benzylate in 10 mL of anhydrous dimethyl sulfoxide was added 0.50 g (1.08 mmol) of tetraester **21**. After the mixture had been stirred for 10 min at room temperature, a clear solution was formed. The mixture was stirred for 5 more min, diluted with benzene, and extracted several times with 1 M phosphoric acid. The acidic aqueous phase was made alkaline with potassium carbonate and extracted with benzene, and the organic phase was washed with saturated sodium chloride solution, dried, and evaporated to give 0.345 g of a yellow oil. Preparative TLC (benzene–ethyl acetate, 3/2) gave 0.32 g (75%) of the benzyl diethyl triester **22**: NMR (CCl_4) δ 1.25 (t, 6 H, J = 7 Hz), 1.70–2.20 (m, 5 H), 2.25–3.55 (m, 7 H), 4.10 (q, 4 H, J = 7 Hz), 5.00 (s, 2 H), 7.20 (s, 5 H); IR 3000, 1730, 1430, 735, 680 cm^{-1}; MS m/e 346 ($M^+ - OC_2H_5$), 318 ($M^+ - CO_2C_2H_5$).

***N*-(3,3-Bis(ethoxycarbonyl)-*n*-propyl)proline (23).** To 0.50 g (1.28 mmol) of *N*-(3,3-bis(ethoxycarbonyl)-*n*-propyl)proline benzyl ester (**22**) dissolved in 25 mL of absolute ethanol was added 60 mg of 10% Pd/C. The mixture was hydrogenated at 50 psi for 18 h, the catalyst was removed, and the solvent was evaporated to give 350 mg (90%) of **23**, which was used without further purification: NMR δ 1.3 (t, 6 H, J = 6 Hz), 1.8–2.6 (m, 6 H), 2.65–4.40 (m, 10 H), 8.9 (br, 1 H).

4,4-Bis(ethoxycarbonyl)pyrrolizidine (Diethyl 1-Azabicyclo[3.3.0]octane-4,4-dicarboxylate, 25). To 0.10 g (0.33 mmol) of *N*-(3,3-bis(ethoxycarbonyl)-*n*-propyl)proline (**23**) was added 0.52 g (3.30 mmol) of phosphorus oxychloride, and the mixture was heated at 100 °C for 2 min. After the solution was cooled, 10 mL of ice water was added, and the pH was adjusted to 6.0 with potassium carbonate, the mixture was left at room temperature for 6 h, then it was saturated with potassium carbonate and extracted with ether. The ether layer was dried, the solvent evaporated, and the residue Kugelrohr distilled, yielding 0.048 g (57%) of pure **25**: NMR δ 1.20 (t, 6 H, J = 7 Hz), 1.60–3.30 (m, 11 H), 4.15 (q, 4 H, J = 7 Hz); IR 3000, 1730, 1250 cm^{-1}; MS m/e 255 (M^+). Anal. Calcd for $C_{13}H_{21}NO_4$: C, 61.2; H, 8.3; N, 5.5. Found: C, 61.1; H, 8.3; N, 5.3.

Formation of iminium ion 27 was carried out from 1.13 g (3.3 mmol) of *N*-(5,5-bis(ethoxycarbonyl)-*n*-pentyl)pipecolic acid (**26**) by adding phosphorus oxychloride (3.2 mL, freshly distilled) and heating and stirring for 4 min. Treatment in the usual way for cyclization led only to polymeric material; none of the 1-azabicyclo[5.4.0]undecane diester **29** could be isolated.

An identical decarbonylation reaction mixture was cooled, and 50 mL of ice–water was added, followed by sodium bicarbonate to pH 4 and 0.5 g of 10% Pd/C. After hydrogenation at 40 psi for 2 h, the solution was filtered, and the filtrate was made alkaline with potassium carbonate and extracted with ether. The ether was washed with water and saturated NaCl, dried, and evaporated to give ***N*-(5,5-bis(ethoxycarbonyl)-*n*-pentyl)piperidine (28)**: 0.84 g; 2.8 mmol; 85%; identical by NMR, IR, and GC with an authentic sample prepared below.

***N*-(5,5,5-Tris(ethoxycarbonyl)-*n*-pentyl)piperidine.** Piperidine (2.3 g, 27 mmol), triethyl 5-bromopentane-1,1,1-tricarboxylate (5 g, 13.5 mmol), and benzene (50 mL) were mixed and placed at room temperature for 24 h. The piperidine hydrobromide was filtered off, and the filtrate was extracted several times with cold 1 M H_3PO_4. The cold acid solution was adjusted to pH 10 with K_2CO_3 and then extracted with ether. Drying and evaporating the ether left an oil weighing 2.5 g (6.7 mmol; 50% yield): NMR δ 1.0–1.8 (m, 19 H), 1.9–2.6 (m, 8 H), 4.2 (q, 6 H); IR 3000, 1760, 1750, 1250 cm^{-1}. Anal. Calcd for $C_{19}H_{33}NO_6$: C, 61.4; H, 8.9; N, 3.8. Found: C, 61.2; H, 8.8; N, 3.8.

***N*-(5,5-Bis(ethoxycarbonyl)-*n*-pentyl)piperidine (28).** *N*-(5,5,5-Tris(ethoxycarbonyl)-*n*-pentyl)piperidine (1.0 g, 2.7 mmol) was added to a solution of sodium metal (0.12 g, 5.25 mmol) in absolute ethanol (10 mL) at room temperature. After 15 min of stirring, the solution was cooled and cold 1 N HCl was added to pH 2. The reaction mixture was washed with ether, adjusted to pH 10 with K_2CO_3 in the cold, and again extracted with ether which was washed with water and saturated NaCl and dried. Evaporation of the ether left analytically pure diester **28**, one peak by GC: NMR δ 1.1–2.2 (m, 18 H), 2.2–2.6 (m, 6 H), 3.3 (t, 1 H), 4.2 (q, 4 H); IR 3000, 1750, 1730, 1360, 1140 cm^{-1}. Anal. Calcd for $C_{16}H_{29}NO_4$: C, 64.2; H, 9.8; N, 4.7. Found: C, 63.9; H, 9.8; N, 4.7.

Registry No. **1** (m = 4), 5227-53-2; **2** (m = 4; R′ = $CH_2C_6H_5$), 61212-37-1; **2** (m = 2; R′ = $CH_2C_6H_5$), 41324-66-7; **2** (m = 3; R′ = $CH_2C_6H_5$), 38068-75-6; **2** (m = 4; R′ = *p*-toluenesulfonate), 71519-04-5; **3** (m = 2; n = 3; R = C_2H_5; R′ = $CH_2C_6H_5$), 71519-05-6; **3** (m = 3; n = 3; R = C_2H_5; R′ = $CH_2C_6H_5$), 71519-06-7; **3** (m = 4; n = 3; R = C_2H_5; R′ = $CH_2C_6H_5$), 61212-38-2; **4** (m = 2; n = 3; R = C_2H_5), 71519-07-8; **4** (m = 3; n = 3; R = C_2H_5), 71519-08-9; **4** (m = 4; n = 3; R = C_2H_5), 61212-39-3; **6** (m = 2; n = 3; R = C_2H_5), 71519-09-0; **6** (m = 3; n = 3; R = C_2H_5), 25647-44-3; **6** (m = 4; n = 3; R = C_2H_5), 61212-41-7; **7**, 31436-28-9; **8**, 71519-10-3; **12**, 69305-74-4; **13**, 36825-10-2; **14**, 71519-11-4; **15**, 71519-12-5; **16**, 71519-13-6; **17**, 71519-14-7; **18**, 71519-15-8; **19**, 71519-16-9; **20**, 71170-82-6; **21**, 71519-17-0; **22**, 71519-18-1; **23**, 71519-19-2; **24**, 71519-20-5; **25**, 71519-21-6; **26**, 71519-22-7; **27**, 71519-23-8; **28**, 71519-24-9; *N*-[5,5,5-tris(ethoxycarbonyl)-*n*-pentyl]piperidine, 71519-25-0; diethyl 3-bromopropylmalonate, 10149-21-0; piperidine, 110-89-4; triethyl 5-bromopentane-1,1,1-tricarboxylate, 71170-83-7.

"K-Region" Imines of Some Carcinogenic Aromatic Hydrocarbons

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Received June 19, 1979

A general synthesis of unsubstituted K-region arene imines from the corresponding arene oxides is described. Reaction of sodium azide with oxiranes gave mixtures of trans azido alcohols, which upon treatment with tri-*n*-butylphosphine yielded the expected arene imines. By this method the K-imines of benz[*a*]anthracene, 7-methlbenz[*a*]anthracene, dibenz[*a*,*h*]anthracene, and benzo[*a*]pyrene were prepared, and means were provided to examine the hypothesis that imines may serve as activated carcinogenic intermediates. The azido alcohols of 7,12-dimethylbenz[*a*]anthracene 5,6-oxide and of benzo[*c*]phenanthrene 5,6-oxide reacted with triisopropylphosphine to give isolable Staudinger adducts which, however, could not be converted into cyclic imines.

Recently[3] we postulated a theory that arene imines[4] are possible transformation products of polycyclic aromatic hydrocarbons in vivo. When an arene oxide alkylates an amino or nucleic acid molecule at a nitrogen atom, and the adduct is dealkylated, cyclyzation of the amino alcohol

(1) Department of Organic Chemistry.
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(3) Ittah, Y.; Shahak, I.; Blum, J. *J. Org. Chem.* **1978**, *43*, 397.
(4) In this context we define an arene imine as an *aziridine* structure fused to a benzene ring.

0022-3263/79/1944-4178$01.00/0

Table I. ^{1}H NMR Spectra (δ) of Some Triisopropylphosphine-Azido Alcohol Adducts[a]

compd	isopropyl CH_3[d]	iso-propyl CH[d]	ring CH_3	OH	H_5	H_6 ($J_{5,6}$, Hz)
5; R = CH_3, R′ = H, R″ = $CH(CH_3)_2$[b]	0.84, 1.00	2.02	2.70	1.80	5.09	5.74 (5)
6; R = CH_3, R′ = H, R″ = $CH(CH_3)_2$[b]	1.14, 1.29	2.48	2.78	2.30	5.27	5.52 (5)
5; R = R′ = CH_3, R″ = $CH(CH_3)_2$[b]	0.88, 1.00	1.95	2.67, 2.94	2.10	5.03	5.63 (4.5)
16[c]	1.26, 1.33	2.53		2.75	4.72	5.27 (10)

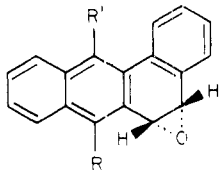
[a] In $CDCl_3$-Me_4Si. [b] 100-MHz NMR. [c] 270-MHz NMR. [d] J = 7 Hz.

intermediate may lead to an arene imine. This theory would suggest that imines are secondary metabolites of polycyclics and may even function, in some cases, as the active carcinogens of the parent hydrocarbons.

In order to test the validity of this hypothesis we studied several synthetic routes to *N*-acetyl,[5] *N*-alkyl,[3,7] and unsubstituted polycyclic arene imines[6] by which the corresponding phenanthrene 9,10-derivatives could be obtained.

We now wish to report the syntheses of K-region imines of some typical carcinogenic structures, namely, derivatives of benz[*a*]anthracene (BA), dibenz[*a*,*h*]anthracene (DBA), and benzo[*a*]pyrene (BP).

As shown previously for phenanthrene 9,10-oxide,[6,8] benz[*a*]anthracene 5,6-oxide (1; R = R′ = H) reacts with aqueous sodium azide. However, in contrast to the symmetrical model compound, 1 (R = R′ = H) yields two trans azido alcohols **2** and **3** (R = R′ = H) in a ratio of 5:3 as evidenced by 270-MHz NMR analysis. The resonance



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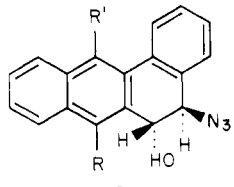

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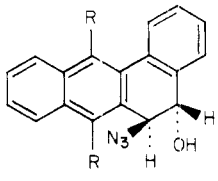

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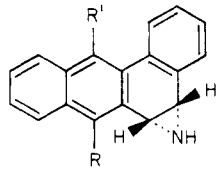

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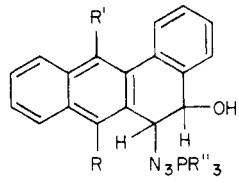
peaks for **2** (R = R′ = H) at 2.43 (d, $J_{H_6H_{OH}}$ = 6 Hz, H_{OH}), 4.68 (d, $J_{H_5H_6}$ = 7 Hz, H_5), and 4.80 ppm (dd, $J_{H_5H_6}$ = 7 Hz, $J_{H_6H_{OH}}$ = 6 Hz, H_6) and for **3** (R = R′ = H) at 2.33 (d, $J_{H_5H_{OH}}$ = 3.5 Hz, H_{OH} = 3.5 Hz, H_{OH}), 4.78 (d, $J_{H_5H_6}$ = 7 Hz, H_6), and 4.81 ppm (ABq, $J_{H_5H_6}$ = 7 Hz, $J_{H_5H_{OH}}$ = 3.5 Hz, H_5) indicate that both azido alcohols have the trans configuration. The stereochemical course of this reaction and its nonregioselectivity are in fair agreement with previous studies of Jeffrey et al.[10] on the addition of azide to arene oxides and with the observation of Harvey et al.[11,12] that the C_5 and C_6 positions in 1 (R = R′ = H) have similar reactivities toward nucleophiles.

Upon treatment of the mixture of **2** and **3** (R = R′ = H) in hexane with cold tri-*n*-butylphosphine[6] followed by 3 h of heating at 56 °C, benz[*a*]anthracene 5,6-imine[13] (**4**; R = R′ = H) was formed in 78% yield. Similar results were obtained when triphenylphosphine was employed, but separation of the aziridine compound from the triphenylphosphine oxide proved difficult. Continuous NMR measurements during the process revealed a significant difference in the reactivities of the two azido alcohols. While the H_5 and H_6 signals of **2** (R = R′ = H) disappear within 25 min at 31 °C, the corresponding peaks of the more stericially hindered isomer **3** are visible for a further 5 h. Nevertheless, it is not advisable to increase the reaction period since in the phosphine-containing solution the imine undergoes slow rearrangement.

When the reaction of **2** (R = R′ = H) with tri-*n*-butylphosphine was conducted above 60 °C most of the imine rearranged to the aromatic amines. However, below 45 °C bright yellow crystals of formula $C_{30}H_{40}N_3OP$ (determined by mass spectroscopy) separated. Their ^{1}H NMR absorption ($CDCl_3$) at 4.79 and 5.30 ppm and ^{31}P resonance peaks ($CDCl_3$) at 39.3 and 39.7 ppm (downfield from 85% H_3PO_4) are consistent with structures **5** and **6** [R = R′ = H, R″ = $(CH_2)_3CH_3$]. This mixture of primary Staudinger



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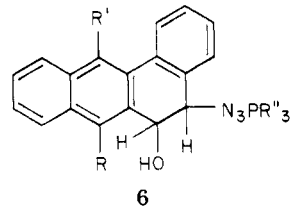

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adducts[14] of the phosphine to **2** and **3** is stable when kept in the refrigerator but decomposes explosively, when dry, upon brief heating at 30 °C. As this deazotization does not lead to **4** (R = R′ = H), it is essential to ensure complete transformation of **5** and **6** while in solution by heating the reaction mixture at 56 °C.

7-Methylbenz[*a*]anthracene 5,6-oxide (1; R = CH_3, R′ = H)[9] reacted nearly as well as the unsubstituted compound to give 7-methylbenz[*a*]anthracene 5,6-imine (**4**; R = CH_3, R′ = H). However, 7,12-dimethylbenz[*a*]anthracene 5,6-oxide (1; R = R′ = CH_3)[15] failed to give an isolable imine. The reaction of the epoxide with sodium azide afforded a mixture of 17% of **2** and 83% of **3** (R = R′ = CH_3) as expected from previous studies of Beland and Harvey.[11] Treatment of the azido alcohols with tri-*n*-butylphosphine at 56 °C gave only small amounts of **4** (R = R′ = CH_3) admixed with phosphorus-containing compounds. At higher temperatures rapid transformation of the aziridine took place. On the other hand, **3** (R = R′ = CH_3) gave a stable triisopropylphosphine adduct, **5** [R =

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(13) For the convenience of the reader we apply trivial names for arene imines throughout the text. IUPAC nomenclature is used only in the Experimental Section.
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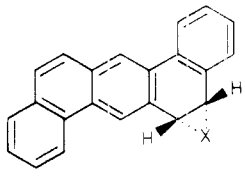
Table II. Some ^{1}H NMR and Mass Spectroscopic Data of Polycyclic Arene Imines

imine	aziridine ring protons, ppm	m/e (rel intensity of fragment ion) M	M − NH	M − NH − 2H	M − NH − CH
phenanthrene 9,10-imine[a]	3.56 (s)	139 (100)	178 (34)	176 (10)	165 (74)
BA 5,6-imine (4; R = R′ = H)[b,d]	3.60, 3.77 (AB q J = 5 Hz)	243 (100)	228 (54)	226 (18)	215 (34)
7-MBA 5,6-imine (4; R = CH_3, R′ = H)[c,d]	3.50, 3.91 (AB q, J = 6 Hz)	257 (100)	242 (25)	240 (9)	229 (15)
7,12-DMBA 5,6-imine (4; R = R′ = CH_3)[c,e,f]	3.56, 3.76 (AB q, J = 6 Hz)	271 (79)	256 (100)	254 (29)	243 (50)
DBA 5,6-imine (7; X = NH)[c,e]	3.63, 3.83 (AB q, J = 5 Hz)	293 (80)	278 (100)	226 (24)	265 (43)
BP 4,5-imine (8; X = NH)[b,d]	3.83, 3.93 (AB q, J = 5 Hz)	267 (100)	252 (43)	250 (15)	239 (27)
BPh 5,6-imine (13; X = NH)[c,d,f]	3.62, 3.84 (AB q, J = 5 Hz)	243 (100)	228 (30)	226 (19)	215 (54)

[a] Data taken from our previous paper.[6] [b] 270-MHz NMR in $CDCl_3$. [c] 100-MHz NMR in $CDCl_3$. [d] Mass spectrum recorded at 100 °C. [e] Mass spectrum recorded at 135 °C. [f] Not isolated as a pure compound.

R′ = CH_3, R″ = $CH(CH_3)_2$], mp 143–144.5 °C. The mass spectrum and elemental analysis indicated the formula $C_{29}H_{38}N_3OP$, and the ^{1}H NMR spectrum showed the characteristic H_5 and H_6 resonance peaks at 5.03 and 5.63 ppm. (See Table I.) We attribute the great stability of **5** [R = R′ = CH_3, R″ = $CH(CH_3)_2$] to a steric effect of the meso methyls on the bulky phosphoazido group at C_6.

The reaction of NaN_3 with dibenz[*a*,*h*]anthracene 5,6-oxide (**7**; X = O)[16] gave two azido alcohols in a ratio of 1.7:1 (cf. ref 12). These pentacyclic compounds hardly react under the conditions given for **2** and **3** (R = R′ = H) but form the expected dibenz[*a*,*h*]anthracene 5,6-imine (**7**; X = NH) in 90% yield when the reaction was conducted at 70 °C.



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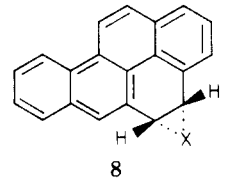

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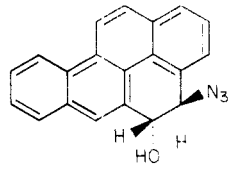

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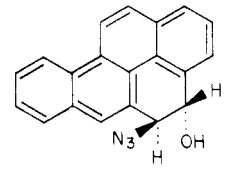

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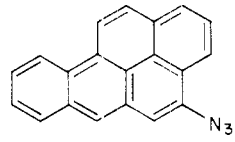

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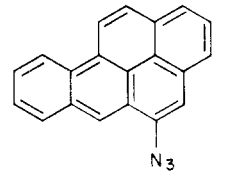

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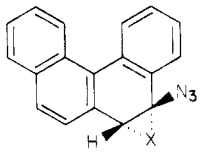
The two trans azido alcohols derived from benzo[*a*]pyrene 4,5-oxide (**8**; X = O) which were obtained in equal amounts (cf. ref 11) have somewhat different solubilities in benzene and methylene chloride. Fractional crystallization provided partial separation of the two isomers, and their structures could be determined by 270-MHz ^{1}H NMR analysis of the fully aromatized 4- and 5-azidobenzo[*a*]pyrenes **11** and **12**. Dehydration of the less soluble azido alcohol with *p*-toluenesulfonic acid in benzene[11] afforded azide **12** in which the H_6 proton was deshielded (in C_6D_6) by 0.66 ppm (from 8.15 to 8.81 ppm) as compared with the value for that of the unsubstituted parent compound.[17] The more soluble azido alcohol gave upon dehydration 4-azidobenzo[*a*]pyrene (**11**) in which the H_3 doublet of BP at 7.79 ppm was shifted to 8.26 ppm. The ortho protons in both **11** and **12** were slightly shielded by the N_3 group as already observed in azidobenzene.[18]

In contrast to the reaction of benzo[*c*]phenanthrene 5,6-oxide (**13**; X = O)[19] with *tert*-butyl mercaptan, which yields exclusively a 6-thio derivative,[11] the S_N2 displacement by azide gave nearly equal amounts of **14** and **15** (270-MHz ^{1}H NMR analysis). The two isomers do not



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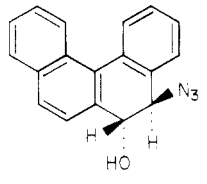
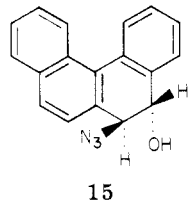
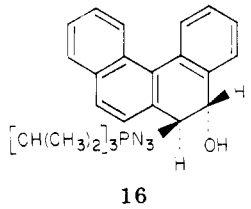


14



15



16

interconvert upon heating. Thus, one should be careful when predicting the regioselectivity of S_N2 displacements on arene oxides just on the basis of relative activity numbers (cf. ref 11 and 12). The two azido alcohols **14** and **15** behave differently, however, in the presence of tertiary phosphines. NMR studies revealed that while **14** is converted into benzo[*c*]phenanthrene 5,6-imine (**13**; X = NH) at 56 °C, the reaction of tertiary phosphines and **15** yields a Staudinger adduct. The product **16** obtained with triisopropylphosphine is particularly stable and could be isolated and analyzed (see Table I). The imine formed from the mixture of azido alcohols and triphenyl- or tri-*n*-butylphosphine could not be separated from the phosphine-containing byproducts.

The structures of the arene imines were established by spectral data, and those that could be isolated were sub-

(16) Boyland, E.; Sims, P. *Biochem. J.* **1965**, *97*, 7.

(17) High, C. W.; Mallion, R. B. *J. Mol. Spectrosc.* **1969**, *29*, 478.

(18) Shapiro, B. L.; Mohrmann, L. E. *J. Phys. Chem. Ref. Data* **1977**, *6*, 919.

(19) Beland and Harvey[11] reacted **13** (X = O) with *tert*-butyl mercaptan but did not report the synthesis or the physical properties of the epoxide.

jected to elemental analysis. The N–H absorptions in the IR spectra appear between 3160 and 3180 cm^{-1}. The ^1H NMR spectra (Table II) prove the existence of pairs of nonequivalent aziridine protons that show up between 3.5 and 4.0 ppm. There is no indication of azepine signals[20] in these spectra. The principal-fragment ions in the mass spectra (Table II) are the molecular ions M, the (M – NH) fragments, and the fluorenyl ions (M – NH – CH) that are characteristic for many 9,10-dihydrophenanthrene derivatives.[21]

The arene imines are converted both upon thermolysis and by protic acids into mixtures of fully aromatized amines (NMR studies). Under nitrosating conditions (isoamyl nitrite and triethylamine[22]) all the imines—including those that could not be isolated in pure state—could be transferred into the corresponding parent hydrocarbons in nearly quantitative yield.

Experimental Section

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are not corrected. Infrared spectra were recorded on a Perkin-Elmer Model 157 spectrophotometer. Proton magnetic resonance spectra were run by using T-60, WP-60, HA-100D, and WH-270 spectrometers. The WP-60 instrument was also used for the recording of ^{31}P magnetic resonance spectra. Mass spectra were measured with a double-focusing Varian MAT-311 spectrometer at 70 eV. The exact masses of ambiguous ions were determined by high-resolution; $R = M/\Delta M > 10\,000$.

1a,11b-Dihydrobenz[*a*]anthr[5,6-*b*]azirine (Benz[*a*]anthracene 5,6-Imine (4; R = R′ = H)). A mixture of 20 g of NaN_3 in 450 mL of 65% aqueous acetone, 0.5 mL of concentrated H_2SO_4, and 0.732 g of benz[*a*]anthracene 5,6-oxide (1; R = R′ = H)[9] was stirred under N_2 at room temperature for 72 h. The acetone was removed in vacuo, and water was added to dissolve the excess of the inorganic salt. The mixture of azido alcohols was filtered, dried, and recrystallized from benzene to yield 0.774 g (87%) of colorless **2** and **3** (R = R′ = H) as hemihydrates. The ratio of **2**:**3** was 5:3 as indicated by 270-MHz ^1H NMR analysis: mp 175–177 °C; IR (Nujol) 2120 (N_3), 3180–3300 cm^{-1} (OH); 270-MHz ^1H NMR ($CDCl_3$) for **2** (R = R′ = H) δ 2.43 (d, $J_{H_6H_{OH}}$ = 6 Hz, disappears upon addition of D_2O), 4.68 (d, $J_{H_5H_6}$ = 7 Hz), 4.80 (dd, $J_{H_5H_6}$ = 7 Hz, $J_{H_6H_{OH}}$ = 6 Hz, decoupled by D_2O), 7.35–8.27 (m); for **3** (R = R′ = H) δ 2.33 (d, $J_{H_5H_{OH}}$ = 3.5 Hz, disappears upon addition of D_2O), 4.78 (d, $J_{H_5H_6}$ = 7 Hz), 4.81 (AB q, $J_{H_5H_6}$ = 7 Hz, $J_{H_5H_{OH}}$ = 3.5 Hz), 7.3–8.87 (m), the H_2O crystallization protons coincide usually with the OH proton but appears separately at ~1.6 upon dilution (this peak disappears upon addition of D_2O or molecular sieve); mass spectrum, *m/e* (rel intensity) 287 ($M^{+\cdot}$, 19), 259 [$(M - N_2)^{+\cdot}$, 14], 258 [$(M - N_2H)^+$, 20], 245 [$(M - N_3)^+$, 16], 231 ($C_{17}H_{11}O^+$, 100), 229 ($C_{18}H_{13}^+$, 15), 215 ($C_{17}H_{11}^+$, 30), 202 ($C_{16}H_{10}^{+\cdot}$, 28). Anal. Calcd for $C_{18}H_{13}N_3O \cdot {}^1/_2\,H_2O$: C, 73.0; H, 4.7; N, 14.2. Found: C, 73.2; H, 4.5; N, 14.5.

Under N_2 a suspension of 0.662 g of the above mixture of azido alcohols in 750 mL of *n*-hexane was stirred at 0 °C for 5 min, and 1.16 mL of freshly purified tri-*n*-butylphosphine was added. After 30 min at 0 °C the mixture was stirred for an additional 30 min at room temperature, and finally the temperature was raised to 56 °C. After 20–30 min a clear yellow solution was formed, and stirring was maintained at this temperature for 2.5 h. The mixture was cooled, the solvent removed in vacuo, and the residue triturated with hexane. The crude imine was washed several times with cold hexane and recrystallized (3×) from anhydrous ether–hexane to yield 0.437 (78%) of pale yellow **4** (R = R′ = H), mp 157 °C dec. Anal. Calcd for $C_{18}H_{13}N$: C, 88.8; H 5.4; N, 5.8. Found: C, 88.5; H, 5.5; N, 5.4.

Deamination of 4 (R = R′ = H). A mixture of 24 mg of the foregoing imine, 1.3 g of isoamyl nitrite, and 0.5 mL of triethylamine was stirred for 45 min at room temperature. Extraction with benzene and PLC on silica afforded almost a quantitative yield of benz[*a*]anthracene.

The other imines were deaminated in the same manner.

7-(Methyl-1a,11b-dihydrobenz[*a*]anthr[5,6-*b*]azirine (7-Methylbenz[*a*]anthracene 5,6-Imine (4; R = CH_3, R′ = H)). As for the lower homologue, 0.243 g of 7-methylbenz[*a*]anthracene 5,6-oxide (1; R = CH_3 R′ = H)[9] was treated at room temperature with 6.5 g of NaN_3, 0.5 mL of concentrated H_2SO_4, 50 mL of acetone, and 100 mL of water for 48 h. The crude mixture of azido alcohols (0.260 g, 92%, ratio of isomers 2:1) softens between 43 and 50 °C and melts at 62 °C: 60-MHz ^1H NMR ($CDCl_3$), δ 1.93 and 2.12 (br s, 1, OH), 2.52 and 2.60 (s, 3, CH_3), 4.45 (m, 1), 5.00 (m, 1), 7.1–8.2 (m, 9); mass spectrum, *m/e* (rel intensity) 301 ($M^{+\cdot}$, 50), 273 [$(M - N_2)^{+\cdot}$, 8], 272 [$(M - H_2O - N)^+$, 11], 259 [$(M - N_3)^+$, 16], 245 ($C_{18}H_{13}O^+$, 100), 242 ($C_{19}H_{15}^+$, 18), 229 ($C_{18}H_{13}^+$, 11), 216 ($C_{17}H_{12}^{+\cdot}$, 21), 202 ($C_{16}H_{10}^{+\cdot}$, 16).

A mixture of 140 mg of the azido alcohols in 200 mL of *n*-heptane was stirred under N_2 for 5 min at 0 °C. Excess tri-*n*-butylphosphine (240 μL) was added, and stirring was continued for 2 h at 0 °C. The mixture was then heated during 10 min at 56 °C. After 2 h at this temperature, the solvent was removed under reduced pressure and the pale yellow residue washed (3×) with cold heptane. The imine (78 mg, 65%) was recrystallized twice from a large volume of cyclohexane. At 138–141 °C **4** (R = CH_3, R′ = H) darkens (decomposes) and melts finally at ~210 °C. Anal. Calcd for $C_{15}H_{14}N$: C, 88.7; H, 5.8; N, 5.4. Found: C, 88.7; H, 5.5; N, 4.9.

***trans*-5,6-Dihydro-7,12-dimethyl-6-[(triisopropylphospho)azido]benz[*c*]anthr-5-ol [5; R = R′ = CH_3, R″ = $CH(CH_3)_2$].** To a solution of 13 g of sodium azide and 0.2 mL of concentrated H_2SO_4 in 200 mL of acetone and 100 mL of water was added 0.544 g of 1 (R = R′ = CH_3),[15] and the mixture was stirred under N_2 at room temperature for 48 h. Evaporation of the acetone afforded 0.549 g (87%) of **2** and **3** (R = R′ = CH_3): ratio of isomers 5:1, respectively; mp 60–75 °C dec; IR (Nujol) 2080 (N_3), 3260–3380 cm^{-1} (OH); 100-MHz ^1H NMR ($CDCl_3$) δ 1.96 (br s, 1), 2.775 (s, 3), 2.92 (s, 3), 4.66 (d, J = 3.5 Hz, 1/6, decoupled by D_2O), 4.76 (d, J = 3.5 Hz, 5/6, decoupled by D_2O), 5.09 (d, J = 3.5 Hz, 5/6), 5.14 (d, J = 3.5 Hz, 1/6), 7.20–8.15 (m, 8); mass spectrum, *m/e* (rel intensity) 315 ($M^{+\cdot}$, 26), 287 [$(M - N_2)^{+\cdot}$, 7], 273 [$(M - N_3)^+$, 9], 272 [$(M - N_2 - CH_3)^+$, 31], 258 ($C_{19}H_{13}O^+$, 100), 256 ($C_{20}H_{15}^+$, 14), 244 ($C_{19}H_{16}^{+\cdot}$, 18), 243 ($C_{19}H_{15}^+$, 16), 242 ($C_{19}H_{14}^{+\cdot}$, 15), 215 ($C_{18}H_{13}^+$, 22), 202 ($C_{16}H_{10}^{+\cdot}$, 9).

A mixture of 0.168 g of the foregoing azides, 0.208 mL of triisopropylphosphine and 200 mL of *n*-heptane was stirred under N_2 at 0 °C for 5.5 h. An additional 0.08-g sample of the phosphine reagent was added, and stirring was continued for 12 h at 20 °C. The cream-colored precipitate (0.165 g, 65%) was recrystallized from benzene–cyclohexane (1:1): mp 143–144.5 °C (dec); ^{31}P NMR ($CDCl_3$, from 85% H_3PO_4) 44.4 ppm. Anal. Calcd for $C_{29}H_{38}N_3OP$: C, 73.2; H, 8.1; N, 8.8; P, 6.5. Found: C, 73.0; H, 8.0; N, 8.5; P, 6.3.

1,13b-Dihydrodibenz[*a*,*h*]anthr[5,6-*b*]azirine (Dibenz[*a*,*h*]anthracene 5,6-Imine (7; X = NH)). Treatment of 0.70 g of dibenz[*a*,*h*]anthracene 5,6-oxide (7; X = O)[16] with 15.5 g of sodium azide in 250 mL of acetone, 125 mL of water, and 0.2 mL of H_2SO_4 for 72 h at room temperature yielded 0.74 g (87%) of the two azido alcohols (ratio 1.7:1): mp 163–166 °C; IR (Nujol) 2090 (N_3), 3400 cm^{-1} (OH); 100-MHz ^1H NMR ($CDCl_3$) δ 1.53 and 1.58 (br peaks, 1) 4.56, 4.76, and 4.86 (ds and AB q, 2), 7.20–8.89 (m, 12); mass spectrum, *m/e* (rel intensity) 337 ($M^{+\cdot}$, 10), 309 [$(M - N_2)^{+\cdot}$, 9], 295 [$(M - N_3)^+$, 40], 280 ($C_{12}H_{16}^{+\cdot}$, 44), 279 ($C_{22}H_{15}^+$, 49), 277 ($C_{22}H_{11}^+$, 36), 252 ($C_{20}H_{12}^{+\cdot}$, 9).

To a stirred solution of 0.615 g of the above azido alcohols in 750 mL of heptane was added under N_2 and with external cooling 1.32 mL of tri-*n*-butylphosphine. The mixture was stirred at room temperature for 1 h and at 57 °C for 4.5 h. After addition of 0.2 mL of the phosphine reagent the mixture was stirred for 2.5 h at 70 °C. The solvent was removed in vacuo, a few drops of hot chloroform were added, and after removal of this solvent the residue was recrystallized (3×) from CH_2Cl_2–heptane to yield 0.485 g (91%) of **7** (X = NH) as pale yellow crystals, mp 172–175 °C. Anal. Calcd for $C_{22}H_{15}N$: C, 90.1; H, 5.1; N, 4.8. Found: C, 90.0; H, 5.0; H, 4.3.

Reaction of Benzo[*a*]pyrene 4,5-Oxide (8; X = O) with Sodium Azide. To a solution of 6 g of sodium azide in 30 mL

(20) Cf. e.g.: Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 11.
(21) See e.g.: Eland, J. H. D.; Danby, C. T., *J. Chem. Soc.* **1965**, 5935.
(22) Carlson, R. M.; Lee, S. Y. *Tetrahedron Lett.* **1969**, 4001.

of water was added a solution of 1.615 g of 8 (X = O)[15] and 0.2 mL of concentrated H_2SO_4 in 110 mL of acetone. The mixture was refluxed for 48 h. The acetone was removed under reduced pressure and the tan precipitate filtered and washed with water to yield 1.742 g (93%) of crude azido alcohols **9** and **10** (ratio of isomers was 1:1): mp 156–158 °C (from benzene–petroleum ether); IR (Nujol) 2110 (N_3), 3320 cm^{-1} (OH); 270-MHz ^1H NMR ($CDCl_3$) δ 1.96 (br s, 0.5), 2.32 (br s, 0.5), 5.035 (d, $J_{4,5}$ = 6 Hz, 0.5), 5.068 (d, $J_{4,5}$ = 6 Hz, 0.5), 5.156 (d, $J_{4,5}$ = 6 Hz, 0.5), 5.184 (d, $J_{4,5}$ = 6 Hz, 0.5), 7.70 (m, 4), 8.04 (m, 4), 8.725 (m, 2); mass spectrum, *m/e* (rel intensity) 311 ($M^{+}\cdot$, 41), 283 [$(M - N_2)^{+}\cdot$, 52], 282 [$(M - N_2H)^{+}$, 23], 269 [$(M - N_3)^{+}$, 68], 268 [$(M - N_3H)^{+}\cdot$, 43], 255 ($C_{19}H_{11}O^{+}$, 28), 254 ($C_{19}H_{10}O^{+}\cdot$, 100), 239 ($C_{19}H_{11}^{+}$, 33), 226 ($C_{18}H_{10}^{+}\cdot$, 25). Anal. Calcd for $C_{20}H_{13}N_3O$: C, 77.2; H, 4.2; N, 13.5. Found: C, 77.1; H, 4.1; N, 13.0.

1a,11b-Dihydrobenzo[*a*]pyren[4,5-*b*]azirine (Benzo[*a*]pyrene 4,5-Imine (8; X = NH)). A suspension of 0.37 g of the above mixture of azido alcohols (**9** and **10**), 0.37 g of tri-*n*-butylphosphine, and 30 mL of hexane was stirred under argon for 3 h at 55 °C (until evolution of N_2 ceased). The mixture was kept at 35 °C for 24 h, and the resulting precipitate was washed with cold ether to yield 0.29 g (83%) of crude imine. An analytical sample was obtained after recrystallization from ether–hexane (6× with heavy losses): light tan crystals; mp 234–236 °C (with decomposition during the heating). Anal. Calcd for $C_{20}H_{13}N$: C, 89.9; H, 4.9; N, 5.2. Found: C, 90.2; H, 4.9; N, 4.9.

***cis*-5,6-Dihydrobenzo[*c*]phenanthrene-5,6-diol.** A solution of 5.02 g of benzo[*c*]phenanthrene and 5.6 g of osmium tetroxide in 4 mL of pyridine and 250 mL of dry benzene was stirred in the dark under N_2 for 10 days. The light tan precipitate was dissolved in 350 mL of CH_2Cl_2 and stirred vigorously (under N_2) for 24 h with 1 L of aqueous KOH (1%)–mannitol (10%). Another portion of 800 mL of the KOH–mannitol solution was added, and stirring was continued for an additional 6 h (until the CH_2Cl_2 solution was decolorized). The organic layer was separated, dried, and concentrated to yield 4.0 g (66%) of the colorless diol hydrate: mp 153–157 °C (from benzene); IR (Nujol) 3290 cm^{-1} (OH); mass spectrum, *m/e* (rel intensity) 262 ($M^{+}\cdot$,83), 83), 244 [$(M - H_2O)^{+}\cdot$, 36], 243 ($C_{18}H_{11}O^{+}$, 20), 232 ($C_{17}H_{12}O^{+}\cdot$, 17), 231 ($C_{17}H_{11}O^{+}$, 66), 228 ($C_{18}H_{12}^{+}\cdot$, 15), 216 ($C_{17}H_{12}^{+}\cdot$, 57), 215 ($C_{17}H_{11}^{+}$, 100), 203 ($C_{16}H_{11}^{+}$, 18), 202 ($C_{16}H_{10}^{+}\cdot$, 40). Anal. Calcd for $C_{18}H_{12}O\cdot H_2O$: C 77.7; H, 5.0. Found: C, 77.7; H, 5.0.

1-Phenylnaphthalene-2,2′-dicarboxaldehyde. A solution of 9.9 g of sodium metaperiodate in 150 mL of water and 800 mL of MeOH was added to a solution of 3.0 g of the above diol in 3 L of MeOH and 600 mL of H_2O. After the mixture was stirred (under N_2) for 96 h, the methanol was removed under reduced pressure and the residue extracted with benzene. The crude product (2.42 g) was chromatographed over Florisil (eluents were petroleum ether, benzene, and finally benzene–5% acetone) to yield 2.22 g (75%) of pure dialdehyde as a yellow oil: IR 1770 cm^{-1} (C=O); 60-MHz ^1H NMR ($CDCl_3$) δ 7.32–8.25 (m, 10), 10.52 (s, 1), 10.81 (s, 1); mass spectrum, *m/e* (rel intensity) 260 ($M^{+}\cdot$, 21), 231 [$(M - 2CO - H)^{+}$, 100], 202 ($C_{16}H_{10}^{+}\cdot$, 37). Anal. Calcd for $C_{18}H_{14}O_2$: C, 83.1; H, 4.6. Found: C, 82.8; H, 4.9.

1a,12b-Dihydrobenzo[*c*]phenanthren[5,6-*b*]oxirene (Benzo[*c*]phenanthrene 5,6-Oxide (13; X = O)).[18] A solution of 1.2 g of tris(dimethylamino)phosphine in 30 mL of dry benzene was added dropwise, under N_2, to a solution of 1.64 g of 1-phenylnaphthalene-2,2′-dicarboxaldehyde in 30 mL of the same solvent. The mixture was stirred at room temperature for 16 h; the solvent was removed and the residue treated with cold anhydrous ether. Upon addition of this solvent a clear solution was formed of which most of the colorless oxide separated on brief standing (2–5 min). Precipitation was completed by careful addition of hexane: yield 1.36 g (88%); mp 93–95 °C (from cyclohexane); 100-MHz ^1H NMR ($CDCl_3$) δ 4.59 and 4.74 (AB q, J = 5 Hz, 2), 7.3–9.0 (m, 10); mass spectrum *m/e* (rel intensity) 244 ($M^{+}\cdot$, 100), 215 ($C_{11}H_{11}^{+}$, 61). Anal. Calcd for $C_{18}H_{12}O$: C, 88.5; H, 4.9. Found: C, 88.3; H, 4.9.

Attempts to prepare **13** (X = O) by the general method of Harvey et al.[15] were unsuccessful.

Reaction of 13 (X = O) with Sodium Azide. A mixture of 32.5 g of NaN_3, 1.12 g of **13** (X = O), 0.2 mL of concentrated H_2SO_4, 500 mL of acetone, and 250 mL of water was stirred under N_2 for 3 days. The acetone was removed under reduced pressure, and the residue (quantitative yield) proved to consist (by 270-MHz ^1H NMR) of nearly equal amounts of **5,6-dihydro-5-azidobenzo[*c*]phenanthr-6-ol (14)** and **5,6-dihydro-6-azidobenzo[*c*]phenanthr-5-ol (15)**: mp 157–158 °C (from benzene); IR (Nujol) 2107 (N_3), 3350 cm^{-1} (OH); 270-MHz ^1H NMR ($CDCl_3$) δ 1.60 (s, H_2O of crystallization), 2.51 (d, J = 6 Hz) and 2.53 (d, J = 6 Hz, OH), 4.61 (d, J = 7.5 Hz) and 4.65 (d, J = 7.5 Hz, H, α to N_3), 4.74 (unresolved, J = 6 Hz) and 4.84 (unresolved d, J = 6 Hz, H α to OH), 7.35–7.98 and 8.55 (m, aromatic); mass spectrum, *m/e* (rel intensity) 287 ($M^{+}\cdot$, 8), 260 [$(MH - N_2)^{+}$, 14], 259 [$(M - N_2)^{+}\cdot$, 33], 258 [$(M - H_2O - N)^{+}$, 16], 245 [$(M - N_3)^{+}$, 8], 231 ($C_{17}H_{11}O^{+}$, 100), 229 ($C_{18}H_{13}^{+}$, 15), 228 ($C_{18}H_{12}^{+}\cdot$, 19), 227 ($C_{18}H_{11}^{+}$, 15), 216 ($C_{17}H_{12}^{+}\cdot$, 10), 215 ($C_{17}H_{11}^{+}$, 21), 203 ($C_{16}H_{11}^{+}$, 26), 202 ($C_{16}H_{10}^{+}\cdot$, 48). Anal. Calcd for $C_{18}H_{13}N_3O\cdot{}^1/_2H_2O$: C, 73.0; H, 4.7; N, 14.2. Found: C, 72.9; H, 4.6; N, 14.2.

***trans*-5,6-Dihydro-6-[(triisopropylphospho)azido]benzo[*c*]phenanthr-5-ol (16).** In the best of several experiments a suspension of 80 mg of the above mixture of azido alcohols **14** and **15** in 200 mL of *n*-heptane and 0.14 mL of triisopropylphosphine was stirred under argon for 30 min at 0 °C. The temperature was gradually raised to 56 °C. During this process a clear solution was formed. After 10 min at 56 °C light pink crystals started to separate. After an additional 50 min at 56 °C the reaction mixture was cooled, and the precipitate was washed with petroleum ether to yield 50 mg (40%) of **16**: mp 134–135 °C dec (from methylene chloride–heptane); ^{31}P NMR ($CDCl_3$, from 85% H_3PO_4) 46.9 ppm. Anal. Calcd for $C_{27}H_{34}N_3OP$: C, 72.5; H, 7.7; N, 9.4; P, 6.9. Found: C, 72.5; H, 7.7; N, 9.0; P, 7.2.

Acknowledgment. We wish to thank Dr. Zeisberg of the Technical University of Berlin for recording the 270-MHz NMR spectra and the Israel Commission for Basic Research, the Israel Academy of Sciences and Humanities, for financial support of this study.

Registry No. **1** (R = R^1 = H), 962-32-3; **1** (R = CH_3; R^1 = H), 1155-38-0; **1** (R = R^1 = CH_3), 39834-38-3; **2** (R = R^1 = H), 71382-38-2; **2** (R = CH_3; R^1 = H), 71382-39-3; **2** (R = R^1 = CH_3), 71382-40-6; **3** (R = R^1 = H), 71382-41-7; **3** (R = CH_3; R^1 = H), 71382-42-8; **3** (R = R^1 = CH_3), 71382-43-9; **4** (R = R^1 = H), 71382-44-0; **4** (R = CH_3; R^1 = H), 71382-45-1; **4** (R = R^1 = CH_3), 71382-46-2; **5** (R = CH_3; R^1 = H; R^{11} = $CH(CH_3)_2$), 71382-47-3; **5** (R = R^1 = CH_3; R^{11} = $CH(CH_3)_2$), 71411-09-1; **6** (R = CH_3; R^1 = H; R^{11} = $CH(CH_3)_2$), 71382-48-4; **7** (X = NH), 71382-49-5; **7** (X = O), 1421-85-8; **8** (X = NH), 71382-50-8; **8** (X = O), 37574-47-3; **9**, 71411-10-4; **10**, 71382-51-9; **11**, 71382-52-0; **12**, 71382-53-1; **13** (X = NH), 71382-54-2; **13** (X = O), 60692-90-2; **14**, 71382-55-3; **15**, 71382-56-4; **16**, 71382-57-5; phenanthrene 9,10-imine, 67464-46-4; benz[*a*]anthracene, 56-55-3; *trans*-5-azido-6-hydroxydibenz[*a*,*h*]anthracene, 71382-58-6; *trans*-5-hydroxy-6-azidodibenz[*a*,*h*]anthracene, 71382-59-7; trisisopropylphosphine, 6476-36-4; *cis*-5,6-dihydrobenzo[*c*]phenanthrene-5,6-diol, 71382-60-0; benzo[*c*]phenanthrene, 195-19-7; 1-phenylnaphthalene-2,2′-dicarboxaldehyde, 71382-61-1.