Electrophilic Substitution of Polycyclic Fluoranthene Hydrocarbons†

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Abstract: The first systematic study of the sites of electrophilic substitution (acylation and/or bromination) of polycyclic fluoranthene hydrocarbons is described. The hydrocarbons studied include indeno[1,2,3-*cd*]pyrene (**1**), benz[*a*]aceanthrylene (**2**), benz[*e*]acephenanthrylene (**3**), and indeno[1,2,3-*hi*]chrysene (**4**). Compounds **1–4** all undergo bromination regioselectively in a single site. The latter are determined by conversion of the bromo derivatives to monodeuterio analogues by metal exchange with butyllithium and analysis of their high-resolution ^1H and ^{13}C NMR spectra in comparison with those of the parent hydrocarbons. This method is potentially generally applicable to determination of the sites of substitution of other complex polycyclic hydrocarbon ring systems. Acylation of **1** is shown to take place in the same site as bromination, i.e., the 12-position. For **2** and **4**, substitution occurs in the 8- and 5-positions, respectively, in good agreement with theoretical prediction by the DEWAR-PI method based on the relative energies of the Wheland intermediates for substitution at various ring positions. However, for **1** and **3** the principal sites of bromination observed experimentally are the 12- and 1-positions, respectively, which do not accord with theoretical prediction of the 3,5- and 8-positions, respectively. In the latter cases, the observed sites of bromination are only slightly less favorable energetically than the theoretically calculated sites and are probably within the limit of accuracy of the calculations.

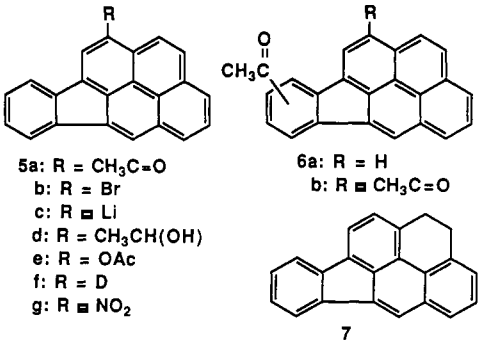
Nonalternant polycyclic hydrocarbons related to fluoranthene are widespread environmental pollutants, some of which are mutagenic and/or carcinogenic.[1] While the chemistry of alternant polycyclic aromatic hydrocarbons has been studied intensively, surprisingly little is known concerning the chemical properties of the polycyclic fluoranthenes, and their patterns of electrophilic substitution are virtually unknown.[2]

As the initial phase of a program to investigate the chemical and biological properties of the polycyclic fluoranthenes, we recently developed a convenient synthetic route to hydrocarbons of this class.[3,4] In this connection, we have also devised a technique for the 2D-NMR analysis of these hydrocarbons that allows complete assignment of their ^1H and ^{13}C resonances.[5] We now report the results of an investigation of the sites of electrophilic substitution (acylation and/or bromination) of indeno[1,2,3-*cd*]pyrene (**1**), benz[*a*]aceanthrylene (**2**), benz[*e*]acephenanthrylene (**3**), and indeno[1,2,3-*hi*]chrysene (**4**) (Figure 1) in relation to theoretical predictions based upon DEWAR-PI molecular orbital calculations described in the accompanying paper.[6]

Results

Indeno[1,2,3-*cd*]pyrene (1) was chosen for initial study. This hydrocarbon is of particular interest because of its environmental prevalence and reported mutagenicity and tumorigenicity.[1] Indeno[1,2,3-*cd*]pyrene is conveniently accessible synthetically from pyrene by the general procedure recently reported.[3,4] The preferred sites of electrophilic substitution on **1** are predicted theoretically by the DEWAR-PI method to be the 3- and 5-positions, and the 12-position is only slightly less energetically favorable (Figure 2).[6] On the other hand, the only experimental information in the literature on the reaction of **1** with electrophiles is the report that nitration of **1** yields its 8- or 9-nitro derivative.[7]

Friedel–Crafts acylation of **1** was carried out at 0 °C using acetyl chloride in the presence of $AlCl_3$ in 1,2-dichloroethane. HPLC analysis of the reaction mixture showed four peaks corresponding to the monoacetyl derivatives and two peaks having longer retention time assigned to the diacetyl derivatives along with recovered unreacted **1**. The ratio of peak intensities of the monoketone products was 50:1:1:1 during the initial phase of the reaction until 60–70% of **1** was converted. Further reaction afforded increasing ratios of diketones at the expense of the monoketone products. Analogous reaction using $AlCl_3$ and $ZnCl_2$ as a catalyst in CS_2 and CH_2Cl_2 gave essentially similar results. The major monoketone product (**5a**), one of the minor isomeric



monoketones (**6a**), and a diketone product (**6b**) were isolated in pure form by chromatography on silica gel followed by recrystallization. Attempted further acetylation of **5a** under similar conditions failed to yield diacetylated products. It appears that the diketone **6b** arises predominantly from **6a**.

The 500-MHz ^1H NMR spectrum of **5a** is consistent with the assignment of the 12-acetylindeno[1,2,3-*cd*]pyrene structure. The most downfield signal is the H_1 proton, which appears as a doublet at δ 8.99 ($J_{1,2}$ = 9.5 Hz) coupled with H_2 (Table I). The sizeable downfield shift of H_1 of **5a** relative to H_1 of **1** (δ 8.10) is consistent with peri interaction of the H_1 proton of **5a** with the adjacent acetyl function. The singlet peaks at δ 8.56 and 8.34 may be assigned to H_{11} and H_6, respectively. Although the downfield shift of H_{11}

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Table I. 500-MHz ^{1}H NMR Chemical Shifts and Coupling Constants for **1** and **5a**[a]

compd	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{10}	H_{11}	H_{12}	CH_3CO
1	8.10	8.04	8.22	8.03	8.37	8.53	8.10	7.40	7.45	8.00	8.33	8.20	
				$J_{1,2}$ = 9.0, $J_{3,4}$ = 7.5, $J_{4,5}$ = 8.0, $J_{7,8}$ = 7.0, $J_{9,10}$ = 6.5, $J_{11,12}$ = 7.5 Hz									
5a	8.99	8.08	8.20	7.98	8.27	8.34	7.97	7.42	7.46	7.92	8.56		2.93
				$J_{1,2}$ = 9.5, $J_{3,4}$ = 7.5, $J_{4,5}$ = 8.0, $J_{7,8}$ = 7.5, $J_{9,10}$ = 7.5 Hz									

[a] Chemical shift data for **1** are taken from ref 5. Spectra were recorded in $CDCl_3$ with Me_4Si as internal standard.

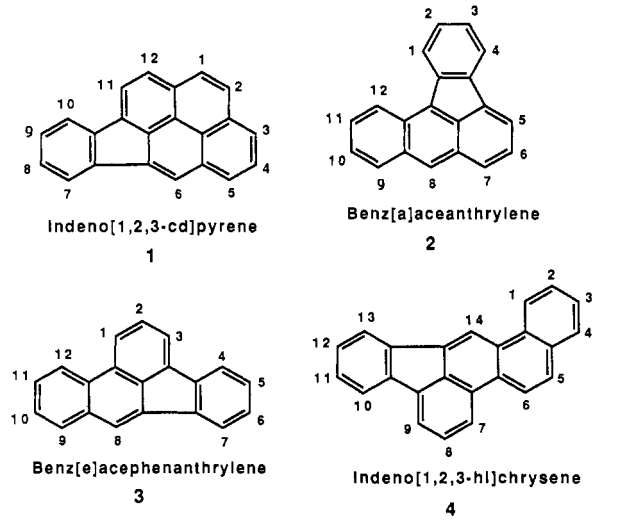

Figure 1. Structural formulas and numbering of polycyclic fluoranthene hydrocarbons.

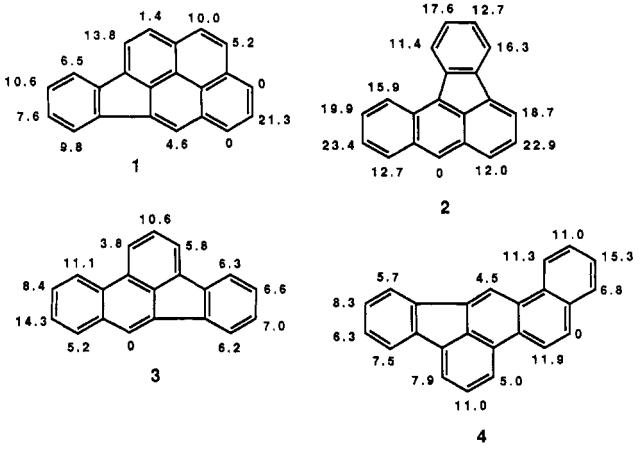

Figure 2. Calculated relative energies of the Wheland intermediates for electrophilic substitution at various ring positions of indeno[1,2,3-*cd*]-pyrene (**1**), benz[*a*]aceanthrylene (**2**), benz[*e*]acephenanthrylene (**3**), and indeno[1,2,3-*hi*]chrysene (**4**). Energies are relative to the Wheland intermediates with the lowest energy calculated by the DEWAR-PI method.[6] We are indebted to Professor Michael J. S. Dewar, The University of Texas at Austin, for these data.

of **5a** relative to H_{11} of **1** (δ 8.33) is somewhat small (0.23 ppm), the direction of the shift is consistent with the effect of the acetyl group. The chemical shifts and coupling patterns of the remaining protons of **5a** closely resemble those of **1** (Table I). Thus, H_3 and H_5 of **5a** appear as doublets at δ 8.20 and 8.27, respectively, and H_4 appears as a triplet at δ 7.98 ($J_{3,4}$ = 7.5 Hz), while the H_3, H_4, and H_5 peaks of **1** are found at δ 8.22, 8.03, and 8.37, respectively. The COSY and long-range COSY (LR-COSY) spectra of **5a** (not shown) are also entirely consistent with its assignment as 12-acetylindeno[1,2,3-*cd*]pyrene. A particularly distinctive feature of the COSY spectrum is the long-range ^5J coupling between the acetyl peak at δ 2.93 and the H_{11} signal at δ 8.56.

Bromination of **1** with bromine in acetic acid was complete in 30 min at room temperature to furnish a single major monobromo derivative **5b** (87%) along with minor amounts of two other isomers. Reaction of **1** with *N*-bromosuccinimide in benzene also gave **5b**, but in lower yield (62%). The bromide **5b** was converted into the corresponding lithio compound **5c** by halogen–lithium exchange with *n*-butyllithium. Reaction of the latter with acetaldehyde gave the expected alcohol **5d**, which underwent oxidation with pyridinium dichromate to yield a ketonic product identical by its NMR spectrum and physical properties with **5a**. Reaction of **5c** with acetonitrile and *N*,*N*-dimethylacetamide furnished **5a** directly. Since **5b** and **5a** are interconvertible, bromination and acetylation must take place preferentially at the same site, namely the 12-position, in indeno[1,2,3-*cd*]pyrene.

Baeyer–Villiger oxidative rearrangement of the ketone **5a** gave the corresponding phenol acetate **5e**. The NMR spectral and physical properties of **5e** were inconsistent with those of the 1-, 2-, and 6-hydroxyindeno[1,2,3-*cd*]pyrene acetates described by Rice et al.,[8] ruling out these positions as the primary sites of electrophilic substitution.

The minor isomeric monoketone **6a**, which was obtained in only trace amounts, was assigned either the 8- or 9-acetylindeno-[1,2,3-*cd*]pyrene structure. The most distinctive feature of the 500-MHz NMR spectrum of **6a** was the presence of two downfield singlets at δ 8.58 and 8.64. The theoretically predicted 3-acetyl and 5-acetyl isomers may be ruled out on this basis, since the coupling patterns of both of these isomers are expected to exhibit only one singlet peak (H_6). The only remaining isomers for which the observed splitting pattern is reasonably consistent are the 8- or 9-acetyl isomers. It is not possible to distinguish between these isomers on the basis of the available data.

The NMR spectrum of the diacetylated product **6b** resembled those of both **5a** and **6a** and is tentatively assigned the 8-, or 9-, 12-diacetylindeno[1,2,3-*cd*]pyrene structure. The H^1 signal of **6b** appeared furthest downfield as a doublet at δ 9.02 ($J_{1,2}$ = 9.5 Hz) coupled with H_2 at δ 8.16. The singlets at δ 8.58, 8.50, and 8.44 may be assigned to H_{11}, H_6, and $H_{7 \text{ or } 10}$. The chemical shifts and coupling patterns of the remaining protons of **6b** are also consistent with its structural assignment (cf. Experimental Section).

Treatment of the lithio compound **5c** with deuterium oxide furnished the deuterated analogue of **1** (**5f**). The ^{1}H NMR spectrum of **5f** in comparison with the previously fully assigned spectrum of the parent hydrocarbon **1**[5] showed the absence of the peak at δ 8.20, and the peak at δ 8.33 appeared as a singlet rather than as a doublet. These two peaks correspond to the 12- and 11-positions of **1**, respectively, assigned by Harvey and Cho by 2D-NMR analysis utilizing a combination of long-range homo- and heteronuclear shift correlation techniques (LR-COSY and LR-HETCOR).[5] The ^{13}C NMR spectrum of **5f** in comparison with that of **1**[5] showed a loss of the signal at 124.819 ppm for C12. These observations further confirm the structural assignments of **5a** and **5b**.

As a potential synthetic route to other isomeric monoacetyl derivatives of **1**, acetylation of the 1,2-dihydro derivative of **1** (**7**) was also investigated. Hydrogenation of **1** over a Pd–C catalyst, known to favor regiospecific hydrogen addition to localized electron-rich K-region bonds,[9] furnished **7**. OsO_4 was shown previously to also add preferentially to the 1,2-bond of **1**.[8] Since the aromatic ring system of **7** is identical with that of **3** for which the 8-position is predicted by MO methods to be most favorable for electrophilic attack,[6] it may be assumed as a first approximation that the analogous 6-position of **7** is its most reactive site. However, Friedel–Crafts acetylation of **7** afforded only **1** and **5a**

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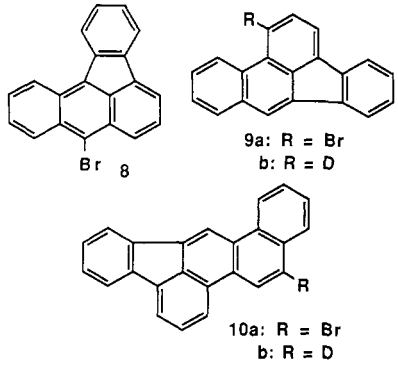
as the main products. Apparently $AlCl_3$-catalyzed dehydrogenation of **7** to **1** competes effectively with acetylation, and **5a** arises mainly from **1**.

Benz[*a*]aceanthrylene (2) is predicted theoretically[6] to undergo electrophilic attack predominantly in the 8-position (Figure 2), equivalent to the 9-position of anthracene. Bromination of **2** was less facile than that of **1**. Reaction of **2** with 1 equiv of Br_2 in CH_2Cl_2 took place overnight to yield of single major monobromo derivative. This was readily identified as 8-bromobenz[*a*]aceanthrylene (**8**) by the absence of the characteristic singlet for the H_8 peak of **2** and the downfield shift of the adjacent H_7 and H_9 signals in its ^1H NMR spectrum in comparison with that of **2**.[10,11]



Benz[*e*]acephenanthrylene (3) (commonly known as benz[*b*]-fluoranthene) is predicted by MO methods[6] to react with electrophiles preferentially in the 8-position (Figure 2), analogous to the 9-position of phenanthrene. Bromination of **3** required a large excess of Br_2 at reflux for 2 days for completion. In order to aid its identification, the monobromo product of **3** (**9a**) was converted to deuterio-**3** (**9b**) by reaction with butyllithium and deuterium oxide. The ^1H NMR spectra of **9a** and **9b** both retained a singlet peak corresponding to H_8 of **3**[5] (δ 8.20), ruling out substitution in the 8-position. The absence of the characteristic H_1 downfield doublet at δ 8.42 and other features of the NMR spectrum of **9b** were only consistent with its assignment as 1-deuterio-**3**. Therefore, the corresponding monobromo derivative **9a** may be assigned as 1-bromobenz[*e*]acephenanthrylene. This assignment is consistent with the large downfield shift of the H_{12} proton of **9a**, which appeared at δ 10.04, in comparison with that of **3**, which was found at δ 8.62.

Indeno[1,2,3-*hi*]chrysene (4) is predicted theoretically[6] to undergo electrophilic substitution preferentially in the 5-position (Figure 2). Bromination of **4** with Br_2 in CH_2Cl_2 at room temperature (39 h) gave a single monobromo derivative **10a** (92%). The high-resolution ^1H NMR spectrum of **10a** was consistent with its assignment as the 5-bromo derivative. Most revealing were the two singlets appearing at low field (δ 8.96 and 9.12) assigned to H_6 and H_{12}, respectively. This structure was confirmed by conversion of **10a** to its monodeuterio analogue **10b** and analysis of its ^1H and ^{13}C NMR spectra in comparison with the previously analyzed spectra of **4**.[5] The ^1H NMR spectrum of **10b** showed a decrease in the H_5 signal at δ 7.98 and a collapse of the H_6 doublet of δ 8.63 to a singlet, while the ^{13}C NMR spectrum exhibited a marked decrease in the intensity of the C5 signal at 127.73 ppm. On the basis of these findings the monobromo derivative **10a** is assigned the 5-bromoindeno[1,2,3-*hi*]chrysene structure.

Discussion

This investigation represents the first systematic exploration of electrophilic substitution of the polycyclic fluoranthene hydrocarbons. The four hydrocarbons selected for this study (**1–4**) are shown to all undergo electrophilic bromination to provide predominantly a single monobromo derivative in good yield. Assignment of isomer structure in these polycyclic hydrocarbon molecules is complicated by the large number of positional isomers possible. The site of bromination in the examples studied is shown to be conveniently determined by conversion of the monobromo derivatives to the corresponding monodeuterio analogues by metal exchange with an alkyllithium reagent and analysis of their high-resolution ^1H (and in some cases ^{13}C) NMR spectra in comparison with those of the parent hydrocarbons previously assigned completely by 2D-NMR techniques.[5] This method appears generally applicable to the assignment of the products of monosubstitution of polycyclic fluoranthenes, since the monobromo derivatives may be readily converted to a wide range of other potentially useful substituted derivatives, e.g., NH_2, NO_2, CHO, CO_2H, OH, etc., by well-established methods.

Acetylation, in the single case examined, is found to take place at the same site in indeno[1,2,3-*cd*]pyrene as does bromination, i.e., the 12-position. The report that nitration of **1** yields its 8- or 9-nitro derivative[7] is inconsistent with MO prediction[6] and with the present experimental findings. However, the reported ^1H NMR data on the mononitro derivative closely resemble that of the ketone **5a** and the bromo compound **5b**. In addition, the presence of the characteristic upfield indeno protons ($H_{8,9}$) in the reported ^1H NMR spectrum strongly supports this argument. Therefore, we tentatively suggest that this mononitro derivative is more likely to be 12-nitrodeno[1,2,3-*cd*]pyrene (**5g**).

The calculated relative energies of the Wheland intermediates for substitution at various ring positions in **1–4** are given in Figure 2. In the case of **2** and **4**, good agreement is observed between the experimentally observed sites of substitution and the MO theoretically predicted sites of electrophilic attack. For **1** and **3** the principal site of substitution observed experimentally is not that for which the Wheland intermediate has the lowest calculated relative energy, i.e., the 3,5-positions in the case of **1** and the 8-position in the case of **3**. However, in both cases the actual site of bromination is calculated to be only slightly less favorable energetically (1.4 and 3.8 kcal/mol) than the position(s) of lowest energy. This difference is probably within the limit of accuracy of the calculations. In neither case is there any obvious steric basis for this difference. It appears, on the basis of the limited data available, that the preferred sites of electrophilic substitution of polycyclic fluoranthene hydrocarbons may be predicted with reasonable accuracy by the method of Dewar and Dennington[6] where the difference in energy between the lowest energy site and other sites is not small. Where this difference is small, the predictions are likely to be unreliable. Further study will be required to establish the validity of this generalization.

Experimental Section

Materials and Methods. The hydrocarbons **1–4** were synthesized by the method described earlier.[3,4] The ^1H NMR spectra were obtained on the University of Chicago 500-MHz NMR spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. Integration was consistent with all structural assignments. The 2D and ^{13}C NMR spectra were recorded with a Varian XL-400 spectrometer. Melting points are uncorrected. HPLC data were obtained by using a Du Pont Zorbax Sil column [4.6 mm (i.d.) × 15 cm] with a flow rate of 2.5 mL/min.

Acetylation of 1. $AlCl_3$ (0.76 g, 5.7 mmol) was added to a solution of **1** (138 mg, 0.5 mmol) in CH_2Cl_2 (20 mL) under an argon atmosphere. To this solution in an ice bath was added 4 mL of a solution of acetyl chloride (0.55 mmol) in ethylene dichloride dropwise with stirring over a 45-min period. The resulting solution was stirred for an additional 30 min, and then the reaction was quenched by the addition of ice. The reaction was worked up conventionally and the crude product was chromatographed on a column of silica gel. Elution with benzene gave initially **1** (7 mg, 5%): mp 163–165 °C (lit.[12] mp 162.5–163 °C). The second yellow fraction afforded **5a** (98 mg, 62%): mp 198–200 °C (from ethanol); mass spectrum *m/e* 388 (M^+), 303, 275; NMR, Table I. Anal. Calcd for $C_{24}H_{14}O$: C, 90.54; H, 4.43. Found: C, 90.47; H, 4.47.

Preparative TLC of the mother liquors on silica gel eluted with 2% ethyl acetate in benzene gave **5a** (mp 198–200 °C) plus **6a**: mp 190–192 °C, light yellow needles; mass spectrum *m/e* 318 (M^+), 303, 275; NMR

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(11) *Selected ^1H Nuclear Magnetic Resonance Spectral Data*; Thermodynamics Research Center, Texas A&M University: College Station, TX, 1982; Suppl. Vol. F-26.
(12) Aitken, I. M.; Reid, D. H. *J. Chem. Soc.* **1956**, 3487.

δ 2.74 (s, 3, CH_3), 7.98–8.42 (m, 9, aryl), 8.58 (s, 1, $H_{6,7\text{ or }10}$), 8.64 (s, 1, $H_{6,7\text{ or }10}$). Anal. Calcd for $C_{24}H_{14}O$: C, 90.54, H, 4.43. Found: C, 90.63; H, 4.48.

Further elution of the column with 10% ethyl acetate in benzene gave **6b** (31 mg, 17%): mp 249–251 °C dec (orange needles from benzene); mass spectrum *m/e* 360 (M^+), 345, 317, 302, 274; NMR δ 2.74 (s, 3, CH_3), 2.93 (s, 3, CH_3), 7.91 (d, 1, $H_{7\text{ or }10}$, J = 8.0 Hz), 8.01 (d, 1, J = 8.0 Hz), 8.02 (t, 1, H_4, J = 7.5 Hz), 8.16 (d, 1, H_2, $J_{1,2}$ = 9.0 Hz), 8.26 (d, 1, H_3, J = 7.5 Hz), 8.33 (d, 1, H_5, J = 7.5 Hz), 8.44, 8.50, 8.58 (s, 3, H_6, $H_{7\text{ or }10}$, H_{11}), 9.02 (d, 1, H_1, $J_{1,2}$ = 9.0 Hz). Anal. Calcd for $C_{26}H_{16}O_2$: C, 86.65, H, 4.47. Found: C, 86.59; H, 4.51. Similar reaction of **5a** with acetyl chloride and $AlCl_3$ failed to afford diacetylated products.

Bromination of 1. A solution of Br_2 (0.16 mL, 3 mmol) in acetic acid (16 mL) was added dropwise to a solution of **1** (826 mg, 3 mmol) in AcOH (300 mL) over 15 min. After being stirred for an additional 15 min, the reaction was quenched by addition of aqueous $Na_2S_2O_5$ (5%, 200 mL) and CH_2Cl_2 (200 mL). The organic layer was dried over $MgSO_4$ and concentrated to 30 mL to give **5b** (923 mg, 87%): mp 203–205 °C dec; mass spectrum *m/e* 355 (M^+), 354, 275, 274; NMR δ 7.42 (t, 1, $H_{8\text{ or }9}$, $J_{8,9}$ = 7.3 Hz), 7.45 (t, 1, $H_{8\text{ or }9}$), 7.95 (d, 1, H_{10}, J = 7.3 Hz), 8.02 (t, 1, H_4, J = 8.2 Hz), 8.05 (d, 1, H_7, J = 7.3 Hz), 8.09 (d, 1, H_2, $J_{1,2}$ = 9.4 Hz), 8.23 (d, 1, H_3, J = 8.2 Hz), 8.30 (d, 1, H_1, $J_{1,2}$ = 9.4 Hz), 8.35 (d, 1, H_5, J = 8.2 Hz), 8.45 (s, 1, $H_{6\text{ or }11}$), 8.49 (s, 1, $H_{6\text{ or }11}$); these tentative assignments are based on comparison with the chemical shifts and coupling constants for **1** and **5a**.

In another experiment, a mixture of **1** (55 mg, 0.2 mmol) and NBS (126 mg, 0.71 mmol) were heated at reflux in dry benzene (20 mL) for 41 h. The HPLC pattern was similar to that for the reaction with Br_2. Workup gave **5b** (44 mg, 62%), in all respects identical with that obtained above.

Conversion of 5b to 5f. To a suspension of the bromide **5b** (107 mg, 0.3 mmol) in dry ether (20 mL) in a three-necked flask purged with argon was added a solution of butyllithium (0.14 mL, 0.35 mmol of a 2.5 M solution in hexane) in ether (1 mL) dropwise at 0 °C for 15 min. Deuterium oxide (0.01 mL, 0.56 mmol) was added to the red solution turning the color to yellow. The usual workup followed by chromatography on silica gel on elution with benzene gave **5f** (40 mg, 48%): mp 161–163 °C (cyclohexane); mass spectrum, *m/e* 277 (M^+) (calcd for 277); the ^1H NMR spectrum of **5f** was essentially identical with that of **1**[5] except for the absence of the H_{12} peak at δ 8.20 and the appearance of the H_{11} peak at δ 8.33 as a singlet rather than a doublet; the ^{13}C NMR spectrum of **5f** matched that of **1** except for the virtual disappearance of the C_{12} signal at 124.819 ppm.

Conversion of 5b to 5a. (a) Preparation of 5c and Its Reaction with Acetaldehyde. A solution of *n*-BuLi (0.15 mL of a 2.6 M solution in hexane, 0.4 mmol) in dry ether (1 mL) under argon was added dropwise into a solution of **5b** (107 mg, 0.3 mmol) in ether (20 mL) at 0 °C over 10 min. Acetaldehyde was introduced into this solution by means of warming an attached flask containing paraldehyde (1 mL) and concentrated H_2SO_4 (0.3 mL) for 5 min. After being stirred for 1 h, the mixture was worked up conventionally and the crude products were purified by chromatography on silica to yield recovered **1** (20 mg, 24%), mp 163–165 °C, and **5d** (38 mg, 40%): mp 184–185 °C; mass spectrum 320 (M^+), 302, 276; NMR δ 1.81 (d, 3, CH_3, J = 8.0 Hz), 2.04 (br s, 1, OH), 6.00 (q, 1, methine, J = 8.0 Hz), 7.41 (t, 1, H_8, $J_{7,8}$ = 7.5 Hz), 7.46 (t, 1, H_9, $J_{9,10}$ = 7.5 Hz), 8.01 (t, 1, H_4, J = 7.5 Hz), 8.02 (d, 1, H_{10}), 8.05 (d, 1, H_2, $J_{1,2}$ = 9.6 Hz), 8.07 (d, 1, H_7), 8.22 (d, H_3, $J_{3,4}$ = 7.5 Hz), 8.30 (d, 1, H_1, $J_{1,2}$ = 9.6 Hz), 8.36 (d, 1, H_5, $J_{4,5}$ = 7.5 Hz), 8.48 (s, 1, $H_{6\text{ or }11}$), 8.57 (s, 1, $H_{6\text{ or }11}$). Anal. Calcd for $C_{24}H_{16}O$: C, 89.97; H, 5.03. Found: C, 89.73; H, 5.07.

(b) Oxidation of 5d. A mixture of **5d** (18 mg, 0.056 mmol) and pyridinium dichromate (Aldrich, 105 mg, 0.28 mmol) in dimethylformamide (10 mL) was stirred at room temperature for 17 h. The usual workup followed by chromatography on silica gel gave **5a** (14 mg, 78%), in all respects identical with **5a** obtained by Friedel–Crafts acylation of **1**.

(c) Reaction of 5c with Acetonitrile. A solution of **5c** was prepared from **5b** (107 mg, 0.3 mmol) as described in (a). To this red solution was added acetonitrile (0.02 mL, 0.38 mmol), turning the color of the solution to dark green. Acetic acid (25 mL) and aqueous HCl (1 N, 10 mL) were added, and the mixture was refluxed for 1 h. The color of the solution changed gradually to yellow. The usual workup followed by chromatography on silica gel furnished **1** (24 mg, 29%) and **5a** (37 mg, 39%) identical in its physical properties with an authentic sample.

(d) Reaction of 5c with *N,N*-Dimethylacetamide. A solution of **5c** was prepared from **5b** (107 mg, 0.3 mmol) as described in (a). Addition of *N,N*-dimethylacetamide (0.04 mL, 0.49 mmol) to this solution at 0 °C was followed by successive color changes from red to black, then to green, and lastly to yellow. The mixture was stirred for 3 h then worked up as usual followed by chromatography on silica gel to yield **1** (25 mg 30%) and **5a** (49 mg, 51%) identical with an authentic sample.

Baeyer–Villiger Oxidation of 5a. A solution of **5a** (127 mg, 0.4 mmol) and *m*-chloroperbenzoic acid (140 mg, 0.8 mmol) in $CHCl_3$ (8 mL) was stirred in the dark for 65 h. Chromatography of the product on silica gel gave on elution with benzene an initial yellow fraction. This was evaporated to dryness, and the residue was treated with KOH (100 mg) in ethanol (10 mL) under reflux for 15 min. Evaporation of the solvent left a residue which was triturated with water (20 mL) to yield recovered **5a** (66 mg, 52%). Acidification of the aqueous phase with dilute HCl gave a yellow precipitate of the crude phenol. This was acetylated with Ac_2O (3 mL) and pyridine (1 mL) for 17 h at room temperature. The usual workup followed by chromatography on silica gel gave the phenol acetate **5e** (11 mg, 8%): mp 192–194 °C dec (CH_2Cl_2–petroleum ether); mass spectrum *m/e* 334 (M^+), 292, 263; NMR δ 2.57 (s, 3, CH_3), 7.39 (t, 1, H_8, $J_{7,8}$ = 7.5 Hz), 7.42 (t, 1, H_9, $J_{9,10}$ = 7.5 Hz), 7.91 (d, 1, H_{10}, $J_{9,10}$ = 7.5 Hz), 7.98 (d, 1, H_1, $J_{1,2}$ = 9.5 Hz), 8.00 (t, 1, H_4, J = 7.5 Hz), 8.02 (d, 1, H_2, $J_{1,2}$ = 9.5 Hz), 8.03 (d, 1, H_7, $J_{7,8}$ = 7.5 Hz), 8.07 (s, 1, H_{11}), 8.17 (d, 1, H_3, $J_{3,4}$ = 7.5 Hz), 8.32 (d, 1, H_5, $J_{4,5}$ = 7.5 Hz), 8.43 (s, 1, H_6); these tentative assignments an based on comparison with the chemical shifts and coupling constants for **1** and **5a** (Table I). Anal. Calcd for $C_{24}H_{14}O_2$: C, 86.21; H, 4.22. Found: C, 86.12; H, 4.25.

Hydrogenation of 1. A solution of **1** (83 mg, 0.3 mmol) in EtOAc (25 mL, distilled over K_2CO_3) was shaken with a 10% Pd–charcoal catalyst (Engelhard, 100 mg) under H_2 (30 psig) at room temperature for 70 h. The catalyst was filtered off and the solution was evaporated to provide a residue which was chromatographed on silica gel. Elution with petroleum ether gave 1,2-dihydroindeno[1,2,3-*cd*]pyrene (**7**; 49 mg, 59%): mp 154–156 °C; mass spectrum 278 (M^+), 276; NMR δ 3.40 (br s, 4, CH_2), 7.34–7.47 (m, 4, aryl), 7.52 (t, 1, aryl, J = 7.5 Hz), 7.85–7.87 (m, 3, aryl), 7.97 (d, 1, aryl, J = 7.0 Hz), 8.19 (s, 1, H_6). Anal. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 94.70; H, 5.10.

Bromination of Benz[*a*]aceanthrylene (2). A solution of **2** (4.2 mg, 0.017 mmol) and Br_2 (0.017 mmol) in CH_2Cl_2 (5 mL) was stirred in an ice bath for 19 h. The usual workup afforded **8** (5.3 mg, 94%): mp 183–185 °C dec; mass spectrum *m/e* 331 (M^+), 330, 251, 250; NMR δ 7.38 (t, 1, J = 7.5 Hz), 7.44 (t, 1, J = 7.5 Hz), 7.59–7.72 (m, 3), 7.94 (d, 1, J = 7.0 Hz), 7.96 (d, 1, J = 7.0 Hz), 8.26 (d, 1, J = 8.7 Hz), 8.31 (d, 1, J = 7.5 Hz), 8.62 (d, 1, J = 8.8 Hz), 8.72 (d, J = 8.8 Hz). Anal. Calcd for $C_{20}H_{11}Br$: C, 72.51; H, 3.35. Found: C, 72.42; H, 3.37.

Bromination of Benz[*e*]acephenanthrylene (3). A solution of **3** (35 mg, 0.14 mmol) and Br_2 (0.84 mmol) in CH_2Cl_2 (20 mL) was heated at reflux for 17 h. Then a second portion of Br_2 (0.84 mmol in 4.5 mL of CH_2Cl_2) was added, and the mixture was refluxed for an additional 25 h. The usual workup gave **9a** (32 mg, 70%): mp 145–147 °C (hexane); mass spectrum *m/e* 332, 331 (M^+), 330, 251, 250; NMR δ 7.4 (m, 2, $H_{5,6}$), 7.65 (t, 1, J = 7.5 Hz), 7.71 (t, 1, J = 7.5 Hz), 7.74 (d, 1, J = 7.5 Hz), 7.84–7.87 (m, 1), 7.93–7.97 (m, 1), 8.03 (t, 2), 8.23 (s, H_8), 10.04 (d, 1, H_{12}, J = 7.5 Hz). Deuteration of **9a** by the procedure employed for the preparation of **5f** gave **9b** (63%). The ^1H NMR spectrum of **9b** closely matched that of **3**[5] except for the loss of the H_1 peak at δ 8.42 and the simplification of the splitting pattern of the H_2 peak.

Bromination of Indeno[1,2,3-*hi*]chrysene (4). Treatment of **4** (29 mg, 0.096 mmol) with Br_2 (0.22 mmol) in CH_2Cl_2 (12 mL) at room temperature for 39 h yielded **10a** (33.5 mg, 92%): mp 211–214 °C (CH_2Cl_2–petroleum ether); mass spectrum *m/e* 381 (M^+) (Calcd for 381), 380, 318, 300; NMR δ 7.40–7.45 (m, 2, $H_{11,12}$), 7.71–8.10 (m, 6, aryl), 8.45 (apparent t, 2), 8.90 (d, 1, H_1, $J_{1,2}$ = 7.5 Hz), 8.96 (s, 1, H_6), 9.12 (s, 1, H_{14}). Conversion of **10a** to the deuterated compound by the usual procedure gave **10b** (ca. 30% deuterium purity). The ^1H NMR spectrum of **10b** closely matched that of **4** except for a decrease of the H_5 signal in the region of δ 7.98 and a partial collapse of the H_6 doublet at δ 8.63 to a singlet; the ^{13}C NMR spectrum of **10b** matched that of **4** except for a marked decrease in the intensity of the C_5 signal at 127.73 ppm.

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