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Silicon–carbon unsaturated compounds.

XLVIII *. Synthesis and reactions of silicon analogs of lithium enolates

Joji Ohshita, Yoshiteru Masaoka, Shin Masaoka and Mitsuo Ishikawa

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724 (Japan)

Akitomo Tachibana, Tasuku Yano and Tokio Yamabe

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606 (Japan)

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Abstract

The reaction of mesitoyl- and (2-methylbenzoyl)tris(trimethylsilyl)silane with 1 equiv. of a silyllithium gave silicon analogs of lithium enolates. Hydrolysis of the lithium silenolates afforded hydrosilanes in high yields. The lithium silenolates can be readily transformed into silenes quantitatively, by treatment with a chlorosilane.

Key words: Silicon; Lithium; Unsaturated compounds; Lithium enolates

Acylpolysilanes are useful compounds as a precursor of silenes. Brook *et al.* [1] have reported the synthesis of various silenes including stable compounds from the photolysis of acylpolysilanes. We have recently demonstrated that the reaction of acylpolysilanes with organolithium reagents affords the silenes *via* a Peterson type reaction [2]. Brook *et al.* [3] have found a similar reaction of acylpolysilanes with a Grignard reagent. During the course of our investigation concerning the synthesis of silenes by the reaction of acylpolysilanes with organolithium compounds, we found that the reaction of acyltris(trimethylsilyl)silane with silyllithium reagents proceeds in a quite different fashion from that of organolithium reagents, giving the silicon analogs of lithium enolates.

The reaction of mesitoyltris(trimethylsilyl)silane (**Ia**) [4] with 1 equiv. of tris(trimethylsilyl)silyllithium [5] in THF at −80°C for 2 h, followed by hydrolysis of the resulting solution gave mesitoylbis(trimethylsilyl)silane (**III**)[1] arising from hydrolysis of the silicon analog of lithium enolate (**IIa**)[2] in 95% yield, along with a quantitative yield of tetrakis(trimethylsilyl)silane (Scheme 1). A similar reaction of **Ia** with 1 equiv. of dimethylphenylsilyllithium in THF at −80°C also affords lithium enolate **IIa**, along with pentamethylphenyldisilane. Hydrolysis of this solution with D_2O produced deuterio(mesitoyl)bis(trimethylsilyl)silane (**III′**) [^2H NMR (in C_6D_6): δ 4.19 (D–Si); exact MS calcd: 323.1668. Found: 323.1667] in 71% yield. The reaction of **Ia** with silyllithium reagents proceeds cleanly to give

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Correspondence to: Dr. M. Ishikawa.

* For Part XLVII, see ref. 8.

[1] For compound **III**: MS: m/z 322 (M^+). ^1H NMR (C_6D_6): δ 0.32 (s, 18H, Me_3Si); 2.14 (s, 3H, *p*-Me); 2.33 (s, 6H, *o*-Me); 4.21 (s, 1H, HSi); 6.70 (s, 2H, ring protons). ^{13}C NMR (in C_6D_6): δ 0.8, 20.3, 21.5, 129.8, 132.8, 138.9, 146.4, 245.7. IR: ν(Si–H) 2081 cm^{-1}; ν(C=O) 1609 cm^{-1}. Exact MS: $C_{16}H_{30}OSi_3$ calcd.: 322.1605. Found: 322.1695.

[2] For compound **IIa**: ^1H NMR (in 70% THF + 30% THF-d_8 at −40°C): δ −0.26 (s, 9H, Me_3Si); 0.17 (s, 9H, Me_3Si); 2.15 (s, 3H, *p*-Me); 2.33 (s, 6H, *o*-Me); 6.64 (s, 2H, ring protons). ^{13}C NMR (in 70% THF + 30% THF-d_8 at −40°C): δ 3.2, 3.9, 20.5, 20.9, 127.9, 132.2, 133.8, 151.2, 262.7. ^{29}Si NMR (in 70% THF + 30% THF-d_8 at −40°C): δ −10.6, −12.8, −59.9.

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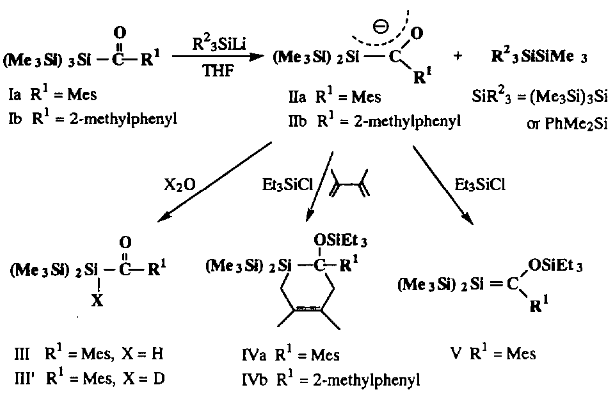

Scheme 1.

lithium enolate **IIa**. In fact, NMR spectra of the reaction mixture, indicate that no other products are produced in this reaction.

The ^{1}H NMR spectrum of **IIa** in THF at −40°C shows two resonances at −0.26 and 0.17 ppm, attributed to two non-equivalent trimethylsilyl protons, in addition to resonances due to the mesityl group. Its ^{29}Si NMR spectrum at −40°C reveals three resonances at −10.6, −12.8 and −59.9 ppm, due to two non-equivalent trimethylsilyl silicons and one bis(silyl)-substituted silicon. On warming to 25°C, the two non-equivalent trimethylsilyl groups coalesced in both ^{1}H and ^{29}Si NMR, while the rest of the NMR was unchanged. When this solution was cooled down to −40°C, two sharp resonances with equal intensities were reproduced in both ^{1}H and ^{29}Si NMR spectra, indicating that the changes are reversible.

Brano-Zhivotovskii *et al.* [6] reported that the reaction of pivaloyl- and adamantoyltris(trimethylsilyl)silane with triethylgermyllithium affords the respective lithium enolates whose ^{29}Si NMR spectra show the resonance at 64.86 and 67.77 ppm, respectively. We followed the reaction of adamantoyltris(trimethylsilyl)silane with triethylgermyllithium. However, we could not observe the ^{29}Si NMR signal at 67.77 ppm reported by those authors. Furthermore, no signals due to the lithium enolate were observed at all, although the formation of triethylgermyltrimethylsilane was detected. Recently, Apeloig *et al.* [7] reported that treatment of adamantoyltris(trimethylsilyl)silane with a twofold excess of trimethylgermyllithium, followed by hydrolysis produces 4-(1-adamantyl)-1-(triethylgermoxy)-1,2,2,3,3-pentakis(trimethylsilyl)-1,2,3-trisilacyclobutane.

As expected, treatment of lithium enolate **IIa** prepared from **Ia** and tris(trimethylsilyl)silyllithium in THF with a mixture of chlorotriethylsilane and 2,3-dimethylbutadiene at −80°C, followed by warming up to room temperature produced 6-mesityl-3,4-dimethyl-6-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silacyclohex-3-ene (**IVa**)[3] in 88% yield, together with a 99% yield of tetrakis(trimethylsilyl)silane. Similar reaction of (2-methylbenzoyl)tris(trimethylsilyl)silane (**Ib**), which was prepared from 2-methylbenzoylchloride in a similar manner to **Ia** in 65% yield, with 1 equiv. of tris(trimethylsilyl)silyllithium in THF, and treatment of the resulting mixture with chlorotriethylsilane and 2,3-dimethylbutadiene afforded 6-(2-methylphenyl)-3,4-dimethyl-6-triethylsiloxy-1,1-bis(trimethylsilyl)-1-silacyclohex-3-ene (**IVb**)[4] and tetrakis(trimethylsilyl)silane in 60% and 67% yields, along with a 27% yield of triethylsilyl[tris(trimethylsilyl)]silane derived from the reaction of tris(trimethylsilyl)silyllithium with chlorotriethylsilane.

Lithium enolate **IIa** can be readily transformed into a silene quantitatively, by treatment with a chlorosilane. Thus, the reaction of a THF solution of **IIa** with chlorotriethylsilane gave 2-mesityl-2-triethylsiloxy[bis(trimethylsilyl)]silene (**V**) [^{1}H NMR (in 70% THF + 30% THF-d_8 at −40°C): δ −0.15 (s, 9H, Me$_3$Si); 0.34 (s, 9H, Me$_3$Si); 0.38 (q, 2H, $J = 7.92$ Hz, CH$_2$Si); 0.83 (t, 3H, $J = 7.92$ Hz, CH$_3$CH$_2$); 2.20 (s, 3H, *p*-Me); 2.39 (s, 6H, *o*-Me); 6.81 (br. s, 2H, ring protons). ^{13}C NMR (in 70% THF + 30% THF-d_8 at −40°C): δ 0.9, 1.7, 5.5, 7.1, 21.0, 128.8, 136.3, 137.1, 142.0, 197.7.] in quantitative yield. Its ^{29}Si NMR spectrum shows four resonances at −13.2, −12.4, 16.6 and 34.3 ppm, due to two non-equivalent trimethylsilyl silicons, siloxy silicon, and sp^2 silicon, respectively.

The experimental finding for the formation of lithium enolate **II** was also confirmed by molecular orbital calculations which were carried out by the Hartree–Fock method using the 6-31G** basis set on the reaction of acetyltris(silyl)silane (**VI**) with silyl-

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[3] For compound **IVa**: MS: m/z 518 (M$^+$). ^{1}H NMR (in C$_6$D$_6$): δ −0.09 (s, 9H, Me$_3$Si); 0.40 (s, 9H, Me$_3$Si); 0.65 (q, 6H, $J = 8.12$ Hz, CH$_2$Si); 0.94 (t, 9H, $J = 8.12$ Hz, CH$_3$CH$_2$); 1.40 (d, 1H, $J = 15.18$ Hz, ring CH$_2$); 1.67 (d, 1H, $J = 15.18$ Hz, ring CH$_2$); 1.91 (s, 3H, MeC=C); 1.93 (s, 3H, MeC=C); 2.09 (s, 3H, *p*-Me); 2.55 (br. s, 3H, *o*-Me); 2.73 (br. s, 3H, *o*-Me); 3.10 (br. s, 2H, ring CH$_2$); 6.70 (br. s, 2H, aromatic ring protons). ^{13}C NMR (in C$_6$D$_6$): 0.5, 2.3, 8.0, 8.4, 20.0, 20.9, 22.3, 27.3, 50.8, 84.4, 127.7, 128.6, 132.5, 133.4, 136.2, 143.8. IR: ν(Si–O) 1050 cm^{-1}. Anal. Found: C, 64.75; H, 10.48. C$_{28}$H$_{54}$OSi$_4$ calcd.: C, 64.79; H, 10.49%.

[4] For compound **IVb**: MS: m/z 490 (M$^+$). ^{1}H NMR (in C$_6$D$_6$): δ −0.01 (s, 9H, Me$_3$Si); 0.56 (s, 9H, Me$_3$Si); 0.71 (q, 6H, $J = 7.92$ Hz, CH$_2$Si); 1.05 (t, 9H, $J = 7.92$ Hz, CH$_3$CH$_2$); 1.56 (d, 1H, $J = 14.19$ Hz, ring CH$_2$); 1.91 (s, 3H, MeC=C); 2.07 (br. d, 1H, $J = 14.19$ Hz, ring CH$_2$); 2.09 (s, 3H, MeC=C); 2.81 (s, 3H, *o*-Me); 3.05 (br. d, 1H, $J = 13.86$ Hz, ring CH$_2$); 3.20 (br. d, 1H, $J = 13.86$ Hz, ring CH$_2$); 7.19–7.42 (m, 4H, aromatic ring protons). ^{13}C NMR (in C$_6$D$_6$): δ 0.9, 1.6, 8.0 (2C), 18.9, 21.8, 22.5, 25.2, 50.8, 81.4, 125.0, 125.5, 126.1, 127.1, 131.7, 132.4, 138.0, 148.3. IR: ν(Si–O) 1029 cm^{-1}. Exact MS: C$_{26}$H$_{50}$OSi$_4$ calcd.: 490.2936. Found: 490.2924.

lithium (**VII**). The enthalpy for this reaction was calculated to be -13.81 kcal mol^{-1}, indicating that the reaction is exothermic, and therefore the formation of lithium enolate (**VIII**) and disilane is thermodynamically favorable.

$$\underset{\textbf{VI}}{(H_3Si)_3SiCOCH_3} + \underset{\textbf{VII}}{H_3SiLi} \rightarrow \underset{\textbf{VIII}}{(H_3Si)_2SiLiCO(CH_3)} + H_3SiSiH_3$$

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