

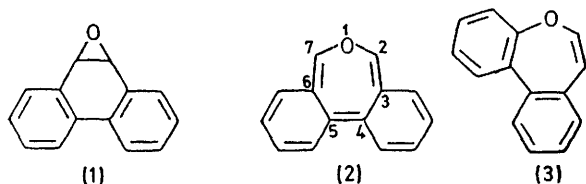
## Photorearrangement of 9,10-Epoxy-9,10-dihydrophenanthrene. Synthesis of 2,3:4,5-Dibenzoxepin

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**Summary** 9,10-Dihydro-9,10-epoxyphenanthrene undergoes photorearrangement to 1,2:3,4-dibenzoxepin, an unknown oxepin, which was synthesized independently.

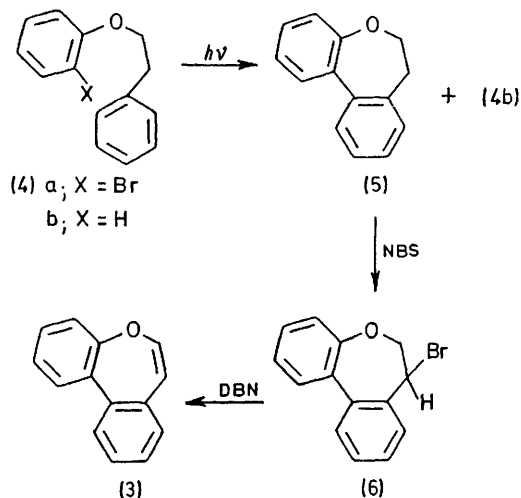
APPLICATION of the Woodward-Hoffmann orbital symmetry rules<sup>1</sup> to the hypothetical valence isomerization of 9,10-epoxy-9,10-dihydrophenanthrene (**1**)<sup>2</sup> reveals that rupture of the key cross link of (**1**) to give 3,4:5,6-dibenzoxepin (**2**) should be an allowed concerted disrotatory process



in the ground state [as would be the retro-electrocyclization of (**2**) to (**1**)] although other factors<sup>3</sup> intervene and in fact the only reported thermolysis product is 9-phenanthrol.<sup>2</sup> Conrotatory opening of (**1**) in the first excited state, however, would lead to a prohibitively strained *trans,cis,cis*-oxepin and consideration of this restriction led us to investigate the photochemistry of (**1**) which unlike most other 2,3-diaryl-oxirans should be constrained to undergo preferential C-O bond cleavage upon photolysis.<sup>4,5</sup>

When (**1**) was irradiated, following degassing by nitrogen purging, in benzene at 254 nm, the major product isolated (20%) was 2,3:4,5-dibenzoxepin (**3**).† Isolation of (**3**) was achieved by thick layer chromatography on silica gel with benzene-hexane (1:4) as eluant and subsequent purification

was accomplished by gas chromatography. Thin layer analyses of aliquots of the photolysis mixture obtained from (**1**) at low conversion indicates that (**3**) is a primary photoproduct. Identical results were obtained with (**1**) when acetonitrile was used as solvent, thus excluding the possibility that benzene is required as a solvent sensitizer.



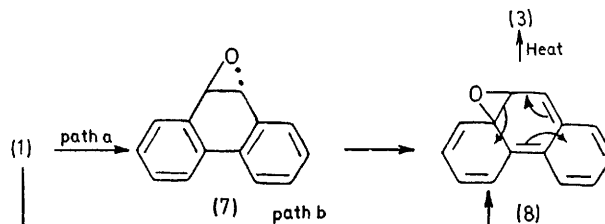
The assignment of structure (**3**) to the photoproduct obtained from (**1**) was confirmed by independent synthesis. The bromo-ether (**4a**) (b.p. 210°/3 mm) was prepared by etherification of *o*-bromophenol with  $\beta$ -phenethyl bromide in acetone using potassium carbonate as a base (60%).<sup>6</sup> Photolysis of (**4a**) in acetonitrile gives the dihydrodi-

† All new compounds had satisfactory u.v., n.m.r., and mass spectra and combustion analyses.

benzoxepin (**5**), m.p. 109—110.5° (35%) in addition to the reduction product (**4b**) (23%). Separation of (**5**) from (**4a**) and (**4b**) and intractable photoproducts was achieved by thick layer chromatography. Henderson and his co-workers<sup>7</sup> had previously employed this photocyclization technique for the synthesis of the aza-analogue of (**5**) from *o*-iodo-(*N*- $\beta$ -phenethyl)aniline. The ether (**5**) was converted into the bromide (**6**) with *N*-bromosuccinimide (NBS) in carbon tetrachloride. Subsequent dehydrobromination of the bromide which was not isolated was accomplished by stirring with 1,5-diazabicyclo[4,3,0]nonene (DBN) in tetrahydrofuran.<sup>8</sup> The spectral properties of the resulting product, isolated by thick layer chromatography and subsequent g.l.p.c., were identical in all respects to that of the photoproduct (**3**) obtained from (**1**).

A stepwise mechanism for the photoconversion of (**1**) into (**3**) may be written involving initial homolysis of the C—O bond to give the diradical (**7**), followed by cyclization to (**8**) (see Scheme) which then would undergo thermal valence isomerization to (**3**) (path a). The suggested intermediate (**7**) may be circumvented if a concerted suprafacial [1,5] interconversion of (**1**) into (**8**) is invoked (path b). Such a process is consistent with orbital symmetry requirements and of lowest energy (allowed) in the first excited state provided inversion at oxygen occurs. We have confirmed that 9-phenanthrol is indeed produced

upon prolonged heating of (**1**) above its melting point (150—200°) and the allowed concerted conversion of (**1**) into (**2**) is apparently by-passed. A sequential mechanism is suggested for the thermal conversion of (**1**) into 9-phenanthrol implicating intermediate (**7**) which suggests that the photoisomerization to (**8**) is concerted (path b).



SCHEME.

The photorearrangement of (**1**) to (**3**) by way of (**8**) may be viewed as an analogue of a photochemical Berson-Willcott rearrangement<sup>9</sup> and formally is related to the photoisomerization of 2,3-benzonorcaradiene to 1,2-benzotropyliene.<sup>10</sup>

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<sup>1</sup> R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.

<sup>2</sup> M. S. Newman and S. Blum, *J. Amer. Chem. Soc.*, **1964**, **86**, 5598.

<sup>3</sup> M. J. S. Dewar and N. Trinajstić, *Tetrahedron*, **1970**, **26**, 4269. Semi-empirical SCF MO calculations conducted by these investigators imply that annelation of benzene with the 3,4 bond of oxepin should be extremely unfavourable and no members of this class of which (**2**) is representative are known.

<sup>4</sup> G. W. Griffin, *Angew. Chem. Internat. Edn.*, **1971**, **10**, 537; *Angew. Chem.*, **1971**, **83**, 604.

<sup>5</sup> D. R. Arnold and L. A. Karnischky, *J. Amer. Chem. Soc.*, **1970**, **92**, 1404.

<sup>6</sup> 'Organic Syntheses,' Coll. vol. III, ed. E. C. Horning, Wiley, New York, 1955, p. 140.

<sup>7</sup> W. A. Henderson, jun., R. Lopresti, and A. Zweig, *J. Amer. Chem. Soc.*, **1969**, **91**, 6049.

<sup>8</sup> E. Vogel and F.-G. Klarner, *Angew. Chem. Internat. Edn.*, **1968**, **7**, 374.

<sup>9</sup> J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **1966**, **88**, 2494.

<sup>10</sup> G. W. Gruber and M. Pomerantz, *J. Amer. Chem. Soc.*, **1969**, **91**, 4004.