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SUPPLEMENTARY MATERIAL

Photochemical Fulleroid to Methanofullerene Conversion via the Di- π -methane (Zimmerman) Rearrangement

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Experimental

Methyl 4-benzoylbutyrate.

This compound was prepared on 25 g scale from 4-benzoyl-butyric acid and MeOH using HCl gas according to a literature procedure.¹ Yield: 92% of a colorless oil, Bp. 132-4o C/2 mm Hg (Lit :¹ 147-8o C/8 Torr). FTIR (neat): 1735, 1686 cm⁻¹.

Methyl 4-benzoylbutyrate *p*-tosyl hydrazone.

A mixture of methyl 4-benzoylbutyrate (20.6 g, 0.1 mole), *p*-toluenesulfonhydrazide (22.3 g, 1.2 equiv.), and MeOH (70 mL) was stirred and refluxed during 5.5 hours. The mixture was left without heating during one day, then cooled to -15o C. The product was collected by filtration, washed with a little cold MeOH, and dried in a desiccator to yield 35.9 g (96%) tosyl hydrazone as white crystals, mp. 122-3o C. ¹H NMR (CDCl₃): 9.3 (s, 1H, NH), 7.93 (d, J = 8.5 Hz, 2H; ortho H-ArSO₂-), 7.66 (m, 2H; ortho H-Ph), 7.34 (m, 3H), 7.28 (d, J = 8.5 Hz, 2H; meta H-Ar-SO₂), 3.79 (s, 3H, OCH₃), 2.64 (m, 2H, N=C-CH₂-), 2.40 (s, 3H, ArCH₃), 2.33 (t, J = 6Hz, -CH₂CO₂R), 1.69 (m, 2H, -CH₂-CH₂CO₂R). ¹³C-NMR (CDCl₃; δ (CDCl₃ = 77.00 ppm)) (Chemical shifts for (E)-isomer with possibly corresponding values for (Z)-isomer in parentheses) :

¹ On leave from the Department of Chemical Engineering, Eindhoven University of Technology, The Netherlands.

174.51 (C=O; 173.43), 153.90 (C=N; 156.98), 143.63 (Ts C₁; 143.95), 136.01 (Ph C₁; 132.45), 135.77 (Ts C₄; 135.08), 129.46 (Ph C₄), 129.36 (Ts C_{2,3}; 129.40), 128.25 (Ts C_{2,3}; 128.35), 127.73 (Ph C_{2,3}; 127.91), 126.06 (Ph C_{2,3}; 126.21), 52.00 (OCH₃; 51.35), 32.01 ($\underline{\text{C}}\text{CO}_2$; 32.75), 25.70 ($\underline{\text{C}}\text{H}_2\text{C}=\text{N}$; 36.98), 21.38 (Ts $\underline{\text{C}}\text{H}_3$), 20.77 ($\underline{\text{C}}\text{H}_2\text{CCO}_2$; 20.92). FTIR (KBr): 3113, 1712, 1369, 1228, 1171 cm^{-1} . HRMS (EI) m/z calcd for C₁₉H₂₃N₂O₄S ((M+1)⁺) 375.1349, found 375.1378. Anal. Calcd for C₁₉H₂₂N₂O₄S: C, 60.94; H, 5.92; N, 7.48; S, 8.56%. Found : C, 61.18; H, 5.91; N, 7.57; S, 8.47%.

1-Phenyl-1-(3-methoxycarbonyl)propyl-diazomethane.

A solution of 10 g (0.0267 mole) p-tosyl hydrazone in dry pyridine (100 mL) was stirred under N₂ at 61-64°C. Sodium methoxide (0.0278 mole, 1.04 equiv.) was added and the mixture was stirred at about 63°C during 2 hrs. The rose-colored mixture was poured on pentane (200 mL)/ice-water (500 mL). After separation of the layers, the aqueous phase was extracted with pentane (2x100 mL). The combined organic phases were washed with ice-water (4x200 mL), dried with MgSO₄/Na₂SO₄, filtered, and concentrated *in vacuo* at 30°C to yield the diazo compound as a red oil. TLC (Al₂O₃/toluene): R_f 0.8. The product was stored at -15°C. Yield: 570 mg (10%). FTIR (neat): 2951, 2037(s), 1737(s), 1596, 1497, 1451, 1163, 751, 693 cm^{-1} .

{6}-1-(3-methoxycarbonyl)propyl-{5}-1-phenyl-[5.6]-C61 (1).

Method A. (One-pot procedure).

Methyl 4-benzoylbutyrate p-tosylhydrazone (1.50g; 4 mmole) was dissolved in 30 mL dry pyridine in a dried three-necked flask provided with N₂ inlet, a thermometer and a magnetic stirring bar. Then, NaOMe (225 mg; 4.16 mmole) was added and the mixture was stirred during 15 min. A solution of 1.44 g (2 mmole) C₆₀ in 100 mL HPLC grade 1,2-dichlorobenzene was added and the homogeneous reaction mixture was stirred at 65-

70°C during 22 hrs. (The course of the reaction was followed by TLC (SiO₂/toluene).

The reaction mixture was transferred to a round bottom flask and concentrated to 70 mL at about .1 mmHg. The solution was poured on a silica gel/toluene column (40x10 cm), pre-eluted with 100 mL chlorobenzene. The mixture was eluted with 200 mL chlorobenzene and then with toluene. The first fraction, containing unreacted C₆₀, was collected, concentrated *in vacuo* to about 20 mL, and transferred to a 150 mL centrifuge tube. Et₂O (120 mL) was added, the mixture was immersed in an ultrasound bath for one minute, the suspension was centrifuged, the supernatant decanted, and the residue was treated with Et₂O (100 mL) twice in the same manner. The pellet was dried *in vacuo* at 70°C. Yield: 837.4 mg (58.1%).

After an intermediate fraction, containing a trace of an unknown brown compound, the fraction containing **1** was collected. The product was obtained and purified in the above described manner for C₆₀, using MeOH instead of Et₂O. Yield: 634.2 mg (35%; or 83% based on converted C₆₀). ¹H NMR (CS₂): major isomer (95%): 7.87 (d, J=7.5 Hz, 2H; *o*-H arom), 7.50 (m, 2H; *m*-H arom), 7.37 (m, 1H; *p*-H arom), 3.50 (s, 3H; OCH₃), 2.01 (t, J= 7.5 Hz, 2H; CH₂CO₂Me), 1.58 (m, 2H; PhCCH₂), 1.37 (m, 2H; CH₂CH₂CO₂Me). Minor isomer (about 5%): 7.19 (m, 2H, *m*-H arom), 7.10 (m, 1H; *p*-H arom), 7.01 (d, J=9 Hz, 2H; *o*-H arom), 3.78 (m, 2H; PhCCH₂), 3.53 (s, 3H; OCH₃), 2.35 (t, J=8 Hz, 2H; CH₂CO₂Me), 1.90 (m, 2H; CH₂CH₂CO₂Me). ¹³C NMR (CS₂; 125 MHz; δ (CS₂) = 192.50 ppm): 171.94 (C=O), 147.39, 146.21, 145.19, 144.81, 144.51, 144.25, 143.98, 143.78, 143.68, 143.63, 143.04, 142.75, 142.47, 142.17, 141.95, 141.35, 141.03, 140.52, 139.70, 139.65, 138.83, 138.21, 137.93, 136.59, 135.02, 130.67, 128.86 (Ph C_{2,3}), 127.83 (Ph C_{2,3}), 60.94 (PhC), 51.04 (OCH₃), 35.58 (PhCC), 33.67 (CCO₂), 20.14 (CCCCO₂). FTIR (KBr): 1735(m), 1432(m), 1171(m), 698(m), 644(w), 589(w), 583(w), 572(w), 559(w), 546(w), 542(w), 526(s) cm⁻¹. UV-vis (hexane): λ_{max} (nm) 222, 262, 336, 424, 542. FABMS (NBA): *m/z* 910 (M⁺), 720 (C₆₀⁺). Anal. Calcd for C₇₂H₁₄O₂: C, 94.94; H, 1.55%. Found: C, 94.66; H, 1.69%.

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Upon elution with CH_2Cl_2 , the fraction containing a mixture of isomeric bis-adducts was collected. Work up as described above (using MeOH) yielded 111.2 mg (5%; or 12% based on converted C_{60}). ^1H NMR (CS_2): 8.1-7.6 (m, 2H; *o*-H Ar), 7.6-7.0 (m, 3H; *m*- and *p*-H Ar), 3.7-3.35 (3H, > 20 peaks for OCH_3), 2.9-2.6 (m, 1H; [6.6]PhCCH₂), 2.6-2.25 (m, 1H; [6.6]CH₂CO₂), 2.25-1.8 (m, 2H; [5.6]CH₂CO₂ + [6.6]CH₂CH₂CO₂), 1.8-1.0 (m, 2H; [5.6]PhCCH₂ + [5.6]CH₂CH₂CO₂). FTIR (KBr): 1736 (s), 1446(m), 1433 (m), 1252 (m), 1201, 1159, 702, 527 cm^{-1} . FABMS (NBA): m/z .1101 ((M+1)⁺), 720 (C_{60}^+). Anal. Calcd for $\text{C}_{84}\text{H}_{28}\text{O}_4$: C, 91.63; H, 2.56. Found: C, 90.90; H, 2.61.

Method B.

To a stirred solution of C_{60} (360 mg, 0.5 mmole) in HPLC grade 1,2-dichlorobenzene (20 mL) was added 3 mL of a stock solution of 570 mg diazoester **2** in 10 mL 1,2-dichlorobenzene (1.5 equiv.). After 24 hrs, another 3 mL aliquot of the stock solution was added, and further reaction was allowed to proceed during 1 hour. The mixture was chromatographed (silica/chlorobenzene) and the three fractions containing C_{60} , **1**, and the bis[5.6]ester, respectively, were worked up as described above. Yield: C_{60} , 106 mg (29%); **1**, 227 mg (50%); bis[5.6]ester, 96 mg (17%).

1-(3-methoxycarbonyl)propyl-1-phenyl-[6.6]- C_{61} (**2**).

General procedure:

Purple solutions of **1** in HPLC grade 1,2-dichlorobenzene (1-10 mg/mL) were stirred and heated to reflux during 2-7 hrs. The isomerization was monitored by HPLC (Analytical reverse phase C_{18} column (Vydac, 25 cm), UV detection at 350 nm, eluent MeOH/ CHCl_3 3:1, flow rate 1.5-2 mL/min, inj. vol. 1-5 mL). The resulting brown solution was concentrated *in vacuo* to 5-20 mL and transferred to a centrifuge tube. The product was precipitated with 50-100 mL MeOH and purified as described for **1**. Yield: 98%. ^1H NMR (CS_2): 7.83 (d, $J=8$ Hz, 2H; *o*-H arom), 7.47 (m, 2H; *m*-H arom),

7.40 (m, 1H; *p*-H arom), 3.56 (s, 3H; OCH₃), 2.84 (m, 2H; PhCCH₂), 2.40 (t, J=7.5 Hz, 2H; CH₂CO₂R), 2.10 (m, 2H; CH₂CH₂CO₂R). ¹³C NMR (CS₂ ; 125 MHz): 171.0 (CO₂Me), 148.2, 147.2, 145.4, 144.8, 144.7, 144.4, 144.3, 144.1, 143.7, 143.4, 142.8, 142.7, 142.6, 141.83, 141.77, 141.67, 140.7, 140.4, 137.8, 137.3, 136.3, 131.7, 128.2 (Ph C_{2,3}), 128.0 (Ph C_{2,3}), 79.3 (bridge head C), 51.5 (OCH₃), 50.7 (PhCCH₂), 33.4, 33.3 (PhCCH₂ and CH₂CO₂Me), 22.3 (CH₂CCO₂Me). FTIR (KBr): 1737(s), 1445(m), 1428(m), 1187 (m), 689 (m), 585 (m), 572 (m), 564 (w), 559 (w), 550 (m), 527 (s). UV-vis (hexane): λ_{max} (nm) 210, 258, 328, 430, 492, 696. FABMS (NBA) : *m/z* 910 (M⁺). Anal. Calcd for C₇₂H₁₄O₂: C, 94.94; H, 1.55%. Found: C, 94.66; H, 1.65%.

References

- (1) Allen, C. F. H.; Cressman, H. W. J. *J. Am. Chem. Soc.* **1933**, *55*, 2953-2959.