Biradical Intermediate in the [2 + 2] Photocycloaddition of Dienes and Alkenes to [60]Fullerene

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The rich chemical and physical properties of all carbon fullerene molecules made them the most studied compounds since their isolation in large quantities in early 1990s. A remarkable array of molecules triggered the study due to their unique electronic, optical, and magnetic properties. Many photochemical reactions for the functionalization of [60]fullerene have been developed in the basis of the electron-deficient behavior of [60]fullerene. In an earlier work, concerning the [2 + 2] photocycloadditions to [60]fullerene, we reported a new type of [2 + 2] functionalization of [60]fullerene with moderately electron-rich p-methoxyalkenes and alkyl-substituted 1,3-butadienes (Scheme 1). 

Scheme 1. Photocycloaddition between C₆₀ and Diene 1

We report here for the first time the nature of the [2 + 2] intermediate of the cycloaddition between dienes or arylalkenes and C₆₀. These results shed light on the mechanism of the [2 + 2] photocycloaddition by providing unambiguous evidence of the involvement of a biradical (not a dipolar) intermediate which is preceded by an electron transfer between the triplet excited state of C₆₀ and the diene or alkene. The results were not sufficient to verify the nature of the intermediate (dipolar or biradical) as well as whether this intermediate is preceded by an electron- or charge-transfer complex between the triplet excited state of C₆₀ and the diene or alkene.

Scheme 2. Mechanistic Probe Capable of Distinguishing between a Radical and a Cation

3-[(E)-3-Phenyl-3-methoxyprop-2-enyl]oxyarylalkenes and alkyl-substituted 1,3-butadienes were designed on the basis that cations often undergo the same rearrangement as their radical counterparts. The cyclopropylcarbinyl probe, as a representative example, was ideal for this study because discrimination between cyclopropyl carbinyl radical and cation is possible in the intermediate formation, during the cycloaddition reaction. Radical or cation rearrangement would provide different products since ring opening will occur toward the phenyl or the methoxy substituent, respectively. A solution of C₆₀ and 30-fold excess of substrate 1 was irradiated with visible light (xenon lamp 300 W), within a few minutes, only one major signal was detected by HPLC accompanied by small amounts of unidentified byproducts which were isolated after purification with flash column chromatography (SiO₂, hexane:CH₂Cl₂:4:1), in 60% yield, based on the recovered C₆₀. The isolated cycloadduct does not cycloreverse to the starting material. Adduct 4 (Scheme 4) was characterized by ¹H, ¹H homonuclear decoupling, DNOE, and HMQC NMR experiments. The ¹H NMR spectrum of the cycloadduct displays an ABC coupling pattern for the hydrogens of the cyclopentane ring, one doublet of doublet which couples with two doublets, in the spectral region between 3.6 and 4.7 ppm. The stereochemistry of cyclopentane ring was determined by DNOE experiments. The doublet of doublet at 4.52 ppm was assigned to the benzylic cyclopentane hydrogen H₂ with no spacial approximation with the other two cyclopentane hydrogens. The doublets at 3.71 and 4.30 ppm were assigned to the cyclopentane hydrogens H₃ and H₅, respectively. However, upon irradiation with visible light (xenon lamp 300 W), within a few minutes, only one major signal was detected by HPLC accompanied by small amounts of unidentified byproducts and only one cycloadduct was isolated after purification with flash column chromatography (SiO₂, hexane:CH₂Cl₂:4:1), in 60% yield, based on the recovered C₆₀. The isolated cycloadduct does not cycloreverse to the starting material. Adduct 4 (Scheme 4) was characterized by ¹H, ¹H homonuclear decoupling, DNOE, and HMQC NMR experiments. The ¹H NMR spectrum of the cycloadduct displays an ABC coupling pattern for the hydrogens of the cyclopentane ring, one doublet of doublet which couples with two doublets, in the spectral region between 3.6 and 4.7 ppm. The stereochemistry of cyclopentane ring was determined by DNOE experiments. The doublet of doublet at 4.52 ppm was assigned to the benzylic cyclopentane hydrogen H₂ with no spacial approximation with the other two cyclopentane hydrogens. The doublets at 3.71 and 4.30 ppm were assigned to the corresponding cyclopentane hydrogens H₃ and H₅. All hydrogens on the cyclopentane ring occupy the three available axial-like positions, while the substituents possess the equatorial-like positions affording the thermodynamically more stable cyclopentane syn-4.

The mechanism that could account for the stereospecific formation of the five-membered ring cycloadduct can be best rationalized via the formation of a geminate radical ion pair, produced by the photoinduced electron transfer from the dienyl group of compound 3 to [60]fullerene, as shown in Scheme 5. The incipient radical cation RC₆₀ undergoes ring opening toward methoxy group, forming exclusively the distonic radical cation RC₆₀⁺ before combining with its...
geminate radical anion of $^3\text{C}_{60}$. In this step, an isomerization of

Coupling of the rearranged radical cation $\text{RC}^{3b}$ with radical anion of $^3\text{C}_{60}$ forms the biradical intermediate $I_1$, which ultimately cyclizes to the cycloadduct $\text{syn}-4$. It is interesting to note here that this photocycloaddition is highly stereospecific since among the 16 possible stereoisomers of $\text{syn}-4$, only the $\text{syn}-4$ product was formed. Also, in product $\text{syn}-4$, the thermodynamically most stable $E$ configuration of the dienyl moiety is formed although the starting material $3$ was a mixture of $E:Z = 70:30$ stereoisomers. If the rearrangement of cyclopropylcarbinyl radical in $\text{RC}'_{3a}$ would be the case, product $5$, through its dipolar intermediate $I_2$, would be expected to be formed (Scheme 5). The former pathway is excluded since $5$ was not observed. Furthermore, we examined the addition of cyclopropyl alkenes to $\text{C}_{60}$. Similar to that in cyclopropyl diene $3$, the photocycloaddition of cyclopropyl alkene $6^\circ$ to $\text{C}_{60}$ gave the rearranged five-membered adduct $\text{syn}-7$ (Scheme 6), under similar experimental conditions. Addition to $\text{C}_{60}$ with the double bond of
deuterium-labeled $6^\circ$ initially a mixture of $E:Z = 70:30$ completely isomerized to a ratio of $E:Z = 50:50$ in the product. Cycloadduct $\text{syn}-7$ was purified by flash column chromatography and was fully characterized by all of the above-mentioned NMR techniques. These results suggest that the [2 + 2] photocycloaddition of an alkene to $\text{C}_{60}$ proceeds through a photoinduced electron-transfer step between the cyclopropylalkene and $^3\text{C}_{60}$, which leads to a biradical intermediate, as shown in Scheme 6.

In conclusion, we have shown here, by using a hypersensitive molecular mechanistic probe, that photocycloaddition of dienes or alkenes to $\text{C}_{60}$ proceeds via a biradical (not dipolar) intermediate, which is preceded by an electron-transfer step between the diene or the alkene and $^3\text{C}_{60}$.

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Supporting Information Available: Detailed experimental procedures and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References


(9) For the preparation of $3$ and $6$, see the Supporting Information.