Polycyclic Fluoranthene Hydrocarbons. 2. A New General Synthesis

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Received May 4, 1987

A novel and efficient synthetic approach to polycyclic fluoranthene hydrocarbons is described. The method entails fusion of an indeno ring to an appropriate alternant hydrocarbon via reaction of its aryllithium derivative with cyclohexene oxide, followed by oxidation, cyclodehydration, and aromatization. Cyclization of the cyclohexanone and cyclohexanol derivatives of the polycyclic aromatic ring systems studied proceeds with high regioselectivity, and the direction of ring closure is predictable by molecular orbital methods. This synthetic approach provides a convenient general route to polyaromatic fluoranthene compounds, including potentially carcinogenic members of this class. Hydrocarbons synthesized by this method include benz[*e*]acephenanthrylene (**1**), indeno[1,2,3-*cd*]pyrene (**2**), indeno[1,2,3-*hi*]chrysene (**3**), benz[*def*]indeno[1,2,3-*hi*]chrysene (**4**), fluoreno[3,2,1,9-*defg*]chrysene (**5**), dibenz[*a,e*]aceanthrylene (**6**), dibenz[*a,j*]aceanthrylene (**7**), benz[*a*]aceanthrylene (**8**), benz[*def*]indeno[1,2,3-*qr*]chrysene (**9**), fluoreno[9,1,2,3-*cdef*]chrysene (**10**), and dibenz[*e,k*]acephenanthrylene (**11**).

While the chemistry of alternant polycyclic aromatic hydrocarbons (PAHs) such as benzo[*a*]pyrene has been studied intensively,[1] much less is known concerning the properties of nonalternant PAHs, i.e., PAHs that are not composed entirely of fused benzenoid rings. Polycyclic aromatic fluoranthenes are an important class of nonalternant PAHs that are derivatives of the parent fluoranthene ring system. Some members of this class, e.g., benz[*e*]acephenanthrylene (**1**) and indeno[1,2,3-*cd*]pyrene (**2**), are widespread environmental pollutants[2] that have been shown to exhibit mutagenic and carcinogenic activities.[3] Chemical and biochemical investigations of the polycyclic fluoranthenes have been hampered, until now, by their relative synthetic inaccessibility. The classical synthetic methods for the preparation of molecules of this type lack broad general applicability and suffer from serious drawbacks due to the severity of the conditions employed and/or the low yields obtained.[1]

In a preliminary report we described[4] a convenient synthetic approach to molecules of this class which is potentially general in scope and makes available for research a wide range of polycyclic aromatic fluoranthenes. We now report full details of this procedure. Polyaromatic fluoranthenes synthesized by this method include benz[*e*]acephenanthrylene (**1**), indeno[1,2,3-*cd*]pyrene (**2**), indeno[1,2,3-*hi*]chrysene (**3**), benz[*def*]indeno[1,2,3-*hi*]chrysene (**4**), fluoreno[3,2,1,9-*defg*]chrysene (**5**), dibenz[*a,e*]aceanthrylene (**6**), dibenz[*a,j*]aceanthrylene (**7**), benz[*a*]aceanthrylene (**8**), benz[*def*]indeno[1,2,3-*qr*]chrysene (**9**), fluoreno[9,1,2,3-*cdef*]chrysene (**10**), and dibenz[*e,k*]acephenanthrylene (**11**). The structures and numbering systems of these ring systems are given in Figure 1.[5]

Results

The synthetic approach adopted for the preparation of the polycyclic fluoranthene hydrocarbons entails fusion of an indeno ring to an appropriate alternant PAH. This procedure, which is illustrated for benz[*e*]acephenanthrylene (**1**, Figure 2), takes advantage of the ready availability of the bromo derivatives of the parent alternant PAHs through direct electrophilic bromination. The method entails conversion of the bromo compound to the corresponding lithio derivative, followed by reaction with cyclohexene oxide, oxidation of the resulting alcohol to a ketone, acid-catalyzed cyclodehydration, and dehydrogenation. In a typical example, reaction of 9-lithiophenanthrene with cyclohexene oxide in ether furnished 2-(9-phenanthryl)cyclohexanol (**12**), which underwent oxidation with pyridinium dichromate (PDC) in DMF or CH_2Cl_2 at room temperature to provide the ketone **13**. Cyclodehydration of **13** in polyphosphoric acid (PPA), followed by aromatization with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), yielded **1** in good overall yield. This method was utilized successfully for the preparation of all of the polycyclic fluoranthenes in Figure 1, with appropriate modifications in individual cases as described below.

While oxidation of the cyclohexanol derivatives of phenanthrene, pyrene, and chrysene with the mild oxidant PDC proceeded smoothly, attempted similar conversion of the analogous derivatives of anthracene and benz[*a*]anthracene resulted in partial oxidation of the aromatic ring system to yield significant amounts of the meso region quinones, anthrone and benz[*a*]anthracene-7,12-dione, and other side products. Similar difficulties were encountered with alternative reagents such as pyridinium chlorochromate[6] and the DMSO–sulfur trioxide–pyridinium complex.[7] However, oxidation of these cyclohexanols was readily effected with the reagent "periodane" recently introduced by Dess and Martin.[8] With short reaction times (<2 h), the corresponding ketones were obtained in good yields with little or no contamination by the related quinones. The Dess–Martin reagent was also found to be particularly effective for the oxidation of the cyclohexanol derivatives of benzo[*a*]pyrene, requiring shorter reaction

(1) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New York, 1964.

(2) *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Polynuclear Aromatic Compounds*; IARC: Lyon: France, 1983; Vol. 32, Part 1.

(3) (a) Deutsch-Wenzel, R. P.; Brune, H.; Grimmer, G.; Dettbarn, G.; Misfeld, J. *JNCI, J. Natl. Cancer Inst.* **1983**, *71*, 539. (b) Rice, J. E.; Hosted, T. J., Jr.; DeFloria, M. C.; LaVoie, E. J.; Fischer, D. L.; Wiley, J. C., Jr. *Carcinogenesis* **1986**, *7*, 1761. (c) Lavit-Lamy, D.; Buu-Hoi, N. P. *J. Chem. Soc., Chem. Commun.* **1966**, 92. (d) Lacassagne, A.; Buu-Hoi, N. P.; Zajdela, F.; Lavit-Lamy, D. *C. R. Hebd. Seances Acad. Sci.* **1963**, *256*, 2728. (e) Busby, W. F., Jr.; Goldman, M. E.; Newberne, P. M.; Wogan, G. N. *Carcinogenesis* **1984**, *5*, 1311.

(4) Cho, B. P.; Harvey, R. G. *Tetrahedron Lett.* **1987**, *28*, 861, 2906.

(5) The names and numbering systems of these hydrocarbons are in accord with the current *Chemical Abstracts* rules. Compounds **1** and **6** are known more commonly as benzo[*b*]fluoranthene and dibenzo[*a,e*]fluoranthene, respectively.

(6) (a) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647. (b) Piancatelli, G.; Scettri, A.; Dauria, M. *Synthesis* **1982**, 245.

(7) Harvey, R. G.; Goh, S. H.; Cortez, C. *J. Am. Chem. Soc.* **1975**, *97*, 3468.

(8) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155. See also: Becker, H. D.; Hansen, L.; Andersson, K. *J. Org. Chem.* **1986**, *51*, 2956.

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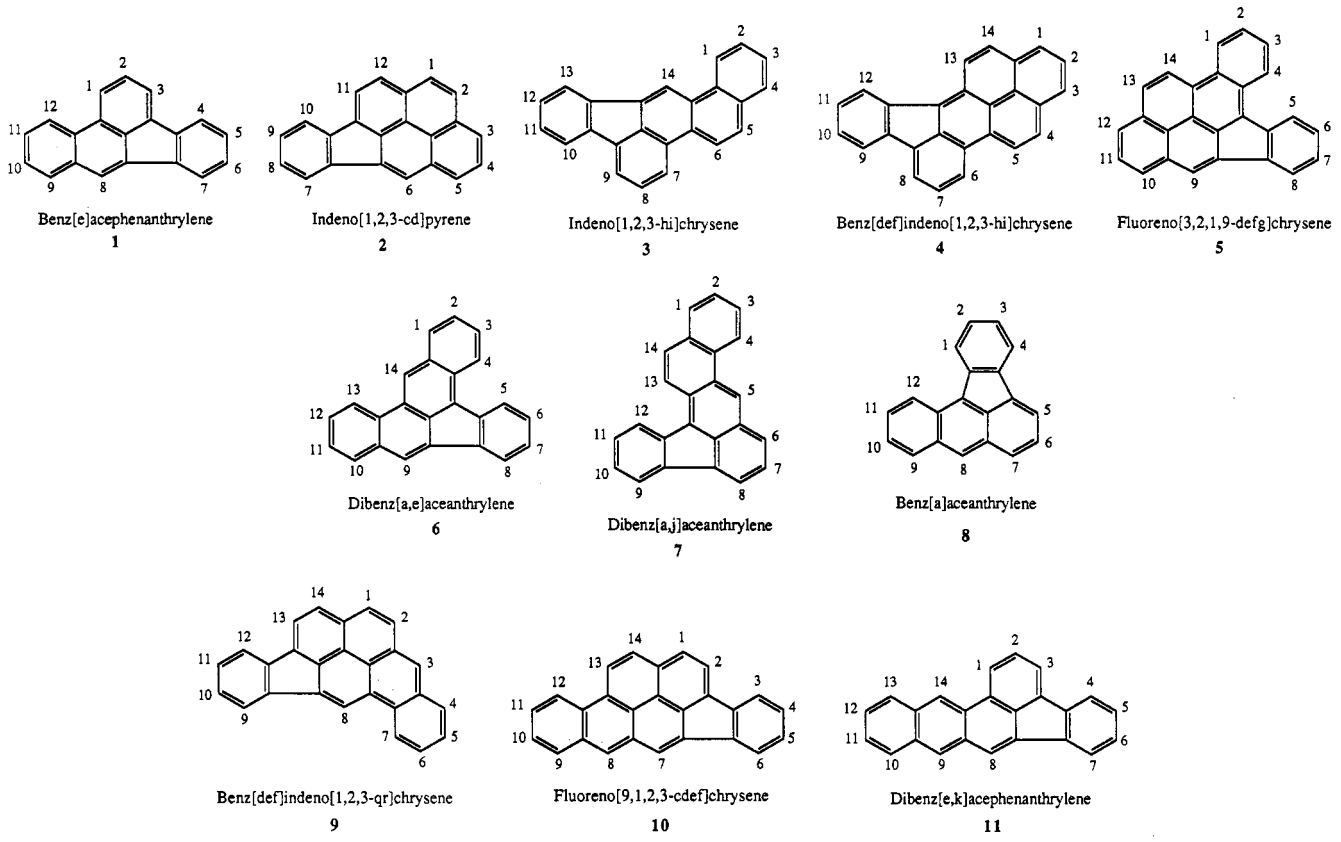


Figure 1.

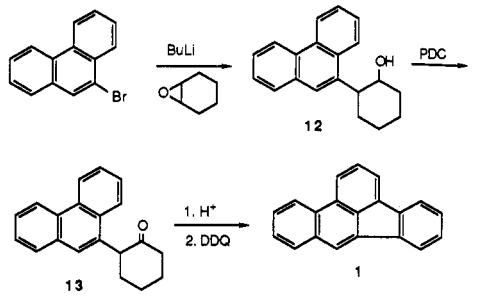


Figure 2.

times and providing higher yields than PDC or PCC.

In the cyclization step, the HPLC profile of the products eluted with pure hexane on a regular silica gel column revealed, in most cases, three well-resolved peaks. Upon treatment of the mixture with DDQ, the two less polar peaks merged with the third peak. This reaction was studied in detail by using the chrysene derivatives as a model (Figure 3). The progress of the cyclization reaction of the ketone **14** was monitored by HPLC and TLC, and the final mixture was separated by preparative HPLC. On the basis of their high-resolution ^1H NMR spectra (500 MHz) and mass spectral analyses, the structures of the three components are readily assigned as the hexahydro product **15**, the expected tetrahydro product **16**, and the fully aromatic target compound indeno[1,2,3-*hi*]chrysene (**3**), in order of increasing polarity (and retention time); the EIMS showed *m/e* 308, 306, and 302, respectively. The proton NMR spectra of these products revealed a characteristic singlet due to H_{14} which shifted downfield with increasing unsaturation of the aromatic ring system. Upon dehydrogenation of the mixture with excess DDQ, the H_{14} singlet peaks of **15** (δ 8.47) and **16** (δ 8.72) merge into that of the fully aromatic compound **3** (δ 9.15). This transformation is also readily detectable by TLC wherein the

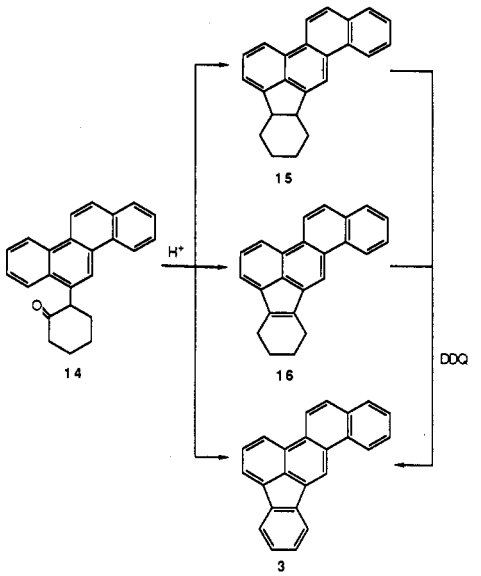


Figure 3.

hydrocarbon product **3** exhibits a more intense absorption at longer wavelength in the UV (bright yellow-orange) than the partially saturated products that are detectable only by short wavelength UV as dim blue colors. These assignments are also consistent with the UV spectra, which show an increasing shift of the UV max to longer wavelengths with increasing unsaturation (Figure 4).

The ratio of **15**:**16**:**3** was 46:29:25 by integration of the H_{14} singlet. The approximate 2:1 ratio of the hexahydro and fully aromatic products is consistent with disproportionation of the initially formed tetrahydro intermediate. Acid-catalyzed disproportionation of hydroaromatic ring systems is well-known, and its driving force is believed to be the thermodynamic energy gain from aromatization.[9]

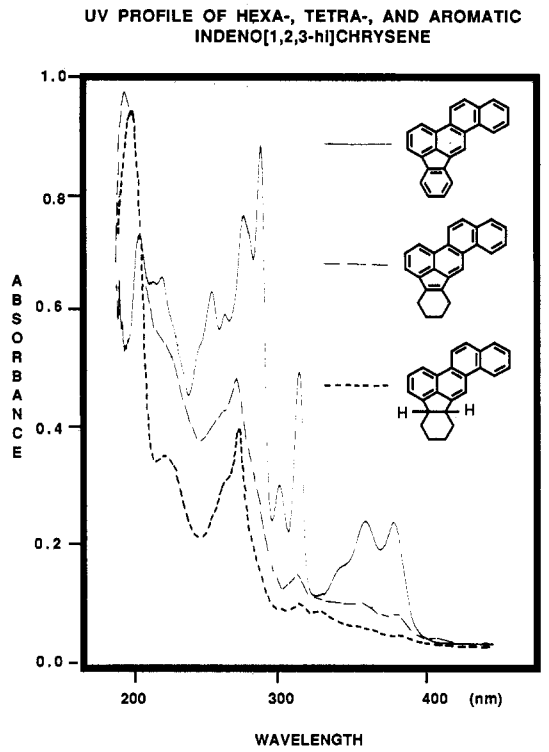
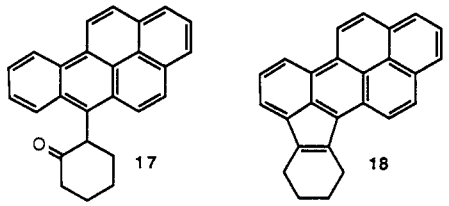


Figure 4.

The dihydro intermediates, which are the presumptive precursors of the fully aromatic products, were not detected. Similar product profiles, indicative of disproportionation, were observed in the other cyclodehydration reactions studied, except in the benzo[*a*]pyrene series. Thus, cyclization of 2-(6-benzo[*a*]pyrenyl)cyclohexanone (**17**) provided the tetrahydro compound **18** as the principal product accompanied by only small amounts of the corresponding hexahydro and fully aromatic products.



Several different strong acids were investigated as potential media for the cyclization reaction. In addition to PPA, these included methanesulfonic acid (MSA), MSA–triflic acid, trifluoroacetic acid (TFA), TFA–triflic acid, and $HClO_4$–AcOH. Although the rates of reaction differed in these media, the course of the reaction, including acid-catalyzed disproportionation of the primary products, was essentially unchanged. The order of relative reactivity in these media was PPA > MSA–triflic acid > MSA > TFA–triflic acid > TFA ≫ $HClO_4$–AcOH. Addition of a few drops of triflic acid to the acidic media generally facilitated cyclization. The optimum conditions were PPA at 110 °C. In most of the examples investigated, cyclization was complete within 1–2 h, although several of the ketonic derivatives of benzo[*a*]pyrene and benz[*a*]anthracene required longer reaction times and higher temperatures, probably due to their low solubilities in PPA.

The cyclization reactions of the series of aryl ketones investigated in these studies are summarized in Table I.

(9) (a) Harvey, R. G.; Halonen, M. *Can. J. Chem.* **1967**, *45*, 2630. (b) Anderson, N. H.; Syrdal, D. P.; Graham, C. *Tetrahedron Lett.* **1972**, 903.

Table I. Cyclodehydration and Aromatization of 2-Arylcyclohexanones

aryl	color in PPA	fluoranthene	yield, %
9-phenanthryl	red-brown	1	74
1-pyrenyl	purple	2	82
4-pyrenyl	purple	2	91
6-chrysenyl	violet-brown	3	71
6-benzo[*a*]pyrenyl	pink violet	4	90
		5	2
1,2,3,4-tetrahydro-6-benzo[*a*]-pyrenyl	pink violet	5	61
7-benz[*a*]anthryl	deep red	6	46
		7	40
9-anthryl	deep red	8	79
6-chloro-1-benzo[*a*]pyrenyl	deep red	9	82
4-benz[*a*]anthryl	light brown	11	91

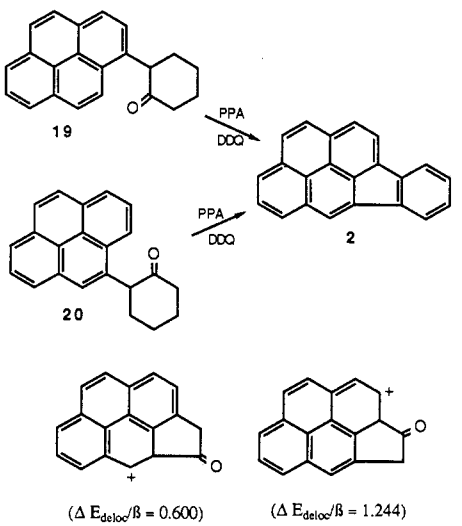


Figure 5.

It is worthy of note that the different ketones in hot PPA gave characteristic colors,[10] and in some cases multiple colors were generated, indicative of the progress of the reaction. The color in PPA and the overall yields of the polycyclic aromatic fluoranthenes are given in Table I.

Surprisingly, cyclodehydration of both 2-(1-pyrenyl)- and 2-(4-pyrenyl)cyclohexanone (**19** and **20**) proceeded smoothly in PPA to furnish excellent yields (82% and 91%, respectively) of indeno[1,2,3-*cd*]pyrene (**2**, Figure 5) following dehydrogenation of the primary product. This finding contrasts with previous reports that attempted acid-catalyzed cyclization of 1-pyrenylacetic acid failed, although cyclization of the isomeric 4-pyrenylacetic acid took place readily.[11] It was reasoned on the basis of theoretical PMO calculations[12] that the low reactivity of the C-4 position of pyrene for electrophilic substitution was responsible for the failure of cyclization to this site. Consistent with this hypothesis, the β-delocalization energy ($\Delta E_{deloc}/\beta$) for cyclization to the 1-position is greater (1.244) than that for reaction in the 4-position (0.600). This explanation appears untenable in view of the present observation that both **19** and **20** cyclize with apparent equal readiness. The failure of 1-pyrenylacetic acid to yield a cyclized product may be due to the greater ease of secondary reactions (e.g., self-condensation) relative to cy-

(10) Pizey, J. S. *Synthetic Reagents*; Vol. 6; New York, 1985; pp 157–414.

(11) (a) Gold, A.; Schultz, J.; Eisenstadt, E. *Tetrahedron Lett.* **1978**, 4491. (b) Konieczny, M.; Harvey, R. G. *J. Org. Chem.* **1979**, *44*, 2158. (c) Ittah, Y.; Jerina, D. M. *Tetrahedron Lett.* **1978**, 4495.

(12) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969; pp 214–217 and 304–306.

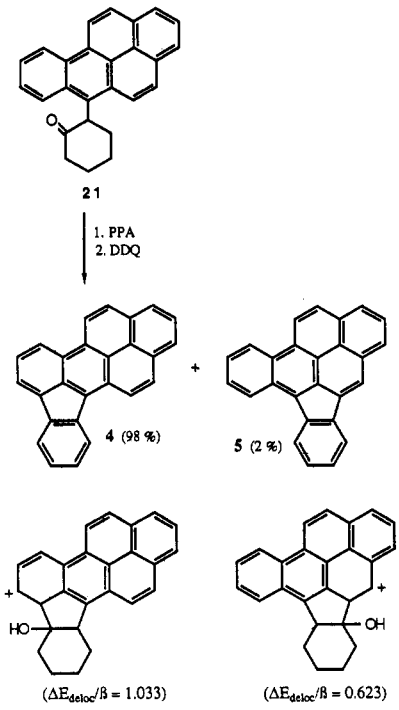


Figure 6.

clization of this isomer. In any case, it is fortuitous that cyclization of 2-(1-pyrenyl)cyclohexanone proceeds readily, since 1-bromopyrene required for its preparation is commercially available, while the isomeric 4-bromopyrene is available only through a complex multistep synthesis.

While the majority of the aryl ketones investigated (Table I) contained only a single peri position adjacent to the position of attachment of the cyclohexanone ring, allowing no ambiguity concerning the direction of cyclization, 2-(6-benzo[*a*]pyrenyl)cyclohexanone (**21**) and 2-(7-benz[*a*]anthracenyl)cyclohexanone (**22**) both contain two such positions, raising the possibility of isomeric products. Cyclodehydration of **21** in PPA, followed by dehydrogenation of the product with DDQ, furnished almost exclusively the isomer arising from covalent bonding to the 7-position in the benzo ring of benzo[*a*]pyrene (**4**, Figure 6). Only a very small amount of the alternative isomer (**5**) formed by cyclization in the alternative direction was detected. The ratio of **4**:**5** was 98:2. These isomers were readily distinguishable by their 500-MHz ^{1}H NMR spectra in comparison with that of benzo[*a*]pyrene, all the chemical shifts and coupling constants of which were previously assigned.[13,14] The most revealing feature of the spectrum of the minor isomer **5** was a sharp singlet at δ 8.52 assigned to H_9 (corresponding to H_4 of the parent benzo[*a*]pyrene ring system). In contrast, the spectrum of the major isomer **4** exhibited a pair of characteristic doublets at δ 8.73 and δ 8.05 (J = 8.5 Hz) assigned to $H_{13,14}$ (corresponding to the $H_{4,5}$ "K-region" protons of benzo[*a*]pyrene). All other spectral features and other properties of **4** and **5** were in accord with their structural assignments.[15,16] The direction

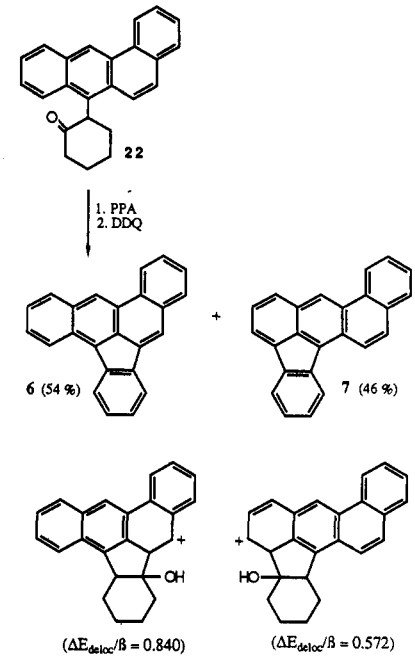


Figure 7.

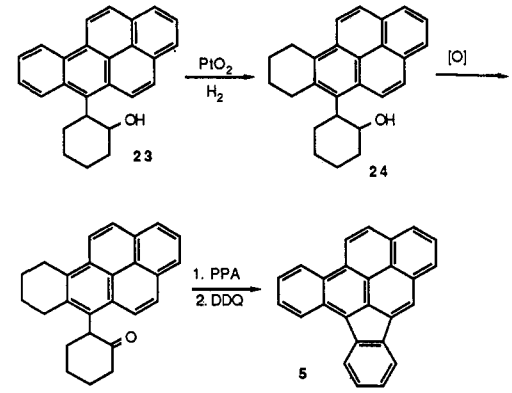


Figure 8.

of the observed highly regioselective cyclization of **21** into the 7-position of benzo[*a*]pyrene is consistent with molecular orbital theoretical calculations that predict preferential formation of the major isomer **4** (for which ΔE_{deloc} = 1.033 β) over the minor isomer **5** (for which ΔE_{deloc} = 0.623 β).

The cyclodehydration of 2-(7-benz[*a*]anthracenyl)-cyclohexanone (**22**), in contrast to that of **21**, exhibited only minimal regioselectivity, affording after dehydrogenation dibenz[*a*,*e*]- and dibenz[*a*,*j*]aceanthrylene (**6** and **7**) in the ratio of 54:46 (Figure 7). The separation of **6** from the mixture was accomplished by repeated chromatography. The isolation of **7** on preparative scale was not pursued, since **7** is obtainable in good yield from the alternative synthetic method reported previously.[17] The low regioselectivity observed in the cyclization of **22** is somewhat unexpected, since PMO calculations of the delocalization energies for cyclization to the H_6 ($\Delta E_{deloc}/\beta$ = 0.840) or the H_8 ($\Delta E_{deloc}/\beta$ = 0.572) positions predict preferred cyclization to the former site, although the difference between the two is small.

Since the cyclodehydration of **21** afforded only one of the two possible isomers with high regioselectivity, a practical synthetic approach to the alternative isomer, **5**,

(13) Thermodynamics Research Center Hydrocarbon Project, *Selected Nuclear Magnetic Resonance Spectral Data*, Suppl. Vol. No. F-26; Thermodynamics Research Center, Texas A&M University, College Station, TX, 1982.

(14) Yagi, H.; Holder, G. M.; Dansette, P. M.; Hernandez, O.; Yeh, H. J.; LeMahieu, R. E.; Jerina, D. M. *J. Org. Chem.* **1976**, *41*, 977.

(15) Complete ^{1}H and ^{13}C NMR assignments of **4** and **5** by the use of 2-D NMR techniques are described in the accompanying paper: Cho, B. P.; Harvey, R. G. *J. Org. Chem.*, following paper in this issue.

(16) The UV spectrum of **5** and its melting point matched closely those reported by Aitken, I. A.; Reid, D. H. *J. Chem. Soc.* **1960**, 663.

(17) Ray, J. K.; Harvey, R. G. *J. Org. Chem.* **1982**, *47*, 3335.

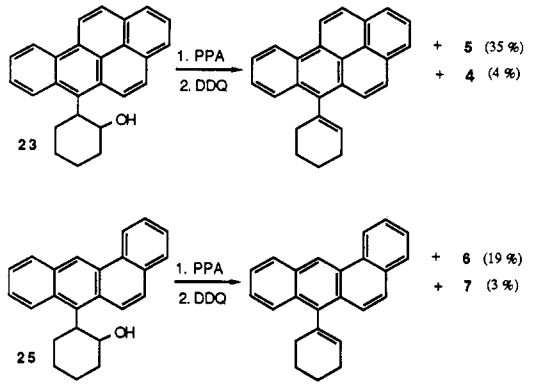


Figure 9.

was required. For this purpose, we decided to take advantage of the previous observation that hydrogenation of benzo[*a*]pyrene can be directed to yield 7,8,9,10-tetrahydrobenzo[*a*]pyrene or 5,6-dihydrobenzo[*a*]pyrene depending upon whether a platinum and palladium catalyst is employed.[18] Hydrogenation of 2-(6-benzo[*a*]pyrenyl)-cyclohexanol (**23**) over a platinum catalyst (PtO_2) took place regioselectively in the terminal benzo ring to yield as the major product 2-(7,8,9,10-tetrahydrobenzo[*a*]pyrenyl)cyclohexanol **24** (>80%), accompanied by lesser amounts of the 4,5-dihydro derivative and further hydrogenated products (<20%) (Figure 8). The mixture was treated with chloranil to convert the perhydrogenated derivatives to **24**, and the product (containing >95% of **24**) was oxidized with the "Dess–Martin" reagent to give the 7,8,9,10-tetrahydro derivative of **21** in acceptable yield. This ketone was cyclized in PPA and aromatized with DDQ to furnish the desired **5** as the sole product.

Cyclodehydration of the alcohol **23** and its benz[*a*]-anthracene analogue (**25**) followed by DDQ dehydrogenation gave somewhat different results than were observed for the related ketones (Figure 9). The major products were the olefins formed by dehydration of both the benzo[*a*]pyrene and benz[*a*]anthracene derivatives (51% and 76%, respectively). In the case of **23**, the accompanying products were **5** (35%) and **4** (4%), indicative of preferential cyclization to the 5-position of benzo[*a*]pyrene. However, this direction of cyclization is contrary to that of the related ketone **21**, which yields almost exclusively the isomer formed by cyclization to the 7-position. Similar cyclodehydration and DDQ treatment of the benz[*a*]-anthracene alcohol **25** yielded, in addition to the olefinic product, polycyclic fluoranthenes **6** and **7** in the ratio of 86:14, representing a substantial improvement over the low regioselectivity observed previously for the cyclization of the related ketone. The reason for the marked difference in the regioselectivity of cyclization exhibited by the alcohol and ketone substrates is uncertain.

Two of the four possible isomeric polycyclic fluoranthene derivatives of benzo[*a*]pyrene (**4**, **5**) were synthesized by direct application of the general synthetic approach in Figure 2. The remaining two isomers, benz[*def*]indeno-[1,2,3-*qr*]chrysene (**9**) and fluoreno[9,1,2,3-*cdef*]chrysene (**10**), were synthesized by a modification of this approach (Figure 10). For this purpose, it was necessary to introduce an appropriate blocking group into the reactive 6-position of benzo[*a*]pyrene. Prior studies on the electrophilic substitution of benzo[*a*]pyrene indicate that the order of positional reactivity is 6 ≫ 1 > 3.[19] Chlorination

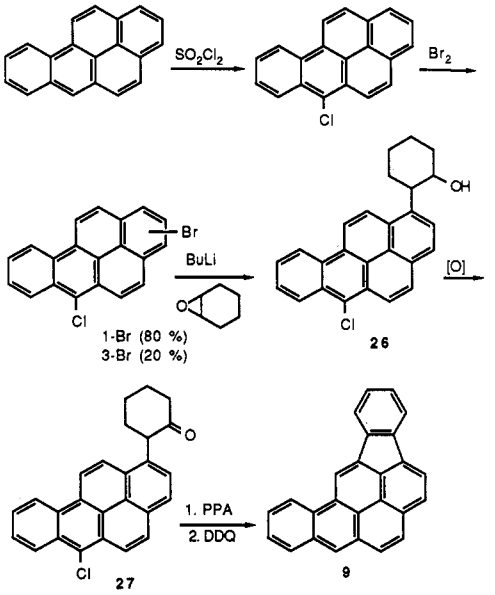


Figure 10.

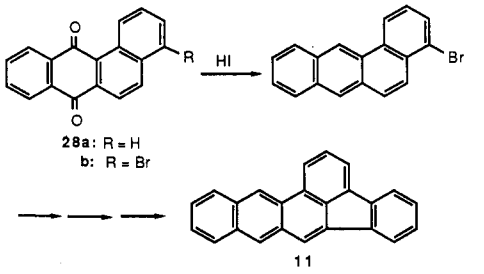


Figure 11.

of benzo[*a*]pyrene with sulfuryl chloride furnished 6-chlorobenzo[*a*]pyrene, which was directly brominated with 1.2 equiv of bromine.[20] The ^1H NMR spectrum of the bromination product showed a mixture of 1-bromo- and 3-bromo-6-chlorobenzo[*a*]pyrene in about 4:1 ratio. Attempts to separate the isomers by recrystallization were unsuccessful. Therefore, the mixture was employed directly in the next step. Reaction of the mixture with phenyllithium followed by treatment of the product with cyclohexene oxide gave the corresponding cyclohexanol derivatives. 2-(6-Chloro-1-benzo[*a*]pyrenyl)cyclohexanol (**26**) was readily separated from the mixture by precipitation with petroleum ether. Oxidation of **26** with the Dess–Martin reagent furnished the ketone **27**, which was cyclized in PPA (150 °C, 5 h) and dehydrogenated with DDQ to yield **9** as the sole product. An unusual feature of the cyclization reaction is the loss of the chlorine atom, as evidenced by the mass spectrum of the product. Although PPA-catalyzed dechlorination of aromatic molecules has apparently not been reported in the literature, a number of strong acids are known to dehalogenate aromatic chlorine or bromine compounds.[21]

The fourth isomer, fluoreno[9,1,2,3-*cdef*]chrysene (**10**), was obtained via a synthetic sequence starting with the mixture of 2-arylcyclohexanols remaining after separation of the major part of **26**. Oxidation of this mixture with the Dess–Martin reagent, followed by treatment with PPA and DDQ, furnished a mixture of **9** and **10** that was readily separated by chromatography on an alumina column using benzene/hexane (8:2) as the solvent system.

(18) Fu, P. P.; Lee, H. M.; Harvey, R. G. *J. Org. Chem.* **1980**, *45*, 2797.
(19) Coffrey, S. *Rodd's Chemistry of Carbon Compounds*; Elsevier: New York, 1979, pp 288–290.
(20) Windaus, A.; Raichle, K. *Liebigs Ann. Chem.* **1939**, *537*, 157.
(21) Pinder, A. R. *Synthesis* **1980**, 425.

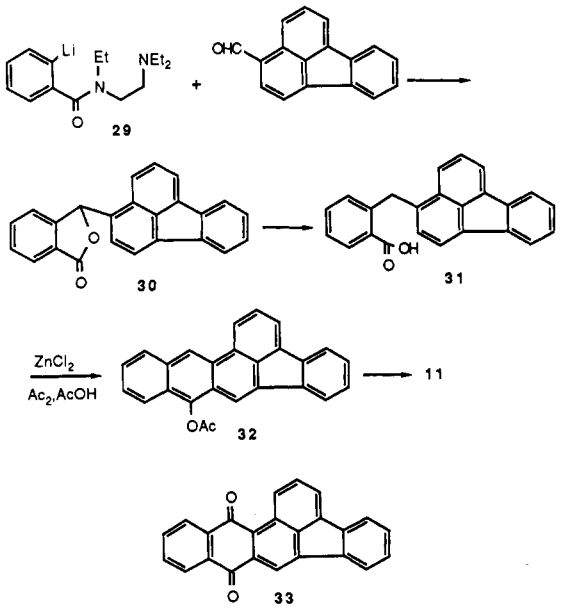


Figure 12.

Three of the four possible polycyclic fluoranthene derivatives of benz[*a*]anthracene were synthesized by application of the general synthetic approach (Figure 2). In addition to **6** and **7**, whose synthesis has been discussed, a third isomer, dibenz[*e*,*k*]acephenanthrylene (**11**), was prepared by the route shown in Figure 11. 4-Bromobenz[*a*]anthracene, required as the starting compound, was synthesized via bromination of benz[*a*]anthracene-7,12-dione (**28a**) by an improved modification of the literature procedure,[23] involving substitution of HI as the reagent for the reduction of 4-bromobenz[*a*]anthracene-7,12-dione (**28b**).[24,25] The yield and purity of the 4-bromobenz[*a*]-anthracene were substantially improved by the use of this reagent. The bromo compound was transformed into **11** by the general method in Figure 2.

Prior to development of the foregoing method for the preparation of **11**, an alternative synthetic route was also investigated (Figure 12). This approach involves application of the ortho-lithiation methodology, which has recently been employed to prepare a broad range of polyaromatic compounds.[26] 2-Lithio-*N*-[2-(diethylamino)-ethyl]-*N*-ethylbenzamide (**29**) was prepared by the method of Comins et al.[27] and reacted with 3-formylfluoranthene[28,29] to provide the lactone **30**. Reduction of **30** with H_2 over a Pd/C catalyst yielded the acid **31**, which underwent cyclization with $ZnCl_2$ in Ac_2O/AcOH to give 9-acetoxydibenz[*e*,*k*]acephenanthrylene (**32**). Reduction of the lactone **30** with Zn in AcOH also provided **31**, but this mode of reduction was very sensitive to the type of zinc used and gave an inferior yield. Treatment of **32** with Zn/NaOH gave dibenz[*e*,*k*]acephenanthrylene (**11**) accompanied by a small amount of the quinone **33**. The physical and spectroscopic properties of **11** prepared via this route were identical with those of a sample prepared through the preceding route.

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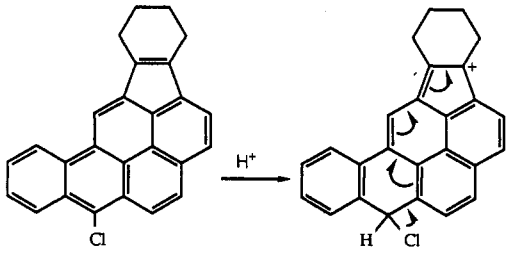
Discussion

In summary, we have described a general synthetic route to polycyclic aromatic fluoranthenes that entails relatively few steps and appears to be applicable to the preparation of most members of this class of nonalternant PAHs. Compounds prepared via this route include the fluoranthene derivatives of phenanthrene (**1**), pyrene (**2**), chrysene (**3**), and anthracene (**8**), for which only a single isomer is possible, as well as three of the four isomeric derivatives of benz[*a*]anthracene (**6**, **7**, **11**) and all four of the isomers derived from benzo[*a*]pyrene (**4**, **5**, **9**, **10**). The main limitation of this approach appears to be the availability of the appropriate lithio derivatives of the parent alternant hydrocarbons. While in many cases these can be obtained from direct bromination followed by metal exchange, in other cases it may be necessary to modify the procedure. One effective strategy, utilized effectively in the synthesis of **9**, is to employ a blocking group such as chlorine to redirect bromination to the desired site. Another useful technique, used in the preparation of **11**, is to brominate the quinone derivatives that generally exhibit different substitution patterns than the parent PAHs and are readily reduced by HI[24,25] to the deoxygenated fully aromatic ring systems.

While cyclization of the majority of the aryl ketones investigated is restricted to only a single available adjacent peri position, 2-(6-benzo[*a*]pyrenyl)- and 2-(7-benz[*a*]-anthracenyl)cyclohexanone (**21** and **22**) contain two such positions, making possible isomeric products. In the case of **21**, cyclization is highly regioselective, furnishing after aromatization mainly the product of cyclization to the 7-position, consistent with prediction based on molecular orbital theoretical calculations of the delocalization energies of the two possible carbocation intermediates. In the case of **22**, cyclization is essentially nonregioselective, furnishing after aromatization only a slight preponderance of isomer **6** relative to **7**. This result is also consistent with theory. While the number of examples is small, these findings suggest that the preferred position of cyclization in reactions of this type may be generally predictable by molecular orbital methods.

The unexpected loss of chlorine from the 6-position of benzo[*a*]pyrene during the cyclodehydration of its cyclohexanone derivative **27** is fortuitous, since it eliminates the necessity for its removal in a subsequent step. The loss of chlorine may be rationalized as proceeding via the intermediate **35** arising from proton addition to the normal cyclodehydration product **34**. The Cl^+ ion formed then abstracts a hydride ion to form dihydrobenz[*def*]indeno-[1,2,3-*qr*]chrysene, which undergoes dehydrogenation to yield **9**.



34 **35**

Surprisingly, little is known concerning the patterns of electrophilic substitution of nonalternant hydrocarbons.[1] Studies of the bromination and acetylation of the polycyclic aromatic fluoranthenes are currently in progress and will be published in due course. Samples of the polycyclic fluoranthenes **1**–**11** synthesized herein will be made available to interested investigators as standards for the

analysis of environmental pollutants and for studies of their biological properties.

Experimental Section

Materials and Methods. Benzo[*a*]pyrene (BP) was prepared from 4-(1-pyrenyl)butyric acid by the procedure reported.[30] 4-Bromopyrene was synthesized from 1,2,3,6,7,8,-hexahydropyrene[31] by the method described previously.[32] 7-Bromobenz[*a*]anthracene was prepared from benz[*a*]anthracene by bromination with NBS.[33] 6-Chlorobenzo[*a*]pyrene was prepared by chlorination of benzo[*a*]pyrene with SO_2Cl_2 by the method reported.[20] *N*-[2-(Diethylamino)ethyl]-*N*-ethylbenzamide was prepared by the literature procedure.[27] *N,N,N',N'*-Tetramethylethylenediamine was distilled from CaH_2 and stored over KOH. *N*-Bromosuccinimide (NBS) was crystallized from water prior to use. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl and $LiAlH_4$. Ether was distilled from CaH_2 and stored over sodium. Benzene was distilled from CaH_2 and stored over molecular sieves (4 Å).

^1H NMR spectra were obtained in $CDCl_3$ on a Varian EM360 spectrometer or the University of Chicago 500-MHz spectrometer; chemical shifts are reported relative to tetramethylsilane (TMS) in $CDCl_3$ unless otherwise noted. Integration was consistent with all structural assignments. ^{13}C NMR spectra were recorded in $CDCl_3$ in 5-mm tubes on a Varian XL-400 spectrometer, operating at 100.57 MHz. Chemical shifts in ppm were determined relative to the $CDCl_3$ absorption and converted to the TMS scale using $\delta(CDCl_3) = 77.00$ ppm. The complete assignments of both proton and carbon spectra of some of the target compounds were made by using a combination of 2D NMR techniques (long-range COSY and long-range ^1H–^{13}C chemical shift correlation spectroscopy) described in the accompanying paper.[15] Infrared spectra were recorded on a Perkin–Elmer infrared spectrophotometer Model 297. UV spectra were obtained on a Perkin-Elmer Model Lamda 5 UV/vis spectrometer using the solvent specified. HPLC separations were carried out on a Perkin-Elmer Series 4 liquid chromatograph equipped with Model LC 95 variable wavelength UV detector using a Dupont Zorbax Sil column (4.6 mm i.d. × 25 cm) using (A) hexane, (B) hexane–THF (7:3), or other solvent as specified. Melting points are uncorrected. All new compounds gave satisfactory microanalysis within ±0.3% and/or high resolution mass spectra (HRMS) consistent with the assigned structures. TLC was run on Merck precoated silica gel 60_{F250} glass plates. Neutral alumina (activity I) was used for the purification of the final compounds.

Organic extracts were routinely dried over anhydrous $MgSO_4$. All lithiations were performed by using syringe–septum cap techniques in oven-dried glassware under an atmosphere of dry, high quality Ar or N_2.

General Procedure for the Synthesis of Polycyclic Aromatic Fluoranthenes: Benzo[*b*]fluoranthene. (1) Reaction of the Aryllithium Compound with Cyclohexene Oxide. *n*-Butyllithium (15.5 mL, 2.6 M in hexane, 0.04 mol) was added over a 20-min period to a solution of 9-bromophenanthrene (5.2 g, 0.02 mol) in anhydrous ether (150 mL) under an Ar or N_2 atmosphere. The resulting milky yellow solution was then stirred for 2 h, and cyclohexene oxide (3.93 g, 0.04 mol) in ether (30 mL) was added dropwise. The mixture was stirred overnight, water (150 mL) was added, and the separated ether layer was washed successively with water and brine and dried. Evaporation of the organic solvent gave a crude viscous residue (8.64 g). Column chromatography (silica gel, 5 × 30 cm) gave a mixture of phenanthrene and the unreacted starting bromo compound (total 1 g) in the first fraction (hexanes) and then 2-(9-phenanthryl)-cyclohexanol (**12**; 3.5 g, 63%) (ethyl acetate–hexanes : 1:9) as white crystals: mp (ethanol) 109–111 °C; HPLC (solvent B, 3 mL/min) t_R 3.3 min; IR (Nujol) 3029 cm^{-1} (br, OH); ^1H NMR δ 8.74 (dd, 1, H_4 or H_5, J = 2.3, 7.0 Hz), 8.64 (d, 1, H_4 or H_5, J = 8.0 Hz), 8.24 (dd, 1, J = 2.0, 8.0 Hz), 7.83 (dd, 1, J = 1.0, 8.5 Hz), 7.73 (s, 1, H_{10}), 7.66–7.54 (m, 4), 4.13 (br m, 1, carbinolic), 3.41 (br m, 1, benzylic), 2.27 (m, 1), 2.08 (m, 1), 1.96 (m, 1), 1.80 (m, 1), 1.77 (s, 1, OH), 1.53 (m, 4); HRMS, calcd for $C_{20}H_{20}O$, 276.1514, *m/e* 276.1513 (M^+). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 87.00; H, 7.36.

(2) Oxidation of the Arylcyclohexanol. A solution of **12** (1.38 g, 5 mmol) in dry DMF (10 mL) was added to a solution of PDC (5.64 g, 15 mmol) in DMF (50 mL) under N_2 and stirred overnight at ambient temperature. The reaction mixture was poured into water (300 mL) and extracted with CH_2Cl_2 (3 × 200 mL). The combined organic extracts were washed thoroughly with water and brine and dried. Evaporation of the solvent gave the crude product (1.3 g), which was passed through a short column of Florisil (ethyl acetate–hexane = 1:9) and recrystallized from ethanol to give pure 2-(9-phenanthryl)cyclohexanone (**13**) as white crystals (1.2 g, 88%): mp 153–155 °C (ethanol); HPLC (solvent B, 3 mL/min) t_R 3.4 min; IR (Nujol) 1760 cm^{-1} (C=O); ^1H NMR δ 8.70 (d, 1, H_4 or H_5, J = 8.0 Hz), 8.6 (d, 1, H_4 or H_5, J = 8.5 Hz), 7.79 (d, 1, J = 8.0 Hz), 7.69 (d, 1, J = 8.0 Hz), 7.60–7.50 (m, 4), 7.56 (s, 1, H_{10}), 4.33 (dd, 1, benzylic, J = 4.75, 12.5 Hz), 2.63 (m, 2), 2.45 (m, 1), 2.35 (m, 1), 2.25 (m, 1), 2.11 (m, 1), 1.92 (m, 2); HRMS, calcd for $C_{20}H_{18}O$; 274.1357, *m/e* 274.1351 (M^+). Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.54; H, 6.66.

(3) Cyclization and Aromatization. A solution of **13** (0.83 g, 3 mmol) in PPA (85%, ca. 40 g) was heated to 110 °C. Reaction progress was monitored by TLC or HPLC. After 2 h, the starting material completely disappeared. The hot brown mixture was then poured directly onto crushed ice (300 g) and allowed to dissolve for 1 h. The resulting dark viscous residue was dispersed by stirring with a spatula, and the resulting suspension was extracted with ether (3 × 200 mL). The combined extracts were washed successively with water, 5% $NaHCO_3$, water, and brine and dried. Removal of the solvent gave a dark viscous residue (0.72 g), which was treated with excess DDQ (2.27 g, 0.01 mol) in dry benzene (50 mL) and refluxed for 30 min under N_2. The solution was cooled and applied directly to an alumina column (neutral, activity I, 5 × 2 cm). Elution with benzene gave benz[*e*]acephenanthrylene (**1**) (0.57 g, 74% from **13**). Recrystallization from ethanol gave analytically pure **1** as white fluffy needles: mp (ethanol) 167.5–168 °C (lit.[34a] mp 168 °C); HPLC (solvent A, 3 mL/min) t_R 7.6 min; complete ^1H and ^{13}C NMR assignments are given in the accompanying paper;[15] HRMS, calcd for $C_{20}H_{12}$, 252.0939, *m/e* 252.0939 (M^+); UV (cyclohexane) max (log ϵ) 348.8 nm (4.01), 300.8 (4.56), 289.2 (4.42), 276.4 (4.44), 255.6 (4.60), 222.0 (4.68), 204.0 (4.74); the UV spectrum essentially matched that reported.[1]

Synthesis of Indeno[1,2,3-*cd*]pyrene from 1-Bromopyrene. (1) 2-(1-Pyrenyl)cyclohexanol. Reaction of 1-lithiopyrene with cyclohexene oxide by the above procedure gave the title alcohol as white leaflets (1.70 g, 57%): mp (ethanol) 152–153 °C; HPLC (solvent B, 3 mL/min) t_R 3.9 min; ^1H NMR δ 8.43 (d, 1, J = 9.5 Hz), 8.18 (d, 1, J = 8.0 Hz), 8.15 (d, 2, J = 7.0 Hz), 8.10 (d, 1, J = 9.0 Hz), 8.03 (m, 3), 7.97 (appt t, 1, J = 7.5 Hz), 4.11 (m, 1, carbinolic), 3.69 (m, 1, benzylic), 2.29 (m, 1), 2.13 (m, 1), 1.99 (m, 1), 1.87 (m, 1), 1.80–1.50 (m, 4); HRMS, calcd for $C_{22}H_{20}O$, 300.1514, *m/e* 300.1512 (M^+). Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.75; H, 6.76.

(2) 2-(1-Pyrenyl)cyclohexanone (19). Oxidation of the above alcohol with PDC furnished **19** as shiny white leaflets (2.10 g, 71%): mp (ethanol) 131.5–132.5 °C; HPLC (solvent B, 3 mL/min) t_R 3.2 min; ^1H NMR δ 8.14 (m, 3), 8.12 (d, 1, J = 6.0 Hz), 8.01 (s, 2), 7.98 (d, 1, J = 9.0 Hz), 7.95 (appt t, 1, 6, J = 7.0 Hz), 7.87 (d, 1, J = 7.5 Hz), 4.62 (dd, 1, benzylic, J = 12.5, 5.5 Hz), 2.68 (m, 2, CH_2C=O), 2.49 (m, 1), 2.40 (m, 1), 2.30 (m, 1), 2.15 (m, 1), 2.00 (m, 2); HRMS, calcd for $C_{20}H_{18}O$, 298.1357, *m/e* 298.1360 (M^+). Anal. Calcd for $C_{20}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.62; H, 6.13.

(3) Indeno[1,2,3-*cd*]pyrene (2). The crude product from reaction of **19** (0.894 g, 3 mmol) in PPA (2 h) followed by the usual workup and treatment with DDQ was chromatographed on alu-

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mina to yield **2** as bright orange needles (0.68 g, 82% from **19**): mp (benzene–petroleum ether) 162–163 °C (lit.[35a] mp 162.5–163 °C); HPLC (solvent A, 3 mL/min) t_R 8.1 min; complete ^1H and ^{13}C NMR assignments are given in the accompanying paper;[15] UV (cyclohexane) max (log ϵ) 359.8 nm (4.05), 315.4 (4.38), 302.9 (4.42), 275.9 (4.28), 250.5 (4.73), 204.0 (4.70), 197.7 (4.66), 192.3 (4.63); the UV spectrum was identical with that reported;[36] HRMS, calcd for 276.0939, *m/e* 276.0927 (M^+).

Indeno[1,2,3-*cd*]pyrene from 4-Bromopyrene. (1) 2-(4-Pyrenyl)cyclohexanol was synthesized from 4-bromopyrene by the usual procedure (1.92 g, 71%): mp (ethyl acetate–hexane) 148–150 °C; HPLC (solvent B, 3 mL/min) t_R 3.3 min; ^1H NMR δ 8.51 (d, 1, J = 8.0 Hz), 8.19 (dd, 1, J = 7.5, 0.5 Hz), 8.14 (d, 2, J = 7.5 Hz), 8.08 (s, 1, H_5), 8.06 (m, 2), 8.03 (appt t, 1, J = 8.0 Hz), 7.98 (appt t, 1, J = 7.0 Hz), 4.25 (m, 1, carbinolic), 3.62 (m, 1, benzylic), 2.32 (m, 1), 2.19 (m, 1), 2.02 (m, 1), 1.86 (m, 1), 1.62 (m, 4); HRMS, calcd for $C_{22}H_{20}O$, 298.1358, *m/e* 298.1358 (M^+).

(2) 2-(4-Pyrenyl)cyclohexanone (20). Oxidation of the alcohol with PDC provided **20** (610 mg, 68%) as white fluffy needles, mp (ethyl acetate–petroleum ether) 161 °C; HPLC (solvent B, 3 mL/min) t_R 3.5 min; ^1H NMR δ 8.13 (m, 3), 8.04 (s, 2), 7.96 (m, 4), 4.55 (dd, 1, benzylic, J = 12.3, 5.3 Hz), 2.71 (m, 2), 2.59 (m, 1), 2.50 (m, 1), 2.31 (m, 1), 2.21 (m, 1), 2.01 (m, 2); HRMS, calcd for $C_{22}H_{18}O$, 298.1358, *m/e* 298.1358 (M^+).

(3) Indeno[1,2,3-*cd*]pyrene (2). Cyclization and aromatization of **20** by the usual procedure gave **2** (0.25 g, 91%), spectroscopically identical (HRMS, ^1H and ^{13}C NMR, UV) with **2** prepared from 1-bromopyrene.

Synthesis of Indeno[1,2,3-*hi*]chrysene (3). (1) 6-Bromochrysene. To a partial suspension of chrysene (2.28 g, 10 mmol) in CS_2 (200 mL) was added bromine (1.76 g, 11 mmol) in CS_2 (20 mL) dropwise over 30 min. Stirring was continued for 2 days at about 40 °C; then the solvent was evaporated and the product was recrystallized from benzene–ethanol (4:1, 200 mL) to give a white powder (0.5 g) containing approximately 30% chrysene. Concentration of the filtrate to about 100 mL gave a second crop (2.53 g, 82%) containing >85% 6-bromochrysene by HPLC analysis (mp 143–146 °C). Recrystallization of the latter twice from benzene gave a product (2.12 g, 69%) that contained <5% chrysene, suitable for the next step: mp (benzene) 152–154 °C (lit.[36] mp 153.6–155 °C); HPLC (solvent A, 3 mL/min) t_R 6.8 min; ^1H NMR δ 8.98 (s, 1, H_5), 8.71 (m, 2), 8.63 (d, 1, J = 8.5 Hz), 8.59 (d, 1, J = 9.0 Hz), 8.39 (dd, 1, J = 6.8, 2.8 Hz), 7.95 (m, 2), 7.69 (m, 2), 7.61 (m, 1); HRMS, calcd for $C_{18}H_{11}Br$, 306.0044, 308.0023, *m/e* 306.0041, 308.0021 (M^+).

(2) 2-(6-Chrysenyl)cyclohexanol was synthesized from 6-bromochrysene by the standard method. It was obtained as white leaflets (1.30 g, 50%): mp (ethyl acetate–hexane) 168–170 °C; HPLC (solvent B, 3 mL/min) t_R 3.2 min; ^1H NMR δ 8.83 (d, 1, J = 8.0 Hz), 8.79 (d, 1, J = 8.5 Hz), 8.74 (s, 1, H_5), 8.68 (d, 1, J = 9.0 Hz), 8.35 (d, 1, J = 8.0 Hz), 7.96 (appt d, 2, J = 8.5 Hz), 7.69 (m, 3), 7.62 (appt t, 1, J = 7.5 Hz), 4.27 (m, 1, carbinolic), 3.57 (m, 1, benzylic), 2.33 (m, 1), 2.14 (m, 1), 2.00 (m, 1), 1.88 (m, 1), 1.60 (m, 4); HRMS, calcd for $C_{24}H_{22}O$, 326.16718 *m/e* 326.1656 (M^+).

(3) 2-(6-Chrysenyl)cyclohexanone was obtained from oxidation of the alcohol as white needles (0.25 g, 62%): mp (ethanol) 178–179 °C; HPLC (solvent B, 3 mL/min) t_R 3.8 min; ^1H NMR δ 8.81 (d, 1, J = 8.50 Hz), 8.72 (d, 1, J = 8.5 Hz), 8.67 (d, 1, J = 9.0 Hz), 8.59 (s, 1, H_5), 7.95 (appt d, 2, J = 9.0 Hz), 7.82 (d, 1, J = 8.5 Hz), 7.65 (appt t, 2, J = 7.5 Hz), 7.58 (appt t, 2, J = 7.0 Hz), 4.51 (dd, 1, benzylic, J = 12.0, 5.3 Hz), 2.70 (m, 2), 2.62–2.46 (m, 2), 2.14 (m, 1), 1.11 (m, 1), 2.02 (m, 2); HRMS, calcd for $C_{24}H_{20}O$, 324.1514, *m/e* 324.1504 (M^+).

(4) Indeno[1,2,3-*hi*]chrysene (3). Cyclization of the above ketone (0.52 g, 1.6 mmol) with PPA (100 g) by the usual procedure furnished a brownish-violet solution, which after the usual workup gave three peaks (8.8, 9.4, and 15.2 min) on HPLC (solvent A, 2 mL/min) that were isolated and were subjected to MS and ^1H NMR analyses. The first peak was identified as **15**: ^1H NMR δ 8.80 (d, 1, H_6 or H_7, J = 8.5 Hz), 8.60 (d, 1, H_6 or H_7, J = 8.5 Hz), 8.47 (s, 1, H_{14}), 8.37 (d, 1, J = 8.0 Hz), 7.96 (d, 1, J = 7.5 Hz), 7.91 (d, 1, J = 9.0 Hz), 7.66 (appt t, 2, J = 8.0 Hz), 7.59 (dd, 1, J = 14.75, 0.4 Hz), 7.42 (d, 1, J = 7.0 Hz), 3.81 (m, 1, methine, H_{13a} or H_{9b}), 3.75 (m, 1, methine, H_{13a} or H_{9b}), 2.60 (m, 2, H_{10} or H_{13}), 2.10 (m, 2, H_{10} or H_{13}), 1.60 (m, 4, $H_{11,12}$); MS, *m/e* 308 (M^+). The second peak was assigned as **16**: ^1H NMR δ 8.82 (d, 1, J = 8.5 Hz), 8.72 (s, 1, H_{14}), 8.62 (d, 1, J = 9.0 Hz), 8.35 (d, 1, J = 8.5 Hz), 7.98 (appt d, 2, J = 8.5 Hz), 7.69 (appt t, 1, J = 7.0 Hz), 7.60 (appt q, 2, J = 8.0 Hz), 7.50 (d, 1, J = 6.5 Hz), 2.90 (m, 2, H_{10} or H_{13}), 2.80 (m, 2, H_{10} or H_{13}), 1.97 (m, 4, $H_{11,12}$); MS, *m/e* 306 (M^+). The third fraction was **3**; see the spectroscopic data below.

The above mixture (0.43 g) was directly treated with DDQ and chromatographed on alumina to yield **3** (0.35 g, 71%): mp 188–189 °C (ethyl acetate/hexane) as long greenish yellow needles; HPLC (solvent A, 2 mL/min) t_R 15.2 min; complete ^1H and ^{13}C NMR assignments are given in the accompanying paper;[15] HRMS, calcd for $C_{24}H_{14}$, 302.1096, *m/e* 302.1080 (M^+); UV (cyclohexane) max (log ϵ) 380.4 nm (4.20), 361.0 (4.20), 315.1 (4.53), 302.2 (4.31), 287.7 (4.78), 276.0 (4.72), 255.1 (4.64), 206.4 (4.73). Anal. Calcd for C, 95.33; H, 4.67. Found: C, 95.19; H. 4.70.

Benz[*def*]indeno[1,2,3-*hi*]chrysene (4). (1) 6-Bromobenzo[*a*]pyrene was prepared from benzo[*a*]pyrene by bromination with NBS in CCl_4 (86%)[37] or by dropwise addition of Br_2 (0.64 g, 4 mmol) in CS_2 (10 mL) to a solution of BP (1.01 g, 4 mmol) in CS_2 (50 mL) at room temperature. The solution was stirred overnight at ambient temperature and evaporated to dryness. Recrystallization of the residue from benzene–ethanol gave a yellow powder (1.13 g, 85%). One more recrystallization gave 6-bromobenzo[*a*]pyrene: mp 222–224 °C (benzene) (lit.[37a] mp 223–224 °C); HPLC (column A, 3 mL/min) t_R 5.1 min; ^1H NMR δ 9.09 (dd, 1, J = 8.3, 1.5 Hz), 8.98 (d, 1, J = 9.0 Hz), 8.84 (dd, 1, J = 8.3, 1.5 Hz), 8.53 (d, 1, J = 9.0 Hz), 8.29 (d, 1, J = 9.0 Hz), 8.09 (d, 1, J = 7.0 Hz), 8.22 (d, 1, J = 8.0 Hz), 7.99 (d, 1, J = 9.0 Hz), 7.96 (appt t, 1, J = 8.0 Hz), 7.84 (m, 2); HRMS, calcd for $C_{20}H_{11}Br$, 330.0041, 332.0024, *m/e* 330.0042, 332.0007 (M^+).

(2) 2-(6-Benzo[*a*]pyrenyl)cyclohexanol (23). 6-Bromobenzo[*a*]pyrene (3.97 g, 12 mmol) was dissolved in dry benzene (200 mL) by heating to 60 °C. Phenyllithium (1.7 M in cyclohexane, 22 mL, 19 mmol) was added dropwise to this solution, and the mixture was stirred under Ar at the same temperature. After 5 h, cyclohexene oxide (1.86 g, 19 mmol) in dry benzene (10 mL) was added to the dark red solution and stirring was continued overnight. The reaction was worked up conventionally. The crude product (5.68 g) was chromatographed on silica gel (5 × 30 cm). Initial elution with hexanes gave debrominated starting material (1.56 g). Further elution with ethyl acetate–hexanes (1:9) furnished the product (2.42 g, 61%), which was utilized directly in the next step: mp (ethanol) 216–218 °C; HPLC (solvent B, 3 mL/min) t_R 5.5 min; ^1H NMR δ 9.12 (d, 1, J = 8.5 Hz), 9.04 (dd, 1, J = 9.0, 4.5 Hz), 8.87 (d, 1, J = 8.5 Hz), 8.75 (m, 1), 8.59 (d, 1, J = 9.5 Hz), 8.51 (d, 1, J = 9.5 Hz), 8.27 (d, 1, J = 9.0 Hz), 8.19 (d, 1, J = 7.5 Hz), 8.05 (d, 1, J = 7.5 Hz), 7.95 (d, 1, J = 7.5 Hz), 7.80 (m, 1), 4.91 (m, 1, carbinolic), 4.26 (m, 1, benzylic), 2.63 (m, 1), 2.36 (m, 1), 2.07 (m, 2), 1.99 (m, 1), 1.66 (m, 3); HRMS, calcd for $C_{26}H_{22}O$, 350.1671, *m/e* 350.1680 (M^+).

(3) 2-(6-Benzo[*a*]pyrenyl)cyclohexanone (21). Oxidation of the above crude alcohol (0.70 g, 2 mmol) with PDC by the usual procedure gave **21** (0.52 g, 75%): mp 232–234 °C (ethyl acetate); HPLC (solvent B, 3 mL/min) t_R 6.6 min; ^1H NMR δ 9.11 (d, 1, J = 8.0 Hz), 9.04 (d, 1, J = 9.5 Hz), 8.27 (d, 1, J = 9.0 Hz), 8.19 (d, 1, J = 8.0 Hz), 8.04 (dd, 1, J = 7.3, 0.4 Hz), 7.94 (d, 1, J = 7.5 Hz), 7.90 (m, 3), 7.78 (appt t, 1, J = 6.5 Hz), 7.73 (m, 1), 5.00 (dd, 1, J = 12.0, 7.0 Hz, benzylic), 2.94 (m, 1), 2.73 (m, 1), 2.64 (m, 1), 2.45 (m, 1), 2.36 (m, 1), 2.22 (m, 2), 2.05 (m, 1); HRMS, calcd 348.1514, *m/e* 348.1487 (M^+).

Analogous oxidation was also conducted with the Dess–Martin reagent. A solution of the alcohol (0.70 g, 2 mmol) and the Dess–Martin reagent (2.55 g, 6 mmol) in CH_2Cl_2 (50 mL) was stirred at room temperature for 30 min.[8] Conventional workup gave a dark green residue (0.8 g), which was chromatographed on silica gel (ethyl acetate–hexanes) to yield **21** as a yellow powder

(35) (a) Aitken, I. M.; Reid, D. H. *J. Chem. Soc.* **1956**, 3487. (b) Lang, K. F.; Buffleb, H. *Chem. Ber.* **1957**, *90*, 2894. (c) Studt, P. *Liebigs Ann. Chem.* **1978**, 528.

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(0.51 g, 73%), spectroscopically identical with **21** obtained from the alternative route.

(4) Benz[*def*]indeno[1,2,3-*hi*]chrysene (4). The above ketone (0.14 g, 4 mmol) was treated with PPA (100 g) by the usual procedure. The color of the solution changed to a dark rose hue and finally to deep violet over 30 min as the temperature reached 110 °C. After 1 h, the hot PPA solution was worked up conventionally. The HPLC profile (solvent B, 2 mL/min) of the viscous residue (126 mg) contained one major peak at 5.2 min along with two other small peaks. The high-field ^{1}H NMR (500 MHz) of the crude product revealed that the main product is the tetrahydro isomer: δ 3.28 (m, 2, H_{12}), 2.89 (m, 2, H_9), 2.05 (m, 2, H_{10} or H_{11}), 1.98 (m, 2, H_{10} or H_{11}). Small amounts of the hexahydro and fully aromatic products were also detected. The mixture was aromatized with DDQ by the usual procedure to yield **4** (118 mg, 92%): ^{1}H NMR analysis of the crude product showed it to be contaminated with approximately 2% of the alternative isomer **5**. This was readily removed by a recrystallization (benzene–ethanol). A second recrystallization from xylene furnished pure **4** as an orange powder: mp 213–215 °C; HPLC (solvent A, 3 mL/min) t_R 8.4 min; ^{1}H NMR δ 8.95 (d, 1, H_5, J = 9.0 Hz), 8.74 (d, 1, H_6, J = 9.0 Hz), 8.73 (d, 1 H_{13}, J = 8.5 Hz), 8.41 (d, 1, H_{12}, J = 7.5 Hz), 8.26 (d, 1, H_4, J = 8.5 Hz), 8.20 (d, 1, H_1 or H_3, J = 8.0 Hz), 8.12 (d, 1, H_8, J = 7.0 Hz), 8.07 (d, 1, H_3 or H_1, J = 7.5 Hz), 8.05 (d, 1, H_{14}, J = 8.5 Hz), 7.99 (dd, 1, H_9, J = 7.5, 1.0 Hz), 7.91 (ddd, 1, H_2, J = 7.5, 1.0, 8.0 Hz), 7.84 (dd, 1, H_7, J = 8.0, 7.0 Hz), 7.43 (dd, 1, H_{11}, J = 7.5, 1.0 Hz), 7.36 (dd, 1, H_{10}, J = 7.0 Hz); ^{13}C NMR δ 140.245, 139.838, 136.683, 131.594, 130.865, 130.424, 130.000 (C10), 129.220, 128.575, 128.575, 128.083 (C4), 127.727 (C11), 127.244 (C7), 126.938 (C14), 126.853 (C1 or C3), 126.082, 125.921 (C2), 125.887 (C3 or C1), 125.768, 125.030, 124.368 (C12), 124.004 (C13), 122.367 (C5), 122.299 (C6), 121.578 (C9), 119.627 (C8); UV (dioxane) max (log ϵ) 455.9 nm (4.50), 430.5 (4.40), 339.6 (4.63), 324.4 (4.37), 303.2 (4.44), 291.8 (4.47), 277.0 (4.50), 254.3 (4.48), 243.0 (4.42), 236.8 (4.31), 230.2 (4.31); HRMS, calcd for $C_{26}H_{14}$ 326.1096, m/e 326.1078 (M^+). Anal. Calcd for $C_{26}H_{14}$: C, 95.68; H, 4.29. Found: C, 95.56; H, 4.35.

Fluoreno[3,2,1,9-*def*]chrysene (5). (1) From the Alcohol. The alcohol **23** (52.5 mg, 1.5 mmol) was cyclized in PPA and dehydrogenated with DDQ by the usual procedures. Chromatography of the product on an alumina column eluted with benzene gave the dehydrated olefin product (24 mg, 48%) in the first fraction (visible only by short UV): mp 216–218 °C (ethyl acetate–hexanes); ^{1}H NMR δ 8.97 (d, 1, J = 9.5 Hz), 8.95 (d, 1, J = 9.5 Hz), 8.33 (dd, 1, J = 8.5, 1.0 Hz), 8.18 (d, 1, J = 9.0 Hz), 8.10 (d, 1, J = 8.0 Hz), 8.08 (d, 1, J = 9.0 Hz), 8.10 (d, 1, J = 8.0 Hz), 7.95 (d, 1, J = 7.5 Hz), 7.85 (appt t, 1, J = 7.5 Hz), 7.79 (d, 1, J = 9.5 Hz), 7.72 (m, 1), 7.67 (m, 1), 2.40 (m, 4, allylic), 1.94 (m, 4, aliphatic); HRMS, calcd for $C_{26}H_2O$ 332.1565, m/e 332.1563 (M^+). Further elution gave a yellow band identified as mainly **5** with a small amount of **4** (~10%) (19 mg, 39%) by ^{1}H NMR analysis. This was recrystallized from xylene to give pure **5** (12 mg, 25% from alcohol) as fine burgundy needles: mp 261–262 °C (xylene) (lit.[16] mp 262–264 °C); ^{1}H NMR δ 9.13 (d, 1, J = 8.0 Hz), 9.04 (d, 1, J = 8.0 Hz), 8.98 (d, 1, J = 9.0 Hz), 8.52 (s, 1, H_9), 8.48 (d, 1, J = 7.5 Hz), 8.36 (d, 1, J = 7.0 Hz), 8.32 (d, 1, J = 8.0 Hz), 8.31 (d, 1, J = 9.0 Hz), 8.17 (d, 1, J = 7.5 Hz), 8.03 (appt t, 1, J = 7.5 Hz), 7.93 (m, 1), 7.86 (m, 1), 7.56 (m, 1), 7.45 (m, 1); UV (cyclohexane) max (log ϵ) 453.1 nm (3.93), 408.6 (3.96), 386.7 (4.01), 335.1 (4.20), 310.8 (4.47), 258.8 (4.80), 206.2 (4.77), 194.9 (4.59); HRMS, calcd for $C_{26}H_{14}$ 326.1096, m/e 326.1067 (M^+).

(2) From the Partially Saturated Alcohol. The alcohol **23** (1.05 g, 3 mmol) in ethyl acetate (150 mL) with platinum oxide (PtO_2, 0.25 g) was hydrogenated (50 psi) at room temperature on a Parr hydrogenator for 20 h. The solution was filtered through a Celite pad and washed with acetone. Evaporation of the filtrate gave a foam containing a mixture of the tetrahydro derivative **24** and small amounts of the di- and hexahydro derivatives (by ^{1}H NMR analysis). The mixture was treated with chloranil (0.37 g, 1.5 mmol) in refluxing dry benzene (100 mL), and the course of reaction was monitored by HPLC, adding addition chloranil as needed to complete the reaction. After conversion was complete (20 h), the mixture was cooled and filtered through a short pad of silica gel. The product (0.72 g) was obtained as white resin on elution with benzene–CH_2Cl_2. Recrystallization from ethyl acetate–hexanes gave **24** (0.61 g, 57%) over 96% pure by ^{1}H NMR analysis: mp 181–183 °C (petroleum ether); ^{1}H NMR δ 8.55 (d, 1, J = 9.5 Hz), 8.24 (d, 1, J = 9.0 Hz), 8.09 (d, 1, J = 7.5 Hz), 8.07 (d, 1, J = 7.5 Hz), 8.03 (d, 1, J = 8.0 Hz), 7.92 (d, 1, J = 9.5 Hz), 7.90 (dd, 1, J = 7.5, 7.5 Hz), 4.81 (m, 1, carbinolic), 3.66 (m, 1, benzylic), 3.41 (m, 2, H_{10}), 3.38 (m, 2, H_7), 3.15 (m, 1), 2.45 (m, 1), 2.26 (m, 1), 2.10 (m, 5), 1.48 (m, 4); MS, m/e 354 (M^+).

Oxidation of **24** (0.177 g, 0.5 mmol) by the Dess–Martin reagent (0.424 g, 1 mmol) in dry CH_2Cl_2 (50 mL) at room temperature gave the corresponding ketone (0.14 g, 80%) as white crystals: mp 205–207 °C (benzene–hexanes); ^{1}H NMR δ 8.23 (d, 1, J = 9.5 Hz), 8.09 (d, 1, J = 7.5 Hz), 8.05 (d, 1, J = 7.5 Hz), 8.02 (d, 1, J = 9.0 Hz), 7.89 (m, 3), 4.42 (m, 1, benzylic), 3.43 (m, 2), 3.03 (m, 2), 2.82 (m, 2), 2.60 (m, 2), 1.90–2.43 (m, 8); MS, m/e 352 (M^+).

The ketone (99 mg, 0.28 mmol) was heated with PPA (20 g) at 110 °C (2 h) and worked up conventionally to give the cyclized product (83 mg). This was directly aromatized by DDQ (0.114 g, 5 mmol) to give **5** (56.1 mg, 61%) identical in its physical and spectroscopic properties with **5** prepared by the alternative procedure.

Dibenz[*a*,*e*]- and Dibenz[*a*,*j*]aceanthrylene (6 and 7). (1) 2-(7-Benz[*a*]anthryl)cyclohexanol (25) was prepared from 7-bromobenz[*a*]anthracene by the usual procedure (66%) and used directly without further purification in the next step.

(2) 2-(7-Benz[*a*]anthracenyl)cyclohexanone (22). A solution of **25** (261 mg, 0.8 mmol) was treated with the Dess–Martin reagent (678 mg, 1.6 mol) in CH_2Cl_2 (30 mL) for 30 min. The crude product (250 mg) was chromatographed on a silica gel column eluted with ethyl acetate–petroleum ether (1:9). Recrystallization from benzene–hexanes furnished **22** as white needles (220 mg, 85%): mp 188–190 °C (benzene–hexanes); HPLC (THF–hexane 2:8, 2 mL/min) t_R 10.0 min; ^{1}H NMR δ 9.15 (s, 1, H_{12}), 8.81 (d, 1, H_1, J = 8.0 Hz), 8.11 (dd, 1, J = 4.8, 5.5 Hz), 7.91 (bs, 1), 7.78 (dd, 1, J = 7.8, 0.5 Hz), 7.65–7.55 (m, 4), 7.49 (m, 2), 4.84 (dd, 1, benzylic, J = 12.5, 6.8 Hz), 2.88 (m, 1), 2.68 (m, 1), 2.53 (m, 1), 2.35 (m, 2), 2.16 (m, 2), 2.00 (m, 1); MS, m/e 324. Anal. Calcd for $C_{24}H_{20}O$: C, 88.86; H, 6.21. Found: C, 88.77; H, 6.25.

(3) Cyclodehydration and Aromatization of 22. The ketone **22** (94 mg, 0.29 mmol) was treated with PPA and aromatized with DDQ by the usual method. ^{1}H NMR analysis showed the crude product (78 mg, 86%) to contain a 54:46 ratio of the two possible isomers (**6** and **7**). The earlier fraction eluted from an alumina column with benzene–hexanes (1:1) was principally **6** (35 mg).[38] The small amount of **7** present was readily removed by two recrystallizations from benzene–ethanol to yield pure **6** (28 mg, 31%): mp 230–234 °C (lit.[38] mp 232 °C); the NMR and UV spectral data matched closely those of the sample obtained via the alternative route below. Repeated column chromatography of the mother liquors gave pure **7** (15 mg): mp 180 °C (lit.[39] mp 181–181.3 °C); ^{1}H NMR data were in good agreement with those previously reported.[17]

(4) Cyclodehydration and Aromatization of 25. The alcohol **25** (1.96 g, 6 mmol) was cyclized in PPA and aromatized with DDQ in the usual manner. TLC showed a less polar spot detectable only by short UV and a visible yellow polar spot. The former was separated by chromatography on neutral alumina and identified as 7-cyclohexenylbenz[*a*]anthracene (1.41 g, 76%), yellow plates: mp 145–147 °C (benzene–hexanes); ^{1}H NMR δ 9.08 (s, 1, H_{14}), 8.80 (d, 1, J = 8.0 Hz), 8.13 (m, 1), 8.07 (m, 1), 7.94 (d, 1, J = 9.0 Hz), 7.80 (d, 1, J = 8.0 Hz), 7.64 (m, 1), 7.57 (m, 2), 7.50 (m, 2), 5.83 (m, 1, olefinic), 2.40 (m, 4, allylic), 1.95 (m, 4, aliphatic); MS, m/e 308. Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.38; H, 6.54.

Further elution gave a mixture of **6** and **7** (84:16) as yellow needles (0.41 g, 22%). Recrystallization gave pure **6** (0.31 g, 17%): mp 231–232 °C (benzene–ethanol) (lit.[38] mp 232 °C); ^{1}H NMR δ 8.97 (s, 1, H_{14}), 8.79 (d, 1, J = 8.5 Hz), 8.77 (d, 1, J = 9.0 Hz), 8.38 (d, 1, J = 8.0 Hz), 8.22 (d, 1, J = 8.5 Hz), 8.21 (s, 1, H_9), 8.06 (d, 1, J = 7.5 Hz), 8.01 (d, 1, J = 7.5 Hz), 7.70 (m, 2), 7.64 (m, 1), 7.58 (m, 1), 7.50 (m, 1), 7.41 (m, 1); UV (cyclohexane) max (log ϵ) 400.7 nm (4.09), 379.8 (4.04), 330.5 (4.39), 315.6 (4.26), 299.0 (4.49), 289.2 (4.54), 264.5 (4.68), 254.2 (4.68), 242.8 (4.70), 217.8 (4.61); HRMS, calcd for $C_{24}H_{14}$ 302.1096, m/e 302.1073 (M^+).

(38) Lavit-Lamy, D.; Buu-Hoi, N. P. *Bull. Soc. Chim. Fr.* **1966**, 2163.
(39) Fieser, L. F.; Seligman, A. M. *J. Am. Chem. Soc.* **1935**, *57*, 2174.

Synthesis of Benz[*a*]aceanthrylene (8). (1) 2-(9-Anthranyl)cyclohexanol. This alcohol was synthesized from 9-bromoanthracene by the usual method (54%) and used without further purification because of its susceptibility to air oxidation.

(2) 2-(9-Anthranyl)cyclohexanone was obtained as white fluffy needles from oxidation of the alcohol using the Dess–Martin reagent (73%): mp 186–188 °C (ethyl acetate–petroleum ether); ^{1}H NMR δ 8.37 (s, 1, H_{10}), 7.98 (m, 2), 7.86 (br s, 2), 7.41 (m, 4), 4.85 (dd, 1, benzylic, J = 12.5, 6.5 Hz), 2.85 (m, 1), 2.65 (m, 1), 2.51 (m, 1), 2.30 (m, 2), 2.15 (m, 2), 1.98 (m, 1); HRMS, calcd for $C_{20}H_{18}O$ 274.1357, m/e 274.1356 (M^+). Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.50; H, 6.64.

(3) Benz[*a*]aceanthrylene (8). The ketone (82.2 mg, 3 mmol) was cyclized in PPA (deep red color) and aromatized by the usual method to give golden needles of **8** (79%): mp 143–145 °C (petroleum ether) (lit.[40a] mp 145–146 °C); HPLC (THF–hexane 1:9, 3 mL/min) t_R 3.5 min; ^{1}H NMR δ 8.74 (d, 1, H_{12}, J = 8.5 Hz), 8.45 (s, 1, H_8), 8.36 (d, 1, H_1, J = 7.5 Hz), 8.12 (d, 1, H_5, J = 7.5 Hz), 7.98 (m, 3, $H_{7,9,4}$), 7.65 (m, 2, $H_{10,11}$), 7.49 (appt t, 1, H_6), 7.46 (m, 1, H_2), 7.38 (m, 1, H_3); UV (cyclohexane) max (log ϵ) 423.0 nm (3.90), 363.5 (3.73), 257.6 (4.81), 203.5 (4.78), 192.4 (4.69); HRMS, calcd for $C_{20}H_{12}$ 252.0939, m/e 252.0909 (M^+).

Benz[*def*]indeno[1,2,3-*qr*]chrysene (9) and Fluoreno-[9,1,2,3-*cdef*]chrysene (10). (1) Bromination of 6-Chlorobenzo[*a*]pyrene. To a solution of 6-chlorobenzo[*a*]pyrene[20] (4.02 g, 14 mmol) in CS_2 (350 mL) was added Br_2 (2.72 g, 18 mmol) in CS_2 (5 mL) dropwise. Precipitation takes place immediately as the bromine is added. After stirring 4 h at the room temperature, the solvent was removed and benzene (200 mL) was added. The resulting suspension was brought to boil on a steam bath and then allowed to sit in the refrigerator overnight. The yellow solid was filtered (5.0 g, 98%) and shown by ^{1}H NMR to be a mixture of 1-bromo- and 3-bromo-6-chlorobenzo[*a*]pyrene (88:22). Attempts to separate the isomers by recrystallization or column chromatography were unsuccessful. Therefore, the mixture was employed directly in the next step; mp 224–229 °C; ^{1}H NMR (of 1-bromo-6-chlorobenzo[*a*]pyrene in the mixture) δ 9.01 (2 doublets, 2, $H_{10,11}$), 8.79 (m, 1), 8.60 (d, 1, J = 9.0 Hz), 8.48 (d, 1, J = 9.0 Hz), 8.19 (d, 1, J = 8.0 Hz), 7.85 (m, 4); MS, m/e (relative intensity) 364 (100), 366 (131), 368 (33).

(2) 2-(6-Chloro-1-benzo[*a*]pyrenyl)cyclohexanol (26). To a suspension of the above mixture (2.56 g, 0.07 mol) in dry benzene (200 mL) was added phenyllithium (7 mL, 2 M in cyclohexane/ether) dropwise at 50 °C. The suspension was stirred until a dark homogeneous solution was obtained (~4 h). Cyclohexene oxide (1.38 g, 14 mmol) was added, and the solution was stirred overnight at the same temperature. The reaction was terminated by the addition of saturated NH_4Cl (200 mL), and the benzene layer was washed with water and saturated brine and dried. The solution was concentrated to a small volume (reddish oil) and directly applied to a silica gel column eluted with ethyl acetate–hexanes (1:9). The product fractions were combined and concentrated to the point where precipitation occurred. The same volume of cold petroleum ether was added; then the solution was refrigerated overnight. The slightly greenish yellow precipitate was collected (0.41 g) and shown by ^{1}H NMR analysis to contain only **26**. A second crop (0.64 g), containing ~40% of the 3-cyclohexanol isomer, was isolated by precipitation using cold petroleum ether. Total yield was 1.05 g (39%): ^{1}H NMR (**26**) δ 9.05 (m, 2), 8.82 (d, 1, J = 9.0 Hz), 8.68 (d, 1, J = 9.5 Hz), 8.51 (d, 1, J = 9.5 Hz), 8.13 (d, 1, J = 8.0 Hz), 8.02 (d, 1, J = 7.5 Hz), 7.99 (d, 1, J = 9.5 Hz), 7.87 (m, 2), 4.12 (m, 1, carbinolic), 3.73 (m, 1, benzylic); ^{1}H NMR (3-isomer) δ 9.05 (d, 1, J = 9.5 Hz), 8.99 (d, 1, J = 9.0 Hz), 8.80 (d, 1, J = 9.5 Hz), 8.57 (d, 1, J = 10.0 Hz), 8.42 (d, 1, J = 10.0 Hz), 8.26 (dd, 1, J = 8.0, 2 Hz), 8.01 (m, 2), 7.86 (m, 2), 4.11 (m, 1, carbinolic), 3.67 (m, 1, benzylic); MS, m/e (relative intensity) 384 (100), 386 (33).

(3) Oxidation of the Alcohol. The alcohol **26** (0.58 g, 0.0015 mol) was treated with the Dess–Martin reagent (1.27 g, 3 mmol) in freshly distilled CH_2Cl_2 (100 mL) at room temperature for 2 h. The product was purified by chromatography on silica gel to yield the ketone **27** as a yellow powder (0.41 g, 71%); recrystallization gave pure **27** as plates: mp 271–272 °C (benzene–ethanol); ^{1}H NMR δ 9.02 (m, 2), 8.82 (d, 1, J = 7.3, 2.3 Hz), 8.51 (d, 1, J = 9.5 Hz), 8.22 (d, 1, J = 9.5 Hz), 8.11 (d, 1, J = 8.0 Hz), 8.00 (d, 1, J = 9.5 Hz), 7.87 (m, 3), 4.68 (dd, 1, benzylic, J = 12.5, 5.0 Hz); MS, m/e (relative intensity) 382 (100), 384 (33).

(4) Benz[*def*]indeno[1,2,3-*qr*]chrysene (9). Treatment of **27** (0.31 g, 0.8 mmol) in PPA (ca. 100 g) at 150 °C for 5 h, followed by the usual workup, gave a reddish residue of crude **9** (0.27 g). ^{1}H NMR and HPLC analyses indicated the presence of only small amounts of partially saturated derivatives; MS showed the absence of chlorine containing products. The crude product was refluxed briefly (10 min) with DDQ (0.18 g, 0.8 mmol) in anhydrous benzene (50 mL) and chromatographed on alumina to afford pure **9** as orange needles (214 mg, 82%: mp 241–242 °C (benzene–hexanes); ^{1}H NMR δ 9.39 (s, 1, H_8), 9.08 (d, 1, H_7, J = 8.0 Hz), 8.50 (s, 1, H_3), 8.24 (d, 1, J = 7.5 Hz), 8.22 (d, 1, J = 8.5 Hz), 8.13 (m, 1), 8.04 (d, 1, J = 7.5 Hz), 7.95 (m, 1), 7.90 (AB q, 2, J_{AB} = 9.5 Hz), 7.80 (appt t, 1, J = 7.5 Hz), 7.69 (appt t, 1, J = 7.5 Hz), 7.39 (m, 2); ^{13}C NMR δ 141.30 (q), 139.54 (q), 135.46 (q), 133.59 (q), 132.17 (q), 131.30 (q), 130.58 (q), 130.55 (q), 129.76, 128.88 (q), 128.23 (q), 128.05, 127.90, 127.33, 127.03, 126.95, 126.77, 126.00, 124.75, 123.05, 122.58, 122.31, 122.13, 121.78, 120.00, 115.98; UV (cyclohexane) max (log ϵ) 428.3 nm (4.46), 406.0 (4.31), 386.7 (4.14), 334.0 (3.88), 307.5 (4.86), 295.7 (4.71), 261.2 (4.80), 252.5 (4.72), 212.7 (4.60); MS, m/e 326. Anal. Calcd for $C_{26}H_{14}$: C, 95.68; H, 4.35. Found: C, 95.47; H, 4.41.

(5) Fluoreno[9,1,2,3-*cdef*]chrysene (10). The mixture of ketones from **3** containing 40% of 2-[3-(6-chlorobenzo[*a*]pyrenyl)]cyclohexanone (96 mg, 0.2 mmol) was treated with PPA and DDQ conventionally to yield 79.6 mg of the mixture of **9** and **10**. Chromatography of the mixture on an alumina column gave on elution with benzene–hexane (8:2) an initial fraction containing mainly **9** (45 mg). Further elution gave mainly **10** (25 mg). Recrystallization of the latter from benzene–hexane provided pure **10** (12 mg): mp 239–240 °C; ^{1}H NMR δ 9.02 (d, 1, H_{13}, J = 8.0 Hz), 8.97 (d, 1, H_{12}, J = 9.5 Hz), 8.78 (s, 1, H_7), 8.55 (s, 1, H_8), 8.36 (d, 1, J = 9.0 Hz), 8.33 (d, 1, J = 8.0 Hz), 8.32 (d, 1, J = 8.0 Hz), 8.28 (d, 1, J = 8.0 Hz), 8.13 (d, 1, J = 7.0 Hz), 8.00 (d, 1, J = 7.5 Hz), 7.86 (m, 1), 7.78 (m, 1), 7.47 (m, 1), 7.42 (m, 1); UV (cyclohexane) max (log ϵ) 417.7 nm (4.80), 388.9 (4.98), 369.2 (4.90), 336.2 (5.18), 329.7 (5.05), 320.6 (5.13), 277.8 (5.39), 266.4 (5.37), 228.3 (5.24), 207.6 (5.19). MS, m/e 326 (M^+). Anal. Calcd for $C_{26}H_{14}$: C, 95.68; H, 4.35. Found: C, 95.62; H, 4.34.

Synthesis of Dibenz[*e*,*k*]acephenanthrylene (11) from 4-Bromobenz[*a*]anthracene. (1) 4-Bromobenz[*a*]-anthracene-7,12-dione (28b). A mixture of benz[*a*]-anthracene-7,12-dione (5.17 g, 0.02 mol), acetic acid (100 mL), and bromine (4 mL) was refluxed for 4 h. After cooling, the solution was filtered, and the yellow crystalline product was recrystallized from acetic acid (ca. 400 mL) to give pure **28b** (5.42 g) as long yellow needles; additional **28b** (1.10 g) was obtained from mother liquor (total 6.52 g, 97%): mp 231–232 °C (lit.[23] mp 230–232 °C); ^{1}H NMR δ 9.70 (d, 1, H_1, J = 9.0 Hz), 8.70 (d, 1, J = 9.0 Hz), 8.47 (d, 1, J = 9.0 Hz), 8.29 (d, 1, J = 7.5 Hz), 8.25 (d, 1, J = 7.0 Hz), 7.96 (d, 1, J = 7.5 Hz), 7.78 (m, 2), 7.57 (m, 1); MS, m/e 336, 338.

(2) 4-Bromobenz[*a*]anthracene. 28b (5.7 g, 17 mmol) was heated under reflux with acetic acid (400 mL), hydriodic acid (57%, 40 mL), and hypophosphorous acid (20 mL) for 18 h.[24] The clear yellow solution was poured onto ice–water (ca. 500 mL) containing sodium bisulfite (ca. 30 g) and stirred at room temperature for 5 h. The solid was filtered and air-dried (5.10 g). In some runs, ^{1}H NMR of the crude product showed a small amount of the dihydro derivative; this can be rearomatized by refluxing with chloranil (2 g) in benzene (200 mL) overnight. Chromatography on an alumina column eluted with benzene followed by recrystallization gave the pure product (4.38 g, 84%) as white needles: mp 215–216 °C (benzene) (lit.[23] mp 210–211 °C);[23] ^{1}H NMR δ 9.12 (s, 1, H_{12}), 8.78 (d, 1, H_1, J = 8.0 Hz), 8.37 (s, 1, H_7), 8.10 (m, 1), 8.08 (d, 1, J = 9.5 Hz), 8.03 (m, 1), 7.86 (m, 2), 7.55 (m, 2), 7.49 (m, 1); UV (cyclohexane) max (log ϵ) 360.7 nm (3.83), 343.6 (3.98), 328.0 (3.93), 296.5 (4.99), 284.8 (4.91), 274.3 (4.61), 254.9 (4.59), 232.1 (4.69), 213.0 (4.42); MS, m/e 306, 308. Anal. Calcd for $C_{18}H_{11}Br$: C, 70.38; H, 3.61; Br, 26.01. Found: C, 70.44; H, 3.59; Br, 25.97.

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(3) 2-(4-Benz[*a*]anthracenyl)cyclohexanol. To a solution of 4-bromobenz[*a*]anthracene (1.54 g, 5 mmol) in anhydrous benzene (100 mL) at 50 °C was added *n*-butyllithium (1.6 M in hexane, 6.3 mL, 10 mmol) dropwise under an Ar atmosphere. After 1 h, a solution of cyclohexene oxide (0.98 g, 10 mmol) in benzene (10 mL) was added, whereupon the turbid solution became homogeneous. Stirring was continued for 5 h at the same temperature; then a saturated NH_4Cl solution (100 mL) was added, and the reaction was worked up conventionally. The crude product (2.40 g) was purified by chromatography to yield the cyclohexanol product (0.81 g, 50%) along with recovered starting material (0.57 g). Recrystallization from benzene–hexane gave an analytical sample of the alcohol as short yellow needles: mp 178–179 °C; ^1H NMR δ 9.16 (s, 1, H_{12}), 8.77 (d, 1, H_1, J = 7.5 Hz), 8.34 (s, 1, H_7), 8.10 (m, 1), 8.02 (m, 2), 7.82 (d, 1, J = 9.5 Hz), 7.68 (m, 1), 7.63 (m, 1), 7.52 (m, 2), 4.01 (m, 1, carbinolic), 3.45 (m, 1, benzylic), 2.26 (m, 1), 2.02 (m, 1), 1.96 (m, 1), 1.83 (m, 1), 1.59 (m, 4). Anal. Calcd for $C_{24}H_{22}O$: C, 88.30; H, 6.80. Found: C, 88.23; H, 6.80.

(4) 2-(4-Benz[*a*]anthracenyl)cyclohexanone. Oxidation of the above alcohol (0.326 g, 1 mmol) with the Dess–Martin reagent (0.85 g, 0.002 mol) (30 min) furnished the ketone (0.276 g, 85%): mp 169–171 °C (benzene–ethanol); ^1H NMR δ 9.12 (s, 1, H_{12}), 8.79 (d, 1, H_1, J = 8.5 Hz), 8.32 (s, 1, H_7), 8.10 (m, 1), 8.00 (m, 1), 7.77 (d, 1, J = 9.5 Hz), 7.65 (m, 1), 7.52 (m, 3), 7.46 (d, 1, J = 7.0 Hz), 4.39 (dd, 1, J = 17.5, 5.0 Hz), 2.67 (m, 2), 2.46 (m, 1), 2.28 (m, 2), 2.15 (m, 1), 1.90 (m, 2). MS, m/e 324 (M^+).

(5) Dibenz[*e*,*k*]acephenanthrylene (11). The above ketone (0.26 g, 0.8 mmol) was treated with PPA (ca. 150 g) at 150 °C for 4 h followed by dehydrogenation with DDQ (0.55 g, 2.4 mmol) in the usual manner. Chromatography of the product on an alumina column gave **11** (220 mg, 91%), which crystallized as fluffy yellow needles from benzene–ethanol: mp 228–229 °C (lit.[41] mp 229–230 °C); ^1H NMR δ 9.10 (s, 1, H_{14}), 8.53 (d, 1, H_1, J = 9.0 Hz), 8.51 (s, 1, H_8), 8.28 (s, 1, H_9), 8.11 (m, 1), 8.05 (m, 1), 8.01 (m, 1), 7.95 (d, 1, J = 7.0 Hz), 7.90 (d, 1, J = 8.0 Hz), 7.75 (appt t, 1, J = 8.0 Hz), 7.56 (m, 2), 7.41 (m, 2); UV (cyclohexane) max (log ϵ) 410.0 nm (4.18), 387.3 (4.11), 368.2 (4.28), 352.2 (4.26), 317.8 (4.70), 304.2 (4.46), 297.0 (4.49), 282.5 (4.85), 252.6 (4.65), 231.4 (4.56); MS, m/e 302. Anal. Calcd for $C_{24}H_{14}$: C, 95.33; H, 4.67. Found: C, 95.24; H, 4.71.

Synthesis of Dibenz[*e*,*k*]acephenanthrylene (11) via the Lactone Route. (1) 3-Formylfluoranthene. To a solution of $SnCl_4$ (24.1 mL, 0.2 mol) in dry CH_2Cl_2 (80 mL) at −10 °C was added 1,1-dichloromethyl methyl ether (14.4 g, 0.13 mol) dropwise for 30 min.[28] A solution of fluoranthene (20.23 g, 0.1 mol) in CH_2Cl_2 (50 mL) was then added dropwise over 1 h. The resulting dark red solution was allowed to come to room temperature and then refluxed for 1 h. The solution was cooled, poured into ice–water, and worked up conventionally. The solution of the product was heated with charcoal (Norit) and then passed through a short silica column and recrystallized from benzene–petroleum ether to give yellow crystals of 3-formylfluoranthene (13.1 g, 57%): mp 97–99 °C (lit.[28] mp 98–99 °C); ^1H NMR δ 10.36 (s, 1, CHO), 8.83 (d, 1, J = 8.5 Hz), 8.05 (d, 1, J = 7.0 Hz), 7.94 (d, 1, J = 7.0 Hz), 7.86 (m, 2), 7.81 (d, 1, J = 7.5 Hz), 7.67 (m, 1), 7.39 (m, 1), 7.34 (m, 1); HRMS, calcd for 230.0732, m/e 230.0731 (M^+).

(2) Synthesis of the Lactone 30. To a stirred solution of *sec*-butyllithium (12 mL, 1.3 M, 16 mmol) and TMEDA (1.86 g, 16 mmol) in anhydrous THF (25 mL) at −78 °C was added dropwise *N*-[2-(diethylamino)ethyl]-*N*-ethylbenzamide[27] (3.2 g, 13 mmol) in THF (10 mL). Stirring was continued for 1 h as the color of the solution changed from yellow to dark green. A solution of 3-formylfluoranthene (2.99 g, 13 mmol) in THF (30 mL) was added, and the solution was allowed to stand at room temperature overnight. After removal of the solvent, 6 N HCl (100 mL) was added, and the mixture was heated at reflux for 18 h. The reaction mixture was cooled and the solid was filtered, washed with water, and air-dried to give **30** as a yellow powder (3.35 g, 80%): mp 235–237 °C (benzene–hexanes); ^1H NMR δ 8.02 (d, 1, J = 7.5 Hz), 7.96 (d, 1, J = 8.5 Hz), 7.94 (d, 1, J = 6.5 Hz), 7.87 (m, 1), 7.84 (m, 1), 7.81 (d, 1, J = 6.5 Hz), 7.67 (m, 1), 7.63 (m, 1), 7.57 (m, 1), 7.36 (m, 4), 7.18 (s, 1, methine); MS, m/e 334.

(3) Dibenz[*e*,*k*]acephenanthrylene (11). A solution of **30** (0.58 g, 1 mmol) in ethyl acetate (100 mL) and 10% palladium-/charcoal (0.30 g) was hydrogenated (50 psi) for 24 h at room temperature. The solution was filtered through Celite and evaporated to dryness, and the residue was recrystallized from benzene–hexane to give the acid **31** as white fluffy needles (0.45 g, 74%): mp 172–174 °C; ^1H NMR δ 4.50 (s, 2, methylene); MS, m/e 336, 318, 289. Anal. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79. Found: C, 85.56; H, 4.84. The same acid was obtained by reduction using zinc (70%), but the reaction is erratic and very sensitive to the quality of zinc. A mixture of **31** (370 mg, 1.1 mmol), acetic anhydride (5 mL), acetic acid (6 mL), and zinc chloride (30 mg) was held at reflux for 1 h and poured onto ice. The usual workup gave 9-acetoxydibenz[*e*,*k*]acephenanthrylene (**32**) as an orange solid (370 mg, 93%): ^1H NMR δ 9.03 (s, 1, H_{14}), 8.23 (s, 1, H_8), 2.72 (s, 3, OAc); MS, m/e 360, 318, 289. A mixture of crude **32** (324 mg, 9 mmol), zinc dust (activated with $CuSO_4$), and 10% NaOH (50 mL) in dioxane (30 mL) was refluxed overnight. The usual workup gave a yellow solid (220 mg) which was chromatographed on an alumina column eluted with benzene to yield crude **11** (201 mg, 74%). Recrystallization from benzene–ethanol provided pure **11** as fluffy yellow needles (120 mg, 57%), identical spectroscopically with **11** prepared via the bromination route. The mmp was not depressed. An orange fraction eluted after **11** was identified as the quinone **33** (10 mg, 3%): mp 249–250 °C (benzene–hexane) (lit.[41] 250–253 °C); ^1H NMR δ 9.35 (d, 1, H_1, J = 8.5 Hz), 8.77 (s, 1 H_8), 8.30 (m, 2), 7.97 (m, 1), 7.92 (d, 1, J = 6.5 Hz), 7.83–7.73 (m, 4), 7.40 (m, 2); UV (cyclohexane) max (log ϵ) 400.7 nm (3.87), 370.0 (3.77), 349.2 (3.65), 332.8 (3.92), 212.8 (4.90), 198.3 (5.08); MS, m/e 332. Anal. Calcd for $C_{24}H_{12}O_2$: C, 86.73; H, 3.64. Found: C, 86.52; H, 3.67.

Acknowledgment. This research was supported by grants from the National Cancer Institute (CA 36097 and CA 14459), the National Institute of Environmental Health Sciences (ES 04266), and the American Cancer Society (BC 132).

Registry No. **1**, 205-99-2; **2**, 193-39-5; **3**, 111189-32-3; **4**, 111189-33-4; **5**, 192-35-8; **6**, 5385-75-1; **7**, 203-20-3; **8**, 203-33-8; **9**, 111189-34-5; **10**, 193-37-3; **11**, 206-06-4; **12**, 111189-35-6; **13**, 73129-94-9; **14**, 111189-36-7; **15**, 111189-37-8; **16**, 111189-38-9; **19**, 111189-39-0; **20**, 111189-40-3; **21**, 111189-41-4; **22**, 111189-42-5; **23**, 111209-31-5; **24**, 111189-43-6; **24** (ketone), 111189-51-6; **25**, 111189-44-7; **26**, 111189-45-8; **26** (3-cyclohexanol isomer), 111189-56-1; **27**, 111189-46-9; **28a**, 2498-66-0; **28b**, 63715-52-6; **29**, 103562-84-1; **30**, 111189-47-0; **31**, 111189-48-1; **32**, 111189-49-2; **33**, 72853-56-6; 9-bromophenanthrene, 573-17-1; cyclohexene oxide, 286-20-4; 2-(1-pyrenyl)cyclohexanol, 111189-50-5; 1-lithiopyrene, 74391-90-5; 2-(4-pyrenyl)cyclohexanol, 111209-32-6; 4-bromopyrene, 1732-26-9; chrysene, 218-01-9; 6-bromochrysene, 7397-93-5; 2-(6-chrysenyl)cyclohexanol, 111209-23-5; benzo[*a*]pyrene, 50-32-8; 6-bromobenzo[*a*]pyrene, 21248-00-0; 7-bromobenz[*a*]anthracene, 32795-84-9; 7-cyclohexenylbenz[*a*]anthracene, 36278-16-7; 2-(9-anthranyl)cyclohexanol, 111189-52-7; 2-(9-anthranyl)cyclohexanone, 111189-53-8; 9-bromoanthracene, 1564-64-3; 6-chlorobenzo[*a*]pyrene, 21248-01-1; 1-bromo-6-chlorobenzo[*a*]pyrene, 111189-54-9; 3-bromo-6-chlorobenzo[*a*]pyrene, 111189-55-0; 4-bromobenz[*a*]anthracene, 61921-39-9; 2-(4-benz[*a*]anthracenyl)cyclohexanol, 111189-57-2; 2-(4-benz[*a*]anthracenyl)cyclohexanone, 111189-58-3; 3-formylfluoranthene, 28440-63-3; fluoranthene, 206-44-0; periodinane, 87413-09-0.

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