

Figure 1.

comparable yields. No interconversion of macrocyclic poly lactones into each other under the conditions of the reaction was observed, and trilactone **2** was recovered unchanged after heating with cyclic distannoxane **1** for 24 h.

This reaction may occur by insertion of several propiolactone molecules into the tin-oxygen bond and subsequent expulsion of the macrocyclic product. Propiolactone insertion into tin-oxygen compounds has been shown to be reversible and together with the possibility of multiple insertions support such a mechanism.²⁶ The reactions of cyclic stannoxanes may be compared with that of some organometallic compounds, which lead to cyclic rather than linear oligomerization of monomers.²⁷ It is, however, different from cationic oligomerization of bicyclooctanone which yields only even multiples of the monomeric unit.¹⁹

The structure of the trimer **2** has been confirmed by X-ray diffraction analysis as shown in Figure 1.²⁸ In the crystal the backbone of the trilactone **2** adopts a crown configuration, with all carbonyl groups on one side of the plane of the ether oxygens. Two enantiomeric conformations are therefore possible, both of which are present in the crystal.

The all-syn arrangement of the carbonyl groups observed in this compound has been reported for both synthetic and natural macrocyclic polycarbonyl compounds. Tri-*o*-thymotide, for instance, a trilactone which forms clathrate inclusion complexes with many guest molecules, assumes a similar conformation²⁹ as do many cyclic tripeptides, both in the solid state and in solution.³⁰ Of particular interest is, however, the iron carrier enterobactin, the cyclic skeleton of which is identical with the trilactone **2**. Although no X-ray diffraction studies of enterobactin or its iron complex have been reported, studies of this compound in solution indicate a propeller-like conformation of the aromatic residues with the ring carbonyl groups pointing down from the cyclic backbone.²¹ We are in the process of applying this synthetic method to the preparation of a number of naturally occurring macrocycles in addition to structural investigations of these novel compounds.

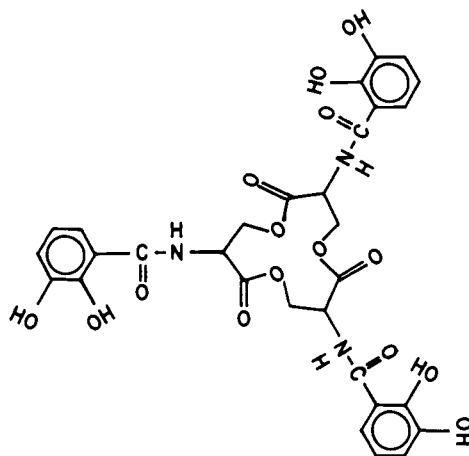
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(28) Compound **2** crystallizes as monoclinic crystals from petroleum ether; space group $P2_1/n$; $a = 8.398$ (8), $b = 8.184$ (4), $c = 14.643$ (5) Å; $\beta = 92.48$ (5)°; $Z = 4$. Intensity data were collected on a CAD-4 diffractometer (1326 unique reflections, $\theta < 23^\circ$), and the structure of the compound (Figure 1) was solved by MULTAN and refined by full-matrix least squares to $R = 0.06$ and $R' = 0.05$.

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Acknowledgment. We thank the Israel Academy for Sciences and Humanities for support.

Supplementary Material Available: X-ray data and specifically atom coordinates (Table 1), hydrogen atom coordinates (Table 2), bond lengths (Table 3), bond angles (Table 4), and physical data (Table 5) as well as the drawing of the packing arrangement (Figure 2) are available (6 pages). Ordering information is given on any current masthead page.

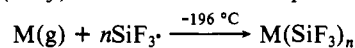
Synthesis of the First Homoleptic Trifluorosilyl σ -Bonded Metal Compounds by Cocondensation of Metal Vapor with Trifluorosilyl Radicals

Thomas R. Bierschenk, T. J. Juhlke, and Richard J. Lagow*

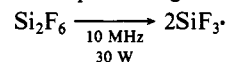
Department of Chemistry
University of Texas at Austin
Austin, Texas 78712

Received January 27, 1981

The first homoleptic trifluorosilyl metal compounds, bis(trifluorosilyl)tellurium, tris(trifluorosilyl)bismuth, and bis(trifluorosilyl)mercury have been formed in moderate yields by cocondensation of tellurium, bismuth, and mercury vapor with trifluorosilyl ($\text{SiF}_3\cdot$) radicals in a low-temperature matrix:



The trifluorosilyl radicals are cleanly generated from hexafluorodisilane in a low-temperature glow discharge:



Hexafluorodisilane is an excellent precursor for the synthesis of trifluorosilyl compounds because the silicon-silicon bond energy of 50 kcal/mol is considerably lower than the silicon-fluorine bond energy of about 140 kcal/mol.^{1,2} The large difference in bond energies leads primarily to plasma generation of trifluorosilyl radicals and production of byproducts such as $\text{Si}_2\text{F}_5\cdot$, $\text{SiF}_2\cdot$, and SiF_4 in quantities too low to detect among the reaction products. The reactor³ used in this work consisted of a metal evaporation source and a radio-frequency generator for production of $\text{SiF}_3\cdot$ radicals. Both species were directed at a -196°C surface. Normally, at least a tenfold stoichiometric excess of Si_2F_6 is used, and of the unreacted Si_2F_6 , 95% may be recycled for other reactions.

Synthesis of $\text{Hg}(\text{SiF}_3)_2$. Mercury (1.5 g) was evaporated over a 3-h period and cocondensed with $\text{SiF}_3\cdot$ radicals. The volatile

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products from the cold finger were then pumped through an ice-salt cooled trap, and the solids were scraped out of the reactor and the ice-cooled trap in an inert atmosphere. The solids were extracted with about 10 mL of freshly dried and degassed acetonitrile. The insoluble portion was removed in a centrifuge, and the acetonitrile was removed by vacuum distillation to give a light yellow solid. The mixture was then sublimed to give 730 mg of $\text{Hg}(\text{SiF}_3)_2$ (26% yield) (mp 205 °C). $\text{Hg}(\text{SiF}_3)_2$ is a white, crystalline solid which is soluble in many organic solvents. Infrared analysis of a KBr disk gave bands at 880 (vs), 825 (s), 800 (vs), 445 (s), and 305 cm^{-1} (w). The ^{19}F NMR spectrum in CH_3CN solution showed a singlet at +29 ppm from external CF_3COOH with $J(^{199}\text{Hg}-\text{F}) = 1160$ Hz. Mass spectral analysis gave a base peak of m/e 85 (SiF_3^+) (100%) and the following comparative abundances of ^{198}Hg isotopes (each envelope possessed the expected peak ratios for mercury and silicon isotopes): Hg^+ , 21%; SiF_2Hg^+ , 1.7%; SiF_3Hg^+ , 1.4%; $\text{Si}_2\text{F}_3\text{Hg}^+$, 0.4%; $\text{Si}_2\text{F}_6\text{Hg}^+$, 0.8%. The identity of the parent was confirmed by high-resolution mass spectroscopy. Reaction of $\text{Hg}(\text{SiF}_3)_2$ with elemental fluorine in a passivated Kel-F and stainless steel system gave SiF_4 . $\text{Hg}(\text{SiF}_3)_2$ is easily hydrolyzed but can be kept for long periods of time in an inert atmosphere. Anal. Calcd for $\text{Hg}(\text{SiF}_3)_2$: Hg, 54.1; Si, 15.15; F, 30.75. Found: Hg, 52.1; Si, 14.5; F, 30.1.

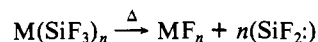
Synthesis of $\text{Bi}(\text{SiF}_3)_3$. Bismuth (1.5 g) was evaporated over a 3-h period with a hexafluorodisilane glow discharge. The volatile products were removed from the cold finger and were collected in a -63 °C trap. Vacuum distillation on a Dobson low-temperature distillation apparatus at -40 °C gave 630 mg of tris(trifluorosilyl)bismuth (21% yield based on metal vaporized). The compound was difficult to obtain in high purity due to its low thermal stability. On the basis of its ^{19}F NMR spectrum, the compound was obtained in greater than 95% purity, with some volatile decomposition products such as SiF_4 and Si_2F_6 also being present. Tris(trifluorosilyl)bismuth is a volatile crystalline solid which reacts with oxygen, water, and many polar organic solvents such as diethyl ether and tetrahydrofuran. The ^{19}F NMR spectrum at -30 °C gave a singlet at +90.4 ppm from external CFCl_3 when dichloromethane was used as a solvent. Upon warming the sample to +15 °C, the height of the peak decreased dramatically while the line width broadened, suggesting that decomposition was occurring. Mass spectral analysis gave a base peak of m/e 85 (SiF_3^+) (100%), and the following bismuth-containing species were observed (each occurred in an envelope having the correct isotope distribution for silicon): Bi^+ , 77%; SiF_2Bi^+ , 22.4%; $(\text{SiF}_3)_2\text{Bi}^+$, 0.2%; $\text{Si}_3\text{F}_6\text{Bi}^+$, 2.4%; $(\text{SiF}_3)_3\text{Bi}^+$, 0.1%. The identity of the parent ion was confirmed by high-resolution mass spectroscopy.

Synthesis of $\text{Te}(\text{SiF}_3)_2$. Tellurium (1.5 g) was evaporated over a 3-h period with a hexafluorodisilane glow discharge. The volatile products were removed from the cold finger and were collected in a -63 °C trap. Low-temperature sublimation of the product mixture at -50 °C gave 773 mg of the dark yellow liquid bis(trifluorosilyl)tellurium (25% yield). Bis(trifluorosilyl)tellurium is a volatile liquid soluble in most organic solvents and, like the bismuth product, reacts with water and polar organic solvents. ^{19}F NMR spectrum at -45 °C gave a singlet at 102.0 ppm from CFCl_3 with $J(^{125}\text{Te}-\text{F}) = 210$ Hz. The compound is sufficiently stable to be vaporized at -30 °C in vacuo with minimal decomposition. Mass spectral analysis gave a base peak of m/e 85 (SiF_3^+) (100%) along with the following tellurium species (each envelope had the isotopically correct pattern for silicon and tellurium): Te^+ , 7.0%; SiFTe^+ , 1.0%; SiF_2Te^+ , 4.5%; SiF_3Te^+ , 1.4%; $\text{Si}_2\text{F}_5\text{Te}^+$, 0.4%; $\text{Si}_2\text{F}_6\text{Te}^+$, 0.2%. The identity of the parent ion was also confirmed by high-resolution mass spectroscopy. Elemental analyses for bis(trifluorosilyl)tellurium and tris(trifluorosilyl)bismuth were not sought because they are unstable at room temperature.

Currently, work under way has produced preliminary evidence for trifluorosilyl compounds such as $\text{Sn}(\text{SiF}_3)_4$, $\text{Ge}(\text{SiF}_3)_4$, $\text{Pd}(\text{SiF}_3)_2(\text{PPh}_3)_2$, and $\text{Pt}(\text{SiF}_3)_2(\text{PPh}_3)_2$.

Trifluorosilyl metal compounds undergo thermolysis and should provide an excellent liquid-phase source of the reactive SiF_2 species

which has previously been shown by Margrave and co-workers to be an intriguing reactant in the gas phase.⁴ Trifluorosilyl metal compounds such as bis(trifluorosilyl)mercury are very soluble in most organic solvents, and a study of the trapping reaction is under way



to determine differences and similarities of the solution-phase reaction of SiF_2 with the gas-phase reagent which has been previously studied.⁴

Acknowledgment. This work was partially supported by a grant from the Robert A. Welch Foundation, The National Science Foundation, and the Air Force Office of Scientific Research (26-0290-2550). We thank Dr. John W. Chinn for kindly obtaining the mass spectral data.

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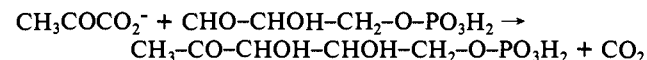
1-Deoxy-D-threo-2-pentulose: the Precursor of the Five-Carbon Chain of the Thiazole of Thiamine

Serge David, Bernard Estramareix,* Jean-Claude Fischer, and Michel Th  risod

Laboratoire de Chimie Organique Multifonctionnelle
Universit   de Paris-Sud
91405 Orsay C  dex, France

Received July 6, 1981

Thiamine pyrophosphate is one of the key coenzymes in metabolism and must be present in all living cells. Thiamine 1, discovered in 1926, is the oldest known vitamin. Nevertheless, many important steps in its biosynthesis are still obscure. It is known that in *Enterobacteria* carbon-2 of the thiazole part, HET (2), comes from C-2 of tyrosine,¹ which also gives its nitrogen.² The fate of the carboxyl is unknown, although it was found in a stray metabolite (3) of obscure significance,³ while the rest of the tyrosine molecule is excreted as 4-hydroxybenzyl alcohol.⁴ In 1978, the presence of glycol 4 in *E. coli* culture media⁵ suggested that a pentose sugar might be the precursor of the five-carbon chain in HET,⁶ while independent experiments on the incorporation of labeled precursors led R. H. White et al.⁷ to postulate the intermediacy of a pentulose derivative, arising by the following mechanism:



We have found since⁸ that the methyl of 1-deoxy-D-threo-2-[1-²H₃]pentulose (not that of the erythro isomer) was a precursor of the methyl of HET. However, the possibility remained that this pentulose was cleaved before incorporation. Besides, R. L. White et al.⁹ interpreted their experiments in yeast as an indication that a pentulose, rather than a deoxypentulose phosphate was the true precursor. The experiments now reported are a strong in-

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