(Figure 2C), the desired lines become well resolved.[13,14]

Although AB spin systems were chosen for these examples, the method is equally successful for two weakly coupled spins. The situation is slightly more complex, however, for three or more coupled nuclei. Several double quantum transitions with different frequencies (which, in general, are not independent of the J couplings) can occur, making the choice of a suitable transmitter position less straightforward. Similarly, the optimum preparation time, τ, is less easily determined.

In practice it is not necessary to have more than an approximate prior knowledge of the shifts and J couplings involved. Given a reasonable choice of transmitter frequency, a few spectra with short t_1 (say <5 ms) once added together often reveal the required line positions. Location of these lines is assisted by the distinctive up-down patterns. Measurements of Ω and J then give the correct ω and τ.

One can envisage a variety of applications for this technique, for example: analysis of complex mixtures such as occur in oil and coal research; detection and monitoring of concentration of metabolites in suspensions of living cells; detection of resonances lying under strong solvent lines; detection of small molecules in the presence of macromolecules. Further work especially on the quantitative aspects of the method is in progress.

Acknowledgment. We are grateful to the Netherlands Organisation for the Advancement of Pure Research (ZWO) for financial support and to the Royal Society, London, for the award of a research fellowship (P.J.H.). It is a pleasure to acknowledge a stimulating discussion with Dr. A. Bax.

Registry No. NADH, 58-68-4; NADPH, 53-57-6.

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(13) Through use of the basic 4-step phase cycling and a 1s relaxation delay between scans, DOUBTFUL spectra of similar quality to Figure 2C could be obtained in 2.5 min.

(14) Previous methods of "editing" NMR spectra[15-20] give subspectra containing, for example, *all* doublets or *all* singlets *and* triplets. DOUBTFUL goes further in selecting *specific* multiplets from such subspectra.

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Molecular and Crystal Structure of 1,1-Bis(*tert*-butyldimethylsilyl)-2,2-bis(trimethylsilyl)ethylene, the Most Twisted Known Olefin, and Unusual Rearrangement during Its Preparation[1]

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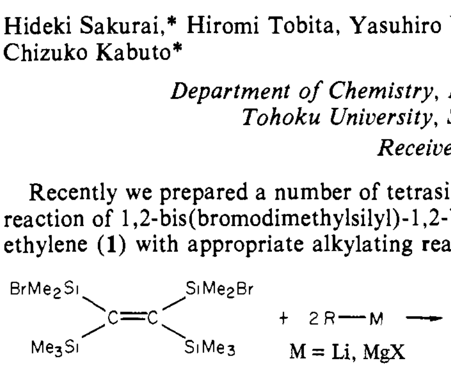
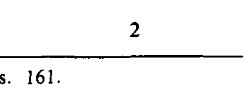
Recently we prepared a number of tetrasilylethylenes by the reaction of 1,2-bis(bromodimethylsilyl)-1,2-bis(trimethylsilyl)ethylene (**1**) with appropriate alkylating reagents.[2]



1



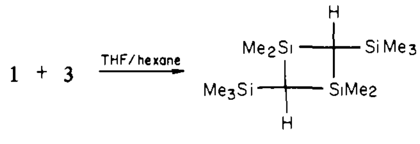
2

Table I. Bond Lengths and Bond Angles with Estimated Standard Deviations for 1,1-Bis(*tert*-butyldimethylsilyl)-2,2-bis(trimethylsilyl)ethylene (5) at 15 °C

	Bond Lengths (Å)		
Si(1)-C(1)	1.926 (4)	Si(2)-C(10)	1.878 (5)
Si(2)-C(2)	1.915 (5)	Si(2)-C(11)	1.873 (5)
Si(1)-C(3)	1.872 (5)	C(5)-C(6)	1.537 (7)
Si(1)-C(4)	1.885 (5)	C(5)-C(7)	1.531 (7)
Si(1)-C(5)	1.917 (4)	C(5)-C(8)	1.545 (7)
Si(2)-C(9)	1.878 (5)	C(1)-C(2)	1.370 (7)
	Bond Angles (Deg)		
C(1)-Si(1)-C(3)	115.8 (2)	C(9)-Si(2)-C(11)	110.8 (2)
C(1)-Si(1)-C(4)	119.7 (2)	C(10)-Si(2)-C(11)	106.7 (2)
C(1)-Si(1)-C(5)	104.6 (2)	Si(1)-C(1)-C(2)	120.5 (3)
C(2)-Si(2)-C(9)	111.9 (2)	Si(2)-C(2)-C(1)	124.2 (3)
C(2)-Si(2)-C(10)	105.9 (2)	Si(1)-C(5)-C(6)	112.5 (3)
C(2)-Si(2)-C(11)	118.6 (2)	Si(1)-C(5)-C(7)	110.8 (3)
C(3)-Si(1)-C(4)	102.9 (2)	Si(1)-C(5)-C(8)	108.9 (3)
C(3)-Si(1)-C(5)	107.5 (2)	C(6)-C(5)-C(7)	109.2 (4)
C(4)-Si(1)-C(5)	105.4 (2)	C(6)-C(5)-C(8)	107.4 (4)
C(9)-Si(2)-C(10)	101.2 (2)	C(7)-C(5)-C(8)	107.9 (4)
Si(1)-C(1)-Si(1')	119.0 (2)		
Si(2)-C(2)-Si(2')	111.6 (2)		

These tetrasilylethylenes are sterically very crowded and show interesting properties; for example, an X-ray crystallographic study on tetrakis(trimethylsilyl)ethylene (**2a**, R = Me) reveals that the double bond of **2a** is twisted by 29.5°.[2c] An obvious approach to more congested olefins involves the reaction of **1** with a bulky alkylating reagent.

However, reactions of **1** with isopropylmagnesium chloride and *tert*-butylmagnesium chloride resulted in the formation of neither expected alkylated products **2** nor hydrosilane (**2b**, R = H). Instead, 1,1,3,3-tetramethyl-2,4-bis(trimethylsilyl)-1,3-disilacyclobutane (**4**) was obtained. The reaction leading to **4** apparently

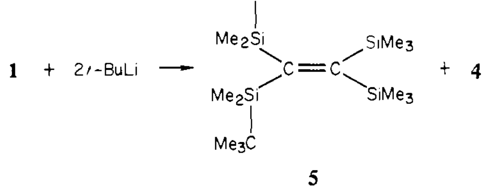


4

3a, $(CH_3)_2CHMgCl$ (reflux, 8 h)
b, $(CH_3)_3CMgCl$ (reflux, 8 h)
c, $[\text{anthracene}]^{-\cdot}\ Li^+$ (reflux, 2.5 h)
d, Na (room temperature, 7 h)

involves an electron-transfer process because lithium anthracenide and even sodium metal can cause the same reaction. Yields in percent and Z/E ratios of **4**, which depend on **3**, were as follows: 22, 9:1 with **3a**; 26, 9:1 with **3b**; 38, 2:1 with **3c**; 14, 1/1 with **3d**.

The reaction of **1** with *tert*-butyllithium at 0 °C gave the unexpected 1,1-bis(*tert*-butyldimethylsilyl)-2,2-bis(trimethylsilyl)ethylene (**5**) in 13% yield along with **4** (Z/E 1:1.05) in 13% yield. A very small amount of an isomer of **5** exists in the reaction mixture as detected by GC-MS and NMR but has not yet been separated.



5

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(1) Chemistry of Organosilicon Compounds. 161.

(2) (a) Sakurai, H.; Nakadaira, Y.; Kira, M.; Tobita, H. *Tetrahedron Lett.* **1980**, *21*, 3077. (b) Sakurai, H.; Tobita, H.; Kira, M.; Nakadaira, Y. *Angew. Chem., Int. Ed. Engl.* **1980**, **19**, 620. (c) Sakurai, H.; Nakadaira, Y.; Tobita, H.; Ito, T.; Toriumi, K.; Ito, H. *J. Am. Chem. Soc.* **1982**, *104*, 300.

0002-7863/82/1504-4288$01.25/0

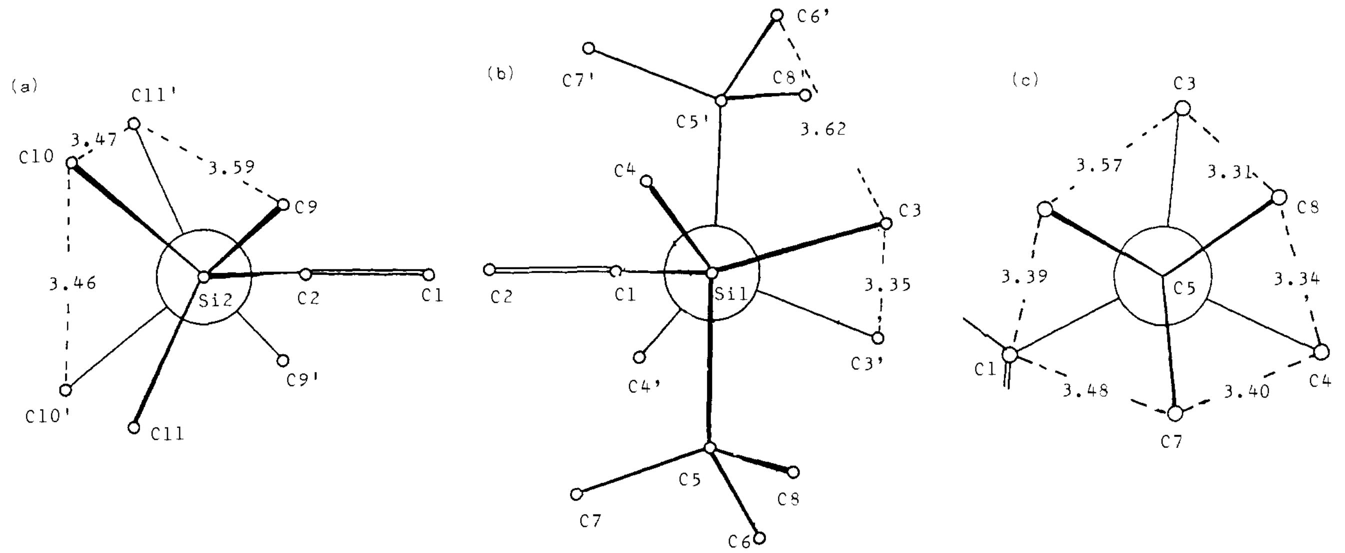

Figure 1. Newman projections: (a) through Si(1) and Si(1′); (b) through Si(2) and Si(2′); (c) through C(5) and Si(1).

Recrystallization from ethanol gave **5** as orange-red crystals, mp 190–191 °C. Spectral data of **5**[3] and correct elemental analyses indicate the structure. The existence of two olefinic carbons in the ^{13}C NMR indicates an unsymmetrical structure for **5**, which has been confirmed by the X-ray diffraction study with a crystal obtained from a hexane solution.[5]

The structure of **5** has crystallographically 2-fold axis symmetry idealized for the molecule, and the molecular packing shows no intermolecular distance less than van der Waals contacts. We may therefore confidently believe that the present structural dimensions reflect straightway the equilibrium configuration of the isolated molecule. The bond lengths and angles are listed in Table I. Several distortions from normal values are found as a part of the mechanism of relieving the strain, displaying a quite similar trend to those in tetrakis(trimethylsilyl)ethylene (**2a**). Notably, the C=C double bond length of 1.370 Å and $C(sp^2)$–Si bond lengths of 1.915 and 1.926 Å are similar to those of **2a** but are exceedingly longer than the normal values.[2c,6]

However, a significant difference caused by the increasing overcrowding is the greater twisting angle of the C=C double bond. The dihedral angle between two $C(sp^2)$ planes, which are strictly planar, is 49.6°, which is apparently the largest known even including cyclic conjugated olefins.[7,8] As evident from the molecular structure, this twisting occurs directly due to the nonbonding interaction between methyl groups C(4) on Si(1) and C(9) on Si(2). Despite the large twisting, the observed separation between C(4) and C(9) is only 3.25 Å, considerably shorter than the accepted value (3.7–3.8 Å).[9]

Another interest in the structure of **5** centers on the conformations around the geminal silicon atoms. Details are shown in Figure 1, illustrating projections of atoms through Si(1) and Si(1′) and Si(2) and Si(2′). In the former part, the close atoms C(3) and C(3′) are separated by 3.35 Å, and thus the C(5) and C(5′) atoms of bulky *tert*-butyl groups are almost in opposite direction. The *tert*-butyl group itself takes a staggered form with nonbonding distances of 3.31–3.57 Å among methyl groups. Distances between the methyl groups of the two Me_3Si groups are 3.46–3.59 Å.

The reaction of **5** with bromine resulted in the quantitative formation of bis(*tert*-butyldimethylsilyl)acetylene (**6**)[10] and bromotrimethylsilane.

$$\mathbf{5} + Br_2 \rightarrow \underset{\mathbf{6}}{Me_3CSiMe_2{-}C{\equiv}C{-}SiMe_2CMe_3} + 2Me_3SiBr$$

Again, a rearrangement is observed. Rearrangements leading to **4**–**6** are mechanistically interesting and are currently under active investigation.

Acknowledgment. This work is supported by the Ministry of Education, Science, and Culture (Grant-in-Aid No. 543007). We are grateful to Toshiba Silicone Co., Ltd., for a gift of chlorosilanes.

Registry No. 1, 74465-54-6; *cis*-**4**, 82113-61-9; *trans*-**4**, 82113-62-0; **5**, 82113-63-1; **6**, 23183-92-8.

Supplementary Material Available: ORTEP view of the structure of **5**, tables of final atomic coordinates, anisotropic temperature factors, and observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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[3] ^1H NMR (CCl_4) δ 0.32 (18 H, s, $SiMe_3$), 0.33 (12 H, s, $SiMe_2$), 0.83 (18 H, s, CMe_3); ^{13}C NMR ($CDCl_3$) δ 0.2 ($SiMe_2$), 5.9 ($SiMe_3$), 20.3 (CMe_3), 27.6 (CMe_3), 208.4 (C=C), 210.8 (C=C); ^{29}Si NMR ($CDCl_3$) δ −4.71, −11.65; IR (KBr, cm^{-1}) 1460 ($\nu_{C=C}$);[4] UV (hexane) λ_{max} (ε) 245.5 (9900), 433 nm (550); MS (*m/e*, %) 400 (0.6), 73 (100).

[4] This is probably one of the lowest records for the C=C stretch, although Warner et al. (Warner, P.; Chang, S.-C.; Powell, D. R.; Jacobson, R. A. *Tetrahedron Lett.* **1981**, *22*, 533) have recently found IR absorption at 1460 cm^{-1} (Raman at 1450 cm^{-1}) for tricyclo[3.3.1.$0^{1,5}$]non-9-ylidene and attributed it to the C=C stretch of a rather short (1.307 (3) Å) and planar double bond with reservations.

[5] A suitably cut platelike crystal with the dimensions of 0.2 × 0.2 × 0.3 mm was mounted on a Rigaku Denki four-circle diffractometer for X-ray measurements with graphite monochromatized Mo Kα radiation (λ 0.71079 Å). The cell constants are a = 18.271 (2) Å, b = 9.949 (1) Å, c = 16.487 (2) Å, and β = 117.60 (2)°. The calculated density is 0.97 g/cm³ for Z = 4 (mol wt 400.94; $C_{20}H_{48}Si_4$). The space group was defined successfully to be $C2/c$. A total of 2170 reflections within 2θ = 55° were measured by the 2θ–θ scan method with a scan rate of 4 °/min. No significant decrease of intensity was shown in the periodic measurements of three check reflections during data collection at room temperature of 15 °C. The intensities were collected for the Lorentz–polarization effects but not for absorption effects. The structure was solved at first by the direct method and then by the successive Fourier synthesis. Approximate coordinates of non-hydrogen atoms were refined by the block-diagonal least-squares method to reduce to an R factor of 0.09. All 24 hydrogen atoms were located from the difference Fourier map and then included in the successive refinements with isotropic temperature factors. The final R factor is 0.067 for all reflections (0.059 for nonzero reflections). The final difference map contained a few noise peaks of ca. 0.20 e/Å³.

[6] The bond length of Si–$C(CH_3)_3$ of **5** compares with Me_3Si–C and $PhMe_2Si$–C bond lengths (an average value of 1.920 (6) Å) of $(Me_3Si)_3C$–$SiMe_2Ph$ reported quite recently: Eaborn, C.; Hitchcock, P. B.; Lickiss, P. D. *J. Organomet. Chem.* **1981**, *221*, 13.

[7] For reviews of crowded olefins, see: (a) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (b) Tidwell, T. T. *Tetrahedron* **1978**, *34*, 1855.

[8] The unknown tetra-*tert*-butylethylene has been predicted to have a twist angle of 45° in the most recent molecular mechanical calculation: Burkert, U. *Tetrahedron* **1981**, *37*, 333. See also: Lenoir, D.; Dauner, H.; Frank, R. M. *Chem. Ber.* **1980**, *113*, 2636.

[9] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

[10] West, R.; Quass, L. C. *J. Organomet. Chem.* **1969**, *18*, 55.