Reactions of K-Region Oxides of Carcinogenic and Noncarcinogenic Aromatic Hydrocarbons. Comparative Studies on Reactions with Nucleophiles and Acid-catalyzed Reactions¹⁾

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Several K-region arene oxides of carcinogenic and noncarcinogenic polycyclic aromatic hydrocarbons were synthesized, and their reactivities with various nucleophiles and their acid-catalyzed reactions were discussed. Relationship between these chemical reactivities and mutagenicity was also discussed.

Keywords—arene oxide; carcinogen; mutagenicity; nucleophilic reaction; substituent effect; alkylation

Introduction

The metabolism of aromatic hydrocarbons involves the conversion of the hydrocarbon to an arene oxide.³⁾ Recent evidence increasingly supports the hypothesis that the arene oxide triggers the induction of tumors. The K-region oxide has been shown to bind covalently to nucleic acid and protein *in vivo*,⁴⁾ to be more active than the parent hydrocarbon in the transformation of cells,⁵⁾ or more mutagenic in bacteria.^{1b,6)} On the other hand, 7,8-diol-9,10-epoxides of benzo[*a*]pyrene have recently been suggested to be one of the principle metabolites bound to deoxyribonucleic acid (DNA) *in vivo*.^{4b,7)}

An understanding of the controlling factors in arene oxide reactivity, regioselectivity, and stereochemistry, is an essential step for any attempt to understand the biological phenomena caused by the chemical. Some systematic works on the chemistry of arene oxides, both K-region and non-K-region oxides have appeared recently. Bruice and coworkers,⁸⁾ and Keller and Heiderberger,⁹⁾ have explored the comparative solvolytic reactions of K-region and non-K-region oxides. Beland and Harvey have studied on the reaction of several K-region oxides with thiol as a nucleophile.¹⁰⁾ Swaisland and others investigated

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- 7) P. Sims, P.L. Grover, A. Swaisland, K. Pal and A. Hewer, *Nature* (London), **252**, 326 (1974); P.G. Wislocki, A.W. Wood, R.L. Chang, W. Levin, H. Yagi, O. Hernandez, D.M. Jerina and A.H. Conney, *Biochem. Biophys. Res. Commun.*, **68**, 1006 (1976); E. Huberman, L. Saches, S.K. Yang and H.V. Gelboin, *Proc. Nat. Acad. Sci., (U.S.A.)*, **73**, 607 (1976).
- 8) P.Y. Bruice, T.C. Bruice, P.M. Dansette, H.G. Selander, H. Yagi and D. Jerina, *J. Am. Chem. Soc.*, **98**, 2965 (1976).
- 9) J.W. Keller and C. Heiderberger, *J. Am. Chem. Soc.*, **98**, 2328 (1976).
- 10) F.A. Beland and R. G. Harvey, *J. Am. Chem. Soc.*, **98**, 4963 (1976).

the reactivity of some K-region oxides with 4-(*p*-nitrobenzyl)pyridine.¹¹⁾ Bruice and coworkers have discussed the nucleophilic displacement on the arene oxides of phenanthrene.¹²⁾ Reactions of benzene oxide and naphthalene oxides with several nucleophiles have been investigated by Jeffery and coworkers.¹³⁾ Works by Newman,¹⁴⁾ Battistini,¹⁵⁾ and Griffin¹⁶⁾ have been reported recently.

We have studied the reactions of several K-region arene oxides, which are listed in Fig. 1, with various nucleophiles, and their acid-catalyzed solvolytic reaction. The chemical reactivity-mutagenicity relationship has been discussed.

Fig. 1

Results

Acid-catalyzed Reactions

Arene oxides rearrange to phenols under acidic conditions. Products and kinetic studies have been reported.^{8,9,17)} More recently, Keller and Heiderberger found *cis*- and *trans*-dihydrodiols in the acid-catalyzed reaction of K-region arene oxides in dioxane-water.⁹⁾ We have investigated a comparative acid-catalyzed reaction of several arene oxides including some substituted phenanthrene-9,10-oxides.

Fig. 2

- 11) A.J. Swaisland, P.L. Grover and P. Sims, *Biochem. Pharmacol.*, **22**, 1547 (1973).
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Solvolytic reaction of phenanthrene-9,10-oxide (**1**) at pH 2.3 in 67% aq. acetone gave 9-phenanthrol (75%) and *trans*-9,10-dihydroxy-9,10-dihydrophenanthrene (17%). Similarly pyrene-4,5-oxide (**2**) gave 4-pyrenol (79%) and *trans*-4,5-dihydroxy-4,5-dihydropyrene (15%). High pressure liquid chromatography (HLC) of the reaction products from other epoxides (**3**–**8**) also suggested the formation of phenols (**9**) in about 70–80% yields and dihydrodiols (**10**) in about 10–20% yields. The acid-catalyzed reaction of these epoxide in 2 N HCl in aqueous acetone rapidly gave the corresponding phenols (**9**) in quantitative yields.

The reaction of unsymmetrical arene oxides, benz[*a*]anthracene-5,6-oxide (**3**) and benzo[*a*]pyrene-4,5-oxide (**4**) gave two isomeric phenols. The distribution of the isomers was examined by nuclear magnetic resonance (NMR) after methylation by conc. HCl–CH₃OH (*vide infra*) or dimethylsulfate. Methylation of the phenolic products from **3** gave a mixture of two methyl ethers (about 1:1.2),¹⁸ and **4** gave two methyl ethers in a 1:1 ratio. Every methyl ether derived from phenolic products obtained from the acid-catalyzed reaction of substituted phenanthrene oxides (**5**–**8**) was homogeneous in respect to NMR, vapor phase chromatography (VPC), thin-layer chromatography (TLC), and HLC, and their structures were determined by unambiguous ways. Methyl ether (**12**) derived from **5** was identified with 2,10-dimethoxyphenanthrene, which was prepared by the photo-oxidation of an enol ether (**13**). The methyl ether (**15**) from **6** was identified with 3,9-dimethoxyphenanthrene prepared from **16**. The methyl ether (**18**) and (**21**) were prepared similarly from **19** and **22**, respectively.

Fig. 3

18) J.C. Wiley, C.S. Menon, D.L. Fischer and J.F. Engel, *Tetrahedron Lett.*, 1975, 2811.

The decomposition rates of these epoxides were measured at pH 2.3 in 67% aqueous acetone at 0° (Table I). Any salt was added since chloride anion can catalyse the rearrangement to phenols.^{1,19)} The disappearance of the epoxide was followed by HLC monitored by UV. The rate constant was first order in the epoxide. The rate of **3** was slightly faster than **4**. Methoxy substitution at the 3-position of phenanthrene oxide greatly enhanced the reaction, while carbomethoxy substitution at the 3-position suppressed the reaction.

TABLE I. Relative Rates of the Acid-catalyzed Decomposition of K-region Arene Oxides at pH 2.3 in Aqueous Acetone

Compound	1	2	3	4	5	6	7	8
Relative rate	1.0	0.9	2.1	1.9	1.8	>20	0.09	0.06

The rate of phenanthrene oxide=1.0 ($k_{\text{obs}}=1.9 \times 10^{-4} \text{ sec}^{-1}$).

When epoxides (**1**—**4**) were heated in conc. HCl-methanol at the refluxing temperature, methyl ethers were formed in good yields. The formation of the corresponding phenols from epoxides is very fast under the conditions. The phenols also gave the methyl ethers under the conditions. Therefore, the formation of methyl ethers from epoxides involves the phenol formation followed by methylation. Naphthols were also methylated by conc. HCl-methanol, though the rates were slow. Monocyclic phenols were not methylated.

Reaction with Phenols

A possible reaction which might be important for the biological (carcinogenic or mutagenic) reaction of a carcinogen is the reaction with nucleophiles as suggested earlier by Miller.²⁰⁾ A phenolic compound is one of models of bionucleophiles. We chose phenol and *p*-cresol as nucleophiles. When a mixture of **1** and sodium phenoxide was heated in dimethyl formamide (DMF) in nitrogen atmosphere at 100°, 9,10-dihydro-9-hydroxy-10-phenoxyphenanthrene (**23**, 19%), 9-phenoxyphenanthrene (**24**, 67%), and a trace of 9-phenanthrol and phenanthrene-9,10-quinone were identified. In the presence of air a significant amount of 9-hydroxy-10-phenoxyphenanthrene (**25**, 29%) was formed instead of **23** and **24**. The structure of **25** was confirmed by dehydroxylation using phenyl tetrazolium chloride. The *trans* configuration for the addition product **23** was deduced from the NMR spectrum ($J_{9,10}=10$ Hz). **23** was transformed into **24** under the reaction condition. In dimethyl sulfoxide (DMSO) at 100°, **24** was the major product and **23** could not be isolated. Very similar results were obtained in the reactions with sodium salts of *p*-cresol, and α - and β -naphthols.

Fig. 4

19) D.M. Johnson and T.C. Bruice, *J. Am. Chem. Soc.*, **97**, 6901 (1975).

20) J.A. Miller, *Cancer Res.*, **30**, 559 (1970).

Since *p*-cresol is a better model for the tyrosine residue, and the presence of the methyl group is convenient for NMR experiment of the reaction products, we studied the alkylation of *p*-cresol with **1** in detail, with the purpose of finding whether C-alkylation occurs or not. Under S_N2 conditions (in DMF or DMSO), the alkylation of sodium *p*-cresolate occurred exclusively at the oxygen atom of the cresol. Thus, **26** and **27** were identified as the reaction products. The addition of a protic solvent such as water or alcohol did really cause the C-alkylation, though the C-alkylation products **28** and **29** were obtained in quite low yields. (Table II). In acetone–water or dioxane–water, the yield of C-alkylation products increased to 2%. Significant amount of C-alkylation was observed in the reaction catalyzed by boron trifluoride-etherate or trifluoroacetic acid at room temperature. As the yield in the reaction catalyzed by BF_3 seems to be dependent on the experimental conditions employed, further experiments are required. The structure of the C-alkylation product (**29**) was determined by an independent synthesis of the methyl ether through Ullman condensation between 9-bromophenanthrene and 3-iodo-4-methoxytoluene in the presence of CuO and CuZn in DMF. The compound **28** was transformed into **29** by dil. hydrochloric acid. The stereochemistry of the 9,10-position was deduced to be *trans* from NMR coupling constant ($J_{9,10} = 10$ Hz).

Fig. 5

TABLE II

Reaction conditions					28 + 29
DMSO–CrONa	0.0	55.7	0.0	0.0 ₁	0.0 ₁
DMSO–H ₂ O(10%)–CrONa	0.1	54.7	0.0 ₁	0.1 ₈	0.2
DMSO–H ₂ O(50%)–CrONa	73.2	0.7	0.8 ₆	0.0 ₈	0.9
DMSO–EtOH(50%)–CrONa	1.7	48.4	0.0 ₁	0.0 ₆	0.1
DMSO–CrOH(50%)–CrONa	54.2	0.7	0.4 ₂	0.1 ₅	0.6
Acetone–H ₂ O(50%)–CrONa	86.4	1.2	1.7 ₇	0.3	2.1
Dioxane–H ₂ O(50%)–CrONa	89.5	0.7	1.9	0.4	2.3
CF ₃ COOH–CrOH	0.0	2.5	0.0	2.4	2.4
BF ₃ ·(C ₂ H ₅) ₂ O–CrOH	0.0	54.8	0.0	5.2	5.2

CrONa=sodium *p*-cresolate, CrOH=*p*-cresol.

The reaction of other K-region oxides (**2**, **3**, **4**) with *p*-cresolate in DMF also afforded (4-methylphenoxy)arenes (50–68%) and *trans*-hydroxy-(4-methylphenoxy)dihydroarenes (1–15%) corresponding to **27** and **26**, respectively. NMR spectra of the products from unsymmetrical epoxide **3** showed that the reaction is not regioselective. The NMR, gas-liquid

chromatography (GLC), and TLC of the reaction products of **4**, both addition and its elimination products, did not give any information on the isomer distribution, suggesting the reaction products were uniform. However, it can not be concluded that the attack of cresol is regio-specific, since the addition reaction of **4** with aniline and methoxide, and the reaction of other unsymmetrical oxides with nucleophiles always gave mixtures of possible isomers.

The reactivity of epoxides including methoxyphenanthrene oxides with cresolate was studied in DMSO and in aqueous acetone. Excess sodium *p*-cresolate was used, which made possible to calculate the pseudo-first order rate constants. The result was summarized in Table III. Benz[*a*]anthracene-5,6-oxide (**3**) is the most reactive epoxide, but only three times more reactive than the least reactive. Though the rate of decrease of 3-methoxyphenanthrene oxide (**6**) was as fast as **1**, the product was only the isomerized phenol 3-methoxy-9-hydroxyphenanthrene, which suggests a much lower reactivity of **6** with the nucleophile than the reactivity of **1**. No exciting change was observed in an aqueous solvent.

TABLE III. Relative Reactivities of Bimolecular Nucleophilic Reactions of Arene Oxides

Compound	1	2	3	4	5	6	7	8
a) Sodium- <i>p</i> -cresolate/DMSO at 65.0°	1.0	0.9	2.2	2.0	0.8	1.0	—	—
b) Sodium- <i>p</i> -cresolate/aq. acetone at 55.6°	1.0	0.6	1.1	1.0	—	—	—	—
c) <i>p</i> -Toluidine/CH ₃ OH at 50.0°	1.0	0.7	2.0	2.1	0.5	0.2	—	—
d) CH ₃ ONa/CH ₃ OH at 50.0°	1.0	0.8	2.8	1.8	0.7	0.9	0.5	0.6

The rate of phenanthrene oxide (**1**)=1.0 $\left(\begin{array}{l} k_{\text{obs}} = \text{a) } 0.98 \times 10^{-4} \text{sec}^{-1} \\ \text{b) } 2.7 \times 10^{-4} \\ \text{c) } 0.87 \times 10^{-4} \\ \text{d) } 1.2 \times 10^{-4} \end{array} \right)$

Reaction with Other Nucleophiles

Amino nucleophile is an attracting one from the biological standpoint, since the nitrogen atom of nucleic acid is one of the reactive sites with active carcinogens. *p*-Toluidine was chosen as the nitrogen nucleophile. The reaction was conducted in methanol and the product was identified as the addition product (**30**). Unsymmetrical epoxides **3** and **4** gave mixtures of isomers judging from NMR. The stereochemistry of the addition is *trans* from NMR coupling constant of the two hydrogens bearing nitrogen and oxygen and from similar mechanistic consideration to other nucleophilic addition reactions. The comparative rate study was performed as the case of *p*-cresol. The result was shown in Table III. Epoxides **3** and **4** are the most reactive epoxides among six epoxides tested, and 3-methoxyphenanthrene oxide (**6**) is the least reactive epoxide.

Reaction with methoxide in methanol was also studied. The products were *trans*-hydroxy-methoxydihydroarenes (**31**). Unsymmetrical oxides gave mixtures of two possible isomers. This was deduced from the methyl absorption of NMR. Products from **5**, **7** and **8** were dehy-

Fig. 6

Fig. 7

drated by methanesulfonyl chloride and the positional isomer ratio was obtained (see Experimental). In every case, the regioselectivity was very poor when experimental error was considered.

Reaction with cyanide in DMF at 100° gave 9-cyanophenanthrene. Reaction with sodium azide in aqueous acetone gave *trans*-9-azide-10-hydroxy-9,10-dihydrophenanthrene.²¹⁾ Though **1** is almost stable at 100° in DMF, the presence of potassium bromide accelerated the rearrangement to 9-phenanthrol. This may be explained by the catalysis of bromide anion. Nucleophilic attack of bromide may give an intermediate hydroxybromide and the dehydrobromination yields 9-phenanthrol.^{1,19)}

Discussion

The present result of the acid-catalyzed reaction of arene oxides agrees with the scheme proposed by Heiderberger,⁹⁾ Bruice,¹²⁾ and Kasperek,¹⁷⁾ and their coworkers. They claim that the rate determining step of the acid catalyzed rearrangement was the formation of a carbocation. This seems to be supported by the present study. In particular, the very fast formation of 3-methoxy-9-hydroxyphenanthrene (**14**) from 3-methoxyphenanthrene oxide (**6**) and the very slow formation of 3-carbomethoxy-10-hydroxyphenanthrene (**20**) from 3-carbomethoxyphenanthrene oxide (**8**) are well interpreted by the simple electronic effect of the methoxy and the carbomethoxy group on the stabilization or destabilization of the carbonium ion. The effect of 2-substituents on the phenanthrene oxide is interesting since the stabilization or destabilization effect on the carbonium ion may be caused by mesomeric effect through the biphenyl conjugation system.

Fig. 8

The difference in the rate constants of four unsubstituted epoxides (**1**–**4**) in the acid catalyzed decomposition is only about two times. The condensation of an additional benzene ring has only small effect on the reactivity. It is not clear whether the different degree of the easiness of planarity of the carbonium ion center has any effect.

The easy methylation of several epoxides or phenols was unexpected. This is a general reaction of polycyclic phenols. The methylation of polycyclic phenols may involve tautomeric ketonic forms of the phenols (Fig. 9), though these phenols do not show any carbonyl absorp-

21) K. Shudo and T. Okamoto, *Chem. Pharm. Bull.* (Tokyo), **24**, 1013 (1976).

tion in their IR spectra. The similar finding on some phenols has been reported by Newman¹⁴⁾ and discussed in relation to carcinogenicity of polycyclic aromatic hydrocarbons.²²⁾

Fig. 9

The reaction with *p*-cresol is interesting. The reaction in DMSO or DMF is S_N2 -type ring opening. Under these conditions, the products are formed by nucleophilic addition of the oxygen atom of cresol. In a protic medium, solvation or protonation of epoxide oxygen may be significant (A_2 -type mechanism).²³⁾ The observed C-alkylation product in protic media may be the reflection of the protonation on the oxygen atom, or a more polarized transition state than S_N2 mechanism. The solvation of phenolate anion also may change the reaction site.²⁴⁾ The present study may suggest that the C-alkylation by arene oxides as well as O- and N-alkylation should be seriously considered in the biological reaction. C-Alkylation by some carcinogenic arylhydroxylamines also has been shown by Miller.²⁰⁾

The order of the reactivity of epoxides with cresolate in DMSO was as follow:

The change of the reactivity was unexpectedly very small, and could not be interpreted by the resonance or inductive effect. Recent work by Harvey and coworkers discussed a nucleophilic addition of thiol in term of the nonbonding molecular orbital coefficients.¹⁰⁾ However, such discussion may be limited to carbonium ion forming reactions (the acid-catalyzed diol or phenol formation).⁹⁾ The poor regioselectivity in the reaction of 3 and 4 is mostly caused by the insensitivity of the reactivity to the electronic effect as well as by the inherent absence of the electronic effect of the condensed benzo ring.

A nitrogen nucleophile also reacted with epoxides. The relative rate constant of the reaction with *p*-toluidine may reflect a chemical reactivity of epoxide with a biological amino group. Benzo[*a*]pyrene-4,5-oxide (4) and benz[*a*]anthracene-5,6-oxide (3) are more reactive epoxides, though the difference in reactivity among the epoxides (1)—(4) is less than 3 times. It is noticeable that 3-methoxyphenanthrene oxide (6) is most stable towards the attack of toluidine among the tested epoxides, showing that the carbonium ion stabilizing group does not facilitate the (bimolecular) reaction with nucleophiles.

The order of the reactivity with methoxide in methanol is similar to that with cresolate in methanol. It is very clear that the nucleophilic attack of the methoxide is non-regio-specific in spite of the presence of, for example, a carbomethoxy group. 3-Methoxyphenanthrene-9,10-oxide (6) gave only 14. This is probably interpreted by methanol- or thermal-catalyzed reaction under the reaction conditions, rather than by the addition-elimination of methanol. The reaction with methoxide may reflect a part of the alkaline decomposition above pH 6 by the "spontaneous" reaction discussed by Jerina and coworkers.⁸⁾ The difference in reactivity among epoxides is again very small.

Though it is rather a matter of fact that S_{N2} reactivity is not always determined by the same electronic factor which governs the S_{N1} (carbonium ion forming) reaction,²⁵⁾ it should

22) A. Dipple, L.S. Levy and P. Thomaslype, *Cancer Res.*, **35**, 652 (1975).

23) J.B. Buchanan and H.Z. Sabel, "Selective Organic Transformation," Vol. 2, ed. by B.S. Thyagarajan, Wiley-Interscience, N.Y., 1970, p. 1.

24) H.O. House, "Modern Synthetic Reactions," 2nd ed., Benjamin, 1972, p. 492.

25) C.G. Swain and W.P. Langsdorf, *J. Am. Chem. Soc.*, **73**, 2813 (1951); W.T. Miller and J. Bernstein, *ibid.*, **70**, 3600 (1948).

be paid attention that S_N2 reactivity of arene oxides is not determined by simple electronic substituent effects.

As reported earlier, the order of mutagenicity of these epoxides tested in *Salmonella typhimurium* strain TA 98 is as follows:^{1b)}

Benzo[a]pyrene-4,5-oxide (4) is most active. Pyrene-4,5-oxide (2) is fairly active. In the nucleophilic reactions, benzo[a]pyrene-4,5-oxide (4) is the epoxide which is more reactive in general. This might look to be significant for the strong mutagenicity of 4. However, the epoxide (3) which is as reactive as 4 showed quite weak mutagenicity. Further, the differences in all nucleophilic reactivity tested are too small to interpret the wide range of the biological activity. The absence of a direct correlation between the biological activity and the acid-catalyzed reactivity (S_{N1} -type reactivity) was also observed. The increasing order of the acid-catalyzed reactivity is shown together with the mutagenic activity (in parentheses) as follows:

This clearly confirmed the absence of the correlation between the mutagenic activity and the easiness of carbonium ion formation. The least reactive epoxide (8) is mutagenic, and the most reactive epoxide (6) is not mutagenic. Therefore, we would like to conclude that the chemical reactivity (both S_{N1} and S_{N2} -type reactions) forming a covalent bond is not the determining the biological activity of arene oxides, though minimum reactivity may be required. Most epoxides may have sufficient reactivity, and the determining factors of the biological activity are the other molecular properties such as the intercalating easiness of a molecule into DNA cavity, participation coefficient, molecular shape, and the relative position of the epoxide moiety in a molecule. The charge transfer ability of arene oxide also may have an important role. Such a consideration has been discussed by Ames.²⁶⁾ Recently Miller also concluded that *in vitro* reactivity of some carcinogenic hydroxylamines with nucleophiles is not the determining factor for their carcinogenicity.²⁷⁾ We also found that the mutagenic activity of arylhydroxylamine derivatives is not correlated with the electrophilic reactivity of the N-O bond.²⁸⁾ We are trying to find the most important molecular property of arene oxides and other carcinogenic compounds.

Experimental

General Method—NMR spectra were recorded on a Jeol PS-100 or a Hitachi-Perkin Elmer 60 Mc apparatus. Ultraviolet (UV) spectra were taken on a Hitachi EPU-2 spectrophotometer with 1 cm cell. Mass spectra were obtained with a Jeol SG spectrometer. Melting points were determined on a Yanagimoto hot plate apparatus and were uncorrected. High pressure liquid chromatography (HLC) separations were performed on 0.2 cm × 25 cm column of MicroPak CH-10 with methanol-water, employing a Variscan ultraviolet detector. Thin-layer chromatography were made from Camag Kiesel Gel DF-5. Gas chromatographic analyses were performed on a Jeol JGC 20K with a flame ionization detector employing 1 m 1% SE 30 or 1 m 1% OV 101 column.

Syntheses of Arene Oxides (1—4)—The K-region arene oxides were synthesized by the general methods previously reported.^{17a,29)} A new method using diphenyl-di (1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxy)-sulfurane³⁰⁾ was applied. A *trans*-dihydrodiol (see below) was suspended in anhydrous methylene chloride,

- 26) B.N. Ames, E.G. Gurney, J.A. Miller, and H. Bartsch, *Proc. Nat. Acad. Sci., (U.S.A.)*, **69**, 3128 (1972).
- 27) P.G. Wislocki, J.A. Miller and E.C. Miller, *Cancer. Res.*, **35**, 880 (1975).
- 28) N-benzoyl-4-methoxyphenylhydroxylamine which is expected to be heterolytically more reactive than muta-carcinogenic N-acyl-biphenylhydroxylamine and N-acetyl-fluorenylhydroxylamines was not mutagenic in bacterial mutation test using *Salmonella typhimurium* TA 100 and TA 98, unpublished result.
- 29) P. Dansette and D.M. Jerina, *J. Am. Chem. Soc.*, **96**, 1224 (1974); S.H. Goh and R.G. Harvey, *ibid.*, **95**, 242 (1973).
- 30) J.C. Martin, J.A. Franz and R.J. Arhart, *J. Am. Chem. Soc.*, **96**, 4604 (1974).

and a three molar excess of the sulfurane was added with stirring. The reaction was almost complete in a minute at room temperature. Quantitative yields were obtained in the syntheses of 1 and 2. The yields were lower (60–65%) in the cases of 3 and 4.

The *trans*-dihydrodiols have been obtained by the reduction of K-region quinones. However the quinones were prepared from *cis*-dihydrodiols, which requires expensive osmium tetroxide. We explored convenient method of preparing the K-region quinones. A polycyclic aromatic compound (for example, 50 g of pyrene) was dissolved in carbon tetrachloride and a catalytic amount of OsO₄ (1/10–1/100 equivalent) was added. A total of 4–5 equivalents of *t*-butylhydroperoxide was added during 24–48 hr at 60°. In most cases a fairly pure K-region quinone was separated out. The yields were 20% (phenanthrene-9,10-quinone), 61% (pyrene-4,5-quinone), 49% (benz[*a*]anthracene-5,6-quinone, and 60% (benzo[*a*]pyrene-4,5-quinone). In the mother liquor could be used for the oxidation of another additional hydrocarbon.

Syntheses of Arene Oxides (5–8)—Phenanthrene oxides (5–8) were prepared using hexamethylphosphorous triamide from corresponding dialdehydes.^{17a)}

(a) 2-Methoxyphenanthrene-9,10-oxide (5): To a solution of 2-acetylphenanthrene³¹⁾ (8.5 g) in CHCl₃ (50 ml) was added *m*-chloroperbenzoic acid (20 g), and the solution was refluxed for 30 hr. After usual work up, 2-acetoxyphenanthrene, mp 146.5–147°, was obtained as needles. *Anal.* Calcd. for C₁₆H₁₂O₂: C, 81.34; H, 5.12. Found: C, 81.56; H, 5.09. The crude acetoxyphenanthrene was hydrolyzed with 10% sodium hydroxide, followed by methylation by dimethyl sulfate (15 ml) at 40–60° for 2 hr. Silica gel chromatography gave 3.3 g of 2-methoxyphenanthrene, mp 99.5–100.5°. *Anal.* Calcd. for C₁₅H₁₂O: C, 86.51; H, 5.81. Found: C, 86.24; H, 5.90. Ozonation of the 2-methyl ether at –35––25° as described³²⁾ gave 4-methoxy-2,2'-diformylbiphenyl, mp 83.5–84°, *Anal.* Calcd., for C₁₅H₁₂O₃: C, 74.99, H, 5.03. Found: C, 74.67; H, 5.07. To the diformyl compound (1.37 g) in dry benzene (10 ml) was added hexamethylphosphorous triamide (2.0 g), and the solution was stood at 35–40° for 3 hr. Evaporation of benzene and purification of the crude product by an alumina column gave 2-methoxyphenanthrene-9,10-oxide (5) (0.97 g, 76%), mp 109–110°. *Anal.* Calcd. for C₁₅H₁₂O₂: C, 80.33; H, 5.39. Found: C, 79.82; H, 5.27.

(b) 3-Methoxyphenanthrene-9,10-oxide (6): This compound was synthesized by similar reaction sequences to 5. 3-Acetoxyphenanthrene, mp 115–116.5°. *Anal.* Calcd. for C₁₆H₁₂O₂: C, 81.34; H, 5.12. Found: C, 81.59; H, 5.17. 3-Methoxyphenanthrene, mp 57–57.5°. *Anal.* Calcd. for C₁₅H₁₂O: C, 86.51; H, 5.81. Found: C, 86.47; H, 5.85. 5-Methoxy-2,2'-diformylbiphenyl, oil. 3-Methoxyphenanthrene-9,10-oxide, mp 67–68°. *Anal.* Calcd. for C₁₅H₁₂O₂: C, 80.33; H, 5.39. Found: C, 80.39; H, 5.37.

(c) 2-Carbomethoxyphenanthrene-9,10-oxide (7): 2-Carbomethoxyphenanthrene³¹⁾ was the starting compound. 4-Carbomethoxy-2,2'-diformylbiphenyl, amorphous. 2-Carbomethoxyphenanthrene-9,10-oxide, mp 147.5–148.5°. *Anal.* Calcd. for C₁₆H₁₂O₃: C, 76.18; H, 4.80. Found: C, 76.33; H, 4.93.

(d) 3-Carbomethoxyphenanthrene-9,10-oxide (8): 3-Carbomethoxyphenanthrene³¹⁾ was the starting compound. 5-Carbomethoxy-2,2'-diformylbiphenyl, mp 104.5–105.5°. *Anal.* Calcd. for C₁₆H₁₂O₄: C, 71.63; H, 4.51. Found: C, 71.21; H, 4.49. 3-Carbomethoxyphenanthrene-9,10-oxide, mp 122–122.5°. *Anal.* Calcd. for C₁₆H₁₂O₃: C, 76.18; H, 4.80. Found: C, 76.05; H, 4.79.

Acid-Catalyzed Reaction of K-Region Oxides—(a) General Procedure for Product Studies: A suspension of the oxide (0.1–0.4 mmol) in 10–40 ml of 67% aqueous acetone adjusted to pH 2.3 by hydrochloric acid ((b)–(e)) or in 2N-HCl-acetone (1:2) ((f)–(i)) was allowed to stand at 0° for 3 hr. The product was extracted with methylene chloride or benzene, and the extract was washed with water, dried over sodium sulfate, and evaporated. The residue was chromatographed on silica gel or recrystallized.

(b) Phenanthrene-9,10-oxide: The products were 9-phenanthrol (mp 154°, 75%), and *trans*-9,10-dihydroxy-9,10 dihydrophenanthrene (mp 182°, 17%).

(c) Pyrene-4,5-oxide: 4-Pyrenol (mp 202°, from benzene, 79%) and *trans*-4,5-dihydroxy-4,5-dihydro-pyrene (mp 211–214°, 15%) were isolated and identified with authentic samples.

(d) Benz[*a*]anthracene-5,6-oxide: The crude product seemed to be unstable, and was methylated with dimethyl sulfate in 20% NaOH solution. The mp of mixture of methyl ethers after chromatography was 86–90° (76% yield). NMR spectra of the methyl ether in CDCl₃ (OCH₃ signals at δ 4.11 and 4.12) suggested that the product is a mixture of about 1:1 of two isomers. The formation of *trans*-dihydrodiol was identified by HLC and the yield was estimated to be about 15% from the peak intensity.

(e) Benzo[*a*]pyrene-4,5-oxide: The methyl ether obtained in the same procedure as in (d) showed mp 125–132°. Yield was 81%. The OCH₃ absorption splitted at δ 4.04 and 4.03 (CDCl₃). HLC showed the formation of dihydroxy compound.

(f) 2-Methoxyphenanthrene-9,10-oxide: The phenol 11 was formed in a quantitative yield. After treatment with dimethyl sulfate in 20% NaOH following chromatography gave dimethyl ether (12), 89%. After purification by sublimation gave a crystalline of mp 112–113°. *Anal.* Calcd. for C₁₆H₁₄O₂: C, 80.64; H, 5.92. Found: C, 80.38; H, 6.03.

31) E. Mosettig and J. Kamp, *J. Am. Chem. Soc.*, **52**, 3704 (1930).

32) P.S. Bailey and R.E. Erickson, *Org. Syn.*, **41**, 41 (1961).

(g) 3-Methoxyphenanthrene-9,10-oxide: The same procedure as (f) gave dimethyl ether **15**, mp 112–113°, in 85% yield. *Anal.* Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 9.52. Found: C, 80.61; H, 5.85.

(h) 2-Carbomethoxyphenanthrene-9,10-oxide: The same procedure as (f) gave methyl ether **18**, mp 130.5–131.5°, in 90% yield. *Anal.* Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.56; H, 5.39.

(i) 3-Carbomethoxyphenanthrene-9,10-oxide: The same procedure as (f) gave methyl ether **21**, mp 133–134°, in 81% yield. *Anal.* Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.45; H, 5.31.

(j) Procedure for Kinetic Study: To a cooled solution of the epoxide (9.0–0.83 mm) in acetone (4 ml) was added 2 ml of aqueous HCl cooled at 0°. The pH of the solution was 2.3. The solution was kept at $0^\circ \pm 0.1^\circ$, and 0.2 ml of the solution was taken at several times (3 min–16 hr). The solution was quenched by mixing 0.1 ml of 10% K_2CO_3 at -5° , and the epoxide remaining was analyzed by HLC using acetone as an internal standard. The result showed a good first order kinetics in respect to the epoxide, during two half lives.

Synthesis of 9- or 10-Methoxyphenanthrenes (12, 15, 18 and 21)—The enol ethers (**13**, **16**, **19** and **22**) were prepared by the procedure according to Krow's method.³³ Photochemical cyclization of the enol ethers was performed in anhydrous ethanol or hexane in the presence of a trace of iodine by the irradiation of a high pressure mercury lamp. The crude reaction mixture was purified by silica gel column chromatography. The major products were the starting enol ether and the hydrolyzed ketone. The next major product isolated was the phenanthrene derivative in yields of 4–8%. Identification with the ether (**12**, **15**, **18** and **21**) obtained from epoxides was performed by infrared (IR) and NMR spectra, and a mixed melting point determination. Possible isomeric methoxyphenanthrenes seemed to be formed in the photochemical cyclization of **13** and **19**, but not identified.

Methylation of Epoxides and Phenols—A suspension of phenol or epoxide (0.1–1 mmol) in methanol (4–40 ml) and conc. HCl (1–10 ml) was heated at the refluxing temperature for 1 hr. The product was extracted with benzene, and the extract was washed with water, dried with sodium sulfate and evaporated. The methyl ether was recrystallized from benzene-hexane. 9-Methoxyphenanthrene from **1** was obtained in 90% yield. mp 95.5–96.5°. *Anal.* Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.22; H, 5.71. A mixture of 5- and 6-methoxybenz[a]anthracene from **3** was obtained in 92% yield. The melting point of the mixture was 80–90°. NMR peak ratio of two methoxy hydrogens was 1:1.1 (δ 4.11 and δ 4.12). 4-Methoxypyrene, mp 131.5–132.5°, was obtained from **2** in 90% yield. *Anal.* Calcd. for $C_{17}H_{12}O$: C, 87.90; H, 5.29. Found: C, 87.85; H, 5.25. 4-Methoxypyrene was also obtained from 4-pyrenol in 85% yield under the same condition. A mixture of 4- and 5-methoxybenzo[a]pyrene was obtained from **4**, mp 125–130°. The NMR peak ratio of the two methoxy hydrogens was 1:1.2 (δ 4.03 and 4.04). *Anal.* Calcd. for $C_{21}H_{14}O$: C, 89.33; H, 5.00. Found: C, 89.12; H, 5.02. A solution of α - and β -naphthols (1 mmol) in 40 ml of methanol and 10 ml of conc. HCl was refluxed for 24 hr. The products were analyzed by HLC, and methoxynaphthalenes were identified in yield of 10% (α -) and 8% (β -). Phenol under the similar conditions resulted in the complete recovery of phenol.

Reaction of Phenanthrene-9,10-oxide and Sodium Phenolate—A mixture of **1** (97 mg) and sodium phenoxide (116 mg) in DMF (5 ml) was heated at 100° for 5 hr in the atmosphere of argon. Water was added to the reaction mixture and extracted with methylene chloride. Products were separated by a silica gel column. *trans*-Hydroxy-phenoxydihydrophenanthrene (**23**, 27.5 mg, 19%) mp 152–155°, (NMR ($CDCl_3$, δ) 5.05 and 5.35 ($J=10$ Hz.)) *Anal.* Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.11; H, 5.47.) and phenoxyphenanthrene (**24**, 91 mg, 67%) mp 78.5–79.5° were isolated. 9-Phenoxyphenanthrene was prepared from 9-bromophenanthrene and sodium phenolate in the presence of copper powder in DMF at 250° for 3 hr. *Anal.* Calcd. for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.80; H, 5.00. TLC of the crude reaction extract showed the presence of trace dihydro diol and phenanthrene-9,10-quinone.

When the same experiment was performed in the presence of air, the major product isolated from 437 mg of **1** by a column chromatography was 9-hydroxy-10-phenoxyphenanthrene (**25**, 205 mg, 29%), whose structure was determined by the conversion to 9-phenoxyphenanthrene by the reaction of phenyltetrazolium chloride followed by the reduction in the presence of Pd catalyst. mp 148–149.5°, *Anal.* Calcd. for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.60; H, 4.87.

Reaction of Epoxides with Sodium *p*-Cresolate—(a) General procedure: To a solution of the epoxide (0.1–1 mmol) dissolved in a solvent was added sodium *p*-cresolate (1–2 mmol). The mixture was degassed or substituted air by nitrogen, and heated at 100° or at the refluxing temperatures. The solvent was evaporated *in vacuo*, and water was added and extracted with methylene chloride. The extract was washed, dried and evaporated, and recrystallized or chromatographed on a silica gel column.

(b) Phenanthrene-9,10-oxide (**1**) in DMF: The reaction was performed in DMF as the general procedure. Products isolated by a silica gel column were 4-methylphenoxyphenanthrene (**27**), mp 74–75° in 40% yield. *Anal.* Calcd. for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 89.06; H, 5.69, and *trans*-9-hydroxy-10-(4-methylphenoxy)phenanthrene (**26**), mp 160–161° (from acetone-hexane) in 15% yield, NMR ($CDCl_3$, δ): 2.35 (CH_3), 5.05 and 5.45 (2H, $J=10$ Hz.), *Anal.* Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.29; H, 6.01.

33) G. R. Krow and E. Michener, *Synthesis*, 1974, 572.

(c) Phenanthrene-9,10-oxide (**1**) in Aqueous Acetone: The reaction of **1** (2 g) with sodium *p*-cresolate (2.6 g) was performed in aqueous acetone. The major product, **27**, was removed by crystallization, and the mother liquor was chromatographed on a silica gel column and successive purification by preparative thin layer chromatography gave **28** (30 mg) and **29** (20 mg).

The product **28** showed mp 195–198° (*Anal.* Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.63; H, 6.06, NMR ($CDCl_3$ - CD_3OD , δ): 2.76 (CH_3), 4.62 and 5.01 ($J=8$), 6.9–7.9 (8H), 6.4 ($J=2$, 1H), 6.64 ($J=9$), 6.78 ($J=2$ and 9)). When **28** was treated with 2*N*-HCl at the refluxing temperature, the phenanthrene derivative (**29**) was obtained in a quantitative yield, and identified with the sample described below.

The compound **29** was sublimed to an amorphous solid (0.1 mmHg/150°). NMR ($CDCl_3$, δ): 2.34 (3H), 6.8–7.2 (3H), 7.4–7.95 (6H), 8.6–8.75 (2H). The methyl ether was prepared by the use of methyl iodide, and a glassy solid was obtained by sublimation at 150°/0.1 mmHg. *Anal.* Calcd. for $C_{22}H_{18}O$: 88.56; H, 6.08. Found: C, 88.54; H, 6.01. Picrate of the methyl ether had mp 168–169°. *Anal.* Calcd. for $C_{28}H_{21}N_3O_8$: C, 63.75; H, 4.01; N, 7.96. Found: C, 63.48; H, 3.96; N, 7.82.

The methyl ether was prepared by Ullman condensation of 2-iodo-4-methylanisole (0.8 g) and 9-bromophenanthrene (0.5 g) in 2 ml DMF in the presence of Cu (500 mg) and CuO (50 mg) at 230–240° for 8 hr. The product was purified by a silica gel column and sublimed as an amorphous solid (170 mg), whose picrate, mp 168–169° was identical with the picrate obtained from **1** in all respects.

(d) Pyrene-4,5-oxide: The major reaction product in DMF was 4-(4'-methylphenoxy)pyrene (66%), whose picrate, mp 140° was analyzed. *Anal.* Calcd. for $C_{26}H_{18}N_3O_8$: C, 64.80; H, 3.56; N, 7.82. Found: C, 64.80; H, 3.61; N, 7.69. The major reaction product in aqueous acetone was the addition product, *trans*-4-hydroxy-5-(4'-methylphenoxy)-4,5-dihydropyrene, mp 178–178.5° in 30% yield. NMR ($CDCl_3$, δ): 2.3 (CH_3), 2.75 (1H, br. OH), 5.48 and 5.76 (1H, 1H, $J=10$). *Anal.* Calcd. for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 85.38; H, 5.60.

(e) Benz[*a*]anthracene-5,6-oxide: The reaction products in DMF were 5- and 6-(4'-methylphenoxy)-derivatives (50%), mp 94–98°, and addition products, two *trans*-hydroxy-(4'-methylphenoxy)-5,6-dihydroanthracenes (5%). The reaction in aqueous acetone gave 34% of the addition products.

(f) Benzo[*a*]pyrene-4,5-oxide: The reaction products obtained in DMF were a mixture of 4- and 5-(4'-methylphenoxy)benzo[*a*]pyrenes, as yellow solid in 68% yield. The reaction in aqueous acetone gave a mixture of two *trans*-hydroxy-(4'-methylphenoxy)-4,5-dihydrobenzo[*a*]pyrenes.

(g) Procedure for Kinetic Study: The epoxide (4–9 mm) and sodium *p*-cresolate (150 mm) in DMSO (purged with nitrogen) or in 67% aqueous acetone were reacted at 65° or 55.6°, respectively. The decrease of the epoxide was followed by HLC. A good first order kinetics was observed in respect to the epoxide through the half life. The change of the amount of the epoxide might effect less than about 5% of error.

(h) Phenanthrene-9,10-oxide. Solvent Effects: The epoxide (**1**, 50 mg) and sodium *p*-cresolate (100.0 mg) was dissolved in a test tube and the solution was purged with purified nitrogen and sealed and heated at 100°. The reaction mixture was dried up at 60° *in vacuo*, water was added to the residue, acidified with 2*N*HCl, and extracted with methylene chloride. Methylene chloride was evaporated by a rotatory evaporator, and cresol was removed at 60°/0.1 mmHg. The residue was separated by a preparative thin-layer chromatography using hexane-methylene chloride as the solvent. Three parts, the top (**27**), the second from the top (**29**) and the starting point (**26** and **28**) were scratched off. Extracts from these parts by methylene chloride-methanol were analyzed by gas chromatography. Under the gas chromatographic conditions employed (SE 30, 1.5%, column temperature 184°, injection temperature 270°) **27** quantitatively decomposed to **29** by dehydration.

Reaction of 1 with Naphthols—(a) A mixture of **1** (485 mg), α -naphthol (540 mg), and *t*-BuOK (622 mg) in DMF (25 ml) were heated at 100° for 5 hr in the atmosphere of argon. The products were isolated by a silica gel column, and 9-(α -naphthoxy)phenanthrene (329 mg, 42%), mp 103–105° (from ethanol-benzene, *Anal.* Calcd. for $C_{24}H_{18}O$: C, 90.14; H, 4.99. Found: C, 89.97; H, 5.03), and *trans*-9-hydroxy-10-naphthoxy-9,10-dihydrophenanthrene (30 mg, 3.6%) as a low melting oil (purified by a molecular distillation at 0.01 mmHg).

(b) The reaction of **1** with β -naphthol as (a) gave 9-(β -naphthoxy)phenanthrene (5%), mp 126.5–127.5° (*Anal.* Calcd. for $C_{24}H_{18}O$: C, 90.14; H, 4.99. Found: C, 89.94; H, 5.02), and *trans*-9-(β -naphthoxy)-10-hydroxy-9,10-dihydrophenanthrene (26%) mp 172–173°, *Anal.* Calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 84.95; H, 5.31).

Reaction of Arene Oxides with *p*-Toluidine—(a) Phenanthrene-9,10-oxide: A solution of **1** (50 mg) and *p*-toluidine (54 mg, 2 equiv) in acetone (2 ml) water (1 ml) was heated under reflux for 21 hr. The mixture was extracted with methylene chloride. A silica gel chromatography gave 64 mg (83%) of amino alcohol as needles (from hexane-methylene chloride), mp 149–150°. *Anal.* Calcd. for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.60; H, 6.33; N, 4.81. NMR ($CDCl_3$, δ): 4.60 and 4.81 (1H, 1H, $J=11$).

(b) Pyrene-4,5-oxide: The reaction of pyrene oxide with *p*-toluidine as (a) gave *trans*-4-hydroxy-5-anilino-4,5-dihydropyrene (63%), mp 149–150° (from hexane-methylene chloride). *Anal.* Calcd. for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30. Found: C, 85.01; H, 5.91; N, 4.59. NMR ($CDCl_3$, δ): 2.19 (3H), 4.97 and 5.14 (1H, 1H, $J=8$).

(c) Benz[*a*]anthracene-5,6-oxide: The reaction gave a mixture of isomeric amino alcohols (95%) as needles from hexane-methylene chloride, mp 173–177°.

(d) Benzo[*a*]pyrene-4,5-oxide: The reaction gave a mixture of isomeric amino alcohols (49%) as thin needles from hexane-benzene, mp 177–182°.

(e) Procedures for Kinetic Study: The solution of about 1 mm of the epoxide in methanol containing *p*-toluidine (93 mm) was heated at 50.0° in a sealed tube. The decrease of the epoxide relative to the internal standard (anisole, toluene or xylene) was followed by HLC. A good first order kinetics was observed in respect to the epoxide through the half life.

Reaction with Methoxide in Methanol—(a) General Procedure: A mixture of an epoxide (0.5 mmol) and sodium methoxide (5 mmol) in 10 ml of methanol was refluxed for 3 hr. The reaction mixture was diluted with water, extracted with methylene chloride. Purification by a silica gel column gave a pure or a mixture of isomeric hydroxy methyl ether.

(b) Phenanthrene-9,10-oxide: The reaction gave *trans*-9-hydroxy-10-methoxy-9,10-dihydrophenanthrene, mp 51–54° (86%). NMR (CDCl₃, δ): 3.6 (3H, CH₃), 4.34 and 4.81 (1H, 1H, *J*=9). *Anal.* Calcd. for C₁₅H₁₄O₂: C, 79.47; H, 6.24. Found: C, 79.21; H, 6.33.

(c) Pyrene-4,5-oxide: The reaction gave *trans*-4-hydroxy-5-methoxy-4,5-dihdropyrene (93%), mp 110–110.5°. NMR (CDCl₃, δ): 3.3 (3H), 4.65 and 5.16 (1H, 1H, *J*=8). *Anal.* Calcd. for C₁₇H₁₄O₂: C, 81.58; H, 5.64. Found: C, 81.32; H, 5.61.

(d) Benz[*a*]anthracene-5,6-oxide: The reaction product was a mixture of isomeric methoxy alcohols (99%), mp 94–98°, NMR (CDCl₃, δ): 3.50 and 3.53 (CH₃). *Anal.* Calcd. for C₁₈H₁₆O₂: C, 82.58; H, 5.84. Found: C, 82.31; H, 5.84.

(e) Benzo[*a*]pyrene-4,5-oxide: The product was a mixture of isomeric methoxy alcohols, mp 151–158° (hexane-methylene chloride, 99%). *Anal.* Calcd. for C₂₁H₁₆O₂: C, 83.98; H, 5.37. Found: C, 83.68; H, 5.37.

(f) 2-Methoxyphenanthrene-9,10-oxide: The product was a mixture of isomeric methoxy alcohols (53%). The mixture was dissolved in pyridine and treated with methanesulfonyl chloride for 2 hr. The composition of the crude dimethoxyphenanthrenes was determined as 3:2 with predominant 2,9-dimethoxyphenanthrene by NMR methoxy signals. The mixture after recrystallization (from hexane-methylene chloride) was analyzed. *Anal.* Calcd. for C₁₆H₁₄O₂: C, 80.64; H, 5.92. Found: C, 80.35; H, 6.01.

(g) 3-Methoxyphenanthrene-9,10-oxide: The reaction with methoxide gave only 9-hydroxy-3-methoxyphenanthrene instead of the hydroxy-methoxy compound. Methylation by dimethylsulafte gave 3,9-dimethoxyphenanthrene in 66% yield.

(h) 2-Carbomethoxyphenanthrene-9,10-oxide: The same treatment as (f) gave a mixture of 2-carbomethoxy-9- and -10-methoxyphenanthrenes (7:6). The mixture after sublimation was analyzed. *Anal.* Calcd. for C₁₇H₁₄O₃: C, 76.67; H, 5.30. Found: C, 76.64; H, 5.43.

(i) 3-Carbomethoxyphenanthrene-9,10-oxide: The same treatment as (f) gave a mixture of 3-carbomethoxy-9- and -10-methoxyphenanthrenes (5:4). The mixture after sublimation was analyzed. *Anal.* Calcd. for C₁₇H₁₄O₃: C, 76.67; H, 5.30. Found: C, 76.62; H, 5.31.

(j) Procedure for Kinetic Study: A solution of an epoxide (0.4–3 mm) in 180 mm-sodium methoxide-methanol was kept at 50°±0.1°. Containing an appropriate amount of biphenyl or anisole as the internal standard for HLC analysis. A good first order kinetics was obtained through the half life or more. The difference of the initial concentration of the epoxide may cause error less than about 3%.

Reaction of 1 with Potassium Cyanide—A mixture of 1 (100 mg), KCN (100 mg) in DMF (10 ml) was heated at 100° for 5 hr. After evaporation of DMF *in vacuo*, the residue was chromatographed on a silica gel column. The major products were 9-cyanophenanthrene (31 mg, 30%) mp 108–109°, which was identified with an authentic sample by a mixed melting point determination and IR spectrum, and 9-phenanthrol (27 mg, 27%) and a mixture of these two products (22 mg) were also obtained.

Reaction of 1 with Potassium Bromide—A solution of 1 (100 mg) and 100 mg of potassium bromide in DMF (10 ml) was heated at 100° for 5 hr. Evaporation of the solvent and washing with water gave 9-phenanthrol in a quantitative yield. In the absence of KBr, more than 70% of 1 was recovered.