



Ring-opening reaction of tetrahydrofuran on the penta(organo)[60]fullerenes: synthesis of hydroxybutyl, methacrylate, and norbornene derivatives

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ABSTRACT

Ring-opening reaction of tetrahydrofuran takes place on penta(methyl)- and penta(*n*-butylphenyl)[60]fullerenes in the presence of chlorotrimethylsilane giving penta(organo) fullerene hydroxybutyl derivatives, $C_{60}R_5(C_4H_8OH)$ ($R = Me, {}^nBuC_6H_4$). The hydroxyl groups were further transformed into methacrylate and norbornylcarbonyloxy groups via esterification with the corresponding acid chlorides. The methacrylate derivative, penta(methyl)[60]fullerenylbutyl methacrylates was crystallographically characterized.

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Functionalized fullerene derivatives have found many promising applications in the areas of materials science and nanotechnology because of their unique electrochemical and photophysical properties.¹ A wide variety of reactions have been utilized for functionalization of fullerenes—cycloadditions,² nucleophilic additions,³ electrophilic substitution,⁴ radical reactions,⁵ and others.⁶ Diversification of these reactions enhances accessibility to functionalized fullerenes. For instance, we have previously reported organozinc-mediated addition of tetrahydrofuran (THF) to C_{60} giving tetrahydrofuranyl fullerene derivatives.⁷ We report herein that an electrophilic ring-opening reaction of THF can selectively proceed with penta(organo)[60]fullerenes in the presence of Me_3SiCl to afford hydroxybutyl derivatives, $C_{60}R_5(C_4H_8OH)$ (**1a**: $R = Me$; **1b**: $R = {}^nBuC_6H_4$). The alcohol products can be further elaborated into a variety of new fullerene-containing methacrylate and norbornene derivatives through esterification of the hydroxyl moieties.

The hydroxybutyl derivatives **1a,b** were obtained in excellent yield, starting from C_{60} in a one-pot reaction (Scheme 1). Treatment of C_{60} with 12 equiv of a methylcopper reagent afforded an intermediate $C_{60}Me_5^-$ (**2a**), to which was added in situ 5 equiv of Me_3SiCl to generate a ring-opening product $C_{60}Me_5(C_4H_8OSiMe_3)$ (**3a**), followed by acid treatment to obtain **1a** in 91% isolated overall yield.^{8,9} When an *n*-butylphenylcopper reagent was employed in this reaction, the product **1b** was obtained in similar yield (92%) even via a bulky intermediate (**2b**). These reactions can be carried out with ease. Purification of the products is also easily performed with normal silica gel column chromatography, because the products have polar hydroxyl groups. The compounds **1a,b**

are very stable and can be stored in air, while compounds **3a,b** gradually decomposed to **1** in air.

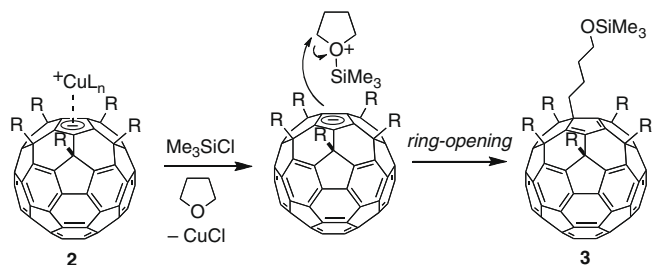
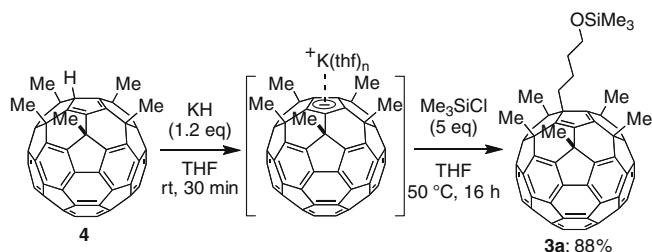
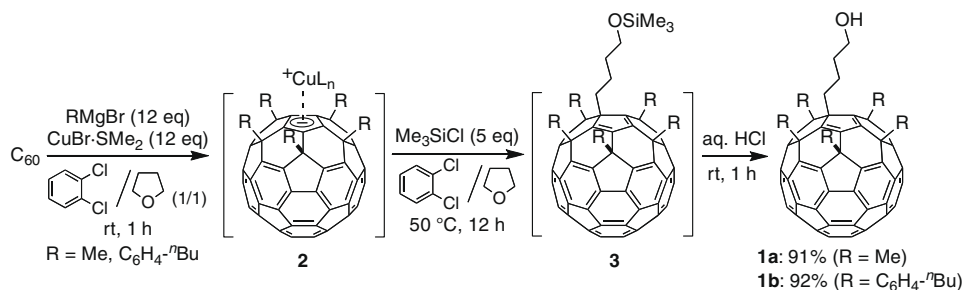
Optimization of the reaction conditions revealed that the use of 5 equiv of Me_3SiCl was the most effective and convenient. We optimized the conditions for the synthesis of **1b**. The use of 1, 3, 5, and 10 equiv of Me_3SiCl resulted in 65%, 77%, 92%, and 92% yield, respectively. Me_3SiBr (5 equiv) and Me_3SiI (5 equiv) were investigated in this reaction, and gave the product in 72% and 57% yield, respectively. Note that trimethylsilyl bromide and iodide themselves can open the cyclic ethers to give, for example, $Br(CH_2)_4OSiMe_3$.¹⁰ We think that these alkyl halides are less reactive than plausible active species, oxonium cations (see below).

The reaction was also performed with the use of a readily available protio compound $C_{60}Me_5H$ (**4**) (Scheme 2). The ring-opening product **3a** was obtained in 88% yield by deprotonation of the hydrogen atom of **4** with KH in THF, followed by addition of Me_3SiCl in similar conditions. On this route, the use of KO^tBu , instead of KH, did not result in any product. This is because of *t*-butanol generated in this reaction. The *t*-butanol deactivates cationic species such as Me_3Si^+ (see below),¹¹ which is absolutely essential for this ring-opening reaction of THF.

The mechanistic aspect of this reaction is discussed with formation of an oxonium compound and a following ring-opening reaction (Scheme 3).¹² A transmetalation reaction of the penta-addition product anion **2** with Me_3SiCl generates a Me_3Si^+ cation formally,¹¹ which immediately forms the oxonium cation of THF. This oxonium species undergoes an electrophilic¹³ ring-opening reaction with the cyclopentadienyl anion of **2** to generate the siloxybutyl product **3**. The present reaction course is quite different from those shown in the syntheses of $CpSiMe_3$ and Cp^*SiMe_3 ($Cp = C_5H_5$; $Cp^* = C_5Me_5$).¹⁴ $NaCp$ and KCp^* react with Me_3SiCl in THF to give the silanes $CpSiMe_3$ and Cp^*SiMe_3 simply via transmetalation reactions. The cyclopentadienyl part of the penta(organo)[60]fullerene is located on the concave cavity, which prevents formation of the

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C_{60} -Si bond. This effect probably gives the tendency to form $C_{60}R_5^-$ and Me_3Si^+ .

The hydroxyl functionality in fullerene derivatives is of importance for building fullerene-based photoelectrochemically and biologically active materials.¹⁵ Here we demonstrated the syntheses of methacrylate and norbornene derivatives via esterification reactions with acid chlorides (Scheme 4). Compounds **1a,b** were treated with methacryloyl chloride in the presence of excess triethylamine in dichloromethane to produce penta(organo)[60]fullerenylbutyl methacrylates **5a,b** in 71–72% yield.¹⁶ A similar reaction with norbornylcarbonyl chloride yielded a norbornene derivative **6**. These products **5** and **6** are stable in air, and can be purified by silica gel column chromatography. The structure of the methacrylate derivative **5a** was unambiguously determined by single-crystal X-ray analysis (Fig. 1).¹⁷ Dark red single crystals containing a 1:1 mixture of **5a** and dichloromethane were obtained by slow diffusion of ethanol into a dichloromethane solution of **5a**. A crystal packing view (Fig. 2) shows a honeycomb-like porous structure, where solvent molecules and part of the methacrylate moiety are located in the hollows. Polymerization¹⁸ of the methacrylate/norbornene parts would be not only interesting but also challenging, because the fullerene part is known to deactivate radical and anionic initiators by radical quenching and the electrophilic properties of fullerenes.

In summary, we have found an efficient and selective ring-opening reaction of THF attaching to the penta(organo)[60]fuller-

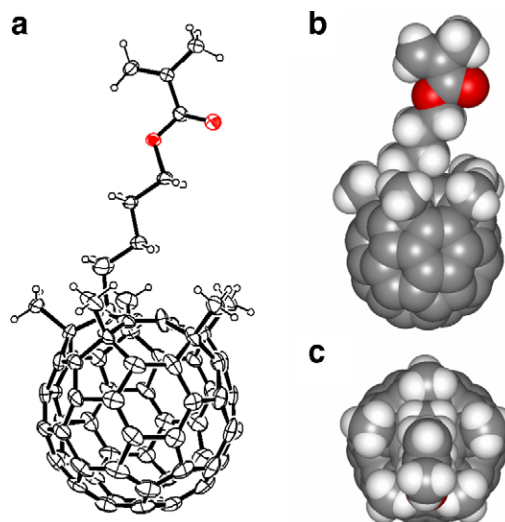
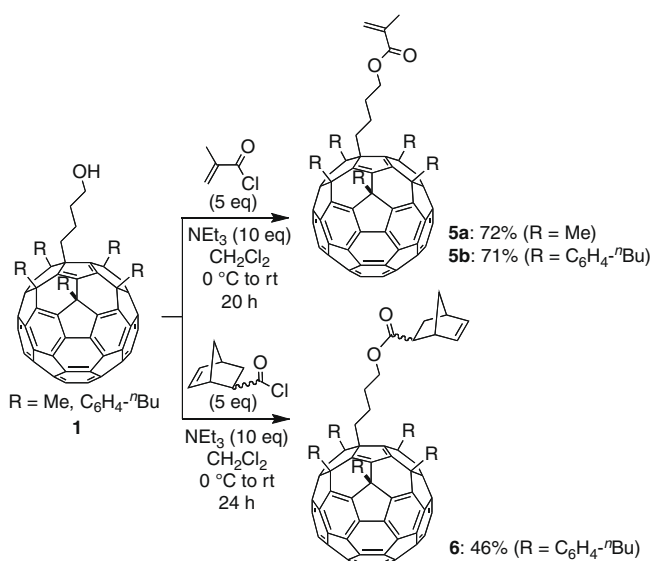


Figure 1. Crystal structure of the fullerene-containing methacrylate **5**. (a) An ORTEP diagram with 30% probability level ellipsoids. (b) Side view of a CPK model. (c) Top view of a CPK model.

ene skeleton. Both pentamethyl and pentaaryl substrates were employed in this reaction to obtain hydroxybutyl derivatives. The usefulness of the alcohol functionalities and the respectable total

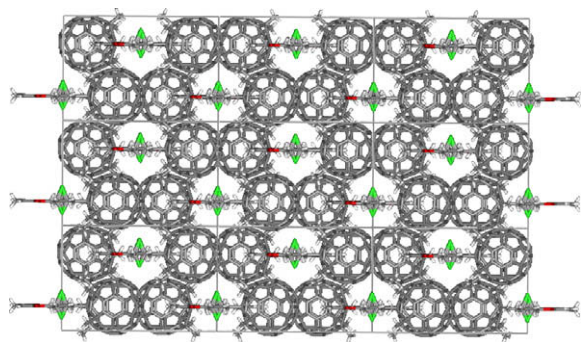


Figure 2. Crystal packing view from C-axis. Oxygen and chlorine atoms are colored red and green, respectively.

yield from C₆₀ are significant for further synthetic elaboration. Fullerene derivatives bearing polymerizing units are potentially unique monomers in materials science.

Acknowledgments

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- Synthesis of 1b:** To a mixture of copper(I) bromide–dimethyl sulfide complex (3.43 g, 16.7 mmol) and *n*-butylphenyl magnesium bromide (17.2 mL, 0.98 M, 16.7 mmol) in THF (25 mL) was added a 1,2-dichlorobenzene (45 mL) solution of C₆₀ (1 g, 1.39 mmol) at room temperature. The reaction mixture was stirred for 1 h at room temperature to complete the penta-addition reaction. Then, chlorotrimethylsilane (1.76 mL, 13.9 mmol) was added to the mixture. After stirring for 12 h at 50 °C, aqueous hydrochloric acid (1 mL, 1 M) was added to the reaction mixture, and then it was stirred for 1 h at room temperature. The solution was passed through a pad of silica gel and evaporated to give a crude product. Purification was performed with silica gel chromatography using toluene/hexane (4/1) as eluent to obtain **1b** (1.84 g, 92%). ¹H NMR (500 MHz, CDCl₃): δ 7.66 (d, 4H), 7.55 (d, 4H), 7.24 (t, 2H), 7.10–7.08 (m, 8H), 6.93 (d, 2H), 3.23 (t, 2H), 2.68–2.60 (m, 8H), 2.50 (t, 2H), 1.65–1.57 (m, 8H), 1.51–1.47 (m, 4H), 1.40–1.33 (m, 8H), 1.30–1.26 (m, 4H), 1.02 (t, 2H), 0.98–0.92 (m, 12H), 0.87 (t, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 156.99, 156.62, 153.58, 151.55, 148.71, 148.60, 148.45, 148.39, 148.18, 148.10, 147.95, 147.75, 147.69, 147.29, 147.22, 147.00, 145.52, 145.44, 144.78, 144.33, 144.29, 144.24, 144.13, 144.04, 143.98, 143.93, 143.68, 142.56, 142.37, 142.25, 141.52, 140.18, 137.82, 136.29, 130.59, 128.72, 128.69, 128.49, 127.99, 127.80, 65.27, 63.09, 62.82, 60.97, 58.33, 40.48, 35.32, 35.17, 35.04, 33.60, 33.42, 33.28, 32.21, 22.34, 22.26, 22.12, 21.65, 14.00, 13.97, 13.90. Anal. Calcd for C₁₁₄H₇₄O: C, 93.79; H, 5.11. Found: C, 93.69; H, 5.14.
- See also, Ref. 3c.
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- Synthesis of 5b:** To a solution of **1b** (1 g, 0.685 mmol) and triethylamine (0.954 mL, 6.85 mmol) in dichloromethane (60 mL) was added methacryloyl chloride (0.277 mL, 3.43 mmol) at 0 °C. After stirring for 2 h at room temperature, aqueous sodium hydrogen carbonate (10 mL) was added to the reaction mixture to quench reactive reagents. The organic phase was extracted and dried over magnesium sulfate. The solution was passed through a pad of silica gel and evaporated to give a crude product. Purification was performed with silica gel chromatography by means of toluene/hexane (1/1) as eluent to obtain **5b** (0.75 g, 72%). ¹H NMR (500 MHz, CDCl₃): δ 7.61 (d, *J* = 8.0 Hz, 4H), 7.50 (d, *J* = 8.0 Hz, 4H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.03–7.01 (m, 8H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.96 (s, 1H), 5.49 (s, 1H), 3.69 (t, *J* = 7.7 Hz, 2H), 2.60–2.53 (m, 8H), 2.43 (t, *J* = 7.8 Hz, 2H), 1.87 (s, 3H), 1.59–1.45 (m, 12H), 1.41–1.21 (m, 12H), 1.03–1.00 (t, *J* = 7.5, 2H), 0.91–0.84 (m, 12H), 0.80 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 167.16, 157.00, 156.77, 153.62, 151.59, 148.80, 148.69, 148.54, 148.47, 148.26, 148.18, 148.05, 147.85, 147.81, 147.37, 147.30, 147.08, 145.59, 145.47, 144.82, 144.39, 144.33, 144.29, 144.15, 144.07, 144.01, 143.98, 142.60, 142.44, 142.32, 141.63, 140.18, 137.80, 136.38, 136.34, 130.62, 128.78, 128.65, 128.54, 127.90, 127.86, 125.31, 65.21, 64.81, 63.13, 60.99, 58.36, 50.90, 40.75, 35.20, 35.18, 35.04, 33.57, 33.42, 33.28, 28.46, 22.36, 22.30, 22.28, 22.15, 18.40, 13.97, 13.94, 13.89. Anal. Calcd for C₁₁₈H₇₉O₂: C, 92.70; H, 5.21. Found: C, 92.67; H, 5.28.
- Crystallographic data for **5b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-716910. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).
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