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1,1,1,5,5,5-HEXAMETHYLTRISILOXANE: PREPARATION AND SOME REACTIONS

DIETMAR SEYFERTH, CHRISTIAN C. PRUD'HOMME * and WEI-LIANG WANG **

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

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Summary

1,1,1,5,5,5-Hexamethyltrisiloxane (I) was prepared by reaction of $(Me_3SiO)_2Mg$ or of Me_3SiOH with dichlorosilane. Its selective chlorination to give mostly $Me_3SiOSiHClOSiMe_3$ and only a small amount of $Me_3SiOSiCl_2OSiMe_3$ was effected by its $PdCl_2$-catalyzed reaction with CCl_4. Photolysis of compound I gave $H(Me_3SiO)_2SiSi(OSiMe_3)_2H$ in 30% yield, as well as polymer.

Introduction

In previous papers we have reported our studies concerning the preparation of cyclic polysiloxanes of type $(H_2SiO)_m$ and linear siloxanes of type $Me_2RSiO(SiH_2O)_nSiMe_2R$ (R = Me, H) by reaction sequences based on H_2SiCl_2 as the starting material [1,2]. In order to study the chemistry of the SiH_2O unit, it was desirable to have 1,1,1,5,5,5-hexamethyltrisiloxane, $Me_3SiOSiH_2OSiMe_3$, as a model compound. This trisiloxane had been produced by cohydrolysis of Me_3SiCl and H_2SiCl_2 and by acid-catalyzed equilibration of $Me_3SiOSiMe_3$ and $(H_2SiO)_m$, but always admixed with higher polysiloxanes, $Me_3SiO(SiH_2O)_nSiMe_3$ [2]. In order to study its chemistry more effectively, a more specific, high yield route was needed.

We report here our work on the synthesis of $Me_3SiOSiH_2OSiMe_3$ and some of its reactions.

Results and discussion

Preparation

As in our earlier studies [1,2] dichlorosilane served well as the starting material. Its reaction with two molar equivalents of Me_3SiOLi in THF/Et_2O medium at

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* Visiting scholar, on leave from Rhône-Poulenc Recherches, St. Fons, (France).

** Visiting scholar, on leave from the Chenguang Chemical Industry Research Institute, Sichuan Province (Peoples Republic of China).

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$-78\,^\circ C$ (adding the silanolate solution to the H_2SiCl_2 in THF) did not give the expected $Me_3SiOSiH_2OSiMe_3$. Rather, a substantial amount of $(Me_3SiO)_3SiH$ was present in the reaction mixture. Obviously, substitution at Si–H as well as at Si–Cl had occurred, so we repeated the preparation using a less nucleophilic silanolate, $Mg(OSiMe_3)_2$. This reagent was prepared by the reaction of two molar equivalents of Me_3SiOLi with one of anhydrous $MgBr_2$ in THF. Its reaction with H_2SiCl_2 in THF at $-78\,^\circ C$, with subsequent warming to room temperature, gave $Me_3SiOSiH_2OSiMe_3$ in 67% yield, in addition to some $(Me_3SiO)_3SiH$. In this preparation it is essential to remove the trisiloxane and solvents from the lithium and magnesium halides by high vacuum trap-to-trap distillation at room temperature. If the reaction mixture is distilled (with application of heat) without prior removal of the lithium and magnesium salts, there is a substantial increase in the amount of $(Me_3SiO)_3SiH$ and the $Me_3SiOSiH_2OSiMe_3$ disappears.

Alternatively, dichlorosilane could be converted to $Me_3SiOSiH_2OSiMe_3$ in 60% yield by reaction with trimethylsilanol in the presence of pyridine. This procedure, carried out in diethyl ether medium at about $-30\,^\circ C$ has as a drawback the voluminous solid product, pyridine hydrochloride, which is formed in the reaction.

Reactions

One reaction of potential interest was the conversion of $Me_3SiOSiH_2OSiMe_3$ to $Me_3SiOSiHClOSiMe_3$ since the latter would be a useful organosilicon intermediate (e.g., in the hydrosilylation of functional olefins to introduce useful groups, then cohydrolysis to generate a functionalized polysiloxane).

We were able to effect a highly selective conversion of $Me_3SiOSiH_2OSiMe_3$ to the desired monochloro compound using a method developed by Nagai et al. for the conversion SiH → SiCl [3] as shown in eq. 1. Initially, it was found that $Me_3SiOSiH_2OSiMe_3$ and CCl_4 reacted exothermally (and less selectively) at room temperature in the presence of a catalytic quantity of $PdCl_2$. The results shown in eq. 1 were obtained by adding the trisiloxane dropwise over 1 h to the stirred $CCl_4/PdCl_2$ mixture at $0\,^\circ C$. The dichlorotrisiloxane, $Me_3SiOSiCl_2OSiMe_3$, is a

$$(Me_3SiO)_2SiH_2 + CCl_4 \xrightarrow[\text{catalyst}]{PdCl_2} \underset{(89\%)}{(Me_3SiO)_2SiHCl} + \underset{(9\%)}{(Me_3SiO)_2SiCl_2} \qquad (1)$$

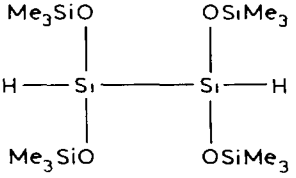
known compound, having been prepared previously by the action of acetyl chloride on $(Me_3SiO)_4Si$ [4] and by the base-catalyzed reaction of hexamethyldisiloxane with silicon tetrachloride [5].

Photochemical chlorination of $Me_3SiOSiH_2OSiMe_3$ using an excess of CCl_4 as the chlorine source was less selective, giving $Me_3SiOSiHClOSiMe_3$ in 68% yield, $Me_3SiOSiCl_2OSiMe_3$ in 18% yield. Similar photochemical chlorination of $Me_3SiO(SiH_2O)_2SiMe_3$ [2] with CCl_4 gave $Me_3SiOSiH_2OSiHClOSiMe_3$ (48%), $Me_3SiO(SiHClO)_2SiMe_3$ (25%), $Me_3SiOSiH_2OSiCl_2OSiMe_3$ (5.5%), $Me_3SiOSiHClOSiCl_2OSiMe_3$ (6.6%) and a trace of $Me_3SiO(SiCl_2O)_2SiMe_3$. These results were obtained after 30 h of irradiation. Longer irradiation increased the amount of polychlorinated products. It would appear that the O_2SiH_2 group is more reactive toward photochemical chlorination than the O_2SiHCl group by a factor of about 2. The two dichlorinated products could not be separated, but the relative intensities of the signals in the ^1H NMR spectrum made the assignments given in the Experimental Section obvious. Mercury sensitization had no beneficial effect on photo-induced chlorination of $Me_3SiOSiH_2OSiMe_3$ by CCl_4. The photo-chlorination of $Me_3SiOSiH_2OSiMe_3$ using sulfuryl chloride as the chlorine source was much more rapid. However, although the consumption of the trisiloxane was complete, the yields of $Me_3SiOSiHClOSiMe_3$ and $Me_3SiOSiCl_2OSiMe_3$ were only 43 and 15%, respectively. It is clear that $PdCl_2$ chlorination by CCl_4 is the most satisfactory route to $Me_3SiOSiHClOSiMe_3$.

Photochemical elimination of hydrogen (as H_2) from silicon hydrides to form silicon–silicon bonds is a known reaction [6], e.g., eq. 2 [6a]. In our hands, the

$$Me(MeO)_2SiH \xrightarrow[\text{vapor phase}]{h\nu,\ Hg} H_2 + Me(MeO)_2SiSi(OMe)_2Me \qquad (2)$$

mercury sensitized photolysis of $Me_3SiOSiH_2OSiMe_3$ gave a disilane (I) in ~ 30% yield and a polymeric polysilane, $[-Si(H)(OSiMe_3)-]_x$, in 60% yield. The chemistry



(I)

of I, which combines a silicon hydride, a disilane and siloxane functionality, should be of some interest. Similar photolysis of $(Me_3SiO)_3SiH$ gave $(Me_3SiO)_3$-$SiSi(OSiMe_3)_3$ in 37% yield.

Experimental

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen.

Dichlorosilane (Union Carbide, Silane A199), MeLi · LiBr (Alfa Products) and Grignard-grade magnesium chips (Alfa) were used as received. Instructions for the handling of H_2SiCl_2 are given in our earlier papers [1,2]. Note the potential hazards associated with this compound [7]. Octamethylcyclotetrasiloxane (General Electric Co.) and 1,2-dibromoethane (Baker) were distilled under nitrogen before use.

GLC analyses were carried out using a Hewlett Packard Model 5750 gas chromatograph equipped with a 6 ft. × 0.25 in. column packed with 15% General Electric SE-30 silicone rubber gum on Chromosorb W which had been acid-washed and treated with Me_3SiCl_2. A 30–250°C temperature program (10°C/min) was used.

Preparation of 1,1,1,5,5,5-hexamethyltrisiloxane

(1) Via magnesium bis(trimethylsilanolate). Lithium trimethylsilanolate was prepared by the reaction of methyllithium with octamethylcyclotetrasiloxane [8].

A one-liter three-necked, round-bottomed flask equipped with a magnetic stir-bar, a nitrogen inlet tube, an addition funnel and a reflux condenser was flame-dried and charged with 371 ml of 1.3 *M* $CH_3Li \cdot LiBr$ in diethyl ether and 50 ml of THF. To this solution was added, with stirring, 35.92 g (0.12 mol) of $[(CH_3)_2SiO]_4$ in 50 ml of THF. The slightly exothermic reaction caused a gentle reflux. The reaction mixture was stirred overnight at room temperature.

In another similarly equipped one-liter flask, 49.7 g (0.265 mol) of 1,2-dibromoethane in 100 ml of THF was added to 6.43 g (0.265 g atom) of magnesium chips in 100 ml of THF to prepare anhydrous $MgBr_2$. After the addition had been completed, the mixture was stirred and heated at reflux for 3 h.

Subsequently the lithium silanolate solution was added slowly to the $MgBr_2$ solution and the resulting mixture was stirred overnight.

Another one-liter flask equipped with a mechanical stirrer, a nitrogen inlet tube, a cold (Dry Ice/isopropanol) condenser and an addition funnel was charged with 100 ml of THF and then 24.4 g (0.24 mol) of dichlorosilane was volatilized from a cold trap into the THF (cooled to $-78\,^\circ C$). To the H_2SiCl_2, at $-78\,^\circ C$, then was added the $(Me_3SiO)_2Mg$ reagent solution, slowly over 3 h, with stirring, under nitrogen. After the addition had been completed, the mixture was allowed to warm to room temperature and was stirred for 2 h. The precipitate which had formed at $-78\,^\circ C$ dissolved at room temperature.

Volatiles were removed from the lithium and magnesium salts by trap-to-trap distillation at room temperature (0.1–0.3 mmHg) into a liquid nitrogen-cooled receiver. The distillate was fractionally distilled to remove solvents and isolate product. 1,1,1,5,5,5-Hexamethyltrisiloxane distilled at 28–29 °C at 10 mmHg and was obtained in 67% yield. Its refractive index and IR and proton NMR spectra were identical with those of an authentic sample obtained in the Me_3SiCl/H_2SiCl_2 cohydrolysis reaction [2].

Further distillation gave $(Me_3SiO)_3SiH$ by-product, b.p. 65–67 °C at 10 mmHg in 5.5% yield. This is a known compound [9].

(2) Via trimethylsilanol. A one-liter flask equipped as in (1) above was charged with 450 ml of diethyl ether, cooled to $-78\,^\circ C$, and then 26.40 g (0.26 mol) of H_2SiCl_2 was added, followed by 25.0 g of dry pyridine. A precipitate resulted. This slurry was stirred at $-78\,^\circ C$ while a mixture of 50.49 g (0.56 mol) of trimethylsilanol [10] and 25.0 g of pyridine was added slowly. Another 100 ml of ether was added in order to facilitate stirring.

The reaction mixture was allowed to warm to room temperature and then was treated with three 500 ml portions of water. The ether layer was dried and fractionally distilled to give 33.0 g (60% yield) of pure $Me_3SiOSiH_2OSiMe_3$.

Photochemically-induced chlorination reactions

A 50 ml single-necked quartz flask equipped with a magnetic stir-bar and a reflux condenser topped with a nitrogen inlet tube was charged with 9.40 mmol of $Me_3SiOSiH_2OSiMe_3$ and 23.0 mmol of carbon tetrachloride (nitrogen atmosphere). The flask was placed in a Rayonet photochemical reactor (λ 2537 Å) and irradiated for 30 h. The resulting clear yellow solution was trap-to-trap distilled (0.3 mmHg) and the distillate was examined by GLC. Two products were present: $Me_3SiOSiHClOSiMe_3$ (68% yield) and $Me_3SiOSiCl_2OSiMe_3$ (18% yield). This represents a 86% conversion of the starting trisiloxane.

3-Chloro-1,1,1,5,5,5-hexamethyltrisiloxane is a new compound. Anal. Found: C, 29.75; H, 7.88. $C_6H_{19}O_2ClSi_3$ calcd.: C, 29.67; H, 7.88%. ^{1}H NMR ($CDCl_3$): δ 0.18 (s, 18H, Me_3Si), 4.97 (s, 1H, SiH) ppm. IR (film, cm^{-1}): ν(SiH) 2231(m).

3,3-Dichloro-1,1,1,5,5,5-hexamethyltrisiloxane is a known compound. It was identified by comparison of its properties with literature data [5,6].

Similar photochemical chlorination of $Me_3SiO(SiH_2O)_2SiMe_3$ [2] was studied. In one experiment, 7.57 mmol of this tetrasiloxane and 31.1 mmol of CCl_4 were irradiated for 30 h. The products were $Me_3SiOSiHClOSiH_2OSiMe_3$ (48%), $Me_3SiO(SiHClO)_2SiMe_3$ (25%), $Me_3SiOSiCl_2OSiH_2OSiMe_3$ (5.5%) and $Me_3SiOSiCl_2OSiHClOSiMe_3$ (6.6%), plus a trace of the tetrachloro derivative. The two dichloro derivatives could not be separated by GLC, but the composition of their mixture could be determined by ^{1}H NMR. Even the separation of the mixture of the dichloro derivatives by GLC was difficult because of the presence of some hexachloroethane.

A 72 h photoreaction of 9.06 mmol of $Me_3SiO(SiH_2O)_2SiMe_3$ and 5.63 mmol of CCl_4 gave $Me_3SiOSiHClOSiH_2OSiMe_3$ (16%), $Me_3SiO(SiHClO)_2SiMe_3$ (35%), $Me_3SiOSiCl_2OSiH_2OSiMe_3$ (8.6%), $Me_3SiOSiCl_2OSiHClOSiMe_3$ (19%) and $Me_3SiO(SiCl_2O)_2OSiMe_3$ (3%).

The following compounds were characterized:

$Me_3SiOSiHClOSiH_2OSiMe_3$, n_D^{20} 1.3907 Anal. Found: C, 25.12; H, 7.39. $C_6H_{21}O_3ClSi_4$ calcd.: C, 24.93; H, 7.32%. ^{1}H NMR ($CDCl_3$): δ 0.16 and 0.19 (s, 9H each, $SiMe_3$), 4.64 (s, 2H, SiH_2), 5.00 (s, 1H, SiHCl) ppm. IR (film, cm^{-1}): ν(SiH) 2230(sh), 2175(s).

82% $Me_3SiO(SiHClO)_2SiMe_3$, 18% $Me_3SiOSiCl_2OSiH_2OSiMe_3$ mixture. Anal. Found: C, 22.08; H, 6.14. $C_6H_{20}O_3Cl_2Si_4$ calcd.: C, 22.28; H, 6.23%.

$Me_3SiO(SiHClO)_2SiMe_3$, ^{1}H NMR ($CDCl_3$): δ 0.19 (s, Me_3Si), 5.03 (s, SiHCl) ppm.

$Me_3SiOSiCl_2OSiH_2OSiMe_3$, ^{1}H NMR ($CDCl_3$): δ 0.15 and 0.21 (s, Me_3Si), 4.64 (s, SiH_2) ppm. IR (mixture; film, cm^{-1}): ν(SiH) 2236(s), 2195(sh).

$Me_3SiOSiCl_2OSiHClOSiMe_3$. Anal. Found: C, 20.41; H, 5.46. $C_6H_{19}O_3Cl_3Si$ calcd.: C, 20.13; H, 5.35%.

The low yield of $Me_3SiO(SiCl_2O)_2SiMe_3$ precluded its GLC collection for analysis.

$PdCl_2$-induced chlorination

A 10 ml two-necked flask equipped with a magnetic stir-bar, a no-air rubber septum and a trap-to-trap distillation head connected to a 10 ml receiver was charged with 0.012 g (0.067 mmol) of $PdCl_2$ and 3.4 g (22.1 mmol) of CCl_4 (under nitrogen) and the mixture was cooled to 0 °C. 1,1,1,5,5,5-Hexamethyltrisiloxane (5.39 mmol) was added dropwise by syringe over a period of 1 h. The color of the mixture changed from dark red to black, indicative of reduction of the $PdCl_2$ catalyst to Pd^0 by the SiH-containing trisiloxane. The reaction mixture was stirred at 0 °C for 70 min, at which time GLC analysis showed that the starting trisiloxane had been completely consumed. Two products were present, $Me_3SiOSiHClOSiMe_3$ (89% yield) and $Me_3SiOSiCl_2OSiMe_3$ (9% yield), in the distillate after volatiles had been separated by trap-to-trap distillation.

Chlorination with sulfuryl chloride

The apparatus and general procedure were the same as in the photo-induced chlorination with CCl_4. A mixture of 4.73 mmol of $Me_3SiOSiH_2OSiMe_3$ and 19.0 mmol of SO_2Cl_2 was irradiated for 2 h. Subsequent trap-to-trap distillation gave 1.713 g of volatile products and left 0.7363 of a colorless, slightly viscous residue. GLC analysis of the distillate showed the presence of $Me_3SiOSiH_2OSiMe_3$ (1%), $Me_3SiOSiHClOSiMe_3$ (43%) and $Me_3SiOSiCl_2OSiMe_3$ (15%).

Photolysis of 1,1,1,5,5,5-hexamethyltrisiloxane

The title trisiloxane (11.1 mmol, no solvent), in a quartz flask, under a nitrogen atmosphere was irradiated in a Rayonet photochemical reactor in the presence of a drop of mercury (λ 2537 Å) for 26 h. Trap-to-trap distillation gave a volatile fraction and a cloudy, viscous residue, the latter in 60% yield.

GLC analysis of the distillate showed the presence of starting material (5%) and $H(Me_3SiO)_2SiSi(OSiMe_3)_2H$ (30% yield). The latter was isolated by GLC (6 ft × 0.25 in., 20% SE-30, 150–250 °C at 5 °C/min; 5 min at 250 °C).

$H(Me_3SiO)_2SiSi(OSiMe_3)_2H$, n_D^{20} 1.4090. Anal. Found: C, 34.65; H, 9.20. $C_{12}H_{38}O_4Si_6$ calcd.: C, 34.74; H, 9.23%. Mass spectrum (Varian MAT-44, 70 eV, m/z (rel. intensity)): 415 (M^+, 0.04), 399 (0.14), 341 (1.58), 326 (0.30), 269 (1.40), 268 (2.05), 267 (8.52), 253 (1.93), 207 ($M/2^+$, 5.47), 191 (3.53), 134 (1.32), 133 (8.99)...73 (Me_3Si^+, 100). ^1H NMR ($CDCl_3$): δ 0.13 (s, 36H), 4.89 (s, 2H) ppm. IR (film, cm^{-1}): $\nu(SiH)$ 2105(m). UV (isooctane) λ_{max} 208, 250 nm.

The nonvolatile residue was dissolved in chloroform and separated from the elemental mercury. The IR spectrum of this material (in $CHCl_3$) was very similar to that of the dimer; $\nu(SiH)$ 2088 cm^{-1}. This suggests that is a higher oligomer, $H[-Si(OSiMe_3)_2-]_nH$.

The polymer in one such experiment, $H[Si(OSiMe_3)_2]_nH$, with $\bar{n} \sim 6$ by integration of the ^1H NMR signals, was found to be quite pure. Anal. Found: C, 34.65; H, 8.87. $6(C_6H_{18}Si_3O_2) + 2H$ calcd.: C, 34.85; H, 8.94%. UV (isooctane): λ_{max} 208, 241, 279, 301, 318 nm.

Photolysis of tris(trimethylsiloxy)silane

The same procedure as described above was used in the photolysis of 5 ml of degassed $HSi(OSiMe_3)_3$ for 42 h. During this time white solid precipitated on the walls of the flask and the liquid phase became yellow.

The solid product was recrystallized from carbon tetrachloride/methanol and sublimed at 70 °C and 0.1 mmHg. The yield of $(Me_3SiO)_3SiSi(OSiMe_3)_3$ was 37%. Anal. Found: C, 36.59; H, 9.19. $C_{18}H_{54}O_6Si_8$ calcd.: C, 36.56; H, 9.20%. ^{29}Si NMR (CCl_4): $\delta(Si)$ 7.899(s) and −76.323(s) ppm.

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