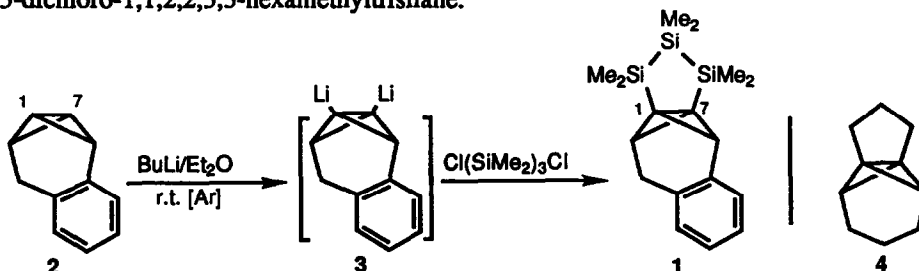


SYNTHESIS AND REACTION OF [3.1.1]TRISILAPROPELLANE

Wataru Ando,* Yoshiyuki Igarashi, Yoshio Kabe, and Norihiro Tokitoh
Department of Chemistry, University of Tsukuba
Tsukuba, Ibaraki 305, Japan

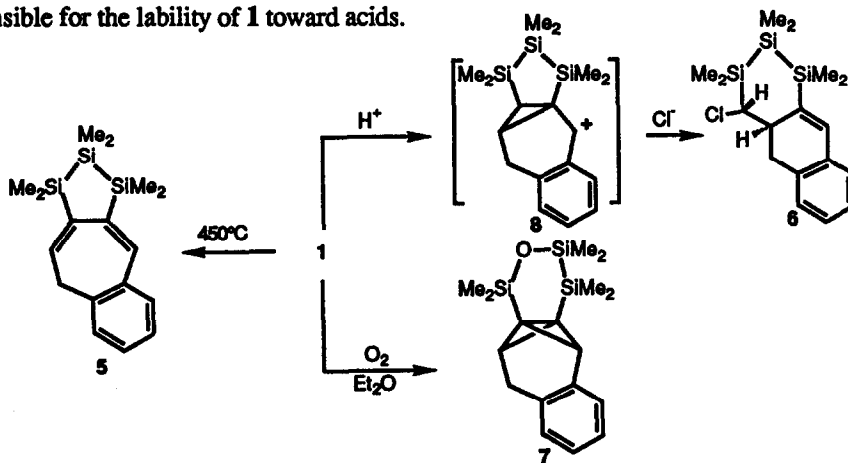
Abstract : [3.1.1]Trisilapropellane **1** which represents the first [n.1.1]silapropellanes was synthesized by treatment of the dilithiated compound **3** with dichlorohexamethyltrisilane. The propellane **1** was thermally stable, while it was labile to acidic contamination and slowly oxidized by air.

Small ring propellanes such as [n.1.1]propellanes¹⁾ have been of considerable recent interest because of the extremely high reactivity attributed to "inverted" tetrahedral geometry at the bridgehead carbons. Most derivatives of propellane have now been prepared, including the parent hydrocarbons! In contrast to rather extensive studies of [n.1.1]propellane chained by methylene unit, there is no report on the preparation of that linked by heteroatom-chains. Our continuous efforts toward the construction of the strained cyclic systems having polysilanylene unit have recently culminated in the synthesis of pentasilacycloheptyne²⁾ and heptasila[7]paracyclophane.³⁾ No mention of [n.1.1]propellanes bridged by polysilanylene chain in the literature prompted us to synthesize [n.1.1]silapropellanes. Here we wish to report the synthesis and characterization of the titled compound **1**⁴⁾ which represents the first [n.1.1]silapropellanes. Connecting the C-1 and C-7 bridgehead positions of tricyclo[4.1.0.0^{2,7}]-heptane **2** by polysilanylene bridge was achieved by the direct reaction of the dilithiated compound **3** with 1,3-dichloro-1,1,2,2,3,3-hexamethyltrisilane.

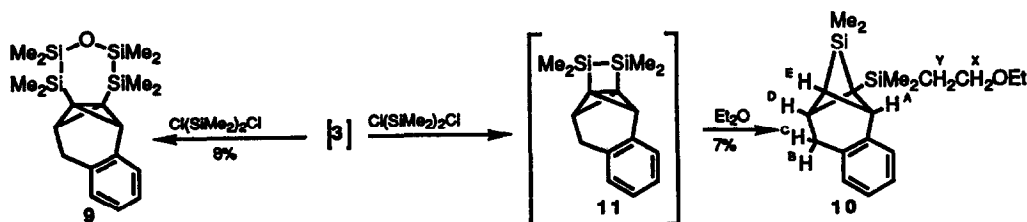


Addition of **2**⁵⁾ to BuLi in ether at room temperature provided **3** and subsequent treatment⁶⁾ with dichlorohexamethyltrisilane produced the [3.1.1]trisilapropellane **1** as a white solid (23% yield). The propellane **1** was purified by distillation under the reduced pressure (125-127°C/0.01mmHg). In the ¹H-NMR and ²⁹Si-NMR spectra of **1**, the protons of SiMe₂ appeared at 0.21, 0.23, 0.26, and 0.27 ppm and the silicon linked by SiMe₂ was shown at -18.4 ppm (middle Si), and -3.70 ppm (end Si).

From these spectra we concluded that **1** had Cs symmetry. The thermal stability of **1** was found to be significantly increased compared to the corresponding carbon analogue **4** which easily isomerizes at 0 °C.^{1b)} When a solution of **1** in C₆D₆, sealed in an NMR tube under 0.001 mmHg was kept at 190 °C for 0.5 h, no decomposition was observed by ¹H-NMR spectrum. However, under the flow pyrolytic conditions at 450 °C, **1** decomposed and finally converted into **5**⁷⁾ in 30% isolated yield.⁸⁾ On the other hand, **1** was labile to acidic contamination such as silica gel in chromatography or HCl present in CHCl₃, and quantitatively rearranged to **6**.⁹⁾ The propellane **1** was also unstable in air to form **7**.¹⁰⁾ It's likely that the intermediate leading to **6** is the cation **8**, which is doubly stabilized by cyclopropyl and silyl substitution.¹¹⁾ The cation **8** is probably attacked by chloride ion with concomitant rearrangement to homoallyl skeleton of **6**. The ease of this reaction seems to be responsible for the lability of **1** toward acids.



Wiberg et al. have shown the convincing evidence for the existence of [2.1.1]propellane in an argon matrix at 20 K via its infrared spectrum. Meanwhile, Szeimies et al. found that the lifetime of bridged [2.1.1]propellane at room temperature seems to be too short for its isolation, and the only ether-adduct was isolated along with the dimer and trimer.^{1a)} We examined the preparation of [2.1.1]disilapropellane from using a similar methodology.



When dichlorotetramethyldisilane was treated with **3** in ether, the [5.1.1]propellane **9**¹²⁾ and the ether incorporated product, conceivably having the structure **10**,¹³⁾ which is probably derived from the reaction intermediate **11** similar to carbon analogous system.¹⁴⁾ Further investigation is needed to establish structure and mechanism of ether-adduct.

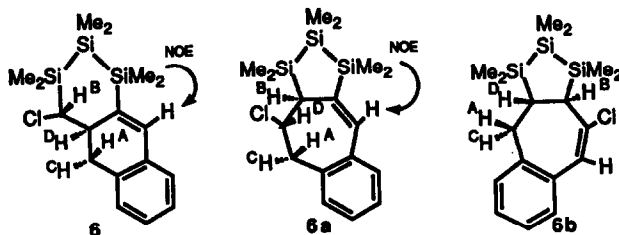
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References and Notes

- 1) Reviews for [n.1.1]propellane, a) G. Szeimies, *Strain and Its Implications in Organic Chemistry*, 1989, 361, b) K. B. Wiberg, *Chem. Rev.*, 1989, 89, 975.
- 2) W. Ando, N. Nakayama, Y. Kabe, and T. Shimizu, *Tetrahedron Letters*, in press.
- 3) W. Ando, T. Tsumuraya, and Y. Kabe, *Angew. Chem. Int. Ed. Engl.*, in press.
- 4) Trisilapropellane **1** : white solid, $^1\text{H-NMR}$ (500MHz, C_6D_6) δ 0.21 (s, 3H), 0.23 (s, 3H), 0.26 (s, 6H), 0.27 (s, 6H), 2.48 (dt, 1H, $J_{\text{AC}}=4.0\text{Hz}$, $J_{\text{BC}}=1.94\text{Hz}$), 2.71 (d, 2H, $J_{\text{BC}}=1.94\text{Hz}$), 2.92 (d, 1H, $J_{\text{AC}}=4.0\text{Hz}$), 6.79-7.15 (m, 4H), $^{13}\text{C-NMR}$ (125MHz, C_6D_6) δ -4.67 (q), -4.62 (q), -2.40 (q), -2.30 (q), 15.4 (s), 26.4 (t), 46.7 (d), 50.7 (d), 126.3 (d), 126.4 (d), 126.8 (d), 128.4 (d), 131.5 (s), 139.8 (s), $^{29}\text{Si-NMR}$ (18MHz, C_6D_6) δ -3.70, -18.4, Exact mass, found m/z 314.1361 : Calcd for $\text{C}_{17}\text{H}_{26}\text{Si}_3$ 314.1341.
- 5) I. Murata, T. Nakazawa, M. Kato, T. Tatsuoka, and Y. Sugihara, *Tetrahedron Letters*, 1975, 19, 1647 .
- 6) a) A. D. Schlüter, H. Huber, and G. Szeimies, *Angew. Chem. Int. Ed. Engl.*, 1985, 24, 404.
b) H. G. Zoch, G. Szeimies, T. Butkowskyj, M. V. Meerssche, G. Germain, and J. P. Declercq, *Chem. Ber.*, 1981, 114, 3896.
- 7) Compound **5** : colorless oil, $^1\text{H-NMR}$ (500MHz, C_6D_6) δ 0.13 (s, 6H), 0.20 (s, 6H), 0.28 (s, 6H), 3.26 (b.s, 2H), 6.80-7.30 (m, 6H), $^{13}\text{C-NMR}$ (125MHz, C_6D_6) δ -8.32 (q), -2.50 (q), -2.47 (q), 39.7 (t), 125.7 (d), 127.5 (d), 128.5 (d), 129.1 (d), 132.3 (d), 132.7 (d), 136.8 (s), 137.3 (s), 151.5 (s), 157.7 (s), $^{29}\text{Si-NMR}$ (18MHz, C_6D_6) δ -11.4, -11.5, -55.0, Exact mass, found m/z 314.1355 : Calcd for $\text{C}_{17}\text{H}_{26}\text{Si}_3$ 314.1367.
- 8) J. Belzner, G. Szeimies, *Tetrahedron Letters*, 1986, 27, 5839.
- 9) Compound **6** : colorless oil, $^1\text{H-NMR}$ (500MHz, CDCl_3) δ 0.06 (s, 3H), 0.09 (s, 3H), 0.18 (s, 3H), 0.22 (s, 3H), 0.29 (s, 3H), 0.30 (s, 3H), 2.62 (ddd, 1H, $J_{\text{AD}}=1.61\text{Hz}$, $J_{\text{BD}}=12.5\text{Hz}$, $J_{\text{CD}}=5.50\text{Hz}$), 2.75 (dd, 1H, $J_{\text{AC}}=15.5\text{Hz}$, $J_{\text{CD}}=5.50\text{Hz}$), 2.93 (d, 1H, $J_{\text{BD}}=12.5\text{Hz}$), 3.41 (dd, 1H, $J_{\text{AC}}=15.5\text{Hz}$, $J_{\text{AD}}=1.61\text{Hz}$), 6.64 (s, 1H), 7.03-7.23 (m, 4H), $^{13}\text{C-NMR}$ (125MHz, CDCl_3) δ -8.47 (q), -7.26 (q), -5.73 (q), -5.63 (q), -4.34 (q), -3.60 (q), 31.7 (t), 38.1 (d), 53.4 (d), 125.6 (d), 126.0 (d), 127.9 (d), 128.8 (d), 133.5 (s), 133.6 (s), 136.4 (d), 143.3 (s), $^{29}\text{Si-NMR}$ (18MHz, CDCl_3) δ -9.8, -19.9, -51.2, Exact mass, found m/z 350.1120 : Calcd for $\text{C}_{17}\text{H}_{27}\text{Si}_3\text{Cl}$ 350.1109.

In the C, H COSY spectrum of **6** the methylene carbon showed the cross peaks to H_A (δ 3.41) and H_C (δ 2.75). J-values of H_A , H_B , H_C , and H_D labelled in the order of increasing chemical shift

established the proton connectivity and trans relationship between H_B and H_D . A reasonable NOE between the olefin proton and protons of $SiMe_2$ (δ 0.29, δ 0.30) appeared on NOESY and NOE difference spectra, and C, H COLOC between carbon in H_D and olefin proton was indicated as long-range coupling, which is unambiguously consistent with the proposed structure 6, not with 6a, and 6b.



- 10) Compound 7 : white solid, 1H -NMR (500MHz, C_6D_6) δ 0.18 (s, 3H), 0.22 (s, 3H), 0.23 (s, 3H), 0.24 (s, 3H), 0.29 (s, 3H), 0.30 (s, 3H), 2.43 (dt, 1H, $J_{AC}=4.0Hz$, $J_{BC}=1.80Hz$), 2.72 (d, 2H, $J_{BC}=1.80Hz$), 2.88 (d, 1H, $J_{AC}=4.0Hz$), 6.81-7.15 (m, 4H), ^{13}C -NMR (125MHz, C_6D_6) δ -3.12 (q), -3.07 (q), 1.04 (q), 1.11 (q), 2.72 (q), 2.76 (q), 6.75 (s), 8.72 (s), 25.5 (t), 41.8 (d), 45.9 (d), 125.9 (d), 126.0 (d), 126.7 (d), 128.2 (d), 130.8 (s), 139.4 (s), ^{29}Si -NMR (18MHz, C_6D_6) δ -27.4, 3.6, 5.7, Exact mass, found m/z 330.1282 : Calcd for $C_{17}H_{26}Si_3O$ 330.1290, IR (KBr) 1000 (Si-O-Si).
- 11) R. T. Taylor and L. A. Paquette, *J. Org. Chem.*, 1978, 43, 242.
- 12) Compound 9 : white solid, 1H -NMR (500MHz, C_6D_6) δ 0.17 (s, 6H), 0.22 (s, 6H), 0.28 (s, 6H), 0.31 (s, 6H), 2.40 (dt, 1H, $J_{AC}=4.0Hz$, $J_{BC}=1.63Hz$), 2.76 (d, 2H, $J_{BC}=1.63Hz$), 2.84 (d, 1H, $J_{AC}=4.0Hz$), 6.80-7.13 (m, 4H), ^{13}C -NMR (125MHz, C_6D_6) δ -2.56 (q), -2.52 (q), 3.05 (q), 9.63 (s), 25.6 (t), 41.3 (d), 45.5 (d), 125.9 (d), 126.0 (d), 126.7 (d), 128.3 (d), 130.5 (s), 139.6 (s), ^{29}Si -NMR (18MHz, C_6D_6) δ 6.86, -19.3, Exact mass, found m/z 388.1518 : Calcd for $C_{19}H_{32}Si_4O$ 388.1529, IR (KBr) 1000 (Si-O-Si).
- 13) Compound 10 : colorless oil, 1H -NMR (500MHz, C_6D_6) δ 0.13 (s, 3H), 0.14 (s, 3H), 0.23 (s, 6H), 0.85 (t, 3H, $J=7.0Hz$), 1.30 (q, 2H, $J=7.0Hz$), 1.45 (t, 2H, $J_{XY}=6.50Hz$), 2.01 (t, 1H, $J_{AE}=J_{DE}=2.40Hz$), 2.36 (q, 1H, $J_{BD}=J_{CD}=J_{DE}=2.40Hz$), 2.66 (dd, 1H, $J_{BC}=17.5Hz$, $J_{CD}=2.40Hz$), 2.68 (dd, 1H, $J_{BC}=17.5Hz$, $J_{BD}=2.40Hz$), 2.76 (d, 1H, $J_{AE}=2.40Hz$), 3.51 (t, 2H, $J_{XY}=6.50Hz$), 6.82-7.12 (m, 4H), ^{13}C -NMR (125MHz, C_6D_6) δ -4.17 (q), -4.10 (q), -0.16 (q), -0.14 (q), 0.84 (s), 11.7 (d), 14.0 (q), 19.3 (t), 24.9 (t), 35.3 (t), 39.2 (d), 43.2 (d), 63.4 (t), 125.8 (d), 126.5 (d), 127.1 (d), 128.3 (d), 130.8 (s), 138.9 (s), ^{29}Si -NMR (18MHz, C_6D_6) δ -22.2, 13.2, Exact mass, m/z 330.1828 : Calcd for $C_{19}H_{30}Si_2O$ 330.1834.
- 14) J. Morf and G. Szeimies, *Tetrahedron Letters*, 1986, 27, 5363.

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