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Photolysis of Diazirines in the Presence of C_{60}: A Chemical Probe for Carbene/Diazomethane Partitioning

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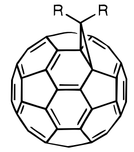
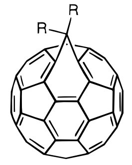
Photolysis and thermolysis of diazirines have been widely used to produce carbenes.[1] Bonneau and Liu have reported that these reactions yield not only a singlet carbene but also a diazo compound as an intramolecular rearrangement product.[2] The nature of the specific substituents on the diazirine determines the formation of the corresponding diazomethane as an intermediate, which may or may not be observed.[3] These authors also reported on the quantum yields of the formation of carbene and diazo compounds derived from the photolysis of diazirines by means of laser flash photolysis.[2]

Numerous chemical transformations have been developed since the isolation of C_{60} in preparatively useful quantities.[4] C_{60} has a unique reactivity, which differs significantly from that of classical planar aromatics.[5] C_{60} reacts with diazomethane to yield fulleroid.[5d,6] Carbene generated from the thermolysis of precursors such as diazirines,[7] sodium trichloroacetate,[8] cyclopropene,[9] oxadiazole,[10] and tosylhydrazone[11] adds onto C_{60}, affording methanofullerene.[4] These differences might be useful in differentiating whether carbene or diazo compound is involved as the reactive intermediate. In this context, we have carried out the photolysis of diazirine in the presence of C_{60}.

Our report demonstrates that C_{60} acts as a mechanistic probe for the formation of carbene and diazo compound in the photolysis of diazirine. As well, our experiment offers the first redox data of methanofullerene and fulleroid bearing the same substituent at the bridging carbon atom on the C_{60} moiety.



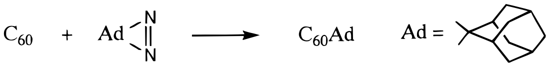
methanofullerene



fulleroid

Irradiation of a benzene solution of 2-adamantane-2,3′-[3H]-diazirine (**1**, 2.5×10^{-4} M) and C_{60} (2.5×10^{-3} M) with a high-pressure mercury arc lamp (cutoff < 300 nm) at 15 °C in a Pyrex tube resulted in the formation of the corresponding adduct C_{60}-Ad (**2**) in 80% yield, which was purified by preparative HPLC with a GPC column. Adduct **2** can be readily separated into two isomers, **2a** and **2b**, by preparative HPLC with a Buckyprep column (Scheme 1). The isomeric ratio of **2a** and **2b** is 49/51.

Scheme 1



1 **2**

FAB mass spectrometry of **2a** and **2b** gives a molecular ion peak ($C_{70}H_{14}$ requires *m/z* 854) at *m/z* 858−854, as well as a peak for C_{60} at *m/z* 724−720, which arises from the loss of the adamantyl group. The UV−visible absorption spectra of **2a** and **2b** are virtually identical to that of C_{60}, except for a subtle difference in the 400−650 nm region. These results suggest that **2a** and **2b** retain the essential electronic and structural character of C_{60}. The UV−visible absorption spectrum of **2a** has an absorption at 434 nm, which is a characteristic feature of a 6,6-adduct of C_{60}.[12] The spectral data of ^{1}H and ^{13}C NMR and 2D NMR (HMQC and HMBC) clearly suggest that **2a** has C_{2v} symmetry.[13] Meanwhile, the analysis of ^{1}H and ^{13}C NMR(HMQC and HMBC) has offered crucial evidence for the identification of C_s symmetry of **2b** as a 5,6-adduct of C_{60}.[14]

We carried out density functional calculations at the BLYP/3-21G level for **2a** and **2b** with the Gaussian 98 program.[15] The optimized structures of **2a** and **2b** have C_{2v} and C_s symmetry, respectively, as shown in Figure 1. These have almost identical stability; **2a** is 3.7 kcal/mol more stable than **2b**. The vertical ionization potentials (Ip) and electron affinities (Ea) calculated at the BLYP/3-21G level are 6.78 and 2.04 eV for **2a** and 6.88

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(13) The ^{1}H NMR spectrum of **2a** displays five proton signals of the adamantyl group at 2.96, 2.34, 2.20, 2.07, and 1.99 ppm. In the ^{13}C NMR spectrum of **2a**, we observed 17 fullerenes resonances (16 between 148 and 138 ppm, three of which show half intensity, and one at 83.3 ppm with half intensity) as well as five non-fullerene signals for the expected C_{2v} symmetrical **2a**. In addition, an analysis of 2D NMR (HMQC and HMBC) also disclosed the assignment of the adamantyl group.

(14) In the ^{1}H NMR spectrum of **2b**, we observed seven signals at 4.87, 2.43, 2.06, 1.92, 1.76 (two overlapped), 1.69, and 1.53 ppm in which one more overlapped signal exists, due to the adamantane ring CH_2 and CH supporting the C_s symmetry of the molecule. The^{13}C NMR spectrum of **2b** shows 32 signals at 148−135 ppm for the sp^2 C_{60} framework carbons, compatible with the fusion across the 5,6-junction. Of the 32, 28 signals have a relative intensity of 2, and four signals have a relative intensity of 1. We observed seven signals due to adamantane ring at 56.95, 38.60, 37.08, 35.35, 34.14, 31.06, and 28.27 ppm in the ^{13}C NMR spectrum. These spectral data confirm the C_s symmetry of **2b**.

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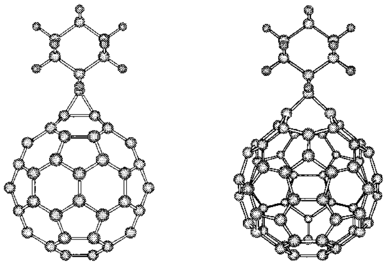

2a **2b**

Figure 1. The optimized structures of **2a** and **2b** at the BLYP/3-21G level.

and 2.05 eV for **2b**, respectively. These values agree with the fact that the HOMO level of −5.24 eV for **2a** is higher than that of −5.30 eV for **2b**, whereas the LUMO levels are almost identical at −3.60 and −3.62 eV for **2a** and **2b**, respectively.

Inasmuch as fulleroid easily rearranges to methanofullerene,[16] we carried out photolysis of pure **2a** and **2b** by themselves. We observed no interconversion between **2a** and **2b** under photolytic conditions.

On the basis of these observations, the isomeric ratio of **2a** and **2b** (49/51) in the photoreaction of C_{60} with adamantyldiazirine **1** reveals the formation ratio of carbene and diazo compound during the reaction. Liu et al. have already determined the formation ratio of adamantylidene and diazoadamantane from **1** by laser flash photolysis technique, which is 1:1.[2] Present results obtained from chemical derivatization of C_{60} by **1** are in agreement with them, which means that C_{60} acts as a chemical probe for the photochemical reaction of diazirine.

To test C_{60} as a chemical probe, we carried out an additional experiment using a different diazirine. We photoirradiated a benzene solution of phenylchlorodiazirine (**3**, 3.3×10^{-4} M) and C_{60} (3.3×10^{-3} M) under the same conditions as those we used in the case of diazirine **1** to afford the corresponding adduct C_{60}-(PhClC)[7b] (**4**) in 99% yield. The HPLC analysis and spectroscopic investigation by means of NMR measurements **4** verify that **4** is a 6,6-adduct of C_{60}. The formation of phenylchlorodiazomethane in the photolysis of diazirine **3** at 10K is only a minor process;[17] therefore, the contribution of this process in the photolysis at room temperature would be minimal. This is in agreement with all of the laser flash photolysis work on **3** at room temperature in which no phenylchlorodiazomethane has been detected.[18] Again, this is consistent with our present observation that only the 6,6-adduct is formed in the C_{60} trapping experiment.

Table 1. Redox Potentials[a] in V of C_{60},[b] **2a**, and **2b**

compd	oxE$_1$	redE$_1$	redE$_2$	redE$_3$
C_{60}	+1.21[c,d]	−1.12	−1.50	−1.95
6,6-C_{60}Ad (**2a**)	+1.07	−1.21	−1.58	−2.06
5,6-C_{60}Ad (**2b**)	+1.10	−1.18	−1.55	−2.02

[a] Half-cell potentials unless otherwise stated. Values are relative to ferrocene/ferrocenium couple. [b] Reference 20. [c] Irreversible. [d] Value was obtained by differential pulse voltammogram (DPV).

In view of the electron-acceptor character of C_{60}, there is a great interest in the electrochemical behavior of C_{60} derivatives bearing an organic addend.[19] We studied the redox potentials of the prepared compounds by cyclic voltammetry (CV) at room temperature. The data are collected in Table 1, together with the C_{60} as reference compound. Although the CV data of the methanofullerenes and the fulleroids have been previously reported, to the best of our knowledge, this experiment demonstrates the first redox data of methanofullerene and fulleroid bearing the same substituent on the C_{60} skeleton. Both adducts exhibit three one-electron reversible reduction waves and one irreversible oxidation, one like that observed for the parent C_{60}. The salient feature is that 6,6-adduct **2a** has a low oxidation potential (+1.16 V) in comparison with the 5,6-adduct **2b** (+1.45 V). The theoretical study supports these results. The HOMO level of **2a** is higher than that of **2b**; the Ip value for **2a** is smaller than that for **2b**. Meanwhile, the first reduction potentials are cathodically shifted, related to C_{60}, which indicates that the introduction of an adamantyl group results in decreasing the electron-accepting properties. This finding is in agreement with that previously observed for other dihydrofullerenes,[21] and it has been explained by the raising of the LUMO energy of the adducts.

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Supporting Information Available: Detailed procedures for the preparation of **2** and **4**, complete spectroscopic characterization of **2** and **4**, CV and DPV voltammograms, and the optimized Cartesian coordinates of **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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