

Bucky-bowls. A general approach to benzocorannulenes: synthesis of mono-, di- and tri-benzocorannulenes

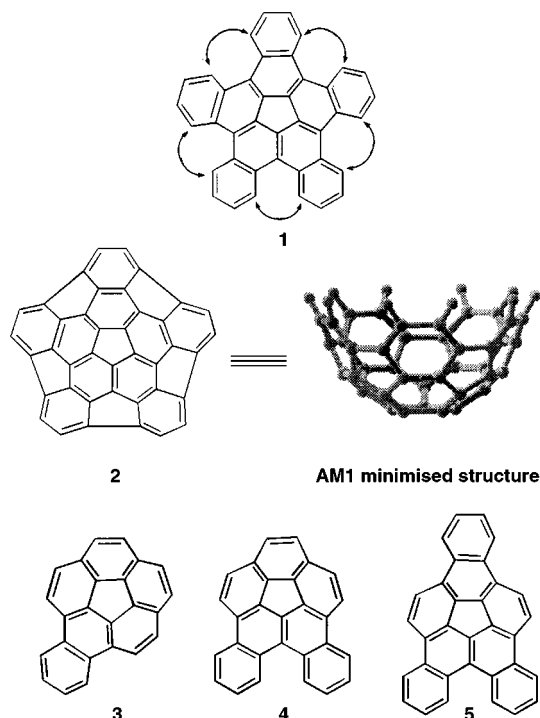
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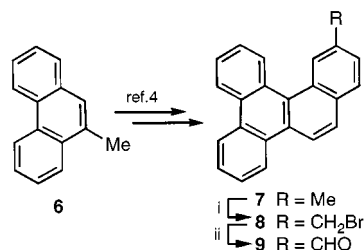
We outline a conceptually simple and general route to bowl-shaped benzocorannulenes based on readily assembled PAHs which on flash vacuum pyrolysis result in the sequential formation of a five- and six-membered ring; following this approach, syntheses of mono-, di- and tri-benzocorannulenes have been achieved.

As a part of our continuing interest in the synthesis of C_{60} fullerene (bucky-ball) and its fragments (bucky-bowls),^{1,2} we became interested in developing a synthetic approach to pentabenzocorannulene **1** *en route* (see transannular bridging indicated in **1**) to the 'deep-bowl' **2**, $C_{40}H_{10}$.³ Bowl-shaped **1** and **2** represent 2/3 of the carbon content of C_{60} with eleven and sixteen rings, respectively, constituting a dominant cross-section on the fullerene surface. Both **1** and **2** evoke considerable synthetic interest and are formidable objectives. As a prelude to efforts towards **1** and **2**, we have developed a new and



general synthetic route to benzoannulated corannulenes in which an appropriately constructed aromatic array upon flash vacuum pyrolysis (FVP) undergoes two-fold C–C bond formation involving cyclodehydrogenation to generate a five-membered ring, followed by insertion of vinylidene carbene or equivalent species to form a six-membered ring. Herein, we report the synthesis of mono-, di- and tri-benzocorannulenes **3–5**.

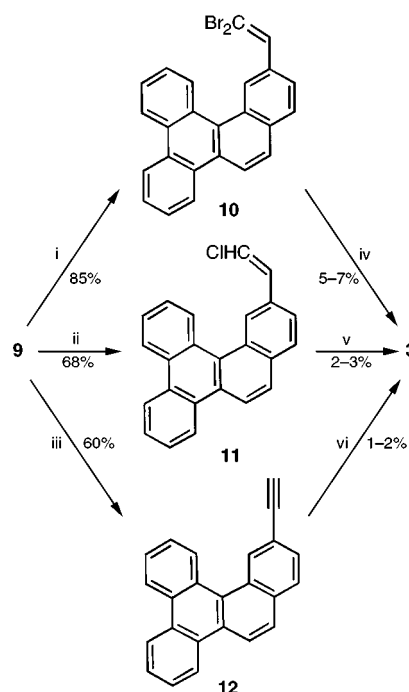
Our approach to benzocorannulene **3** emanated from 13-methylbenzo[*g*]chrysene **7**, readily available from 9-methylphenanthrene **6** through a tactical modification of the reported



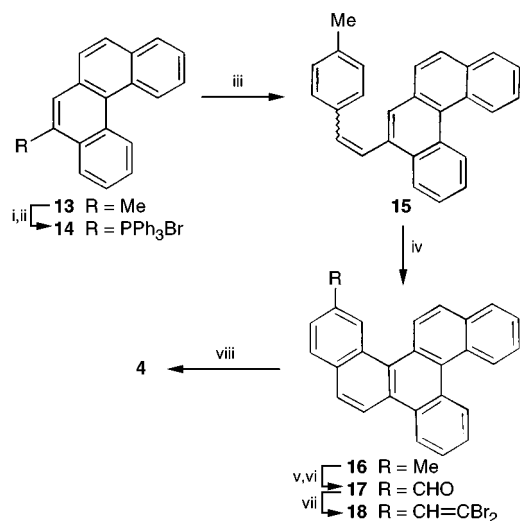
Scheme 1 Reagents and conditions: i, NBS, AIBN, CCl₄, 73%; ii, (Bu₄N)₂Cr₂O₇, CHCl₃, 76%.

procedure.⁴ The methyl group in **7** was oxidised to the required aldehyde **9** in two steps *via* the intermediate bromide **8** (Scheme 1). The aldehyde functionality in **9** was then elaborated to **10–12** having active functionalities, which on thermal activation under FVP conditions were expected to result in the projected two-fold cyclization. Indeed, FVP of **10–12** furnished **3**, albeit in low yields characteristic of such reactions (Scheme 2).² Benzocorannulene **3** was readily identified through its spectral characteristics (UV, 2D NMR, mass).^{5,6}

Our approach to dibenzocorannulene **4** originated from 5-methylbenzo[*c*]phenanthrene **13**, in turn readily accessible from commercial 2-methylnaphthalene.⁷ Naphthoannulation on **13** through the intermediacy of the Wittig salt **14** and photocyclization of the resulting stilbene derivative **15** led to 13-methyldibenzo[*c,p*]chrysene **16** (Scheme 3). The methyl



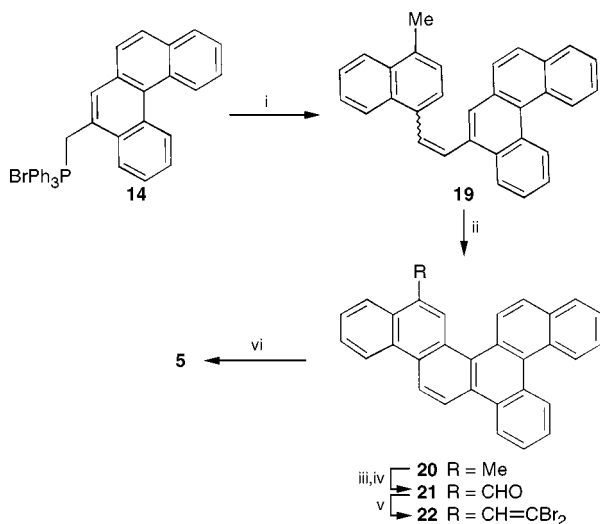
Scheme 2 Reagents and conditions: i, CBr₄, PPh₃, Zn, CH₂Cl₂, 85%; ii, ClCH₂PPh₃Cl, Bu^tOK, 0.5 h, 68%; iii, ClCH₂PPh₃Cl, Bu^tOK, 2 h, 60%; iv, FVP, 1150 °C, 5–7%; v, FVP, 1150 °C, 2–3%; vi, FVP, 1150 °C, 1–2%.



Scheme 3 Reagents and conditions: i, NBS 99%; ii, PPh_3 , C_6H_6 , 79%; iii, $p\text{-MeC}_6\text{H}_4\text{CHO}$, Cs_2CO_3 , Pr^iOH , 80%; iv, $h\nu$, I_2 , C_6H_6 , propylene oxide, 65%; v, NBS, CCl_4 , 44%; vi, $(\text{Bu}_4\text{N})_2\text{Cr}_2\text{O}_7$, CHCl_3 , 77%; vii, CBr_4 , PPh_3 , Zn , CH_2Cl_2 , 85%; viii, FVP, 1150 °C, 5–7%.

group in **16** was oxidised to the aldehyde **17** and in the light of the relatively more efficient conversion **10**→**3** was further transformed to the hexacyclic *gem*-dibromoalkene **18**, the desired FVP precursor. On thermal activation **18** underwent the expected double cyclization to furnish the new dibenzocorannulene **4** and was fully characterised on the basis of incisive spectral analyses⁵ (Scheme 3).

Interestingly, 5-methylbenzo[*c*]phenanthrene **13** and the Wittig salt **14** derived from it also served as the precursor for the synthesis of tribenzocorannulene **5**. Wittig coupling between **14** and 4-methylnaphthaldehyde gave **19** which on photocyclization led to the naphtho[1,2-*f*]picene derivative **20** (Scheme 4). The methyl group in **20** was again elaborated to the aldehyde **21** and further to the FVP precursor **22**. As planned, FVP on **22**



Scheme 4 Reagents and conditions: i, 4-methylnaphthaldehyde, Cs_2CO_3 , Pr^iOH ; ii, $h\nu$, I_2 , C_6H_6 , propylene oxide, 50% (2 steps); iii, NBS, CCl_4 , 45%; iv, $(\text{Bu}_4\text{N})_2\text{Cr}_2\text{O}_7$, CHCl_3 , 70%; v, CBr_4 , PPh_3 , Zn , CH_2Cl_2 , 55%; vi, FVP, 1150 °C, 1–2%.

furnished the desired tribenzocorannulene **5**, which was spectroscopically characterised (Scheme 4).^{5,6}

In short, we have accomplished the syntheses of bowl-shaped benzocorannulenes **3–5** from appropriate polycyclic aromatics employing FVP as the key step, in which a five- and a six-membered rings are sequentially formed. The precursor polycyclic platforms were assembled from simple aromatic starting materials through an iterative sequence involving Wittig olefination and photocyclization steps. Notwithstanding the low yields in the final FVP step, which is not uncommon for such cyclizations,^{1,2} this work demonstrates the generality of our approach and sets the stage for the synthesis of **1** and **2**.

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Notes and references

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- All new compounds reported here were fully characterised on the basis of their spectral (UV, IR, 2D ^1H and ^{13}C NMR, MS) and analytical data. Selected data for **3**: mp 253 °C; λ_{max} (MeOH)/nm 305, 275, 260 and 240; δ_{H} (300 MHz; CDCl_3), 8.68 (2H, dd, *J* 6 and 3.3), 8.26 (2H, d, *J* 8.7), 7.95 (2H, d, *J* 8.7), 7.84 (4H, ABq, *J* 8.7), 7.76 (2H, dd, *J* 5.7 and 3.3); δ_{C} (75 MHz; CDCl_3) 137.6 (qC), 135.4 (qC), 134.6 (qC), 133.1 (qC), 130.8 (qC), 130.5 (qC), 128.9 (qC), 127.5 (CH), 127.3 (CH), 127.1 (CH), 126.9 (CH), 125.1 (CH) and 124.3 (CH); *m/z* 300 (M^+). For **4**: mp > 250 °C (decomp.); λ_{max} (MeOH)/nm 319, 272, 257 (sh), 242 (sh); δ_{H} (300 MHz; CDCl_3) 9.41 (2H, d, *J* 8.4), 8.83 (2H, d, *J* 7.5), 8.35 (2H, d, *J* 8.7), 8.01 (2H, d, *J* 8.4), 7.91 (2H, s), 7.88–7.77 (4H, m); δ_{C} (75 MHz; CDCl_3) 136.7 (qC), 134.2 (qC), 134.0 (qC), 133.9 (qC), 133.7 (qC), 130.2 (qC), 128.5 (qC), 127.8 (CH), 127.5 (CH), 127.1 (CH), 127.0 (CH), 126.5 (CH), 125.5 (CH), 124.5 (qC), 123.9 (CH); *m/z* 350 (M^+). For **5**: λ_{max} (MeOH)/nm 347, 334, 279, 252; δ_{H} (400 MHz; CDCl_3) 9.41 (2H, d, *J* 8), 8.86 (2H, d, *J* 7.2), 8.73 (2H, dd, *J* 6.4 and 3.6), 8.45 (4H, ABq, *J* 8.4), 7.87 (2H, d, *J* 8), 7.83 (2H, d, *J* 9.2), 7.79 (2H, dd, *J* 6 and 3.2); *m/z* 400 (M^+).
- Mono- **3** and tri-benzocorannulene **5** reported here have been prepared previously by Scott *et al.* [ref. 1(b), (e)] following entirely different routes. See also: B. McMahon, B.S. Thesis, Boston College, 1997; C. C. McComas, B.S. Thesis, Boston College, 1996. Since the details of this work are not published, we have provided here the spectral data and also compared the spectra of our synthetic compounds with theirs. Dibenzocorannulene **4** has been prepared for the first time.
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