Communications to the Editor

There Is a Hole in My Bucky

Jan C. Hummelen,[†] Maurizio Prato,[‡] and Fred Wudl*,[†]

Institute for Polymers and Organic Solids
Department of Chemistry and Physics
University of California, Santa Barbara
Santa Barbara, California 93106
Dipartimento di Scienze Farmaceutiche
Piazzale Europa 1, 34127 Trieste, Italy

From the beginning, the discovery of C_{60} and the other fullerenes has ignited the imagination of many scientists, in particular those working in supramolecular chemistry. These carbon cages are the simplest hollow structures which might give rise to interesting host−guest complexes with potential applications that would include complexation, catalysis, constrictive binding, and protection of unstable species.[1]

The first examples of endohedral metallofullerenes were prepared in 1991 with a high-temperature laser vaporization method.[2] The preferred way to prepare endohedral complexes has been the carbon arc burning method using mixtures of graphite and the guest-to-be materials in composite rods.[2] Noble gases can also be forced into the cages by high-temperature−high-pressure conditions.[3] The yields of endohedral complexes in these reactions are very low, and separation from the hollow fullerenes for purification of the desired products has been a major problem. The above-mentioned methods are not likely to be suitable for the encapsulation of small molecules as well as molecular and atomic ions.

Another approach to endohedral complexes would comprise controlled opening of the fullerene, encapsulation of the guest material, and restoration of the original fullerene structure, a strategy that Hawkins very likely considered in his pioneering work on osmylation of C_{60} and C_{70}.[4,5] Hydrolysis of the osmate esters apparently did not afford the diol, and this approach failed.

Here we report the first regioselective and efficient synthetic method for severing two adjacent bonds in C_{60}.[6]

Reaction of C_{60} with azides yields [5.6]azafulleroids in good yields.[7] In the azafulleroid, one C−C bond is cleaved (see **1**), and the C=C bonds adjacent to the nitrogen atom are susceptible to regiospecific formation of bisazafulleroids.[8]

The previously reported elegant work on the self-sensitized photooxygenation of certain C_{60} adducts[9] was applied to *N*-methoxyethoxymethyl (MEM)-substituted [5.6]azafulleroid **1**[1]
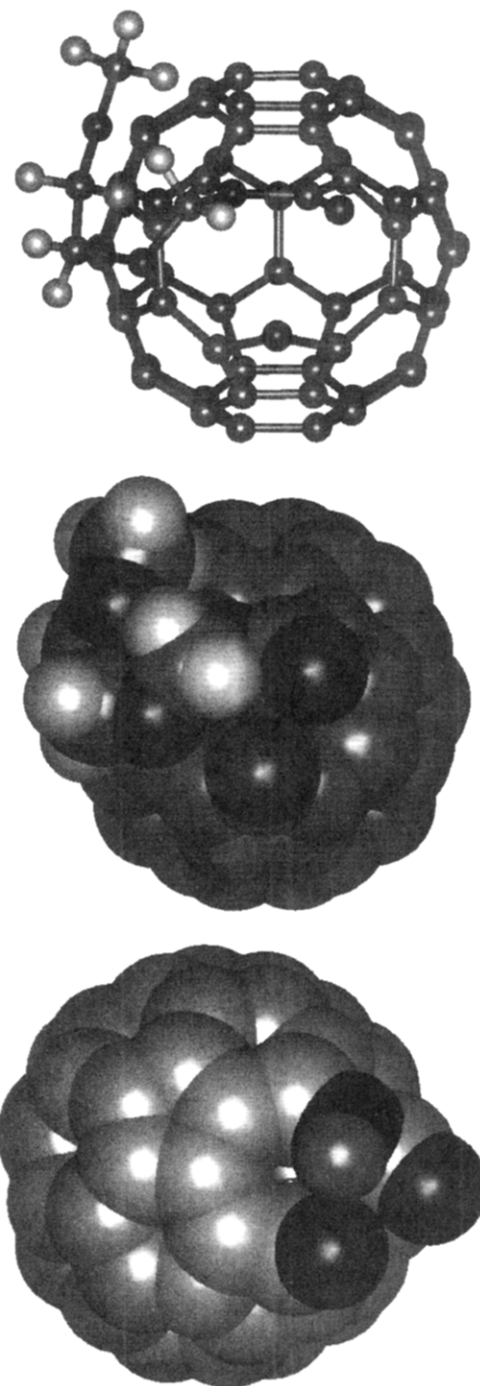

Figure 1. (A) Ball and stick molecular model of **3** (top). The dark sphere on the near bottom center is the keto oxygen, and the dark sphere on the center right is the lactam carbonyl oxygen. (B) CPK molecular model of **3** (middle) in exactly the same position as in (A). The hole described in note 14 is just to the right of the lactam carbonyl and is clearly visible in (C). The group of atoms wrapping around the upper left is the lowest energy conformer of the MEM group. (C) Same as (B), except the ball was rotated and the MEM group replaced by a hydrogen atom to better reveal the orifice, which is part of a longer slit (bottom).

to afford the ring-opened *N*-MEM-ketolactam **3** in high yield (Scheme 1 and Figure 1).

The reaction, using 1,2-dichlorobenzene (ODCB) as the solvent and a Kapton 500HN (DuPont) filtered flood lamp as

[†] University of California, Santa Barbara.
[‡] Dipartimento di Scienze Farmaceutiche.
(1) Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests*; The Royal Society of Chemistry: Cambridge, 1994.
(2) Chai, Y.; Guo, T.; Jin, C.; Haufler, R. E.; Chibante, L. P. F.; Fure, J.; Wang, L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 7564.
(3) Saunders, M.; Jiménez-Vazquez, H. A.; Cross, R. J.; Poreda, R. J. *Science* **1993**, *259*, 1428.
(4) Hawkins, J. M.; Meyer, A.; Solow, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 7499.
(5) Hawkins, J. M.; Meyer, A. *Science* **1993**, *260*, 1918.
(6) A nonspecific oxidative cluster opening was reported: Taliani, C.; Ruani, G.; Zamboni, R.; Danieli, R.; Rossini, S.; Denisov, V. M.; Burk, V. M.; Burlakov, F.; Negri, G.; Orlandi, F.; Zerbetto, X. *J. Chem. Soc., Chem. Commun.* **1993**, 220.
(7) Prato, M.; Li, Q.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148.
(8) Grösser, T.; Prato, M.; Lucchini, V.; Hirsch, A.; Wudl, F. *Angew. Chem.*, in press.
(9) Zhang, X.; Romero, A.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 11024−11025.

Scheme 1
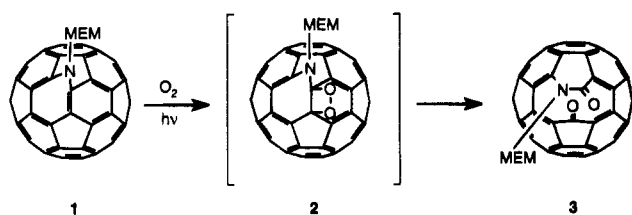
the light source, is virtually complete within 3 h at 25—30 °C. The Kapton filter is a convenient alternative for the commonly used aqueous dichromate solution filter.[10] The reaction is highly regioselective, most likely because the anti-Bredt carbon—carbon double bonds in 1 are more strained. We assume the product was formed through the 1,2-dioxetane intermediate 2. Keto-lactam 3 was separated from traces of starting material and obtained in pure form (~70% yield) by column chromatography (silica gel/ toluene—EtOAc 9:1). Compound 3 shows two carbonyl absorptions in the FT-IR, one at 1727 (ketone) and the other at 1693 (lactam) cm⁻¹. These values deviate slightly from the corresponding ones for fluorenone (1714 cm⁻¹) and 5-methyl-5H-phenanthridin-6-one (1645 cm⁻¹),[11] respectively, reflecting some extra strain and/or less aromaticity in 3 compared to the model compounds. The UV—vis spectrum of 3 in chloroform is distinctly different from those of the well-described [5.6]- and [6.6]-, 1,2-adducts of C₆₀, showing absorption maxima at 260, 328, 428 (sh), 466 (sh), 616 (sh), and 688 nm. The 500 MHz ¹H NMR spectrum of 3 in CS₂/TMS reveals that the MEM group is unaffected by the photooxygenation reaction. The two diastereotopic N-methylene protons of the asymmetric compound give rise to an AB system (J_{AB} = 10.5 Hz; ∂ = 6.19 and 5.83 ppm), the ethoxy methylenes appear as multiplets at 3.89 and 3.48 ppm, and the terminal methoxy group shows a singlet at 3.23 ppm. The asymmetry of 3 is most clearly revealed in its 500 MHz ¹³C NMR spectrum in CDCl₃: 51 sp² carbon resonances appear at 128.0—150.1 ppm. The ketone and lactam carbon atoms appear at 198.5 and 163.6 ppm, respectively. The four carbon atoms of the MEM group show resonances at 59.1 (OCH₃), 70.0, 71.6 (ethylene), and 80.6 (N-methylene) ppm. FAB-MS showed a strong (M + H)⁺ peak at m/z 856. Hence, both ¹³C NMR and FAB-MS rule out the possibility that the product would actually be the result of a double photooxygenation reaction, i.e., diketoimide 4.[12]

Compound 3 is stable under the reaction conditions; no new products were detected after 4 h of photooxygenation in ODCB at 25—30 °C. Thereafter, methylene blue was added as a sensitizer, and the photooxygenation was resumed; no further reaction occurred within 5 h.

4   5
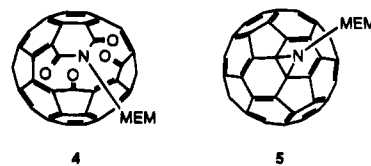
Recently, we reported the efficient (oxygen-suppressed) photochemical rearrangement of a fulleroid to the corresponding methanofullerene isomer.[13] In our laboratory, this photochemical rearrangement is an effective and convenient method for the preparation of a number of methanofullerenes. When azafulleroid 1 was irradiated under the same anaerobic conditions (Kapton 500HN-filtered light), no isomerization occurred (a fundamental difference in reactivity between azafulleroids and fulleroids),[13] but a very slow conversion to 3 took place, indicating the very high efficiency of traces of O₂ sensitization by 1.

When solutions of [6.6]-N-MEM-fulleroaziridine 5 in ODCB were irradiated, no reaction took place with O₂, neither in the presence nor in the absence of methylene blue, and no photochemical isomerization under anaerobic conditions could be detected; this indicates a fundamental equivalence in reactivity between fulleroaziridines (e.g., 5) and methanofullerenes.

A ball and stick molecular model generated with Insight (Insight II Molecular Modeling v. 2.3.5, Biosym Technologies, 1994) on a Silicon Graphics Iris workstation shows the relatively large size of the hole (Figure 1A); however, a CPK model (Figure 1B) clearly indicates that compound 3, at its minimum energy conformation, does not have an opening large enough to allow any guest molecule to enter the cage. Some flexibility in the keto and lactam moieties at elevated temperatures is expected and should increase the size of the opening;[14] also, removal of the MEM protecting group should further increase access to the cavity.

The work presented here can be considered a first step toward the controlled opening of the fullerene cage. Further elaboration of ketolactam 3 in this direction is currently under active investigation.

Supporting Information Available: Experimental details for the preparation, purification, and characterization of 3 (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA951186I

(10) Hummelen, J. C. Ph.D. Dissertation, University of Groningen, The Netherlands, 1985.

(11) Lüdersdorf, R.; Martens, J.; Pakzad, B.; Preafcke, K. *Liebigs Ann. Chem.* **1977**, 1992.

(12) Elemental analysis for 3, calcd for C₆₄H₉NO₄: C, 89.82; H, 1.06; N, 1.64. Found: C, 87.21; H, 1.32; N, 1.61.

(13) Janssen, R. A. J.; Hummelen, J. C.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 544.

(14) Approximately 0.3 × 0.5 Å (within the certainty of the calculation method of Insight, see Figure 1C), sufficient for the penetration of He.