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The First Bicyclic System with σ(Si-Si)-π Conjugation. Synthesis of Bicyclo[6.6.0]-1,8-diisopropyl-4,4,5,5,11,11,12,12-octamethyl-1,4,5,8,11,12-hexasila-2,6,9,13-tetrayne

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Treatment of 1,2-diisopropyltetrachlorodisilane with 2 equiv. of di-Grignard reagent of 1,2-diethynyltetramethyldisilane led to a good yield of the bicyclic title compound , which has a UV absorption at 260 nm.

Bicyclic systems consisting of σ(Si-Si)-π conjugations are of some interest, since such a fused system may lead to unusual electronic and physical properties through unique σ(Si-Si)-π conjugation. Quite interesting properties are observed for the bicyclic [2.2.0] hexasilane compound reported by Nagai et al.$^{1)}$

Recently we have reported a new route to a good yield of strained cyclic disilanylene-acetylenes using di-Grignard reagents of 1,2-diethynyldisilane in dilute THF solutions.$^{2)}$ We now wish to report the first synthesis of a bicyclic compound, bicyclo[6.6.0]-1,8-diisopropyl-4,4,5,5,11,11,12,12-octa-methyl-1,4,5,8,11,12-hexasila-2,6,9,13-tetrayne $\underline{1}$, possessing an effective σ(Si-Si)-π conjugation. Fused polycycles constructed exclusively from a σ-π conjugated system were previously unknown.$^{3)}$ Compound $\underline{1}$ can be regarded as a basic unit for ladder-type polymers containing a σ-π conjugated system.

The bicyclic compound $\underline{1}$ can be obtained by the reaction of 1,2-diisopropyltetrachlorodisilane $\underline{2}$ with 2 equiv. of di-Grignard reagent $\underline{3}$ of 1,2-diethynyltetramethyldisilane in dilute THF solution as shown in

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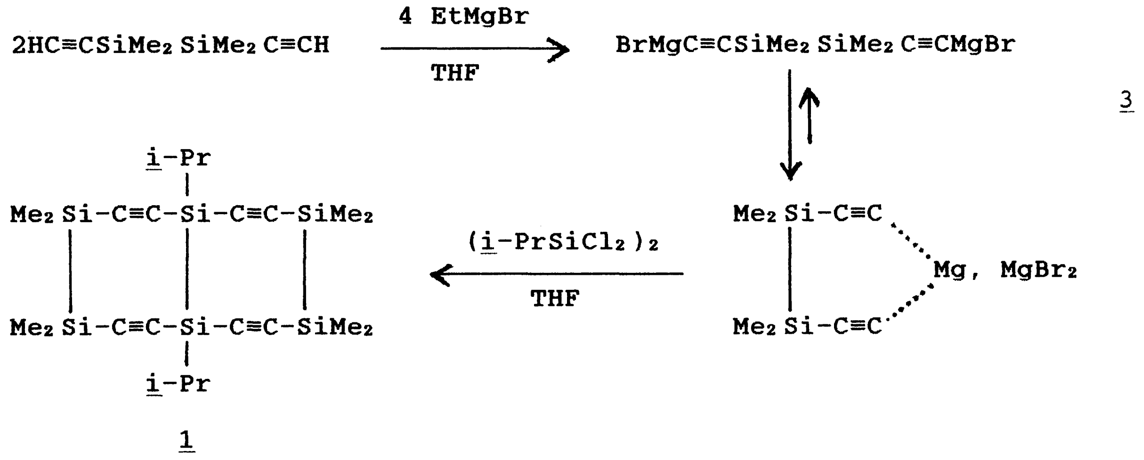
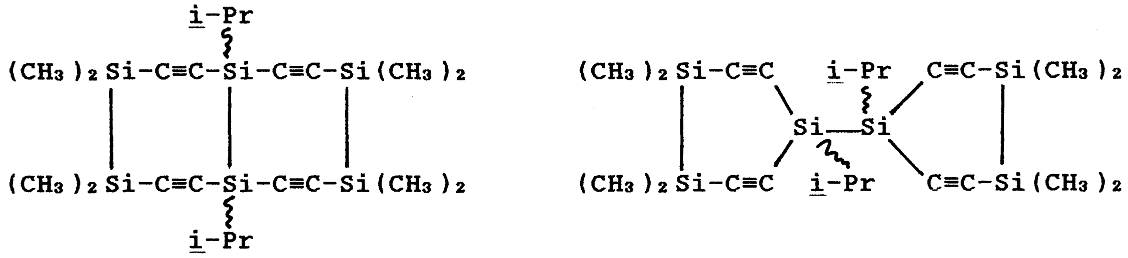


Scheme 1. Synthetic Route to 1.

Scheme 1.[4] A typical procedure is as follows: 100 mL of the di-Grignard reagent THF solution from 1.66 g (10 mmol) of 1,2-diethynyltetramethyldisilane[5] and ethylmagnesium bromide (20 mmol) and 100 mL THF solution of 1.42 g (5 mmol) of 1,2-diisopropyltetrachlorodisilane[6] were simultaneously added to 300 mL of THF under N_2 over 2 h at room temperature. After completion of addition, the THF solution was refluxed for 3 d.[7] The THF was removed under vacuum and 150 mL of hexane was added to the residue. The solution was washed with aqueous NH_4Cl solution (100 mL x 2), water (100 mL x 1), and dried over Na_2SO_4. After filtration, evaporation, and drying under vacuum, 1.9 g of pale yellow solid was obtained. Recrystallization of 1.14 g of the crude product from 50 mL of ethanol gave 0.31 g (22%) of compound 1 as colorless crystals, mp 156-157 °C.[8] Compound 1 is stable to atmospheric oxygen and water, and easily soluble in hydrocarbons (benzene, toluene, hexane) as well as ether and THF, but poorly soluble in MeOH.

Four possible structures (A) – (D) (Fig. 1) were considered for compound 1. Structures (C) and (D) can be ruled out both by the ^{29}Si NMR and their great cyclic strain energy. If seven-membered rings were present as in structures C or D, the ^{29}Si chemical shift of the two central silicon atoms would be expected to be much more deshielded.[9] Structure A seems more likely than B, because molecular models show that the trans isomer B is much more strained than A.

Interestingly two signals for the methyl groups on the non-bridged silicons were observed in both ^1H and ^{13}C NMR spectra. Both cis (A) and trans (B) structures can actually have two different kinds of methyl groups because the fused ring cannot be flipped. The lowest



(A) cis (B) trans (C) cis (D) trans

Fig. 1. Four possible structures for 1.

energy absorption of 1 in the UV region occurs at 260 nm, which is longer by 10 nm than that of the corresponding monocyclic compound.[2] The bathochromic shift compared to the monocyclic analog may reflect destabilization of the HOMO resulting from greater ring strain in 1.

The structural analysis of compound 1 by X-ray and synthetic approaches to the higher homologs as well as the ladder polymer are now being explored.

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References

1) H. Matsumoto, H. Miyamoto, N. Kojima and Y. Nagai, J. Chem. Soc., Chem. Commun., 1987, 1316; H. Matsumoto, H. Miyamoto, N. Kojima and Y. Nagai, Chem. Lett., 1988, 629.

2) T. Iwahara and R. West, J. Chem. Soc., Chem. Commun., 1988, 954.

3) Bicyclic compound 1 was described at the Fifth International Symposium on Inorganic Ring Systems, August 1988, Univ. of Massachusetts, and at the Ninth International Symposium on Organosilicon Chemistry, July 1990, Univ. of Edinburgh.

4) An alternative route to 1 is the reaction of the tetra-Grignard reagent of 1,1,2,2-tetraethynyldisilane with 2 equiv. of 1,2-dichlorodisilane. But in this case, a polymerization reaction was predominant, accompanied by formation of a small amount of the bicyclic compound 1 detected by GLC.

5) A. Seabald, P. Seiberlich, and B. J. Wrackmeyer, J. Organomet. Chem., 303, 73 (1986).

6) To prepare 2, Ph_2SiCl_2 was treated with i-PrMgCl in refluxing THF for 7 d giving 74% of Ph_2i-PrSiCl (3); 3 was coupled with Li in THF at 25 °C for 4 d to give 57% of (Ph_2i-PrSi)$_2$ (4); 4 was treated with HCl and $AlCl_3$ (cat.) for 20 min at 25 °C to give 86% of 2, Bp 55-57 °C/0.45 Torr.

7) A shorter reaction time or on-and-off reaction decreased the yield. In these cases, a pale yellow viscous liquid and small amounts of white solid were obtained as crude products; after purification by column chromatography on silica gel with hexane/AcOEt (50/1) followed by recrystallization from EtOH, about 5% of compound 1 was obtained.

8) Spectroscopic data for 1: IR (KBr disk) cm^{-1} 2960(s), 2920(m), 2890(m), 2870(s), 1470(m), 1410(m), 1250(s), 990(m); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.24 [s, 12H, Si($C\underline{H}_3$)$_2$], 0.27 [s, 12H, Si($C\underline{H}_3$)$_2$], 1.04-1.07 [m, 14H, SiC$\underline{H}$($C\underline{H}_3$)$_2$]; MS (30 eV) m/e (rel. inten.) 4.71 (M^++1, 4.4), 470 (M^+, 11), 428 (23), 427 (19), 113 (100); exact mass determination calcd for $C_{21}{}^{13}CH_{38}Si_6$: 471.1623, measd. 471.1608; calcd for $C_{22}H_{38}Si_6$: 470.1589, measd. 470.161. Calcd for $C_{19}H_{31}Si_6$ (M^+-iPr) 427.1042, measd. 427.1047. UV (solution in n-hexane) λ_{max} = 211, 239, 250(sh), 260. ^{13}C NMR ($CDCl_3$) δ -3.21 [Si($\underline{C}H_3$)$_2$], -3.07 [Si($\underline{C}H_3$)$_2$], 13.49 [$\underline{C}$H(CH_3)$_2$], 18.49 [CH($\underline{C}H_3$)$_2$], 112.41, 132.34 (-$\underline{C}$≡$\underline{C}$-); ^{29}Si NMR ($CDCl_3$) δ -42.87, -33.08.

9) H. Sakurai, Y. Nakadaira, A. Hosomi, Y. Eriyama and C. Kabato, J. Am. Chem. Soc., 105, 3359 (1983).

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