1-(Trimethylsilyl)-2-acetylacenaphthylene (4d): mp 119–120 °C; ^{1}H NMR 0.43 (s, 9 H, $SiMe_3$), 2.60 (s, 3 H, COMe), 7.10–7.85 (m, 5 H, H_4, H_5, H_6, H_7, H_8); as expected H_3 exhibits 2 d at 7.90 and 8.02 ($J_{3,4} \simeq 7$ Hz, $J_{3,5} \simeq 0.7$ Hz).

Acknowledgment. We thank Professor Dietmar Seyferth (Massachussetts Institute of Technology), who agreed to check our article for correct English and Rhône-Poulenc Industries for providing us with the Me_3SiCl necessary for the synthesis of the silyl derivatives.

Registry No. **1a**, 60989-58-4; **1b**, 6861-64-9; **1c**, 31202-24-1; **1d**, 10047-18-4; **1e**, 80262-61-9; **2a**, 71582-67-7; **2b**, 80262-62-0; **2b′**, 65726-91-2; **2c**, 80262-63-1; **2d**, 80262-64-2; **2e**, 80262-65-3; **3a**, 80262-66-4; **4a**, 71582-66-6; **4b**, 80262-67-5; **4b′**, 80262-68-6; **4c**, 80262-69-7; **4c′**, 80262-70-0; **4d**, 80262-71-1; **5a**, 71582-69-9; **5b**, 80262-72-2; **5b″**, 80262-73-3; **5c**, 80262-74-4; **5c′**, 80262-75-5; **5d**, 80262-76-6; **5d″**, 80262-77-7; **6**, 80287-49-6; **7**, 80262-78-8; 5-bromoacenaphthene, 2051-98-1; acenaphthene, 83-32-9.

Reactions of the K-Region Epoxides of Polycyclic Aromatic Hydrocarbons with Phosphodiesters. A Potential Detoxification Reaction

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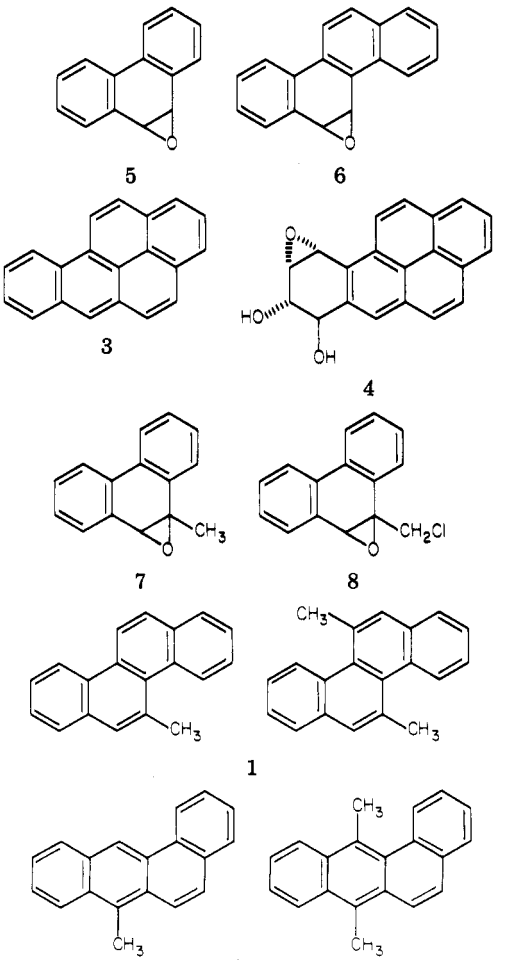
Phenanthrene 9,10-oxide reacts with diethyl hydrogen phosphate to give 9-phenanthrol. The reaction was first order in both epoxide and phosphate concentrations, with a pseudo-first-order rate constant $k_\psi = 6.2 \times 10^{-1}$ mol^{-1} L s^{-1}. Similarly, chrysene 5,6-oxide on reaction with phosphate opened regiospecifically to give 6-chrysenol. Several anilinium phosphate salts were prepared and reacted with phenanthrene 9,10-oxide. The extent of reaction was markedly influenced by the pK_a of the anilinium salt. The biological implications of this study in understanding the relative noncarcinogenicity of K-region arene oxides are discussed.

Polycyclic aromatic hydrocarbons (PAH) are considered as the most prevalent environmental carcinogens.[1] They are universal products of the combustion of organic matter. Burning of wood or refuse and, indeed, cigarette smoking can all contribute to the concentration of PAH in the environment. PAH are also present in fossil fuels such as petroleum or coal. There is no question that many of these PAH are carcinogenic. As early as 1930, dibenz[*a*,*h*]anthracene was found to induce tumors in mouse skin.[2] In 1933, the carcinogen benzo[*a*]pyrene (BP) was isolated from coal tar extract.[3] Since that time many PAH have been identified as carcinogens according to in vivo testings.

Because PAH as such do not bind covalently to DNA, RNA, proteins, and other biomolecules, it is generally accepted that they must be metabolically activated in vivo to a chemically reactive form which then combines covalently with the macromolecular target. Several theories have been put forward to established correlations between the structure of PAH, metabolism, covalent binding, and carcinogenicity. Among these, the "K-region" theory of Pullman and Pullman has received wide attention.[4] This theory suggests that it is the "K region" of a PAH which is transformed during metabolic activation and is responsible for the carcinogenic activity for the hydrocarbon. With this theory, it is possible to provide a reasonable ranking of carcinogenic activity of a number of PAH. It is also in apparent agreement with some structure–activity relationships observed for substituted chrysenes (**1**) and benz[*a*]anthracenes (**2**) where substitution by fluoro or methyl groups on the K region has a dramatic effect on the biological activity of the hydrocarbon[5,6] (see Chart I).

Chart I



Recently, the "bay region" theory of carcinogenesis by PAH has been proposed mainly through the effort of

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Jerina.[7-9] He suggests that the critical feature responsible for carcinogenic activity is an epoxide on a saturated, angular benzo ring which forms part of a bay region in the PAH. For example, benzo[a]pyrene (3) is found to be metabolized in vivo to 7β,8α-dihydroxy-9α,10α-epoxy-7,8,9,10-tetrahydrobenzo[a]pyrene (BP diol epoxide, 4).[10] There is also strong evidence to indicate that it is the covalent binding of cellular DNA with BP metabolites which is the primary event leading to carcinogenesis.[11] The theory has also been used to account for the carcinogenic activity of the diol epoxide of benz[a]anthracene.[12,13] The bulk of chemical evidence suggests that the nature of the covalent binding is likely to be the reaction of the epoxides with the amino group of the DNA bases (N-alkylation). An alternative possibility, involving phosphate alkylation in the reaction of PAH epoxides with DNA has also been proposed.[14] The bay-region epoxides act as electrophiles in trapping the various nucleophiles of the target biomolecules, and, indeed, theoretical calculations[9] suggest that the bay-region epoxides are particularly effective.

While the bay-region theory appears to have superceded the K-region theory, there is a dilemma which requires explanation. The K-region theory correctly predicts the reactivity of the K region in PAH and that K-region epoxides are formed as metabolites of PAH, indeed, sometimes as the major metabolites. These K-region epoxides behave also as effective electrophiles in reacting with a number of nucleophiles such as mercaptides,[15] amines,[16] and hydroxides.[16] In fact, Nakanishi and co-workers have found that 7,12-dimethylbenzanthracene 5,6-oxide and guanosine react to give N-alkylation and O-alkylation products.[17] These reactions indicate that K-region epoxides may well react with biomolecules in a manner very similar to that of the bay-region types. Yet, in contrast to the bay-region epoxides, K-region epoxides appear to be weak carcinogens, and no in vivo adduct of K-region epoxide with DNA has thus far been observed. This is generally attributed to various detoxification mechanisms, including hydration of the K-region epoxides to the corresponding diols and isomerization to the corresponding phenols. While these detoxification mechanisms may indeed occur, bay-region epoxides may be susceptible to these events as well, perhaps to a smaller extent.[10] One must postulate, therefore, either that K-region epoxides are selectively detoxified to the extent they do not reach the target biomolecules at all or that if they do reach the target biomolecules, they do not cause the necessary damage.

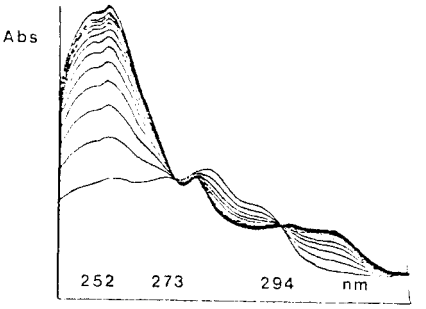
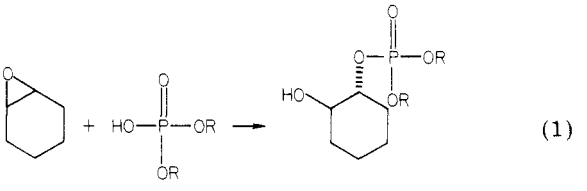
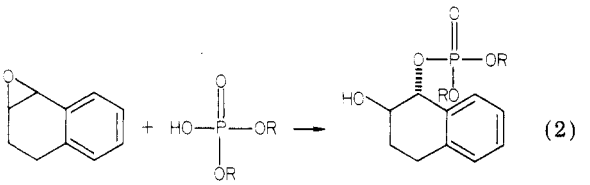


Figure 1. UV spectrum for the increase in absorption of 9-phenanthrol at 252 nm with time taken at 50-s intervals.

Recently, we have examined the reaction of cyclohexene oxides with dialkyl and diaryl hydrogen phosphates as a model to understanding the reaction of PAH epoxides with nucleic acids.[18] From these results, we have concluded that phosphodiesters can be converted efficiently to phosphotriesters by cyclohexene oxides according to eq 1.



(1)



(2)

Furthermore, it is clear from the regiochemistry of the reaction that a neighboring hydroxy group or aromatic ring can direct the attack of the phosphate on the epoxide. We have now extended our study to the reaction of phosphodiesters with K-region epoxides of some PAH, and the results indicate that they show a different reactivity pattern from the cyclohexene oxides.

Results and Discussion

Phenanthrene 9,10-oxide (5) and chrysene 5,6-oxide (6) were prepared from the parent hydrocarbons by using the phase-transfer catalytic conditions recently reported by Hamilton with slight modification.[19] 9-Methylphenanthrene was prepared from 9-bromophenanthrene by metalation followed by methylation.[20] Epoxidation using the PTC conditions gave a mixture of 9-methylphenanthrene 9,10-oxide (7) and possibly 9-chloromethylphenanthrene 9,10-oxide (8) in a ratio of 3:1.

The reaction of phenanthrene 9,10-oxide with phosphate gave exclusively 9-phenanthrol which was identified by UV, NMR, and HPLC comparison with authentic sample. CI mass spectroscopy gave correct $(M + 1)^+$ values. Under identical conditions phenanthrene 9,10-oxide and aniline gave only starting material (NMR), even with extended reaction times.

The kinetics of the reaction of phenanthrene 9,10-oxide with diethyl phosphate in dichloromethane was studied spectrophotometrically. The ultraviolet spectrum of 9-

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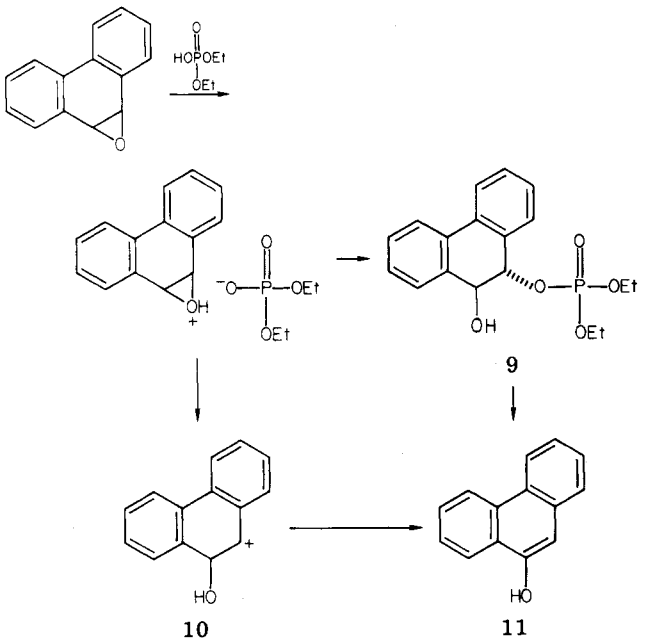
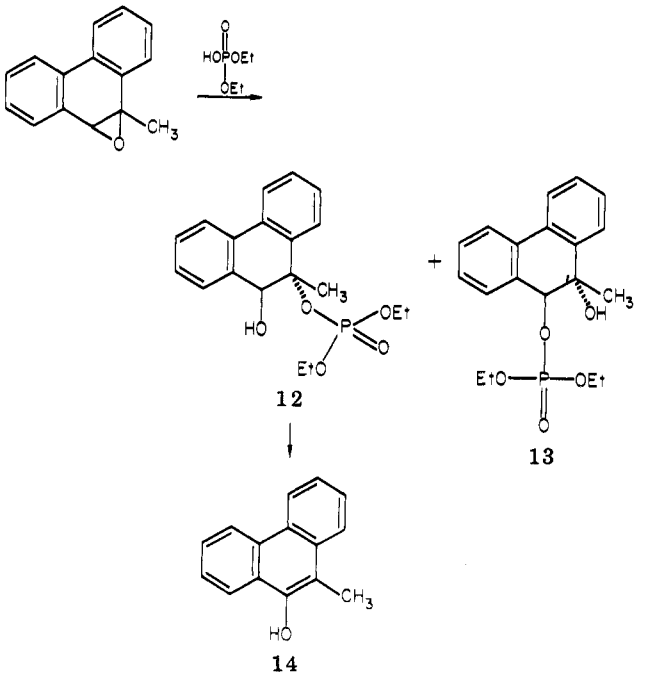
Scheme I



Scheme II



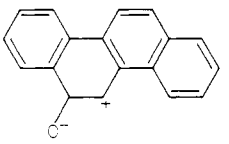
phenanthrol is sufficiently different from that of the starting material. Indeed, Figure 1 shows the change in UV absorption as the reaction proceeds, with very good isosbestic points. With diethyl phosphate present in excess, the rate of the reaction can be followed under pseudo-first-order conditions by monitoring the increase in phenol absorption at 252 nm. This establishes a first-order dependence on epoxide concentration. By varying the concentration of diethyl phosphate, a first-order dependence of rate on diethyl phosphate concentration was also established.

At least two mechanisms which are consistent with the kinetics can be considered for the formation of 9-phenanthrol. In mechanism A, the protonated epoxide reacts with the phosphate anion to give the phosphotriester adduct **9** in accordance with our results from eq 1. The adduct **9** suffers a fast elimination to give **11** (Scheme I). The elimination has to be a fast step in order to account for the presence of isosbestic points in the UV study.

In mechanism B, the adduct is not formed at all. The protonated species undergoes ring opening to **10** followed by either NIH shift[21] or proton elimination to give the product 9-phenanthrol.

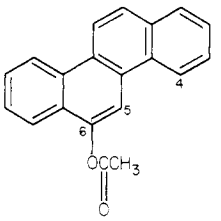
Two lines of evidence suggest that the phosphotriester adduct is not formed as the intermediate in the reaction. First, we have prepared compound **9** by an independent method as follows. 9,10-Dihydro-*trans*-phenanthrene-9,10-diol[22] was reacted with equimolar amounts of diethyl chlorophosphate and pyridine in CH_2Cl_2 to give after workup a solid product. Its NMR is consistent with structure **9**. In addition, its mass spectrum (CI) showed a strong peak at m/e 331 $[(M + 1)^+ - H_2O]$. The compound was found to be stable under the reaction conditions in which phenanthrene 9,10-oxide was transformed to 9-phenanthrol. Second, we have reacted 9-methylphenanthrene 9,10-oxide with diethyl hydrogen phosphate. If a phosphotriester were the intermediate, we would expect in this case a mixture of at least two compounds, **12** and **13** (Scheme II), and only compound **12** can eliminate to 10-methyl-9-phenanthrol. However, the reaction product showed only 10-methyl-9-phenanthrol (**14**) with no indication of formation of any phosphotriester.

Similarly, chrysene 5,6-oxide (**6**) on reaction with dibenzyl phosphate gave a phenolic compound. It was acetylated to the acetyl derivative and methylated to the methyl ether. In both cases the NMR showed a single peak at the chemical shift corresponding to the 6-isomer. The regiospecificity of the reaction in giving a single isomer can be explained by the mechanism proposed and is in agreement with molecular orbital calculations. The preferred carbocation (see I) formed upon opening of the



I

epoxide ring will be that giving the smaller Dewar reactivity number ($N\tau$).[23] The carbocation at C-6 has $N\tau$ = 1.90 and that at C-5 has $N\tau$ = 1.67 (see II). Hence the favored zwitterionic form is in agreement with our experimental result.



II

Our study demonstrates clearly that cyclohexene oxides and K-region arene oxides react quite differently with phosphodiesters. With cyclohexene oxides (and presumably bay-region epoxides) alkylation occurs, leading to phosphotriesters, whereas K-region arene oxides are converted to the corresponding phenols. Herein may lie one of the contributing detoxification mechanisms; that is, even

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Table I

salt of dibenzyl phosphate	pK_a	% reaction
(i) *p*-chloroaniline	4.10	0
(ii) *m*-chloroaniline	3.46	0
(iii) *m*-nitroaniline	2.46	100
(iv) free acid	0.70^{25}	100

if K-region arene oxides reach the target DNA (or RNA) molecules, they may be rendered harmless by the phosphate groups inevitably present.

We of course recognize that the phosphate groups of nucleic acids do not exist in the acid form but in the salt form with inorganic counterions or with ammonium ions from the nitrogen of adjacent bases or amino acids in the form of histones. We expect that the reaction of phosphate with epoxides depends on, among other things, the pK_a of the counter ammonium ion. Thus, we prepared the phosphate salts of several aniline bases and measured the extent of reaction by NMR. The results are shown in Table I.

These results indicate that the rearrangement of K-region arene oxides to phenol can occur with *m*-nitroanalinium dibenzyl phosphate. It is interesting to note that whereas *m*-chloroanilinium dibenzyl phosphate is incapable of converting phenanthrene 9,10-oxide to 9-phenanthrol under these conditions, it can nevertheless convert 1,2,3,4-tetrahydronaphthalene 1,2-oxide to 2-hydroxy-1,2,3,4-tetrahydronaphth-1-yl dibenzyl phosphate (15).

Conclusion

Our results show that K-region arene oxides rearrange to phenols in the presence of phosphodiesters. In contrast to cyclohexene oxides, they show no tendency to form phosphotriesters, despite their obvious reactivity as electrophiles in trapping other nucleophiles such as amines or thiols. We suggest that this rearrangement process may be one of the contributing factors to the detoxification of K-region arene oxides even if K-region arene oxides were stable enough in vivo to reach the target DNA (or RNA) molecules.

Experimental Section

NMR spectra were recorded on a Varian T-60 or XL-200 spectrometer in $CDCl_3$; chemical shifts are reported relative to Me_4Si. Mass spectra were obtained on a Hewlett-Packard 5980A or a LKB 9000 mass spectrometer at 70 eV with a direct insertion probe (chemical ionization, isobutane). Infrared spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer calibrated with the 1602-cm^{-1} band of polystyrene. Melting points were determined on a Gallenkamp apparatus and are uncorrected. HPLC was performed on an Altex Model 300 liquid chromatograph with a 1 × 10 cm column of 10-μm silica.

Kinetic Measurements. Kinetic studies were performed in freshly distilled dichloromethane (from P_2O_5), which was eluted through a column of Na_2CO_3 to remove traces of acid, and stored over 3-Å molecular sieves. Phenanthrene 9,10-oxide was recrystallized from methylene chloride–pentane as a white solid, mp 99–101 °C. Diethyl phosphate was prepared from the chloro compound by adding aqueous NaOH to pH 13, neutralizing to pH 7, passing the mixture through a Dowex H^+ exchange resin, and extracting with ethyl acetate. The rate of phenol formation was monitored by the increase in absorption at 252 nm, observed with a Unicam SP 800 spectrophotometer with a thermostated cell block maintained at 26.0 °C. The instrument was set to scan automatically from λ 325 to 248 nm at 50-s intervals. The concentration of phosphate, [P], used was $\sim 3 \times 10^{-3}$ mmol and that of arene oxide, [E], was ~100-fold less.

The reaction showed isosbestic points at 273 and 294 nm. It exhibits pseudo-first-order kinetic behavior with linear plots of log ($A_\infty - A$) vs. time. A plot of log k vs. log [P] gave a slope of 1.05 with a ρ (correlation coefficient) of 0.998. The pseudo first order rate constant $K_\varphi = K_{obsd}/[P] = 6.2 \times 10^{-1}$ mol^{-1} L s^{-1}.

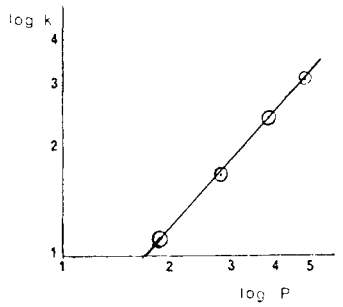

Figure 2. Plot of the logarithm of the observed rate constant for the reaction of diethyl phosphate with phenanthrene 9,10-oxide vs. the logarithm of the phosphate concentration.

Table II. Change in the Observed Rate Constant with Phosphate Concentration[a,c]

10^{-3} [phosphate], M	$10^{-3}k_{obsd}$,[b] s^{-1}	10^{-3} [phosphate], M	$10^{-3}k_{obsd}$,[b] s^{-1}
1.86	1.14	3.73	2.42
2.79	1.68	4.67	3.04

[a] Epoxide concentration was constant at 2.92×10^{-5} M. [b] Obtained as the slope of log ($A_\infty - A$) vs. time over at least 2 half-lives. [c] Procedure: to 0.3 mL of epoxide stock solution and dichloromethane in a cuvette was added phosphate solution. The total volume was 2.8 mL. The cuvette was shaken by inversion and the increase in absorption measured.

All runs were repeated in duplicate. First-order rates could be observed for at least 2 half-lives. The values of the pseudo-first-order rate constant were calculated by the method of least squares. Sample data are given in Figure 2 and Table II.

Phenanthrene 9,10-Oxide (5). To 0.15 g of phenanthrene (0.84 mmol) in 18 mL of dichloromethane and 42 mL of freshly prepared sodium hypochlorite (pH 8.6) was added 0.071 g (0.25 equiv) of tetrabutylammonium hydrogen sulfate. The reaction flask was maintained in a room-temperature water bath. This was sitrred vigorously for 15 min. The reaction was quenched with 25 mL of CH_2Cl_2 and washed with a large quantity of ice-cold water. The organic layer was dried (K_2CO_3) and the solvent evaporated at ambient temperature to give 0.13 g (80%) of a bright yellow solid. Recrystallization from methylene chloride–pentane furnished a white solid: mp 99–101 °C (lit.[21] mp 104–105 °C); NMR ($CDCl_3$) δ 4.5 (2, 2 H, oxiranyl H); UV (95% EtOH) λ_{max} 279 nm (log ε 4.04).

Chrysene 5,6-Oxide (6). To 0.18 g of chrysene in 50 mL of CH_2Cl_2 and 30 mL of freshly prepared sodium hypochlorite was added 0.057 g (0.20 equiv) of tetrabutylammonium hydrogen sulfate. The mixture was stirred for 14 h. A conventional workup gave chrysene 5,6-oxide as a light yellow solid: 0.15 g (78%); mp >250 °C; NMR ($CDCl_3$) δ 4.6 (d, 1 H, 2-oxiranyl, J = 4 Hz), 5.3 (d, 1 H, 1-oxiranyl, J = 4 Hz).

9-Phenanthrol. To 98 mg of phenanthrene 9,10-oxide (0.50 mmol) in 2 mL of CH_2Cl_2 at 0 °C was added dropwise an equimolar amount diethyl phosphate (78 mg) in 3 mL of CH_2Cl_2. After being stirred 5 min, the mixture was quenched with 10 mL of CH_2Cl_2 and washed with 10% $NaHCO_3$ (2 × 15 mL). Drying (K_2CO_3) and evaporating of the solvent at ambient temperature gave 81 mg of orange solid: 83% yield; NMR ($CDCl_3$) δ 4.4 (s, 1 H, br); IR ($CHCl_3$) 3540 cm^{-1} (OH); UV (95% EtOH) λ_{max} 252 nm. It is identical with an authentic sample (Aldrich) by HPLC (EtOAc–petroleum ether, 5:95 (v/v); flow rate 2 mL/min). Its mass spectrum (CI, isobutane) showed $(M + 1)^+$ at m/e 195.

6-Chrysenol. To a solution of chrysene 5,6-oxide in 2 mL of CH_2Cl_2 (0.17 g, 0.70 mmol) at 0 °C was added dibenzyl phosphate (0.19 g) in 3 mL of CH_2Cl_2. Stirring 5 min and workup gave 0.12 g of orange solid (76%) which is very slightly soluble in $CHCl_3$. The reaction was repeated with 50 mg of *p*-toluene sulfonic acid. In both cases ^1H NMR showed loss of the oxiranyl signal which is replaced by a broad absorption at δ 4.7–5.3. The identity of

6-chrysenol was established by acetylation and methylation.

6-Acetoxychrysene. A solution of pyridine (0.16 mL) and acetic anhydride (16 mL), both previously distilled, was refluxed for 15 min and cooled to room temperature. This was added to 30 mg of 6-chrysenol and stirred for 14 h at room temperature. The solution was concentrated, and the green solid obtained was dissolved in minimum of benzene and eluted through Florisil with 25-50% benzene-hexane. A tan yellow solid was obtained: 12 mg (34%); mp 111-113 °C (hexane); NMR ($CDCl_3$) δ 2.50 (s, 3 H, CH_3CO_2) (lit.[24] δ 2.50). The chemical shift is identical with that of the acetoxychrysene derived from the TsOH-catalyzed rearrangement of chrysene 5,6-oxide to chrysenol. Its mass spectrum (EI) showed m/e 286 (M^+) and 244 ($M - CH_2{=}C{=}O$). The crude acetoxy compound before Florisil purification showed only one acetoxy peak at δ 2.50 in its ^1H NMR.

6-Methoxychrysene. To 30 mg of chrysenol (0.12 mmol) in 5 mL of dimethylformamide were added 1 mL of dimethyl sulfate and 1 g of barium oxide. The suspension was stirred for 19 h at room temperature. Concentrated NH_4OH (5 mL) was added and stirring continued for 30 min. The mixture was taken up in 15 mL of ethyl ether, washed with water (4 × 15 mL), 5% HCl (2 × 15 mL), and H_2O (1 × 15 mL), and dried ($MgSO_4$). Evaporation of solvent gave 20 mg of orange solid. Chromatography (Florisil) on elution with benzene gave yellow solid: 14 mg (43%); mp 115-119 °C (lit.[24] mp 121-122 °C); NMR ($CDCl_3$) δ 4.15 (s, 3 H, OCH_3) (lit.[24] δ 4.10). Its structure was confirmed by CI mass spectroscopy (isobutane): $(M + 1)^+$ at m/e 259.

9-Methylphenanthrene 9,10-Oxide (7). To 80 mg of 9-methylphenanthrene (0.42 mmol) in 10 mL of $CHCl_3$ and 80 mL of hypochlorite (pH 8.6) equilibrated with a room-temperature water bath was added at once 0.15 g of tetrabutylammonium hydrogen sulfate (0.44 mmol) with vigorous stirring. After 0.3 min the reaction was quenched with 30 mL of $CHCl_3$. The aqueous phase was decanted off, and the organic layer was washed with an excess of ice cold water. Drying (K_2CO_3) and removal of solvent at ambient temperature gave 70 mg of brownish solid (81%). This was used at once because of its instability. Its NMR ($CDCl_3$) [δ 1.93 (s, 3 H, CH_3), 4.23 (s, 1 H, oxiranyl H) 4.50 (s, 2 H, CH_2Cl)] showed the product to be a mixture of 7 and 9-(chloromethyl)phenanthrene 9,10-oxide (8) in a ratio of 3:1. This is also in agreement with the mass spectrum (CI, isobutane), m/e 243, 245 (3:1), 209.

10-Methyl-9-phenanthrol. 9-Methylphenanthrene 9,10-oxide (70 mg) in 2 mL of CH_2Cl_2 was added dropwise at 0 °C to 1.0 equiv of diethyl phosphate in 3 mL of CH_2Cl_2. After stirring for 5 min, the reaction was quenched with 5 mL of CH_2Cl_2 and washed with 10% $NaHCO_3$ (1 × 10 mL) and H_2O (2 × 10 mL). Drying and removal of solvent at ambient temperature gave 50 mg of light brown solid (72%). Recrystallization (CH_3OH-H_2O) gave a white solid: mp 119-122 °C (lit.[26] mp 125 °C); NMR ($CDCl_3$) δ 2.67 (s, 3 H, CH_3), 3.80 (s, 1 H, OH); UV λ_{max} (95% EtOH) 255 nm. No adduct with an ethoxy group was observed at all in the ^1H NMR. The same results were obtained from acid hydrolysis of the epoxide.

Reactions of Phenanthrene 9,10-Oxide with Amine Salts of Dibenzyl Phosphate. An equimolar amount of a freshly prepared sample of phenanthrene 9,10-oxide and 2,3-diphenylbutane (as an internal standard) were mixed, and the NMR ($CDCl_3$) was recorded. To a solution of the aniline derivative (1.4 equiv) and dibenzyl phosphate (1.1 equiv) in 1.0 mL of $CDCl_3$ was added a solution of the former two reagents in 1.0 mL of $CDCl_3$. The flask was stirred vigorously at room temperature for 5 min, an aliquot removed, and the NMR taken. We measured any change in the ratio of the 2-oxiranyl protons (δ 4.5) with respect to the methine protons of 2,3-diphenylbutane (δ 2.8). No reaction (i and ii, Table I) means no change was measured. Complete reaction (iii and iv) means the oxiranyl protons were absent in the NMR.

Registry No. 5, 585-08-0; 6, 15131-84-7; 7, 80641-44-7; 8, 80641-45-8; 11, 484-17-3; *p*-chloroanilinium dibenzyl phosphate, 80641-46-9; *m*-chloroanilinium dibenzyl phosphate, 80641-47-0; *m*-nitroanilinium dibenzyl phosphate, 80641-48-1; dibenzyl phosphate, 1623-08-1; diethyl phosphate, 598-02-7; phenanthrene, 85-01-8; chrysene, 218-01-9; 6-chrysenol, 37515-51-8; 6-acetoxychrysene, 7499-59-4; 6-methoxychrysene, 51361-87-6; 9-methylphenanthrene, 883-20-5; 10-methyl-9-phenanthrol, 16430-50-5.

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Peroxy Esters. 7. Base-Catalyzed Reaction of 5-(Acylmethyl)-2,6-di-*tert*-butyl-4-oxa-2-cyclopentenones Derived Selectively from Acid Catalysis of 2,6-Di-*tert*-butyl-*p*-peroxyquinol Acetates[1]

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The reaction of 5-(acylmethyl)-2,5-di-*tert*-butyl-4-oxa-2-cyclopentenones, easily available from acid treatment of 2,6-di-*tert*-butyl-*p*-peroxyquinol acetates with *t*-BuOK in *t*-BuOH at 70 °C, gave 3-alkyl-2,5-di-*tert*-butyl-2,4-cyclopentadienones in good yield, providing a new convenient synthetic route to 3-alkyl-2,5-di-*tert*-butylcyclopentadienones from 4-alkyl-2,6-di-*tert*-butylphenols via oxygenation by which the phenols are selectively converted to the above *p*-peroxyquinols. Treatment of the 4-oxa-2-cyclopentenones with the same base in *t*-BuOH containing petroleum ether at 0 °C, on the other hand, led to the quantitative formation of 1,6-di-*tert*-butyl-8-oxabicyclo[3.2.1]octane-3,7-diones resulting from an intramolecular Michael addition of a carbanion generated on the acyl group of the acylmethyl group in the starting 4-oxa-2-cyclopentenones. Heating of these bicyclic products with *t*-BuOK in *t*-BuOH at 70 °C gave the cyclopentadienones quantitatively. A plausible mechanism involving equilibria among carbanions generated on the acylmethyl group is discussed.

Cyclopentadienones have received much attention because of their potential intermediacy in organic synthesis.[2] For example, many aromatic compounds including hetero aromatics have been synthesized by the Diels-Alder reaction with various cyclopentadienones as dienophiles as well as diene systems.[2] *tert*-Butylated cyclopentadienones have also been synthesized by rather complicated methods.[3-5] Recently, we have reported a one-step method to

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