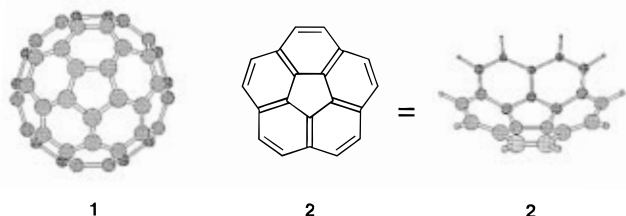


Corannulene. A Three-Step Synthesis¹Lawrence T. Scott,* Pei-Chao Cheng, Mohammed M. Hashemi,[†]
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Abstract: Thermal cyclization of 7,10-diethynylfluoranthene (**3**) in the gas phase gives corannulene (**2**), the smallest bowl-shaped polycyclic hydrocarbon fragment of C₆₀ with fullerene-like curvature. Bromocorannulene (**10**) and 1,6-dibromocorannulene (**9**) have also been obtained from flash pyrolysis of 7,10-bis(2,2-dibromovinyl)fluoranthene (**8**). Short, practical syntheses of several corannulene precursors from acenaphthenequinone are described which have made corannulene available in gram quantities.

Background

By the time C₆₀ (**1**) first came into the hands of chemists,² the bowl-shaped 20-carbon fullerene fragment corannulene (**2**) had already been known for some 20 years, thanks to the pioneering synthesis of Barth and Lawton in 1966.³



This forerunner of the fullerenes features five pyramidalized trigonal carbon atoms in its hub, all of which sit at the confluence of one five-membered ring and two six membered rings, as does every carbon atom of C₆₀. An X-ray crystal structure of corannulene confirmed its anticipated bowl-shaped geometry and revealed the distortion of all five benzene rings out of planarity.⁴ A few spectroscopic studies were also reported in the early days;^{3,5} however, the 17 steps required to synthesize this novel hydrocarbon precluded any systematic investigation of its chemical behavior, and the first chapter of the corannulene story came to a close not long after it began. Numerous attempts by others to find more efficient syntheses of corannulene over the following two decades all ended in failure, and some of these have been recorded.⁶

[†] On leave from Sharif University of Technology, Tehran, Iran.

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(3) (a) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380–1. (b) Lawton, R. G.; Barth, W. E. *J. Am. Chem. Soc.* **1971**, *93*, 1730–45.

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In 1989, motivated by the challenge to design a rational laboratory synthesis of C₆₀, we set our sights on corannulene as a preliminary synthetic objective in order to test the viability of a strategy for introducing curvature into preexisting polycyclic aromatic hydrocarbon (PAH) networks. Our plan was to rely on the high temperatures imparted by gas-phase pyrolyses⁷ to populate nonplanar geometries of normal PAHs, which could then be trapped by prearranged cyclization reactions.⁸ Confidence in this strategy stemmed from the recognition, even in 1989, that the curved surfaces of fullerenes could be formed under high-energy conditions in the gas phase, the energy coming from either a laser⁹ or a flame.¹⁰ All subsequent syntheses of fullerenes, e.g., by vaporization of graphite in an electric arc,² have likewise involved high-energy conditions in the gas phase.

Inspired by the reports of R. F. C. Brown *et al.* that vinylidenes generated thermally from terminal acetylenes in the gas phase can be trapped intramolecularly to construct both five-membered rings¹¹ and six-membered rings^{11,12} (eq 1), we worked out a short synthesis of 7,10-diethynylfluoranthene (**3**) and found that it does indeed provide a convenient new route to corannulene (eq 2).^{1a,b} The utility of our new synthetic strategy for constructing curved PAHs was thereby established, and the

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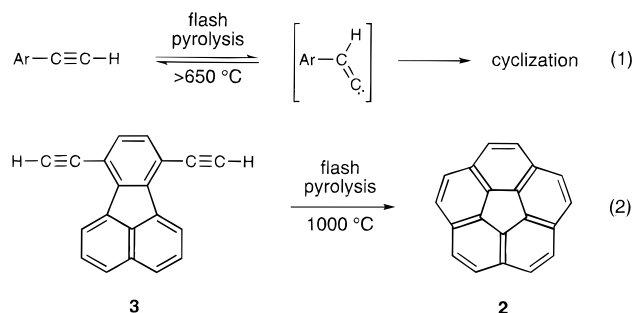
(9) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162–3.

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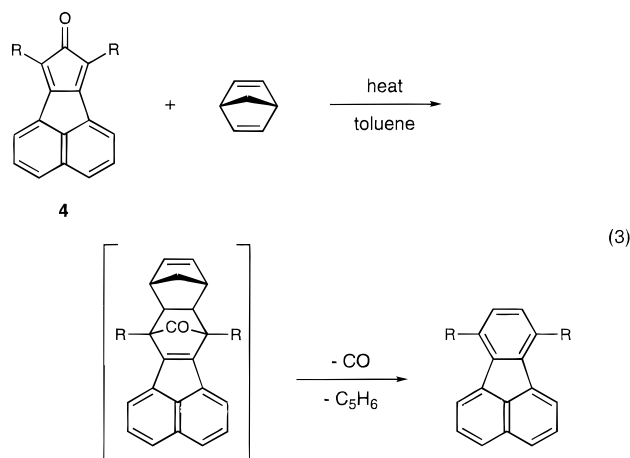
success of the experiment provided validation for the concept on which the strategy was based.



Shortly after the first communication of our results, J. S. Siegel *et al.* reported a third synthesis of corannulene, one that also uses a flash vacuum pyrolysis (FVP) in the final step.¹³ Concurrently, we made a number of improvements to our original approach, which streamlined it considerably and ultimately culminated in an efficient three-step synthesis of corannulene from commercially available starting materials.^{14,e} More recently, Zimmermann,¹⁴ Rabideau,¹⁵ and Mehta¹⁶ have found still other ways to make corannulene using FVP, and in 1996, Siegel *et al.* reported a new route to the corannulene ring system that requires no pyrolysis.¹⁷ The present paper provides details concerning our original route to corannulene and the subsequent improvements thereto.

Synthesis and Pyrolysis of 7,10-Diethynylfluoranthene (3)

At the outset of this project, we were pleased to learn that earlier workers had already discovered a versatile route to 7,10-disubstituted fluoranthenes based on Diels-Alder additions of a “masked acetylene” to cyclopentadienones of type 4.^{6a} When norbornadiene is used as the dienophile in this reaction, carbon monoxide and cyclopentadiene are lost spontaneously under the normal reaction conditions (refluxing toluene), unveiling the final fluoranthene in an exceptionally direct way (eq 3).^{6a,18}



(13) Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921–3.

(14) Zimmermann, G.; Nuechter, U.; Hagen, S.; Nuechter, M. *Tetrahedron Lett.* **1994**, *35*, 4747–50.

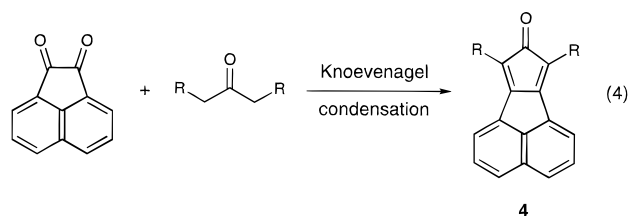
(15) Liu, C. Z.; Rabideau, P. W. *Tetrahedron Lett.* **1996**, *37*, 3437–3440.

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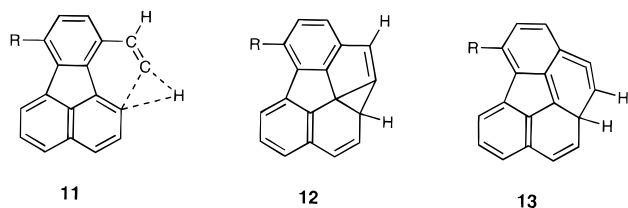
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The requisite cyclopentadienones, in turn, are easily available in one step by the double Knoevenagel condensation of disubstituted acetones with acenaphthenequinone (eq 4).¹⁹



By the simple expedient of running the Knoevenagel condensation in the presence of norbornadiene at 100 °C, rather than in pure toluene, we succeeded in compressing these two powerful C–C bond-forming reactions into a single operation, thus providing a remarkably easy one-step synthesis of dimethyl fluoranthene-7,10-dicarboxylate (5) from acenaphthenequinone, acetone dicarboxylic ester, and norbornadiene (Scheme 1). Conversion of the ester groups in 5 to aldehydes, *via* the corresponding diol (6) by sequential LiAlH_4 reduction²⁰ and PCC oxidation, set the stage for a Corey–Fuchs acetylene synthesis²¹ *via* 7,10-bis(2,2-dibromovinyl)fluoranthene (8, Scheme 1). Flash pyrolysis of diyne 3 then completed our original six-step synthesis of corannulene (eq 2).

Of course we cannot say with certainty whether the thermally generated vinylidene inserts into the C–H bond protruding from the naphthalene below (11), giving a new benzene ring directly, or whether it first adds to make a norcaradiene (12) that subsequently isomerizes to the observed ring system.^{12,22} Furthermore, we cannot exclude on experimental grounds the alternative of a direct electrocyclicization from 2 to an “isobenzene” intermediate such as 13.²³ These intriguing mechanistic intricacies remain open to speculation.²⁴



The apparatus used for the final pyrolysis step consists of a simple horizontal quartz tube heated by an electric tube furnace and is described in detail in the Experimental Section. Unfor-

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(20) Over-reduction to 7,10-dimethylfluoranthene was encountered when the LiAlH_4 reaction was conducted in refluxing THF.

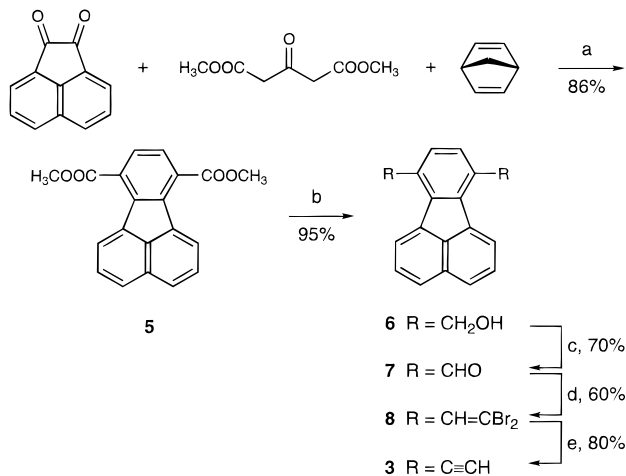
(21) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769–72.

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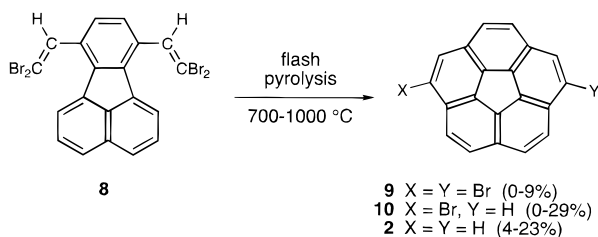
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(24) The work of Hopf *et al.* on the isomerization of simple hexa-1,3-dien-5-yne to benzenes may be relevant here: (a) Hopf, H.; Musso, H. *Angew. Chem.* **1969**, *81*, 680 (see also: *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 680). (b) Roth, W. R.; Hopf, H.; Horn, C. *Chem. Ber.* **1994**, *127*, 1765–79. (c) Hopf, H.; Berger, H.; Zimmermann, G.; Nuechter, U.; Jones, P. G.; Dix, I. *Angew. Chem.* **1997**, *109*, 1236–1238 (see also: *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1187–1190). (d) Nuechter, U.; Zimmermann, G.; Francke, V.; Hopf, H. *Liebigs Ann./Recl.* **1997**, 1505–1515. (e) Personal communication.

Scheme 1



Scheme 2

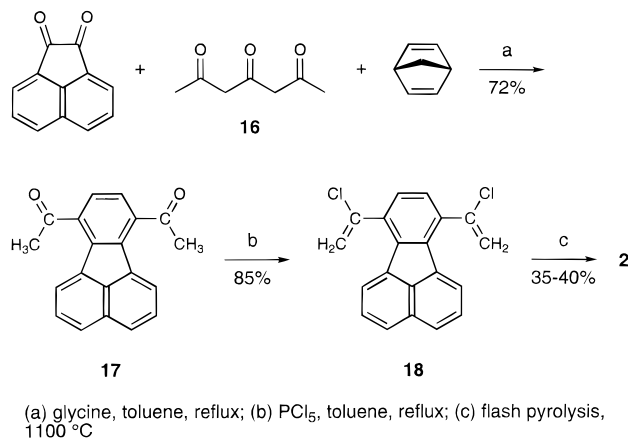


tunately, the volatility of diyne **3** is so low that heat had to be applied to the solid sample to induce vaporization, and this resulted in considerable polymerization of the starting material. Neither high vacuum conditions (10^{-5} Torr) nor a strong flow of nitrogen carrier gas over the surface of the sample at atmospheric pressure resulted in efficient sublimation of this corannulene precursor. The best conditions found comprised a hybrid of the vacuum and the flow pyrolysis protocols: a slow bleed of nitrogen gas was passed over the sample in a chamber attached to one end of the quartz tube while a mechanical pump pulled a vacuum through the traps attached to the other end of the tube (final vacuum = *ca* 0.6 Torr). Under these conditions, 10–15% of the diyne **3** sublimed out of the sample chamber and was carried through the hot tube where it cyclized to corannulene (eq 2). The optimum pyrolysis temperature was found to be 1000 °C; at lower temperatures, an isomer with only one side closed was obtained.

Our first improvement on this synthesis resulted from the discovery that pyrolysis of 7,10-bis(2,2-dibromovinyl)fluoranthene (**8**) also gives corannulene and that **8** suffers less thermal polymerization during sublimation. Depending on the temperature employed, we also isolated 1,6-dibromocorannulene (**9**) and monobromocorannulene (**10**) from this pyrolysis (Scheme 2).^{1c}

An increase in the relative amount of corannulene obtained from this pyrolysis at higher temperatures, accompanied by a decrease in the relative yields of brominated corannulenes **9** and **10**, is consistent with the view that 1,6-dibromocorannulene (**9**) constitutes the initial product of the reaction and that bromine atoms are subsequently lost by homolytic cleavage of weak C–Br bonds at high temperatures. The corannulenyl radicals thus generated can scavenge hydrogen atoms from other gas-phase species or from the nonvolatile organic material that accumulates on the walls of the tube. In fact, we believe these cyclizations themselves probably involve vinyl radicals gener-

Scheme 3

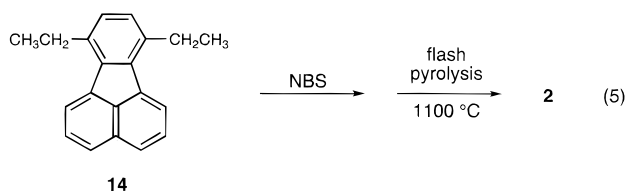


ated by just such homolytic cleavages of weak C–Br bonds.²⁵ Regardless of the mechanism for this transformation, it shortened our earlier synthesis of corannulene to five steps and increased our overall yield of the corannulene ring system sevenfold.

Development of a Three-Step Synthesis of Corannulene

Driven by the conviction that still simpler variants of the above route must be possible, we modified our one-step synthesis of 7,10-disubstituted fluoranthenes (Scheme 1) to make 7,10-diethylfluoranthene (**14**)²⁶ from acenaphthenequinone, 4-heptanone, and norbornadiene. This hydrocarbon has the virtue of already containing all 20 carbon atoms of the target corannulene; the side chains simply need to be raised to a higher oxidation state. Unfortunately, but not surprisingly, direct pyrolysis of **14** gave no trace of corannulene, even when various dehydrogenation catalysts were placed in the hot zone of the apparatus. Cleavage of the weak benzylic C–C bonds in **14** dominated all of these reactions.

Bromination of **14** with NBS, on the other hand, introduces labile benzylic halides, and the α,α' -dibromo derivative does give small amounts of corannulene when subjected to flash pyrolysis (eq 5).



We then found that the mixtures of tri- and tetrabromo derivatives of 7,10-diethylfluoranthene obtained by further bromination with NBS give much higher yields of corannulene, and this discovery quickly led to the design and development of our final, highly-efficient, three-step synthesis, which is outlined in Scheme 3.^{1c,d}

Using heptane-2,4,6-trione (**16**)²⁷ in the initial Knoevenagel/Diels–Alder reaction, we now prepare 7,10-diacetylfluoranthene (**17**) in 70–75% yield on a 20-g scale. Conversion of the acetyl

(25) We earlier speculated^{1c} that ring formation might involve an initial electrocyclization followed by thermal loss of HBr, but subsequent work with other systems supports the radical cyclization mechanism: Bratcher, M. S. Ph.D. Dissertation, Boston College, 1996 (details to be published elsewhere).

(26) For an earlier stepwise synthesis of 7,10-diethylfluoranthene (**14**), see: Fuchs, B. *J. Chem. Soc. C* **1968**, 68–71.

(27) (a) Parish Chemical Company. (b) Feist, F.; Belert, H. *Chem. Ber.* **1895**, 28, 1817–1829.

groups to 1-chlorovinyl side chains with PCl_5^{28} also proceeds in good yield (80–85%) on a 10-g scale to give **18**, and pyrolysis of **18** gives corannulene in yields of 35–40% on a 1.0-g scale. Thus, from an easily prepared stockpile of **18**, it is now possible to turn out 250–300-mg samples of corannulene routinely in a single pyrolysis run. Combining the crude pyrolysates from several runs gives gram quantities of corannulene after purification.²⁹

We do not expect to find a corannulene precursor that is superior to **18** and have ended our search for alternatives. Not only can **18** be prepared by simple reactions on a large scale in just two steps from commercially available starting materials, it sublimes quantitatively in our pyrolysis apparatus and does not suffer from the competing polymerizations that plagued our earlier precursors.

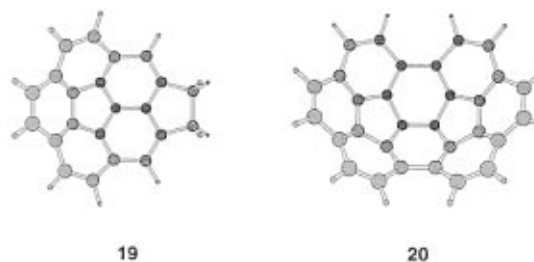
As a mechanistic comment, we have good evidence that the first steps in the conversion of **18** to corannulene involve thermal loss of two molecules of HCl to generate diyne **3** in the hot zone of the pyrolysis apparatus; if the temperature of the oven is lowered from 1100 to 900 °C, diyne **3** can be isolated as the sole product. We recommend 1-chlorovinyl groups as superb latent ethynyl groups for flash pyrolyses.³⁰

Opportunities and Extensions

With corannulene available in our laboratory by this route for several years now, we have carried out extensive studies on its chemical behavior in a wide range of reactions and have found many surprises.³¹ From low-temperature NMR measurements on a simple corannulene derivative, we determined the bowl-to-bowl inversion barrier to be only 10.2 kcal/mol.^{1c} Reduction of corannulene with lithium in THF gives a dianion that is best described as an aromatic cyclopentadienide core and an antiaromatic 16-electron rim.³² Further reduction with lithium produces the corresponding tetraanion, which is best described as an aromatic cyclopentadienide core and an aromatic 18-electron rim, *i.e.*, two concentric aromatic rings.^{32,33} This latter species aggregates to form unprecedented high-order dimers with four of the lithium ions sandwiched between the

two hydrocarbon tetraanions.³⁴ Numerous collaborations with other chemists throughout the world have yielded, *inter alia*, experimental values for the heat of formation of corannulene (111 kcal/mol),³⁵ the electron affinity of corannulene in the gas phase (0.50 ± 0.10 eV),³⁶ and the oxidation potential of corannulene in the gas phase (7.7 ± 0.1 eV),³⁷ as well as evidence for the formation of a 1:1 complex between corannulene and the cation radical of C_{60} ,³⁷ evidence for the formation of corannulene in fuel-rich hydrocarbon flames,³⁸ and a new synthesis of C_{60} by pyrolysis of corannulene.³⁹

Extensions of our corannulene synthesis by P. W. Rabideau *et al.* have yielded the “locked” corannulene **19** (inversion barrier = 27.6 kcal/mol)⁴⁰ and the $\text{C}_{30}\text{H}_{12}$ “semibuckminsterfullerene” **20**.^{41,42} Since our introduction of the 1-chlorovinyl group as a latent ethynyl group in flash pyrolysis, this synthetic method has been used with considerable success for the preparation of numerous other new PAHs unrelated to corannulene.^{30,43}



In the coming years, we can expect to see a wealth of new corannulene chemistry as a result of the dramatically increased availability of this intriguing compound. The strategy for constructing curved fullerene fragments from “normal” PAH derivatives has already been successfully applied to many larger members of this fascinating family of hydrocarbons.⁴⁴

Experimental Section

General Procedures. Tetrahydrofuran (THF) was purified by distillation under nitrogen from the potassium ketyl of benzophenone.

(28) Kagan, J.; Arora, S. K.; Bryzgis, M.; Dhawan, S. N.; Reid, K.; Singh, S. P.; Tow, L. *J. Org. Chem.* **1983**, *48*, 703–6.

(29) Byproducts identified include benzo[ghi]fluoranthene (from loss of one side chain), cyclopenta[cd]pyrene (a known rearrangement product of benzo[ghi]fluoranthene), and fluoranthene (from loss of both side chains). Varying amounts of dicyclopenta[cd, fg]pyrene^{30c} are also obtained. We thank Dorin Preda for tracking down and identifying these side products by comparisons with authentic samples.

(30) We have used 1-chlorovinyl groups as latent ethynyl groups for the synthesis of a wide range of polycyclic aromatic hydrocarbons by flash pyrolytic methods. See, for example: (a) Necula, A.; Scott, L. T. Northeast Regional Meeting of the American Chemical Society, Burlington, VT, June 19–22, 1994, Abstract No. 60. (b) Necula, A.; Scott, L. T. Eighth International Symposium on Novel Aromatic Compounds; Braunschweig, Germany, July 31–August 4, 1995, Abstract No. 114. (c) Scott, L. T.; Necula, A. *J. Org. Chem.* **1996**, *61*, 386–8. (d) Necula, A. Ph.D. Dissertation, Boston College, 1996. (e) Scott, L. T.; Necula, A. *Tetrahedron Lett.* **1997**, *38*, 1877–1880.

(31) Several preliminary accounts of the chemistry of corannulene have been presented.^{1d–g} See also: (a) Scott, L. T.; Cheng, P.-C.; Bratcher, M. S.; Corpuz, E. 12th IUPAC Conference on Physical Organic Chemistry; Padova, Italy, August 28–September 2, 1994, Abstract No. 34. (b) Cheng, P.-C.; Scott, L. T. National Meeting of the American Chemical Society; Washington, DC, August 21–26, 1994, organic division Abstract No. 87. (c) Cheng, P.-C.; Scott, L. T., Eighth International Symposium on Novel Aromatic Compounds; Braunschweig, Germany, July 31–August 4, 1995, Abstract No. 8.

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Proton and carbon NMR chemical shifts are reported in ppm downfield from tetramethylsilane with chloroform as the reference standard, unless otherwise specified. Preparative thin layer chromatographies were performed on 20 × 20 cm Analtech Uniplat Taper plates, Silica Gel GF. For column chromatographies, Silica Gel 60–200 mesh and aluminum oxide (activated, neutral, Brockmann I, *ca.* 150 mesh) were used. High-resolution mass spectrometry (HRMS) was performed by the Midwest Center for Mass Spectrometry at the University of Nebraska–Lincoln and by the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois.

Dimethyl Fluoranthene-7,10-dicarboxylate (5). A mixture of acenaphthenequinone (5.00 g, 24.7 mmol), dimethyl 1,3-acetone dicarboxylate (9.0 mL, 65 mmol), and glycine (4.5 g, 60 mmol) in 75 mL of 2,5-norbornadiene was stirred at reflux for 3.5 days. The reaction flask was equipped with a modified Hickman still reflux condenser (or a Dean-Stark trap) to remove the water generated from the reaction. Excess solvent was removed at the end of the reaction either by simple distillation or by evaporation under reduced pressure to give a brown solid which was chromatographed on silica gel with 2:2:1 benzene/hexane/ethyl acetate as eluant. The product was further purified by crystallization from methanol to give 7.51 g (86%) of light brown to pale peach colored solid: mp 144–145 °C, lit.^{6a} mp 147–148 °C.

7,10-Bis(hydroxymethyl)fluoranthene (6). A solution of diester **5** (1.00 g, 3.2 mmol) in 30 mL of dry THF was added dropwise with stirring to a solution of lithium aluminum hydride (1.21 g, 32 mmol) in 30 mL of dry THF at 0 °C. The reaction mixture was stirred at room temperature for 6 h and then hydrolyzed with 15 mL of water, 15 mL of 10% aqueous sodium hydroxide, and 15 mL of water. The mixture was subsequently extracted with 3 × 50 mL of 1:1 ether/THF. Note: Diol **6** is not sufficiently soluble in pure ether to be efficiently extracted with ether alone. The combined organic layers were washed with 50 mL of water, then dried over magnesium sulfate. Removal of the solvents under reduced pressure gave a brown oil that was purified by column chromatography on silica gel with 6:4 ethyl acetate/hexane as eluant. The material thus isolated was crystallized from anhydrous ether to give 800 mg (95%) of white crystals: mp 213–215 °C, lit.^{6a} mp 217–220 °C. ¹³C NMR (100 MHz, DMSO-*d*₆): δ 133.7, 132.3, 131.8, 127.8, 125.6, 124.5, 122.9, 122.6, 120.6, 57.8 (not previously reported).

7,10-Diformylfluoranthene (7). A mixture of diol **6** (800 mg, 3.0 mmol) and pyridinium chlorochromate (2.15 g, 10 mmol) in 15 mL of dry THF was stirred at room temperature for 5 h. The resulting brown solution was then diluted with 50 mL of ether to give a brown precipitate. The organic layer was separated, and the brown residue was washed with 2 × 30 mL of ether. The combined ethereal solutions were filtered through a short pad of florisil to give a light yellow solution, which was concentrated under reduced pressure to give 530 mg (70%) of **7** as yellow crystals: mp 195 °C dec. ¹H NMR (400 MHz, CDCl₃): δ 10.75 (s, 2H), 8.75 (d, 2H, *J* = 7.2 Hz), 8.02 (d, 2H, *J* = 8.1 Hz), 7.99 (s, 2H), 7.74 (dd, 2H, *J* = 8.1 and 7.2 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 191.6, 140.9, 136.0, 134.0, 133.0, 132.0, 130.1, 129.5, 128.5, 127.7. IR (KBr): 1722 cm⁻¹ (C=O). MS (EI, 70 eV) *m/z* (rel abundance) 258 (74, M⁺), 230 (21), 229 (34), 202 (100), 201 (70), 200 (84), 100 (53). HRMS Calcd for C₁₈H₁₀O₂: 258.0680. Found: 258.0688.

7,10-Bis(2,2-dibromovinyl)fluoranthene (8). A mixture of zinc powder (2.08 g, 31.8 mmol), triphenylphosphine (8.24 g, 31.5 mmol), and carbon tetrabromide (8.80 g, 27.5 mmol) in 150 mL of methylene chloride was stirred under nitrogen for 36 h, during which time a pink color developed.²¹ A solution of dialdehyde **7** (2.08 g, 8.06 mmol) in methylene chloride was then added, and the reaction mixture was stirred at room temperature for 8 h. The reaction mixture was poured into 100 mL of hexane to give a milky solution with a brown residue. The organic layer was separated, and the brown residue was dissolved in 25 mL of methylene chloride. The methylene chloride solution was poured into another 100 mL of fresh hexane to give another milky solution with a brown residue. The organic layer was again separated and combined with the first one and filtered through a short pad of florisil to give a clear solution. Removal of the solvent gave pale crystals which were recrystallized from methanol to give 2.77 g (60%) of white crystals: mp 188–190 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.95 (s, 2H), 7.95 (d, 2H, *J* = 6.9 Hz), 7.91 (d, 2H, *J* = 8.1 Hz), 7.69

(dd, 2H, *J* = 8.1 and 6.9 Hz), 7.47 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 137.0, 136.0, 135.9, 132.7, 132.1, 130.1, 128.5, 127.9, 127.7, 123.7, 94.0. MS (EI, 70 eV) *m/z* (rel abundance) 574 (2), 572 (8), 570 (13), 568 (9), 566 (2), 492 (6), 490 (17), 488 (18), 486 (7), 412 (10), 410 (18), 408 (11), 330 (21), 328 (23), 250 (100), 249 (47), 248 (59). HRMS Calcd for C₂₀H₁₀Br₄: 565.7518. Found: 565.7517.

7,10-Diethynylfluoranthene (3). To a mixture of diisopropylamine (1.44 g, 14.4 mmol) in 20 mL of dry THF under nitrogen at –78 °C was added *n*-BuLi in hexane (2.5 M, 5.6 mL, 14 mmol). After 15 min, a solution of tetrabromide **8** (2.00 g, 3.50 mmol) in 10 mL of THF was added, and the reaction mixture was stirred at –78 °C for 5 h. The resulting mixture was poured into 50 mL of water, the aqueous solution was extracted with 3 × 50 mL of ether, the combined organic layers were washed with 30 mL of 5% aqueous hydrochloric acid and 30 mL of 10% aqueous sodium bicarbonate and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with use of 9:1 hexane/ethyl acetate as eluant to give 719 mg (80%) of **3** as pale yellow crystals: mp 143.0–145.0 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.62 (d, 2H, *J* = 6.9 Hz), 7.94 (d, 2H, *J* = 9.0 Hz), 7.71 (dd, 2H, *J* = 9.0 and 6.9 Hz), 7.47 (s, 2H), 3.63 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 140.2, 135.0, 132.6, 131.6, 129.8, 128.2, 127.6, 123.9, 117.2, 83.4, 82.4. MS (EI, 70 eV) *m/z* (rel abundance): 251 (22), 250 (100, M⁺), 249 (22), 248 (30), 125 (8), 124 (10). HRMS Calcd for C₂₀H₁₀: 250.0782. Found: 250.0781.

7,10-Diacetylfluoranthene (17). A 1000-mL round-bottomed flask, equipped with a magnetic stirrer and a modified Hickman still reflux condenser to remove the water generated from the reaction, was charged with acenaphthenequinone (20.0 g, 0.11 mol), glycine (8.24 g, 0.11 mol), and 100 mL of toluene. This reaction mixture was heated with stirring over a period of 20 min to a temperature of approximately 100 °C, at which point 2,4,6-heptanetrione²⁷ (15.60 g, 0.11 mol) was added all at once. After another 30 min at 100 °C, 2,5-norbornadiene (250 mL) was introduced to the flask, and the solution was brought to reflux in a 120 °C oil bath. After 24 h, a second equivalent of 2,4,6-heptanetrione (15.60 g, 0.11 mol) was added. This brown solution was maintained at reflux with stirring for a total of 72 h. At the end of this period, the mixture was cooled, then diluted with 200 mL of methylene chloride and washed 3 × 300 mL of water and 3 × 300 mL of saturated sodium chloride solution. The combined organic layers were dried over magnesium sulfate, filtered, and concentrated on the rotary evaporator. The crude solid was digested in 100 mL of acetone and put in the freezer overnight. Filtration gave relatively pure **17** as a yellow solid. More **17** was obtained from the acetone solution by chromatography on silica gel with use of 1:1 hexane/ethyl acetate as eluant to give a combined yield of 22.70 g (72%): mp 193–194 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.34 (d, *J* = 7.2 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.64 (dd, *J* = 8.0, 7.2 Hz, 2H), 7.59 (s, 2H), 2.77 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 202.83, 138.75, 138.31, 134.38, 133.67, 130.46, 129.15, 128.52, 126.82, 126.30, 30.81. IR (neat): 3059 (w), 3002 (w), 1688 (s), 1428 (s), 1360 (m), 781 (s) cm⁻¹. MS (EI, 70 eV) *m/z* (rel abundance): 286 (62, M⁺), 271 (100), 243 (26), 228 (10). HRMS: Calcd for C₂₀H₁₄O₂: 286.0994. Found: 286.1001.

7,10-Bis(1-chlorovinyl)fluoranthene (18). To a solution of 7,10-diacetylfluoranthene (10.0 g, 0.034 mol) in 150 mL of toluene at 90–100 °C under a nitrogen atmosphere was added phosphorus pentachloride (18.9 g, 0.090 mol) in small portions with stirring. Stirring was maintained at the same temperature for 7 h; then the reaction mixture was chilled and hydrolyzed by careful addition of crushed ice (3.0 g). The cold toluene layer was quickly washed with 2 × 150 mL of water, dried immediately over magnesium sulfate, and concentrated to dryness under vacuum. The residue was chromatographed on silica gel with use of 5:1 hexane/benzene as eluant to afford 9.40 g (83%) of **18** as light yellow crystals: mp 137–138 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.32 (d, *J* = 7.2 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.64 (dd, *J* = 8.1, 7.2 Hz, 2H), 7.30 (s, 2H), 5.88 (d, *J* = 1.4 Hz, 2H), 5.72 (d, *J* = 1.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 138.81, 137.20, 136.08, 135.23, 133.28, 130.56, 128.74, 128.59, 128.25, 125.04, 117.94. IR (neat): 3100 (w), 3052 (m), 1628 (s), 1427 (s), 1345 (m), 891 (s), 827 (s) cm⁻¹. MS (EI, 70 eV) *m/z* (rel abundance): 326 (3, M⁺+4), 324 (20, M⁺+2), 322 (31, M⁺), 289 (13), 287 (40), 252 (40), 251 (100),

250 (87), 226 (19), 125 (39). HRMS: Calcd for $C_{20}H_{12}Cl_2$: 322.0316. Found: 322.0306.

Pyrolysis Reactions: General Procedure. The pyrolysis apparatus used in these experiments resembles the Trahanovsky design sold by Kontes Scientific Glassware (Vineland, NJ 08360) and consists of an unpacked horizontal quartz tube (28 mm o.d.) heated in a single zone electric furnace equipped with a digital single setpoint temperature controller (Lindberg model 55035; hot zone length 35 cm). The outlet of the pyrolysis tube makes a 90° bend (referred to below as “the elbow”) to the vertical product trap, which is cooled in a Dewar flask with liquid nitrogen and is connected through a manifold to a second trap and the vacuum pump (Precision Vac Torr 150 model 69151). A pressure gauge is attached to the manifold between the two traps. A small glass boat containing the solid sample to be pyrolyzed is placed in a chamber that has a ground joint at one end for attachment to the head of the pyrolysis tube.

To sublime compounds of the size described here, we have found it desirable not only to warm the sample chamber, either with a heat gun or with a heating tape connected to a variable AC controller, but also to leak a light flow of nitrogen carrier gas into the sample chamber through an inlet located upstream from the sample. The flow of nitrogen can be controlled simply by means of a screw clamp on the flexible tubing that connects the nitrogen cylinder to the pyrolysis apparatus. With mechanical pumping downstream from the product trap and the nitrogen leaking in, an operating pressure of 0.4–0.7 Torr was measured at the manifold during typical pyrolysis runs. The time required for each pyrolysis and the individual workup procedures are recorded below.

At the highest operating temperatures (1000–1100 °C), considerable black carbonaceous material develops on the walls of the tube in the hot zone. Best results are obtained if the tube is cleaned between pyrolysis runs.

Corannulene (2) from 7,10-Diethynylfluoranthene (3).⁴⁵ Diethynylfluoranthene **3** (40 mg) was pyrolyzed at 1000 °C as described above. The sample chamber was heated to 80 °C. After 18 h a small amount of corannulene appeared as white crystals on the elbow above the trap, but the rest of the starting material had degraded to a brown polymer in the sample chamber. Washing the elbow with 30 mL of dichloromethane gave 4 mg (10%) of pure corannulene: mp 265–266 °C [lit.³ mp 268–269 °C]. ¹H NMR (300 MHz, $CDCl_3$): δ 7.81 (s). ¹³C NMR (75 MHz, $CDCl_3$): δ 135.81, 130.84, 127.18. MS (EI, 70 eV) m/z (rel abundance): 251 (22), 250 (100), 248 (18), 125 (7).

Corannulene (2), 1,6-Dibromocorannulene (9), and Bromocorannulene (10) from 7,10-Bis(2,2-dibromovinyl)fluoranthene (8). Bis(2,2-dibromovinyl)fluoranthene **8** (50 mg, 0.088 mmol) was pyrolyzed at 900 °C over a period of 24 h as described above, after which time only a very small amount of material was left in the boat. The products were isolated by washing the elbow and the trap with 100 mL of dichloromethane. Evaporation of the solvent and preparative thin layer chromatography of the crude pyrolysate on silica gel with cyclohexane

(45) Alternative methods for introduction of diethynylfluoranthene **3** into the pyrolysis tube met with only marginal success. A 4% yield of corannulene was obtained with use of the solution spray method of Rubin et al.: Rubin, Y.; Lin, S. S.; Knobler, C. B.; Anthony, J.; Boldi, A. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 6943–6949. A 17% yield of corannulene was obtained with use of the frozen matrix/flash sublimation method of Magrath and Fowler: Magrath, J.; Fowler, F. W. *Tetrahedron Lett.* **1988**, *29*, 2174–7.

as eluant gave 1,6-dibromocorannulene (**9**, 1.2 mg, 2.4%), bromocorannulene (**10**, 10.3 mg, 29%), and corannulene (**2**, 5.1 mg, 23%), eluting in that order. An analogous pyrolysis at 750 °C gave a 9% isolated yield of 1,6-dibromocorannulene (**9**), 16% bromocorannulene (**10**), and 9% corannulene (**2**). At 1000 °C, corannulene (**2**) was obtained in 21% yield as the only isolable product; no bromocorannulenes survived at this temperature. **1,6-Dibromocorannulene (9)**: yellow crystals, mp 256–258 °C. ¹H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 2H), 7.97 (d, 2H, $J = 8.7$ Hz), 7.90 (d, 2H, $J = 8.7$ Hz), 7.73 (s, 2H). ¹³C NMR (100 MHz, $CDCl_3$): $\delta = 137.2, 136.6, 135.3, 132.1, 131.6, 130.4, 128.6, 127.9, 127.4, 127.0, 122.4$. MS (EI, 70 eV) m/z (rel abundance) 410 (49), 408 (100), 406 (50), 329 (17), 327 (15) 248 (52), 124 (34). HRMS Calcd for $C_{20}H_8Br_2$: 405.8992. Found: 405.8982. **Bromocorannulene (10)**: pale yellow crystals, mp 185–186 °C. ¹H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.93 (d, 1H, $J = 8.6$ Hz), 7.87 (d, 1H, $J = 8.6$ Hz), 7.82 (s, 2H), 7.81 (d, 1H, $J = 8.8$ Hz), 7.79 (d, 1H, $J = 8.6$ Hz), 7.78 (d, 1H, $J = 8.8$ Hz), 7.71 (d, 1H, $J = 8.6$ Hz). ¹³C NMR (100 MHz, $CDCl_3$): δ 136.57, 136.42 (2C), 135.75, 135.46, 132.65, 131.77 (2C), 131.52, 130.88, 130.12, 128.77, 128.44 (2C), 127.97, 127.94, 127.72, 127.24, 126.72, 122.09. MS (EI, 70 eV) m/z (rel abundance) 330 (100), 328 (99), 249 (53), 248 (43), 124 (34). HRMS Calcd for $C_{20}H_9Br$: 327.9887. Found: 327.9873.

Corannulene (2) from 7,10-Diethylfluoranthene (14). In a 250-mL two-necked round-bottomed flask, a solution of 7,10-diethylfluoranthene²⁶ (**14**, 258 mg, 1.00 mmol), *N*-bromosuccinimide (392 mg, 2.2 mmol), and dibenzoyl peroxide (8 mg, 0.03 mmol) in 20 mL of benzene was irradiated with a 275 W sun lamp and heated to reflux for 4 days. At the end of each 24-h interval, additional NBS (267 mg, 1.50 mmol) and dibenzoyl peroxide (8 mg, 0.03 mmol) were added. At the end of 4 days, the solution was cooled to room temperature and concentrated on the rotary evaporator. The crude brown solid was chromatographed on silica gel with 10:1 hexane/ethyl acetate as eluant to give 326 mg of a yellow solid. Analysis of this material (¹H NMR and GC/MS) revealed it to be an inseparable mixture of the di-, tri-, and tetrabromo compounds resulting from multiple benzylic brominations. Pyrolysis of the mixture at 1100 °C as described above (0.5–0.6 torr with nitrogen flow) on a scale of 150–260 mg over 24 h gave 8–21 mg (10–15%) of corannulene after chromatographic purification.

Corannulene (2) from 7,10-Bis(1-chlorovinyl)fluoranthene (18). Bis(1-chlorovinyl)fluoranthene (**18**, 1.0 g) was pyrolyzed at 1100 °C as described above (*ca.* 1.0 Torr with nitrogen flow) over a period of 24 h, after which time, no more than a few milligrams of material was left in the sample boat. Washing the elbow of the tube and the cold trap with 120 mL of methylene chloride and evaporation of the solvent under reduced pressure gave 450 mg of crude yellow material. The crude product was chromatographed on an alumina column with cyclohexane as eluant. The product thus obtained was further purified by crystallization from ethanol to give 299 mg (39%) of corannulene (**2**) as light yellow crystals, identical in all respects with the corannulene prepared by the less efficient methods described above.

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