

Short synthetic approach towards the triindenotriphenylene (hemifullerene) system

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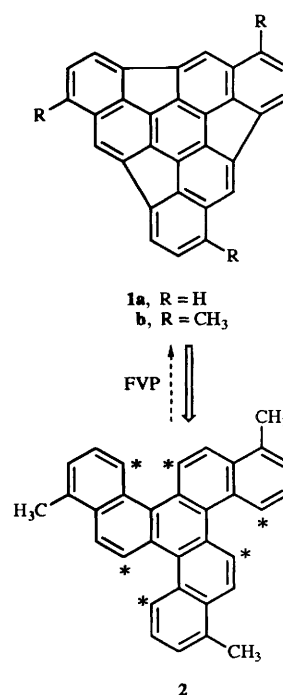
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A two-step synthesis of trimethyltribenzotriphenylene **2** from readily available starting materials involving three-fold Wittig reaction and three-fold oxidative photocyclization along a C_3 -symmetry path is reported. Flash vacuum pyrolysis of **2** in the quest for the triindenotriphenylene (hemifullerene) system has so far led only to the formation of mono-coupled products **6** and **7**.

The discovery of [60]fullerene and its emerging rich chemistry¹ has rekindled widespread interest in the bowl-shaped polycyclic aromatic hydrocarbons (PAHs) that constitute a significant cross-section of the bucky-ball. For nearly quarter of a century,^{2a} C_{20} -corrannulene² remained the seminal example of a bowl shaped PAH but in the last couple of years many new, curved aromatic hydrocarbons of enchanting shape and symmetry have been identified as prominent C_{60} siblings.³ Among them, C_3 -symmetric triindenotriphenylene **1a** ($C_{30}H_{12}$, hemifullerene), cup-shaped and composed of 10 rings, holds special interest and its molecular structure has been the object of several theoretical studies at semi-empirical as well as *ab initio* levels.⁴ However, contemporaneous synthetic studies directed towards **1a** have not yet surfaced in the literature,⁵ despite the formidable challenge and interest associated with this class of compounds. In this communication, we wish to disclose an exceptionally short strategy aimed at hemifullerene system and the progress made so far.

At the outset, we identified **1b**, a symmetrically substituted trimethyl derivative of hemifullerene as the target structure, in which the benzylic methyl groups could be readily activated and exploited for further synthetic manipulations at the rim *en route* to deeper bowls and eventually to C_{60} itself. Retrosynthetically (**1b** \rightarrow **2**), we identified a C_3 -symmetric trimethyltribenzotriphenylene **2** as the pivotal precursor in which key connectivities could be established at the starred positions through transannular cyclo-dehydrogenations employing the flash vacuum pyrolysis (FVP) technique. In this context, we evaluated the feasibility of this three-fold transannular C–C coupling process in **2** employing MNDO calculations.⁶ Sequential C–C connections in **2** ($C_{33}H_{24}$) leading to $C_{33}H_{22}$, $C_{33}H_{20}$ and finally to the desired $C_{33}H_{18}$ (**1b**) showed an increase in ΔH_f of 9.3, 33.3 and 55.8 kcal mol⁻¹, respectively.† The average interatomic distance between the starred positions in **2** was 3.15 Å, well within the acceptable range for such transannular coupling. Corresponding distances in the mono-coupled product $C_{33}H_{22}$ were marginally longer (3.19 Å) and in the di-coupled product substantially longer (3.45 Å). These results were encouraging enough for us to develop a synthesis of the precursor **2** and attempt thermally induced C–C coupling reactions.

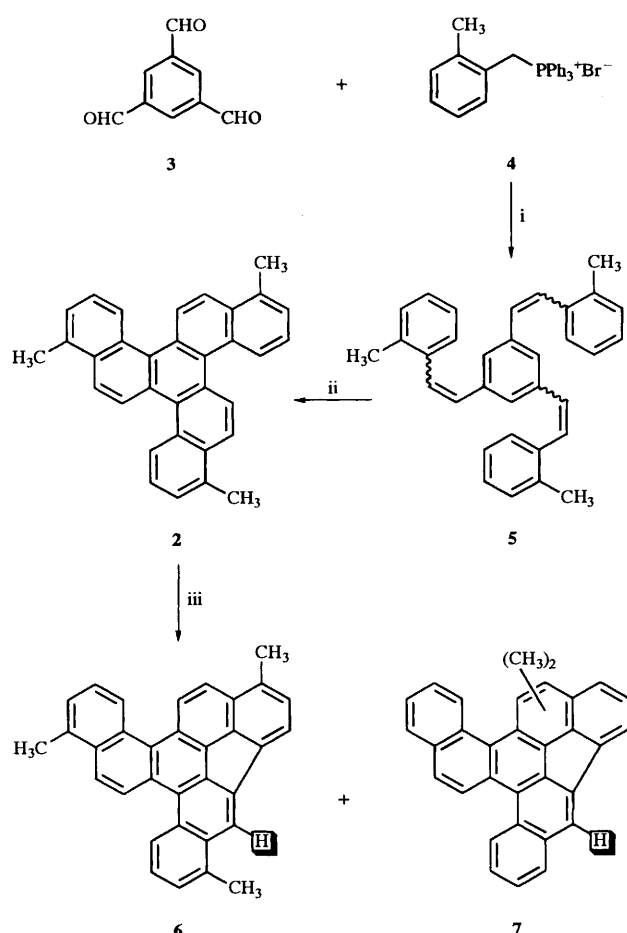
The three-fold Wittig reaction between 1,3,5-triformylbenzene **3**⁷ and the ylide derived from 2-methylbenzyltriphenylphosphonium bromide **4** furnished **5** as a mixture of *E* and *Z* isomers. This mixture was as such subjected to oxidative three-fold photocyclization by irradiation through a 450 W Hg lamp in the presence of cat. I_2 to furnish the desired C_3 -



tribenzotriphenylene **2** in just two steps. The structural identity of **2** (m/z 420, M^+) was secured on the basis of its 1H NMR spectrum (fully assigned on the basis of 1H - 1H COSY) and 11 line ^{13}C NMR spectrum which indicated its C_3 -symmetry. Thus, **2** is attained through formation of six C–C bonds, in just two steps, retaining the C_3 -symmetry of the precursor **3**.

When **2** was subjected to FVP at 900° (0.1 Torr) through a quartz tube, packed with quartz chips,^{3b} two products **6** and **7** (3:1) could be isolated from the pyrolysate by column chromatography (silica gel). The major product was identified as **6** on the basis of its mass spectrum (m/z 418, M^+), appearance of three methyl singlets in the 1H NMR spectrum at δ 2.95, 3.02 and 3.11 indicating complete loss of symmetry and the assignment of all the aromatic proton resonances through the 1H - 1H COSY spectrum. Particularly significant was the appearance of a sharp singlet at δ 8.64 (1 H) due to the indicated proton in **6**. The minor compound **7** (m/z 404, M^+) had only two methyl resonances at δ 2.95 and 3.12 in the 1H NMR spectrum and indicated the loss of a methyl group during the pyrolysis. However, the position of the two remaining

† 1 cal = 4.184 J.



Reagents and conditions: i, BuLi, THF, room temp., 12 h, 55%; ii, *hν*, cat. I₂, cyclohexane, 450 W Hg lamp, vycor filter, 1.5 h, ≈10%; iii, FVP, 900 °C, 0.1 mmHg, quant. (based on recovered 2)

methyl groups in 7 could not be fixed unambiguously with the available data. Although, we have been unable to observe the formation of 1b from the FVP of 2 so far, the characterization of 6 and 7 demonstrates the feasibility of our approach and augurs well for continuing efforts along this approach employing suitable substituted (halogen) derivatives of 2.

Experimental

1,7,13-Trimethyltribenzo[*c,i,o*]triphenylene 2

To a suspension of the Wittig salt 4 (2.23 mg, 5 mmol), prepared from 2-bromomethyltoluene and triphenylphosphine, in dry tetrahydrofuran (THF) (8 cm³) was added butyllithium (4.5 mmol) at -78 °C and the mixture stirred for about 15 min. 1,3,5-Triformylbenzene 3 (200 mg, 1.23 mmol) in THF (2 cm³) was introduced and the stirring continued for 5 h at room temperature (30 °C). The reaction mixture was diluted with diethyl ether, washed with brine, dried and concentrated. The residue was passed through a silica gel column to remove triphenylphosphine oxide and other impurities. The 1% ethyl acetate-hexane eluent was concentrated to give 5 (289 mg, 55%) as a mixture of *E,Z*-isomers as revealed by the ¹H NMR spectrum. A solution of 5 (100 mg, 0.24 mmol) in dry

cyclohexane was purged with dry N₂ and a few crystals of I₂ introduced. This solution was irradiated with a 450 W Hanovia medium pressure Hg lamp in a quartz immersion vessel using a vycor filter for 90 min. The reaction mixture was concentrated and chromatographed over a silica gel column. Elution with 1% ethyl acetate-hexane furnished a fraction which on crystallization from hexane furnished pure 2 (9 mg, ~10%), mp > 300 °C; *m/z* (FAB) 420, M⁺; δ_H(200 MHz; CDCl₃; *J*/Hz) 8.92 (3 H, d, *J* 9), 8.81 (3 H, br d, *J* 7), 8.12 (3 H, d, *J* 9), 7.54, 3 H, dd, *J* 9 and 7), 7.50 (3 H, d, *J* 9) and 2.90 (9 H, s); δ_C(50.0 MHz; CDCl₃) 134.05, 131.96, 130.01, 128.65, 127.82, 127.58, 127.18, 126.81, 125.14, 121.59 and 20.05.

Flash vacuum pyrolysis of 2

The tribenzotriphenylene derivative 2 (5 mg) was subjected to flash vacuum pyrolysis in a quartz vessel at 900 °C (0.1 mmHg) in a slow stream of N₂ employing a home-built system similar to that described by Staab and Haenel.⁸ The material collected on the cold-finger (~5 mg) was carefully chromatographed on a silica gel column (2% ethyl acetate-hexane eluent) to furnish 2 (~1 mg), 6 (~3 mg) and 7 (~1 mg). 6: *m/z* (FAB) 418 (M⁺); δ_H(200 MHz; CDCl₃; *J*/Hz) 9.41 (1 H, d, *J* 9), 9.18 (1 H, br d, *J* 8), 9.02 (1 H, d, *J* 9), 8.64 (1 H, s), 8.47 (1 H, d, *J* 9), 8.45 (1 H, d, *J* 8), 8.36 (1 H, d, *J* 9), 8.34 (1 H, d, *J* 8), 7.94 (1 H, d, *J* 8), 7.66 (1 H, dd, *J* 8), 7.58 (1 H, d, *J* 9), 7.50 (1 H, dd, *J* 8), 7.28 (1 H, d, *J* 9), 3.11 (3 H, s), 3.02 (3 H, s) and 2.95 (3 H, s). 7: *m/z* (FAB) 404 (M⁺); δ_H(200 MHz; CDCl₃; *J*/Hz) 9.44 (1 H, d, *J* 8), 9.22 (1 H, d, *J* 8), 9.01 (1 H, d, *J* 8), 8.63 (1 H, s), 8.58-7.40 (10 H, m), 3.12 (3 H, s) and 2.95 (3 H, s).

Acknowledgements

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References

- 1 A. Hirsch, *The Chemistry of the Fullerene*, Georg Thieme Verlag, Stuttgart, 1994.
- 2 (a) W. E. Barth and R. G. Lawton, *J. Am. Chem. Soc.*, 1971, **93**, 1730; (b) L. T. Scott, M. M. Hashemi and M. S. Batcher, *J. Am. Chem. Soc.*, 1992, **114**, 1920; (c) A. Borchardt, A. Fuchicello, K. V. Kilway, K. K. Baldrige and J. S. Siegel, *J. Am. Chem. Soc.*, 1992, **114**, 1921; (d) A. H. Abdourazak, A. Sygula and P. W. Rabideau, *J. Am. Chem. Soc.*, 1993, **115**, 3010; (e) S. Magen, U. Nuechter, M. Nuechter and G. Zimmermann, *Tetrahedron Lett.*, 1994, **35**, 7013.
- 3 (a) C. Fabre and A. Rassat, *C.R. Acad. Sci. Paris, Sec. 2*, 1989, 1223; (b) G. Mehta, S. R. Shah and K. Ravikumar, *J. Chem. Soc., Chem. Commun.*, 1993, 1006; (c) P. W. Rabideau, A. H. Abdourazak, H. E. Folsom, Z. Marciniow, A. Sygula and R. Sygula, *J. Am. Chem. Soc.*, 1994, **116**, 7891; (d) G. Mehta and K. Venkateswara Rao, *Synlett*, 1995, 319.
- 4 (a) R. Faust and K. P. C. Vollhardt, *J. Chem. Soc., Chem. Commun.*, 1993, 1471; (b) A. Sygula and P. W. Rabideau, *J. Chem. Soc., Chem. Commun.*, 1994, 1497; (c) M. J. Plater, H. S. Rzepa and S. Stossel, *J. Chem. Soc., Chem. Commun.*, 1994, 1567.
- 5 (a) F. Sbrogio, F. Fabris, O. De Lucchi and V. Lucchini, *Synlett*, 1994, 761; (b) M. J. Plater, Abstract ISP-28, International Conference on Organic Synthesis, December, 1994, Bangalore, India.
- 6 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4599.
- 7 B. Raju and G. S. Krishna Rao, *Synthesis*, 1987, 197.
- 8 H. A. Staab and M. Haenel, *Chem. Ber.*, 1973, **106**, 2090.

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