

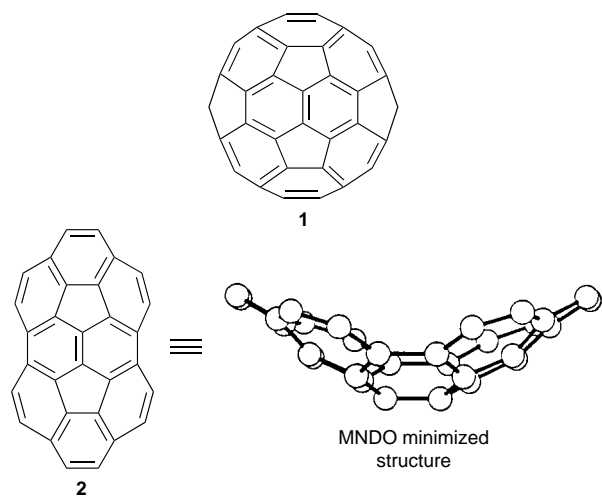
Buckybowls: a simple, conceptually new synthesis of C_{2v} -semibuckminsterfullerene ($C_{30}H_{12}$, [5,5]-fulvalene circulene)

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An extremely simple synthesis of decacyclic, $C_{30}H_{12}$ 'bucky-bowl' **2** from *m*-xylene, employing a strategy of wider applicability for the synthesis of diverse curved aromatic surfaces, is described.

The onset of the fullerene era, following the discovery of buckminsterfullerene **1**, has generated a great deal of interest in the synthesis and chemistry of 'bowl-shaped' polycyclic aromatic hydrocarbons (PAHs), particularly those representing a dominant motif on the fullerene surface.¹ Such PAHs, with curved surfaces, can be expected to exhibit novel physico-chemical characteristics and mimic some of the properties of fullerenes. Since buckybowls have never been encountered during the graphite vapourization processes, the only way to access them is through logically orchestrated synthetic methodologies. Efforts in this direction have been mounted in several laboratories during the past few years¹ and among the notable successes is the synthesis of C_{2v} -semibuckminsterfullerene **2**,² representing half the carbon content of **1** and endowed with substantial curvature (calculated bowl depth 2.7 Å).^{2a}

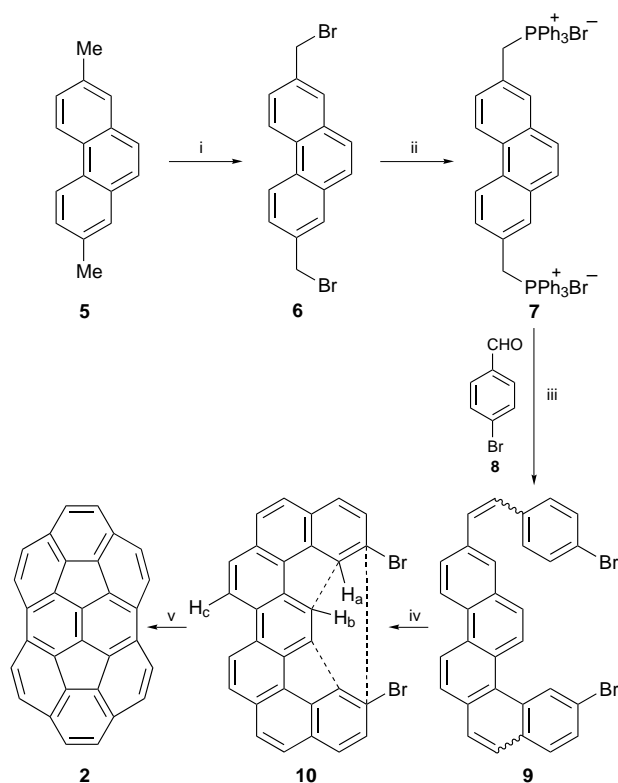


Rabideau *et al.*^{2a} were the first to report the synthesis of **2** via flash vacuum pyrolysis (FVP) of **3**, following a variant of the Scott's seminal synthesis of corannulene (Scheme 1).³ Very

Scheme 1

recently, in 1997, the groups of Scott and Zimmermann accomplished^{2b} a synthesis of **2** via FVP of **4**, a compound obtained serendipitously from cyclopenta[def]phenanthrene. We now report a new synthesis of **2** which is conceptually different from the earlier efforts and notable for its simplicity and brevity.⁴

Readily available 2,7-dimethylphenanthrene **5**⁵ was transformed to the bis-ylide precursor **7** via the bis(2,7-bromomethyl)phenanthrene **6** (Scheme 2). Two-fold Wittig coupling between the ylide derived from **7** and *p*-bromobenzaldehyde **8** furnished **9** as a mixture of *E*- and *Z*-isomers. **9** underwent facile two-fold oxidative photocyclization with high regioselectivity to furnish the desired **10** as the only characterizable product. The symmetry of **10** and its structure followed from its characteristic ¹H NMR spectrum [bay-region protons: δ 9.41 (s, H_a), 9.02 (s, H_b), 8.93 (d, *J* 9 Hz, H_c)] and 15 line ¹³C NMR spectrum [δ 132.0, 131.4, 131.3, 130.6, 130.0(2C), 129.3, 128.1, 127.2(2C), 127.0(2C), 125.7, 122.7, 120.6]. We had planned to effect in tandem, three-fold cyclization in **10** (see dotted lines) as the pivotal step and for that purpose strategically positioned the two bromine atoms as promoters of such a process.^{2b} To our great delight, we found that **10** on FVP furnished **2**, which was isolated from the pyrolysate through



Scheme 2 Reagents and conditions: i, NBS, CCl_4 , heat, 4 h, 80%; ii, PPh_3 , benzene, room temp., 2–3 days, 79%; iii, K_2CO_3 , THF, 18-crown-6, 10 h, 40%; iv, $h\nu$ (450 W), Pyrex, benzene, 2 h, 60%; v, FVP, 1150 °C, 0.5 mm, N_2 , 2–3%

extensive chromatography (alumina) and characterized through its mass spectrum [m/z 372 (M^+)] and diagnostic three line ^1H NMR spectrum [δ 7.92 (d, J 9 Hz, 4 H), 7.55 (d, J 9 Hz, 4 H), 7.42 (s, 4 H)] which was found to be identical with the reported values.² Admittedly, the yield (2–3%) of **2** in the FVP step is low and as yet unoptimised, but it compares well with the earlier reports (2.1 and 5% in FVP).²

Our approach to **2** from dimethylphenanthrene **5** involves the following sequence: NBS bromination–Wittig olefination–photocyclization and pyrolysis. Interestingly, the phenanthrene precursor **5** itself is assembled from *m*-xylene through the same sequence involving NBS bromination–Wittig olefination–photocyclization.⁵ Thus, in an overall sense, through an iterative three step sequence and a final pyrolysis step, *m*-xylene is elaborated into the decacyclic, $\text{C}_{30}\text{H}_{12}$, aromatic 'bowl' **2**. We believe that the simple strategy outlined here can be adapted towards the synthesis of several bowl-like non-planar PAHs. Efforts along these lines are currently underway.

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Footnote and References

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