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Interconversions of Aryl Radicals by 1,4-Shifts of Hydrogen Atoms. A Synthesis of Benzo[*a*]corannulene

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Abstract: Aryl radicals generated ortho to aryl substituents by flash vacuum pyrolysis (FVP) of the corresponding aryl chlorides are shown to be capable of transferring hydrogen atoms between the ortho and ortho′ positions (1,4-shifts of hydrogen atoms). In the examples described here, the rearranged aryl radicals are trapped by subsequent radical cyclization reactions. For example, FVP of 2-(*o*-chlorophenyl)-benzo[*c*]phenanthrene gives 1-phenylbenzo[*ghi*]fluoranthene as the major product by homolysis of the C−Cl bond, 1,4-shift of a hydrogen atom out of the sterically congested cove region to the radical center, cyclization of the rearranged radical, and rearomatization of the molecule by loss of the other cove region hydrogen. In a control experiment run under the same conditions, FVP of 2-phenylbenzo[*c*]phenanthrene, which lacks a radical precursor, gave primarily recovered starting material. When the FVP was repeated using 2-(2,6-dichlorophenyl)benzo[*c*]phenanthrene as the starting material, benzo[*a*]corannulene was obtained as the major product, presumably by the same cascade of events to produce 1-(*o*-chlorophenyl)benzo[*ghi*]-fluoranthene, which then suffers a second radical cyclization spontaneously under the high-temperature conditions to give the geodesic polyarene.

Introduction

The C−H bonds of aromatic hydrocarbons are exceptionally strong. A bond dissociation energy of 113.5 ± 0.5 kcal/mol has been measured for the C−H bond of benzene,[1] for example. Consequently, thermodynamics disfavor the abstraction of hydrogen atoms from aromatic hydrocarbons by all but the most reactive radical species (e.g., •OH). Abstraction of a hydrogen atom from an aromatic hydrocarbon by an aryl radical (•Ar), however, should be nearly thermoneutral and ought not to suffer from any significant thermodynamic penalty. *Intramolecular* hydrogen atom abstractions of this sort represent potentially reversible pathways for the rearrangement of aryl radicals that can be thought of nominally as "radical center migrations" in aryl radicals.

We first became interested in such radical rearrangements in connection with the 1,2-shift of hydrogen atoms in aryl radicals[2] and report here an extension of our work on that rearrangement to the related 1,4-shifts (Figure 1). To search for examples of the latter rearrangement, we adopted the same strategy as the one used to demonstrate the feasibility of 1,2-shifts. Thus, specific aryl radicals are generated in the gas phase at low pressure by flash vacuum pyrolysis (FVP) of the corresponding aryl halides. At the high temperatures of the FVP experiment, the initially formed radicals have sufficient energy to surmount the rather significant energy barriers expected for these hydrogen atom shifts.[3] In the systems studied, special structural features

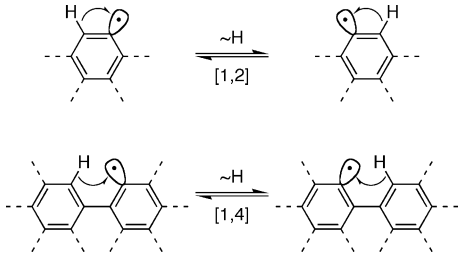

Figure 1. Basic features of the 1,2- and 1,4-shifts of hydrogen atoms in aryl radicals.

were incorporated to simultaneously (1) render the hydrogen atom shift exothermic and (2) provide an escape channel for the rearranged radical to yield a product that could serve as a diagnostic for the hydrogen shift.

As shown in Figure 2, the driving force we built in for the 1,2-shift was the relief of steric congestion in the cove region of a [4]helicene. The escape channel for the rearranged radical was C−C bond formation across the mouth of the cove region, followed by loss of the other cove region hydrogen atom to rearomatize the molecule. Deuterium labeling confirmed that the hydrogen atom in the product attached at the original site of the halogen atom (shown in Figure 2) was indeed the hydrogen that came from the ortho-position in the cove region.[2]

(1) Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590−2599.
(2) Brooks, M. A.; Scott, L. T. *J. Am. Chem. Soc.* **1999**, *121*, 5444−5449.
(3) Density functional calculations predict relatively high activation energies for these hydrogen shifts: (a) An activation energy of nearly 60 kcal/mol has been calculated for the 1,2-shift of hydrogen in phenyl radical.[2] (b) An activation energy of 24 kcal/mol has been calculated for the 1,4-shift of hydrogen between the ortho and ortho' positions in the 2-biphenyl radical: Cioslowski, J.; Liu, G.; Moncrieff, D. *J. Org. Chem.* **1996**, *61*, 4111−4114.

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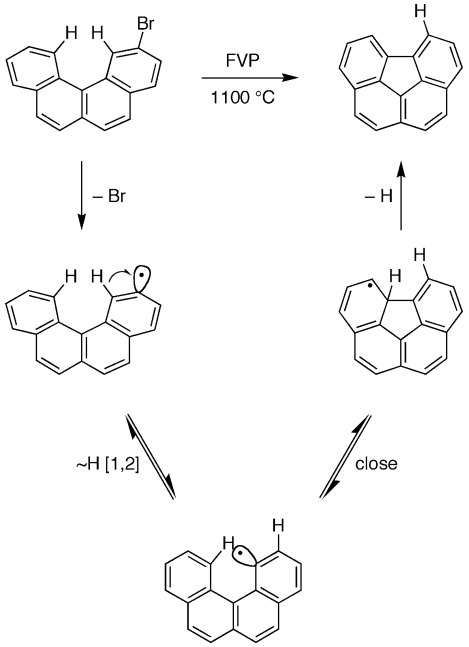


Figure 2. Strain relief provides a driving force for this 1,2-shift of a hydrogen atom in an aryl radical, and ring closure traps the rearranged radical.

Results and Discussion

To test for the 1,4-shift of a hydrogen atom in an aryl radical, we prepared 2-(*o*-chlorophenyl)benzo[*c*]phenanthrene (**1**) by a Suzuki−Miyaura coupling of 2-chlorophenylboronic acid with 2-bromo[4]helicene[4] and subjected it to FVP. A chlorine atom was chosen as the radical precursor instead of a bromine atom in this case in order to minimize secondary Suzuki−Miyaura couplings of the desired product with the boronic acid. A minor drawback of this substitution is the recovery of some unchanged starting material after the FVP, owing to the greater strength of the C−Cl bond, relative to that of a C−Br bond; however, this problem could be abated somewhat by loosely packing a section of the pyrolysis tube with quartz wool.

Figure 3 outlines the course we expected this reaction to take if the initially formed radical were able to rearrange by a 1,4-shift of hydrogen. Thus, homolysis of the C−Cl bond should generate the initial radical, a 1,4-shift of hydrogen would transform that into a cove region radical, and the rearranged radical would cyclize to give 1-phenylbenzo[*ghi*]fluoranthene (**2**).

When the FVP of **1** was conducted at 1100 °C/0.7 mmHg, hydrocarbon **2** was indeed obtained as the major product (33% isolated yield by HPLC), together with a small amount of benzo[*ghi*]fluoranthene (**3**), traces of benzo[*a*]corannulene (**8**), and recovered starting material (**1**) in a ratio of 56:7:3:34, respectively[5] (material balance 55−60%).[6] The $C_{18}H_{10}$ hydrocarbon **3** is an analogue of the major product (**2**) that is missing the phenyl ring. We do not know the fate of the lost phenyl ring or the mechanism by which the C−C bond was cleaved, but it is important to note that no significant amounts of products such as **4** or **5** were formed in which the five-membered ring had failed to close; essentially every product molecule obtained that had lost a chlorine atom had also cyclized. The trace quantities of benzo[*a*]corannulene (**8**) presumably arise from a "cascade" cyclization process similar to that seen in other radical cyclization reactions.[7]

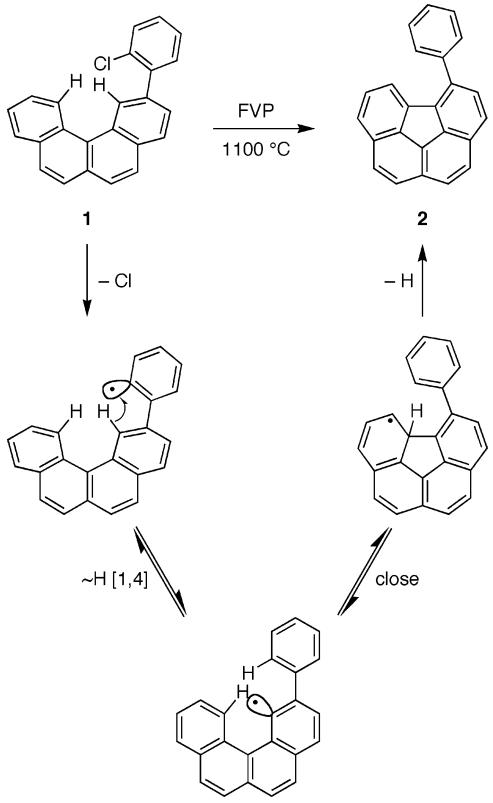
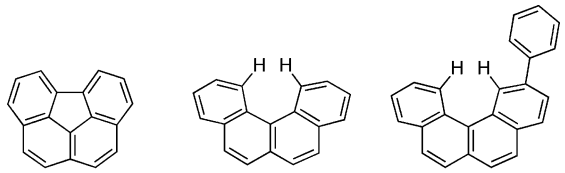


Figure 3. Strain relief provides a driving force for this 1,4-shift of a hydrogen atom in an aryl radical, and ring closure traps the rearranged radical.



As a control experiment, to determine whether the incorporation of a radical precursor is really necessary to promote ring closure across the mouth of the [4]helicene cove region ("cyclodehydrogenation"), we synthesized 2-phenyl[4]helicene (**5**), the analogue of **1** with no chlorine atom attached, and subjected it to FVP under the same conditions. In this case, the product mixture consisted predominantly of unchanged starting material (**5**), accompanied by small amounts of the cyclized material (**2**) and phenyl-loss products, both closed (**3**) and open (**4**), in a ratio[5] of 55:15:15:15 (material balance[6] 60%). Thus, the background "cyclodehydrogenation" reaction, although not zero, is low under our conditions. Taken together, these data strongly implicate the 1,4-shift of a hydrogen atom depicted in Figure 3 as the most reasonable explanation for the efficient five-membered ring closure in the FVP of **1**.

(4) The 2-bromo[4]helicene = 2-bromobenzo[*c*]phenanthrene was synthesized as described in ref 2.
(5) The molar ratio of products in the pyrolysate was determined by integration of the ^{1}H NMR spectrum of the mixture.
(6) The material balance as a percent was calculated from the weight material balance, correcting for the different molecular weights and abundances[5] of the various components.
(7) Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 4994−5007.

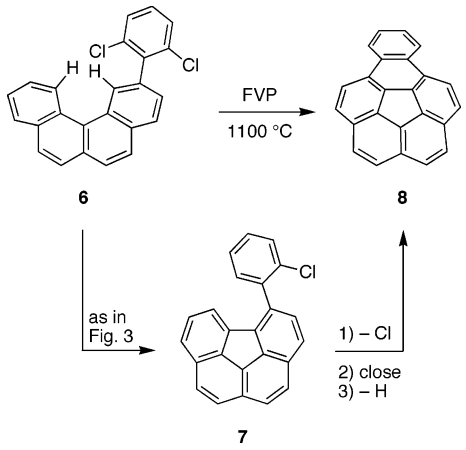


Figure 4. A synthesis of benzo[*a*]corannulene (**8**) that exploits the 1,4-shift of a hydrogen atom in an aryl radical to promote the first ring closure.

In the light of these results, we devised a scheme to exploit the 1,4-shift of hydrogen as the key step in a synthesis. Toward this end, 2-(2,6-dichlorophenyl)benzo[*c*]phenanthrene (**6**) was prepared by a Negishi coupling[8] of 2,6-dichlorophenylzinc with 2-bromo[4]helicene. FVP of this starting material, we reasoned, should give a cyclized product analogous to **2** but with the second chlorine atom still attached (i.e., **7**). Homolysis of the second C−Cl bond at that stage would then be expected to lead to the closure of a new six-membered ring, thereby producing the bowl-shaped polycyclic aromatic hydrocarbon benzo[*a*]-corannulene (**8**) (Figure 4).[9] Gratifyingly, FVP of the 2,6-dichlorophenyl compound **6** at 1100 °C/0.7 mmHg gave benzo[*a*]corannulene (**8**) as the major product. A small amount of the starting material survived again in this case, but the other byproducts formed (**3** and **7**) both lost their cove region hydrogens and closed the five-membered ring. The ratio of products obtained,[5] in order of decreasing abundance, was **8**:**7**:**3**:**6** = 47:28:14:11. From this mixture, benzo[*a*]corannulene (**8**) was obtained by chromatographic purification in 16% isolated yield. The only other synthesis of benzo[*a*]corannulene (**8**) published to date also employed a FVP in the final step that gave the hydrocarbon in ca. 6% yield.[10]

Conclusions

Evidence has been found that confirms the feasibility of 1,4-shifts of hydrogen atoms in aryl radicals at high temperatures in the gas phase, under the conditions of flash vacuum pyrolysis (1100 °C/0.7 mmHg). Such radical rearrangements can lead to chemical reactions in regions of a molecule that are four atoms away from the site where a radical is initially generated. These hydrogen migrations between aryl carbon atoms are not expected to be facile under ordinary laboratory conditions in solution, but they can expand the utility of flash vacuum pyrolysis as a method for building polycyclic aromatic hydrocarbon ring systems, including strained geodesic polyarenes. A synthesis of benzo[*a*]corannulene (**8**) that depends on the 1,4-shift of a hydrogen atom is presented as a demonstration of this strategy.

Experimental Section

General. Tetrahydrofuran was purified by distillation under nitrogen from the potassium ketyl of benzophenone. All other solvents and commercial chemicals were of the best available grade and were used without further purification, unless otherwise stated. Proton NMR chemical shifts are reported in ppm downfield from tetramethylsilane with deuteriochloroform (δ = 7.26 ppm) as the reference standard, unless otherwise specified. Carbon NMR shifts are reported in ppm downfield from tetramethylsilane with deuteriochloroform (δ = 77.16 ppm) as the reference standard. Preparative thin layer chromatographies were performed on 20 cm × 20 cm Analtech Uniplate Taper plates, Alumina GF. For column chromatographies, silica gel 32−63 μm was used. High-performance liquid chromatographies (HPLC) were performed on a Waters Delta 600 with a Supelcosil LC-PAH (25 cm × 21.2 mm) reversed-phase column. Gas chromatograph−mass spectrometer (GC−MS) analyses were performed on a Thermo Finnigan Trace DSQ with electron impact ionization with a Thermo TR-5MS (15 m × 0.25 mm i.d. × 0.25 μm film) column. High-resolution mass spectrometry (HRMS) was performed by the Mass Spectroscopy Laboratory, School of Chemical Sciences, University of Illinois. Elemental analyses were performed by Robertson Microlit Laboratories. Melting points are uncorrected.

2-(*o*-Chlorophenyl)benzo[*c*]phenanthrene (1). $Pd(PPh_3)_4$ (30 mg, 0.026 mmol), K_2CO_3 (208 mg, 1.5 mmol), 2-chlorophenylboronic acid (468 mg, 3.0 mmol), and 2-bromobenzo[*c*]phenanthrene[4] (420 mg, 1.5 mmol) were added to a 10-mL oven-dried pressure tube equipped with a magnetic stirring bar. The tube was evacuated and refilled with nitrogen three times, and then THF (1.5 mL) and water (0.3 mL) were added. The reaction mixture was stirred at 90 °C for 15 h, cooled back to room temperature, and flashed through a short pad of silica gel, using dichloromethane to flush the silica. The filtrate was concentrated and purified by column chromatography on silica gel with dichloromethane and hexanes (1:9) as eluant to yield 393 mg (85%) of 2-(*o*-chlorophenyl)benzo[*c*]phenanthrene (**1**) as a white solid: mp 106−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, J = 1.2 Hz, 1 H), 9.18 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 8.0, 1H), 8.02 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.73 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.68 (ddd, J = 6.8 Hz, J = 8.4 Hz, J = 1.6 Hz, 1H), 7.62 (ddd, J = 8.0 Hz, J = 6.8 Hz, J = 1.2 Hz, 1H), 7.58 (dd, J = 7.2 Hz, J = 2.0 Hz, 1H), 7.47 (dd, J = 7.2 Hz, J = 2.4 Hz, 1H), 7.41−7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.84, 137.19, 133.49, 132.82, 132.72, 131.87, 131.27, 130.26, 130.14, 130.01, 128.82, 128.66, 128.53, 128.25, 127.96, 127.68, 127.56, 127.34, 127.28, 127.16, 127.03, 126.83, 126.36, 125.93. Anal. Calcd for $C_{24}H_{15}Cl$: C, 85.07; H, 4.46. Found: C, 84.90; H, 4.38.

1-Phenylbenzo[*ghi*]fluoranthene (2). Flash vacuum pyrolysis was performed on 50 mg of 2-(*o*-chlorophenyl)benzo[*c*]phenanthrene (**1**) at 1100 °C, with a steady flow of nitrogen carrier gas (final pressure 0.65−0.75 mmHg), as previously described.[11] The crude pyrolysate (25 mg) was dissolved in dichloromethane and flashed through a short pad of alumina to yield a mixture of 1-phenylbenzo[*ghi*]fluoranthene (**2**), unchanged starting material (**1**), benzo[*ghi*]fluoranthene (**3**), and benzo[*a*]corannulene (**8**), in a ratio of 56:34:7:3, respectively.[5] The crude pyrolysate was partially purified by flash chromatography on alumina with dichloromethane and hexanes (1:9) as eluant. Further purification by HPLC on a C18 reversed-phase column with acetonitrile and water

(8) The Suzuki−Miyaura couplings did not work as well in this more hindered case as it did for the syntheses of **1** and **5**.

(9) The closely related dibenzo[*a*,*g*]corannulene has been synthesized by a FVP route involving two aryl radical cyclizations of the type **7** → **8**: (a) Bratcher, M. S.; Scott, L. T. In *Abstracts of Papers, 207th National* Meeting *of the American Chemical Society;* American Chemical Society: Washington, DC, March 1994, San Diego, CA.; abstr. ORGN 420. (b) Bratcher, M. S., Ph.D. dissertation, Boston College, Chestnut Hill, MA, 1996. (c) Reisch, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1427−1430.

(10) Mehta, G.; Srirama Sarma, P. V. V. *Chem. Commun.* **2000**, 19−20. See also: McComas, C. C.; Scott, L. T. In *Abstracts of Papers, 211th National Meeting of the American Chemical Society*; American Chemical Society: Washington, DC, March 1996, New Orleans, LA; abstr. CHED-556.

(11) (a) Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8743−8744. (b) Necula, A.; Scott, L. T. *J. Anal. Appl. Pyrolysis* **2000**, *54*, 65−87. A 4 cm section of the pyrolysis tube near the center of the hot zone was loosely packed with quartz wool in order to diminish the amount of starting material that passed through the tube without change.

(9:1) as eluant yielded 15 mg (33%) of 1-phenylbenzo[*ghi*]fluoranthene (**2**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 6.8 Hz, 1H), 8.03−7.97 (m, 3H), 7.95 (d, J = 8.8 Hz, 2H), 7.95 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.63 (brt, 2H), 7.57 (dd, J = 7.2 Hz, J = 6.8 Hz, 1H), 7.53 (tt, J = 7.6 Hz, J = 1.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.56, 139.94, 137.33, 133.94, 133.71, 133.47, 132.97, 130.34, 129.45, 128.92, 128.40, 128.22, 127.89, 127.22, 127.14, 127.01, 126.92, 126.62, 126.57, 125.14, 125.05, 124.80; HRMS (EI, *m*/*z*) calcd for $C_{24}H_{14}$ (M^+) 302.1096, found 302.1088.

2-Phenylbenzo[*c*]phenanthrene (5). $Pd(PPh_3)_4$ (30 mg, 0.026 mmol), K_2CO_3 (208 mg, 1.5 mmol), phenylboronic acid (368 mg, 3.0 mmol), and 2-bromobenzo[*c*]phenanthrene[4] (420 mg, 1.5 mmol) were added to a 10-mL oven-dried pressure tube equipped with a magnetic stirring bar. The tube was evacuated and refilled with nitrogen three times, and then THF (1.5 mL) and water (0.3 mL) were added. The reaction mixture was stirred at 90 °C for 15 h, cooled back to room temperature, and flashed through a short pad of silica gel, using dichloromethane to flush the silica. The filtrate was concentrated and purified by column chromatography on silica gel with dichloromethane and hexanes (1:9) as eluant to yield 435 mg (95%) of 2-phenylbenzo[*c*]phenanthrene (**5**) as a white solid: mp 132−133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (d, J = 0.8 Hz, 1H), 9.20 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.4, 1H), 8.05 (dd, J = 7.8 Hz, J = 1.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.90 (dd, J = 8.4 Hz, J = 2.0 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.81 (dd, J = 8.0 Hz, J = 1.6 Hz, 2H), 7.71 (ddd, J = 8.4 Hz, J = 7.0 Hz, J = 1.4 Hz, 1H), 7.65 (ddd, J = 8.0 Hz, J = 6.8 Hz, J = 1.2 Hz, 1H), 7.54 (brt, J = 8.0 Hz, J = 6.0 Hz, 2H), 7.43 (tt, J = 7.6 Hz, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.53, 138.87, 133.57, 132.62, 131.33, 130.63, 130.38, 129.01, 128.63, 127.83, 127.62, 127.60, 127.37, 127.12, 126.98, 126.89, 126.32, 125.90, 125.34. Anal. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30. Found: C, 94.59; H, 5.31.

2,6-Dichlorophenylzinc Chloride (0.18 M in THF). To a stirred solution of 1,3-dichlorobenzene (1.47 g, 10 mmol) in THF (25 mL) at −78 °C was slowly added (20 min) *n*-BuLi (5.5 mL, 11 mmol, 2.0 M in hexane) from a syringe. The reaction mixture was stirred at −78 °C for 1.5 h to form a white slurry. Then $ZnCl_2$ (24 mL, 0.5 M in THF) was added via syringe. The mixture was allowed to warm slowly to room temperature and was then stirred for another 15 min.

2-(2,6-Dichlorophenyl)benzo[*c*]phenanthrene (6). $Pd_2(dba)_3$ (13.6 mg, 0.015 mmol), ligand S-Phos (24.8 mg, 0.060 mmol), and 2-bromobenzo[*c*]phenanthrene[4] (420 mg, 1.5 mmol) were added to an oven-dried Schlenk tube equipped with a magnetic stirring bar. The tube was evacuated and refilled with nitrogen three times, and then 2,6-dichlorophenylzinc chloride (12.4 mL, 2.23 mmol, 0.18 M) was added. The reaction mixture was stirred at 70 °C for 15 h, cooled back to room temperature, and flashed through a short pad of silica gel, using dichloromethane to flush the silica. The filtrate was concentrated and purified by column chromatography on silica gel with dichloromethane and hexanes (15:85) as eluant to yield 502 mg (83%) of 2-(2,6-dichlorophenyl)benzo[*c*]phenanthrene (**6**) as a white solid: mp 160−162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (d, J = 8.0 Hz, 1H), 9.03 (d, J = 0.8 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.02 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.67 (ddd, J = 8.4 Hz, J = 6.8 Hz, J = 1.6 Hz, 1H), 7.61 (ddd, J = 8.0 Hz, J = 6.8 Hz, J = 1.2 Hz, 1H), 7.55 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.80, 135.29, 134.66, 133.50, 132.98, 131.21, 130.26, 130.01, 129.20, 129.03, 128.53, 128.35, 128.25, 127.88, 127.72, 127.56, 127.47, 127.26, 127.23, 126.79, 126.40, 125.95. Anal. Calcd for $C_{24}H_{14}Cl_2$: C, 77.22; H, 3.78. Found: C, 76.92; H, 3.62.

Benzo[*a*]corannulene (8). Flash vacuum pyrolysis was performed on 62 mg of 2-(2,6-dichlorophenyl)benzo[*c*]phenanthrene (**6**) at 1100 °C, with a steady flow of nitrogen carrier gas (final pressure: 0.65−0.75 mmHg), as previously described.[11] The crude pyrolysate (15 mg) was dissolved in dichloromethane and flashed through a short pad of alumina to yield a mixture of benzo[*a*]corannulene (**8**), 1-(*o*-chlorophenyl)benzo[*ghi*]fluoranthene (**7**), benzo[*ghi*]fluoranthene (**3**), and unchanged starting material (**6**) in a ratio[5] of approximately 47:28:14:11. The crude pyrolysate was partially purified by flash chromatography on alumina with dichloromethane and hexanes (1:9) as eluant. Further purification by HPLC on a C18 reversed-phase column with acetonitrile and water (8:2) as eluant yielded 8 mg (16%) of benzo[*a*]corannulene (**8**): mp 252−253 °C (lit.[10] mp 253 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (AA′ of AA′BB′, 2H), 8.26 (d, J = 8.8 Hz, 2H), 7.96 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.76 (BB′ of AA′BB′, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.77, 135.57, 134.79, 133.30, 130.92, 130.63, 129.03, 127.70, 127.47, 127.30, 127.11, 125.24, 124.42; HRMS (EI, *m*/*z*) calcd for $C_{24}H_{12}$ (M^+) 300.0939, found 300.0933. The NMR data reported above match closely the NMR data reported previously for benzo[*a*]corannulene (**8**).[10]

Acknowledgment. We thank the Department of Energy Office of Basic Energy Sciences for financial support of this research and D.V. Preda for stimulating discussions.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **1**, **2**, **5**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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