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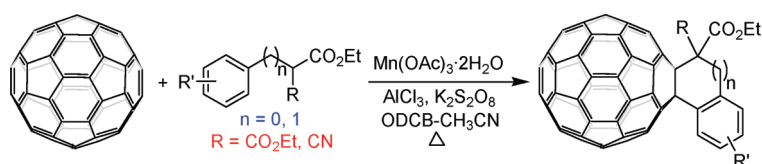
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## ABSTRACT



The addition of aluminum chloride to the manganese acetate-mediated radical reaction of [60]fullerene with 2-arylmalonates, 2-benzylmalonates, and 2-arylcianoacetates can switch the reaction pathway and affords a variety of structurally novel and scarce [60]fullerene-fused tetrahydronaphthalene and indane derivatives. These products are formed probably through radical addition, followed by Friedel–Crafts-type annulation.

Due to immense potential applications of fullerenes in medicinal chemistry, materials, and nanotechnology,<sup>1</sup> a number of chemical reactions to functionalize fullerenes have been developed, and numerous fullerene products with widely structural diversities have been prepared over the past 20 years.<sup>2</sup> Radical reactions are important tools in organic synthetic chemistry. We have recently investigated radical reactions of [60]fullerene (C<sub>60</sub>) mediated by metal

salts such as Mn(OAc)<sub>3</sub>,<sup>3,4</sup> Cu(OAc)<sub>2</sub>,<sup>4c</sup> Pb(OAc)<sub>4</sub>,<sup>4h</sup> and Fe(ClO<sub>4</sub>)<sub>3</sub>.<sup>5</sup> Among them the Mn(OAc)<sub>3</sub>-mediated reaction of C<sub>60</sub> with substituted malonate esters in refluxing chlorobenzene or toluene generated 1,4-adducts and 1,16-adducts of C<sub>60</sub>.<sup>4a,b,5c</sup> We also revealed that replacing Mn(OAc)<sub>3</sub> with Fe(ClO<sub>4</sub>)<sub>3</sub> altered the pathway for the reaction of C<sub>60</sub> with substituted malonate esters including diethyl 2-benzylmalonate and diethyl 2-phenylmalonate

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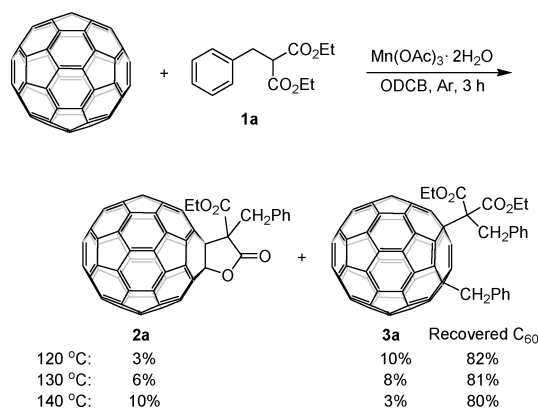
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and afforded disubstituted C<sub>60</sub>-fused lactones.<sup>5c</sup> Herein, we disclose that another type of products, i.e., C<sub>60</sub>-fused tetrahydronaphthalene and indane derivatives, can be obtained from the reaction of C<sub>60</sub> with malonates and cyanoacetates substituted with an aryl or a benzyl group mediated by Mn(OAc)<sub>3</sub> in combination with AlCl<sub>3</sub>, via a radical addition and aryl annulation sequence.

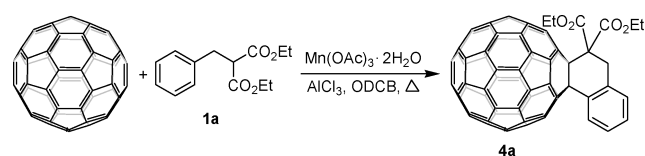
At the onset, the reaction of C<sub>60</sub> with diethyl 2-benzylmalonate (**1a**) was performed in the presence of only Mn(OAc)<sub>3</sub> in a molar ratio of 1:5:2 in *o*-dichlorobenzene (ODCB) and under an argon atmosphere (Scheme 1). Disubstituted C<sub>60</sub>-fused-lactone **2a** and benzyl-substituted unsymmetrical 1,4-adduct **3a** could be isolated as major products albeit in low yields, along with other unidentified minor byproducts. The product distribution of **2a** and **3a** was highly dependent on the reaction temperature. 1,4-Adduct **3a** was the dominant product when the reaction was conducted at 120 °C, whereas the major product was lactone **2a** at 140 °C. In comparison with the Mn(OAc)<sub>3</sub>-mediated reaction of C<sub>60</sub> with diethyl 2-methylmalonate, the reaction with **1a** gave an unsymmetrical 1,4-adduct **3a** instead of symmetrical 1,4- and/or 1,16-adducts with a formula of C<sub>60</sub>(CCH<sub>2</sub>Ph(CO<sub>2</sub>Et))<sub>2</sub> besides a similar C<sub>60</sub>-fused lactone **2a**. Reaction of **1a** with Mn(OAc)<sub>3</sub> gave a  $\cdot\text{CCH}_2\text{Ph}(\text{CO}_2\text{Et})_2$  radical, and subsequent addition to C<sub>60</sub> afforded a  $\cdot\text{C}_{60}(\text{CCH}_2\text{Ph}(\text{CO}_2\text{Et})_2)$  radical. Following similar sequential processes as promoted by Fe(ClO<sub>4</sub>)<sub>3</sub> provided lactone **2a**.<sup>5c</sup> Coupling of the  $\cdot\text{C}_{60}(\text{CCH}_2\text{Ph}(\text{CO}_2\text{Et})_2)$  radical with the  $\cdot\text{CH}_2\text{Ph}$  radical generated in situ from the  $\cdot\text{CCH}_2\text{Ph}(\text{CO}_2\text{Et})_2$  species would give benzyl-substituted unsymmetrical 1,4-adduct **3a**.

**Scheme 1.** Mn(OAc)<sub>3</sub>-Mediated Reaction of C<sub>60</sub> with **1a** Affording C<sub>60</sub>-Fused Lactone **2a** and 1,4-Adduct **3a**



The poor results shown in Scheme 1 prompted us to search for better conditions in order to improve the

**Table 1.** Optimization of Reaction Conditions for the Mn(OAc)<sub>3</sub>-Mediated Reaction of C<sub>60</sub> with **1a**



entry	molar ratio <sup>a</sup>	oxidant	reaction temp (°C) <sup>b</sup>	reaction time (h)	Yield of <b>4a</b> (%) <sup>c</sup>
1	1:5:2:15	—	120	3	11 (42)
2	1:5:2:15	—	130	3	15 (48)
3	1:5:2:15	—	140	3	12 (60)
4	1:5:2:15	Cu(OAc) <sub>2</sub> <sup>d</sup>	130	3	19 (90)
5	1:5:2:15	Oxone <sup>d</sup>	130	3	24 (65)
<b>6</b>	<b>1:5:2:15</b>	<b>K<sub>2</sub>S<sub>2</sub>O<sub>8</sub><sup>d</sup></b>	<b>130</b>	<b>3</b>	<b>28 (85)</b>
7	1:5:2:15	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> <sup>d</sup>	130	2	27 (68)
8	1:5:2:15	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> <sup>d</sup>	130	4	24 (60)
9	1:5:1:15	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> <sup>d</sup>	130	3	13 (68)
10	1:5:3:15	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> <sup>d</sup>	130	3	30 (75) <sup>e</sup>

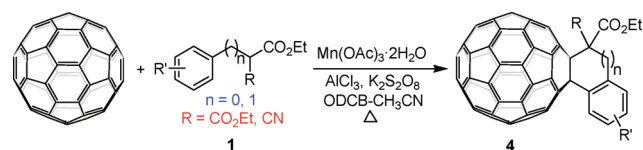
<sup>a</sup> Molar ratio refers to C<sub>60</sub>/**1a**/Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O/AlCl<sub>3</sub>. <sup>b</sup> Oil bath temperature. <sup>c</sup> Isolated yield; that in parentheses was based on consumed C<sub>60</sub>. <sup>d</sup> 2 equiv of oxidant were employed. <sup>e</sup> Recovered C<sub>60</sub> was impure.

product yield and selectivity, and even to obtain a new product by changing the reaction pathway. Olah and co-workers described the formation of multihydroarylated fullerenes by the AlCl<sub>3</sub>-mediated Friedel–Crafts-type reaction of C<sub>60</sub> with benzene or toluene.<sup>6a,b</sup> Later Nakamura, Kokubo, and their co-workers systematically investigated the Friedel–Crafts-type reaction that selectively produced a series of mono-, di-, and trihydroarylation of [60]fullerene.<sup>6c–e</sup> Kokubo's group also reported the AlCl<sub>3</sub>-catalyzed acetylation of monohydroarylated [60]-fullerenes with acetyl chloride.<sup>6c</sup> Recently we disclosed that the reaction of a C<sub>60</sub>-fused 1,3-dioxolane with chlorobenzene and 1,2-dichlorobenzene in the presence of AlCl<sub>3</sub> afforded the rare arylated 1,4-fullerenols.<sup>5b</sup> Intriguingly, we discovered that the addition of AlCl<sub>3</sub> (15 equiv) to the Mn(OAc)<sub>3</sub>-promoted reaction of C<sub>60</sub> with diethyl 2-benzylmalonate switched the reaction pathway and afforded the aryl-annulated product **4a**.

We found that AlCl<sub>3</sub> played a crucial role on the selectivity and product yield. For example, if 5 equiv of AlCl<sub>3</sub> were employed lactone **2a** was also formed besides **4a**. To achieve the selective formation of **4a**, 15 equiv of AlCl<sub>3</sub> were necessary. Product **4a** was obtained in 11% yield when the reaction of C<sub>60</sub> with **1a** and Mn(OAc)<sub>3</sub> in a molar ratio of 1:5:2 was allowed to proceed in an oil bath preset at 120 °C for 3 h (Table 1, entry 1). The presence or absence of an inert atmosphere had a negligible effect on the product yield. Consequently, the reaction was then performed in open air. The yield was improved to 15% at 130 °C under otherwise the same conditions (Table 1, entry 2). However, the yield dropped to 12% if the reaction temperature was further increased to 140 °C (Table 1, entry 3 vs 2). An oxidant was then added to examine if it had a beneficial

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**Table 2.** Reaction Conditions and Yields for the Reaction of C<sub>60</sub> with 2-Benzylmalonates/2-Arylmalonate/2-Arylcynoacetates in the Presence of Mn(OAc)<sub>3</sub> and AlCl<sub>3</sub><sup>a</sup>



entry	product	reaction temp (°C) <sup>b</sup>	reaction time (h)	yield of 4 (%) <sup>c</sup>
1		130	3	28 (78)
2		130	3	24 (71)
3		130	3	18 (60)
4		140	4	13 (59)
5		140	4	14 (64) <sup>d</sup>
6		140	4	20 (61) <sup>d</sup>

<sup>a</sup> Unless otherwise indicated, all reactions were performed with a molar ratio of C<sub>60</sub>/1/Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/AlCl<sub>3</sub> = 1:5:2:2:15.

<sup>b</sup> Oil bath temperature. <sup>c</sup> Isolated yield; that in parentheses was based on consumed C<sub>60</sub>. <sup>d</sup> The reaction was carried out in the absence of acetonitrile.

effect on the product yield at the reaction temperature of 130 °C. Both Cu(OAc)<sub>2</sub> and Oxone increased the yield to 19% and 24%, respectively (Table1, entries 4 and 5). To our delight, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> could further enhance the yield to 28% (85% based on consumed C<sub>60</sub>) (Table1, entry 6). Prolonging or shortening the reaction time gave inferior results (Table1, entries 7 and 8). Decreasing the amount of Mn(OAc)<sub>3</sub> from 2 to 1 equiv significantly reduced the yield to 13% (Table1, entry 9). Increasing the quantity of Mn(OAc)<sub>3</sub> to 3 equiv only afforded a comparable product yield, yet more byproducts were formed and the recovered C<sub>60</sub> was contaminated by impurities (Table1, entry 10).

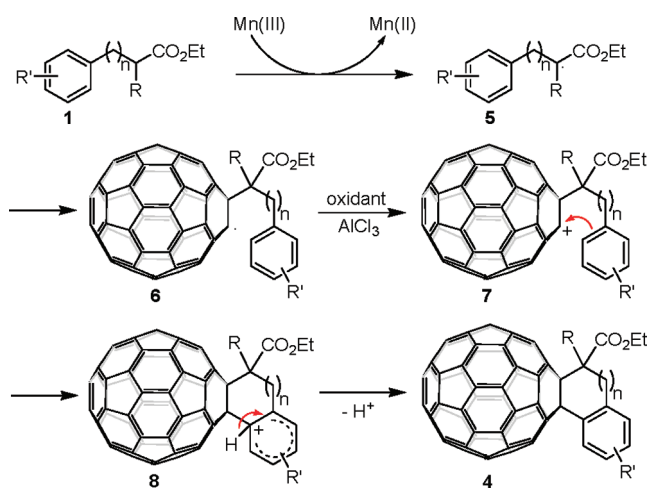
It should be noted that other Lewis acids such as BF<sub>3</sub> were also examined; both selectivity and yield were poorer than those for AlCl<sub>3</sub> under the same conditions. Product **2a** could not be obtained in the presence of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> without the aid of

AlCl<sub>3</sub>. Therefore, AlCl<sub>3</sub> was essential for the selective formation of **2a**. Acetonitrile was added as the cosolvent to increase the solubility of the employed inorganic oxidant, and it gave better results than THF, DMF, DMSO, and CH<sub>3</sub>CH<sub>2</sub>OH. Therefore, the molar ratio of 1:5:2:2:15 for the reagents C<sub>60</sub>, **1a**, Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and AlCl<sub>3</sub> and the reaction temperature of 130 °C in ODCB/CH<sub>3</sub>CN were chosen as the optimized reaction conditions.

With the optimized conditions in hand, the scope of the present Mn(OAc)<sub>3</sub>/AlCl<sub>3</sub>-mediated reaction was extended to other 2-benzylmalonates (**1b–1d**), 2-arylmalonates (**1e**), and 2-arylcynoacetates (**1f** and **1g**). The reaction conditions and yields are summarized in Table 2. The Mn(OAc)<sub>3</sub>/AlCl<sub>3</sub>-mediated reaction of C<sub>60</sub> with 2-benzylmalonates (**1b–1d**) bearing a substituent at the *para*, *meta*, or *ortho* position of the phenyl ring could successfully produce C<sub>60</sub>-fused tetrahydronaphthalenes **4b–4d** in synthetically acceptable yields (Table 2, entries 1–3). When 2-arylmalonate **1e** and 2-arylcynoacetates (**1f** and **1g**) were used to replace 2-benzylmalonates, C<sub>60</sub>-fused indanes **4e–4g** were obtained. Compared with **1a–1d**, **1e–1g** displayed a lower reactivity and required a higher temperature (140 °C) and longer reaction time (4 h), yet generally gave lower yields probably because the in situ formed radical was delocalized to the phenyl ring and, thus, retarded the radical addition to C<sub>60</sub>. The isolated yields of **4a–4g** were relatively low because we stopped the reactions at an early stage to avoid the formation of bisadducts and byproducts. In this way, we could recover more C<sub>60</sub> and achieve higher yields based on consumed C<sub>60</sub>.

Lactone **2a** is a known product, and its identity was confirmed by comparison of its spectral data with the reported ones.<sup>5c</sup> The structures of 1,4-adduct **3a**, C<sub>60</sub>-fused tetrahydronaphthalenes **4a–4d**, and C<sub>60</sub>-fused indanes **4e–4g** were fully established by their HRMS, <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, and UV–vis spectra. All products exhibited correct molecular weights in their high-resolution mass spectra and the expected chemical shifts as well as the splitting patterns for all protons in their <sup>1</sup>H NMR spectra. The <sup>13</sup>C NMR spectrum of **3a** displayed 51 peaks with 6 overlapping ones in the 136–157 ppm range for the 58 sp<sup>2</sup>-carbons of the C<sub>60</sub> moiety, two peaks for the two sp<sup>3</sup>-carbons of the C<sub>60</sub> skeleton at about 60 and 62 ppm, and the signals for the CH<sub>2</sub>Ph and C(CH<sub>2</sub>Ph)(CO<sub>2</sub>Et)<sub>2</sub> groups, fully consistent with its molecular structure with C<sub>1</sub> symmetry. The UV–vis spectrum of **3a** showed a broad peak at 445 nm, which is a characteristic absorption band for a 1,4-adduct of C<sub>60</sub>.<sup>4</sup> There were at least 38 lines including some overlapped ones in the range of 132–160 ppm for the 58 sp<sup>2</sup>-carbons of the C<sub>60</sub> cage in the <sup>13</sup>C NMR spectra of **4a–4g** except for that of **4e**, agreeing well with their C<sub>1</sub> molecular symmetry due to the nonplanar geometry of the annulated six-membered ring of **4a–4d** or nonequivalent ester and cyano substituents of **4f** and **4g**. In contrast, 26 peaks with three overlapping and two half-intensity ones in the 134–154 pm range for the 58 sp<sup>2</sup>-carbons of the C<sub>60</sub> skeleton and 2 peaks at ca. 74 and 75 ppm for the two sp<sup>3</sup>-carbons of the C<sub>60</sub> cage were observed for **4e**, consistent with its C<sub>s</sub> molecular symmetry.

**Scheme 2.** Proposed Reaction Mechanism for the Formation of **4a–g**



The reaction of  $\text{C}_{60}$  with 2-benzylmalonate **1a** in the presence of  $\text{Mn(OAc)}_3$  gave  $\text{C}_{60}$ -fused-lactone **2a** and unsymmetrical 1,4-adduct **3a**. However, the addition of  $\text{AlCl}_3$  switched the reaction pathway and afforded aryl-annulated product **4a**. The exact role played by  $\text{AlCl}_3$  is not clear right now. We suspect that  $\text{AlCl}_3$  helps to oxidize the

(7) It was noted that coordination of  $\text{C}_{60}$  to  $\text{FeCl}_3$  may change oxidation and reduction potentials, see: Hashiguchi, M.; Watanabe, K.; Matsuo, Y. *Org. Biomol. Chem.* **2011**, *9*, 6417.

(8) A strong electron-withdrawing group such as  $\text{NO}_2$  on the phenyl ring prohibited the cyclization process and instead afforded the corresponding  $\text{C}_{60}$ -fused lactone, thus supporting the proposed mechanism.

fullerenyl radical to the fullerenyl cation,<sup>7</sup> hence altering the reaction pathway. The plausible reaction mechanism for the cascade formation of **4a–g** is shown in Scheme 2. Radical **5** is formed via the reaction of **1** with  $\text{Mn(OAc)}_3$ . Addition of radical **5** to  $\text{C}_{60}$  provides fullerenyl radical **6**, which is oxidized by another molecule of  $\text{Mn(OAc)}_3$  with the assistance of  $\text{AlCl}_3$  to generate fullerenyl carbocation **7**. Intramolecular cyclization of carbocation **7** via the Friedel–Crafts-type process affords aryl-annulated product **4**.<sup>8</sup>  $\text{K}_2\text{S}_2\text{O}_8$  is a stronger oxidant than  $\text{Mn(OAc)}_3$  and facilitates the formation of intermediate **7**, thus leading to a higher product yield.

In summary, we have disclosed that the addition of  $\text{AlCl}_3$  to the  $\text{Mn(OAc)}_3$ -mediated reaction of  $\text{C}_{60}$  with active methylene compounds substituted with an aryl or a benzyl group can switch the reaction mechanism and selectively afford aryl-annulated products. The intriguing formation of  $\text{C}_{60}$ -fused tetrahydronaphthalene and indane derivatives is believed to proceed via the  $\text{Mn(OAc)}_3$ -mediated radical addition, followed by the Friedel–Crafts-type annulation with the assistance of  $\text{AlCl}_3$ .

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**Supporting Information Available.** Experimental procedures, spectral data, and NMR spectra of products **3a** and **4a–g**. This material is available free of charge via the Internet at <http://pubs.acs.org>.