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SCRAMBLING OF PSEUDOHALOGEN GROUPS ON THE DIMETHYLSILICON MOIETY

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Scrambling reactions of the substituents chlorine, methoxy and dimethylamino on the dimethylsilicon moiety have been reported previously[1]. In this study we extended the work by including the isocyano, isocyanato and isothiocyanato groups. Earlier investigators[2] have shown qualitatively in a few selected examples that pseudohalogengroups attached to silicon do undergo exchange with chlorine and methoxy groups. This paper reports a systematic quantitative study of the substituent-exchange equilibria involving pseudohalogen groups on the dimethylsilicon moiety, under conditions where the methyl groups do not undergo exchange.

EXPERIMENTAL

Reagents

Dimethyldichlorosilane and dimethyldimethoxysilane were purchased from Peninsular Chem Research, Inc. and Anderson Chemical Company respectively. Dimethyldibromosilane was obtained in 60% yield by heating 0.75 mole of octamethylcyclotetrasiloxane with 2 moles of boron tribromide at 200° and distilling off the resulting dimethyldibromosilane, b.p. 111°/760 mm. Dimethylbis(thiomethyl)-silane[3], dimethyldiisocyanosilane[4], dimethyldiisocyanatosilane[5] and dimethyldiisothiocyanatosilane[6] were prepared according to literature methods. The purity of the compounds was checked by proton NMR (< 0.2% hydrogen containing impurities).

Equilibrations and analysis

Due to hydrolytic sensitivity of the silicon compounds involved, all materials were handled in an atmosphere of dried nitrogen. Equilibrations were carried out by sealing the correct proportions of starting materials in 5 mm o.d. precision NMR tubes and heating. In each case, pilot kinetic runs were undertaken to establish the conditions for reaching equilibrium.

A Varian A-60 analytical NMR spectrometer operating at a frequency of 60 Mc/s was employed for the NMR determinations at a sweep rate of 0.1 cps/s, using the greatest available sweep width (50 cycles for the entire scale). A thermostated NMR probe held at 72° was employed in the measurements on some of the systems involving the isocyano group. The NMR measurements on all of the other systems were made at 33°. Samples held at 120° were run at 33° immediately after quenching to room temperature so that the obtained data correspond to 120°. Uncorrected ^{1}H NMR chemical shifts (as measured, not corrected for bulk magnetic susceptibilities) of the protons in CH_3–Si, CH_3–O–Si and CH_3–S–Si groups of the compounds involved are reported in Table 1. The peaks for mixed compounds were identified from material-balance calculations and on the basis of the linear increase of their chemical shifts on substitution.

TABLE 1

OBSERVED PROTON NMR CHEMICAL SHIFTS IN THE SYSTEMS $(CH_3)_2SiX_2$ *vs.* $(CH_3)_2SiY_2$
In ppm relative to tetramethylsilane as internal standard[a].

X	*Y*	$(CH_3)_2SiX_2$	$(CH_3)_2SiXY$	$(CH_3)_2SiY_2$
NC	Cl	−0.187	−0.362	−0.547[b]
NC	Br	−0.648	−0.858	−1.068[b]
NC	SCH_3	−0.673	−0.575[c]	−0.475[d]
NC	NCS	−0.033	−0.013	+0.037[b]
NCO	Cl	−0.392	−0.550	−0.750
NCO	Br	−0.392	−0.697	−1.040
NCO	OCH_3	−0.367	−0.192[e]	−0.083[f]
NCO	NCS	−0.411	−0.456	−0.496
NCS	Cl	−0.500	−0.625	−0.750
NCS	SCH_3	−0.547	−0.533[g]	−0.478[h]

[a] Determined in the neat liquid samples when $R \sim 1$ (unless otherwise specified). [b] In benzene 3:1 (v/v). TMS internal standard. [c] SCH_3 resonance at −2.108 ppm. [d] SCH_3 resonance at −1.983 ppm. [e] OCH_3 resonance at −3.472 ppm. [f] OCH_3 resonance at −3.433 ppm. [g] SCH_3 resonance at −2.125 ppm. [h] SCH_3 resonance at −1.975 ppm.

The peak areas (determined by electronic integration or weighing of cut-out Xerox copies of the spectra) of the proton NMR signals of the methyl groups directly attached to silicon were utilized for determining the equilibrium concentrations in the systems. The equilibrium data reported in Tables 2, 3 and 4 correspond to the temperature and reaction times given although equilibrium in many cases was reached in considerably shorter times (given in footnotes in the Tables).

RESULTS AND DISCUSSION

Although it has been accepted for some years that the known organosilicon pseudohalides are iso compounds, the evidence is not compelling[7]. Disregarding these structural controversies, we therefore will refer for convenience to all pseudohalides as the iso compounds. Consequently, they will be written in the form $\gtrdot$SiNC, $\gtrdot$SiNCO and $\gtrdot$SiNCS, without implying any conclusions on our part about their structure.

Scrambling of the isocyano group

The experimental data are presented in Table 2. These data were employed to calculate[8] the equilibrium constants (listed in Table 5) for the reactions of eqn. (1).

$$(CH_3)_2Si(NC)_2 + (CH_3)_2SiY_2 \rightleftharpoons 2\,(CH_3)_2Si(NC)Y \qquad (1)$$

These equilibrium constants then were used to calculate[8] the values given in paren-

TABLE 2

EQUILIBRIUM DATA FOR THE INTERCHANGE OF THE ISOCYANO GROUP WITH OTHER SUBSTITUENTS ON THE DIMETHYLSILICON MOIETY

Parameter	*Mole ratio*	*Mole percentage*		
	$R \equiv NC/Si$	$(CH_3)_2SiY_2$	$(CH_3)_2SiY(NC)$	$(CH_3)_2Si(NC)_2$
Y = Cl[a]	0.306[b]	72.7	26.0	1.3
	(0.286)[c]	(71.5)[d]	(26.4)	(2.1)
	0.656	45.6	45.0	9.5
	(0.640)	(44.5)	(45.5)	(10.0)
	0.931	28.3	50.9	20.8
	(0.926)	(27.7)	(51.6)	(20.8)
	1.247	13.7	49.3	37.0
	(1.233)	(13.4)	(48.6)	(38.0)
	1.547	4.4	36.9	58.7
	(1.543)	(4.7)	(35.9)	(59.4)
Y = Br[e]	0.322	73.4	25.4	1.2
	(0.278)	(69.9)	(28.0)	(2.1)
	0.778	41.1	47.9	11.0
	(0.699)	(38.3)	(49.5)	(12.2)
	0.950	27.1	53.0	19.9
	(0.928)	(25.9)	(53.2)	(20.9)
	1.242	12.5	50.4	37.1
	(1.247)	(12.9)	(50.0)	(37.1)
	1.566	4.0	31.9	64.2
	(1.602)	(4.0)	(35.5)	(60.6)
Y = SCH_3[f]	0.316	67.8	31.0	1.1
	(0.332)	(68.6)	(31.2)	(0.2)
	0.640	38.5	58.7	2.8
	(0.643)	(37.5)	(61.1)	(1.4)
	0.895	17.8	78.3	3.9
	(0.861)	(16.0)	(78.5)	(5.5)
	1.243	3.9	72.5	23.6
	(1.198)	(2.6)	(70.5)	(26.9)
	1.688	1.8	31.4	66.8
	(1.650)	(0.2)	(30.8)	(68.9)
Y = NCS[g]	0.325	73.6	26.3	0.1
	(0.265)	(71.2)	(25.1)	(3.7)
	0.667	49.8	37.2	13.1
	(0.633)	(47.0)	(39.2)	(13.8)
	0.993	26.0	41.1	32.9
	(1.068)	(28.6)	(43.5)	(27.9)
	1.312	17.1	42.5	40.1
	(1.233)	(14.5)	(39.7)	(45.7)
	1.631	5.3	31.3	63.5
	(1.582)	(4.7)	(27.5)	(67.8)

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[a] Data obtained after 27 h at 25°; equilibrium reached in less than 3 h at 25°, measured in 3:1 benzene solution. [b] Calculated from ingredients. [c] Values in parentheses are calculated from NMR peak areas. [d] Values in parentheses are calculated from equilibrium constants in Table 5. [e] Data obtained after 18 h at 25°; equilibrium reached in less than 3 h at 25°. [f] Data obtained after 150 h at 72°; equilibrium reached in less than 8 days at 25°; data correspond to 72° (probe temperature). [g] Data obtained after 21 days at 72°; equilibrium reached in less than 160 h at 72°; because of rapid exchange (see text), the equilibria in this system probably correspond to the NMR probe temperature of 33°.

TABLE 3

EQUILIBRIUM DATA FOR THE INTERCHANGE OF THE ISOCYANATO GROUP WITH OTHER SUBSTITUENTS ON THE DIMETHYLSILICON MOIETY

Parameter	*Mole ratio*	*Mole percentage*		
	$R \equiv NCO/Si$	$(CH_3)_2SiY_2$	$(CH_3)_2SiY(NCO)$	$(CH_3)_2Si(NCO)_2$
Y = Cl[a]	0.348[b]	69.7	26.2	4.2
	(0.345)[c]	(68.5)[d]	(28.3)	(3.2)
	0.681	44.0	43.4	12.7
	(0.686)	(44.1)	(43.7)	(12.2)
	1.014	24.0	48.8	27.2
	(1.033)	(25.1)	(48.5)	(26.4)
	1.354	10.5	42.3	47.3
	(1.368)	(11.0)	(42.6)	(46.4)
	1.697	2.1	26.3	71.6
	(1.695)	(2.5)	(25.3)	(72.2)
Y = Br[e]	0.091	91.5	8.3	0.3
	(0.088)	(91.2)	(8.5)	(0.3)
	0.348	66.6	28.5	4.9
	(0.383)	(69.2)	(26.8)	(4.0)
	0.651	44.9	40.7	14.4
	(0.695)	(47.6)	(39.7)	(12.7)
	1.066	21.4	44.4	34.2
	(1.127)	(24.4)	(44.5)	(31.0)
	1.490	7.2	32.6	60.2
	(1.531)	(8.1)	(34.8)	(57.1)
Y = OCH_3[f]	0.356	61.8	36.7	1.6
	(0.398)	(65.4)	(33.6)	(1.0)
	0.687	45.5	42.6	11.9
	(0.664)	(36.6)	(58.1)	(5.3)
	0.984	15.4	69.2	15.4
	(1.000)	(17.1)	(67.5)	(15.4)
	1.209	9.7	64.0	26.3
	(1.166)	(8.0)	(63.1)	(28.9)
	1.565	1.8	39.0	59.3
	(1.575)	(1.6)	(40.3)	(58.1)
Y = NCS[g]	0.353	68.1	29.0	2.8
	(0.347)	(67.6)	(29.6)	(2.9)
	0.673	43.8	45.6	10.6
	(0.667)	(43.5)	(45.8)	(10.7)
	1.026	23.2	52.0	24.8
	(1.015)	(23.0)	(51.5)	(25.5)
	1.352	10.6	46.7	42.8
	(1.322)	(9.9)	(44.9)	(45.2)
	1.680	2.7	30.6	66.7
	(1.640)	(2.3)	(27.3)	(70.4)

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[a] Data obtained after 40 h at 120°; equilibrium reached in less than 20 h at 120°, equilibrium data correspond to 120°. [b] Calculated from ingredients. [c] Values in parentheses are calculated from NMR peak areas. [d] Values in parentheses are calculated from the equilibrium constants in Table 5. [e] Data obtained after 32 days at 120°; equilibrium reached in less than 20 days at 120°, equilibrium data correspond to 120°. [f] Data obtained after 112 h at 120°; equilibrium reached in less than 20 h at 120°, equilibrium data correspond to 120°. [g] Data obtained after 600 h at 25°; equilibrium reached in less than 100 h at 25°, equilibrium corresponds to 25°.

theses in Table 2. It is apparent from the equilibrium constants listed in Table 5 that the exchange on the dimethylsilicon moiety of the isocyano group with chlorine or bromine atoms is quite close to the ideally random case ($K_{rand} = 0.250$). However, the exchange equilibrium resulting from interchange of isocyano with thiomethyl groups deviates from the random case, with the mixed species being preferred. For the system involving the exchange of isocyano and isothiocyanato groups the equilibrium constants were found to be somewhat larger than expected for randomness. However, due to overlap of the three peaks observed in this system and to broadening of the signals (attributable to rapid exchange of NC and NCS groups on the dimethylsilicon moiety), the peak areas could not be determined as accurately as in the other systems. Therefore, the equilibrium constant for this system exhibits a larger standard error than the others. By applying the proper equation for the calculation of average lifetimes from saddle-shaped NMR spectra[9], the lifetime at 33° for scrambling in this system was estimated to be *ca.* 0.1 sec for the neat liquids. Furthermore on increasing dilution, the resolved NMR signal at 1:1 dilution with benzene, for the mixed compound $(CH_3)_2Si(NC)(NCS)$ was seen to shift more and more downfield so that, at a dilution with 31 parts of benzene, it completely merged with the signal due to $(CH_3)_2Si(NCS)_2$. Line broadening was also observed in the spectra of certain compositions ($R \equiv$ NC/Si = 1.6 to 1.0) of the system $(CH_3)_2SiCl_2$ *vs.* $(CH_3)_2Si(NC)_2$,

TABLE 4

EQUILIBRIUM DATA FOR THE INTERCHANGE OF THE ISOTHIOCYANATO GROUP WITH OTHER SUBSTITUENTS ON THE DIMETHYLSILICON MOIETY

Parameter	*Mole ratio*	*Mole percentage*		
	$R \equiv NCS/Si$	$(CH_3)_2SiY_2$	$(CH_3)_2SiY(NCS)$	$(CH_3)_2Si(NCS)_2$
Y = Cl[a]	0.344[b]	68.6	27.8	3.6
	(0.350)[c]	(69.0)[d]	(27.6)	(3.4)
	0.665	46.6	41.8	11.6
	(0.650)	(45.6)	(42.4)	(12.1)
	1.038	22.7	47.0	30.4
	(1.077)	(24.4)	(47.4)	(28.3)
	1.368	10.2	41.0	48.8
	(1.387)	(11.0)	(41.3)	(47.8)
	1.712	1.9	23.3	74.8
	(1.729)	(2.4)	(24.0)	(73.6)
Y = SCH₃[e]	0.344	64.8	29.4	5.8
	(0.410)	(68.5)	(28.6)	(2.9)
	0.779	34.2	47.8	18.1
	(0.839)	(37.1)	(47.8)	(15.0)
	1.014	21.8	51.1	27.1
	(1.053)	(24.1)	(50.3)	(25.6)
	1.442	6.6	41.1	52.3
	(1.456)	(7.7)	(40.4)	(51.9)
	1.726	3.3	25.6	71.0
	(1.677)	(1.8)	(23.8)	(74.4)

[a] Data obtained after 40 h at 120°; equilibrium reached in less than 23 h at 120°, equilibrium data correspond to 120°. [b] Calculated from ingredients. [c] Values in parentheses are calculated from the NMR peak areas. [d] Values in parentheses are calculated from the equilibrium constants in Table 5. [e] Data obtained after 27 days at 25°; equilibrium reached in less than 90 h at 25°, equilibrium data correspond to 25°.

TABLE 5

EQUILIBRIUM CONSTANTS FOR SUBSTITUENT INTERCHANGE ON THE DIMETHYLSILICON MOIETY AT 25°

X	*Y*	K^a	*Standard error*
NC	Cl	0.22	0.01
NC	Br	0.19	0.03
NC	SCH_3	0.014^b	0.006
NC	NCS	0.42^b	0.10
NCO	Cl	0.28^c	0.01
NCO	Br	0.38^c	0.07
NCO	OCH_3	0.058^c	0.010
NCO	NCS	0.22	0.03
NCS	Cl	0.31^c	0.03
NCS	SCH_3	0.24	0.05
Ideal randomness		0.250	

[a] $K = [(CH_3)_2SiX_2][(CH_3)_2SiY_2]/[(CH_3)_2SiXY]^2$. [b] Constant corresponds to 72°. [c] Constant corresponds to 120°.

indicating also rapid exchange of NC groups with Cl atoms on the dimethylsilicon moiety.

The NMR chemical shift of dimethyldiisocyanosilane, which is —0.056 ppm in dilute benzene solution, is seen in Table 1 to vary greatly from one system to another. Moreover, over the composition range studied (see the *R* values in Table 2), the shifts were found to be quite constant within each system. There is also a large difference between the chemical shift of $(CH_3)_2SiCl_2$ when going from a benzene solution of the equilibrated system $(CH_3)_2Si(NC)_2$ *vs.* $(CH_3)_2SiCl_2$ (—0.547 ppm) to the pure neat liquid or its benzene solution (—0.75 ppm). We have tentatively chosen to ascribe these anomalies to rapidly exchanging complexes formed between the various molecules appearing at equilibrium in the systems involving the isocyano group. According to the usual simple-minded viewpoint based on a direct correlation of NMR shielding with "electron density", a considerable amount of charge transfer may probably be attributed to the presumed complex involving $(CH_3)_2Si(NC)_2$ and $(CH_3)_2SiCl_2$, since the shifts of these two compounds are moved towards each other by the same amount (*ca.* 0.2 ppm) upon complex formation. In the case of the presumed interaction of the diisocyano compound with the dibromo or bisthiomethyl compounds, the large change in chemical shift is observed only for $(CH_3)_2Si(NC)_2$, a finding which might be interpreted to mean that the "complexing effect" in these two cases may be a change in an assumed rapid equilibrium between the cyano and isocyano forms of the NC group.

Scrambling of the isocyanato group

The experimental and calculated data presented in Table 3 and the equilibrium constants of these systems shown in Table 5 indicate that the exchange of NCO groups according to eqn. (2) with Y = chlorine, bromine or NCS groups is close to the distribution expected for ideal randomness.

$$(CH_3)_2Si(NCO)_2 + (CH_3)_2SiY_2 \rightleftharpoons 2\,(CH_3)_2Si(NCO)Y \qquad (2)$$

However, scrambling of methoxyl groups with isocyanato groups is nonrandom with the mixed compound being preferred.

Scrambling of the isothiocyanato group

The experimental and calculated data for the equilibria resulting from exchange of isothiocyanato groups with chlorine atoms or thiomethyl groups are presented in Table 4. The equilibrium constant for the reactions of eqn. (3) are listed in Table 5. It is seen that these constants, for Y = Cl or SCH_3, are very close to the ideal random value.

$$(CH_3)_2Si(NCS)_2 + (CH_3)_2SiY_2 \rightleftharpoons 2\,(CH_3)_2Si(NCS)Y \qquad (3)$$

GENERAL CONCLUSION

With respect to deviations from randomness in scrambling with other groups on the dimethylsilicon moiety, the pseudohalogens appear to act similarly to the halogens. In previous studies, it has been demonstrated that halogen–halogen exchange equilibria on a central moiety follow the laws of random statistics[10,11]. In agreement with this, we found that the equilibria resulting from the exchange of pseudohalogen groups with halogens or with other pseudohalogen groups on the dimethylsilicon moiety are also random. Furthermore, nonrandom behavior was observed when pseudohalogen groups were exchanged with alkoxyl and thiomethyl groups [exception: $(CH_3)_2Si(NCS)_2$ *vs.* $(CH_3)_2Si(SCH_3)_2$] a behavior which also has been observed to about the same amount for halogen–alkoxyl[1] and halogen–thiomethyl[11] exchange equilibria on the dimethyl silicon moiety.

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SUMMARY

Proton nuclear magnetic resonance was employed in a quantitative study of most of the equilibria resulting from scrambling on dimethylsilicon of isocyano, isocyanato, and isothiocyanato groups with each other and with the chloro, bromo, methoxy, and methylthio groups. The pseudohalogen groups behave similarly to the halogens with respect to deviations from additivity in Pauling-type bond energies.

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