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Cyclic Germanosilthianes

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Received February 16, 1967

Proton nmr data for equilibrated mixtures of hexamethylcyclotrisilthiane and hexamethylcyclotrigermanium trisulfide are evaluated in terms of three equilibrium constants. Two fo these interrelate the four trimeric cyclic molecules resulting from permuting dimethylsilicon and dimethylgermanium moieties between the three sulfur atoms of the ring structure. A third constant relates one of the hexatomic rings to the tetratomic-ring molecule in which two dimethylsilicon groups are bridged by two sulfur atoms. These data establish the existence of new cyclic structures having sulfur atoms alternating with silicon or germanium atoms.

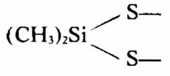
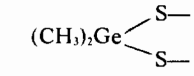
Organosilicon ring compounds in which silicon atoms alternate with more than one kind of heteroatoms have been reported only recently.[1] Examples of these types of cyclic molecules are the hexa- or octatomic silicon-oxygen ring structure in which one or more of the bridging oxygens are replaced by bridging NH or NCH_3 groups. In addition, it has been demonstrated[2,3] that compounds of this type, *e.g.*, the cyclic «silthiazanes» in which silicon atoms alternate with sulfur and nitrogen atoms in the ring, may be obtained by redistribution of bridging NCH_3 groups in nonamethylcyclotrisilazane with the bridging sulfur atoms in hexamethylcyclotrisilthiane. This paper describes related studies dealing with the redistribution of dimethylsilicon and dimethylgermanium moieties in hexatomic silicon-sulfur and germanium-sulfur ring structures to give cyclic germanosilthianes. The latter therefore represent derivatives of hexamethylcyclotrisilthiane in which one or two of the silicon atoms are replaced by germanium.

Experimental Section

Reagents. Hexamethylcyclotrisilthiane[4] and hexamethylcyclotrigermanium trisulfide[5,6] were prepared according to methods of the literature. The purified substances did not exhibit any proton-containing impurities detectable by proton nuclear magnetic resonance (nmr).

Sample Preparation, Equilibration and Data Evaluation. Various proportions of hexamethylcyclotrisilthiane and hexamethylcyclotrigermanium trisulfide were heated at 140° in sealed 5-mm o.d. precision nmr tubes. The reported equilibrium data correspond to 61 days at this temperature. For all samples, the results obtained at 61 days were identical to those found at 28 days. Preliminary runs indicated equilibration within less than half of this shorter time. The quantitative proton nmr spectra were obtained on samples which, immediately upon quenching to room temperature, were diluted with 5 parts of carbon tetrachloride, since poor nmr resolution was observed in the neat samples. Except for the difference in resolution, the peak-area distributions were the same for the undiluted and diluted samples. Also spectra taken on the neat liquids at 140° with a heated probe (again lower peak resolution than the diluted samples) agreed with the spectra obtained at the normal probe temperature of 33° for the Varian A-60 spectrometer. This spectrometer had been modified to obtain spectra at a sweep width of 25 cps for the entire scale. Since the observed peaks could not be completely resolved even at this sweep width, electronic integration of their areas was inaccurate. Therefore, peak areas were determined by cutting out and weighing Xerox copies of the spectra. The proton nmr chemical shifts observed for various molecular segments in the cyclic molecules seen at equilibrium are presented in Table I.

Table I. Proton NMR Chemical Shifts[a] of Methyl Groups in an Equilibrated Sample of a Mixture of $[(CH_3)_2SiS]_3$ and $[(CH_3)_2GeS]_3$

	 $(CH_3)_2Si\langle^{S-}_{S-}$		 $(CH_3)_2Ge\langle^{S-}_{S-}$	
	Resonance in Fig. 1	Chem. Shift	Resonance in Fig 1	Chem. Shift
[SiSi][b]	D	—0.739		
[SiSiSi][c]	E	—0.681		
[SiSiGe][d]	A′	—0.670 (2)	A	—0.958 (1)
[SiGeGe][e]	B′	—0.661 (1)	B	—0.946 (2)
[GeGeGe][f]			C	—0.932

[a] Measured in 5: 1 CCl_4 solution in a sample having a composition $R \equiv Si/(Si+Ge) = 0.632$. Shifts are given in ppm relative to internal tetramethylsilane. Area ratios of corresponding peaks in the compounds given are listed in parentheses. [b] Tetramethylcyclodisilthiane. [c] Hexamethylcyclotrisilthiane. [d] Hexamethylcyclogermanodisilthiane. [e] Hexamethylcyclodigermanosilthiane. [f] Hexamethylcyclotrigermanium trisulfide.

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(1) R. L. Elliot and L. W. Breed, *Inorg. Chem.*, *4*, 1455 (1965) and the references cited therein.

(2) K. Moedritzer and J. R. Van Wazer, *J. Phys. Chem.*, *70*, 2030 (1966).

(3) K. Moedritzer and J. R. Van Wazer, *Inorg. Nucl. Chem. Létters*, 2, 45 (1966).

(4) T. Nomura, N. Yokoi, and K. Yamasaki, *Proc. Japan Acad.*, *29*, 342 (1954); *Chem. Abstr.*, *49*, 12274 (1955).

(5) E. G. Rochow, *J. Am. Chem. Soc.*, *70*, 1801 (1948).

(6) M. P. Brown and E. G. Rochow, *J. Am. Chem. Soc.*, *82*, 4166

The calculation of equilibrium constants was performed as previously described[7,8] by treating the assemblage of three sulfur atoms in the ring molecules as being equivalent to a trifunctional central moiety and the dimethylsilicon and dimethylgermanium moieties as the exchanging substituents. In this way, the computer programs developed for redistribution equilibria in systems QZ_ν *vs.* QT_ν (Q being a central moiety of functionality ν and Z and T being monofunctional exchangeable substituents) could be utilized to calculate equilibrium constants from the data and the theoretical molecular distributions corresponding to these constants.

Results and Discussion

When hexamethylcyclotrisilthiane, $[(CH_3)_2SiS]_3$, is heated at 140° for several days with hexamethylcyclotrigermanium trisulfide, $[(CH_3)_2GeS]_3$, exchange of dimethylsilicon and dimethylgermanium moieties occurs. As a result, two new compounds are formed which contain silicon as well as germanium in the ring molecule. At equilibrium, therefore, four kinds of hexatomic-ring molecules must be considered; the two starting materials and the two rings containing silicon as well as germanium. The concentration of all species present at equilibrium was determined by proton nmr. The assignment of the observed nmr signals to the pertinent structural segments of the various cyclic molecules was aided by the known chemical shifts of the two starting materials and the tetratomic silicon-sulfur ring compound which at equilibrium is seen here also. The further assignment took into account certain constant-area relationships of pairs of peaks seen in a series of spectra obtained from equilibrated mixtures of differing over-all composition. The sample spectrum in Figure 1 shows, in addition to the signals for the cyclic dimeric and trimeric silthiane (SiSi) and (SiSiSi) and the germanium sulfide trimer (GeGeGe), a pair of signals assigned to hexamethylcyclogermanodisilthiane (SiSiGe) appearing throughout the series of spectra in the constant area ratio A:A' = 1:2. Similarly, the pair of signals lettered B and B' exhibit the constant area ratio 2:1 and therefore were assigned to hexamethylcyclodigermanosilthiane (SiGeGe). These assignments were corroborated by material-balance calculations.

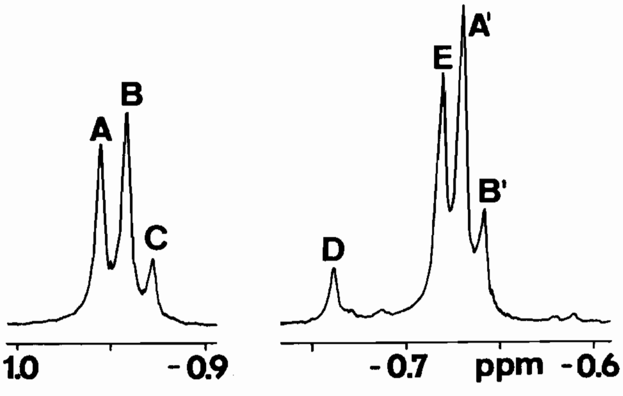
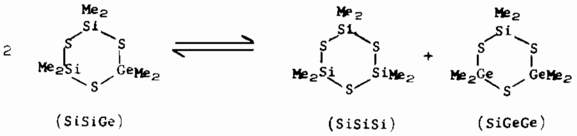


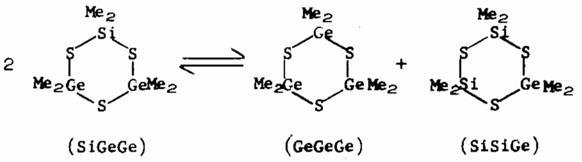
Figure 1. Proton nmr spectrum of an equilibrated sample (diluted with 5 parts of CCl_4) in the system $[(CH_3)_2SiS]_3$ *vs* $[(CH_3)_2GeS]_3$ of the composition $R \equiv Si/(Si+Ge) = 0.632$. The assignment of the resonances is given in Table I (tetramethylsilane = 0 ppm).

In most studies[9] of families of equilibrated compounds which have been carried out in our laboratory, the presence of neighboring groups having an upfield (downfield) shift with respect to the particular group in question causes the shift of that group to be upfield (downfield). In Table I, it is noted that the opposite order of arrangement of the nmr signals holds for the ring compounds studied here. Thus the nmr signals of the dimethylgermanium methyl groups in the silicon-substituted cyclics appears downfield of the resonance for the all-germanium ring molecule even though the resonance of the all-silicon ring lies upfield. Similar behavior is found for the shifts of the dimethylsilicon groups in the mixed cyclic structures.

The equilibria involving the hexatomic-ring molecules may be fully represented by the reactions of equations (1) and (2), with the methyl groups being denoted by Me.



(1)



(2)

Since under the condition of the equilibration tetramethylcyclodisilthiane has been found to be present in substantial amounts, an additional equilibrium expression is required. This requirement is fulfilled by the reaction of equation 3 which, in conjunction with equations 1 and 2, relates the silicon-sulfur dimer to the set of four trimeric ring molecules.

$$3[(CH_3)_2SiS]_2 \rightleftharpoons 2[(CH_3)_2SiS]_3 \qquad (3)$$

The nmr spectra do not provide any evidence for the presence at equilibrium of other tetratomic-ring molecules, such as the tetramethylcyclogermanosilthiane or the tetramethylcyclodigermanium disulfide. Also cyclic molecules larger than the hexatomic-ring stuctures do not seem to be present since at equilibrium no separate detectable nmr resonances were observed other than the ones assigned in Table I and quantitatively accounted for.

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(7) L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, 36, 303 (1964).

(8) K. Moedritzer, J. R. Van Wazer, and C. H. Dungan, *J. Phys. Chem.*, 42, 2478 (1965).

(9) For references, see J. R. Van Wazer and K. Moedritzer, *Angew. Chem. Intern. Ed. Engl.*, 5, 341 (1966) or «Exchange Reactions», International Atomic Energy Agency, Vienna, 1965, pp. 23-28. (1960).

The experimental data have been evaluated in terms of equilibrium constants for the reaction of equations 1, 2, and 3. Weighted- average values for these constants at 140° are given below:

$$K^{\infty}_{3Si,2Si} = [SiSiSi]^2/[SiSi]^3 = 36.0 \pm 10.8\ l/mole \qquad (4)$$

$$K^{\infty}_{SiGeGe} = [GeGeGe][SiSiGe]/[SiGeGe]^2 = 0.38 \pm 0.02 \qquad (5)$$

$$K^{\infty}_{SiSiGe} = [SiSiSi][SiGeGe]/[SiSiGe]^2 = 0.45 \pm 0.02 \qquad (6)$$

The two equilibrium constants describing the equilibria between the hexatomic rings, K^{∞}_{SiSiGe} and K^{∞}_{SiGeGe} are quite close to the value for ideally random sorting of dimethylsilicon and dimethylgermanium moieties between the three sulfur atoms, $K_{rand} = 0.333$. This means that the amounts of the two germanium-and-silicon-containing ring molecules at equilibrium is governed by simple statistics so that the reactions involving the interchange equilibria are entropy controlled.

The constant relating the different sizes of silthiane rings, $K^{\infty}_{3Si,2Si}$, is significantly dependent on temperature and has been determined for various temperatures in earlier studies.[2,8] For 200°, $K^{\infty}_{3Si,2Si} = 3.5$ l/mole, for 120° it is 130 l/mole, and for 25°, 7200 l/mole. The value reported here for 140° fits on the straight line resulting from a plot of log $K^{\infty}_{3Si,2Si}$ *vs.* 1/T involving the available data for different temperatures. The fact that the silthiane dimer-trimer equilibrium is established at the relatively low temperature of 140° indicates that this equilibration is catalyzed by the dimethylgermanium sulfide. The rate of dimer-trimer equilibration of pure hexamethyltrisilthiane has been found[8] to be extremely slow below 180°, but fairly rapid at about 200°. A similar rapid rate of equilibration at a temperature below 180° has been observed for the silthiane dimer-trimer equilibrium in the system of the cyclic silthiazanes.[2] Also in the present case, it seems likely that the ring-ring equilibrations proceed *via* chain intermediates, with undetectable amounts of chain-terminating groups initiating the reaction.

The experimental proton-nmr data of the equilibrated mixture, expressed in mole percent of the total molecules present, are shown in Table II. From these, the equilibrium constants presented in equations 4, 5, and 6 were determined. These constants were then used to calculate the distribution of molecules at equilibrium for the over-all compositions for which experimental data were obtained. These values are listed in parentheses in Table II where excellent agreement between the experimental and calculated concentrations is observed.

Table II. Experimental and Calculated Equilibrium Concentrations in Mole Per Cent for the System $[(CH_3)_2SiS]_3$ *vs* $[(CH_3)_2GeS]_3$ at 140°

$R \equiv Si/(Si+Ge)$	[SiSi]	[SiSiSi]	[SiSiGe]	[SiGeGe]	[GeGeGe]
0.140[a]	—	0.5	4.5	31.0	64.0
(0.138)[b]	(0.6)[c]	(0.4)	(5.2)	(29.6)	(64.2)
0.226	0.2	1.5	8.9	34.0	55.5
(0.189)	(0.9)	(1.0)	(8.8)	(35.3)	(54.1)
0.382	2.2	5.8	24.7	40.5	26.9
(0.375)	(3.2)	(6.1)	(23.6)	(40.6)	(26.6)
0.632	6.8	23.5	37.1	26.5	6.1
(0.630)	(7.3)	(24.0)	(36.9)	(25.3)	(6.6)
0.753	9.1	33.6	37.6	17.5	2.2
(0.728)	(9.7)	(34.5)	(36.1)	(16.8)	(3.0)
0.874	14.4	52.4	24.6	7.9	0.7
(0.851)	(12.4)	(52.1)	(28.1)	(6.8)	(0.6)

[a] Determined from the ingredients. [b] Calculated from the nmr peak area. [c] Theoretical values calculated from the equilibrium constants of equations 4, 5, and 6.

Acknowledgment. We wish to thank Raymond E. Miller for the experimental work and Dr. L. C. D. Groenweghe for assistance in using the computer programs developed by him.