

74. Homolytic Substitution Reaction at a Silicon Atom

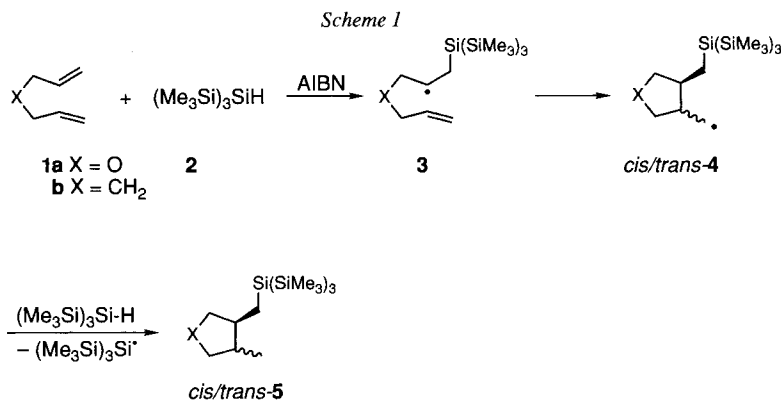
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Tris(trimethylsilyl)silane (**2**) is an efficient hydrosilylating agent of 1,6-dienes **1** operating *via* a free-radical chain mechanism. The intermediate alkyl radical **3** attacks the second olefinic bond of the diene **1** and forms cyclopentylalkyl radical **4**. Using a low concentration of the hydrogen donor **2**, a radical substitution reaction at the Si-center of *cis*-**4** occurs and yields the bicyclic silane **6**. The rate of this homolytic substitution at the Si-atom is $2.4 \cdot 10^5 \text{ s}^{-1}$ (80°).

1. Introduction. – Homolytic substitution reactions at sp^3 -hybridized Si-centers are uncommon [1]. Although examples were reported of radical displacement reactions at Si by halogen [2] and benzophenone triplet [3], to our knowledge no homolytic substitutions at Si by C-centered radicals in the liquid phase are reported²⁾. Reactions with tris(trimethylsilyl)silane (**2**) provide the first examples of this reaction type. Silane **2** is an efficient hydrosilylating agent of alkenes operating *via* a free-radical chain mechanism [5]. With 1,6-diene **1b**, the intermediate alkyl radical **3** attacks the second olefinic bond and forms cyclopentylalkyl radical **4b** (Scheme 1). Under high concentrations of silane **2**, this radical is trapped by H to yield **5b** as a *cis/trans*-mixture [5a]³⁾. Experiments with low concentration of silane **2** now demonstrate that attack of the radical C-atom at the Si-center of the radicals **4a,b** competes successfully with H-abstraction.



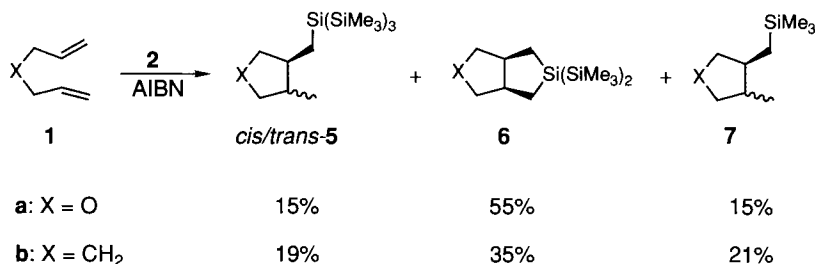
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²⁾ A 1,2 migration of a Me_3Si group from a Si-atom to an adjacent C-centered radical was reported to occur in the gas phase only [4].

³⁾ The ^{13}C -NMR signals of the CH_2 and Me groups at the five-membered rings are at lower field for *trans*-**5a,b** than for *cis*-**5a,b**; for analogous compounds, see [6].

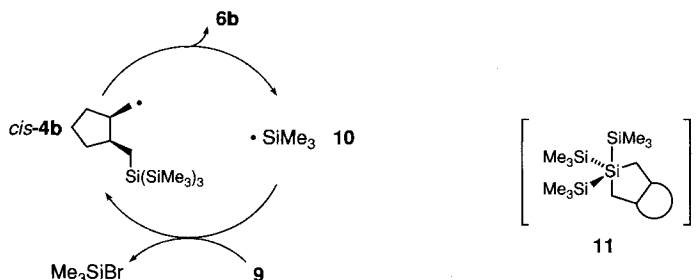
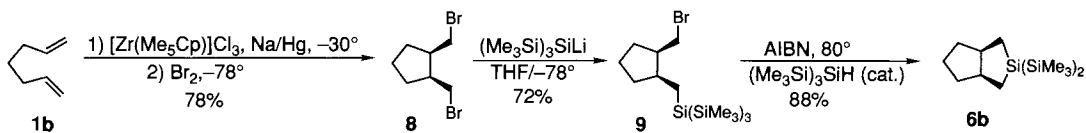
2. Results and Discussion. – Addition of a dilute solution of tris(trimethylsilyl)silane (**2**) to 1,6-dienes **1a,b** within 9 h, under radical-producing conditions (AIBN = 2,2'-azobis(isobutyronitrile) = 2,2'-dimethyl-2,2'-azobis[propanenitrile]) at 80° gave silabicycloalkanes **6a,b** in 35–55% yield besides *cis/trans*-**5a,b** and **7a,b** (Scheme 2). The structure of silabicycles **6a,b** was elucidated by NMR spectroscopy. Because of their symmetry, **6a** shows only 5 and compound **6b** only 6 ¹³C-NMR signals.

Scheme 2

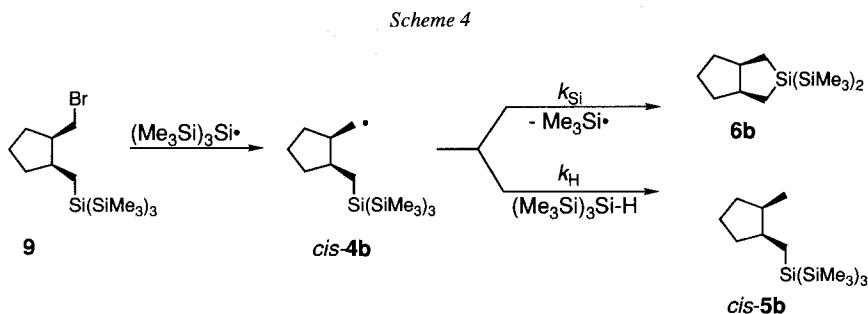


To check, whether products **6a,b** were formed *via* intramolecular attack of the primary alkyl radical center of **4a,b** at the Si-atom, we synthesized silylated bromide **9** from **1b** *via* dibromide **8** (Scheme 3). Radical Br-abstraction from **9** gave silabicycloalkane **6b** in 88% yield. The reduced product **5b** was formed only in 10%. It is interesting, that the reaction needs only catalytic amounts of silane **2**. We assume that trimethylsilyl radical (**10**), generated during this intramolecular substitution at the central Si-atom, carries the chain. This could also explain the formation of product **7** in Scheme 2: in the presence of 1,6-diene **1**, **10** is trapped by the olefinic bond and yields the monocyclic trimethylsilylated product **7**.

Scheme 3



These experiments leave no doubt that the intermediate alkyl radicals **4a,b** undergo intramolecular substitution reactions. Yet it is not clear, whether intermediate **11** with a pentavalent Si-center is formed or this is only the transition state of the radical substitution. To learn how fast this radical substitution at the Si-center occurs, we carried out kinetic competition reactions with excess of silane **2** (Scheme 4). Thus, alkyl radical *cis*-**4b** was formed from the corresponding bromide **9** (ca. 0.05M) and **2** (ca. 1.3–2.0M) by an AIBN initiated radical chain reaction in toluene as solvent. The alkyl radical *cis*-**4b** gave rise to products *cis*-**5b** and **6b** for product ratios at 80°, see *Exper. Part*.



Since the silane concentration remains essentially constant under these pseudo-first-order conditions, Eqn. 1 is obeyed,

$$\frac{k_{\text{Si}}}{k_{\text{H}}} = \left[(\text{Me}_3\text{Si})_3\text{SiH} \right] \frac{\left[\text{Cyclopentane-Si}(\text{SiMe}_3)_2 \right]}{\left[\text{Cyclopentane-Si}(\text{SiMe}_3)_3 \right]} \quad (1)$$

where k_{H} is the rate constant of the H-abstraction from silane **2** and k_{Si} the rate constant of the homolytic substitution at the Si-center. From the product ratio **6b**/*cis*-**5b**, the ratio of the rate constants $k_{\text{Si}}/k_{\text{H}} = 0.198$ (80°) is obtained. Since k_{H} is ca. $1.2 \cdot 10^6 \text{ M}^{-1}\text{s}^{-1}$ at 80° [7] for a primary alkyl radical, the homolytic substitution at the Si-atom is $2.4 \cdot 10^5 \text{ s}^{-1}$ (80°). This rate is surprisingly high and indicates that also bimolecular homolytic substitutions ($S_{\text{H}}2$ reactions) at Si should occur, if they lead to the cleavage of a Si–Si bond.

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Experimental Part

General. All radical reactions were carried out under Ar. Column chromatography: silica gel C 560KV, 35–70 μm (Chemische Fabrik Uetikon). FC = flash chromatography. GC: Carlo Erba 6000 flame ionization detector coupled to a Shimadzu-C-R4A integrator; 25 m SE-54 DF, 50 \rightarrow 260° at 10°/min). GC/MS: Hewlett-Packard 5790A gas chromatograph coupled to a Hewlett-Packard 5970A mass-selective detector; 25 m SE-30, 50 \rightarrow 260

at 10°/min. ¹H- and ¹³C-NMR spectra: **5a**, **6a**, **8**, and **9**: Varian Gemini 300 (¹H, 300 MHz; ¹³C, 75 MHz); CDCl₃ as solvent and as standard (δ 7.27 ppm); **5b** and **6b**: Varian VXR 400 (¹H, 400 MHz; ¹³C, 101 MHz); CDCl₃ as solvent. MS: VG 70-250.

1. *Hydrosilylation of Diallyl Ether (1a)*. To a soln. of **1a** (196 mg, 2 mmol) in toluene (20 ml) under Ar, tris(trimethylsilyl)silane (**2**; 595.2 mg, 2.4 mmol), and AIBN (76 mg, 0.46 mmol) in toluene (4 ml) were added by syringe within 9 h. During the addition, the soln. was heated at 80°. The mixture was cooled and evaporated. Distillation gave **6a** (295 mg, 54%; b.p. 100°/0.4 mbar) and *cis/trans*-**5a** (104 mg, 15%; *cis/trans* 3:1; b.p. 150°/0.4 mbar). Product **7a** was identified by GC/MS prior to distillation (estimated yield (GC) ca. 15%).

cis/trans-Tetrahydro-3-methyl-4-[[tris(trimethylsilyl)silyl]methyl]furan (*cis/trans*-**5a**). The anal. data were determined from the mixture. ¹H-NMR: *cis*-**5a**: 4.06–3.96 (*m*, 2 H); 3.43 (*m*, 2 H); 1.80–1.68 (*m*, 2 H); 1.17 (*dd*, *J* = 2.9, 14.4, 1 H); 1.00 (*d*, *J* = 6.3, 3 H); 0.63 (*dd*, *J* = 10.5, 14.4, 1 H); 0.16 (*s*, 27 H); *trans*-**5a**: 3.94–3.86 (*m*, 2 H); 3.46 (*m*, 2 H); 2.30–2.25 (*m*, 2 H); 1.05–0.91 (*m*, 1 H); 0.93 (*d*, *J* = 6.3, 3 H); 0.72 (*dd*, *J* = 10.8, 14.9, 1 H); 0.14 (*s*, 27 H); ¹³C-NMR: *cis*-**5a**: 74.8, 74.0, 46.1, 37.5, 12.5, 9.5, 0.9; *trans*-**5a**: 75.9, 74.7, 46.7, 41.8, 15.6, 10.3, 0.9. FI-MS: 346 (*M*⁺), 73. Anal. calc. for C₁₅H₃₈OSi₄ (346.75): C 51.95, H 11.04; found: C 51.79, H 10.98.

cis-7,7-Bis(trimethylsilyl)-3-oxa-7-silabicyclo[3.3.0]octane (**6a**): ¹H-NMR: 3.91 (*dd*, *J* = 6.7, 8.2, 2 H); 3.42 (*dd*, *J* = 5.3, 8.2, 2 H); 2.69–2.68 (*m*, 2 H); 1.05 (*dd*, *J* = 8.2, 14.8, 2 H); 0.75 (*dd*, *J* = 6.1, 14.8, 2 H); 0.12 (*s*, 18 H). ¹³C-NMR: 74.6, 46.1, 10.3, 1.20, 1.03. GC/MS: 272 (*M*⁺), 73. Anal. calc. for C₁₂H₂₈OSi₃ (272.59): C 52.81, H 10.35; found: C 52.63, H 10.42.

cis/trans-Tetrahydro-3-methyl-4-[(trimethylsilyl)methyl]furan (**7a**). GC/MS: 157 ([*M* – 15]⁺), 99 ([*M* – 73]⁺), 73.

2. *Hydrosilylation of Hepta-1,6-diene (1b)*. As described for the reaction of **1a**. The yields of *cis/trans*-**5b**, **6b**, and **7b** reported in Scheme 2 were obtained by GC analysis using an internal standard.

cis/trans-1-Methyl-2-[[tris(trimethylsilyl)silyl]methyl]cyclopentane (*cis/trans*-**5b**). The anal. data were determined from the mixture. ¹H-NMR: *cis*-**5b**: 1.93–1.11 (*m*, 8 H); 0.94 (*dd*, *J* = 4.0, 14.3, 1 H); 0.82 (*d*, *J* = 6.9, 3 H); 0.62 (*dd*, *J* = 10.0, 14.3, 1 H); 0.17 (*s*, 27 H); *trans*-**5b**: 1.93–1.11 (*m*, 8 H); 1.20 (*dd*, *J* = 2.3, 14.1, 1 H); 0.96 (*d*, *J* = 6.3, 3 H); 0.52 (*dd*, *J* = 10.8, 14.1, 1 H); 0.17 (*s*, 27 H). ¹³C-NMR: *cis*-**5b**: 43.0, 38.4, 32.8, 32.7, 22.5, 14.9, 7.7, 1.42; *trans*-**5b**: 47.6, 44.6, 35.3, 34.3, 23.1, 18.9, 12.5, 1.40. GC/MS: 344 (*M*⁺), 271 ([*M* – 73]⁺), 73. Anal. calc. for C₁₆H₄₀Si₄ (344.84): C 55.73, H 11.69; found: C 55.83, H 11.58.

cis-3,3-Bis(trimethylsilyl)-3-silabicyclo[3.3.0]octane (**6b**): ¹H-NMR: 2.31–2.25 (*m*, 2 H); 1.79–1.66 (*m*, 3 H); 1.55–1.45 (*m*, 1 H); 1.32–1.26 (*m*, 2 H); 0.97 (*dd*, *J* = 6.2, 14.7, 2 H); 0.65 (*dd*, *J* = 8.0, 14.7, 2 H); 0.11 (*s*, 9 H); 0.09 (*s*, 9 H). ¹³C-NMR: 46.6, 33.2, 23.3, 13.1, –0.77, –0.57. GC/MS: 270 (*M*⁺), 197 ([*M* – 73]⁺), 73. Anal. calc. for C₁₃H₃₀Si₃ (270.63): C 57.69, H 11.17; found: C 57.49, H 11.16.

cis/trans-1-Methyl-2-[(trimethylsilyl)methyl]cyclopentane (**7b**). GC/MS: 170 (*M*⁺), 155 ([*M* – 15]⁺), 96 ([*M* – 73]⁺), 73.

3. *cis*-1-(Bromomethyl)-2-[[tris(trimethylsilyl)silyl]methyl]cyclopentane (**9**). Cyclization of **1b** with (pentamethylcyclopentadienyl)zirconium trichloride and sodium amalgam followed by bromination [8] afforded *cis*-1,2-bis(bromomethyl)cyclopentane (**8**) in 78% yield. A soln. of **8** (2.0 g, 7.81 mmol) in dry THF (30 ml) was cooled at –78°, and freshly prepared tris(trimethylsilyl)silyllithium [9] in THF (ca. 20 ml) was added slowly, until most of **8** was consumed. (GC control). The mixture was quenched with 2M HCl (100 ml), extracted 4 times with pentane (100 ml), dried (Na₂SO₄) and evaporated. FC (silica gel, pentane) and bulb-to-bulb distillation (100–150°/0.5 mbar) afforded **9** (2.37 g, 72%). ¹H-NMR: 3.46 (*dd*, *J* = 7.6, 9.7, 1 H); 3.34 (*dd*, *J* = 8.2, 9.7, 1 H); 2.33–2.23 (*m*, 1 H); 2.20–2.09 (*m*, 1 H); 1.87–1.36 (*m*, 6 H); 1.00 (*dd*, *J* = 2.7, 13.7, 1 H); 0.54 (*dd*, *J* = 12.3, 13.7, 1 H); 0.19 (*s*, 27 H). ¹³C-NMR: 47.4, 41.7, 35.7, 32.9, 29.2, 22.6, 6.4, 1.37. GC/MS 351, 349 ([*M* – 73]⁺). Anal. calc for C₁₆H₃₉BrSi₄ (423.72): C 45.35, H 9.28; found: C 45.51, H 9.18.

4. *Cyclization of Bromide 9*. To a soln. of **9** (101.6 mg, 0.24 mmol) and tetradecane (89.2 mg, 0.45 mmol) in 5 ml of benzene, under N₂, **2** (54 mg, 0.22 mmol) and AIBN (17.8 mg, 0.11 mmol) in 1 ml of benzene were added by syringe within 4 h. During the addition, the soln. was heated at 80°. After heating for another h, the yield was determined by GC: 88% of **6b** and 10% of **5b**.

5. *Kinetic Studies.* In a 10-ml graduated flask, **9** (423.5 mg, 1.00 mmol), tetradecane (283.5 mg, 1.43 mmol) as internal standard, and AIBN (5 mg) were dissolved in toluene, and the soln. was degassed. This 0.1M standard soln. had a density of $d = 0.865 \text{ g/cm}^3$ (20°). A small ampoule with a magnetic stirrer and a septum was degassed and filled with this 0.1M standard soln. of **9** (242–418 mg, 0.0335–0.0483 mmol) and with **2** (246–383 mg, 1.092–1.540 mmol). The tube was heated 3 h at $80 \pm 2^\circ$. After cooling, the product ratios were determined by GC (see *Table*).

Table. Product Ratios Obtained from **9** at Various Concentrations of Silane **2** at 80°

(Me ₃ Si) ₃ SiH [M]	Bromide 9 [M]	6b/cis-5b
1.33	0.0589	0.128
1.43	0.0558	0.120
1.77	0.0451	0.0938
1.90	0.0414	0.0832

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