

Extended projection of C₆₀ spheres into three-dimensional space—three-fold cycloaddition of [60]fullerene to hericene

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Heating 2,3,5,6,7,8-hexamethylidenebicyclo[2.2.2]octane with an excess of C₆₀ in toluene for 3–4 d gives the 1:3 multiple Diels–Alder adduct in low (*ca.* 10%) yield.

With the advent of a means for the macro-scale preparation of C₆₀^{1,2} has come an avalanche of reports on the properties and chemistry of this spherical allotrope of carbon.^{3–5} Among the many rapid advances are those that have demonstrated the capability of this fullerene for serving as a reactive dienophile. Diels–Alder cycloaddition invariably occurs across the shorter interconnective double bond positioned between two six-membered rings. Many intermolecular cycloadditions have been reported and intramolecular variants have begun to make their appearance.⁶ As a consequence of the predictable regioselectivity of [4 + 2] cyclocondensations, adducts can be readily obtained in a high state of purity.

Despite these accomplishments, little attention has been accorded to the capping of polyfunctional dienes with C₆₀. At the present time, it is recognized that two molecules of [60]fullerene are captured by bis-*o*-quinodimethane to deliver a bisadduct.⁷ Our own interest in this field has led to the preparation of dumbbell-like systems, *e.g.* **3** and **4**, Scheme 1, in which two C₆₀ units are linked by cyclohexa-1,4-dienyl 'ladders' having differing spacer requirements.⁸ The precursor polyalkenes **1** and **2** are readily available.⁹

Here we describe an extension of this principle of structural assembly into a three-dimensional format. The acceptor molecule used was 2,3,5,6,7,8-hexamethylidenebicyclo[2.2.2]octane **5**, a hydrocarbon originally prepared by Vogel, who also proposed the trivial name hericene.¹⁰ The synthesis of **5** commenced with double addition of maleic anhydride to coumalic acid and required 12 steps.^{10,11} Although this hexaene exhibited limited solubility in aromatic hydrocarbon solvents,

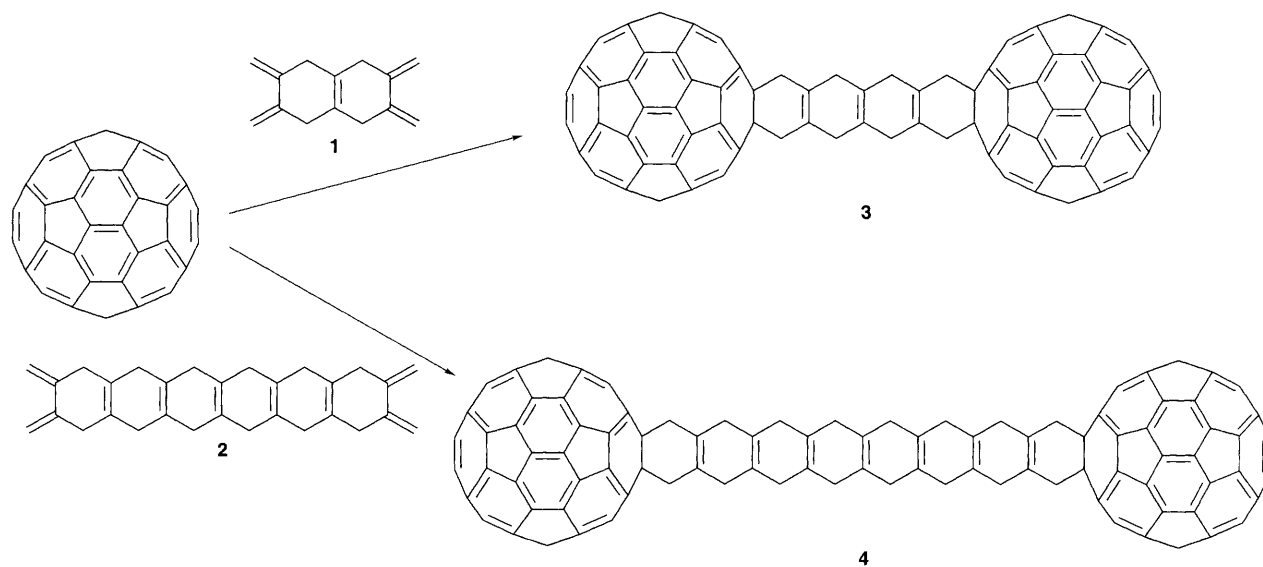
the extent of its dissolution in hot toluene was sufficient for the present purposes.

In a typical experiment, a solution of C₆₀ (353 mg, 0.46 mmol) in 250 ml of freshly distilled and deoxygenated toluene was treated with **5** (26 mg, 0.14 mmol) and refluxed for 3 d under nitrogen. After cooling, a red–brown precipitate was separated by filtration and washed extensively with toluene until the washings were colourless. The remaining solid, consisting mainly of compound **6**, weighed 29 mg (9%).

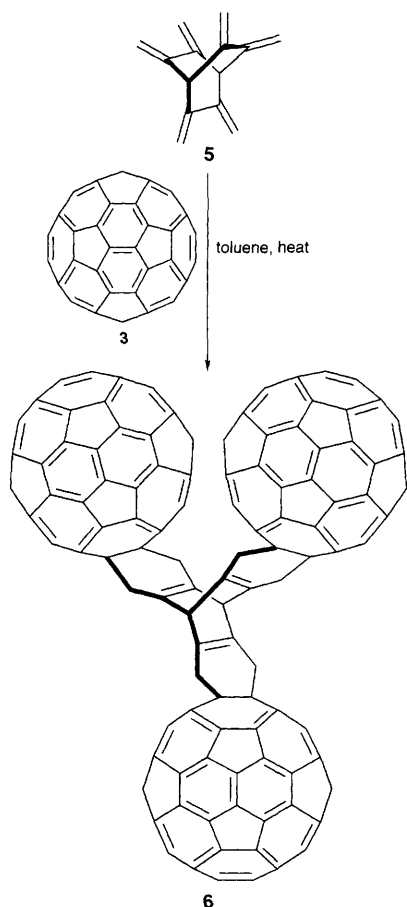
Not unexpectedly, **6** proved to be totally insoluble in all of the many solvents examined. As in the case of **3** and **4**,⁹ molecular ion analysis by mass spectrometry was to no avail, presumably because of fragmentation under the conditions of measurement.¹²

Ultimately, recourse was made to the TOSS CPMAS solid state ¹³C NMR technique¹³ for insight into sample purity (>85%) and structural analysis. By means of the total suppression of sidebands cross-polarization magic-angle spinning technique, it became possible to observe those carbon atoms central to the tris-adduct. In the upfield sector, intense peaks make their appearance at 68.9, 64.1 and 46.0 ppm. The first of these was recognized to arise from those tetrahedral carbon atoms of the fullerene that have become the centres linked to the former hericene sub-structure.^{9,14} The weakest central signal can be assigned with confidence to the pair of bridgehead carbons, which in less structurally ornate scenarios can be found in the vicinity of 60 ppm.¹⁵ The methylene carbon spacers combine to provide the most prominent peak at δ 46.0, in complete agreement with precedent.⁹ The simplicity of this region of the spectrum was uniquely consistent with the D_{3h} symmetry inherent in **6**.

The skeletal carbons of the fullerene framework resonate below δ_c 129, with the most prominent absorptions (δ_c 157.8,



Scheme 1



Scheme 2

150.3, 146.0, 143.0, 137.5 and 130.0) conforming well to the expected shifts.¹⁶

In summary, we have shown that the dienophilic reactivity of C_{60} , which compares favourably to that of *N*-phenylmaleimide,¹² allows for the ready implementation of triple addition to **5**. The end product **6** is an unusual hydrocarbon in many respects. It is constructed of a barrelene core,¹⁷ each bridge of

which is hinged to a C_{60} cage by way of monomethylene units. On this basis, **6** represents the first 'radiafullerene,' with three carbon spheres radiating out symmetrically from the staging framework. Thus, two constitutional patterns are present in **6**, the combination representing super-positioning of two strained and fundamentally interesting components. The only restriction to exploitation of such systems is the striking insolubility of the underivatized parent compound.

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