Tetrahedron Letters Vol. 21, pp 3077 - 3080
0040-4039/80/0801-3077$02.00/0

TETRAKIS(TRIMETHYLSILYL)ETHYLENE AND RELATED COMPOUNDS, CROWDED OLEFINS[1]

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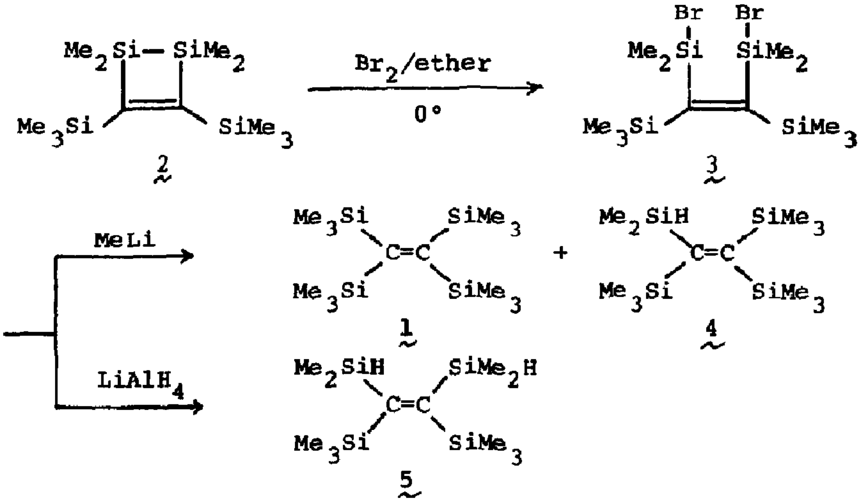
Summary: Tetrakis(trimethylsilyl)ethylene (1), tris(trimethylsilyl)(dimethylsilyl) ethylene and 1,2-bis(trimethylsilyl)-1,2-bis(dimethylsilyl)ethylene have been prepared and spectral properties are described. ESR spectra of anion and cation radicals of 1 are also recorded, indicating a nonplanar twisted structure for 1. These crowded olefins show interesting reversible thermochromism.

Preparation of crowded olefins has been an intriguing target in the organic chemistry because one can anticipate unusual properties due to molecular distortion for these olefins. We report preparation and some properties of tetrakis-(trimethylsilyl)ethylene (1) and related compounds.[2]

An exothermic reaction of 1,1,2,2-tetramethyl-3,4-bis(trimethylsilyl)-1,2-disilacyclobut-3-ene (2),[3] prepared by our new method,[4] in ether with 0.93 equivalent of bromine resulted in the formation of a clear pale yellow solution of 3 which was subjected to a further reaction with methyllithium without isolation. After usual work-up, 1 was obtained in 41% yield as a yellow crystal.[5]

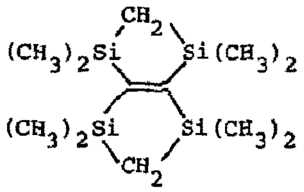


Tris(trimethylsilyl)(dimethylsilyl)ethylene (4) was also isolated from the reaction mixture in ca. 5% yield as a pale yellow crystal.[7] Reduction of 3 with excess $LiAlH_4$ gave 1,2-bis(trimethylsilyl)-1,2-bis(dimethylsilyl)ethylene (5) in 81% yield as a white crystal.[8]

Reduction of **1** with potassium in dimethoxyethane gave an anion radical and a well-characterized ESR spectrum was obtained as shown in Fig. 1. Small but definite temperature dependence of the ESR spectra was observed; temperature (°C) and hyperfine coupling constants (hfcc, in gauss) are: +20, 0.185(a_H), 4.65($a_{^{29}Si}$), 2.61($a_{^{13}C}$); -20, 0.188(a_H), 4.43($a_{^{29}Si}$); -80, 0.190(a_H), 4.22($a_{^{29}Si}$).

A cationic radical of **1** was also obtained upon oxidation with $AlCl_3$ in dichloromethane.[9] The ESR spectrum of $\mathbf{1}^{\cdot +}$ shows no temperature dependence and is shown in Fig. 2: hfcc (gauss) (0°C) 0.30 (a_H), 17.75($a_{^{29}Si}$).

An interesting comparison may be made between these data and those of both anion and cation radicals of 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasilabicyclo-[3.3.0]oct-1-ene (**6**). Bock, Fritz et al. reported larger ^{29}Si and ^{1}H coupling constants for both $\mathbf{6}^{\cdot -}$ ($a_{^{29}Si}$=6.72G, $a_H^{CH_2}$=$a_H^{CH_3}$=0.48G at 300 K) and $\mathbf{6}^{\cdot +}$ ($a_{^{29}Si}$=22.71 G, $a_H^{CH_2}$=2.48G, $a_H^{CH_3}$=0.62G at 180 K).[9]



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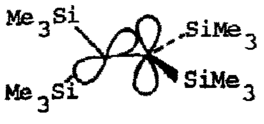

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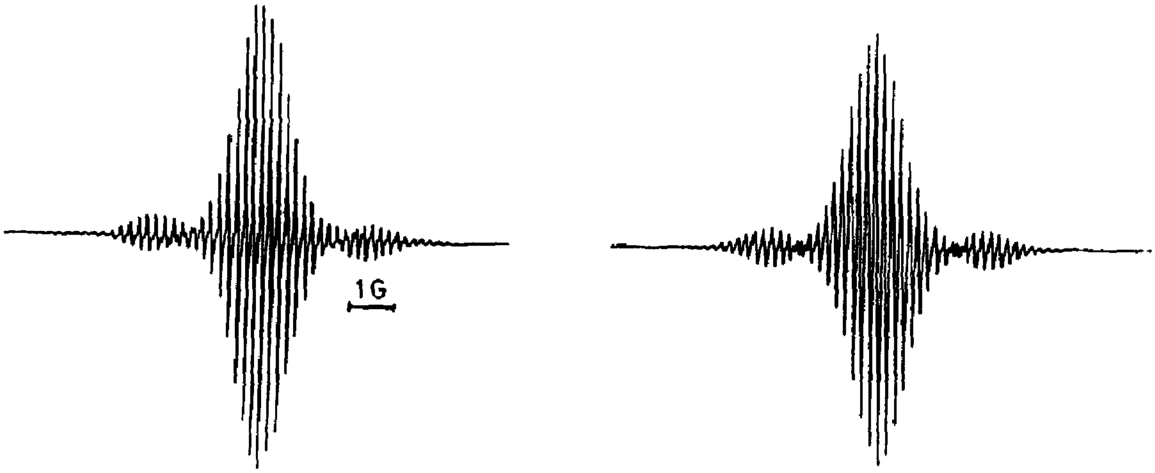
The marked difference in the magnitude of $a_{^{29}Si}$ can be explained in terms of the distorted nonplanar structure of **1**. Thus, examination of a molecular model demonstrated that **1** cannot be planar and therefore twisted conformations are important even in the ground state of the molecule. An interesting and important feature of **1** is that extensive σ(Si-C)-p mixing is possible in the twisted conformation (**7**), while nonbonding repulsion of methyl groups for **1** is dissolved by forming five-membered rings in **6**, so that the tetrasilyl-substituted ethylene arrangement of **6** is fixed to be planar. Since both spin polarization and hyperconjugation can determine the magnitude of the ^{29}Si hfcc and countervails each other,[10] the magnitude of ^{29}Si hfcc should be smaller for nonplanar radical ions of **1** than for radical ions of **6**. The temperature effect on the $a_{^{29}Si}$ of $\mathbf{1}^{\cdot -}$ supports the explanation. The twisted structure being the prefered conformation, smaller $a_{^{29}Si}$ should be observed at lower temperature as indeed it is shown experimentally.

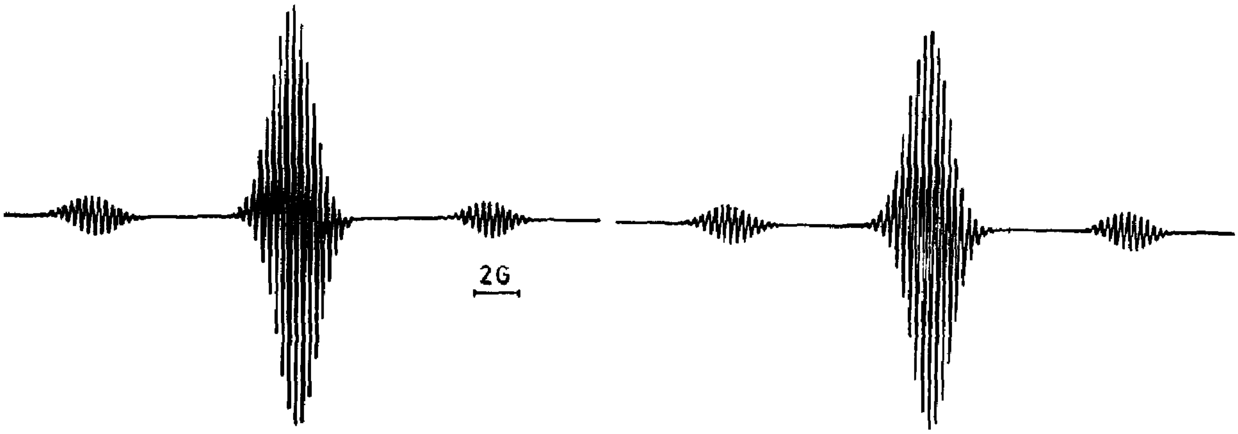
As another indication as crowded olefins, **1**, **4**, and **5** show interesting reversible thermochromism. Thus, at ca. 200°C **1** and **4** become orange yellow and deep yellow, respectively. The color of **5** also changes to yellow at ca. 200°C. At -78°C, both **1** and **4** become colorless. These observations merit further detailed spectroscopic investigation and theoretical calculation on the molecule which are currently under way.

Figure 1. ESR spectra of the anion radical of tetrakis(trimethylsilyl)ethylene (1). (a) Experimental at 20°C; (b) Simulated with hfcc(gauss) 0.185(36 ^{1}H), 4.65 (4 ^{29}Si), 2.61(1 ^{13}C) and line width of 0.06G.


(a) Experimental

(b) Simulated

Figure 2. ESR spectra of the cation radical of tetrakis(trimethylsilyl)ethylene (1). (a) Experimental at 0°C; (b) Simulated with hfcc(gauss) 0.30(36 ^{1}H), 17.75 (4 ^{29}Si) and line width of 0.12G.


(a) Experimental

(b) Simulated

Acknowledgment

We thank Dr. A. Hosomi for helpful advice. We also thank the Mitsubishi Foundation and Toshiba Silicone Co., Ltd., for partial supports to the work.

References and Notes

(1) Chemistry of Organosilicon Compounds 132.

(2) Generation of **1** has been reported by C. Chung and R. J. Lagow, J. C. S. Chem. Comm., 1078 (1972), but no data on the physical properties was recorded. See also, R. J. Wroczynski, M. W. Baum, D. Kost, K. Mislow, S. C. Vick, and D. Seyferth, J. Organometal. Chem., 170, C29 (1979).

(3) D. Seyferth, and S. C. Vick, J. Organometal. Chem., 125, C11 (1977).

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(5) **1**; mp 102°C; ^{1}H NMR (CCl$_4$) δ 0.24 (s); ^{13}C NMR (CDCl$_3$) δ 4.2 (Si-$\underline{C}$H$_3$), 195.3 ($\underline{C}$=$\underline{C}$); ^{29}Si NMR (CDCl$_3$) δ -8.63(high-field shift, relative to external TMS); M$^+$ 316 (4.1%), m/e 155(100%); λ_{max}(n-hexane) nm(ε) 223.7 (17,900), 370 (710). Anal.: Calcd for $C_{14}H_{36}Si_4$: C, 53.08; H, 11.46. Found: C, 53.34; H, 11.62. Very weak C=C stretching was found at 1533 cm^{-1} in the Raman spectrum.[6]

(6) We thank Prof. M. Ito and Dr. N. Mikami for taking the Raman spectra.

(7) **4**; mp 66°C; ^{1}H NMR (CCl$_4$) δ 0.25 (s, 27H), 0.29(d, J=3.7Hz, 6H), 4.28(sep, J=3.7Hz, 1H); M$^+$ 302 (3.1%) m/e 155 (100%); λ_{max}(n-hexane) nm(ε) 223.5 (18.000), 357(610). Anal.: Calcd for $C_{13}H_{34}Si_4$: C, 51.57; H, 11.32. Found: C, 51.56; H, 11.26.

(8) **5**, presumably the Z-isomer; mp 101°C; ^{1}H NMR (CCl$_4$) δ 0.25 (s, 18H), 0.28(d, J=3.7Hz, 12H), 4.38(sep, J=3.7Hz, 2H); decoupled ^{13}C NMR (CDCl$_3$) δ -1.55 (SiHMe$_2$), 3.6 (SiMe$_3$) 188.2 (C=C); gated decoupling (NOE mode) changes the signal at δ -1.55 to qdq ($^1J_{CH}$=120.4, $^2J_{CH}$=6.2, $^3J_{CH}$=2.2Hz) and the signal at δ 3.6 to qsep ($^1J_{CH}$=119.4, $^3J_{CH}$=2.2Hz); ^{29}Si NMR (CDCl$_3$) δ -9.64 (SiMe$_3$) -20.58 (SiHMe$_2$); M$^+$ 288 (3.5%), m/e 155 (66.8%) m/e 73 (100%); λ_{max}(n-hexane) nm(ε) 224.2(16.500), 344(370). Anal.: Calcd for $C_{12}H_{32}Si_4$: C, 49.92; H, 11.17. Found: C, 49.92; H, 11.28.

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(Received in Japan 17 May 1980)