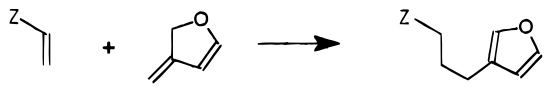
Ene Reaction of C_{60} and 3-Methylene-2,3-Dihydrofuran

William H. Miles* and Patricia M. Smiley

Department of Chemistry, Lafayette College, Easton, Pennsylvania 18042

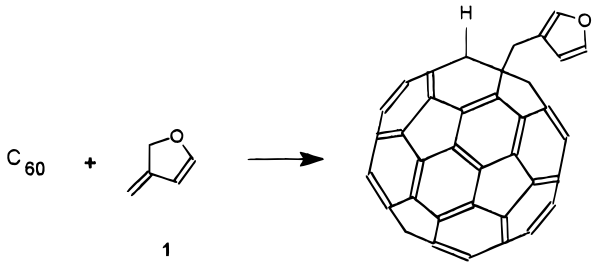
Received August 10, 1995 (Revised Manuscript Received January 25, 1996)

The fascinating chemical, physical, and biological properties of fullerenes have incited a flurry of research activity.[1] Although C_{60} reactivity is extensive and multifaceted,[2−8] the preparation and isolation of pure, well-characterized fullerene derivatives remains an important objective. Among the most useful methods for the functionalization of fullerenes are the cycloaddition reactions[2−4] such as the Diels−Alder reaction. The facile participation of C_{60} in electrocyclic reactions as a dieneophile[9] and dipolarophile prompted Wu[5a] and Komatsu[5b] to study the enophilic behavior of C_{60}. The reaction of C_{60} with 1-heptene,[5a] 4-allylanisole,[5a] and 3,5-di-*tert*-butyl-4-[(trimethylsiloxy)allyl]benzene[5b] were the first published reports of an ene reaction[10] with a fullerene. We have independently investigated the ene reaction of C_{60} with 3-methylene-2,3-dihydrofuran (**1**), the alicyclic isomer of 3-methylfuran, which readily undergoes the ene reaction with simple electron deficient alkenes.[11] We now report that the ene reaction of C_{60} with 3-methylene-2,3-dihydrofuran gives an easily isolated fullerene addition product in good yield.



1

The reaction of C_{60} with 3-methylene-2,3-dihydrofuran (10 equivs) in toluene at 25 °C for 22 h gave 1-(3-furylmethyl)-1,9-dihydrofullerene-60 (**2**) as a brown solid in 46% yield (50% yield based on recovered C_{60}), along with recovered C_{60} and fullerene products tentatively identified as the multiple addition products.[12,13] Longer reaction times, higher concentrations of **1**, and/or higher temperatures gave higher conversion of C_{60} but also gave higher yields of the multiple addition products. Dihydrofullerene **2** was easily separated from C_{60} and the other fullerene products by flash chromatography on silica gel.



1 **2**

The ^{1}H NMR of **2** had resonances for the three furyl protons at δ 8.03, 7.64, and 6.92, and for the methylene protons at δ 4.60. These protons were shifted substan-

(1) Reviews: Hammond, G. S.; Kuck, V. J., Eds.; *Fullerenes: Synthesis, Properties, and Chemistry of Large Carbon Clusters*; ACS Symposium Series 481; American Chemical Society: Washington, DC, 1992. *Acc. Chem. Res.* **1992**, *25*, entire issue. Hirsch, A. *The Chemistry of Fullerenes*; George Thieme Verlag: New York, 1994. Hirsch, A. *Synthesis* **1995**, 895.

(2) [4 + 2]: (a) Khan, S. I.; Oliver, A. M.; Paddon-Row, M. N.; Rubin, Y. *J. Am. Chem. Soc.* **1993**, *115*, 4919. (b) Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretzian, C. *J. Am. Chem. Soc.* **1993**, *115*, 344. (c) An, Y.; Anderson, J. L.; Rubin, Y. *J. Org. Chem.* **1993**, *58*, 4799. (d) Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 1594. (e) Rotello, V. M.; Howard, J. B.; Yadav, T.; Conn, M. M.; Viani, E.; Giovane, L. M.; Lafleur, A. L. *Tetrahedron Lett.* **1993**, *34*, 1561. (f) Wilson, S. R.; Li, Q. *Tetrahedron Lett.* **1993**, *34*, 8043. (g) Komatsu, K.; Murata, Y.; Sugita, N.; Takeuchi, K.; Wan, T. S. M. *Tetrahedron Lett.* **1993**, *34*, 8473. (h) Tago, T.; Minowa, T.; Okada, Y.; Nishimura, J. *Tetrahedron Lett.* **1993**, *34*, 8461. (i) Zhang, X.; Foote, C. S. *J. Org. Chem.* **1994**, *59*, 5235. (j) Krautler, B.; Puchberger, M. *Helv. Chim. Acta* **1993**, *76*, 1626. (k) Nie, B.; Hasan, K.; Greaves, M. D.; Rotello, V. M. *Tetrahedron Lett.* **1995**, *36*, 3617. (l) Paquette, P. A.; Graham, R. J. *J. Am. Chem. Soc.* **1995**, *60*, 2958. (m) Belik, P.; Gugel, A.; Kraus, A.; Walter, M.; Mullen, K. *J. Org. Chem.* **1995**, *60*, 3307. (n) An, Y.; Ellis, G. A.; Viado, A. L.; Rubin, Y. *J. Org. Chem.* **1995**, *60*, 6353.

(3) [3 + 2] and [2 + 1]: Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798. Meier, M. S.; Poplawska, M. *J. Org. Chem.* **1993**, *58*, 4524. Yamago, S.; Tokuyama, H.; Nakamura, E.; Prato, M.; Wudl, F. *J. Org. Chem.* **1993**, *58*, 4796. Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479. Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson. O. *J. Am. Chem. Soc.* **1992**, *114*, 7300. Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 5829. Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1993**, *115*, 10366. Prato, M.; Li, Q. C.; Wudl. F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148. Zhang, X.; Willems, M.; Foote, C. S. *Tetrahedron Lett.* **1993**, *34*, 8187. Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; Goldschmidt, R. J.; King, R. C. *J. Am. Chem. Soc.* **1995**, *117*, 5492. Paolucci, F.; Marcaccio, M.; Roffia, S.; Orlandi, G; Zerbetto, F.; Prato, M.; Maggini, M.; Scorrano, G. *J. Am. Chem. Soc.* **1995**, *117*, 6572.

(4) [2 + 2]: (a) Hoke, S. H., II; Molstad, J.; Dilettato, D.; Jay, M. J.; Carlson, D.; Kahr, B.; Cooks, R. G. *J. Org. Chem.* **1992**, *57*, 5069. (b) Wilson, S. R.; Kaprinidis, N.; Wu, Y.; Schuster, D. I. *J. Am. Chem. Soc.* **1993**, *115*, 8495. (c) Zhang, X.; Romero, A.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 11024. (d) Zhang, X.; Foote, C. S. *J. Am. Chem. Soc.* **1995**, *117*, 4271.

(5) Ene Reaction: (a) Wu, S.; Shu, L.; Fan, K. *Tetrahedron Lett.* **1994**, *35*, 919. (b) Komatsu, K.; Murata, Y.; Sugita, N.; Wan, T. M. S. *Chem. Lett.* **1994**, 635.

(6) Nucleophilic addition: (a) Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697. (b) Hirsch, A.; Soi, A.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 766. (c) Hirsch, A.; Grosser, T.; Skiebe, A.; Soi, A. *Chem. Ber.* **1993**, *126*, 1061. (d) Bestmann, H. J.; Hadawi, D.; Roder, T.; Moll, C. *Tetrahedron Lett.* **1994**, *35*, 9017. (e) Komatsu, K.; Murata, Y.; Takimoto, N.; Mori, S.; Sugita, N.; Wan, T. S. M. *J. Org. Chem.* **1994**, *59*, 6101. (f) Yamago, S.; Yanagawa, M.; Nakamura, E. *J. Chem. Soc., Chem. Commun.* **1994**, 2093. (g) Kitagawa, T.; Tanaka, T.; Takata, Y.; Takeuchi, K.; Komatsu, K. *J. Org. Chem.* **1995**, *60*, 1490. (h) Ganapathi, P. S.; Friedman, S. H.; Kenyon, G. L.; Rubin, Y. *J. Org. Chem.* **1995**, *60*, 2954. (i) Keshavarz, K. M.; Knight, B.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 11371.

(7) Transition metal complexes: Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, *252*, 1160. Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J. *Science* **1991**, *252*, 312. Douthwaite, R. E.; Green, M. L. H.; Stephens, A. H. H.; Turner, J. F. C. *J. Chem. Soc., Chem. Commun.* **1993**, 1522.

(8) Radical addition: Yoshida, M.; Morishima, A.; Morinaga, Y.; Iyoda, M. *Tetrahedron Lett.* **1994**, *35*, 9045. Chiang, L. Y.; Wang, L.-Y.; Swirczewski, J. W.; Soled, S.; Cameron, S. *J. Org. Chem.* **1994**, *59*, 3960.

(9) Studies by Wilson (ref 2f) suggest that the reactivity of C_{60} as a dieneophile is comparable to *N*-phenylmaleimide.

(10) For reviews of the ene reaction see Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. Mikami, K.; Shimizu, M. *Chem. Rev.* **1992**, *92*, 1021.

(11) Miles, W. H.; Berreth, C. L.; Smiley, P. M. *Tetrahedron Lett.* **1993**, *34*, 5221.

(12) The black solid had numerous peaks in the ^{1}H NMR between δ 4.0−4.9, 5.9−7.2 and 7.5−8.1. Mass spectral analysis suggests that the compound is a mixture of the isomeric bis-adducts: HRMS calcd for $C_{70}H_{10}O_2$ 884.0837; found 884.1167.

(13) Although the Diels−Alder reaction of a furan-containing resin with C_{60} has been reported (ref 2k), we did not observe Diels−Alder products of C_{60} or fullerene **2** with 3-methylfuran (an unavoidable side product in the preparation of 3-methylene-2,3-dihydrofuran).

0022-3263/96/1961-2559$12.00/0

tially downfield due to the deshielding effect of the C_{60} moiety.[14] The singlet at δ 6.72 for the C_{60}-H underwent slow exchange with D_2O. The 35 peaks in the ^{13}C NMR spectrum suggest C_S symmetry, assuming that two carbon resonances are overlapping in the δ 142−148 region.[15] The signals appearing at δ 42.65 for the CH_2 group, δ 59.33 and 65.52 for the sp^3 carbons of the C_{60} core, δ 112.99 and 120.37 for the C-3 and C-4 furyl carbons, and between δ 136−157 for the remaining furyl carbons and sp^2 carbons of the C_{60} core are consistent with the structure depicted for fullerene **2**. The notable bands in the UV-vis of **2** are at 432 and 704 nm, consistent with the spectra of other C_{60} fullerene 6,6-addition products.[2j,4d,5,6] The addition of 3-methylene-2,3-dihydrofuran across a 6,6 junction is not surprising in view of the numerous examples of addition reactions in the literature and the theoretical calculations for the stability of the addition products of nonsterically demanding groups.[6d,6g,8,16]

The facile ene reaction of C_{60} with 3-methylene-2,3-dihydrofuran provides further evidence that the ene reaction will be an important method for the functionalization of fullerenes. The chemical manipulation of the furan ring[17] of **2** may provide a means of obtaining a whole host of new fullerene compounds, including water soluble fullerenes.[2i] Furthermore, the utility of 3-methylene-2,3-dihydrofuran in the functionalization of C_{60} underscores the potential for alicyclic isomers of aromatic compounds in synthesis of organic compounds.[11,18]

(14) Prato, M.; Suzuki, T.; Wudl, F.; Lucchini, V.; Maggini, M. *J. Am. Chem. Soc.* **1993**, *115*, 7876. For comparative purposes, the furyl and C-5 protons of 5-(3-furyl)-2-pentanone appear at δ 7.26, 7.12, 6.16, and 2.28 in the ^1H NMR (300 MHz, CS_2:$(CD_3)_2CO$, 5:1).

(15) Addition across a 6,5 junction would lead to a fullerene having C_1 symmetry, and hence 58 chemically distinct sp^2 carbons for the fullerene core. The 1,4-dihydrofullerene product (see Fagan's example in ref 6a and Kitagawa's example in ref 6g) also would have C_1 symmetry.

(16) Henderson, C. C.; Cahill, P. A. *Science* **1993**, *259*, 1885. Henderson, C. C.; Cahill, P. A. *Chem. Phys. Lett.* **1992**, *198*, 570. Matsuzawa, N.; Dixon, D. A.; Fukunaga, T. *J. Phys. Chem.* **1992**, *96*, 7594.

(17) Lipshultz, B. H. *Chem. Rev.* **1986**, *86*, 795.

(18) Gajewski, J. J.; Gortva, A. M. *J. Org. Chem.* **1989**, *54*, 373. Tidwell, J. H.; Senn, D. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 4685. Ojida, A.; Abe, A.; Kanematsu, K. *Heterocycles* **1994**, *38*, 2585.

Experimental Section

General. All reactions and purifications were carried out under argon in flame-dried glassware. Toluene was distilled from sodium/benzophenone immediately before use. The solvents used for column chromatography, UV-vis, and NMR were degassed before use. C_{60} was purchased from Fullerenes Enterprise and used without further purification.

NMR spectra were obtained on a Brucker AC-300 NMR spectrophotometer. Infrared spectra were obtained on a Mattson Cygnus 100 FT/IR spectrometer. UV-vis were obtained on a Hewlett Packard Model 8452 Diode array UV-vis spectrometer. Microanalysis was performed at Atlantic Microlab, Inc.

1-(3-Furylmethyl)-1,9-dihydrofullerene-60 (2). To a solution of C_{60} (0.360 g, 0.50 mmol) in toluene (150 mL) was added 3-methylene-2,3-dihydrofuran (0.50 mL of a 4:1 mixture of 3-methylene-2,3-dihydrofuran: 3-methylfuran, 4.9 mmol). After stirring at 25 °C for 22 h, silica gel (4 g) was added, and the volatile organic compounds were removed under reduced pressure at room temperature. Flash chromatography (silica gel, 200 g) with 99:1 cyclohexane:toluene first gave C_{60} (0.031 g, 9%) as a purple solid and then **2** (0.184 g, 46% yield, 50% based on recovered C_{60}) as a brown solid. Further elution with 98:2 cyclohexane:toluene gave a black solid tentatively identified as multiple addition products (0.047 g).[12] For **2**: mp > 250 °C; ^1H NMR (300 MHz, CS_2:$(CD_3)_2CO$, 5:1) δ 8.03 (1H, br s), 7.64 (1H, m), 6.92 (1H, br s), 6.72 (1H, s), 4.65 (2H, s); ^{13}C NMR (75 MHz, CS_2:$(CH_3)_2CO$, 4:1, 0.03 M $Cr(acac)_3$) 155.89, 154.38, 147.75, 147.58, 147.34, 146.71, 146.63, 146.54, 146.48, 146.10, 145.87, 145.75, 145.71, 145.68, 145.05, 144.90, 144.07, 143.57, 143.40, 142.90, 142.69, 142.58, 142.38, 142.31, 142.20, 141.97, 140.55, 140.48, 136.67, 136.54, 120.37, 112.99, 65.52, 59.33, 42.65; IR (KBr pellet) 1510, 1461, 1427, 1258, 1214, 1182, 1160, 1024, 872, 777, 759, 744, 725, 599, 580, 526 cm^{-1}; UV-vis (hexane) λ_{max} 222, 256, 306, 324, 404, 432, 704; HRMS calcd for $C_{65}H_6O$ 802.0419; found 802.0593. Anal. Calcd for $C_{65}H_6O$: C, 97.25; H, 0.75. Found: C, 96.42; H, 1.15.

Acknowledgment. We would like to thank Dr. Paul J. Fagan (DuPont) for helpful discussions and Dr. Joseph Lazar (DuPont) for the mass spectral analysis.

Supporting Information Available: Copies of the ^1H and ^{13}C NMR spectra, UV-vis spectrum, and IR spectrum of **2** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO951486I