duced sialosides to glycosyl donors, should be widely applicable for the syntheses of various NeuAc-containing glycoconjugates.

Acknowledgment. This research was supported by grants from the NSF (DMB-88-21049) and NIH (GM-27904).

Supplementary Material Available: Experimental details for the synthesis of **2**, **3**, **6–8**, and **1b**, enzymatic sialylation of **2**, 300-MHz ^{1}H-NMR spectra of **5** and synthetic GM3, and Lineweaver–Burk plot for the determination of kinetic parameters (10 pages). Ordering information is given on any current masthead page.

Reaction of C_{60} with Silylene, the First Fullerene Silirane Derivative

Takeshi Akasaka and Wataru Ando*

Department of Chemistry, University of Tsukuba
Tsukuba, Ibaraki 305, Japan

Kaoru Kobayashi and Shigeru Nagase

Department of Chemistry, Faculty of Education
Yokohama National University, Yokohama 240, Japan

Received November 25, 1992

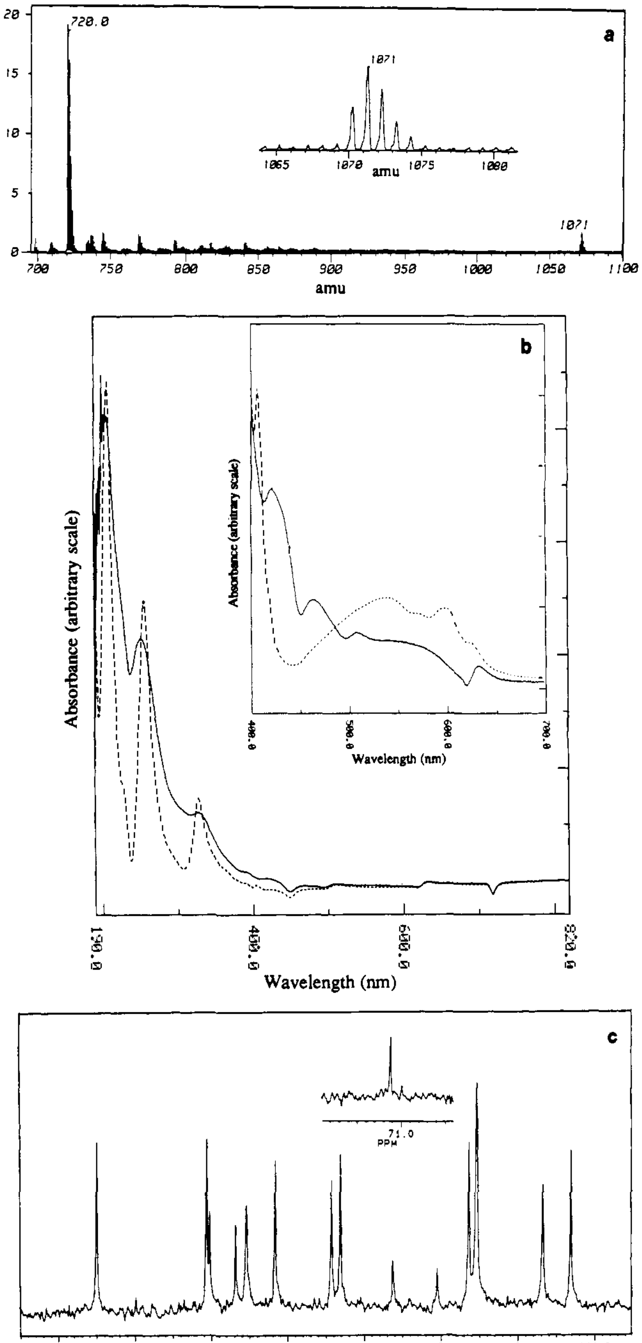


Figure 1. (a) FAB mass spectrum of **2** from 700 to 1100 amu. Inset: expanded view of the 1065–1080-amu region. (b) UV–Vis spectra of C_{60} (---) and **2** (—) from 400 to 700 nm in toluene. Inset: spectra of C_{60} (---) and **2** (—) from 190 to 829 nm in hexane. (c) ^{13}C NMR spectrum of **2**.

Since the isolation of Buckminsterfullerene (C_{60})[1] in preparatively useful quantities,[2] much attention has been devoted to its chemical reactivities[3] toward nucleophiles,[4] radicals,[5] reducing agents,[6] dienes,[4] dipoles,[4,7] zero-valent transition metals,[8] oxygen,[9] and also electrophiles.[10] Several functionalizations have been attempted, but only a few discrete individual products such as the

---

[1] (1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

[2] (2) (a) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. (b) Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167.

[3] (3) (a) Bethune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J. *Chem. Phys. Lett.* **1990**, *174*, 219. (b) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423. (c) Ajie, H.; Alvarez, M. M.; Anz, S. A.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630. (d) Johnson, R. D.; Meijer, G.; Bethune, D. S. *J. Am. Chem. Soc.* **1990**, *112*, 8983. (e) Ettl, R.; Chao, I.; Diederich, F.; Whetten, R. L. *Nature* **1991**, *353*, 149. (f) Tycko, R.; Haddon, R. C.; Dabbagh, G.; Glarum, S. H.; Douglass, D. C.; Mijsce, A. M. *J. Phys. Chem.* **1991**, *95*, 518. (g) Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sensharma, D.; Wudl, F.; Khemani, C.; Koch, A. *Science* **1991**, *252*, 548. (h) Koch, A.; Khemani, K. C.; Wudl, F. *J. Org. Chem.* **1991**, *56*, 4543. (i) Parker, D. H.; Wurtz, P.; Chatterjee, K.; Lykke, K. R.; Hunt, J. E.; Pellin, M. J.; Hemminger, J. C.; Gruen, D. M.; Stock, L. M. *J. Am. Chem. Soc.* **1991**, *113*, 7499. (j) Peters, G.; Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 223. (k) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050. (l) Allemand, P.-M.; Srdanov, G.; Koch, A.; Khemani, K.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *1123*, 2780. (m) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364. (n) Ehoulet, C.; Bard, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 5456. (o) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773.

[4] (4) (a) Hirsch, A.; Li, Q.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1309. (b) Wudl, F.; Hirsch, A.; Khemani, K. C.; Suzuki, T.; Allemand, P.-M. Koch, A.; Eckert, H.; Srdanov, G.; Webb, H. m. In *Fullerenes: Synthesis, Properties, and Chemistry of Large Carbon Clusters*; Hammond, G. S.; Kuck, V. J., Eds.; American Chemical Society: Washington, DC, 1992; p 161.

[5] (5) (a) Krusic, P. J.; Wasserman, E.; Keiser, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991**, *254*, 1183. (b) Krusic, P. J.; Wasserman, E.; Parkinson, B. A.; Malone, B.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *J. Am. Chem. Soc.* **1991**, *113*, 6274. (c) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Wasserman, E. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1425. (d) Loy, D. A.; Assink, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 3977. (e) McEwen, L. N.; McKay, R. G.; Larsen, B. S. *J. Am. Chem. Soc.* **1992**, *114*, 4412.

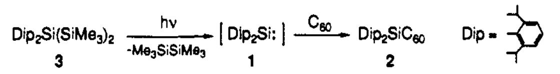
[6] (6) (a) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634. (b) Bausch, J. W.; Prakash, S. G. K.; Olah, G. A. *J. Am. Chem. Soc.* **1991**, *113*, 3205.

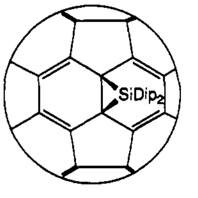
[7] (7) (a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ō. *Science* **1991**, *254*, 1186. (b) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157. (c) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarrson, Ō. *J. Am. Chem. Soc.* **1992**, *114*, 7300. (d) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301.

[8] (8) (a) Hawkins, J. M.; Lewis, T. A.; Loren, S. D.; Meyer, A.; Heath, J. R.; Shibata, Y.; Saykally, R. J. *J. Org. Chem.* **1990**, *55*, 6250. (b) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J. *Science* **1991**, *252*, 312. (a) Hawkins, J. M.; Loren, S.; Meyer, A.; Nunlist, R. *J. Am. Chem. Soc.* **1991**, *113*, 7770. (d) Hawkins, J. *Acc. Chem. Res.* **1991**, *25*, 150. (e) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, *252*, 1160. (f) Fagan, P. J.; Calabrese, J. C.; Malone, B. *J. Am. Chem. Soc.* **1991**, *113*, 9408. (g) Fagan, P. *Acc. Chem. Res.* **1992**, *25*, 134. (h) Koefod, R. S.; Hudgens, M. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 8957.

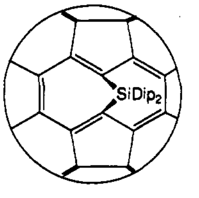
0002-7863/93/1515-1605$04.00/0

Scheme I

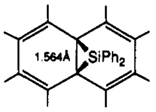




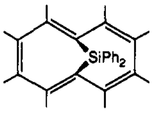
2a



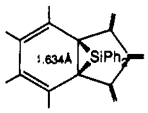
2b



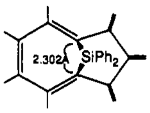
4a



4b



5a



5b

fullerene epoxide,[9d,e] the fulleroids,[7] and the metal complexes[8] have been prepared and completely characterized. In this communication we report that addition of bis(2,6-diisopropylphenyl)silylene (**1**) as a reactive divalent species to C_{60} furnishes adduct **2**[11] as the isolable product (Scheme I).

Trisilane **3**[12] as a silylene precursor[13] was photolyzed with a low-pressure mercury lamp in a toluene solution of C_{60}. The color of the solution changed from purple to dark brown. Flash chromatography on silica gel furnished thermally stable **2** in 58% yield.[14] The dark brown powder exhibits slightly lower solubility than to that of C_{60} but a different TLC R_f value.

FAB mass spectrometry of **2** ($C_{84}H_{34}Si$) displays a peak for **2** at 1074–1070 as well as one for C_{60} at 723–720 which arises from loss of **1**, as shown in Figure 1a. The isolated **2** is not contaminated by C_{60} according to HPLC. The UV–vis absorption spectra of **2** is virtually identical to that of C_{60} except for subtle differences in the 400–700-nm region (Figure 1b). **2** exhibits a new band at 421 nm but lacks the C_{60} band at 406 nm. Relative to C_{60}, **2** shows stronger absorptions at 463 and 508 nm and weaker absorptions at 539 and 599 nm. The FTIR spectrum of **2** contains no detectable absorptions above 1500 cm^{-1} except those at 3048.7 and 2961.9 cm^{-1}. Seven relatively strong bands and eight weaker ones are observed, with four bands at 1429.0, 1182.9, 575.9, and 527.0 cm^{-1} which correspond to those in the C_{60} spectrum.

The FAB mass, UV–vis, and FTIR spectra of **2** contain a number of unique features but also suggest that this new fullerene retains the essential electronic and structural character of C_{60}. The silirane structure **2a**, of C_{2v} symmetry,[6a,7,8d,e] would derive from addition of **1** across the reactive 6-ring-6-ring junction. Silamethano[10]annulene **2b**, analogous to the structure proposed for Ph_2C_{61}, could arise via isomerization of **2a**.

The ^{13}C NMR spectrum of **2**[15] shows 17 signals for the C_{60} skeleton, of which four correspond to two carbon atoms and 13 correspond to four carbon atoms: one at $\delta = 71.12$ and the remainder between $\delta = 140$ and 150 (Figure 1c). The signal at $\delta = 142.54$ consists of three peaks each corresponding to four carbon atoms. This is the appropriate number and ratio of peak intensities for a C_{60} adduct of C_{2v} symmetry. The ^{13}C NMR signal at $\delta = 71.12$ strongly supports **2a** rather than **2b**; an sp^2 C–Si should give rise to a signal below $\delta = 130$.[16] Methyl-substituted silirane carbons typically resonate at $\delta = 15$–25.[17] A downfield shift by 20 ppm may occur when a vinyl group is attached to the ring carbon.[18] Although the resonance at $\delta = 71.12$ is at low field for the silirane carbons, the downfield shift is probably caused by the anisotropy of the partially broken fullerene, which was also reported in $C_{60}O$.[8e] The ^{29}Si NMR spectrum of **2** shows a peak at $\delta = -72.74$ which is also assigned to the silicon atom of **2a**. The chemical shift of the silicon atom on a silirane ring typically appears at high field ranging from $\delta = -50$ to -85.[17] The ^{29}Si chemical shift of diphenyldivinylsilane can be anticipated to appear at $\delta = -20$.[16] Thus, the chemical shifts of the two-carbon signal at $\delta = 71.12$ and the silicon one at $\delta = -72.74$ are fully consistent with expectations for the silirane carbon atoms and silicon atom in **2a**.

The experimental finding for **2a** was confirmed by AM1 molecular orbital calculation[19,20] on the reaction of C_{60} and diphenylsilylene. Diphenylsilylene adds across the junction of two six-membered rings in C_{60} to give silirane **4a** (a 6-6 adduct) with an exothermicity of 61.3 kcal/mol. The isomeric **4b** was not located on the potential energy surface. The 6-6 adduct **4a** was 19.4 and 10.7 kcal/mol more stable than the 5-6 adducts **5a** and **5b**, respectively.[21] Interestingly, this is in contrast with the addition of diphenylmethylene, for which the 6-6 adduct was calculated to be only 1.2 kcal/mol more stable than the 5-6 adduct.

Supplementary Material Available: Detailed procedures for the preparation of **2**, complete spectroscopic characterization of **2**, and computer-generated models of **4a**, **5a**, and **5b** (8 pages). Ordering information is given on any current masthead page.

---

(9) (a) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11. (b) Kalsbeck, W. A.; Thorp, H. H. *J. Electroanal. Chem.* **1991**, *314*, 363. (c) Wood, J. M.; Kahr, B.; Hoke, S. H., II; Dejarme, L.; Cooks, R. G.; Ben-Amotz, D. *J. Am. Chem. Soc.* **1991**, *113*, 5907. (d) Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McCauley, J. P., Jr.; Jones, D. R.; Gallaghar, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 1103. (e) Elemes, Y.; Silverman, S. K.; Sheu, C.; Kao, M.; Foote, C. S.; Alvarez, M. M.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 351.

(10) (a) Avent, A. G.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M.; Holloway, J. H.; Hope, E. G.; Langley, G. J. *Nature* **1991**, *355*, 27. (b) Holloway, J. H.; Hope, E. G.; Taylor, R.; Langley, G. J.; Avent, A. G.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1991**, 966. (c) Selig, H.; Lifshitz, C.; Peres, T.; Fischer, J. E.; Smith, A. B., III; McGhie, A. R.; Romanow, W. J.; McCauley, J. P., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 5475. (d) Olah, G. A.; Bucsi, I.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.; Sensharama, D.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1991**, *113*, 9385, 9387. (e) Tebbe, J. N.; Becker, J. Y.; Chase, D. B.; Firment, L. E.; Holler, E. R.; Malone, B. S.; Krusic, P. J.; Wasserman, E. *J. Am. Chem. Soc.* **1991**, *113*, 9900. (f) Birkett, P. R.; Hitchcock, P. B. H.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Nature* **1992**, *357*, 479. (g) Tebbe, F. N.; Harlow, R. L.; Chase, D. B.; Thorn, D. L.; Campbell, G. C., Jr.; Calabrese, J. C.; Herron, N.; Young, R. J., Jr.; Wasserman, E. *Science* **1992**, *256*, 822.

(11) The title compound could be considered a silylene analog of $C_{60}O$.[9d]

(12) **3**: ^{1}H NMR ($CDCl_3$) δ 7.20 (d, $J = 7.8$ Hz, 2 H), 7.13(4) (d, $J = 7.8$ Hz, 1 H), 7.12(7), (d, $J = 7.8$ Hz, 1 H), 6.94(0) (d, $J = 7.8$ Hz, 1 H), 6.93(5) (d, $J = 7.8$ Hz, 1 H), 3.38 (sep, $J = 6.3$ Hz, 2 H), 2.91 (sep, $J = 6.3$ Hz, 2 H), 1.32 (d, $J = 6.3$ Hz, 6 H), 1.30 (d, $J = 6.3$ Hz, 6 H), 1.10 (d, $J = 6.3$ Hz, 6 H), 0.23 (s, 18 H), 0.04 (d, $J = 6.3$ Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 155.70, 153.44, 137.02, 128.61, 123.96, 36.46, 34.74, 27.02, 26.09, 25.97, 23.57, 2.57; ^{29}Si NMR (CS_2/CD_2Cl_2) δ −11.61, −52.73; MS, *m/z* 496 (M^+), 423 ($M^+ - SiMe_3$). Anal. Calcd for $C_{30}H_{52}Si_3$: 496.3377. Found: 496.3353.

(13) (a) Gasper, P. P. In *Reactive Intermediates*; Jones, M., Ed.; Wiley: New York, 1978; Vol. 1 p 229. (b) Gasper, P. P. In *Reactive Intermediates*; Jones, M., Ed.; Wiley: New York, 1981; Vol. 2, p 335. (c) Gasper, P. P. In *Reactive Intermediates*; Jones, M., Ed.; Wiley: New York, 1985; Vol. 3, p 333. (d) Gasper, P. P.; Holten, D.; Konieczny, S. *Acc. Chem. Res.* **1987**, *20*, 329.

(14) $(Dip_2Si)_2C_{60}$ (FAB MS, *m/z* 1424–1420($(Dip_2Si)_2C_{60}$), 723–720 (C_{60})) was also obtained in 27% yield; details will be reported elsewhere.

(15) The proton NMR was consistent with that of the Dip_2Si adduct of C_{60}.

(16) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 518.

(17) (a) Lambert, R. C.; Seyferth, D. *J. Am. Chem. Soc.* **1972**, *94*, 9426. (b) Seyferth, D.; Annarelli, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 2273. (c) Seyferth, D.; Annarelli, D. C. *J. Organomet. Chem.* **1976**, *117*, C51. (d) Seyferth, D.; Lambert, R. L., Jr.; Annarelli, D. C. *J. Organometal. Chem.* **1976**, *122*, 311. (e) Ando, W.; Fujita, M.; Yoshida, H.; Sekiguchi, A. *J. Am. Chem. Soc.* **1988**, *110*, 3310.

(18) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Tokyo Kagaku Dojin: Tokyo, 1981; p 231.

(19) Dewar, M. J.; Jie, C. X. *Organometallics* **1987**, *6*, 1486.

(20) All calculations were carried out using the GAUSSIAN 92 program: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*; Gaussian, Inc.: Pittsburgh, PA, 1992.

(21) The less stable **5a** isomerizes to **5b** with a small barrier of 2.0 kcal/mol.