JOC The Journal of Organic Chemistry

Article

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Synthesis and Functionalization of Symmetrical 2,5-Diaryl Fulleropyrrolidines: Ferric Perchlorate-Mediated One-Step Reaction of [60]Fullerene with Arylmethanamines

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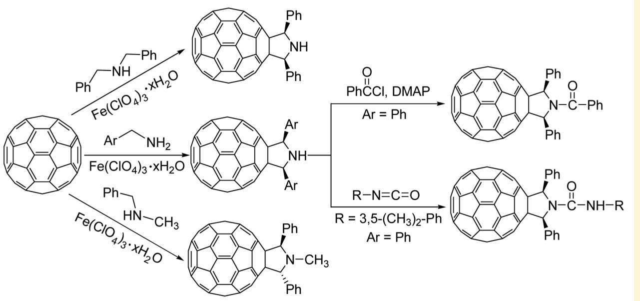
Supporting Information

ABSTRACT: A series of scarce N-unsubstituted 2,5-diaryl fulleropyrrolidines as cis isomers could be prepared via the facile one-step reaction of [60]fullerene with N-unsubstituted arylmethanamines promoted by cheap and easily available ferric perchlorate. Nevertheless, the reaction of N-substituted arylmethanamines with [60]fullerene under the same conditions gave different experimental results. *N*-Methylbenzylamine formed *N*-methyl 2,5-diphenyl fulleropyrrolidine as a trans isomer, and *N*,*N*-dibenzylamine unexpectedly afforded the N-unsubstituted 2,5-diphenyl fulleropyrrolidine as a cis isomer. Intriguingly, high stereoselectivity for all 2,5-diaryl fulleropyrrolidines could be observed although both cis and trans isomers were possibly formed. N-Unsubstituted fulleropyrrolidine could be further converted to N-substituted fulleropyrrolidines under the assistance of an acid chloride or an isocyanate. A possible reaction pathway leading to 2,5-diaryl fulleropyrrolidines is also proposed.



■ INTRODUCTION

Since the availability of fullerenes in a macroscopic amount,[1] the functionalization of fullerenes has become one of the most developing fields of fullerene research because a large variety of fullerene derivatives exhibit a wide range of valuable properties and have therefore been utilized in many fields such as medicinal chemistry, material science, and nanotechnology.[2] 1,3-Dipolar cycloaddition reaction is one of the most powerful and versatile methods for functionalizing fullerenes because they were found to be easily controlled and tend to give the readily separable and well-defined products with good yields.[3,4] Among a large number of fullerene derivatives obtained via the 1,3-dipolar cycloadditions, fulleropyrrolidines[4] have occupied a prominent place attributed to their increasing application in the target-directed synthesis of new materials and potential biologically active compounds. For instance, some synthesized fulleropyrrolidine derivatives have recently served as the acceptors of photovoltaic solar cells and have exhibited a higher power conversion efficiency (PCE) than that of [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) under the same conditions.[5] Pioneering work on fulleropyrrolidine derivatives was conducted by Prato and co-workers through the reaction of [60]fullerene (C_{60}) with azomethine ylides generated in situ by decarboxylation of immonium salts derived from condensation of α-amino acids with aldehydes/ketones (Prato reaction).[6] Fulleropyrrolidines could also be synthesized through several alternative methods such as thermal ring opening of aziridines,[6,7] thermal loss of CO_2 from oxazolidinones,[6,8] acid-catalyzed[9a] or thermal desilylation[9b] of trimethylsilyl amino derivatives, tautomerization of imines,[10] reaction with aldehydes in the presence of aqueous ammonia,[11a] picolylamines,[11b] and dibenzylamine,[11c] thermal reaction of α-amino acids and amino acid esters,[12] or reaction of halides and amino acids.[13] Photochemical treatment of tertiary amines,[14] α-amino acid esters,[15a,b] or aminopolycarboxylic esters[15c] with C_{60} was also applied to prepare pyrrolidine derivatives. Although many fulleropyrrolidines have been synthesized by the aforementioned approaches, these known protocols still have some synthetic limitations, that is, the difficulty in the preparation of

Received: October 17, 2015
Published: February 4, 2016

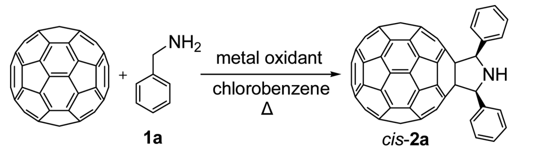
2,5-diaryl fulleropyrrolidines together with the poor stereoselectivity of 2,5-disubstituted fulleropyrrolidines. For example, the Prato reaction has almost never been utilized for the synthesis of 2,5-diaryl fulleropyrrolidines since starting α-aryl-substituted amino acids are hardly available.[4a,b] The tautomerization of imine reported by Troshin's group only afforded a few 2,5-dipyridyl fulleropyrrolidines owing to the very limited scope of substrates.[11b] Moreover, 2,5-disubstituted fulleropyrrolidines with rare exceptions always afford a mixture of cis and trans isomers.[4a,b,16] On the other hand, 2,5-diaryl fulleropyrrolidines may have a great potential application in designing a broad range of diad and triad donor−acceptor systems to study their photophysical and electrochemical properties.[4b,c] Therefore, it is still necessary to develop a more practical and convenient method for the preparation of fulleropyrrolidines, especially the rare 2,5-diaryl fulleropyrrolidines with high stereoselectivity.

Recently, some transition metal salts[17,18] have been successfully employed as promoters to functionalize fullerenes to obtain a large variety of fullerene derivatives with different structural motifs. For example, a large number of novel fullerene derivatives including oxazolines, 1,3-dioxolanes, disubstituted lactones, boronic esters, 1,2-fullerenols, hemiketals, oxazolidinofullerenes/thiazolidinofullerenes, and dioxanes/dioxepanes have been prepared by $Fe(ClO_4)_3$-mediated reactions of C_{60} with nitriles,[19a] aldehydes/ketones,[19b] malonate esters,[19c] arylboronic acids,[19d] acid chlorides,[19e] β-keto esters,[19f] isocyanates/isothiocyanates,[19g] and diols,[19h] respectively. In continuation of our interest in the $Fe(ClO_4)_3$-mediated reactions of C_{60},[19] herein we describe the synthesis of symmetrical 2,5-diaryl fulleropyrrolidines with high stereoselectivity by the $Fe(ClO_4)_3$-mediated reaction of C_{60} with arylmethanamines and also disclose further conversion of N-unsubstituted fulleropyrrolidine into N-substituted fulleropyrrolidines in the presence of an acid chloride or an isocyanate.

■ RESULTS AND DISCUSSION

At the onset, benzylamine (**1a**) as the typical substrate was chosen to react with C_{60} without the addition of any promoter. To our disappointment, no obvious product *cis*-**2a** could be observed when the reaction was conducted in the absence of promoter (entry 1, Table 1), which meant that the existence of promoter played a crucial role in the successful synthesis of *cis*-**2a**. In our previous study, $Fe(ClO_4)_3$ as a metal oxidant has been proved to be an efficient promoter for a large variety of fullerene reactions,[19] and thus $Fe(ClO_4)_3$ was first selected as a promoter. Much to our satisfaction, the reaction was found to proceed well and gave the desired 2,5-diaryl fulleropyrrolidine **2a** as a cis isomer in as high as 44% yield when the reaction mixture of C_{60}, $Fe(ClO_4)_3$, and **1a** in a molar ratio of 1:2:20 was stirred in chlorobenzene at 120 °C for 23 h under air conditions (entry 2, Table 1). Increasing the reaction temperature to 130 °C only led to a comparable yield of *cis*-**2a** (entry 3, Table 1), while decreasing the reaction temperature to 100 °C drastically reduced the isolated yield of *cis*-**2a** (entry 4, Table 1). It was found that changing the amount of $Fe(ClO_4)_3$ (from 1 to 5 equiv) and benzylamine (from 5 to 30 equiv) had no benefit to improving the reaction efficiency (entries 5−9, Table 1). When the reaction was performed under a nitrogen atmosphere, the yield of *cis*-**2a** was almost the same as that under air conditions, indicating that oxygen in air has no influence on the reaction (entry 2 vs entry 10, Table 1). Accordingly, the reagent molar ratio of C_{60}/

Table 1. Optimization of Reaction Conditions for the $Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Benzylamine 1a[a]



1a *cis*-**2a**

entry	metal oxidant	molar ratio[b]	temp (°C)	time (h)	yield (%) of *cis*-**2a**[c]
1	none	1:0:20	120	23	0
2	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:20	120	23	44 (85)
3	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:20	130	24	43 (80)
4	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:20	100	24	<5
5	$Fe(ClO_4)_3{\cdot}xH_2O$	1:1:20	120	25	23 (88)
6	$Fe(ClO_4)_3{\cdot}xH_2O$	1:5:20	120	21	36 (77)
7	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:5	120	24	<5
8	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:10	120	24	12 (33)
9	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:30	120	24	44 (73)
10[d]	$Fe(ClO_4)_3{\cdot}xH_2O$	1:2:20	120	24	42 (91)
11	$Mg(ClO_4)_2$	1:2:20	120	51	16 (50)
12	$CuCl_2{\cdot}2H_2O$	1:2:20	120	24	trace
13	$CuCl_2$	1:2:20	120	23	trace
14	$FeCl_3{\cdot}6H_2O$	1:2:20	120	28	trace
15	$FeCl_3$	1:2:20	120	27	trace
16	$Mn(OAc)_3{\cdot}H_2O$	1:2:20	120	23	trace
17	$Cu(OAc)_2{\cdot}H_2O$	1:2:20	120	1.5	trace
18	$Pb(OAc)_4$	1:2:20	120	24	<5
19	$(NH_4)_2Ce(NO_3)_6$	1:2:20	120	24	trace

[a]Unless otherwise indicated, all reactions were performed under air conditions. [b]Molar ratio refers to $C_{60}/Fe(ClO_4)_3{\cdot}xH_2O/$**1a**. [c]Isolated yield; those in parentheses were based on consumed C_{60}. [d]The reaction was conducted under nitrogen conditions.

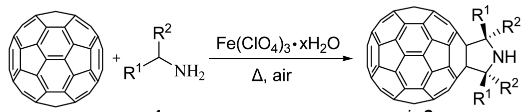
$Fe(ClO_4)_3$/**1a** as 1:2:20, the reaction temperature as 120 °C together with the air conditions were chosen as the optimized reaction conditions. It should be noted that metal oxidants such as $Mg(ClO_4)_2$, $CuCl_2{\cdot}2H_2O$, $CuCl_2$, $FeCl_3{\cdot}6H_2O$, $FeCl_3$, $Mn(OAc)_3{\cdot}2H_2O$, $Cu(OAc)_2{\cdot}H_2O$, $Pb(OAc)_4$, and $(NH_4)_2Ce(NO_3)_6$ have also been examined as promoters under the optimized conditions (entries 11−19, Table 1), and it was found that $Fe(ClO_4)_3$ was obviously superior to other metal oxidants. For example, only 16% yield of product *cis*-**2a** was obtained in the presence of $Mg(ClO_4)_2$ even by extending the reaction time to 51 h (entry 11, Table 1). As for $CuCl_2{\cdot}2H_2O$, $CuCl_2$, $FeCl_3{\cdot}6H_2O$, $FeCl_3$, $Mn(OAc)_3{\cdot}2H_2O$, $Cu(OAc)_2{\cdot}H_2O$, $Pb(OAc)_4$, and $(NH_4)_2Ce(NO_3)_6$ (entries 12−19, Table 1), less than 5% or a trace amount of product yield was generally observed.

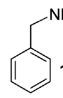
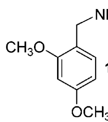
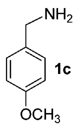
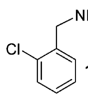
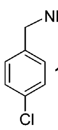
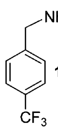
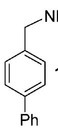
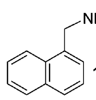
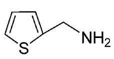
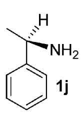
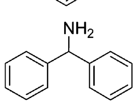
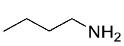
With the optimized conditions in hand, this reaction could be extended to other arylmethanamines such as 2,4-dimethoxybenzylamine (**1b**), 4-methoxybenzylamine (**1c**), 2-chlorobenzylamine (**1d**), 4-chlorobenzylamine (**1e**), 4-(trifluoromethyl)-benzylamine (**1f**), 4-phenylbenzylamine (**1g**), 1-naphthalenemethylamine (**1h**), and 2-thiophenemethylamine (**1i**), and were found to generate the desired 2,5-diaryl fulleropyrrolidine *cis*-**2b−i**, respectively. Additionally, (*R*)-(+)-α-methylbenzylamine (**1j**), aminodiphenylmethane (**1k**), and *n*-butylamine (**1l**) were also investigated. The reaction conditions and yields for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with amines **1a−l** are summarized in Table 2.

As can be seen from Table 2, all of the examined arylmethanamines including phenylmethanamines bearing

DOI: 10.1021/acs.joc.5b02412
J. Org. Chem. 2016, 81, 1769−1777

Table 2. Reaction Conditions and Yields for the Reaction of C_{60} with Amines 1a–l in the Presence of $Fe(ClO_4)_3$[a]

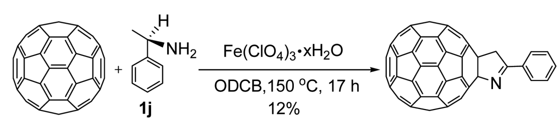


amine **1**	time (h)	yield of *cis*-**2**[b] (%)
 **1a**	23	44 (85)
 **1b**	12	56 (74)
 **1c**	36	25 (93)
 **1d**	24	36 (82)
 **1e**	24[c]	30 (73)
 **1f**	24	21 (78)
 **1g**	23	33 (75)
 **1h**	22	18 (82)
 **1i**	25	22 (92)
 **1j**	48	0
 **1k**	24	0
 **1l**	21	0

[a]All reactions were performed in chlorobenzene (10 mL) under air conditions at 120 °C unless otherwise indicated, molar ratio refers to $C_{60}/Fe(ClO_4)_3{\cdot}xH_2O/1$ = 1:2:20. [b]Isolated yield, those in parentheses were based on consumed C_{60}. [c]The reaction of C_{60} with **1e** was conducted in *o*-dichlorobenzene (6 mL) at 150 °C.

either electron-donating or electron-withdrawing groups (**1a**–**g**), 1-naphthalenemethylamine (**1h**), and 2-thiophenemethylamine (**1i**) could be successfully utilized to synthesize symmetrical 2,5-diaryl fulleropyrrolidines **2a**–**i** as cis isomers in valuable yields ranging from 18 to 56% (73–93% based on consumed C_{60}). In the case of 4-chlorobenzylamine (**1e**), raising the reaction temperature to 150 °C together with changing the reaction solvent to *o*-dichlorobenzene (ODCB) could provide an acceptable yield (29%) of fulleropyrrolidine *cis*-**2e**. The Cl group of *cis*-**2d** or *cis*-**2e** is a valuable precursor and could be further transformed to other moieties. Compared with benzylamine (**1a**), 1-naphthalenemethylamine (**1h**) obviously decreased the product yield (18%), probably due to the great steric hindrance of two naphthyl groups. As for (*R*)-(+)-*α*-methylbenzylamine (**1j**), aminodiphenylmethane (**1k**), and *n*-butylamine (**1l**), no anticipated fulleropyrrolidine derivatives were observed even by increasing the amount of **1j**–**l** or by raising the reaction temperature and prolonging the reaction time. However, a few nonfullerene products from **1j** were observed probably due to the partial oxidation of **1j**. Interestingly, the reaction with **1k** could not afford any products, and thus starting material **1k** totally remained. As for *n*-butylamine (**1l**), the entire starting material **1l** had been completely consumed, and many nonfullerene products had been formed. Therefore, the reason for the failure to produce fulleropyrrolidine derivatives via the reaction of C_{60} with **1j**–**l** under the assistance of $Fe(ClO_4)_3$ was mainly attributed to the easy oxidation or degradation for **1j**,**l** together with the great steric hindrance for **1j**,**k**. It should be noted that the reaction of C_{60} with **1j** at 150 °C in ODCB for 17 h unexpectedly produced the fulleropyrroline **3** in 12% of isolated yield (Scheme 1), although **1j** could not afford the desired fulleropyrrolidine under various reaction conditions, and the suggested reaction pathway for the formation of fulleropyrroline **3** is outlined in Scheme S1 in Supporting Information.

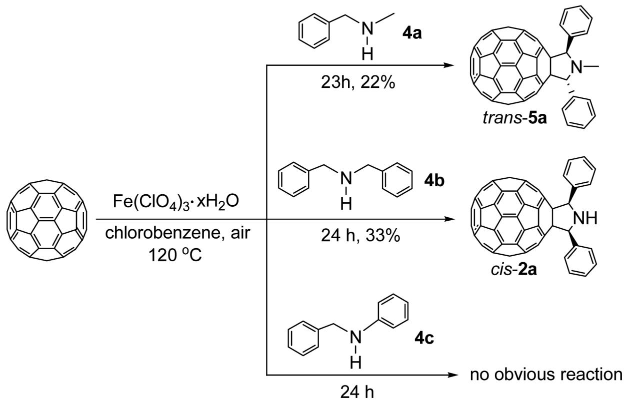
Scheme 1. Reaction of C_{60} with (*R*)-(+)-*α*-Methylbenzylamine 1j Promoted by $Fe(ClO_4)_3$, Affording Fulleropyrroline 3



To expand the scope of the reaction, three representative N-substituted arylmethanamines, that is, *N*-methylbenzylamine (**4a**), *N*,*N*-dibenzylamine (**4b**), and *N*-phenylbenzylamine (**4c**), were also selected to react with C_{60} in the presence of $Fe(ClO_4)_3$ (Scheme 2). We found that the reaction of C_{60}, $Fe(ClO_4)_3$, and *N*-methylbenzylamine (**4a**) under standard conditions, that is, in a molar ratio of $C_{60}/Fe(ClO_4)_3{\cdot}xH_2O/\mathbf{4a}$ as 1:2:20 in chlorobenzene at 120 °C under air conditions, afforded the desired *N*-methyl 2,5-diphenyl fulleropyrrolidine **5a** as a trans isomer in 22% yield. However, similar treatment of C_{60} with *N*,*N*-dibenzylamine (**4b**) and *N*-phenylbenzylamine (**4c**) failed to produce the anticipated N-substituted 2,5-diayl fulleropyrrolidines. The reaction of C_{60} with *N*,*N*-dibenzylamine (**4b**) mainly gave the unexpected N-unsubstituted 2,5-diphenyl fulleropyrrolidine **2a** as a cis isomer in 33% yield, while the reaction of C_{60} with *N*-phenylbenzylamine (**4c**) could not afford obvious fullerene products although different reaction conditions were attempted. Intriguingly, the isolated yield of fulleropyrrolidine *trans*-**5a** could be drastically increased from 22% to 52% and the reaction time could also be noticeably shortened from 23 to 4 h when the reaction of C_{60}, $Fe(ClO_4)_3$, and *N*-methylbenzylamine (**4a**) was conducted in

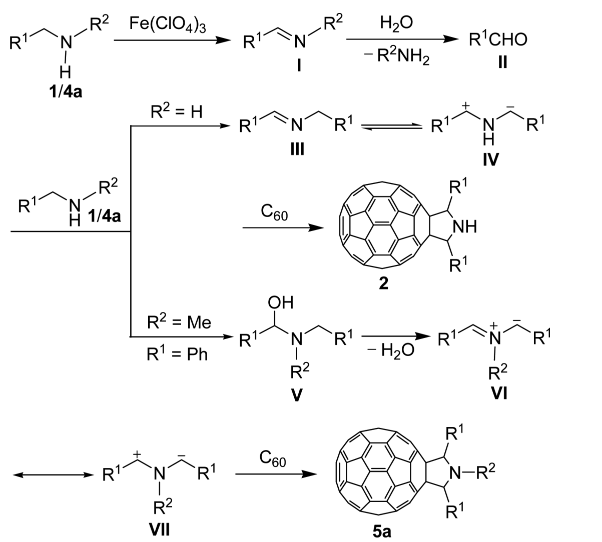
DOI: 10.1021/acs.joc.5b02412
J. Org. Chem. 2016, 81, 1769–1777

Scheme 2. Reaction of C_{60} with *N*-Methylbenzylamine, *N*,*N*-Dibenzylamine, and *N*-Phenylbenzylamine in the Presence of $Fe(ClO_4)_3$



the presence of 5 equiv of benzaldehyde under standard conditions. These experimental results would provide strong evidence for our suggested mechanism for the formation of fulleropyrrolidines **2**/**5a** shown in Scheme 3. Furthermore, we

Scheme 3. Proposed Reaction Mechanism for the Formation of 2,5-Diaryl Fulleropyrrolidines



had also studied the reaction of C_{60}, $Fe(ClO_4)_3$, and *N*-phenylbenzylamine (**4c**) with the addition of 5 equiv of benzaldehyde under the same conditions for 24 h. Unfortunately, the desired fulleropyrrolidine was still not obviously observed even by increasing the amount of benzaldehyde to 20 equiv. The direct conjugation between the phenyl and amine groups may play a crucial role in reducing the reactivity of *N*-phenylbenzylamine (**4c**). In addition, a plausible reaction mechanism for the formation of *cis*-**2a** from **4b** was provided in Scheme S3 in Supporting Information.

Products *cis*-**2a**,[16] **3**,[20] and *trans*-**5a**[14c] are known compounds, and their identities were confirmed by comparing their spectral data with those reported previously. As for new compounds *cis*-**2b**−**i**, their structures were fully characterized by their HRMS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectra. All high-resolution mass spectra of these new products gave the correct $[M + H]^+$ peaks along with the signals at about 720 arising from the loss of the addends. Their UV−vis spectra resemble those of other fulleropyrrolidine derivatives[6−16] and showed a peak at 431−434 nm, which is a characteristic absorption for the 1,2-adduct of C_{60}. Their IR spectra displayed the absorptions at 3309−3330 cm^{-1}, corresponding to the stretching vibrations of the NH group. In their ^{1}H NMR spectra, the expected chemical shifts along with the splitting patterns for all protons were observed. In their ^{13}C NMR spectra, there were no more than 30 peaks including some overlapped ones due to the 58 sp^2-carbons of the fullerene moiety, agreeing with the C_s symmetry of the molecular structures, and the peaks for the two sp^3-carbons of the C_{60} cage appeared at 75.23−76.17 ppm. It should be noted that the stereochemistry of the products **2a**−**i** and **5a** could be assigned based on their ^{13}C NMR spectra. For symmetrical fulleropyrrolidines **2a**−**i** and **5a**, the cis isomers should theoretically display 32 peaks including 4 half-intensity ones (corresponding to 1C) for the carbons of fullerene skeleton because of their C_s symmetry, while the trans isomers should show 30 peaks with equal intensity owing to their C_2 symmetry. Experimentally, half-intensity peaks were found in all ^{13}C NMR spectra of fulleropyrrolidines **2a**−**i**, yet equal intensity 30 peaks were only observed in the ^{13}C NMR spectrum of fulleropyrrolidine **5a**. Accordingly, fulleropyrrolidines **2a**−**i** and **5a** were unambiguously assigned as cis isomers and trans isomer, respectively.

Up to now, fulleropyrrolidines have been mainly synthesized via the 1,3-dipolar cycloaddition reactions of azomethine ylides with fullerenes.[6−13,16] Azomethine ylides can be generated in different ways such as decarboxylation of immonium salts (Prato reaction)[6] and tautomerization of imines.[10,11b,c] Recently, thermal tautomerization of imines to azomethine ylides to prepare fulleropyrrolidines has been extended by different research groups.[10c,11b,c] Imines can be easily formed by the direct condensation reaction[11b,c] of aldehydes and amines or by the oxidation of arylmethanamines in the presence of metal oxidants.[21] We thus conjectured that the reaction pathway for the formation of 2,5-diaryl fulleropyrrolidines via the $Fe(ClO_4)_3$-mediated reaction of C_{60} with arylmethanamines might undergo the tautomerization of imines because $Fe(ClO_4)_3$ as a metal oxidant has the ability to transform arylmethanamines to the corresponding imines.

On the basis of the previously suggested reaction mechanisms for the formation of fulleropyrrolidines via thermal tautomerization of imines[10,11b,c] together with the proposed reaction pathways for the preparation of imines by the oxidation of arylmethanamines with the aid of metal oxidants,[21] the possible formation mechanism for 2,5-diaryl fulleropyrrolidines **2**/**5a** from the reaction of C_{60} and arylmethanamines **1**/**4a** in the presence of $Fe(ClO_4)_3$ is shown in Scheme 3. A chosen arylmethanamine **1**/**4a** is first dehydrogenated by the reaction of **1**/**4a** with $Fe(ClO_4)_3$ to generate Schiff-base imine intermediate **I**. The oxidative dehydrogenation reactions of arylmethanamines in the presence of metal oxidants have been extensively reported in previous literature.[21] Hydrolysis of imine intermediate **I** accompanied by the elimination of R^2NH_2 forms the corresponding aldehyde **II**. When R^2 = H, the direct condensation of aldehyde **II** with another molecule of arylmethanamine forms a new imine intermediate **III**, followed by tautomerization to produce azomethine ylide **IV**, which can undergo a concerted 1,3-dipolar cycloaddition to C_{60} to afford fulleropyrrolidines **2**. When R^2 = Me, the nucleophilic addition of aldehyde **II** with arylmethanamine **4a** leads to the formation of intermediate **V**. Subsequent dehydration of intermediate **V**

DOI: 10.1021/acs.joc.5b02412
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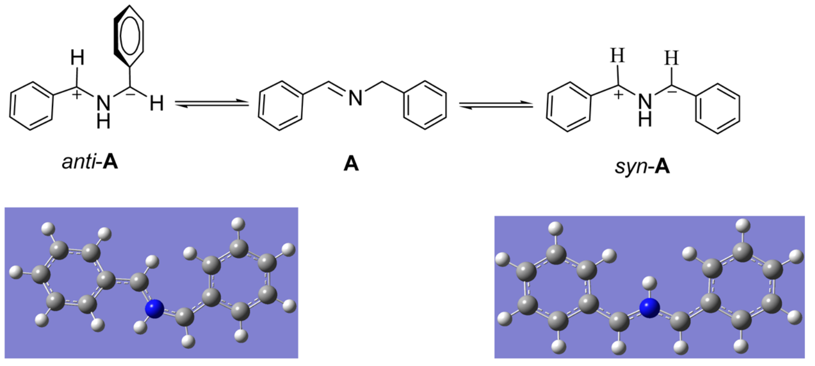
Scheme 4. Thermal Tautomerization of Imine A



results in the generation of dipoles **VI**, which can give its resonance structure **VII**, followed by cycloaddition to C_{60} to generate fulleropyrrolidine **5a**.

It should be noted that 2,5-diaryl fulleropyrrolidines **2**/**5a** obtained through the reaction of C_{60} with arylmethanamines in the presence of $Fe(ClO_4)_3$ exhibited high stereoselectivity, that is, fulleropyrrolidines **2a**−**i** were formed as cis isomers and fulleropyrrolidine **5a** was obtained as a trans isomer based on their ^{1}H NMR and ^{13}C NMR spectra. Intriguingly, no obvious trans isomers of fulleropyrrolidines **2a**−**i** along with cis isomer of fulleropyrrolidine **5a** were observed although they were also possibly formed, probably because their yields were too low to permit their isolation and spectroscopic characterization. As for the stereoselectivity of fulleropyrrolidines **2**/**5a** during the reaction progress, benzylamine (**1a**) as the representative substrate has been investigated. The experimental results indicated that no obvious *trans*-**2a** was produced based on the ^{1}H NMR measurement when the reaction was manipulated under the same experimental conditions for 7, 12, 18, and 24 h, respectively (see Supporting Information). Therefore, the stereoselectivity of **2**/**5a** has no correlation with reaction time. Although the exact reasons for the stereoselective synthesis of 2,5-diaryl fulleropyrrolidines **2**/**5a** are not completely clear, the stability of azomethine ylides should play a crucial role in the successful realization of their high stereoselectivity. In the case of arylmethanamines **1a**−**i**, benzylamine (**1a**) was chosen as the typical substrate to elucidate the stereoselectivity of fulleropyrrolidines **2a**−**i**. As shown in Scheme 4, imine **A** from the transformation of benzylamine (**1a**) with the aid of $Fe(ClO_4)_3$ can undergo a thermal tautomeric equilibration between **A** and *anti*-**A**, or between **A** and *syn*-**A**. The formed *anti*-**A** and *syn*-**A** may further react with C_{60} via 1,3-dipolar cycloaddition of azomethine ylides to afford the expected *trans*-**2a** and *cis*-**2a**, respectively. However, azomethine ylide *anti*-**A** is less stable than *syn*-**A**, because the interactions between the bulky phenyl group and the α-hydrogen atom prevent the phenyl ring from becoming coplanar with the nitrogen atom. Also, the out-of-plane phenyl group of *anti*-**A** can hinder the approach of azomethine ylide to the surface of C_{60}. Additionally, a B3LYP/6-31G(d) energy calculation for *anti*-**A** and *syn*-**A** at 393.15 K had also been conducted, and the optimized results indicated that *syn*-**A** was planar and about 16.36 kJ/mol more stable than the structure of *anti*-**A** with one out-of-plane phenyl group. Therefore, the cis isomer is expected to be the predominant product. In fact, no obvious *trans* isomers could be isolated for all the reaction of arylmethanamines **1a**−**i**.

As for arylmethanamine **4a**, its N-substituted 2,5-diaryl fulleropyrrolidine **5a** was obtained as a trans isomer, in contrast to the cis isomers of above-described N-unsubstituted 2,5-diaryl fulleropyrrolidines **2a**−**i**. The reversed stereoselectivity of **5a** is obviously attributed to the presence of a bulky group attached to the nitrogen atom. Scheme 3 have indicated that dipoles **VI** can give its resonance structure **VII** (azomethine ylide), which exists in three conformations, that is, W-shaped, U-shaped, and S-shaped (Figure 1). 1,3-Dipolar cycloaddition reaction of the

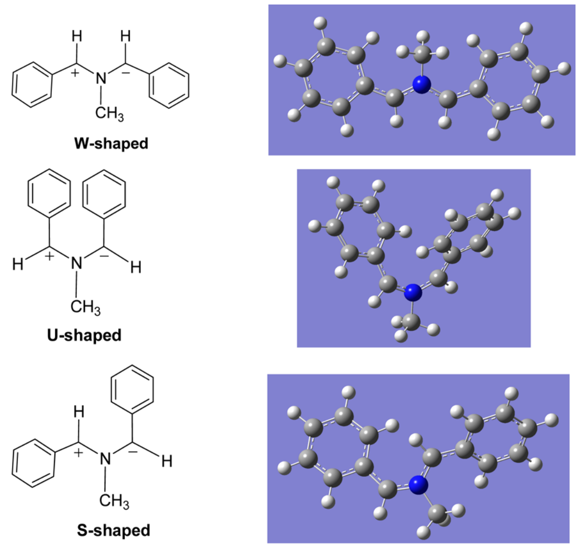


Figure 1. Conformations of intermediate **VII**.

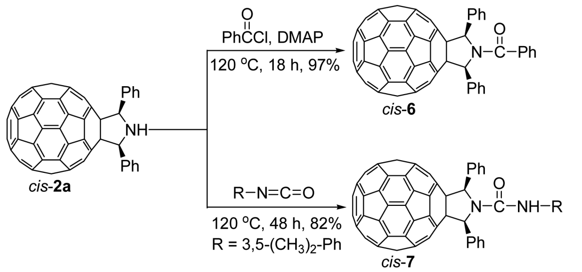
S-shaped ylide should generate a *trans* fulleropyrrolidine, while W- and U-shaped ylides are expected to give a cis product. Theoretical B3LYP/6-31G(d) calculations at 393.15 K disclosed that the S-shaped conformation is 1.97 and 11.92 kJ/mol more stable than the U- and W-shaped geometries, respectively. Thus, the computational results are in line with the experimental data although the energy difference between S-shaped and U-shaped is relatively small.

The N-unsubstituted 2,5-diaryl fulleropyrrolidines are valuable precursors and can be employed for further functionalization via the transformation of their NH group. However, the reactivity of the NH group in fulleropyrrolidine is sometimes quite different from that of NH group in the nonfullerene analogues. For instance, the basicity of fulleropyrrolidine N has been found to drop several orders of magnitude compared with that of the corresponding pyrrolidine N, and thus functionalization of the N is quite

DOI: 10.1021/acs.joc.5b02412
J. Org. Chem. 2016, 81, 1769−1777

difficult under normal conditions.[4a,22] To our delight, the reactions of N-unsubstituted 2,5-diaryl fulleropyrrolidine *cis*-**2a** with benzoyl chloride and 3,5-dimethylphenyl isocyanate were found to proceed readily under mild conditions and could produce the rare N-substituted 2,5-diaryl fulleropyrrolidines as cis isomers (Scheme 5), which would be extremely difficult to synthesize by traditional methods. As shown in Scheme 5, the treatment of *cis*-**2a** with benzoyl chloride under the assistance of 4-dimethylaminopyridine (DMAP) at 120 °C for 18 h successfully afforded the rare N-substituted 2,5-diphenyl fulleropyrrolidine *cis*-**6** in 97% yield. As for 3,5-dimethylphenyl isocyanate, the reaction with *cis*-**2a** without the addition of DMAP at 120 °C for 48 h yielded the desired fulleropyrrolidine *cis*-**7** in 82% yield. It should be noted that C_{60} was also formed as a byproduct through the partial decomposition of *cis*-**2a**, but in a much lower amount than that of the desired product, in the reactions of *cis*-**2a** with benzoyl chloride and 3,5-dimethylphenyl isocyanate.

Scheme 5. Reaction of N-Unsubstituted 2,5-Dipheyl Fulleropyrrolidine *cis*-2a with Benzoyl Chloride and 3,5-Dimethylphenyl Isocyanate



Products *cis*-**6** and *cis*-**7** were also fully characterized by their HRMS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectra. In their ^{1}H NMR spectra, the disappearance of the singlet for NH indicated that the proton from NH had been substituted by other motifs. In their ^{13}C NMR spectra, the typical peak for the C═O carbon appeared at 157.88−172.80 ppm, and no more than 27 peaks including some overlapped ones for the 58 sp^2-carbons of the C_{60} moiety were observed in the range of 135−154 ppm, consistent with the C_s symmetry of their molecular structures, which meant that *cis*-**6** and *cis*-**7** were also cis isomers. In their IR spectra, the strong absorptions at 1648−1675 cm^{-1} further confirmed the presence of the C═O moiety.

■ CONCLUSION

In summary, symmetrical 2,5-diaryl fulleropyrrolidines with high stereoselectivity have been effectively prepared by the $Fe(ClO_4)_3$-mediated one-step reaction of C_{60} with various arylmethanamines. The successful synthesis of symmetrical 2,5-diaryl fulleropyrrolidines, especially the unprecedented 2,5-di(diphenyl) fulleropyrrolidine, 2,5-di(naphthyl) fulleropyrrolidine, and 2,5-di(thienyl) fulleropyrrolidine, would provide an immense opportunity for researchers in material field to design and synthesize a large variety of novel organic photovoltaic materials. In addition, further derivation of N-unsubstituted 2,5-diphenyl *cis*-fulleropyrrolidine through the reaction with benzoyl chloride and 3,5-dimethylphenyl isocyanate afforded the unreported N-substituted 2,5-diaryl fulleropyrrolidines as cis isomers. A possible reaction mechanism together with a plausible explanation for the stereoselective formation of 2,5-diaryl fulleropyrrolidines are provided.

■ EXPERIMENTAL SECTION

General Methods. All reagents and solvents were used directly as obtained commercially without further purification. All reactions were carried out under air conditions without the use of air-sensitive techniques. Reactions were monitored by thin layer chromatography (TLC) using carbon disulfide/toluene as developing solvent. All of the fullerene products were purified by flash chromatography over silica gel. The UV−vis spectra were taken in $CHCl_3$. IR spectra were measured with KBr pellets. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a 400 MHz NMR spectrometer. Chemical shifts in ^{1}H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm, and chemical shifts in ^{13}C NMR spectra were referenced to residual $CHCl_3$ at 77.16 ppm or DMSO at 39.52 ppm. High-resolution mass spectrometry (HRMS) was performed by MALDI-TOF in positive-ion mode with 4-hydroxy-α-cyanocinnamic acid as the matrix.

General Procedure for the $Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Arylmethylamines 1a−l. A mixture of C_{60} (36.0 mg, 0.0500 mmol), $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.100 mmol), and a given amount of arylmethylamine **1** (1.00 mmol) was added to a 50 mL round-bottom flask. After they were completely dissolved in chlorobenzene (10 mL, 6 mL of ODCB for **1e**) by sonication, the resulting solution was heated with stirring in an oil bath preset at 120 °C (150 °C for **1e**) under air conditions. The reaction was carefully monitored by thin-layer chromatography (TLC) and stopped at the designated time. The reaction mixture was filtered through a silica gel plug in order to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent to afford first unreacted C_{60} and then fulleropyrrolidine *cis*-**2** as an amorphous brown solid.

$Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Benzylamine 1a under Different Conditions. A 50 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer was charged with C_{60} (36.0 mg, 0.0500 mmol), metal oxidant (0.0500−0.250 mmol), and **1a** (0.250−1.50 mmol). After the added compounds were completely dissolved in chlorobenzene (10 mL) by sonication, the resulting solution was heated with stirring in an oil bath preset at 100−130 °C under air or nitrogen conditions for a designated time (1.5−51 h, monitored by TLC). The reaction mixture was filtered through a silica gel plug to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent to give unreacted C_{60} and fulleropyrrolidine *cis*-**2a**.[16]

Fulleropyrrolidine *cis*-2a. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.0500 mmol) with **1a** (109 μL, 1.00 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.100 mmol) for 23 h afforded first unreacted C_{60} (17.2 mg, 48%) and then *cis*-**2a**[16] (20.0 mg, 44%) as an amorphous brown solid.

Fulleropyrrolidine *cis*-2b. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.0500 mmol) with **1b** (157 μL, 1.00 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.100 mmol) for 12 h afforded first unreacted C_{60} (8.7 mg, 24%) and then *cis*-**2b** (28.9 mg, 56%) as an amorphous brown solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.99 (br.s, 2H), 6.52 (s, 1H), 6.50 (s, 1H), 6.42 (s, 2H), 6.23 (br.s, 2H), 3.75 (s, 6H), 3.70 (s, 6H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 159.47 (aryl C), 157.39 (aryl C), 154.66, 154.36, 146.13, 145.93, 145.27, 144.96, 144.94, 144.77, 144.68, 144.55, 144.01, 143.96, 143.82 (4C), 143.36, 143.25, 141.84 (1C), 141.79 (1C), 141.56, 141.46, 141.42, 141.11, 140.97, 140.84, 140.73, 140.46, 138.26 (4C), 135.31, 133.83, 128.97 (aryl C), 118.12 (aryl C), 104.33 (1C, aryl C), 104.21 (1C, aryl C), 97.71 (aryl C), 76.17 (sp^3-C of C_{60}), 67.22, 53.97 (4C); FT-IR ν/cm^{-1} (KBr) 3310, 2922, 2853, 1610, 1586, 1504, 1460, 1435, 1420, 1378, 1294, 1282, 1261, 1207, 1183, 1155, 1129, 1039, 918, 860, 834, 821, 798, 687, 616, 573, 526; UV−vis ($CHCl_3$) λ_{max}/nm 259, 313, 434; MALDI-TOF MS m/z calcd for $C_{78}H_{22}NO_4$ [M + H]$^+$ 1036.1549, found 1036.1548.

Fulleropyrrolidine *cis*-2c. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.0500 mmol) with **1c** (131 μL, 1.00 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.100 mmol) for 36 h afforded first unreacted C_{60} (26.4 mg, 73%) and then *cis*-**2c** (12.4 mg, 25%) as

DOI: 10.1021/acs.joc.5b02412
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an amorphous brown solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.81 (d, J = 8.2 Hz, 4H), 6.85 (d, J = 8.2 Hz, 4H), 5.82 (s, 2H), 4.09 (s, 1H), 3.73 (s, 6H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 158.58 (aryl *C*), 153.64, 153.14, 146.20, 146.14, 145.46, 145.26, 145.23, 145.10, 144.85 (3C), 144.62 (1C), 144.50, 144.27, 144.20, 144.14, 143.72, 143.42, 142.17 (1C), 142.02 (1C), 141.66, 141.59, 141.44, 141.25, 141.11 (4C), 141.00, 140.55, 139.01, 138.43, 136.06, 135.09, 129.48 (aryl *C*), 128.93 (aryl *C*), 128.84 (aryl *C*), 113.22 (aryl *C*), 113.13 (aryl *C*), 75.96 (sp^3-*C* of C_{60}), 73.81, 54.16 (1C), 54.08 (1C); FT-IR ν/cm^{-1} (KBr) 3330, 2924, 2851, 1609, 1584, 1510, 1460, 1434, 1424, 1370, 1284, 1248, 1182, 1171, 1089, 1039, 825, 685, 610, 573, 545, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 310, 432; MALDI-TOF MS m/z calcd for $C_{76}H_{18}NO_2$ [M + H]$^+$ 976.1338, found 976.1339.

Fulleropyrrolidine *cis*-2d. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.0500 mmol) with **1d** (122 μL, 1.00 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.100 mmol) for 24 h afforded first unreacted C_{60} (20.2 mg, 56%) and then *cis*-**2d** (17.0 mg, 36%) as an amorphous brown solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 8.43 (d, J = 8.2 Hz, 2H), 7.40−7.34 (m, 4H), 7.25 (t, J = 7.5 Hz, 2H), 6.48 (s, 2H), 4.33 (s, 1H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 153.43, 153.23, 146.26, 146.15, 145.24 (4C), 145.07, 144.99, 144.93, 144.72 (1C), 144.64 (1C), 144.41, 144.33, 144.19 (4C), 143.55, 143.45, 142.05 (1C), 142.01 (1C), 141.70, 141.65, 141.61, 141.32, 141.11, 140.93, 140.89, 140.84, 138.81, 138.59, 135.83, 135.80, 134.63 (aryl *C*), 133.67 (aryl *C*), 130.41 (aryl *C*), 129.07 (aryl *C*), 128.50 (aryl *C*), 126.43 (aryl *C*), 75.26 (sp^3-*C* of C_{60}), 69.03 (1C), 68.90 (1C); FT-IR ν/cm^{-1} (KBr) 3321, 2918, 2848, 1511, 1474, 1462, 1427, 1376, 1266, 1182, 1048, 1035, 780, 754, 743, 712, 686, 547, 527; UV−vis ($CHCl_3$) λ_{max}/nm 258, 314, 431; MALDI-TOF MS m/z calcd for $C_{74}H_{12}ClN$ [M + H]$^+$ 949.0658, found 949.0659.

Fulleropyrrolidine *cis*-2e. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.0500 mmol) with **1e** (123 μL, 1.00 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.100 mmol) in ODCB (6 mL) at 150 °C for 24 h afforded first unreacted C_{60} (21.2 mg, 59%) and then *cis*-**2e** (14.2 mg, 30%) as an amorphous brown solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.91 (d, J = 7.4 Hz, 4H), 7.34 (d, J = 7.4 Hz, 4H), 5.87 (s, 2H), 4.54 (s, 1H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 146.18, 145.75, 145.24, 145.20, 145.08, 144.99, 144.83 (3C), 144.67 (1C), 144.50 (4C), 144.24 (6C), 144.12, 143.63, 143.36, 142.14 (1C), 142.00 (1C), 141.65, 141.56, 141.31, 141.18, 141.04, 140.97 (4C), 140.53, 139.02, 138.48, 136.38 (aryl *C*), 136.05, 135.13, 133.22 (aryl *C*), 129.22 (4C, aryl *C*), 127.84 (4C, aryl *C*), 75.45 (sp^3-*C* of C_{60}), 73.29; FT-IR ν/cm^{-1} (KBr) 3312, 2922, 2851, 1594, 1512, 1462, 1427, 1369, 1338, 1257, 1230, 1181, 1167, 1089, 856, 797, 786, 772, 612, 574, 527; UV−vis ($CHCl_3$) λ_{max}/nm 257, 311, 434; MALDI-TOF MS m/z calcd for $C_{74}H_{12}ClN$ [M + H]$^+$ 949.0658, found 949.0658.

Fulleropyrrolidine *cis*-2f. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.0500 mmol) with **1f** (143 μL, 1.00 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.100 mmol) for 24 h afforded first unreacted C_{60} (26.4 mg, 73%) and then *cis*-**2f** (11.0 mg, 21%) as an amorphous brown solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 8.14 (d, J = 7.7 Hz, 4H), 7.66 (d, J = 7.7 Hz, 4H), 5.98 (s, 2H), 4.82 (s, 1H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 152.31, 152.27, 146.26, 145.68, 145.31, 145.30, 145.16, 144.92, 144.83, 144.70 (1C), 144.60 (3C), 144.33 (4C), 144.20, 143.67, 143.43, 142.17 (3C), 142.10 (1C), 141.75, 141.64, 141.35, 141.25, 141.10, 141.01 (4C), 140.63, 139.11, 138.58, 136.20, 135.28, 129.13 (q, J_{C-F} = 31.9 Hz, aryl *C*), 128.42 (4C, aryl *C*), 124.51 (4C, aryl *C*), 120.44 (q, J_{C-F} = 271.2 Hz, aryl *C*), 75.41 (sp^3-*C* of C_{60}), 73.44; FT-IR ν/cm^{-1} (KBr) 3316, 2923, 2854, 1618, 1462, 1421, 1376, 1319, 1216, 1169, 1129, 1113, 1089, 1064, 1017, 880, 839, 764, 688, 575, 526; UV−vis ($CHCl_3$) λ_{max}/nm 255, 314, 433; MALDI-TOF MS m/z calcd for $C_{76}H_{12}F_6N$ [M + H]$^+$ 1052.0874, found 1052.0875.

Fulleropyrrolidine *cis*-2g. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.0500 mmol) with **1g** (183 mg, 1.00 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.100 mmol) for 23 h afforded first unreacted C_{60} (20.0 mg, 56%) and then *cis*-**2g** (17.8 mg, 33%) as an amorphous brown solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 8.04 (d, J = 7.6 Hz, 4H), 7.62 (d, J = 7.6 Hz, 4H), 7.53 (d, J = 6.9 Hz, 4H), 7.35 (t, J = 7.3 Hz, 4H), 7.25 (d, J = 6.4 Hz, 2H), 5.97 (s, 2H), 4.37 (s, 1H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 153.12, 152.90, 146.16, 146.01, 145.32, 145.22 (4C), 145.06, 144.81, 144.76 (1C), 144.57 (1C), 144.51, 144.22 (4C), 144.10, 143.64, 143.37, 142.10 (1C), 141.99 (1C), 141.62, 141.54, 141.38, 141.19, 141.06 (4C), 140.97, 140.53, 139.90, 139.52, 139.01, 138.48, 136.78, 136.17, 135.11, 128.43 (aryl *C*), 128.38 (aryl *C*), 128.09 (4C, aryl *C*), 126.63 (aryl *C*), 126.23 (4C, aryl *C*), 126.19 (4C, aryl *C*), 75.76 (sp^3-*C* of C_{60}), 73.97; FT-IR ν/cm^{-1} (KBr) 3315, 2927, 2855, 1601, 1520, 1486, 1462, 1427, 1410, 1376, 1356, 1278, 1215, 1182, 1156, 1116, 1073, 1007, 836, 762, 737, 694, 611, 573, 552, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 307, 431; MALDI-TOF MS m/z calcd for $C_{86}H_{22}N$ [M + H]$^+$ 1068.1752, found 1068.1751.

Fulleropyrrolidine *cis*-2h. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.0500 mmol) with **1h** (147 μL, 1.00 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.100 mmol) for 22 h afforded first unreacted C_{60} (28.0 mg, 78%) and then *cis*-**2h** (9.1 mg, 18%) as an amorphous brown solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 8.69 (d, J = 5.3 Hz, 4H), 7.80 (t, J = 8.8 Hz, 4H), 7.60 (t, J = 7.4 Hz, 2H), 7.45−7.37 (m, 4H), 6.98 (s, 2H), 4.27 (s, 1H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 154.17, 152.81, 146.47, 146.07, 145.07 (4C), 144.91, 144.80, 144.70, 144.54 (1C), 144.47 (1C), 144.32, 144.13, 144.04, 143.98, 143.47, 143.19, 141.96 (1C), 141.77 (1C), 141.51, 141.47, 141.27, 141.06, 140.94, 140.87, 140.78, 140.47, 138.48, 138.41, 135.38, 134.94, 134.02 (aryl *C*), 133.02 (aryl *C*), 131.25 (aryl *C*), 128.37 (1C, aryl *C*), 128.34 (1C, aryl *C*), 127.76 (1C, aryl *C*), 127.71 (1C, aryl *C*), 126.54 (aryl *C*), 125.17 (aryl *C*), 125.11 (aryl *C*), 124.85 (aryl *C*), 123.73 (aryl *C*), 75.88 (sp^3-*C* of C_{60}), 68.67; FT-IR ν/cm^{-1} (KBr) 3314, 2928, 2856, 1595, 1510, 1462, 1427, 1395, 1367, 1355, 1339, 1258, 1231, 1182, 1088, 1006, 946, 913, 864, 796, 784, 771, 694, 609, 573, 526; UV−vis ($CHCl_3$) λ_{max}/nm 258, 311, 432; MALDI-TOF MS m/z calcd for $C_{82}H_{18}N$ [M + H]$^+$ 1016.1439, found 1016.1439.

Fulleropyrrolidine *cis*-2i. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.0500 mmol) with **1i** (103 μL, 1.00 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.100 mmol) for 25 h afforded first unreacted C_{60} (27.4 mg, 76%) and then *cis*-**2i** (10.0 mg, 22%) as an amorphous brown solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.40 (br.s, 2H), 7.30 (d, J = 4.9 Hz, 2H), 7.00 (t, J = 3.7 Hz, 2H), 6.19 (s, 2H), 4.80 (s, 1H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 152.67, 152.30, 146.23, 146.01, 145.36, 145.30, 145.22, 145.06, 144.83 (3C), 144.59, 144.55 (1C), 144.30, 144.22, 144.14, 143.70, 143.36, 142.15 (1C), 141.99 (1C), 141.65, 141.62, 141.26 (6C), 141.14, 141.03, 141.00, 140.54, 139.00, 138.42, 136.30, 135.04, 126.02 (aryl *C*), 125.48 (aryl *C*), 124.99 (aryl *C*), 75.23 (sp^3-*C* of C_{60}), 69.93 (1C), 69.87 (1C); FT-IR ν/cm^{-1} (KBr) 3309, 2923, 2851, 1510, 1457, 1426, 1380, 1355, 1299, 1235, 1187, 1091, 1075, 1035, 853, 831, 764, 700, 614, 574, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 311, 431; MALDI-TOF MS m/z calcd for $C_{70}H_{10}NS_2$ [M + H]$^+$ 928.0255, found 928.0254.

Fulleropyrroline 3. By following the same experimental procedure as for the $Fe(ClO_4)_3{\cdot}xH_2O$-mediated reaction of C_{60} with amines **1a**−**l**, the reaction of C_{60} (36.0 mg, 0.0500 mmol) with **1j** (127 μL, 1.00 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.100 mmol) in ODCB (6 mL) at 150 °C for 17 h afforded first unreacted C_{60} (17.1 mg, 48%) and then **3**[20] (4.9 mg, 12%) as an amorphous brown solid.

Fulleropyrrolidine *trans*-5a. By following the same experimental procedure as for the $Fe(ClO_4)_3{\cdot}xH_2O$-mediated reaction of C_{60} with amines **1a**−**l**, the reaction of C_{60} (36.0 mg, 0.0500 mmol) with **4a** (129 μL, 1.00 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.100 mmol) for 23 h afforded first unreacted C_{60} (26.7 mg, 74%) and then *trans*-**5a**[14c] (10.3 mg, 22%) as an amorphous brown solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.89 (br.s, 4H), 7.43 (t, J = 7.9 Hz, 4H), 7.31 (t, J = 6.9 Hz, 2H), 6.11 (s, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 154.91, 153.02, 146.29, 145.31, 145.21, 145.15 (4C), 144.96, 144.92, 144.53, 144.45, 144.23, 144.21, 144.06, 143.52 (4C), 142.11, 141.61, 141.50, 141.14, 141.08 (4C), 140.96, 140.69, 140.65, 139.01, 138.61, 137.32, 135.81,

DOI: 10.1021/acs.joc.5b02412
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134.82 (aryl C), 129.30 (4C, aryl C), 127.95 (4C, aryl C), 127.62 (aryl C), 78.23(sp^3-C of C_{60}), 73.88, 34.51 (1C).

Fulleropyrrolidine *cis*-2a. By following the same experimental procedure as for the $Fe(ClO_4)_3{\cdot}xH_2O$-mediated reaction of C_{60} with amines **1a–l**, the reaction of C_{60} (36.0 mg, 0.0500 mmol) with **4c** (192 μL, 1.00 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.100 mmol) for 24 h afforded first unreacted C_{60} (17.0 mg, 47%) and then *cis*-**2a**[16] (15.0 mg, 33%) as an amorphous brown solid.

Preparation of Fulleropyrrolidine *trans*-5a in the Presence of Benzaldehyde. By following the same experimental procedure as for the $Fe(ClO_4)_3{\cdot}xH_2O$-mediated reaction of C_{60} with amines **1a-l**, the reaction of C_{60} (36.0 mg, 0.0500 mmol), **4a** (129 μL, 1.00 mmol), benzaldehyde (26 μL, 0.25 mmol), and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.100 mmol) for 4 h afforded first unreacted C_{60} (11.7 mg, 33%) and then *trans*-**5a**[14c] (23.8 mg, 52%).

Preparation of Fulleropyrrolidine *cis*-6. A mixture of *cis*-**2a** (22.9 mg, 0.0250 mmol), benzoyl chloride (58 μL, 0.50 mmol), and DMAP (15.3 mg, 0.125 mmol) was dissolved in chlorobenzene (6 mL) and was heated with vigorous stirring in an oil bath preset at 120 °C for 18 h. The resulting solution was directly separated on a silica gel column with CS_2/toluene as the eluent to give the N-substituted 2,5-diphenyl fulleropyrrolidine *cis*-**6** (24.7 mg, 97%) along with a trace amount of unreacted *cis*-**2a**. mp >300 °C; ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.75 (d, *J* = 7.5 Hz, 4H), 7.28–7.23 (m, 6H), 7.17 (t, *J* = 7.4 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.0 Hz, 2H), 6.90 (s, 2H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 172.80 (1C, C═O), 153.72, 152.81, 146.41, 145.22 (4C), 145.07, 144.84, 144.65 (1C), 144.54 (5C), 144.40, 144.24, 144.17, 144.00 (4C), 142.17 (1C), 142.14 (1C), 141.60, 141.53, 141.12 (6C), 140.76, 140.62, 140.55, 139.06, 138.57, 138.15, 136.61 (1C, aryl C), 135.32, 133.75 (aryl C), 128.24 (1C, aryl C), 128.22 (1C, aryl C), 128.15 (aryl C), 127.99 (1C, aryl C), 127.61 (4C, aryl C), 127.05 (aryl C), 126.82 (aryl C), 125.75 (aryl C), 74.75 (sp^3-C of C_{60}), 72.83; FT-IR ν/cm^{-1} (KBr) 2924, 2854, 1648, 1493, 1455, 1428, 1383, 1336, 1296, 1269, 1209, 1152, 1119, 1099, 696, 661, 597, 574, 552, 526; UV–vis ($CHCl_3$) λ_{max}/nm 256, 315, 431; MALDI-TOF MS *m/z* calcd for $C_{81}H_{18}NO$ $[M + H]^+$ 1020.1388, found 1020.1389.

Preparation of Fulleropyrrolidine *cis*-7. By following the same experimental procedure as for the preparation of *cis*-**6**, the reaction of *cis*-**2a** (22.9 mg, 0.0250 mmol) and 3,5-dimethylphenyl isocyanate (70 μL, 0.50 mmol) for 48 h afforded the N-substituted 2,5-diphenyl fulleropyrrolidine *cis*-**7** (21.8 mg, 82%) together with a small amount of unreacted *cis*-**2a**. mp >300 °C; ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 8.89 (s, 1H), 8.04 (d, *J* = 6.9 Hz, 4H), 7.37 (t, *J* = 7.4 Hz, 4H), 7.27 (t, *J* = 7.3 Hz, 2H), 6.85 (s, 2H), 6.50 (s, 1H), 6.17 (s, 2H), 2.16 (s, 6H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 157.88 (1C, C═O), 153.22, 152.62, 146.43, 145.65, 145.39 (5C), 145.20, 145.01 (4C), 144.75 (1C), 144.71, 144.43 (4C), 144.15, 143.75, 143.53, 142.28 (1C), 142.14 (1C), 141.76, 141.69, 141.44, 141.34, 141.15, 140.95, 140.79, 140.73, 139.10, 138.43, 137.53 (aryl C), 136.84, 136.02, 135.75 (aryl C), 135.10 (aryl C), 128.89 (aryl C), 128.79 (aryl C), 127.90 (6C, aryl C), 116.46 (1C, aryl C), 116.33 (1C, aryl C), 77.43 (sp^3-C of C_{60}), 73.63, 20.85; FT-IR ν/cm^{-1} (KBr) 3393, 2916, 2847, 1675, 1610, 1538, 1491, 1454, 1427, 1354, 1278, 1268, 1218, 1204, 1154, 1115, 1077, 1027, 832, 773, 737, 703, 685, 573, 526; UV–vis ($CHCl_3$) λ_{max}/nm 256, 314, 430; MALDI-TOF MS *m/z* calcd for $C_{83}H_{23}N_2O$ $[M + H]^+$ 1063.1810, found 1063.1811.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02412.

Proposed formation mechanisms of compounds **3** and *cis*-**2a**, computational results for *anti*-**A**, *syn*-**A**, S-shaped, W-shaped, and U-shaped ylides as well as the NMR spectra of products *cis*-**2a–i**, **3**, *trans*-**5a**, *cis*-**6**, and *cis*-**7**, ^{1}H NMR spectra of fulleropyrrolidine *cis*-**2a** for 7, 12, 18, and 24 h, UV–vis spectrum of *cis*-**2h**, HRMS of *cis*-**2b**, *cis*-**2h**, *cis*-**2i**, and *cis*-**6** (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful for the financial support from National Natural Science Foundation of China (nos. 21102041, 21071049, and 21272236), Natural Science Foundation of Hubei Province (nos. 2014CFB550 and 2013CFA087), Natural Science Fund for Creative Research Groups of Hubei Province of China (no. 2014CFA015), and Innovation and Entrepreneurship Training Program for Undergraduates of Hubei Province (no. 201310512011).

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