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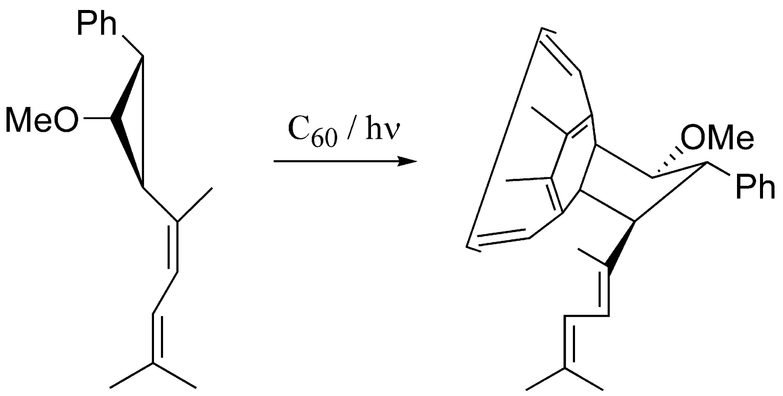

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Biradical Intermediate in the [2 + 2] Photocycloaddition of Dienes and Alkenes to [60]Fullerene

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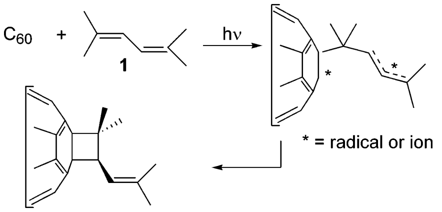
The rich chemical and physical properties of all carbon fullerene molecules made them the most studied compounds since their isolation in large quantities in early 1990s. A remarkable array of their chemical reactions has been explored over the last 15 years.[1] Many photochemical reactions for the functionalization of [60]-fullerene[2] have been developed on the basis of the electron-deficient behavior of $^3C_{60}$.[3] In an earlier work, concerning the [2 + 2] photocycloadditions to C_{60}, we reported[4] a new type of [2 + 2] functionalization of C_{60} with moderately electron-rich *p*-methoxyarylalkenes and alkyl-substituted 1,3-butadienes[5] (Scheme 1). Stereoisotopic studies showed that the first rate-determining step of the reaction involves the formation of an open biradical or dipolar intermediate between the triplet excited state of C_{60} and the diene or alkene. Those 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 C_{60} and the diene or the alkene.

Scheme 1. Photocycloaddition between C_{60} and Diene **1**

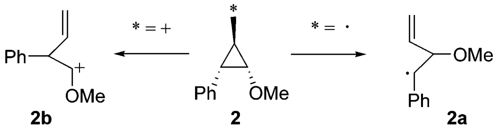


We report here for the first time the nature of the [2 + 2] intermediate of the cycloaddition between dienes or arylalkenes and C_{60}. These results shed light on the mechanism of the [2 + 2] photocycloaddition by providing unambiguous evidence of the involvement of a biradical (not a dipolar) intermediate which is preceded by an electron transfer between the triplet excited state of C_{60} and the unsaturated substrate.

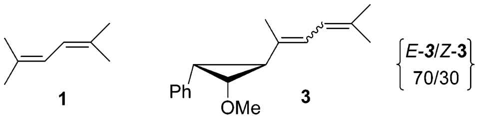
In an earlier work, Newcomb and co-workers developed the hypersensitive molecular mechanistic probe[6] 2-methoxy-3-phenylcyclopropylcarbinyl probe, **2**, shown in Scheme 2. Probe **2** provides a reliable mean of determining the nature of an intermediate generated in the course of a stepwise reaction mechanism.[6,7] **2** was designed on the basis that cations often undergo the same rearrangement as their radical counterparts. The cyclopropylcarbinyl radical **2** (* = ·) results in ring opening to a benzylic radical **2a**, whereas the cyclopropylcarbinyl cation (* = +) leads to fragmentation favoring an oxonium ion **2b**. Moreover, rearrangement of radical cations of vinylcyclopropanes has been reported in cycloadditions involving electron-transfer process.[8]

Thus, to further probe the [2 + 2] cycloaddition mechanism of dienes to C_{60} and to obtain information on the nature of the intermediate, 2-(2-methoxy-3-phenylcyclopropyl)-5-methyl-2,4-hexadiene (**3**) was prepared.[9] Diene **3** is derived from the replacement of an (*E*)-methyl group in substrate **1**, with the substituted cyclopropyl moiety (Scheme 3). Substrate **3** is 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 C_{60} and 30-fold excess of **3** as a 70:30 *E*:*Z* mixture in deoxygenated toluene, in the absence of light, did not react after 24 h at solvent reflux.

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



Scheme 3



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 (SiO_2, hexane:CH_2Cl_2 4:1), in 60% yield, based on the recovered C_{60}. 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 cycloproduct 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 H^2 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 H^3 and H^1. 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 $^3C_{60}$, as shown in Scheme 5. The incipient radical cation RC_{3a} undergoes ring opening toward methoxy group, forming exclusively the distonic radical cation RC_{3b} before combining with its

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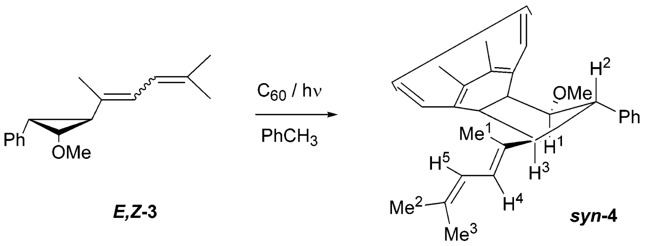
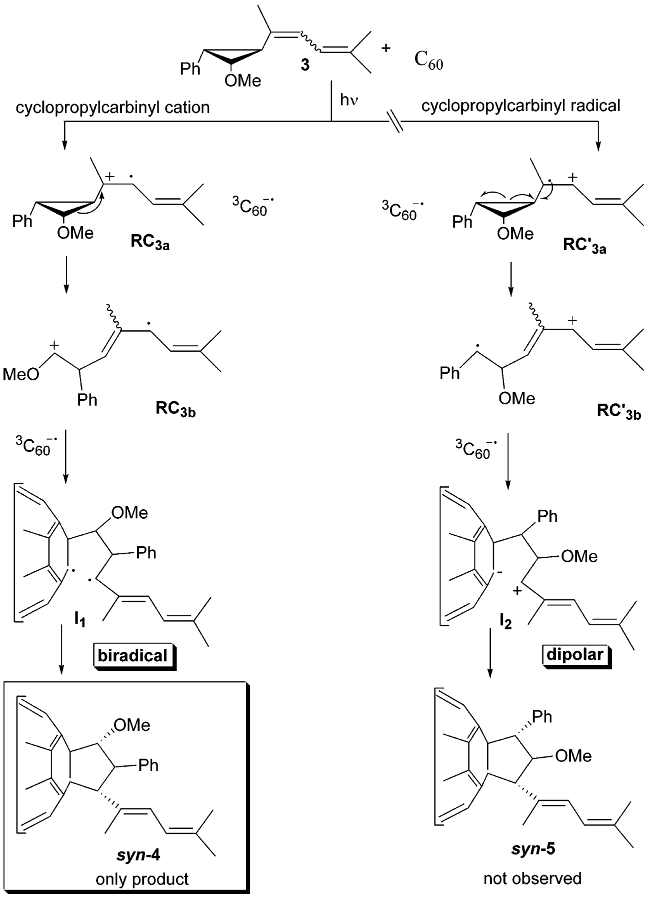
Scheme 4. Photochemical Cycloaddition of (*E*,*Z*)-**3** to C_{60}



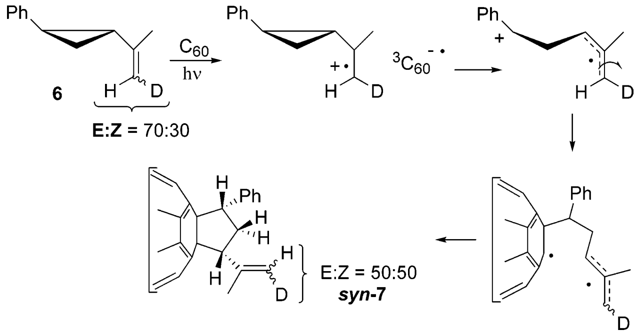
Scheme 5. Proposed Mechanism for the Formation of *syn*-**4**



geminate radical anion of $^3C_{60}$. In this step, an isomerization of the radical cation can take place.

Coupling of the rearranged radical cation RC_{3b} with radical anion of $^3C_{60}$ forms the biradical intermediate I_1, which ultimately cyclizes to the cycloadduct **4**. It is interesting to note here that this photocycloaddition is highly stereospecific since among the 16 possible stereoisomers of **4**, only the *syn*-**4** product was formed. Also, in product *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 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 C_{60}. Similar to that in cyclopropyl diene **3**, the photocycloaddition of cyclopropyl alkene **6**[9] to C_{60} gave the rearranged five-membered adduct *syn*-**7** (Scheme 6), under similar experimental conditions. Addition to C_{60} with the double bond of deuterium-labeled **6**—initially a mixture of $E{:}Z = 70{:}30$—completely isomerized to a ratio of $E{:}Z = 50{:}50$ in the product. Cycloadduct *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 $^3C_{60}$ proceeds through a photoinduced electron-transfer step between the cyclopropylalkene and $^3C_{60}$, which leads to a biradical intermediate, as shown in Scheme 6.

Scheme 6. Proposed Mechanism for the Formation of *syn*-**7**



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

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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.

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

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