Silanol Synthesis: Reaction of Hexaphenylcyclotrisiloxane with Organometallic Reagents

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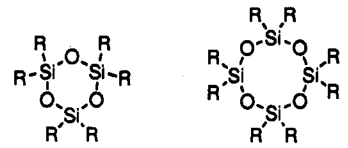
Silanols and their corresponding oxygen anions (silanolates) find increasing use in organic synthesis as organic-soluble equivalents of water and hydroxide[1] and in organometallic chemistry as stable, bulky ligands.[2] In addition, silanols are good hydrogen-bond acceptors and even better hydrogen-bond donors,[3] properties conducive to applications in molecular recognition[4] and biomodulation.[5] While a few silanols such as triethylsilanol, triphenylsilanol, and *tert*-butyldimethylsilanol are commercially available, the well-known tendency of silanols to undergo self-condensation to give siloxanes has hindered their use and investigations into their chemistry. We describe here a simple, general, and inexpensive method for silanol synthesis.

Typically, silanols are prepared by hydrolysis of the corresponding chlorosilane or aminosilane. While this can be an efficient process, rigorous control of pH is often required to prevent siloxane formation.[3] Moreover, in cases where the silanol precursor is not commercially available, its preparation often requires the use of highly reactive and moisture-sensitive aminochloro- or dichlorosilanes. An alternative and potentially general method for the preparation of silanols would be the reaction of organometallic reagents with siloxanes (silicones). Siloxanes are inexpensive, largely insensitive to moisture, and often available as easily handled solids. For example, the commercially available dimethyl- and diphenylsiloxane trimers 1 and tetramers 2 are all crystalline and soluble in standard organic solvents. Reaction of siloxanes with organolithium reagents directly produces a lithium silanolate and, on hydrolysis, silanols.



1 **a** R = Me 2
b R = Ph

While the polymerization of cyclic siloxanes with catalytic amounts of lithium reagents has been the subject of many studies,[6] few reports detail the reaction of *stoichiometric* amounts of lithium reagents (relative to silicon).[7] In a very brief report, Rudisch and Schmidt found that dimethylsiloxanes react quantitatively with methyllithium in ether to yield lithium trimethylsilanolate and mention that THF is not a suitable solvent for the reaction.[8] A seminal study by Frye found that *n*-butyllithium and hexamethylcyclotrisiloxane (**1a**) gave lithium *n*-butyldimethylsilanolate in hexane.[9] We recently reported[10] that this reaction can be extended to the use of aryllithium reagents with dimethylsiloxanes. To further explore the generality of this transformation, we have studied the reactions of hexaphenylcyclotrisiloxane (**1b**). The alkyldiphenylsilanol products are not volatile and do not easily condense to siloxanes, making product isolation and characterization practical.

Results

All reactions were performed by adding the organometallic reagent (1.1–1.2 equiv based on silicon) to a −78 °C solution of the siloxane in the indicated solvent (Table I). In the case of hexane, where solubility at low temperatures was a problem, a suspension of the siloxane was used. The mixture was slowly warmed in stages, with monitoring by TLC. When the starting siloxane was no longer present by TLC, the reaction was assumed to be complete and the reaction mixture was poured into aqueous acid, isolated, and purified by column chromatography. Four commercially available lithium reagents, a Grignard reagent, and four solvents were surveyed (Table I). For each combination of organometallic reagent and solvent, the temperature at which the disappearance of starting siloxane was observed and the time of reaction at that temperature are indicated.

On the basis of the yields of product 3 (Table I), several points are immediately clear. The Grignard reagent is only marginally reactive with the siloxane, and after 16–18 h of reflux up to 97% of the starting siloxane was recovered. For each of the lithium reagents, at least one solvent was found that gave an excellent yield of silanol, but no solvent was universally useful. The use of THF uniformly led to rapid consumption of the siloxane by the lithium reagents but also led to complex mixtures from which pure silanol could not be isolated.

Methyllithium, as a solution in ether, performed poorly with only ether as solvent but gave an excellent yield in hexane. In contrast, *tert*-butyllithium gave the cleanest reaction in ether and both *n*-butyllithium and *sec*-butyllithium gave the highest yield of silanol in toluene.

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Table I

$(Ph_2SiO)_3 + 3.3\ RM \rightarrow RPh_2SiOH$

RM	yield[a] (°C, h)[b]			
	hexane	toluene	ether	THF
MeLi[c]	**93** (25, 3)	**51** (110, 15)	**34** (0, 34)	**0** (0, 0.3)
n-BuMgBr[d]	**27** (69, 16)	**34** (110, 16)	**0** (35, 18)	**0** (67, 16)
n-BuLi[e]	**35** (69, 21)	**91** (110, 1.5)	**86** (25, 3)	**0** (25, 3)
s-BuLi[f]	**32** (62, 0.5)	**86** (110, 1)	**58** (0, 1)	**0** (−70, 2.5)
t-BuLi[g]	**0** (45, 2.5)	**69** (110, 3)	**93** (0, 1.5)	**0** (0, 1.5)

[a] Isolated yield of silanol based on starting siloxane. [b] Reactions were initiated at −78 °C and warmed at intervals with monitoring by TLC for disappearance of starting siloxane. Final temperature and time at that temperature are shown. [c] 1.1 M in ether. [d] 2.0 M in ether. [e] 2.0 M in hexane. [f] 1.3 M in cyclohexane. [g] 1.7 M in pentane.

Probable intermediates containing diphenylsilyl diethers (Scheme I) are known to be unstable on silica gel;[11] however, with methyllithium in ether and in toluene a small amount of trisiloxanol derived from **4a** was isolated.

The facility with which *tert*-butyllithium reacted with siloxane **2a** in ether seemed surprising and potentially useful. Substituting hexamethylcyclotrisiloxane (**1a**) gave the versatile *tert*-butyldimethylsilanol[12] in 98% isolated yield. *tert*-Butyldimethylsilanol has been shown to be easily convertible to the chloride[12] and useful for direct silylation of alcohols under Mitsunobu conditions.[13]

Discussion

The reaction of organometallic reagents with cyclotrisiloxanes to yield silanols is superficially similar to the formation of primary alcohols with the formaldehyde trimer 1,3,5-trioxane. Mechanistically, however, these reactions are quite distinct. Formaldehyde polymers undergo depolymerization and subsequent reaction of the monomers,[14] whereas the reaction of siloxanes would be expected to involve initial formation of a pentacoordinate silicon intermediate or transition state.[15] Such a reaction path would yield the intermediate species **4** (Scheme I), and the selectivity of a subsequent nucleophilic attack for the α-silicon would ultimately determine the byproducts and the yield of silanol. A high yield of silanol **3** requires that the α-silicon (Scheme I) carrying the negatively charged oxygen be the kinetically reactive center. An additional complication of the reaction scheme (not shown) is the potential for the silanolate intermediates, and the desired silanolate product **3**, to react with the starting siloxane. Anionic polymerization of cyclic siloxanes, via lithium silanolates, is known to be promoted by polar solvents including THF.[16] Silanolate–siloxane reactivity would greatly complicate the chemistry and be a source of poor yields and complex mixtures, as is observed for reactions in THF. Nevertheless, stoichiometric reaction of lithium reagents with siloxanes in less polar solvents does lead predominantly, and in some cases exclusively, to silanol product. It should be noted that while the trisiloxane ring is inherently strained, Frye et al. found that the intermediate formed on ring opening of **1a** (the hexamethyl analog of **4**) is consumed much more rapidly by *n*-butyllithium than trisiloxane **1a** itself.[9]

The selectivity for nucleophilic attack at the α-silicon of **4** could stem from coordination of the lithium reagent by the oxygen anion. Reaction at the α-silicon would then involve a four-centered pathway, whereas reaction at the β-silicon would involve a six-centered pathway. Alternatively, the negative charge on oxygen could induce rehybridization at silicon, making the α-silicon more reactive. Relevant to these two points are the recently published X-ray structures of di-*tert*-butysilanediol and its monolithium salt (Figure 1).[17,18] These structures show a change in geometry at silicon on deprotonation of one oxygen as well as coordination (activation?) of the adjacent neutral oxygen by the lithium counterion.

The nature of α-silicon selectivity notwithstanding, treatment of siloxanes with lithium reagents is a general method for synthesis of triorganosilanes and silanolates. Primary, secondary, and tertiary organolithium reagents, with a judiscous choice of solvent, give high yields of silanol(ate) with both diphenyl- and dimethylsiloxanes.

Experimental Section

General. Melting points were obtained by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were obtained with a Perkin-Elmer Model 1600 FT-IR. NMR spectra were recorded on a GE QE-300 (300 MHz ^1H) or a Bruker AC-250 (250 MHz ^1H). Mass spectra were recorded on a VG-7070ENF or VG-ZAB1FHF. Column and thin layer chromatography were performed on silica gel with the indicated solvent system. Ether and THF were distilled from sodium benzophenone ketyl. Hexane and toluene were distilled from calcium hydride. Hexaphenylcyclotrisiloxane was purified by recrystallization from ethyl acetate. Hexamethylcyclotrisiloxane was purified by sublimation at 55 °C (55 Torr). All reactions were performed under a positive pressure of nitrogen.

***n*-Butyldiphenylsilanol (3b).** To a solution of hexaphenylcyclotrisiloxane (**1b**) (0.3077 g, 0.5172 mmol) in toluene (20 mL) at −78 °C was added dropwise *n*-butyllithium (0.85 mL of a 2.25 M solution in hexane, 1.9 mmol). The resulting solution was stirred at −78 °C for 1.5 h and then allowed to slowly warm, with monitoring by TLC. No change was observed until the reaction had reached 0 °C (3 h). On heating to reflux, no starting material was observed by TLC. After the solution was cooled to 0 °C, 10% HCl was added and the aqueous phase was extracted with ether. The combined organics were dried over $MgSO_4$ and concentrated. Flash chromatography (1:9, ethyl acetate:hexanes) gave **3b** (0.3604 g, 91%) as a colorless solid: $R_f = 0.29$ (1:9 ethyl acetate:hexanes); mp 53.5–54.0 °C (lit.[19] mp 58 °C); ^1H NMR ($CDCl_3$) δ 7.62 (d, 4 H, $J = 7.6$ Hz), 7.40 (m, 6 H), 1.88 (bs, 1 H), 1.40 (m, 2 H), 1.18 (m, 2 H), 0.95 (t, 2 H, $J = 7.1$ Hz), 0.88 (t, 3 H, $J = 6.9$ Hz); ^{13}C NMR ($CDCl_3$) δ 134.1, 129.6, 127.8, 104.9, 26.1, 25.2, 14.9, 13.3; IR (neat) 3274, 3069, 2957, 2922, 1427, 1118, 834, 730, 699 cm^{-1}; MS (CI/NH_3) *m/e* (rel intensity) 274 (62, MNH_4^+), 256 (5, M^+), 216 (59), 196 (100).

Diphenylmethylsilanol (3a):[20] $R_f = 0.24$ (1:9 ethyl acetate: hexanes); ^1H NMR ($CDCl_3$) δ 7.66 (d, 4 H, $J = 7.0$ Hz), 7.4 (m, 6 H), 2.0 (bs, 1 H), 0.69 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 133.9, 129.7, 127.6, 104.9, −1.4; IR (neat) 3301, 3068, 2958, 1428, 1120, 852,

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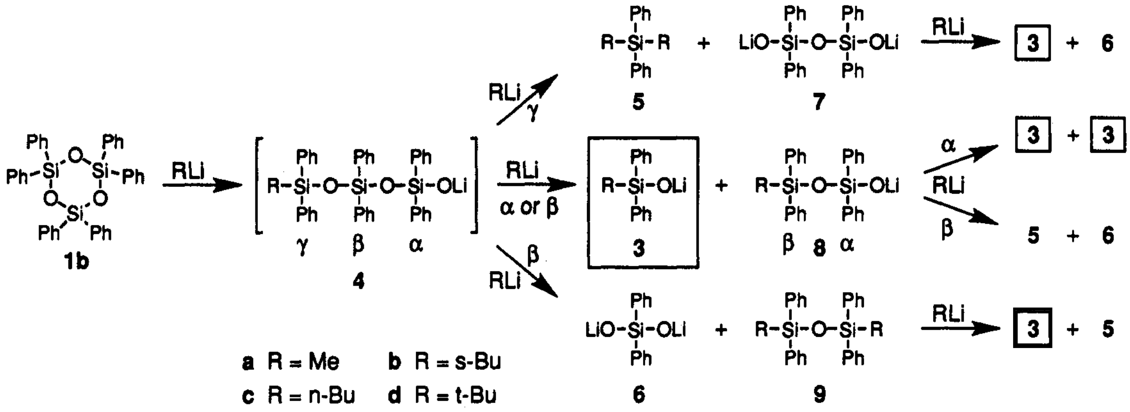
Scheme I



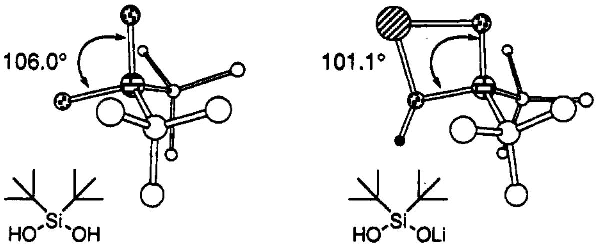


Figure 1. Comparison of crystal structures reported for di-*tert*-butylsilanediol[17] and its monolithium salt.[18]

791, 697 cm^{-1}; MS (CI/NH$_3$) *m/e* (rel intensity) 232 (80, MNH$_4^+$), 216 (61), 199 (31), 154 (100).

***sec*-Butyldiphenylsilanol (3c):** R_f = 0.33 (1:9 ethyl acetate:hexanes); mp 66–67 °C (lit.[19] mp 68–71 °C); ^{1}H NMR (CDCl$_3$) δ 7.64 (d, 4 H, *J* = 7.2 Hz), 7.41 (m, 6 H), 2.04 (bs, 1 H), 1.73 (m, 1 H), 1.26 (m, 2H), 1.09 (d, 3 H, *J* = 6.8 Hz), 0.96 (t, 3 H, *J* = 7.0 Hz); ^{13}C NMR (CDCl$_3$) δ 134.4, 129.6, 127.7, 104.9, 24.3, 21.4, 13.3, 13.2; IR (neat) 3340, 2958, 1644, 1426, 1115, 820, 699 cm^{-1}; MS (CI/NH$_3$) *m/e* (rel intensity) 274 (72, MNH$_4^+$), 256 (6, M$^+$), 216 (74), 196 (100); HRMS (CI/NH$_3$) calcd for $C_{16}H_{24}NOSi$ 274.1627, found 274.1629.

***tert*-Butyldiphenylsilanol (3d):** R_f = 0.31 (9:1 ethyl acetate:hexanes); mp 57–59 °C (lit.[21] mp 62–64 °C); ^{1}H NMR (CDCl$_3$) δ 7.62 (d, 4 H, *J* = 7.6 Hz), 7.41 (m, 6 H), 2.16 (bs, 1 H), 1.08 (s, 9 H); ^{13}C NMR (CDCl$_3$) δ 134.8, 129.5, 127.6, 104.9, 26.6; IR (neat) 3395, 3418, 3070, 2958, 1652, 1427, 1114, 820, 699, 608 cm^{-1}; MS (CI/NH$_3$) *m/e* (rel intensity) 274 (64, MNH$_4^+$), 236 (6), 216 (78), 196 (100).

***tert*-Butyldimethylsilanol.** To a solution of hexamethylcyclotrisiloxane (**1a**) (0.661 g, 2.97 mmol) in ether (40 mL) at 0 °C was added dropwise *tert*-butyllithium (5.9 mL of a 1.67 M solution in pentane, 9.9 mmol). After 1 h the solution was warmed to 25 °C for 1.5 h, recooled to 0 °C, and quenched with 10% HCl. The aqueous layer was extracted with ether and the combined extracts were dried with MgSO$_4$. Kugelrohr distillation at 125–140 °C (lit.[12] bp 139 °C) gave the product as a colorless oil (1.15 g, 98%): ^{1}H NMR (CDCl$_3$) δ 3.92 (bs, 1 H), 0.91 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR (CDCl$_3$) δ 25.6, 0.80, −3.2; IR (neat) 3376, 2959, 1472, 1260, 1090, 837, 799 cm^{-1}.

1,1,3,3,5,5-Hexaphenyl-5-methyltrisiloxan-1-ol: R_f = 0.29 (1:9 ethyl acetate:hexanes); ^{1}H NMR (CDCl$_3$) δ 7.7–7.2 (m, 30 H), 2.25 (bs, 1 H,), 0.50 (s, 3 H); IR (neat) 3417, 3068, 1428, 1120, 1070, 792, 698 cm^{-1}; MS (CI/NH$_3$) *m/e* (rel intensity) 628 (100, MNH$_4^+$), 550 (12), 430 (65), 352 (34); HRMS (CI/NH$_3$) calcd for $C_{37}H_{38}NO_3Si_3$ 628.2160, found 628.2180.

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