Supplementary Materials

First synthesis of a new fullerene oximes bis(9-[hydroxo]-1-[1'-hydroxymino-2'-oxo-2'-alkyl-ethyl])1,9-dihydro-[C₆₀-I_h][5,6]fullerenes via reaction of C₆₀ with ketones and NaNO₂ promoted by HCl

Ramil G. Bulgakov, Zemfira S. Kinzyabaeva¹

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, Ufa, Russia

1. Experimental

We used a commercial C₆₀ (99.9%), produced by arc discharge between graphite electrodes (Institute of Organometallic Chemistry. G.A. Razuvaev, RAS, Nizhny Novgorod). The solvent CCl₄ was purified according to the procedure.² NaNO₂, acetone, acetophenone, methyl ethyl ketone and methyl isopropyl ketone were analytical grade and used as purchased. HPLC chromatography was performed on Hewlet Packard, series 1090, with a UV detector ($\lambda_{\text{max}} = 340$ nm), Buckyprep Waters 4.6×250 mm column at a temperature of 30°C, toluene as a mobile phase, flow rate 1.0 ml/min. The components of the mixture were separated using a Cosmosil Buckyprep Waters semicolumn 250 x 10 mm at room temperature; mobile phase: toluene; flow rate: 2.0 mL/min. UV-Visible spectra were recorded on a Perkin Elmer Lambda 750 spectrometer ($l = 0.1$; 1 cm). IR spectra have been recorded

¹Address correspondence to Zemfira S. Kinzyabaeva, Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 141 pr. Oktyabrya, Ufa, 450075, Russia. E-mail: zefa5@rambler.ru

² Gordon, A., Ford, R. (1972) A Handbook of practical data, techniques, and references, J. Wiley and Sons: New York.

by a Vertex 70V spectrometer (Bruker) in CHCl_3 . The NMR spectra of ^1H and ^{13}C were recorded on Bruker Avance-400 spectrometer (operating frequency of 400.13 MHz and 100.62). CDCl_3 was used as a solvent (δ 77.1 ppm), internal standard – $(\text{CH}_3)_4\text{Si}$. Mass spectra were obtained on the Bruker MALDI TOF/TOF Autoflex-III instrument with a laser desorption and registration of positive and negative ions in the reflective mode. The elementary sulfur S_n was used as a matrix.

2. General procedure for the synthesis of the C_{60} bisadducts 1-4

To solution of C_{60} in CCl_4 (30 mg, 0.04 mmol) were sequentially added ketones (Me_2CO , EtMeCO , i-PrMeCO , PhMeCO) (0.4 mol), NaNO_2 (0.1 mol), and HCl (0.2 mol). Immediately after the addition of HCl , were observed vigorous evolution of brown gas and the deep purple solution became dark brown and white precipitate is formed. The reaction solution was mixed in 30 min and then neutralized by CaCO_3 . The liquid phase was separated by filtration and analyzed by HPLC. Reaction kinetics was monitored by the decrease of the C_{60} peak up to the 100% conversion. HPLC of the solution after reaction contains the single broadened peak with the retention time equal to 6.2 min. The reaction products were isolated by semipreparative HPLC with toluene as an eluent. Unfortunately, the replacement of toluene by the polar eluent $\text{CH}_3\text{CN}:\text{H}_2\text{O} = 4:1$ also did not allow separating the regioisomeric bisadducts. Additional purification was successfully performed by water washing (3×50 mL). When water added, two liquid layers aroused, so by-products were removed to the water layer. A liquid organic residue was dried under anhydrous MgSO_4 , and toluene was distilled off. The obtained precipitates 1-4 were dried in vacuo.

1-[hydroxo]-9-[1'-hydroximino-2'-oxo-2'-methyl-ethyl]-1,9-dihydro-[C₆₀-*I_h*][5,6]fullerene 1. 95% (37 mg). ¹³C NMR (100.62 MHz, CDCl₃): δ 17.85–30.76, 69.94, 76.86, 107.18, 113.59, 138.6, 141.91, 142.06, 143.29, 144.80, 145.99, 147.93, 149.00, 151.27, 162.66, 166.85, 167.30, 167.54, 185.79, 189.15, 193.45. ¹H NMR (400.13 MHz, CDCl₃): δ 2.34 (s, 3H); 6.44 (s, 1H), 6.50 (s, 1H); 8–10 (s, 1H). MALDI TOF (m/z): 926.876 [M] (C₆₆H₁₀O₆N₂) (calcd 926.825). IR ν/cm⁻¹: 3651, 3402 (O–H), 3013, 2926, 2852, 1803 (C=O), 1709 (C=N), 1606, 1420, 1367, 1159, 947 (N–O), 596.

1-[hydroxo]-9-[1'-hydroximino-2'-oxo-2'-ethyl-ethyl]-1,9-dihydro-[C₆₀-*I_h*][5,6] fullerene 2. 91% (36 mg). ¹³C NMR (100.62 MHz, CDCl₃): δ 7.96–10.54, 18.84–28.76, 66.84, 74.86, 103.56, 108.06, 135.6, 141.31, 140.06, 143.99, 144.85, 146.99, 147.83, 149.33, 152.26, 161.40, 166.85, 167.30, 167.54, 173.26, 183.17, 189.15, 192.77. ¹H NMR (400.13 MHz, CDCl₃): δ 1.74 (s, 3H); 2.65 (s, 2H); 6.25 (s, 1H); 8–10 (s, 1H). MALDI TOF (m/z): 954.868 [M] (C₆₈H₁₄O₆N₂) (calcd 954.879). IR ν/cm⁻¹: 3410 (O–H), 1800 (C=O), 1700 (C=N), 1604, 1369, 1155, 940 (N–O), 615.

1-[hydroxo]-9-[1'-hydroximino-2'-oxo-2'-isopropyl-ethyl]-1,9-dihydro-[C₆₀-*I_h*][5,6]fullerene 3. 89% (36 mg). ¹³C NMR (100.62 MHz, CDCl₃): δ 18.96–20.54, 30.94–35.77, 62.34, 75.67, 100.56, 110.15, 136.87, 137.64, 138.11, 140.98, 142.29, 143.14, 144.85, 146.27,

155.21, 160.39, 162.44, 168.53, 170.16, 175.57, 180.66, 190.07. ^1H NMR (400.13 MHz, CDCl_3): δ 1.64 (s, 3H); 2.81 (s, 1H). 6.00 (s, 1H); 8-10 (s, 1H); MALDI TOF (m/z): 982.970 [M] ($\text{C}_{70}\text{H}_{18}\text{O}_6\text{N}_2$) (calcd 982.933). IR ν/cm^{-1} : 3409 (O–H), 1799 (C=O), 1705 (C=N), 1600, 1367, 1158, 947 (N–O), 600.

1-[hydroxo]-9-[1'-hydroximino-2'-oxo-2'-phenyl-ethyl]-1,9-dihydro-[$\text{C}_{60}\text{-I}_h$][5,6]fullerene 4. 90% (39 mg). ^{13}C NMR (100.62 MHz, CDCl_3): δ 75.66, 99.56, 128.58, 134.35, 132.57, 130.64, 184.67, 138.7, 139.88, 141.22, 143.15, 144.66, 145.01, 144.90, 149.90, 151.54, 155.44, 165.39, 182.22, 184.67. ^1H NMR (400.13 MHz, CDCl_3): δ 7.02 (s, 1H), 7.20–7.25 (Ph). 7.45–7.48 (Ph), 8.00-8.40 (s, 1H); MALDI TOF (m/z): 1050.969 [M] ($\text{C}_{76}\text{H}_{14}\text{O}_6\text{N}_2$) (calcd 1050.968). IR ν/cm^{-1} : 3415 (O–H), 1800 (C=O), 1706 (C=N), 1601, 1363, 1156, 948 (N–O), 595.

3. Analysis carbonyl groups of the 1 adduct

To 1 mL of 1 solution (15 mg) in methanol we added 1 mL of 2,4-dinitrophenylhydrazine solution and a drop of concentrated HCl. The test-tube was closed and heated at water bath at 70 °C for 5 min. A yellow precipitate occurred. After the cooling and addition of 5 mL of 10% aqueous solution of KOH, the solution immediately obtained intensive red color as a manifestation of formation of quinoid ion 6 (Scheme 1).

Scheme 1

4. Analysis oxime groups of the 1 adduct

Distilled water (10 mL) and concentrated HCl (0.5mL) was added to solid yellow adduct 1 (37 mg). This mixture was heated in 30 min at reflux of liquid phase. Then solid was washed by water to pH = 7 and dried in vacuum. This way, solid powder 7 was obtained. (Scheme 2).

Scheme 2

1-[hydroxo]-9-[1', 2'-dioxo-2'-methyl-ethyl]-1,9-dihydro-[C₆₀-I_h][5,6]fullerene 7. 98% (35 mg). ¹³C NMR (100.62 MHz, CDCl₃): δ 27.97, 28.14, 29.69, 67.76, 69.95, 95.31, 98.15, 103.82, 129.76, 137.31, 139.53, 139.85, 142.44, 143.99, 145.17, 145.59, 146.15, 147.96, 148.95, 150.48, 151.17, 151.36, 151.64, 153.65, 153.48, 189.45, 190.34, 191.51, 192.99, 193.45, 193.96. ¹H NMR (400.13 MHz, CDCl₃): δ 2.64-2.67(s, 3H). MALDI TOF (m/z): 896.701 (calcd 896.796).

5. a) ^1H NMR spectra of 1

b) ^{13}C NMR spectra of 1

Current Data Parameters

NAME kz-261-6
EXPNO 13
PROCNO 1

F2 - Acquisition Parameters

Date_ 20140620
Time 16.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 138585
DS 2
SWH 25252.525 Hz
FIDRES 0.770646 Hz
AQ 0.6488064 sec
RG 2050
DW 19.800 usec
DE 6.50 usec
TE 298.3 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 40

===== CHANNEL f1 =====

SFO1 100.6248425 MHz
NUC1 ^{13}C
P1 10.00 usec
PLW1 34.00000000 W

===== CHANNEL f2 =====

SFO2 400.1316005 MHz
NUC2 ^1H
CPDPRG[2] waltz16
PCPD2 90.00 usec
PLW2 8.89999962 W
PLW12 0.24067000 W
PLW13 0.19495000 W

F2 - Processing parameters

SI 65536
SF 100.6127690 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

6. IR spectrum of 1

7. UV-Vis spectra of 1

8. Mass spectra of 1

9. UV-Vis spectra of 6

10. a) ^1H NMR spectra of 7

b) ^{13}C NMR spectra of 7

11. Mass spectra of 7