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A New Synthesis of Corannulene

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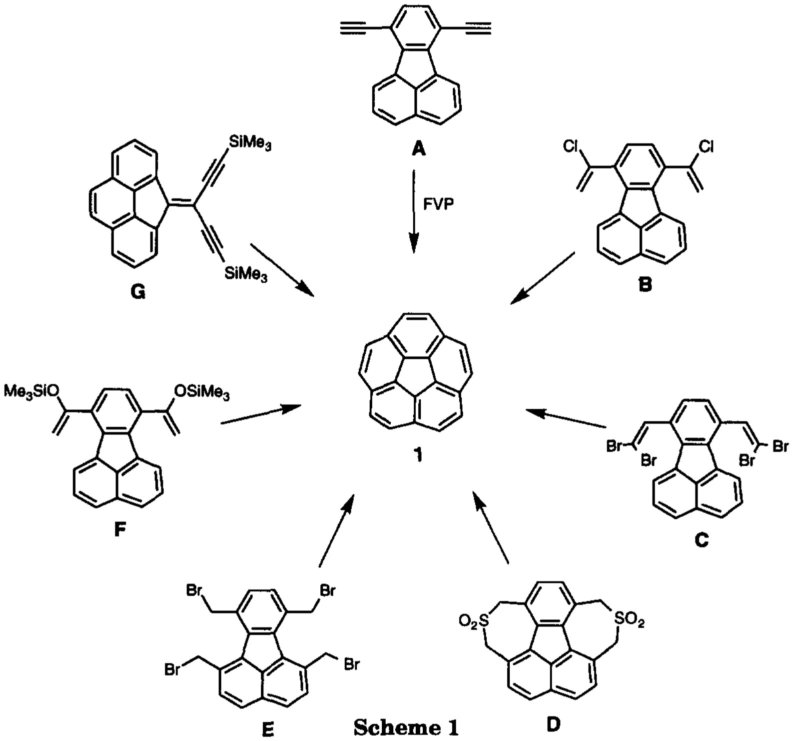
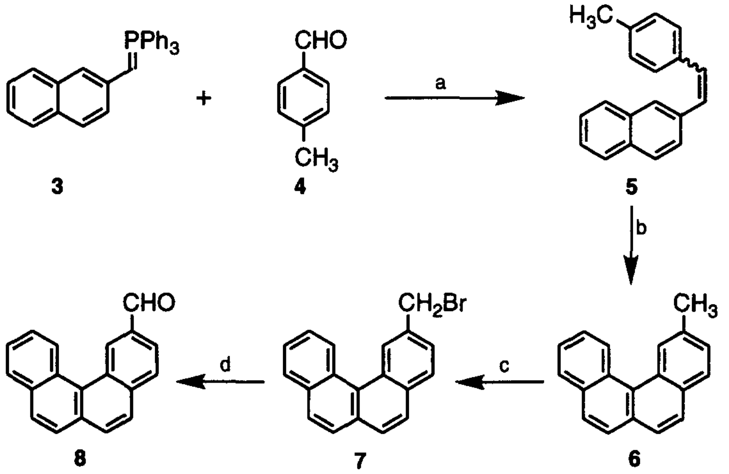
Abstract: Flash vacuum pyrolysis of 2-substituted benzo[c]phenanthrene has been exploited as a pivotal step in a new, simple synthesis of the 'bowl-shaped' hydrocarbon corannulene **1**. © 1997 Elsevier Science Ltd.

The 'bowl-shaped' $C_{20}H_{10}$-hydrocarbon, corannulene **1**, is a fascinating molecular entity whose synthesis was first accomplished over a quarter of a century ago in what was a pioneering effort at that time.[1] However, the advent of the fullerene era has rekindled world-wide interest in **1**, as it constitutes a dominant, readily recognizable motif on the curved surface of buckminsterfullerene (C_{60}). During the past five years, several syntheses of **1** have appeared, Scheme 1,[2] most of which



Scheme 1

(A-F→**1**) are tactical variations of the Scott strategy (A→**1**)[2a] involving the flash vacuum pyrolysis (FVP) of 7,10-disubstituted fluoranthene derivatives. Zimmermann *et al.*,[2d] on the other hand, have employed FVP on a *bis*-trimethylsilyl derivative of cyclopenta[def]phenanthrene system (G→**1**) to access **1**. In these syntheses of corannulene, Scheme 1, the central five-membered ring is pre-formed and two six-membered aromatic rings are added during the key FVP process to complete the 'rim' of the curved surface of **1**. Herein, we outline a new approach to **1** employing bench-top starting materials and text-book reactions, and generating a five- and a six-membered ring during a pivotal FVP step on the precursor 2-substituted benzo[c]phenanthrene derivatives **2a-d**.[3,4]

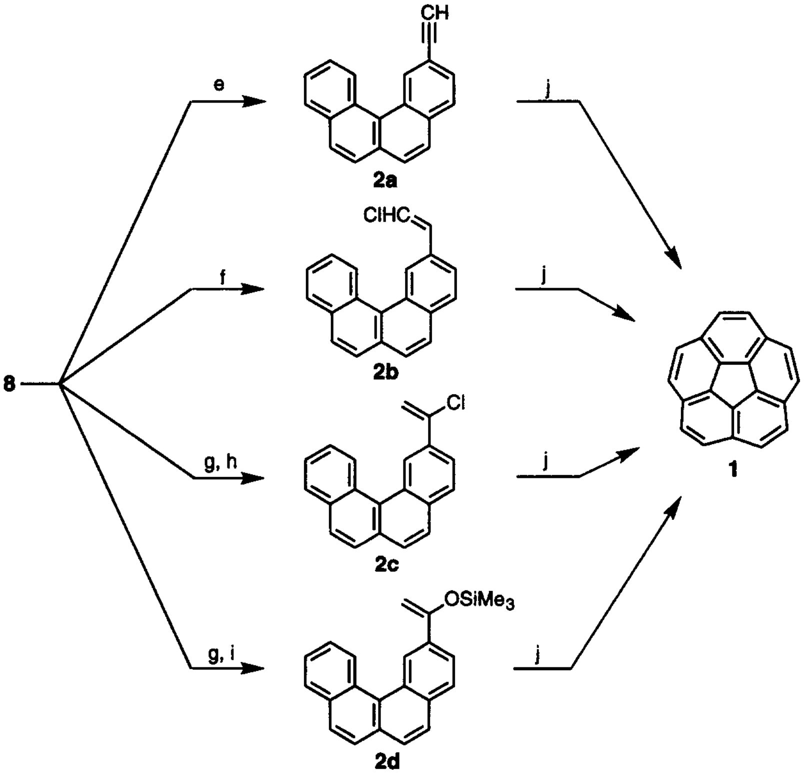


Reagents and yield: a, K_2CO_3, THF, 18- crown- 6, 65%; b, hν (450w Hg lamp), C_6H_6, I_2, propylene oxide, 2h, 35%; c, NBS,CCl_4, AIBN,75%; d, $(Bu_4N)_2Cr_2O_7$, $CHCl_3$, 60%

Scheme2

The requisite benzo[c]phenanthrenes **2a-d** were assembled as shown in Scheme 2. Wittig reaction between the ylide **3** (derived from 2-bromomethyl-naphthalene) and *p*-tolualdehyde **4** furnished **5** as an E:Z mixture. Irradiation of **5** in the presence of iodine led to the desired photocyclization and isolation of 2-methylbenzo[c]phenanthrene **6** as the major product.[5-7] The methyl group in **6** was oxidized to the formyl derivative **8**[7c] *via* the 2-bromomethyl intermediate **7**[7b], Scheme 2. The formyl derivative **8** was elaborated to **2a-d**, the precursors identified for FVP studies, through functional group transformations summarized in Scheme 3.

When **2a-d** were subjected to FVP in a quartz tube (30 cm x 1 cm) at 1200°C (0.5 torr, N_2 flow), corannulene **1** could be isolated, in each case, through column chromatography on silica gel (hexane eluent) and was readily identified through its characteristic ^1H NMR (δ 7.82, s) and ^{13}C NMR (δ 135.84, 130.89, 127.04) spectral data.[2a] While **2b** and **2c** furnished **1** in 8% isolated yield (based on several runs) in the FVP reaction, **2a** and **2d** were less efficient (2-4%). The yields in the FVP step leading to **1** are generally low (being 10% for A→**1** in the first report by Scott[2a] and 8% for F→**1** in the most recent publication by Rabideau,[2e] Scheme 1) although somewhat better yields have been realized in some other cases.[2]



Reagents and yield: e, $ClCH_2PPh_3^+Cl^-$, t-BuO^- K^+, 2h, 60%; f, $ClCH_2PPh_3^+Cl^-$, t-BuO^- K^+, 0.5h, 70%; g, (i) CH_3MgI, THF, 0.5h, 80%; (ii) PCC, DCM, 2h, 60%; h, PCl_5, C_6H_6, 40%; i,LDA,THF,TMSCl, 60%; j, FVP,~1200°C, 0.5 torr, N_2 flow.

Scheme3

Formation of **1** from **2a-d**, with the concurrent formation of a five- and six-membered ring during FVP reaction, was an encouraging outcome of preparative value, as the hexacyclic hydrocarbon corannulene can now be accessed readily from cheap starting materials through a simple, straightforward sequence.

Acknowledgements

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References & Notes

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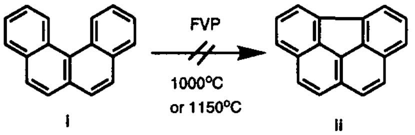
3. Initially, we were a bit pessimistic about the projected **2a-d**→**1** transformation in the light of the recent report[4a] that benzo[c]phenanthrene **i** does not cyclise to **ii** under FVP conditions. However, during the course of the present work, a report describing the successful transformation of **i**→**ii** under optimized temperature and pressure regimes appeared[4b] and raised the confidence in the eventual success of our synthetic route.



i

ii

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5. All new compounds were characterized on the basis of their spectroscopic (IR, ^{1}H & ^{13}C NMR) characteristics. Selected data for some of the compounds is as follows: **6**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.17 (d, 1H, J=8Hz), 8.96 (s, 1H), 8.04 (d, 1H, J=8Hz), 7.96-7.60 (m, 7H), 7.48 (d, 1H, J=8Hz), 7.48 (d, 1H, J=8Hz), 2.68 (s, 3H); ^{13}C NMR (50.0 MHz, $CDCl_3$): δ 135.87, 133.51, 131.65, 131.20, 130.49, 128.53, 128.41, 127.86, 127.69, 127.44, 127.28, 126.92, 125.99, 125.68.**8**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.27 (s, 1H), 9.57 (s, 1H), 9.05 (d, 1H, J=8Hz), 8.10 - 7.70 (m, 9H); ^{13}C NMR (50.0 MHz, $CDCl_3$): δ 192.38, 136.98, 134.16, 133.85, 133.36, 131.43, 130.14, 129.56, 129.98, 128.84, 128.36, 128.08, 127.69, 127.02, 126.88, 126.63, 126.54, 123.73.**2a**: 9.30 (s, 1H), 9.08 (d, 1H, J=8Hz), 8.02-7.68 (m, 9H); ^{13}C NMR (50.0 MHz, $CDCl_3$): δ 132.17, 131.33, 128.63, 127.98, 127.74, 127.04, 126.67, 126.13. MS: *m/z* 252[M^+] .**2b**: (mixture of E:Z isomers): 9.49 (s, 1H), 9.21 (d, 1H, J=8Hz), 8.06-7.62 (m, 9H), 6.90 (d, 1H, J=8Hz), 6.42 (d, 1H, J=8Hz); ^{13}C NMR (50.0 MHz, $CDCl_3$): δ 133.95, 133.57, 131.84, 131.28, 130.07, 129.12, 128.72, 128.56, 128.44, 127.98, 127.74, 127.55, 127.29, 127.09, 126.83, 126.30, 126.02, 117.67 MS: *m/z* 288[M^+]; **2c**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.46(s, 1H), 9.12(d, 1H, J= 8Hz), 8.07-7.65(m, 9H), 6.00(s, 1H), 5.70(s, 1H); ^{13}C NMR (50.0 MHz, $CDCl_3$): δ 138.2, 137.0, 134.2, 133.4, 130.1, 129.5, 128.8, 128.3, 128.0, 127.8, 124.3, 123.7, 117.1.; MS: *m/z* 288[M^+]; **2d**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.60(s, 1H), 9.18(d,1H, J= 8Hz), 8.06- 7.66(m, 9H), 4.89(s, 1H), 4.61(s, 1H), 0.1(s, 9H); ^{13}C NMR (50.0 MHz, $CDCl_3$): δ 133.5, 130.2, 129.6, 128.8, 128.0, 127.7, 127.1, 126.9, 126.6, 124.3, 117.2, 0.1.; MS: *m/z* 264(base peak) , M^+ peak not observed.
6. Syntheses of **6** and **7** were patterned along the routes reported earlier.[4a,7]
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