cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 [9 H, s, OC(CH_3)$_3$] 1.75 (1 H, m, H-3), 2.20–2.30 (1 H, m, H-3′), 2.50–2.75 (2 H, m, H-4 and *p*-MeOPhC*H*), 3.18 (1 H, m, *p*-MeOPhC*H*′), 3.75 (3 H, s, OCH_3), 3.98 (1 H, t, J = 7.7 Hz, H-2), 5.88 (1 H, s, NH), 6.76 (2 H, m, *p*-MeOAr*H*), 7.15 (2 H, m, *p*-MeOAr*H*); MS m/z 305 (M$^+$, 31), 249 (49), 248 (22), 205 (100). Anal. Calcd for $C_{17}H_{23}NO_4$: C, 66.89; H, 7.59; N, 4.59. Found: C, 66.98; H, 7.32; N, 4.45.

***tert*-Butyl (2*S*)-4β-((*p*-fluorophenyl)methyl)pyroglutamate (7e)**: white solid (EtOAc–hexane) (95 mg, 65%); mp 105–106 °C; $[\alpha]^{25}_D$ +31.8° (c 0.66, MeOH); IR (KBr) 1720, 1745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 [9 H, s, OC(CH_3)$_3$], 1.70–1.80 (1 H, m, H-3), 2.32–2.40 (1 H, m, H-3′), 2.50–2.68 (2 H, m, H-4 and *p*-FPhC*H*), 3.15 (1 H, dd, J = 3.9, 11.8 Hz, *p*-FPhC*H*′), 4.02 (1 H, t, J = 7.6 Hz, H-2), 6.05 (1 H, s, N*H*), 7.02 (2 H, m, *p*-FAr*H*), 7.13 (2 H, m, *p*-FAr*H*); MS m/z 293 (M$^+$, 20), 238 (9), 192 (100). Anal. Calcd for $C_{16}H_{20}NO_3F$: C, 65.53; H, 6.87; N, 4.78. Found: C, 65.84; H, 6.62; N, 4.59.

Alkylation of 1a or 1b with Benzyl Bromide. Compounds **1a** (0.95 g, 3 mmol) and **1b** (285 mg, 1 mmol) were benzylated with benzyl bromide according to the procedure described in the literature[10] to give **8a** and **8b**, respectively.

***tert*-Butyl (2*S*)-1-(benzyloxycarbonyl)-4α-(phenylmethyl)pyroglutamate (8a)**: white solid (EtOAc–hexane) (430 mg, 35%); mp 112–114 °C; $[\alpha]^{25}_D$ −59.2° (c 1.75, $CHCl_3$); IR (KBr) 1740, 1792 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.34 [9 H, s, OC(CH_3)$_3$], 1.95–2.10 (2 H, m, H-3 and H-3′), 2.55–3.05 (2 H, m, H-4 and PhC*H*), 3.25 (1 H, dd, J = 2.5, 12 Hz, PhC*H*′), 4.35 (1 H, dd, J = 4.5, 6.5 Hz, H-2), 5.25 (2 H, s, PhCH_2O), 7.30 (10 H, m, Ar*H*); MS m/z 410 (M + 1, 20), 409 (M$^+$, 35), 353 (30), 319 (11), 275 (35), 265 (20), 264 (15); 91 (100). Anal. Calcd for $C_{24}H_{27}NO_5$: C, 70.41; H, 6.6; N, 3.42. Found: C, 70.82; H, 6.92; N, 3.1.

***tert*-Butyl (2*S*)-1-(*tert*-butyloxycarbonyl)-4α-(phenylmethyl)pyroglutamate (8b)**: white crystalline solid (150 mg, 40%); mp 129–131 °C; $[\alpha]^{25}_D$ −34.09° (c 0.44, MeOH); IR (KBr) 1742, 1800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 [9 H, s, OC(CH_3)$_3$], 1.49 [9 H, s, C(CH_3)$_3$], 1.83–2.05 (2 H, m, H-3 and H-3′), 2.5–2.95 (2 H, m, H-4 and PhC*H*), 3.25 (1 H, dd, J = 2.5, 12 Hz, PhC*H*′), 4.30 (1 H, dd, J = 5, 6.6 Hz, H-2), 7.23 (5 H, m, ArH); ^{13}C NMR ($CDCl_3$) δ 27.9, 36.3, 43.3, 57.7, 82.2, 83.2, 126.5, 128.6, 128.9, 138.3, 149.4, 170.2, 174.3; MS m/z 375 (M$^+$, 5). Anal. Calcd for $C_{21}H_{29}NO_5$: C, 67.2; H, 7.73; N, 3.73. Found: C, 67.05; H, 8.15; N, 3.68.

Removal of the Benzyloxycarbonyl Group from 8a. Removal of the benzyloxycarbonyl group from **8a** (0.4 g, 1 mmol) using a similar procedure as described for **4** or **5** gave **6c** (200 mg, 75%).

Removal of the *tert*-Butyloxycarbonyl Group from 8b. **8b** (0.23 g, 0.6 mmol) was deprotected with TFA–CH_2Cl_2 according to the literature procedure[10] to give **6c** (95 mg, 56%), identical in all respects to the product obtained by the aldol pathway.

Conversion of 6c and 7c to 8b and 9. To a solution of **6c** or **7c** (0.14 g, 0.5 mmol) in dry CH_2Cl_2 were added Et_3N (0.07 mL, 0.5 mmol), di-*tert*-butyl dicarbonate (0.22 g, 1 mmol), and DMAP (0.06 g, 0.5 mmol). The solution was stirred for 6–8 h at 25 °C under a N_2 atmosphere. The volatiles were removed, and the residue was chromatographed on a column of Florisil (30% EtOAc–hexane) to give **8b** and **9**, respectively.

***tert*-Butyl (2*S*)-1-(*tert*-butyloxycarbonyl)-4β-(phenylmethyl)pyroglutamate (9)**: white solid (EtOAc–hexane) (140 mg, 73%); mp 115–116 °C; $[\alpha]^{25}_D$ +3.57° (c 0.56, MeOH); IR (KBr) 1745, 1800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 [9 H, s, OC (CH_3)$_3$], 1.50 [9 H, s, C(CH_3)$_3$], 1.72 (1 H, m, H-3), 2.25 (1 H, m, H-3′), 2.46–2.75 (2 H, m, H-4 + PhC*H*), 3.28 (1 H, d, J = 12.4 Hz, Ph-C*H*′), 4.33 (1 H, dd, J = 5.9, 8.8 Hz, H-2), 7.18 (5 H, m, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 26.5, 27.9, 36.9, 44.5, 58.1, 82.2, 83.4, 126.6, 128.7, 128.9, 138.6, 149.5, 170.6, 174.6; MS m/z 375 (M$^+$, 4), 320 (43), 319 (65), 263 (15), 246 (22), 219 (40), 174 (35), 91 (100). Anal. Calcd for $C_{21}H_{29}NO_5$: C, 67.20; H, 7.73; N, 3.73. Found: C, 66.95; H, 7.95; N, 3.45.

***tert*-Butyl (2*S*)-4α-(Phenylmethyl)-5-thioxoprolinate (10).** To a solution of **6c** (275 mg, 1 mmol) in dry THF was added Laweson's reagent (202 mg, 0.5 mmol). The solution was stirred for 4 h at 25 °C. The volatiles were removed, Et_2O (25 mL) was added, and the mixture was poured into cold saturated sodium bicarbonate solution. The Et_2O layer was separated, and the aqueous layer was extracted twice with Et_2O. The Et_2O extract was washed with water, dried over Na_2SO_4, concentrated, and chromatographed by flash chromatography using 20% EtOAc–hexane as eluent to afford compound **10** as a white crystalline solid (recrystallized from EtOAc–hexane) (195 mg, 67%); mp 88–91 °C; IR (KBr) 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 [9 H, s, OC(CH_3)$_3$], 2.15 (2 H, m, H-3 and H-3′), 2.65 (1 H, m, PhC*H*), 2.95–3.18 (1 H, m, H-4), 3.35 (1 H, dd, J = 2.5, 12 Hz, PhC*H*′), 3.96 (1 H, dd, J = 5, 9 Hz, H-2), 6.43 (1 H, s, N*H*), 7.14 (5 H, m, Ar*H*); MS m/z 293 (M + 2, 5), 292 (M + 1, 20), 291 (M$^+$, 35), 237 (2), 236 (6), 235 (32), 234 (48), 202 (12), 91 (100). Anal. Calcd for $C_{16}H_{21}NO_2S$: C, 65.98; H, 7.21; N, 4.8. Found: C, 66.32; H, 7.17; N, 4.52.

***tert*-Butyl (2*S*)-4α-(Phenylmethyl)prolinate (11).** Sodium borohydride (912 mg, 24 mmol) was added in portions to a solution of **10** (290 mg, 1 mmol) and $NiCl_2$·$6H_2O$ (2.2 g, 8 mmol) in 50 mL of THF–MeOH (1:1) at 0 °C. The reaction mixture was stirred at room temperature until the starting material had disappeared as monitored by TLC; the reaction mixture was filtered through Celite, concentrated, and chromatographed on a column of alumina to afford **11** (130 mg, 50%); IR (neat) 1742 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 [9 H, s, OC(CH_3)$_3$], 1.85 (1 H, ddd, J = 10, 9, 13 Hz, H-3α), 1.95 (1 H, ddd, J = 8, 5, 13 Hz, H-3β), 2.32 (2 H, m, H-4 and PhC*H*), 2.58 (1 H, dd, J = 8, 11 Hz, H-5α), 2.66 (1 H, dd, J = 2.5, 7 Hz, PhC*H*′), 3.16 (1 H, dd, J = 7, 11 Hz, H-5β), 3.72 (1 H, dd, J = 5.0, 9.0 Hz, H-2), 6.64 (1 H, s, NH), 7.12–7.30 (5 H, m, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 27.8, 36.4, 39.4, 40.4, 52.5, 60.0, 80.9, 125.8, 128.2, 128.5, 140.7, 174.4; MS m/z 262 (M + 1, 44), 206 (9), 205 (4), 161 (35), 160 (95), 91 (90), 57 (100).

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Registry No. **1a**, 81470-51-1; **1b**, 91229-91-3; **2c**, 127949-78-4; **2d**, 138858-32-9; **2e**, 138858-33-0; **2f**, 138858-34-1; **2g**, 138858-35-2; **2h**, 138858-36-3; **4c**, 138858-37-4; **4d**, 138858-38-5; **5c**, 138858-39-6; **5d**, 138858-40-9; **6c**, 127949-77-3; **6d**, 138858-41-0; **6e**, 138858-42-1; **7c**, 138858-43-2; **7d**, 138858-44-3; **7e**, 138858-45-4; **8a**, 138858-46-5; **8b**, 127949-74-0; **9**, 138858-47-6; **10**, 138858-48-7; **11**, 138858-49-8; Z-pGlu-OH, 32159-21-0; PhCHO, 100-52-7; 4-$MeOC_6H_4CHO$, 123-11-5; 4-FC_6H_4CHO, 459-57-4; 4-ClC_6H_4CHO, 104-88-1; 3-$MeOC_6H_4CHO$, 591-31-1; $PhCH_2Br$, 100-39-0; furan-2-carboxaldehyde, 98-01-1.

Supplementary Material Available: ^{1}H NMR and in some cases ^{13}C NMR spectra for compounds for which elemental analyses were not obtained (19 pages). Ordering information is given on any current masthead page.

Efficient Preparative Separation of C_{60} and C_{70}. Gel Permeation Chromatography of Fullerenes Using 100% Toluene as Mobile Phase

Mark S. Meier* and John P. Selegue

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

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The scientific community is becoming increasingly interested in the chemistry and physics of the fullerene family of carbon allotropes.[1] A number of studies have uncovered interesting properties of C_{60}: rubidium- and potassium-doped C_{60} are high-temperature superconductors[2-5] and C_{60} thin films display a number of interesting

(1) Diederich, F.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 678–680.
(2) Chen, C.-C.; Kelty, S. P.; Lieber, C. M. *Science* **1991**, *253*, 886–888.

0022-3263/92/1957-1924$03.00/0

optical and electronic properties.[6-8] The isolation of pure C_{60} and pure C_{70} is tedious and has proven to be a major throttle on the pace at which research on these compounds can proceed. In this paper we report a method for the purification of C_{60} and C_{70} which we feel will help alleviate this bottleneck.

Fullerenes are usually prepared by evaporating graphite rods in arc reactors under a helium atmosphere,[9-11] producing a soot that contains C_{60}, C_{70}, higher fullerenes,[12-14] and uncharacterized insoluble material. The soot is then stirred with benzene or toluene to extract the soluble compounds. The preparative separation of C_{60} and C_{70} from this extract is usually performed by column chromatography[15] on alumina using hexane to slowly elute C_{60},[16] followed by elution of C_{70} with toluene/hexane mixtures.[17] C_{60} is very poorly soluble in hexane, requiring very large volumes of solvent and long elution times to purify even small samples. Solvent systems in which the compounds are more soluble lead to very poor separation. Addition of as little as 10% toluene to the mobile phase causes C_{60} and C_{70} to elute together. Reversed-phase HPLC using toluene/2-propanol mobile phase[18] and chromatography on a Pirkle column[17] using hexane as the mobile phase both offer excellent separation, but the low solubility of the fullerenes in these solvent systems severely limits column loadings, and therefore very little material can be purified in one run. The use of pure toluene as the mobile phase, a solvent in which the fullerenes are much more soluble, leads to no appreciable separation of these compounds on adsorption-type (C_{18}, silica gel, or alumina) columns. Clearly, a high-resolution chromatographic method that allows for the use of pure toluene would be greatly superior to existing methods, as larger quantities of material could be separated rapidly using a much smaller volume of solvent.

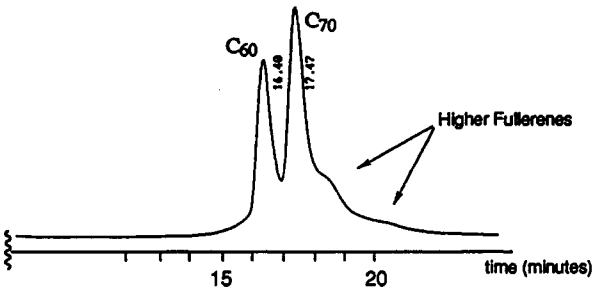

Figure 1. GPC chromatogram of fullerene extract. Conditions: 100-μL injection of saturated fullerene extract, 19-mm × 30-cm 500-Å Ultrastyragel column, toluene mobile phase (5 mL/min), UV/vis detection at 600 nm. Larger injections saturated the detector. Completely excluded materials elute in 42 mL, and the column volume is 85 mL.

We have found that it is possible to separate C_{60} from C_{70} using a gel permeation column and *100% toluene as the mobile phase*. Injection of toluene *saturated with fullerenes* (ca. 6–8 mg/mL) onto a Waters 7.8-mm × 30-cm Ultrastyragel gel permeation column (500-Å pore size) and elution with pure toluene lead to near-baseline separation of C_{60} from C_{70}. Collection of a violet C_{60} band followed by an orange-brown C_{70} band gave pure fullerene samples, whose identities were confirmed by HPLC analysis on reversed-phase C_{18}-silica. Their retention times matched those of C_{60} and C_{70} samples purified by conventional alumina column chromatography. Samples purified by GPC were at least as pure as samples chromatographed on alumina columns.

Over the range of injection volumes from 20 μL to 1.0 mL of saturated extract, we do not observe any distortion of peak shapes, suggesting that the column has not been overloaded. However, since the separation of the bands is 0.8 mL, injection volumes of greater than 1 mL (containing 6–8 mg of material) cannot completely separate on this analytical size column. The use of two columns in series increases the separation, allowing the injection of larger volumes of saturated extract. With two 7.8-mm diameter analytical Ultrastyragel columns (500 Å and 100 Å) in series, we have been able to inject 1 mL of concentrated extract and obtain good separations. The use of a larger diameter Ultrastyragel column (19 mm) increases the allowed injection volume to 5 mL of saturated extract, leading to a C_{60} fraction containing ca. 95% C_{60} and 5% C_{70}, followed by a C_{70} fraction containing ca. 74% C_{70}, 24% C_{60}, and a few percent of the higher fullerenes (Figure 1). Samples of even higher purity could be obtained by peak-shaving. Reinjection of the C_{60} and the C_{70} fractions gives 99.5% pure C_{60} and 95% pure C_{70}. Two 19-mm columns in series improve the resolution, and this can be used to increase the purity of the fractions obtained or to increase the amount of material that can be purified in a single injection. Injections of 10 mL of saturated extract onto this two-column bank lead to the isolation of 23 mg of 93% pure C_{60}.

Since C_{60} (7-Å spheres) and C_{70} (7- × 7- × 9-Å ellipsoids) are about the same size, it is unlikely that separation can be achieved by true size-selective filtration. The 500-Å pore size of this resin and the fact that the *smaller molecule elutes first* indicate that filtration is not responsible for the separation. No change in resolution was observed when the column was equilibrated with 5% DMF in toluene or 5% DMSO in toluene, suggesting that any strongly polar sites that may exist in the packing are not involved in the separation. Warming the column to 60 °C also had

(3) Holczer, K.; Klein, O.; Huang, S. M.; Kaner, R. B.; Fu, K. J.; Whetten, R. L.; Diederich, F. *Science* **1991**, *252*, 1154–1157.
(4) Hebard, A. F.; Roseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* **1991**, *350*, 600.
(5) McCauley, J. P.; Zhu, Q.; Coustel, N.; Zhou, O.; Vaughan, G.; Idziak, S. H. J.; Fischer, J. E.; Tozer, S. W.; Groski, D. M.; Bykovetz, N.; Lin, C. L.; McGhie, A. R.; Allen, B. H.; Romanow, W. J.; Denenstein, A. M.; Smith, A. B., III. *J. Am. Chem. Soc.* **1991**, *113*, 8537–8538.
(6) Ren, S. L.; Wang, Y.; Rao, A. M.; McRae, E.; Holden, J. M.; Hager, T.; Wang, K.-A.; Lee, W.-T.; Ni, H. F.; Selegue, J. P.; Eklund, P. C. *Appl. Phys. Lett.* **1991**, *59*, 2678–2680.
(7) Mort, J.; Okumura, K.; Machonkin, M.; Ziolo, R. G.; Huffman, D. R.; Ferguson, M. I. *Appl. Phys. Lett.* In press.
(8) Krummacher, S.; Cramm, S.; Szot, K.; Krätschmer, W.; Eberhardt, W. *Phys. Rev. B.* In press.
(9) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634–8636.
(10) Koch, A. S.; Khemani, K. C.; Wudl, F. *J. Org. Chem.* **1991**, *56*, 4543–4545.
(11) C_{60} and C_{70} have been isolated from soot produced by the combustion of benzene: Howard, J. B.; McKinnon, J. T.; Makarovsky, Y.; Lafleur, A. L.; Johnson, M. E. *Nature* **1991**, *352*, 139–141.
(12) Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sensharma, D.; Wudl, F.; Khemani, K. C.; Koch, A. *Science* **1991**, *252*, 548–551.
(13) Ettl, R.; Chao, I.; Diederich, F.; Whetten, R. L. *Nature* **1991**, *353*, 149–153.
(14) Parker, D. H.; Wurz, P.; Chatterjee, K.; Lykke, K. R.; Hunt, J. E.; Pellin, M. J.; Hemminger, J. C.; Gruen, D. M.; Stock, L. M. *J. Am. Chem. Soc.* **1991**, *113*, 7499–7503.
(15) Taylor, R.; Hare, J. P.; Abdul-Sada, A. D.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, *1423*–1424.
(16) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630–8633.
(17) Hawkins, J. M.; Lewis, T. A.; Loren, S. D.; Meyer, A.; Heath, J. R.; Shibato, Y.; Saykally, R. J. *J. Org. Chem.* **1990**, *55*, 6250–6252.
(18) Haddon, R. C.; Schneemeyer, L. F.; Waszcak, J. V.; Glarum, S. H.; Tycko, R.; Dabbagh, G.; Kortan, A. R.; Muller, A. J.; Mujsce, A. M.; Rosseinsky, M. J.; Zahurak, S. M.; Makhija, A. V.; Thiel, F. A.; Raghavachari, K.; Cockayne, E.; Elser, V. *Nature* **1991**, *350*, 46–47.

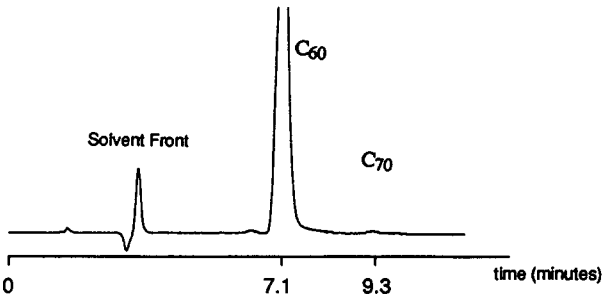

Figure 2. Reversed-phase analysis of the C_{60} fraction. Conditions: 20-μL injection of C_{60} fraction in toluene, 8-mm × 10-cm Novapak C_{18}, 60% 2-propanol/40% toluene mobile phase (1 mL/min), UV/vis detection at 590 nm.

a minimal effect on the separation. We are unable to identify the mechanism by which these compounds are separated, but we feel that hydrophobic interactions are involved rather than size filtration.

The purification protocol described above is largely free of the difficulties involved in other techniques for the isolation of the fullerenes and should increase the supply of pure C_{60} and C_{70} available for research. The use of pure toluene as the eluent leads to several substantial advantages: much smaller volumes of eluting solvent, much higher column loading, and ready recovery and reuse of the solvent. The speed and convenience of HPLC, including the option of complete automation increases the value of the method. We believe that a fully automated system, built around the components used here, will allow for the daily isolation of gram quantities of C_{60} as well as hundreds of milligrams of C_{70}.

Experimental Section

Preparation of Crude Fullerene Extract. A reactor similar to that of Krätschmer et al.[16,19] was used to pass an AC discharge between graphite electrodes in a 200-mTorr He atmosphere. The resulting fullerene-rich soot (10.5 g) was stirred with toluene (750 mL), suction-filtered (Whatman no. 1 filter paper), and evaporated to dryness, leaving 0.77 g of a dark solid. This solid was sonicated for 5 min with toluene (50 mL) and then suction filtered through a medium-porosity glass frit. The filtrate was evaporated to leave 0.46 g of fullerenes. This was suspended in 50 mL of toluene and filtered through a 0.2-μm nylon filter. The filtrate was diluted by 10% with toluene before injection.

Chromatographic Procedures. Toluene and 2-propanol were filtered through 0.2-μm nylon membrane filters. All separations and analyses were carried out on Waters 600E HPLC/GPC systems using UV/vis detection. The strong absorption of the fullerenes often leads to detector saturation, so during high concentration preparative runs the detector was set at 600 nm for the lowest available sensitivity. During C_{18} reversed-phase analysis of the collected fractions the detector was set to 590 nm, where the ratio of extinction coefficients is known to be 1:1.2 (C_{60}/C_{70}).[20]

GPC Separations. Waters Ultrastyragel (500-Å pore size) GPC columns, either 7.8 mm × 30 cm or 19 mm × 30 cm, were used for separations. Fractions were collected manually. Large injections (>2.0 mL) were accomplished by placing the concentrated extract in a solvent reservoir and pumping the desired volume onto the column and then switching to 100% toluene for elution.

Retention times on a single 19 mm × 30 cm GPC column (5 mL/min of toluene mobile phase) were 16.4 min (C_{60}) and 17.5 min (C_{70}), with the higher fullerenes eluting as a shoulder on the tail of the C_{70} peak. Typical 5-mL injections produced 10–15 mg of C_{60} (92–95% pure), 7–10 mg of an overlapping fraction (ca. 1:1 C_{60}/C_{70}), and 6–10 mg of C_{70} (24% C_{60}, 76% C_{70}, and several percent of higher molecular weight fullerenes). The amount of material in each fraction depends on manual fraction cutting technique, leading to large variations between runs. Fraction cutting times are not optimized.

Higher purity samples were obtained by reinjection and peak-shaving. For example, reinjection of 12 mg of the C_{60} fraction onto a 19-mm × 30-cm Ultrastyragel column produced 5.5 mg of 99.5% pure C_{60}; reinjection of 9 mg of the C_{70} fraction produced 4.5 mg of 95% pure C_{70}. The remainder of each sample was recovered as a C_{60}/C_{70} mixture. With two 7.8- × 30-cm columns connected in series (500-Å and 100-Å Ultrastyragel) using 1 mL/min of toluene as mobile phase, the retention times were 27 min (C_{60}) and 29 min (C_{70}).

HPLC Analyses. Samples were analyzed on Waters Novapak C_{18} reversed-phase, 8-mm × 10-cm Radial-Pak cartridges in a RCM 8 × 10 cartridge holder. Authentic C_{60} and C_{70} samples purified by chromatography on alumina were used as standards (Figure 2). Elution with 60% 2-propanol–40% toluene (1 mL/min) and detection at 590 nm gave retention times of 7.1 min (C_{60}) and 9.3 min (C_{70}).[21]

Acknowledgment. We acknowledge Mr. Michael Davis of Waters Corporation for suggesting the 500-Å Ultrastyragel column, and we thank Mr. Davis, Allen Anderson, and Michael Woodman of Waters for valuable assistance. We also thank the research group of Professor Peter Eklund of the University of Kentucky Department of Physics and the Center for Applied Energy Research (CAER) for fullerene-containing soot and alumina-purified standards. Financial support was provided by the University of Kentucky, CAER, and the U.S. Department of Energy (DE-FG05-85ER13432 to J.P.S.).

Registry No. C_{60}, 99685-96-8; C_{70}, 115383-22-7.

(21) The physiological effects of the fullerenes are unknown. Appropriate precautions should be taken against skin contact and against breathing the dust of these materials. See: Foote, C. S.; Diederich, F. N.; Whetten, R.; Wudl, F. *Chem. Eng. News* **1990**, Dec 17, p 2.

(19) Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167.

(20) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050–1051.

Ring Expansions of Simple Cyclic Conjugated Cyclopropyl Ketones by the Nozaki Method Are Not Regiospecific

Harry D. Ward, David S. Teager, and Roger K. Murray, Jr.*

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

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Since cyclic conjugated cyclopropyl ketones (**1**) have significant synthetic utility,[1] it is surprising that a general method has not been developed for the ring enlargement of these compounds that maintains the conjugation of the functional groups. On the contrary, reported homologations of **1** give predominantly or exclusively the corresponding nonconjugated ring-expanded ketones. For example, ring expansion of nortricyclanone (**2**) by the three-step Tiffeneau–Demjanov procedure provides a mixture of **3** and **4** in a ratio of 90:10, respectively.[2] Similar treatment of 8,9-didehydro-2-adamantanone (**5**) gives only **6**.[3]

(1) For reviews, see: (a) Tunemoto, D.; Kondo, K. *Yuki Gosei Kagaku Kyokaishi* **1977**, *35*, 1070. (b) Reissig, H.-L. In *The Chemistry of the Cyclopropyl Group*; Rapport, Z., Ed.; John Wiley: New York, 1987; pp 385–391.

(2) Lumb, J. T.; Whitham, G. H. *Tetrahedron* **1965**, *21*, 499.

0022-3263/92/1957-1926$03.00/0