JOC Article

Aziridination of C_{60} with Simple Amides and Catalytic Rearrangement of the Aziridinofullerenes to Azafulleroids

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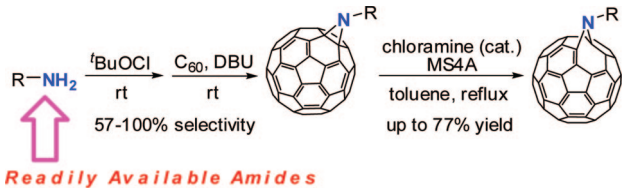
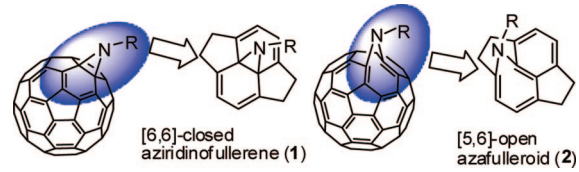


The selective formation of aziridinofullerene and azafulleroid, which are isomers of the fullerene derivatives-introduced N_1 unit, is achieved. The ionic aziridination is a very convenient and risk-free procedure compared with the conventional method with azides as nitrogen sources, and gives aziridinofullerenes from various readily available amides (carbamates, ureas, carboxamides, and phosphamides). For example, benzyl carbamate was chlorinated by *tert*-butyl hypochlorite (*tert*-BuOCl) and then reacted with C_{60} in the presence of base to give *N*-benzyloxycarbonyl aziridinofullerene exclusively and without formation of its isomer, an azafulleroid. The reaction enabled the synthesis of functional fullerene derivatives having a trialkoxysilyl group and an amino acid moiety. Azafulleroids were obtained through the rearrangement of corresponding aziridinofullerenes by using the combination of a chloramine catalyst and MS4A. Among other chloramines used, chloramine B (CB) showed superior ability as a catalyst in the rearrangement. It was found that MS4A functions as a Lewis acid in the reaction.

Introduction

The development of a basic and facile method for the functionalization of C_{60} remains an important challenge because of recent demands for carbon nanomaterials.[1,2] Among various methodologies for the functionalization, aziridination of C_{60} is a powerful method for the direct introduction of a heteroatom to the molecule, leading to closed [6,6]-bridged aziridinofullerenes **1** (Scheme 1). Moreover, isomers of **1** and opened [5,6]-bridged azafulleroids **2** are key precursors for azafullerene "$C_{59}N$" synthesis.[3] Azides are commonly used as nitrogen sources for the synthesis of nitrogen unit-substituted fullerenes.[4]

SCHEME 1. Partial Illustration of Aziridinofullerene and Azafulleroid



Some problems remain, however, namely that control of the distribution of the two products **1** and **2** is rather difficult, and that azides require careful handling due to their high reactivity, explosiveness, and toxicity. Other than azides, examples of aziridination using nitrene[5] or iminoiodane[6] as an N_1 source have been developed, but generality of the substituents for nitrogen remains limited. On the other hand, although photochemical[7] and thermal[5c,8] conversion between **1** and **2** was revealed, the studies would not test synthetic generality.

Quite recently, our group reported a new method for the ionic aziridination of C_{60} using chloramine-T (CT, **3a**) as a readily

(1) (a) Hirsch, A.; Brettreich, M. *Fullerenes: Chemistry and Reactions*; Wiley-VCH: Weinheim, Germany, 2005. (b) Kadish, K. M.; Ruoff, R. S., Eds. *Fullerenes: Chemistry, Physics, and Technology*; Wiley: New York, 2000. (c) Martin, N. *Chem. Commun.* **2006**, 2093.

(2) For recent reports, see: (a) Minakata, S.; Tsuruoka, R.; Komatsu, M. *J. Am. Chem. Soc.* **2008**, *130*, 1536. (b) Matsuo, Y.; Kanaizuka, K.; Matsuo, K.; Zhong, Y.-W.; Nakae, T.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 5016. (c) Yang, C.; Kim, J. Y.; Cho, S.; Lee, J. K.; Heeger, A. J.; Wudl, F. *J. Am. Chem. Soc.* **2008**, *130*, 6444.

(3) (a) Hummelen, J. C.; Knight, B.; Pavlovich, J.; Gonzalez, R.; Wudl, F. *Science* **1995**, *269*, 1554. (b) Nuber, B.; Hirsch, A. *Chem. Commun.* **1996**, 1421.

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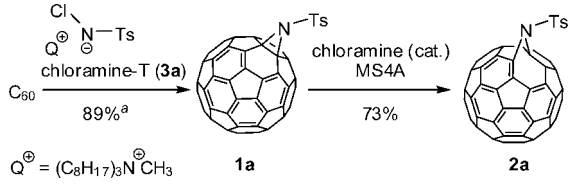
SCHEME 2. Aziridination of C_{60} with Chloramine-T and Rearrangement of Aziridinofullerene



[a] Based on converted C_{60}.

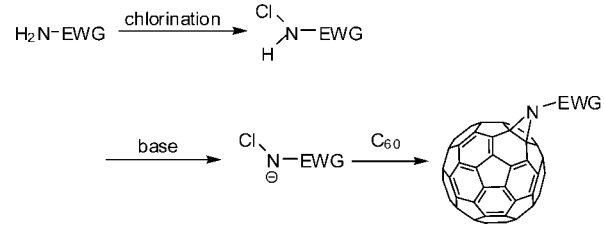
available N_1 source, giving predominantly *N*-tosylated aziridinofullerene **1a** with high selectivity[9] (89%), and the unique rearrangement of **1a** to **2a** using the combination of a catalytic amount of chloramine and molecular sieves 4A (MS4A), as well as a thermal rearrangement (Scheme 2).[8] Although the aziridination is unique and unprecedented, the method essentially requires the use of chloramine salts, some of which are not stable. However, to our knowledge, ionic aziridination is not well established, either for fullerenes or for electron-deficient olefins.[10]

From this point of view, a new practical and highly selective aziridination of C_{60} with alternative nitrogen sources instead of azides and generally applicable isomerization of an aziridinofullerene to an azafulleroid are desired. Here we report a new type of selective aziridination of C_{60} with a variety of simple amides, many of which are either commercially available or readily prepared from either corresponding acids,[11] alcohols,[12] or amines.[13] Moreover, catalytic rearrangement of the resulting aziridinofullerenes to azafulleroids with use of a chloramine salt and an MS4A system was investigated.

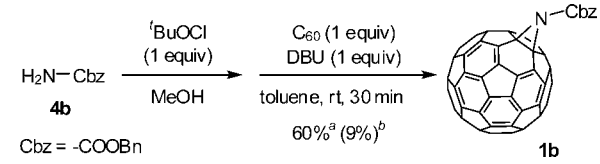
Results and Discussion

Preliminary Results of Aziridination of C_{60} with Benzyl Carbamate. Provided the ionic reaction path proposed in our previous aziridination with CT is suitable, the development of a new methodology for the generation of chloramine anions from readily accessible amides would directly lead to a general synthesis of a variety of aziridinofullerenes. As mentioned in the Introduction, most chloramine salts, even those with an electron-withdrawing group, cannot be isolated due to their unstable nature. To expand the generality of the aziridination of C_{60}, a facile method for the chlorination of amides and their deprotonation in situ should be explored (Scheme 3). As an initial experiment for the new aziridination of C_{60}, *tert*-butyl hypochlorite (*t*-BuOCl) was employed in the chlorination of benzyl carbamate (**4b**).[14] The reaction was carried out in MeOH and the solvent was exchanged with toluene followed by addition of C_{60} and DBU, affording *N*-benzyloxycarbonyl aziridinofullerene in moderate selectivity (60%), as shown in Scheme 4.

SCHEME 3. Working Hypothesis of Ionic Aziridination of C_{60} with Amides

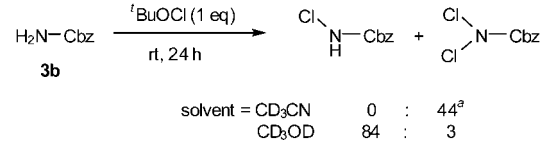


SCHEME 4. Aziridination of C_{60} with Benzyl Carbamate



[a] Based on converted C_{60}. [b] Isolated yield is given in parentheses.

SCHEME 5. Chlorination of Benzyl Carbamate



[a] Yields determined by ^{1}H NMR.

Optimization of the Conditions of Aziridination of C_{60} with Benzylcarbamate. Although the desired aziridinofullerene was obtained with this method, the efficiency was unsatisfactory. To first learn the details of the process, the chlorination of carbamate was investigated. The chlorination of benzyl carbamate was monitored by using ^{1}H NMR. Chlorination of the carbamate with an equimolar amount of *t*-BuOCl in d_3-acetonitrile gave only the dichlorinated product. In contrast, monochlorinated carbamate was predominantly produced by using d_4-methanol (Scheme 5).

The reaction of the resulting monochlorinated carbamate with C_{60} should be carried out in toluene because the solvent is suitable for the modification of C_{60} and is available for organic reaction. As with our previous report of the aziridination of C_{60} with CT[8] in which the sodium ion of CT was exchanged with the ammonium ion prior to use, the *N*-chlorinated nitrogen anion generated from the resulting carbamate obtained by chlorination

(4) (a) Prato, M.; Li, Q. C.; Wudl, F.; Luccini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148. (b) Ishida, T.; Tanaka, K.; Nogami, T. *Chem. Lett.* **1994**, 561. (c) Banks, M. R.; Cadogan, J. I. G.; Gosney, I.; Hodgson, P. K. G.; Langridge-Smith, P. R. R.; Rankin, D. W. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1365. (d) Yan, M.; Cai, S. X.; Keana, J. F. W. *J. Org. Chem.* **1994**, *59*, 5951. (e) Banks, M. R.; Cadogan, J. I. G.; Gosney, I.; Hodgson, P. K. G.; Langridge-Smitha, P. R. R.; Millar, J. R. A.; Parkinson, J. A.; Rankin, D. W. H.; Taylor, A. T. *J. Chem. Soc., Chem. Commun.* **1995**, 887. (f) Averdung, J.; Mattay, J.; Jacobi, D.; Abraham, W. *Tetrahedron* **1995**, *51*, 2543. (g) Schick, G.; Grösser, T.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2289. (h) Smith, A. B., III; Tokuyama, H. *Tetrahedron* **1996**, *52*, 5257. (i) Bellavia-Lund, C.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 943. (j) Ulmer, L.; Mattay, J. *Eur. J. Org. Chem.* **2003**, 2933.

(5) (a) Kuwashima, S.; Kubota, M.; Kushida, K.; Ishida, T.; Ohashi, M.; Nogami, T. *Tetrahedron Lett.* **1994**, *35*, 4371. (b) Banks, M. R.; Cadogan, J. I. G.; Gosney, I.; Hodgson, P. K. G.; Langridge-Smith, P. R. R.; Millar, J. R. A.; Taylor, A. T. *Tetrahedron Lett.* **1994**, *35*, 9067. (c) Nakahodo, T.; Okada, M.; Moria, H.; Yoshimura, T.; Ishitsuka, M. O.; Tsuchiya, T.; Maeda, Y.; Fujihara, H.; Akasaka, T.; Gao, X.; Nagase, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 1298.

(6) Zhang, X.; Gan, L.; Huang, S.; Shi, Y. *J. Org. Chem.* **2004**, *69*, 5800.

(7) (a) Averdung, J.; Mattay, J. *Tetrahedron* **1996**, *52*, 5407. (b) Ouchi, A.; Hatsuda, R.; Awen, B. Z. S.; Sakuragi, M.; Ogura, R.; Ishii, T.; Araki, Y.; Ito, O. *J. Am. Chem. Soc.* **2002**, *124*, 13364.

(8) Minakata, S.; Tsuruoka, R.; Nagamachi, T.; Komatsu, M. *Chem. Commun.* **2008**, 323.

(9) Selectivity/100 = (isolated yield of product)/(conversion of C_{60}).

(10) Shen, Y.-M.; Zhao, M.-X.; Xu, J.; Yian, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 8005, and references cited therein. .

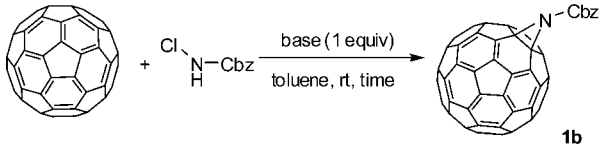
(11) For example, see: Khalafi-Nezhad, A.; Parhami, A.; Rad, M. N. S.; Zarea, A. *Tetrahedron Lett.* **2005**, *46*, 6879.

(12) For example, see: Gorodetskii, L. S.; Volzhina, O. N.; Kuznetsova, I. A.; Alekseeva, E. N. *Pharm. Chem. J.* **1982**, *16*, 474.

(13) For example, see:(a) Weisel, C. A.; Mosher, H. S.; Whitmore, F. C. *J. Am. Chem. Soc.* **1945**, *67*, 1055. (b) Durant, G. J. *Chem. Ind.* **1965**, *32*, 1428. (c) Mosvhel, R. C.; Hudgins, W. R.; Dipple, A. *J. Org. Chem.* **1986**, *51*, 4180.

(14) (a) Herranz, E.; Sharpless, K. B. *J. Org. Chem.* **1980**, *45*, 2710. (b) Angert, G.; Li, H. H.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2813.

TABLE 1. Aziridination of C_{60} with *N*-Chlorobenzyl Carbamate



1b

entry	carbamate (equiv)	base	time (min)	entry (%)[a,b]
1	1	NaH	300	NR[c]
2	1	^{t}BuONa	300	NR
3	1	^{t}BuONa[d]	300	85 (15)
4	1	^{n}Pr$_3$N	300	NR
5	1	DBU	300	50 (10)
6	2	DBU	300	25 (12)
7	1	DBU	30	60 (9)
8	1.5	DBU	30	80 (12)
9	2	DBU	30	53 (10)

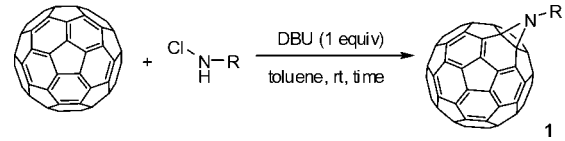
[a] Based on converted C_{60}. [b] The numbers in parentheses are isolated yields. [c] NR: no reaction. [d] Triethylbenzylammonium chloride was used as the phase-transfer catalyst.

should be dissolved in toluene. In fact, while the reaction did not proceed with only NaH or *t*-BuONa because of their insolubility, the desired product was obtained by using a combination of *t*-BuONa and an equimolar amount of triethylbenzylammonium chloride (Table 1, entrys 1−3). To facilitate the manipulation, organic bases were investigated. Although tripropylamine was ineffective for the aziridination (entry 4), DBU, which would be a sufficient strong organic base for abstraction of the hydrogen on the chloroamide, was found to be a good base for the reaction (entry 5). The use of 2 equiv of the carbamate decreased the selectivity (entry 6). A decrease of the reaction time improved the selectivity due to a reduction of the multiaddition of the amide. Consequently, when 1.5 equiv of carbamate was employed, the desired aziridinofullerene was obtained in high selectivity (80%), which compares to the results of entry 3. The structure of the resulting aziridinofullerene was easily identified by using ^{1}H and ^{13}C NMR techniques and FAB-MS. In the study of ^{13}C NMR in $CDCl_3$, 15 signals within the range of δ 135−150 ppm, derived from the C_{2v} symmetry of the [6,6]-closed adduct,[15] were observed. We were able to assign signals at δ 80.60 and 156.30 ppm to the sp^3 carbon of the aziridine ring and to the carbonyl carbon of the Cbz group, respectively. This evidence indicates a closed structure of the C_{60} sphere.

Aziridination of C_{60} with Various Simple Amides. A variety of simple amides were applied to the aziridination of C_{60}. Carbamates having a *tert*-butoxycarbonyl (Boc, **4c**) group and having either long-liner or branched-alkyl chains (**4d** and **4e**, respectively) gave the corresponding aziridinofullerenes (Table 2, entries 1−3). Ureas were also applicable to the reaction, affording the desired products in good yields (entries 4 and 5), and representing the first example for synthesis of aziridinofullerenes having urea moieties. Although the yields should be left for improvement, the aziridinofullerenes derived from benzamide and picolinamide (**1h** and **1i**) were yielded in good selectivity (entries 6 and 7). When phosphamides were subjected to the reaction, phosphoryl-substituted aziridinofullerene was furnished (entries 8 and 9). The bulkiness of the diphenylphosphoryl (Dpp) group of **1k** would prevent further addition of the amide and the corresponding aziridinofullerene was produced with high efficiency. In addition, this aziridinofullerene **1k** was easily converted to *N-H*

(15) The method for identification of aziridinofullerene and azafulleroid with ^{13}C NMR was well established by the literature cited in ref 4.

TABLE 2. Aziridination of C_{60} with Various Amides

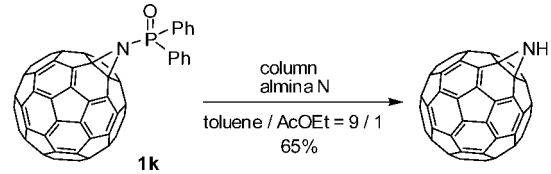


1

entry	amide (equiv)		time (min)	yield (%)[a,b]	product
1	H_2N O O^tBu	**4c** (1.5)	15	80 (26)	**1c**
2	H_2N O $O^nC_{16}H_{33}$	**4d** (1.0)	300	60 (15)	**1d**
3	H_2N O O	**4e** (1.0)	300	57 (17)	**1e**
4	H_2N O NMe_2	**4f** (1.5)	30	77 (35)	**1f**
5	H_2N O $N(^nC_{12}H_{25})_2$	**4g** (1.0)	10	66 (35)	**1g**
6	H_2N O Ph	**4h** (1.0)	60	99 (7)	**1h**
7	H_2N O N	**4i** (1.5)	120	61 (11)	**1i**
8	H_2N O P OEt OEt	**4j** (1.5)	30	60 (28)	**1j**
9	H_2N O P Ph Ph	**4k** (1.5)	30	100 (50)	**1k**

[a] Based on converted C_{60}. [b] The numbers in parenthesss are isolated yields.

SCHEME 6. Preparation of *N-H* Aziridinofullerene



1k

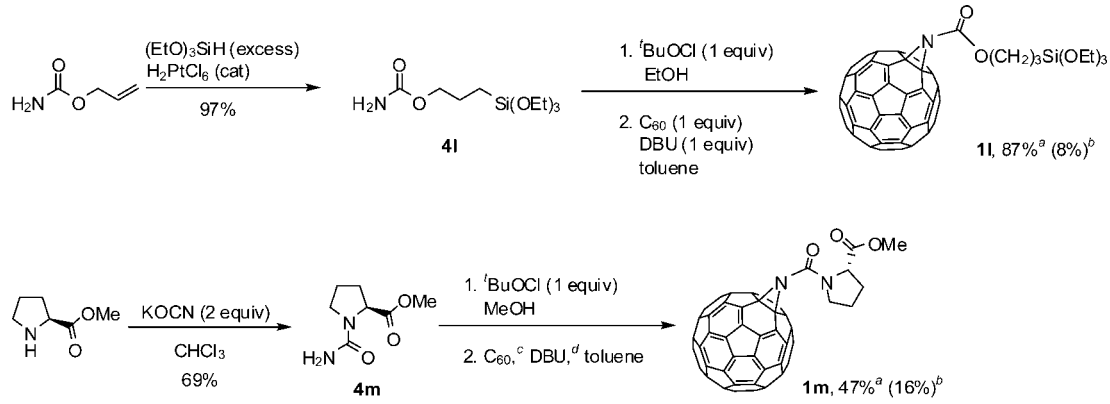
aziridinofullerene as shown in Scheme 6 (33% from C_{60} vs 21% by the previous route[16]).

Functionalization of C_{60} by the Aziridination. Recently, to leverage the unique properties of C_{60}, fullerene derivatives having functional groups, for example, either a trialkoxysilyl group[17] or an amino acid moiety,[18,19] have been given a great deal of attention in the fields of nanotechnology and biochem-

(16) The Boc group of aziridinofullerene **1c** can be easily detached and substituted, see: (a) Averdung, J.; Luftmann, H.; Mattay, J.; Claus, K.-U.; Abraham, W. *Tetrahedron Lett.* **1995**, *36*, 2957. (b) Averdung, J.; Wolff, C.; Mattay, J. *Tetrahedron Lett.* **1996**, *37*, 4683.

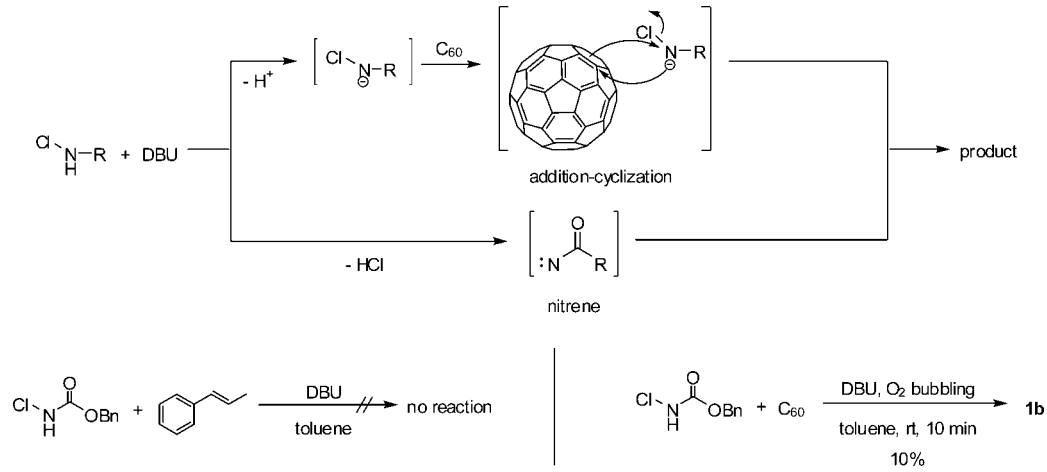
(17) (a) Kraus, A.; Schneider, M.; Gugel, A.; Mullen, K. *J. Mater. Chem.* **1997**, *7*, 763. (b) Kordatos, K.; Da, R. T.; Bosi, S.; Pantarotto, D.; Georgakilas, V.; Spalluto, G.; Prato, M. *J. Org. Chem.* **2001**, *66*, 4915. (c) Gasparrini, F.; Misiti, D.; Della, N. F.; Maggini, M.; Scorrano, G.; Villani, C. *Tetrahedron* **2001**, *57*, 6997. (d) Bochio, M.; Carraro, M.; Scoorano, G.; Bango, A. *Adv. Synth. Catal.* **2004**, *346*, 648. (e) Cho, Y.-J.; Ahn, T. K.; Song, H.; Kim, K. S.; Lee, C. Y.; Seo, W. S.; Lee, K.; Kim, S. K.; Kim, D.; Park, J. T. *J. Am. Chem. Soc.* **2005**, *127*, 2380. (f) Bianco, A.; Maggini, M.; Nogarole, M.; Scorrano, G. *Eur. J. Org. Chem.* **2006**, 2934. (g) Whitnall, W.; Cademartiri, L.; Ozin, G. A. *J. Am. Chem. Soc.* **2007**, *129*, 15644.

SCHEME 7. Synthesis of Functionalized Aziridinofullerene



[a] Based on converted C_{60}. [b] The numbers in parentheses are isolated yields. [c] **4m**/C_{60} = 1.5. [d] **4m**/DBU = 1.5.

SCHEME 8. Considered Pathways for the Aziridination



istry. The aziridination discovered here would be a powerful tool for the synthesis of these functional materials. Aziridinofullerenes possessing either a triethoxysilyl group or a proline moiety were easily synthesized from simple substrates via two steps (Scheme 7). Carbamate bearing a triethoxysilyl group (**4*l***) was prepared by the hydrosilylation of allyl carbamate, and the carbamate obtained was chlorinated with *t*-BuOCl, followed by a reaction with C_{60} to produce the desired aziridinofullerene with a triethoxy functional group. In the same way, an optically active unit could be introduced to C_{60} by reaction with a *N*-carbamoyl proline ester (**4m**) prepared from a proline ester and potassium cyanate.

Consideration of the Reaction Pathway of Aziridination. For the present aziridination of C_{60}, there are two dominant pathways: ionic addition−cyclization, as in the case of CT, and the addition of nitrene generated by α-elimination of the haloamide (Scheme 8). To confirm the pathway, the following reactions were examined. Since it is known that nitrene had reacted with β-methylstyrene to afford an aziridine derivative,[20] if an active species in the reaction is nitrene, the corresponding aziridine should be produced when using styrene. However, when the styrene was treated with *N*-chloroamide in the presence of DBU, the aziridination did not proceed. Moreover, O_2 is a well-known radical scavenger such as triplet nitrene, but O_2 bubbling did not affect the reaction efficiency compared with the results shown in Table 1 (entry 7). These results indicate that the active species of this reaction was not nitrene, but was instead anionic nitrogen generated by the deprotonation of chloroamide. Therefore, the addition−cyclization pathway was strongly suggested for the aziridination of C_{60}. In addition, the completely selective formation of aziridinofullerene (no azafulleroid)[21] corroborates this proposed pathway.

The Catalytic Rearrangement of Aziridinofullerenes to Azafulleroids. We have already revealed that *N*-tosylated aziridinofullerene (**1a**) was catalytically rearranged to a corresponding azafulleroid (**2a**) by using a chloramine salt and MS4A.[8] However, the role of the chloramine catalyst and MS4A is yet to be clarified and the substrate was limited to **1a**. Since a wide range of aziridinofullerenes have been synthesized by using our original procedure, the catalytic rearrangement of aziridinofullerenes to azafulleroids was examined.

First, to tune the catalytic activity of chloramine salt, several chloramines were employed in the rearrangement of aziridi-

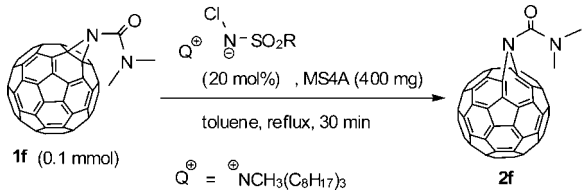
(18) For recent reports, see: (a) Watanabe, L. A.; Bhuiyan, M. P. I.; Jose, B.; Kato, T.; Nishino, N. *Tetrahedron Lett.* **2004**, *45*, 7137. (b) Enes, R. F.; Tome, A. C.; Cavaleiro, J. A. S. *Tetrahedron* **2005**, *61*, 1423. (c) Rouse, J. G.; Yang, J.; Ryman-Rasmussen, J. P.; Barron, A. R.; Monteiro-Riviere, N. A. *Nano. Lett.* **2007**, *7*, 155. (d) Yang, J.; Wang, K.; Driver, J.; Yang, J.; Barron, A. R. *Org. Biomol. Chem.* **2007**, *5*, 260.

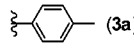
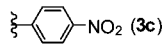
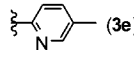
(19) For reviews, see: (a) Vol'pin, M. E.; Parnes, Z. N.; Romanova, V. S. *Russ. Chem. Bull.* **1998**, *47*, 1021. (b) Burley, G. A.; Keller, P. A.; Pyne, S. G. *Fullerene Sci. Technol.* **1999**, *7*, 973. (c) Bianco, A.; Da, R. T.; Prato, M.; Toniolo, C. *J. Pet. Sci.* **2001**, *7*, 208.

(20) Minakata, S.; Kano, D.; Fukuoka, R.; Oderaotoshi, Y.; Komatsu, M. *Heterocycles* **2003**, *60*, 289.

(21) It is known that aziridinofullerenes as well as azafulleroids were produced by the reaction of C_{60} with a nitrene species. For example, see ref 4j.

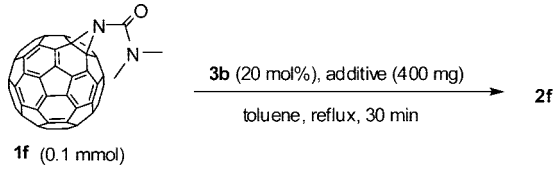
TABLE 3. Optimization of a Chloramine Catalyst for the Rearrangement



entry	R		yield (%)[a]	recovery of **1f** (%)
1		(**3b**)	77	23
2		(**3a**)	49	34
3		(**3c**)	9	80
4		(**3d**)	2	98
5		(**3e**)	17	76

[a] Determined by ^{1}H NMR.

TABLE 4. Optimization of Additives



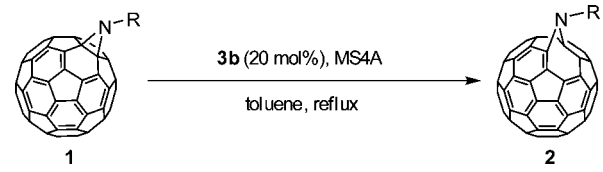
entry	additive	yield (%)[a]	recovery of **1f** (%)
1	MS4A	77	23
2	MS3A	0	91
3	MS5A	0	84
4	aluminum oxide 90 active basic	8	74
5	aluminum oxide 90 active neutral	2	74

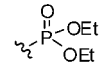
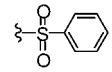
[a] Determined by ^{1}H NMR.

nofullerene **1f** as a model substrate. Chloramine having a benzenesulfonyl group, chloramine-B (CB), **3b**, which is one of the commercially available chloramines, was effective in rearrangement to give the corresponding azafulleroid **2f** in good yield (Table 3, entry 1). More than 29 signals within the range of δ 130−150 ppm were observed in the ^{13}C NMR spectra of **2f**, indicating that the product had C_s symmetry.[15] It was possible to assign the signals at δ 162.68 ppm to the carbonyl carbon of urea, and the signal of the sp^3 carbon of aziridinofullerene **1f** disappeared. Thus, the structure of the product was determined to be [5,6]-open azafulleroid. Although the yield of the reaction with **3a** as a catalyst was lower than that of CB, CT could also catalyze the reaction (entry 2). Chloramines having an electron-withdrawing group were ineffective for the rearrangement, and most of the starting **1f** was recovered (entries 3−5).

Since an additive plays an important role in the rearrangement, some inorganic porous materials were evaluated in the reaction. MS3A and MS5A did not function as an additive for the rearrangement (Table 4, entries 2 and 3), although they have an elemental composition that is similar to that of MS4A with the exception of the pore size, owing to the cation species on the surface (MS3A: K^+; MS4A: Na^+; MS5A: Ca^{2+}).[22] Although both the basic and neutral aluminum oxides were ineffective in the rearrangement, the addition of basic alumina gave the azafulleroid with a relatively better yield than that of the neutral alumina (entries 4 and 5). From observation of the X-ray fluorescence, basic alumina contained more than 3-fold the amount of sodium (0.17 wt %), compared with neutral alumina (<0.05 wt %), but any other compositional differences between them were not identified. These results suggest that the surface cation, especially Na^+, might participate in the generation of azafulleroid.

TABLE 5. Rearrangement of Aziridinofullerenes to Azafulleroids



entry	R		Time (h)	yield (%)
1		(**1f**)	0.5	77[a] (**2f**)
2	Cbz	(**1b**)	6	47[b] (**2b**)
3		(**1j**)	0.5	31[a] (**2j**)
4[c]		(**1n**)	3	50[b] (**2n**)

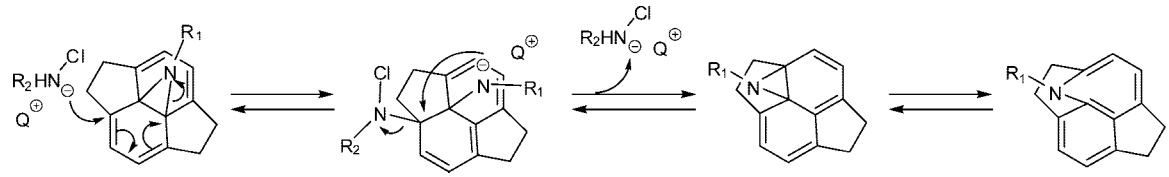
[a] Determined by ^{1}H NMR. [b] Isolated yield. [c] cat: 10 mol%.

On the basis of the present study results, various aziridinofullerenes were applied to rearrangement under optimized conditions. Fortunately, the reaction shows a generality of substituents on the nitrogen of aziridinofullerene. For example, azafulleroid having a Cbz group (**2b**) was afforded in 47% yield (Table 5, entry 2). Although the yield was insufficient, the rearrangement was also applicable to aziridinofullerenes **1j** to give the corresponding azafulleroids (entry 3). Aziridinofullerene **1n** was also efficiently isomerized to **2n** even though 10 mol % of **3b** was used (entry 4).

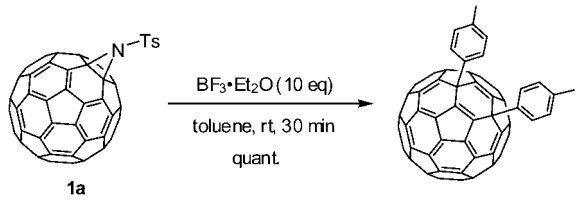
Consideration of the Reaction Pathway for Rearrangement. We had already proposed a pathway for rearrangement that deserves consideration.[8] As shown in Scheme 9, the reaction proceeds by the initial attack of chloramine salt, followed by elimination of the catalyst along with the transformation of the cage of C_{60}. While the function of MS4A was not clarified at the time, the role of MS4A was newly investigated. In the absence of MS4A the reaction of aziridinofullerene **1a** with a catalytic amount of **3b** gave a complex mixture of poly adducts bearing heterosubstituents in ca. 10% yield. This result indicates that MS4A would assist the elimination of the catalyst. From the results of the optimization of additives (Table 4), the following points were considered. Because the pore size of all molecular sieves (3−5 nm) used in this examination was sufficiently less than the diameter of C_{60} (ca. 10 nm), it is quite unlikely that the pore contributed to the formation of azafulleroids. Therefore, we focused on the surface

(22) See the Supporting Information.

SCHEME 9. Considered Pathways for the Rearrangement



SCHEME 10. Nucleophilic Addition of Toluene Promoted by Lewis Acid



cation of MS4A as described above, namely, that the cation might function as a weak Lewis acid to promote the elimination of the chloramine catalyst. To confirm the prediction, aziridinofullerene **1a** was treated with a typical Lewis acid: boron trifluoride etherate. As a result, the quantitative addition of the solvent (toluene) occurred smoothly even in the absence of a chloramine salt (Scheme 10). This phenomenon is similar to the case of fullerene epoxide,[23] as reported by Tajima et al., and the result supported our hypothesis in that MS4A promotes the elimination of chloramine as a very weak acid. In contrast to the strong acidity of $BF_3 \cdot Et_2O$, which led to the complete elimination of the nitrogen unit, the weaker acidity of MS4A successfully enabled rearrangement to take place.

Conclusions

A variety of simple amides are useful for the efficient ionic aziridination of C_{60}, and the resulting aziridinofullerenes are rearranged to azafulleroids by the combination of a chloramine catalyst and MS4A. Monochloroamides, which are key reagents for the aziridination of C_{60}, were easily synthesized by *t*-BuOCl in methanol. In the present study, treatment of the chlorinated amides with C_{60} in the presence of an organic base smoothly gave the desired aziridinofullerene as a single isomer. The aziridination pathway is deduced to be addition−cyclization. The rearrangement of aziridinofullerenes to azafulleroid was applicable to the broad aziridinofullerenes prepared by using our original method, and was promoted by a chloramine catalyst and by MS4A. In the rearrangement, MS4A functions as a weak Lewis acid for the elimination of the catalyst. Thus far, the introduction of a N_1 unit to C_{60} by using organic azides has been the only procedure for the general formation of aziridinofullerenes and/or azafulleroids. This efficient and convenient method for the introduction of a N_1 unit to C_{60}, including the unique rearrangement, could be included among the general methods for the synthesis of functionalized C_{60} derivatives.

Experimental Section

General Procedure for the Synthesis of Aziridinofullerenes. A solution of amides (0.15 mmol) and *t*-BuOCl (16 mg, 0.15 mmol) was stirred in MeOH (1 mL) at room temperature for 2 h. The solvent was then concentrated under vacuum and the residue dissolved in toluene (5 mL), followed by addition of the solution to a toluene solution (50 mL) of C_{60} (72 mg, 0.1 mmol). DBU (13.8 mg, 0.1 mmol) was then added to the solution and the mixture was stirred at room temperature for the indicated times. The solution was passed through a short column of silica gel (3 g) and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel.

1,2-*N*-(Benzyloxycarbonyl)aziridino[60]fullerene (1b). Black crystalline solid. FT-IR (KBr) 3429, 2924, 2852, 1743, 1225, 1186, 527 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 5.53 (s, 2H), 7.39−7.43 (m, 3H), 7.52−7.55 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 70.0, 80.6, 128.6, 128.9, 134.8, 140.0, 141.0, 142.06, 142.10, 142.7, 143.0, 143.1, 143.4, 143.6, 143.8, 144.35, 144.43, 144.8, 145.0, 145.1, 156.3. UV−vis (CH_2Cl_2) λ_{max} 421, 410, 323, 255, 227 nm. FAB-MS 869 ($[M]^+$). HR-MS calcd for ($C_{68}H_7NO_2$) 869.0476, found 869.0579. R_f 0.50 (TLC, SiO_2, hexane:toluene = 1:1).

1,2-*N*-(*tert*-Butyloxycarbonyl)aziridino[60]fullerene (1c). Black crystalline solid. FT-IR (KBr) 3440, 1739, 1254, 1147, 1095, 806, 524 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 1.70 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$:CS_2 = 2:1) δ 28.2, 81.3, 84.7, 139.9, 141.1, 142.2, 142.3, 142.8, 143.15, 143.16, 143.8, 144.0, 144.1, 144.5, 144.6, 144.78, 144.81, 145.1, 145.2, 154.8. UV−vis (CH_2Cl_2) λ_{max} 422, 410, 325, 256, 229 nm. FAB-MS *m*/*z* 835 ($[M]^+$). HR-MS calcd for ($C_{65}H_9NO_2$) 835.0668, found 835.0633. R_f 0.62 (TLC, SiO_2, hexane:toluene = 1:1).

1,2-*N*-(*n*-Hexadecyloxycarbonyl)aziridino[60]fullerene (1d). Black solid. FT-IR (KBr) 3427, 2920, 2848, 1745, 1462, 1228, 1095, 527 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3H), 1.19−1.54 (m, 26H), 1.84 (t, J = 7.2 Hz, 2H), 4.51 (t, J = 6.5 Hz, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 22.7, 25.8, 28.8, 29.2, 29.3, 29.55, 29.58, 29.7, 31.9, 68.4, 80.7, 139.8, 140.9, 142.0, 142.6, 142.9, 143.0, 143.5, 143.8, 144.27, 144.32, 144.6, 144.7, 144.9, 145.0, 156.2. FAB-MS *m*/*z* 1003 ($[M]^+$). UV−vis (CH_2Cl_2) λ_{max} 421, 409, 323, 256, 227 nm. HR-MS calcd for ($C_{77}H_{33}NO_2$) 1003.2511, found 1003.2502. R_f 0.65 (TLC, SiO_2, hexane:toluene = 1:1).

1,2-*N*-(2-Ethylhexyloxycarbonyl)aziridino[60]fullerene (1e). Black crystalline solid. FT-IR (KBr) 3442, 2921, 1743, 1654, 1403, 1226 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 0.90 (t, J = 7.0 Hz, 3H), 0.97 (t, J = 7.4 Hz, 3H), 1.26−1.55 (m, 8H), 1.77−1.82 (m, 1H), 4.44 (dd, J = 1.1 Hz, 5.7 Hz, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.1, 14.1, 23.1, 23.9, 28.9, 30.4, 39.1, 70.6, 80.9, 140.1, 141.1, 142.3, 142.8, 143.20, 143.23, 143.80, 143.84, 144.0, 144.5, 144.6, 144.86, 144.90, 145.2, 145.3, 156.6. FAB-MS *m*/*z* 891 ($[M]^+$). UV−vis (CH_2Cl_2) λ_{max} 325, 256, 227 nm. HR-MS calcd for ($C_{69}H_{17}NO_2$) 891.1259, found 891.1265. R_f 0.63 (TLC, SiO_2, hexane:toluene = 1:1).

1,2-*N*-(*N*′,*N*′-Dimetylaminocarbonyl)aziridino[60]fullerene (1f). Black crystalline solid. FT-IR (KBr) 3436, 2924, 2852, 1691, 1381, 1150, 527 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 3.27 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$:CS_2 = 2:1) δ 37.1, 37.3, 80.8, 140.5, 141.0, 142.2, 142.3, 142.9, 143.09, 143.10, 143.9, 144.1, 144.4, 144.6, 144.89, 144.93, 145.2, 145.3, 156.8. UV−vis (CH_2Cl_2) λ_{max} 423, 410, 324, 257, 228 nm. FAB-MS *m*/*z* 806 ($[M]^+$). HR-MS calcd for ($C_{63}H_6N_2O$) 806.0480, found 806.0504. R_f 0.20 (TLC, SiO_2, toluene).

1,2-*N*-(*N*′,*N*′-Didodecylylaminocarbonyl)aziridino[60]fullerene (1g). Black solid. FT-IR (KBr) 3448, 2922, 2850, 1689, 1462, 1417, 527 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 0.85−0.88 (m, 6H), 1.15−1.58 (m, 36H), 1.71 (m, 2H), 2.01 (m, 2H), 3.58 (t, J =

(23) Tajima, Y.; Hara, T.; Honma, T.; Matsumoto, S.; Takeuchi, K. *Org. Lett.* **2006**, *8*, 3203.

7.3 Hz, 2H), 3.93 (t, J = 7.6 Hz, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.2, 22.7, 27.0, 27.1, 28.0, 28.5, 29.4, 29.4, 29.4, 29.6, 29.6, 29.7, 31.9, 47.5, 48.3, 80.7, 140.1, 140.7, 141.9, 142.0, 142.6, 142.79, 142.82, 143.6, 143.9, 144.3, 144.4, 144.6, 144.9, 145.0, 156.4. UV−vis (CH_2Cl_2) λ_{max} 423, 325, 257, 228 nm. FAB-MS m/z 1114 ([M]$^+$). HR-MS calcd for ($C_{85}H_{50}N_2O$) 1114.3923, found 1114.3904. R_f 0.38 (TLC, SiO_2, hexane:toluene = 1:1).

1,2-*N*-Benzoylaziridino[60]fullerene (1h). Black crystalline solid. FT-IR (KBr) 3436, 2923, 2856, 1699, 1645, 1392, 1259, 1176, 1089, 1033, 806, 700 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73−7.63 (m, 3H), 8.55 (d, J = 4.3 Hz, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 81.0, 125.2, 128.1, 128.9, 129.1, 129.3, 130.9, 134.1, 140.0, 141.1, 142.0, 142.1, 142.7, 143.1, 143.5, 143.7, 144.0, 144.5, 144.8, 145.1, 145.2, 170.8. UV−vis (CH_2Cl_2) λ_{max} 421, 410, 323, 257, 229 nm. FAB-MS m/z 840 ([M]$^+$ + 1). HR-MS calcd for ($C_{67}H_5NO$) 839.0371, found 839.0391. R_f 0.27 (TLC, SiO_2, hexane:toluene = 1:1).

1,2-*N*-(2-Picolylcarbonyl)aziridino[60]fullerene (1i). Black crystalline solid. FT-IR (KBr) 3448, 2924, 2852, 1653, 1637, 1585, 1429, 1086, 527 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$:CS_2 = 2:1) δ 7.16−7.20 (m, 1H), 7.62−7.66 (m, 1H), 7.82−7.88 (m, 1H), 8.53−8.55 (m, 1H). ^{13}C NMR (68 MHz, $CDCl_3$:CS_2 = 2:1) δ 82.6, 115.8, 119.5, 137.7, 140.0, 140.7, 141.89, 141.93, 142.4, 142.5, 142.8, 143.5, 143.8, 144.2, 144.4, 144.5, 144.8, 144.9, 148.4, 157.2. UV−vis (CH_2Cl_2) λ_{max} 325, 258, 227 nm. HR-MS calcd for ($C_{66}H_4N_2O$) 840.0324, found 840.0300. R_f 0.40 (TLC, SiO_2, toluene).

1,2-*N*-(Diethoxyphosphino)aziridino[60]fullerene (1j). Black crystalline solid. FT-IR (KBr) 3450, 2978, 1275, 1051, 1024, 968, 527 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.51 (t, J = 7.0, 3H), 4.49 (q, J = 7.0 Hz, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 16.5, 16.6, 65.0, 65.1, 78.4, 78.8, 140.6, 141.0, 141.8, 141.9, 142.5, 142.86, 142.91, 143.7, 143.8, 144.1, 144.3, 144.8, 144.90, 145.0, 145.1. UV−vis (CH_2Cl_2) λ_{max} 421, 409, 324, 255, 227 nm. FAB-MS m/z 872 ([M]$^+$ + 1). HR-MS calcd for ($C_{64}H_{10}NO_3P$) 871.0398, found 871.0422. R_f 0.40 (TLC, SiO_2, toluene:AcOEt = 10:1).

1,2-*N*-(Diphenylphosphino)aziridino[60]fullerene (1k). Black crystalline solid; FT-IR (KBr) 3444, 1635, 1431, 1381, 1223, 1117, 858, 831, 729, 696, 525 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.63 (m, 6H), 8.31 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 79.6, 79.6, 129.3, 129.4, 131.2, 132.1, 132.37, 132.43, 133.1, 133.2, 141.0, 141.6, 142.4, 143.0, 143.33, 143.34, 143.4, 144.2, 144.3, 144.7, 144.8, 145.1, 145.1, 145.4, 145.5, 145.86, 145.89. UV−vis (CH_2Cl_2) λ_{max} 423, 410, 325, 256, 228 nm. FAB-MS m/z 936 ([M]$^+$ + 1). HR-MS calcd for ($C_{72}H_{10}NOP$) 935.0500, found 935.0490. R_f 0.45 (TLC, SiO_2, toluene:AcOEt = 10:1).

1,2-*N*-(3-Trimethoxysilylpropyloxycarbonyl)aziridino[60]fullerene (1*l*′). In the step of the chlorination of amide **4*l*** in MeOH, ethoxy groups on the silicon atom were exchanged with methoxy groups. Because of high reactivity of the alkoxysilyl group toward the surface of silica, isolation of this product by silica gel column chromatography was very difficult (3% yield). FT-IR (KBr) 3425, 3203, 2924, 2854, 1741, 1425, 1230, 1093, 527 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.77−0.83 (m, 2H), 1.95−2.01 (m, 2H), 3.59 (s, 9H), 4.49 (t, J = 6.6, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 5.3, 22.4, 50.6, 70.1, 80.7, 139.9, 140.9, 142.0, 142.6, 142.8, 142.94, 142.96, 143.5, 143.6, 143.8, 144.26, 144.33, 144.60, 144.64, 144.9, 145.0, 156.1. FAB-MS m/z 941 ([M]$^+$). UV−vis (CH_2Cl_2) λ_{max} 495, 421, 325, 255, 228 nm. HR-MS calcd for ($C_{67}H_{15}NO_5Si$) 941.0719, found 941.0743. Aziridinofullerene **1*l*** was obtained without exchanging the alkoxy groups by using EtOH in the step of the chlorination of **4*l***. ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.74−0.81 (m, 2H), 1.20−1.56 (m, 9H), 1.92−2.04 (m, 2H), 3.79−3.88 (m, 6H), 4.50 (t, J = 6.9, 2H).

1,2-*N*-[{(*S*)-2-(Methoxycarbonyl)-1-pyrrolidino}carbonyl]-aziridino[60]fullerene (1m). Black crystalline solid. FT-IR (KBr) 3448, 2924, 2852, 1743, 1687, 1388, 1184, 52 cm^{-1}7. ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.21−2.45 (m, 4H), 3.81 (s, 3H), 4.34−4.38 (m, 2H), 4.76 (dd, J = 4.2, 8.2, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.1, 29.7, 47.8, 52.5, 56.0, 80.5, 140.36, 140.39, 140.9, 142.05,142.11, 142.2, 142.7, 143.0, 143.7, 144.0 144.07, 144.11, 144.37, 144.43, 144.8, 145.0, 145.1, 155.3, 172.0. UV−vis (CH_2Cl_2) λ_{max} 421, 323, 256, 227 nm. FAB-MS m/z 840 ([M]$^+$ + 1). HR-MS calcd for ($C_{67}H_5NO_2$) 839.0371, found 839.0391. R_f 0.20 (TLC, SiO_2, toluene:AcOEt = 98:2).

General Procedure for the Synthesis of Azafulleroids. In the presence of 400 mg of MS4A, a solution of aziridinofullerenes (0.1 mmol) and ion-exchanged chloramine B[8] (11 mg, 0.02 mmol) in toluene (30 mL) was heated for the indicated times under reflux and vigorous stirring. The solution was passed through a short column of silica gel (3 g) and the solvent was then evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give corresponding azafulleroid **2** and C_{60}.

1,6-*N*-(Benzyloxycarbonyl)aza[60]fulleroid (2b). Black crystalline solid. FT-IR (KBr) 3423, 2922, 2852, 1743, 1655, 1390, 1336, 987, 526 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.77 (s, 2H), 7.48 (m, 3H), 7.65 (d, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 74.0, 128.0, 128.4, 128.6, 128.8, 134.5, 136.0, 138.1, 139.3, 140.1, 141.5, 141.8, 141.9, 142.1, 142.5, 142.6, 143.1, 143.5, 144.1, 144.4, 144.9, 145.0, 145.3, 145.6, 145.9, 146.1, 146.2, 147.7, 148.1, 148.3, 164.6. UV−vis (CH_2Cl_2) λ_{max} 316, 255, 228 nm. FAB-MS m/z 870 ([M]$^+$ + 1). HR-MS calcd for ($C_{67}H_7NO_2S$) 869.0477, found 869.0579. R_f 0.40 (TLC, SiO_2, hexane:toluene = 1:1).

1,6-*N*-(*N*′,*N*′-Dimetylaminocarbonyl)aza[60]fulleroid (2f). Black crystalline solid. FT-IR (KBr) 3444, 1654, 1382, 1103, 972, 800 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$:CS_2 = 2:1) δ 3.41 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$:CS_2 = 2:1) δ 38.3, 135.7, 138.4, 139.3, 140.2, 141.8, 141.98, 142.03, 142.2, 142.2, 142.56, 142.58, 142.64, 142.7, 144.3, 144.66, 144.70, 145.0, 145.1, 145.4, 145.5, 145.6, 146.00, 146.03, 146.1, 146.3, 146.4, 147.8, 148.2, 150.4, 162.7. UV−vis (CH_2Cl_2) λ_{max} 316, 255, 228 nm. FAB-MS m/z 807 ([M]$^+$ + 1), 720 (C_{60}). HR-MS calcd for ($C_{63}H_6N_2O$) 806.0480, found 806.0465. R_f 0.10 (TLC, SiO_2, toluene).

1,6-*N*-(Diethoxyphosphino)aza[60]fulleroid (2j). Black crystalline solid. FT-IR (KBr) 3448, 2923, 2852, 1737, 1720, 1639, 1093, 526 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.48 (t, 3H, J = 7.0), 1.49 (t, 3H, J = 7.0 Hz), 4.46 (m, 4H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 16.5, 16.6, 64.6, 64.7, 134.2, 134.3, 134.4, 136.7, 136.8, 137.6, 137.7, 138.4, 139.1, 139.7, 141.3, 141.9, 142.7, 142.8, 142.9, 143.1, 143.3, 143.4, 143.6, 143.9, 144.06, 144.14, 144.3, 144.4, 144.7, 146.4, 146.5, 147.3. UV−vis (CH_2Cl_2) λ_{max} 328, 260, 228 nm. FAB-MS m/z 872 ([M]$^+$ + 1). HR-MS calcd for ($C_{64}H_{10}NO_3P$) 871.0398, found 871.0414. R_f 0.30 (TLC, SiO_2, toluene:AcOEt = 10:1).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all fullerene derivatives and experimental procedure for the preparation of new amides and their characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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