Functionalization of buckminsterfullerene by hypervalent iodine reagents

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10.1070/MC2001v011n02ABEH001413

Fullerene C_{60} reacts with hypervalent iodine reagents (azido-, acetoxy-, sulfonyloxy- and chloroiodanes) under mild conditions with the formation of the appropriate functionalized fullerenes.

There is currently a significant interest in the chemistry of fullerenes and their derivatives.[1] The common procedures for fullerene functionalization are based on the ability of fullerenes to accept extra electrons in reactions with reducing reagents (such as alkali metals) or nucleophiles (for example, the Bingel reaction). Functionalization of fullerenes with electrophilic reagents has also been reported.[2] Bromine reacts with C_{60} to afford the adducts $C_{60}Br_6$, $C_{60}Br_8$ and $C_{60}Br_{24}$, depending on the reaction conditions.[2(a),(b)] Fullerenes can be chlorinated,[2(c)–(e)] fluorinated,[2(f),(g)] nitrated[2(h)] and cyclosulfated[2(i)] by reactions with the appropriate electrophilic reagents. Preliminary results on the functionalization of C_{60} by hypervalent iodine reagents will be discussed here. In the last few years, organic derivatives of hypervalent iodine have found broad synthetic applications as mild oxidising and electrophilic agents for functionalization of various organic substrates.[3]

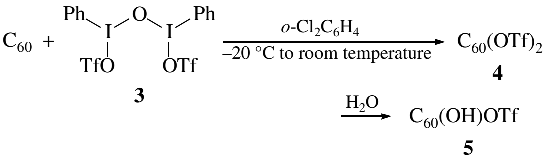
We have investigated the reaction of C_{60} with hypervalent iodine azide $PhI(N_3)_2$ **1**, which was generated *in situ* from iodosobenzene and azidotrimethylsilane. The PhIO/2TMSN$_3$ combination was shown to be a premier reagent for azidation of various organic substrates.[4] The reaction of C_{60} with 6.1 equivalents of $PhI(N_3)_2$ was carried out under typical azidation conditions[4] in a solution of *o*-dichlorobenzene (Scheme 1).[†]

$$\underset{}{C_{60}} + \underset{\substack{\mathbf{1}\\(6.1\ \text{equiv.})}}{PhI(N_3)_2} \xrightarrow[-20\ ^\circ\text{C to room temperature}]{o\text{-}Cl_2C_6H_4} \underset{\mathbf{2}}{C_{60}(N_3)_6}$$

Scheme 1

After stirring for about 2 h at –20 °C, the reaction mixture changed from the original purple solution to a dark brown mixture. The solvent and all volatile products were removed in a high vacuum to afford azide **2** as a black highly explosive powder. The IR spectrum of this powder displayed a very intense absorption peak at 2100 cm^{-1}, typical of organic azides. NMR spectroscopy of this product was difficult to perform due to the very low solubility in all common NMR solvents. The ^{1}H NMR spectrum of the low-concentration sample displayed very weak signals between δ 7.6 and 7.2 ppm, which are likely attributed to residual iodobenzene trapped in the solid product. Elemental analysis of product **2** showed a nitrogen content of 21.27–21.34%, which is consistent with the average presence of six azido groups in the molecule of product **2**·PhI.[‡] Due to the low stability of the product, we failed to obtain meaningful results from mass-spectrometric measurements. Azidation of C_{60} with one equivalent of $PhI(N_3)_2$ under similar conditions resulted in the formation of $C_{60}(N_3)_2$ as indicated by elemental analysis of the product.

A similar reaction of C_{60} with hypervalent iodine triflate **3** (Zefirov's reagent) afforded triflate **5** as the final product resulting from the partial hydrolysis of initial bis-triflate **4** (Scheme 2).[§] Product **5** was obtained as a black solid after removal of the solvent and volatile by-products in a high vacuum. The IR spectrum of **5** displayed a very broad absorption band at 3233 cm^{-1} characteristic of hydroxylated fullerenes.[2(i)] The characteristic absorptions of covalent triflate were present at 1250, 1179 and 1033 cm^{-1}. A broad signal of the hydroxy group was observed at δ 1.58. Elemental analysis of the product showed a sulfur content of 2.8%, which is consistent with the presence of one triflate in the molecule of **5**.



Scheme 2

The reaction of C_{60} fullerene with (diacetoxy)iodobenzene **6** was carried out in tetrachloroethane at 80 °C (Scheme 3). The reaction was monitored using TLC by detecting the disappearance of the initial C_{60} in the mixture. After the reaction was complete, the solvent and all volatile products were removed in a high vacuum to afford product **7** as a brown solid. The IR spectrum of **7** displayed the characteristic absorption of the acetoxy group at about 1720 cm^{-1}. The ^{1}H NMR spectrum of the sample showed the expected signal of the acetyl methyl at 2.13 ppm. The laser desorption mass spectrum of **7** displayed the 786 and 788 a.m.u. ion peaks corresponding to $C_{60}O_2(OH)_2$ and $C_{60}(OH)_4$, as well as an intense peak of the acetyl cation at *m*/*z* 43.

$$C_{60} + \underset{\mathbf{6}}{2PhI(OAc)_2} \xrightarrow[150\ \text{h}]{C_2H_2Cl_4,\ 80\ ^\circ\text{C}} \underset{\mathbf{7}}{C_{60}(OAc)_4}$$

Scheme 3

C_{60} smoothly reacts with (dichloro)iodobenzene **8** in tetrachloroethane at –25 to 25 °C with the formation of polychlorinated fullerenes **9** (Scheme 4).[¶] IR and ^{13}C NMR spectroscopic data for **9** were virtually identical to the published data[2(c)] for $C_{60}Cl_n$ (n = 12–15). Specifically, the IR spectrum of **9** displayed the characteristic C–Cl stretching frequencies between 875 and 840 cm^{-1}. The ^{13}C NMR spectrum of the sample showed a broad featureless peak centered near 148 ppm. MALDI-TOF or laser desorption mass-spectrometric analysis of $C_{60}Cl_n$ in the

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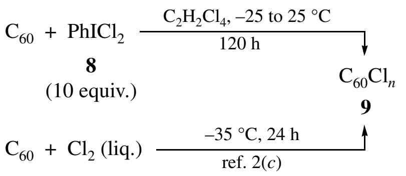
[†] *Preparation of* **2**. A sample of C_{60} (20 mg, 0.028 mmol) was dissolved in 2–3 ml of freshly distilled *o*-dichlorobenzene at room temperature. The resulting purple solution was cooled to –20 °C, and iodosobenzene (40 mg, 0.18 mmol) and then azidotrimethylsilane (39 mg, 0.34 mmol) were added under nitrogen. The resulting mixture was stirred at –20 °C for 2 h; then, the solvent and all volatile products were removed in a high vacuum to afford a black, highly explosive powder. ^{1}H NMR (CDCl$_3$) δ: 7.6–7.2 (group of multiplets). IR (KBr, ν/cm^{-1}): 2100 (very strong). Found (%): C, 63.68; H, 0.74; N, 21.34; I, 8.75. Calc. for $C_{60}N_{18}{\cdot}C_6H_5I$ (%): C, 67.35; H, 0.43; N, 21.43; I, 10.78.

[‡] Azidofullerene **2** and other fullerene products (**4**, **5**, **7**) are shown in this paper as single formulas, which are in the closest agreement with the results of elemental analysis. However, all these products most likely represent a distribution of compounds rather than a specific polyadduct.

[§] *Preparation of* **5**. A sample of C_{60} (20 mg, 0.028 mmol) was dissolved in 2–3 ml of freshly distilled *o*-dichlorobenzene at room temperature. The resulting purple solution was cooled to –20 °C, and iodosobenzene (6.2 mg, 0.028 mmol) and then trimethylsilyl triflate (10.5 mg, 0.048 mmol) were added under nitrogen. The resulting mixture was warmed to room temperature and stirred for three days; then, the solvent and all volatile products were removed in a high vacuum to afford a dark brown material. ^{1}H NMR (CDCl$_3$) δ: 7.7–7.2 (group of multiplets), 1.58 (br. s, OH). IR (KBr, ν/cm^{-1}): 3400–3200 (br., OH), 1250, 1179, 1033 (strong, OTf). Found (%): C, 70.64; H, 1.16; S, 2.80; I, 9.93. Calc. for $C_{60}(OH)OSO_2CF_3{\cdot}C_6H_5I$ (%): C, 73.78; H, 0.55; S, 2.94; I, 11.63.

positive mode showed only the peak of C_{60} ($M = 720$).[2(c)–(e)] MALDI-TOF analysis for negative ions using a 2,5-dihydroxybenzoic acid matrix, as previously reported,[5] was unsuccessful, whereas a dithranol matrix afforded weak signals indicative of $C_{60}Cl_5$, $C_{60}Cl_7$ and $C_{60}Cl_9$. Laser desorption analysis in the negative mode (in the absence of a matrix), however, nicely provided a spectrum consistent with the expected distribution of polychlorinated products,[5,††] with $C_{60}Cl_7$ and $C_{60}Cl_9$ as prevalent species. Elemental analysis of product **9**, consistent with the molecular composition of $C_{60}Cl_{16}$, suggests a slightly higher chlorine content than MS analysis. The previously reported preparation of $C_{60}Cl_n$ involved the chlorination of C_{60} with chlorine gas at 250 °C or liquid chlorine at –35 °C for one day.[2(c)–(e)]



$n = 12–16$

Scheme 4

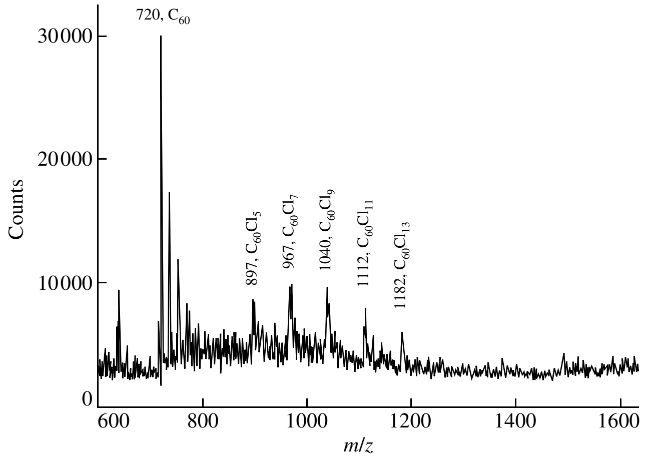


Figure 1 Laser desorption mass spectrum of $C_{60}Cl_n$ showing negative ions. Averaged over 87 scans.

In conclusion, the first functionalization of fullerene C_{60} with hypervalent iodine reagents is reported. The treatment of C_{60} with an excess of azidoiodinane **1** results in addition of up to six azido groups, while a similar reaction with hypervalent iodine triflate **3** affords mono triflate **5** as the main product. (Diacetoxy)iodobenzene reacts with C_{60} with the formation of tetraacetate **7**, which was identified by IR and NMR spectroscopy and mass spectrometry. Chlorination of C_{60} with (dichloro)iodobenzene affords polychlorinated fullerene **9**, whose IR, ^{13}C NMR and mass spectra are identical with the previously reported data for $C_{60}Cl_n$ obtained by direct chlorination of C_{60}.

This work was supported by the National Science Foundation (grant no. NSF/CHE-9802823), the National Science and Engineering Research Council of Canada, and the University of Alberta. We thank PerSeptive Biosystems for the loan of a Voyager Elite equipped with delayed extraction and Dr. R. Whittal for help with the MS analysis. We are grateful to Professor V. I. Sokolov for thoughtful discussions.

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Received: 25th December 2000; Com. 00/1739

¶ *Preparation of* **9**. A sample of C_{60} (24 mg, 0.033 mmol) was dissolved in 10 ml of 1,1,2,2-tetrachloroethane under nitrogen. The solution was cooled to –25 °C. (Dichloro)iodobenzene (91 mg, 0.33 mmol) was dissolved in 2 ml of dry dichloromethane and added to the cool C_{60} solution. The mixture was warmed to room temperature and stirred for 120 h. The solvent and all volatile products were removed in a high vacuum. The precipitate was washed with hexane to afford 18 mg of product **9** as an orange-brown solid. ^{13}C NMR, δ: 148 (br.). IR (KBr, ν/cm^{-1}): 875 to 840 (br.). Found (%): C, 54.8; Cl, 43.6. Calc. for $C_{60}Cl_{16}$ (%): C 55.96; Cl 44.04.

[††] Although in some cases low resolution limited matching of the isotopic pattern to the most intense m/z signal for each isomer $C_{60}Cl_x$, there is no question that the spectrum confirms polychlorination of C_{60}.