## Synthesis and Functionalization of [60]Fullerene-Fused Imidazolines

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## **Received February 3, 2013**



The silver carbonate promoted reaction of [60]fullerene with (Z)-N-arylbenzamidines afforded the unprecedented C<sub>60</sub>-fused imidazoline derivatives in high yields. Substrates with both electron-donating and -withdrawing groups on aromatic rings could be employed. In addition, the electrochemistry and further selective functionalization of the obtained C<sub>60</sub>-fused imidazolines were investigated.

Owing to potential applications in materials, medical chemistry, and nanotechnology,<sup>1</sup> various methodologies have been explored to functionalize fullerenes, and a large number of fullerene products have been prepared over the past two decades.<sup>2</sup> Transition-metal-mediated reactions of [60]fullerene (C<sub>60</sub>) have attracted increasing attention.

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Although various reactions of  $C_{60}$  mediated by Mn(OAc)<sub>3</sub><sup>3</sup> and  $Fe(ClO_4)_3^4$  have been reported, the utilization of other transition metal salts including silver salts in the radical reactions of fullerenes is underdeveloped.<sup>5</sup> In our previous work, we found that Fe(ClO<sub>4</sub>)<sub>3</sub> could efficiently promote the radical reactions of  $C_{60}$  and afforded  $C_{60}$ -fused oxazolines,<sup>6</sup> dioxolanes,<sup>7</sup> and dioxaborolanes,<sup>8</sup> where an oxygen and a nitrogen atom or two oxygen atoms are connected to the C<sub>60</sub> cage. Herein, we disclose that silver carbonate can promote the radical reaction of  $C_{60}$  with

LETTERS XXXX Vol. XX, No. XX 000-000

ORGANIC

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(Z)-N-arylbenzamidines to provide  $C_{60}$ -fused imidazolines, in which two nitrogen atoms are attached to the fullerene moiety. In addition, further selective functionalization of the obtained  $C_{60}$ -fused imidazolines by a Grignard reagent and 3-chloroperbenzoic acid (*m*CPBA) is demonstrated.

At the outset of our studies, the  $Ag_2CO_3$ -promoted reaction of  $C_{60}$  with (Z)-N-phenylbenzamidines (1a) was chosen to screen the reaction conditions. The reaction of  $C_{60}$  with 1a and  $Ag_2CO_3$  in a molar ratio of 1:1:1 at 110 °C for 10 h gave 2a in 10% yield (Table 1, entry 1). Increasing the amount of  $Ag_2CO_3$  to 2 equiv provided 2a in 24% yield (Table 1, entry 2). An additional increase of 1a to 2 equiv resulted in a 42% yield (Table 1, entry 3). When the molar ratio was enhanced to 1:3:2, the product yield could be further improved to 56% (Table 1, entry 4). It was found that an inert atmosphere was important, as the reaction in open air or an oxygen atmosphere significantly decreased the product yield (Table 1, entries 5 and 6).





<sup>*a*</sup> All reactions were carried out under a nitrogen atmosphere unless otherwise indicated. <sup>*b*</sup> Molar ratio refers to  $C_{60}/1a$ /oxidant. <sup>*c*</sup> Isolated yield; the values in parentheses were based on consumed  $C_{60}$ . <sup>*d*</sup> The reaction was carried out in open air, and 1a was recovered in 96% yield when  $C_{60}$  was omitted from the system under the same conditions. <sup>*e*</sup> The reaction was carried out under an oxygen atmosphere, and 1a was recovered in 98% yield when  $C_{60}$  was omitted from the system under the same conditions.

Increasing the amount of either **1a** or Ag<sub>2</sub>CO<sub>3</sub> further was not beneficial to achieve a higher yield, yet more C<sub>60</sub> was consumed (Table 1, entries 7 and 8). When the temperature was lowered to 90 °C, **2a** was obtained in only 18% yield (Table 1, entry 9). When the temperature was increased to 130 °C, the yield dropped slightly to 54% accompanied by more byproducts (Table 1, entry 10). Shortening or prolonging the reaction time led to a lower yield (Table 1, entries 11 and 12). The efficiency of other silver salts was also examined. Ag<sub>2</sub>O and AgOAc could promote the reaction, but both of them gave an inferior yield compared to Ag<sub>2</sub>CO<sub>3</sub> (Table 1, entries 13 and 14). Disappointingly, when Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O, Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, or FeCl<sub>3</sub>·6H<sub>2</sub>O was employed as the oxidant, **2a** was isolated in much lower yields (Table 1, entries 15–17). Therefore, the molar ratio of 1:3:2 for the regents C<sub>60</sub>, **1a**, and Ag<sub>2</sub>CO<sub>3</sub> and the temperature of 110 °C in chlorobenzene under a nitrogen atmosphere were chosen as the optimized reaction conditions (Table 1, entry 4).

With the optimized conditions in hand, we started to investigate the scope of the reaction. We were pleased to find that (Z)-N-arylbenzamidines (1a-g) with both electrondonating and -withdrawing groups could be employed and furnished the desired [60]fullereoimidazolines 2a-gin 42–59% isolated yields, higher than those of most monoadducts. (Z)-N-Arylbenzamidines bearing a methyl, chlorine, or methoxy group in both aryl rings could undergo the Ag<sub>2</sub>CO<sub>3</sub>-promoted cycloaddition reaction to C<sub>60</sub>. Intriguingly, ortho-substituted substrates proceeded well and even provided higher product yields (Table 2, entries 3 and 5). In addition, the chlorine group in products **2c**, **2d**, and **2g** (Table 2, entries 3, 4, and 7) may be used as a handle for coupling reactions.

The structures of  $C_{60}$ -fused imidazolines 2a-g were fully established by their MALDI-TOF MS, <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, and UV-vis spectra. All products 2a-gexhibited correct molecular weights in their mass spectra. The <sup>13</sup>C NMR spectra of 2a-g except 2c clearly exhibited no more than 30 peaks in the range of 134–149 ppm for the  $sp^2$ -carbons of the fullerene cage and two peaks at 85-87and 93–94 ppm for the two sp<sup>3</sup>-carbons of the fullerene skeleton, consistent with the  $C_s$  symmetry of their molecular structures. However, because of the steric hindrance of Cl at the ortho position, the <sup>13</sup>C NMR spectrum of 2c exhibited 45 peaks for the sp<sup>2</sup>-carbons of the fullerene skeleton, along with two peaks for the two sp<sup>3</sup>-carbons of  $C_{60}$  cage, agreeing with its  $C_1$  symmetry. The chemical shifts for the two  $C_{60}$  sp<sup>3</sup>-carbons of 2a-g are close to those of fullerene derivatives with the nitrogen atom attached to the  $C_{60}$  skeleton.<sup>6,9</sup> The typical chemical shifts at 163–164 ppm in the <sup>13</sup>C NMR spectra indicated the presence of the amidine moiety. The UV-vis spectrum of all products showed a peak at 427-428 nm, which is the characteristic peak for 1,2-adducts of C<sub>60</sub>.

Although the exact pathway leading to 2a-g remains to be clarified, a plausible mechanism is outlined in Scheme 1. First, the reaction of *N*-arylbenzimidamide 1 with Ag<sub>2</sub>CO<sub>3</sub> generates 3, which undergoes homolytic cleavage of the nitrogen-silver bond to provide radical species 4. A similar Cu-catalyzed process was recently reported.<sup>10</sup>

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Ê	+ R + NH2 NH2	Ag <sub>2</sub> CO <sub>3</sub> PhCl, N <sub>2</sub> 110 °C		
entry	product	time (h)	yield of $2$ (%) <sup>b</sup>	recovered C <sub>60</sub>
1		10	56 (95)	41
2		12	49 (80)	39
3		10	59 (76)	22
4	2d	24	44 (71)	38
5		6	56 (74)	24
6	2f	18	47 (85)	45
7		24	42 (75)	44

**Table 2.** Reaction Conditions and Yields for the Reaction of  $C_{60}$  with 1a-g in the Presence of  $Ag_2CO_3^a$ 

<sup>*a*</sup> All reactions were carried out at 110 °C under a nitrogen atmosphere with a molar ratio of C<sub>60</sub>/1/Ag<sub>2</sub>CO<sub>3</sub> = 1:3:2. <sup>*b*</sup> Isolated yield; the values in parentheses were based on consumed C<sub>60</sub>.

The radical addition of 4 to  $C_{60}$  will give fullerenyl radical 5. Alternatively, the intermediate 5 may also be formed by the homolytic addition of 3 to  $C_{60}$ .<sup>6</sup> Intramolecular cyclization of 5 produces radical 6.

Although the addition of a carbon-centered radical to the N-terminus of the C=N bond is rare, the formed radical in **6** is stabilized by two nitrogen substituents and a phenyl group.<sup>11</sup> Oxidation of radical **6** by another  $Ag^+$  species with the loss of H<sup>+</sup> affords **2**. Therefore, 2 molar equiv of Ag(I) were required, and the molar ratio of

Scheme 1. Proposed Reaction Mechanism for the Formation of 2a-g



 $C_{60}/1a/Ag_2CO_3 = 1:3:2$  was used to achieve higher conversions and product yields. However, the concerted [3 + 2] annulation process of amidines to  $C_{60}$  via a nitrene intermediate cannot be excluded.<sup>10</sup>

Table 3 shows the half-wave reduction potentials of products  $2\mathbf{a}-\mathbf{g}$  together with C<sub>60</sub>. The first reduction potentials are generally shifted anodically by ca. 100 mV for most monoadducts of C<sub>60</sub>. However, the  $E^1$  of  $2\mathbf{a}-\mathbf{g}$  showed a smaller negative shift (30–50 mV) relative to that of C<sub>60</sub>, due to the two attached heteroatoms.<sup>9d,12</sup> Therefore, fullereoimidazolines  $2\mathbf{a}-\mathbf{g}$  may be utilized as low-lying LUMO acceptors in organic photovoltaic devices by choosing appropriate donor material.<sup>12</sup>

compd	$E^1$	$E^2$	$E^3$
C <sub>60</sub>	-1.077	-1.456	-1.911
2a	-1.117	-1.493	-2.013
2b	-1.119	-1.493	-2.013
2c	-1.114	-1.493	-2.016
2d	-1.111	-1.485	-1.997
<b>2e</b>	-1.114	-1.490	-2.010
2 <b>f</b>	-1.124	-1.504	-2.026
$2\mathbf{g}$	-1.116	-1.498	-2.018

<sup>*a*</sup> Potential in V versus a ferrocene/ferrocenium couple. Experiment conditions: 0.20 mM of  $2a-g/C_{60}$  and 0.1 M of *n*-Bu<sub>4</sub>NClO<sub>4</sub> in anhydrous *o*-dichlorobenzene; reference electrode: SCE; working electrode: Pt; auxiliary electrode: Pt wire; scanning rate: 50 mV s<sup>-1</sup>.

Further functionalization of the synthesized fullereoimidazolines was also attempted by using 2a as a representative compound. After 2a was treated with CH<sub>3</sub>MgBr in chlorobenzene at 0 °C for 5 min and subsequently quenched by NH<sub>4</sub>Cl, the regioselective product 7a with a

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Scheme 2. Further Functionalization of 2a





Figure 1. Partial NBO charge distribution of 2a.

1.2.3.4-configuration was isolated in 70% yield (Scheme 2). In the <sup>1</sup>H NMR spectrum of **7a**, two singlets for the methyl group and fullerenyl proton were located at 2.71 and 5.94 ppm besides those for the two phenyl groups. The <sup>13</sup>C NMR of 7a exhibited 53 peaks in the 152–129 ppm range for the sp<sup>2</sup>-carbons of the fullerene skeleton and four peaks at 87.46, 82.98, 59.58, and 57.39 ppm for the four  $sp^3$ -carbons of the C<sub>60</sub> cage. The amidino carbon showed little chemical shift compared to that of 2a, suggesting that it remained unchanged. The UV-vis spectrum of 7a exhibited the typical feature of fullerene products with a 1,2,3,4-configuration (see Figure S1 in the Supporting Information).<sup>13</sup> To better understand the regioselectivity for the Grignard addition reaction, the NBO charge distribution of 2a was calculated at the B3LYP/3-21G\* level. As shown in Figure 1, the fullerenyl carbon with a positive charge of +0.125 should be the site of attack by CH<sub>3</sub>MgBr.



Figure 2. Optimized structures and relative energies of 7a and its regioisomer 7a-1.

The protonation of the formed fullenenyl anion could afford **7a** or its regioisomer **7a-1**. The introduction of an unfavorable [5,6] double bond in isomeric **7a-1** would increase its formation energy.

Indeed, theoretical calculations at the B3LYP/3-21G\* level showed that **7a** was more stable than **7a-1** by 28.6 kJ·mol<sup>-1</sup> (Figure 2). It should be pointed out that although the amidino carbon atom had the largest positive charge of +0.628, the Grignard reagent did not attack the C=N bond. The addition mode of CH<sub>3</sub>MgBr to C<sub>60</sub>-fused imidazolines here is different from that to C<sub>60</sub>-fused lactones, which underwent either a reductive ring opening<sup>14</sup> or addition to the C=O bond of the lactone moiety.<sup>15</sup>

Furthermore, the nitroxide **8a** could be prepared in 44% yield after treatment of **2a** with *m*CPBA at 60 °C for 3 h. Product **8a** was also fully characterized. The addition of the oxygen atom to **2a** lowered the symmetry from  $C_s$  to  $C_1$ , and thus the <sup>13</sup>C NMR of **8a** exhibited 52 peaks for the sp<sup>2</sup>-carbons of the fullerene cage in the range of 149–135 ppm. The  $\delta_C$  of the amidino carbon that was located at 162.96 ppm indicated that the oxygenation did not occur at the C=N bond. This result was supported by the calculated larger negative density at the nitrogen atom bearing the phenyl group (-0.765) compared to the imino nitrogen atom (-0.476) (Figure 1).

In summary,  $Ag_2CO_3$  has been successfully applied to the radical reaction of  $C_{60}$  with (*Z*)-*N*-arylbenzamidines affording unprecedented  $C_{60}$ -fused imidazolines. [60]-Fulleroimidazolines can be further functionalized to give regioisomeric products with a 1,2,3,4-configuration or nitroxide products, which would be difficult to synthesize by existing methods.

Acknowledgment. We are grateful for financial support from NSFC (21132007) and Specialized Research Fund for the Doctoral Program of Higher Education (20123402130011).

**Supporting Information Available.** Experimental procedures, spectral data, spectra, and computation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.