DYE-SENSITIZED PHOTOOXIDATION OF PHENANTHRENE*

B. J. Dowty, N. E. Brightwell, J. L. Laseter, and G. W. Griffin
Departments of Biological Sciences and Chemistry
Louisiana State University in New Orleans
New Orleans, Louisiana 70122

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SUMMARY. The dye-sensitized photooxidation of phenanthrene has been studied in a two-phase system employing n-hexane and water. Rose bengal was used as a sensitizer. A number of volatile oxidation products are observed and characterized by GC-MS-COM methods. The data suggest that one oxidation route involves the conversion of phenanthrene to 9,10-epoxy-9,10-dihydrophenanthrene which is related to the potentially carcinogenic arene oxides of more highly condensed polynuclear hydrocarbons. These results may have significance in connection with the enhancement of aberrant effects on biological systems produced by polynuclear hydrocarbons upon exposure to light.

INTRODUCTION. The growing recognition that arene oxides may play a significant role in carcinogenesis by polynuclear hydrocarbons has prompted us to investigate possible mechanistic routes for their formation (1). In a recent review of carcinogenicity of such arene oxides it has been pointed out that both natural and synthetic compounds are active, or metabolized to active, substances which are reactive toward cellular nucleophiles (2). As a continuation of our studies on the interaction of singlet oxygen at the interface of lipophilic surfaces including biological systems we have studied the dye-sensitized photooxidation of phenanthrene under such conditions to determine whether the arene oxide 1 is among the products (3,4,5).

METHODS AND MATERIALS. In a typical case rose bengal (~5.0 x 10^{-5}M) was introduced as a sensitizer into an aqueous phase (400 ml:pH 8.2) to which 20 ml of n-hexane containing 50 mg of phenanthrene was added. The resulting two-phase system was irradiated for periods ranging from 1 to 7 hr at 0-5° (6). Oxygen was simultaneously introduced through two fritted inlets at a rate of approximately 120 ml/min which provides adequate agitation to maintain a relatively uniform dispersion at the interface. Controls were performed in the same manner with ground state oxygen. The organic phase was separated and the

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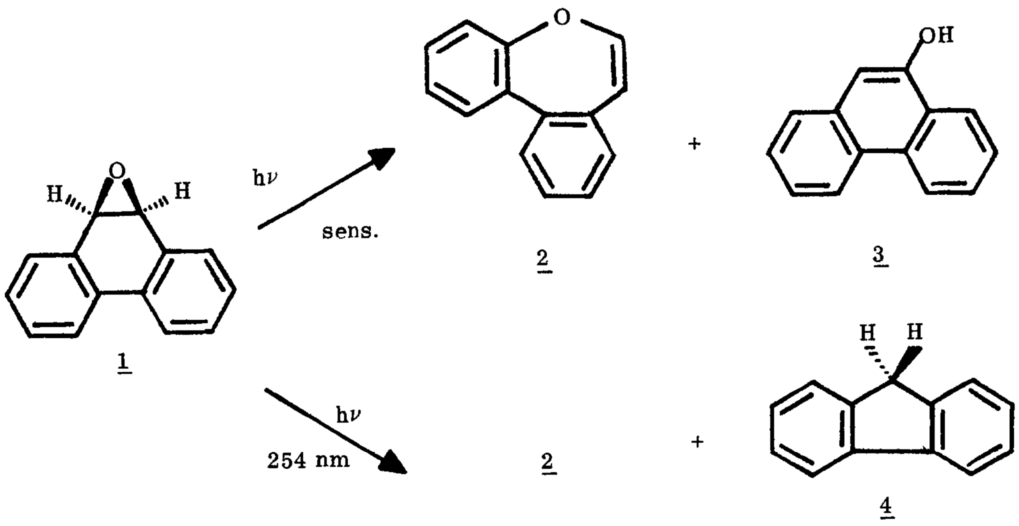
aqueous layer extracted repeatedly with benzene-chloroform (2:1) and the volatile solvents removed from the resulting organic extract under vacuum at ambient temperature. Separation of the oxidation products was achieved by GC on a stainless steel column (1.83 m x 2 mm id) packed with UCW-98 (Silicon-gum) operated isothermally at 200° with a helium carrier flow rate of 10 ml/min. The products were characterized by techniques involving a combined gas chromatograph-mass spectrometer-computer so that the components in general could be identified by comparison with authentic samples and quantified with confidence.

RESULTS AND DISCUSSION. While identification of certain products remains to be achieved it is clear that after 3 hr exposure the volatile constituents derived from phenanthrene upon oxidation with singlet oxygen, listed in order of increasing elution times, include fluorene (m/e 166), fluorenone (m/e 180), 9-phenanthrol (m/e 194), 9,10-phenanthrenequinone (m/e 208). In certain runs an additional product, 2,2'-diformylbiphenyl (m/e 210), was also detected and its structure verified by mass spectrometry; however, complete resolution from residual phenanthrene has not been achieved. The GC peak due to phenanthrene is off-scale and unfortunately obscures a broad and significant region of the chromatogram. Another unresolved component which appears on the leading edge of the phenanthrene peak has a retention time and a molecular weight identical to that of an authentic sample of 2,3:4,5-dibenzoxepin (2)(7).

It is noteworthy that under identical conditions 9,10-epoxy-9,10-dihydrophenanthrene (1)(5) undergoes interconversion to 2,3:4,5-dibenzoxepin (2)(9%) and 9-phenanthrol (3)(~20%). Other products obtained from 1 under these conditions include fluorenone (3%), 2,2'-diformylbiphenyl (15%), 2-hydroxybiphenyl-2'-carboxylic acid lactone (16%), diphenic acid anhydride (4%) and 9,10-phenanthrenequinone (~28%). Undoubtedly hydration of 1 is a competing reaction as is photorearrangement to 2 (*vide infra*) with both processes ultimately leading to reaction products which are sensitive to attack by singlet oxygen, namely 3 and 2, respectively, which in fact may be the primary precursors for many of the substances identified. Despite these complicating features, on the basis of comparative GC profiles we are led to believe that 1 may be formed as a primary product in a phenanthrene singlet oxidation process which competes with the 2 + 2 addition of singlet oxygen across the 9,10 pi-bond (1). The formation of oxiranes by end-on addition of singlet oxygen to alkenes is a reaction not without precedent (7). It is of further significance that a control study employing ground state oxygen and phenanthrene gives an entirely different GC profile of products. Our failure to date to identify 1 (the only reasonable precursor for 2) and 2 among the oxidation products of phenanthrene stems from our present inability to resolve gas



chromatographically small quantities of 1 and 2 (obtained in low conversion runs required to minimize competing secondary reactions) from the more abundant products phenanthrol (3) and phenanthrene, respectively.

The origin of fluorene (4) from phenanthrene and 1 upon irradiation remains to be elucidated; however, it should be noted that 4 is formed upon direct irradiation of 1 (254 nm),in addition to the oxepin 2 (6b,8). In the latter case this hydrocarbon may be formed by C-O cleavage of the oxirane ring followed by ring contraction and photodecarbonylation of the resulting aldehyde. The absorption spectrum for 1 interestingly rises steeply at 298 nm (λmax 273, ε - 45,000) and trails to ~ 330 nm (8b) so that it is not surprising that photoinduced processes might occur without more efficient filtering. The ring contraction also might be rationalized by invoking an open zwitterionic mechanism for the singlet oxygen addition at least in the case of phenanthrene.

In view of the above facts and the known thermolability of the oxide 1 it is not unexpected that some difficulty has been encountered in observing the steady state concentration levels at which 1 exists under the specific reaction conditions discussed above (8,9); however, in one experiment a GC peak was observed which upon addition of an authentic sample of the oxide showed enhancement. Modification of experimental conditions and use of milder separation techniques such as liquid-liquid chromatography with recycle capability should permit observation of this sensitive product. We feel that these results may have significance in connection with the enhancement of aberrant effects on biological systems produced by polycyclic hydrocarbons following exposure to light (10).

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3. Dowty, B., Laseter, J. L., Griffin, G. W., Politzer, I. R., and Walkinshaw, C. H. (1973) Science 181, 669.
4. The reactions of ground state oxygen with phenanthrene is under study by Professor R. M. Wilson, University of Cincinnati. We are indebted to him for helpful discussions concerning the course of the reaction of phenanthrene with triplet oxygen.
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6. (a) Photooxygenations were conducted in a 800 ml Pyrex vessel fitted with two fritted inlets for oxygen and a water cooled Pyrex Hanovia type immersion well which accommodates a double Pyrex filter and a Sylvania EHC 500 watt tungsten lamp.
   (b) Irradiations at 254 nm were conducted in serum-capped Vycor test tubes employing a Rayonet RPR-100 Chamber Reactor equipped with 16 8-watt lamps and a "merry-go-round" apparatus (The Southern New England Ultraviolet Co., Middletown, Conn.). All samples were

degassed by purging with nitrogen for a period of 45 min prior to irradiation.

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   (b) Schaap, A. P., and Faler, G. R. (1973) J. Amer. Chem. Soc. 95, 3381.
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9. In independent studies it has been shown that sensitized irradiation of 1 affords 9-phenanthrol (3) as the major product (8a). Similarly, benzene oxide gives phenol upon photolysis in the presence of acetone as a solvent sensitizer; Holovka, J. M., and Gardner, P. D. (1967) J. Amer. Chem. Soc. 89, 6390.
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