A Practical, Large Scale Synthesis of the Corannulene System

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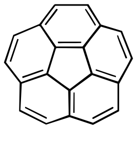
Corannulene (**1**), whose C_{20} carbon network may be considered to represent the polar cap of buckminsterfullerene C_{60}, was first synthesized by Barth and Lawton in 1966 by a 16-step process.[1]



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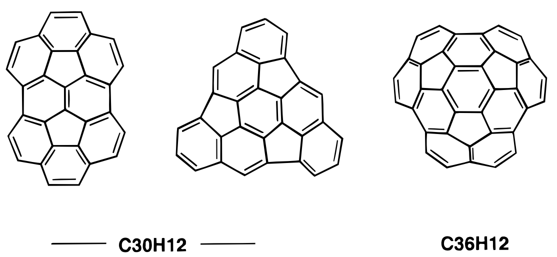
Several attempts to improve the synthesis failed until Scott and co-workers applied flash vacuum pyrolysis methodology (FVP) to the ring-forming step.[2] This high-temperature (ca. 1000 °C) gas-phase process promotes intramolecular ring closures that can lead to the formation of strained systems such as **1**. In 1996 Siegel and co-workers reported a modest yield synthesis of dimethylcorannulene via high-dilution, low-valent titanium coupling on both sides of 1,6-bis(bromomethyl)-7,10-bis(1-bromoethyl)fluoranthene, followed by DDQ dehydrogenation.[3] Recently, we[4] and Siegel's group[5] improved the synthesis by the employment of dibromomethyl derivatives; the low-valent titanium or vanadium treatment of 1,6,7,10-tetrakis(dibromomethyl)fluoranthene (**2**) produces corannulene in 70−80% yield. However, these reactions require high dilution techniques with reaction times of 2−4 days, as well as strict oxygen- and moisture-free conditions. Herein we report an inexpensive, convenient synthesis of 1,2,5,6-tetrabromocorannulene from **2** in over 80% yield that only requires refluxing for 15 min in aqueous dioxane containing a small amount of NaOH.

Curved surface polynuclear aromatics with carbon frameworks identifiable on the buckminsterfullerene surface, sometimes called "buckybowls", are novel structures of considerable interest for their chemical and physical properties. They have both concave and convex surfaces, and aromatics in this series may possess fullerene-like properties with increasing numbers of carbon atoms.

To date, larger buckybowls have generally been prepared by flash vacuum pyrolysis in low yield. This includes two $C_{30}H_{12}$ semibuckminsterfullerenes, first synthesized by our group,[6] and so far the largest buckybowl, a $C_{36}H_{12}$ from the Scott group.[7] Most recently we have been working on the development of solution-phase syntheses for these systems since, if they could be prepared in substantial amounts, they could serve as synthetic intermediates for the synthesis of even larger buckybowls and perhaps provide an organic synthesis of buckminsterfullerene itself.[8]



Serendipity reared its head as we attempted the hydrolysis of **2** in acetone/water mixtures containing either sodium carbonate or sodium hydroxide to generate the tetraaldehyde as a precursor to cabonyl coupling. To our surprise no aldehyde was formed under these conditions, but rather a mixture of dibromo- and tribromocorannulenes as demonstrated by GC/MS. Separation of the products was not attempted, but when the mixture was treated with *n*-butyllithium in THF at −78 °C, and then quenched carefully at that temperature, corannulene was formed in yields of 50 to 55% overall for the two steps combined! Optimization of the reaction conditions ultimately allowed us to cleanly produce tetrabromocorannulene (**3**) in 83% isolated yield (Scheme 1).[9] For example, refluxing 6.5 g of **2** in 250 mL of dioxane and 100 mL of water containing 3 g of NaOH afforded 3.4 g of **3**.

This simple procedure, which can provide very large amounts of a well-defined and functionalized corannulene, has, in our opinion, extraordinary potential. For example, production of corannulene itself on a very large scale is already possible by this method (Scheme 1), and we hope for considerable improvement as we begin to explore methods for the inexpensive, high-yield debromination of **3**.[10] Of course the presence of functionalizable bromine in **3** represents a major feature of this synthesis. For example, the bromine atoms can easily be replaced by methyl groups (Scheme 2, path a)[11] or TMS-acetylene (Scheme 2, path c),[12] and this will allow for further elaboration of this novel structure.

The coupling of benzyl halides, and related compounds, is well-known in the literature,[13] and recently this protocol has been used

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(2) (a) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082−7084. (b) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920−1921. (c) Scott, L. T.; Cheng, P.-C.; Hashemi, M. M.; Bratcher, M. S.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 10963−10968.

(3) Seiders, T. J.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2754−2755.

(4) (a) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1998**, *120*, 12666−12667. (b) Sygula, A.; Rabideau, P. W. *Abstracts*; National Meeting of the American Chemical Society, New Orleans, Louisiana, August 1999, ORGN-065. (c) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1999**, *121*, 7800−7803.

(5) (a) Seiders, T. J.; Baldrige, K. K.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7439−7440. (b) Seiders, T. J.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804−7813.

(6) (a) Rabideau, P. W.; Abdourazak, A. H.; Folsom, H. E.; Marcinow, Z.; Sygula, A.; Sygula, R. *J. Am. Chem. Soc.* **1994**, *116*, 7891−7892. (b) Abdourazak, A. H.; Marcinow, Z.; Sygula, A.; Sygula, R.; Rabideau, P. W. *J. Am. Chem. Soc.* **1995**, *117*, 6410−6411.

(7) (a) Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8743−8744. (b) Ansems, R. B. M.; Scott, L. T. *J. Am. Chem. Soc.* **2000**, *122*, 2719−2724.

(8) For a conceptually different approach to the synthesis of fullerenes, see: Buntz, U. H. F.; Rubin, Y.; Tobe, Y. *Chem. Soc. Rev.* **1999**, 28, 107−119 and references therein.

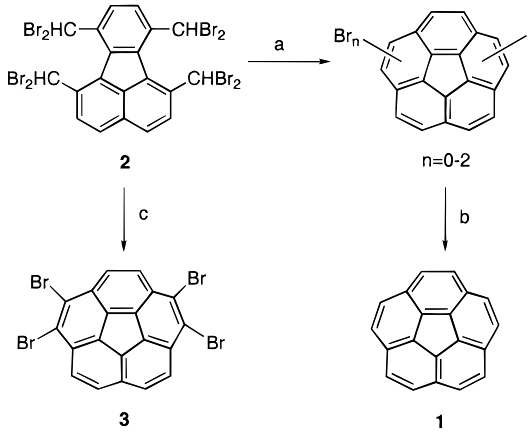
(9) Colorless solid (from xylenes); mp 338−340 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, $J = 8.9$ Hz, 2H), 7.95 (d, $J = 8.9$ Hz, 2H), 7.98 (s, 2H). ^{13}C NMR was not obtained due to the very poor solubility of **3** in common deuterated solvents. MS (EI, 70 eV) *m*/*z*, (rel intensity >10%) 569 (13), 568 (33), 567 (36), 566 (55), 565 (47), 564 (42), 563 (40), 562 (15), 560 (19), 407 (11), 406 (14), 405 (23), 403 (14), 283 (16), 281 (17), 250(23), 246 (100), 244 (13), 203 (15), 202 (10), 162 (19), 123 (72). HRMS (EI, 70 eV) calcd for $C_{20}H_6Br_4$ (M^+) 565.7165, found 565.7162.

(10) Although the mixture of di- and tribromocorannulenes is smoothly converted to corannulene by metalation with *n*-butyllithium followed by quenching with dilute HCl (Scheme 1, path b), a similar method applied to **3** produces a mixture of corannulene and mono- and dibutylcornannulenes. Under similar conditions, methyllithium produces a mixture of di-, tri-, and tetramethylcorannulenes. Refluxing **3** with $LiAlH_4$ in THF gives corannulene and some dihydro- and tetrahydrocorannulenes. This mixture can be converted to pure corannulene with DDQ, but the yield of the two steps is only ca. 30%.

(11) Tetramethylcorannulene **4** was previously synthesized by low-valent titanium coupling of 1,6,7,10-tetrakis(1-bromoethyl)fluoranthene, followed by DDQ dehydrogenation to afford a 6% yield for the two steps combined.[5b]

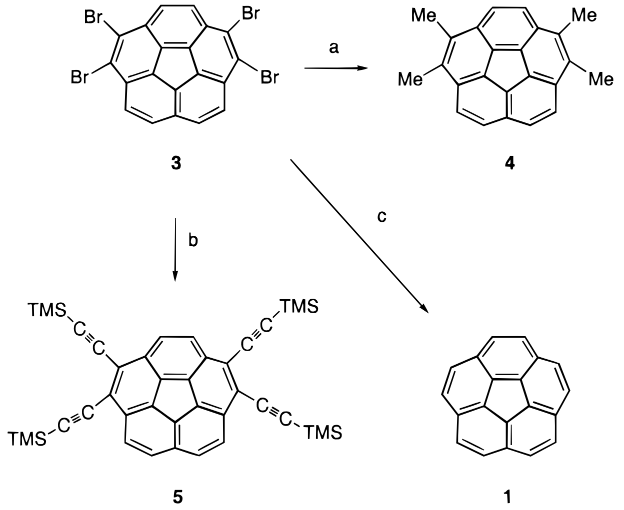
10.1021/ja0011461 CCC: $19.00

Scheme 1[a]



[a] Reagents and yields: (a) acetone/water (3:1), NaOH, reflux, 1 h; (b) *n*-BuLi, THF, −78 °C, 30 min, then quenched with dilute HCl, 50−55% yield for the two steps combined; (c) dioxane/water (2.5:1), NaOH, refluxed 15 min, 83% yield after crystallization (xylenes).

Scheme 2[b]



[a] Reagents and yields: (a) AlMe$_3$, NiCl$_2$(dppp), DME, reflux 12 h, 76% isolated yield; (b) (TMS) acetylene, Pd(PPh$_3$)$_2$Cl$_2$, CuI, N(Et)$_3$, reflux 3 h, 86% isolated yield; (c) LiAlH$_4$, DDQ, 30%.

for making enediynes[14a] and [5]-helicene.[14b] Generally, the couplings are performed in anhydrous media and the mechanism is often assumed to be carbenoid. However, the exact pathway of these transformations is a matter of some controversy. After the initial deprotonation step, several mechanistic routes for the carbon−carbon bond formation have been proposed including nucleophilic attack by the carbanion, the intermediacy of carbenes (α-elimination), or formation of radicals by electron transfer from the carbanionic center.[13−15] Similarly, the mechanism for the transformation of **2** to the corannulene core is open to speculation. Deprotonation of dibromomethyl is certainly the first step since refluxing **2** in acetone/water mixtures without base (or with dilute hydrochloric acid) affords unchanged starting material. Bromocarbene formation from the dibromocarbanion may be a viable option for the next step since nucleophilic attack of the latter on the neighboring dibromomethyl group may be unlikely due to steric congestion. The resulting bromocarbene could insert into either the C−H or more likely the C−Br bond of the adjacent dibromomethyl group, followed by HBr elimination. This, of course, would lead to tetrabromocorannulene, the observed product. However, other reaction pathways are possible and likely responsible for the mixture of products, including di- and tribrominated corannulenes, formed in acetone/water (Scheme 1, path a).[16] Further investigations of the reaction pathway are underway.

In conclusion, we regard this new synthetic pathway as a major step toward the practical, large-scale syntheses of corannulene and related bowl-shaped aromatics. The overall process begins with easily available 2,7-dimethylnaphthalene,[17] and the sequence of chloromethylation, cyanation, hydrolysis, ring closure, and oxidation to produce 2,7-dimethylacenaphthenone is very straightforward and affords good yields.[18] The conversion of this quinone to 1,6,7,10-tetramethylfluoranthene is achieved either by the original two-step process[18b] or by a one-pot reaction using the method developed by the Scott group.[2a] Bromination of the hydrocarbon gives **2** in yields above 80%,[4c,5b] so this key precursor can be easily prepared, and on a very large scale. Thus we expect tetrabromocorannulene to become a key intermediate for the synthesis and study of larger bowl systems, and perhaps for the synthesis of buckminsterfullerene itself. The latter process would be important since it may provide a method of trapping atoms, molecules, or ions within the fullerene cavity during the final closure steps.[19]

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Supporting Information Available: Details of the experimental procedures for **1**, **3**, **4**, and **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] Compound **5** was isolated as a yellow solid (from ethanol/benzene): changes color above 240 °C, mp 277−280 °C dec. ^{1}H NMR (400 MHz, CDCl$_3$) δ (strongly dependent on the concentration of the sample) 0.35 (s, 18H), 0.355 (s, 18H), 7.77 (d, $J = 8.8$ Hz, 2H), 7.92 (d, $J = 8.8$ Hz, 2H), 7.96 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 0.45, 101.71, 101.84, 104.64, 104.79, 125.08, 125.36, 126.52, 126.91, 127.94, 130.57, 131.15, 131.57, 133.83, 134.57, 134.88. MS (EI, 70 eV) *m*/*z* (rel intensity) 636 (18), 635 (40), 634 (100), 633 (71), 630 (10), 618 (22), 531 (21). HRMS (EI, 70 eV) calcd for C$_{40}$H$_{42}$Si$_4$ (M$^+$) 634.2364, found 634.2375.

[13] See for example: (a) Hauser, C. R.; Brasen, W. R.; Skell, P. S.; Kantor, S. W.; Brodhag, A. E. *J. Am. Chem. Soc.* **1956**, *78*, 1653−1658. (b) Ledwith, A.; Shih-Lin, Y. *Chem. Ind. (London)* **1964**, 1867−1868. (c) Hoeg, D. F.; Lusk, D. I. *J. Organomet. Chem.* **1966**, *5*, 1−12. (d) Hanna, S. B.; Wideman, L. G. *Chem. Ind. (London)* **1968**, 486. (e) Vernigor, E. M.; Shalaev, V. K.; Luk'yanets, E. A. *J. Org. Chem. USSR* **1981**, *17*, 317−321.

[14] (a) Huber, R. S.; Jones, G. B. *Tetrahedron Lett.* **1994**, *35*, 2655−2658. (b) Dubois, F.; Gingras, M. *Tetrahedron Lett.* **1998**, *39*, 5039−5040.

[15] Kharash, M. S.; Nudenberg, W.; Fields, E. K. *J. Am. Chem. Soc.* **1944**, *66*, 1276−1279.

[16] Overnight reflux of tetrabromocorannulene **3** in acetone/water/NaOH affords unchanged starting material indicating that **3** is not an intermediate in the coupling of **2** in this solvent system.

[17] Wolinska-Mocydlarz, J.; Cannone, P.; Leitch, L. C. *Synthesis* **1974**, 566−568.

[18] (a) Buu-Hoi; Cagniant, P. *Rev. Sci.* **1942**, *80*, 130−133. (b) Borchart, A.; Hardcastle, K.; Gantzel, P.; Siegel, J. S. *Tetrahedron Lett.* **1993**, *34*, 273−276.

[19] A non-pyrolytic synthesis of dibenzo[*a*,*g*]corannulene by palladium-catalyzed intramolecular aryl−aryl coupling of 7,10-di(2-bromophenyl)-fluoranthene has just been reported: (a) Scott, L. T.; Reisch, H. *Abstracts*; National Meeting of the American Chemical Society, San Francisco, CA, March 2000, ORGN-515. (b) Reisch, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1427−1430. We thank Professor Larry Scott for sharing the manuscript with us.