

## Solvent-free Synthesis of Dihydrofuran-fused [60]Fullerene Derivatives by High-speed Vibration Milling

Xin CHENG<sup>1</sup>, Guan Wu WANG<sup>1\*</sup>, Yasujiro MURATA<sup>2</sup>, Koichi KOMATSU<sup>2</sup>

<sup>1</sup>Department of Chemistry, University of Science and Technology of China, Hefei 230026

<sup>2</sup>Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

**Abstract:** Solvent-free reactions of 1, 3-cyclohexanedione, 5, 5-dimethyl-1, 3-cyclohexanedione, 2, 4-pentanedione and ethyl acetoacetate with C<sub>60</sub> in the presence of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O and ceric ammonium nitrate (CAN) under the high-speed vibration milling conditions afforded dihydrofuran-fused C<sub>60</sub> derivatives. CAN is the better oxidant than Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O in these mechanochemical reactions.

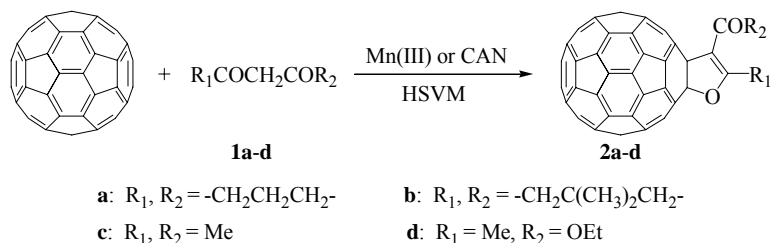
**Keywords:** [60]Fullerene, mechanochemical, solvent-free, β-dicarbonyl compounds.

Solvent-free organic reactions have been attracting great interest of chemists due to the elimination of the usage of harmful organic solvents, low costs, and simplicity in the procedure<sup>1</sup>. Solvent-free mechanochemical reactions of fullerenes were explored and are significant for the reactions of fullerenes because the low solubility of fullerenes in common organic solvents requires large quantity of organic solvents and some novel fullerene reactions could only occur in the solid-state reaction<sup>2</sup>. Since the first solid-state reaction involving C-C bond formation of C<sub>60</sub> under high-speed vibration milling (abbreviated as HSVM) was studied in 1996<sup>3</sup>, there are many reports on reactions of C<sub>60</sub> catalyzed by various potassium salts, alkali metals, or solid amines to prepare fullerene dimers and trimers<sup>4</sup>, [4+2] reaction of C<sub>60</sub> with condensed aromatic compounds<sup>5</sup>, phthalazine<sup>6</sup> and di(2-pyridyl)-1, 2, 4, 5-tetrazine<sup>7</sup>, reaction of C<sub>60</sub> with dichlorodiphenylsilane or dichlorodiphenylgermane in the presence of lithium<sup>8</sup>, reactions of C<sub>60</sub> with organic bromides and alkali metals<sup>9</sup>, reaction of C<sub>60</sub> and N-alkylglycines with and without aldehydes<sup>10</sup>, reaction of C<sub>60</sub> with active methylene compounds<sup>11</sup>, and reaction of C<sub>60</sub> with diazo compounds<sup>12</sup> under the HSVM conditions. We recently investigated the Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O-promoted radical reactions of active methylene compounds with C<sub>60</sub> in chlorobenzene and toluene<sup>13</sup>. More recently, we and others found that the reactions of β-diketones and β-keto esters with C<sub>60</sub> in the presence of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O afforded dihydrofuran-fused C<sub>60</sub> derivatives<sup>14</sup>. As a continuation of our work on the mechanochemical reactions of fullerenes under the HSVM conditions, in this paper we report the mechanochemical reaction of C<sub>60</sub> with β-dicarbonyl compounds in the presence of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O and ceric ammonium nitrate (CAN).

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\* E-mail: gwang@ustc.edu.cn

Scheme 1

**Table 1** The yields of dihydrofuran-fused C<sub>60</sub> derivatives **2** in the presence of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O and CAN

Substrate	Product	Yield <sup>a</sup>	
		Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	(NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>
	<b>2a</b>	22 (85)	29 (88)
	<b>2b</b>	28 (90)	36 (88)
CH <sub>3</sub> COCH <sub>2</sub> COCH <sub>3</sub>	<b>2c</b>	0	23 (82)
CH <sub>3</sub> COCH <sub>2</sub> CO <sub>2</sub> Et	<b>2d</b>	0	27 (84)

<sup>a</sup>Yield in parenthesis based on consumed C<sub>60</sub>.

The reactions of 1, 3-cyclohexanedione **1a**, 5, 5-dimethyl-1, 3-cyclohexanedione **1b**, 2,4-pentanedione **1c** and ethyl acetoacetate **1d** with C<sub>60</sub> in the presence of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O were examined under the HSVM conditions. Thus, the mixture of C<sub>60</sub> (14.4 mg, 0.02 mmol), β-dicarbonyl compound **1** (0.03 mmol) and Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (5.3 mg, 0.02 mmol) was vigorously milled at a frequency of 3500 cycles per minute for 45 min under the HSVM conditions. It was found that only **1a** and **1b** could react with C<sub>60</sub> in the presence of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O. The combined reaction mixture from two runs was separated on a silica gel column with CS<sub>2</sub>/toluene as the eluent to give unreacted C<sub>60</sub> and dihydrofuran-fused C<sub>60</sub> derivative **2a** or **2b** (Scheme 1).

The failure for the above mechanochemical reaction of C<sub>60</sub> with **1c** and **1d** prompted us to investigate other oxidants instead of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O. We found that CAN could promote the reactions of all of the four β-dicarbonyl compounds with C<sub>60</sub> under the same conditions (Scheme 1). The yields of dihydrofuran-fused C<sub>60</sub> derivatives **2** from the mechanochemical reactions of **1a-e** with C<sub>60</sub> in the presence of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O and CAN are listed in Table 1.

The <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS, IR and UV-Vis spectral data of **2a-d** were identical with those reported<sup>11,14</sup>. From Table 1, it is obvious that CAN is a better oxidant than Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O in the mechanochemical reactions of β-dicarbonyl compounds with C<sub>60</sub>, and the yields based on consumed C<sub>60</sub> are pretty high. The yields, especially those based on converted C<sub>60</sub>, for the mechanochemical reactions promoted by CAN are better than those in chlorobenzene mediated by Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O alone<sup>14a</sup> or those mediated by bases under HSVM conditions<sup>11a,11b</sup> in most cases.

In conclusion, the solvent-free reactions of β-dicarbonyl compounds with C<sub>60</sub> have

been investigated in the presence of  $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$  and CAN under the HSVM conditions. CAN is a better oxidant than  $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$  in these mechanochemical reactions.

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