

be unexpected in view of the susceptibility of silacyclopropanes to nucleophilic ring opening.¹²

Attempts to observe the type A product (8) at low temperature and in nonnucleophilic solvents have been unsuccessful. The dienones were photostable, neat at 77°K, and only polymeric products were observed in solvents other than *tert*-butyl alcohol.

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Photolysis of Arene Oxides at Low Temperatures. Oxygen Walks and Keto Tautomers of Phenols

Sir:

Walk reactions, rearrangements in which a divalent group (-O-, -NR-, CR₂-) that is part of a three-membered ring undergoes migration along the surface of a cyclic π system, have been detected under a variety of conditions. Thermal isomerizations of substituted tropilidenes¹ and norcaradienes² occur with migration of the methylene group of a cyclopropane ring. Azepins undergo related thermal rearrangements.³ In contrast to these thermal reactions, oxido-⁴⁻⁶ and iminoannulenes⁴ as well as arene oxides⁷⁻⁹ undergo similar migrations of oxygen and substituted nitrogen probably by ionic pathways. Finally, several substituted norcaradienes¹⁰⁻¹² show this type of isomerization under the influence of light. The present study describes the photolysis of arene oxides at reduced temperature. An arene oxide in equilibrium with an oxepin (1), a K-region arene oxide (2), and a non-K-region arene oxide (3) have been examined as they represent the major classes of arene oxides.¹³

Keto tautomers of phenols have been postulated¹⁴ as nonenzymatic isomerization products of arene oxides since such tautomers readily explain the intramolecular migration and retention of aromatic ring substituents¹⁵ (the NIH shift) observed during enzymatic hydroxylation. While the keto tautomer of phenol itself has never been detected, several reports of the chemical¹⁶⁻¹⁸ and photochemical generation of keto tautomers of phenols bearing bulky substituents at the 2,6-positions have appeared.^{19,20} Keto tautomers of naphthols and phenanthrols are unknown. In certain higher polycyclic systems, the keto tautomers predominate;²¹ 9-anthrol has 89% of the keto form at equilibrium and only the keto form of 10-hydroxypentacene is known. Despite the fact that oxiranes with aryl substituents tend to undergo reactions other than C-O bond cleavage on photolysis,²² arene oxides readily photoisomerize to phenols.^{23,24} The isomerization is accompanied by the NIH shift.²³

Photolysis of benzene oxide-oxepin (1) with 3100 Å light gives 2-oxabicyclo[3.2.0]hepta-3,6-diene,²⁵ while irradiation with 2537 Å light at -80° produces mainly phenol and only minor amounts of the above diene and benzene.²⁴ Under the latter conditions, sensitization by acetone (solvent) produced phenol exclusively. We have reexamined the photolysis of 1. After 30-min irradiation (2537 Å) of 1-3,6-*d*₂^{26,27} in acetone-*d*₆ at room temperature in a quartz tube, nmr analysis indicated 40% of the sample had been converted to phenol. About 12% of the remaining oxide had undergone an oxygen migration to 1-1,4-*d*₂ as evidenced by the appearance of β -hydrogens as a broad apparent doublet at δ 5.83 and by increasing complexity of the signal at

(13) See D. M. Jerina, H. Yagi, and J. W. Daly, *Heterocycles*, **1**, 267 (1973), for a review on the synthesis and chemistry of the arene oxide-oxepin system.

(14) D. R. Boyd, D. M. Jerina, and J. W. Daly, *Biochemistry*, **11**, 1961 (1972). Isomerization of either [1-²H]- or [2-²H]naphthalene 1,2-oxide to 1-naphthol at neutral pH occurs with 80% retention of deuterium from either substrate, a result which suggests the keto tautomer of 1-naphthol as the common intermediate from both substrates. Discussion of the involvement of keto tautomers in the aromatization of other arene oxides is available.^{13,15}

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(25) E. Vogel and H. Gunther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967).

(26) For the synthesis of 1-3,6-*d*₂, 1,4-cyclohexadiene-3,3,6,6-*d*₄, obtained from Merck, was converted to the desired oxide as previously described.²⁷ The nmr spectrum of the oxide in acetone showed two sharp singlets at δ 5.27 and 6.20 for the α - and γ -hydrogens of 1.

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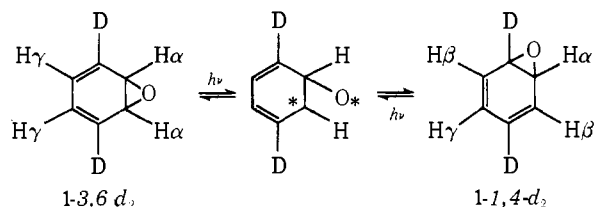
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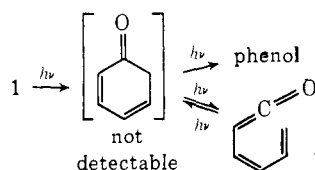
(10) G. W. Gruber and M. Pomerantz, *J. Amer. Chem. Soc.*, **91**, 4004 (1969).

(11) L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **93**, 5128 (1971).

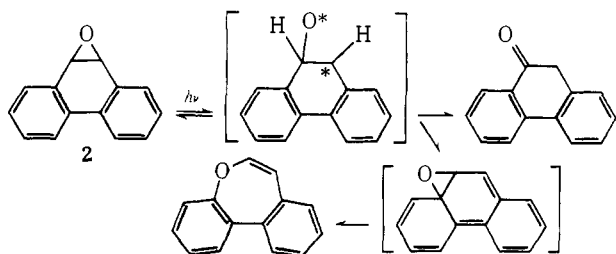
(12) H. E. Zimmerman and W. Eberbach, *J. Amer. Chem. Soc.*, **95**, 3970 (1973).



the α - and γ -hydrogen positions. Further irradiation led to complete isomerization to phenol, possibly due to acid catalysis by the photoexcited phenol. When **1** as a thin film was irradiated through Pyrex at 77°K, its absorption at 1660 cm^{-1} decreased and a strong, sharp absorption at 2112 cm^{-1} attributable to a ketene appeared. After a total of 10 min of irradiation, a photostationary state was reached at which the amount of ketene remained constant and phenol began to appear (1590 cm^{-1}) at the expense of **1**. At no point could a band attributable to carbonyl absorption be detected in the region 1600–1800 cm^{-1} . The keto tautomer was assumed to be present in low concentration, since both a ketene and phenol were formed.²⁸ On warming to –90 to –100°, the ketene signal rapidly disappeared.



Irradiation of phenanthrene, 9,10-oxide (**2**) as a suspension in Nujol at 77°K led to a new band at 1695 cm^{-1} attributable to a carbonyl as well as new bands at 1600 and 1650 cm^{-1} . Repetitive spectra taken during photolysis gave no indication of ketenes or CO. As the sample was allowed to reach room temperature, the carbonyl absorption disappeared. A new band at 1625 cm^{-1} appeared, while absorption at 1600 cm^{-1} broadened and increased due to the formation of 9-phenanthrol. As the 1650- cm^{-1} region remained unchanged on warming, a thermally stable product, identified as 2,3,4,5-dibenzoxepin,²⁹ formed. It also forms on photolysis at room temperature but to a lesser extent relative to phenanthrol. In a preparative experiment at room temperature, 60 mg of **2** as a stirred suspension in 3 ml of ether was irradiated with 2537 Å light for 40 min. Preparative tlc on silica gel with CHCl_3 containing 5% triethylamine led to isolation of 9-phenanthrol (40%), 2,3,4,5-dibenzoxepin (30%), phenanthrene (10%), and recovered **2** (10%) in addition



to other minor and unidentified components.³⁰ In

(28) Photoequilibria between nonenolizable cyclohexadienones and ketenes have ample precedent. D. Lemmer and H. Perst, *Tetrahedron Lett.*, 2735 (1972).

(29) Distinct bands all of medium or greater intensity at 1600, 1650, 1430, 1260, 1100, and 1025 cm^{-1} were present.

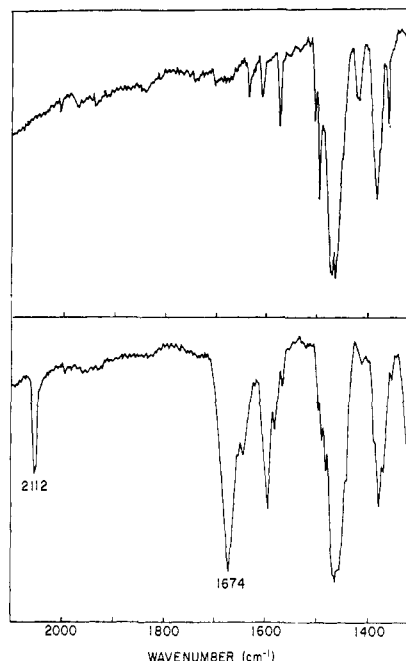


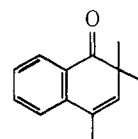
Figure 1. Infrared absorption spectra at 77°K of naphthalene 1,2-oxide before (top) and after (bottom) irradiation for 30 min with a medium-pressure Hg lamp as a suspension in Nujol. The appearance of bands at 2112 and 1674 cm^{-1} after irradiation is due to a ketene and the keto tautomer of 1-naphthol, respectively.

contrast to **1**, the keto form of 9-phenanthrol is readily observable at low temperature. A ketene cleavage is not detected here, since that would interfere with the aromaticity of both rings. Migration of oxygen for **2** proceeds by ring expansion to the resonance stabilized dibenzoxepin. This reaction may proceed stepwise as shown, or *via* a synchronous rearrangement.

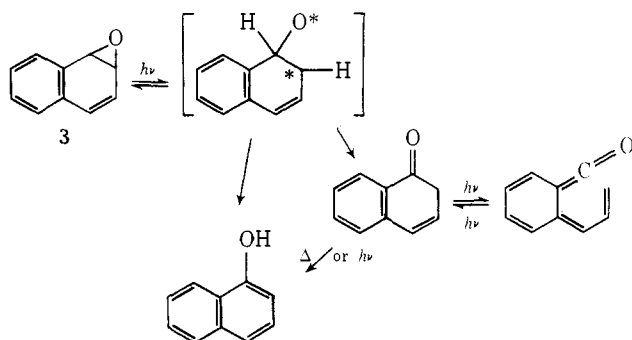
When a suspension of naphthalene 1,2-oxide (**3**) in Nujol was irradiated at 77°K through quartz for 2 min, a carbonyl band (1674 cm^{-1}),³¹ 1-naphthol (1595 cm^{-1}),³² and a small ketene absorption (2112 cm^{-1}) were detected. The bands due to ketene and ketone maximized after a total of 10 min of irradiation, while the ratio of ketene to ketone was constant after 2 min (Figure 1). Irradiation for longer than 10 min led only to increased amounts of 1-naphthol. Both the ketene and ketone absorptions disappeared with concurrent increase in the absorption for 1-naphthol when the sample was allowed to warm to –100°. Only 1-naphthol was detected when **3** was irradiated at –80° in CH_2Cl_2 solu-

(30) The structures of all of these products were confirmed by R_f on tlc and by nmr and mass spectra. During the course of this study N. E. Brightwell and G. W. Griffin, *J. Chem. Soc., Chem. Commun.*, 37 (1973), have described the photoisomerization of **2** into the dibenzoxepin which they synthesized by an unambiguous route. They subsequently reported the formation of fluorene as a minor photoisomerization product of **2**; B. J. Dowty, N. E. Brightwell, J. L. Laseter, and G. W. Griffin, *Biochem. Biophys. Res. Commun.*, 57, 452 (1974).

(31) H. Hart and R. K. Murray, *J. Org. Chem.*, 35, 1535 (1970), report a carbonyl absorption at 1673 cm^{-1} for



(32) Neither cooling of 1-naphthol to 77°K nor irradiation at that temperature gives any indication for the formation of the keto tautomers considered in this study.



tion. Formation of a ketene from **3** is presumed to be minor since aromaticity must be destroyed. Significant amounts of products resulting from migration of oxygen were not detected.

In summary, only **2** produces a keto tautomer without a detectable amount of the corresponding phenol at 77°K. This ketone gains the least amount of resonance stabilization on enolization. Despite the large amount of ketone from **2**, this is the only oxide for which a ketene could not be detected as aromaticity in two rings must be destroyed. In contrast **1** produced the largest amount of ketene even though the concentration of the keto tautomer was below detection at 77°K. Migration of oxygen was readily detected for **1** and **2**. In principle these isomerizations might be explicable in terms of the generation of an oxene or oxygen atom from the parent oxide followed by readdition at a different pair of ring carbons to form an isomerized arene oxide. The extrusion of oxygen, though previously observed²⁴ for **1** and detected here for **2**, is an unlikely explanation for these isomerizations, since attempts to trap the oxygen liberated from arene oxides by reactive aromatic acceptors, such as anisole, have been unsuccessful.³³

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(33) Unpublished observations by D. R. Boyd, previously at NIH.

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Rhodophytin, a Halogenated Vinyl Peroxide of Marine Origin

Sir:

Marine algae have recently received considerable attention due to their synthesis of unusual secondary metabolites. In particular, members of the genus *Laurencia*¹⁻⁵ (Rhodomelaceae, Rhodophyta) are noted

(1) J. J. Sims, W. Fenical, P. Radlick, and R. M. Wing, *J. Amer. Chem. Soc.*, **93**, 3774 (1971).

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(3) A. G. González, J. Darias, J. D. Martín, and C. Pérez, *Tetrahedron Lett.*, 1249 (1974).

(4) T. Irie, M. Suzuki, and T. Masamune, *Tetrahedron*, **24**, 4193 (1968).

(5) J. J. Sims, G. H. Y. Lin, R. M. Wing, and W. Fenical, *J. Chem. Soc., Chem. Commun.*, 470 (1973).

for their unique synthesis of bromine- and chlorine-containing compounds. Recently, we reported⁶ the X-ray structure of chondriol (**1**), an antiviral acetylene-containing metabolite identified first as a constituent of *Chondria oppositoclada* Dawson. Subsequent chemotaxonomic studies of this morphologically complex group of seaweeds have revealed the origin of chondriol as a distinct *Laurencia* species⁷ indigenous to the Gulf of California. In this communication I wish to report the structure of rhodophytin (**2**), a most unusual natural product obtained from the same *Laurencia* source. Rhodophytin contains the first example of a vinyl peroxide moiety.

Rhodophytin, $[\alpha]_D^{25} -141.5^\circ$ (*c* 6.85, hexane), is a light mobile oil obtained in high yield (0.05% dry weight) by column chromatography of a chloroform extract of the alga. The high resolution mass spectrum of rhodophytin showed an intense *M* - 16 fragment at 328/330/332, which established its halogen content ($C_{15}H_{18}OBrCl$). The facile loss of an oxygen atom under mass spectral conditions was the first indication of the peroxide functionality of this metabolite.

The infrared absorption of **2** showed the terminal acetylene (3300 cm^{-1}), the multiple double bonds (3030 and 1648 cm^{-1}), and the carbon-oxygen single bond stretch (1109 cm^{-1}), in close analogy to the spectral characteristics of chondriol. Bands were not observed for either the hydroxyl or carbonyl functional groups.

Hydrogenation of rhodophytin with platinum in ether gave 7-chloro-6-hydroxypentadeca-12-one. The nmr and mass spectra of this keto-alcohol, *m/e* 276 ($C_{15}H_{29}O_2Cl$), established that rhodophytin was based on an *n*-pentadecane skeleton and confirmed the presence of two oxygen atoms. An intense fragment at *m/e* 86 in the mass spectrum was strong evidence⁸ for positioning the carbonyl at C-12. Jones oxidation⁹ converted the keto-alcohol to 7-chloropentadeca-6,12-dione in high yield. A comparison of the 220-MHz nmr spectra of these products, aided by double resonance experiments, proved the vicinal arrangement of oxygen and chlorine atoms on C-6 and C-7 in these derivatives.

A comparison of the ¹³C nmr spectra of rhodophytin and chondriol (Table I) showed six identical olefin carbon atoms in each structure. It follows from the molecular weight and the total of 18 hydrogen atoms that rhodophytin must contain seven double-bond equivalents: one assigned to two halogen substituents, five for unsaturation, and one for the ring system. Since rhodophytin is based on an *n*-pentadecane skeleton, and, since neither oxygen atom component is part of a hydroxyl or carbonyl function, ring formation must involve peroxide bond formation. In confirmation, rhodophytin gives a strong iodine coloration upon treatment with acidified potassium iodide in aqueous methanol.¹⁰

(6) W. Fenical, K. B. Gifkins, and J. Clardy, *Tetrahedron Lett.*, 1507 (1974).

(7) W. Fenical and J. N. Norris, *J. Phycology*, in press.

(8) An *m/e* fragment = 86 is strongly suggestive of a ketone β scission reaction to yield $CH_2CH_2CH_2C(=OH^+)CH_2$. See F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1967.

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