

Communications to the Editor

Synthesis, Structure, and Stabilities of *trans*-1,2-Diphenyl-4,4,5,5,6,6-hexamethyl-4,5,6-trisilacycloheptene

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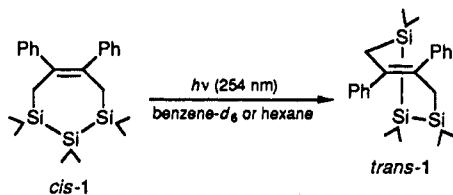
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Medium-ring *trans*-cycloalkenes have been the subject of considerable interest as strained cyclic compounds. *trans*-Cyclooctene is well-known as the smallest *trans*-cycloalkene that is stable at room temperature.¹ *trans*-Cycloheptenes have been generated at low temperature and their existence was confirmed by chemical trapping with isobenzofuran² or acidic methanol³ and ¹H NMR spectroscopy.⁴ Even *trans*-cyclohexene has been generated.⁵ However, isolation of the *trans*-cycloheptenes has been unsuccessful except for homoadamant-3-ene stabilized by bulky substituent⁶ because of the transient thermal stability caused by the strained structure.^{4,7} Recently, we reported the synthesis of pentasilacycloheptyne as the smallest stable polysilacyclic acetylene; it is stabilized by long bond lengths of Si-Si bonds.⁸ In the present paper we report the isolation of *trans*-trisilacycloheptene stabilized by long Si-Si bond lengths.

cis-1,2-Diphenyl-4,4,5,5,6,6-hexamethyl-4,5,6-trisilacycloheptene (*cis*-1) was prepared by the reaction of 2,3-diphenylbutadiene with 1,3-dichlorohexamethyltrisilane in the presence of magnesium in 23% yield. When the benzene-*d*₆ solution of *cis*-1 (9.0×10^{-3} M) was irradiated with an 80-W low-pressure mercury lamp through a Quartz NMR tube, it was observed by ¹H NMR measurements that the resonances for *cis*-1 decreased in intensity and new resonances (three singlets at -0.29, 0.37, and 0.39 ppm and an AB quartet at 1.76 and 3.22 ppm, $J = 14.0$ Hz) appeared upon irradiation. After 5 h, purification by preparative-TLC (hexane) and crystallization gave *trans*-1,2-diphenyl-4,4,5,5,6,6-hexamethyl-4,5,6-trisilacycloheptene (*trans*-1) in 12.5% yield. Irradiation of a hexane solution of *cis*-1 also gave *trans* isomer (*trans*-1) in 19% yield.



The structure of the *trans*-trisilacycloheptene (*trans*-1) was determined by NMR, UV, mass, and X-ray analysis.^{9,10} The UV

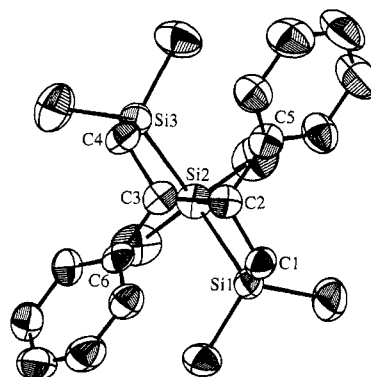


Figure 1. ORTEP plot of *trans*-1 with hydrogen atoms removed for clarity; selected bond lengths (Å) and bond angles (deg): C(1)-C(2), 1.506 (7); C(2)-C(3), 1.344 (8); C(3)-C(4), 1.515 (8); C(4)-Si(3), 1.905 (6); Si(3)-Si(2), 2.378 (2); Si(2)-Si(1), 2.386 (3); Si(1)-C(1), 1.905 (5); C(1)-C(2)-C(3), 122.4 (5); C(2)-C(3)-C(4), 124.0 (5); C(3)-C(4)-Si(3), 110.0 (3); C(4)-Si(3)-Si(2), 112.9 (2); Si(3)-Si(2)-Si(1), 120.62 (9); Si(2)-Si(1)-C(1), 113.4 (2); Si(1)-C(1)-C(2), 109.6 (4); C(1)-C(2)-C(3), 115.8 (5); C(4)-C(3)-C(6), 113.6 (5); C(3)-C(2)-C(5), 120.5 (5); C(2)-C(3)-C(6), 121.2 (5).

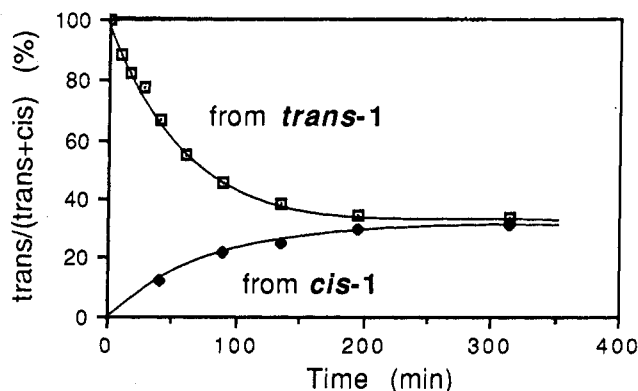


Figure 2. Plot of *trans* percentage as a function of time for the photo *trans*-*cis* isomerization of 1 in benzene-*d*₆.

spectrum shows characteristic absorption of *trans*-stilbene derivatives at 321 nm (hexane).

The molecular structure of *trans*-1 was determined by X-ray crystallographic analysis.¹⁰ The X-ray structure of *trans*-1 is shown in Figure 1. Previously, an unsymmetrical structure was proposed for *trans*-cycloheptene based on ¹H NMR measurements^{4,11} and force-field calculation.¹¹ However, the ¹H and ¹³C

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(9) Spectral data of *trans*-1: mp 115-117 °C; IR (CCl₄) 3100-2900, 1620-1480, 1250, 1070-1020 cm⁻¹; UV (hexane) 223 (ε 7500, sh), 250 (ε 2800, sh) 321 (ε 2800) nm; ¹H NMR (500 MHz, C₆D₆) δ -0.29 (s, 6 H, CH₃), 0.37 (s, 6 H, CH₃), 0.39 (s, 6 H, CH₃), 1.76 (d, $J = 14.0$ Hz, 2 H, CH), 3.22 (d, $J = 14.0$ Hz, 2 H, CH), 7.05-7.77 (m, 10 H, Ar); ¹H NMR (500 MHz, CDCl₃) δ -0.58 (s, 6 H, CH₃), 0.10 (s, 6 H, CH₃), 0.22 (s, 6 H, CH₃), 1.50 (d, $J = 14.1$ Hz, 2 H, CH), 2.90 (d, $J = 14.1$ Hz, 2 H, CH), 7.18-7.23 (m, 2 H, Ar), 7.30-7.58 (m, 8 H, Ar); ¹³C NMR (125 MHz, CDCl₃) δ -3.4, -0.6, 0.2, 26.6, 126.7, 128.3, 128.4, 136.1, 145.5; ²⁹Si NMR (18 MHz, C₆D₆) δ -44.9 (Si-Si-Si), -1.4 (Si-Si-Si); LRMS, m/e 380, 320, 307, 174, 116; HRMS, m/e calcd for C₂₂H₃₂Si₃ 380.1812, found 380.1812.

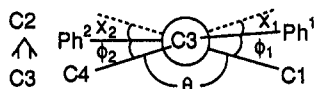
(10) Crystal data for *trans*-1: Compound *trans*-1 crystallized in the monoclinic space group $P2_1/c$, with $a = 8.671$ (2) Å, $b = 25.238$ (0) Å, $c = 10.812$ (0) Å, $\beta = 101.51$ (0)°, $V = 2318.6$ Å³, $Z = 4$, and ρ (calcd) = 1.09 g cm⁻³. Data were collected on an Enraf-Nonius CAD4 diffractometer at 23 °C. Of the 3184 unique data collected with Mo K α radiation ($\lambda = 0.70930$ Å), the 2022 with $I > 3\sigma(I)$ were used in the least-squares refinement to yield $R = 5.2\%$, $R_w = 5.6\%$.

Table I. Time Constants for Thermal Trans–Cis Isomerization of *trans*-Cycloheptenes

| compd | solvent | temp, °C | time const, s ⁻¹ |
|------------------------------------|-----------------------------|----------|-------------------------------------|
| <i>trans</i> -1 | DMSO- <i>d</i> ₆ | 80 | 1.59 (±0.10) × 10 ⁻⁶ |
| | | 100 | 8.86 (±0.35) × 10 ⁻⁶ |
| | | 120 | 4.72 (±0.68) × 10 ⁻⁵ |
| <i>trans</i> -cycloheptene | MeOH | 1.0 | 1.19 × 10 ^{-3^a} |
| <i>trans</i> -1-phenylcycloheptene | cyclohexane | ambient | 2.77 × 10 ^{-3^b} |

^a Calculated on the basis of ref 15. ^b Calculated on the basis of ref 16.

NMR measurements at room temperature and the X-ray crystallographic analysis of *trans*-1 show a symmetrical conformation. ¹H NMR measurement of *trans*-1 at low temperature (–70 °C) is also consistent with a symmetrical form. A molecular mechanics calculation (MM2) of *trans*-1 also supports the symmetrical structure as the one having 11.4 kcal less strain compared with the unsymmetrical form. The most interesting point of the structure of *trans*-1 is the twisting around the C=C double bond. The torsion angle of C(1)–C(2)–C(3)–C(4) was found to be 180° – θ = 32.7°. This value is, however, in fair agreement with the value for the unsymmetrical calculated structure rather than that of the symmetrical form. The twist angle Φ [(φ₁ + φ₂)/2] and the pyramidal deformation X [(χ₁ + χ₂)/2] were also found



X-ray: θ = 147.3°, φ₁ = 19.9°, φ₂ = 19.2°, χ₁ = 12.8°, χ₂ = 13.5°
 MM2(symmetrical): 131.5° 42.2° 40.7° 6.3° 7.8°
 MM2(unsymmetrical): 147.7° 31.0° 17.2° 1.3° 15.1°

to be 19.6° and 13.2°, respectively. The bond angles around the ring atoms of *trans*-1 are almost normal except for the expanded Si(1)–Si(2)–Si(3) bond angle. Interestingly, the bond lengths of C(1)–C(2) and C(3)–C(4) are slightly shortened while those of C(1)–Si(1), C(4)–Si(3), Si(1)–Si(2), and Si(2)–Si(3) are stretched from corresponding normal bond lengths. These deformations of the bond angle and lengths must occur to mitigate the twist of the C=C double bond. The C=C double bond [C(2)–C(3) = 1.344 Å] is slightly stretched compared with that of *trans*-stilbene in the solid state (1.228–1.330 Å).^{12,13} The expansion of the C=C double bond may result from the twisting of the double bond. Furthermore, two benzene rings incline at 47.3° and 51.1° from the planes of C(3)–C(2)–C(5) and C(2)–C(3)–C(6), respectively, though the torsion angles of *trans*-stilbene are ranged between 3.6 and 5.7° in the solid state.¹²

Photochemical reaction of *trans*-1 was examined as a general property of the olefins. Irradiation (254 nm) of *trans*-1 in benzene-*d*₆ gave photoisomerized *cis*-1. In this isomerization, it was found that a photoequilibrium existed and the photostationary *trans*/*cis* ratio was 0.49 (Figure 2). This value is higher than the photosensitized isomerization of *trans*-cycloheptene.¹⁴

Thermal stabilities of *trans*-1 were also examined. When a benzene-*d*₆ solution of *trans*-1 in an NMR tube was heated at 80 °C, *trans*-1 was stable even after 72 h. However, heating of the DMSO-*d*₆ solution at 80 °C tended to initiate the reaction and gave isomerized *cis*-1. These results may be explained by stabilization of the transition state caused by solvation with the polar solvent. At several temperatures, the measurements of the *trans*/*cis* ratio by ¹H NMR at regular time intervals in DMSO-*d*₆ gave a straight line for a plot of log [*trans*-1] as a function of time,

and the rate constants obtained are shown in Table I. The rate constants of the thermal *trans*–*cis* isomerization are very small compared with those of *trans*-cycloheptene¹⁵ and *trans*-1-phenylcycloheptene.¹⁶ It is found that the introduction of the three silicon atoms in *trans*-cycloheptene is useful to stabilize the *trans*-trisilacycloheptene. A plot of log *k* as a function of reciprocal of temperature also gave a good linear relationship, and the following thermodynamic parameters were obtained: *E*_a = 23.2 ± 1.3 kcal mol⁻¹, log *A* = 8.6 ± 0.7, Δ*G*₃₇₃[‡] = 30.6 ± 2.6 kcal mol⁻¹, Δ*H*₃₇₃[‡] = 22.5 ± 1.3 kcal mol⁻¹, Δ*S*₃₇₃[‡] = –21.7 ± 11 cal K⁻¹ mol⁻¹. At 120 °C, continued heating gave other minor products, which include 2,3-diphenylbutadiene, *cis*-1,2-diphenyl-4,4-dimethyl-4-silacyclopentene, and *cis*-1,2-diphenyl-4,4,5,5-tetramethyl-4,5-disilacyclohexene which were identified by GCMS and ¹H NMR measurements of the mixture and unidentified silicon compounds. These products were found to be formed from *trans*-1 because the heating of *cis*-1 under the same conditions gave no reaction.

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Supplementary Material Available: Detailed information of the X-ray crystal analysis of *trans*-1 including data collection and reductions and structure solution and refinement, the Arrhenius plot for the thermal *trans*–*cis* isomerization of 1 in DMSO-*d*₆, and tables of experimental details, positional and thermal parameters, general temperature factor expressions, root-mean-square amplitudes of thermal vibration, and bond distances and angles (22 pages); listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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Observation of a Weakly Bound Mn(CO)₅⁺/CH₄ Complex

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Intramolecular reductive elimination of an alkane molecule from alkyl hydride organometallic complexes (e.g., [(Cp)₂Re(H)CH₃]Cl and (Cp)₂W(H)CH₃) has received considerable attention recently.^{1–4} This is partly due to the intense interest in the reverse oxidative addition process, which, in the case of alkanes, results in hydrocarbon activation.⁵

To explain exchange of deuterium from the hydride position with hydrogen in the methyl ligand and an inverse kinetic isotope effect for the elimination of methane, organometallic/methane σ complexes were invoked as intermediates. The structure of the complexes could not be established with certainty, but involvement

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