# Zinc-Mediated Reductive Cyclization of [60]Fullerene with Enones and Subsequent Dehydration under Solvent-Free and Ball-Milling **Conditions**

Hong-Wei Liu,<sup>†</sup> Hui Xu,<sup>†</sup> Gang Shao,<sup>†</sup> and Guan-Wu Wang<sup>\*,†,‡</sup>

<sup>†</sup>CAS Key Laboratory of Soft Matter Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, *i*ChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Center for Excellence in Molecular Synthesis of CAS, and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

<sup>‡</sup>State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, Gansu 730000, P. R. China

Supporting Information



ABSTRACT: The zinc-mediated solvent-free reaction of [60] fullerene with enones and water and the subsequent treatment of a base afford various [60] fullerene-fused cyclopentanols using the ball-milling technique. A plausible reaction mechanism is proposed on the basis of control experiments. In addition, the formed [60]fullerene-fused cyclopentanols can be further dehydrated to provide [60]fullerene-fused cyclopentenes.

eveloping efficient methods toward functionalized fullerene derivatives are prevalent in modern organic synthesis due to their great potential applications in the fields of materials, biology, and nanoscience.<sup>1</sup> However, the chemical functionalizations and applications of fullerenes are severely restricted because of their poor solubility in common organic solvents. To solve this problem, mechanochemistry has emerged as a powerful tool for constructing various fullerene derivatives under solvent-free conditions.<sup>2</sup> The first mechanochemical reaction of [60] fullerene ( $C_{60}$ ) was reported in 1996 by Wang et al.<sup>3</sup> After that, diverse types of reactions, including nucleophilic additions,<sup>3,4</sup> radical additions,<sup>5</sup> cycloadditions,<sup>6</sup> and oxidations,<sup>7</sup> have been established successfully under the mechanochemical conditions. Compared with the analogous solution-based reactions, these reactions feature many unique advantages, such as avoiding hazardous solvents, higher product yields, much shorter reaction times, and even different chemical reactivities.4a,6b

On the other hand, because of the high reactivity of fullerene anions, various chemical reactions of fullerene anions generated by electrochemical or chemical reduction have been reported.<sup>8-10</sup> Among these methods, the use of metals such as Li, Na, K, and Zn is a convenient way to reduce fullerenes via both liquid-phase and solvent-free reactions.<sup>10</sup> In light of these successful studies, we attempted more mechanochemical reactions of C<sub>60</sub> mediated by Zn.<sup>3</sup> Herein, we report the zincmediated solvent-free reaction of  $C_{60}$  with various enones and water to afford C<sub>60</sub>-fused cyclopentanols and the subsequent dehydration to provide C<sub>60</sub>-fused cyclopentenes under ballmilling conditions.

It has been reported that zinc can reduce  $C_{60}$ .<sup>10c-e</sup> We surmised that the formed fullerene anions could undergo Michael addition to enones. A proton source such as an acid or water might be required to protonate the generated carbanions. At the outset, a mixture of  $C_{60}$  (0.05 mmol), chalcone 1a (0.10 mmol), zinc dust (0.10 mmol), and p-toluenesulfonic acid (p-TSA, 0.25 mmol) was introduced into a stainless steel jar (5 mL) together with 4 stainless steel balls (5 mm in diameter) and milled vigorously (41.7 Hz) in a Spex SamplePrep 5100 mixer mill at room temperature for 60 min, but only trace amounts of products were detected (Table 1, entry 1). Then, p-TSA was replaced with camphorsulfonic acid (D-CSA), acetic acid (AcOH), and water. Although the former two were fruitless, water was effective in promoting this reaction and provided products **2a** and **3a** in yields of 4% and 11%, respectively (Table 1, entries 2-4). The spectral characterization showed that 2awas a  $C_{60}$ -fused cyclopentanol derivative and 3a was a hydrofullerene derivative. However, we were more interested in the C<sub>60</sub>-fused cyclopentanol instead of the hydrofullerene derivative. We envisaged that 3a might be converted to 2a with the assistance of a base, as deduced from their molecular structures. Accordingly, after milling for 60 min in step 1, 5 equiv of Et<sub>3</sub>N was then added and milled for 15 min. To our satisfaction, almost all 3a disappeared, and 2a could be isolated

Received: February 18, 2019

#### Table 1. Optimization of the Reaction Conditions<sup>4</sup>

Table 1. Optimization of the Reaction Conditions					
	+ 1a 2n 2n additiv ball-mi t Step	e 1 additive 2 ball-milling 15 min 1 Step 2	HO Za	Ja Sa	H
entry	C <sub>60</sub> :1 <b>a</b> :Zn molar ratio	additive 1 (equiv)	additive 2 (equiv)	<i>t</i> (h)	yield of 2a (%) <sup>b</sup>
1 <sup>c</sup>	1:2:2	<i>p</i> -TSA (5)	_	1	trace
2 <sup><i>c</i></sup>	1:2:2	D-CSA (5)	_	1	trace
3 <sup>c</sup>	1:2:2	AcOH (5)	_	1	trace
4 <sup><i>c</i></sup>	1:2:2	$H_2O(5)$	_	1	$4(23)^{d}$
5	1:2:2	$H_2O(5)$	$Et_3N(5)$	1	14 (68)
6	1:2:2	$H_2O(8)$	$Et_3N(5)$	1	30 (77)
7	1:2:2	$H_2O(10)$	$Et_3N(5)$	1	34 (69)
8	1:2:2	$H_2O(12)$	$Et_3N(5)$	1	32 (66)
9	1:1:2	$H_2O(10)$	$Et_3N(5)$	1	11 (73)
10	1:3:2	$H_2O(10)$	$Et_3N(5)$	1	33 (65)
11	1:2:1	$H_2O(10)$	$Et_3N(5)$	1	16 (53)
12	1:2:3	$H_2O(10)$	$Et_3N(5)$	1	34 (72)
13	1:2:2	$H_2O(10)$	$Et_3N(5)$	1.5	41 (67)
14	1:2:2	$H_2O(10)$	$Et_3N(5)$	2	38 (59)
15	1:2:2	$H_2O(10)$	Et <sub>3</sub> N (4)	1.5	42 (66)
16	1:2:2	$H_2O(10)$	$Et_{3}N(3)$	1.5	39 (65)
17 <sup>f</sup>	1:2:2	$H_2O(10)$	$Et_3N(4)$	1.5	43 (65)
18	1:2:2	$H_2O(10)$	$Na_2CO_3(4)$	1.5	20 (37) <sup>e</sup>
19	1:2:2	$H_2O(10)$	KOAc (4)	1.5	38 (59)
20	1:2:2	$H_2O(10)$	DMAP (4)	1.5	37 (57)
21 <sup>g</sup>	1:2:2	$H_2O(10)$	$Et_{3}N(4)$	1.75	36 (56)
22 <sup><i>h</i></sup>	1:2:2	$H_2O(10)$	$Et_{3}N(4)$	12	0
23 <sup>i</sup>	1:2:2	$H_2O(10)$	$Et_3N(4)$	12	0
24 <sup>j</sup>	1:2:2	$H_2O(10)$	$Et_{3}N(4)$	12	0

<sup>*a*</sup>Unless otherwise noted, reactions were performed in a Spex SamplePrep 5100 mixer mill with 0.05 mmol of  $C_{60}$ . <sup>*b*</sup>Isolated yields based on  $C_{60}$ . Values in parentheses were based on the amount of  $C_{60}$ consumed. <sup>*c*</sup>Only step 1 of this reaction was carried out. <sup>*d*</sup>Product **3a** was isolated in 11% yield. <sup>*e*</sup>Product **3a** was isolated in 21% yield. <sup>*f*</sup>Preactivated zinc dust was used. <sup>*g*</sup>The Et<sub>3</sub>N was added together with  $C_{60}$  **1a**, Zn, and water. The reaction time was 105 min. <sup>*h*</sup>The reaction was performed in chlorobenzene at 80 °C. <sup>*i*</sup>The reaction was performed in 1,1,2,2-tetrachloroethane at 80 °C.

in 14% yield (Table 1, entry 5). The amount of water was subsequently screened. When the dosage of water was increased to 8 equiv, an improved yield of 30% was obtained (Table 1, entry 6). Further increasing the amount of water to 10 equiv led to a slightly increased yield of 34% (Table 1, entry 7). However, a slightly decreased yield was attained when 12 equiv of water was employed (Table 1, entry 8), indicating that 10 equiv of water was the optimal choice. Afterward, the C<sub>60</sub>:1a:Zn molar ratio was investigated. It was found that decreasing or increasing the dosage of **1a** or Zn did not produce better results (Table 1, entries 9–12). Next, with the optimal  $C_{60}$ : 1a:Zn:water molar ratio (1:2:2:10), the reaction time of step 1 was examined. As the reaction time was extended to 1.5 h, the yield of product 2a was increased to 41%, yet a reduced yield of 38% was obtained when the reaction time was further prolonged to 2 h (Table 1, entries 13 and 14). In addition, the employed base should play a crucial role in promoting the intermediate to the cyclized product; thus, the amount of Et<sub>3</sub>N was examined. The reaction was carried out with an amount of Et<sub>3</sub>N decreased from 5 equiv to 4 equiv and 3 equiv, and product 2a was delivered in yields of 42% and 39%,

respectively (Table 1, entries 15 and 16). Consequently, the optimal amount of Et<sub>3</sub>N was 4 equiv. Furthermore, the zinc dust preactivated by HCl was found to provide nearly the same yield as that for the commercial zinc dust (Table 1, entry 17 vs entry 15). Finally, several bases, including Na<sub>2</sub>CO<sub>3</sub>, KOAc, and 4dimethylaminopyridine (DMAP), were screened in a bid to improve the yield, yet all of these bases failed to afford higher yields (Table 1, entries 18-20). On the basis of the success of the one-pot two-step protocol described above, we further investigated this reaction by a one-pot, one-step process. As a result, a good yield of 36% was obtained, yet it was slightly lower than that for the one-pot, two-step procedure (Table 1, entry 21 vs entry 15). To compare the mechanochemical reaction with its liquid-phase counterpart, the reaction was performed in several solvents (6 mL), including chlorobenzene, o-dichlorobenzene, and 1,1,2,2-tetrachloroethane at 80 °C for 12 h (step 1), and then 4 equiv of Et<sub>3</sub>N was added. The reaction mixture was allowed to react for 2 h (step 2), but no desired product could be isolated (Table 1, entries 22-24). On the basis of the results presented above, the optimized reaction conditions were established as follows: step 1,  $C_{60}$  (0.05 mmol), 1a (0.10 mmol), zinc dust (0.10 mmol), water (0.50 mmol), mixer mill, 41.7 Hz, 90 min; step 2, Et<sub>3</sub>N (0.20 mmol), mixer mill, 41.7 Hz, 15 min.

With the optimized conditions in hand, we then investigated the scope of this reaction by employing various chalcones under the optimal reaction conditions, and the results are summarized in Scheme 1. Chalcones with an electron-donating group, including methyl and methoxy groups at the para position on the phenyl ring of R<sup>1</sup>, afforded **2b** and **2c** in yields of 30% and 33%, respectively. Satisfyingly, the chloro and bromo substituents were well tolerated in this reaction; products 2d and 2e could be isolated in 36% and 32% yields, respectively. Furthermore, reactions of chalcones containing the meta- and orthosubstituted methyl group also proceeded smoothly and afforded the corresponding products 2f and 2g in 37% and 34% yields, respectively. Then, the chalcone with a methyl group on the phenyl ring in  $R^2$  at the para position reacted fluently and provided product 2h in 33% yield. However, the chalcone bearing a *para*-substituted methoxy group retarded the reaction obviously, giving product 2i in a lower yield of 25%. The substrate with a *meta*-substituted methyl group also worked well under our optimal conditions, providing product 2j in 38% yield. Furthermore, substrates with other aryl, heteroaryl, and alkyl groups were also explored. The results revealed that 2-naphthyl-, 2-thienyl-, methyl-, and dimethyl-substituted enones were compatible with our protocol, and products 2k-n were isolated in 19-32% yields. The assigned structures of products were unambiguously confirmed by the single-crystal X-ray diffraction analysis of **2a** as an example.<sup>1</sup>

A scale-up solvent-free mechanochemical reaction of 100 mg of  $C_{60}$  (0.14 mmol) with chalcone **1a** (0.28 mmol) was conducted under the optimal reaction conditions. Product **2a** was obtained in 33% yield, indicating that this protocol could be performed for a larger-scale preparation.

A set of control experiments were conducted to shed light on the reaction mechanism. Without step 2, we performed the reaction under the step 1 conditions. Intermediate **3a** was isolated in 27% yield, along with product **2a** in 15% yield (Scheme 2a). When pre-prepared intermediate **3a** was allowed to be milled for 15 min with Et<sub>3</sub>N, product **2a** was isolated in 87% yield (Scheme 2b). These results inferred that **3a** was a key intermediate in this reaction. Subsequently, when H<sub>2</sub>O was

#### Scheme 1. Results for the Reaction of $C_{60}$ with Enones 2a-n<sup>a</sup>



<sup>*a*</sup>All reactions were performed in a Spex SamplePrep 5100 mixer mill with 0.05 mmol of  $C_{60}$ . Isolated yields based on  $C_{60}$ . Values in parentheses were based on the amount of  $C_{60}$  consumed.

replaced by D<sub>2</sub>O under the identical reaction conditions, we found the H/D scrambling on product 2a and intermediate 3a, which confirmed that water could act as a hydrogen donor (Scheme 2c). However, it was found that the hydroxyl group of compound  $d_1$ -2a was undeuterated because of the facile hydrogen-deuterium exchange with water during the workup process, consistent with the literature.<sup>12</sup> Because the single electron transfer (SET) from Zn to  $\alpha_{\beta}$ -unsaturated ketones would generate the corresponding radical enolates,<sup>13</sup> we investigated whether this process was involved under our reaction conditions. The reaction in the absence of  $C_{60}$  under the optimized reaction conditions afforded polysubstituted cyclopentanol derivative 4a in 30% yield (Scheme 2d). Compound 4a was produced by the radical coupling of radical enolates formed by SET and subsequent intramolecular aldol cyclization.<sup>13</sup> In addition, 4a could also be isolated in the same yield without the addition of Et<sub>3</sub>N. However, 4a could not be isolated when  $C_{60}$  was present. Therefore, the enolate radical anion was unlikely involved, and Zn preferentially reduced C<sub>60</sub> rather than the enones.

On the basis of the control experiments and the literature,  $^{8,10}$  a plausible reaction mechanism is proposed (Scheme 3). At first, the C<sub>60</sub> dianion is readily produced through the acceptance of two electrons from Zn. Subsequently, the Michael addition of the C<sub>60</sub> dianion to substrate 1 followed by protonation generates fullerenyl anion 5. Finally, anionic 5 undergoes an intra-



not observed (0.5 equiv C<sub>60</sub>)

Scheme 3. Proposed Reaction Mechanism



molecular cyclization and protonation to deliver cyclized product 2. In the absence of a base, part of anionic 5 is protonated to afford hydrofullerene 3, which can be converted back to 5 by the added base.

Further dehydration to provide  $C_{60}$ -fused cyclopentenes **6** was investigated by employing **2a** and **2b** as representative examples (Scheme 4). As desired,  $C_{60}$ -fused cyclopentene **6a** was obtained in 73% yield when **2a** was treated with 4 equiv of trifluoromethanesulfonic acid (TfOH) for 30 min under ball-milling conditions. Although MgSO<sub>4</sub> alone could not promote the dehydration of **2a**, the combination of 4 equiv of TfOH with 4 equiv of MgSO<sub>4</sub> afforded a higher yield of 91%. Similarly, **6b** 

Letter

#### Scheme 4. Dehydration Reaction



could be successfully isolated in 84% yield under the same reaction conditions.

In summary, we have developed a solvent-free reductive cyclization reaction of  $C_{60}$  with enones mediated by zinc in the presence of water and triethylamine under ball-milling conditions, affording a series of  $C_{60}$ -fused cyclopentanols. On the basis of the control experiments, a plausible reaction mechanism has been proposed. In addition, the formed  $C_{60}$ -fused cyclopentanols can be efficiently transformed into  $C_{60}$ -fused cyclopentene derivatives via dehydration reaction with TfOH and MgSO<sub>4</sub>. Our protocol features solvent-free conditions and easily available and cheap reagents.

### ASSOCIATED CONTENT

### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00612.

Detailed experimental procedures and characterization data, NMR spectra of 2a-n,  $d_1$ -2a, 3a,  $d_2$ -3a, 4a, 6a, and 6b, and crystal data of 2a (PDF)

### **Accession Codes**

CCDC 1859109 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: gwang@ustc.edu.cn. ORCID <sup>©</sup>

Guan-Wu Wang: 0000-0001-9287-532X

## Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors are grateful for financial support from the National Natural Science Foundation of China (21372211) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB20000000).

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