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Published in:
Journal of the American Chemical Society

DOI:
10.1021/ja00131a024

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1995

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
There Is a Hole in My Bucky

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Received April 12, 1995

From the beginning, the discovery of C₆₀ and the other fullerences 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 fullerences 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 fullerence structure, a strategy that Hawkins very likely considered in his pioneering work on osmylation of C₆₀ and C₂₆.⁴⁵ 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 C₆₀:⁶

Reaction of C₆₀ 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 bisazafulleoloids.⁸

The previously reported elegant work on the self-sensitized photooxygenation of certain C₆₀ adducts⁹ was applied to N-methoxyethoxymethyl (MEM)-substituted [5,6]azafulleloid ¹¹.

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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
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. 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. Compound 3 was separated from traces of starting material and obtained in pure form (~70% yield) by column chromatography.

Recently, we reported the efficient (oxygen-suppressed) photochemical rearrangement of a fulleroid to the corresponding methanofullerene isomer. 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 azafullerenoids and fulleroids), 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; 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.

Acknowledgment. We thank the National Science Foundation for support through the Materials Research Laboratory as well as Grants DMR-91-22536, DMR-91-11097, and CHE 93-00954 to F.W. M.P. and F.W. thank NATO for a travel grant (CRG 930451).

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.