

# Hypervalent Iodine Reagent Mediated Diamination of [60]Fullerene with Sulfamides or Phosphoryl Diamides

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**S** Supporting Information

**ABSTRACT:** A hypervalent iodine-promoted intermolecular diamination reactions of  $C_{60}$  with sulfamides or phosphoryl diamides affords two classes of novel  $C_{60}$ -fused cyclic sulfamide or phosphoryl diamide derivatives. The reaction between  $C_{60}$  and sulfamides can be effectively controlled to selectively synthesize diamination products or azafulleroids under  $PhIO/I_2$  or  $PhI(OAc)_2/I_2$  conditions, respectively. Moreover, phosphoryl diamides were first used as an amine source in the diamination of alkenes.

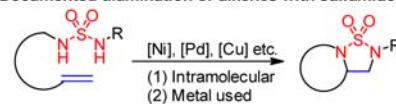


Chemical modification on the sphere of  $C_{60}$  allows the preparation of large quantities of fullerene derivatives with different structures and properties for the investigation of their application in biological and material science. Until now, a variety of methods for chemical functionalization of fullerenes have been explored involving various  $[2 + n]$  ( $n = 1-4$ ) reactions, redox reactions, cycloadditions, radical additions, nucleophilic additions, and multiadditions.<sup>1</sup> Free-radical reactions were one of the most investigated reactions in fullerene chemistry and continue to be an effective strategy for the functionalization of fullerenes. To date, the addition of different kinds of radicals (e.g., C-, Si-, O-, S-, and P-centered radicals) to fullerenes has been well documented.<sup>2</sup> Multiaddition is liable to occur when free radicals react with fullerenes and tend to give a reaction mixture containing many and hardly separable products.<sup>3</sup> Therefore, controlling the single-addition of free-radicals to  $C_{60}$  is a challenge. Later, radical reactions of fullerenes promoted by transition-metal salts such as Mn(III),<sup>4</sup> Cu(II),<sup>2d,5</sup> Fe(III),<sup>6</sup> and Pb(IV)<sup>7</sup> to generate the monoadduct were developed. The Orfanopoulos group explored a photochemical addition of acyl and  $\alpha$ -oxygen C-centered radicals to fullerene catalyzed by TBADT  $[(n-Bu_4N)_4W_{10}O_{32}]$ .<sup>8</sup> Recently, cobalt-catalyzed radical hydroalkylation or cycloaddition of  $C_{60}$  with active alkyl bromides or dibromides was demonstrated.<sup>2e,9</sup> In contrast to the most investigated addition of C-centered radicals to fullerenes, the addition of N-centered radicals to fullerenes was rather rare. Only a few reactions of  $C_{60}$  with nitriles, amidines, amides, and carbamates based on N-centered radicals were exploited.<sup>2c,10</sup> Recently, we developed a hypervalent iodine reagent/ $I_2$  system-mediated or CuI-catalyzed N-centered radical reactions of  $C_{60}$  with amines/amides/amidines.<sup>5c,11</sup>

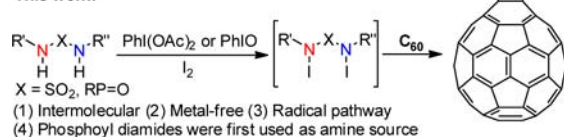
Oxidative diamination of olefins with sulfamides has recently emerged as a suitable approach to generate bicyclic sulfamides. This strategy has been successfully employed by using [Ni], [Pd] catalysts, or stoichiometric copper reagents (Scheme 1).<sup>12</sup> Recently, the nonmetal-based methods received more attention in alkene diamination with different amine sources.<sup>13</sup> However,

## Scheme 1

Documented diamination of alkenes with sulfamides:



This work:

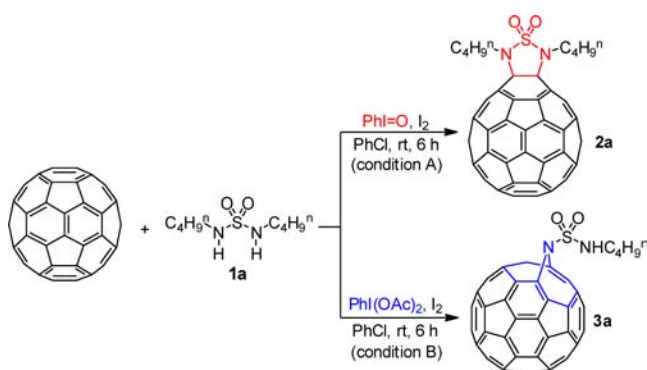


this approach was limited to an intramolecular addition fashion, and the use of phosphoryl diamides as amine source has never been investigated. The new methods for the preparation of fullerooxazoles and iminofullerenes explored by us and Minakata's group<sup>11,14</sup> disclosed the nitrogen radicals were easy to generate through N–I bond cleavage from the  $N,N$ -diiodo intermediate and took place radical reaction with  $C_{60}$ . Inspired by these results, we could envision that treatment of sulfamides or phosphoryl diamides with hypervalent iodine reagents/ $I_2$  would generate the  $N,N'$ -diiodo intermediate, which might be captured by  $C_{60}$  in a radical pathway to generate novel  $C_{60}$ -fused cyclic diamine derivatives (Scheme 1).

We began our investigation with the  $PhI(OAc)_2/I_2$ -mediated reaction of  $C_{60}$  with  $N,N'$ -dibutylsulfamide **1a** (Table 1). When a mixture of  $C_{60}$  and 2 equiv of **1a** was treated with 2 equiv of  $PhI(OAc)_2$  and 2 equiv of  $I_2$  in chlorobenzene at room temperature for 6 h, to our disappointment, one of the butyl groups on the nitrogen atom was leaving, and azafulleroid **3a** was obtained as the main product along with trace of diamination product **2a** (Table 1, entry 5). We were fortunate to find that the ratio of **2a** to **3a** could be inverted in favor of diamination when

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**Table 1. Selective Reaction of C<sub>60</sub> with N,N'-Dibutylsulfamide Mediated by PhIO/I<sub>2</sub> or PhI(OAc)<sub>2</sub>/I<sub>2</sub>**


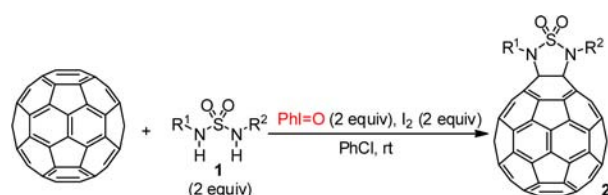
entry	conditions	[C <sub>60</sub> /1a/hypervalent iodine/I <sub>2</sub> ]	time (h)	yield <sup>b</sup> (%)	
				2	3
1	A	1:2:2:2	6	28 (82)	trace
2	A	1:2:2:0.2	24	10 (86)	trace
3	A	1:2:3:1	12	22 (83)	trace
4	A	1:2:4:1	6	30 (69)	trace
5	B	1:2:2:2	6	trace	24 (79)
6	B	1:2:2:0.2	24	trace	11 (89)
7	B	1:2:3:1	12	trace	21 (75)
8	B	1:2:4:1	6	trace	19 (63)

<sup>a</sup>C<sub>60</sub> (36 mg), rt, 10 mL of chlorobenzene. <sup>b</sup>Isolated yield; values in parentheses are based on consumed C<sub>60</sub>.

PhI(OAc)<sub>2</sub> was replaced by PhIO. Under PhIO/I<sub>2</sub> conditions, **2a** was obtained in 28% yield accompanied by a trace of **3a** (Table 1, entry 1). Catalytic loading of I<sub>2</sub> led to a dramatic decrease in the yield (Table 1, entries 2 and 6). Increasing the amount of hypervalent iodine to 3–4 equiv did not result in notable improvement on the yield (Table 1, entries 3, 4, 7, and 8). It should be pointed out that both hypervalent iodine and I<sub>2</sub> were essential to the reaction, and no reaction occurred in the absence of either one.

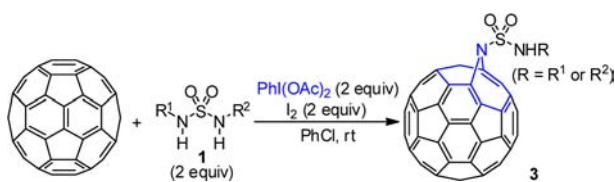
It was intriguing that **2a** and **3a** could be selectively obtained under PhIO/I<sub>2</sub> and PhI(OAc)<sub>2</sub>/I<sub>2</sub> systems, respectively. To investigate the generality of the two kinds of selective transformations, the optimized conditions (Table 1, entries 1 and 5) were applied for a number of different substituted sulfamides **1a–i** (Tables 2 and 3). Under PhIO/I<sub>2</sub> conditions, when R<sup>1</sup> and R<sup>2</sup> are both aliphatic groups, the reaction proceeded well to give the diamination products **2** (Table 2, entries 1–6). If one of the substituents on the nitrogen atom was ester group, the yield decreased notably (Table 2, entry 7). The cyclic sulfamide **1h** also afforded the desired product **2h** in lower yield with the assistance of photoirradiation (Table 2, entry 8). It was a pity that an aromatic substituent on the nitrogen atom resulted in the failure of the reaction (Table 2, entry 9).

As can be seen from the results mentioned in Table 1, one substituent disappeared in the product. The symmetric sulfamides gave the main product **3a** and **3b** as expected (Table 3, entries 1 and 2). When the R<sup>1</sup> and R<sup>2</sup> were different aliphatic groups, an interesting phenomenon was observed (Table 3, entries 3–5). Only one main product was observed for **1c–e**. The sequence of leaving ability of the group is Bn- > *n*-butyl- > cyclohexyl-. For the substrate **1e**, 5% of the diamination product **2e** was isolated accompanying with the main product **3d**. In terms of substrates **1f** and **1g**, only the diamination product **2f**

**Table 2. Reaction of C<sub>60</sub> with Sulfamides under PhIO/I<sub>2</sub> Conditions**


entry	sulfamides	product	time (h)	yield (%) <sup>a</sup>
1	<b>1a</b> C <sub>4</sub> H <sub>9</sub> <sup>n</sup> -N(SO <sub>2</sub> )-C <sub>4</sub> H <sub>9</sub> <sup>n</sup>	<b>2a</b>	6	28 (82)
2	<b>1b</b> Bn-N(SO <sub>2</sub> )-Bn	<b>2b</b>	6	32 (76)
3	<b>1c</b> C <sub>4</sub> H <sub>9</sub> <sup>n</sup> -N(SO <sub>2</sub> )-Bn	<b>2c</b>	8	25 (80)
4	<b>1d</b> C <sub>4</sub> H <sub>9</sub> <sup>n</sup> -N(SO <sub>2</sub> )-C <sub>6</sub> H <sub>11</sub>	<b>2d</b>	8	23 (79)
5	<b>1e</b> Bn-N(SO <sub>2</sub> )-C <sub>6</sub> H <sub>11</sub>	<b>2e</b>	8	27 (69)
6	<b>1f</b> C <sub>4</sub> H <sub>9</sub> <sup>n</sup> -N(SO <sub>2</sub> )-CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> Et	<b>2f</b>	8	30 (81)
7	<b>1g</b> Bn-N(SO <sub>2</sub> )-CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> Et	<b>2g</b>	10	13 (81)
8 <sup>b</sup>	<b>1h</b> HN(SO <sub>2</sub> )NH	<b>2h</b>	6	11 (67)
9	<b>1i</b> Bn-N(SO <sub>2</sub> )-C <sub>6</sub> H <sub>5</sub>	<b>2i</b>	10	0

<sup>a</sup>Isolated yield; values in parentheses are based on consumed C<sub>60</sub>. <sup>b</sup>Irradiation with 125 W fluorescent high pressure mercury amp.

**Table 3. Reaction of C<sub>60</sub> with Sulfamides under PhI(OAc)<sub>2</sub>/I<sub>2</sub> Conditions**


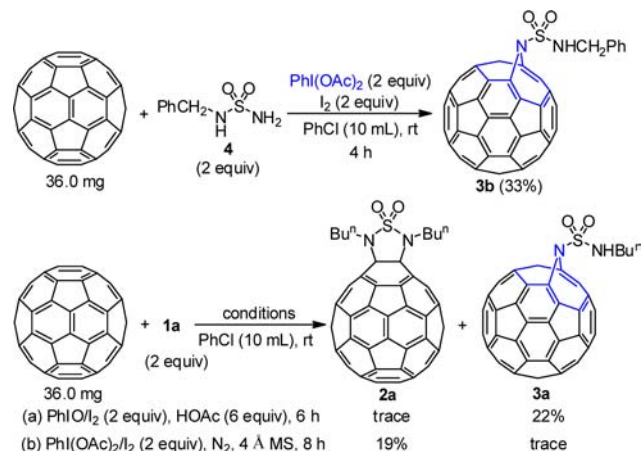
entry	sulfamides	time (h)	product and yield <sup>a</sup>
1	<b>1a</b>	8	<b>3a</b> , 24% (82%) (R = C <sub>4</sub> H <sub>9</sub> <sup>n</sup> )
2	<b>1b</b>	8	<b>3b</b> , 29% (87%) (R = Bn)
3	<b>1c</b>	8	<b>3a</b> , 22% (79%)
4	<b>1d</b>	8	<b>3d</b> , 27% (85%) (R = cyclohexyl)
5	<b>1e</b>	8	<b>3d</b> , 23% (65%) and <b>2e</b> , 5% (14%)
6	<b>1f</b>	6	<b>2f</b> , 20% (71%)
7	<b>1g</b>	6	<b>2g</b> , 18% (67%)
8	<b>1h</b>	8	NR
9	<b>1i</b>	12	NR

<sup>a</sup>Isolated yield; values in parentheses are based on consumed C<sub>60</sub>.

and **2g** was afforded under either PhI(OAc)<sub>2</sub>/I<sub>2</sub> or PhIO/I<sub>2</sub> conditions. For cyclic sulfamide **1g**, no product was observed under PhI(OAc)<sub>2</sub>/I<sub>2</sub> conditions.

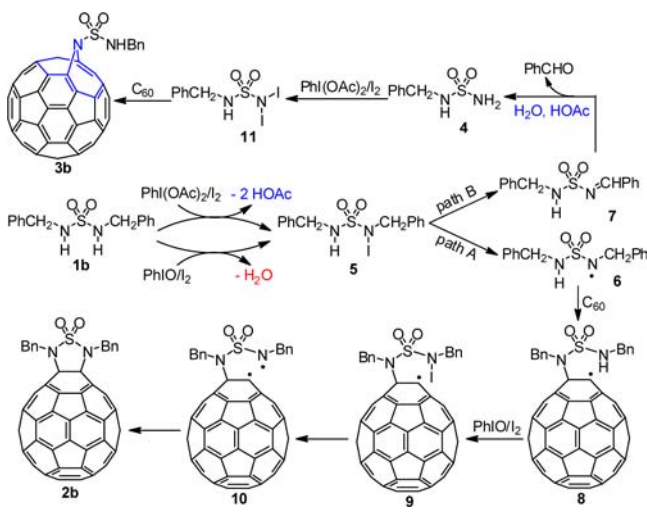
To gain insight into the selective transformation, several control experiments were carried out (Scheme 2). Togo and co-

## Scheme 2. Controlled Experiments



workers have reported the oxidative dealkylation of *N*-alkylsulfonamides to free sulfonamides and aldehydes under  $\text{PhI}(\text{OAc})_2/\text{I}_2$  conditions.<sup>15</sup> Treatment of  $C_{60}$  and *N*-benzylsulfamide **4** with  $\text{PhI}(\text{OAc})_2/\text{I}_2$  indeed afforded the azafulleroid **3b**. This meant that **1b** might be transformed to **4** promoted by  $\text{PhI}(\text{OAc})_2/\text{I}_2$ . Why was the diamination product was the main product under  $\text{PhIO}/\text{I}_2$  conditions? We thought that the essential factor was whether the imine intermediate **7**, which was generated from **5** via oxidative elimination of  $\text{HI}$ , could be easily decomposed to **4** (Scheme 3). When the reaction of  $C_{60}$

## Scheme 3. Proposed Reaction Mechanism



with **1a** and  $\text{PhIO}/\text{I}_2$  was performed with 6 equiv of  $\text{HOAc}$  as the additive, only a trace of **2a** could be observed on TLC and **3a** was obtained in 22% yield. Moreover, if the reaction of  $C_{60}$  with **1a** and  $\text{PhI}(\text{OAc})_2/\text{I}_2$  was performed under  $\text{N}_2$  atmosphere with 4 Å molecular sieves as the additive, diamination product **2a** was formed in 19% yield accompanying with trace of **3a**. This could be explained by the trace of water, and acidic conditions were favorable to the hydrolysis of **7**, which led to the formation of **3a**.

On the basis of these results and our previous work on the hypervalent iodine-mediated reaction of  $C_{60}$  with amines,<sup>11</sup> a radical reaction mechanism for the selective transformation is proposed in Scheme 3. *N*-Iodo intermediate **5** was generated under both reaction conditions. *N*-I bond cleavage and elimination of  $\text{HI}$  would afford radical **6** and imine **7**, respectively.

Addition of **6** to  $C_{60}$  gave the fullerene radical **8**. Subsequent *N*-iodination, *N*-I bond cleavage, and intramolecular coupling afforded the diamination product. Under  $\text{PhI}(\text{OAc})_2/\text{I}_2$  conditions,  $\text{HOAc}$  was generated in the first step of iodination, which promoted the hydrolysis of **7** to **4** in the presence of a trace of water in the air. *N,N*-Diodination of **4** provided **11**, which underwent a radical reaction with  $C_{60}$  to give azafulleroid **3b**. Under  $\text{PhIO}/\text{I}_2$  conditions, the absence of acid inhibited the decomposition of **7**. Therefore, the formation of azafulleroid **3b** was suppressed and diamination product **2b** was predominant.

Encouraged by the good results, we next turned our attention to phosphoryl diamides **12a** and **12b**, which have never been used as the amine source in the diamination of olefins (Table 4).

Table 4. Reaction of  $C_{60}$  with Phosphoryl Diamides

entry	substrate	conditions	time (h)	yield <sup>a</sup> (%)	
				13	14
1	<b>12a</b>	$\text{PhIO}/\text{I}_2$	6	0	29 (82)
2	<b>12a</b>	$\text{PhI}(\text{OAc})_2/\text{I}_2$	6	0	26 (79)
3	<b>12a</b>	$\text{PhI}(\text{OAc})_2/\text{I}_2$ , $h\nu$	6	trace	25 (70)
4	<b>12a</b>	$\text{PhI}(\text{OAc})_2/\text{I}_2$ , $h\nu$ , $\text{N}_2$ , 4 Å MS	12	16 (77)	trace
5	<b>12b</b>	$\text{PhI}(\text{OAc})_2/\text{I}_2$	6	0	24 (76)
6	<b>12b</b>	$\text{PhI}(\text{OAc})_2/\text{I}_2$ , $h\nu$	6	trace	25 (69)
7	<b>12b</b>	$\text{PhI}(\text{OAc})_2/\text{I}_2$ , $h\nu$ , $\text{N}_2$ , 4 Å MS	12	14 (65)	trace

<sup>a</sup>Isolated yield; values in parentheses are based on consumed  $C_{60}$ .

In contrast to sulfamides,  $\text{PhIO}$  and  $\text{PhI}(\text{OAc})_2$  did not show obvious distinction for phosphoryl diamides. Under either  $\text{PhIO}/\text{I}_2$  or  $\text{PhI}(\text{OAc})_2/\text{I}_2$  conditions, the reaction of  $C_{60}$  with **12a** did not furnish the anticipated diamination product **13a**. Instead, the aziridinofullerene **14** generated from the *P*-*N* bond cleavage was produced as the main product (Table 4, entries 1 and 2). It should be noted that only trace of *cis*-1-bisaziridinofullerene, which was inevitably generated in our previously reported  $\text{PhI}(\text{OAc})_2/\text{I}_2$ -mediated reaction of  $C_{60}$  with alkyl amine,<sup>11b</sup> was observed in this reaction. Thus, this method was a good choice for selectively preparing aziridinefullerene (single-addition) bearing an alkyl group on the nitrogen atom. If the reaction was performed under the irradiation of a 125 W fluorescent high pressure Hg lamp, although the aziridinofullerene **14** was still the main product, trace of diamination product **13a** was observed on TLC (Table 4, entry 3). When the reaction was carried out under  $\text{N}_2$  atmosphere with the addition of 4 Å molecular sieve, to our delight, the formation of **14** was suppressed notably and the diamination product **13a** was isolated as the main products. In case of phosphoryl diamide **12b**, similar result was obtained as that of **12a**.

Although the addition of diamines to  $C_{60}$  under photoirradiation or heating has been well investigated for the synthesis of cyclic diamine-fused  $C_{60}$  derivatives,<sup>18</sup> the substrates were limited to *N,N'*-dialkyl-substituted ethylenediamine and piperazine compounds. Moreover, an electron-transfer process, which



was quite different with the present method, was involved in the reaction. The recently emerged intramolecular diamination of alkenes under metal-free conditions mostly underwent an ionic pathway.<sup>13</sup>

The structures of new diamination products **2** and **13** and azafulleroids **3** were fully assigned on the basis of their MALDI-TOFMS, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and UV-vis spectra. Taking **2a** as an example, the TOFMS spectrum of **3a** showed the [M + Na]<sup>+</sup> peak at *m/z* 949.0981. The <sup>1</sup>H NMR spectrum of **3a** displayed four signals for the butyl group. The <sup>13</sup>C NMR spectrum of **3a** exhibited 16 signals (3 × 2C, and 13 × 4C) for the sp<sup>2</sup>-C of the C<sub>60</sub> skeleton in the range of 137.74–148.31 ppm and one peak at 79.32 ppm for the sp<sup>3</sup>-C of the C<sub>60</sub> cage, agreeing well with the C<sub>2v</sub> symmetry of its molecular structure.

In summary, we have developed a hypervalent iodine-mediated intermolecular diamination of C<sub>60</sub> with sulfamides or phosphoryl diamides for the synthesis of novel C<sub>60</sub>-fused cyclic sulfamide or C<sub>60</sub>-fused cyclic phosphoryl diamide derivatives, which constitute two new classes of the fullerene family. Compared with previously reported methods for the diamination of olefins with sulfamides, this novel protocol is distinguished by (1) an intermolecular addition fashion; (2) metal-free conditions; (3) radical pathway; (4) first use of phosphoryl diamides as amine source; and (5) mild conditions.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details and NMR spectra of the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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