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A New Reaction of Fullerenes: [2 + 2] Photocycloaddition of Enones

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Since the discovery by Huffmann and Krätschmer[1] of a method for the preparation of buckminsterfullerene (C_{60})[2] in macroscopic quantities, a wide range of reactions of this material have been reported.[3–9] We now report functionalization of C_{60} by [2 + 2] photocycloaddition of cyclic enones, allowing the simple preparation of a large new class of C_{60} derivatives. This is another application of a classic photochemical reaction[10] which is widely used synthetically.[11] The mechanistic features also are of considerable interest.[12]

One of us[13] has been developing the new technique of electrospray ionization mass spectrometry (ESI-MS)[14] for study of organic reactions in solution. The discovery of these photochemical cycloaddition reactions was made possible through the use of the "electrospray-active" tagged fulleroid **1**.[15,16] Analysis of complexes of **1** containing metal cations using ESI-MS cleanly gives only the respective molecular ions without fragmentation.[17,18] The use of **1** to monitor the reactions of C_{60} provides the simplest way yet found to explore the chemistry of this material. Thus, the course of reaction upon UV irradiation of crown ether fulleroid **1** and 3-methylcyclohexen-2-one (**2a**) in benzene solution was followed by ESI-MS as shown in Figure 1. Irradiation was performed with the broad spectrum output of a Hanovia high-pressure mercury lamp and with a XeCl excimer laser operating at 308 nm. The time-dependent incorporation of up to seven enone units is readily observable

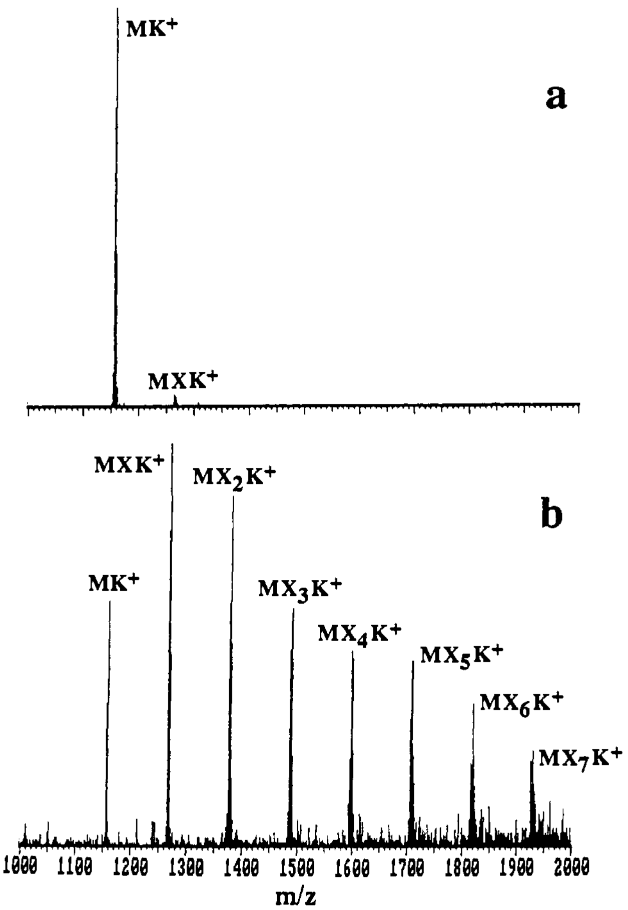
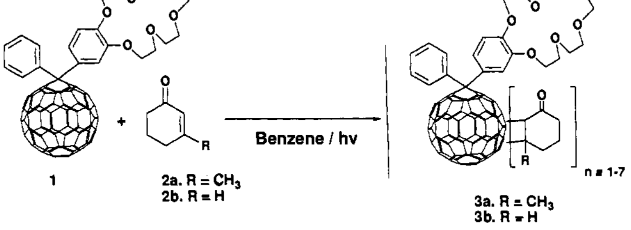


Figure 1. ESI-MS spectra of reaction mixture from irradiation of fullerene adduct **1** with 3-methyl-2-cyclohexenone (**2a**) in benzene after dilution of an aliquot with an equal volume of potassium acetate in methanol. Spectra a and b were recorded after irradiation with a Hanovia high-pressure lamp through Pyrex for 2 and 12 min, respectively. Peak assignments (*m/z*) are MK^+ (1159), MXK^+ (1269), MX_2K^+ (1379), MX_3K^+ (1489), MX_4K^+ (1599), MX_5K^+ (1709), MX_6K^+ (1819), and MX_7K^+ (1929), where M = compound **1**, X = units of enone **2a**.



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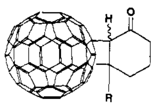
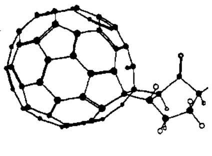
under these conditions. A similar result was found when the irradiation time was held constant at 12 min and the enone concentration was increased (see supplementary material). Photoadducts of type **3** were formed from 2-cyclohexenone (**2b**), 4,4-dimethyl-2-cyclohexenone, testosterone acetate, and 2-cycloheptenone, but not from 2-cyclopentenone (CP). No adducts could be detected upon laser excitation of a mixture of **1** and **2a** at 532 nm, where the only light-absorbing species is **1**.

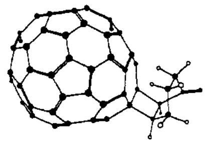
In order to characterize the photoadduct of C_{60} and enone **2a**, C_{60} itself and the enone in benzene were irradiated to ~20–25% conversion. The monoadduct **4** (R_f 0.36, toluene, silica gel TLC) was isolated in 20% yield (31% based on recovered C_{60}) by silica gel chromatography. After being tagged,[15] the adduct gave a single peak at m/z 1269 ($M + K^+$), as found for the monoadduct derived from irradiation of **1** and **2a**. Analysis of this material by FAB mass spectrometry and microanalysis confirmed its formulation as an adduct of one enone unit to C_{60}. ^1H NMR and IR and "Buckyclutcher" HPLC[19] analysis showed that the isolated monoadduct is a mixture of two compounds in a ratio of 57:43. This material has two carbonyl bands at 1707 and 1730 cm^{-1}, the latter more intense, and two sets of resonances at 4.91, 4.10, 2.00, and 1.79 ppm corresponding to bridgehead protons and methyl groups in structure **4a**.[20] Since additions to C_{60} generally occur across reactive 6/6 pyracyclene ring junctions,[3–9,21,22] we propose that these cycloadducts are the *cis*- and *trans*-fused stereoisomers arising from [2 + 2] cycloaddition across the 6/6 ring junction in C_{60}, the major product being *trans*. Adducts of cyclohexenones and alkenes are formed with both *cis* and *trans* four–six ring fusions, the latter often being the major product.[11,23,24]



4a. R = CH$_3$
4b. R = H



trans- 4b



cis- 4b

The procedure for preparation and isolation of monoadducts **4b** from C_{60} and 2-cyclohexenone (**2b**) was essentially the same as described above. In this case, however, the stereochemistry of the four–six ring fusion can be derived directly from the NMR coupling constant between the two bridgehead protons. As with **2a**, the 400-MHz ^1H NMR spectrum (see supplementary material) again gave clear indication of the formation of two products. In the major isomer A, a doublet at 4.57 ppm ($J = 10.7$ Hz) is coupled to a doublet of triplets centered at 4.45 ppm ($J_{ab} = 10.7$, $J_{bc} = J_{bd} = 6.8$ Hz). In the minor isomer B, a downfield doublet ($J_{ab} = 14.9$ Hz) centered at 4.76 ppm is coupled to an upfield overlapping doublet of doublets at 4.37 ppm ($J_{ab} = 14.8$, $J_{bc} = 11.7$, $J_{bd} = 4$ Hz). By analogy with literature on cyclohexenone cycloadducts,[11,23,24] these data indicate that B is the *trans*-fused [2 + 2] cycloadduct and that A is the corresponding *cis*-fused cycloadduct of [2 + 2] photoaddition across the 6/6 fusion.[3–9,21,22] In this case, the major product is the *cis* isomer. These assignments are supported by the strikingly different IR carbonyl stretching frequencies: 1707 and 1730 (major band) cm^{-1} for **4a** and 1707 (major band) and 1726 cm^{-1} for **4b**.[23,24]

The fact that these adducts are not formed upon irradiation at 532 nm where the fullerene is the only light-absorbing component, indicates that fullerene triplets, which are known to be efficiently produced from fullerene singlets,[25] do not undergo addition to ground-state enones. Thus, enone photocycloaddition to fullerenes most likely proceeds by the same mechanism operating in photoaddition of enones to ordinary alkenes,[12] namely stepwise addition of enone triplet excited states to the fullerene *via* an intermediate triplet 1,4-biradical. Consistent with this is the observation that alkenes (cyclopentene, cyclohexene) do not undergo photoaddition to fullerenes. While initial photoaddition of CP triplets to C_{60} to give a triplet 1,4-biradical should not be particularly inhibited,[12] the results suggest that this particular 1,4-biradical prefers to fragment to regenerate starting materials rather than to close to a relatively strained cycloadduct.[26]

We were initially surprised that the photocycloaddition reaction occurred at all, since triplet energy transfer (TET) from cyclohexenones (E_T 63–72 kcal/mol)[27] to fullerenes (E_T 38 kcal/mol)[26] is energetically favorable by at least 25 kcal/mol. TET was expected to take place at a diffusion-controlled rate (5×10^9 M^{-1} s^{-1} in benzene), which is larger than that expected for chemical addition of enone triplets, 10^6–10^8 M^{-1} s^{-1}.[12,28] Since fullerene triplets are low-energy long-lived, highly delocalized species,[26] they are expected to be chemically unreactive. We propose that enone-to-fullerene TET does not compete, precisely because it is so exothermic, that is, the rate of TET is low due to an inverted Marcus region effect.[29]

In conclusion, we have shown (a) that ESI-MS is a uniquely suitable tool for studying the reactions of fullerenes, (b) that a variety of functionally substituted derivatives of C_{60} can be prepared by [2 + 2] photocycloaddition to cyclic enones, and (c) that these adducts arise by the stepwise addition of enone triplets to the fullerenes.

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Supplementary Material Available: Experimental details, ESI-MS spectral determination of the concentration dependence of the addition **1** to enone **2a**, ESI-MS spectra of **3a** and **3b**, 400-MHz NMR and FAB mass spectra of **4a** and **4b**, and "Buckyclutcher" HPLC separation of *cis*- and *trans*-**4a** (11 pages). Ordering information is give on any current masthead page.

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