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Synthesis of a New $C_{32}H_{12}$ Bowl-Shaped Aromatic Hydrocarbon: Acenaphtho[3,2,1,8-*ijklm*]diindeno[4,3,2,1-*cdef*:1′,2′,3′,4′-*pqra*]triphenylene

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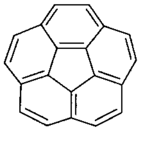
Abstract: The flash vacuum pyrolysis (FVP) of 1,2-bis(2-bromophenyl)-4,9-dibromocorannulene leads to a new $C_{32}H_{12}$ buckybowl.

Since the discovery of C_{60}, curved fullerene fragments known as "buckybowls" have been the subject of an active field of research.[1] Two general strategies for the synthesis of these novel polycyclic aromatic hydrocarbons have been developed. Methods incorporating flash vacuum pyrolysis (FVP) introduced by the Scott group[2a] have been successful in the production of corannulene (**1**),[2] the smallest member of this family, and other larger buckybowls including $C_{32}H_{12}$ (**2**)[3] and $C_{36}H_{12}$ (**3**),[4] the largest fullerene fragments synthesized to date. More recently, Scott et al.[5] have employed the FVP method for the synthesis of buckminsterfullerene itself.



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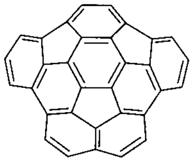

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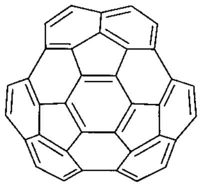

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While the high temperature, low concentration conditions in FVP appear to promote the formation of intramolecular, highly strained bonds, yields not only vary from moderate to very low but also are on a milligram scale. Furthermore, the required conditions generally exclude the possibility of functionality in the products. In contrast, the nonpyrolytic methods, reported by Siegel[6] and later by Scott[7] as well as our group,[8] have shown substantial yield improvements, allow for larger scale, and can give functionalized products since nonvolatile precursors can be used in the critical ring-forming step. These benefits suggest that nonpyrolytic schemes will be important routes for the preparation of larger buckybowls or perhaps even buckminsterfullerene in the future.

Following our recent discovery that tetrabromocorannulene can be conveniently prepared on a large scale by sodium hydroxide-promoted coupling of tetrakis(dibromomethyl)fluoranthene,[8] we began exploring a solution-phase approach to the synthesis of a number of corannulene derivatives.[9] Herein, we report that the pyrolysis of one of these derivatives, 1,2-bis(2-bromophenyl)-4,9-dibromocorannulene (**7**), leads to the formation of a new $C_{32}H_{12}$ buckybowl, **6**, isomeric with **2** (see Scheme 1).

Thus, condensation of 3,8-dimethylacenaphthenequinone with 3-pentanone under Knoevenagle conditions gave the carbinol[10] that, without purification, underwent a Diels−Alder cycloaddition with bis(2-bromophenyl)ethyne[11] to give the hexasubstituted fluoranthene **4** in 36% yield. Treatment of **4** with an excess of *N*-bromosuccinimide under irradiation with a lamp led to the formation of hexabromide **5** exclusively.[12] Refluxing **5** with sodium hydroxide in dioxane/water (∼3:1) afforded, almost quantitatively, the desired product **7**. Encouraged by results in our laboratory on a related system,[14] we applied the recently published strategy for dibenzo[*a*,*g*]corannulene[7] and its dihydrocyclopenta analogue[13] to **7** in the hope of achieving formation of two five-membered rings resulting in **8**. To this end, we examined several palladium catalysts (specifically, Pd(PCy$_3$)$_2$Cl$_2$, Pd(PPh$_3$)$_2$Cl$_2$, and palladacycles) with organic bases (DBU, *N*-methyldicyclohexylamine) in different solvents (DMAc, DMF) with no success. Only debromination, without the desired ring closures, was observed.

Therefore, having gram quantities of **7**, we decided to pursue the pyrolytic method. Several years ago, we reported the synthesis of **2** by FVP, albeit in very low yield (0.1%). We thought precursor **7**, already possessing a curved surface with four bromines in the desired positions, should be a better choice. To our surprise, we accomplished not the two expected ring closures but

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(1) For recent reviews see: (a) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242. (b) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291−300. (c) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325−13370. (d) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Amselms, R. B. M.; Bratcher, M. S.; Hagen, S. *Pure Appl. Chem.* **1999**, *71*, 209−219.

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

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(7) Reish, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1427−1430.

(8) Sygula, A.; Rabideau, P. W. *J. Am. Chem.* **2000**, *122*, 6323−6324.

(9) (a) Xu, G.; Sygula, A.; Marcinow, Z.; Rabideau, P. W. *Tetrahedron Lett.* **2000**, *41*, 9931−9934. (b) Xu, G.; Sygula, A.; Marcinow, Z.; Rabideau, P. W. *Tetrahedron* **2001**, *57*, 3637−3644.

(10) Borchart, A.; Hardcastle, K.; Gantzel, P.; Siegel, J. S. *Tetrahedron Lett.* **1993**, *34*, 273.

(11) Diercks, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 266.

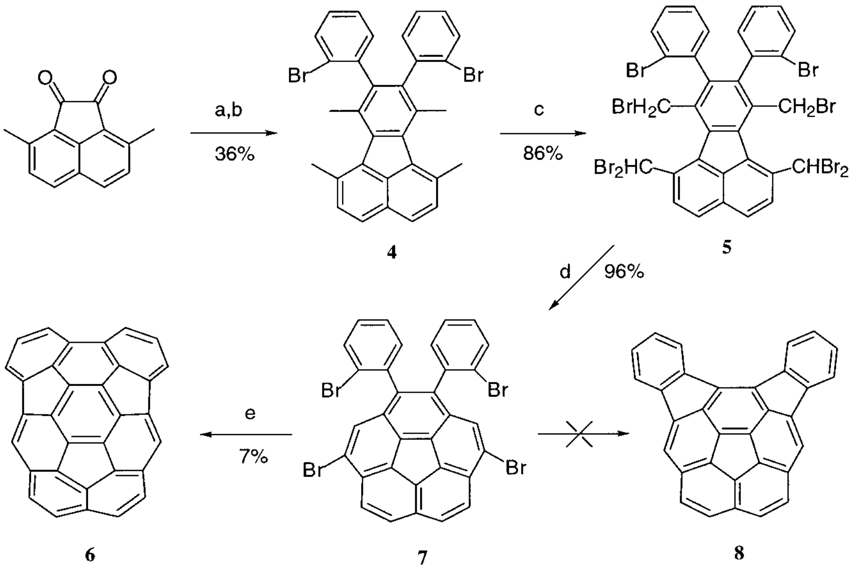
(12) In our preliminary study, 1,6,7,10-tetramethyl-8,9-diphenylfluoranthene was used as an intermediate. However, even with a very large excess of NBS and refluxing for several days, the single major product contained six bromines instead of the expected eight. From these observations, it is clear that the presence of phenyl or bromophenyl groups ortho to the methyl groups inhibits the further addition of bromines.

(13) Marcinow, Z.; Sygula, A.; Ellern, A.; Rabideau, P. W. *Org. Lett.* **2001**, *3*, 3527−3529.

(14) Preliminary results on the palladium-catalyzed coupling of 2-(trifluoromethanosulfonyloxy)phenylcorannulene gave monoindenocorannulene in modest yield.

10.1021/jo025645r CCC: $22.00

Scheme 1[a]



[a] Reagents and conditions: (a) 3-pentanone, NaOH/MeOH, rt, overnight; (b) bis(2-bromophenyl)ethyne, Ac_2O, 160 °C, sealed tube, 24 h; (c) NBS (excess), *hν*, benzene, benzoyl peroxide, 24 h; (d) dioxane/water (~3:1), NaOH, reflux 30 min; (e) FVP, 1050 °C, 1 mmHg.

three, and with a significant improvement in yield as compared with isomer **2**. Indeed, FVP of **7** at 1050 °C (400 mg in ca. 80 mg batches) following a quick silica gel chromatography of pyrolysate gave 16 mg (7%) of **6**, shown to be a $C_{32}H_{12}$ hydrocarbon by mass spectroscopy. In agreement with the assigned structure, ^1H NMR shows the expected four doublets, one singlet and a doublet of doublets, while the ^{13}C NMR spectrum shows the expected six methine carbons and 11 quaternary signals. The most distinctive features were significant shifts of two quaternary signals to lower field (δ 151.3 and 153.5), consistent with other large buckybowls such as **2** and **3**.

The procedure described here provides a short route to the previously unknown $C_{32}H_{12}$ fullerene fragment. Our attempts to achieve the desired ring closures in the final step by solution-phase chemistry have, so far, not met with success, hence the rather unusual combination of both solution and FVP methods in buckybowl synthesis.

Experimental Section

General Methods. ^1H (300 MHz) and ^{13}C (75.4 MHz) NMR spectra were recorded in $CDCl_3$ (δ = 7.26 and 77.23 ppm, respectively) unless otherwise noted. High-resolution mass spectroscopy (HRMS) was preformed by the Mass Spectroscopy Laboratory at ISU. Melting points are uncorrected. The flash vacuum pyrolysis apparatus was purchased from Kontes Glass, Inc., and the following procedure was employed. The sample was dissolved in CH_2Cl_2 and transferred to a small glass boat filled with glass wool. The solvent was evaporated, and the boat was placed in the inlet chamber wrapped with a heating mantle that allowed sublimation of the substrate under vacuum with a small flow of nitrogen. The pyrolysate condensed on the sidearm of the quartz tube, exiting the chamber, which was cooled with dry ice/acetone. Bis(2-bromophenyl)ethyne[11] and 3,8-dimethylacenaphthenequinone[10] were both synthesized according to published procedures.

1,6,7,10-Tetramethyl-8,9-bis(bromophenyl)fluoranthene (4). To a suspension of 3,8-dimethylacenaphthenequinone (3 g, 14.3 mmol) and 3-pentanone (5 mL) in 50 mL of methanol was added a 20% methanolic solution of potassium hydroxide (3 mL). The mixture was stirred at room temperature overnight, diluted with water, and extracted with dichloromethane (DCM). The organic layer was washed with aqueous ammonium chloride and water (three times), dried, and evaporated to give the cyclopentadienone (2.43 g, 65%). The crude product was transferred to a 200 mL sealed reaction vessel. Bis(2-bromophenyl)ethyne (3.19 g, 9.5 mmol) and acetic anhydride (60 mL) were added, and the vessel was sealed and placed in an oil bath at 160 °C for 24 h. After cooling, the mixture was poured onto ice, and the dark brown solid that separated was chromatographed on silica gel with hexane/DCM (10:1) to yield 2.92 g (36% for two steps) of the desired product (yellow solid): mp 188−190 °C; ^1H NMR δ 7.72 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.42−7.34 (m, 4H), 7.14 (t, J = 7.5 Hz, 2H), 7.01 (t, J = 7.5 Hz, 2H), 2.83 (s, 6H), 2.41 (s, 6H); ^{13}C NMR δ 142.37, 140.31, 140.15, 135.01, 134.06, 132.37, 132.26, 131.89, 130.66, 128.81, 128.58, 127.33, 126.72, 126.40, 125.16, 24.92, 22.11. Anal. Calcd for $C_{32}H_{24}Br_2$: C, 67.63; H, 4.26. Found: C, 67.31; H, 4.17.

1,6-Bis(dibromomethyl)-7,10-bis(bromomethyl)-8,9-bis(2-bromophenyl)fluoranthene (5). A 1.32 g (2.3 mmol) portion of **4**, *N*-bromosuccinimide (4.0 g, 22.5 mmol), and benzoyl peroxide (20 mg) in dry benzene (100 mL) were irradiated with a sun lamp and refluxed for 20 h. The solution was washed (three times) with water, dried over magnesium sulfate, filtered, and evaporated to yield, after recrystallization from toluene−ethanol, a yellow solid (2.08 g, 86%): mp 180−182 °C; ^1H NMR δ 8.35 (d, J = 8.7 Hz, 2H), 7.98 (d, J = 8.7 Hz, 2H), 7.91 (s, 2H; $CHBr_2$), 7.53−7.39 (m, 4H), 7.13−7.08 (m, 4H), 4.66 (s, 4H); ^{13}C NMR δ 144.33, 139.86, 138.66, 137.24, 133.51, 133.23, 133.02, 132.61, 132.19, 131.69, 130.49, 129.79, 129.09, 129.04, 126.94, 42.90, 33.24; MS (EI, 70 eV) *m/z* (rel intensity) 1040 (4), 959 (12), 879 (8), 800 (21), 720 (10), 642 (18), 561 (13), 481 (32), 400 (100). Anal. Calcd for $C_{32}H_{18}Br_8$: C, 36.90; H, 1.74. Found: C, 36.69; H, 1.87.

1,2-Bis(2-bromophenyl)-4,9-dibromocorannulene (7). A 370 mg portion of sodium hydroxide pellets was added to a stirred suspension of **5** (850 mg) in 40 mL of dioxane and 12 mL of water. The reaction mixture was refluxed for 30 min, cooled, poured into water, and acidified with hydrochloric acid. The precipitate was filtered, washed thoroughly with water and ethanol, and dried to give a pale yellow solid (560 mg, 96%): mp 258−260 °C; ^1H NMR δ 7.93 (m, 4H), 7.63−7.60 (m, 2H), 7.56 (s, 2H), 7.41−7.38 (m, 2H), 7.23−7.12 (m, 4H); ^{13}C NMR δ 138.51, 137.81, 135.74, 135.45, 133.67, 132.56, 131.66, 131.48, 131.05, 130.67, 129.75, 129.49, 128.54, 127.57, 127.35, 124.51, 122.11; MS (EI, 70 eV) *m/z* (rel intensity) 719 (45), 717 (58), 715 (38), 557 (30), 397 (100); HRMS (EI, 70 eV) calcd for $C_{32}H_{14}Br_4$ 717.7788, found 717.7800.

Acenaphtho[3,2,1,8-*ijklm*]diindeno[4,3,2,1-*cdef*:1′,2′,3′,4′-*pqra*]triphenylene (6). Flash vacuum pyrolysis of **7** (400 mg in ca. 80 mg portions) at 1050 °C under vacuum with a slow nitrogen bleed (~1 mmHg) over a period of 2 h gave 28 mg of pyrolysate. Column chromatography with hexane/dichloromethane (10:1) on silica gel gave 16 mg of **6** (7% yield): mp 290−292 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.01 (d, $J = 8.4$ Hz, 2H), 7.56 (s, 2H), 7.55 (d, $J = 7.2$ Hz, 2H), 7.46 (d, $J = 8.8$ Hz, 2H), 7.37 (d, $J = 8.8$ Hz, 2H), 7.37 (dd, $J = 7.2$, 8.4 Hz, 2H); ^{13}C NMR (75.4 MHz, CDCl$_3$) δ 153.50, 151.30, 148.40, 144.37, 140.46, 138.59, 138.29, 136.79, 135.34, 134.92, 132.05, 129.11, 128.76, 128.72, 127.09, 126.93, 123.52, 119.29 (last six CH by NMR attached proton test); MS (EI, 70 eV) *m/z* (rel intensity) 396 (100), 324 (60), 198 (56); HRMS (EI, 70 eV) calcd for $C_{32}H_{12}$ 396.0939, found 396.0946.

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