Organic LETTERS

Letter

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Cu-Catalyzed C−H Amination of Hydrofullerenes Leading to 1,4-Difunctionalized Fullerenes

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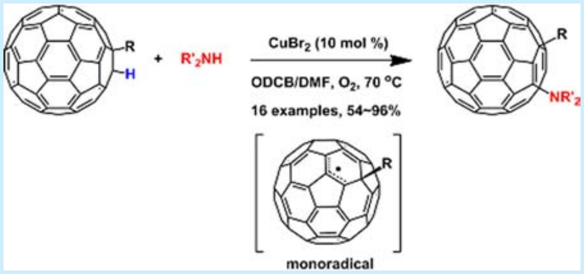
Ⓢ *Supporting Information*

ABSTRACT: A novel and highly efficient Cu-catalyzed C−H amination of the monofunctionalized hydrofullerenes for the synthesis of 1,4-difunctional fullerenes has been reported. A new series of 1,4-fullerene derivatives having various monoamine addends were synthesized in good to high yields under mild reaction conditions. The controlled experiments revealed that the reaction proceeds through the formation of a fullerene monoradical as a key intermediate followed by coupling with an amine radical.



Fullerene derivatives with versatile functional groups on a fullerene core not only increase their solubilities in various organic solvents but also tune the energy levels and the packing structures, while maintaining the electron affinity and the electron transport ability of C_{60}. These merits make functional fullerenes attractive as excellent n-type materials in organic electronics.[1] The continuous creation of a new series of functional fullerenes possessing a potential functionality in materials science and medicinal chemistry is still highly desirable.[1,2] The transition-metal-catalyzed methodology has been demonstrated as one of the most efficient methodologies for functionalization of fullerenes, which offers much opportunity for creating novel functional fullerenes.[3] Recently, we have reported that a fullerene monoradical can be readily formed from the monofunctionalized hydrofullerenes catalyzed by the $Cu(OAc)_2$ oxidant or NaOH base under an air atmosphere, affording the single-bonded fullerene dimers in high yields.[3k,4] The interesting catalytic generation and reactivity of the fullerene monoradical species[5] led us to further explore its function as a useful intermediate for the synthesis of new functional fullerenes. Indeed, the research groups of Komatsu and Nakamura have reported that a fullerene monoradical can be oxidized to a fullerene cation by using excess amounts of strong acids or $CuCl_2$, which reacted with nucleophiles to produce the corresponding 1,4- or 1,2-fullerenes, respectively.[6] However, to the best of our knowledge, direct and selective intermolecular radical coupling between a fullerene monoradical and a certain radical species generated *in situ* under a catalyst system has never been reported.[7] Herein, we report a novel Cu-catalyzed C−H amination of the monosubstituted hydrofullerenes with various amines to afford a new series of monoamine functionalized 1,4-bisadducts in good to high yields. The controlled experiments clearly revealed the involvement of a radical coupling between a fullerene monoradical and an amine radical species under the optimal reaction conditions.

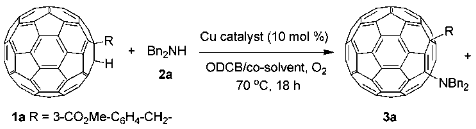
1,4-Difunctionalized fullerenes possess two alkyl or aryl functional groups on the 1,4-position of the fullerene core and exhibit a higher absorption extinction coefficient in the visible region than that of methanofullerene, which have been used as n-type semiconductors for high performance organic photovoltaics and thin film transistors.[1,8] Those 1,4-fullerenes were generally prepared by the reactions of fullerene anions with alkyl halides and fullerene cations with aryl nucleophiles.[6a,8−10] Only one example of the monoamine functionalized 1,4-bisadduct has been reported by Wudl et al.,[11] in which the aniline substituted 1,4-bisadduct was prepared by the acid-mediated reaction of 1,4-disubstituted fullerenol with aniline. It was noted that, while the addition of amines to C_{60} resulted in the formation of multiadducts,[12] the present Cu-catalyzed C−H amination afforded the corresponding 1,4-bisadducts in a high monoselectivity. In this article, we provide not only a novel transformation for selective functionalization of fullerenes but also a new series of 1,4-fullerens with a wide range of monoamine addends.[13]

On the basis of our previous Cu-catalyzed dimerization of the monofunctionalized hydrofullerenes,[3k] we initiated our investigation by examining various copper catalysts in the reaction of hydrofullerene **1a** and dibenzylamine **2a** in a 1:100 mixture of DMF and ODCB (1,2-dichlorobenzene) at 70 °C under an oxygen atmosphere (Table 1). The yields were determined by HPLC analysis using C_{70} as an internal standard. The $Cu(OAc)_2$ catalyst which was the most sufficient catalyst for dimerization of **1a** exhibited low catalytic activity in producing the amine-substituted 1,4-bisadduct **3a**; instead, the single-bonded fullerene dimer **4a** was obtained in high yield (entry 1;

Received: December 10, 2013
Published: December 30, 2013

dx.doi.org/10.1021/ol403573r | *Org. Lett.* 2014, 16, 620−623

Table 1. Optimization Reaction Conditions for C−H Amination of Hydrofullerene 1a[a]

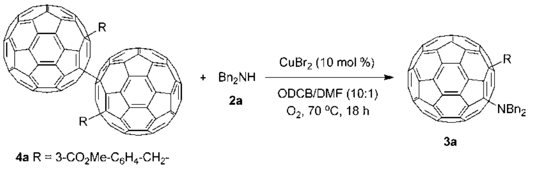


entry	catalyst	solvent (100:1)	3a (%)[b]	4a (%)[b]
1	$Cu(OAc)_2$	ODCB/DMF	5	85
2	$Cu(OTf)_2$	ODCB/DMF	38	38
3	$CuCl_2$	ODCB/DMF	37	54
4	$CuBr_2$	ODCB/DMF	67	20
5	Cu_2O	ODCB/DMF	40	54
6	CuCl	ODCB/DMF	34	60
7	CuBr	ODCB/DMF	58	34
8	CuI	ODCB/DMF	21	70
9	$CuBr_2$	ODCB/THF	40	39
10	$CuBr_2$	$ODCB/CH_3CN$	38	39
11[c]	$CuBr_2$	ODCB	27	13
12[d]	$CuBr_2$	ODCB/DMF (10:1)	75 (71)	0
13[e]	$CuBr_2$	ODCB/DMF (10:1)	43	0
14	none	ODCB/DMF (10:1)	0	90
15[f]	none	ODCB/DMF (10:1)	0	trace

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), Cu catalyst (10 mol %), ODCB/cosolvent (10 mL), oxygen balloon, 70 °C for 18 h. [b] Yields determined by HPLC by using C_{70} as an internal standard. Yield of **3a** isolated by silica gel chromatography is shown in parentheses. [c] **1a** was recovered in 56% yield. [d] C_{60} was obtained in 9% yield. [e] The reaction was conducted under an air atmosphere. **1a** was recovered in 23% yield. [f] The reaction was conducted under an argon atmosphere. **1a** was recovered in 90% yield.

for the structure of **4a**, see Table 2). Among the other Cu(II) species such as $Cu(OTf)_2$, $CuCl_2$, and $CuBr_2$ tested, the use of $CuBr_2$ obviously increased the yield of **3a** up to a 67% yield together with a 20% yield of **4a** (entries 2−5). The Cu(I) species such as Cu_2O, CuCl, CuBr, and CuI are also active, but the yields of **3a** are lower than that with $CuBr_2$ (entries 6−8). In contrast, several other metal catalysts, such as $AuBr_3$, $FeCl_3$, $CoBr_2$, $PdCl_2$, and $Mn(OAc)_3$, were totally inactive for the formation of **3a** and the dimer **4a** was obtained in comparable yields. The use of THF or CH_3CN as a cosolvent instead of DMF or ODCB as a single solvent did not result in increasing the yield of **3a** (entries 9−11). Changing the ratio of ODCB and DMF from 100:1 to 10:1 increased the yield of **3a** to 71% (entry 12). It was noted that the reaction produced the corresponding amination product **3a** in 43% yield under an air atmosphere, indicating that the oxygen atmosphere is indispensable in achieving the high chemical yield of **3a** (entry 13).

Table 2. Control Experiments of Amination by Using the Single-Bonded Fullerene Dimer 4a[a]



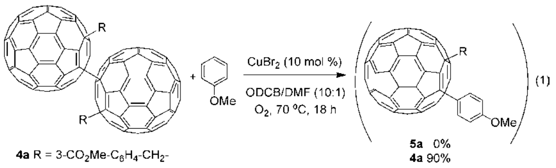
entry	catalyst	oxidant	3a (%)[b]	4a (%)[b]
1	$CuBr_2$	O_2	77	trace
2	$CuBr_2$	argon	9	80
3	none	O_2	0	90

[a] Reaction conditions: a mixture of *meso* and *racemic* dimer **4a** (0.1 mmol), **2a** (0.4 mmol), $CuBr_2$ (10 mol %), ODCB/DMF (10:1, 10 mL), oxygen balloon, 70 °C, 18 h. [b] Yields determined by HPLC using C_{70} as an internal standard.

We noticed that, in the absence of a copper catalyst, the present reaction produced the dimerization product **4a** in over 90% yield without formation of **3a** (entry 14), while it is not surprising that we have demonstrated that the strong NaOH base can be used as a catalyst for the efficient dimerization of the hydrofullerene **1a** at room temperature.[4] However, the similar reaction under an argon atmosphere afforded a trace amount of **4a** (entry 15). These results indicate that amine acts as a base to promote the dimerization of **1a** in the presence of oxygen and implied that the present amination might proceed through the dimerization of **1a** to form **4a** by the amine base followed by amination of the dimer **4a** by a copper catalyst to form the dibenzylamine-substituted 1,4-bisadduct **3a**.

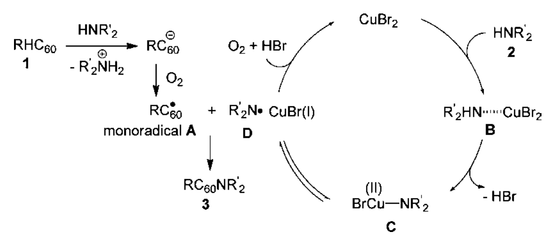
The aforementioned results led us to examine the reaction pathway from the single-bonded fullerene dimer to the amine-substituted 1,4-bisadduct as shown in Table 2. When **4a** was treated with dibenzylamine **2a** in the presence of a $CuBr_2$ catalyst and oxygen, the corresponding 1,4-bisadduct **3a** was obtained in 77% yield, while the reaction produced **3a** in a very poor yield of 9% under an Ar atmosphere (entries 1 and 2). It was noted that the reaction did not proceed in the absence of the $CuBr_2$ catalyst (entry 3). These results clearly indicate that the amination of the single-bonded fullerene dimer is promoted by the $CuBr_2$ catalyst and oxygen is indispensable for the present transformation. It was well demonstrated that the single-bonded fullerene dimers dissociate to the stable monoradicals in solution.[3k,4,5] Consequently, the results in both Tables 1 and 2 indicate that the present C−H amination of hydrofullerene to the 1,4-bisadduct might proceed through the formation of a fullerene radical intermediate followed by coupling with an amine.

As aforementioned, Matsuo and Nakamura et al. reported that a fullerene cationic species can be generated from a fullerene radical by using an excess amount of $CuCl_2$ at high temperature.[6b,c] Komatsu et al. demonstrated the fullerene cationic species by the electrophilic addition to allylsilane or benzene to form the corresponding 1,4-bisadducts.[6a] To confirm whether our amination reaction conditions generate the fullerene cation or not, the fullerene dimer **4a** was treated with anisole under our standard $CuBr_2$-catalyzed reaction conditions in the absence of amines (eq 1). However, the reaction did not produce any anisole-substituted 1,2- or 1,4-bisadduct and **4a** was recovered in over 90% yield. This result indicated that our reaction conditions are unable to generate the fullerene cationic species from the fullerene radical.



On the basis of these results, the reaction mechanism is proposed as shown in Scheme 1. Deprotonation of an acidic proton in hydrofullerene **1** by an amine base forms a fullerenyl monoanion, which converts to a monoradical **A** by an O_2-promoted one-electron oxidation.[4] Meanwhile, coordination of

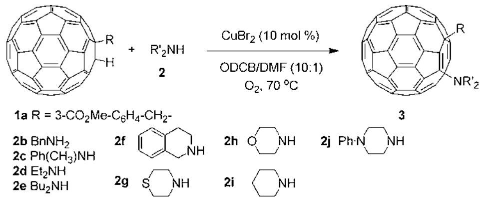
Scheme 1. Proposed Reaction Mechanism



$CuBr_2$ to amine **2** forms the Cu(II)-amine intermediate **C** along with HBr. Intermediate **C** would be in equilibrium with amine radical **D** and the Cu(I) species. Subsequent intermolecular radical coupling between the fullerene monoradical **A** and the amine radical **D** produces the corresponding 1,4-bisadduct **3**. The improved efficiency for formation of **3a** by using DMF as the cosolvent and the increased amount of DMF indicated that the DMF polar solvent should stabilize both fullerene and amine radicals, assisting the sufficient intermolecular radical coupling.[3k] Finally, oxidation of CuBr under an oxygen atmosphere in the presence of HBr regenerates the $CuBr_2$ catalyst. The results of entries 4 and 7 in Table 1 suggest that the bromide salts can improve the oxidation ability of the Cu(I) species under the present reaction conditions.[14]

Under the optimized conditions, the scope of the $CuBr_2$-catalyzed amination of the monofunctionalized hydrofullerene **1a** with various amines was examined (Table 3). All of the reactions were monitored by TLC and HPLC analysis, and the corresponding 1,4-bisadducts **3** were isolated by using silica gel column chromatography. In some cases, a small amount of the fullerene dimer **4a** remained, and the HPLC analysis did not show any amine multiadducts (see Supporting Information). A variety of acyclic amines, such as benzylamine (**2b**), *N*-methylaniline (**2c**), diethylamine (**2d**), and dibutylamine (**2e**), were tolerated, affording the corresponding amination 1,4-bisadducts **3b**−**e** in 54−64% yields (entries 1−4). The reactions with cyclic amines, such as tetrahydroisoquinoline (**2f**), thiomorpholine (**2g**), morpholine (**2h**), piperidine (**2i**), and 1-phenylpiperazine (**2j**), produced the corresponding 1,4-fullerenes **3f**−**j** in high chemical yields; the yield of **3j** was up to 96% by using **2j** (entries 5−9). It should be mentioned that the amine-substituted 1,4-fullerenes showed good solubility in chloroform, toluene, and ODCB.

Table 3. $CuBr_2$-Catalyzed C−H Amination of Hydrofullerene 1a with Various Amines[a]

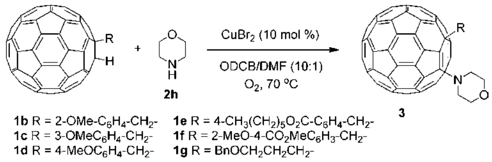


entry	2	time (h)	3	yield (%)[b]	dimer **4a** (%)[c]
1	**2b**	16	**3b**	64	7
2[d]	**2c**	20	**3c**	54	7
3	**2d**	16	**3d**	64	6
4	**2e**	29	**3e**	61	10
5	**2f**	36	**3f**	73	10
6	**2g**	55	**3g**	70	9
7	**2h**	12	**3h**	86	6
8	**2i**	13	**3i**	85	0
9	**2j**	17	**3j**	96	0

[a] Reaction conditions: **1a** (0.1 mmol), **2** (0.2 mmol), $CuBr_2$ (10 mol %), ODCB/DMF (10:1, 10 mL), oxygen balloon, 70 °C. [b] Yields of isolated products. [c] Yields determined by HPLC using C_{70} as an internal standard. A less than 2% yield of C_{60} was obtained in every example unless otherwise noted. [d] C_{60} was obtained in 5% yield

The reaction was further examined by using various monofunctionalized hydrofullerenes (**1**) and morpholine (**2h**) under the standard conditions (Table 4). The reaction using the monobenzyl hydrofullerenes **1b**−**d** having a methoxy group at the 2- or 3- or 4-position of the benzene ring afforded the corresponding 1,4-fullerenes **3k**−**m** in good yields (entries 1−3). The monobenzyl hydrofullerenes **1e** and **1f** having an ester or both ester and methoxy groups on the benzene ring were also tolerated, producing the desired 1,4-fullerenes **3n** and **3o** in 72% and 71% yields, respectively (entries 4 and 5). The alky-substituted hydrofullerene **1g** with a benzyl-protected alcohol gave the corresponding product **3p** in 73% yield under longer reaction times (entry 6). It was noted that, in every example, a small amount of C_{60} was formed probably by the elimination of the fullerene anions or the monoradicals shown in Scheme 1.

Table 4. $CuBr_2$-Catalyzed Amination of Various Hydrofullerenes 1 with Morpholine 2h[a]



entry	1	time (h)	3	yield (%)[b]
1	**1b**	13	**3k**	58
2	**1c**	13	**3l**	74
3	**1d**	24	**3m**	41
4	**1e**	13	**3n**	72
5	**1f**	13	**3o**	71[c]
6	**1g**	42	**3p**	73[d]

[a] Reaction conditions: **1** (0.1 mmol), **2h** (0.2 mmol), $CuBr_2$ (10 mol %), ODCB/DMF (10:1, 10 mL), oxygen balloon, 70 °C. [b] Yields of isolated products. A less than 2% yield of C_{60} was observed in every example unless otherwise noted. [c] C_{60} was obtained in 6% yield. [d] C_{60} was obtained in 9% yield.

The structures of 1,4-bisadducts **3** were characterized by ^1H NMR, ^{13}C NMR, and high resolution mass spectra (Supporting Information). The UV−vis absorption spectra of compounds **3** exhibit a characteristic broad absorption band around 450 nm as shown in Figure S1 (Supporting Information), which further supports the 1,4-bisadduct structure of **3**.[8−11] The low symmetry of 1,4-bisadducts **3** showed an increased absorption in the visible region compared to [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) which is a well-used benchmark acceptor in bulk heterojunction (BHJ) solar cells.[1] For example, the extinction coefficients of **3a** and **3i** are 7000 mol^{-1} cm^{-1} at 444 and 447 nm, respectively, which are approximately 2.5 times higher than that of $PC_{61}BM$ (2800 mol^{-1} cm^{-1} at 431 nm) (Table S1, Supporting Information). The electrochemistry of 1,4-fullerenes was investigated by electrochemical cyclic voltammetry (CV) in ODCB (Supporting Information, Figure S2). The LUMO levels of **3a** and **3h** having a dibenzylamine or morpholine group on the C_{60} core were estimated be −3.64

and −3.65 eV, respectively, which are sufficiently low to be used as the potential n-type materials.

In conclusion, we have described a novel and selective Cu-catalyzed C−H amination of the monofunctionalized hydrofullerenes with various amines. A variety of the new monoamine-substituted 1,4-bisadducts were synthesized in good to high yields. The experimental results indicated that the present reaction proceeds through the formation of a fullerene monoradical by an amine followed by coupling with an amine radical generated by a $CuBr_2$ catalyst under an oxygen atmosphere. The optical properties of the new 1,4-fullerenes compared to the methanofullerene showed increased absorption bands in the visible region. This methodology provides a valuable and general synthetic tool for the synthesis of a new series of 1,4-fullerenes having various monoamine addends which are expected to be useful in electronic device applications.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data. 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

This work was supported by a Scientific Research (B) from the Japan Society for Promotion of Science (JSPS) (No. 25288043), a Grant-in-Aid for Scientific Research on Innovative Areas “Organic Synthesis Based on Reaction Integration. Development of New Methods and Creation of New Substances” from the MEXT (Japan), and World Premier International Research Center Initiative (WPI), MEXT (Japan). We also thank the support of Showa Denko Group Institute for Advanced and Core Technology. W.S. acknowledges the support of the China Scholarship Council (CSC).

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