Organometallic Chemistry

Lithium and sodium *tris*(trimethylsilyl)silanolates. Synthesis and reactivity

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Lithium and sodium tris(trimethylsilyl)silanolates were obtained by the reaction of tris(trimethylsilyl)silanol with Bu^nLi or Pr^iONa in hexane. The degree of association of silanolates in benzene solution was found to be 2 and 4 for the sodium and lithium derivatives, respectively. $(Me_3Si)_3SiONa$ is noticeably more active than the lithium derivative in the reaction with Me_3SiCl. Tris(trimethylsilyl)silanol reacts with trimethylchlorosilane to give $(Me_3Si)_3SiCl$. The hydrolysis of $(Me_3Si)_3SiONa$ (Li) in benzene and hexane yields the corresponding silanol, whereas in HMPA the splitting of Si—Si bonds and hydrogen evolution were observed.

Key words: silanols, silanolates, polysilanes.

Silanols and metal silanolates are of interest as convenient intermediate products for the synthesis of various polysiloxanes and heterosiloxanes.

The primary silanols and silanolates of the $R_nSi(OH)_m(OM)_{4-n-m}$ $(n+m \leq 4)$ type and siloxane hydroxyl derivatives have been investigated in detail,[1] while the analogous polysilanyl derivatives were not sufficiently investigated. Thus, only two sodium silanolates that contain chains of silicon atoms are known.[2,3] The present work reports the synthesis and some reactions of lithium and sodium tris(trimethylsilyl)silanolates. The tris(trimethylsilyl)siloxy group has a considerable steric effect and can be used, along with other analogous bulky groups (*i.e.*, Bu^t_3CO[4], $(Bu^tO)_3SiO$[5], Bu^t_3SiO[6]), for the synthesis of new complexes of transition metals with the necessary steric protection of a central atom.

Triorganyl silanolates of alkaline metals are usually prepared by the treatment of triorganyl silanols with alkaline metals.[1] However, the attempt to isolate the derivatives of tris(trimethylsilyl)silanol[7] by this method has failed. The authors[7] pointed out that the treatment of $(Me_3Si)_3SiOH$ with a Na/K alloy resulted in several products that have a molecular mass higher or lower than that of the target product and exhibited the absorption bands of the Si—H and Si—O groups in the IR spectra.

The treatment of silanol with alkaline metal hydrides is considered as the other convenient method for the synthesis of silanolates.[1] However, our preliminary stud-

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ies showed that sodium hydride does not react with tris(trimethylsilyl)silanol in benzene at 25°C. After stirring for 48 h, the starting silanol was recovered intact.

Sodium tris(trimethylsilyl)silanolate was obtained by an unconventional method, *viz.*, by the addition of a solution of tris(trimethylsilyl)silanol in hexane to a suspension of sodium isopropylate in the same solvent. The exchange reaction proceeds virtually with the rate of mixing of the reagents:

$$(Me_3Si)_3SiOH + Pr^iONa \xrightarrow{\text{hexane, 20 °C}} (Me_3Si)_3SiONa + Pr^iOH. \quad (1)$$

Sodium isopropylate rapidly dissolves in hexane during the reaction. After removing the solvent the residue is obtained as colorless crystals readily soluble in common organic solvents (hexane, benzene, diethyl ether, tetrahydrofuran). This product is sodium tris(trimethylsilyl)silanolate contaminated with the starting silanol (the reaction is carried out with a small excess of silanol). The latter is removed by heating the product in a vacuum ($1 \cdot 10^{-2}$ Torr) for 5 h at 80 °C.

Lithium tris(trimethylsilyl)silanol was isolated after the reaction of exactly equivalent amounts of silanol and *n*-butyllithium in hexane.

$$(Me_3Si)_3SiOH + Bu^nLi \xrightarrow{\text{hexane, 20 °C}} (Me_3Si)_3SiOLi + Bu^nH \quad (2)$$

Lithium and sodium tris(trimethylsilyl)silanolates differ in their reactivity. Thus, the lithium derivative does not react with trimethylchlorosilane in heptane or benzene at 20 °C. The reaction in these solvents slowly proceeds only when the reaction mixture is refluxed, whereas the sodium derivative rapidly affords the product of silylation.

$$(Me_3Si)_3SiOLi\ (Na) + Me_3SiCl \xrightarrow[(PhH,\ 20\ °C)]{PhH,\ 80\ °C} (Me_3Si)_3SiOSiMe_3 + LiCl\ (NaCl) \quad (3)$$

If the starting sodium (lithium) silanolate contains bonded silanol, treatment with an excess of Me_3SiCl results in two products, *i.e.*, 1,1,1-tris(trimethylsilyl)trimethyldisiloxane and tris(trimethylsilyl)chlorosilane.

$$(Me_3Si)_3SiONa \cdot (Me_3Si)_3SiOH \xrightarrow[PhH,\ 20\ °C]{Me_3SiCl} (Me_3Si)_3SiOSiMe_3 + (Me_3Si)_3SiCl + (Me_3Si)_2O \quad (4)$$

A control experiment showed the reaction of pure tris(trimethylsilyl)silanol with excess trimethylchlorosilane to give tris(trimethylsilyl)chlorosilane.

$$(Me_3Si)_3SiOH \xrightarrow[PhH]{Me_3SiCl} (Me_3Si)_3SiCl \quad (5)$$

Reaction (5) is uncommon for silanols because in acidic media mainly the condensation to yield disiloxanes is observed. Exchange reaction (5) is probably caused by two factors: first, a high hydrolytic stability of tris(trimethylsilyl)chlorosilane and, second, the impossibility of the condensation to give $[(Me_3Si)_3Si]_2O$ due to steric hindrances. The equilibrium in reaction (5) is shifted due to the formation of hydrolytically stable $(Me_3Si)_3SiCl$ and the rapid elimination of trimethylsilanol, which reacts with trimethylchlorosilane (equations 6a-f). The hydrogen chloride formed in this process can also transform $(Me_3Si)_3SiOH$ to $(Me_3Si)_3SiCl$. At the same time the hydrolysis of $(Me_3Si)_3SiCl$ does not take place (water can be formed during the condensation of Me_3SiOH and in the reactions of HCl with $(Me_3Si)_3SiOH$ and Me_3SiOH).

$$(Me_3Si)_3SiOH + Me_3SiCl \longrightarrow (Me_3Si)_3SiCl + Me_3SiOH \quad (6a)$$

$$Me_3SiOH + Me_3SiCl \longrightarrow Me_3SiOSiMe_3 + HCl \quad (6b)$$

$$2\ Me_3SiOH \longrightarrow Me_3SiOSiMe_3 + H_2O \quad (6c)$$

$$Me_3SiCl + H_2O \longrightarrow Me_3SiOH + HCl \quad (6d)$$

$$(Me_3Si)_3SiOH + HCl \longrightarrow (Me_3Si)_3SiCl + H_2O \quad (6e)$$

$$(Me_3Si)_3SiCl + H_2O \not\longrightarrow (Me_3Si)_3SiOH + HCl \quad (6f)$$

In previous works[8,9] contradictory data on the hydrolysis of $(Me_3Si)_3SiCl$ were reported. The authors of Ref. 8 reported the preparation of tris(trimethylsilyl)silanol by the hydrolysis of $(Me_3Si)_3SiCl$ in a water-tetrahydrofuran medium. However, in later work[9]

it was shown that silanol can not be obtained by this method, and intact starting chlorosilane was recovered after prolonged stirring of the reaction mixture. We carried out the reaction under the conditions described and found that, in a neutral medium (H_2O:THF), the reaction actually does not occur. The chlorine atom can be replaced with the hydroxyl group only by boiling the solution of $(Me_3Si)_3SiCl$ with 20 % KOH for 30 h with vigorous stirring.

Powdered lithium and sodium tris(trimethylsilyl)-silanolates are stable in dry air but they are very sensitive to water. The hydrolysis of these compounds in non-polar media (hexane, benzene) gives the silanol quantitatively. The hydrolysis of silanolates in ionizing solvents (HMPTA, pyridine) is accompanied by the evolution of hydrogen and the destruction of the molecule. Thus, the hydrolysis of sodium tris(trimethylsilyl)silanolate in HMPTA involves the quantitative evolution of hydrogen caused by the cleavage of all three Si—Si bonds of the molecule. The dissolution of silanolates in pyridine also gives rise to the slow destruction of the pyridine ring and the resinification of the reaction mixture. This reaction probably occurs due to rearrangements that proceed in ionizing solvents to yield sodium silyl compounds analogously to the Sakurai reaction[10].

$$Me_6Si_2 + MeONa \xrightarrow{HMF} Me_3SiNa + Me_3SiOMe$$

It is known that silanols form associates in a solution or in a solid state,[1] and the degree of association decreases with increasing the size of the organosilicon substituents. Thus, for example, sodium trimethylsilanolate is a decamer in benzene solution.[11] The degree of association of the obtained silanolates in benzene solution measured by cryoscopic method was 2 and 4 for $(Me_3Si)_3SiONa$ and $(Me_3Si)_3SiOLi$, respectively.

We studied the thermal stability of the powdered silanolates. Lithium and sodium tris(trimethylsilyl)-silanolates are not affected by heating (2—3 h) at 95 °C. At 110 °C melting begins, accompanied by the decomposition of lithium tris(trimethylsilyl)silanolate. During a slow heating to 180 °C, in the cooled side of a sealed evacuated tube, a liquid is collected, which contains four components with different molecular masses according to GC. Some of the products were identified chromatographically, *i.e.*, $(Me_3Si)_3SiOH$ (13 %), $(Me_3Si)_3SiOSiMe_3$ (10 %), and $(Me_3Si)_3SiH$ (55 %). The IR spectrum of the liquid, besides the absorption bands of O—H (3620, 3420), Si—Me (1255, 840), and Si—O (1040), contains an intense band at 2030 cm^{-1}, which is characteristic of the Si—H group of tris(trimethylsilyl)silane.[12] In the gas phase hydrogen was detected. It is quite possible that the complicated thermolysis proceeds simultaneously by ionic and radical mechanisms. More detailed data about the thermal decay of tris(trimethylsilyl)silanolates will be reported later.

Experimental

^1H NMR spectra were obtained on a Tesla BS-487-C (100 MHz) instrument in $CDCl_3$; the internal standard was $CHCl_3$. GC analysis was performed on a Tsvet-500 chromatograph with a 0.4×200 cm stainless steel column, sorbents 5 % SE-30 and OV-17 on Chromaton-N-Super, and a heat conductivity detector. The carrier gas was helium. IR spectra were registered on a Perkin-Elmer 577 spectrophotometer with a thin layer of the compound between the KBr windows.

Solvents were purified by common procedures: hexane and benzene were distilled over phosphorous pentoxide, THF and pyridine were distilled over KOH, and hexamethylphosphoric triamide was distilled *in vacuo* over calcium hydride.

All operations, starting from the synthesis of tris(trimethylsilyl)silanol, were done in argon or *in vacuo*.

Tris(trimethylsilyl)silanol. A round-bottom three-necked flask supplied with a stirrer, reflux condenser, and dropping funnel was charged with $(Me_3Si)_3SiBr$ [12] (59.0 g, 0.18 mol), 200 mL of THF, 20 mL of water, and 0.005 g of methyl orange indicator.

A 10 % solution of NaOH (75 mL) was added dropwise to the reaction mixture with vigorous stirring until the water layer turned intensely purple. The hydrolysis of tris(trimethylsilyl)bromosilane occurs much more easily than that of tris(trimethylsilyl)chlorosilane; the former occurs simultaneously with the mixing of the reagents at ambient temperature without noticeable heat release. The water layer was separated and washed with hexane. The organic layer was combined with the hexane extract, the solvent was removed, and a residue was distilled *in vacuo* to give 42.8 g (90 %) of $(Me_3Si)_3SiOH$, b.p. 81 °C (1.5 Torr) (*cf.* Ref. 9: 81 °C/1.5 Torr). IR, ν/cm^{-1}: 3620, 3420 (O—H), 1240, 840 (Si—Me), 1040 (Si—O). ^1H NMR, δ: 0.16 (27 H, Me); 125 (1 H, OH).

Lithium tris(trimethylsilyl)silanolate. A round-bottom three-necked flask supplied with a stirrer, reflux condenser, and dropping funnel was flushed with argon and charged with $(Me_3Si)_3SiOH$ (4.1 g, 0.015 mol) and 15 mL of absolute hexane. Butyl lithium (0.015 mol, 13.6 mL of a 1.1 *M* solution) was added dropwise with stirring. The reaction mixture grew somewhat warmer, and butane evolution was observed. Then the solution was stirred for an additional 1 h, and the solvent was removed *in vacuo*. The crystalline mass obtained was vacuumed for 5 h at 60 °C to yield 3.9 g (96 %) of lithium tris(trimethylsilyl)silanolate. Found (%): C, 39.87; H, 9.36. Mol. mass 1107.0. Calculated (%): C, 39.95; H, 10.06. Mol. mass 270.5.

Reaction of lithium tris(trimethylsilyl)silanolate with trimethylchlorosilane. A threefold excess of trimethylchlorosilane (2.9 g) was added to a solution of lithium tris(trimethylsilyl)silanolate (2.4 g, 9 mmol) in hexane or benzene (20 mL). After storing for three days at 20—25 °C, the solution remained transparent. Boiling of the reaction mixture for 5 h resulted in precipitation of LiCl. The precipitate was filtered off, the solvent was removed by distillation, and the residue was sublimated *in vacuo* at 0.01 Torr to give 2.5 g (83 %) of 1,1,1-tris(trimethylsilyl)trimethyldisiloxane, m.p. 198—200 °C. Found (%): C, 43.20; H, 10.73; Si, 39.25. $C_{12}H_{36}OSi_5$. Calculated (%): C, 42.81; H, 10.78; Si, 41.66. ^1H NMR, δ: 0.14 (27 H, Me); 0.02 (9 H, Me). IR, ν/cm^{-1}: 1245, 840 (Si—Me), 1080 (Si—O).

Sodium tris(trimethylsilyl)silanolate. A tube was charged with sodium isopropylate (1.24 g, 0.015 mol) and hexane (20 mL). A solution of tris(trimethylsilyl)silanol (4.80 g, 0.018 mol) in hexane (10 mL) was added to the suspension formed.

The reaction mixture became homogeneous. After stirring for 1 h, isopropanol and the solvent were removed *in vacuo*. The residue was vacuumed for 5 h at 0.01 Torr at 80°C to give 4.0 g (93 %) of sodium tris(trimethylsilyl)silanolate. Found (%): C, 37.89; H, 9.39. Mol. mass 595. Calculated (%): C, 37.71; H, 9.49. Mol. mass 286.

Reaction of sodium tris(trimethylsilylsilanolate with trimethylchlorosilane occurs under more mild conditions (20 °C) to yield a precipitate of NaCl. A mixture of $(Me_3Si)_3SiONa$ and a three fold excess of Me_3SiCl was stirred for an additional 3 h and was worked-up similarly to the reaction of $(Me_3Si)_3SiOLi$ + Me_3SiCl. The yield of $(Me_3Si)_3SiOSiMe_3$ was 90 % based on the starting sodium tris(trimethylsilyl)silanolate.

Reaction of tris(trimethylsilyl)silanol with an excess of trimethylchlorosilane. A threefold molar excess of trimethylchlorosilane was added to a solution of $(Me_3Si)_3SiOH$ (2.9 g, 0.011 mol) in hexane (20 mL). The mixture was stored for 30 min, then the solvent and light reaction products were distilled off, and the residue was distilled *in vacuo* to give 2.8 g (90 %) of tris(trimethylsilyl)chlorosilane, b.p. 90—93 °C (1.5 Torr) (*cf.* Ref. 12: 93 °C/1.8 Torr). Found (%): C, 39.19; H, 10.26; Si, 38.70. $C_9H_{27}Si_4Cl$. Calculated (%): C, 38.20; H, 9.62; Si, 39.66. ^1H NMR, δ: 0.22 (27 H, Me). IR, ν/cm^{-1}: 1240, 840 (Si—Me), 485 (Si—Cl).

Hydrolysis of sodium tris(trimethylsilyl)silanolate in hexamethylphosphoric triamide. A specified amount of sodium tris(trimethylsilyl)silanolate (0.1 g) was put in a tube and degassed. 5 mL of HMPTA was added *in vacuo*, and the solution turned intensely yellow. The coloring vanished when the solution was exposed in air. The tube was filled with argon and connected to a buret, and water was added slowly dropwise from another tube also connected to the buret. The volume of the hydrogen evolved was 23.2 mL (normal conditions). After the addition of excess water, a precipitate of silicon dioxide was formed.

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