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Redistribution Equilibria on Dimethylsilicon

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Equilibrium constants are reported for the exchange on the dimethylsilicon moiety of the substituent pairs halogen or pseudohalogen *vs.* phenoxyl, aceto, methylthio, or dimethylamino groups and of methylthio *vs.* aceto groups. These constants are included in a general tabulation of the random *vs.* nonrandom character of pairs of exchangeable substituents on the dimethylsilicon moiety.

Equilibria involving exchange of pairs of monofunctional substituents on the dimethylsilicon moiety have been studied quite extensively.[1] Owing to the ready availability of derivatives of dimethylsilane and the simple equilibrium involved, exchange reactions on the dimethylsilicon moiety have served as a test case for determining the deviations from randomness in the scrambling of a given pair of substituents. Such studies are noteworthy since as a general rule[1,2] the random or nonrandom behavior of a given pair of substituents is independent to a first order of the central moiety. This allows extrapolation of the results obtained on dimethylsilicon to other central moieties. Therefore the study of the exchange equilibria of as many pairs of substituents as possible on any one kind of central moiety is desirable. The present paper reports additional equilibrium constants for dimethylsilicon systems involving the exchange of halogens or pseudohalogens with phenoxyl, aceto, methylthio, or dimethylamino groups and of methylthio with aceto groups.

Experimental Part

Materials.—Dimethyldichlorosilane was purchased from Peninsular ChemResearch Inc., Gainesville, Fla., and redistilled before use. Dimethyldibromosilane,[3] dimethyldiphenoxysilane,[4] diacetodimethylsilane,[5] dimethyldi(methylthio)silane,[6] dimethylbis(dimethylamino)silane,[7] dicyanodimethylsilane,[8] and diisocyanatodimethylsilane[9] were prepared according to methods of the literature.

Procedures and Data Treatment.—The experimental procedures for obtaining the equilibrium data and the calculations of the equilibrium constants were the same as described previously.[3] Proton nuclear magnetic resonance (nmr) chemical shifts of the compounds as seen at equilibrium are presented in Table I, for which the parameter R is closest to unity. The shifts are reported to the third decimal place only to show the kind of resolution found for each system. Changes in the over-all composition as denoted by R led to shift changes in the range of 0.05 ppm. The conditions for reaching equilibrium are listed in Table II showing the equilibrium constants.

In addition to the systems described in this paper several other pairs of dimethylsilane derivatives were investigated, the evaluation of which however had to be abandoned owing to extensive side reactions occurring at the temperatures required for equilibration. These are the systems: $(CH_3)_2Si(OCH_3)_2$ *vs.* $(CH_3)_2Si(OOCCH_3)_2$ (apparent equilibrium reached after 25 days at 120°); $(CH_3)_2Si(NCO)_2$ *vs.* $(CH_3)_2Si[N(CH_3)_2]_2$ (apparent equilibrium reached after 90 hr at 120°); $(CH_3)_2Si[N(CH_3)_2]_2$ *vs.* $(CH_3)_2Si(OOCCH_3)_2$ (apparent equilibrium reached after 17 days at 120°; solid reaction products were formed in some of the samples); $(CH_3)_2Si(CN)_2$ *vs.* $(CH_3)_2Si(OCH_3)_2$ (apparent equilibrium reached after 21 days at 120°; solid reaction products were formed in some of the samples).

For the systems $(CH_3)_2Si(SCH_3)_2$ *vs.* $(CH_3)_2Si(NCO)_2$ and $(CH_3)_2Si(CN)_2$ *vs.* $(CH_3)_2Si[N(CH_3)_2]_2$ fairly good equilibrium data could be obtained. However, in the first system, the material balance was off by more than 15% owing to unknown reasons and some of the samples of the second system had decomposed before equilibrium was reached. Therefore these data are not presented in this paper although they were used for an estimate of the respective equilibrium constants.

Results and Discussion

Redistribution equilibria in systems $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_2SiT_2$, where Z and T are monofunctional exchangeable substituents and $(CH_3)_2Si$ is a moiety which under the conditions of the equilibration remains intact, are described by the reaction

$$2(CH_3)_2SiZT \rightleftarrows (CH_3)_2SiZ_2 + (CH_3)_2SiT_2 \qquad (1)$$

Accordingly a single equilibrium constant corresponding to eq 1 is sufficient to determine the concentrations of the three species present at equilibrium in such systems

$$K = [(CH_3)_2SiZ_2][(CH_3)_2SiT_2]/[(CH_3)_2SiZT]^2 \qquad (2)$$

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Table I

Proton Nmr Chemical Shifts Observed in Equilibrated Samples of the Systems $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_2SiT_2$ in Ppm Relative to Internal Tetramethylsilane in the Neat Liquid Samples

Z	T	$(CH_3)_2SiZ_2$	$(CH_3)_2SiZT$	$(CH_3)_2SiT_2$
Cl	OC_6H_5	−0.662	−0.500	−0.305
Br	OC_6H_5	−0.983	−0.662	−0.312
Cl	$OOCCH_3$	−0.773	−0.590[a]	−0.417[b]
SCH_3	$OOCCH_3$	−0.480[c]	−0.473[d]	−0.423[e]
Br[f]	$N(CH_3)_2$	−0.825	−0.548[g]	−0.047[h]
CN	$N(CH_3)_2$	−0.636	−0.324[i]	+0.013[j]
SCH_3	NCO	−0.475[k]	−0.463[l]	−0.400

[a] $OOCCH_3$, −2.018. [b] $OOCCH_3$, −1.993. [c] SCH_3, −1.994. [d] SCH_3 and $OOCCH_3$, −2.087 and −2.012; assignment could not be made. [e] $OOCCH_3$, −2.018; [f] In benzene, 1:1. [g] $N(CH_3)_2$, −2.412. [h] $N(CH_3)_2$, −2.295. [i] $N(CH_3)_2$, −2.530. [j] $N(CH_3)_2$, −2.480. [k] SCH_3, −2.084. [l] SCH_3, −2.028.

Data obtained by evaluating quantitatively the proton nmr spectra of equilibrated samples have been used to calculate the equilibrium constants of the form of eq 2 summarized in Table II.

Table II

Weighted-Average Equilibrium Constants for Interchange of the Substituents Z and T on the Dimethylsilicon Moiety

Z	T	$K = [(CH_3)_2SiZ_2][(CH_3)_2SiT_2]/[(CH_3)_2SiZT]^2$	Time[a]	Temp, °C
Cl	OC_6H_5	0.16 ± 0.01[b]	31 days (<27 days)	150
Br	OC_6H_5	0.14 ± 0.01	14 days (<8 days)	150
Cl	$OOCCH_3$	0.34 ± 0.03	17 days (<8 days)	120
SCH_3	$OOCCH_3$	8.6 ± 1.2	21 days (<17 days)	120
Br[c]	$N(CH_3)_2$	$(4.2 \pm 4.2) \times 10^{-4}$	15 hr (<1 hr)	120
CN[d]	$N(CH_3)_2$	$\sim 1 \times 10^{-4}$	24 days (<5 days)	72
SCH_3[d]	NCO	~4.6	26 days (<7 days)	120
Ideal randomness		0.25		

[a] The time given is the one when equilibrium was measured; times listed in parentheses are the minimum times required for reaching equilibrium. [b] The weighted mean values of the equilibrium constants and their standard errors are calculated according to L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, **36**, 303 (1964), using only the concepts given on pp 305–308. [c] In benzene, 1:1. [d] Experimental data did not permit an exact determination of the equilibrium constant; the value given is estimated.

The experimental nmr data from which the equilibrium constants were calculated are shown in Table III where they are compared with the respective mole fractions of the various molecules calculated from the equilibrium constants in Table II. It is seen that generally good agreement between experimental and calculated equilibrium concentrations is observed.

The deviation from randomness of the free energies corresponding to the equilibrium constants of eq 2 are presented below and in Figure 1 for the data obtained in this study (Table II) and the published values[1–3,10–13] for other exchanges of two monofunctional substituents on the dimethylsilicon moiety. This deviation from randomness, $\delta\Delta F°$, is approximately equal to the enthalpy per mole for eq 1, on the assumption that the entropy change in the reaction is due predominantly to the exchange of the Z and T ligands and not to other factors such as preferential solvation

$$\delta\Delta F° = -(RT/2)\ln(K_{\text{obsd}}/K_{\text{rand}}) \qquad (3)$$

The following is an ordered listing of $\delta\Delta F°$ (in kcal/mol) of all pairs of monofunctional substituents for which exchange has been studied on the dimethylsilicon moiety (except for the F–H and CH_3O–H exchanges which were studied[13] on $CH_3(C_6H_5)Si$): CN–$N(CH_3)_2$, 2.7; Br–$N(CH_3)_2$, 2.5; Cl–$N(CH_3)_2$, 2.2; Cl–CH_3, 1.8; Br–OCH_3, 1.4; Cl–OCH_3, 1.3; CN–SCH_3, 1.0; Br–SCH_3, 0.6; NCO–OCH_3, 0.6; Cl–H, 0.4; Br–OC_6H_5, 0.3; Cl–OC_6H_5, 0.2; Cl–SCH_3, 0.1; Br–CN, 0.1; OCH_3–$N(CH_3)_2$, 0.1; Cl–CN, 0.04, NCO–NCS, 0.04; NCS–SCH_3, 0.01; OCH_3–OC_2H_5, −0.1; Cl–NCO, −0.1; Cl–Br, −0.1; Cl–NCS, −0.1; Cl–$OOCCH_3$, −0.1; Br–NCO, −0.2; CN–NCS, −0.2; Cl–I, −0.4; OCH_3–SCH_3, −1.0; NCO–SCH_3, −1.1; SCH_3–$OOCCH_3$, −1.4; OCH_3–H, −1.7; F–H, −1.9.

Some order may be made out of the confusing sequence of these data by tabulating the values of $\delta\Delta F°$ for exchange of the various substituents (here labeled T) *vs.* each of a number of given substituents (labeled Z) and placing these tabulations for each given substituent (Z) in a sequence which leads to increasing (or decreasing) trends in the value of $\delta\Delta F°$ for any one of the various substituents (T). This has been done in Figure 1, from which it can be seen that reasonably good ordering of the majority of the substituents is achieved by the series: CN > Br > Cl > NCS > NCO > SCH_3 > H > OCH_3 > $N(CH_3)_2$.

By taking this series of the Z substituents, we find that the T substituents fall into two families. One of them, consisting of the $N(CH_3)_2$, OCH_3, SCH_3, and perhaps H substituents, shows a diminution in $\delta\Delta F°$ when going from left to right in the above series. On the other hand, the two halogens Cl and Br and the pseudohalogen CN exhibit a $\delta\Delta F°$ around zero on the left side of this series and a pronounced increase in $\delta\Delta F°$ on the right side—so that the slope of the trend line for this second group has a sign opposite to that of the first group.

In the first group of T substituents shown in Figure

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TABLE III

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA IN MOLE PER CENT IN SYSTEMS $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_2SiT_2$

A. System $(CH_3)_2SiCl_2$ vs. $(CH_3)_2Si(OC_6H_5)_2$

$R \equiv Cl/Si$	$(CH_3)_2SiCl_2$	$(CH_3)_2SiCl(OC_6H_5)$	$(CH_3)_2Si(OC_6H_5)_2$
0.302[a] (0.308)[c]	1.8[b] (1.7)[d]	27.2 (26.9)	71.0 (71.5)
0.639 (0.656)	8.3 (8.3)	49.0 (47.4)	42.7 (44.4)
0.989 (1.011)	23.3 (21.8)	54.6 (55.2)	22.2 (22.9)
1.540 (1.531)	56.9 (58.1)	39.4 (37.9)	3.8 (4.0)
1.628 (1.630)	65.7 (65.4)	31.5 (32.1)	2.8 (2.6)

B. System $(CH_3)_2SiBr_2$ vs. $(CH_3)_2Si(OC_6H_5)_2$

$R \equiv Br/Si$	$(CH_3)_2SiBr_2$	$(CH_3)_2SiBr(OC_6H_5)$	$(CH_3)_2Si(OC_6H_5)_2$
0.316[a] (0.297)[c]	1.5[b] (1.5)[d]	26.8 (28.4)	71.7 (70.0)
0.655 (0.652)	8.3 (7.9)	48.7 (49.7)	43.1 (42.4)
0.997 (0.966)	19.1 (21.0)	58.4 (57.7)	22.5 (21.3)
1.314 (1.320)	41.1 (40.1)	49.8 (51.1)	9.1 (8.8)
1.648 (1.647)	66.9 (66.8)	30.9 (31.3)	2.2 (2.0)

C. System $(CH_3)_2SiCl_2$ vs. $(CH_3)_2Si(OOCCH_3)_2$

$R \equiv Cl/Si$	$(CH_3)_2SiCl_2$	$(CH_3)_2SiCl(OOCCH_3)$	$(CH_3)_2Si(OOCCH_3)_2$
0.622[a] (0.634)[c]	11.3[b] (11.1)[d]	40.8 (40.0)	47.9 (48.9)
0.993 (1.000)	27.1 (26.5)	45.8 (46.2)	27.1 (27.3)
1.313 (1.333)	45.8 (44.7)	41.7 (41.9)	12.5 (13.4)
1.572 (1.584)	64.4 (62.7)	31.0 (31.6)	4.6 (5.5)
1.802 (1.836)	84.0 (80.8)	15.6 (17.8)	0.4 (1.3)

D. System $(CH_3)_2Si(OOCCH_3)_2$ vs. $(CH_3)_2Si(SCH_3)_2$

$R \equiv SCH_3/Si$	$(CH_3)_2Si(SCH_3)_2$	$(CH_3)_2Si(SCH_3)(OOCCH_3)$	$(CH_3)_2Si(OOCCH_3)_2$
0.539[a] (0.514)[c]	20.1[b] (20.6)[d]	11.2 (12.6)	68.7 (66.8)
0.966 (0.995)	42.6 (41.0)	14.3 (14.5)	43.1 (44.4)
1.271 (1.274)	56.0 (56.6)	15.4 (13.9)	28.6 (29.5)
1.549 (1.553)	71.8 (71.6)	11.7 (11.8)	16.5 (16.7)
1.794 (1.781)	85.2 (85.7)	7.7 (7.9)	7.1 (6.3)

E. System $(CH_3)_2SiBr_2$ vs. $(CH_3)_2Si[N(CH_3)_2]_2$

$R \equiv Br/Si$	$(CH_3)_2SiBr_2$	$(CH_3)_2SiBr[N(CH_3)_2]$	$(CH_3)_2Si[N(CH_3)_2]_2$
0.371[a] (0.371)[c]	--[b] (0.0)[d]	36.7 (37.1)	63.3 (62.9)
0.699 (0.697)	-- (0.1)	72.0 (69.7)	28.0 (30.2)
1.032 (1.032)	4.1 (4.1)	95.0 (94.9)	0.9 (0.9)
1.367 (1.371)	38.1 (36.8)	60.9 (63.2)	1.1 (0.0)
1.703 (1.715)	71.5 (70.3)	28.5 (29.7)	-- (0.0)

[a] From the ingredients. [b] From the nmr spectra. [c] Calculated from the nmr data. [d] Calculated from the equilibrium constants in Table II for the *R* values as determined from the ingredients.

1, one observes that the greatest deviations from randomness are found with the dimethylamino group. Following this (about 1 kcal lower) is the methoxyl group and then the methylthio group. The phenoxy and aceto groups lie about 1 kcal below the methoxyl group in Figure 1. Presumably participation of the unshared electron pairs of the silicon-bonded oxygen in resonance structures involving the benzene ring of the phenoxy group or the carbonyl of the aceto group results in this modification of the enthalpy. A similar difference between the methoxy and phenoxy groups has been found for exchange on monomethylsilicon[14] and on phosphorus[15,16] as the central moieties.

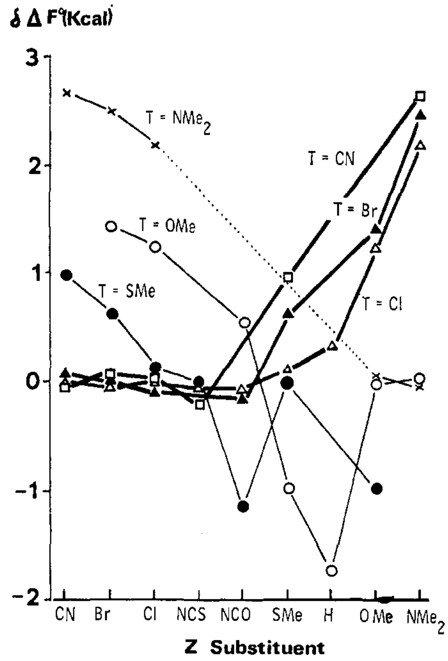

Figure 1.—Systematic plots of the deviation from randomness as a function of variations in the Z substituent for different kinds of T substituents. The sequence of Z substituents was chosen arbitrarily to give reasonably smooth curves for the majority of the T substituents.

It is apparent from Figure 1 that additional data are needed to round out the tentative correlation given therein. In particular, more exchange-equilibrium data should be obtained with one of the exchangeable substituents being either hydrogen or fluorine. Figure 1 can obviously be used for predictions. However, such predictions will necessarily be suspect in view of the V shape of the loci of the methoxy values ($T = OCH_3$) in this figure.

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