl and T=Br, the four constants determining this particular system are derived from the reactions of equations (1)-(4) and are of the form of K_1, K_7, K_8, and K_{23} in Table I. Of these constats, K_1 describes the sorting of chlorine and bromine on the dimethylgermanium moiety, K_7 and K_8 the same process on the methylgermanium moiety, and K_{23} the distribution of the two kinds of substituents between the two central moieties.

Three-Substituent System. Upon addition of a third exchanging substituent to the above system, such as iodine in the form of CH_3GeI_3 or $(CH_3)_2GeI_2$, the latter will equilibrate with the molecular species originally present which contain chlorine and bromine as substituents, and thus generate additional species. This situation corresponds to System I in Table I of this paper. Accordingly, in addition to the equilibria listed above (equations (1)-(4) for Z=Cl and T=Br), similar ones will be required for the pairs of substituents chlorine/iodine (equations (1)-(4) for Z=Cl and T=I) and bromine/iodine (Z=Br and T=I).

For the equilibria involving the dimethylgermanium moiety, the corresponding constants are derived from equation (1) and are of the form of K_2 and K_3 in Table I and, for the methylgermanium moiety, they are derived from equations (2) and (3) and are of the form of K_9, K_{10}, K_{11}, and K_{12}. With three different exchangeable substituents present, the methylgermanium compound

Table I. Equilibrium constants[a] as calculated from the experim ental data at 33°

	System I[b]	System II[c]	Literature[d] values
Exchanges on $(CH_3)_2Ge<$			. . .
$K_1 = [Cl_2][Br_2]/[BrCl]^2$	0.28 ± 0.02	0.30 ± 0.01	0.30 ± 0.02
$K_2 = [Cl_2][I_2]/[ClI]^2$	0.67 ± 0.22	0.62 ± 0.06	0.67 ± 0.07
$K_3 = [Br_2][I_2]/[BrI]^2$	0.45 ± 0.17	0.37 ± 0.04	0.34 ± 0.01
$K_4 = [Cl_2][(OPh)_2]/[Cl(OPh)]^2$	—	0.08 ± 0.03	0.14 ± 0.01[e]
$K_5 = [Br_2][(OPh)_2]/[Br(OPh)]^2$	—	0.25 ± 0.10	0.24 ± 0.01[e]
$K_6 = [I_2][(OPh)_2]/[I(OPh)]^2$	—	$1.3\ \pm3.9$	1.61 ± 0.05[e]
Exchanges on $CH_3Ge\leqslant$			
$K_7 = [Cl_3][Br_2Cl]/[BrCl_2]^2$	0.49 ± 0.04	0.32 ± 0.03	0.42 ± 0.03
$K_8 = [Br_3][BrCl_2]/[Br_2Cl]^2$	0.28 ± 0.06	0.38 ± 0.03	0.41 ± 0.03
$K_9 = [Cl_3][ClI_2]/[Cl_2I]^2$	0.73 ± 0.08	0.68 ± 0.13	0.79 ± 0.07
$K_{10} = [I_3][Cl_2I]/[ClI_2]^2$	0.76 ± 0.14	0.69 ± 0.16	0.72 ± 0.06
$K_{11} = [Br_3][BrI_2]/[Br_2I]^2$	0.39 ± 0.09	0.43 ± 0.07	0.42 ± 0.03
$K_{12} = [I_3][Br_2I]/[BrI_2]^2$	0.41 ± 0.09	0.40 ± 0.07	0.44 ± 0.03
$K_{13} = [Cl_3][Cl(OPh)_2]/[Cl_2(OPh)]^2$	—	0.16 ± 0.04	0.14 ± 0.01[e]
$K_{14} = [(OPh)_3][Cl_2(OPh)]/[Cl(OPh)_2]^2$	—	0.05 ± 0.02	0.24 ± 0.02[e]
$K_{15} = [Br_3][Br(OPh)_2]/[Br_2(OPh)]^2$	—	0.19 ± 0.07	0.17 ± 0.04[e]
$K_{15} = [(OPh)_3][Br_2(OPh)]/[Br(OPh)_2]^2$	—	0.26 ± 0.11	0.37 ± 0.02[e]
$K_{17} = [I_3][I(OPh)_2]/[I_2(OPh)]^2$	—	$1.7\ \pm1.8$	0.99 ± 0.05[e]
$K_{18} = [(OPh)_3][I_2(OPh)]/[I(OPh)_2]^2$	—	0.30 ± 0.22	1.32 ± 0.10[e]
$K_{19} = [Br_2Cl][ClI_2]/[BrClI]^2$	0.33 ± 0.04	0.34 ± 0.05	0.35 ± 0.03[f]
$K_{20} = [Br_2Cl][Cl(OPh)_2]/[BrCl(OPh)]^2$	—	0.28 ± 0.04	0.16 ± 0.02[f]
$K_{21} = [BrI_2][Br(OPh)_2]/[BrI(OPh)]^2$	—	0.35 ± 0.14	0.55 ± 0.08[f]
$K_{22} = [ClI_2][Cl(OPh)_2]/[ClI(OPh)]^2$	—	0.80 ± 0.23	0.55 ± 0.08[f]
Exchanges between $(CH_3)_2Ge<$ and $CH_3Ge\leqslant$			
$K_{23} = [Br_3]^2[Cl_2]^3/\{[Cl_3]^2[Br_2]^3\}$	3.71 ± 0.95	0.73 ± 0.43[g]	5.92 ± 0.42[e,h]
$K_{24} = [I_3]^2[Cl_2]^3/\{[Cl_3]^2[I_2]^3\}$	$(7.62\pm0.20)\times10^{+2}$	$(4.72\pm0.28)\times10^{+2}$[g]	$(1.73\pm0.14)\times10^{+3}$[e]
$K_{25} = [(OPh)_3]^2[Cl_2]^3/\{[Cl_3]^2[(OPh)_2]^3\}$	—	$(5.81\pm3.98)\times10^{+5}$[g]	$(7.07\pm1.24)\times10^{+5}$[e]

[a] Weighted average values and their standard error; only the exchanging substituents, omitting the $CH_3Ge\leqslant$ or $(CH_3)_2Ge<$ central moieties, are shown. [b] Exchange of Cl, Br and I between CH_3Ge and $(CH_3)_2Ge$. [c] Exchange of Cl, Br, I and OC_6H_5 between CH_3Ge and $(CH_3)_2Ge$. [d] As determined in systems $(CH_3)_2GeZ_2$ *vs.* $(CH_3)_2GeT_2$ or CH_3GeZ_3 *vs.* CH_3GeT_3, respectively (References 8 and 9). [e] From data of systems[7] $(CH_3)_2GeZ_2$ *vs.* CH_3GeT_3. [f] From data of the system[3] CH_3GeCl_3 *vs.* CH_3GeBr_3 *vs.* CH_3GeI_3 *vs.* $CH_3Ge(OC_6H_5)_3$. [g] In System II the literature values of the intersystem constants K_{23}-K_{25} were used for calculating theoretical distributions. [h] Two values for this compound were reported,[7] 4.63 ± 0.12 and 5.92 ± 0.42. The latter was used for the calculation of the theoretical distribution in System II.

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(7) K. Moedritzer and J. R. Van Wazer, *J. Organometal. Chem.* (Amsterdam), in press.

$CH_3GeBrClI$ will also appear at equilibrium, thus requiring an additional equilibrium constant defined by K_{19}. The distribution of chlorine and bromine between the two central moieties, $CH_3Ge\leqslant$ and $(CH_3)_2Ge<$, is determined by an "intersystem constant" of the form of K_{23}, similarly K_{24} determines the distribution of iodine and chlorine and the analogous distribution of bromine and iodine by another intersystem constant which does not need to be listed as an independent one since it may be calculated from the two others,

$$K_{I(Br/I)} = K_{24}/K_{23} \tag{5}$$

In total, therefore in System I, 16 compounds are expected at equilibrium, 6 based on dimethylgermanium and 10 based on methylgermanium. These require as a minimum-number set 12 equilibrium constants. Values for the chosen minimum-number set of constants are presented in Table I.

The experimental data presented in Table II show that of the 16 different compounds expected, two appear at equilibrium in amounts of the order of 1% or less in the composition studied. These are $(CH_3)_2GeI_2$ and CH_3GeBr_3. Obviously this is a consequence of the nonrandom value of the intersystem constants K_{23}, K_{24}, and the constant of equation (6) which favors the placing of the lower-atomic-weight halogen on the dimethylgermanium moiety.

The minimum-number set of constants for system I in Table I has been used to calculate theoretical equilibrium distributions corresponding to the experimental over-all compositions. These data are listed in parentheses in Table II and it is seen that generally good agreement between experimental and calculated equilibrium concentrations is observed.

The intersystem equilibrium constant for the sorting of the iodine and chlorine substituents,

$$K_{I(Br/I)} = [CH_3GeI_3]^2[(CH_3)_2GeBr_2]^3/[CH_3GeBr_3]^2[(CH_3)_2GeI_2]^3 \tag{6}$$

although not required for the above calculations, may, of course, be determined from the experimental data of Table II, $K_{I(Br/I)} = (1.47 \pm 0.30) \times 10^{+2}$. The value of this constant as calculated according to equation (5) is $2.06 \times 10^{+2}$ and as determined previously for the system[7] CH_3GeBr_3 *vs.* $(CH_3)_2GeI_2$: $K_{I(Br/I)} = (3.39 \pm 0.35) \times 10^{+2}$.

Table II. Equilibrium data (in mole per cent) for the multicomponent system involving the exchange of Cl, Br, and I between CH_3Ge and $(CH_3)_2Ge$ at 33°

Signal	Chem. Shift[a]	Assignment	Experiment Number				
			1	2	3	4	5
A	–2.771	CH_3GeI_3	2.4[b]	1.1	0.7	2.9	0.4
			(2.3)[c]	(1.6)	(0.7)	(3.1)	(0.5)
B	–2.508	CH_3GeBrI_2	5.7	3.4	1.2	3.1	1.9
			(5.8)	(3.5)	(1.3)	(3.6)	(2.0)
C	–2.325	CH_3GeClI_2	3.6	3.2	2.6	5.7	1.5
			(3.5)	(3.5)	(2.8)	(5.6)	(1.8)
D	–2.265	CH_3GeBr_2I	6.1	3.1	1.0	1.7	3.0
			(6.0)	(3.2)	(1.0)	(1.8)	(3.1)
E	–2.107	$CH_3GeBrClI$	8.8	7.7	5.2	7.3	6.2
			(9.1)	(8.2)	(5.4)	(7.1)	(7.4)
F	–2.060	CH_3GeBr_3	2.8	0.9	0.5	0.3	1.7
			(2.4)	(1.1)	(0.3)	(0.3)	(1.9)
G	–1.958	CH_3GeCl_2I	3.9	5.7	7.5	9.1	4.0
			(3.9	(5.9)	(8.1)	(7.8)	(4.9)
H	–1.917	CH_3GeBr_2Cl	6.6	7.8	2.9	2.8	7.5
			(7.9)	(6.3)	(3.4)	(2.9)	(9.8)
I	–1.871	$(CH_3)_2GeI_2$	1.1	0.6	1.4	0.9	0.4
			(1.2)	(0.8)	(0.4)	(1.5)	(0.3)
J	–1.791	$CH_3GeBrCl_2$	7.8	9.8	10.8	8.0	10.4
			(7.2)	(9.6)	(11.0)	(6.9)	(13.9)
K	–1.708	CH_3GeCl_3	4.4	7.3	16.6	10.3	7.2
			(3.2)	(7.2)	(17.3)	(7.9)	(9.7)
L	–1.664	$(CH_3)_2GeBrI$	3.8	2.3	0.8	2.0	2.1
			(4.3)	(2.7)	(1.1)	(2.6)	(1.7)
M	–1.500	$(CH_3)_2GeClI$	4.3	4.7	4.0	6.0	3.8
			(4.8)	(5.1)	(4.2)	(7.5)	(2.9)
N	–1.455	$(CH_3)_2GeBr_2$	6.8	3.7	1.4	1.8	5.9
			(7.1)	(3.9)	(1.3)	(2.0)	(4.2)
O	–1.313	$(CH_3)_2GeBrCl$	18.4	17.1	12.4	12.9	21.2
			(18.2)	(16.9)	(11.7)	(13.6)	(16.8)
P	–1.183	$(CH_3)_2GeCl_2$	13.6	21.7	32.1	25.1	22.9
			(13.2)	(20.7)	(30.2)	(25.6)	(19.1)
Composition parameters:		$R_1 \equiv Cl/Ge$	1.015[d]	1.340	1.754	1.468	1.337
			(1.055)[e]	(1.368)	(1.777)	(1.500)	(1.364)
		$R_2 \equiv Br/Ge$	0.938[d]	0.709	0.427	0.484	0.815
			(0.919)[e]	(0.722)	(0.425)	(0.468)	(0.797)
		$R_3 \equiv I/Ge$	0.559[d]	0.452	0.308	0.576	0.298
			(0.549)[e]	(0.412)	(0.310)	(0.542)	(0.279)
		$R_1 \equiv CH_3Ge/Ge$	0.512[d]	0.499	0.488	0.528	0.450
			(0.521)[e]	(0.500)	(0.490)	(0.512)	(0.438)

[a] In ppm relative to internal tetramethylsilane in the neat liquid sample. [b] From the nmr data. [c] Calculated from the equilibrium constants of Table I, System I. [d] From the ingredients. [e] From the experimental nmr data.

Table III. Equilibrium data (in mole per cent) for the multicomponent system involving the exchange of Cl, Br, I, and OC_6H_5 between CH_3Ge and $(CH_3)_2Ge$ at 33°

Signal	Chem. Shift [a]	Assignment	Experiment Number								
			1	2	3	4	5	6	7	8	9
I	−2.717	CH_3GeI_3	2.1 [b]	1.4	6.3	0.6	1.3	0.2	14.2	—	—
			(2.0) [c]	(1.2)	(6.0)	(0.8)	(1.2)	(0.3)	(12.3)	(0.1)	(0.1)
II	−2.443	CH_3GeBrI_2	4.6	2.9	6.9	3.8	2.7	0.7	6.1	1.1	0.3
			(4.7)	(2.5)	(6.7)	(4.1)	(2.9)	(0.6)	(5.7)	(1.2)	(0.4)
III	−2.262	CH_3GeClI_2	2.8	1.3	4.1	1.1	3.3	0.3	3.2	0.3	1.0
			(2.9)	(1.2)	(4.0)	(1.3)	(3.1)	(0.2)	(3.5)	(0.2)	(1.2)
IV	−2.208	CH_3GeBr_2I	4.3	2.2	2.9	8.1	2.8	0.5	1.1	9.2	0.6
			(4.4)	(2.2)	(3.0)	(8.4)	(2.9)	(0.6)	(1.1)	(9.6)	(0.5)
V	−2.035	$CH_3GeClBrI$	7.1	2.5	4.2	6.6	7.6	0.5	1.4	4.1	3.7
			(6.4)	(2.6)	(4.3)	(6.6)	(7.4)	(0.5)	(1.6)	(3.3)	(3.6)
VI	−2.028	$CH_3GeI_2(OPh)$	—	—	1.4	—	—	0.8	1.5	—	—
			(0.6)	(1.0)	(1.4)	(0.2)	(0.3)	(0.7)	(1.5)	(0.0)	(0.0)
VII	−1.988	CH_3GeBr_3	1.9	0.7	0.3	8.0	1.2	0.2	0.1	32.2	0.2
			(1.7)	(0.8)	(0.6)	(7.6)	(1.2)	(0.2)	(0.1)	(32.8)	(0.2)
VIII	−1.882	CH_3GeCl_2I	3.0	1.1	1.8	1.4	5.6	—	0.7	0.6	7.5
			(2.8)	(0.9)	(1.8)	(1.5)	(5.6)	(0.2)	(0.7)	(0.3)	(8.3)
IX	−1.918	$CH_3GeBrI(OPh)$	—	2.5	2.4	2.8	1.3	2.6	—	0.7	—
			(3.0)	(4.5)	(3.2)	(2.6)	(1.4)	(3.3)	(1.5)	(0.8)	(0.1)
X	−1.840	CH_3GeBr_2Cl	6.1	3.1	2.5	10.6	6.1	—	0.7	20.7	3.7
			(5.0)	(1.9)	(1.6)	(11.4)	(5.9)	(0.4)	(0.2)	(21.5)	(3.7)
XI	−1.828	$(CH_3)_2GeI_2$	1.5	1.5	3.5	0.4	0.3	1.3	15.4	—	—
			(0.9)	(1.4)	(4.0)	(0.3)	(0.3)	(1.4)	(16.1)	(0.0)	(0.0)
XII	−1.705	$CH_3GeBrCl_2$	4.6	4.8	1.7	5.8	10.3	0.4	0.3	5.4	20.3
			(5.4)	(1.6)	(1.7)	(6.6	(11.3)	(0.3)	(0.3)	(5.3)	(21.2)
XIII	−1.675	$CH_3GeClI(OPh)$	2.7	0.4	2.5	1.3	2.5	—	1.4	1.4	1.5
			(2.8)	(3.3)	(2.9)	(1.3)	(2.3)	(2.0)	(1.4)	(0.2)	(0.5)
XIV	−1.638	$CH_3GeBr_2(OPh)$	2.8	3.5	2.0	5.0	1.4	—	—	5.5	0.3
			(2.5)	(3.6)	(1.3)	(4.9)	(1.2)	(2.7)	(0.2)	(5.7)	(0.1)
XV	−1.610	$(CH_3)_2GeBrI$	3.4	6.4	7.4	2.9	1.5	5.3	13.2	0.2	—
			(3.7)	(5.5)	(7.9)	(2.6)	(1.5)	(5.7)	(13.4)	(0.6)	(0.1)
XVI	−1.582	$CH_3GeI(OPh)_2$	—	—	0.6	—	—	3.6	—	—	—
			(0.3)	(1.4)	(0.5)	(0.1)	(0.1)	(2.8)	(0.3)	(0.0)	(0.0)
XVII	−1.572	CH_3GeCl_3	1.9	0.6	0.3	1.3	7.0	2.6	0.6	1.5	40.5
			(1.9)	(0.4)	(0.6)	(1.2)	(6.9)	(0.1)	(0.1)	(0.4)	(39.0)
XVIII	−1.512	$CH_3GeBrCl(OPh)$	6.5	7.3	3.5	7.0	5.4	5.4	0.7	3.5	1.8
			(6.1)	(6.9)	(3.1)	(6.4)	(5.3)	(4.3)	(0.6)	(3.2)	(1.5)
XIX	−1.457	$(CH_3)_2GeClI$	3.5	4.9	8.0	1.4	2.4	3.6	13.2	0.1	0.7
			(3.8)	(4.4)	(8.0)	(1.4)	(2.7)	(3.8)	(13.8)	(0.1)	(0.5)
XX	−1.413	$(CH_3)_2GeBr_2$	5.3	7.3	6.1	9.2	2.8	8.0	4.5	8.2	0.3
			(5.7)	(8.0)	(5.9)	(9.2)	(2.5)	(8.8)	(4.2)	(8.3)	(0 2)
XXI	−1.397	$CH_3GeCl_2(OPh)$	4.9	3.7	2.5	3.2	6.6	2.3	—	0.4	6.2
			(5.0)	(4.4)	(2.5)	(2.8)	(7.6)	(2.2)	(0.5)	(0.6)	(6.4)
XXII	−1.292	$CH_3GeBr(OPh)_2$	1.6	4.5	0.7	1.1	0.6	1.8	—	—	—
			(0.7)	(2.8)	(0.6)	(0.6)	(0.2)	(6.1)	(0.1)	(0.2)	(0.0)
XXIII	−1.273	$(CH_3)_2GeBrCl$	14.6	15.5	13.8	12.1	10.2	19.0	10.6	5.0	2.9
			(13.9)	(15.2)	(14.0)	(11.8)	(10.5)	(13.6)	(10.1)	(4.6)	(2.5)
XXIV	−1.242	$(CH_3)_2GeI(OPh)$	0.1	0.5	0.3	—	—	0.3	0.9	—	—
			(0.1)	(0.4)	(0.3)	(0.0)	(0.0)	(1.0)	(0.6)	(0.0)	(0.0)
XXV	−1.168	$CH_3GeCl(OPh)_2$	2.2	4.9	1.7	0.7	1.7	15.5	0.2	—	0.3
			(2.1)	(7.1)	(1.7)	(1.0)	(1.4)	(12.5)	(0.4)	(0.1)	(0.2)
XXVI	−1.138	$(CH_3)_2GeCl_2$	10.9	8.9	10.1	4.9	14.6	3.7	7.6	0.9	9.6
			(10.1)	(8.6)	(9.9)	(4.5)	(13.3)	(6.3)	(7.3)	(0.8)	(9.6)
XXVII	−1.052	$(CH_3)_2GeBr(OPh)$	0.5	2.5	0.9	0.3	0.2	6.7	1.0	0.1	—
			(0.5)	(1.9)	(0.8)	(0.3)	(0.1)	(5.9)	(0.7)	(0.1)	(0.0)
XXVIII	−0.918	$(CH_3)_2GeCl(OPh)$	1.0	3.4	1.7	0.4	0.6	8.2	1.7	—	—
			(1.1)	(3.6)	(1.8)	(0.4)	(0.6)	(9.0)	(1.7)	(0.0)	(0.0)
XXIX	−0.910	$CH_3Ge(OPh)_3$	0.1	1.6	0.1	—	—	5.0	—	—	—
			(0.0)	(0.6)	(0.1)	(0.0)	(0.0)	(3.5)	(0.0)	(0.0)	(0.0)
XXX	−0.710	$(CH_3)_2Ge(OPh)_2$	—	0.2	—	—	—	1.4	—	—	—
			(0.0)	(0.1)	(0.0)	(0.0)	(0.0)	(1.0)	(0.0)	(0.0)	(0.0)
Composition parameter:											
		$R_1 \equiv Cl/Ge$	0.963 [d]	0.749	0.750	0.759	1.355	0.645	0.509	0.484	2.218
			(0.990) [e]	(0.821)	(0.751)	(0.757)	(1.350)	(0.731)	(0.521)	(0.542)	(2.243)
		$R_2 \equiv Br/Ge$	0.846 [d]	0.775	0.675	1.323	0.694	0.661	0.457	2.080	0.392
			(0.856) [e]	(0.832)	(0.694)	(1.322)	(0.696)	(0.600)	(0.462)	(2.039)	(0.394)
		$R_3 \equiv I/Ge$	0.513 [d]	0.408	0.819	0.387	0.409	0.265	1.250	0.180	0.170
			(0.482) [e]	(0.361)	(0.808)	(0.369)	(0.402)	(0.232)	(1.269)	(0.191)	(0.166)
		$R_4 \equiv OPh/Ge$	0.281 [d]	0.541	0.231	0.225	0.225	0.865	0.106	0.112	0.090
			(0.264) [e]	(0.478)	(0.236)	(0.236)	(0.226)	(0.833)	(0.076)	(0.116)	(0.104)
		$R_1 \equiv (CH_3)_2Ge/Ge$	0.397 [d]	0.492	0.525	0.306	0.317	0.565	0.678	0.146	0.130
			(0.408) [e]	(0.511)	(0.518)	(0.316)	(0.326)	(0.575)	(0.681)	(0.145)	(0.131)

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[a] In ppm relative to internal tetramethylsilane in the neat liquid sample. [b] From the experimental nmr data. [c] Calculated from the constants in Table I, System II. [d] From the ingredients. [e] From the experimental nmr data.

Four-Substituent System. A similar treatment of the redistribution equilibria of the four exchangeable substituents Cl, Br, I, and OC_6H_5 between the dimethylgermanium and methylgermanium moieties in System II leads to a maximum of 30 species participating in the equilibria. Ten of these are dimethylgermanium derivatives; *i.e.*, in addition to the dimethylgermanium compounds of System I, the three mixed species with the substituents being a phenoxyl group and a halogen (Cl, Br, or I) plus one other species, the dimethyldiphenoxygermane. All of these are in equilibrium with the over-all equilibria determined by the constants K_1 to K_6 of Table I. In the corresponding equilibria on the methylgermanium moiety, a total of 20 different compounds are involved with the equilibria being described by the constants K_7 through K_{22} of Table I. Relating the sorting of the four exchangeable substituents between dimethylgermanium and methylgermanium are six intersystem equilifrium constants, one for each pair of substituents as defined by equation (4), three of which are independent ones. We selected the constants represented by K_{23}, K_{24}, and K_{25} as the three independent ones from which the others may be calculated. Thus at equilibrium in this system, the relative concentrations of the thirty different species are determined by the twenty five constants of Table I.

The experimentally determined equilibrium constants of Systems I and II in Table I compare well with values for these constants as determined independently in much simpler systems, *i.e.* in systems where only pairs of substituents were scrambled.[8,9] Constants involving the compounds having three different substituents (K_{19} through K_{22}), of course, could only be determined in systems[3] in which at least three of the four substituents were present.

Generally good agreement is observed between the values of the constants as obtained in Systems I and II and the literature values. The constants K_4, K_5, and K_6 of System II perhaps are less reliable as indicated by the large standard error which is due to the small equilibrium concentrations of $(CH_3)_2Ge(OC_6H_5)_2$ as shown in Table III for almost all of the samples in this system. Similar reasons hold for the constants, K_{14}, K_{16}, and K_{18} all of which show a relatively large standard error due to the small equilibrium concentration of $CH_3Ge(OC_6H_5)_3$. They also deviate considerably from the literature values. Furthermore, the intersystem constants as determined from the data of System II proved to be less accurate since second and third powers of small concentrations were involved in their calculation. Therefore in the latter instances, the literature values for K_{23}, K_{24}, and K_{25} were used for the calculations of the theoretical distributions.

In all other cases, however, the values of the constants as determined from the data of System II were used to calculate the theoretical distribution of the thirty species at equilibrium for the compositions as defined by the proportions of starting ingrediens. Surprisingly good agreement is seen in Table III between experimental and calculated equilibrium concentrations data.

An important feature in checking the assignments of nmr peaks to certain compounds is the material-balance concept. Good agreement of the composition parameters R as determined from the starting ingredients of the mixture with the same values as calculated from the nmr peak areas is generally an indication of the correctness of the assignments made. As shown in Tables II and III, this condition is met.

In view of the presence at equilibrium of thirty species, the absolute equilibrium concentrations of any given species is always quite small. Therefore the preferences for substituents to be associated with either the dimethylgermanium or methylgermanium moiety, as expressed by the intersystem constants is not obvious from simple inspection of the data of Table III. As in System I, the low-atomic-weight halogens prefer to be associated with the dimethylgermanium moiety; and, when paired against the phenoxyl group, all three halogens prefer the dimethylgermanium moiety — chlorine and bromine to about the same extent and the iodine to a somewhat lesser degree.

Additional intersystem constants, although not required for the calculation of theoretical distributions, have been computed from the experimental data of System II in Table III. Again, since the computation of these constants involved powers of sometimes quite small concentrations, their standard error is larger than the one obtained in simpler systems[7] consisting of less species at equilibrium.

For the distribution of bromine and iodine between methyl-and dimethylgermanium in System II, the intersystem constant as defined by equation (6) has been found to be $(1.58\pm0.29)\times10^{+2}$ [lit.:[7] $(3.39\pm0.35)\times10^{+2}$]. The constant for the sorting of bromine with phenoxyl groups, defined by equation (7), has a literature value[7] of $(1.89\pm0.29)\times10^{+5}$ whereas the data of System II yieldede $(3.00\pm1.10)\times10^{+5}$;

$$K_{I(Br/OPh)} =$$

$$[MeGe(OPh)_3]^2[Me_2GeBr_2]^3/\{[MeGeBr_3]^2[Me_2Ge(OPh_2]^3\} \quad (7)$$

For the sorting of iodine with phenoxyl groups described by equation (8)

$$K_{I(I/OPh)} =$$

$$[MeGe(OPh)_3]^2[Me_2GeI_2]^3/\{[MeGeI_3]^2[Me_2Ge(OPh_2]^3\} \quad (8)$$

the constant was found to be $(1.87\pm0.85)\times10^{+2}$ [lit.:[7] $(1\ 48\pm0.23)\times10^{+2}$].

Acknowledgment. We wish to thank Raymond E. Miller for experimental work, the Germanium Information Center for a gift of elemental germanium, and Mrs. Celeste Frank for editorial assistance.

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