Synthesis and Reactivity of [3.1.1] and [2.1.1]Silapropellanes

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Abstract; The dilithiated compound 3 reacted with 1, 3-dichlorotrisilane to give [3.1.1]trisilapropellane 1 as a stable form. The reaction of 3 with 1, 2-dichlorodisilane gave the ether-incorporated product 9 through [2.1.1]disilapropellane 13. Reductive coupling of the bissilylated tricyclo $[4.1.0.0^{2,7}]$ heptane 23a also provided [3.1.1]disiloxapropellane 25 via the intermediate of [2.1.1]disilapropellane 24a. The compounds 1 and 25 show an unique reactivity in the presence of acid to give 7 and 27. The structures of 7 and 27 sharing common ring system have been determined by 2D-NMR and X-ray crystal analysis, respectively. Theoretical studies are also carried out by MNDO method.

Introduction

The name of propellane was proposed by Ginsburg for the compound having three nonzero bridges and one zero bridge between a pair of bridgehead carbons. The small ring propellanes have the interesting characteristic of having an "inverted" tetrahedral geometry at the bridgehead carbons. Within the group of small ring propellanes, [n.1.1]propellanes have doubtlessly attracted most attention.¹⁾ Most derivatives of propellane have now been prepared, including the parent hydrocarbons! In contrast to rather extensive studies of [n.1.1]propellane²⁾ 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 pentasilacycloheptyne,³⁾ heptasila[7]paracyclophane,⁴⁾ and trisilabicyclo[1.1.1]pentane.⁵⁾ We also reported the formation of [3.1.1]trisilapropellane 1 by the reaction of the dilthiated compound 3 of tricyclo[4.1.0.0^{2,7}]heptane 2 with 1, 3-dichlorotrisilane.⁶⁾ Here we wish to report further study of the synthesis of [n.1.1]silapropellane's derivatives (n=1, 2) as well as some chemical reaction and MNDO calculation.

Results and Discussion

1: Synthesis of [3.1.1]trisilapropellane 1. Addition of 2^{7} to BuLi in ether at room temperature provided the dilithiated compound 3^{8}) and subsequent treatment with 1, 3-dichlorohexamethyltrisilane produced the [3.1.1]trisilapropellane 1 as a white solid in 23 % yield. In the ¹H-NMR and ²⁹Si-NMR spectra of 1, the proton of SiMe₂ was shown at 0.21, 0.23, 0.26, and 0.27 ppm, the silicon linked by SiMe₂ was shown at -18.4 ppm (center Si), and -3.70 ppm (end Si). These spectra indicates the structure of Cs symmetry. The thin plate in crystal shape of 1 was not suitable for X-ray crystal analysis.



Reactivity of [3.1.1]trisilapropellane 1. The active site of [3.1.1]trisilapropellane 1 is expected on the bridgehead carbon and Si-Si bond. The propellane 1 was oxidized by air to afford 5 in solution. The thermal stability of 1 was found to be significantly increased compared to the corresponding carbon analogue 4 which was unstable at $0 \, {}^{\circ}C.^{9)}$ When a solution of 1 in C_6D_6 , sealed in an NMR tube under 0.001 mmHg was kept at 190 °C for 0.5h, no decomposition was observed by ¹H-NMR spectrum. However, under the flow pyrolytic conditions at 450 °C,¹⁰⁾ 1 was converted into 6 in 30 % isolated yield. On the other hand, 1 was decomposed to acidic contamination such as silica gel in chromatography, and labile to HCl present in CHCl₃ to quantitatively give 7 presumably via cation 8.¹¹) The cation 8 is probably attacked by chloride ion with concomitant rearrangement to homoallyl skeleton of 7. The stabilization of 8 by cyclopropyl and silyl groups seems to be responsible for the lability of 1 toward acids. The C, H COSY spectrum of compound 7 showed the methylene



carbon with the cross peaks at H_A (δ 3.41) and H_C (δ 2.75) (see Figure 1a). The 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 (see Figure 1c). A reasonable NOE between the olefin proton and protons of SiMe₂ (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 (see Figure 1b), which is unambiguously consistent with the proposed structure 7, not with 7a and 7b.



Figure 1 a) C,H COSY spectrum of 7, b) C, H COLOC spectrum of 7, c) ¹H-NMR methylene and methine region of 7.

Photolysis of [3,1,1]trisilapropellane 1 in ether solution was carried with a low pressure mercury lamp in quartz tube under argon atmosphere for 5 h.¹²) After volatile compounds were distilled under reduced pressure followed by preparative HPLC, the compounds 9 and 10 were isolated in a trace amount. Interestingly, replacing the solvent from ether to diethyl sulfide and ethanol, the compounds 11 and 12 were obtained in 17 and 13 % yields, respectively. With the inspection of environment of SiMe groups, it would be elucidated whether the reaction proceeded on bridgehead carbons or Si-Si bonds. In the ¹H-NMR spectrum, six distinct signals assigned to SiMe of compounds 11 and 12 were observed. In contrast, ¹H-NMR spectrum of compounds 9 and 10 exhibited only three singlets assigned to SiMe in ratio 1:1:2. These data required that compounds 11 and 12 retained three SiMe₂ groups in ring system, and one of two SiMe₂ groups in compounds 9 and 10 was held in ring system, and the other SiMe₂ group split out of ring. The similarity of ¹H, ¹³C, and ²⁹Si-NMR spectra, especially high-field carbons at 0.84 ppm (quaternary bridgehead carbons substituted by two silvl groups), established that compound 10 shared common skeleton with 9. The formation of compounds 9 and 10 may involve the intermediate of [2.1.1] disilapropellane 13, formed by silvlene extrusion of [3.1.1]trisilapropellane 1. The detailed NMR of 9 will be shown in the following section. The introduction of ethylthic or ethoxy group gave not only two nonequivalent benzylic protons, but also five protons spin-relaying systems in the 1 H-NMR spectrum of compounds 9-11. With the respect of 11 and 12, assignments of proton connectivity and C-H correlation by H, H and C, H COSY spectra established the structures. As the 12 has three membered ring, it's characteristics to be shown at -0.1 and 1.11 ppm in ¹H-NMR spectrum. According to the elucidated structures of 11 and 12, ethanethiol adds to a central carbon-carbon bond of [3.1.1]trisilapropellane 1, while ethanol adds into external carbon-carbon bond of [3.1.1]trisilapropellane 1.







2: Attempted synthesis of [2.1.1]disilapropellane. [2.1.1]Propellane was reported to be very unstable, and only the convincing evidence for existence of [2.1.1]propellane was found in an argon matrix at 20 K via its infrared spectrum.¹³) Meanwhile, Szeimies et al.

studied the lifetime of bridged [2.1.1]propellane 14 at room temperature, but 14 was too unstable for its isolation, and the only ether-adduct 15 was isolated along with the dimer and trimer.⁹⁾ We examined the preparation of [2.1.1]disilapropellane 13 by the reaction of 1, 2dichlorotetramethyldisilane with 3 in ether, and found the formation of the [5.1.1]propellane 16 and the ether incorporated product, conceivably having the structure 9, which was probably derived from the reaction intermediate 13 similar to carbon analogous system. However, the mode of ether-incorporation was different from that of carbon analogous system. The H, H COSY spectrum of compound 9 showed the methylene protons as the cross peaks between H_Y (δ 1.45) and H_X (δ 3.51) (J_{XY}=6.5 Hz). These data suggested that compound 9 possessed 2-ethoxyethyl group, not 1-ethoxyethyl group. The three ¹H-NMR signals were shown at 0.13, 0.14, and 0.23 ppm in a ratio 1:1:2, while two signals in ²⁹Si-NMR were observed with fairly different chemical shifts (-21.4 ppm, and 13.2 ppm). These data led to the conclusion that 9 possessed the silyl substituted silabicyclo[1.1.1]pentane skeleton, not disila[2.1.1]bicyclohexane skeleton, shown in the following scheme. This conclusion is also evidenced by a high-field quaternary bridgehead carbon (0.84 ppm) detected by C, H COLOC



spectrum. Although there are several mechanistic possibilities, the unique rearrangement of 1,2-silyl shift may proceed through the intermediate of bissilene 17 or biradical 18 to produce silyl radical 19. Meanwhile, the radical disproportionation of ether affording vinyl ether was initiated by biradicals (18 or 19), finally silyl radical 19 added to vinyl ether.

In the hope of stabilizing the intermediate 13 by bulky substituent, the dilithiated compound 3 was treated with 1, 2-dichlorotetraisopropyl- or tetraphenyldisilane, but no coupling products were formed. Therefore we chose alternative route, which consisted of bis-silylation of 3 with monohydrosilanes followed by chlorination and reductive coupling. The selection of substituent R was important. The reductive coupling reaction of compound 23b was complicated for methyl group (R=Me), and the chlorination of Si-H on mesityl group 22c (R=Mes) could not complete by means of BPO/CCl₄ and PdCl₂/CCl₄. Chlorine was used as chlorinating reagent, but the reaction proceeded vigorously to give unidentified products. Fortunately, the chlorination of compound 22a (R=Ph) by the addition of PdCl₂/CCl₄ at room temperature gave 23a in quantitative yield. Then the resulting 23a was introduced to Na/K dispersion in toluene at room temperature.¹⁴⁾ Purification of the reaction mixture by preparative HPLC provided sets of products with varying eluates. The compounds 26 and 27 were isolated with CHCl₃ as an elution solvent in 6 and 7 % yields, respectively, The compounds 28 and 25 were isolable with toluene as an elution solvent in 11 and ca. 0.5 % The structures of those compounds have been identified by ¹H, ¹³C, vields, respectively.



²⁹Si -NMR, and Mass spectroscopy. Especially IR absorptions in the region of 1000-1150 cm^{-1} and 3400-3450 cm^{-1} for 25-28 were assigned as SiOSi and SiOH groups. The ¹H-NMR, and ¹³C-NMR spectra of 27 were very close to those of 7. Furthermore the compound 27 would be formed through similar rearrangement of [3,1,1]disiloxapropellane 25. The molecular ring system and stereochemistry of 27 are the same as that of 7 except the Si-O-Si linkage. Fortunately, the recrystallization of 27 in hexane-benzene yielded well-formed prisms to serve X-ray crystal analysis. The molecule crystallized as benzene solvate in space group P1bar : An ORTEP drawing is shown in Figure 3 together with bond distances and dihedral angles of three rings. The inspection of the structures of 25-28 left little doubt that 26-28 was formed at the expense of unstable [3.1.1]disiloxapropellane 25. When 25 was exposed into preparative HPLC, 26 and 27 were produced in CHCl₃, and 28 was produced in Toluene. The compound 25 might be obtained by oxidation of [2.1.1]disilapropellane 24a, since 23a was not easily hydrolyzed to 25 in water, and compound 28 was not converted to 25 in refluxing benzene. An ¹H-NMR spectrum of reaction mixture, obtained with strict exclusion of water and oxygen, revealed that none of compounds 25-28 are present prior to work up. However, the complexity of the mixture does not permit unambiguous identification of intermediate 24a and thus alternative explanations that could account for the formation of product 25-28 cannot be rejected.



Figure 3 ORTEP drawing of 27. Selected Bond Distances (Å) and Dihedral Angles (Deg) : Si(1)-O, 1.637(2); Si(2)-O, 1.640(2); Si(1)-C(3), 1.899(4); Si(2)-C(4), 1.858(3); C(3)-Cl, 1.821(3); C(2)-C(3), 1.537(5); C(1)-C(2), 1.529(5); C(2)-C(4), 1.532(4). C(11)-C(12)-C(13)-C(14)-C(15)-C(16) // C(2)-C(1)-C(11)-C(16)-C(5)--C(4), 11.58; C(2)-C(1)-C(11)-C(16)-C(5)-C(4) // C(2)-C(3)-Si(1)-O--Si(2)-C(4), 49.06.

With the inspection of ORTEP drawing of 27, the three six-membered rings were fused in diagonal direction. The planes of C11-C12-C13-C14-C15-C16 and C1-C2-C4-C5-C16-C11 were almost coplanner, but plane C2-C3-Si1-O-Si2-C4 was pseudo boat style slipping out the other two planes. This ring system, and orientation of double bond as well as trans configuration of H2 and H3 were in agreement with the structure of 7 determined from NMR technique. The C4-Si2 bond was slightly shorter than the C3-Si1 bond.

Lastly, the reaction of 3 with dimesithyldichlorosilane failed to get [1.1.1]silapropellane instead of the formation of Si-alkylation product. So far three-membered rings containing silicon and two carbons, i. e. siliranes have never been prepared by this route, 15 while Szeimies et al. succeeded in synthesis of [1.1.1]propellane using similar route. 16

3: MNDO Calculations of [n.1.1]Silapropellanes. In order to understand reactivity of [n.1.1]silapropellanes in contrast to the corresponding carbon analogous, [n.1.1]propellanes,²⁾ we calculated orbital energy, energy of two-center terms, enthalpy of these propellanes by MNDO method, taking the experimental results into consideration. Calculation was performed using the MOPAC Ver. 5 program.¹⁷)



Table 1 MNDO Energy Level Calculation of [n.1.1] silapropellanes and [n.1.1]propellanes a) The energy values of non-bridged [n.1.1]silapropellanes bearing SiMe₂ groups

shown in parenthesis.

b) The energy values of non-bridged [n.1.1]propellanes shown in parenthesis.

[2.1.1]Disilapropellane is found to have relatively high HOMO energy level, and are small difference of energy level between HOMO and LUMO, shown in Table 1. This result indicates that [2.1.1]disilapropellane acts as either of electron donor and acceptor, and the radical reaction might occur. This accords with the formation of ether adduct 9 via free radical reaction mechanism. What the order of HOMO energy level in [n.1.1]silapropellanes is [3.1.1] < [1.1.1] < [2.1.1] agrees with only successful isolation of [3.1.1]trisilapropellane 1. The order of HOMO energy level in [n.1.1]propellanes is [1.1.1] < [2.1.1], and correlated with thermal stability of these [n.1.1]propellanes in practice.



Table 2 The energy of two-center terms of [n.1.1]silapropellanes (upper) and energy of two-center terms of [n.1.1]propellanes (bottom) with HOMO orbitals

From the energy of two-center terms, we found that [n.1.1] silapropellanes would be able to easily cleave and react in the place of both bridgehead carbon and silicon-silicon bond. So we thought that reaction of [2.1.1] disilapropellane was complicated in contrast to one of [2.1.1] propellane.⁹

Experimental

¹H-, ¹³C-, and ²⁹Si-NMR spectra were recorded on a JEOL JNN-PMX-60SI, a JEOL FX-90Q, and a Bruker AM-500 spectrometer. Chemical shifts were shown in parts per million (ppm) relative to internal tetramethylsilane as 0 ppm. IR and mass spectra were obtained on a Hitachi 260-50 and a Hitachi RMU-6M spectroscopy, respectively. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-D300 mass spectrometer. Preparative HPLC was carried out on a LC-08 (Japan Analytical Ind. Co., LTD.). Preparative gas chromatographic separations were carried out on an Ohkura Model-802 using a 8 mm x 1.8 m glass column of 2 % Silicone OV-1 on 60/80 mesh Uniport HP. H, H NOESY, C, H COSY, C, H COLOC, ¹H-NOE spectra were observed on the Bruker AM-500. All melting points were uncorrected.

Materials 4, 5-Benzotricyclo[$4.1.0.0^{2,7}$]heptane 2,⁷) octamethyltrisilane,¹⁸) 1, 3dichlorohexamethyltrisilane,¹⁹) hexamethyldisilane,²⁰) 1, 2-dichlorotetramethyldisilane,¹⁹) and diphenylchlorosilane²¹) were synthesized according to the literature procedures. Other materials were commercially available and purified before use.

Synthesis of [3.1.1]Trisilapropellane 1. To ether (5.0 ml) solution of BuLi (7.2 mmol) 4, 5-benzotricyclo[4.1.0.0^{2,7}]heptane 2 (426 mg, 3.0 mmol) was added, and stirred at room temperature for 24 h. This suspension of dilithiated compound 3 and ether (5.0 ml) solution of 1, 3-dichlorohexamethyltrisilane (735 mg, 3.0 mmol) were simultaneously added to 15 ml of ether solution under N₂ over 1h at room temperature, and stirred for 24 h. After concentrated, addition of hexane and filtration through Celite, followed by removal of solvent in vacuo provided a viscous brown oil. The product 1 from this reaction mixture was distilled under reduced pressure by Kugel Rohr (125-127 °C / 0.01 mmHg) as a white solid in 23 % yield. 1 : m. p. 125-127 °C ; ¹H-NMR (500 MHz, C₆D₆) δ 0.21 (s, 3H), 0.23 (s, 3H), 0.26 (s, 6H), 0.27 (s, 6H), 2.48 (dt, 1H, J_{AC}=4.0 Hz, J_{BC}=1.94 Hz), 2.71 (d, 2H, J_{BC}=1.94 Hz), 2.92 (d, 1H, J_{AC}=4.0 Hz), 6.79-7.15 (m, 4H) ; ¹³C-NMR (125 MHz, C₆D₆) 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) ; ²⁹Si-NMR (18 MHz, C₆D₆) δ -3.70, -18.4 ; Exact mass, found m/z 314.1361 : Calcd for C₁₇H₂₆Si₃ 314.1341.

Flow pyrolysis of 1. The flow pyrolysis of hexane (50 ml) solution of 1 (50 mg, 0.16 mmol) at 450 °C under N₂ was converted into 6. The compound 6 was purified by Al₂O₃ TLC from hexane as an elution solvent, and obtained in 30 % yield. 6 : colorless oil; ¹H-NMR (500 MHz, C₆D₆) δ 0.13 (s, 6H), 0.20 (s, 6H), 0.28 (s, 6H), 3.26 (b.s., 2H), 6.80-7.30 (m, 6H); ¹³C-NMR (125 MHz, C₆D₆) 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); ²⁹Si-NMR (18 MHz, C₆D₆) δ -11.4, -11.5, -55.0; Exact mass, found m/z 314.1355 : Calcd for C₁₇H₂₆Si₃ 314.1367.

Reaction of 1 with acid. The compound 1 (50 mg, 0.16 mmol) was stirred in CHCl₃ for 3 h at room temperature to form 7 quantitatively. The 7 was purified by HPLC. 7 : colorless oil ; ¹H-NMR (500 MHz, CDCl₃) 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_{AD}=1.61 Hz, J_{BD}=12.5 Hz, J_{CD}=5.50 Hz), 2.75 (dd, 1H, J_{AC}=15.5 Hz, J_{CD}=5.50 Hz), 2.93 (d, 1H, J_{BD}=12.5 Hz), 3.41 (dd, 1H, J_{AC}=15.5 Hz, J_{AD}=1.61 Hz), 6.64 (s, 1H), 7.03-7.23 (m, 4H); ¹³C-NMR (125 MHz, CDCl₃) 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) ; ²⁹Si-NMR (18 MHz, CDCl₃) δ -9.8, -19.9, -51.2 ; Exact mass, found m/z 350.1120 : Calcd for C₁₇H₂₇Si₃Cl 350.1109.

Oxygenation of 1. The compound 1 (50 mg, 0.16 mmol) was stirred in Et₂O under O₂ for 30 h to form siloxy compound 5. The 5 was purified by Al₂O₃ TLC (hexane as an elution solvent), and isolated in 30 % yield. 5 : white solid ; m. p. 60-61 *C; ¹H-NMR (500 MHz, C₆D₆) 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}=4.0 Hz, J_{BC}=1.80 Hz), 2.72 (d, 2H, J_{BC}=1.80 Hz), 2.88 (d, 1H, J_{AC}=4.0 Hz), 6.81-7.15 (m, 4H) ; ¹³C-NMR (125 MHz, C₆D₆) 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) ; ²⁹Si-NMR (18 MHz, C₆D₆) δ -27.4, 3.6, 5.7 ; Exact mass, found m/z 330.1282 : Calcd for C₁₇H₂₆Si₃O 330.1290 ; IR (KBr) 1000 cm⁻¹ (Si-O-Si) ; The 1 was stable in solid condition, and 1 could not be oxidized, however, 1 could be slowly oxidized by air in solution condition.

Attempted Synthesis of [2.1.1]Disilapropellane. The ether (5.0 ml) solution of the dilithiated compound 3 (3.0 mmol) and the ether (5.0 ml) solution 1,2dichlorotetramethyldisilane (561 mg, 3 mmol) were simultaneously added to 15 ml ether under N₂ over 1 h at room temperature, and stirred overnight. After concentrated, addition of hexane and filtration through Celite, followed by removal of solvent in vacuo provided a viscous brown oil. The volatile part from the reaction mixture was obtained as colorless oil under reduced pressure (110-120 °C / 0.01 mmHg). This volatile part was separated by HPLC. The

ether-adduct 9 and siloxane 16 were obtained in 7 % and 8 %, respectively. 9 : colorless oil; ¹H-NMR (500 MHz, C_6D_6) δ 0.13 (s, 3H), 0.14 (s, 3H), 0.23 (s, 6H), 0.85 (t, 3H, J=7.0 Hz), 1.30 (q, 2H, J=7.0 Hz), 1.45 (t, 2H, J_{XY} =6.50 Hz), 2.01 (t, 1H, J_{AE} = J_{DE} =2.40 Hz), 2.36 (q, 1H, J_{BD} = J_{CD} = J_{DE} =2.40 Hz), 2.66 (dd, 1H, J_{BC} =17.5 Hz, J_{CD} =2.40 Hz), 2.68 (dd, 1H, J_{BC} =17.5 Hz, J_{BD} =2.40 Hz), 2.76 (d, 1H, J_{AE} =2.40 Hz), 3.51 (t, 2H, J_{XY} =6.50 Hz), 6.82-7.12 (m, 4H) ; ¹³C-NMR (125 MHz, C₆D₆) δ -4.17 (q), -4.10 (q), -0.12 (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) ; ²⁹Si-NMR (18 MHz, C₆D₆) δ -21.4, 13.2 ; Exact mass, m/z 330.1828 : Calcd for C₁₉H₃₀Si₂O 330.1834. 16 : white solid ; m. p. 69-71 °C; ¹H-NMR (500 MHz, C₆D₆) δ 0.17 (s, 6H), 0.22 (s, 6H), 0.28 (s, 6H), 0.31 (s, 6H), 2.40 (dt, 1H, J_{AC} =4.0 Hz, J_{BC} =1.63 Hz), 2.76 (d, 2H, J_{BC} =1.63 Hz), 2.84 (d, 1H, J_{AC} =4.0 Hz), 6.80-7.13 (m, 4H) ; ¹³C-NMR (125 MHz, C₆D₆) 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) ; ²⁹Si-NMR (18 MHz, C₆D₆) δ 6.86, -19.3 ; Exact mass, found m/z 388.1518 : Calcd for C₁₉H₃₂Si₄O 388.1529 ; IR (KBr) 1000 cm⁻¹ (Si-O-Si). Synthesis of 22a. The diphenylchlorosilane (2.7 g, 12 mmol) was added to ether (30 ml) solution of the dilithiated 3 (6 mmol) formed from 2 (852 mg, 6 mmol) and BuLi (14 mmol), and the reaction mixture was stirred at room temperature for 10 h. The reaction mixture was quenched with 15 ml of water, and the aqueous layer was extracted with ether (20 ml x 3). The combined organic phase was dried over MgSO₄. After removal of solvent at reduced pressure, the residual brown oil was chromatographed on a 3 cm by 15 cm column of alumina (deactivated with 5% of water) and eluted with hexane. Evaporation of the solvent yielded a white solid, which was purified by recrystallization from hexane in 38% yield (1.15 g). 22a

: white solid; m. p. 90-92 °C; ¹H-NMR (500 MHz, C_6D_6) δ 2.44 (q, 1H, J_{AC} =4.0 Hz, J_{BC} =2.0 Hz), 2.73 (b.s, 2H), 2.93 (d, 1H, J_{AC} =4.0 Hz), 5.61 (s, 2H), 6.79- 7.13 (m, 16H), 7.56-7.58 (m, 8H); ¹³C-NMR (125 MHz, C_6D_6) δ 7.45 (s), 24.8 (t), 41.6 (d), 45.6 (d), 126.2 (d), 126.3 (d), 127.1 (d), 128.1 (d), 128.4 (d), 129.9 (d), 130.4 (s), 134.1 (s), 135.9 (d), 138.2 (s). ²⁹Si-NMR (18 MHz, C_6D_6) δ -15.9; Mass m/e 506 (M⁺).

Chlorination of 22a. PdCl₂ (88.7 mg, 0.5 mmol) was added to CCl₄ solution of **22a** (254 mg, 0.5 mmol) at room temperature for 3 h under N₂. After concentrated, addition of hexane and filtration through a Celite, followed by removal of solvent in vacuo provided a white solid quantitatively. This solid was purified with hexane, and used in the following reaction. **23a**: ¹H-NMR (500 MHz, C₆D₆) δ 2.11 (b.s, 1H), 2.67 (b.s, 2H), 3.21 (d, 1H, J=4.0 Hz), 6.80-7.13 (m, 16H), 7.63-7.68 (m, 8H); ¹³C-NMR (125 MHz, C₆D₆) δ 12.8 (s), 24.3 (t), 41.0 (d), 44.9 (d), 126.5 (d), 126.8 (d), 127.4 (d), 128.0 (d), 128.2 (d), 128.4 (d), 130.2 (s), 130.7 (d), 130.8 (d), 133.6 (s), 133.7 (s), 135.1 (d), 135.3 (d), 136.8 (s); ²⁹Si-NMR (18 MHz, C₆D₆) d 5.69; Mass m/e 574 (M⁺).

Reductive coupling reaction of 23a. The toluene (2 ml) solution of 23a (287 mg, 0.5 mmol) was added to toluene (2.0 ml) of Na/K (7 mg, 0.3 mmol) / (35 mg, 0.9 mmol) at room temperature, and the reaction mixture was stirred for 10 h under N2. Addition of hexane and filtration through a Celite, followed by removal of solvent in vacuo provided a viscous white solid. The reaction mixture was separated by HPLC. (a): With CHCl₃ as an elution solvent, the products were 26 and 27 in 6 % and 7 % yields, respectively. 26 : colorless oil; ¹H-NMR (500 MHz, C_6D_6) δ 1.11 (t, 3H, J_{XY} =5.0 Hz), 2.61 (dt, 1H, J_{AD} =4.0 Hz, $J_{BD}=J_{CD}=2.2$ Hz), 2.68 (dd, 1H, $J_{BC}=16.5$ Hz, $J_{CD}=2.2$ Hz), 2.74 (dd, 1H, $J_{BC}=16.5$ Hz, $J_{BD}=2.2$ Hz), 3.15 (d, 1H, $J_{AD}=4.0$ Hz), 3.55 (q, 2H, $J_{XY}=5.0$ Hz), 4.83 (s, 1H), 6.82-7.13 (m, 16H), 7.57-7.85 (m, 8H); ¹³C-NMR (125 MHz, C₆D₆) δ 9.71 (s), 11.2 (s), 18.0 (q), 24.8 (t), 42.1 (d), 45.7 (d), 60.8 (t), 126.2 (d), 126.3 (d), 126.9 (d), 128.06 (d), 128.1 (d), 128.26 (d), 128.3 (d), 128.4 (d), 129.8 (d), 129.9 (d), 130.4 (d), 130.5 (d), 130.6 (s), 133.5 (s), 133.6 (s), 134.9 (d), 135.0 (d), 135.5 (d), 135.6 (d), 136.9 (s), 137.0 (s), 138.2 (s); ²⁹Si-NMR (18 MHz, C₆D₆) δ -9.25, -3.63; IR (KBr) 3400 cm⁻¹; Exact mass, found m/z 566.2102 : Calcd for C37H34Si2O2 566.2107. 27 : white solid ; m. p. 179-181 °C; ¹H--NMR (500 MHz, C_6D_6) § 3.07 (dd, 1H, J_{BD} =7.47 Hz, J_{CD} =16.0 Hz), 3.12 (dd, J_{BC} = 6.40 Hz, J_{CD} =16.0 Hz), 3.39 (ddd, J_{AB} =13.2 Hz, J_{BC} =6.40 Hz), J_{BD} =7.47 Hz), 3.85 (d, 1H, J_{AB} =13.2 Hz), 6.62-7.25 (m, 16H), 7.69-7.90 (m, 8H); ¹³C-NMR (125 MHz, C₆D₆) δ 31.2 (1), 40.9 (d), 49.1 (d), 127.1 (d), 127.4 (d), 128.1 (d), 128. 4 (d), 128.5 (d) 128.6 (d), 128.8 (d), 129.2 (d), 130.6 (s), 130.7 (d), 130.8 (d), 132.6 (s), 133.1 (s), 133.8 (s), 134.7 (s), 134.9 (s), 135.1 (d), 135.4 (d), 135.6 (d), 136.4 (d), 137.0 (s), 142.3 (d) ; ²⁹Si-NMR (18 MHz, C₆D₆) δ -12.6, -14.4; IR (KBr) 1000 cm⁻¹; Exact mass, found m/z 556.1447: Calcd for C35H29Si2ClO 556.1448.

X-Ray Crystal Analysis for 27. The crystals were triclinic, with a=9.406(7) Å, b=10.996(2) Å, c=16.453(9) Å, α =100.227(2)°, β =95.477(9)°, γ =107.047(2)°, V=1581.5 Å³, space group P1bar, Z=2, μ (Mok α)=2.2 cm⁻¹, ρ calkd=1.17 g/cm³, 5585 reflection. The size of crystal used for data colection was approximately 0.4 x 0.5 x 0.5 mm. The 3674 independent reflection [2 θ < 50°; IFo²I >3 σ IFo²I] were measured on an Enraf Nonius CAD4 diffractometer using MoK α irradiation and ω -2 θ scan. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically and hydrogen atoms refined with fixed thermal parameters to R=0.043 and Rw=0.045.

(b) With Toluene as an elution solvent, the product was 25 and 28 in 0.5 % and 11 % yields, respectively. 25 : ¹H-NMR (500 MHz, C_6D_6) δ 2.64 (s, 2H), 2.70 (d, 1H, J=4.0 Hz), 3.10 (d, 1H, J=4.0 Hz), 6.78-7.13 (m, 16H), 7.75-7.91 (m, 8H) ; ¹³C-NMR (125 MHz, C_6D_6) δ 11.4 (s), 24.8 (t), 43.3 (d), 46.9 (d), 126.2 (d), 126.5 (d), 127.0 (d), 128.2 (d), 128.3 (d), 128.4 (d), 130.2 (d), 130.3 (d), 130.5 (s), 135.0 (d), 135.1 (d), 135.8 (s), 135.9 (s), 137.8 (s) ; ²⁹Si-NMR (18 MHz, C_6D_6) δ -9.46 ; IR (KBr) 1150-1000 cm⁻¹ ; MS m/e 520 (M⁺). 28: white solid ; m. p. 168-170 °C; ¹H-NMR (500 MHz, C_6D_6) δ 2.58 (d, 1H, J=4.0 Hz), 2.70 (s, 2H), 3.11 (d, 1H, J=4.0 Hz), 4.35 (b.s, 2H), 6.82-7.13 (m, 16H), 7.64-7.77 (m, 8H) ; ¹³C-NMR (125 MHz, C_6D_6) δ 10.5 (s), 24.8 (t), 42.1 (d), 45.7 (d), 126.2 (d), 126.3 (d), 127.0 (d), 128.1 (d), 128.2 (s) ; ²⁹Si-NMR (18 MHz, C_6D_6) d -7.06 ; IR (KBr) 3450 cm⁻¹ ; Mass m/e 538 (M⁺)

(a) An ether (5.0 ml) solution of 1 (100 mg, 0.32 mmol) was Photolysis of 1. irradiated with low pressure mercury lamp in quartz tube under argon atmosphere for 5 h. After concentrated, the reaction mixtures were separated by HPLC (toluene as an elution solvent). Besides the 1 (30 mg) was recovered, oligomer which was unknown was main product, so 9 and 10 were obtained in only a trace. 10: colorless oil; ¹H-NMR (500 MHz, C₆D₆) δ 0.11 (s, 3H), 0.12 (s, 3H), 0.21 (s, 6H), 1.06 (t, 3H, J=7.0 Hz), 2.01 (t, 1H, $J_{AE}=J_{DE}=2.2$ Hz), 2.35 (q, 1H, $J_{BD}=J_{CD}=J_{DE}=2.2$ Hz), 2.63 (dd, 1H, $J_{BC}=16.5$ Hz, $J_{CD}=2.2$ Hz), 2.68 (dd, 1H, $J_{BC}=16.5$ Hz, $J_{BD}=2.2$ Hz), 2.75 (d, 1H, $J_{AE}=2.2$ Hz), 3.50 (q, 2H, J=7.0 Hz), 6.80-7.11 (m, 4H); 13 C-NMR (125 MHz, C₆D₆) δ -4.15 (q), -4.08 (q), -0.07 (q), 0.84 (s), 11.7 (d), 18.9 (q), 24.9 (t), 39.2 (d), 43.1 (d), 59.3 (t), 125.9 (d), 126.0 (d), 127.5 (d), 128.4 (d), 130.9 (s), 138.9 (s); 29 Si-NMR (18 MHz, C₆D₆) δ 13.0, -22.2; Mass m/e $302 (M^+)$. (b) A diethyl sulfide (10 ml) solution of 1 (200 mg, 0.66 mmol) was irradiated with low pressure mercury lamp in quarts tube under argon atmosphere for 5 h. After concentrated, the reaction mixtures were separated and purified by preparative GLC. Besides siloxy 5 which 1 was oxidized was obtained, there were two main products. As one showed complicated spectrum in ¹H-NMR, we couldn't determine structure in it. The other was determined as structure of 11 in 17 % yield. 11: pale yellow oil; ¹H-NMR (500 MHz, C6D6) & 0.02 (s, 3H), 0.11 (s, 3H), 0.22 (s, 3H), 0.30 (s, 3H), 0.37 (s, 3H), 0.39 (s, 3H), 0.66 (t, 3H, $J_{XZ}=J_{YZ}=7.5$ Hz), 1.35 (s, 1H), 1.91 (dq, 1H, $J_{XY}=11.5$ Hz, $J_{YZ}=7.5$ Hz),

2.22 (q, 1H, J_{XY} =11.5 Hz, J_{XZ} =7.5 Hz), 2.56 (dt, 1H, J_{AD} = J_{CD} =2.5 Hz, J_{BD} =4.7 Hz), 2.75 (dd, 1H, J_{AC} =19.5 Hz, J_{CD} =2.5 Hz), 3.15 (d, 1H, J_{BD} =4.7 Hz), 3.45 (dd, 1H, J_{AC} =19.5 Hz, J_{AD} =2.5 Hz), 6.80-7.13 (m, 4H) ; ¹³C-NMR (125 MHz, C₆D₆) δ -6.29 (q), -6.05 (q), -4.39 (q), -4.06 (q), -3.53 (q), -3.07 (q), 15.0 (q), 24.7 (t), 35.7 (t), 38.2 (d), 41.1 (d), 42.2 (s), 47.2 (d), 124.4 (d), 125.1 (d), 126.7 (d), 128.5 (d), 137.1 (s), 148.2 (s) ; ²⁹Si-NMR (18 MHz, C₆D₆) δ -57.3, -16.4, -9.40 ; Mass m/e 361 (M⁺-15)

(c) An ethanol (5 ml) solution of 1 (100 mg, 0.32 mmol) was irradiated with low pressure mercury lamp in quarts tube under argon atmosphere for 5 h. After concentrated, the reaction mixtures were separated by HPLC. The 12 was obtained in 13 % yield. The product 12 was purified with preparative GLC. 12 : colorless oil ; ¹H-NMR (500 MHz, C₆D₆) δ -0.1 (d, J_{CD}=2.0 Hz), 0.09 (s, 3H), 0.18 (s, 3H), 0.22 (s, 3H), 0.27 (s, 3H), 0.48 (s, 3H), 0.64 (s, 3H), 1.04 (t, 3H, J_{XZ}=J_{YZ}=5.5 Hz), 1.11 (b.s., 1H), 2.92 (d, 1H, J_{AB}=15 Hz), 3.18 (quint, 1H, J_{XY}=J_{YZ}=5.5 Hz), 3.27 (quint, 1H, J_{XY}=J_{XZ}=5.5 Hz), 3.46 (d, 1H, J_{AB}=15 Hz), 4.60 (s, 1H), 6.80-7.20 (m, 4H) ; ¹³C-NMR (125 MHz, C₆D₆) δ -8.24 (q), -5.99 (q), -4.32 (q), -3.62 (q), -2.15 (q), -1.80 (q), 12.9 (d), 15.7 (q), 18.6 (d), 22.2 (s), 30.3 (t), 64.0 (t), 82.3 (d), 125.9 (d), 128.6 (d), 129.9 (d), 130.3 (d), 134.5 (s), 135.4 (s) ; Mass m/e 345 (M⁺-15)

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References.

- Reviews for [n.1.1]propellane, a) G. Szeimies, <u>Strain and Its Implications in Organic</u> Chemistry, 1989, vol. 273, pp361-381. b) K. B. Wiberg, <u>Chem. Rev., 89</u>, 975-983 (1)(1989).
- (2)a) K. B. Wiberg, J. Am. Chem. Soc., 105, 1227-1233 (1983). b) M. D. Newton, and J. M. Schulman, J. Am. Chem. Soc., <u>94</u>, 773-778 (1972). c) D. P. G. Hamon, and V. C. Trenerry, J. Am. Chem. Soc., <u>103</u>, 4962-4965 (1981). d) P. G. Gassman, and G. S. Proehl, <u>J. Am. Chem. Soc.</u>, <u>102</u>, 6862-6863 (1980). e) K. B. Wiberg, and F. H. Walker, <u>J. Am. Chem. Soc.</u>, <u>104</u>, 5239-5240 (1982).
- (3) W. Ando, N. Nakayama, Y. Kabe, and T. Shimizu, Tetrahedron Letters, 31, 3597-3598 (1990)
- (4) W. Ando, T. Tsumuraya, and Y. Kabe, Angew. Chem. Int. Ed. Engl., 29, 778-780 (1990).
- W. Ando, H. Yoshida, K. Kurishima, and M. Sugiyama, J. Am. Chem. Soc., in (5) press
- W. Ando, Y. Igarashi, Y. Kabe, and N. Tokitoh, Tetrahedron Letters, 31, 4185-4188 (6) (1990)
- I. Murata, T. Nakazawa, M. Kato, T. Tatsuoka, and Y. Sugihara, Tetrahedron Letters, (7) 16, 1647-1650 (1975).
- a) A. -D. Schlüter, H. Huber, and G. Szeimies, <u>Angew. Chem. Int. Ed. Engl.</u>, <u>24</u>, 404-405 (1985). b) H. -G. Zoch, G. Szeimies, T. Butkowskyj, M. Van Meerssche, (8) G. Germain, and J. -P. Declercq, <u>Chem. Ber.</u>, 114, 3896-3905 (1981).
 J. Morf, and G. Szeimies, <u>Tetrahedron Letters</u>, 27, 5363-5366 (1986).
 J. Belzner, G. Szeimies, <u>Tetrahedron Letters</u>, 27, 5839-5842 (1986).
 R. T. Taylor, and L. A. Paquette, J. Org. Chem., 43, 242-249 (1978).
 J. Belzner, and G. Szeimies, <u>Tetrahedron Letters</u>, 28, 3099-3102 (1987).
- (9)
- (10)
- (11)
- (12)
- K. B. Wiberg, F. H. Walker, W. E. Pratt, and J. Michl, J. Am. Chem. Soc., 105, (13) 3638-3641 (1983).
- K. Shiina, J. Organomet. Chem., 310, C57-C59 (1986). (14)
- a) D. Seyferth, J. Organomet. Chem., 100, 237-256 (1975). b) W. Ando. and H. (15)Saso, Tetrahedron Letters, 27, 5625-5628 (1986).
- (16) K. Semmler, G. Szeimies, and J. Belzner, J. Am. Chem. Soc., 107, 6410-6411 (1985).
- M. J. S. Dewar, and W. Thiel, J. Am. Chem. Soc., 99, 4899-4907 (1977). (17)
- (18)H. Gilman, R. L. Harrell, J. Organomet. Chem., 5, 201-202 (1966).
- H. Sakurai, K. Tominaga, T. Watanabe, and M. Kumada, Tetrahedron Letters, 7, (19) 5493-5497 (1966).
- H. Gilman, K. Shiina, D. Aoki, B. J. Gaj, D. Wittenberg, and T. Brennan, J. (20)Organomet. Chem., 13, 323-328 (1968).
- (21)H. J. Emeléus, and S. R. Robinson, J. Chem. Soc., 151, 1592-1594 (1947).