7630 *J. Org. Chem.* **1993**, *58*, 7630–7631

Synthesis of $C_{60}H_2$ by Rhodium-Catalyzed Hydrogenation of C_{60}

Luann Becker,[*,†] Theodore P. Evans,[‡] and Jeffrey L. Bada[†]

Scripps Institution of Oceanography, and Department of Chemistry, University of California, San Diego, La Jolla, California 92093

Received June 29, 1993 (Revised Manuscript Received November 5, 1993[●])

Summary: Reduction of C_{60} with rhodium(0) on alumina and hydrogen in deuterated benzene (C_6D_6) at ambient temperature and pressure yields a mixture of hydrogenated compounds; $C_{60}H_2$ has been characterized as the major product in 14% yield based on ^1H NMR.

The detection and synthesis of fullerenes has had a major impact on chemistry.[1,2] The development of techniques capable of producing macroscopic quantities of fullerenes, particularly C_{60}, has allowed investigation of the physical and chemical properties of these compounds.[3,4] Previously, C_{60} has been reduced by Birch reduction[5] and transfer hydrogenation[6] resulting in $C_{60}H_{18}$ and $C_{60}H_{36}$ as the principal products. However, these results have recently been disputed.[7] We report here the first catalytic reduction of C_{60} to give a mixture of hydrogenated products of which $C_{60}H_2$ was characterized as the major product.

Recently, BH_3–THF in toluene was shown to react with C_{60} to give $C_{60}H_2$ upon hydrolysis in 10% isolated yield.[8] The $C_{60}H_2$ product was isolated and fully characterized.[9] We observed that the HPLC chromatogram and the ^1H NMR spectrum for this reaction were remarkably similar to the rhodium-catalyzed hydrogenation of C_{60}. In our procedure, 2 mg of C_{60} was reacted with 4 mg of rhodium in 4 mL of deuterated benzene (C_6D_6) at ambient temperature while the mixture was stirred under constant balloon pressure of hydrogen (see supplementary material for more details). The ^1H NMR (C_6D_6) spectrum of the BH_3–THF reduction product displayed a sharp singlet at 5.89 ppm that was identical to the product isolated from the rhodium-catalyzed hydrogenation of C_{60}. In addition, an HPLC chromatogram of a mixture of the reacted products showed that the two peaks coelute and have the same electronic absorption spectra.

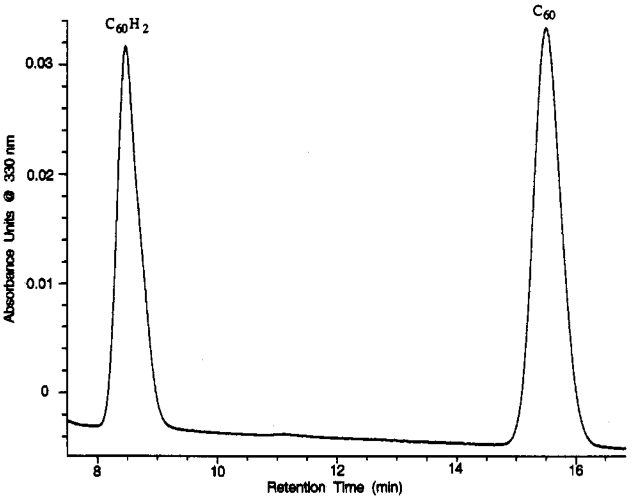

Figure 1. HPLC chromatogram of the reduced C_{60} mixture separated using a Phenomenex "buckysep" column.

The high-performance liquid chromatography (HPLC) chromatogram of the C_{60}-hydrogenated reaction mixture separated using a Phenomenex "buckysep" column with a mobile phase of 55% toluene and 45% acetonitrile is shown in Figure 1. The HPLC chromatogram of the C_{60}-hydrogenated mixture revealed several smaller peaks in the 2–6-min retention time range and two larger peaks at 8.5 min and 15.5 min. Electronic absorption spectra of collected fractions revealed that the peak at 8.5 min was $C_{60}H_2$ and the peak at 15.5 min was unreacted C_{60}. Unreacted C_{60} is clearly separated from the $C_{60}H_2$ product. The HPLC peaks in the 2–6-min range are attributed to more highly hydrogenated species.

A ^1H NMR spectrum (500 MHz, C_6D_6) was obtained for the crude reaction mixture, and several sharp resonance peaks were observed at δ 5.89, δ 3.97, and δ 2.09 ppm (Figure 2). A ^{13}C NMR (50 MHz, CS_2–$(CD_3)_2CO$ (9:1)) spectrum was also obtained for the crude reaction mixture, and sharp resonance peaks were observed at δ 117.3, δ 127.1, and δ 143.5 ppm with the latter attributed to C_{60}. Neither the control reaction run under the same conditions but without C_{60} nor the C_{60} starting material displayed peaks in the ^1H NMR or the ^{13}C NMR that we have assigned to products. It seems likely that the δ 117.3 and δ 127.1 ppm resonances in the ^{13}C NMR are due to the $C_{60}H_2$ product.

An estimate of the yield on the rhodium catalytic reaction was determined by adding an equimolar amount of anisole as an internal standard to the crude reaction mixture which had been degassed with argon. The yields

---

[†] Scripps Institution of Oceanography.

[‡] Department of Chemistry.

[●] Abstract published in *Advance ACS Abstracts*, December 1, 1993.

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. E.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(2) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(3) For reviews, see: *Acc. Chem. Res.* **1992**, 25.

(4) For reviews, see: *Carbon* **1992**, 30.

(5) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634.

(6) Ruchardt, C.; Gerst, M.; Ebenhoch, J.; Beckhaus, H.; Campbell, E.; Tellgmann, R.; Schwarz, H.; Weiske, T.; Pitter, S. *Angew. Chem.* **1993**, *32*, 584.

(7) It has recently been shown that the products reported by Birch reduction, detected using laser desorption/ionization time-of-flight mass spectrometry (L^2MS) and electron impact mass spectrometry (EIMS), are actually a mixture of polyhydrofullerenes, containing $C_{60}H_{18}$ through $C_{60}H_{36}$. The resolution obtained using L^2MS was insufficient to resolve the product distribution. We attempted to characterize our $C_{60}H_2$ product using L^2MS and experienced similar resolution problems. In addition, the composition of the polyhydrofullerenes was shown to vary when subjected to the elevated temperatures (>250 °C) required for EIMS and other mass spectrometric techniques using direct-insertion heated probes. For example, see: Banks, M. R. *et. al. Chem. Commun.* **1993**, *14*, 1149.

(8) Henderson, C. C.; Cahill, P. A. *Science* **1993**, *259*, 1885.

(9) Both negative- and positive-ion fast atom bombardment mass spectrometry (FAB MS) were used to obtain high-resolution measurements to confirm the masses of the isolated products. There are a number of uncertainties in these measurements. McKinnon *et al.* (1992) have observed isotope ratios determined by FAB MS for C_{60} that were different than the predicted abundance ratios of $^{13}C/^{12}C$. Since McKinnon *et al.* were measuring C_{60} and not hydrogenated C_{60} products, it was concluded that hydrogenation may be occurring under the conditions of the FAB MS analysis. For example, see: McKinnon *et al. Combust. Flame*, **1992**, *88*, 102. On the basis of these results, we feel FAB MS does not provide an accurate evaluation of the degree of hydrogenation in C_{60} hydrogenated mixtures.

0022-3263/93/1958-7630$04.00/0

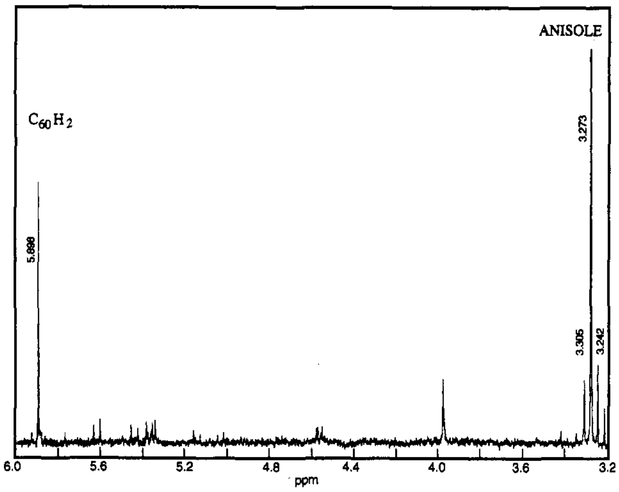

Figure 2. ^1H NMR spectrum of the crude reaction mixture shows a sharp singlet at 5.89 ppm assigned to $C_{60}H_2$. The peak at 3.27 ppm is anisole, the internal standard used for estimating the $C_{60}H_2$ yield.

of $C_{60}H_2$ in the reaction mixture were then calculated by integration of the anisole peak (δ 3.27) and the $C_{60}H_2$ peak (δ 5.89). A ^1H NMR spectrum of the crude reaction mixture taken at 24 h gave the product $C_{60}H_2$ in 14% yield.

The $C_{60}H_2$ yield was shown to vary over time. HPLC analysis over a 48-h period indicated that the maximal concentration of the $C_{60}H_2$ was reached in approximately 24 h, after which the yield began to decrease. There is a concomitant increase in the relative area of the peaks in the 2–6 min range, suggesting production of higher hydrogenated species in the mixture. The ^1H NMR spectrum taken at 2 and 24 h gave the product $C_{60}H_2$ in yields of 5% and 14%, respectively. In addition, the $C_{60}H_2$ product was much more stable in the C_{60}-hydrogenated mixture than in its isolated form. When separated out of the mixture, $C_{60}H_2$ is readily converted back to C_{60} in the presence of oxygen. Therefore, fractions of $C_{60}H_2$ were collected in vials under argon to ensure preservation of the product.

Acknowledgment. This work was supported by a grant for a NASA Specialized Center of Research and Training in Exobiology at UCSD. We thank Bill Paplawsky, at SIO, for the use of his HPLC for separation and collection of fractions analyzed in this study and Dr. J. Faulkner, at SIO, for the use of his laboratories.

Supplementary Material Available: Additional experimental procedures and spectral data (^1H NMR, ^{13}C NMR, HPLC, UV, and IR spectra) of the reaction products (15 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.