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# *Communications to the Editor*

## Osmylation of $C_{70}$: Reactivity versus Local Curvature of the Fullerene Spheroid

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Unlike $C_{60}$, the higher fullerenes[1] and carbon nanotubes[2] contain carbons with different degrees of pyramidalization corresponding to different degrees of local curvature of the fullerene spheroid. In the simplest case, $C_{70}$ contains eight types of C–C bonds, each positioned differently on the oblong fullerene surface.[3] Here, we report an analysis of the regiochemistry of the osmylation of $C_{70}$ where the observed ratio of isomeric 1:1 adducts **1**, **2**, **3**, and **4** (2.1:1.0:<0.1:<0.1) demonstrates greater kinetic reactivity at sites of greater local curvature, rather than at sites of greater bond order. These results complement the thermodynamically controlled regiochemistry observed by Balch and co-workers.[4]

Osmylation[5,6] of $C_{70}$ with 0.75 equiv of $OsO_4$ in pyridine/toluene at 0 °C yielded two isomers of $C_{70}(OsO_4py_2)$ which were cleanly separable by HPLC on silica gel (9% pyridine in toluene). The pyridine ligands were exchanged for 4-*tert*-butylpyridine to increase solubility for NMR analysis. Both isomers showed cleanly resolved $^{13}C$ and $^{1}H$ NMR spectra, which are summarized in Table I (see also supplementary material).[7] $^{1}H$ NMR recorded before chromatography showed that the major and minor isomers form in a 2.1:1 ratio. No other isomers were detectable to a limit of 5%.

Within the limits of detection by $^{1}H$ and $^{13}C$ NMR, $C_{60}$ adds $OsO_4$ to the fusion of two six-membered rings.[8,9] Assuming that $C_{70}$ also adds $OsO_4$ to 6–6 ring fusions, four $C_{70}(OsO_4L_2)$ isomers are possible (Figure 1A). In these four isomers, the osmyl groups are positioned differently with respect to the mirror planes of $C_{70}$ such that they each correspond to a characteristic number of symmetry independent carbons and protons (Table I). Comparing the NMR data for the two purified isomers with the number of possible peaks for isomers **1**–**4** (Table I), the major and minor isomers correspond to **1** and **2**, respectively, where the spectra of both isomers contain one pair of coincident fullerene carbon peaks. Both isomers show five pyrene-type carbons[1] in the 127–133 ppm range, as expected for $C_s$-symmetric structures.

**Table I.** Number of Independent Carbons and Protons in $C_{70}OsO_4$(4-*tert*-butylpyridine)$_2$ Isomers

| isomer | trivalent fullerene carbons (intensity) | *C*–O | sets of 4-*tert*-butylpyridine carbons and protons |
|---|---|---|---|
| major | 1 (1C), 32 (2C), 1 (3C) | 2 | 2 |
| minor | 4 (1C), 30 (2C), 1 (4C) | 1 | 1 |
| **1** | 2 (1C), 33 (2C) | 2 | 2 |
| **2** | 4 (1C), 32 (2C) | 1 | 1 |
| **3** | 68 (1C) | 2 | 2 |
| **4** | 6 (2C), 14 (4C) | 1 | 1 |

Resubmission of purified **1** and **2** to the osmylation conditions gives two different sets of $C_{70}(OsO_4py_2)_2$ isomers according to HPLC. Isomer **1** gives six 2:1 adducts, isomer **2** gives seven 2:1 adducts, and four of the $C_{70}(OsO_4py_2)_2$ isomers overlap between the two sets. This is consistent with the second osmylation of $C_{70}$ occurring at a pyracylene-type position (as found for the first additions), with proximate sites being sterically blocked by the first osmyl group (as found for $C_{60}$[9]). That is, isomer **1** could give seven 2:1 isomers and isomer **2** could give eight 2:1 isomers, with four of the $C_{70}(OsO_4py_2)_2$ isomers coinciding between the two sets (Figure 1B,C). The formation of distinct sets of $C_{70}(OsO_4py_2)_2$ isomers from **1** and **2** establishes that the $C_{70}$ osmate esters do not equilibrate under the reaction conditions; thus osmylation is kinetically controlled.

The observed kinetically controlled regioselectivity for the osmylation of $C_{70}$ agrees qualitatively with ab initio calculations on $C_{70}$ in that osmylation occurs at bonds categorized as double bonds (corresponding to isomers **1** and **2**), but not at bonds designated as single bonds or intermediate (aromatic) bonds (corresponding to isomers **4** and **3**, respectively).[10] However, the ratio of isomers **1** and **2** (2.1:1) does not quantitatively correspond to the relative calculated bond orders for the respective bonds in $C_{70}$, 1.66 and 1.74,[11] in that the bond with lower calculated bond order is more reactive. (Bonds corresponding to isomers **1** and **2** are each represented 10 times in $C_{70}$.) Three calculated $C_{70}$ structures show that major isomer **1** corresponds to a longer bond in $C_{70}$ than minor isomer **2**,[10–12] and the crystal structure of a $C_{70}$ clathrate confirms these calculations.[13,14] In contrast to bond lengths and bond orders, the degree of local curvature of the $C_{70}$ spheroid, as described by the $\sigma$–$\pi$ interorbital angles[15] of an ab

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(4) Under conditions where regiochemistry is controlled by the thermodynamics of both reaction and crystallization, $C_{70}$ adds one or two $Ir(CO)Cl(PR_3)_2$ moieties at sites analogous to osmate ester isomer **1**. $C_{70}\{Ir(CO)Cl(PPhMe_2)_2\}_2$ appears to exist as several equilibrating regioisomers in solution. Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M.; Parkin, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 8953. Balch, A. L.; Lee, J. W.; Olmstead, M. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1356.

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(7) $C_{70}(OsO_4)$(4-*tert*-butylpyridine)$_2$, major isomer (**1**): $^{13}C$ NMR (125 MHz, 17.4 mg in 0.45 mL of $CDCl_3$) $\delta$ 166.01 (L), 165.89 (L), 157.68 (2C), 155.03 (2C), 151.57 (2C), 151.46 (2C), 151.21 (2C), 151.19 (2C), 150.81 (2C), 150.35 (2C), 150.30 (2C), 149.84 (2C), 149.66 (L), 149.44 (L), 149.39 (2C), 149.34 (2C), 149.17 (2C), 149.06 (2C), 148.86 (2C), 148.54 (2C), 148.09 (2C), 147.53 (2C), 147.51 (2C), 147.49 (1C), 146.83 (2C), 146.24 (2C), 145.44 (2C), 143.76 (3C), 143.57 (2C), 143.49 (2C), 141.75 (2C), 141.32 (2C), 138.15 (2C), 133.31 (2C), 132.74 (2C), 132.24 (2C), 131.58 (2C), 131.52 (2C), 122.88 (L), 122.74 (L), 102.15 (*C*–O), 100.92 (*C*–O), 35.19 (L), 35.08 (L), 30.55 (L), 30.49 (L). Minor isomer (**2**): $^{13}C$ NMR (100 MHz, 9.3 mg in 0.45 mL of $CDCl_3$) $\delta$ 165.86 (L), 155.40 (1C), 153.21 (2C), 152.26 (2C), 151.62 (2C), 150.08 (2C), 149.88 (1C), 149.67 (L), 149.41 (2C), 149.33 (2C), 149.24 (1C), 149.06 (2C), 148.86 (2C), 148.36 (2C), 147.99 (2C), 147.89 (2C), 147.24 (2C), 147.22 (2C), 147.18 (2C), 146.71 (1C), 146.61 (2C), 146.33 (2C), 145.88 (2C), 145.48 (4C), 145.03 (2C), 144.82 (2C), 144.69 (2C), 144.07 (2C), 143.90 (2C), 143.24 (2C), 142.92 (2C), 141.82 (2C), 132.60 (2C), 132.46 (2C), 131.02 (2C), 130.17 (2C), 127.18 (2C), 122.75 (L), 98.56 (*C*–O), 35.10 (L), 30.50 (L). L denotes coordinated 4-*tert*-butylpyridine carbons. The intensities of the L and *C*–O signals are not listed because the relaxation times of these carbons significantly differ from those of the fullerene-type carbons.

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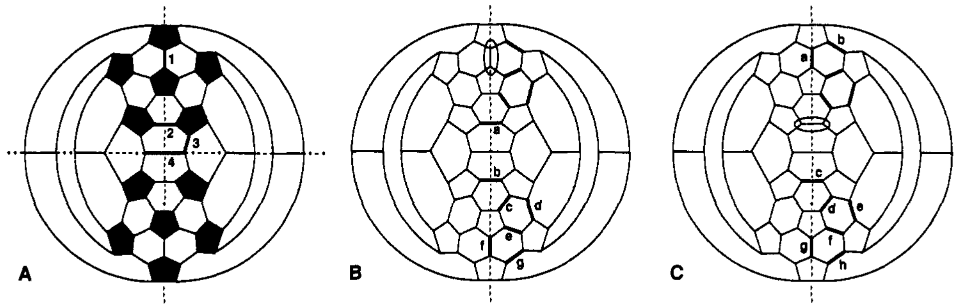

**Figure 1.** (A) Representation of $C_{70}$ showing the four types of 6–6 ring fusions (bold) corresponding to $C_{70}(OsO_4L_2)$ isomers **1** ($C_s$), **2** ($C_s$), **3** ($C_1$), and **4** ($C_{2v}$). Dashed lines indicate two of the six mirror planes of $C_{70}$; five-membered rings are blackened. (B) $C_{70}(OsO_4L_2)$ isomer **1** with the position of osmylation marked with an oval and the mirror plane indicated by a dashed line. Bold bonds indicate independent pyracylene-type positions with sights corresponding to sterically accessible $C_{70}(OsO_4L_2)_2$ isomers lettered a–g. (C) Analogous representation of $C_{70}(OsO_4L_2)$ isomer **2**. $C_{70}(OsO_4L_2)_2$ isomers **1a**, **1b**, **1d**, and **1g** are equivalent to **2a**, **2g**, **2f**, and **2d**, respectively.

initio calculated structure,[12] agrees well with the observed regioselectivity. Isomers **1**, **2**, **3**, and **4** correspond to osmylation at bonds between pairs of carbons with $\sigma$–$\pi$ interorbital angles of 102.0 and 101.9°, 101.5 and 101.5°, 100.0 and 98.9°, and 98.9 and 98.9°, respectively. Thus, osmylation occurs mainly at the bond between the highly pyramidalized carbons, to a lesser extent at the bond between carbons pyramidalized like those in $C_{60}$ (101.6°), and little or not at all at the bond between the less pyramidalized carbons, giving isomers **1** > **2** ≫ **3** and **4**.

The O-bonded carbons of osmylated $C_{60}$ are nearly tetrahedral.[5] Greater reactivity at the more pyramidalized carbons of $C_{70}$ corresponds to greater strain relief as the fullerene carbons become four-coordinate. Crystalline adducts of $C_{70}$ with $Ir(CO)Cl(PR_3)_2$ moieties similarly show reaction at positions which require the least distortion of the carbon cluster.[4] The regioselectivity observed with $C_{70}$ suggests that the higher fullerenes may show more discrete chemistry than suggested by their complex structures. Our recent kinetic resolutions of the chiral fullerenes $C_{76}$ and $C_{84}$ by asymmetric osmylation are consistent with this prediction.[16] Extrapolating from $C_{70}$ to carbon nanotubes, the osmium-mediated oxidation at sites of greatest local curvature in $C_{70}$, observed here, provides a model for the lead-mediated oxidation of carbon nanotubes at the tips, proposed by Ajayan and Iijima.[17]

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**Supplementary Material Available:** $^{13}C$ NMR spectra of $C_{70}$-$OsO_4$(4-*tert*-butylpyridine)$_2$ isomers **1** and **2** (13 pages). Ordering information is given on any current masthead page.

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