



## An effective system to synthesize methanofullerenes: substrate–ionic liquid–ultrasonic irradiation

Zhu Yinghuai,<sup>a,\*</sup> Stefan Bahnmüller,<sup>a</sup> Ching Chibun,<sup>a</sup> Keith Carpenter,<sup>a</sup> Narayan S. Hosmane<sup>b</sup> and John A. Maguire<sup>c,\*</sup>

<sup>a</sup>*Institute of Chemical and Engineering Sciences, Block 28, #02-08, Ayer Rajah Crescent, Singapore 139959*

<sup>b</sup>*Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL 60115, USA*

<sup>c</sup>*Department of Chemistry, Southern Methodist University, Dallas, TX 75275, USA*

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**Abstract**—Dehalogenation of the polyhalides,  $\text{CHCl}_3$ ,  $\text{C}_{60}(\text{CCl}_2)$ ,  $\text{CH}_2\text{I}_2$ , and 7,7-dibromobicyclo(4,1,0)heptane, by treatment with zinc, magnesium or NaOH powder, followed by the in situ reaction with fullerene in the presence of ultrasonic irradiation and in the ionic liquid solvents, [bmim][PF<sub>6</sub>] or [omim][BF<sub>4</sub>], provided [6,6]-junction cycloaddition products in 53–79% yields. Only single isomers of the products were detected in the reaction solutions. © 2003 Published by Elsevier Science Ltd.

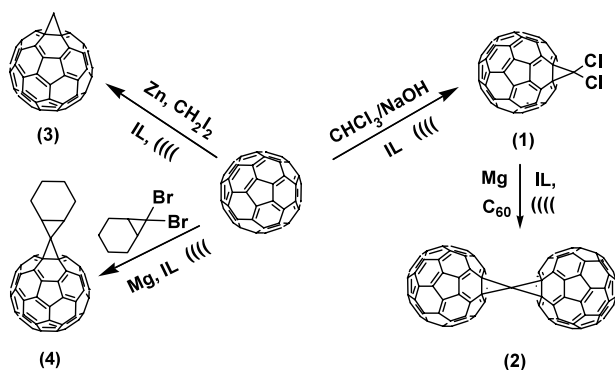
There has been a great deal of attention focused on the derivatization of fullerenes. Not only are these molecules of inherent interest in themselves, but they have potential applications in medicine, optics and material science.<sup>1–18</sup> Some of the most important routes to functionalized fullerenes are through fulleroid and methanofullerene precursors.<sup>1–18</sup> Parent methanofullerene can be formed in yields of ~21% by thermolysis or photolysis of fullerene pyrazoline,  $(\text{CH}_2\text{N}_2)\text{C}_{60}$ .<sup>4b,6b</sup> The pyrazoline can be produced in 44% yield from the reaction of fullerene and diazomethane.<sup>4b</sup>

Two isomers of the methanofullerenes have been reported, a [6,6] cyclopropane where the  $\text{CH}_2$  moiety adds across a [6,6] ‘short’ bond of the  $\text{C}_{60}$  and a [6,5] annulene, in which the  $\text{CH}_2$  group inserts into a ‘long’ [6,5] bond. Thermolysis leads to the latter compound,<sup>4b</sup> while photolysis gives a mixture of the [6,6] and [6,5] products.<sup>6b</sup> Concentration also seems to be important in product distribution in that photolysis of the pyrazoline at low concentrations favor the [6,6] isomer, while at high concentrations the [6,5] isomer prevailed.<sup>6c</sup> It is of interest to note that neither heat nor photolysis could bring about the interconversion of the [6,6] and [6,5] isomers.<sup>6c</sup> The thermolysis of a substituted methanofullerene with the parent  $\text{C}_{60}$  at high temperature, such as  $\text{C}_{60}\text{CBr}_2/\text{C}_{60}$  at 450°C and  $\text{C}_{60}\text{CHCO}_2\text{Et}/\text{C}_{60}$  at 550°C, resulted in the low yield (10%) formation

of a fullerene dimer,  $\text{C}_{121}$ , through a proposed carbene intermediate.<sup>15</sup> We have been interested in the use of ionic liquids as solvents in organic reactions.<sup>19</sup> While there have been a number of studies on hydrogenation, oxidation, epoxidation, hydroformylation, allylation, and cross-coupling reactions in ionic liquids<sup>19–31</sup> relatively little work has been done on the use of ionic liquids as reaction media for carbene mediated reactions.<sup>32</sup> In order to expand our knowledge of the use of ionic liquids in such reactions and to develop procedures for higher yield methanofullerene syntheses, we have begun to explore the use of ionic liquids as media for fullerene carbene reactions. Herein, we describe our initial results concerning this study.

Scheme 1 summarizes the carbene/fullerene reactions leading to the syntheses of [6,6] $\text{C}_{60}\text{CCl}_2$  (**1**), [6,6]-[6,6] $\text{C}_{121}$  (**2**), [6,6] $\text{C}_{60}\text{CH}_2$  (**3**) and [6,6] $\text{C}_{60}\text{C}_7\text{H}_{10}$  (**4**). Except for compound **1**, the carbene was generated, by the standard reaction of a dihalide with either Mg or Zn, in the presence of fullerene.<sup>33</sup> In the case of **1**, carbene generation was accomplished by the reaction of  $\text{CHCl}_3$  with base. In all cases, ultrasonic irradiation and continuous stirring was used to facilitate distribution of substrates in the multiphase reaction media. Duplicate reactions were run in two ionic liquid solvents, 1-methyl-3-octylimidazolium tetrafluoroborate, [omim][BF<sub>4</sub>] and 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF<sub>6</sub>]. The results, listed in Table 1, indicate no substantial advantage of one ionic liquid over the other.

\* Corresponding authors.



Scheme 1.

However, Table 1 clearly illustrates the advantages of the combined use of ionic liquid solvents and ultrasonic irradiation. The yields of the methanofullerenes ranged from a low of 53% for **2** in [omim][BF<sub>4</sub>] to a high of 79% for **3** in [bmim][PF<sub>6</sub>]; even the lowest yield represents a significant improvement over those reported in the literature.<sup>15a</sup> All compounds were characterized by FAB-MS and <sup>13</sup>C NMR spectroscopy. Compound **2** was further characterized by <sup>1</sup>H NMR, IR and UV/vis spectroscopy. The <sup>13</sup>C NMR spectrum of **1** agrees with that reported by Nogami and co-workers,<sup>3</sup> except that the single resonance at  $\delta$  145.22 ppm reported by these workers could be resolved into two peaks at  $\delta$  145.08 and 145.01 ppm. Both the <sup>13</sup>C NMR and the mass spectra of **3** agree with the literature values for methanofullerene reported by Smith and co-workers.<sup>6e</sup>

The <sup>13</sup>C NMR spectrum of **2** consists of 14 resonances in the  $\delta$  140.24–147.98 ppm region with an additional peak at 67.86 ppm. There are three possible isomers for C<sub>121</sub>, [6,6]–[6,6] (**A**), [6,6]–[6,5] (**B**) and [6,5]–[6,5] (**C**) (see Fig. 1). The <sup>13</sup>C NMR spectra of isomers **A**, **B** and **C** should consist of 16, 62 and 60 resonances, respectively, in the *sp*<sup>2</sup> region ( $\delta$  125–150 ppm).<sup>15c,d</sup> The 14 peak pattern found for **2** clearly establishes its identity as that of isomer **A**. A comparison of the experimental <sup>13</sup>C NMR spectrum with the 16-peak pattern found by Dragoe and co-workers<sup>15a</sup> shows that the two most intense peaks in **2**, at  $\delta$  145.41 and 142.55 ppm, were resolved into two resonances each by these workers. Ab initio molecular orbital calculations by Shimotani, Dragoe and Kitazawa showed that, while isomer **C** had the highest energy, isomers **A** and **B** had about the same energy, but the  $\Delta G_f^\circ$  for **B** was slightly lower than that of **A** due mainly to the contributions of  $\Delta H_{\text{vib}}(T)$  and  $S_{\text{vib}}(T)$  terms. Such terms would be significant at the reaction temperatures of 450–550°C used in their syn-

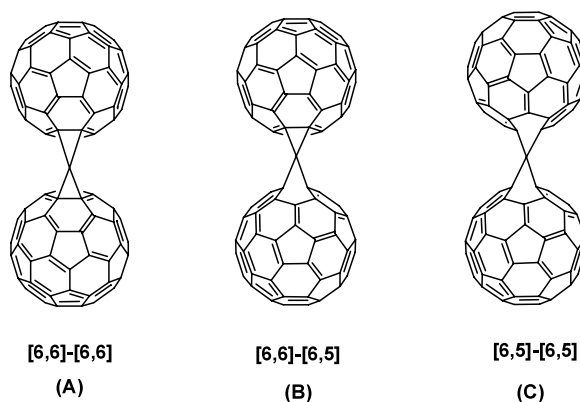


Figure 1.

theses.<sup>15a,c</sup> In our work compound **2** was synthesized at 25°C, hence the vibrational terms would not be as important. Therefore, it is not surprising that we obtained exclusively **A**, while Dragoe obtained a mixture of **A** and **B**.<sup>15a,c</sup> It should be pointed out that there is no universal agreement as to the relative energies of the C<sub>121</sub> isomers. On the basis of tight-binding molecular-dynamics simulation calculations, Yu, Zhang and Lee concluded that isomer **C** would be the more stable one.<sup>18</sup> However, in all calculations the energy differences are small and must be viewed with some caution. Be that as it may, in our synthesis, no evidence was found for the existence of either **B** or **C**, or for any higher carbon content species, such as C<sub>122</sub>.

The structure of compound **4**, shown in Scheme 1, shows a [6,6] bonding of the C<sub>60</sub> unit to the cyclopropanyl carbon of bicyclo(4,1,0)heptane, forcing the cyclohexane ring to adopt a boat conformation and imparting an overall C<sub>s</sub> symmetry to the compound. All spectroscopic analyses confirm this structure. The <sup>1</sup>H NMR spectra of **4** show resonances for the CH<sub>2</sub> and CH protons at  $\delta$  1.15–2.05 and 2.00–2.10 ppm, respectively. The <sup>13</sup>C NMR spectra gives the expected 14 peak pattern between  $\delta$  137.18–148.83 ppm, and a typical *sp*<sup>3</sup>-C<sub>(6,6-bridge)</sub> peak at 77.21 ppm, in addition to the bicyclo(4,1,0)heptane resonances. The UV/vis spectra of **4** shows an absorption at 428 nm which is diagnostic for [6,6] coupling of the fulleroid.<sup>6e</sup> The FAB-MS spectra of **4** shows molecular ion peaks at *m/z* = 814.6 which further confirms the assigned structure.

Although the detailed mechanism for the fullerene carbene reactions in an ionic liquid has yet to be determined, the high yields and the exclusive [6,6]-cycloaddition, suggests that ionic liquid solvents

Table 1. Methanofullerene yields in ionic liquids

Ionic liquid	CHCl <sub>3</sub> /C <sub>60</sub> /NaOH	C <sub>60</sub> (CCl <sub>2</sub> )/C <sub>60</sub> /Mg	C <sub>7</sub> H <sub>10</sub> Br <sub>2</sub> /C <sub>60</sub> /Mg	CH <sub>2</sub> I <sub>2</sub> /C <sub>60</sub> /Zn
[bmim][PF <sub>6</sub> ]	67	58	65	79
[omim][BF <sub>4</sub> ]	70	53	59	73
Time (days)	3	4	3	2.5

play a special role in the formation of specific intermediates that lead to single products. Mechanistic studies of these reactions are currently underway in our laboratory.

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33. (a) *Synthesis and characterization of 4*. A 20 mL sample of the ionic liquid [bmim][PF<sub>6</sub>] was placed in a 50 mL two-necked round-bottomed flask, equipped with a magnetic stirring bar, and the vessel was degassed by three vacuum/argon-filling cycles. Then 7,7-dibromobicyclo(4,1,0)heptane (53 mg, 0.209 mmol, in 4 mL dry THF), C<sub>60</sub> (241 mg, 0.334 mmol) and magnesium powder (10 mg, 0.411 mmol) were added to the flask under argon. After addition, the mixture was irradiated by ultrasound (ultrasonic frequency 50 KHz) for 3 days with continuous stirring under an argon atmosphere at 25°C. At the end of this time, methanol (5 mL) was added to the vessel to trap the reaction. The resulting mixture was poured into 300 mL CS<sub>2</sub> to extract the products and any unreacted fullerene. After drying the CS<sub>2</sub> phase under reduced pressure, the crude mixture was separated by flash chromatography (SiO<sub>2</sub> column, eluted with toluene/hexane (v/v=1/10) to recover 78 mg of unreacted C<sub>60</sub>, followed by preparative HPLC (4.5 mm×25 cm, cosmosil column, elution with toluene/hexane 1:1 at 10 mL/min, 330 nm detection) for further separation to give **4** as a dark brown powder, (110 mg, 65% yield). When the reaction was repeated in [omim][BF<sub>4</sub>] ionic liquid, the yield of **4** was 59%. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a BRUKER-400 instrument at 400 and 100.62 MHz respectively, in CS<sub>2</sub>/C<sub>6</sub>D<sub>6</sub> with Cr(acac)<sub>3</sub> as a relaxation agent (15 mM). 60° pulse and more than 50000 scans were used in collecting the <sup>13</sup>C NMR data. <sup>1</sup>H NMR: δ (ppm), 1.15–1.30 (m, 2H), 1.35–1.45 (m, 2H), 1.75–1.90 (m, 2H), 1.95–2.05 (m, 2H), 2.00–2.10 (m, 2H); <sup>13</sup>C NMR (δ, ppm): 148.83 (4C), 145.72 (4C), 144.70 (6C), 144.22 (4C), 144.13 (4C), 143.78 (4C), 143.21 (4C), 142.63 (6C), 142.45 (2C), 142.22 (4C), 142.08 (4C), 141.78 (4C), 140.77 (4C), 137.18 (4C), 77.21 (2C<sub>C<sub>60</sub>-sp<sup>3</sup></sub>), 35.78 (1C), 26.90 (2C), 23.81 (2C), 23.18 (2C), two signals are missing. UV/vis spectrum in CS<sub>2</sub>/benzene (1.80×10<sup>-4</sup> M), λ<sub>max</sub> at 428 and 650 nm. FAB-MS: *m/z*=719.5, 814.6 (M<sup>+</sup>). IR (cm<sup>-1</sup>, KBr pellet): 472 (vs, br), 616 (m, s), 792 (s, m), 960 (m, s), 1007 (m, s), 1087 (s, br), 1123 (vs, s), 1389 (m, s), 1641 (m, br), 3049 (m, m).
- (b) *Synthesis and characterization of 1*. In a process similar to that used in the preparation of **4**, CHCl<sub>3</sub> (0.01 mL, 0.125 mmol in 2 mL dry THF), NaOH powder (20 mg, 0.426 mmol), and C<sub>60</sub> (220 mg, 0.305 mmol), were added to the particular ionic liquid solvent and irradiated by ultrasound for 3 days to give **1** as a dark brown solid in 67% ([bmim][PF<sub>6</sub>]) or 70% ([omim][BF<sub>4</sub>]) yields. <sup>13</sup>C NMR (δ, ppm): 145.08 (4C), 145.01 (4C), 144.69 (6C), 144.52 (4C), 144.47 (4C), 144.06 (2C), 143.77 (4C), 143.60 (4C), 143.31 (4C), 143.09 (4C), 142.61 (2C), 142.33 (4C), 141.89 (4C), 141.09 (4C), 138.68 (4C), 79.72 (2C<sub>C<sub>60</sub>-sp<sup>3</sup></sub>), 63.10 (1C), one signal is missing. FAB-MS: *m/z*=720.1, 803.2 (M<sup>+</sup>).
- (c) *Synthesis and characterization of 2*. In a process similar to that used in the preparation of **4**, compound **1** (100 mg, 0.124 mmol), Mg powder (8 mg, 0.329 mmol), and C<sub>60</sub> (230 mg, 0.319 mmol), were added to the particular ionic liquid solvent and irradiated with ultrasound for 4 days to give **2** as a dark brown powder in 58% ([bmim][PF<sub>6</sub>]) or 53% ([omim][BF<sub>4</sub>]) yield. <sup>13</sup>C NMR (δ, ppm): 147.98 (4C), 147.67 (4C), 146.77 (4C), 146.46 (4C), 146.18 (4C), 145.41 (6C), 144.66 (4C), 143.10 (2C), 142.55 (6C), 142.41 (4C), 142.34 (4C), 141.39 (4C), 140.90 (4C), 140.24 (4C), 67.86 (2C<sub>C<sub>60</sub>-sp<sup>3</sup></sub>), three signals are missing. FAB-MS: *m/z*=720.2, 732.3, 1453.1 (M<sup>+</sup>).
- (d) *Synthesis and characterization of 3*. In a process similar to that used in the synthesis of **4**, CH<sub>2</sub>I<sub>2</sub> (0.01 mL, 0.123 mmol in 2 mL dry THF), Zn powder (24 mg, 0.368 mmol), and C<sub>60</sub> (225 mg, 0.312 mmol) were added to the particular ionic liquid solvent and irradiated for 2.5 days to give **3** as a dark brown solid in 79% ([bmim][PF<sub>6</sub>]) or 73% ([omim][BF<sub>4</sub>]) yield. <sup>1</sup>H NMR: δ 3.95 ppm (s, 2H). <sup>13</sup>C NMR (δ, ppm): 149.84 (4C), 145.62 (4C), 145.07 (4C), 144.87 (4C), 144.71 (6C), 143.95 (4C), 143.68 (4C), 142.72 (2C), 142.64 (4C), 142.52 (6C), 142.32 (4C), 142.06 (4C), 140.64 (4C), 137.20 (4C), 71.78 (2C<sub>C<sub>60</sub>-sp<sup>3</sup></sub>), 30.60 (1C), two signals are missing. FAB-MS: *m/z*=720.0, 734.5 (M<sup>+</sup>).