

Reactions of Lithium Silenolates with Acyl Halides. First Synthesis of Di- and Tetraacylsilanes

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Acylsilanes play an important role in both organosynthetic and organosilicon chemistry. They are actively used as versatile synthetic tools, such as acyl anion equivalents and radicalophiles.^{1,2} In organosilicon chemistry, acylpolysilanes are of particular importance, since they can be used as the efficient precursors of silenes. The photolysis^{2,3} and thermolysis^{3,4} of acyltris(trimethylsilyl)silanes cleanly produce various silenes, including stable ones,³ via a 1,3-trimethylsilyl shift from the tris(trimethylsilyl)silyl unit to the carbonyl oxygen. Peterson type reactions of acylpolysilanes with alkyl- and aryllithium reagents also afford high yields of silenes at low temperature.⁵ However, the acylsilanes reported so far involve monoacyl-substituted silicon atom(s), and no compounds having a silicon atom substituted with two or more acyl groups have been reported.

In an effort to develop novel organosilicon reagents based on the transformation of acylpolysilanes, we have found that the reactions of acyltris(trimethylsilyl)silanes with silyllithium reagents give the corresponding lithium silenolates by replacement of a trimethylsilyl group with lithium, if the acylpolysilanes have no enolizable protons and involve a sterically bulky group on the carbonyl carbon.⁶ Lithium silenolates are silicon analogues of lithium enolates and react readily with several electrophiles, such as alkyl halides,⁶ carbonyl compounds,⁷ and dienes.⁸ We have also demonstrated that oxidative coupling of lithium silenolates with palladium dichloride leads to the formation of bis(acyl)polysilanes as the first example of polysilanes with two Si-acyl bonds on the adjacent silicon atoms.⁹ In this paper, we report the first synthesis of compounds having a silicon atom with di- and tetraacyl substitution, by the reactions of lithium silenolates with acyl halides.

When we carried out the reaction of lithium 2-mesitylbis(trimethylsilyl)silenolate (**1a**), prepared from the reaction of mesityltris(trimethylsilyl)silane with tris(trimethylsilyl)silyllithium ((Me₃Si)₃SiLi), with a slight excess of acyl chlorides at -80 °C in THF, the corresponding diacylbis(trimethylsilyl)silanes

Scheme 1

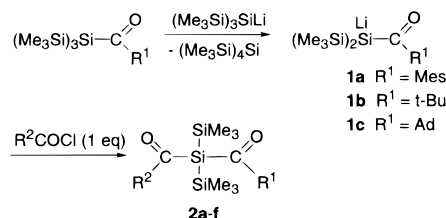
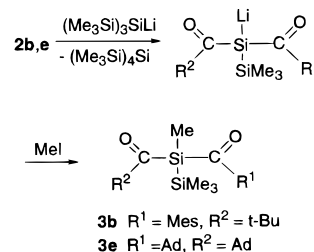


Table 1. Preparation of Diacylsilanes

compound	R ¹	R ²	yield/% isolated ^a NMR ^b
2a	Mes	Mes	76 95
2b	Mes	t-Bu	81 97
2c	Mes	Ad	75 95
2d	t-Bu	Ad	76 95
2e	Ad	Ad	75 93
2f	Mes	OCH ₂ Ph	73 93

^a Isolated yield. ^b Determined by integration of ¹H NMR spectrum of the reaction mixture.

Scheme 2



2a–c were obtained in good isolated yields (Scheme 1, Table 1). Similar reactions of lithium silenolates **1b,c** also proceeded smoothly to give diacylsilanes **2d–e** in moderate isolated yields. With a chloroformate, **1a** afforded compound **2f** again in good isolated yield.

The structures of **2a–f** were verified mainly by NMR spectrometries, and their ²⁹Si NMR spectra reveal a signal of dicarbonyl-substituted silicon around -50 ppm. The rather low isolated yields of **2a–f** are presumably due to the decomposition of the products during workup, especially on treating them with gel permeation chromatography (GPC). Indeed, direct analysis of the reaction mixtures by NMR spectroscopy indicated the formation of **2a–f** in more than 90% yields, as shown in Table 1.

Products **2a–f** are the first examples of compounds which have a silicon atom bearing two or more carbonyl groups. They are silicon analogues of acetylacetones and acetoacetic esters, and the Si(SiMe₃)₂ unit behaves like activated methylenes as expected. Thus, treatment of **2b,e** with (Me₃Si)₃SiLi gave the corresponding lithium acylsilenolates, as indicated by the formation of substitution products **3b,e** by treating the anionic species with methyl iodide, as shown in Scheme 2. The yields of **3b,e** were determined, by integration of ¹H NMR spectra of the reaction mixtures, to be 89 and 87%, respectively.

Interestingly, when lithium silenolate **1a** was treated with acyl chlorides in excess and the reaction mixtures were analyzed by NMR spectrometries, tetraacylsilanes **4a,c** were found to be produced in 41 and 70% yields, together with 9 and 11% yields of the corresponding diacylsilanes **2a** and **2c**, respectively (Scheme 3). Tetraacylsilanes **4a,c** were readily isolated in 24 and 40% yields, respectively, from the mixtures by preparative GPC. Their ²⁹Si NMR spectra reveal a signal at -90.5 ppm for **4a** and -81.4

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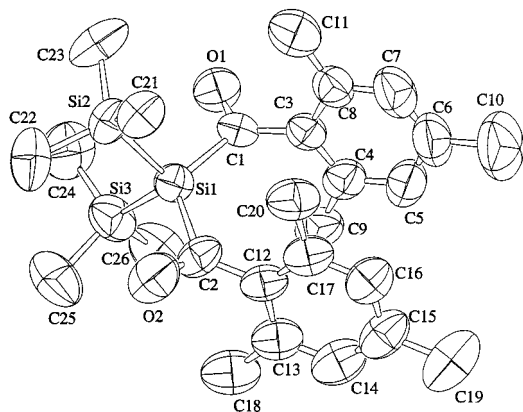
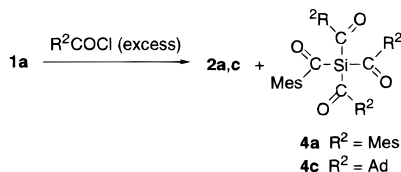


Figure 1. ORTEP drawing of compound **2a**. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Si1–Si2 = 2.35(2), Si1–Si3 = 2.368(3), Si1–C1 = 1.94(2), Si1–C2 = 1.969(9), O1–C1 = 1.210(8), O2–C2 = 1.21(2), C1–C3 = 1.48(1), C2–C12 = 1.48(1), Si2–Si1–Si3 = 108.1(1), Si2–Si1–C1 = 108.3(8), Si2–Si1–C2 = 106.9(7), Si3–Si1–C1 = 105.5(5), Si3–Si1–C2 = 107.5(3), C1–Si1–C2 = 120.0(4), Si1–C1–O1 = 113.8(6), Si1–C1–C3 = 124.4(6), O1–C1–C3 = 121.3(8), Si1–C2–O2 = 110.1(7), Si1–C2–C12 = 126.8(9), O2–C2–C12 = 123.1(9).

Scheme 3



ppm for **4c**, and the ¹³C NMR spectra show carbonyl signal(s) at 237.2 ppm for **4a** and 237.6 and 240.7 ppm for **4c** which are at lower field relative to standard dialkyl ketones, characteristic of carbonyl carbons of acylsilanes.

The crystal structures of diacylsilane **2a** and tetra(acyl)silane **4a** were determined by X-ray diffraction studies.¹⁰ ORTEP drawing of **2a** and **4a** are depicted in Figures 1 and 2, which show no unusual bondings involved in these structures. The Si–Si bond lengths in **2a** are in the normal range (2.33–2.37 Å).¹¹ The Si–C–O angles in **2a** and **4a** range from 110.1 to 113.8°

(10) Crystal data for **2a**: C₂₆H₄₀O₂Si₃, MW = 468.86, space group P2₁/c with *a* = 8.3(1) Å, *b* = 30.6(1) Å, *c* = 11.6(1) Å, β = 101.3(9)°, *V* = 2906(51) Å³, *Z* = 4, density (calcd) = 1.071 g/cm³, *F*(000) = 1016.00, μ (Mo Kα) = 1.81 cm⁻¹. 6691 Intensity data were collected on a Rigaku AFC7R diffractometer using a 0.6 × 0.2 × 0.2 mm³ sized crystal. 2584 unique reflections; with *I* > 3σ(*I*) used in refinement; *R* = 8.2%, *R*_w = 8.1%. Crystal data for **4a**: C₄₀H₄₄O₄Si, MW = 616.87, space group C2/c with *a* = 16.986(2) Å, *b* = 15.016(4) Å, *c* = 14.781(2) Å, β = 110.975(9)°, *V* = 3520(1) Å³, *Z* = 4, density (calcd) = 1.164 g/cm³, *F*(000) = 1320.00, μ (Mo Kα) = 1.05 cm⁻¹. 4049 Intensity data were collected on a Rigaku AFC7R diffractometer using a 0.8 × 0.2 × 0.1 mm³ sized crystal. 2187 unique reflections; with *I* > 3σ(*I*) were used in refinement; *R* = 5.5%, *R*_w = 5.2%.

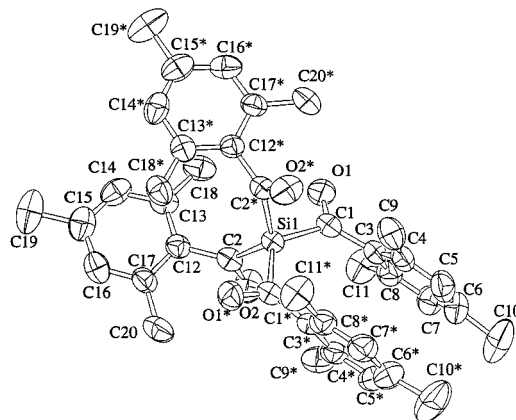


Figure 2. ORTEP drawing of compound **4a**. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Si1–C1 = 1.940(3), Si1–C2 = 1.946(3), O1–C1 = 1.216(4), O2–C2 = 1.218(4), C1–C3 = 1.499(5), C2–C12 = 1.503(5), C1–Si1–C1* = 124.2(2), C1–Si1–C2 = 101.1(1), C1–Si1–C2* = 104.7(1), C2–Si1–C2* = 123.1(2), Si1–C1–O1 = 110.8(3), Si1–C1–C3 = 127.4(2), O1–C1–C3 = 121.5(3), Si1–C2–O2 = 111.8(3), Si1–C2–C12 = 126.4(3), O2–C2–C12 = 121.6(3).

and so are smaller than those of Si–C(carbonyl)–C(Mes) (124.4–127.4°) and O–C–C(Mes) angles (121.3–123.1°), reflecting the steric congestion of these compounds. The sum of bond angles at carbonyl carbons is 359.5–360.0°, indicating the high planarity of the bondings of these carbons.

In conclusion, we have studied the reactions of lithium silenolates with acyl chlorides which afforded di- or tetraacylsilanes, depending on the reaction conditions. These are the first examples of compounds having a silicon or a heavier group 14 element substituted with two or more carbonyl groups. Although the synthesis of carbon tetracarboxylates has been reported previously, tetraacylsilanes are the first example of compounds with a tetraacyl-substituted group 14 element including carbon.¹² Studies concerning the chemical behavior of di- and tetraacylsilanes and the reaction mechanism leading to tetraacylsilanes are in progress.

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Supporting Information Available: Experimental details for the preparation of compounds **2a–f**, **3b,d**, and **4a,b** and X-ray diffraction studies for compounds **2a** and **4a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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