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

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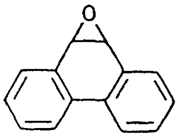
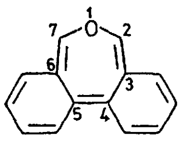
Summary 9,10-Dihydro-9,10-epoxyphenanthrene undergoes photorearrangement to 1,2:3,4-dibenzoxepin, an unknown oxepin, which was synthesized independently.

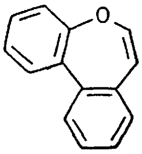
Application of the Woodward–Hoffmann orbital symmetry rules[1] to the hypothetical valence isomerization of 9,10-epoxy-9,10-dihydrophenanthrene (**1**)[2] reveals that rupture of the key cross link of (**1**) to give 3,4:5,6-dibenzoxepin (**2**) should be an allowed concerted disrotatory process in the ground state [as would be the retro-electrocyclization of (**2**) to (**1**)] although other factors[3] intervene and in fact the only reported thermolysis product is 9-phenanthrol.[2] 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-diaryloxirans should be constrained to undergo preferential C–O bond cleavage upon photolysis.[4,5]



(**1**)

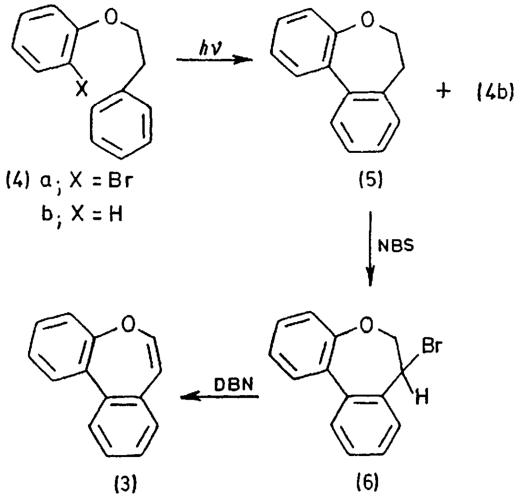


(**2**)



(**3**)

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.

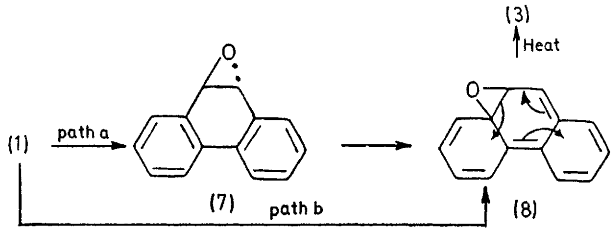


The assignment of structure (**3**) to the photoproduct obtained from (**1**) was confirmed by independent synthesis. The bromo-ether (**4a**) (b.p. 210°/3 mm) was prepared by etherification of *o*-bromophenol with β-phenethyl bromide in acetone using potassium carbonate as a base (60%).[6] Photolysis 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[7] had previously employed this photocyclization technique for the synthesis of the aza-analogue of (**5**) from *o*-iodo-(*N*-β-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.[8] 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[9] and formally is related to the photoisomerization of 2,3-benzonorcaradiene to 1,2-benzotropylidene.[10]

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