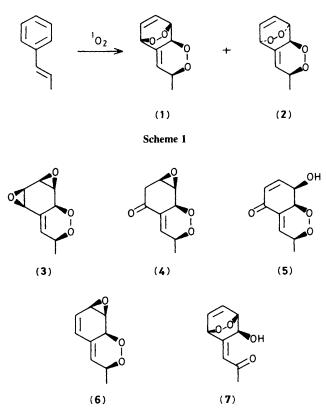
Polyoxygenated Cyclohexenes from Aromatic Compounds: Selective Reactions of Bis(endoperoxides)

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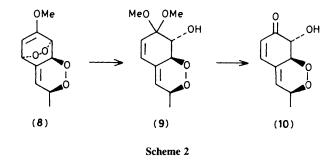
Selective rearrangements of the styrene bis(endoperoxide) (1) at a single endoperoxide ring have been observed on thermolysis, photolysis, or treatment with triethylamine; reduction by phosphorus(\mathfrak{m}) reagents gives reaction at the bicyclic endoperoxide ring of the bis(endoperoxides) (1) and (8).

The reaction of singlet oxygen $({}^{1}O_{2})$ with styrenes is unusual, in that the aromatic ring is attacked along with the exocyclic double bond, to give bis(1,4-endoperoxides) [*e.g.* (1) and (2), formed from β -methylstyrene as shown in Scheme 1].^{1,2} Although 1,4-endoperoxides have been much used as a convenient functional group for subsequent synthetic transformations,^{3,4} very little is known about the chemistry of bis(endoperoxides). We now show that compounds such as (1) are capable of being transformed selectively at either endoperoxide ring, by stereospecific reactions. Sensitised photooxidation of β -methylstyrene gives the bis(endoperoxide) (1) as the major product,¹ separable by column chromatography



in yields up to 30%. Thermolysis or photolysis[†] of (1) gave diepoxide (3) as the minor product (30–35%), whilst the major component (65–70%) was the β , γ -epoxy-ketone (4), clearly identifiable from the ¹H and ¹³C n.m.r. spectra of the crude reaction mixtures. On chromatography using silica gel, the epoxy-ketone (4) rearranged cleanly to give the hydroxyenone (5). N.m.r. spectra suggested that compounds (4) and (5) were each a single stereochemical and positional isomer.[‡] The presence of a single olefinic proton in the products (3) and (4) shows that selective rearrangement of the more strained *bicyclic* peroxide bridge has occurred.⁵ In the present example, the formation of (4) as the major component is curious, since the thermolysis of endoperoxides has often been assumed to give *syn*-diepoxides as the sole products.^{5,6}

The reaction of (1) with trimethyl phosphite in dichloromethane or with triphenylphosphine in benzene at 20 °C gave, in high yield (70% after chromatography), the epoxyendoperoxide (6) whose conjugated diene structure was obvious from its u.v. absorption. This reduction is the first simple example of attack by a reagent on a bicyclic peroxide ring, in the



presence of a monocyclic peroxide. Alternatively, treatment of (1) with triethylamine in dichloromethane at 0 °C led within a few hours to an essentially quantitative yield of a simple compound, assigned the hydroxyenone structure (7). The high selectivity observed in this latter case is most likely due to the accessibility of the α -proton on the *monocyclic* peroxide ring towards attack by triethylamine acting as a base.⁷

These rearrangements are not restricted to monosubstituted styrenes; introduction of a masked carbonyl group into the ring is possible, for example. Thus, the reaction of *p*-methoxy- β -methylstyrene with ${}^{1}O_{2}$ gave the bis(endoperoxide) (8) (35%).§ Treatment of (8) with triphenylphosphine and methanol gave the acetal (9) (73%), easily deprotected to yield dienone (10), as shown in Scheme 2. Alternatively, compound (10) was obtained by treatment of the bis(endoper-oxide) (8) with trimethyl phosphite in dichloromethane, followed by chromatography on moist silica gel (50% overall yield).

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[†] Thermolysis: heated in benzene solution under reflux, 3 h, to give (3) and (4) in a ratio of 35:65. Photolysis: medium-pressure mercury arc, 1% solution in benzene, quartz apparatus, giving (3) and (4) in a ratio of 30:70; compound (1) in benzene shows u.v. absorption tailing to *ca.* 400 nm, with $\varepsilon = 26$ at 313 nm.

 $[\]ddagger$ Satisfactory ¹H and ¹³C n.m.r. spectra, i.r. spectra, and elemental analysis and/or mass spectra were obtained for all new compounds, with the exception of the epoxy-ketone (4) which could not be isolated without isomerisation to (5).

[§] The stereochemistry shown for the adduct was clearly discernible by comparison of ¹H n.m.r. chemical shifts with related examples: see ref. 1 and H. Kotsuki, I. Saito, and T. Matsuura, *Tetrahedron Lett.*, 1981, 469.