

Concise Route to Symmetric Multiadducts of [60]Fullerene: Preparation of an Equatorial Tetraadduct by Orthogonal Transposition

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The discovery of the fullerenes by Kroto and Smalley et al.¹ and the development of a preparative method for their synthesis by Krätschmer and Huffman et al.² has opened a new dimension of carbon chemistry.³ Special interest has been devoted lately^{4–9} to the exploration of preparative entries to regioselectively multifunctionalized derivatives of these carbon spheres, achieving the sequential addition of up to six organic addends to [60]fullerene (**1**) by cyclopropanation and/or [4 + 2]-cycloaddition reactions.^{5–9} A particularly versatile and elegant approach in this respect is Diederich's method of "tether-directed remote functionalization".^{6,9} The highly symmetric [60]-fullerene accordingly represents a particularly versatile scaffold for the covalent assembly of a variety of regular three-dimensionally structured molecules, some of which may enlarge the existing repertoire of programmed molecular components¹⁰ for the construction of useful ordered solid materials. We describe here a highly efficient route to symmetric mixed hexaadducts and to an equatorial D_{2h} -symmetric tetraadduct of **1**, introducing and exploring the strategy of an "orthogonal transposition".

Recently, we have reported the development of a uniform and topochemically controlled refunctionalization of **1**, which provided an efficient way to the antipodal anthracene bis-[4 + 2]-cycloadduct **2**.¹¹ In **2** the two anthracene addends are placed "strategically" at opposing ends (at the poles) of the carbon sphere. From there, the anthracene addends of **2** were expected to control further reactions and to steer them toward the molecular equator,¹² opening a concise route to mixed symmetric hexaadducts: indeed, when a suspension of **2** in dichloromethane was treated with an excess of diethyl bromomalonate

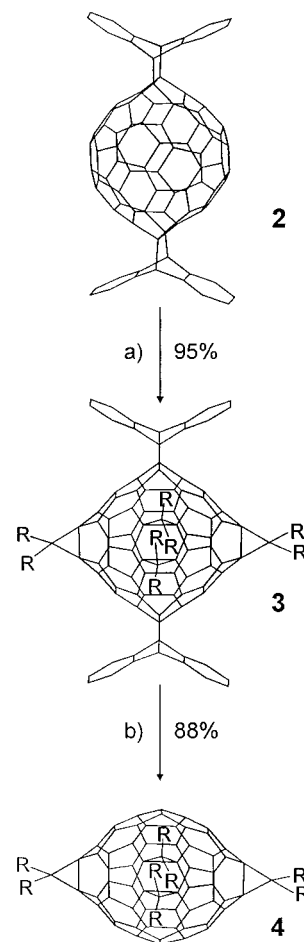


Figure 1. Synthetic scheme: (a) $\text{BrHC}(\text{CO}_2\text{Et})_2/\text{DBU}$ in $\text{CH}_2\text{Cl}_2/\text{room temperature}$; (b) 195° , 5 min; $\text{R} = \text{CO}_2\text{CH}_2\text{CH}_3$.

and of the amidine base diazabicycloundecene (DBU) at room temperature, after 2 days from the reaction mixture, the mixed hexaadduct **3** could be isolated in 95% yield as a crystalline and yellow solid (see Figure 1).¹³ The structure of the hexaaddition product **3** was deduced spectroscopically (FAB-MS, ^1H NMR, and ^{13}C NMR, UV/vis spectra):¹⁴ (i) the UV/vis spectrum reflected the regular addition pattern at the fullerene sphere (see, e.g., ref 6a); (ii) the molecular ion in the FAB-MS spectrum at $m/z = 1709.7$ was consistent with the molecular formula of **3**; and (iii) the indication of seven sets of equivalent

(12) This expectation was based (so far) on the observed selectivity of formation (in solution, at room temperature) of anthracene bisadducts of **1** (see: Kräutler, B. *Fullerenes: Recent Advances*; Kadish, K. M., Ruoff R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1996; Vol. 3, pp 1284–1295).

(13) **Preparation of Hexaadduct 3:** Diethyl bromomalonate (36.5 μL , 0.22 mmol) and DBU (32.6 μL , 0.22 mmol) were added to a stirred suspension of bisadduct **2** (11.7 mg, 10.9 mmol) in dichloromethane (2 mL) under argon. An orange solution was obtained after 10 min. Diethyl bromomalonate (36.5 μL , 0.22 mmol) and DBU (32.6 μL , 0.22 mmol) were added after 24 h, and the mixture stirred again for 24 h, during which time a yellow precipitate formed. The mixture was centrifuged, the precipitate was washed with pentane and recrystallized from chloroform/hexane to give the hexaadduct **3** (17.5 mg, 95%) as yellow crystals. **Tetraadduct 4:** Crystalline hexaadduct **3** (5.0 mg, 2.9 mmol) was heated under vacuum in a sealed tube at 195°C for 5 min. The mixture was taken up in dichloromethane and was purified by column chromatography (silica Merck, Type 9385, dichloromethane). The green fraction was evaporated to dryness, and the residual tetraadduct **4** was recrystallized from dichloromethane/pentane to give 3.5 mg (88%) of dark green-brown crystals. **Hexaadduct 5:** Freshly distilled cyclopentadiene (9 mL) was added to a stirred suspension of **2** (9.4 mg, 8.6 mmol) in dichloromethane (9 mL) under argon. An orange solution was obtained after several hours. The reaction mixture was stirred for a total of 160 h (pale precipitate), then centrifuged; the precipitate was washed with pentane and dried under high vacuum to give the hexaadduct **5** (11.4 mg, 79%) as slightly yellow powder.

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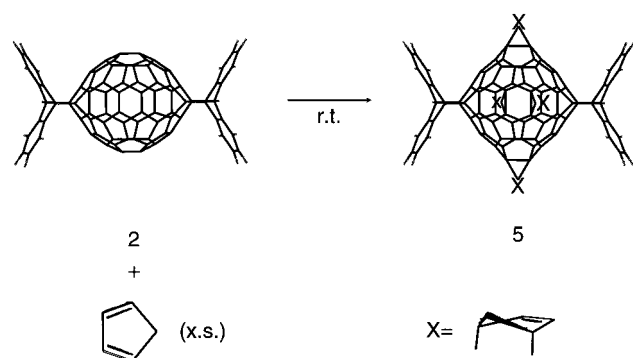
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Scheme 1



proton sites (in the ^1H NMR spectrum) and of 21 sets of equivalent carbons (in the ^{13}C NMR spectrum) was consistent with the proposed constitution of the D_{2h} -symmetric hexaaddition product **3**. Likewise, from **2** and an excess of cyclopentadiene, the mixed hexaadduct **5** resulted in 79% yield (see Scheme 1).^{13,14} The hexaadduct **5** ($\text{C}_{108}\text{H}_{44}$; MW = 1341.4), despite a uniform pattern of pseudooctahedral [4 + 2]-cycloaddition at the fullerene core (UV/vis),¹⁴ actually represents a mixture of five stereoisomers, due to the low symmetry of the cyclopentadiene addend.

Heating of a solid sample of **3** with protection from oxygen to 195 °C for 5 min produced free anthracene and the D_{2h} -symmetric tetraadduct **4**, isolated as a dark brown-green crystalline solid in 88% yield (see Figure 1).¹³ The tetraadduct **4**, obtained in this way, was identified spectroanalytically with that recently prepared by Diederich and co-workers^{9a,15} using a combined approach of a tether-directed multifunctionalization^{6,9,16} and Rubin's method of oxidative removal of the diene addend.¹⁷

We have reported here, on one hand, on a rational synthetic entry to symmetric mixed hexaadducts of the [60]fullerene (**1**),

(14) **Spectroscopic Data for 3**: UV/vis (CH_2Cl_2) 361 sh (4.27), 309.5 (4.80), 288.5 (4.83); ^1H NMR (500 MHz, CDCl_3): δ 1.23 (t, $J = 7.5$, 12H), 1.36 (t, $J = 7.0$, 12 H), 4.18 (q, $J = 7.5$, 8H), 4.34 (q, $J = 7.0$, 8H), 5.17 (s, 4H), 7.23 (m, 8H), 7.41 (m, 8H); ^{13}C NMR (125 MHz, CDCl_3): δ 13.93 (q), 14.10 (q), 47.64 (s), 48.64 (s), 58.24 (d), 62.63 (t), 62.65 (t), 66.10 (s), 68.52 (s), 70.10 (s), 125.31 (d), 126.70 (d), 139.30 (s), 139.90 (s), 141.71 (s), 144.71 (s), 145.03 (s), 145.74 (s), 153.64 (s), 163.82 (s), 164.16 (s); FAB-MS (NOBA-matrix, m/z (%int)): 1711.7 (3), 1710.7 (4), 1709.7 (4, $[M + 1]^+$), 1355.0 (42), 1354.0 (100), 1353.0 (87, $[M + 1 - \text{C}_{28}\text{H}_{20}]^+$). **5**: UV/vis (CH_2Cl_2) 352 (4.1), 310 (sh, 4.4), 295 (4.5), 249 (sh, 4.4); ^1H NMR (500 MHz, $\text{CS}_2/\text{C}_6\text{D}_6$ (9:1)) 1.4–2.2 (m, 8H), 3.14 (broad s, 4H), 3.4–3.6 (m, 4H), 4.6–4.8 (m, 4H), 5.99 (s, 4H), 6.2–6.4 (m, 4H), 6.9–7.4 (m, superimposed by m of $\text{C}_6\text{D}_5\text{H}$); ^{13}C NMR (125 MHz, $\text{CS}_2/\text{C}_6\text{D}_6$ (9:1)) from HMQC spectra¹⁹ 45.3 (t), 56 (d), 57.6 (d), 125 (d), 126 (d), 136 (d), 137 (d); FAB-MS (NOBA-matrix, m/z (%int)): 1341 (3, $[M + 1]^+$), 721 (95), 720 (100, C_{60}^+).

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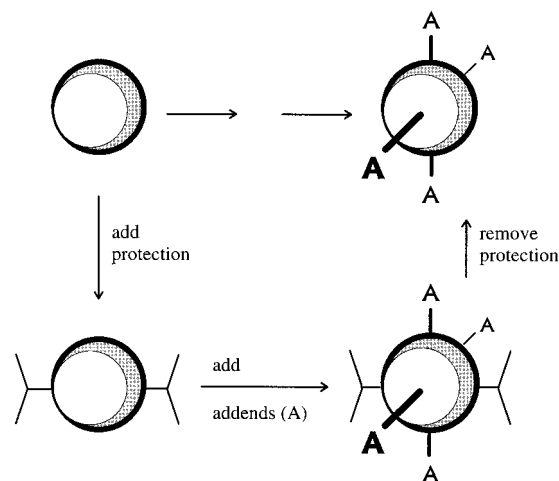


Figure 2. “Orthogonal transposition” as a synthetic strategy to equatorial tetraadducts of the [60]fullerene (**1**).

in which two types of addends are bound and spatially segregated into an equatorially bound set of four, and a set of two (other) addends, that are bound at the two poles of the functionalized carbon sphere.

By exploiting the thermal lability of anthracene adducts of fullerenes,^{5b,8,11} the mixed hexaadduct **3** then furnished an efficient entry to the equatorial tetraadduct **4**. Over all, the two-step transformation of the antipodal bisadduct **2** into the equatorial tetraadduct **4** then achieved a remarkable and specific refunctionalization of the fullerene sphere, in which a set of (two) addends (bound at the molecular poles of **2**) are replaced by a second set of (four) addends, that is now (re)positioned at the molecular equator in **4** (see Figure 2). The four substituents in **4** are (approximately) bound in a plane, that is, orthogonal to the original molecular axis in **2**.

The transformation **2** \rightarrow **4** formally represents (the first example of) an “orthogonal transposition” (of fullerene-bound addends) and defines a strategy that may be of considerable value for the preparation of specific multifunctionalized fullerenes with a symmetric addition pattern. Such and related approaches^{9,15} will provide rational entries to new structural motives based on the versatile spheric carbon scaffolds of the fullerenes. Cycloaddition reactions at these regularly structured and unsaturated carbon networks may have a central position in this respect. Clearly, the spheric buildup of the fullerenes adds a dimension to the work-space of supramolecular chemistry¹⁰ and opens exceptional routes to the design and synthesis of regularly and three-dimensionally structured molecules.

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