Supporting Information

Ring-Opening Reaction of Cyclopropanated [60]Fullerenes: Unexpected Transformation of Methano[60]fullerenes Having an Electron-Donating Group on the Methano-Bridge Carbon

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(i) General

¹H NMR spectra were recorded on a Varian Mercury 300 or a JEOL Alpha 500 operating at 300 or 500 MHz, respectively. ¹³C NMR spectra were recorded on a Varian Mercury 300 or a JEOL Alpha 500 operating at 75 and 125 MHz, respectively. IR spectra were recorded on a JASCO model FT/IR-480plus. MALDI-TOF-MS spectra were recorded on an Applied Biosystems Voyager-DE STR. Gel permeation chromatography was conducted on a recycling HPLC system (Japan Analytical Industry, Co.) equipped with a UV detector: column, JAIGEL-1H/2H; eluent, CHCl₃; flow rate, 3.5 mL min⁻¹. 2,2-[60]Fullerenoalkylamine trifluoromethanesulfonic acid salts (**1a–g**•HOTf) were prepared according to the reported method (Tada, T.; Ishida, Y.; Saigo, K. *Org. Lett.* **2005**, 7, 5897 and Tada, T.; Ishida, Y.; Saigo, K. *Synlett* **2007**, 235). All the reactions were conducted under argon atmosphere.

(ii) Experimental details for the preparation of ketones/aldehyde 2a–g

1-Formyl-1,2-dihydro[60]fullerene (2a):

To a toluene solution (30 mL) of pyridine (31.5 μmol) and 4-(*N,N*-dimethylamino)pyridine (3.0 μmol) was added 2,2-[60]fullerenomethylamine trifluoromethanesulfonic acid salts (**1a**•HOTf) (13.5 mg, 15.0 μmol) at 0 °C with stirring. The reaction mixture was then allowed to warm up to room temperature and stirred for 12 h. After concentration of the resultant mixture under reduced pressure, CS₂ (20 mL) was added to the residual solid. The insoluble mass was filtered off, and the filtrate was concentrated under reduced pressure. Residual toluene was azeotropically removed with CHCl₃ (3 x 10 mL) to afford a mixture of **2a** (7.9 mg, 10.5 μmol , 70% yield) and 1,2-dihydro[60]fullerene (2.3 mg, 3.2 μmol , 21% yield). Because of the poor solubility of **2a** to common organic solvents, the mixture was used for the next reaction without further purification.

¹H NMR (1,2-C₆D₄Cl₂/CS₂ = 1:1, v/v): δ = 7.65 (s, 1H), 10.80 (s, 1H).

¹³C NMR (1,2-C₆D₄Cl₂ = 1:1, v/v): δ = 51.89, 77.82, 134.82, 135.02, 137.27, 140.46, 140.66, 141.33, 141.60, 141.69, 141.97, 142.17, 142.56, 142.70, 143.26, 144.20, 144.72, 145.37, 145.70, 145.78, 145.89, 146.28, 146.33, 146.69, 147.16, 147.56, 147.97, 152.62, 192.40.

FT-IR (KBr): 2919, 2849, 1730, 1427, 1181, 576, 526 cm⁻¹.

MALDI-TOF-MASS (dithranol): calcd. for C₆₁H₃O [M + H]⁺ 751.0184, found 751.0978.

1-Propionyl-1,2-dihydro[60]fullerene (2c):

To a toluene solution (30 mL) of pyridine (34.0 μmol) and 4-(*N,N*-dimethylamino)pyridine (3.2 μmol) was added 2,2-[60]fullerenopropylamine trifluoromethanesulfonic acid salts (**1b**•HOTf) (15.0 mg, 16.2 μmol) at 0 °C with stirring. The reaction mixture was then allowed to warm up to room temperature and stirred for 12 h. The resultant mixture was concentrated under reduced pressure and subjected to preparative thin-layer chromatography developed with CS₂ to afford **2c** as a brown solid (11.0 mg, 14.1 μmol , 87% yield).

¹H NMR (1,2-C₆D₄Cl₂/CS₂ = 1:1, v/v): δ = 1.60 (t, 3H, *J* = 7.3 Hz), 3.79 (q, 2H, *J* = 7.3 Hz), 7.75 (s, 1H).

¹³C NMR (1,2-C₆D₄Cl₂/CS₂ = 1:1, v/v): δ = 9.10, 33.85, 55.87, 78.36, 135.02, 136.26, 140.10, 140.53, 141.39, 141.50, 141.63, 141.94, 142.07, 142.27, 142.51, 142.61, 143.17, 144.04, 144.62, 145.12, 145.19, 145.43, 145.72, 146.03, 146.10, 146.38, 146.85, 147.04, 147.11, 147.44, 150.31, 153.35, 203.14.

FT-IR (KBr): 2927, 2849, 1725, 1427, 1339, 1185, 1105, 572, 552, 527 cm⁻¹.

MALDI-TOF-MASS (dithranol): calcd. for C₆₃H₇O [M + H]⁺ 779.0497, found 779.1171.

1-Acetyl-1,2-dihydro[60]fullerene (2b):

The ketone **2b** was synthesized in a similar procedure to that for the synthesis of **2c** (86% yield).

¹H NMR (1,2-C₆D₄Cl₂/CS₂ = 1:1, v/v): δ = 3.29 (s, 3H), 7.77 (s, 1H).

^{13}C NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v): $\delta = 27.30, 55.42, 78.95, 135.08, 136.54, 140.29, 140.59, 141.45, 141.63, 141.72, 142.04, 142.19, 142.40, 142.60, 142.70, 143.27, 144.15, 144.73, 145.22, 145.31, 145.59, 145.84, 146.16, 146.24, 146.52, 147.00, 147.13, 147.26, 147.56, 150.32, 153.35, 200.57$.

FT-IR (KBr): 2850, 1717, 1426, 1165, 574, 526 cm^{-1} .

MALDI-TOF-MASS (dithranol): calcd. for $\text{C}_{62}\text{H}_5\text{O}$ $[\text{M} + \text{H}]^+$ 765.0340, found 765.1027.

1-Phenylacetyl-1,2-dihydro[60]fullerene (**2d**):

The ketone **2d** was synthesized in a similar procedure to that for the synthesis of **2c** (90% yield).

^1H NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v): $\delta = 5.11$ (s, 2H), 7.40–7.45 (m, 7H, overlapped with internal 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$), 7.50–7.53 (m, 2H), 7.59–7.60 (m, 2H), 7.78 (s, 1H).

^{13}C NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v): $\delta = 46.13, 55.96, 78.87, 128.99, 129.44, 132.21, 133.72, 135.11, 136.74, 140.25, 140.60, 141.48, 141.66, 141.73, 142.05, 142.19, 142.36, 142.61, 142.72, 143.27, 144.14, 144.74, 145.21, 145.31, 145.58, 145.65, 145.81, 146.15, 146.24, 146.52, 147.05, 147.26, 147.51, 149.80, 153.24, 200.96$.

FT-IR (KBr): 2853, 1718, 1452, 1428, 1184, 765, 711, 574, 527 cm^{-1} .

MALDI-TOF-MASS (dithranol): calcd. for $\text{C}_{69}\text{H}_9\text{O}$ $[\text{M} + \text{H}]^+$ 841.0653, found 841.1452.

1-Benzoyl-1,2-dihydro[60]fullerene (**2e**):

To a toluene solution (30 mL) of pyridine (31.5 μmol) and 4-(*N,N*-dimethylamino)pyridine (3.0 μmol) was added 2,2-[60]fullerenobenzylamine trifluoromethylsulfonic acid salts (**1e**•HOTf) (14.6 mg, 15.0 μmol) at 0 °C with stirring. The reaction mixture was then allowed to warm up to room temperature and stirred for 12 h. The resultant mixture was concentrated under reduced pressure and subjected to preparative gel permeation column chromatography developed with CHCl_3 to afford **2e** as a brown solid (11.1 mg, 13.4 μmol , 90% yield).

^1H NMR ($\text{CDCl}_3/\text{CS}_2 = 1:1$, v/v): $\delta = 7.34$ (s, 1H), 7.65–7.77 (m, 3H), 8.67–8.70 (m, 2H).

^{13}C NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v): $\delta = 57.75, 77.33, 129.06, 129.38, 129.63, 132.24, 133.37, 135.87, 135.96, 136.40, 140.04, 140.57, 141.57, 141.71, 142.03, 142.06, 142.10, 142.58, 142.68, 142.97, 143.21, 144.34, 144.63, 145.34, 145.43, 145.65, 145.69, 146.17, 146.36, 146.91, 146.94, 147.18, 147.34, 150.84, 151.94, 196.92$.

FT-IR (KBr): 2919, 1671, 1427, 1224, 1180, 868, 690, 576, 526 cm^{-1} .

MALDI-TOF-MASS (dithranol): calcd. for $\text{C}_{67}\text{H}_6\text{O}$ $[\text{M}]^+$ 826.0419, found 826.1705.

1-(4-Methoxybenzoyl)-1,2-dihydro[60]fullerene (**2f**):

The ketone **2f** was synthesized in a similar procedure to that for the synthesis of **2e** (88% yield).

^1H NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v): $\delta = 3.96$ (s, 3H), 7.24 (d, 2H, $J = 8.4$ Hz), 7.26 (s, 1H), 8.97 (d, 2H, $J = 8.4$ Hz).

^{13}C NMR ($1,2\text{-C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v): $\delta = 55.30, 58.34, 76.93, 114.38, 128.38, 129.02, 129.35, 132.32, 135.74, 136.08, 140.05, 140.54, 141.57, 141.68, 141.92, 142.01, 142.12, 142.58, 142.65, 143.21, 144.41, 144.60, 145.35, 145.42, 145.60, 145.65, 146.15, 146.28, 146.35, 146.82, 146.93, 151.56, 151.79, 164.02, 194.95$.

FT-IR (KBr): 2923, 1666, 1507, 1419, 1239, 1169, 1015, 728, 526 cm^{-1} .

MALDI-TOF-MASS (dithranol): calcd. for $\text{C}_{68}\text{H}_8\text{O}_2$ $[\text{M}]^+$ 856.0524, found 856.1498.

1-[4-(4-Isopropylphenyl)benzoyl]-1,2-dihydro[60]fullerene (**2g**):

The ketone **2g** was synthesized in a similar procedure to that for the synthesis of **2e** (76% yield).

^1H NMR (CDCl_3): $\delta = 1.33$ (d, 6H, $J = 6.9$ Hz), 2.94–3.08 (m, 2H), 7.30 (s, 1H), 7.43 (d, 2H, $J = 8.4$ Hz), 7.69 (d, 2H, $J = 8.4$ Hz), 7.95 (d, 2H, $J = 8.6$ Hz), 8.91 (d, 2H, $J = 8.6$ Hz).

^{13}C NMR ($\text{C}_6\text{D}_6/\text{CS}_2 = 1:1$, v/v): $\delta = 24.25, 34.42, 58.17, 77.47, 130.67, 134.76, 136.21, 136.28, 137.25, 140.43, 140.90, 141.95, 142.06, 142.33, 142.38, 142.48, 142.94, 143.03, 143.59, 144.75, 144.96, 145.68, 145.77, 146.02, 146.36, 146.52, 146.68, 146.71, 147.27, 147.30, 147.53, 147.66, 149.44, 151.41, 152.30, 196.27$.

FT-IR (KBr): 2957, 2923, 1671, 1458, 1427, 1261, 1184, 1028, 818, 803, 526 cm^{-1} .

MALDI-TOF-MASS (dithranol): calcd. for $\text{C}_{76}\text{H}_{16}\text{O}$ $[\text{M}]^+$ 944.1201, found 944.1973.

(iii) Experimental detail for the hydrolysis 2g

To a toluene solution (100 mL) of the ketone **2g** (88 mg, 93.1 μmol) was added 1 M aqueous NaOH (100 mL) at 0 °C with stirring. The reaction mixture was then allowed to warm up to room temperature and vigorously stirred for 12 h. After successive addition of toluene (50 mL) and 3 M aqueous HCl (50 mL), the reaction mixture was stirred for 1 h. The organic layer was separated, washed with brine (50 mL), dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure. The resultant residue was dissolved in $\text{CHCl}_3/\text{CS}_2$ (1:1, v/v, 10 mL), and methanol (80 mL) was added to the mixture to give the solid mass. The solid was collected by filtration, washed with MeOH (20 mL), and crystallized from $\text{CS}_2/\text{Et}_2\text{O}$ (1:5, v/v, 12 mL) to afford 1,2-dihydro[60]fullerene **3** (58.3 mg, 80.7 μmol , 87%) as a brown solid. The filtrate and MeOH used for the washing of the solid were combined and concentrated under reduced pressure to afford a white solid. The solid thus obtained was dissolved in Et_2O (10 mL) and extracted with 1 M aqueous KOH (2 x 10 mL). The combined aqueous layers were treated with 3 M aqueous HCl (20 mL) and extracted with Et_2O (3 x 10 mL). The combined organic layers were successively washed with water (20 mL) and brine (20 mL), dried over anhydrous MgSO_4 , and concentrated under reduced pressure to afford 4-(4-isopropylphenyl)benzoic acid (13.5 mg, 56.2 μmol ,

60%) as a white solid.

1,2-Dihydro[60]fullerene (3):

^1H NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v): $\delta = 6.89$ (s, 1H).

^{13}C NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2 = 1:1$, v/v): $\delta = 53.30, 136.34, 140.39, 141.60, 141.96, 142.53, 144.70, 145.42, 145.51, 146.31, 146.37, 147.75, 152.41$.

FT-IR (KBr) 2943, 1426, 1177, 575, 523 cm^{-1} .

MALDI-TOF-MASS (dithranol) calcd. for C_{60}H_2 $[\text{M}]^+$ 722.0157, found 722.2320.

4-(4-Isopropylphenyl)benzoic acid:

^1H NMR ($\text{CDCl}_3/\text{CD}_3\text{OD} = 20:1$, v/v): $\delta = 1.30$ (d, 6H, $J = 6.9$ Hz), 2.92–3.02 (m, 1H), 7.33 (d, 2H, $J = 8.4$ Hz), 7.57 (d, 2H, $J = 8.4$ Hz), 7.66 (d, 2H, $J = 8.4$ Hz), 8.11 (d, 2H, $J = 8.4$ Hz).

^{13}C NMR ($\text{CDCl}_3/\text{CD}_3\text{OD} = 20:1$, v/v): $\delta = 23.70, 33.66, 126.62, 126.84, 127.00, 128.57, 130.19, 137.30, 145.52, 148.90, 168.86$.

FT-IR (KBr) 3465, 2923, 2853, 1677, 1605, 1428, 1319, 1298, 831, 778 cm^{-1} .

FAB-HR-MASS calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$ 240.1150, found 240.1158.

(iv) Experimental detail for the synthesis of the authentic sample of 4-(4-isopropylphenyl)benzoic acid

To a THF solution (20 mL) of 4-iodobenzoic acid methyl ester (560 mg, 2.14 mmol) was successively added bis[1,2-bis(diphenylphosphino)ethane]palladium (19 mg, 21 μmol), 4-isopropylphenylboronic acid (350 mg, 2.14 mmol) in THF/MeOH (1:1, v/v, 6.0 mL), and K_2CO_3 (700 mg, 5.04 mmol) in water (2.5 mL) at room temperature with stirring. After being stirred at this temperature for 2 h, the reaction mixture was treated with water (20 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure to afford 4-(4-isopropylphenyl)benzoic acid methyl ester (510 mg, 2.01 mmol, 94%) as a white solid. Thus obtained sample was satisfactorily pure and was used for the next step without further purification. To a MeOH/THF/water solution (5:1:1, v/v/v, 28 mL) of 4-(4-isopropylphenyl)benzoic acid methyl ester (426 mg, 1.68 mmol) was added $\text{LiOH}\cdot\text{H}_2\text{O}$ (211 mg, 5.04 mmol) at room temperature with stirring. After being stirred at this temperature for 96 h, the reaction mixture was concentrated under reduced pressure, treated with 1 M aqueous HCl (10 mL), and extracted with diethyl ether (2 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous MgSO_4 , and concentrated under reduced pressure to dryness. The resultant solid was crystallized from acetonitrile (20 mL) to afford 4-(4-isopropylphenyl)benzoic acid (194 mg, 0.807 mmol, 48%) as a white solid.

4-(4-Isopropylphenyl)benzoic acid:

^1H NMR ($\text{CDCl}_3/\text{CD}_3\text{OD} = 4:1$, v/v): $\delta = 1.30$ (d, 6H, $J = 6.6$ Hz), 2.92-3.02 (m, 1H), 7.34 (d, 2H, $J = 8.4$ Hz), 7.57 (d, 2H, $J = 8.4$ Hz), 7.66 (d, 2H, $J = 8.4$ Hz), 8.11 (d, 2H, $J = 8.4$ Hz).

^{13}C NMR ($\text{CDCl}_3/\text{CD}_3\text{OD} = 4:1$, v/v): $\delta = 23.51$, 33.55, 126.47, 126.71, 126.86, 128.56, 130.02, 137.19, 145.37, 148.79, 168.66.

FT-IR (KBr) 3458, 2927, 2870, 1678, 1605, 1426, 1319, 1297, 830, 777 cm^{-1} .

EI-MASS calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$ 240, found 240.

(v) ^1H NMR, ^{13}C NMR, FT-IR, and MALDI-TOF-MS spectra

1-Formyl-1,2-dihydro[60]fullerene (2a):

FT-IR (KBr)

MALDI-TOF-MS (dithranol)

1-Acetyl-1,2-dihydro[60]fullerene (2b):

^1H NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v)

^{13}C NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v)

1-Propionyl-1,2-dihydro[60]fullerene (2c):

^1H NMR ($\text{CDCl}_3/\text{CS}_2 = 1:1$, v/v)

^{13}C NMR ($1,2\text{-C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v)

FT-IR (KBr)

MALDI-TOF-MS (dithranol)

1-Phenylacetyl-1,2-dihydro[60]fullerene (2d):

^1H NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v)

^{13}C NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v)

1-Benzoyl-1,2-dihydro[60]fullerene (2e):

^1H NMR ($\text{CDCl}_3/\text{CS}_2 = 1:1$, v/v)

^{13}C NMR ($1,2\text{-C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v)

FT-IR (KBr)

MALDI-TOF-MS (dithranol)

1-(4-Methoxybenzoyl)-1,2-dihydro[60]fullerene (2f):

^1H NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v)

^{13}C NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v)

1-[4-(4-Isopropylphenyl)benzoyl]-1,2-dihydro[60]fullerene (2g):

^1H NMR (CDCl_3)

^{13}C NMR ($\text{C}_6\text{D}_6/\text{CS}_2 = 1:1, \text{v/v}$)

1,2-Dihydro[60]fullerene (3):

^1H NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2/\text{CS}_2 = 1:1$, v/v)

^{13}C NMR (1,2- $\text{C}_6\text{D}_4\text{Cl}_2$)

FT-IR (KBr)

MALDI-TOF-MS (dithranol)

4-(4-Isopropylphenyl)benzoic acid

^1H NMR ($\text{CDCl}_3/\text{CD}_3\text{OD} = 20:1$, v/v)

^{13}C NMR ($\text{CDCl}_3/\text{CD}_3\text{OD} = 20:1$, v/v)