

## High-pressure Diels–Alder Reaction of [60]Fullerene with several Tropones.† Characterization of the 1:1-Cycloadducts

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The high-pressure Diels–Alder reaction of fullerite with tropone and several of its derivatives under 300 MPa gave 1:1-[4 + 2] cycloadducts of C<sub>60</sub> in good yields. Their <sup>1</sup>H and <sup>13</sup>C NMR spectra were consistent with the structures depicted. These compounds quantitatively regenerate starting materials upon thermolysis.

Additions with [60]fullerene (C<sub>60</sub>) are of current interest.<sup>1</sup> Indeed, a recent paper has shown that C<sub>60</sub> reacts with cyclopentadiene to form a 1:1-cycloadduct, which cycloreverses at 90 °C.<sup>2</sup> In addition, a 1:6-cycloadduct of C<sub>60</sub> with cyclopentadiene, which has been shown to be highly thermally stable towards cycloreversion, has been isolated.<sup>3</sup> There have been several reports on the cycloadditions of C<sub>60</sub> *viz.* with a carbene,<sup>4</sup> a nitrene,<sup>5</sup> and a 5,6-dimethylenecyclohexa-1,3-diene.<sup>6</sup> Quite recently, the Diels–Alder adducts of C<sub>60</sub> with the Danishefsky diene and arylbutadiene derivatives have been isolated and shown to be characterizable.<sup>7</sup> The torsional strain of the spherical  $\pi$ -system makes C<sub>60</sub> sufficiently reactive towards dienes, and it is classified as an electron-deficient olefin with a low-lying LUMO and a high reduction potential.<sup>8</sup>

However, apparently no examples of additions to C<sub>60</sub> using high-pressure conditions are known. In view of the observed thermal instability<sup>2</sup> of the Diels–Alder adducts of C<sub>60</sub>, the addition reaction should become more favourable under high-pressure conditions, with even the least reactive dienes becoming reactive. We have now investigated such high-pressure cycloadditions with tropones, which are typical electron-deficient conjugated compounds being reactive as 2 $\pi$ -, 4 $\pi$ -, 6 $\pi$ - and 8 $\pi$ -components.<sup>9</sup> Herein described are the isolation and characterization of the Diels–Alder adducts of C<sub>60</sub> with various tropones (**1a–e**).<sup>10</sup>

### Results and Discussion

The Diels–Alder reaction of fullerite with tropone **1a** occurred smoothly at 300 MPa, to give the product **2a** after chromatography (see Scheme 1); its <sup>1</sup>H NMR spectrum showed signal patterns characteristic of the bicyclo[3.2.2]nona-3,6-dien-2-one system, although these signals appeared at considerably lower field than those for the parent compound **3a**.<sup>11</sup> For example, two kinds of the methine proton signals, C-1 and C-5 of the bicyclo[3.2.2]nonadienone moiety, appeared at  $\delta$  5.15 (ddm, *J* 8.8, 7.3) and 5.27 (ddd, *J* 7.7, 1.8, 1.1), respectively, for **2a**, while corresponding signals for **3a** appeared at  $\delta$  3.36 and 3.53. Namely, the chemical-shift differences ( $\Delta\delta$ ) are *ca.* 1.8. The FAB mass spectrum of **2a** showed it to be the 1:1-cycloadduct [ $m/z$  827, (M + H)<sup>+</sup> for C<sub>67</sub>H<sub>6</sub>O] of C<sub>60</sub> and **1a** (see Fig. 1).

The <sup>13</sup>C NMR spectrum of **2a** disclosed 62 lines, five of which are accidentally-overlapping 2C signals (see Fig. 2). Therefore, all of the possible 67 carbons were identified. Moreover, the UV–VIS spectrum was quite similar to those of reference compounds in the literature.<sup>12</sup> Taken together, these

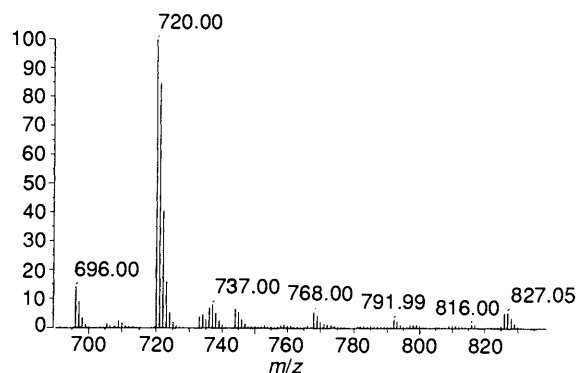


Fig. 1 High resolution, positive ion FAB-mass spectrum of **2a**. The ion at  $m/z$  827 corresponds to the composition of (C<sub>67</sub>H<sub>6</sub>O + H)<sup>+</sup> from exact mass measurements.

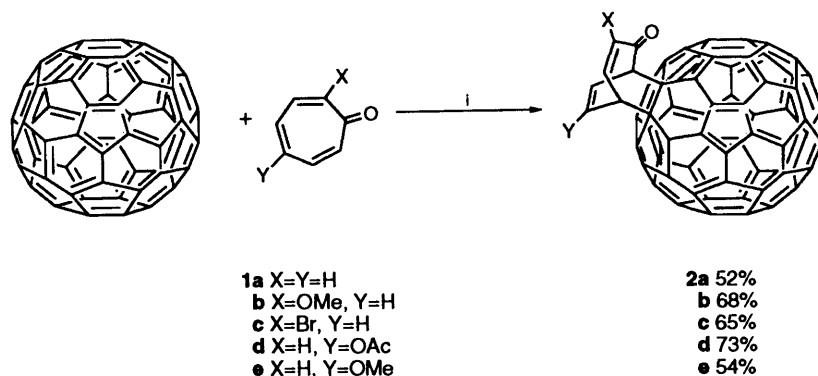
findings left no ambiguity as to the structure of **2a** as depicted in Scheme 1.

This cycloaddition occurred even under atmospheric pressure; by refluxing a toluene solution of fullerite and **1a**, **2a** was detected by HPLC, but its yield was < 1%. As predicted, the higher fullerene, [70]fullerene (C<sub>70</sub>), was relatively inert under these conditions; the ratio of recovered fullerite showed an enrichment in C<sub>70</sub> (ratio C<sub>60</sub>:C<sub>70</sub> of 70:30).

Furthermore, the adduct **2a** regenerated C<sub>60</sub> and **1a** when heated at 160 °C in *o*-dichlorobenzene. Thus **2a** is thermally more stable than the Diels–Alder adduct of a reactive diene, cyclopentadiene, which was stated to cycloreverse at 90 °C.<sup>2</sup> The fragmentation process could be monitored by thermochemical analyses. In the thermogravimetric analysis (TGA), a loss of 12.6% of the original mass occurred in the range 110–200 °C; the loss of tropone from **2a** requires 12.8% [see Fig. 3(a)]. In the differential scanning calorimetric (DSC) analysis, a broad endothermic peak appeared around this temperature range, and the integration of the peak area gave a value of 128.3 mJ mg<sup>-1</sup>, equivalent to 106 kJ mol<sup>-1</sup>, a reasonable figure for the retro-Diels–Alder reaction [see Fig. 3(b)].

In the reaction of fullerite and 2-methoxytropone **1b**, where the ratio of **1b**:fullerite is 5:2, a single Diels–Alder adduct **2b** was obtained in 68% yield after HPLC fractionation. The mass spectrum of **2b** showed it to be a 1:1-adduct of C<sub>60</sub>. Its <sup>1</sup>H NMR spectrum was markedly different from that of **2a** in respect of its chemical shifts, *i.e.*, the  $\beta$ -proton of the  $\alpha,\beta$ -unsaturated keto system in the bicyclo[3.2.2]nonadienone moiety appeared at considerably higher field,  $\delta$  6.73 (d, *J* 9.9) compared with that of **2a** at  $\delta$  7.73 (dd, *J* 11.0, 8.8), clearly

† Tropone = Cyclohepta-2,4,6-trienone.



Scheme 1 Reagents and conditions: i, 300 MPa, 100 °C, toluene

indicating it to be a 3-methoxybicyclo[3.2.3]nona-3,6-dien-2-one derivative.\* Yet the chemical shift is considerably lower ( $\Delta\delta$  ca. 1.7) than those of simple 3-methoxy derivatives, 9-*exo*-cyano-3-methoxybicyclo[3.2.2]nona-3,6-dien-2-one (**3y**) ( $\delta$  6.00) and 9-*endo*-cyano-3-methoxybicyclo[3.2.2]nona-3,6-dien-2-one (**3z**) ( $\delta$  5.95), obtained from **1b** and acrylonitrile (see Scheme 2).† The  $^{13}\text{C}$  NMR spectrum showed 60 lines including five  $\text{sp}^3$ -carbon signals ( $\delta$  48.60, 55.82, 65.90, 67.70 and 71.33) and five newly-introduced  $\text{sp}^2$ -carbon signals ( $\delta$  119.24, 128.83, 139.91, 152.47 and 189.68); therefore, eight lines are overlapping since the structure of this unsymmetrical compound, **2b**, requires 68 lines. The UV-VIS spectrum was again similar to those of reference compounds in the literature<sup>12</sup> and of **2a**. The structure of **2b** is, therefore, a [4 + 2] cycloadduct obtained from the reaction at the double bond between two six-membered rings of  $\text{C}_{60}$ .

Similarly, fullerite and 2-bromotropone **1c** gave 1:1-Diels-Alder  $\text{C}_{60}$ -adduct **2c** in 65% yield after reaction for 40 h. Its mass spectrum was also consistent with a 1:1-adduct and its  $^1\text{H}$  NMR spectrum revealed three olefinic proton signals ( $\delta$  7.19, 7.50 and 8.32) and two methine proton signals ( $\delta$  5.20 and 5.58), indicating that the bromine atom is not at the bridgehead position. The chemical shift of the  $\beta$ -proton signal of the  $\alpha,\beta$ -unsaturated keto system, appearing at very low field,  $\delta$  8.32 (d,  $J$  9.5), is also fully consistent with the depicted structure. The  $^{13}\text{C}$  NMR spectrum of **2c** revealed 57 lines of separated signals, indicating that 10 signals were overlapping. Both **2b** and **2c** were stable at room temperature in the solid state and in solution; no cycloreversion occurred. However, by heating to ca. 160 °C, the cycloreversion occurred to give  $\text{C}_{60}$  and **1b** or **1c**, respectively.

The cycloaddition can be extended to 4-substituted tropones; 4-acetoxytropone (**1d**) and 4-methoxytropone (**1e**)<sup>14</sup> gave 1:1-Diels-Alder adducts **2d** and **2e** in good yields. Again, their substituents were not at the bridgehead positions. To date, only one example of a Diels-Alder reaction of **1e** is known; that is with maleic anhydride, the structure of the adduct having been established as an *endo*-5-methoxybicyclo[3.2.2]nona-3,6-dien-2-one derivative.<sup>15</sup>

However, tropolone **1f** was unreactive under these conditions with fullerite, the starting materials being quantitatively recovered. Although it is difficult to explain this negative result, no further work was carried out.

In conclusion, tropones having either electron-donating or

electron-withdrawing substituents gave the same type of products. This has opened a general and facile route for direct functionalization of  $\text{C}_{60}$ ; in particular, the present oxygen-carrying cycloadducts **2** offer promise as starting materials for further functionalization. Studies on the chemical transformations of various compounds **2** are in progress and the results will be reported in the near future.

### Experimental

**General.**—Fullerite was purchased from Kurita Co. Ltd. and was of composition  $\text{C}_{60}:\text{C}_{70}$  of 80:16. Elemental analyses were performed by Mr. M. Shido of the Elemental Analyses Centre, Department of Chemistry, Faculty of Science, Kyushu University. NMR spectra were measured on a JEOL GX 500 Model spectrometer (500 MHz for  $^1\text{H}$  and 125 MHz for  $^{13}\text{C}$  spectra) in the solvents indicated.  $J$  Values are given in Hz and chemical shifts in  $\delta$  units.  $^{13}\text{C}$  NMR signals due to the tropone skeleton are italicized. The FAB mass spectra were measured with a JEOL 102A spectrometer. HPLC was run on a Nippon Waters Model 600E apparatus with a column equipped with a stationary phase YMC, R-ODS-5, S-5, 120A ODS; the solvent for elution was 1:1 acetonitrile-toluene.

**Diels-Alder Reaction of Fullerite with Tropones 1 (General Method).**—A toluene solution (5  $\text{cm}^3$ ) of fullerite (50 mg) and **1** (ca. 20 mg) in a high-pressure furnace was heated at 100 °C for 36 h. After the apparatus had cooled, the dark mixture was chromatographed on a silica gel column. The fractions obtained with hexane-benzene (1:1) to benzene as eluent were further purified by HPLC and recrystallized from benzene- $\text{CS}_2$  (1:1) to give the products **2**.

**2a** Black powders from benzene, decomp. point 142 °C (Found: C, 96.75; H, 1.2.  $\text{C}_{67}\text{H}_6\text{O}$  requires C, 97.34; H, 0.73%.  $\text{C}_{67}\text{H}_6\text{O}\cdot\text{C}_6\text{H}_6$  requires C, 96.82; H, 1.36%);  $\delta_{\text{H}}(\text{CDCl}_3)$  5.15 (1 H, ddm,  $J$  8.8, 7.3), 5.27 (1 H, ddd,  $J$  7.7, 1.8, 1.1), 6.54 (1 H, ddd,  $J$  11.0, 1.8, 0.7), 7.13 (1 H, ddd,  $J$  8.8, 7.7, 1.1), 7.45 (1 H, ddd,  $J$  8.8, 7.3, 1.1) and 7.73 (1 H, dd,  $J$  11.0, 8.8);  $\delta_{\text{C}}[0.035 \text{ mol dm}^{-3} \text{Cr}(\text{acac})_3 \text{ in } \text{CDCl}_3\text{-CS}_2 (3:1)]$  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 (2 C), 140.23, 141.51, 141.70 (2 C), 141.72, 141.75, 141.98, 142.08, 142.10, 142.12, 142.22, 142.26, 142.37, 142.60, 142.67, 142.68 (2 C), 143.15, 143.18, 144.14, 144.58, 144.64, 144.65, 144.78, 144.80, 144.86, 145.48, 145.49, 145.55 (2 C), 145.60, 145.61, 145.62, 145.63, 145.67, 145.74, 145.92, 146.28, (2 C), 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;  $\nu_{\text{max}}/\text{cm}^{-1}$  2930, 1670, 1635, 1460, 1430, 1380, 1350, 1250, 1180, 1160, 920, 890, 840, 825, 820, 780, 770, 760, 750, 700, 680 and 660;  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$  408.2 ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  5400), 435.8 (4000), 481.5 (1900), 542.3 (1200), 606.3 (600), 635.8 (500) and 703.0 (400);  $m/z$  (FAB) 827 [(M + H)<sup>+</sup>, 5.4] and 720 (100).

**2b** Black powders from benzene, decomp. point ca. 150 °C;

\* In most cases, Diels-Alder reactions of **1b** with dienophiles give 1-methoxybicyclo[3.2.2]nona-3,6-dien-2-one derivatives as the major products. For the first example of a 3-methoxybicyclo[3.2.2]nona-3,6-dien-2-one derivative, see ref. 13.

† The  $^1\text{H}$  NMR data for the parent 3-methoxybicyclo[3.2.2]nona-dienone **3b** are not available. However, the small  $\Delta\delta$  (0.05) between *exo*- and *endo*-9-cyano derivatives **3y** and **3z** can be taken as alternatives for **3b**.

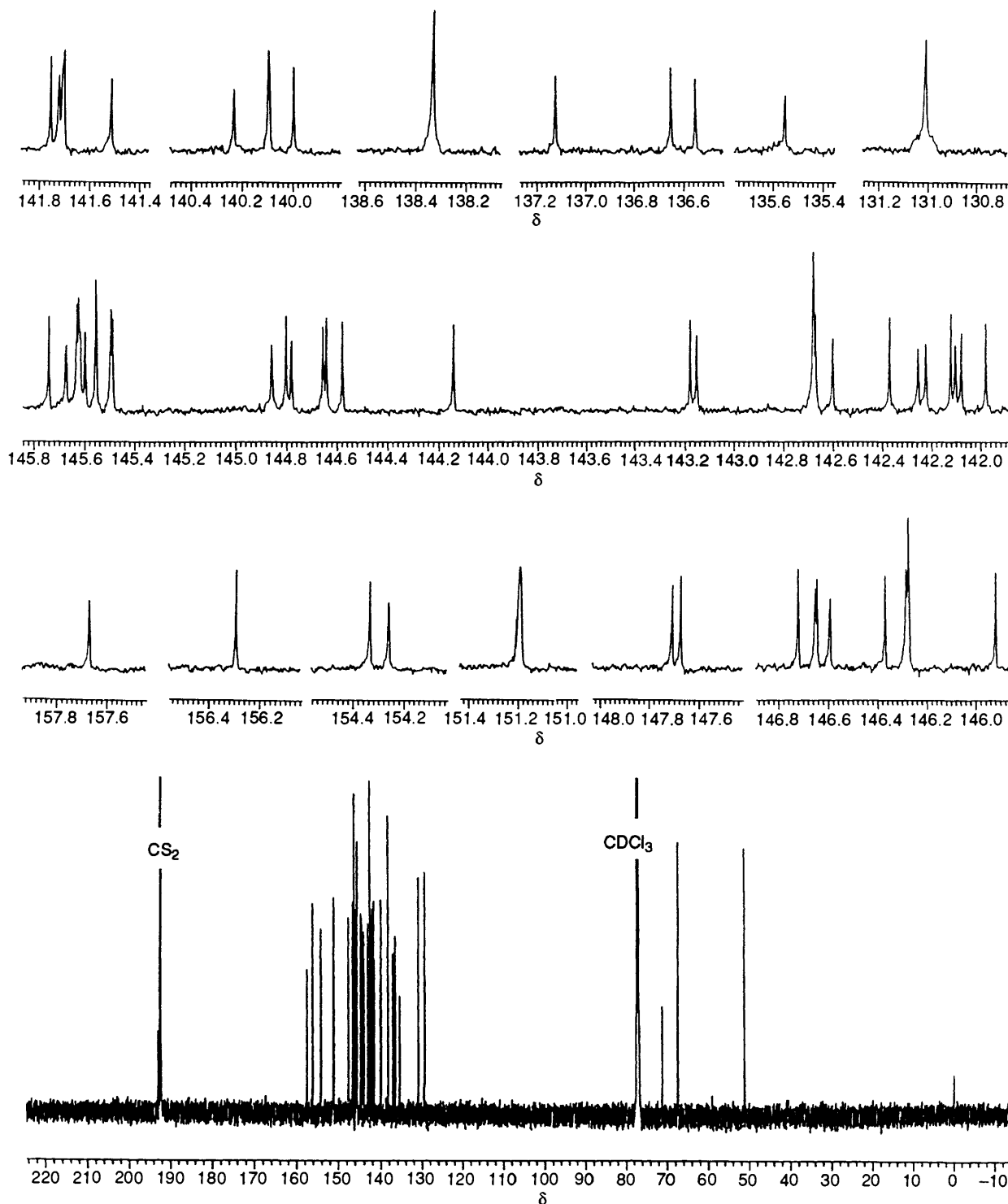


Fig. 2 The  $^{13}\text{C}$  NMR spectrum of **2a**

$\delta_{\text{H}}(\text{CDCl}_3)$  3.89 (3 H, s), 5.16 (1 H, ddd,  $J$  9.9, 7.3, 1.1), 5.42 (1 H, dd,  $J$  7.3, 1.1), 6.73 (1 H, d,  $J$  9.9), 7.13 (1 H, ddd,  $J$  8.4, 7.3, 1.1) and 7.53 (1 H, ddd,  $J$  8.4, 7.3, 1.1);  $\delta_{\text{C}}(\text{CDCl}_3)$  48.60, 55.82, 65.90, 67.70, 71.33, 119.24, 128.83, 135.84, 136.60, 136.80, 136.82, 139.91, 140.07, 140.12, 140.14, 140.28, 141.54, 141.80, 141.81 (2 C), 141.96, 142.04, 142.16, 142.18, 142.24, 142.27, 142.33, 142.59, 142.67, 142.75 (3 C), 143.21, 143.24, 144.24, 144.67, 144.72, 144.77, 144.87, 144.97, 145.06, 145.45, 145.56, 145.64, 145.66 (4 C), 145.71, 145.75, 145.80, 145.97, 146.37 (3 C), 146.46, 146.67, 146.72, 146.76, 146.77, 147.80, 147.81, 152.47, 154.10, 155.30, 156.42, 157.77 and 189.68;  $\nu_{\text{max}}/\text{cm}^{-1}$  2920, 1681, 1639, 1621,

1476, 1460, 1428, 1375, 1240, 1169, 1131, 924, 752, 675, 574 and 526;  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$  406.9 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  4449), 433.4 (3207), 480.5 (1570), 541.0 (972), 607.5 (495), 637.6 (376) and 700.6 (323).

**2c** Black powders from chloroform and carbon disulfide, decomp. point ca. 140 °C (Found: C, 88.7; H, 1.2.  $\text{C}_6\text{H}_5\text{BrO}$  requires C, 88.85; H, 0.56%.  $\text{C}_6\text{H}_5\text{BrO}\cdot\text{C}_6\text{H}_6$  requires C, 89.13; H, 1.12%);  $\delta_{\text{H}}(\text{CDCl}_3)$  5.20 (1 H, ddd,  $J$  9.5, 7.3, 1.1), 5.58 (1 H, dd,  $J$  7.7, 1.1), 7.19 (1 H, ddd,  $J$  8.4, 7.7, 1.1), 7.50 (1 H, ddd,  $J$  8.4, 7.3, 1.1) and 8.32 (1 H, d,  $J$  9.5);  $\delta_{\text{C}}[\text{CDCl}_3\text{-CS}_2$  (3:1)] 52.32, 65.74, 67.17, 70.65, 126.63, 129.59, 135.66, 136.47, 136.62, 136.81,

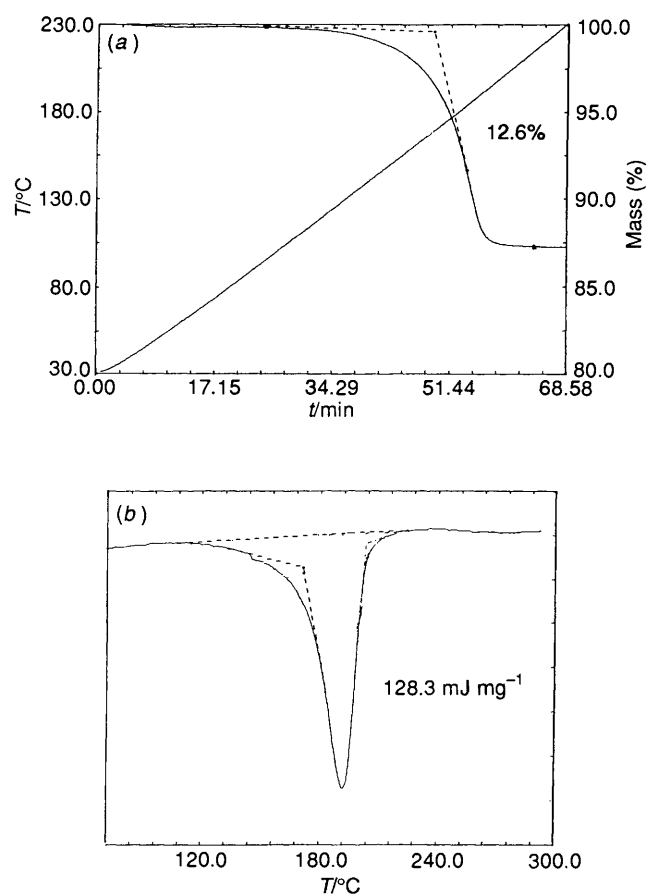
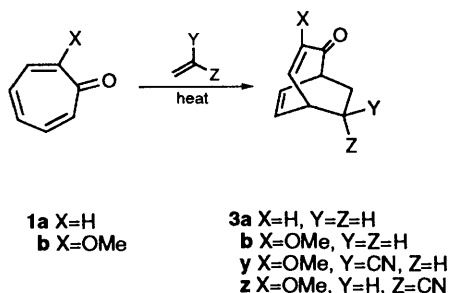


Fig. 3 Thermochemical analysis of cycloreversion of **2a** to  $C_{60}$  and **1a**: (a) thermogravimetry; (b) differential scanning calorimetry



Scheme 2

138.27, 140.11 (2 C), 140.12 (2 C), 140.33, 141.55, 141.76 (2 C), 141.86, 141.97, 142.08, 142.11, 142.13, 142.19, 142.29 (2 C), 142.65, 142.71 (3 C), 142.72 (2 C), 143.14, 143.18, 143.95, 144.57, 144.58, 144.61, 144.66 (2 C), 144.85, 145.45 (2 C), 145.52, 145.55, 145.57, 145.60, 145.62, 145.66, 145.68, 145.81, 145.97, 146.32 (2 C), 146.40, 146.64, 146.69, 146.76, 147.73, 147.76, 151.68, 153.41, 153.71, 155.48, 156.95 and 186.31;  $\nu_{\max}/\text{cm}^{-1}$  2922, 1680, 1396, 1180, 1035, 716, 675, 565 and 526;  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)$  405.6 ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  4700), 432.8 (3307), 478.2 (1764), 536.2 (1107), 607.5 (576), 634.7 (458) and 698.7 (374);  $m/z$  (FAB) 905 and 907 [(M + H)<sup>+</sup>, 3.1] and 720 (100).

**2d** Black powders from chloroform, decomp. point ca. 130 °C (Found: C, 93.6; H, 1.3.  $C_{69}H_8O_3$  requires C, 93.66; H, 0.91%.  $C_{69}H_8O_3 \cdot C_6H_6$  requires C, 93.56; H, 1.45%;  $\delta_{\text{H}}(\text{CDCl}_3)$  2.40 (3 H, s), 5.03 (1 H, ddd,  $J$  9.2, 2.2, 0.7), 5.22 (1 H, dd,  $J$  8.4, 1.8), 6.64 (1 H, ddd,  $J$  11.0, 1.8, 0.7), 6.72 (1 H, dd,  $J$  8.4, 2.2) and 7.75 (1 H, dd,  $J$  11.0, 9.2);  $\delta_{\text{C}}(\text{CDCl}_3)$  21.26, 55.39, 65.47, 67.55, 71.60, 110.85, 130.35, 135.62, 136.82, 136.83, 137.37, 139.98, 140.15, 140.17, 140.35, 141.61, 141.73, 141.78, 141.81, 141.85, 142.08,

142.17, 142.22, 142.32, 142.34, 142.43, 142.71, 142.76, 142.78, 142.80, 143.23, 143.27, 144.09, 144.60, 144.62, 144.65, 144.73, 144.76, 144.98, 145.62 (2 C), 145.63 (2 C), 145.64, 145.66, 145.68, 145.70, 145.71, 145.74, 145.85, 145.96, 146.37, 146.38, 146.39, 146.44, 146.44, 146.71 (2 C), 146.74, 146.83, 147.76, 147.82, 149.80, 153.58, 153.68, 155.14, 157.25, 157.60, 169.20 and 193.75;  $\nu_{\max}/\text{cm}^{-1}$  2920, 1758, 1669, 1426, 1380, 1367, 1197, 1178, 1142, 900, 770, 670, 550 and 526;  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  4545), 432.3 (3153), 478.7 (1623), 537.9 (999), 609.3 (497), 635.8 (379) and 696.6 (316);  $m/z$  (FAB) 885 [(M + H)<sup>+</sup>, 4.3] and 720 (100).

**2e** Black powders from chloroform, decomp. point ca. 160 °C;  $\delta_{\text{H}}(\text{CDCl}_3)$  3.99 (3 H, s), 4.93 (1 H, ddd,  $J$  9.0, 2.2, 0.7), 5.10 (1 H, dd,  $J$  8.4, 1.8), 5.72 (1 H, dd,  $J$  8.4, 2.2), 6.64 (1 H, ddd,  $J$  10.6, 1.8, 0.7) and 7.69 (1 H, dd,  $J$  10.6, 9.0);  $\delta_{\text{C}}(\text{CDCl}_3)$  55.23, 56.42, 65.40, 67.85, 71.28, 90.55, 131.50, 135.57, 136.78, 137.22, 139.95, 140.02, 140.19, 140.36, 141.57, 141.77, 141.80, 141.83, 142.08, 142.14, 142.22, 142.33, 142.36, 142.46, 142.49, 142.68, 142.71, 142.76, 142.78, 143.20, 143.24, 144.30, 144.62, 144.63, 144.77, 144.78, 145.01 (2 C), 145.56 (2 C), 145.62 (3 C), 145.64, 145.69, 145.70, 145.86, 145.90, 146.90, 146.04, 146.35 (2 C), 146.38, 146.42, 146.66, 146.69, 146.71, 146.80, 147.73, 147.79, 148.89, 153.95, 153.99, 155.68, 157.87, 166.34 and 195.52;  $\nu_{\max}/\text{cm}^{-1}$  2924, 1671, 1520, 1430, 1353, 1222, 1160, 1020, 850, 760, 674, 580 and 526;  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  4959), 433.1 (3331), 482.5 (1679), 542.0 (1014), 606.2 (534), 636.0 (414) and 700.0 (336);  $m/z$  (FAB) 857 [(M + H)<sup>+</sup>, 7.7] and 720 (100).

*Attempted Diels–Alder Reaction of Fullerite with 1f.*—A toluene solution (5 cm<sup>3</sup>) of fullerite (72 mg) and **1f** (30 mg) was heated under 500 MPa at 100 °C for 36 h. After the apparatus had cooled, work-up as above gave recovered starting materials, fullerite and **1f**, quantitatively.

*Cycloreversion of 2a, 2b and 2c.*—*o*-Dichlorobenzene solutions (1 cm<sup>3</sup>) of **2** (1 mg) were heated at 160 °C for 30 min. HP chromatographic analysis confirmed a quantitative generation of  $C_{60}$  together with **1a**, **1b** or **1c** in a ratio of 1 : 1.

## References

- M. Tsuda, T. Ishida, T. Nogami, S. Kurono and M. Ohashi, *Chem. Lett.*, 1992, 2333; Y. Rubin, S. Khan, D. I. Freedberg and C. Yeretian, *J. Am. Chem. Soc.*, 1993, **115**, 344; 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.*, 1993, **115**, 1594; S. I. Khan, A. M. Oliver, M. N. Paddon-Row and Y. Rubin, *J. Am. Chem. Soc.*, 1993, **115**, 4919; S. H. Hoke II, J. Molstad, D. Dilettato, M. J. Jay, D. Carlson, B. Kahr and R. G. Cooks, *J. Org. Chem.*, 1992, **57**, 5069; H. Tokuyama, M. Nakamura and E. Nakamura, *Tetrahedron Lett.*, 1993, **34**, 7429.
- V. M. Rotello, J. B. Howard, T. Yadav, M. M. Conn, E. Viani, L. M. Giovane and A. L. Lafleur, *Tetrahedron Lett.*, 1993, **34**, 1561.
- M. F. Meidine, R. Roers, G. J. Langley, A. G. Avent, A. D. Darish, S. Firth, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1993, 1342.
- S. R. Wilson and Y. Wu, *J. Chem. Soc., Chem. Commun.*, 1993, 784; H. Tokuyama, M. Nakamura and E. Nakamura, *Tetrahedron Lett.*, 1993, **34**, 7429.
- M. Prato, Q. Chan and F. Wudl, *J. Am. Chem. Soc.*, 1993, **115**, 1148.
- P. Belik, A. Gügel, J. Spickermann and K. M. Müllen, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 78.
- S. R. Williams and Q. Lu, *Tetrahedron Lett.*, 1993, **34**, 8043.
- R. C. Haddon, *Acc. Chem. Res.*, 1992, **25**, 127.
- H. Takeshita, Y. Wada, A. Mori and T. Hatsui, *Chem. Lett.*, 1973, 335.
- Part of the content of this paper has been preliminarily reported: H. Takeshita, J. Liu, N. Kato and A. Mori, *Chem. Lett.*, 1993, 1697.
- T. Uehara and Y. Kitahara, *Chem. Ind. (London)*, 1971, 354;

- H. Takeshita, T. Hatsui, I. Shimooda and H. Mametsuka, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2291.
- 12 A. Vasella, P. Uhlmann, C. A. A. Waldraff, F. Diederich and C. Thilgen, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1338.
- 13 S. Itô, H. Takeshita and Y. Shoji, *Tetrahedron Lett.*, 1969, 1815.
- 14 Y. Ikeda, A. Mori and H. Takeshita, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 2779.
- 15 O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, 1960, **82**, 3642.

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