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Isocorannulenofuran: A Versatile Building Block for the Synthesis of Large Buckybowls

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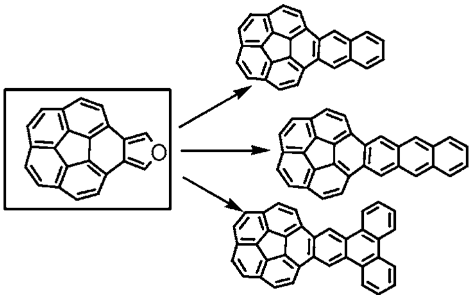
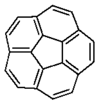
ABSTRACT



Isocorannulenofuran, synthesized in two steps from accessible bromocorannulene, gives Diels–Alder adducts with benzynes which can be deoxygenated to produce large polycyclic aromatic hydrocarbons (PAHs) combining the bowl-shaped corannulene subunit with planar fragments.

Buckybowls, a novel class of polycyclic aromatic hydrocarbons (PAHs) with bowl-shaped carbon networks structurally related to fullerenes have been a subject of significant research due to their unusual structures as well as their potential applications in material sciences.[1] The smallest buckybowl, corannulene (**1**, $C_{20}H_{10}$), has been known for decades, but its limited availability has hampered systematic studies of its chemistry.[2] Development of flash vacuum pyrolytic (FVP) methodology in the 1990s by the Scott research group made corannulene and related systems more accessible.[1b] However, only recent advances in practical, condensed-phase synthetic methods have allowed for gram-scale production of several novel curved-surface systems, including corannulene derivatives as well as larger molecular architectures previously not available by FVP methods.[1]



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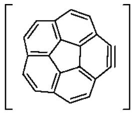

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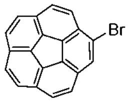

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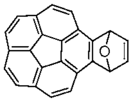

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Recently, we reported the formation of bowl-shaped aryne **2** (corannulyne) by HBr elimination from bromocorannulene **3**, an easily accessible precursor, and its reaction with furan which led to the Diels−Alder cycloaddition product **4**.[3] Removal of the oxygen demonstrated the potential of **2** to produce larger PAHs with corannulene subunits. We have now achieved the elimination of acetylene from **4** to produce isocorannulenofuran (**5**), a reactive diene complementing dienophilic **2** in our pursuit of practical synthetic methodologies leading to large buckybowls. Hence, we report herein the efficient synthesis of isofuran **5** and its successful

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[1] For reviews, see: (a) Sygula, A.; Rabideau, P. W. In *Carbon Rich Compounds*; Haley, M. M., Tykwinski, R. R. Eds.; Willey-VCH: Weinheim, 2006; p 529. (b) Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 4994. (c) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. *Pure Appl. Chem.* **1999**, *71*, 209. (d) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325. (e) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291. (f) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235.

[2] Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380. Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730.

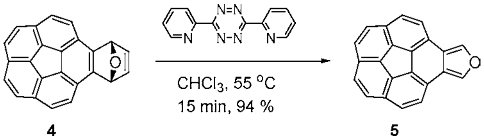
[3] Sygula, A.; Sygula, R.; Rabideau, P. W. *Org. Lett.* **2005**, *7*, 4999.

10.1021/ol0625839 CCC: $33.50

applications in the formation of large conjugated PAHs containing bowl-shaped corannulene subunits.

Considering the importance of [2+4] cycloadditions in the synthesis of large conjugated systems, we recognized the potential of isocorannulenofuran (**5**) as a precursor for novel, bowl-shaped PAHs. Following the well-established "s-tetrazine approach",[4] brief heating of **4** with commercially available 2,6-bis-2-pyridyl-1,2,4,5-tetrazine in chloroform, followed by filtration of the purple reaction mixture through a plug of silica gel, provided isocorannulenofuran **5** in 94% yield (Scheme 1).

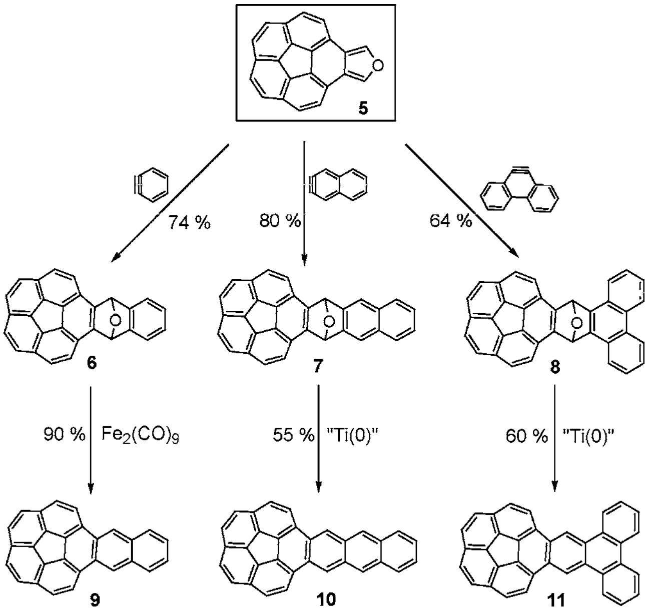
Scheme 1. Synthesis of Isocorannulenofuran



Isobenzofurans, with few exceptions, are too unstable to be isolated. We were pleased to observe that **5** is one of the exceptions and can be isolated and fully characterized by NMR and MS.[5] Although solutions of **5** undergo slow decomposition when exposed to air and light, solid isocorannulenofuran stored under an inert atmosphere in a refrigerator does not show any signs of decomposition for weeks. On the other hand, isofuran **5** is sufficiently reactive to give Diels−Alder cycloaddition products with reactive dienophiles such as benzynes (Scheme 2).

Endoxides **6**[6] and **7**[7] were obtained by gentle reflux of **5** in 1,2-dichloroethane with benzene-diazonium-2-carboxylate and naphthalene-2-diazonium-3-carboxylate, respectively. In contrast, **8**[8] was obtained by overnight heating of **5** with 9-bromophenanthrene at 50 °C in THF with excess $NaNH_2$ and a catalytic amount of KO^{t}Bu. The adducts **6**−**8** were formed in good yields, proving the synthetic usefulness of **5** as a dienophile in [4+2] cycloadditions.

Scheme 2. Reactions of Isocorannulenofuran with Arynes



Despite their significant sizes, adducts **6**−**8** are quite soluble in common organic solvents due to the high degree of nonplanarity introduced by both the corannulene subunits and the presence of two sp^3 hybridized carbon atoms at the oxygen bridge. This allowed for easy characterization of the addition products by both ^{1}H and ^{13}C NMR spectroscopy.

Deoxygenation of the 1,4-endoxides formed by Diels−Alder addition of benzynes to furans is a well-established general method for the construction of aromatic systems.[9] Oxygen extrusion from adducts **6**−**8** provides a synthetic route to extended PAHs which combine bowl-shaped corannulene subunits with planar fragments such as naphthalene, anthracene, and triphenylene. We reacted **5** with diiron nonacarbonyl as the deoxygenating agent resulting in clean formation of naphtho[2,3-*a*]corannulene **9** in an excellent yield of 90%. NMR spectra were identical with the recently published spectra of **9** synthesized by a different route.[10]

In contrast, heating of **7** and **8** in benzene with diiron nonacarbonyl resulted in the formation of mixtures of products as evidenced by NMR spectra. Therefore, we switched to an alternative low-valent titanium method ("Ti(0)") which was previously shown to be a method of choice for the deoxygenation of large 1,4-endoxides.[11] Thus, heating of the adducts with a mixture of $TiCl_4$, $LiAlH_4$, and Et_3N in THF afforded hydrocarbons **10** and **11** in modest yields (Scheme 2, yields not optimized).

Hydrocarbons **10** and **11** have significantly lower solubilities in common organic solvents as compared to their precursors **7** and **8**, respectively. However, the solubilities

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(4) Warrener, R. N. *J. Am. Chem. Soc.* **1971**, *93*, 2346. Russell, R. A.; Marsden, D. E.; Sterns, M.; Warrener, R. N. *Aust. J. Chem.* **1981**, *34*, 1223.

(5) Yellow solid, darkens above 200 °C, mp 225−226 °C. ^{1}H NMR (THF-d_8, 600 MHz) δ 8.46 (2H, s), 7.82 (4H, AB, $\Delta\nu = 10.2$ Hz, $J = 8.6$ Hz), 7.77 (4H, AB, $\Delta\nu = 15.7$ Hz, $J = 8.7$ Hz). ^{13}C NMR (THF-d_8, 75.5 MHz) δ 138.38, 136.93, 136.31, 131.53, 131.27, 129.12, 128.64, 128.10, 127.53, 125.86, 125.39, 124.46. MS *m/z* (rel intensity) 290 (100), 262 (33). HRMS (EI, 25 eV) calcd for $C_{22}H_{10}O$ 290.0732, found 290.0733.

(6) Yellow oily solid. ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 7.88 (2H, d, $J = 8.8$ Hz), 7.84 (2H, d, $J = 8.8$ Hz), 7.79 (4H, AB, $\Delta\nu = 3.9$ Hz, $J = 8.9$ Hz), 7.24 (2H, m), 6.76 (2H, m), 6.66 (2H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 149.12, 148.42, 136.00, 135.04, 134.95, 131.02, 130.72, 127.81, 127.34, 127.28, 127.08, 125.66, 123.56, 120.38, 81.90. HRMS (EI, 25 eV) calcd for $C_{28}H_{14}O$ 366.1039, found 366.1036.

(7) ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.88 (2H, d, $J = 8.8$ Hz), 7.80 (2H, d, $J = 8.8$ Hz), 7.73 (4H, AB, $\Delta\nu = 5.9$ Hz, $J = 8.7$ Hz), 7.55 (2H, s), 7.52 (2H, m), 7.25 (2H, m), 6.78 (2H, s). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 148.00, 143.73, 136.07, 135.46, 134.95, 132.03, 131.10, 130.83, 128.17, 127.95, 127.42, 127.27, 127.03, 126.30, 123.64, 118.81, 81.50. HRMS (EI, 25 eV) calcd for $C_{32}H_{16}O$ 416.1196, found 416.1207.

(8) ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.48 (2H, d, $J = 8.3$ Hz), 8.13 (2H, d, $J = 8.1$ Hz), 7.93 (2H, d, $J = 8.9$ Hz), 7.74 (2H, d, $J = 8.9$ Hz), 7.67 (4H, AB, $\Delta\nu = 14.8$ Hz, $J = 8.6$ Hz), 7.61 (2H, t, $J = 7.4$ Hz), 7.48 (2H, t, $J = 7.4$ Hz), 7.36 (2H, s). ^{13}C NMR (THF-d_8, 75.5 MHz) δ 152.77, 148.42, 136.73, 135.32, 132.28, 131.58, 130.19, 129.76, 129.21, 128.45, 128.29, 127.97, 127.90, 127.67, 126.94, 125.25, 124.53, 124.36, 82.41. HRMS (EI, 25 eV) calcd for $C_{36}H_{18}O$ 466.1352, found 466.1354.

(9) Wong, H. N. C.; Ng, T.-K.; Wong, T.-Y. *Heterocycles* **1983**, *20*, 1815 and references therein.

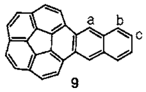
(10) Aphrahamian, I.; Preda, D. V.; Bancu, M.; Belanger, A. P.; Shedarsky, T.; Scott, L. T.; Rabinovitz, M. *J. Org. Chem.* **2006**, *71*, 290.

(11) Wong, H. N. C. *Acc. Chem. Res.* **1989**, *22*, 145. Man, Y.-M.; Mak, T. C. W.; Wong, H. N. C. *J. Org. Chem.* **1990**, *55*, 3214.

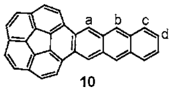
were sufficient to characterize both **10** and **11** by ^{1}H NMR spectroscopy.[12,13] HRMS provided the final proof for the presence of the expected molecular ions of both hydrocarbons.[12,13]

Hydrocarbons **9**−**11** exhibit characteristic low-field signals in their ^{1}H NMR spectra. To facilitate analysis of the spectra, we calculated the GIAO[14] chemical shifts. Application of the Hybrid Density Functional model of Perdew, Burke, and Ernzerhof[15] with a standard 6-31G(d) basis set produced an excellent fit between the calculated and experimental proton chemical shifts with an average deviation of 0.04 ppm for 24 distinct protons in the three hydrocarbons.[16] Both experimental and calculated chemical shifts for the "planar" fragments of **9**−**11** are presented in Table 1. The protons located on the benzene rings abutting the corannulene fragment show the unusually low-field absorptions at 9.11, 9.27, and 9.93 ppm in **9**, **10**, and **11**, respectively. The hydrogen atoms of the corannulene subunits, not shown in Table 1, absorb in the range of 7.82−8.52 ppm, and their experimental chemical shifts are also very well reproduced by the calculations with an average deviation of 0.02 ppm for 12 distinct protons.

Table 1. Experimental (Top Line) and GIAO Calculated (Bottom Line, Italics) ^{1}H NMR Chemical Shifts in Hydrocarbons **9**−**11**



9



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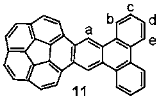

11

	H_a	H_b	H_c	H_d	H_e
9	9.11	8.17	7.64		
	9.08	*8.18*	*7.75*		
10	9.27	8.81	8.16	7.57	
	9.27	*8.72*	*8.19*	*7.68*	
11	9.93	9.04	7.84	7.79	8.74
	9.97	*9.09*	*7.86*	*7.79*	*8.73*

One obvious route to a large, dual-bowl PAH would be reaction of corannulyne **2** with isocorannulenofuran **5**. Unfortunately, all attempts so far with this reaction have failed because no cycloaddition products were isolated at low temperatures while complex mixtures of products were formed at elevated temperatures. Reasons for the failure of this reaction are yet to be determined.

In summary, we described a simple synthesis of isocorannulenofuran which is sufficiently stable to be isolated and stored. Its potential as a synthon for the formation of large PAHs with embedded corannulene subunits is demonstrated by a facile Diels−Alder addition to benzynes which deliver 1,4-endoxides with good yields. The adducts were deoxygenated to form large hydrocarbons **9**−**11** representing a class of PAHs combining both bowl-shaped and planar fragments. Further efforts to apply isocorannulenofuran to the synthesis of even larger molecular scaffolds (molecular tweezers and clips) with corannulene subunits are underway.

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[12] ^{1}H NMR (1,1,2,2-tetrachloroethane-d_2, 600 MHz) δ 9.27 (2H, s), 8.81 (2H, s), 8.36 (2H, d, $J = 8.5$ Hz), 8.16 (2H, m), 8.02 (2H, d, $J = 8.5$ Hz), 7.90 (2H, d, $J = 8.6$ Hz), 7.86 (2H, d, $J = 8.6$ Hz), 7.57 (2H, m). HRMS (EI, 25 eV) calcd for $C_{32}H_{16}$ 400.1247, found 400.1247.

[13] ^{1}H NMR (1,1,2,2-tetrachloroethane-d_2, 600 MHz) δ 9.93 (2H, s), 9.04 (2H, d, $J = 7.9$ Hz), 8.74 (2H, d, $J = 7.9$ Hz), 8.54 (2H, d, $J = 8.5$ Hz), 8.09 (2H, d, $J = 8.5$ Hz), 7.95 (2H, d, $J = 8.6$ Hz), 7.90 (2H, d, $J = 8.6$ Hz), 7.84 (2H, t, $J = 7.0$ Hz), 7.79 (2H, t, $J = 7.0$ Hz). HRMS (EI, 25 eV) calcd for $C_{36}H_{18}$ 450.1403, found 450.1420.

[14] Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

[15] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

[16] The Gaussian03 program package was used for all calculations. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.