Synthesis and Isolation of One Isomer of $C_{60}H_6$

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The preparation of hydrogenated fullerenes by Birch reduction of C_{60} was one of the first chemical reactions of a fullerene to be reported in the literature.[1,2] Since that time, a number of different hydrogenated fullerenes have been isolated, including $C_{60}H_2$,[3−6] $C_{70}H_2$,[7] $C_{60}H_4$,[8] $C_{60}H_{18}$,[9] and $C_{60}H_{36}$.[1,2,10] Clearly, a wide range of different levels of reduction can be achieved with appropriate conditions. Efficient preparation of any one reduced fullerene is made difficult by the large number of adjacent oxidation states, and structures have been determined for only a few such compounds because of the numerous isomers that are possible for each. We now report a reaction that produces $C_{60}H_6$ with essentially no contamination by adjacent oxidation states. This compound is formed as one dominant isomer and one minor isomer, and we report the assignment of the structure of the major isomer through a comparison of its C−H coupled ^{13}C NMR spectrum with that of 1,2-$C_{60}H_2$.[11]

The reaction of C_{60} with Zn−Cu couple at 50 °C in toluene containing a small amount of water proceeds rapidly, with essentially 100% consumption of C_{60} in about 2 h. After 4 h, virtually all of the products observed are $C_{60}H_6$ isomers or oxides.[12] Furthermore, analysis by HPLC indicates that roughly 50% of the soluble material is a single component, one isomer of $C_{60}H_6$. Large amounts of Zn−Cu (5 g or more for 50 mg of C_{60}) result in very rapid reduction but with poor mass balances, presumably due to adsorption. Analysis of the crude reaction mixture by HPLC (Figure 1) reveals two isomeric $C_{60}H_6$ species (**1** and **2**) in a 6:1 ratio, as well as several $C_{60}H_6O$ species. Only minute traces of C_{60}, $C_{60}H_2$, and $C_{60}H_4$ are present. Anhydrous conditions, using dry methanol as a proton source, result in a very slow reaction that does not produce significant conversion to $C_{60}H_6$, suggesting that the proton source is actually residual water on the metal rather than methanol itself.

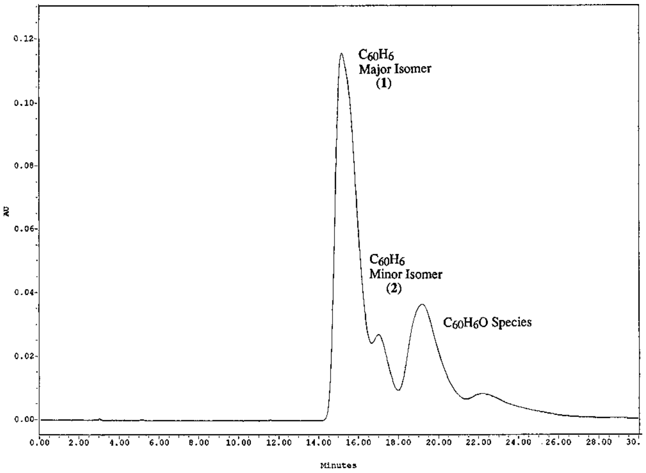

Figure 1. HPLC chromatogram of the crude reaction mixture. Conditions: semipreparative Buckyclutcher column, 4.5 mL/min 1:1 toluene/hexane mobile phase, detection at 335 nm.

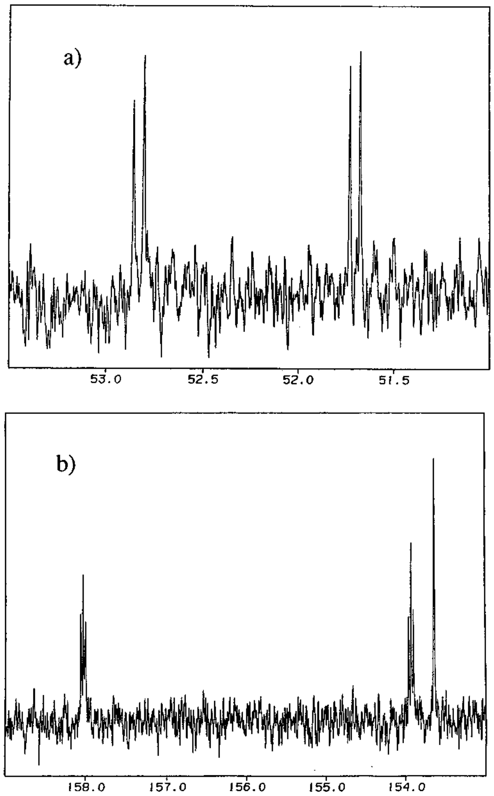

Figure 2. Expansions of the $^1H-^{13}C$ coupled ^{13}C NMR spectrum of **1** in 9:1 CS_2/acetone-d_6: (a) the upfield, sp^3 resonance at 52.28 ppm, J_1 = 142 Hz, J_2 = 6.8 Hz; (b) the three most downfield resonances showing two triplets with J = 3.7 Hz.

Isolation of the major $C_{60}H_6$ band was accomplished by HPLC using a preparative Buckyclutcher column and an automated injector/fraction collector. Analysis of the fraction containing **1** (a cranberry-colored solution when concentrated) by Buckyclutcher and C_{18} HPLC in several different solvent systems has failed to produce evidence of more than one component. The typical isolated yield is 35%.

The ^1H NMR spectrum of the major isomer (**1**) shows only a singlet at 5.18 ppm in toluene-d_8 (6.0 ppm in $CS_2/CDCl_3$), which fits nicely into the upfield progression of resonances in the $C_{60}H_2$ (δ 5.93 ppm, toluene-d_8),[3] $C_{60}H_4$ (δ 5.0−6.3 ppm depending on the isomer, toluene-d_8),[8] $C_{60}H_6$ series. A total of

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(10) A recent report has shown that similar reactions can be driven to the $C_{60}H_{36}$ level: Darwish, A. D.; Abdul-Sada, A. K.; Langley, J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1995**, 2359−2365.

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(12) Note: The reaction times are highly dependent on efficient stirring.

10 lines are observed in the ^{1}H-decoupled ^{13}C NMR spectrum of **1**, which include resonances for a single sp^3 carbon with an NOE at 52.28 ppm and for nine carbons in the sp^2 region. The nine sp^2 resonances have similar intensities and have line widths of less than 0.4 Hz fwhm, suggesting that superimposed resonances are unlikely.

The observation of ten carbon resonances indicates a structure with both 2-fold and 3-fold symmetry axes. Several such structures are possible, although only one places the hydrogens on adjacent carbons and positions all double bonds in six-membered rings, characteristics common to the majority of fullerene derivatives. A 1,2-regiochemistry of hydrogen addition in **1** was confirmed by comparison of the ^{1}H-coupled ^{13}C spectrum of **1** (Figure 2) with the ^{1}H-coupled ^{13}C spectrum of $C_{60}H_2$. The ^{13}C spectrum of $C_{60}H_2$, a compound with established 1,2-regiochemistry,[3] shows an sp^3 carbon at 53.11 ppm that splits into a doublet of doublets with a 142-Hz one-bond C−H coupling and a 6.8-Hz two-bond C−H coupling. The 52.28-ppm resonance of **1** also splits into a doublet of doublets with 142- and 6.8-Hz C−H couplings. In addition, the most downfield resonance of $C_{60}H_2$ splits into a triplet with a coupling constant of 3.9 Hz. The two most downfield resonances in the spectrum of **1** split into triplets with apparent 3.7-Hz coupling constants. The striking similarity in chemical shifts and coupling constants observed in the spectra of these two compounds indicates that the hydrogens in **1** are on adjacent carbons as they are in $C_{60}H_2$.

Given the constraints of the ^{1}H (only one type of hydrogen atoms) and the ^{13}C NMR (only 10 types of carbon atoms, hydrogens on adjacent carbons) data, we believe that the only viable structure for **1**, the major isomer of $C_{60}H_6$ produced under our conditions, is the 1,2,33,41,42,50 isomer shown in Figure 3. This pattern has a 3-fold symmetry axis and three 2-fold symmetry axes, and would exhibit both a singlet in the ^{1}H NMR spectrum and a total of 10 resonances in the ^{13}C NMR spectrum.

This reaction is, to the best of our knowledge, the only example of the preferential formation of the highly symmetrical 1,2,33,41,42,50 addition pattern. The structures of two other $C_{60}R_6$ species, $C_{60}Br_6$[13] and $C_{60}Cl_6$,[14] both show a 1,2,5,10,21,24 addition pattern, and this pattern is predicted to be one of the low energy isomers for $C_{60}H_6$.[15] We believe that **1** is a kinetic product, although attempts to isomerize **1** to a thermodynamic isomer have only resulted in dehydrogenation to a mixture of C_{60}, $C_{60}H_2$, and $C_{60}H_4$. We believe that **1** results from rapid reduction of 1,2,41,42-$C_{60}H_4$, and we are currently investigating the details of this conversion.

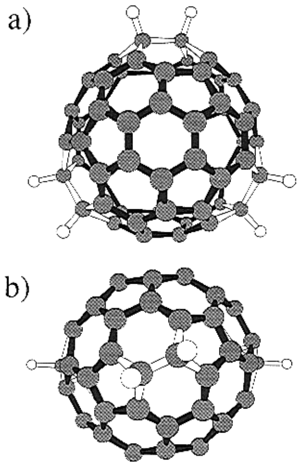

Figure 3. Two views of **1**: (a) looking down the 3-fold axis; and (b) looking down one of three 2-fold axes.

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Supporting Information Available: Experimental procedures and ^{1}H NMR, ^{13}C NMR, UV/visible, and FABS mass spectra (6 pages). See any current masthead page for ordering and Internet access instructions.

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