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Preparation of a Novel Cyclic Silylmercurial

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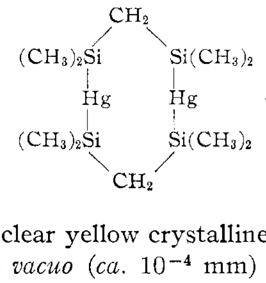
Gilman and his coworkers[2] proposed silicon–mercury compounds as intermediates to account for the products observed for reactions of triphenylsilyllithium with mercuric halides. The first adequate characterization of such a compound, however, was reported by Wiberg, *et al.*,[3] in 1963. They isolated and characterized bis(trimethylsilyl)mercury in good yield and high purity from the reaction of trimethylbromosilane with sodium amalgam. This most interesting class of compounds has generated considerable interest in the published literature. Reactions with lithium,[4] multiple bonds,[5,6] carbenes,[7] silicon hydrides,[8] aryl halides,[9] ethers,[10] and mercuric salts[11] have been reported and these reports illustrate the high degree of utility these reagents possess. In the present work we wish to describe the preparation of a novel cyclic dimercurial, 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclooctane, and some of its properties.

Results and Discussion

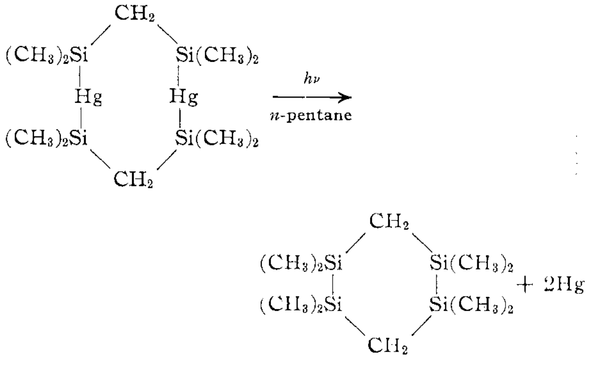
The new cyclic silylmercurial was prepared in 56% yield by a reaction analogous to that discovered by Wiberg.[3] A very slow reaction occurs at room temperature between sodium amalgam and 2,4-dichloro-2,4-dimethyl-2,4-disilapentane as shown in

$$2(CH_3)_2ClSi{-}CH_2{-}SiCl(CH_3)_2 + Na{-}Hg \longrightarrow$$



$$+\ 4NaCl \quad (1)$$

The product is a clear yellow crystalline solid which sublimes rapidly *in vacuo* (*ca.* 10^{-4} mm) without decomposition at 107°. The characterization of this compound was possible by elemental analysis and mass spectrometry, and the proposed structure is strongly supported by the nature of its photolytic decomposition which occurs according to



(2)

The use of the new dimercurial in the preparation of other heterocyclics possessing silicon–silicon bonds is presently being studied.

Experimental Section

Reagents.—**2,4-Dichloro-2,4-dimethyl-2,4-disilapentane** was prepared according to Lyukas and coworkers.[12] **One per cent sodium amalgam** was prepared according to Vogel.[13] ***n*-Pentane** (Fisher) was distilled from lithium aluminum hydride before using.

Apparatus and Methods.—All operations were carried out in an N_2-flushed glove bag or in standard vacuum-line apparatus. Mass spectra were obtained using Consolidated Electronics Corp. 21-104 and Hitachi RMU-6D mass spectrometers. Proton nmr spectra were obtained using a Varian A-60A. Infrared spectra were obtained with a Perkin-Elmer Model 621 spectrophotometer. Analyses were obtained from Schwarzkopf Microanalytical Laboratory and Stephen Nagy microchemical Laboratory.

Preparation of 2,2,4,4,6,6,8,8-Octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclooctane.—A mixture of 1% sodium amalgam (70 g, *ca.* 0.03 g-atom of Na), 2,4-dichloro-2,4-dimethyl-2,4-disilapentane (2.702 g, 13.4 mmol), and *n*-pentane (9 ml) was placed in a reaction vessel. The vessel then was evacuated, sealed, and placed on a mechanical shaker. After 1 month of shaking in the dark at room temperature the vessel was removed from the shaker. The contents of the vessel at this point were a yellow crystalline solid, a clear yellow solution, and mercury. The yellow solution and the yellow crystalline solid were decanted from the mercury and the mixture was filtered. The yellow crystalline solid was washed with additional *n*-pentane (15 ml) and then dried *in vacuo*. Elemental analysis characterized it as $[C_5H_{14}Si_2Hg]_n$. *Anal.* Calcd for $[C_5H_{14}Si_2Hg]_n$: C, 18.15; H, 4.26; Si, 16.98; Hg, 60.6. Found: C, 18.46; H, 4.55; Si, 16.71; Hg, 60.5.

The low solubility of the yellow crystalline solid precluded a molecular weight determination by any solution method. Fortunately, the molecular ion peak was observed in the mass spectrum [*m/e* (relative per cent)]: M, 664 (0.5); M–Hg, 462 (8.2); M–2Hg, 260 (9.6).

The relative sizes of the peaks in the isotopic clusters of these ions were consistent with the molecular formula $[C_5H_{14}Si_2Hg]_2$. The method of preparation and the preceding data identify the product as 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclooctane, shown by the following structure.

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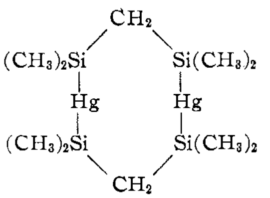

In this reaction 2.499 g of pure product was isolated. This corresponds to a yield of 56% based upon the amount of 2,4-dichloro-2,4-dimethyl-2,4-disilapentane used.

Photolysis of 2,2,4,4,6,6,8,8-Octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclooctane.—A solution prepared by mixing 0.7106 g (1.07 mmol) of 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclooctane with 10 ml of *n*-pentane sealed in an evacuated Pyrex vessel was irradiated by a commercial sunlamp for 5 days. Initially some yellow crystalline solid was present due to the limited solubility of the cyclic dimercurial in *n*-pentane. During the course of the irradiation this solid dissolved to form a clear colorless solution and a bead of mercury. When no further change could be noted, the reaction tube was opened and the solvent was removed. Remaining behind was 4.1 g (2.03 mmol) of mercury, 96% of the amount expected from eq 2, and 0.237 g of a white crystalline solid identified as 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrasilacyclohexane by its analysis and melting point of 48.8–50.0° (lit. mp 42°,[14] 51–52°[15]). *Anal.* Calcd for $[C_5H_{14}Si_2]_n$: C, 46.1; H, 10.85; Si, 43.1. Found: C, 46.3; H, 10.56; Si, 42.9. The amount of this cyclotetrasilane isolated is 85% of that expected from eq 2.

Other physical data were obtained for this previously reported compound. Nmr spectrum (in methylene chloride): τ 9.91, 10.10, area ratio 6.3:1 (expected 6.0:1). Mass spectrum [*m/e* (relative per cent)]: M, 260 (5.6); $M-CH_3$, 245 (4.4); $M-Si(CH_3)_3$, 187 (1.9); $Si(CH_3)_3$, 73 (100). Infrared spectrum (cm^{-1}) (CsBr): 2950 (m), 2890 (m, sh), 2860 (m, sh), 1400 (m), 1350 (m), 1250 (m), 1245 (m, sh), 1023 (m), 830 (s, sh), 810 (s), 789 (s, sh), 740 (w), 683 (w), 665 (w), 622 (w), 575 (w).

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Stereospecific Isomerization of Some Cobalt(III) Complexes with Flexible Tetramine Ligands

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In the course of a continuing study of the stereochemistry of various cobalt(III) complexes with flexible tetradentate ligands,[1] we have reexamined the complexes *trans*-dichloro(3,7-diaza-1,9-diaminononane)cobalt(III) perchlorate (*trans*-$[Co(2,3,2\text{-tet})Cl_2]ClO_4$) and *trans*-dichloro(4,7-diaza-1,10-diaminodecane)cobalt(III) perchlorate (*trans*-$[Co(3,2,3\text{-tet})Cl_2]ClO_4$) described by Hamilton and Alexander.[2,3] We have extended this series to several mixed-ligand complexes with bidentate ligands, including the oxalate dianion. Three topological isomers are possible for the diacidotetramine complexes (Figure 1), though not all have yet been observed; of these, the two *cis* forms should exist for the oxalato complexes.

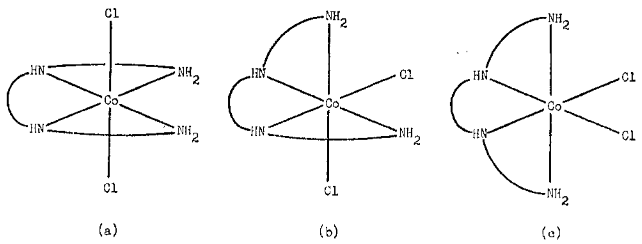

Figure 1.—The geometrical isomerism of flexible tetramine ligands: (a) *trans;* (b) β or unsymmetrical *cis;* (c) α or symmetrical *cis*.

The complexes $Co(2,3,2\text{-tet})OX^+$, and $Co(3,2,3\text{-tet})OX^+$ may be prepared from the corresponding *trans*-dichloro derivatives by the action of concentrated aqueous oxalic acid. The optical antipodes of these mixed-ligand oxalatotetramine complexes may be separated by fractional crystallization of the monohydrogen bis(benzoyl)-*d*-tartrate salts.

We have assigned the β-*cis* configuration to the complex $Co(2,3,2\text{-tet})OX^+$ and the α-*cis* configuration to the complex $Co(3,2,3\text{-tet})OX^+$ by comparing the ORD curves of these complexes (Figure 2) with those of the

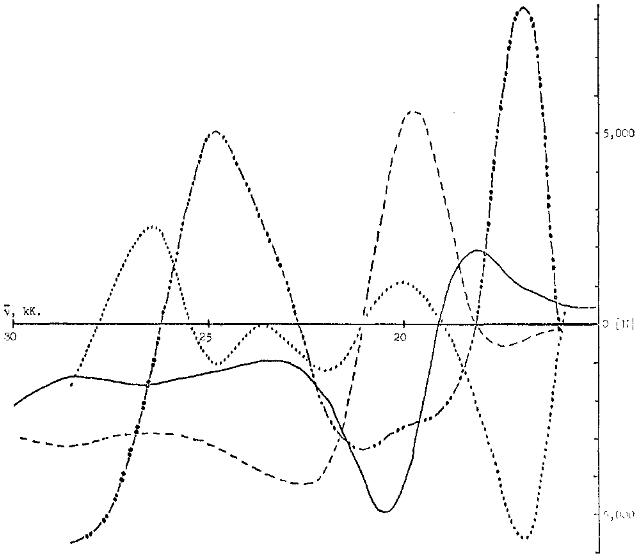

Figure 2.—The optical rotatory dispersion (15–30 kK) of Λ-β-(*RR*)-$Co(2,3,2\text{-tet})OX^+$ (———), Λ-α-(*RR*)-$Co(3,2,3\text{-tet})OX^+$ (– – – – –), *trans*-(*RR*)-$Co(2,3,2\text{-tet})Cl_2^+$ (×10) (–· · –· · –· · –), and *trans*-(*RR*)-$Co(3,2,3\text{-tet})Cl_2^+$ (×5) (· · · · · · · ·).

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