CHEMISTRY LETTERS, pp. 1697-1698, 1993.

High-Pressure Diels-Alder Reaction between Buckminsterfullerene and Tropone

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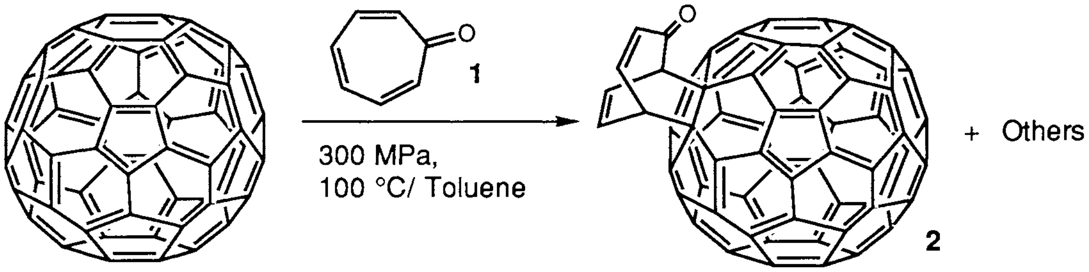
Heating buckminsterfullerene and tropone in toluene under high-pressure conditions (300 MPa) gave a stable [4+2] monoadduct in 55% yield. It was cycloreversed upon heating around 140 °C. Its ^{13}C-NMR spectrum revealed 62 lines of signals.

Recently, cycloaddition reactions between buckminsterfullerene (C_{60}) and dienes$^{1)}$ or benzyne$^{2)}$ are intensively investigated to explore the reactivity of C_{60}. It is estimated to be similar to electron-deficient olefins with a low LUMO level and a high reduction potential.$^{3)}$ Since it has been observed that Diels-Alder adducts of C_{60} undergo facile cycloreversion,$^{1a,b)}$ transformation of adducts to stable molecules is usually required prior to characterization. In this paper, we report high-pressure cycloaddition of C_{60} to tropone (**1**) to obtain the original adduct; under the conditions, retro Diels-Alder process could be prevented.



When a toluene solution (5 cm^3) of C_{60} (50 mg)$^{4)}$ and **1** (**1**:C_{60}=2.5:1) was heated at 100 °C under 300 MPa for 36 h,$^{5)}$ at least three products were detected from HPLC analysis (YMC, R-ODS-5, S-5, 120A ODS, toluene/MeCN=1). The major product (**2**)$^{6)}$ was isolated in 55% yield based on converted C_{60} after silica gel chromatography (hexane/benzene) and HPLC (toluene/MeCN).$^{7)}$

This product **2** is stable both in the solid state and in solution. No cycloreversion was observed at room temperature. However, around 140 °C, it reverted to C_{60} and **1**. Mass spectrum indicated that **2** is a 1:1 adduct. Elemental analysis showed that **2** includes 1 mole of benzene by recrystallization.$^{8)}$ The ^{1}H-NMR spectrum of **2** showed the characteristic splitting patterns of the bicyclo[3.2.2]nona-3,6-dien-2-one moiety with rather lower-field shifted signals ascribable to four olefinic and two methine protons than those of many other derivatives.$^{9)}$ The ^{13}C-NMR spectrum showed 62 lines, in which the signals of the bicyclo[3.2.2]nonadienone moiety were observed at δ 51.31, 67.36, 129.43, 131.01, 138.33, 151.19, and 193.23. Five lines are overlapping since the structure of **2** requires 67 lines. It is rather surprising that only five lines are overlapping in the ^{13}C-NMR spectrum of an unsymmetrical buckminsterfullerene derivatives. 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}.[1c, 10] The structure of **2** is, therefore, likely to be a [4+2] adduct at a double bond between two six-membered rings.[11]

Amounts of two minor products were increased when a large amount of **1** (**1**:C_{60}=5:1) was used. The ^{1}H-NMR spectrum of the mixture of two minor products showed that they have an element of symmetry, which indicates that they are 1:2 adducts.

High-pressure cycloadditions between C_{60} and other troponoids and further transformations from **2** are under way and the X-ray crystallographic studies of **2** should be desirable to investigate the precise structure.

References

1) For example, a) P. Belik, A. Gügel, J. Spickermann, and K. Müllen, *Angew. Chem., Int. Ed. Engl.*, **32**, 78 (1993); b) 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); c) Y. Rubin, S. Khan, D. I. Freedberg, and C. Yeretzian, *J. Am. Chem. Soc.*, **115**, 344 (1993); d) 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, *ibid.*, **115**, 1594 (1993); e) S. I. Khan, A. M. Oliver, M. N. Paddon-Row, and Y. Rubin, *ibid.,* **115**, 4919 (1993).

2) 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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4) Fullerene used here is a mixture of C_{60} and C_{70} (84/16).

5) Alternatively, the reaction was also carried out in a refluxing toluene under atmospheric pressure, in which a small amount of **2** was detected by HPLC.

6) Black powders (benzene/CS_2=1), mp 142 °C (decomp). Found : C, 96.75; H, 1.24%. Calcd for $C_{67}H_6O$: C, 97.34: H, 0.73%. Calcd for $C_{67}H_6O \cdot C_6H_6$: C, 96.82; H, 1.36%. FAB Mass: m/z 827 $(M+H)^+$ (5.4%), 720 (100%). ^{1}H-NMR ($CDCl_3$) δ 5.15 (1H, ddm, *J*=8.8, 7.3 Hz), 5.27 (1H, ddd, *J*=7.7, 1.8, 1.1 Hz), 6.54 (1H, ddd, *J*=11.0, 1.8, 0.7 Hz), 7.13 (1H, ddd, *J*=8.8, 7.7, 1.1 Hz), 7.45 (1H, ddd, *J*=8.8, 7.3, 1.1 Hz), and 7.73 (1H, dd, *J*=11.0, 8.8 Hz). ^{13}C-NMR (125 MHz) ($CDCl_3/CS_2$=3 with 0.035 M Cr(acac)$_3$ as a relaxation agent) δ 51.31, 67.36, 67.50, 71.16, 129.43, 131.01, 135.55, 136.55, 136.65, 137.12, 138.33, 139.99, 140.09 (2C), 140.23, 141.51 (2C), 141.70, 141.72, 141.75, 141.98, 142.08, 142.10, 142.12, 142.22, 142.26. 142.37, 142.60, 142.67, 142.68 (2C), 143.15, 143.18, 144.14, 144.58, 144.64, 144.65, 144.78, 144.80, 144.86, 145.48, 145.49, 145.55 (2C), 145.60, 145.61, 145.62, 145.63, 145.67, 145.74, 145.92, 146.28 (2C), 146.29, 146.37, 146.59, 146.64, 146.65, 146.72, 147.68, 147.71, 151.19, 154.26, 154.33, 156.29, 157.67, and 193.23. IR (KBr) 2930, 1670, 1635, 1460, 1430, 1380, 1350, 1250, 1180, 1160, 920, 890, 840, 825, 820, 780, 770, 760, 750, 740, 700, 680, and 660 cm^{-1}. UV-vis (toluene) 408.2 nm (ε=5400), 435.8 (4000), 481.5 (1900), 542.3 (1200), 606.3 (600), 635.8 (500), and 703.0 (400).

7) The recovered fullerene (18 mg, ca. 70% conversion) consisted of C_{60} and C_{70} as 70:30.

8) This was confirmed by δ 7.36 (s) in ^{1}H-NMR spectrum.

9) For example, Z.-H. Li, A. Mori, N. Kato, and H. Takeshita, *Bull. Chem. Soc. Jpn.*, **64**, 2778 (1991).

10) B. Kräutler and M. Puchberger, *Helv. Chim. Acta,* **76**, 1626 (1993).

11) We admit that the structure depicted for **2** is tentative; another probable structure, which should be formed by the reaction at a double bond between six- and five-membered rings, has not been eliminated.

(Received July 5, 1993)