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Novel Open-Cage Fullerenes Having a 12-Membered-Ring Orifice: Removal of the Organic Addends from the Rim of the Orifice

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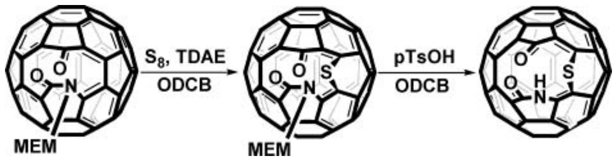
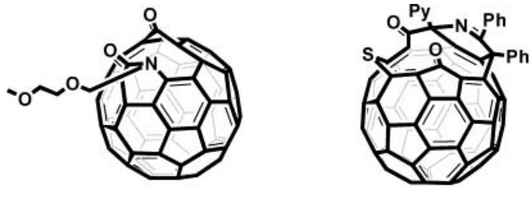
ABSTRACT



Two novel open-cage fullerene derivatives bearing a 12-membered-ring orifice on the fullerene cage have been isolated. Removal of the N-MEM protective group leads to the first open-cage [60]fullerene derivative without organic addends on the rim of the orifice.

N-MEM-ketolactam **1** (Scheme 1), the first reported open-cage fullerene derivative, was isolated in 1995 by Wudl and co-workers.[1] Since then, several synthetic procedures toward the formation of an orifice in the fullerene shell have been developed.[2−6] Opened species, bearing sufficiently large apertures to incorporate atoms, molecules or ions such as He, Ne, H_2, N_2, or Li^+, are important members in the fullerene family because of their potential use in the production of endohedral fullerene derivatives. Endohedral fullerenes are currently being formed by utilizing the evaporation of graphite-metal composites, high-temperature and high-pressure conditions, ion implantation, or high-energy plasma insertions into pure fullerenes.[7−10] The chemical creation and then closure of the opening, following the encapsulation of the desired species within the fullerene cage, known as the “molecular surgery” approach, has been proposed as an alternative route to the synthesis of endohedral fullerenes. This has proven to be possible quite recently by the gas-phase generation of $H_2@C_{60}$ during MALDI-TOF mass spectrometry experiments of an open-cage fullerene derivative.[11]

Scheme 1



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Following the work of Wudl,[1] Rubin and co-workers prepared an open-cage bislactam [60]fullerene derivative with

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(1) Hummelen, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 7003−7004.
(2) Schick, G.; Jarrosson, T.; Rubin, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 2360−2363.
(3) Murata, Y.; Murata, M.; Komatsu, K. *Chem. Eur. J.* **2003**, *9*, 1600−1609.
(4) Iwamatsu, S.-I.; Ono, F.; Murata, S. *Chem. Commun.* **2003**, 1268−1269.
(5) Murata, Y.; Murata, M.; Komatsu, K. *J. Org. Chem.* **2001**, *66*, 8187−8191.
(6) Inoue, H.; Yamaguchi, H.; Iwamatsu, S.-I.; Uozaki, T.; Suzuki, T.; Akasaka, T.; Nagase, S.; Murata, S. *Tetrahedron Lett.* **2001**, *42*, 895−897.
(7) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843−892.

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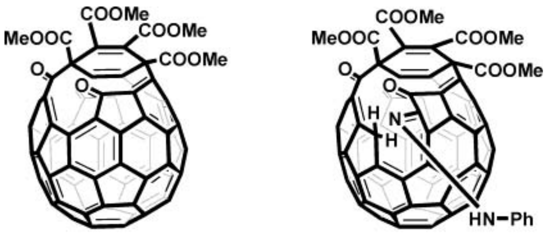
a 14-membered-ring orifice by the scission of four bonds of the fullerene cage[2] and succeeded in introducing inside the cage both He atoms and H_2 molecules with yields of 1.5 and 5%, respectively.[12] In addition, Komatsu and co-workers isolated the open-cage fullerene derivative **2** (Scheme 1),[3] within which they encapsulated H_2 molecules in 100% yield at an applied H_2 pressure of 800 atm at 200 °C.[11]

Moreover, a regioselective addition reaction between the α,β-unsaturated carbonyl structure of the open-cage fullerene adduct **3** and aromatic hydrazines was recently reported.[4] The reaction proceeds with migration of two hydrogen atoms from the hydrazine to the fullerene, affording adduct **4**, which has a methylene carbon along the orifice (Scheme 2).

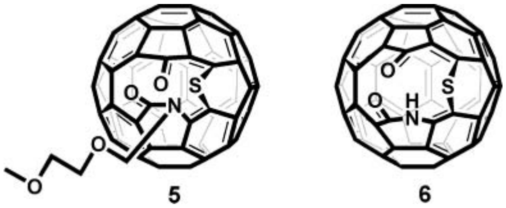
Scheme 2



3 **4**

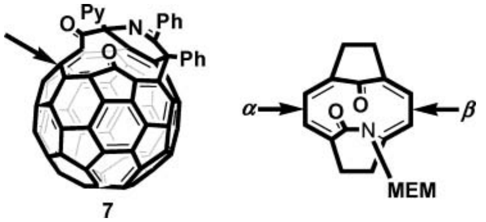
In this communication we report the synthesis, isolation, and characterization of the two new open-cage fullerene derivatives **5** and **6** presented in Scheme 3, containing a 12-membered ring on the surface of the [60]fullerene. To the best of our knowledge, adduct **6** is the first open-cage [60]-fullerene adduct without any organic addend on the rim of the orifice.

Scheme 3



5 **6**

Scheme 4



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The resemblance of the structure of the *N*-MEM-ketolactam **1** to the α,β-unsaturated carbonyl structure of **7** (Scheme 4), which is the precursor of adduct **2**,[3] prompted us to examine its reactivity toward elemental sulfur. Heating of **1** at 180 °C together with S_8 in 1,2-dichlorobenzene (ODCB) for 30 min in the presence of tetrakis(dimethylamino)ethylene (TDAE) afforded **5** in very good yield (72% based on the amount of the isolated adduct). This successful and efficient sulfur insertion indicates that Komatsu's procedure is of general applicability.[3] The molecular ion peak of **5** was clearly observed (*m*/*z* 887) in the MALDI-TOF mass spectrum of the new adduct. The ^{1}H NMR spectrum of adduct **5** is almost identical to that of the starting material **1** apart from a slight downfield shift of all peaks. The ketone ^{13}C NMR absorption shifted from δ 198.5 ppm in the starting material **1** to δ 190.2 ppm in the adduct **5**, while the lactam ^{13}C chemical shift change was insignificant (the lactam carbon resonances are at 163.6 and 163.5 ppm in **1** and **5**, respectively). The ketone carbonyl absorption in the IR spectrum of **5** shifted to 1738 from 1727 cm^{-1} in the starting material **1**, while the lactam carbonyl was practically unaffected since it moved to 1695 from 1693 cm^{-1}. The UV−VIS spectrum of the new adduct in chloroform is almost identical to the starting material *N*-MEM-ketolactam, showing absorption maxima at 256 and 320 nm, whereas the corresponding absorptions of **1** are at 260 and 328 nm, respectively.

Both ^{13}C NMR and IR spectra of the new adduct rule out the possibility that the sulfur atom is inserted into the central C−C bond, α, of the butadiene unit of the starting material (Scheme 4) as one might expect from the reaction of **7** with elemental sulfur. In such a case, the lactam carbonyl absorption shift would have been comparable to that of the ketone. Consequently, we arrive at the conclusion that reaction with sulfur occurs at bond β in **1**, thereby affording adduct **5** (Scheme 3).

We next tried to remove the MEM protecting group, aiming at the synthesis and isolation of the thio-aza-[60]-fullerene **8** via the intermediate radical **9** (Scheme 5) by utilizing the azafullerene production method.[13] For this reason, we heated **5** in a degassed ODCB solution at 150 °C in the presence of 30 equiv of *p*-toluenesulfonic acid monohydrate for 2 h. However, after column chromatographic purification, instead of **8** we isolated adduct **6**, the solubility of which is very low even in ODCB, in 58% yield.

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(8) Nagase, S.; Kobayashi, K.; Akasaka, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2131−2142.

(9) (a) Mauser, H.;. Van Eikema Hommes, N. J. R.; Clark, T.; Hirsch, A.; Pietzak, B.; Weidinger, A.; Dunsch, L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2835−2838. (b) Pietzak, B.; Waiblinger, M.; Murphy, T. A.; Weidinger, A.; Hφhne, M.; Dietel, E.; Hirsch, A.; *Chem. Phys. Lett.* **1997**, *279*, 259−263.

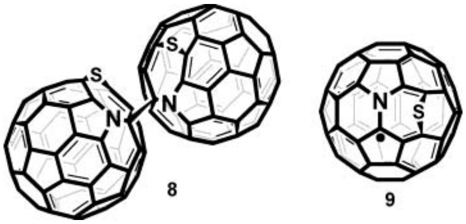
(10) Stevenson, S.; Rice, G.; Glass, T.; Harich, K.; Cromer, F.; Jordan, M. R.; Craft, J.; Hadju, E.; Bible, R.; Olmstead, M. M.; Maitra, K.; Fisher, A. J.; Balch, A. L. Dorn, H. C. *Nature* **1999**, *401*, 55−57.

(11) Murata, Y.; Murata, M.; Komatsu, K. *J. Am. Chem. Soc.* **2003**, *125*, 7152−7153.

(12) Rubin, Y.; Jarrosson, T.; Wang, G.-W.; Bartberger, M. D.; Houk, K. N.; Schick, G.; Saunders, M.; Cross, R. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1543−1546.

(13) Hummelen, J. C.; Knight, B.; Pavlovich, J.; Gonzalez, R.; Wudl, F. *Science* **1995**, *269*, 1554−1556.

Scheme 5



8

9

Apparently, the insertion of the sulfur atom in the fullerene cage has extensively changed the chemical behavior of the ketolactam as well as the MEM deprotection mechanism.

The molecular ion peak of **6** was observed at *m*/*z* 799 in its MALDI-TOF mass spectrum. The ^{1}H NMR spectrum of adduct **6** (ODCB-d_4) showed only a D_2O exchangeable singlet at δ 9.27 ppm. This time both the ketone and the lactam carbon absorption shifts in the ^{13}C NMR spectrum (ODCB/benzene-d_6 = 6/1) were insignificant. They were observed at δ 191.2 (190.2 in **5**) and 161.7 ppm (163.5 in **5**), respectively. The ketone carbonyl absorption in the IR spectrum of **6** moved to 1725 from 1738 cm^{-1} in the starting material **5**, while the lactam carbonyl remained again unaffected since it moved to 1694 from 1695 cm^{-1}. The UV−VIS spectrum of the new adduct in ODCB/benzene = 6/1 shows absorption maxima at 295, 320, and 406(sh) nm.

In conclusion, the sulfur-atom insertion[3] into the butadiene unit of *N*-MEM ketolactam **1** significantly changes the chemical behavior of the *N*-MEM protective group, providing the first open-cage fullerene derivative without organic addends on the rim of the orifice.

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Supporting Information Available: Detailed experimental procedures, NMR, FT-IR, and UV−VIS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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