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Selective Electrosynthesis of $(CH_3)_2C_{60}$: A Novel Method for the Controlled Functionalization of Fullerenes

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There is a growing interest in the chemical derivatization of fullerenes in general and C_{60} in particular.[1] This includes cycloaddition,[2] radical addition,[3] addition across the double bond,[4] metal complex formation[1d,5] and nucleophilic substitution.[6] Nucleophilic substitution, such as methylation involving chemically generated C_{60}^{n-} anions, is facile but leads to a mixture of polymethylated $(CH_3)_pC_{60}$ products, where $p \leq 24$.[6] That is, there is no control over the number of addends on the fullerene cage by this method. Both the stability of the C_{60}^{n-} anions in many deaerated aprotic solvents and the large difference in formal redox potentials between the consecutive $C_{60}^{n-/(n+1)-}$ redox couples[7] are promising for electrochemical generation of C_{60}^{n-} anions, in a desired oxidation state, which can then be employed as nucleophiles in substitution reactions.

We describe here the first selective synthesis of $(CH_3)_2C_{60}$ (**1**), i.e., the simplest dialkylated derivative of C_{60}. The selectivity is achieved by electrochemical control of the charge, n, on C_{60}^{n-}, generated prior to methylation. The addition of methyl iodide to a solution of C_{60}^{2-}, generated by controlled-potential bulk electroreduction of C_{60} in an aprotic solvent,[8] yields predominantly a dimethylated product **1** and free iodide in solution.

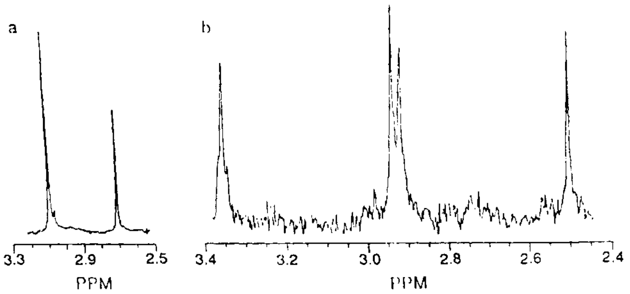

Figure 1. ^1H NMR spectrum of the product mixture **1**, isolated by GP-HPLC: (a) without ^{13}C enrichment, (b) with ^{13}C enrichment.

A 50-mg sample of C_{60} was dissolved in 120 mL of 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) benzonitrile solution and exhaustively electroreduced at −1.1 V, in a drybox, to yield a dark-red solution of the C_{60}^{2-} dianion.[8,9] After the potential was turned off, a 100-fold excess of neat methyl iodide was added all at once to the solution. The solution turned progressively darker as the reaction proceeded. The extent of reaction was monitored *in situ* by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) at a Pt disk working electrode. After ca. 40 min the solution was brownish-black, and the CV and DPV peaks of the products no longer increased while the peaks corresponding to the $C_{60}^{n-/(n+1)-}$ electroreductions, although decreased by ca. 50%, were still present. At this point exhaustive electrooxidation was performed at −0.2 V, i.e., at a value sufficiently positive to electrooxidize the unreacted starting material but not the liberated iodide. When the electrooxidation was completed, the mixture was taken out of the drybox and the solvent evaporated. The solid was washed repeatedly with acetonitrile to remove TBAP and dried *in vacuo* to yield 44 mg of a reddish-brown residue. Semipreparative gel permeation high-performance liquid chromatography (GP-HPLC) of the residue showed a single peak of the desired product, with a shoulder on its rising portion, from which 7 mg of **1** was isolated.[10] The overall yield of **1** was ca. 22 mg (44% with respect to C_{60}), as estimated by CV and GP-HPLC. CV and DPV of **1** in 0.1 M TBAP benzonitrile showed three diffusion-controlled reversible one-electron electroreductions of $E_{1/2}$ values equal to −0.58, −1.00, and −1.55 V (vs SCE) in the potential window, limited by solvent decomposition.[12] These electroreductions can be ascribed to the 0/1−, 1−/2−, and 2−/3− electron transfers of **1**. The single GP-HPLC peak of **1** was resolved into two peaks on an analytical "Buckyclutcher I" column[13] with a peak height ratio of about 1:1.4 and a selectivity factor, $\alpha = 1.27$.

Surface analysis by laser ionization (SALI)[15] indicated that the molecular composition of the GP-HPLC product **1** is $(CH_3)_2C_{60}$ (MW 750). Therefore, the two HPLC peaks of **1** eluted from the "Buckyclutcher I" column indicate the presence of two different $(CH_3)_2C_{60}$ isomers.

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(9) All experiments were performed at ambient temperature (22 ± 1 °C) in a drybox under nitrogen atmosphere. The instruments used in this study are described elsewhere.[8]

(10) This sample of **1** was obtained from the central portion of the $(CH_3)_2C_{60}$ fraction eluted from the semipreparative GP-HPLC[11] using an Ultrastyragel 500 Å, 300 ×40 mm column (Waters, Millipore Corp., Milford, MA); a 90/10 (v/v) dichloromethane/cyclohexane mixture as eluent; a 1.125 mL min^{-1} flow rate; and UV–vis detection, 405-nm filter. Attempts are underway to isolate the two isomers on a semipreparative "Buckyclutcher I" column.

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(13) The "Buckyclutcher I" 250 × 4.6 mm column (Regis, Morton Grove, IL) is packed with a 5-μm silica gel modified with trident-tris(2,4-dinitrophenyl) covalently attached to silica through a C_{10} spacer.[14]

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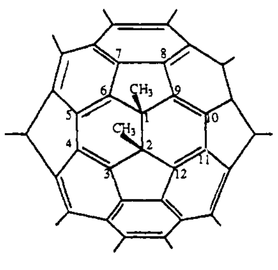
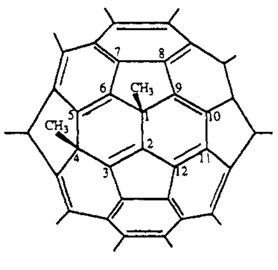
^1H NMR spectroscopy[16] of **1** (Figure 1a) shows two singlets at δ 3.11 ppm and δ 2.72 ppm with the similar peak intensity ratio of about 1.4:1 as observed by HPLC. In accord with the HPLC and SALI results, this also points to two isomeric forms of **1**, each containing two equivalent methyl groups.

The presence of the two isomers was also confirmed by ^1H NMR spectroscopy of the product mixture **1** obtained by using ^{13}C-enriched methyl (Figure 1b) iodide where two doublets, centered at δ 3.11 ppm and δ 2.72 ppm ($J_{C\text{-}H}$ = 131 Hz), were observed. The ^1H-decoupled ^{13}C NMR spectrum of the same product mixture shows two peaks at δ 29.9 ppm and δ 30.3 ppm (not shown) corresponding to two sets of equivalent methyl groups. The coupling constant determined from the ^1H-coupled ^{13}C NMR spectum, displaying two quartets centered at 29.9 and 30.3 ppm, was the same as the one determined from the ^1H NMR spectrum ($J_{C\text{-}H}$ = 131 Hz).

Semiempirical calculations based on the Schrieffer–Su–Heeger (SSH) model[17] suggest that, of the 23 possible dimethylbuckminsterfullerene isomers, the 1,2- and 1,4-isomers are those of the lowest heats of formation, and that the heat of formation of the 1,4-isomer is larger than that of the 1,2-isomer.[19,20] Similar calculations performed on $(CH_3)C_{60}^-$, i.e., a probable intermediate in the reaction, suggest that the 1,2-isomer would be preferred over the 1,4-isomer since the electron density is largest at C_2 (25%) followed by $C_{4/11}$ (9% each). However, the actual ratio of the two isomers should depend also on kinetic factors, since there are two sites for 1,4 addition while there is only one site for 1,2 addition.



$1,2\text{-}(CH_3)_2C_{60}$



$1,4\text{-}(CH_3)_2C_{60}$

On the basis of the electrochemical, chromatographic, spectroscopic, and computational results, we assign the two compounds to the 1,2- and 1,4-isomers. An exact assignment of the isomers cannot be made at this time and must await X-ray structural determinations.

In summary, dimethylbuckminsterfullerene, $(CH_3)_2C_{60}$, has been selectively synthesized through the reaction of electrogenerated C_{60}^{2-} with methyl iodide and obtained as a mixture of two separable regio isomers in a 44% yield. The presented preparation method provides a convenient route for controlled alkylation of C_{60} in large quantities and opens the door for selective fullerene functionalization with other addends.

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(16) NMR spectra were recorded on a General Electric QE 300-MHz spectrometer with CS_2 as solvent and C_6D_6 as the internal reference.

(17) The independent electron approximation is adopted and the energy differences due to electron–electron interactions are neglected in the SSH model.[18]

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