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# $^3$He NMR as a Sensitive Probe of Fullerene Reactivity: [2 + 2] Photocycloaddition of 3-Methyl-2-cyclohexenone to $C_{70}$[†]

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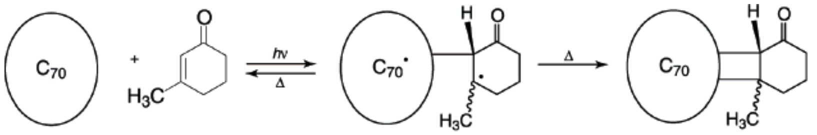
*Received November 7, 2005*



*14 possible regioisomers and diastereomers*

The [2 + 2] photoadditions of 3-methyl-2-cyclohexenone to $C_{70}$ and $^3He@C_{70}$ have been studied by a combination of HPLC chromatography and FAB-MS, as well as IR and $^1$H and $^3$He NMR spectroscopies. The total yield of the mixture of monoadducts was 55% (67% on the basis of the recovered $C_{70}$). The use of $^3$He NMR was especially powerful in determining the regioselectivity of the photoaddition reaction of enone to $C_{70}$. Results of the $^3$He NMR experiments conducted on the product mixture implicate the two [6,6] bonds closest to the poles of the fullerene (C1−C2 and C5−C6) in the photoaddition process. This reaction mode is analogous to that of most thermal addition reactions to $C_{70}$. Separation and characterization of the product mixture shows that eight distinct monoadducts are formed in the photoaddition, namely, the four diastereomeric adducts to the C1−C2 and C5−C6 bonds of the $C_{70}$ cage, each consisting of cis- and trans-fused isomers in a ratio of 2:3. The major mode of photoaddition, accounting for 65% of the product mixture, involves addition to the C1−C2 bond of the ovoid fullerene. Mechanistic implications of these findings are discussed.

## Introduction

The photochemical [2 + 2] addition of enones to $C_{60}$ is a general and well-documented reaction.[1−4] A large variety of cyclic enones add across the most reactive bond of the $C_{60}$ molecule, namely, the [6,6] bond between two adjacent six-membered rings, when a mixture of the fullerene and the enone is subjected to light in the UV region (ca. 300 nm). Photoexcitation at longer wavelengths where only the fullerene absorbs does not induce the addition process. Only two monoadducts are formed in the reaction with $C_{60}$, corresponding to cis and trans fusion of the four- and six-membered rings to the fullerene core (Figure 1). These diastereomeric products have been separated and definitively characterized using standard spectroscopic techniques (i.e., MS, IR, and $^1$H, $^{13}$C, and $^3$He NMR).[4−7] Such reactions are thought to take place via a mechanism analogous to that for the [2 + 2] photocycloaddition of enones to simple olefins in the presence of UV light, namely, the stepwise addition of the enone triplet excited state to ground-state alkenes via 1,4-biradical intermediates.[8−12]

The analogous photoaddition of 3-methyl-2-cyclohexenone (MCH) to $C_{70}$ (Scheme 1) is an inherently much more complex reaction. The ovoid shape of $C_{70}$ (Scheme 1), with its four chemically distinct [6,6] bonds (as opposed to only one such

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[†] Dedicated in memoriam to Christopher Spencer Foote, 1935−2005.

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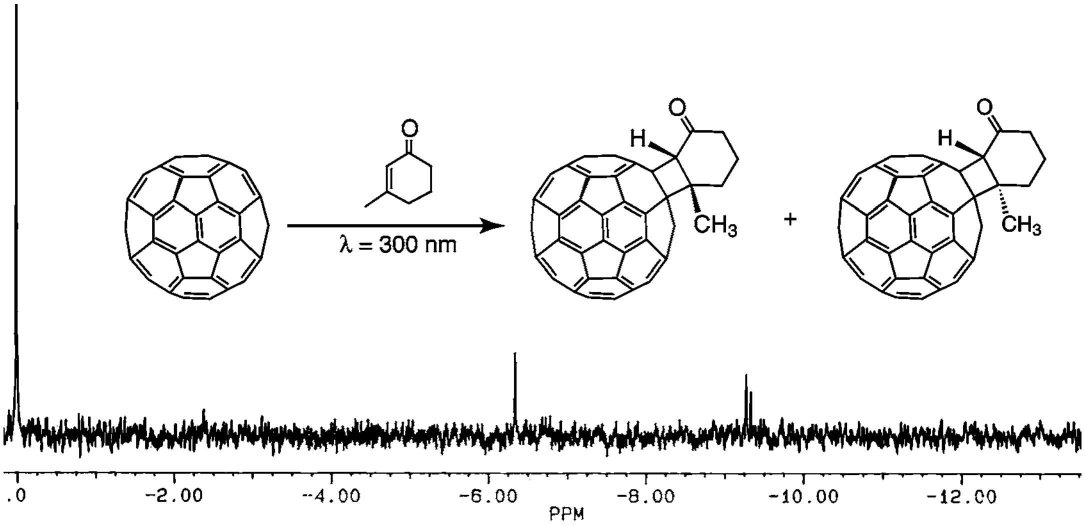
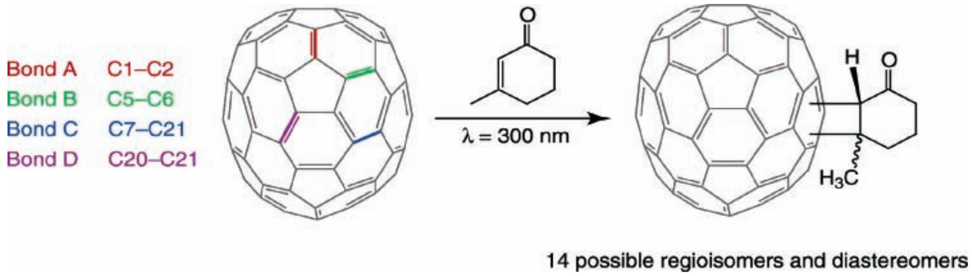


**FIGURE 1.** $^3$He NMR spectrum of the product mixture resulting from the [2 + 2] photocycloaddition of 3-methyl-2-cyclohexen-1-one to $C_{60}$. The resonances at −9.28 and −9.34 ppm relative to free $^3$He (0.0 ppm) correspond to trans- and cis-fused monoadducts, respectively. The resonance at −6.34 ppm corresponds to $^3He@C_{60}$.

**SCHEME 1**



bond in $C_{60}$), gives rise to the possibility of forming as many as 14 different regioisomeric and diastereoisomeric monoadducts of enone to $C_{70}$ (not counting enantiomers).[13−18] Because the addend (MCH) is unsymmetrical, regioisomers are generated by the addition across bond A (C1−C2) and bond C (C7−C21), while diastereomers can result from the addition across bond B (C5−C6), corresponding to the six-membered ring of the enone adduct pointing toward either the pole or the equator of the ovoid fullerene, respectively (Scheme 1). Only a single isomer can be formed as a result of an addition across bond D (C20−C21), which is on the equator of the fullerene. Furthermore, cis- and trans-fused structures are possible for each of the above isomers. From the well-established course of the ground-state addition reactions of $C_{70}$, it was anticipated that photoaddition across the more strained [6,6] bonds associated with the regions of greatest curvature on the $C_{70}$ surface, namely, bonds A and B, would predominate over the addition at the much less strained bonds (C and D).[19−24] The degree of selectivity in photochemical versus thermal addition to $C_{70}$ could not be predicted.

An additional consideration is the regioselectivity associated with the addition of unsymmetrical polarized addends such as alkyl azides[25] and diazomethane derivatives[26,27] across bond A, a process which is strongly influenced by the marked polarity of this particular bond as a result of the curvature on the fullerene surface.[28] The calculated Mulliken charges on the carbon atom closest to the fullerene pole (C1) is +0.0045, while the charge on C2 is −0.0098.[26,29,30] The addition of $N_3CH_2CO_2Me$ to $C_{70}$ in 1-chloronaphthalene at 50 °C leads to the formation of the three isomeric triazolines (**1**−**3**, Chart 1) in yields of 36, 7, and 1%, respectively.[25] Identical regioselectivity has been observed for the thermal addition of diazomethane derivatives to $C_{70}$.[26,27] This is an excellent demonstration of the enhanced reactivity of bond A of $C_{70}$ relative to bond B, as

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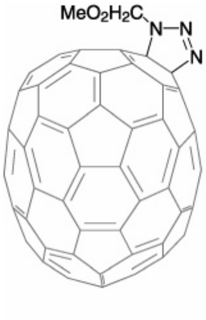
**CHART 1**



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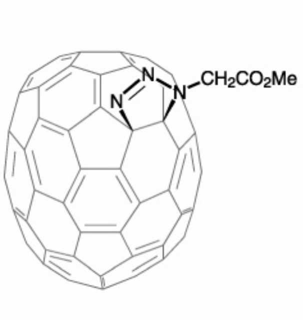

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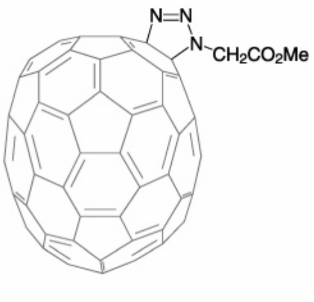

**3**

well as the preferred interaction of the negatively polarized atom of the dipolar addend, in this case, the nitrogen atom bearing the substituent, with the more positively polarized carbon of bond A (C1). One motivation of the present study was to see if analogous regioselectivity is observed for [2 + 2] photochemical addition pathways. In this connection there are two fundamental issues: (1) the degree of regioselectivity observed for the addition of substrates in high-energy excited states versus substrates in the ground state to $C_{70}$, and (2) the question of the direction and extent of polarization of the electron density in the reactive triplet excited state of the enone. This latter issue has been a matter of considerable controversy in the organic photochemistry literature.[31−46]

The major challenge of the present study centered on the separation and structural characterization of the large number of monoadducts expected from photocycloaddition of MCH to $C_{70}$. From the beginning of this study, we had planned to take advantage of the powerful $^3$He NMR technique developed by Saunders and co-workers at Yale as a sensitive analytical probe of fullerene reactivity.[47,48] When fullerenes containing an endohedral magnetically active $^3$He atom (spin $^1/_2$) are used, prepared at Yale by a high-pressure/high-temperature method, it is possible to follow the course of reactions on the fullerene surface by $^3$He NMR spectroscopy. We have previously utilized this technique extensively in studies of a variety of processes involving both $C_{60}$ and $C_{70}$ in collaboration with the Yale group.[4,49−54] $^3$He NMR can be a powerful tool for the study of equilibrium processes involving fullerenes,[55,56] and additionally, the $^3$He NMR spectrum of the crude reaction mixture allows for the determination of the number and ratio of products in a given reaction involving a fullerene because each isomer appears as a singlet with its own characteristic chemical shift. Furthermore, no signals are observed that are derived from nonfullerene reaction components. With very few exceptions thus far, $^3$He NMR is able to distinguish between all regioisomers and diastereomers produced in a given reaction as well as between monoadducts, bisadducts, and higher adducts. This is exemplified by Figure 1 in which the diastereomeric cis- and trans-fused adducts from the photoaddition of MCH to $^3He@C_{60}$ appear as two distinct peaks separated by 0.05 ppm and centered at about −9.2 ppm in the $^3$He NMR spectrum; the signal for the starting material is at −6.2 ppm relative to gaseous $^3$He. The major product was shown to be the trans-fused isomer by IR and $^1$H NMR analysis of the individual isomers following separation by HPLC using a Buckyclutcher column.[1,4] An additional feature of the $^3$He NMR technique that turned out to be critical in the present study is that characteristic chemical shifts are associated with adducts at each of the [6,6] bonds on the surface of $^3He@C_{70}$, allowing for tentative structural assignments for the photoadducts of MCH with $C_{70}$ to be made.

## Results and Discussion

**Initial Findings.** The [2 + 2] photoaddition of MCH to $C_{70}$ was carried out on both analytical and preparative scales in deoxygenated toluene. The reaction mixtures of enone and $C_{70}$ were irradiated using a 300-W Hanovia lamp at about 300 nm

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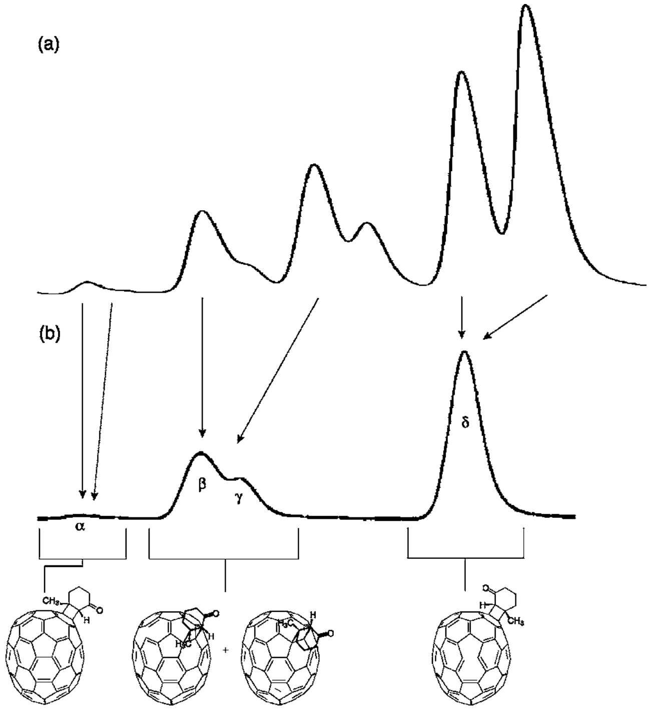

**FIGURE 2.** HPLC chromatograph for the MCH$-$C$_{70}$ monoadduct product mixture both (a) before and (b) after acid-catalyzed epimerization of the trans-fused diastereomers to the corresponding cis-fused homologues.

for 16$-$20 h. The resultant product mixture was partially resolved by flash chromatography on silica using toluene as the eluent, allowing for the separation of a mixture of isomeric MCH$-$C$_{70}$ monoadducts from unreacted C$_{70}$ and higher adducts. The overall yield of the mixture of monoadducts was 55% (67% on the basis of the recovered C$_{70}$).

Analysis of the monoadduct product mixture by HPLC chromatography, using both analytical and semipreparative Cosmosil and Buckyclutcher columns, indicated the presence of eight separable isomers (Figure 2a). The IR spectrum of the isomeric mixture showed two distinct carbonyl stretching bands at 1701 and 1724 cm$^{-1}$ that correspond to cis- and trans-fused [2 + 2] adducts, respectively, as was shown previously.[57−59] It has been shown by HPLC analysis of the well-characterized C$_{60}$ photoadducts that Cosmosil columns are unable to separate cis- and trans-fused diastereomeric adducts, which can be separated on the Buckyclutcher column.[60,61] Thus, the Cosmosil column can be used to separate the regioisomeric C$_{70}$ monoadducts, while the Buckyclutcher column can be used to separate regioisomers as well as the chemically distinct cis- and trans-fused diastereomers.

HPLC analysis indicates the presence of eight monoadduct isomers in total (four trans-fused diastereomers and four cis-fused diastereomers), corresponding to four distinct regioisomers labeled $\alpha-\delta$. Note that the two peaks corresponding to isomer $\alpha$, the lowest yield product, are poorly resolved. Isolation and characterization of the isomers corresponding to the individual peaks show that peaks $\alpha$ and $\delta$ correspond to C$_{70}$ bond A adducts, while peaks $\beta$ and $\gamma$ correspond to bond B adducts.

The HPLC analysis indicated that four sets of isomers (not counting enantiomers) were formed upon photoaddition of MCH to C$_{70}$. Separation of these isomers was later accomplished by preparative HPLC. $^{1}$H and $^{13}$C NMR analysis of the product mixture afforded limited information concerning the electronic environment of the bridgehead proton and the methyl protons and the symmetry of the fullerene portion of the various regioisomers, as each monoadduct is $C_1$ symmetric. In the absence of X-ray crystal structures for each of the eight individual isomers, we relied upon $^{3}$He NMR analysis of the mixture of monoadducts for discernment of the reactive fullerene [6,6] bonds involved in the [2 + 2] photoaddition process.

**Characterization of the Isomeric Monoadducts.** Repetition of the photoaddition reaction using MCH and $^{3}$He@C$_{70}$ was followed by the analysis of the mixture of monoadducts by $^{3}$He NMR. The resultant spectrum is shown in Figure 3a. Four pairs of peaks separated by 0.01$-$0.02 ppm, centered at $-24.16$, $-24.24$, $-27.15$, and $-27.23$ ppm, are observed. The detection of four sets of cis- and trans-fused regioisomeric monoadducts by $^{3}$He NMR correlates with the observed HPLC traces using Cosmosil and Buckyclutcher columns. The $^{3}$He NMR shifts are downfield from $^{3}$He@C$_{70}$ ($-28.8$ ppm) and can be compared with those observed for fulleropyrrolidines prepared by our group at $-27.0$ and $-23.8$ ppm, in which the addend is fused at bond A (C1$-$C2) and bond B (C5$-$C6) of C$_{70}$, respectively.[62−64] This good agreement between the $^{3}$He NMR shifts for the C$_{70}$ photoadducts and the previously studied fulleropyrrolidines suggests that [2 + 2] photoaddition of MCH to C$_{70}$ takes place at the [6,6] bonds closest to the poles of the C$_{70}$ cage where the local curvature is greatest. There is no evidence for the formation of any [5,6] bond adduct, which would introduce increased strain by placing double bonds onto the fullerene pentagons.[65] Moreover, only [6,6] photoadducts were isolated for the corresponding reaction with C$_{60}$, suggesting that [5,6] addition is not a major factor for the stepwise triplet diradical addition of enones to fullerenes.[1,4]

Therefore, it follows that the products of the photoaddition of MCH to C$_{70}$ correspond to structures **4**$-$**7** (Chart 2). Furthermore, from the $^{3}$He NMR and IR spectra and HPLC analysis, it is evident that each of these isomers is formed as a mixture of cis- and trans-fused diastereomers because a pair of peaks for each isomer is observed with a separation of 0.01$-$0.02 ppm in the $^{3}$He NMR spectrum, very similar to what was seen for the MCH$-$C$_{60}$ photoadducts.[2] In the latter case, it was shown that the trans isomer, which is the major product, corresponds to the upfield peak. Similar assignments can be made for the MCH$-$C$_{70}$ photoadducts (vide infra).

Accordingly, acid-catalyzed epimerization of the less stable trans-fused isomers to the more stable cis-fused isomers was carried out to reduce the number of monoadducts present in the product mixture and to simplify the problem of structural

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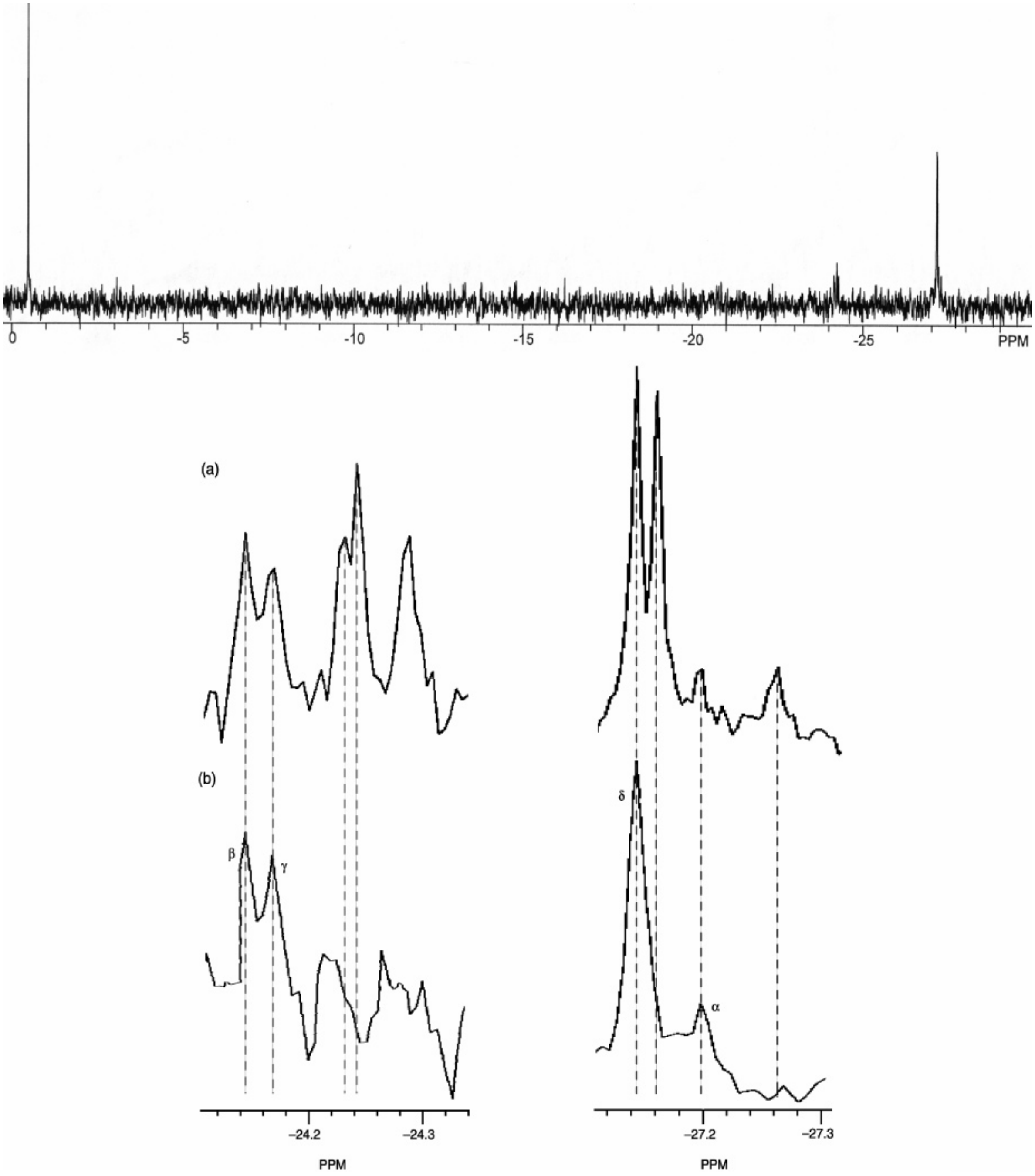

**FIGURE 3.** $^3$He NMR spectra for the MCH$-$C$_{70}$ monoadduct product mixture both (a) before and (b) after acid-catalyzed epimerization of trans-fused diastereomers to the corresponding cis-fused homologues. The four resonances centered at $-$24.20 ppm correspond to the C$_{70}$ bond B adducts, while those centered at $-$27.20 correspond to the bond A adducts. Note the disappearance of the four resonances corresponding to the trans-fused diastereomers following epimerization.

assignment. $^3$He NMR, IR, and HPLC analysis of the reaction mixture, following treatment with *p*-toluenesulfonic acid in toluene, demonstrated that epimerization had indeed occurred. A likely mechanism for the trans-to-cis epimerization involving keto$-$enol tautomerization is depicted in Scheme 2a. The IR spectrum for the mixture following acid treatment showed only a single carbonyl band at 1700 cm$^{-1}$, which corresponds to the cis-fused monoadducts.[4,66] A corresponding simplification of the Buckyclutcher HPLC trace and $^3$He NMR spectra were also observed (Figures 2b and 3b).

A clear difference can be seen between the $^3$He NMR spectrum for the mixture before and the spectrum for the mixture after acid treatment (Figure 3b). Thus, the major peak at about $-$27.16 ppm is assigned to the cis-fused bond A monoadduct because it was in great excess following the acid-catalyzed epimerization. Accordingly, the slightly upfield resonance at $-$27.14 observed prior to treatment with acid (Figure 3a) is assigned to the corresponding trans-fused diastereomer. Along similar lines, the isomer corresponding to the resonance at $-$27.26 ppm is converted to a resonance at $-$27.20 ppm, while the resonances at $-$27.23 and $-$27.24 are converted to reso-

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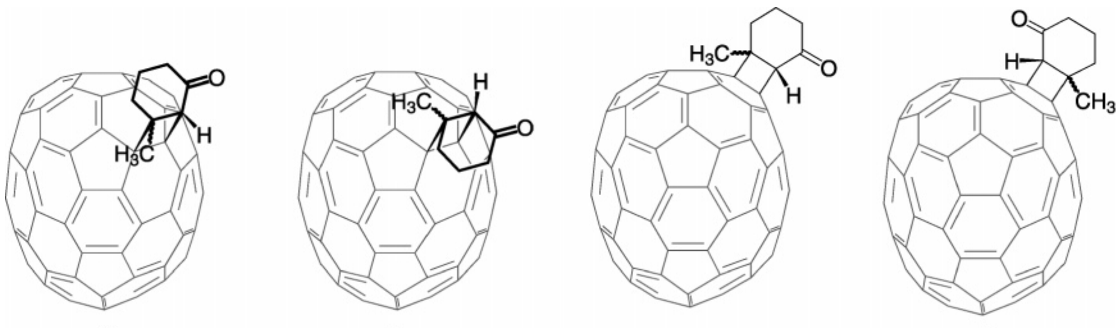
(66) Identical results have been observed previously for MCH$-$C$_{60}$ adducts by our group.

CHART 2



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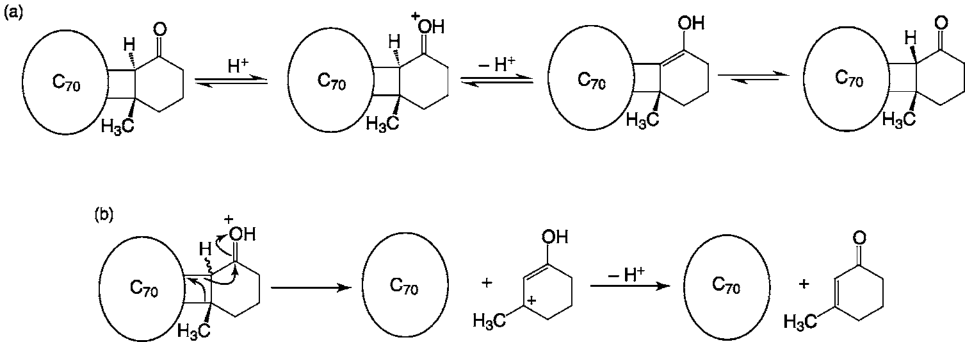
SCHEME 2



nances at −27.17 and −27.15 ppm, respectively. Similarly, HPLC traces of the product mixture using the Buckyclutcher column are greatly simplified following acid treatment and indicate the presence of four cis-fused isomers (α−*δ*; Figure 2b) as a result of the epimerization of the trans monoadducts to the corresponding cis-fused diastereomers. From the comparison of the HPLC traces and from the $^3$He NMR spectra obtained for the monoadduct mixture before and after the acid-catalyzed epimerization, it is clear that the photoaddition reaction in toluene shows a slight preference for the formation of the trans-fused diastereomers (trans/cis ∼ 3:2)

Additionally, a large peak at −28.8 ppm is observed in the $^3$He NMR spectrum, following acid treatment, which corresponds to $^3$He@C$_{70}$. Pristine C$_{70}$ was not present in the monoadduct mixture prior to the treatment of the reaction mixture with acid. The dissociation of the enone addend from the fullerene cage, which occurs in competition with the acid-catalyzed cis−trans epimerization, can be mechanistically rationalized as shown in Scheme 2b. HPLC experiments also verified the presence of pristine C$_{70}$ in the mixture following treatment with acid.

Semipreparative HPLC performed following the acid treatment allowed for the purification and separation of the major C$_{70}$ adduct (peak *δ* from the adduct mixture). The adducts corresponding to peaks *β* and *γ* were purified and separated together. Attempts to separate isomers *β* and *γ* from one another were unsuccessful. The minor product corresponding to peak α in the HPLC trace (Figure 2b) was collected separately but comprised less than 1% of the overall monoadduct product mixture, making its subsequent spectroscopic characterization unfeasible. The assignment of the structures of these purified products was finally made using $^3$He and $^1$H NMR analysis.

The isomer corresponding to peak *δ* (major product) showed a single $^3$He NMR resonance at −27.14 ppm (Figure 3b), indicating that this isomer is indeed a bond A (C1−C2) adduct,[62−64] corresponding either to structure **6** or to structure **7**. The $^1$H NMR spectrum for this predominate MCH−C$_{70}$ adduct shows that the bridgehead proton adduct is upfield relative to that of the analogous cis-fused MCH−C$_{60}$ adduct (4.07 vs 4.58 ppm, respectively, in CDCl$_3$/CS$_2$). Our group and others have shown that functional groups placed closer to the fullerene poles are shielded relative to those oriented toward the equator of C$_{70}$.[25−27,67,68] Thus, we can conclude that the enone addend shows a strong propensity to undergo the [2 + 2] photoaddition to C$_{70}$ in a geometry in which the carbonyl moiety and, hence, the bridgehead proton are directed toward the fullerene pole, while the bridgehead methyl group is directed toward the equator. Accordingly, the major MCH−C$_{70}$ photoadduct is concluded to be isomer **7**. We assign structure **6** to the minor product corresponding to peak α in the HPLC on the basis of its $^3$He resonance at −27.20 ppm.

$^3$He NMR of the mixture of HPLC peaks *β* and *γ* proved equally informative. On the basis of $^3$He NMR studies of C$_{70}$ adducts mentioned earlier, the resonances at −24.15 and −24.17 ppm (Figure 3b) clearly indicate that both isomers in the *β*−*γ* mixture are bond B adducts. The formation of both diastereomeric bond B isomers **4** and **5** can be rationalized on the basis of the chirotropic nature of the enone addend. Integration of the HPLC chromatograph and $^3$He NMR spectra in Figures 2 and 3, respectively, shows that these two isomers are formed in yields of 23 and 11%, respectively, accounting for roughly one-third of the overall monoadduct mixture. Because we were unable to separate the two isomers, we do not know whether **4** or **5** is the major bond B photoadduct.

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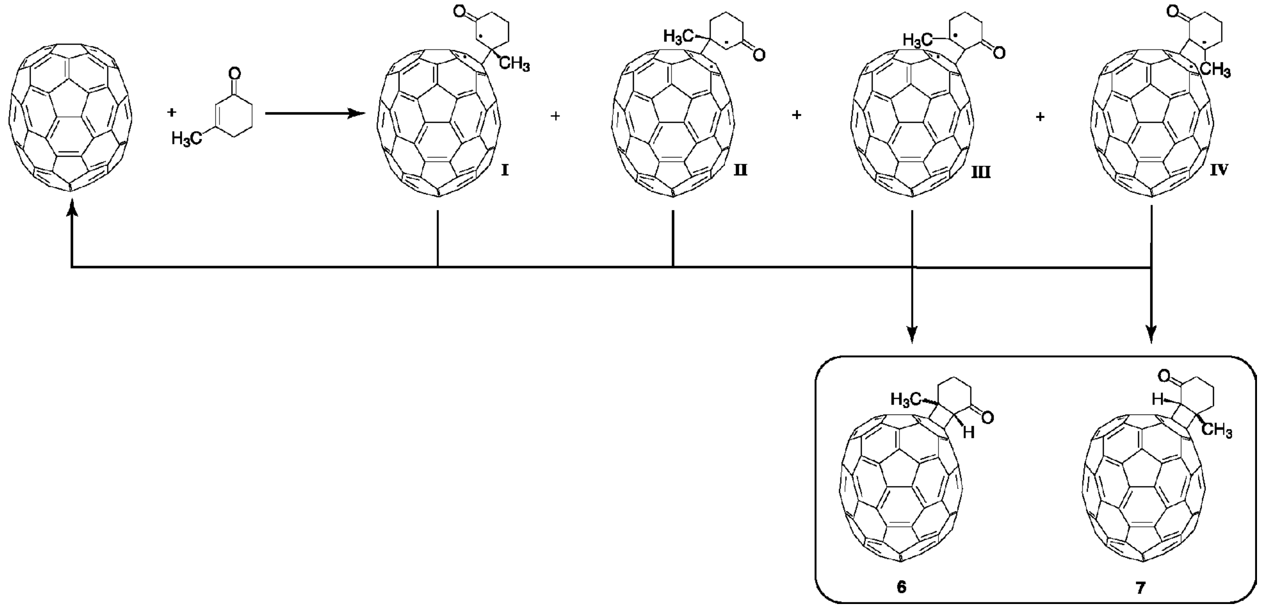
**SCHEME 3**



Nonetheless, it is clear that the [2 + 2] photochemical cycloaddition of MCH to $C_{70}$ proceeds in a manner similar to previously studied thermal cycloadditions to $C_{70}$ in which the most highly curved [6,6] bond (bond A) is the most reactive on the fullerene cage, with bond B displaying slightly lower reactivity.[19−24] It is worth noting that, on the basis of the $^3$He NMR and HPLC studies described above, the two bond A monoadducts represent the principle (66%) and minor products (<1%) of the enone photoaddition, while the two bond B adducts (**4** and **5**) are formed to an intermediate extent (34% for **4** and **5** combined).

**Mechanistic Discussion.** From a mechanistic standpoint, the addition of the triplet excited state of MCH to bond A of the $C_{70}$ cage via a 1,4-biradical intermediate (see Introduction) suggests that the formation of isomer **7** should predominate over that of **6**. Following the excitation of the enone and intersystem crossing to generate the lowest triplet excited state, addition to bond A of the fullerene can take place to give any of the four 1,4-biradical intermediates (**I**−**IV**) shown in Scheme 3. From a purely thermodynamic standpoint, one would expect biradicals **I** and **II** to be less stable than **III** and **IV**, respectively, on the basis of the relative stability of 2°, 3°, and enoxyl radicals.[69,70] Accordingly, it is expected that intermediates **III** and **IV** will be more readily formed as compared to intermediates **I** and **II**. Furthermore, we expect that biradical **IV** will be more stable than **III** because the unpaired electron on the fullerene in **IV** will experience an environment of lower local curvature, allowing for greater stabilization by delocalization. Previous studies have shown that $C_{70}$ radicals such as **IV** show a slightly higher stability as compared to those such as **III**.[71,72] Following this line of thinking, isomer **7**, the product of the ring closure of **IV**, should be the preferred product from the addition to bond A, as observed. The relative instability of **III** will serve to deter the formation of isomeric adduct **6**.

On the basis of these arguments, it is not difficult to rationalize the manner in which the difference in stability of **III** and **IV** gives rise to the disparate yields of **6** (<1%) and **7** (66%). The overall product distribution observed is strikingly reminiscent of that observed for the addition of alkyl azides or diazonium derivatives to $C_{70}$, as discussed earlier.[25−27]

On similar grounds, it is difficult to rationalize from a mechanistic standpoint why either **4** or **5** should predominate over one another on the addition to bond B through tertiary biradicals **V** and **VI**, respectively (Scheme 4). In both of these biradicals, the locations of the radical centers on the fullerene cage are essentially identical (i.e., essentially the same curvature and Mulliken charge). Indeed, the formation of **4** versus **5** is essentially controlled by the manner in which the first bond forms at the α carbon of the enone, with the addend directed either toward the fullerene pole or toward the equator. The structural and electronic factors that effect this competition are not at all obvious at this time.

A further consideration centers on the well-established fact that in general the product ratio observed for the enone−alkene [2 + 2] photocycloaddition is not related in a simple way to the stability of the various 1,4-biradical intermediates involved in a given reaction because of the fact that biradical reversion to ground-state starting materials can compete with ring closure to form adducts.[12] That is, the product ratio may not, and usually does not, reflect the ratio of the biradicals formed in the initial step.[60] The factors that control the conformation of 1,4-biradical intermediates, which in turn affect the competition between ring closure and ring scission, are subtle and involve both molecular structure and solvent polarity.[12,73] Accordingly, small changes in reaction conditions, as well as the substrate identity, can have dramatic effects on product distributions in [2 + 2] photocycloadditions.

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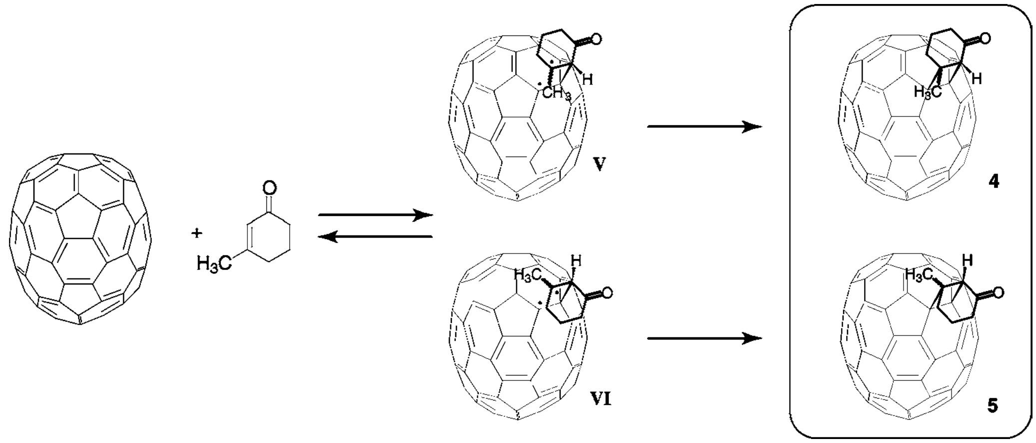
**SCHEME 4**



## Concluding Remarks

The [2 + 2] photoadditions of MCH to $C_{70}$ and $^3He@C_{70}$ have been carried out, and the complex reaction mixture has been studied by a combination of chromatographic and spectroscopic techniques. The total yield of the mixure of monoadducts was 55% (67% on the basis of the recovered $C_{70}$). The use of $^3He$ NMR was crucial to the determination of the [6,6] bonds involved in the photoaddition of enone to $C_{70}$. The $^3He$ NMR results clearly indicate that the two [6,6] bonds closest to the poles of the fullerene (C1−C2 and C5−C6) react most readily with MCH triplet excited states. The four regioisomeric products are formed in a ratio of 2:1:0.03 [**7**:(**4** + **5**):**6**]. This product distribution is similar to that obtained for typical thermal addition reactions to $C_{70}$. The fact that the degree of regioselectivity observed for the addition of substrates in high-energy excited states is similar to that observed for ground-state reactants reflects the mechanism of the [2 + 2] photocycloaddition, specifically the intermediacy of the 1,4-biradical intermediates. Such biradicals, formed upon the addition of enone triplet excited states to any of the four [6,6] bonds of $C_{70}$, can either cyclize to give adducts or decay to regenerate ground-state starting materials. The relative rate at which various 1,4-biradical intermediates close to generate [2 + 2] photoaddition products or fragment to regenerate enone and fullerene is a major factor in determining the ultimate MCH−$C_{70}$ adduct distribution. In principle, biradicals could be formed upon the addition of triplet MCH to any of the [6,6] bonds of $C_{70}$. The fact that products of addition to bonds A and B of the ovoid fullerene predominate in the monoadduct product mixture could reflect the relief of strain associated with the ring closure of the biradicals generated at the most highly curved [6,6] bonds on the fullerene surface. The corollary of this argument is that the analogous biradical intermediates formed at the more planar [6,6] bonds on $C_{70}$, namely, bonds C and D, would be more likely to fragment to regenerate reactants because the driving force for ring closure is greatly reduced.

Polarization of the enone triplet state is yet another factor that has to be taken into account.[12] Such polarization, which remains controversial, will surely play a role in the addition of enone triplet states to polarized carbon−carbon double bonds, such as bond A of $C_{70}$, where charge polarization is known to be significant. Accordingly, the mechanism that emerges for the photoaddition of enones such as MCH to fullerenes that are less symmetric than $C_{60}$ is quite complex. It is remarkable that the selectivity in this high-energy photochemical addition reaction is not significantly different from that of the ground-state thermal addition reactions to $C_{70}$.[19−30]

## Experimental Section

**Materials and Methods.** See Supporting Information.

**Photoaddition of 3-Methyl-2-cyclohexen-1-one to $C_{70}$.** The mixture of $C_{70}$ monoadducts was prepared by the irradiation of a mixture of enone and $C_{70}$ in toluene. The reaction mixture was prepared by dissolving 200 mg of $C_{70}$ (0.238 mmol) and 1.0 mL of 3-methyl-2-cyclohexen-1-one (0.881 mmol) in 600 mL of reagent grade toluene. After the solution was degassed with argon for 30 min, photoirradiation at about 300 nm was carried out using a 450-W Hanovia lamp equipped with a water-cooled condenser through Pyrex glass. The solution was continuously stirred using a magnetic stirrer. Following unperturbed irradiation for 16−20 h, the solvent was removed and the monoadducts were isolated together by flash chromatography on silica using toluene as the eluent. Following the removal of the solvent, the mixture of monoadducts was washed sequentially with ether to remove residual solvent and enone and then dried in vacuo. The total yield of monoadducts was 55% (67% on the basis of the recovered $C_{70}$). The reaction was repeated with $^3He@C_{70}$. Generally about 50 mg of $^3He$-labeled $C_{70}$ was used for these reactions. The amount of enone was scaled accordingly for the reaction with $^3He@C_{70}$, but 600 mL of toluene was used to ensure that the Hanovia lamp was completely immersed in the reaction mixture (the same yields were attained in the case of $^3He@C_{70}$). $^3He$ NMR (500 MHz, $CDCl_3/CS_2$, 25 °C, $\delta$): −24.15, −24.17, −24.23, −24.24, −27.15, −27.16, −24.20, −24.26. The mixture of monoadducts was characterized by FAB mass spectrometry: FAB-MS ($m/z$, $M^+$) calcd for $C_{77}H_{10}O$, 950.90; found, 950.91. IR analysis showed a set of carbonyl stretching frequencies at 1700 and 1724 $cm^{-1}$ corresponding to cis- and trans-fused cycloadducts, respectively.

**Acid-Catalyzed Epimerization of $C_{70}$ Monoadducts.** For the characterization of the reaction products, the mixture of monoadducts was heated at reflux in acidic media to catalyze the isomerization of trans-fused diastereomers to the cis form. This isomerization was completed by dissolving 40 mg of the mixture of monoadducts (with endohedral $^3He$) and 1 mg of *p*-toluenesulfonic acid in 70 mL of toluene. The solution was then heated at reflux for 72 h, after which it was washed three times with 50 mL of saturated $NaHCO_3$ and once with water. The organic phase was separated and dried over $MgSO_4$. The drying agent was removed by vacuum filtration, and the solvent was removed. The resultant mixture of monoadducts was then washed sequentially with ether to remove residual solvent and dried in vacuo. $^3He$ NMR (500 MHz, $CDCl_3/CS_2$, 25 °C, $\delta$): −24.15, −24.17, −27.16, −24.20. IR analysis showed a single carbonyl stretching frequency at 1700 $cm^{-1}$.

**Separation and Characterization of cis-Fused Isomeric $C_{70}$ Monoadducts.** The mixture of monoadducts was isolated together from the reaction mixture by flash chromatography on silica using toluene as the eluent. Following the epimerization to the cis-fused isomers, the isomeric mixture monoadduct was separated by HPLC using analytical and semipreparative Cosmosil and Buckyclutcher columns with toluene and hexanes (1:1, v/v) as the eluent. Two main fractions were collected corresponding to isomer cis-**7** and a mixture of isomers cis-**4** and cis-**5**, respectively. Isomer cis-**7**: FAB-MS (*m*/*z*, $M^+$) calcd for $C_{77}H_{10}O$, 950.90; found, 951.07. $^3$He NMR (500 MHz, $CDCl_3/CS_2$, 25 °C, $\delta$): $-27.16$. $^1$H NMR (200 MHz, $CDCl_3/CS_2$, 25 °C): 4.07 (s, 1H), 3.48 (t, 2H), 1.46 (m, 2H), 1.84 (s, 3H), 1.03 (t, 2H). Isomers cis-**4** and cis-**5**: FAB-MS (*m*/*z*, $M^+$) calcd for $C_{77}H_{10}O$, 950.90; found, 950.94. $^3$He NMR (500 MHz, $CDCl_3/CS_2$, 25 °C, $\delta$): $-24.15$, $-24.17$.

**Acknowledgment.** J.R. thanks New York University College of Arts and Sciences for a Myron Kove Research Fellowship—Dean's Undergraduate Research Grant and is grateful to Pfizer Pharmaceuticals for a summer research fellowship. This work was supported by NSF Grant CHE-9712735.

**Supporting Information Available:** General experimental methods (one page). This material is available free of charge via the Internet at http://pubs.acs.org.

JO0523060