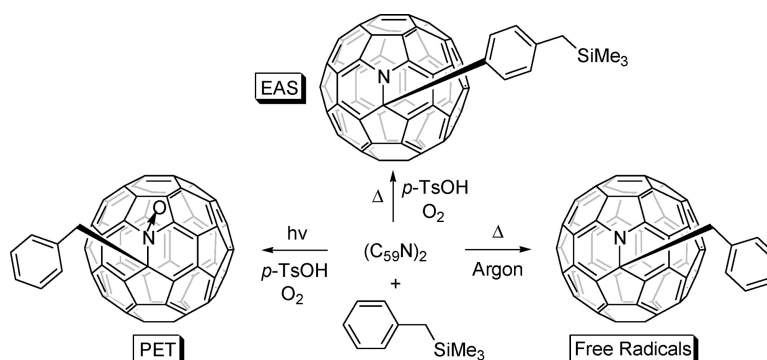


Photoinduced Electron Transfer Reactivity of Aza[60]fullerene: Three Discrete Functionalization Pathways with a Single Substrate

Georgios C. Vougioukalakis, and Michael Orfanopoulos

J. Am. Chem. Soc., **2004**, 126 (49), 15956-15957 • DOI: 10.1021/ja045495x • Publication Date (Web): 16 November 2004

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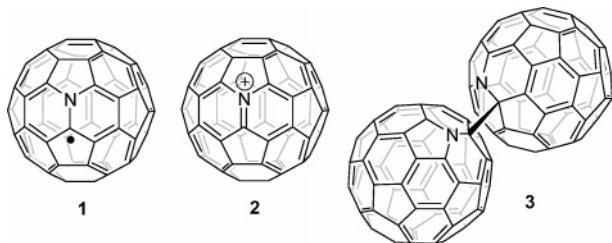
Georgios C. Vougioukalakis and Michael Orfanopoulos*

Department of Chemistry, University of Crete, 71409 Iraklion, Crete, Greece

Received July 27, 2004; E-mail: orfanop@chemistry.uoc.gr

Azafullerenes, $(C_{59}N)_2$ and $(C_{69}N)_2$, are the only heterofullerenes that have been synthesized and isolated in bulk quantities by "chemical procedures".^{1,2} In the past few years, research on the properties of the $(C_{59}N)_2$ dimer has attracted considerable experimental³ and theoretical⁴ attention. Since its discovery, two basic strategies have been developed for the preparation of monomeric aza[60]fullerene adducts.⁵ The first one, which was developed by Wudl and co-workers,^{6,7} is based on the trapping of the azafullerenyl radical $C_{59}N^\bullet$ (**1**). By using this methodology, we recently isolated four new aza[60]fullerene adducts via its radical reactions with 9-alkyl-substituted fluorenes.⁸ The second and more frequently used route was developed by Hirsch and collaborators^{9–13} and is based on the trapping of the azafullerenium carbocation $C_{59}N^+$ (**2**) by a number of nucleophiles. Carbocation **2**, which is isoelectronic to [60]fullerene, is produced and reacted in situ by thermal treatment of dimer **3** in the presence of oxygen, toluene-*p*-sulfonic acid (*p*-TsOH), and the nucleophile. The monomeric $C_{59}N^+$ cation has been isolated lately as the carborane anion salt by oxidation of the sp^3 – sp^3 C–C bond of **3** with hexabromo(phenyl)carbazole.¹⁴

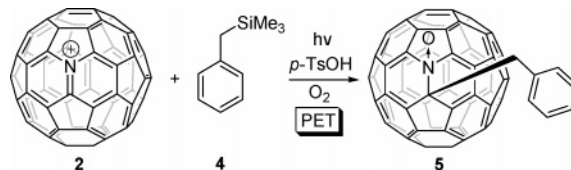
Chart 1



It is also well-known that iminium cations participate in a wide variety of photoinduced electron transfer (PET) reactions, with several neutral electron donors, leading to the generation of stabilized α -amino radicals.¹⁵ Neutral α -amino radicals produced in this way have been shown to participate in secondary reactions, such as radical coupling. A highly selective reaction pathway followed by donor cation radicals that bear α -trialkylsilyl substituents is desilylation.^{15,16}

This interesting reactivity of iminium cations prompted us to investigate the photochemical and thermal behavior of azafullerenium carbocation **2**, which bears structural resemblance to the ordinary iminium cation species. Herein, we report on the photoinduced electron transfer reaction between **2** and benzyltrimethylsilane **4** to afford the new aza[60]fullerene monoadduct **5** (Scheme 1). This kind of $C_{59}N^+$ reactivity has not been previously recognized and provides a new, promising functionalization method for azafullerenes. We will also show that depending on reaction conditions, aza[60]fullerene monoadducts **6** and **7** (Chart

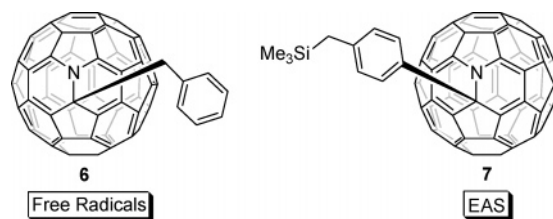
Scheme 1. Photoinduced Electron Transfer Reaction between Aza[60]fullerenium Carbocation **2** and Benzyltrimethylsilane **4**



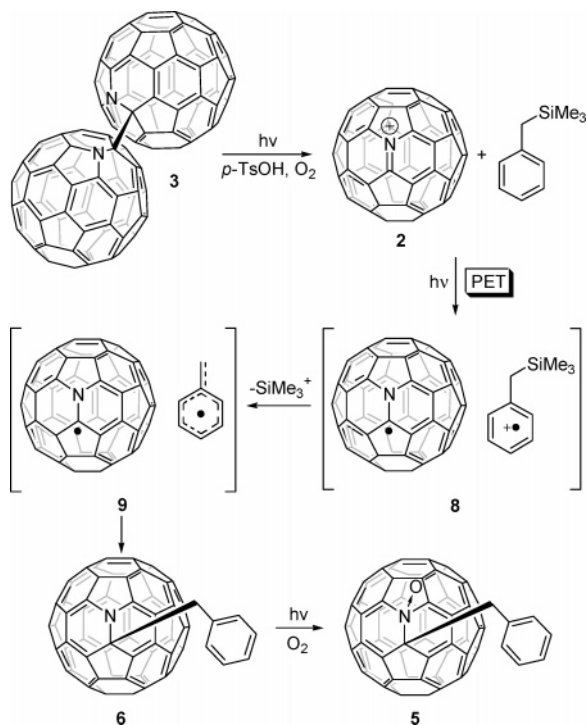
2) are exclusively produced by two distinct mechanisms, namely, free radicals and electrophilic aromatic substitution (EAS), respectively.

A solution of $(C_{59}N)_2$ together with a large excess of benzyltrimethylsilane in *o*-dichlorobenzene (ODCB) was irradiated in the presence of oxygen and *p*-TsOH with a 300 W xenon lamp (>300 nm) as the light source. After 40 min, adduct **5** was obtained in 28% isolable yield by semipreparative HPLC. Adduct **5** was characterized by 1H , ^{13}C , DEPT, and HMQC NMR experiments, as well as with FT-IR, UV–vis, and mass spectrometry. On the other hand, thermal treatment of $(C_{59}N)_2$ at 150 °C with a large excess of benzyltrimethylsilane in ODCB for 1.5 h, again, in the presence of oxygen and *p*-TsOH, exclusively afforded the electrophilic aromatic substitution monoadduct **7** in 65% yield. Monoadduct **7** was purified by HPLC and fully characterized by all of the above-mentioned spectroscopic techniques. Finally, thermal or photochemical treatment of $(C_{59}N)_2$ in thoroughly degassed ODCB, in the presence of benzyltrimethylsilane under argon, afforded monoadduct **6**, though with very low yield ($<8\%$).

Chart 2. New Aza[60]fullerene Monoadducts **6** and **7** Produced via Free Radical and Electrophilic Aromatic Substitution Reactions

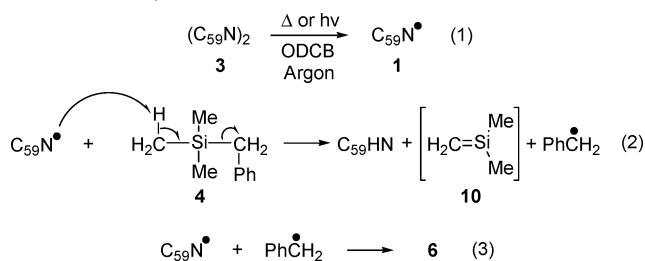


The formation of adduct **5** is satisfactorily explained by the intervention of a PET mechanism, from benzyltrimethylsilane to the azafullerenium cation **2**, in the key step of the reaction. According to the proposed mechanism (Scheme 2), the first step involves the photochemical homolysis of $(C_{59}N)_2$ to $C_{59}N^\bullet$. In the presence of *p*-TsOH and oxygen, $C_{59}N^\bullet$ is readily oxidized to the iminium cation $C_{59}N^+$.⁷ Photoinduced electron transfer from benzyltrimethylsilane to $C_{59}N^+$ gives the radical cation pair **8**, while concomitant loss of the electrofugal group $SiMe_3^+$ from the benzylic position leads to the neutral radical pair **9**.^{15,16} Eventually, radical coupling leads to monoadduct **6**, which upon irradiation in the presence of oxygen, is self-photo-oxygenated to **5**.¹⁷

Scheme 2. Proposed Mechanism for the Formation of **5**

Moreover, the formation of aza[60]fullerene monoadduct **7** may be attributed to an EAS reaction between $C_{59}N^+$ and benzyltrimethylsilane. This regioselective reaction has been shown to be effective principally with electron-rich aromatics.^{9,11,13} A recent mechanistic study on the EAS reaction between **2** and electron-rich aromatic compounds has shown that the arenium cation is formed by the electrophilic attack of $C_{59}N^+$ on the aromatic ring in the first step, followed by hydrogen abstraction in a rate-determining second step.¹⁸

The thermal and photochemical formation of adduct **6**, in the absence of oxygen and *p*-TsOH, may be rationalized by a free radical reaction mechanism (Scheme 3) quite similar to the one

Scheme 3. Proposed Mechanism for the Formation of **6**

proposed for the reaction between $(C_{59}N)_2$ and diphenylmethane or substituted fluorenes.^{7,8} We assume that hydrogen abstraction from the methyl group, instead of from the benzylic position of **4**, by $C_{59}N^+$ (eq 2) is favored for two reasons: (a) the greater stability of the incipient benzyl radical at the transition state of the concerted decomposition step, and (b) the steric hindrance offered by the bulky

$SiMe_3$ group during the attack at the benzylic position. If this is the case, production of the highly reactive intermediate **10** (dipolar or biradical),¹⁹ which can multiply add to the aza[60]fullerene carbon shell, could rationalize the low yield of **6**. Multiple additions of other radical species cannot be also excluded. This working hypothesis may rationalize the slow disappearance of **3**, the formation of monoadduct **6**, and the formation of unidentified aza[60]fullerene multiadducts (observed by HPLC).

In conclusion, a promising azafullerene functionalization method that uses the unprecedented PET reactivity of $C_{59}N^+$ has been elaborated. $(C_{59}N)_2$ displays three different modes of reactivity toward benzyltrimethylsilane **4**, giving three novel aza[60]fullerene monoadducts. Studies on the physicochemical characteristics and applications of the $C_{59}N^+$ PET reactivity are currently underway.

Acknowledgment. Dedicated to Professor Zvi Rappaport. Leonidas Zervas Foundation and the Greek National Scholarships Foundation (IKY) are acknowledged for providing fellowships to G.C.V. We also thank Professor G. J. Karabatsos for valuable comments and discussions.

Supporting Information Available: Detailed experimental procedures, ¹H and ¹³C NMR, MS, 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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JA045495X