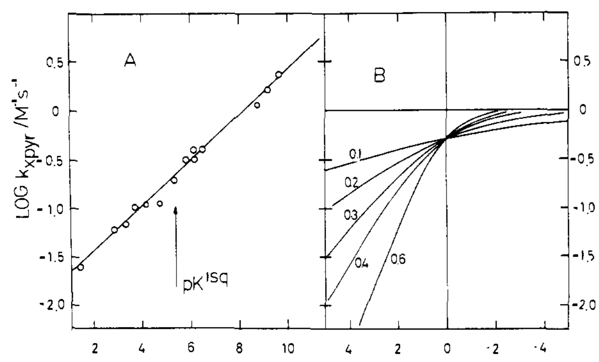

Figure 1. (A) Plot of log k_{xpyr} vs. pK^{xpyr} for the pyridinolysis of isoquinoline-*N*-sulfonate; 25 °C, 0.1 M ionic strength. The line is theoretical from the text; points in increasing value of pK^{xpyr}: 3-CN, 3-Br, 4-MeOCO, 3-CHO, 3-CH_2CN, 4-CHO, H, 3-Me, 3,5-Me_2, 4-Me, 3,4-Me_2, 4-morpholino, 4-NH_2, 4-Me_2N. General base catalysis is excluded by the observation that $k_{2,6\text{-lutidine}}$ ($10^{-2.4}$ M^{-1} s^{-1}) is some 2 orders of magnitude lower than that predicted from the Brønsted equation given in the text. (B) Family of normalized curves (log k/k_0) vs. ΔpK for the theoretical rate law governing a preassociation stepwise mechanism (eq 2). Numbers refer to the chosen value of β_N for the rate law.

a family of normalized curves for different values of β_N, and it is clear that none of these β_N values generates a theoretical curve to fit the data. The curves will only approximate to a straight line when $\beta_N < 0.1$. The data may be force fitted to the equation for the stepwise process and a best fit obtained to a least-squares program where $\beta_N = 0.4$. The correlation coefficient for this fit is quite good, but the residuals possess a nonrandom variation with pK, whereas those for the linear fit have a random distribution.

The conclusion of a preassociation concerted mechanism is very similar to that for the analogous pyridine-*N*-phosphonate transfer reactions.[7] The comparison extends to a similar reactivity and a low value of the bond order in the transition state as measured by the ratio of β_N to the value of β for the equilibrium (β_N/β_{EQ} = 0.19, β_{EQ} = 1.24[5]). The absence of free or solvated sulfur trioxide as an intermediate in solvolysis reactions in solvents of low water content[8] and of the preassociative stepwise mechanism are consistent with the known high reactivity of monomeric sulfur trioxide.[9] Analogues of sulfur trioxide such as sulfen,[10] aminosulfen ($MeN{=}SO_2$),[11] and paraoxosulfen (p-$OC_6H_4SO_2$)[12] are expected to be less reactive than sulfur trioxide and have been demonstrated as *discrete* intermediates in transfer reactions.[10-12] Since these "sulfen" intermediates ($X{=}SO_2$) exhibit a spectrum of reactivity, it is quite possible that an intermediate could be devised that would participate in a preassociation stepwise mechanism.

Registry No, Isoquinoline-*N*-sulfonate, 53854-50-5; 3-cyanopyridine, 100-54-9; 3-bromopyridine, 626-55-1; methyl 4-pyridinecarboxylate, 2459-09-8; 3-pyridinecarboxaldehyde, 500-22-1; 3-pyridineacetonitrile, 6443-85-2; 4-pyridinecarboxaldehyde, 872-85-5; pyridine, 110-86-1; 3-methylpyridine, 108-99-6; 3,5-dimethylpyridine, 591-22-0; 4-methylpyridine, 108-89-4; 3,4-dimethylpyridine, 583-58-4; 4-morpholinopyridine, 2767-91-1; 4-aminopyridine, 504-24-5; 4-dimethylaminopyridine, 1122-58-3; 2,6-lutidine, 108-48-5; sulfur trioxide, 7446-11-9.

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(7) Bourne, N.; Williams, A., preceding paper in this issue.

(8) Hopkins, A.; Williams, A. *J. Chem. Soc., Chem. Commun.* **1983**, 37.

(9) (a) Gilbert, E. E. *Chem. Rev.* **1962**, *62*, 549. (b) The reactivity against nucleophiles of monomeric sulfur trioxide has to our knowledge never been measured but must be very much greater than that of the polymeric forms, which are themselves exceptionally reactive.

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(11) Williams, A.; Douglas, K. T. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1727.

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3,4,7,8-Tetrasilacycloocta-1,5-diyne, 3,6,7-Trisilacyclohepta-1,4-diyne, and Related Compounds. New Class of Cyclic Compounds Composed of Polysilanes and Acetylenes[1]

Hideki Sakurai,* Yasuhiro Nakadaira, Akira Hosomi,
Yuichi Eriyama, and Chizuko Kabuto

Department of Chemisty, Tohoku University
Sendai 980, Japan

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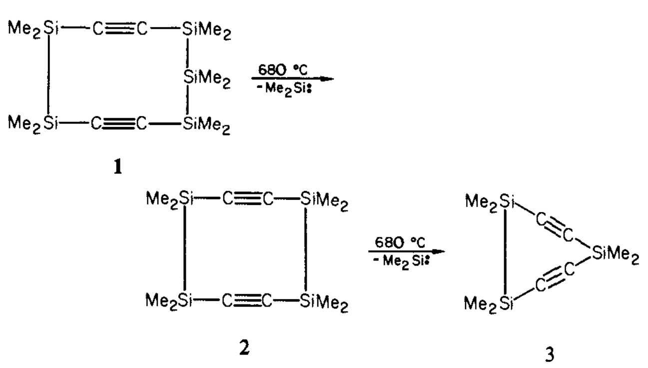
Although several types of cyclic polysilanes having carbon-carbon multiple bonds in the ring are known,[2] no cyclic ethynylene polysilane has been reported. As shown in a qualitative molecular orbital diagram of 3,4,7,8-tetrasilacycloocta-1,5-diyne in Figure 1, two Si–Si σ orbitals can overlap with one of two π orbitals[3,4] of each C≡C bond to make up new molecular orbitals with through-conjugation. Therefore, it is extremely intriguing to examine the properties of 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacycloocta-1,5-diyne (**1**), if it can be prepared. On the other hand, neither spatial nor through-bond interaction between two acetylenes has been observed for the corresponding cycloocta-1,5-diyne, the smallest known cyclic diyne.[5]

We have adopted a ring-contraction method[6] for the preparation of **1** (Scheme I). Irradiation with a low-pressure mercury lamp[6] or flash vacuum pyrolysis (FVP, 650 °C (10^{-2}–10^{-3} mmHg)) of **2**, prepared in 37% yield by the reaction of a di-Grignard reagent from 1,2-diethynyl-1,1,2,2-tetramethyldisilane with 1,3-dichlorohexamethyltrisilane, resulted in the formation of **1** as a crystal in 10% and 63% yield, respectively, with concomitant extrusion of dimethylsilylene, which was trapped with diethylsilane. Poorer yield in the photochemical process than in FVP may be ascribed to the fact that the product (**1**) has stronger absorption than the precursor in the 240–260-nm region, as shown later.

Surprisingly, from the pyrolysis products, 3,3,6,6,7,7-hexamethyl-3,6,7-trisilacyclohepta-1,4-diyne (**3**) was isolated as a white crystal in 3% yield. Apparently, **1** is the direct precursor to **3**, as evidenced by the fact that the FVP of **1** (680 °C (10^{-2}–10^{-3} mmHg)) gave **3** in 6.3% yield.

As far as we know, **3** is the smallest known cyclic diyne. Although unstable in air, **3** can be purified by sublimation to give correct analyses. Several interesting features can be pointed out from Table I, which lists physical properties of ethynylene polysilanes, but the most striking fact is an enhanced bathochromic

Scheme I



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(1) Chemistry of Organosilicon Compounds. 167.

(2) Inter alia (a) Disilacyclobutanes: Sakurai, H.; Kobayashi, T.; Nakadaira, Y. *J. Organomet. Chem.* **1978**, *162*, C43. (b) Disilacyclohexadienes: Nakadaira, Y.; Kanouchi, S.; Sakurai, H. *J. Am. Chem. Soc.* **1974**,, *96*, 5623.

(3) For a review: Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261.

(4) Ensslin, W.; Bock, H.; Becker, G. *J. Am. Chem. Soc.* **1974**, *96*, 2757 and references therein.

(5) Koster-Jensen, E.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 671.

(6) (a) Sakurai, H.; Kobayashi, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1971**, *93*, 5272; (b) **1974**, *96*, 2656.

0002-7863/83/1505-3359$01.50/0

Table I, Some Physical Properties of Cyclic and Acyclic Ethynylene Polysilanes

compd	mp, °C	^{1}H NMR,[a] ppm	^{13}C NMR,[a] ppm	^{29}Si NMR,[a] ppm	Raman (IR),[b] cm^{-1}	UV, nm (log ϵ)
2	55-56	0.17 (6 H, s), 0.23 (12 H, s), 0.24 (12 H, s)	−7.57, −3.46, −2.81, 115.67, 116.39	−45.61, −35.77, −34.21	2091.5 (2080)	226.5 (4.21), 236 sh (4.03)
1	139	0.25 (24 H, s)	−3.07, 119.46	−33.62	2082.4	242 sh (3.97), 250 (4.13)
3	64-65	0.34 (12 H, s), 0.35 (6 H, s)	−3,13, −1.11, 126.70, 132.25	−26.85, 1.57	2042.0	243 sh (3.64), 251 (3.70), 260 sh (2.41)
4[c]	44-44,5	0.05 (18 H, s),[d] 0.24 (12 H, s)[d]	−3.20, −0.07, 111.62, 116.91	−38.17, −19.08	2097.5 (2100)	223 (4.03), 230 (4.06)

[a] In $CDCl_3$. [b] In *n*-hexane. [c] $Me_3Si{-}C{\equiv}C{-}SiMe_2SiMe_2{-}C{\equiv}C{-}SiMe_3$. [d] In$CCl_4$.

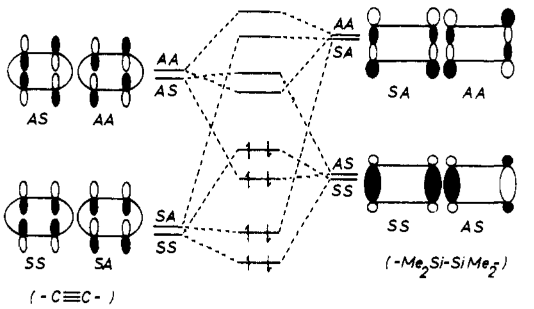

Figure 1, Qualitative molecular orbital diagram of 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacycloocta-1,5-diyne (**1**).

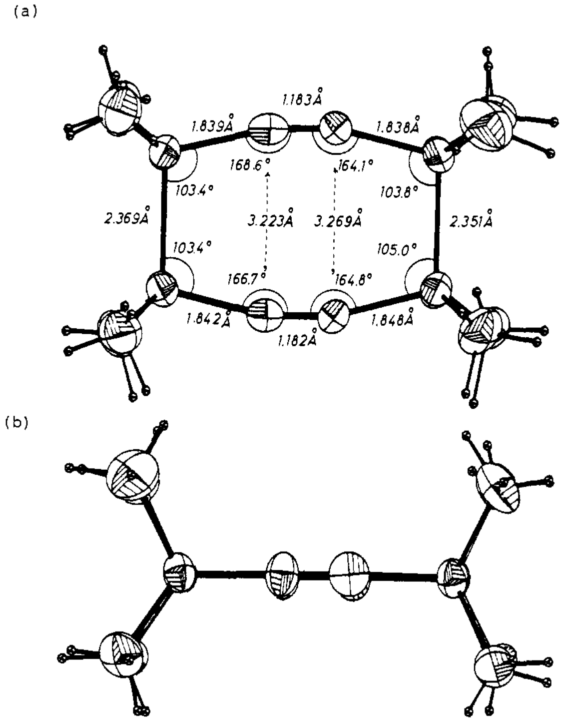

Figure 2, Molecular structure of **1**: (a) ORTEP view with appropriate data of bond lengths and angles; (b) side view.

shift in the UV spectra for **1** and **3**. Thus, **1** shows an absorption maximum at 250 nm (ϵ 13,400).

Two major factors, i.e., ring strain and σ–π conjugation, may be considered to account for the UV shift. However, judging from ^{13}C NMR data of acetylene units, the ring strain of **1** is not very significant; i.e., only a 2.55 ppm shift is observed for the ^{13}C NMR chemical shift of the sp carbon of **1** in comparison with **4**. Moreover, the molecular structure of **1** as determined by X-ray crystallography (Figure 2)[7] demonstrates rather little distortion in both disilane and acetylene units. Therefore, the enhanced bathochromic shift in the UV spectra of **1** should primarily be caused by the unique electronic structure of **1**, in which the HOMO is raised due to extensive σ–π mixing.[8]

The carbon–carbon triple bonds of **3** are very much distorted as judged by ^{13}C NMR. Thus ^{13}C NMR chemical shifts of the triple bond appeared with large low-field shifts at 126.70 and 132.25 ppm. These values are rather close to those of 1,2-bis(trimethylsilyl)ethylenes.[9] Therefore, the bond order of the triple bond of **3** decreases considerably.[10] Correspondingly, the C≡C stretching frequencies (Raman) decreased in the order of **2** > **1** > **3**.[11]

Registry No. 1, 85263-68-9; **2**, 85442-77-9; **3**, 85442-78-0; **4**, 85442-79-1; 1,2-diethynyl-1,1,2,2-tetramethyldisilane, 54773-31-8; 1,3-dichlorohexamethyltrisilane, 812-36-2.

Supplementary Material Available: ORTEP view of the structure of **1** and tables of crystal data, bond angles, bond lengths with estimated deviations, final atomic coordinates and isotropic temperature factors for hydrogen atoms, final anisotropic factors of non-hydrogen atoms, and observed and calculated structure factors (17 pages). Ordering informations is given on any current

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(7) Crystal data for **1**, $C_{12}H_{24}Si_4$ (fw 280.68), are as follows: monoclinic *Pc*; $a = 7.676$ Å; $b = 6.348$ Å; $c = 19.909$ Å; $\beta = 111.908°$; $V = 900.157$ Å; $Z = 2$; number of reflections 1707; $D_{calcd} = 1.035$ g cm^{-3}; $R = 0.0441$. Since the X-ray crystallographic determination of **1** revealed several interesting facts, we will report the experimental details as well as the structural parameters in a forthcoming paper.

(8) A referee pointed out that the σ–π mixing of a sort proposed for **1** should take place equally well in **2**. However, this is highly unlikely, since the HOMO of trisilane is composed of the antibonding combination of two δ(Si–Si) orbitals, which requires the SA combination of the two acetylene π orbitals for conjugation (Figure 1) as a logical consequence. The SA combination of two acetylene π orbitals cannot conjugate with the HOMO of disilane, so that cyclic through-conjugation observed for **1** does not exist for **2**. Indeed, the UV spectrum of **2** can be reconstructed almost perfectly simply by adding the spectra of **4** and octamethyltrisilane.

(9) Block, H.; Seidl, H. *J. Organomet. Chem.* **1968**, *13*, 87. For a discussion of ^{13}C NMR and UV spectra of polysilylethylenes: Sakurai, H.; Tobita, H.; Nakadaira, Y. *Chem. Lett.* **1982**, 1251.

(10) The ^{29}Si NMR chemical shifts of **3** are also anomalous. We will discuss the structure and reactions of **3** in detail later.

(11) All new compounds in this report gave correct elemental analyses and exact mass spectra.

A Stereorational Synthesis of Optically Active *trans*-Cycloalkenes and [10.10]Betweenanene

James A. Marshall* and Katherine E. Flynn

Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

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Early studies on medium-ring *trans*-cycloalkenes contributed significantly to perceptions of transannular effects,[1] restricted rotation,[2] and molecular chirality.[3] More recently the discovery of new biologically active unsaturated macrocyclic natural products[4] has underscored the importance of fundamental work