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COMPETITION EQUILIBRIA OF EXCHANGEABLE SUBSTITUENTS BETWEEN METHYL AND DIMETHYLGERMANIUM MOIETIES

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SUMMARY

Redistribution of the exchangeable substituents halogen *vs.* halogen, phenoxy, methoxy or methylthio between the moieties methylgermanium and dimethylgermanium have been studied by proton nuclear magnetic resonance. The resulting equilibria have been evaluated in terms of sets of four equilibrium constants, one for the distribution of the pair of substituents on the dimethylgermanium moiety, two for the sorting on the methylgermanium moiety and one for the distribution of the substituent pair between the methyl and dimethylgermanium moieties. In the halogen–halogen exchanges the lower atomic weight halogen at equilibrium prefers association with the dimethylgermanium moiety. In the halogen *vs.* phenoxy, methoxy or methylthio exchanges halogens favor attachment to the dimethylgermanium moiety.

INTRODUCTION

In earlier studies[1-3] from this laboratory we have demonstrated that competition equilibria of pairs of exchangeable substituents between two differently methyl-substituted silicon moieties result in distinctly nonrandom distributions of substituents about the two moieties of silicon. In continuing these broad studies of redistribution equilibria, it is desirable for purposes of comparison to undertake similar competition experiments between various methylgermanium moieties. This paper reports an experimental study of the equilibria resulting from exchange of halogens with each other and with the substituents phenoxy, methoxy, and methylthio between methyl- and dimethylgermanium moieties. Equilibrium constants for the remaining possible pairings of substituents may be calculated from constants obtained in this paper.

EXPERIMENTAL

Materials

The dimethyldihalogermanes and methyltrihalogermanes were prepared according to the "Direct Synthesis"[4,5] from elemental germanium and methyl halide. Methyltriphenoxygermane and dimethyldiphenoxygermane were prepared from the respective chloride or bromide, phenol, and triethylamine; dimethyldimethoxygermane[6] and dimethylbis(methylthio)germane[7] were synthesized as reported previously. All reagents, in addition to having the correct boiling or melting points, had less than 1 % of hydrogen-containing impurities, as determined by proton nuclear-magnetic resonance (NMR).

Procedures

Reagent admixing, equilibration, proton NMR measurements and the calculation of both the equilibrium constants and theoretical equilibrium distributions have been performed as reported earlier[3,8,9]. Equilibration in the exchange of the methylthio group with bromine was the only slow process among all of the systems investigated in this study. Equilibration in this case was carried out at 33°, with the same NMR results being obtained at 48 and at 119 h. Equilibrium for the exchange of all other substituent pairs was achieved by holding the samples for several days at room temperature. Since other studies[10-12] have shown that the equilibrations for these systems are rapid at room temperature, the respective equilibrium data correspond to 33°, the temperature of the NMR probe. The proton NMR spectra obtained on a Varian A-60 spectrometer were measured on the neat liquids. Proton NMR chemical shifts of the methyl- and dimethylgermanium moieties in the species present at equilibrium are reported in Table 1. The general principle of the calculation of equilibrium constants in systems involving the redistribution of two kinds of monofunctional substituents between two kinds of central moieties has been discussed elsewhere[8,9]. The calculations and statistical-data evaluations were done on an IBM 7044 computer.

TABLE 1

PROTON NMR CHEMICAL SHIFTS OF THE METHYL- AND DIMETHYLGERMANIUM MOIETIES OBSERVED IN EQUILIBRATED MIXTURES OF EQUIMOLAR AMOUNTS OF CH_3GeT_3 *vs.* $(CH_3)_2GeZ_2$

Z and T are exchangeable monofunctional substituents.

Values in ppm relative to internal tetramethylsilane in the neat liquids.

Z	T	Me_2GeZ_2	Me_2GeZT	Me_2GeT_2	$MeGeZ_3$	$MeGeZ_2T$	$MeGeZT_2$	$MeGeT_3$
Cl[a]	Br	−1.200	−1.333	−1.471	−1.692	−1.808	−1.942	−2.083
Cl[b]	Br	−1.177	−1.310	−1.450	−1.657	−1.777	−1.907	−2.053
Cl	I	−1.232	−1.558	−1.935	−1.735	−2.028	−2.410	−2.858
Br	I	−1.473	−1.733	−1.892	−2.087	−2.290	−2.525	−2.793
Cl	OC_6H_5	−0.982	−0.788	−0.595	−1.317	−1.178	−0.990	−0.772
Br	OC_6H_5	−1.128	−0.835	−0.541	−1.600	−1.291	−0.995	−0.694
I	OC_6H_5	−1.679	−1.101	−0.592	−2.605	−1.862	−1.278	−0.775
Br	OCH_3	−1.488	−0.961[c]	−0.452[d]	−2.047	−1.577[e]	−1.053[f]	−0.593[g]
Br	SCH_3	−1.510	−1.122[h]	−0.735[i]	−2.097	−1.758[j]	−1.378[k]	−1.003[l]

[a] Mixtures prepared from CH_3GeBr_3 and $(CH_3)_2GeCl_2$. [b] Mixtures prepared from CH_3GeCl_3 and $(CH_3)_2GeBr_2$. [c] OCH_3: −0.348. [d] OCH_3: −3.454. [e] OCH_3: −3.628. [f] OCH_3: −3.564. [g] OCH_3: −3.556. [h] SCH_3: −2.178. [i] SCH_3: −2.057. [j] SCH_3: −2.335. [k] SCH_3: −2.226. [l] SCH_3: −2.140.

RESULTS AND CONCLUSIONS

In the studies described herein the methyl- or dimethylgermanium moieties remain intact as such under conditions where facile exchange of the other substituents on germanium, such as halogens, oxygen- and sulfur-bonded groups, takes place. Therefore, when describing the totality of the equilibria involving pairs of monofunctional substituents on methyl- and dimethylgermanium only seven different compounds will have to be considered as participating in the equilibria. These seven different species will be determined by a set of four independent equilibrium constants in addition to (*a*) two composition parameters and (*b*) the obvious provision that the mole fractions of all species sum up to 1.00. Of the many ways of expressing four independent equilibria, we have chosen the equations given below.

$$2\,(CH_3)_2GeZT \rightleftarrows (CH_3)_2GeZ_2 + (CH_3)_2GeT_2 \tag{1}$$

$$2\,CH_3GeZ_2T \rightleftarrows CH_3GeZ_3 + CH_3GeZT_2 \tag{2}$$

$$2\,CH_3GeZT_2 \rightleftarrows CH_3GeT_3 + CH_3GeZ_2T \tag{3}$$

$$2\,CH_3GeZ_3 + 3\,(CH_3)_2GeT_2 \rightleftarrows 2\,CH_3GeT_3 + 3\,(CH_3)_2GeZ_2 \tag{4}$$

Whereas the equilibrium of eqn. 1 deals with the sorting of the two kinds of monofunctional, exchangeable substituents, Z and T, on the dimethylgermanium moiety, the equilibria of eqns. 2 and 3 describe the exchange of the same substituents on the methylgermanium moiety. The equilibrium of eqn. 4 deals with the distribution of the pair of substituents between the methyl- and dimethylgermanium moieties. Accordingly, one may set up the four equilibrium constants which correspond to the equilibrium reactions of eqns. 1–4; and when their values are known, the equilibrium concentrations of the seven components at any over-all composition in this system are defined.

$$K_1 = [(CH_3)_2GeZ_2]\cdot[(CH_3)_2GeT_2]/[(CH_3)_2GeZT]^2 \tag{5}$$

$$K_2 = [CH_3GeZ_3]\cdot[CH_3GeZT_2]/[CH_3GeZ_2T]^2 \tag{6}$$

$$K_3 = [CH_3GeT_3]\cdot[CH_3GeZ_2T]/[CH_3GeZT_2]^2 \tag{7}$$

$$K_1 = [CH_3GeT_3]^2\cdot[(CH_3)_2GeZ_2]^3/\{[CH_3GeZ_3]^2\cdot[(CH_3)_2GeT_2]^3\} \tag{8}$$

Values of the equilibrium constants of eqns. 5–8 for several pairs of monofunctional substituents determined from the proton NMR spectra are presented in Table 2. From these data it is seen that values of K_1 as determined in the competitive equilibria reported here agree well with those (listed in brackets in Table 2) obtained previously in separate studies[6,7,10] of the systems $(CH_3)_2GeZ_2$ *vs.* $(CH_3)_2GeT_2$. Similarly the values of K_2 and K_3 in this work agree with data[11,12] from separate studies of systems CH_3GeZ_3 *vs.* CH_3GeT_3. The comments made in these papers[6,7,10–12] with regard to random sorting and deviations from ideal randomness apply here also. No previous data, however, were available for the scrambling equilibria involving halogens and phenoxy groups on either the methylgermanium or the dimethylgermanium moiety. The constants K_1, K_2 and K_3 for the latter exchanges are reported here for the first time; and it is interesting to note that the constants for the exchange of either chlorine or bromine with phenoxy groups on either the dimethylgermanium or the methylgermanium moiety are about ten times larger than the ones for the related exchange of these halogens with methoxy groups, a situation which has been observed also in the cases of the corresponding equilibria on methyl[13] or dimethylsilicon[14]. The values for the exchange of iodine with the phenoxy group are quite different from those obtained for the exchange of either chlorine or bromine with this group. This is in accord

TABLE 2

EQUILIBRIUM CONSTANTS[a] OBSERVED IN SYSTEMS CH_3GeT_3 *vs.* $(CH_3)_2GeZ_2$ AT 33°
Z and T are exchangeable monofunctional substituents.

Z	T	$K_1 = \frac{[Me_2GeZ_2]\cdot[Me_2GeT_2]}{[Me_2GeZT]^2}$	$K_2 = \frac{[MeGeZ_3]\cdot[MeGeZT_2]}{[MeGeZ_2T]^2}$	$K_3 = \frac{[MeGeZ_2T]\cdot[MeGeT_3]}{[MeGeZT_2]^2}$	$K_t = \frac{[MeGeT_3]^2\cdot[Me_2GeZ_2]^3}{[MeGeZ_3]^2\cdot[MeSiT_2]^3}$
Cl[b]	Br	0.30±0.01 [0.30±0.02][d]	0.40±0.06 [0.42±0.03][e]	0.40±0.06 [0.41±0.03][e]	4.63±0.12
Cl[c]	Br	0.31±0.01 [0.30±0.02][d]	0.39±0.02 [0.42±0.03][e]	0.39±0.03 [0.41±0.03][e]	5.92±0.42
Cl	I	0.65±0.03 [0.67±0.07][d]	0.81±0.05 [0.79±0.07][e]	0.72±0.08 [0.72±0.06][e]	(1.73±0.14) × 10^3
Br	I	0.35±0.01 [0.34±0.01][d]	0.46±0.02 [0.42±0.03][e]	0.45±0.03 [0.44±0.03][e]	(3.39±0.35) × 10^2
Cl	OC_6H_5	0.14±0.01 —[f]	0.14±0.01 —[f]	0.24±0.02 —[f]	(7.07±1.24) × 10^5
Br	OC_6H_5	0.24±0.01 —[f]	0.17±0.04 —[f]	0.37±0.02 —[f]	(1.89±0.29) × 10^5
I	OC_6H_5	1.61±0.05 —[f]	0.99±0.05 —[f]	1.32±0.10 —[f]	(1.48±0.23) × 10^2
Br	OCH_3	1.21 × 10^{-2} [(1.1±0.2) × 10^{-2}][g]	(1.56±0.33) × 10^{-2} [(2.14±0.75) × 10^{-2}][h]	(3.16±0.10) × 10^{-2} [(3.98±1.41) × 10^{-2}][h]	(2.09±0.72) × 10^9
Br	SCH_3	(1.44±0.26) × 10^{-2} [(2.5±0.8) × 10^{-2}][i]	(2.98±7.01) × 10^{-2} [(3.13±0.72) × 10^{-2}][h]	(2.82±0.36) × 10^{-2} [(3.19±0.78) × 10^{-2}][h]	(5.03±1.04) × 10^8
Ideal randomness		0.25	0.33	0.33	1.00

[a] Weighted average values[8] and corresponding standard errors. [b] Mixtures prepared from CH_3GeBr_3 and $(CH_3)_2GeCl_2$. [c] Mixtures prepared from CH_3GeCl_3 and $(CH_3)_2GeBr_2$. [d] Ref. 10. [e] Ref. 11. [f] Data not available. [g] Ref. 6; this constant was used for the calculations since only one equilibrium composition yielded values for the constant. [h] Ref. 12. [i] Ref. 7 (at 120°).

with the fact that in the interhalogen exchange, iodine also shows up as being quite different from either chlorine or bromine.

The intersystem constants K_1 for the assignments of Z and T substituents used in Table 2 are all larger than the random value ($K_{1(\text{rand})} = 1.00$) to a varying degree. This means that at equilibrium the preferred species are CH_3GeT_3 and $(CH_3)_2GeZ_2$. Thus for the halogen–halogen exchanges, the preferred distribution at equilibrium is characterised by a preference of the lower atomic weight halogen for the dimethylgermanium moiety and the higher atomic weight halogen for the methylgermanium moiety. In the equilibria involving the exchange of halogens with phenoxy, methoxy and methylthio groups the halogens are always preferentially on the dimethylger-

TABLE 3

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA (IN MOLE %) IN SYSTEMS CH_3GeT_3 *vs.* $(CH_3)_2GeZ_2$

R	CH_3Ge /Ge_{total}	$CH_3GeT_{3-n}Z_n$ ($n=0$–3)				$(CH_3)_2GeT_{2-n}Z_n$ ($n=0$–2)		
		T_3	T_2Z	TZ_2	Z_3	T_2	TZ	Z_2
A. System CH_3GeBr_3 *vs.* $(CH_3)_2GeCl_2$ *(R≡Cl/Ge) where T=Br*								
0.328[a]	0.836[a]	55.7[b]	20.1	2.8	0.1	15.8	5.1	0.4
(0.319)[c]	(0.787)[c]	(59.1)[d]	(21.3)	(3.1)	(0.2)	(11.9)	(4.0)	(0.4)
0.653	0.673	28.8	24.4	8.7	1.3	18.2	14.9	3.7
(0.680)	(0.632)	(31.7)	(26.0)	(8.5)	(1.1)	(16.7)	(12.9)	(3.0)
0.949	0.525	14.5	20.7	11.3	2.8	17.4	23.8	9.4
(0.943)	(0.493)	(15.4)	(21.9)	(12.4)	(2.8)	(16.5)	(22.1)	(8.8)
1.236	0.382	5.9	13.8	13.3	4.9	13.2	29.2	19.7
(1.237)	(0.379)	(5.9)	(14.0)	(13.3)	(5.0)	(13.1)	(29.2)	(19.4)
1.542	0.229	1.5	5.4	10.1	7.2	7.4	30.7	37.7
(1.533)	(0.242)	(1.2)	(5.3)	(9.6)	(6.7)	(7.2)	(30.7)	(39.2)
B. System CH_3GeCl_3 *vs.* $(CH_3)_2GeBr_2$ *(R≡Cl/Ge) where T=Cl*								
0.774[a]	0.258[a]	0.9[b]	4.6	11.6	9.9	10.9	32.3	30.0
(0.776)[c]	(0.270)[c]	(0.8)[d]	(4.8)	(10.7)	(9.5)	(10.9)	(32.9)	(30.4)
1.146	0.382	3.8	11.9	15.1	8.2	16.6	29.2	15.2
(1.127)	(0.390)	(3.8)	(12.0)	(15.0)	(7.4)	(17.4)	(29.3)	(15.1)
1.581	0.527	12.2	21.3	15.0	4.3	21.2	20.1	6.0
(1.567)	(0.528)	(12.2)	(21.6)	(14.8)	(4.0)	(21.6)	(20.0)	(5.7)
2.049	0.683	29.2	27.7	9.8	1.4	20.2	10.2	1.5
(2.034)	(0.681)	(30.0)	(27.3)	(9.7)	(1.4)	(20.5)	(9.8)	(1.4)
2.517	0.839	57.5	22.0	3.6	0.2	13.8	2.8	0.1
(2.367)	(0.833)	(58.4)	(22.1)	(3.3)	(0.2)	(13.3)	(2.6)	(0.2)
C. System CH_3GeBr_3 *vs.* $(CH_3)_2GeI_2$ *(R≡Br/Ge) where T=Br*								
0.604[a]	0.201[a]	—[b]	1.6	5.4	13.5	10.3	32.8	34.5
(0.620)[c]	(0.205)[c]	(0.1)[d]	(1.1)	(5.8)	(13.1)	(9.8)	(32.5)	(37.5)
1.106	0.369	2.0	8.0	15.4	12.5	23.1	27.6	11.4
(1.112)	(0.379)	(1.9)	(7.7)	(15.0)	(12.3)	(23.3)	(28.1)	(11.8)
1.663	0.554	12.3	20.5	17.0	6.0	28.4	13.5	2.4
(1.652)	(0.558)	(12.4)	(21.0)	(16.5)	(5.5)	(28.3)	(13.9)	(2.4)
2.144	0.715	33.5	26.9	9.8	1.3	22.6	5.4	0.5
(2.147)	(0.715)	(33.4)	(26.6)	(9.8)	(1.5)	(22.9)	(5.3)	(0.4)
2.624	0.877	65.2	19.8	2.1	—	12.0	1.0	—
(2.623)	(0.871)	(66.2)	(18.9)	(2.5)	(0.1)	(11.3)	(0.9)	(0.0)

(*continued on next page*)

TABLE 3 (*continued*)

R	CH_3Ge /Ge_{total}	$CH_3GeT_{3-n}Z_n$ (n=0–3)				$(CH_3)_2GeT_{2-n}Z_n$ (n=0–2)		
		T_3	T_2Z	TZ_2	Z_3	T_2	TZ	Z_2
D. System CH_3GeI_3 vs. $(CH_3)_2GeCl_2$ ($R \equiv Cl/Ge$) where $T = I$								
0.555[a]	0.723[a]	48.9[b]	16.2	5.3	1.0	9.2	10.6	8.7
(0.578)[c]	(0.714)[c]	(49.7)[d]	(16.9)	(4.7)	(0.9)	(9.3)	(10.6)	(7.9)
0.835	0.583	32.3	16.7	6.8	2.1	9.4	15.7	17.0
(0.863)	(0.579)	(33.6)	(16.3)	(6.5)	(1.8)	(9.6)	(15.6)	(16.6)
1.158	0.421	18.1	13.4	7.9	3.3	8.5	18.9	30.1
(1.182)	(0.427)	(18.8)	(13.0)	(7.3)	(3.0)	(8.5)	(19.6)	(29.8)
1.455	0.272	8.2	8.5	6.7	4.0	5.7	21.1	45.7
(1.464)	(0.274)	(8.3)	(8.3)	(6.7)	(3.9)	(6.3)	(20.9)	(45.6)
1.748	0.126	1.6	3.5	4.5	4.1	2.7	17.6	66.0
(1.744)	(0.137)	(1.6)	(2.8)	(4.0)	(4.1)	(3.0)	(17.4)	(67.0)
E. System CH_3GeCl_3 vs. $(CH_3)_2Ge(OC_6H_5)_2$ ($R \equiv Cl/Ge$) where $T = Cl$								
0.887[a]	0.296[a]	—[b]	1.2	8.1	17.3	17.1	42.2	14.2
(0.869)[c]	(0.266)[c]	(0.0)[d]	(1.6)	(10.6)	(17.3)	(17.2)	(40.4)	(12.9)
1.553	0.518	2.5	18.6	21.2	5.8	36.3	14.7	0.9
(1.532)	(0.481)	(2.7)	(21.2)	(22.2)	(5.6)	(34.9)	(12.7)	(0.6)
2.010	0.670	16.6	36.6	11.1	1.0	31.5	3.3	—
(2.004)	(0.653)	(17.1)	(37.8)	(11.3)	(0.8)	(29.9)	(3.1)	(0.0)
2.421	0.807	44.5	32.1	2.4	—	20.3	0.7	—
(2.414)	(0.790)	(45.8)	(31.8)	(3.0)	(0.1)	(18.7)	(0.6)	(0.0)
2.720	0.907	71.6	17.9	1.1	—	9.3	0.1	—
(2.704)	(0.906)	(72.7)	(17.4)	(0.6)	(0.0)	(9.2)	(0.1)	(0.0)
F. System $CH_3Ge(OC_6H_5)_3$ vs. $(CH_3)_2GeBr_2$ ($R \equiv Br/Ge$) where $T = OC_6H_5$								
1.743[a]	0.129[a]	0.9[b]	3.7	6.0	1.4[b]	1.2	19.2	67.6
(1.743)[c]	(0.120)[c]	(0.9)[d]	(4.0)	(6.3)	(1.6)	(0.8)	(19.9)	(66.5)
1.527	0.236	4.2	9.1	7.9	1.1	2.8	24.1	50.9
(1.541)	(0.223)	(4.2)	(9.8)	(8.4)	(1.2)	(1.9)	(26.3)	(48.1)
1.316	0.342	9.9	14.9	8.2	1.2	4.2	25.7	35.8
(1.322)	(0.342)	(9.8)	(15.0)	(8.6)	(0.8)	(3.1)	(28.3)	(34.4)
0.886	0.557	26.4	21.4	6.7	0.5	6.8	21.6	16.6
(0.911)	(0.550)	(27.7)	(21.5)	(6.2)	(0.3)	(5.3)	(24.2)	(14.8)
0.644	0.672	40.8	22.3	4.1	—	7.5	16.8	8.5
(0.643)	(0.672)	(41.5)	(21.5)	(4.1)	(0.1)	(6.2)	(18.9)	(7.7)
G. System CH_3GeI_3 vs. $(CH_3)_2Ge(OC_6H_5)_2$ ($R \equiv I/Ge$) where $T = I$								
2.572[a]	0.857[a]	66.6[b]	13.9	3.5	1.2	13.0	1.5	0.3
(2.586)[c]	(0.852)[c]	(65.0)[d]	(15.8)	(3.8)	(1.2)	(12.7)	(1.4)	(0.2)
2.196	0.732	43.3	18.3	7.6	4.1	21.6	4.3	0.9
(2.216)	(0.735)	(42.4)	(18.4)	(7.9)	(4.5)	(21.7)	(4.1)	(0.9)
1.676	0.559	19.6	14.6	10.6	10.4	30.7	10.2	3.9
(1.702)	(0.552)	(19.0)	(14.6)	(11.1)	(11.1)	(30.0)	(10.1)	(4.0)
1.212	0.404	5.5	7.5	9.5	15.3	32.5	18.1	11.6
(1.241)	(0.378)	(5.9)	(7.7)	(9.9)	(17.0)	(30.4)	(17.5)	(11.7)
0.749	0.250	0.6	1.8	4.3	16.0	21.9	24.2	31.3
(0.777)	(0.227)	(0.7)	(1.9)	(5.0)	(17.3)	(20.2)	(23.4)	(31.4)

(*continued on next page*)

TABLE 3 (*continued*)

R	CH_3Ge $/Ge_{total}$	$CH_3GeT_{3-n}Z_n$ $(n=0–3)$				$(CH_3)_2GeT_{2-n}Z_n$ $(n=0–2)$		
		T_3	T_2Z	TZ_2	Z_3	T_2	TZ	Z_2
H. System CH_3GeBr_3 *vs.* $(CH_3)_2Ge(OCH_3)_2$ $(R\equiv Br/Ge)$ *where* $T=Br$								
0.686[a]	0.229[a]	—[b]	—	5.8	14.3	2.1	58.3	19.6
(0.707)[c]	(0.236)[c]	(0.0)[d]	(0.1)	(6.4)	(16.4)	(2.1)	(57.8)	(17.2)
1.306	0.435	—	9.5	30.5	3.1	26.4	30.6	—
(1.329)	(0.431)	(0.0)	(8.9)	(31.1)	(3.5)	(25.6)	(30.5)	(0.4)
1.829	0.610	2.2	42.7	13.0	—	37.8	4.3	—
(1.849)	(0.579)	(2.0)	(44.0)	(14.8)	(0.2)	(35.0)	(4.0)	(0.0)
2.290	0.763	30.6	44.9	0.9	—	23.4	0.2	—
(2.295)	(0.764)	(30.2)	(45.1)	(1.0)	(0.0)	(23.5)	(0.2)	(0.0)
2.693	0.900	71.6	18.1	—	—	10.3	—	—
(2.716)	(0.897)	(69.4)	(20.2)	(0.1)	(0.0)	(10.2)	(0.0)	(0.0)
I. System $CH_3Ge(SCH_3)_3$ *vs.* $(CH_3)_2GeBr_2$ $(R\equiv Br/Ge)$ *where* $T=SCH_3$								
0.332[a]	0.834[a]	61.0[b]	20.7	—	—	5.3	12.7	0.3
(0.340)[c]	(0.817)[c]	(62.3)[d]	(20.9)	(0.2)	(0.0)	(5.0)	(11.3)	(0.4)
0.797	0.602	22.3	36.0	1.7	—	3.1	32.0	5.0
(0.814)	(0.600)	(23.4)	(35.3)	(1.5)	(0.0)	(3.1)	(32.0)	(4.7)
1.182	0.409	5.0	29.2	4.9	—	0.7	38.6	21.7
(1.210)	(0.391)	(5.6)	(30.6)	(4.7)	(0.0)	(1.0)	(38.0)	(20.1)
1.472	0.264	0.8	16.9	7.3	—	0.5	31.3	43.2
(1.492)	(0.250)	(1.3)	(18.1)	(6.9)	(0.1)	(0.3)	(31.5)	(41.8)
1.795	0.103	1.8	5.4	5.8	0.2	—	14.5	72.3
(1.767)	(0.132)	(0.1)	(4.3)	(5.7)	(0.2)	(0.1)	(16.2)	(73.5)

[a] From the ingredients. [b] From the NMR spectra. [c] Calculated from the NMR data. [d] Calculated from the equilibrium constants K_1, K_2, K_3 and K_I in Table 2 for the *R* values as determined from the ingredients.

manium moiety, whereas the other substituents are associated with the methylgermanium moiety.

The experimental data obtained from the NMR peak areas of the spectra of the equilibrated samples are presented in Table 3 where they are compared with the molecular distributions calculated from the corresponding sets of equilibrium constants of Table 2. Good agreement between the experimental and calculated values is generally observed without having to resort to use of activity coefficients.

For the exchange of chlorine with bromine atoms between the methyl and dimethylgermanium moieties, the equilibrium has been approached from both sides, using as starting materials in one case (system A in Table 3) CH_3GeBr_3 and $(CH_3)_2GeCl_2$ and in the other (system B) CH_3GeCl_3 and $(CH_3)_2GeBr_2$. The differences in the equilibrium constants for these separate two series of experiments are within the standard deviations for K_1, K_2 and K_3 as shown in Table 2. However, for K_I, the somewhat larger difference must also be attributed to measurement errors rather than to incomplete equilibration since the values of $K_I=4.6$ for System A and $K_I=5.9$ for System B correspond to a crossing over of the rate-of-equilibration curves obtained by approaching the equilibrium from both sides.

DISCUSSION

The reliability of the values for the intersystem constants in Table 2 is evidenced by the good agreement of the value of an intersystem constant calculated from the corresponding equilibrium data with the value calculated from the other intersystem constants. Thus K_I for the chlorine–iodine exchange may be calculated from those of the chlorine–bromine and bromine–iodine exchanges: $K_I(\text{Cl/I}) = K_I(\text{Cl/Br}) \cdot K_I(\text{Br/I}) = 1.79 \times 10^3$, whereas the directly determined value from Table 2 is 1.73×10^3. Similarly $K_I(\text{Cl/Br}) = K_I(\text{Cl/OPh})/K_I(\text{Br/OPh}) = 3.74$, with the corresponding values from Table 2 being 4.63 and 5.92.

The good agreement demonstrated above for the values of the intersystem constants from these two sources prompted analogous calculations to yield intersystem constants for pairs of substituents for which experimental data were not obtained. These constants are shown in Table 4. Again it is seen that for the exchanges of the halogens chlorine and iodine with either methoxy or methylthio groups the preferred distribution is the one which places the halogen on the dimethylgermanium moiety. The equilibria involving phenoxy with methoxy (or methylthio) groups place the phenoxy group preferentially on the dimethylgermanium moiety. Such differences between the phenoxy and methoxy oxygens might possibly be due to a feed-back of the oxygen electrons not involved in the σ-bond structure into the benzene ring of the phenoxyl group, thereby changing the availability of the electrons for p_π–d_π bonding between the oxygen and the neighboring germanium atom (as compared to the methoxy case).

TABLE 4

NEW INTERSYSTEM EQUILIBRIUM CONSTANTS K_I AT 33° CALCULATED FROM THE EXPERIMENTAL ONES OF TABLE 2

Z	T	$K_1 = \dfrac{[\text{MeGeT}_3]^2 \cdot [\text{Me}_2\text{GeZ}_2]^3}{[\text{MeGeZ}_3]^2 \cdot [\text{Me}_2\text{GeT}_2]^3}$
Cl	OCH_3	$K_1(\text{Br/OCH}_3) \cdot K_1(\text{Cl/I}) = 1.10 \times 10^{10}$
I	OCH_3	$K_1(\text{Br/OCH}_3)/K_1(\text{Br/I}) = 6.17 \times 10^6$
Cl	SCH_3	$K_1(\text{Br/SCH}_3) \cdot K_1(\text{Cl/Br}) = 2.65 \times 10^9$
I	SCH_3	$K_1(\text{Br/SCH}_3)/K_1(\text{Br/I}) = 1.48 \times 10^6$
OC_6H_5	OCH_3	$K_1(\text{Br/OCH}_3)/K_1(\text{Br/OPh}) = 1.11 \times 10^4$
SCH_3	OCH_3	$K_1(\text{Br/OCH}_3)/K_1(\text{Br/SCH}_3) = 4.16$
OC_6H_5	SCH_3	$K_I(\text{Br/SCH}_3)/K_I(\text{Br/OPh}) = 2.66 \times 10^3$

Comparing the intersystem equilibrium constants obtained in this paper with analogous constants for the corresponding silicon compounds[1], parallel behavior is observed. For halogen *vs.* methoxy, methylthio or dimethylamino, the halogen atoms in the silicon case are also preferentially found on the dimethyl-substituted moiety. However, for the chlorine-bromine exchange in the silicon system the chlorine atoms are somewhat favored to be on the methylsilicon moiety; whereas, as indicated by the data in Table 2, in the corresponding germanium system there is a small preference for the chlorine atoms to be on the dimethylgermanium.

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