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# *Communications to the Editor*

## The First Non-Pyrolytic Synthesis of a Semibuckminsterfullerene

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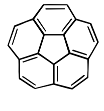
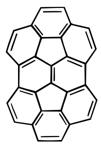
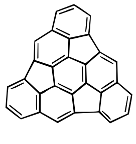
The considerable amount of research attention given to $C_{60}$ and the family of fullerenes has led to a growing interest in polynuclear aromatic hydrocarbons that may be considered to be fullerene fragments; that is, aromatic hydrocarbons with carbon frameworks that can be identified on the buckminsterfullerene surface.[1] Corannulene (**1**, $C_{20}H_{10}$), the polar cap of buckminsterfullerene, is the simplest example of such a hydrocarbon that exhibits curvature. And while **1** has been known since 1966,[2] it was the recent syntheses by Scott et al.[3] and by Siegel et al.[4] that spawned substantial progress in the field.[1] While significantly bowl-shaped, **1** undergoes rapid bowl-to-bowl inversion, and so there was considerable interest in preparing higher members of the series to learn if more highly strained and highly curved systems might be synthetically accessible. Indeed, a number of such systems have since been prepared, perhaps most notably a $C_{22}H_{10}$,[5] two $C_{30}H_{12}$ semibuckminsterfullerenes (**2** and **3**),[6,7] a $C_{32}H_{12}$,[8] and a $C_{36}H_{12}$.[9] A third member in the series of semibuckminsterfullerenes that appears to possess an accessible structure, **4**, has yet to be prepared.[1e] Another reason for the interest in semibuckminsterfullerenes is their role as possible intermediates in the total organic synthesis of buckminsterfullerene itself,[10−13] especially with **3** and **4** since they represent exactly half of $C_{60}$. Of course, it could also be possible, in principle, to synthesize $C_{60}$ by the chemical elaboration of a $C_{30}H_{xx}$ or higher system. However, all syntheses to date of "buckybowls" beyond corannulene employ flash vacuum pyrolysis (FVP) as the critical, curvature-producing step. FVP is ordinarily a small-scale and often low-yield process, and so the methodology of employing a semibuckminsterfullerene as a synthetic intermediate in a multistep route to $C_{60}$ has not been realistic. The total synthesis of $C_{60}$ notwithstanding, perhaps an even more serious consequence of the relative inaccessibility of semibuckminsterfullerenes is the inability to fully explore their chemistry. We now report the first non-pyrolytic route to a semibuckminsterfullerene (**2**) that lends itself to large-scale synthesis and should allow the elaboration of this $C_{30}H_{12}$ to larger structures as well as an examination of its chemistry.



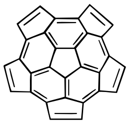
**1**



**2**

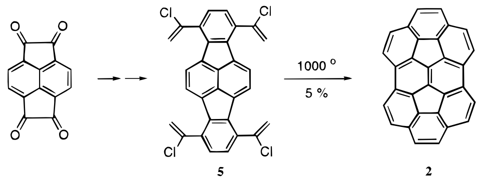


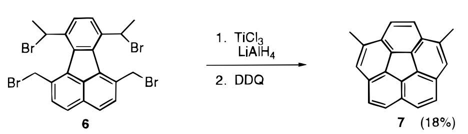
**3**



**4**

The original synthesis of **2** was first accomplished by the pyrolysis of the tetra(chlorovinyl) derivative **5**, affording milligram quantities of the first known semibuckminsterfullerene.[6] Subsequently, two additional precursors that give **2** upon FVP were discovered by Hagen et al.[14] and Mehta and Panda,[15] providing yields of 2.1% and 2−3%, respectively, for the pyrolysis step. Our interest in developing a new route to **2** was piqued by the recent work of Seiders et al.,[16] who reported a non-pyrolytic synthesis of 1,4-dimethylcorannulene (**7**) via reductive coupling of tetrabromide **6**. To explore the application of this same process to the synthesis of **2**, we developed a synthesis of the octamethylated hydrocarbon **8**.[17] Indeed, treatment of **8** with 8 molar equiv of NBS in benzene with reflux under sun lamp irradiation led to formation of the octakis-bromomethyl derivative **9** as the major product.[18] Intramolecular coupling of **9** would potentially





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(1) For recent reviews on bowl-shaped, fullerene-related hydrocarbons, see: (a) Siegel, J. S.; Seiders, T. J. *Chem. Br.* **1995**, 313−316. (b) Faust, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1429−1432. (c) Rabideau, P. W.; Sygula, A. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; Jai Press Inc.: Greenwich, CT, 1995; Vol. 3, pp 1−36. (d) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242. (e) Scott, L. T. *Pure Appl. Chem*. **1996**, *68*, 291−300.

(2) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc*. **1966**, *88*, 380−381. See also: Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc*. **1971**, *93*, 1730−1745.

(3) (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.

(4) Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc*. **1992**, *114*, 1921−1923.

(5) Abdourazak, A. H.; Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc*. **1993**, *115*, 3010−3011. Sygula, A.; Abdourazak, A. H.; Rabideau, P. W. *J. Am. Chem. Soc*. **1996**, *118*, 339−343.

(6) Rabideau, P. W.; Abdourazak, A. H.; Folsom, H. E.; Marcinow, Z.; Sygula, A.; Sygula, R. *J. Am. Chem. Soc*. **1994**, *116*, 7891−7892. Clayton, M. D.; Marcinow, Z.; Rabideau, P. W. *J. Org. Chem.* **1996**, *61*, 6052−6054.

(7) Abdourazak, A. H.; Marcinow, Z.; Sygula, A.; Sygula, R.; Rabideau, P. W. *J. Am. Chem. Soc*. **1995**, *117*, 6410−6411.

(8) Clayton, M. D.; Rabideau, P. W. *Tetrahedron Lett.* **1997**, *38*, 741−744.

(9) Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc*. **1996**, *118*, 8743−8744. See also: Forkey, D. M.; Attar, S.; Noll, B. C.; Koerner, R.; Olmstead, M.; Balch, A. L. *J. Am. Chem. Soc*. **1997**, *119*, 5766−5767.

(10) Loguercio, D. Ph.D. Thesis, UCLA, Los Angeles, CA, 1988.

(11) Faust, R.; Vollhardt, K. P. C. *J. Chem. Soc., Chem. Commun*. **1993**, 1471−1473.

(12) Diederich, F.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1101−1123 and references therein. See also: McElvany, S. W.; Ross, M. M.; Goroff, N. S.; Diederich, F. *Science* **1993**, *259*, 1594−1596.

(13) Sastry, G. N.; Jemmis, E. D.; Mehta, G.; Shah, S. R. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1867−1871.

(14) Hagen, S.; Bratcher, M. S.; Erickson, M. S.; Zimmerman, G.; Scott, L. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 406−408.

(15) Mehta, G.; Panda, G. *Chem. Commun*. **1997**, 2081−2082.

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

(17) Sygula, A.; Fronczek, F. R.; Rabideau, P. W. *Tetrahedron Lett.* **1997**, 5095−5098.

(18) Isolated as a yellow powder from benzene. Darkens gradually above 250 °C and melts (dec) at 278−280 °C (sealed capillary). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 4.7 (very broad, 4H), 5.0 (vb, 4H), 5.3 (br multiplet, 8H), 7.51 (s, 4H). The broad C**H$_2$**Br signals sharpen into two singlets at 5.02 and 5.44 (intensity 1:1) in nitrobenzene-*d$_5$* at 70 °C. $^{13}$C NMR was not obtained due to very limited solubility of **9** in common deuterated solvents.

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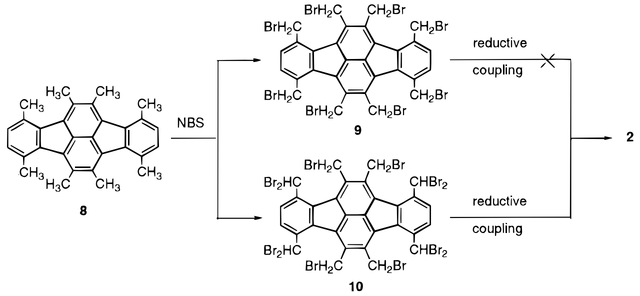
lead to octahydro-**2** ($C_{30}H_{20}$), presumably convertible to **2** by treatment with DDQ. Several such attempts were made employing various reductive systems including $TiCl_3/LiAlH_4$,[19] $TiCl_3$, Zn/Cu,[20] $VCl_3$/ $LiAlH_4$,[21] and $TiCl_2$[22] in both THF and DME. Unfortunately, even in the best cases, only inseparable traces of **2** were formed after DDQ treatment, as detected by GC/MS. Moreover, only minute portions of soluble organic materials were recovered from these attempts, indicating that despite the high dilution technique employed, competing intermolecular coupling prevailed, leading to polymerization. Apparently, the higher strain of the $C_{30}$ framework, as compared to corannulene, prohibits intramolecular coupling in this case, in contrast to the success, albeit with modest yields, for the latter system.[16]

Looking for a "hotter" intermediate, we decided to brominate **8** beyond the octabromide **9**. Thus, treatment of **8** with a large excess of NBS led to the formation of a single major product containing 12 bromine atoms. Considering the high symmetry of the $^1$H NMR spectrum, and the expected steric congestion of the "inner" methyl groups in **8**, we suspected that double bromination had occurred only on the four "outer" methyls leading to **10**.[23] Indeed, this prediction was confirmed by X-ray crystal structure determination (Figure 1).[24] In contrast to the failure with **9**, dodecabromo **10** did, in fact, lead to modest yields of the semibuckminsterfullerene framework under treatment with low-valent titanium or vanadium. The major isolated product of the reductive coupling of **10** is (aromatized) **2**, accompanied by some dihydro-**2** and also by some incompletely cyclized byproducts. In this regard, the low-valent titanium protocols were superior to the vanadium alternative since the latter produced more dihydro-**2**. While coupling was successful with both $TiCl_3/LiAlH_4$ and $TiCl_3$/Zn/Cu reductive systems, we also found that the recently developed inexpensive and convenient activated titanium powder method[25] works as well as the former alternatives.



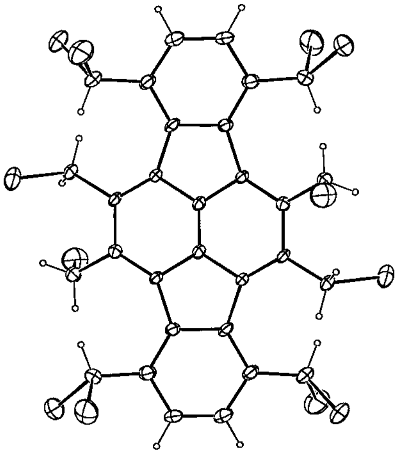


**Figure 1.** ORTEP drawing of **10**. The solvating toluene is not shown for clarity.

While so far our best yields of **2** are rather modest (ca. 20%) despite variations in the reaction conditions—reductive system, solvent, temperature, rate of the bromide addition—we continue to work on optimization of the procedure.[26] However, even with present yields, this "wet chemistry" synthesis offers a big advantage over pyrolytic alternatives, and this has important consequences not only for the exploration of buckybowl chemistry but also for the organic synthesis of fullerenes. To date, the most likely route to a total synthesis of $C_{60}$ has appeared to be from cyclophanes.[27] However, the availability of **2** in significant amounts suggests that further elaboration of this bowl-shaped fullerene fragment should also be considered as a plausible route to $C_{60}$.

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**Supporting Information Available:** Synthetic details, characterization of intermediates for the preparation of **2**, and X-ray data table for **10** (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[19] McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 4708–4709.

[20] McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255–3266. McMurry, J. E.; Lectka, T.; Rico, J. G. *J. Org. Chem.* **1989**, *54*, 3748–3749.

[21] Ho, T.-L.; Olah, G. A. *Synthesis* **1977**, 170–171.

[22] Eisch, J. J.; Shi, X.; Lasota, J. *Z. Naturforsch.* **1995**, *50b*, 342–350.

[23] Isolated as orange crystals from toluene, **10**$\cdot 2C_6H_5CH_3$. Darkens and decomposes but does not melt below 350 °C. $^1$H NMR (250 MHz, THF-$d_8$): $\delta$ 5.1 (vb, 4H), 5.5 (vb, 4H), 7.50 (b, 4H), 8.16 (s, 4H); toluene peaks at $\delta$ 2.31 (s) and 7.05–7.20 (m). $^{13}$C NMR (50.3 MHz, $CDCl_3$): broad peaks at $\delta$ 30.52, 40.37, 133.87, 135.03 135.53, 139.9, and 139.86, and sharp toluene peaks at 21.69, 125.53, 128.45, 129.27, and 137.37.

[24] Full details of the X-ray crystal structure will be published later.

[25] Fürstner, A.; Hupperts, A. *J. Am. Chem. Soc.* **1995**, *117*, 4468–4475.

[26] Since we needed to carry out a number of reactions to determine optimum conditions, runs were typically limited to approximately 500 mg of **10**. We are presently rebuilding our supply of **10** to conduct reactions on a relatively large scale, and these results will be reported in the full paper.

[27] For leading references, see: Rubin, Y.; Parker, T. C.; Pastor, S. J.; Jalisatgi, S.; Boulle, C.; Wilkins, C. L. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1226–1229. See also: Tobe, Y.; Nakagawa, N.; Naemura, K.; Wakabayashi, T.; Shida, T.; Achiba, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4544–4545.