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# The High-Pressure Diels–Alder Reaction of [5,6]-Fullerene-$C_{60}$ with Cycloheptatriene. Formation of Diels–Alder Adducts with Improved Thermal Stability

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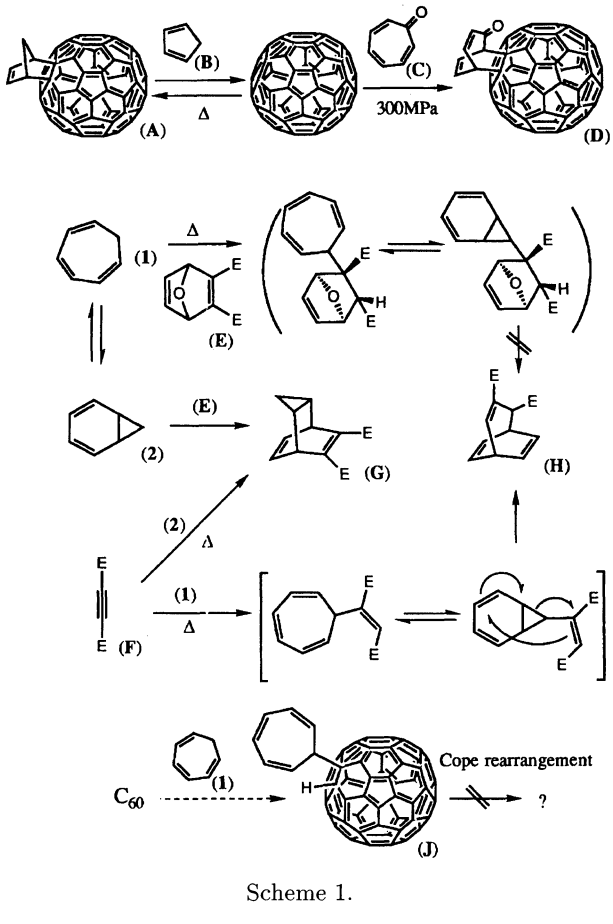
(Received January 5, 1994)

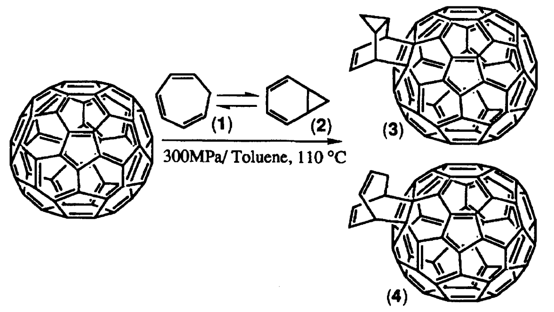
**Synopsis.** The high-pressure Diels–Alder reaction of $C_{60}$ with cycloheptatriene under 300 MPa gave two [4+2] cycloadducts derived from two valence isomers, cycloheptatriene and norcaradiene. The thermolysis of the adducts indicated the tricyclo[3.2.2.$0^{2,4}$]non-6-ene derivative is a kinetically-controlled product.

The addition reactions with [5,6]-fullerene-$C_{60}$ ($C_{60}$) are of current interest.1,2) The torsional strain of the spherical $\pi$-system makes sufficiently reactive towards dienes. It is particularly noteworthy that the characterization of a 1:1-cycloadduct (**A**) with a hydrocarbon, cyclopentadiene (**B**), has been proven to occur in the manufacturing process of $C_{60}$; in addition, **A** cycloreversed to **B** and $C_{60}$ upon heating at 90 °C.1) We have recently found a smooth cycloaddition of $C_{60}$ with tropone (**C**) under high-pressure conditions, 300 MPa, to form a 1:1-cycloadduct (**D**).3) Therefore, cycloheptatriene (**1**), a conjugated triene, might be worth investigating since **1** exists as both forms of **1** and the valence isomer, norcaradiene (**2**),4) under the Diels–Alder reaction conditions, where **2** is more reactive than **1** because the doubly allylic C-7 hydrogens of **1** tend to cause the ene reaction. The ene-products of **1** then cause an intramolecular Cope rearrangement to give stable bicyclo[3.2.2]nonene derivatives. In this respect, we have already shown the high-pressure Diels–Alder reaction of **1** with dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dioate (**E**), as a synthetic equivalent of dimethyl butynedioate (**F**), were pressure dependent;5) the higher pressure favored the formation of the cycloadduct (**G**) over the ene-reaction product (**H**). Based on this finding, we have solved a long-time dispute on the mechanism of formation of the ene-reaction product.6) In the case of $C_{60}$, it is interesting to know whether or not the precursor of the ene-reaction product, 7-cycloheptatrienyl derivative (**J**), might be formed. Since the subsequent Cope rearrangement can not be taken place, an outcome of this reactive **J** is also of interest (Scheme 1). This prompted us to extend the study to $C_{60}$ with **1**.

A mixture of $C_{60}$ and **1** dissolved in toluene was heated at 100 °C under 300 MPa. After 36 h, the mixture was chromatographed to give the cycloadducts; the major product (**3**), obtained in a 52% yield, was identified to be the [4+2] cycloadducts derived from $C_{60}$ and the valence-isomeric **2**. Its $^{1}$H NMR spectrum showed a presence of a cyclopropane ring, i.e., four proton signals appeared at high field region, and its $^{13}$C NMR spectrum revealed 35 lines of signals to indicate a presence of a symmetry element; for the structure depicted for **3**, theoretically 36 lines of carbon signals should appear. As a by-product, the [4+2] cycloadduct (**4**) was obtained in a 14.5% yield (Scheme 2). Its $^{13}$C NMR spectrum assured an absence of any symmetry element; there were 66 lines of separate carbon signals and only one overlapped 2C signal. In the $^{1}$H NMR spectrum, there were four vinyl proton signals and a signal ascribable to an allylic methylene group. Therefore, **4** is bicyclo[3.2.2]nonadiene derivative. Appearance of four olefinic proton signals identified its formation as via the direct Diels–Alder route, not via the ene reaction and



Scheme 1.



Scheme 2.

Cope rearrangement process.

Heating **3** at 140 °C in a sealed tube afforded $C_{60}$ in a quantitative yield. However, heating **3** in a solid state caused apparent isomerization to **4**; during the determination of the melting point of **3**, each once-sintered sample solidified again, and the ${}^1$H NMR spectrum of the collected sample was indeed **4**. This does not necessarily mean that the isomerization is intramolecular, since the thermal treatment of **3** in solution gave no **4**. Therefore, the cycloreversion of **3** could take place quite easily. Moreover, a brief thermal reaction with a neat mixture of **1** and **2** afforded **3** (20%) and **4** (3%), to show that the former was a kinetically controlled product, but prolonged reaction afforded a complicated product mixture; apparently, multiple introductions of **1** into $C_{60}$ occurred, and neither **4** nor **3** was any longer obtained. When the reaction was carried out in refluxing toluene, a small amount of **4** and **3** were detected on a high-pressure liquid chromatogram. The yields were 1% for **4** and only 0.2% for **3**, respectively (Scheme 3).

Predominant formation of **4** over **3** under thermodynamic conditions is different from the previous cases; in general, tricyclo[3.2.2.0$^{2,4}$]non-6-enes were major products and the bicyclo[3.2.2]nonenes were accompanying by-products. Also occurrence of no cyclopropene (**5**) in the cycloreversion mixture is predictable, since a cheletropic removal of **5** should leave the dihydrobenzene skeleton.

The present results, facile C–C bond formations with **1** (or **2**) via thermal reactions proved the general capability of $C_{60}$ for addition reactions with cycloolefins. When compared with **A** from $C_{60}$ and cyclopentadiene (**B**), **4** is relatively stable under cycloreversion conditions, as could be judged from its decomposition point, ca. 250 °C. This is parallel to the finding of accumulation of **4** under the thermodynamically controlled conditions. Recently, thermal instability of Diels–Alder adducts from $C_{60}$ in general has been questioned as the cycloadducts of $C_{60}$ and several arylbutadienes are quite stable in this respect.$^{7)}$.

$$\mathbf{(3)} \xrightarrow[\text{0.1 MPa}]{\text{140 °C}} C_{60} + \mathbf{(1)} \xrightarrow[\text{0.1 MPa}]{\text{110 °C}} \mathbf{(3)} + \mathbf{(4)}$$

Scheme 3.

Further study will be reported in due course.

## Experimental

**Diels–Alder Reaction of $C_{60}$ with 1 and Its valence Isomer (2).** A toluene solution (5 cm$^3$) of $C_{60}$ (50 mg)$^{8)}$ and **1** (20 mg) was placed in a high-pressure furnace and heated at 100 °C under 300 MPa for 36 h. After the apparatus was cooled, the dark-colored mixture was chromatographed on a silica-gel column. Then, the fractions obtained from hexane–$C_6H_6$ (1 : 1) were further purified with HPLC and recrystallized from benzene and $CS_2$ (1 : 1) to give **3** [black powders, mp ca. 160 °C (decomp), 16.1 mg, 52% (based on the consumed $C_{60}$). FAB MS $m/z$ 813 ($[M+1]^+$, 6.8) and 720 (100). ${}^1$H NMR ($CDCl_3$) $\delta=0.77$ (1H, td, $J=7.3$, 5.5 Hz), 0.86 (1H, dt, $J=5.5$, 3.7 Hz), 2.33 (2H, br m), 4.41 (2H, dm, $J=3.3$ Hz), and 6.84 (2H, dd, $J=4.8$, 3.3 Hz). ${}^{13}$C NMR ($CDCl_3/CS_2$, 3 : 1 with 0.035 M Cr (acac)$_3$ as a relaxation agent, at 125 MHz) $\delta=\underline{10.88}$ (2C), $\underline{29.83}$, $\underline{45.54}$ (2C), 72.10 (2C), $\underline{130.63}$ (2C), 136.54 (2C), 137.57 (2C), 139.97 (2C), 140.13 (2C), 141.64(2C), 141.66 (2C), 141.99, 142.14 (2C), 142.17 (2C), 142.55 (2C), 142.57 (2C), 142.62 (2C), 143.10 (2C), 144.63 (2C), 144.75 (2C), 145.24 (2C), 145.33 (2C), 145.45 (2C), 145.51 (2C), 145.57 (2C), 145.92 (2C), 146.18 (3C), 146.24 (2C), 146.40 (2C), 146.54 (2C), 147.52, 147.97 (2C), 150.52, 156.40 (2C), and 156.76 (2C). IR(KBr) $\nu$ 2922, 1427, 1260, 1183, 1096, 1034, 913, 847, 800, 738, 725, 671, 563, and 526 cm$^{-1}$ UV-vis ($CH_2Cl_2$) $\lambda_{max}=407.7$ nm ($\varepsilon=3397$), 435.8 (2790), 467.5 (1717), 539.8 (1135), 608.6 (515), 641.0 (414), and 710.1 (350)], together with **4** [black powder, mp ca. 250 °C (decomp); 4.5 mg, 14.5% (based on consumed $C_{60}$). FAB MS $m/z$ 813 ($[M+1]^+$, 7.9) and 720 (100). ${}^1$H NMR ($CDCl_3$) $\delta=3.10$ (1H, dtd, $J=19.4$, 3.3, 2.2 Hz), 3.63 (1H, dtd, $J=19.4$, 3.7, 2.2 Hz), 4.20 (1H, dt, $J=7.3$, 3.7 Hz), 4.42 (1H, dd, $J=8.4$, 7.7 Hz), 6.15 (1H, dt(br), $J=10.6$, 3.7 Hz), 6.45 (1H, ddt, $J=10.6$, 8.4, 2.2 Hz), 7.08 (1H, ddd, $J=8.4$, 7.3, 1.1 Hz), and 7.36 (1H, ddd, $J=8.4$, 7.7, 1.1 Hz). ${}^{13}$C NMR ($CDCl_3/CS_2=3:1$ with a relaxation agent 0.035 M Cr(acac)$_3$, at 125 MHz) $\delta=\underline{34.73}$, $\underline{47.41}$, $\underline{47.61}$, 69.42, 73.18, $\underline{129.67}$, $\underline{131.94}$, $\underline{132.13}$, 135.16, 136.13, 137.17, 137.57, $\underline{138.15}$, 139.89, 139.94, 140.03, 141.10, 141.46, 141.49, 141.61, 141.66, 141.88, 142.03, 142.09, 142.18, 142.19, 142.46, 142.49, 142.57, 142.62, 142.65), 142.70, 143.15, 143.20, 144.62, 144.64, 144.80, 144.88, 145.22, 145.26, 145.29, 145.33, 145.41 (2C), 145.42, 145.50, 145.52, 145.53, 146.75, 145.88, 146.15, 146.17, 146.19, 146.24, 146.25, 146.44, 146.45, 146.50, 146.55, 147.59, 147.65, 147.95, 150.49, 156.33, 156.73, 157.52, and 159.84. IR(KBr) $\nu$ 2918, 1455, 1429, 1261, 1182, 1123, 1034, 803, 748, 726, 687, 591, 575, and 527 cm$^{-1}$; UV-vis ($CH_2Cl_2$) $\lambda_{max}=406.7$ nm ($\varepsilon=3500$), 435.2 (2976), 464.6 (2361), 545.6 (1135), 609.0 (473), 639.4 (339), and 706.9 (183)].

**Thermolysis of 3.** A toluene solution (1 cm$^3$) of **3** (2 mg) was heated in a sealed tube at 140 °C for 2 h. The mixture was then heated in vacuo to remove the volatile material. The residue thus obtained was analyzed with high-pressure liquid chromatography; it showed a quantitative regeneration of $C_{60}$, as a single component. No trace of **3** or **4** could be identified.

**Thermal Addition Reaction of $C_{60}$ and 1 under Atmospheric Pressure. Formation of 3 and 4.** A toluene solution (8 cm$^3$) or $C_{60}$ (10 mg) and **1** (4 mg) was refluxed at 110 °C for 24 h. The mixture was then analyzed by high-pressure liquid chromatography to give **3** (0.2%) and **4** (1%) with recovered $C_{60}$ (9.8 mg, 98%).

**Addition Reaction of a Neat Mixture of $C_{60}$ and 1. Formation of 3 and 4.** A neat mixture of $C_{60}$ (50 mg) and **1** (5 $cm^3$) was refluxed at 120 °C for 2 min. Characterization by means of high-pressure liquid chromatography showed **3** (20%) and **4** (3%) together with recovered $C_{60}$ (65%). Prolonged heating caused a formation of an intractable mass.

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8) The sample was purchased from Kurita Co., Ltd., which provided the analytical figures: $C_{60} : C_{70} = 80 : 16$.