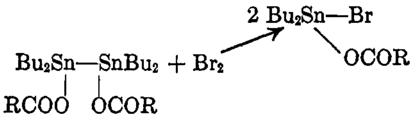
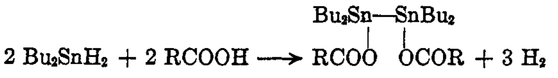


$$\underset{\text{RCOO}\ \ \text{OCOR}}{\text{Bu}_2\text{Sn—SnBu}_2} + \text{Br}_2 \longrightarrow 2\,\text{Bu}_2\text{Sn}\begin{matrix}\text{—Br}\\ \text{\\OCOR}\end{matrix}$$

The number of moles of gas produced during the formation of B was calculated as equal to 3 times the number of moles of B by the reaction:



$$2\,\text{Bu}_2\text{SnH}_2 + 2\,\text{RCOOH} \longrightarrow \underset{\text{RCOO}\ \ \text{OCOR}}{\text{Bu}_2\text{Sn—SnBu}_2} + 3\,\text{H}_2$$

The number of moles of gas formed in producing A was considered equal to the total number of moles of gas minus the number of moles of gas obtained in forming B.

The number of moles of A produced could then be calculated by the equation:

$$\text{Bu}_2\text{SnH}_2 + 2\,\text{RCOOH} \longrightarrow \text{Bu}_2\text{Sn(OCOR)}_2 + 2\,\text{H}_2$$

The percentages of A and B produced are based on di-*n*-butyltin dihydride.

Thermal decomposition of 1,1,2,2-tetraphenyl-1,2-diacetoxyditin. A sample of 1,1,2,2-tetraphenyl-1,2-diacetoxyditin (2.00 g., 0.00301 mole, m.p. 152°) in a test tube was placed in an oil bath preheated to 156° and suction applied (23 mm.). Over a three-hour period, with the oil bath temperature kept between 153 and 161°, colorless needles sublimed and filled the tube above the oil level, and a tan residue (1.73 g.) remained in the bottom of the tube. Treatment of the residue with hot benzene (15 ml.) dissolved 1.56 g. from which on cooling 0.87 g. (68%) of colorless crystals were deposited which were shown to be tetraphenyltin by melting point (224–226°) and mixture melting point with an authentic sample. The sublimate 0.18 g. (25%), m.p. 189–190° was shown to be tin(II) acetate by comparison with an authentic sample prepared from tin(II) hydroxide and acetic acid.[8] During the sublimation at 23 mm. and 180–200° of 10.2 g. of product prepared by the latter method, 5.1 g. (43%) of stannous acetate, was obtained melting clear at 189–190°, and 5.1 g. of yellow-black residue, evidently from decomposition at elevated temperature. The sensitivity of stannous acetate to air was shown by exposing a sample for 17 days to air during which time it changed from colorless to yellow and its melting point changed to 180–183° (with residue). These observations and the literature references to stannous acetate as a yellowish powder, m.p., 182°, point to preparation of an improved product by sublimation.

Reaction of 1,1,2,2-tetra-n-butyl-1,2-diacetoxyditin with bromine. To 5.85 g. (0.0100 mole) of 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin was added 4% bromine solution in carbon tetrachloride until the bromine color persisted. Evaporation of the solvent on a steam bath followed by vacuum at 0.5 mm. gave 7.39 g. (99.5%) of colorless crystals of di-*n*-butylacetoxytin bromide, melting at 66–67°. Two recrystallizations from light petroleum ether gave the analytical sample 4.61 g. (62%), m.p. 67.0–68.5°.

Anal. Calcd. for $C_{10}H_{21}SnO_2Br$: Sn, 31.92; C, 32.29; H, 5.69; Br, 21.49. Found: Sn, 32.21, 31.98; C, 32.52; H, 5.71; Br, 21.62.

DURHAM, N. H.

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[8] E. H. Baker, *J. Appl. Chem.*, **3**, 323 (1953).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY]

Siloxanes and Silanols Derived from Perphenylated Polysilanes

A. W. P. JARVIE, H. J. S. WINKLER, AND H. GILMAN

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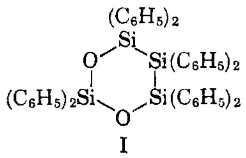
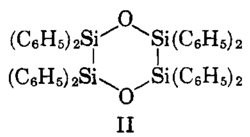
From hydrolysis of 1,4-dichloro- and 1,4-diiodooctaphenyltetrasilane there was isolated a cyclic siloxane containing four silicon atoms and one oxygen atom. This siloxane was obtained from octaphenylcyclotetrasilane by recrystallization from tetralin. The structure of one of the cyclic siloxanes isolated by Kipping[1] was identified as 2,2,3,3,5,5,6-octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane by its synthesis.

Several siloxanes were isolated by Kipping from the hydrolysis of the dihalooctaphenyltetrasilane and the oxidation of either Compound (A), octaphenylcyclotetrasilane, or Compound (B), dodecaphenylcyclohexasilane.[1–4] One of these, designated as octaphenylsilicotetrane oxide, was proposed to be a five-membered ring containing one atom and four diphenylsilylene units.[1] Analytical data and hydrogen values[5] confirmed the suggested structure. This "monoxide" was obtained by hydrolysis of 1,4-diiodooctaphenyltetrasilane.[1] It was also prepared from Compound (A) either by the action of several oxidizing agents[2a] or from attempted halogenations in the presence of either water or oxygen.[1,2a]

Two isomeric oxides with the molecular formula $(C_6H_5)_8Si_4O_2$ were also isolated in many of the reactions discussed above. The tentative structures proposed for these compounds were I and II:



I



II

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[1] F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830 (1921).

[2] (a) F. S. Kipping, *J. Chem. Soc.*, **123**, 2590 (1923); (b) F. S. Kipping, *J. Chem. Soc.*, **123**, 2598 (1923).

[3] F. S. Kipping, *J. Chem. Soc.*, 2978 (1927).

[4] The compounds designated by F. S. Kipping as Compound (A) and Compound (B) have been shown to be octaphenylcyclotetrasilane and dodecaphenylcyclohexasilane. See H. Gilman, D. Peterson, A. W. Jarvie, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **82**, 2076 (1960); **83**, 4089 (1961).

[5] F. S. Kipping, *J. Chem. Soc.*, **119**, 848 (1921); see also H. J. S. Winkler and H. Gilman, *J. Org. Chem.*, **26**, 1265 (1961).

The available data supported the structures I or II for the isomers but did not permit the assignment of either one of these to a particular isomer. One of these, termed the "rhomboidal oxide," was obtained from the "monoxide" by oxidation with nitric acid or moist iodine.[1] Oxidation of Compound A with hot nitrobenzene yielded the other isomeric dioxide.[1]

We have assigned the structure II to the isomer designated as the "rhomboidal oxide" on the basis of an unambiguous synthesis from *sym*-tetraphenyldisilanediol[6]:

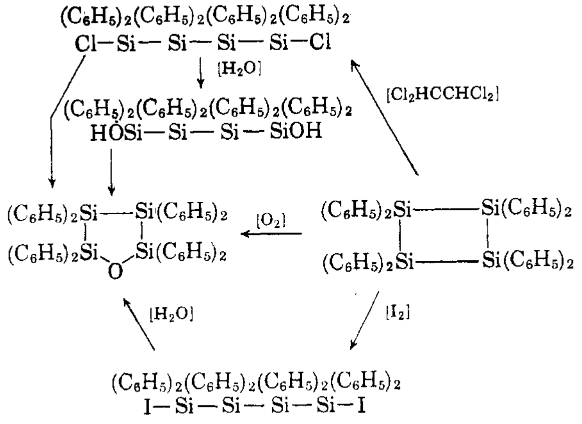
II

Having assigned the structure II to one of the isomers, it may be assumed on the basis of Kipping's analytical data that the other isomer has the structure I.

We have repeated the preparation of the "monoxide" from 1,4-diiodooctaphenyltetrasilane by hydrolysis according to Kipping's procedure.[1] There was obtained from this preparation a compound melting at 226–228°.[7] Samples with the same melting point were obtained from the 1,4-dichlorooctaphenyltetrasilane[8–10] by hydrolysis. A compound with the same infrared spectrum, but melting at 234–236°, was obtained by passing the 1,4-dichlorooctaphenyltetrasilane through a column packed with alumina.

The infrared spectra of all these samples of the monoxide showed a very intense band at 955 cm.$^{-1}$, an abnormally low frequency for the siloxane group. A similar shift of the Si—O—Si vibration has recently been reported for a five-membered ring containing one oxygen, two carbon, and two silicon atoms.[11] This type of compound showed the siloxane vibration in the region 925–905 cm.$^{-1}$. The normal Si—O—Si vibrations occur for unstrained siloxanes in the region 1090–1010 cm.$^{-1}$.[12]

Hydrolysis of 1,4-dichlorooctaphenyltetrasilane under milder conditions gave a crude product, the infrared spectrum of which indicated the presence of strongly hydrogen-bonded silanols. However, attempts to isolate a 1,4-disilanol failed, as the disilanol very rapidly underwent dehydration to the cyclic siloxane.



During the early attempts in these laboratories to purify octaphenylcyclotetrasilane, tetralin was used as a solvent for recrystallization. It was noticed that recrystallization from this solvent did not raise the melting point. The recrystallized product showed a broad, strong absorption at 955 cm.$^{-1}$ characteristic of the "monoxide." Tetralin is known to absorb atmospheric oxygen forming hydroperoxides.[13] These may be responsible for the oxidation of octaphenylcyclotetrasilane during its recrystallization. The presence of any undissolved Compound A may even promote the absorption of oxygen and peroxide formation by the tetralin. Powdered glass wool, bismuth carbonate, and barium sulfate are known to catalyze the oxidation of tetralin.[14]

In contrast to the very ready dehydration of the 1,4-dihydroxyoctaphenyltetrasilane to the "monoxide," it was possible to isolate the 1,6-dihydroxydodecaphenylhexasilane from the hydrolysis of 1,6-dibromododecaphenylhexasilane obtained by the action of bromine on dodecaphenylcyclohexasilane.[15]

EXPERIMENTAL[16]

Hydrolysis of 1,4-diiodooctaphenyltetrasilane. A mixture of 10 ml. of ethanol, 5 ml. of aniline, and 5 ml. of water was added to 2 g. (0.002 mole) of 1,4-diiodooctaphenyltetrasilane.[10] The mixture was refluxed for 2 hours, cooled, and filtered to yield 1.8 g. (81%) of an insoluble product, m.p. 218–228°. Several recrystallizations from benzene–petroleum ether (b.p. 60–70°) raised the melting point to 226–228°. The infrared spectrum of this compound showed a very strong band at 955 cm.$^{-1}$

Anal. Calcd. for $C_{48}H_{40}Si_4O$: C, 77.48; H, 5.40; Si, 15.04. Found: C, 77.44, 77.45; H, 5.87, 5.64; Si, 14.86, 14.90.

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[6] H. J. S. Winkler and H. Gilman, *J. Org. Chem.*, **26**, 1265 (1961).

[7] Kipping reports[1] a melting range as follows: "the melting of such preparations were most indefinite and irregular; some samples sintered from 205–210° and melted complete at about 220°; others did not sinter until about 220° and melted gradually up to 245° or occasionally as high as 250–260°."

[8] A. W. P. Jarvie and H. Gilman, *Chem. & Ind.*, 965 (1960).

[9] J. Krämer, and H. Gilman, *J. Org. Chem.*, in press.

[10] A. W. P. Jarvie, H. J. S. Winkler, D. Peterson, and H. Gilman, *J. Am. Chem. Soc.*, **83**, 1921 (1961).

[11] W. A. Piccoli, G. G. Haberland, and R. L. Merker, *J. Am. Chem. Soc.*, **82**, 1883 (1960).

[12] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen & Co., Ltd., 2nd ed., London, 1958, p. 334.

[13] A. Robertson and W. A. Waters, *Transay Farad. Soc.*, **42**, 201 (1946).

[14] P. George, *Trans. Faraday Soc.*, **42**, 210 (1946).

[15] H. J. S. Winkler, A. W. P. Jarvie, D. Peterson, and H. Gilman, *J. Am. Chem. Soc.*, **83**, 4089 (1961).

[16] All reactions involving halosilanes were performed in an atmosphere of dry, oxygen-free nitrogen.

Hydrogen value: Calcd. for three Si—Si bonds per $C_{48}H_{40}Si_4O$: 90.4. Found: 94.7, 92 (ml./g.).

Hydrolysis of 1,4-dichlorooctaphenyltetrasilane (I). The same aqueous alcoholic aniline mixture described in the previous section was used to hydrolyze 0.55 g. (0.7 mmole) of 1,4-dichlorooctaphenyltetrasilane.[8-10] In this case refluxing was continued for 20 hours. After cooling, filtration gave 0.3 g. (58.3%) of a compound, m.p. 220–228°. Recrystallization from benzene–petroleum ether (b.p. 60–70°) raised the melting point to 226–228°. A mixed melting point with the product from the hydrolysis of the diiodo compound was not depressed and the infrared spectra were superimposable.

Hydrolysis of 1,4-dichlorooctaphenyltetrasilane (II). To a mixture of 50 ml. of *tert*-amyl alcohol, 40 ml. of toluene, and 140 ml. of water was added 8 g. (0.01 mole) of 1,4-dichlorooctaphenyltetrasilane. The mixture was stirred for 24 hours at room temperature. The layers were separated and the insoluble material was filtered off to yield 2.5 g. (33.6%), m.p. 215–220°. Several recrystallizations from benzene–petroleum ether (b.p. 60–70°) raised the melting point to 226–228°. The mixture melting point and the infrared spectrum identified this compound as the "monoxide."

Chromatography of 1,4-dichlorooctaphenyltetrasilane. Two grams of 1,4-dichlorooctaphenyltetrasilane were dissolved in benzene and chromatographed through an alumina column. Elution with petroleum ether (b.p. 60–70°) gave 0.9 g. (50%) of a product, m.p. 234–236°. This compound had an infrared spectrum identical with those of the above isolated samples.

Formation of 1,6-dihydroxydodecaphenylhexasilane. To a mixture of 25 ml. of *tert*-amyl alcohol, 20 ml. of toluene, and 70 ml. of water was added 4 g. (0.003 mole) of 1,6-dibromododecaphenylhexasilane.[15] The reaction mixture was stirred for 24 hours at room temperature. The layers were separated and the aqueous layer was extracted with ether. The organic extracts were combined and dried. Evaporation of the solvents gave 3.5 g. of a product melting over a range (100–130°). After several recrystallizations from benzene-petroleum ether (b.p. 60–70°) there was obtained 2 g. (56%) of a compound melting at 170–172°. This material showed strong Si—O—H bonding in the infrared. An identical product was obtained when 1,6-dibromododecaphenylhexasilane was hydrolyzed with 0.1*N* hydrochloric acid.

Anal. Calcd. for $C_{72}H_{62}Si_6O_2$: C, 76.80; H, 5.51; Si, 14.93. Found: C, 77.00, 77.03; H, 5.72, 5.63; Si, 14.86, 14.74. Hydrogen value: Calcd. for five Si—Si bonds per $C_{72}H_{62}Si_6O_2$: 99.7. Found: 103, 99.8.

Preparation of 2,2,3,3,5,5,6,6-octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane. A suspension of 2 g. of *sym*-tetraphenyldisilanediol[6] in 30 ml. of 88% formic acid was heated 30 min. to boiling. The solution was cooled and poured into 100 ml. of ice water. The white crystalline compound which was collected melted at 219–220° after one recrystallization from benzene–petroleum ether (b.p. 60–70°). The pure siloxane weighed 1.8 g. (95%).

Anal. Calcd. for $C_{48}H_{40}Si_4O_2$: C, 75.75; H, 5.30; Si, 14.75; O, 4.21. Found: C, 75.55, 75.75; H, 5.30, 5.36; Si, 14.60, 14.81. Hydrogen value: Calcd. for two Si—Si bonds per $C_{48}H_{40}Si_4O_2$: 59. Found: 59.5.

Acknowledgment. This research was supported in part by the United States Air Force under contract AF 33(616)-6127 monitored by the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

AMES, IOWA

[CONTRIBUTION FROM THE DEVELOPMENT DEPARTMENT, UNION CARBIDE CHEMICALS CO.,
DIVISION OF UNION CARBIDE CORP.]

Synthesis of 1,1′-Bis(tri-*n*-dodecylsilyl)ferrocene

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Received September 15, 1961

The previously unreported 1,1′-bis(tri-*n*-dodecylsilyl)ferrocene has been synthesized in a yield of about 54% from chlorotri-*n*-dodecylsilane via the intermediate tri-*n*-dodecylsilylcyclopentadiene. The procedure utilizes modifications of previously developed synthetic methods and should be applicable to the preparation of other disubstituted silylferrocenes. Some aspects of the preparation of the intermediate compounds and the ferrocene derivative are discussed.

During an investigation of potential high temperature lubricants and hydraulic fluids in this laboratory, the need arose for fairly large quantities of 1,1′-bis(tri-*n*-dodecylsilyl)ferrocene. At the time of our study, only two heteroannularly disubstituted trialkylsilylferrocenes had been reported in the literature, namely 1,1′-bis(trimethylsilyl)ferrocene[1] and 1,1′-bis(tri-*n*-hexylsilyl)ferrocene.[2] Each of these compounds had been prepared by two possible routes: (A) the metalation of ferrocene followed by reaction with the appropriate bromotrialkylsilane,[1,2] and (B) *via* coupling of the appropriate trialkylsilylcyclopentadiene with iron(II) chloride.[2] The former method also was used to prepare tri-*n*-dodecylsilylferrocene; however, in this instance isolation of 1,1′-bis(tri-*n*-dodecylsilyl)ferrocene from the resulting reaction mixture was not attempted.[2a]

In studies elsewhere the reaction of lithiated ferrocene with bromotrialkylsilanes led to low yields of a mixture of the mono- and disubstituted silylferrocenes contaminated with substantial amounts of the corresponding *n*-butyltrialkylsilanes (from the reaction of the bromosilanes with *n*-butyllithium used in the metalation reaction).[2a] The 1,1′-bis(trimethylsilyl)ferrocene was isolated in a yield of 27%,[1] while the yield of the *n*-hexyl derivative was 35%.[2b] The latter compound was

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(1) M. Rausch, M. Vogel, and H. Rosenberg, Wright Air Development Center Technical Report 57-62, Part I (1958).

(2) (a) M. Rausch, M. Vogel, H. Rosenberg, D. Mayo, and P. Shaw, Wright Air Development Center Technical Report 57-62, Part II (1958). (b) S. I. Goldberg, D. W. Mayo, M. Vogel, H. Rosenberg, and M. Rausch, *J. Org. Chem.*, 24, 824 (1959).