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Regio- and Stereoselectivity of the [2 + 2] Photocycloaddition of Acyclic Enones to C_{60}

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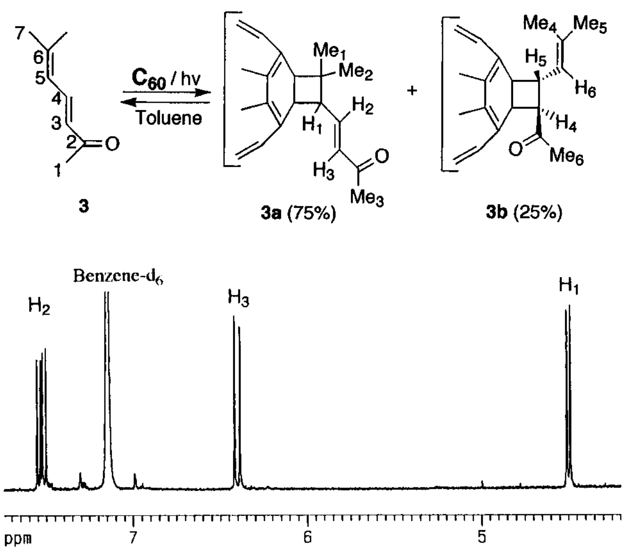
Buckminsterfullerene C_{60} is an electron deficient, electrophilic molecule[1] and behaves like an electron poor alkene rather than an aromatic compound. The triplet excited state of C_{60} ($^3C_{60}$) that is formed with a quantum yield of about unity has a reduction potential close to 0.98 V and is more electrophilic than the ground state.[2] The chemistry of the triplet excited state and ground state of C_{60} encompasses a large variety of reactions.[3] However, [2 + 2] cycloadditions of fullerenes are less common.

The triplet excited state has been reported to be responsible for the [2+2] photocycloadditions of C_{60} with electron rich alkynes (ynamines), such as *N,N*-diethylpropynylamine,[4] *N,N*-diethyl-4-methylpenten-3-yn-1-amine,[5] and electron rich alkenes such as tetraalkoxyethylenes.[5] Recently, we reported two types of [2 + 2] functionalizations of C_{60} with moderately electron rich substrates such as *p*-methoxyarylalkenes[6] and the alkyl-substituted 1,3-butadienes.[7] The stereochemical studies and the secondary isotope effects of these reactions showed that the [2 + 2] photocycloaddition is stepwise involving the formation of a dipolar or a biradical intermediate in the rate-determining step between the triplet excited state of C_{60} and the unsaturated substrate. Schuster and co-workers have recently reported a new photochemical [2 + 2] cycloaddition of cyclic enones[8] and cyclic 1,3-diones[9] to C_{60}. The photocycloaddition cannot be achieved by irradiation at 532 nm wavelength where C_{60} is the only light absorbing component.[8] This result indicates that fullerene triplets do not undergo addition to the ground state of enones. The authors proposed that the addition of the enones to C_{60} proceeds by a stepwise addition of the enone triplet excited states to ground-state fullerene, via intermediate triplet 1,4-biradicals, as occurs in the [2 + 2] photoadditions of enones to alkenes.[10]

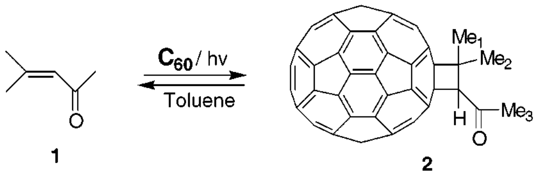
In this paper we report a study of the regio- and stereoselectivity of the [2 + 2] photocycloaddition of acyclic enones and dienones to C_{60}. Upon irradiating a mixture of C_{60} and a 1000-fold molecular excess of mesityl oxide in deoxygenated toluene with a 300 W xenon lamp as the light source, the [2 + 2] adduct was formed within 30 min (Scheme 1). The reaction is reversible and reaches equilibrium. Since the equilibrium constant of the reaction is very small, irradiation of the [2 + 2] adduct **2**, free of enone, cycloreverses to starting materials. Similar photocycloreversion reactions have been reported previously.[5] The ^1H NMR spectrum of **2** shows two single absorptions due to the diastereotopic methyls (Me_1, Me_2) at 2.04 and 2.16 ppm, one single absorption at 2.29 ppm which corresponds to the methyl next to the carbonyl group (Me_3), and a singlet at 4.72 ppm which corresponds to the cyclobutane hydrogen. This is the first example of [2 + 2] cycloaddition of an acyclic enone to C_{60}.



3 **3a** (75%) **3b** (25%)

Figure 1. [2 + 2] photocycloaddition of *trans*-6-methyl-3,5-heptadien-2-one to C_{60}.

Scheme 1. [2 + 2] Photocycloaddition of Mesityl Oxide to C_{60}



1 **2**

To study the regio- and stereoselectivity of this reaction, the photochemical cycloadditions of the dienones *trans*-6-methyl-3,5-heptadien-2-one (**3**) and *trans*-2-methyl-2,5-heptadien-4-one (**4**) to C_{60} were studied. The reactive dienones **3** and **4** are ideally suited for this purpose. Compound **3** bears two unequally substituted conjugated double bonds, both available for the [2 + 2] cycloaddition to C_{60}, whereas in compound **4** the carbonyl moiety isolates the two unequal stericaly and electronically double bonds of the dienone. The equilibrium of the cycloaddition of **3** and **4** to C_{60} is more shifted toward the products compared to the cycloaddition of mesityl oxide to C_{60}. Because of that, less excess of the starting substrates (~100-fold excess) was required to achieve the reaction.

The photochemical addition of **3** to C_{60} leads to the formation of two regioisomers **3a** and **3b** in a 3/1 ratio (Figure 1). The two adducts were separated by flash column chromatography using toluene:hexane (2:1) as eluent and characterized by ^1H NMR spectroscopy (Figure 1). The ^1H NMR spectrum of **3a** shows two singlets at 1.99 and 2.08 ppm (Me_1 and Me_2), a singlet at 2.19 ppm (Me_3), a doublet

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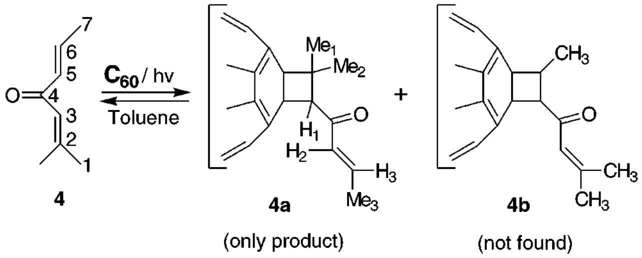
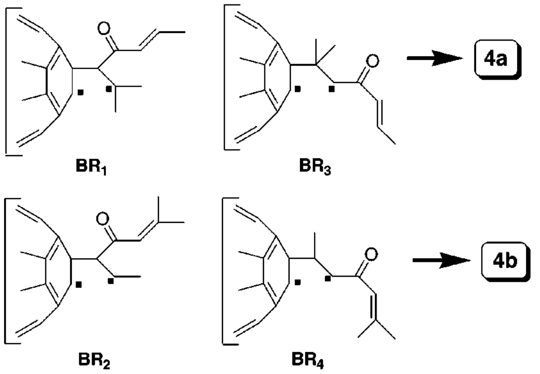
Scheme 2. [2 + 2] Photocycloaddition of *trans*-2-Methyl-2,5-heptadien-4-one to C_{60}



Scheme 3. Four Possible Biradical Intermediates in the [2 + 2] Photocycloaddition of *trans*-2-Methyl-2,5-heptadien-4-one to C_{60}



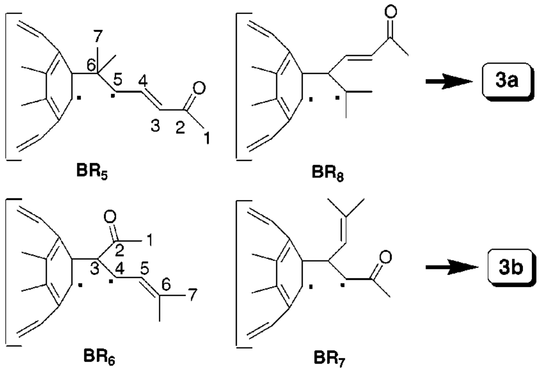
with allylic coupling at 4.49 ppm (H_1), a doublet with allylic coupling at 6.40 ppm (H_3), and a doublet of doublets at 7.53 ppm (H_2). The value of the coupling constant between H_2 and H_3 ($J = 15.7$ Hz) is typical for a *trans*-substituted double bond.

The ^{1}H NMR of **3b** shows two singlets with allylic coupling at 1.86 and 1.93 ppm (Me_4 and Me_5), a singlet at 2.39 ppm (Me_6), a doublet at 4.77 ppm (H_4), a doublet of doublets at 5.50 ppm (H_5), and a doublet with allylic coupling at 6.12 ppm (H_6). The coupling constant between H_4 and H_5 ($J = 8.3$ Hz) is typical for a *trans*-substituted cyclobutane ring.[6,7] FAB-MS of **3a** and **3b** gave the expected M + 1 ion at 845 amu which corresponds to the molecular formula $C_{68}H_{12}O$. These results show that the [2 + 2] photoaddition of dienone **3** to C_{60} is regioselective for the trisubstituted terminal double bond. It is constructive to emphasize that the stereochemistry of the unreacted double bond in **3a** remains *trans*, while the stereochemistry on the cyclobutane ring of **3b** adduct is also *trans*.

The photochemical addition of compound **4**,[11] where the double bonds are isolated by the carbonyl group, to C_{60} is regiospecific and affords exclusively one of the two possible [2 + 2] regioisomeric adducts. The photocycloaddition occurs on the more substituted double bond, leading exclusively to the [2 + 2] adduct **4a** (Scheme 2). The ^{1}H NMR spectrum of **4a** shows a doublet at 1.99 ppm (Me_3) with allylic coupling, two singlets at 2.01 and 2.21 ppm (Me_1 and Me_2), a singlet at 4.97 ppm (H_1), a doublet with allylic coupling at 6.36 ppm (H_2), and a multiplet at 7.03 ppm (H_3). The coupling constant between H_2 and H_3 ($J = 15.4$ Hz) is typical for a *trans*-substituted double bond.

According to the mechanism proposed by Schuster and co-workers,[8] the four possible biradical intermediates during the addition of **4** to C_{60} are shown in Scheme 3. The biradical intermediates $\mathbf{BR_1}$ and $\mathbf{BR_3}$ collapse to the only [2 + 2] cycloadduct **4a**. If we assume that a fraction of the adduct **4a** comes from $\mathbf{BR_3}$, then formation of **4b** from $\mathbf{BR_4}$ would be expected, because the transition state, leading to the formation of BR_4, is less sterically hindered than the transition state leading to the BR_3 biradical intermediate (Scheme 3). The absence of the [2 + 2] adduct **4b** in the less substituted double bond of the dienone suggests a negligible contribution of the intermediate biradicals $\mathbf{BR_3}$ and $\mathbf{BR_4}$ to the reaction pathways. Because in the intermediates $\mathbf{BR_3}$ and $\mathbf{BR_4}$ the double bond of the enone moiety is conjugated with the carbonyl group, the stabilization of the alkyl radicals due to the conjugation with the carbonyl group is substantially reduced. As a result, the intermediate $\mathbf{BR_1}$ which leads to the formation of adduct **4a** is the more stable than the three other possible intermediates.

Scheme 4. Four Possible Biradical Intermediates in the [2 + 2] Photocycloaddition of *trans*-6-Methyl-3,5-heptadien-2-one to C_{60}



Although these and previous results[8] support a biradical mechanism, the possibility of a concerted mechanism cannot be excluded. In this case the electron rich trisubstituted double bond in **4** would probably be the favored donor in such a concerted process, leading to the observed regiospecificity.

The fact that the adduct **3a** is the major product in the photoaddition of **3** to C_{60} is consonant with the relative stability of the intermediate biradicals. Particularly, biradical $\mathbf{BR_5}$ that leads to **3a** is more stable than the intermediate biradicals $\mathbf{BR_6}$, $\mathbf{BR_7}$, and $\mathbf{BR_8}$ due to the extented spin delocalization through conjugation with the α,β-unsaturated carbonyl moiety (Scheme 4).

It is noteworthy that retention of stereochemistry of the unreacted $C_3{-}C_4$ double bond in the product **3a** is in agreement with the known propensity of allylic radicals to resist rotation around the partial double bond.[7] Despite the biradical nature of the intermediate, ring closure occurs sterospecifically, forming the thermodynamically most stable *trans* cyclobutane adduct **3b**. This is in accordance with previous results in the photochemical [2 + 2] cycloaddition of *cis*/*trans*-4-propenylanisole to C_{60}.[6a] It is important to note here that in an effort to simplify the discussion, the mechanistic rationale of the regioselectivity was based on the relative stability of the biradical intermediates. However, the stability of the transition states leading to the corresponding biradical intermediates dictates the observed regioselectivity of the title reaction.

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Supporting Information Available: ^{1}H NMR spectra for **2**, **3a**, **3b**, **4**, and **4a** and high-resolution FAB-MS for **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] *trans*-2-Methyl-2,5-heptadien-4-one was prepeared in 97% geometrical purity by an aldol condensation under kinetic control (−78 °C) between the enolate of mesityl oxide and acetaldehyde, followed by dehydration of the aldolate under acidic conditions.