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Published in:
Journal of the American Chemical Society

DOI:
10.1021/ja00106a068

Published: 01/01/1995

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

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Link to publication

Citation for published version (APA):
Photochemical Fulleroid to Methanofullerene Conversion via the Di-\(\pi\)-methane (Zimmerman) Rearrangement

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Received June 15, 1994

The preparation of functionalized fullerenes is a rapidly growing area of scientific interest. One of the objectives in chemically modifying buckminsterfullerene (C\(_{60}\)) is to add novel features to the remarkable set of properties of fullerenes, most noticeably its ability to accommodate up to six electrons in a reversible fashion. A reliable and versatile route to functionalization has been found via the addition of diazo compounds to C\(_{60}\). This route offers the possibility of obtaining monoad-
gloration has been found via the addition of diazo compounds to C\(_{60}\) and the reaction of 1-phenyl-1-(3-(methoxycarbonyl)propyl)diazo-methane with C\(_{60}\). Purification of the reaction mixture offered traces of 2. Based on \(^{13}\)C NMR (e.g., quaternary C(61) at 60.9 ppm and bridgehead carbons in the aromatic region), the fulleroid structure was assigned to 1. Fulleroid 1 was converted thermally into methanofullerene 2 by heating in \(\alpha\)-dichlorobenzene at 180 °C for 6 h. The isomerization was followed by HPLC (reversed-phase C18 column, MeOH/CHCl\(_3\) 3:1). The \(^{13}\)C NMR spectrum of 2 reveals C(61) at 50.7 ppm and bridgehead carbons at 79.3 ppm, in accordance with a methanofullerene structure. UV/vis spectra are in agreement with typical features of fulleroids and methanofullerenes. There are

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Figure 1. UV/vis spectra of 1, 2, and C\(_{60}\) in \(p\)-xylene.

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Figure 2. UV/vis spectra taken at different time intervals during the photochemical 1 \(\rightarrow\) 2 conversion.

60 \(\pi\) electrons in the [5,6]methanoannulene 1, and the visible region of its electronic spectrum is almost identical to that of C\(_{60}\) (cf. Figure 1), suggesting the same \(\pi\)-bonding. Cyclopropane 2, on the other hand, has 58 \(\pi\) electrons, and the spectrum exhibits a hypsochromic shift in addition to two diagnostic peaks at 434 and 697 nm.

We found that irradiation of 1 in deoxygenated \(p\)-xylene (3 \(\times\) \(10^{-4}\) M) at ambient temperature with light from an Ar ion laser (488 nm, 50 mW, 10 mm path length) gives rise to a quantitative conversion to 2 in approximately 1 h. The UV/vis spectra (Figure 2) taken at different time intervals reveal three isosbestic points in the visible region at 430, 550, and 662 nm, indicating the interconversion of two species. The final spectrum is superimposable with that of an independently synthesized sample of 2, and NMR as well as HPLC confirm the quantitative conversion.

The sp\(^3\) carbon of 1, formally carrying two vinyl groups, represents the basic structural moiety required for a photochemical di-\(\pi\)-methane rearrangement, described by the following formal mechanistic scheme:

In acyclic systems, the di-\(\pi\)-methane rearrangement is known to proceed preferentially via the singlet state, although in case of 3-methyl-1-(9-phenanthryl)-1-buten, also reactivity from the
triplet state has been observed.\(^5\) Rigid (bicyclic) molecules are known to react via the triplet state.\(^2\) Based on this general rule and the fact that intersystem crossing in \(C_{60}\) is very efficient,\(^6\) it is likely that \(1\) rearranges via the triplet manifold. Consistent with a triplet intermediate, we find that the rate of conversion \(1 \rightarrow 2\) decreases by a factor of more than 20 in air-saturated \(p\)-xylene, due to triplet quenching by oxygen.

Metastable triplet states can readily be detected using near-steady-state photoinduced absorption (PIA) spectroscopy. The PIA spectrum of \(C_{60}\) (Figure 3) in \(p\)-xylene exhibits a triplet band at \(1.65\) eV with a shoulder at \(1.80\) eV. The PIA spectrum of \(2\) shows that intersystem crossing to the triplet state is also efficient for functionalized fullerenes; triplet PIA bands appear at \(1.50\) and \(1.73\) eV (Figure 3). The spectra in Figure 3 show a close resemblance to PIA results on \(C_{60}\) and [6,6]diphenyl-\(C_{60}\) incorporated in polystyrene glasses at \(4\) K, assigned to absorptions within the triplet manifold using optically detected magnetic resonance.\(^7\) The initial PIA spectrum of \(1\) is weak (Figure 3). Although one can speculate on the absence of an equally strong PIA spectrum for \(1\) as compared to \(2\) and \(C_{60}\), a possible explanation is the efficient reaction of \(1\) to \(2\). When intersystem crossing to the singlet manifold occurs before cyclization, \(2\) is obtained in the (singlet) ground state, and PIA features will be absent. Continued irradiation of \(1\), however, produces \(2\), and, concomitant with the change in the UV/vis spectrum, the PIA spectrum recorded after \(2\) h is identical to that of \(2\) (Figure 3).

We conclude that the photochemical reaction of fulleroid \(1\) to methanofullerene \(2\) is an example of the di-\(\pi\)-methane rearrangement via the triplet manifold. The rearrangement is efficient for \(1\) but does not take place for [5,6]C\(_{61}\)H\(_2\), consistent with the general requirement for the di-\(\pi\)-methane rearrangement that the methane carbon carries substituents.\(^2\) Evidently, the intermediate 1,3-diradical of \(1\) will be stabilized by the phenyl ring. This photochemical interconversion is of potential synthetic interest, especially when a thermal rearrangement of fullerenes is not feasible due to product instability.

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. R.A.J.J. acknowledges the Eindhoven University of Technology for financial support.

Supplementary Material Available: Experimental details for the preparation, purification, and characterization of \(1\) and \(2\) (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.