Hydrogenation of Silyl-Substituted Alkynes Using Diimide: Application to the Synthesis of Saturated Sila-Macrocycles

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(Received October 11, 2000; CL-000923)

The hydrogenation of bistrimethylsilylactylene, bis(trimethylsilyl)-1,3-diynes, and related silylalkynes giving the corresponding saturated compounds were achieved by using diimide prepared in situ from *p*-toluenesulfonyl hydrazide in diglyme. The present method was applicable to the synthesis of saturated 12- and 18-membered oligosilacycloalkanes.

We have found that the hydrogenation of various silylalkynes with diimide provides a convenient and versatile method for the syntheses of the corresponding saturated compounds.[1,2] The results are particularly interesting, because though various silylalkynes are prepared rather easily, their hydrogenation by other conventional methods such as the hydrogenation with transition metal catalysts was unsuccessful.[3] The present method was applied to the synthesis of saturated sila-macrocycles such as 1,4,7,10-tetrasilacyclododecane and 1,4,7,10,13,16-hexasilacyclooctadecane.

$$R_3Si{-}C{\equiv}C{-}SiR_3 \xrightarrow[\text{diglyme, 162 °C}]{TsNHNH_2} R_3Si{-}CH_2{-}CH_2{-}SiR_3 \quad (1)$$

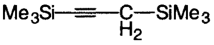
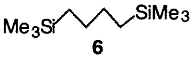
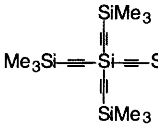
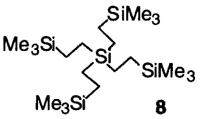
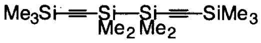
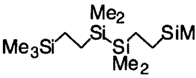
Typically, the hydrogenation of bis(trimethylsilyl)acetylene (**1**) with diimide was performed as follows: A mixture of **1** (2.00 g, 11.8 mmol) and *p*-toluenesulfonyl hydrazide (4.38 g, 23.5 mmol) in diglyme (20 mL) was heated under reflux for 10 h. After cooling the mixture to room temperature, water (20 mL) was added. The mixture was neutralized with aqueous $NaHCO_3$ and then extracted with pentane. The organic layer was dried over anhydrous sodium sulfate. Evaporation of solvents followed by silicagel column chromatography gave pure 1,2-bis(trimethylsilyl)ethane (**2**, 1.70 g, 83% yield) as a colorless oil (Table 1, entry 1). The reduction of **1** with an equimolar amount of *p*-toluenesulfonyl hydrazide afforded a mixture of the corresponding bissilylethane and ethylene.

The present method for the synthesis of silaalkanes is useful because the precursor silylalkynes are obtained easily by the reactions of ethynyllithiums and ethynyl Grignard reagents with halosilanes. Not only 1,2-bissilylethanes but 1,3-bissilyl- and 1,4-bissilylalkanes were prepared by the hydrogenation of the corresponding 3-silylpropargylsilanes and 1,4-bis(trialkylsilyl)-diynes, respectively. These results are summarized in Table 1.

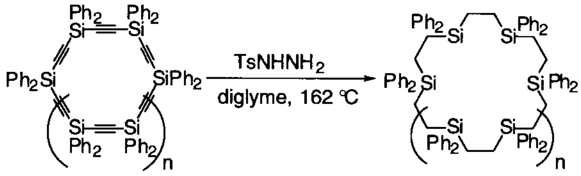
The hydrogenation of tetrakis(trimethylsilylethynyl)silane **7**[4] afforded tetrakis(2-trimethylsilylethyl)silane **8** in 88% yield. Dendrimeric silaalkanes may be synthesized by the present hydrogenation of the corresponding dendrimers having silaalkyne skeletons.[5] No cleavage of Si–Si bonds occurred during the hydrogenation of bis(trimethylsilylethynyl)disilane **9**[6] using diimide; the reaction gave the corresponding saturated compound **10**[7] in 77% yield (Table 1, entry 5).

Crown-like silaalkanes **11** and **12** were prepared in 74 and 82% yields,[8] respectively, by the hydrogenation of the corresponding cyclic oligosilaalkynes **13**[9] and **14**[9] (eq 2).

Table 1. Hydrogenation of various silylalkynes

Entry	Silylalkyne	Product	Yield/%[a]
1	$Me_3Si{-}C{\equiv}C{-}SiMe_3$ **1**	 **2**	83
2	 $Me_3Si{-}C{\equiv}C{-}CH_2{-}SiMe_3$ **3**	 **4**	79
3	$Me_3Si{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3$ **5**	 **6**	92
4	 **7**	 **8**	88
5	 $Me_3Si{-}C{\equiv}C{-}SiMe_2{-}SiMe_2{-}C{\equiv}C{-}SiMe_3$ **9**	 **10**	77

[a]Isolated yields.



13: n = 0
14: n = 1

11: n = 0 (74%)
12: n = 1 (82%)

Structures of **11** and **12** were determined by spectroscopic, elemental, and X-ray crystallographic analyses.[10,11] As shown in Figure 1, **11** and **12** were found by X-ray crystallography to have roughly rectangular molecular skeletons, where the deviations of all silicon atoms in **11** and **12** from the least squares planes were within 0.08 Å and 0.86 Å, respectively.

Phenyl groups in **12** were completely converted into chlorine, hydrogen, and fluorine atoms by conventional procedures to give the corresponding new macrocyclic silaalkanes **15**, **16**, and **17**,[12] respectively (Scheme 1). Chlorination of **12** was performed using hydrogen chloride in the presence of aluminum chloride to give **15** in 92% yield. Reduction of **15** by lithium aluminum hydride at room temperature afforded hexasilacyclooctadecane **16** in 87% yield. Compound **15** was converted into the fluorinated derivative **17** in 81% yield by fluorination using antimony(III) fluoride at room temperature. The highly symmetric structures

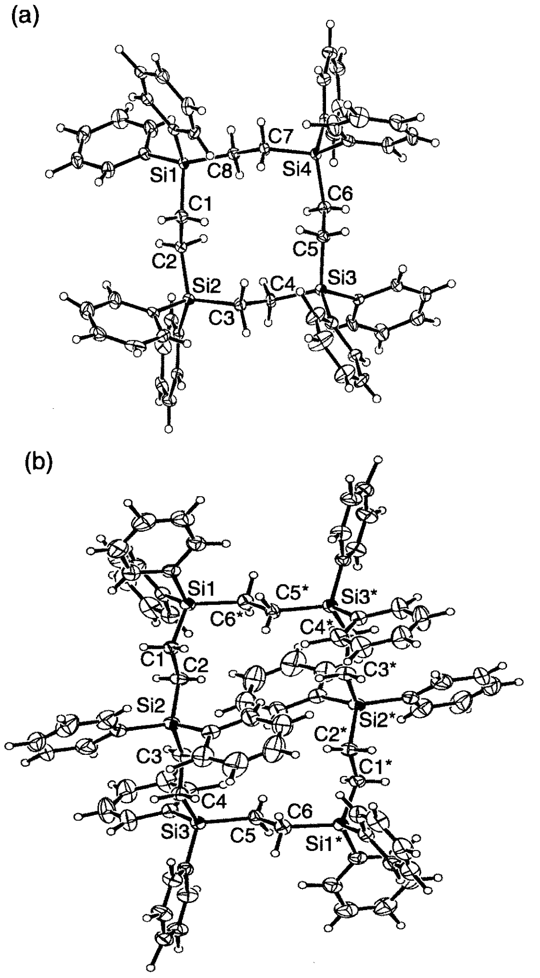
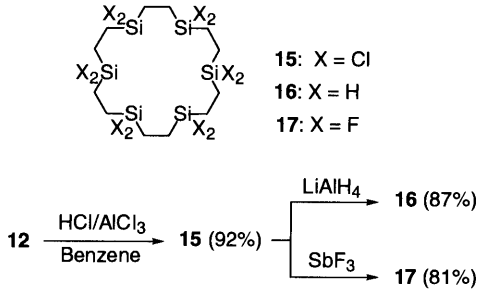


Figure 1. Molecular structures of **11** and **12** with selected bond lengths (Å) and bond angles (deg). Thermal ellipsoids are drawn at the 30% probability level. (a) **11**; Si1–C1 = 1.877(8), C1–C2 = 1.55(1), C2–Si2 = 1.868(8); C8–Si1–C1 = 107.4(4), Si1–C1–C2 = 114.0(6), C1–C2–Si2 = 114.3(6), C2–Si2–C3 = 118.8(4). (b) **12**; C2–Si2 = 1.880(5), Si2–C3 = 1.862(5), C3–C4 = 1.539(7), C4–Si3 = 1.867(5); C2–Si2–C3 = 106.9(2), Si2–C3–C4 = 116.7(3), C4–Si3–C5 = 110.4(2), Si3–C5–C6 = 113.9(3).

Scheme 1.



of these silacycles were confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. In the ^{13}C NMR spectrum of **17**, a single methylene carbon resonance was observed at δ 2.1 as a triplet due to the coupling with two equivalent fluorine atoms ($^{2}J_{\mathrm{C-F}}$ = 16 Hz). The ^{29}Si NMR signal of **17** appeared at δ –1.5 as a triplet due to the coupling with the two equivalent fluorine atoms ($^{1}J_{\mathrm{Si-F}}$ = 306 Hz). The ^{19}F NMR spectrum shows a sharp singlet at δ –138.0 with satellite signals due to ^{29}Si nuclei ($^{1}J_{\mathrm{Si-F}}$ = 360 Hz). Because these sila-macrocycles have flexible structures and functional silicon moieties, the compounds would be employed for new components in the supramolecular chemistry.

References and Notes

1 For a recent review, see: D. J. Pasto and R. T. Taylor, *Org. React.*, **40**, 91 (1991).

2 R. S. Dewey and E. E. von Tamelene, *J. Am. Chem. Soc.*, **83**, 3729 (1961); T. N. Mitchell and B. Kowall, *J. Organomet. Chem.*, **481**, 137 (1994).

3 The hydrogenation with hydrogen in the presence of various transition metal catalysts ($RhCl(PPh_3)_3$, Pd/C, Pt/C, etc.) was unsuccessful.

4 N. V. Komarov and O. G. Yarosh, *Zh. Obshch. Khim.*, **37**, 264 (1967).

5 T. Matsuo, K. Uchida, and A. Sekiguchi, *Chem. Commun.*, **1999**, 1799.

6 Compound **9** was prepared by the reaction of [(trimethylsilyl)-ethynyl]magnesium bromide with 1,1-dichloro-1,1,2,2-tetramethyldisilane in THF. **9**: 78% yield, colorless crystals; mp 41.8–43.6 °C; ^{1}H NMR (C_6D_6, 298 K, δ) 0.13 (s, 18 H), 0.34 (s, 12 H); ^{13}C NMR (C_6D_6, 298 K, δ) –3.0, –0.4, 111.9, 117.3; ^{29}Si NMR (C_6D_6, 298 K, δ) –38.1, –19.1; MS (70 eV) *m/z* (%) 310 (M$^+$, 32), 295 (78), 237 (32), 155 (68), 140 (36), 73 (100); HRMS Calcd for $C_{14}H_{30}Si_4$: 310.1425. Found: 310.1421.

7 Yu. E. Ovchinnikov, V. E. Shklover, Yu. T. Struchkov, Yu. P. Polyakov, and L. E. Guselnikov, *Makromol. Chem.*, **187**, 2011 (1986).

8 **11**: mp 225.8–226.0 °C; ^{1}H NMR ($CDCl_3$, 298 K, δ) 1.04 (s, 16 H), 7.25–7.39 (m, 40 H); ^{13}C NMR ($CDCl_3$, 298 K, δ) 2.5, 127.7, 129.1, 134.9, 135.9; ^{29}Si NMR ($CDCl_3$, 298 K, δ) –3.8; MS (70 eV) *m/z* (%) 840 (M$^+$, 9), 522 (15), 468 (87), 343 (56), 259 (100), 183 (50); Anal. Calcd for $C_{56}H_{56}Si_4$: C, 79.94; H, 6.71%; Found: C, 79.90; H, 6.97%. **12**: mp 256.4 °C; ^{1}H NMR ($CDCl_3$, 298 K, δ) 1.00 (s, 24 H), 7.19–7.44 (m, 60 H); ^{13}C NMR ($CDCl_3$, 298 K, δ) 3.7, 127.8, 129.2, 135.0, 135.3; ^{29}Si NMR ($CDCl_3$, 298 K, δ) –3.2; Anal. Calcd for $C_{84}H_{84}Si_6$: C, 79.94; H, 6.71%; Found: C, 79.72; H, 6.72%.

9 R. Bortolin, B. Parbhoo, and S. S. D. Brown, *J. Chem. Soc., Chem. Commun.*, **1988**, 1079; M. Unno, T. Saito, and H. Matsumoto, *Chem. Lett.*, **1999**, 1235.

10 Intensities of reflections were collected on a Rigaku/MSC Mercury CCD diffractometer using Mo Kα radiation (λ = 0.71069 Å). The structures were solved by direct method using SIR92. Crystal data for **11**: $C_{56}H_{56}Si_4 \cdot 2CHCl_3$, fw = 1080.16, monoclinic, space group $P2_1/c$, a = 12.5464(6) Å, b = 21.075(1) Å, c = 22.394(1) Å, β = 102.6227(5)° V = 5778.3(6) Å^3, Z = 2, d_{calc} = 1.212 g/cm^3, temperature 190 K. Full matrix least-squares refinement yielded the final R value of 0.080 (R_w = 0.085) for 4750 independent reflections [I > 3.00σ(I)]. Crystal data for **12**: $C_{84}H_{84}Si_6 \cdot 4H_2O$, fw = 1334.16, monoclinic, space group $P2_1/n$, a = 12.0616(7) Å, b = 21.008(1) Å, c = 15.987(1) Å, β = 101.3450(7)° V = 3971.8(4) Å^3, Z = 2, d_{calc} = 1.115 g/cm^3, temperature 293 K. Full matrix least-squares refinement yielded the final R value of 0.061 (R_w = 0.074) for 4329 independent reflections [I > 5.00σ(I)].

11 Compound **12** was obtained previously by the hydrosilylation of diphenylbis(2-diphenylsilylethyl)silane with diphenylbis[2-diphenyl-(vinyl)silylethyl]silane under highly dilute conditions in 1.8% yield; M. Ichinohe, Y. Hayashi, and M. Kira, 73th Annual Meeting of the Chemical Society of Japan, Morioka, September 1997, Abstr., No. 3D801.

12 **15**: mp 162.2–164.9 °C; ^{1}H NMR (CD_2Cl_2, 298 K, δ) 1.23 (s, 24 H); ^{13}C NMR (CD_2Cl_2, 298 K, δ) 13.4; ^{29}Si NMR (CD_2Cl_2, 298 K, δ) 31.3; MS (70 eV) *m/z* (%) 761 (M$^+$, trace), 71 (37), 58 (100); HRMS Calcd for $C_{12}H_{24}{}^{35}Cl_9{}^{37}Cl_3Si_6$: 761.6667. Found: 761.6642. **16**: mp 21.3–23.1 °C; ^{1}H NMR ($CDCl_3$, 298 K, δ) 0.71–0.72 (m, 24 H), 3.68 (bs, 12H); ^{13}C NMR ($CDCl_3$, 298 K, δ) 3.5; ^{29}Si NMR ($CDCl_3$, 298 K, δ) –21.8; MS (70 eV) *m/z* (%) 348 (M$^+$, 4), 289 (19), 231 (77), 203 (36), 173 (100), 145 (57), 115 (45), 89 (50); HRMS Calcd for $C_{12}H_{36}Si_6$: 348.1433. Found: 348.1432. **17**: mp 73.4 °C; ^{1}H NMR (THF-d_8, 298 K, δ) 0.97 (bs, 24 H); ^{13}C NMR (THF-d_8, 298 K, δ) 2.1 (t, $^{2}J_{\mathrm{C-F}}$ = 16 Hz); ^{29}Si NMR (THF-d_8, 298 K, δ) –1.5 (t, $^{1}J_{\mathrm{Si-F}}$ = 306 Hz); ^{19}F NMR (THF-d_8, 298 K, δ) –138.0 (s, $^{1}J_{\mathrm{Si-F}}$ = 306 Hz); MS (70 eV) *m/z* (%) 564 (M$^+$, 3), 295 (71), 207 (100), 193 (50), 163 (58); HRMS Calcd for $C_{12}H_{24}F_{12}Si_6$: 564.0302. Found: 564.0325.