Photochemical Cycloaddition of C_{78} with Disilirane

Aihong Han, Takatsugu Wakahara, Yutaka Maeda, Yasuyuki Niino, Takeshi Akasaka,*† Kazunori Yamamoto,††
Masahiro Kako,††† Yasuhiro Nakadaira,††† Kaoru Kobayashi,†††† and Shigeru Nagase†††††
Graduate School of Science and Technology, Niigata University, Niigata 950-2181
†*Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577*
††*Japan Nuclear Fuel Cycle Development Institute, Tokai, Ibaraki 319-1100*
†††*The University of Electro-Communications, Chofu, Tokyo 182-8585*
††††*Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397*
†††††*Institute for Molecular Science, Myodaiji, Okazaki 444-8585*

(Received July 18, 2001; CL- 010670)

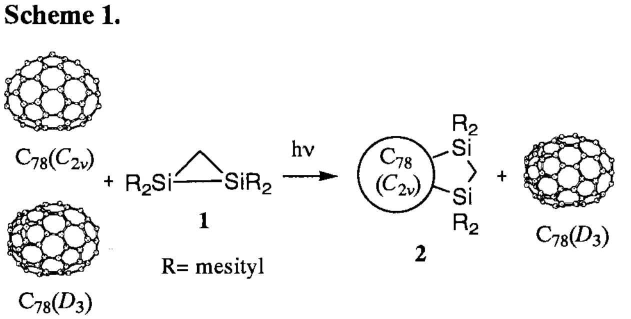
The photochemical cycloaddition of $C_{78}(C_{2v}+D_3)$ with disilirane **1** only gave the adducts of $C_{78}(C_{2v})$. The D_3 isomer of C_{78} did give no adduct with **1**. The two mono-adducts were firstly isolated by a multi-stage HPLC, and characterized on the basis of the spectroscopic data. The electrochemical properties were also investigated by means of differential pulse voltammetry.

The chemical reactivity of C_{60} and C_{70} has been systematically investigated over the past decade. Recently, isolation and structure determination of D_2-C_{76},[1] C_{78}[2–4] and C_{84}[5–7] have allowed investigation on the chemical reactivity of the higher fullerenes. Diederich et al. reported that the mono-adduct of C_{76} had been prepared by the Bingel reaction and Diels–Alder reaction.[8,9] They also reported the multi-adduct of C_{78} (mixture of C_{2v} and D_3) by the Bingel reaction.[10] Those results revealed the unique properties of higher fullerenes different significantly from the known chemistry of C_{60} and C_{70}.

In the course of our study on the chemical functionalization of fullerenes with organosilicon compounds, we found the photochemical mono- and bis-silylation of C_{60} and C_{70}.[11] We report here the first photochemical silylation of C_{78} with disilirane.

We used the 2 : 1 mixture of C_{2v}- and D_3-C_{78} as a starting material.[12] Irradiation of a toluene solution of 1,1,2,2-tetramesityl-1,2-disilirane (**1,** 1.6 equiv) and $C_{78}(C_{2v}+D_3)$ with a halogen-tungsten lamp (cutoff < 400 nm) gave the formation of 1,1,3,3-tetramesityl-1,3-disilolane (**2**) in 38% yield with 33% unreacted C_{78} and 6% bis-adduct (Scheme 1). It is very interesting to note that HPLC analysis of unreacted C_{78} showed the existence of only one isomer, D_3-C_{78} (Figure 1.)[13] We also carried out the reaction of D_3-C_{78} with **1** under the same reaction conditions. However, we did not get any adduct. These observations revealed that the adduct **2** formed in the reaction of $C_{78}(C_{2v}+D_3)$ with **1** is the $C_{78}(C_{2v})$ derivatives.

Scheme 1.



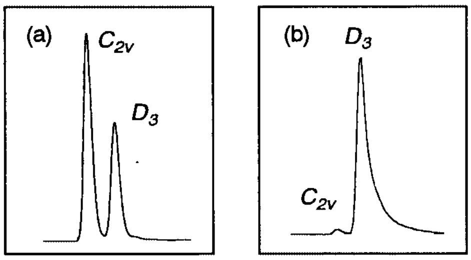


Figure 1. HPLC profiles of (a) $C_{78}(C_{2v}+D_3)$ and (b) unreacted C_{78}.

After three-stage HPLC separation,[14] two major isomers **2a** and **2b** were isolated in pure form, accompanied with at least two minor isomers, which were not further investigated. Mass spectrometry of both **2a** and **2b** displayed a peak at *m/z* 1486–1482 as well as one for C_{78} at *m/z* 940–936, which arises from the loss of **1** from **2**. The UV–vis absorption spectra of **2a** and **2b** revealed that the spectra of the two isomers are very similar to each other.

The symmetries of the two mono-adduct isomers were determined by ^1H and ^{13}C NMR measurements. The ^1H NMR spectrum of **2a**[15] displayed 12 methyl signals with equal intensity between 1.9 and 3.5 ppm and 8 meta-proton signals of the mesityl groups between 6.4 and 7.0 ppm. An AB quartet (J = 15.0 Hz) for the two methylene protons was observed at 2.09 and 2.12 ppm. The ^{13}C NMR spectrum showed that the adduct **2a** is a C_1-symmetrical compound. Except for the peaks at 65.3 and 64.3 ppm assigned to the two bridgehead carbons, all fullerene ^{13}C NMR signals appeared in the spectral range between 165 and 125 ppm. In the HMQC NMR spectrum, two cross-peaks due to the methylene protons at 2.09 and 2.12 ppm and the methylene carbon atom of the disilirane component at 7.2 ppm were observed. No change on the symmetry was observed below 120 °C. These spectral data suggest that the cycloadduct **2a** has C_1 symmetry. The ^1H, ^{13}C, ^{29}Si, HMQC and HMBC spectra were also measured for **2b**.[16] The results also indicate that **2b** has C_1 symmetry.

Disilirane **1** adds to C_{60} at the 6–6 ring junctions giving the corresponding 5-membered ring.[11b] It would be assumed that **1** also adds to C_{78} at the 6–6 ring junctions. While all the positions in C_{60} are identical, 21 sets of carbons and 18 distinct types of C–C bonds at the 6–6 ring junctions are available in C_{78} (C_{2v}). Although 18 isomers are conceivable for **2**, interestingly, we isolated only two adducts **2a** and **2b** as major products in the reaction of C_{78} with disilirane. Because **2a** and **2b** have C_1 symmetry, 11 isomers have to be considered. At this point, the exact assignment of the isomers, however, may await X-ray structural determinations.

The fact that the adducts are formed upon irradiation at > 400 nm where C_{78} is the only light-absorbing component indicates the triplet C_{78} undergoes interaction with **1** forming an exciplex intermediate, similar to the case of C_{60}.

In order to know the electronic property,[11c] the redox-potentials of **2a** and **2b** have been measured by means of differential pulse voltammetry. The data are collected in Table 1, together with the C_{60}, C_{78} and 1:1 adduct (**3**) of C_{60} with **1**,[11b] as reference compounds. The salient feature is that **2b** has a low oxidation potential (+0.48 V) as compared with C_{78} (+0.65 V) itself. On the other hand, the reduction potentials of **2a** and **2b** relative to C_{78} are cathodically shifted, which indicates that the introduction of a silyl group results in decreasing the electron-accepting properties. These findings agree with those previously observed for other silylfullerenes.[11c]

Table 1. Redox potentials[a] of C_{60}, $C_{78}(C_{2v}+D_3)$, $C_{78}(D_3)$, **2a**, **2b**, and **3**

Compd	$^{Ox}E2$	$^{Ox}E1$	$^{Red}E1$	$^{Red}E2$	$^{Red}E3$	$^{Red}E4$
C_{60}		1.32	–1.13	–1.50	–1.94	–2.41
$C_{78}(C_{2v}+D_3)$	0.87	0.63	–0.79	–1.11	–1.47	–2.10
$C_{78}(D_3)$		0.65	–0.76	–1.06	–1.79	–2.15
2a	0.92	0.67	–1.11	–1.40	–1.64	–2.00
2b		0.48	–1.27	–1.63	–2.02	–2.45
3[b]	1.23	0.73	–1.35	–1.70	–2.22	

[a]Values are in volts relative to ferrocene/ferrocenium couple and obtained by DPV. [b]Reference 11. Conditions: 0.1 M (n-Bu)$_4$NPF$_6$ in 1,2-dichlorobenzene, working electrode and counter electrode are Pt wire, reference electrode Ag/0.01 M $AgNO_3$ and 0.1 M (n-Bu)$_4$NClO$_4$ in CH_3CN. Pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV/s.

In conclusion, we found the selective silylation of $C_{78}(C_{2v})$. The low reactivity of D_3 isomer must originate from its photophysical property. It may be applicable to the separation of these isomers.

This work was supported in part by a grant from the Asahi Glass Foundation and by a grant from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Note

1 R. Ettl, I. Chao, F. Diederich, and R. l. Whetten, *Nature*, **353**, 149 (1991).

2 F. Diederich, R. L. Whetten, C. Thilgen, R. Ettl, I. Chao, and M. M. Alvarez, *Science*, **254**, 1768 (1991).

3 K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, and Y. Achiba, *Nature*, **357**, 142 (1992).

4 R. Taylor, G. J. Langley, T. J. S. Dennis, H. W. Kroto, and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, **1992**, 1043.

5 T. J. S. Dennis, T. Kai, T. Tomiyama, and H. Shinohara, *Chem. Commun.*, **1998**, 619.

6 T. J. S. Dennis, T. Kai, T. Tomiyama, H. Shinohara, T. Yoshida, Y. Kobayashi, H. Ishiwatari, Y. Miyake, K. Kikuchi, and Y. Achiba, *J. Chem. Phys. A*, **103**, 8747 (1999).

7 N. Tagmatarchis, A. G. Avent, K. Prassides, T. J. S. Dennis, and H. Shinohara, *Chem. Commun.*, **1999**, 1023.

8 A. Herrmann, F. Diederich, C. Thilgen, H.-U. ter Meer, and W. H. Muller, *Helv. Chim. Acta*, **77**, 1689 (1994).

9 A. Herrmann and F. Diederich, *Helv. Chim. Acta*, **1996**, 1741.

10 A. Herrmann and F. Diederich, *J. Chem. Soc., Perkin Trans.* 2, **1997**, 1679.

11 a) T. Akasaka, W. Ando, K. Kobayashi, and S. Nagase, *J. Am. Chem. Soc.*, **115**, 1605 (1993). b) T. Akasaka, W. Ando, K. Kobayashi, and S. Nagase, *J. Am. Chem. Soc.*, **115,** 10366 (1993). c) T. Suzuki, Y. Maruyama, T. Akasaka, W. Ando, K. Kobayashi, and S. Nagase, *J. Am. Chem. Soc.*, **116**, 1359 (1994). d) T. Akasaka, E. Mitsuhida, W. Ando, K. Kobayashi, and S. Nagase, *J. Am. Chem. Soc.*, **116**, 2627 (1994). e) T. Akasaka, E. Mitsuhida, W. Ando, K. Kobayashi, and S. Nagase, *J. Chem. Soc., Chem. Commun.*, **1995**, 1529. f) T. Akasaka, T. Suzuki, Y. Maeda, M. Ara, T. Wakahara, K. Kobayashi, S. Nagase, M. Kako, Y. Nakadaira, M. Fujitsuka, and O. Ito, *J. Org. Chem.*, **64**, 566 (1999). g) T. Akasaka, T. Wakahara, S. Nagase, and K. Kobayashi, *J. Synth. Org. Chem. Jpn.*, **58** , 1066 (2000).

12 $C_{78}(C_{2v}+D_3)$ was isolated from the toluene extracts of the soot by preparative HPLC with Buckyprep column (Nacalai Tesque: 20 mmϕ × 250 mm) with toluene as an eluent. The isomer ratio was confirmed by HPLC analysis[13] and ^{13}C NMR measurement.[2–4]

13 K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, K. Saito, I. Ikemoto, and Y. Achiba, *Synth. Met.*, **55–57**, 3208 (1993).

14 1st stage; JAIGEL 1H and 2H columns (Japan Analytical Industry Co., Ltd.)/toluene. 2nd stage; Buckyprep column (Nacalai Tesque)/toluene. 3rd stage; Buckyclutcher column (Regis)/toluene / hexane (3:7).

15 **2a**: UV–vis (CS_2): λ_{max}: 838, 744, 599(sh), 555(sh), 507(sh) 462(sh) nm. ^{1}H NMR (300 MHz, $CDCl_3/CS_2$): δ 6.85(s, 2H), 6.71(s, 3H), 6.64(s, 1H), 6.57(s, 1H), 6.55(s, 1H), 3.34(s, 3H), 3.33(s, 3H), 2.38(s, 3H), 2.28(s, 3H), 2.27(s, 3H), 2.21(s, 3H), 2.14(s, 3H), 2.13(s, 3H), 2.12(d, J = 15.0 Hz, 1H), 2.09(d, J = 15.0 Hz, 1H), 2.03(s, 3H), 2.01(s, 3H), 2.00(s, 3H), 1.96(s, 3H). ^{13}C NMR (125 MHz, $CS_2/CDCl_3$): δ 164.69, 163.48, 154.62, 151.34, 149.43, 148.74, 148.24, 148.01, 147.60, 147.41, 147.00, 146.96, 146.90, 146.82, 146.61, 146.40, 145.92, 145.63, 145.60, 145.45, 145.33, 145.27, 145.22, 145.04, 145.00, 144.97, 144.75, 144.59, 144.37, 144.35, 144.09, 144.06, 144.03, 143.98, 143.92, 143.89, 143.63, 143.45, 143.36, 143.15, 142.96, 142.86, 142.74, 142.72, 142.68, 142.29, 142.11, 141.57, 141.44, 141.11, 141.06, 141.03, 141.01, 140.68, 140.40, 140.20, 140.12, 139.86, 139.82, 139.78, 139.63, 139.46, 139.40, 139.32, 139.28, 138.70, 138.38, 138.35, 137.83, 136.48, 135.70, 135.00, 134.88, 134.38, 134.13, 133.95, 133.09, 133.04, 132.73, 132.57, 132.14, 131.87, 131.81, 131.35, 131.16, 130.79, 130.40, 130.27, 130.22, 130.14, 130.07, 129.67, 128.21, 128.16, 65.26, 64.31, 28.79, 28.52, 25.57, 25.26, 25.19, 24.64, 23.50, 23.45, 21.14, 21.05, 21.00, 20.98, 7.17. ^{29}Si NMR (100 MHz, $CS_2/CDCl_3$): δ –8.46, –10.49. FABMS: *m/z* 1486–1482.

16 **2b**: UV–vis (CS_2): λ_{max}: 883, 790(sh), 748, 610, 560, 502 nm. ^{1}H NMR (300 MHz, $CDCl_3/CS_2$): δ 6.87(s, 2H), 6.72(s, 1H), 6.70(s, 1H), 6.64(s, 1H), 6.61(s, 1H), 6.54(s, 1H), 6.53(s, 1H), 3.47(s, 3H), 3.41(s, 3H), 2.51(s, 3H), 2.35(s, 3H), 2.29(d, J = 14.5 Hz, 1H), 2.27(s, 6H), 2.16(s, 3H), 2.15(d, J = 14.5 Hz, 1H), 2.12(s, 3H), 2.11(s, 3H), 2.06(s, 3H), 2.02(s, 3H), 1.95(s, 3H). ^{13}C NMR (125 MHz, $CDCl_3/CS_2$): δ 171.86, 157.40, 157.30, 153.29, 151.54, 150.56, 150.53, 149.50, 148.96, 148.91, 148.74, 148.50, 148.34, 148.04, 147.75, 147.73, 147.45, 147.37, 146.73, 146.60, 146.41, 146.37, 146.11, 146.06, 146.05, 146.00, 145.73, 145.57, 145.50, 145.40, 145.21, 144.94, 144.67, 144.41, 144.31, 144.15, 144.14, 144.09, 144.01, 143.94, 143.91, 143.76, 143.75, 143.64, 143.59, 143.54, 143.10, 142.80, 142.71, 142.41, 142.26, 142.07, 141.70, 141.07, 141.03, 141.00, 140.94, 140.61, 140.03, 139.72, 139.68, 139.65, 139.54, 139.35, 139.31, 138.58, 138.49, 138.38, 138.16, 138.13, 137.66, 137.23, 136.56, 136.03, 135.87, 135.28, 135.07, 134.79, 134.18, 134.15, 133.81, 133.71, 133.67, 132.97, 131.84, 131.81, 130.51, 130.46, 130.41, 130.32, 130.23, 130.03, 129.84, 129.55, 128.84, 128.77, 128.38, 128.09, 128.03, 66.23, 65.11, 29.01, 28.86, 26.04, 25.68, 25.56, 24.82, 23.58, 23.39, 21.01, 9.20. ^{29}Si NMR (100 MHz, $CS_2/CDCl_3$): δ –8.51, –11.28. FABMS: *m/z* 1486–1482.