



Mendeleev Communications

Synthesis of fullerene-containing methacrylates

Seda A. Torosyan,^{*a*} Yulia N. Biglova,^{*b*} Vladimir V. Mikheev,^{*b*} Zarina T. Khalitova,^{*b*} Fanuza A. Gimalova^{*a*} and Mansur S. Miftakhov^{**a*}

^a Institute of Organic Chemistry, Ufa Scientific Centre of the Russian Academy of Sciences, 450054 Ufa,

Russian Federation. Fax: +7 347 235 6066; e-mail: bioreg@anrb.ru

^b Department of Chemistry, Bashkir State University, 450074 Ufa, Russian Federation

DOI: 10.1016/j.mencom.2012.06.009

The Bingel–Hirsch reaction between fullerene C_{60} and 2-methacryloyloxyethyl methyl malonate or 2-methacryloyloxyethyl dichloroacetate afforded the corresponding monocyclopropanation products.

Fullerene C_{60} exhibits electron-withdrawing properties¹ and is used in the composite materials that show high-temperature superconductivity,² as electron-accepting components of plastic solar batteries,^{3–7} *etc.*⁸

In this paper, we report the syntheses of new methacrylate monomers **1** and **2** (Scheme 1)[†] containing covalently attached fullerene C_{60} in the side chain. Compounds **1** and **2** were accessed by cyclopropanation of fullerene C_{60} with reactants **3** and **4** (for their formulae see Scheme 2) according to the Bingel–Hirsch reaction.⁹ Note that the coupling $C_{60} + 4$ did not require the use of CBr₄.

Compound **5** was obtained by controlled esterification of methacrylic acid with ethylene glycol.¹⁰ Esterification of hydroxy group in compound **5** with methyl hydrogen malonate by the Mitsunobu reaction¹¹ proceeded smoothly (method i, Scheme 2).[‡]

{(1-Methoxycarbonyl)-1-[2-(methacryloyloxy)ethyloxycarbonyl]-1,2methane}-1,2-dihydro-C₆₀-fullerene 1. Fullerene C₆₀ (0.1 g, 0.14 mmol) was dissolved in toluene (30 ml); CBr₄ (0.045 g, 0.14 mmol), compound 3 (0.03 g, 0.14 mmol) and diazabicyclo[4.2.0]undec-7-ene (DBU) (0.13 g, 0.14 mmol) were added, and the mixture was stirred for 5 min at room temperature. The mixture was filtered, the filtrate was washed with 5% hydrochloric acid, dried with MgSO4 and concentrated, and the residue was treated with column chromatography on silica gel using toluene-light petroleum (4:1) as the eluent to give 0.060 g (46%) of monoadduct $\mathbf{1}$ and 0.04 g of non-reacted C₆₀. Dark brown powder. Mp > 360 °C. IR (ν /cm⁻¹): 2980, 2953, 2924, 1746, 1719, 1452, 1433, 1319, 1296, 1267, 1234, 1213, 1163, 1111, 1095, 943, 813, 756, 667, 527. UV (CHCl₃, λ_{max}/nm): 257, 326, 425. ¹H NMR (CDCl₃) δ: 1.97 (s, 3 H, Me), 4.01 (s, 3 H, OMe), 4.55 (t, 2H, CH₂O, J 4.4 Hz), 4.75 (m, 2H, CH₂O, J 4.5 Hz), 5.62 (br. s, 1H) and 6.17 (s, 1H, =CH₂). ¹³C NMR (CDCl₃) δ : 18.31 (Me), 53.80 (C¹_{cycloprop}), 54.11 (OMe), 62.05, 64.80 (2 CH₂O), 71.30 ($C_{fullerene}^{sp3}$), 126.57 (=CH₂), 135.67 (=CMe), 138.78, 139.27, 140.97, 141.19, 142.19, 142.94, 143.02 (3C), 143.07, 143.85, 143.89, 144.56, 144.63, 144.65, 144.69, 144.91, 145.06, 145.11, 145.14, 145.20, 145.27 (C_{fullerene}), 163.46 (CO₂), 163.90 and 166.99 (CO₂). MS, m/z: 948.061 [M⁺] (calc. for C₇₀H₁₂O₆, m/z: 948.0634).





[†] NMR spectra were recorded on a Bruker AM-300 spectrometer at 300 (¹H) and 75.47 MHz (¹³C) and a Bruker AVANCE-500 spectrometer at 500 (¹H) and 125.77 MHz (¹³C), using TMS as the internal standard. IR spectra were measured on an IR Prestige-21 Fourier Transform Shimadzu spectrophotometer using samples prepared as thin films or dispersed in Nujol. Mass spectra were recorded on a MALDI Voyager-D STR TOF spectrometer. Elemental analyses of the compounds obtained match the calculated values. The progress of reactions was monitored by TLC on Sorbfil plates (Russia); spots were detected by calcinations or by treatment with an alkaline solution of potassium permanganate. The products were isolated by column chromatography on silica gel (30–60 g of sorbent per gram of substrate); freshly distilled solvents were used as the eluents.

However, the use of methyl malonate chloride (method ii) was more practical for it provided almost the same yield of the product **3**. For the preparation of compound **4**, we used the corresponding acid chloride (method iii).

The electron-withdrawing properties of fullerene C_{60} moieties in methanefullerenes 1 and 2 are further enhanced by additional inductive effects of the ester group and the Cl atom, respectively, which seems promising for practical use. The monomers 1 and 2 will be tested in polymerization and copolymerization reactions.

The authors are grateful to Professor L. M. Khalilov and V. M. Yanybin for recording MALDI TOF mass spectra.

References

- 1 F. Zhou, C. Jehoulet and A. J. Bard, J. Am Chem. Soc., 1992, 114, 11004.
- 2 A. Hebard, M. Rossienski, R. Haddon, D. Murphy, S. Glarum, T. Palstra, A. Ramires and A. Kortan, *Nature*, 1991, **350**, 600.
- 3 K. Moriwaki, F. Matsumoto, Y. Takao, D. Shimizu and T. Ohno, *Tetrahedron*, 2010, **66**, 7316.
- 4 Y.-J. Cheng, Sh.-H. Yang and Ch.-S. Hsu, Chem. Rev., 2009, 109, 5868.

- 5 Ch.-Y. Chang, Ch.-E. Wu, Sh.-Y. Chen, C. Cui, Y.-J. Cheng, Ch.-S. Hsu, Y.-L. Wang and Y. Li, *Angew. Chem. Int. Ed.*, 2011, **50**, 9368.
- 6 D. Guidi, B. M. Illescas, C. M. Atienza, M. Wielopolski and N. Martin, *Chem. Soc. Rev.*, 2009, 38, 1587.
- 7 P. A. Troshin and N. S. Sariciftci, in *Supramolecular Chemistry: From Molecules to Nanomaterials*, eds. J. W. Steed and P. A. Gale, John Wiley & Sons, Ltd., Chichester, UK, 2012, p. 2725.
- 8 P. A. Troshin, R. N. Lyubovskaya and V. F. Razumov, *Rossiiskie Nano*tekhnologii, 2008, **3**, 6 (in Russian).
- 9 X. Camps and A. Hirsch, J. Chem. Soc., Perkin Trans. 1, 1997, 1595. 10 K. Ramalinga, P. Vijayalakshmi and T. N. B. Kaimal, Tetrahedron Lett.,
- 2002, **43**, 879.
- 11 O. Mitsunobu and M. Eguchi, Bull. Chem. Soc. Jpn., 1971, 44, 3427.

Received: 23rd January 2012; Com. 12/3866

2-*Methacryloyloxyethyl dichloroacetate* **4**. iii) Dichloroacetyl chloride (0.1 g, 0.68 mmol) was added with cooling to a solution of compound **5** (0.056 g, 0.55 mmol) in pyridine (0.5 ml) and the mixture was stirred at room temperature for 12 h until the starting compound was consumed (the progress of the reaction was monitored by TLC). The mixture was then diluted with CH₂Cl₂ (30 ml), washed with 5% HCl to remove pyridine, and dried with MgSO₄; the solvent was evaporated. The product was purified on a column with SiO₂ using CH₂Cl₂ as the eluent. Yield 75% (0.1 g). IR (ν /cm⁻¹): 3013, 2963, 1769, 1751, 1718, 1635, 1454, 1369, 1323, 1296, 1159, 1055, 1031, 966, 945, 814. ¹H NMR (CDCl₃) δ : 1.90 (t, 3 H, Me, *J* 1.1 Hz), 4.40 and 4.50 (2 m, 2×2 H, OCH₂CH₂O), 5.57 (t, 1H, =CH₂, *J* 1.4 Hz), 5.96 (s, 1H, CHCl₂), 6.09 (s, 1H, =CH₂). ¹³C NMR (CDCl₃) δ : 18.15 (Me), 61.59 (CH₂O), 63.93 (CHCl₂), 64.81 (CH₂O), 126.40 (=CH₂) and 135.57 (=CMe), 164.32 and 166.86 (2 CO₂).

2-Hydroxyethyl methacrylate **5**. Ethylene glycol (105.4 ml, 1.7 mol) and iodine (0.1 g) were added to methacrylic acid (15 ml, 0.17 mol) and the mixture was refluxed for 4 h. After cooling of the mixture, a solution of NaCl was added. The mixture was extracted with CH_2Cl_2 , the combined organic layers were washed with 5% aqueous $Na_2S_2O_3$ and with saturated NaCl solutions and then dried with MgSO₄. The solvent was distilled off in a rotary evaporator and the product was purified by distillation *in vacuo*. Bp 83–85 °C (20 Torr). Yield 85%. IR (ν/cm^{-1}): 3425, 2957, 2930, 2884, 1714, 1635, 1454, 1321, 1298, 1170, 1080, 1033, 945, 903, 816. ¹H NMR (CDCl₃) δ : 1.90 (t, 3 H, Me, *J* 1.3 Hz), 3.80 (t, 2 H, CH₂O, *J* 6.5 Hz), 4.25 (t, 2 H, CH₂O, *J* 6.5 Hz), 5.10 (t, 1H, =CH₂, *J* 1.3 Hz), 6.10 (s, 1H, =CH₂). ¹³C NMR (CDCl₃) δ : 18.20 (Me), 61.01 and 66.24 (2OCH₂), 126.01 (=CH₂), 135.90 (=CMe), 167.73 (CO₂).

[‡] 2-Methacryloyloxyethyl methyl malonate 3. i) Diisopropyl diazodicarboxylate (0.424 g, 2.10 mmol) and PPh₃ (0.55 g, 2.10 mmol) were added with stirring in an argon flow to a solution of compound 5 (0.27 g, 2.60 mmol) and methyl hydrogen malonate (0.3 g, 2.50 mmol) in THF (5 ml) and the mixture was stirred at room temperature until the starting compound was consumed (the progress of the reaction was monitored by TLC). The solvent was then removed on a rotary evaporator. The residue was purified on a column with SiO2 using CH2Cl2-MeOH (20:1) as the eluent. Yield 55% (0.25 g). ii) Methyl malonate chloride (0.25 g, 1.83 mmol) was added to a solution of compound 5 (0.2 g, 1.52 mmol) in pyridine (3 ml) and the mixture was stirred at room temperature until the starting compound was consumed (TLC control). The mixture was then diluted with chloroform (30 ml), washed with 5% HCl and dried with MgSO₄; the solvent was evaporated. The product was purified on a column with SiO₂ using EtOAc–light petroleum (1:3) as the eluent. Yield 57% (0.19 g). IR (v/cm⁻¹): 2958, 2932, 2895, 1757, 1718, 1638, 1439, 1412, 1371, 1338, 1321, 1298, 1279, 1161, 1151, 1055, 1039, 1024, 949, 851, 815, 785, 851, 758, 656, 603, 581, 521, 482. ¹H NMR (CDCl₃) δ: 1.96 (t, 3 H, Me, J 1.0 and 1.6 Hz), 3.45 (s, 2H, CH₂), 3.75 (s, 3H, OMe), 4.40 (m, 4H, 2CH₂O), 5.61 (t, 1H, =CH₂, J 1.6 Hz), 6.15 (s, 1H, =CH₂). ¹³C NMR (CDCl₃) δ : 18.06 (Me), 40.97 (CH₂), 52.38 (OMe), 61.90 and 62.91 (2OCH₂), 126.00 (=CH₂), 135.64 (=CMe), 166.10, 166.53 and 166.84 (CO₂).