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[1 + 2] and [3 + 2] Cycloaddition Reactions of Vinylcarbenes with C_{60}

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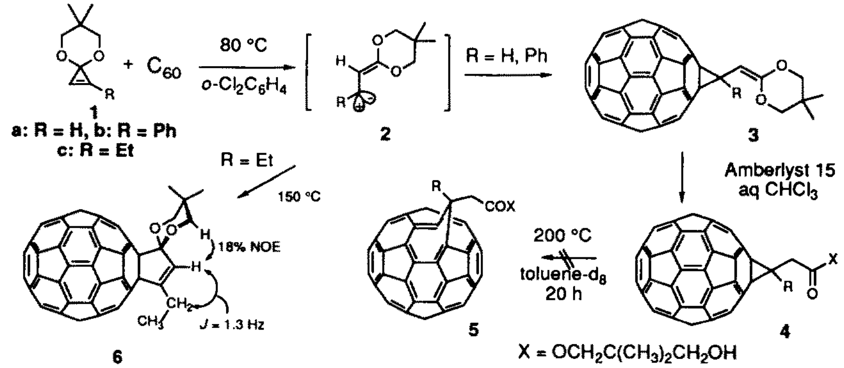
Abstract: Thermolysis of a mixture of C_{60} and the cyclopropenone acetal **1a** or **1b** gives the methanofullerene **4a** or **b**, whereas the ethyl-substituted compound **1c** gives the cyclopentenone acetal **6**. The thermal stability of **4** and the semi-empirical molecular orbital calculations performed for the parent methanofullerenes and fulleroids indicated that the fulleroid structure such as **5** may be unstable.

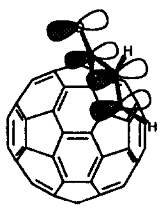
Synthesis and structure of organic derivatives of buckminsterfullerene,[1,2,3]continue to attract interests of broad scientific community. Cyclopropenone acetal **1**[4,5] is a unique source of carbene reactive species in that it generates a vinylcarbene **2** by a purely thermal process without intervention of any intermediates.[4] Therefore, **2** is an attractive carbene to be studied in fullerene chemistry, since diazo compounds, a conventional source of carbene species, fail to react with C_{60} via a simple carbene mechanism and unexpectedly gives fulleroids rather than methanofullerenes.[2b,c] We report here that the reaction of an equimolar mixture of a cyclopropenone acetal **1** and C_{60} produces a [1 + 2] cycloadduct **4** and a [3 + 2] cycloadduct **6** depending on the substituent R (Scheme I). The methanofullerene **4a** represents the novel fullerene which has been established unambiguously to have a all carbon three-membered ring fused to the C_{60} skeleton.[3] The cyclopentenone acetal **6**, on the other hand, provides an intriguing orbital arrangement, wherein the cyclopentene π-orbital is placed close to but orthogonal to the π-sphere of the fullerene. The methanofullerene **4** was found to be thermally stable (200 °C), showing no tendency to rearrange to the isomeric fulleroid **5** having methano[10]annulene structure. Semi-empirical molecular orbital calculations suggested that **5** is less stable than **4**. These results are strongly suggesting that the fulleroid having methano[10]annulene structure dose not exist.[6]

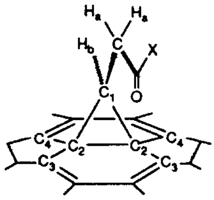
Scheme I.



The cyclopropenes **1a**, **b**, **c** are available in one or two steps from the corresponding 1,3-dichloroacetone acetal on a multi-gram scale,[7] and, upon mild thermolysis at 80-100 °C, reversibly generate vinylcarbenes **2a**,**b**,**c**.[4,5] When a mixture of the cyclopropene **1a** (1.2 equiv) and C_{60} (50 mg) in *o*-dichlorobenezene (60 mL) was heated at 80 °C for 24 hour, a reddish adduct **4a** was obtained in 44% yield (58% based on recovered C_{60}) after treatment of the hydrolytically labile ketene acetal **3** with aqueous acid.[8] The polar ester **4** can be readily isolated from the less polar C_{60} on silica gel. Similarly, the phenylcyclopropene **1b** gave **4b** in 10% isolated yield.

Curiously, the reaction of the ethylcyclopropene **1c** afford the [3 + 2] cycloadduct **6** in 40% yield rather than **3**.[9] The formation of a cyclopentenone acetal by the reaction of **1** with an electron-deficient olefin has previously been reported.[4, 5] Both the ^{13}C NMR spectrum (1:1 $CS_2/CDCl_3$) of **6** showing only 38 signals (31 at δ 110-155) and the ^1H NMR spectra, especially, the acetal signals, indicated the C_s symmetry of the molecule and therefore the ring fusion at the 6,6-ring juncture as shown. Irradiation of the axial acetal protons caused 18% nuclear Overhauhauser enhancement of the olefinic proton signal, clearly indicating the 3-ethylcyclopent-2-en-1-one structure. The orbital picture shown below for the prototypical cyclopentenone illustrates the unique spatial arrangement of the olefinic π-orbitals with respect to the C_{60} sphere. Given the possibility of introducing further olefinic conjugation with suitable carbon-carbon chain elongation reactions (e.g., Wittig reaction), one can envision the possibility of constructing an unprecedented π-orbital array over the C_{60} sphere. Overwhelming effects of the C_{60} group so far precluded identification of any particular electronic consequence of the interaction of the olefin and the fullerene π-orbitals, and this subject is left for further studies.





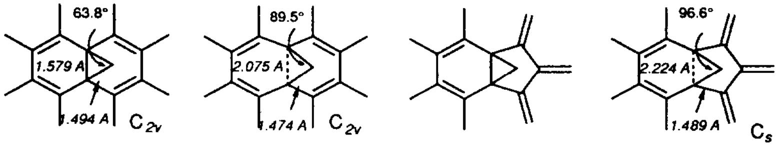
$\delta(C_1) = 33.34$ ppm
$\delta(C_2) = 75.18$ ppm
$\delta(C_3$ or $C_4) = 146.91$ or 149.50 ppm

$^1J(C_1\text{-}H_b) = 166.9$ Hz
$^2J(C_1\text{-}H_a) = 5.7$ Hz
$^2J(C_2\text{-}H_b) = {}^3J(C_2\text{-}H_a) = 3.8$ Hz
$^3J(C_3\text{-}H_b)$ or $^3J(C_4\text{-}H_b) = 3.8$ or 4.8 Hz

Figure 1. ^{13}C NMR data for the cyclopropane structure in 4a

The structural analysis of the [1 + 2] cycloadduct **4a** was carefully carried out, since the previous structural assignment of the fulleroid and methanofullerene were made on rather ambiguous evidence.[2b,3a] The proton-decoupled ^{13}C NMR spectra showed only 39 signals indicating C_s symmetry of the molecule. Of the 32 carbon signals assigned to the C_{60} skeleton, 27 signals of relative intensity of 2, and 4 signals of intensity of 1 are due to sp^2 carbons and a 2-carbon intensity signal at δ 75.18 is due to the sp^3 C_2 carbon (see below). Analysis of the C-H coupling in the proton-non-decoupled ^{13}C NMR spectra gave the crucial evidence for the identification of the cyclopropane structure in **4** (Figure 1). The two equivalent protons α to the ester group (H_a, δ 3.64) are coupled ($J = 7.3$ Hz) to an adjacent proton (H_b, δ 4.44), which experiences strong deshielding by the C_{60} group.[2b,c] The C_1 atom (δ 33.34), which is directly connected to H_b, was found to exhibit a very large $^1J_{C\text{-}H}$ coupling of 166.9 Hz, a value compatible only with a cyclopropane sp^3 carbon, and not with the fulleroid structure such as **5**.[10] The signal at δ 75.18 with relative intensity of 2 appears as quartet ($J = 3.8$ Hz) with 2- and 3-bond coupling to H_b and H_a, and thus assigned to the C_2 atom at the cyclopropane/C_{60} juncture. In addition, the chemical shift value of δ 75.18 is reasonable as an sp^3 carbon in the C_{60} skeleton rather as an sp^2 one in **5a**: this is a conventional protocol for assinging methanofullerene structure.[2] We could also assign two signals appearing in the "aromatic region" at δ 146.91 (J = 3.8 Hz) and 149.05 (J = 4.8 Hz) to C_3 and C_4,[11] since they exhibit 3-bond coupling with H_b. The above ^{13}C NMR data present the first unequivocal evidence of the methanofullerene structure,[12] and gives a support to the structural assignment of related compounds.[3a] For instance, the phenyl compound **4b** shows signals at δ 47.11 and 79.19 assignable to the C_1 and C_2 atoms, and thus must also have the methanofullerene structure. In addition, the UV-visible spectrum of **4a** (λ = 259, 326, 428, 490, and 688 nm) was found to be virtually identical with those previously assigned to fullerene epoxide (λ = 256, 328, 424, 496, and 680 nm) and the sugar-connected methanofullerene (λ = 433 and 499 nm).[13]

With a methanofullerene[3a] and fulleroids[2b] reported in the literature, there has arisen considerable ambiguity as to their exact structure and their interrelationship. Among four structural prototypes A-D (Figure 2), all except C are recorded in the literature, and only the identity of A (this work and ref. 3c, d) and D[2c,d] is conclusive. In order to obtain information on the stability of these structures, the AM1 and PM3 semi-empirical molecular orbital calculations[14] were carried out. In the 6,6-ring fusion pair, the methanofullerene A was found to be much more stable than the corresponding fulleroid B:[2a,b] at the AM1 level, B is 6.9 kcal/mmol higher in energy than A, and, at the PM3 level, B could not be located as a stationary point on the potential surface. In the 5,6-ring fusion series, on the other hand, the fulleroid structure D[2c] was found to be stable and the methanofullerene C could not be located as a stationary point at both levels of calculations.[15] The energy barriers separating methanofullerene and fulleroid seem generally low as is expected from the bicyclo[4.1.0]hepta-1,3-triene partial structure.[16] Experiments supported the calculations. Thus, we found that **4a** is thermally stable and does not isomerize either to **5a** or to the compound corresponding to D upon heating in toluene-d_8 at 200 °C for 20 h as monitored by ^1H NMR.[17]



A (6.8 kcal/mol) [0.4 kcal/mol]
B (13.7 kcal/mol) [not located]
C (not located) [not located]
D (0.0 kcal/mol) [0.0 kcal/mol]

Figure 2. Relative heat of formation calculated at the (AM1 level) and at the [PM3 level], and the geometry at the AM1 level

The flexibility in regard of the carbene structure, the uniqueness of the rigid cyclopropane and cyclopentene rings built on the fullerene sphere and the possibility of further elaboration of functional groups promises a variety of chemistry to be examined for these new fullerene derivatives.[18,19]

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8. R_f = 0.20, 10% EtOAc in toluene; IR ($CHCl_3$) 3625, 2925, 2870, 1730, 1430, 1380, 1190, 1040, 580, 530. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (s, 6 H, two CH_3), 1.98 (br s, 1 H, OH), 3.45 (s ,2 H, CH_2OH), 3.64 (d, J = 7.3 Hz, 2 H, CH_2CO_2), 4.21 (s, 2 H, CO_2CH_2), 4.44 (t, J = 7.3 Hz, 1 H $CHCH_2$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.61 (two CH_3), 31.84 (CH_2), 33.34 (CH), 36.54 (C), 68.37 (CH_2), 70.33 (CH_2), 75.18 (C_{60}, cyclopropyl carbon), 136.34, 137.97, 141.11, 141.12, 142.15, 142.17, 142.37, 142.65, 413.02, 143.05, 143.10, 143.65, 143.73, 144.30, 144.40, 144.42, 144.57, 144.71, 144.79, 144.81, 145.10, 145.19, 145.20, 145.25, 145.72, 146.91, 149.50, 171.26 (C=O). Anal. Calcd for $C_{68}H_{14}O_3\cdot 3/4CHCl_3$: C, 85.27; H, 1.54. Found: C, 85.29; H, 1.31.
9. R_f = 0.41, 50% hexane in toluene; IR (CS_2) 2950, 2925, 2850, 1180, 1100, 1020, 760, 520; ^{1}H NMR (500 MHz, $CS_2/CDCl_3$ 1/1) δ 0.99 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3), 1.57 (t, J = 7.2 Hz, 3 H, CH_2CH_3), 3.08 (dq, J = 1.4, 7.2 Hz, 2 H, CH_2CH_3), 3.84 (d, J = 11.5 Hz, 2 H, acetal methylene), 4.18 (d, J = 11.5 Hz, 2 H, acetal methylene), 7.13 (t, J = 1.3 Hz, 1 H, vinyl H); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$ 1/1) δ 12.70, 21.94, 22.87, 22.96, 29.92, 73.42,79.17, 114.30, 119.34, 134.64, 136.64, 139.64, 139.66, 141.44, 141.54, 141.77, 141.79, 142.11, 142.32, 142.34, 142.49, 142.90, 144.15, 144.53, 144.90, 145.16, 145.28, 145.41, 145.72, 145.82, 145.86, 146.18, 146.48, 146.83, 147.20, 153.87, 154.15, 154.94.
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11. If one assumes steric compression effects, the δ 146.91 ppm signal may be assigned to the C_3 carbon.
12. The location of the cyclopropane at the 6,6-ring junction is still tentative. However, the formation of only a single diastereomer of **4** is consistent with this assignment, since the reaction at the 5,6-ring junction *can* give two diastereomers. Finally, the spectral similarity mentioned in the text suggests that all these compounds are in the same structural series.
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