Highly Thermally-Stable Diels-Alder Adducts of [60]Fullerene with 2-Cycloalkenones and Their Acetals

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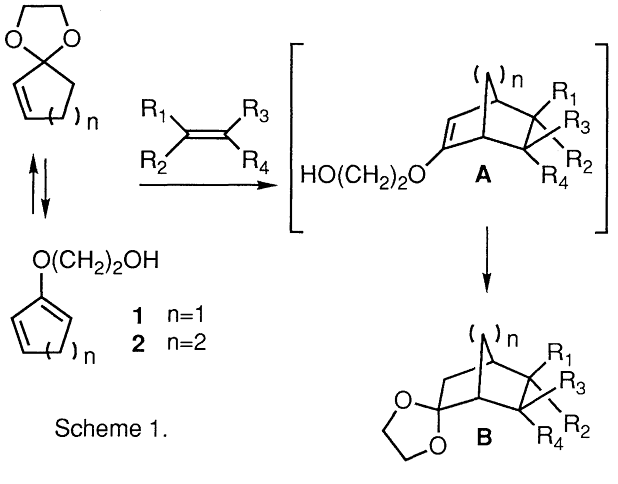
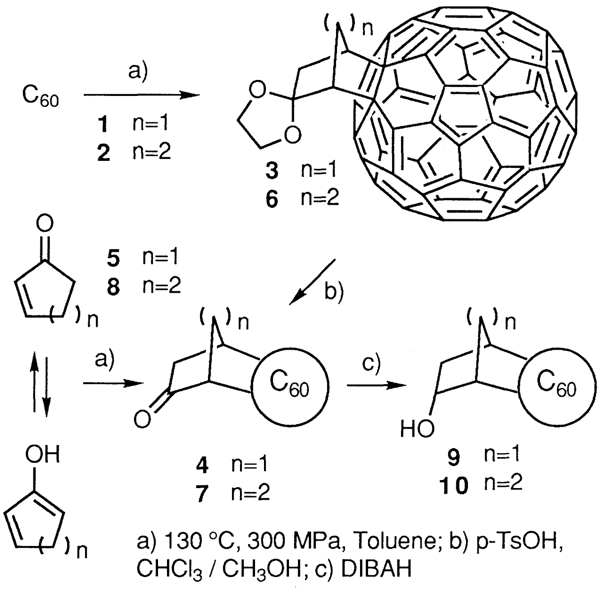
A [4+2] monoadduct with improved thermal stability was obtained from the reaction of [60]fullerene with 2,5-dioxaspiro-[4.4]non-6-ene, a masked 4π-component, under high-pressure conditions (300 MPa) at 130 °C in toluene in 85% yield. Hydrolysis of the adduct gave the corresponding ketone, which was also obtained by the reaction of [60]fullerene with cyclopentenone. Even at 150 °C for 15 h, no cycloreversion of the adducts was observed.

It is now recognized that the Diels-Alder reaction of [60]fullerene (C_{60}) is useful for functioalization of C_{60}.[1] However, the cycloadditions of C_{60} usually have a disadvantage, a facile cycloreversion. Recently we applied high-pressure conditions for the reactions of C_{60} with troponoids[2] and cycloheptatriene[3] to improve the reactivities by suppressing the cycloreversion. On the basis of the similar concept, the Diels-Alder reaction of C_{60} with masked 4π-components[4,5] such as 2,5-dioxaspiro[4.4]non-6-ene (**1**) and 2,5-dioxaspiro[4.5]dec-6-ene (**2**), should afford the [4+2] cycloadducts with improved thermal stability; the primary cycloadduct (**A**) bearing a 2-hydroxyethoxyethene group may be transformed to an acetal (**B**) under the reaction conditions, and such an *in-situ*-acetalization could prevent the cycloreversion of the adduct.



Scheme 1.

When a toluene solution of C_{60}[6] and **1** (C_{60}:**1**=1:1.5) was heated at 130 °C for 24 h under 300 MPa, a single product **3**[7] was obtained from HPLC separation (YMC, R-ODS-5, S-5, 120A ODS, toluene/CH_3CN=1) in 85% yield with high chemical conversion (80%). At atmospheric pressure in xylene (130 °C, 36 h, N_2), the yield of **3** was 82% (48% recovery of C_{60}). The ^1H NMR spectrum showed a norbornanone framework. The UV-vis spectrum is quite similar to those of Diels-Alder adducts at a double bond between two six-membered rings of C_{60}.[1f,8] The elemental analysis showed that **3** is a 1:1 adduct of C_{60} and **1**, but the intensity of the molecular ion peak was too weak to determine the molecular formula from the high-resolution FAB-MS spectrum. Heating a toluene solution of **3** at 115 °C for 8 h caused no cycloreversion. At 160 °C for 8 h, ca. 5% of C_{60} were detected on the chromatogram.



a) 130 °C, 300 MPa, Toluene; b) p-TsOH, $CHCl_3$ / CH_3OH; c) DIBAH

Scheme 2.

Hydrolysis of **3** with *p*-TsOH in a mixture of $CHCl_3$ and CH_3OH gave a ketone **4**[7] quantitatively, which was prepared independently from the Diels-Alder reaction of C_{60} and cyclopentenone (**5**)[9] under 300 MPa at 130 °C for 24 h in 81% yield (49% recovery of C_{60}).

Similarly, the reaction of C_{60} and **2** gave **6** in 82% yield under 300 MPa with 50% conversion, which was stable on heating at 160 °C for 15 h. At atmospheric pressure in xylene (130 °C, 36 h, N_2), the yield of **6** was 71% (80% recovery of C_{60}). Hydrolysis of **6** gave **7**,[7] which could be prepared from C_{60} and cyclohexenone (**8**).

The DIBAH reduction of **4** and **7** gave alcohols **9** and **10**, respectively. Treatment of **9** and **10** in CH_3OH gave no tetrahydrofuran derivative, unlike the cases of the alcohols obtained from the DIBAH reduction of the Diels-Alder adducts of tropones and C_{60}.[10] This should mean that the distance between the hydroxy group and the C_{60} skeleton is too remote to make a

C-O bond.

The preparation of the adducts with high thermal stability from C_{60} and the masked 4π-components should be valuable.

References and Notes

1 For example, a) X. Zhang and C. S. Foote, *J. Org. Chem.*, **59**, 5253 (1994); b) W. Bidell, R. E. Douthwaite, M. L. H. Green, A. H. H. Stephens, and J. F. C. Turner, *J. Chem. Soc., Chem. Commun.*, **1994**, 1641; c) A. Gügel, A. Kraus, J. Spickermann, P. Belik, and K. Müllen, *Angew. Chem. Int. Ed. Engl.*, **33**, 559 (1994); d) P. Belik, A. Gügel, J. Spickermann, and K. Müllen, *Angew. Chem. Int. Ed. Engl.*, **32**, 78 (1993); e) V. M. Rotello, J. B. Howard, T. Yadav, M. M. Conn, E. Viani, L. M. Giovane, and A. L. Lafleur, *Tetrahedron Lett.*, **34**, 1561 (1993); f) Y. Rubin, S. Khan, D. I. Freedberg, and C. Yeretzian, *J. Am. Chem. Soc.*, **115**, 344 (1993); g) M. Prato, T. Suzuki, H. Foroudian, Q. Li, K. Khemani, F. Wudl, J. Leonetti, R. D. Little, T. White, B. Rickborn, S. Yamago, and E. Nakamura, *J. Am. Chem. Soc.*, **115**, 1594 (1993); h) S. I. Khan, A. M. Oliver, M. N. Paddon-Row, and Y. Rubin, *J. Am. Chem. Soc.*, **115**, 4919 (1993); S. H. Hoke II, J. Molstad, D. Dilettato, M. J. Jay, D. Carlson, B. Kahr, and R. G. Cooks, *J. Org. Chem.*, **57**, 5069 (1992); M. Tsuda, T. Ishida, T. Nogami, S. Kurono, and M. Ohashi, *Chem. Lett.*, **1992**, 2333.

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6 Fullerene used here contains more than 85% of C_{60}.

7 **3**: Anal. Found: C, 94.56; H, 1.66%. Calcd for $C_{67}H_{10}O_2$: C, 95.03; H, 1.19%. ^{1}H NMR ($CDCl_3$:CS_2=1:1) δ 2.83 (1H, dt, *J*=11.4, 1.5 Hz), 2.85 (1H, ddd, *J*=14.3, 4.8, 1.1 Hz), 3.30 (1H, dd, *J*=14.3, 3.3 Hz), 3.55 (1H, dquint, *J*=11.4, 1.8 Hz), 3.73 (1H, br m), 3.80 (1H, dq, *J*=4.8, 1.5 Hz), and 4.05~4.23 (4H, m). IR ν 2868, 1511, 1460, 1428, 1327, 1184, 1103, 1059, 1015, 932, 856, 764, 671, 572, and 527 cm^{-1}. UV-vis (CH_2Cl_2) λ_{max} 407 nm (ε=7447), 434.2 (6120), 458.2 (4766), 533.8 (2999), 631.1 (1480), and 709.8 (828). **6**: Anal. Found: C, 94.67; H, 1.85%. Calcd for $C_{68}H_{12}O_2$: C, 94.88; H, 1.41%. ^{1}H NMR ($CDCl_3$:CS_2=1:1) δ 2.40~2.55 (1H, m), 2.79 (1H, dd, *J*= 15.0, 4.0 Hz), 2.80~3.22 (2H, m), 3.10~3.20 (1H, m), 3.21~3.25 (1H, m), 3.33~3.38 (1H, m), 3.61 (1H, td, *J*= 15.0, 2.6 Hz), and 4.10~4.28 (4H, m). IR ν 2926, 1461, 1427, 1359, 1116, 1087, 1021, 942, 810, 764, 671, 572, and 526 cm^{-1}. UV-vis (CH_2Cl_2) λ_{max} 407 nm (ε=5611), 436.2 (4608), 472.0 (3672), 536.0 (2456), 607.7 (1363), and 706.9 (792). **4**: Anal. Found C, 97.71; H, 0.89%. Calcd for $C_{65}H_6O$: C, 97.25; 0.75%. FAB MS Found: m/z 803.0480. Calcd for $C_{65}H_7O$: 803.0497. ^{1}H NMR ($CDCl_3$) δ 2.86 (1H, dt, *J*=11.7, 1.5 Hz), 3.12 (1H, ddd, *J*=18.7, 5.5, 1.8 Hz), 3.61 (1H, dd, *J*=18.7, 4.4 Hz), 3.81 (1H, dm, *J*=11.7 Hz), and 4.21~4.25 (2H, m). ^{13}C NMR ($CDCl_3$) δ 35.41, 45.24, 48.72, 63.22, 70.97, 72.62, 136.51, 136.66, 137.35, 137.81, 139.84, 139.96, 140.26, 140.29, 141.55, 141.67, 141.76, 141.84, 141.85, 141.87 (3C), 141.93, 141.95, 142.00, 142.08, 142.46, 142.54, 142.56, 142.57, 142.95, 142.96, 144.24, 144.28, 144.33, 144.54 (2C), 145.12, 145.14, 145.18, 145.23 (2C), 145.31, 145.32, 145.34, 145.38, 145.40, 145.50, 145.81, 145.87, 145.95, 145.96, 146.07, 146.08, 146.10, 146.13, 146.25, 146.29, 147.19, 147.20, 152.58, 152.88, 153.73, 153.95, and 210.87. IR ν 2926, 1754, 1460, 1428, 1260, 1183, 1161, 1096, 929, 814, 799, 763, 573, and 527 cm^{-1}. UV-vis (CH_2Cl_2) λ_{max} 405.1 nm (ε=6696), 432.6 (5443), 454.4 (4400), 533.1 (2593), 608.3 (1247), and 696.3 (658). **7**: FAB MS Found: m/z 817.0672. Calcd for $C_{66}H_9O$: 817.0653. ^{1}H NMR ($CDCl_3$:CS_2=1:1) δ 2.54~2.84 (2H, m), 3.26 (1H, dd, *J*=19.8, 3.3 Hz), 3.25~3.46 (2H, m), 3.66~3.71 (1H, m), 3.82 (1H, t, *J*=2.9 Hz), and 3.96 (1H, dt, *J*=19.8, 2.9 Hz). ^{13}C NMR ($CDCl_3$:CS_2= 1:1) δ 23.52, 24.97, 42.39, 44.68, 55.34, 66.04, 67.03, 135.65, 136.08, 136.37, 136.84, 140.30, 140.41 (2C), 140.48, 141.62, 141.71, 141.74, 141.77 (2C), 141.89, 141.92, 141.95, 142.00, 142.03, 142.09, 142.11, 142.61, 142.62, 142.63, 142.70, 143.18, 143.22, 144.53, 144.60, 144.66, 144.73, 145.11, 145.14, 145.25, 145.48 (4C), 145.49, 145.52, 145.58 (3C), 145.70, 145.72, 146.25, 146.27, 146.29, 146.36, 146.42 (2C), 146.49, 146.54, 147.64, 147.65, 153.54, 154.10, 154.12, and 154.25. (no C=O signal was observed). IR ν 2926, 1729, 1461, 1426, 1395, 1211, 1181, 1109, 920, 814, 748, 667, 575, 552, and 525 cm^{-1}. UV-vis (CH_2Cl_2) λ_{max} 405.1 nm (ε=4691), 434.9 (6891), 458.2 (5884), 529.2 (3441), 609.6 (1448), and 696.3 (667).

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