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PHOTOLYSIS OF SATURATED BICYCLIC PEROXIDES

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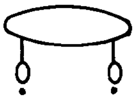
Abstract. Under direct photolysis, [*n*.2.1]-peroxides (*n* = 3-5) isomerise chiefly to epoxyaldehydes, [*n*.2.2]-peroxides (*n* = 2-4) mainly undergo dehydrogenation to cycloalkane-1,4-diones, and 2,3-dioxabicyclo[2.2.1]heptane exhibits both types of behaviour; photo-isomerisation of 6,7- into 6,8-dioxabicyclo[3.2.1]octane occurs when benzophenone is present as sensitizer.

Several saturated bicyclic peroxides have recently been prepared for the first time, largely in response to the need for chemical models of the naturally occurring 2,3-dioxabicyclo[2.2.1]heptane derivatives that play a central role in the arachidonic acid cascade.[1] Homolytic cleavage of the O-O bond in these saturated bicyclic peroxides offers a route to an interesting new class of diradicals, the cycloalkanedioxyls (1). It has already been established[2] that the chemistry of oxygen-centred diradicals (2) derived from monocyclic peroxides is distinct from that of caged (3) or free alkoxyl radicals obtained from acyclic peroxides, and it is of interest to see how this is further modified by the additional constraints imposed by the presence of the cycloalkane ring.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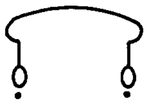
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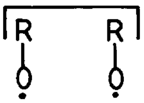

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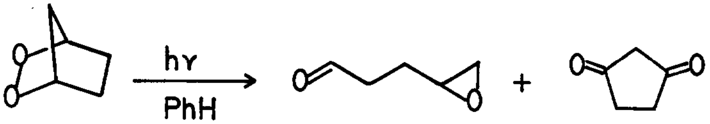
Studies of the thermolysis of saturated bicyclic peroxides in the gas phase[3,4] and in solution[5,6] have provided a fair body of information on the behaviour of thermally generated cycloalkanedioxyls. In contrast, the photolysis of these compounds is virtually unexplored, yet the potential facility for isolating thermally labile primary products and the possibility of the photolytically generated diradicals behaving differently to the thermally derived species by virtue of possessing different spin multiplicities and/or electronic configurations,[2] suggest that new transformations might be achieved. Indeed, in the one example of which we are aware, the direct photolysis of 1,5-dimethyl-6,7-dioxabicyclo[3.2.1]octane afforded a completely different product to that of thermolysis, while benzophenone-sensitized photolysis provided a quantitative yield of the pheromone frontalin.[4] We now report the preliminary results of a study of the photolysis of seven unsubstituted dioxabicycloalkanes, namely the [2.2.1]-peroxide, three [*n*.2.1]-homologues (*n* = 3-5), and three [*n*.2.2]-homologues (*n* = 2-4).

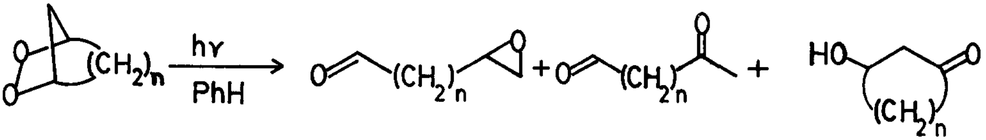
A solution of each peroxide (100-150 mg) in benzene (1 cm^3) in an n.m.r. tube was irradiated for 20-40 h with a Hanovia medium pressure mercury arc fitted with a pyrex sleeve, and the progress of the reaction was followed by ^1H n.m.r. spectroscopy. Products were identified by comparison with authentic samples, and product distributions were estimated by ^1H-decoupled ^{13}C n.m.r. spectroscopy.

The major product from 2,3-dioxabicyclo[2.2.1]heptane was 4,5-epoxypentanal as found previously for thermolysis in the gas phase[3a] or in solvents of low polarity,[5b] but cyclopentane-1,3-dione (25%) was also obtained (equation 1) and was readily isolated since it crystallised out during the photolysis.



(1)

It is interesting to note that the two types of product obtained for the [2.2.1]-peroxide reflect the major transformations observed for the two different types of higher homologue. Thus, the [*n*.2.1]-peroxides afforded mainly epoxyaldehyde (*n* = 3, 70%; *n* = 4, 60%; *n* = 5, 45%) together with ketoaldehyde and about 10% of 3-hydroxycycloalkanone (equation 2), while the [*n*.2.2]-compounds gave predominantly cycloalkane-1,4-diones (equation 3).



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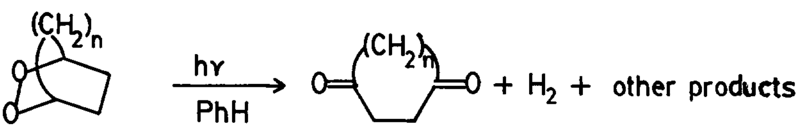
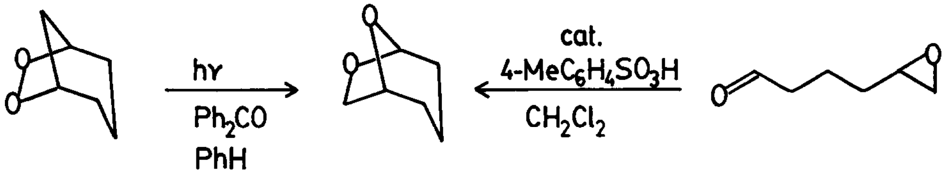


(3)

The product distributions for the [*n*.2.1]-peroxides are markedly different to those from gas phase thermolysis[3b] where the ketoaldehydes are obtained in over 90% yield. The small amounts of 3-hydroxycycloalkanone probably arise by induced decomposition and have been observed also in the thermolysis of the [4.2.1]-peroxide in solution.[6] For the [*n*.2.2]-peroxides, on the other hand, the major pathway for photodecomposition is the same as that for thermolysis.[3b] A solution of the [3.2.2]-peroxide in C_6D_6 was evacuated and sealed, and after photolysing the sample, the gas phase was examined by laser Raman spectroscopy.[7] That H_2 was detected while HD was not lends some support to our earlier suggestion[3b] that molecular hydrogen is extruded from the intermediate cycloalkanedioxyl. The competing elimination of ethylene to form α,ω-dialdehydes which occurs thermally,[3b] was not identified with certainty in the photolyses, although aldehydic protons were detected in the ^1H n.m.r. spectra of the products. Photolysis of the [4.2.2]-peroxide was less clean than that of the other [*n*.2.2]-compounds. This resembles the thermal behaviour, where 25% of a product originally described as 7-ethenyloxepan-2-ol was obtained.[3b] The same product was obtained in lower yield in the photolysis, but its structure has now been unambiguously identified as 2-hydroxy-5-(3-butenyl)tetrahydrofuran, which suggests that some four-carbon bridge cleavage takes place in the decompositions.

Benzophenone-sensitized photolysis of the [3.2.1]-peroxide afforded 6,8-dioxabicyclo[3.2.1]octane as major product (50-60%) and this could also be prepared by acid-catalysed isomerisation of the corresponding epoxyaldehyde (equation 4).



(4)

This change in the pathway of photo-isomerisation upon introduction of a sensitizer parallels the behaviour of the 1,5-dimethyl derivative,[4] and a similar explanation can be offered. Cleavage of the one-carbon bridge after, or in concert with, O-O homolysis affords a 1,3-diradical containing an aldehyde group. In the direct photolysis this is a singlet species which can collapse to the epoxyaldehyde, but in the sensitized photolysis it is a triplet species in which there is time for bond rotation and intramolecular addition to the aldehyde group to precede spin inversion. The observation that the [4.2.1]- and [5.2.1]-peroxides did not undergo analogous rearrangements is consistent with this picture, since such processes would require the formation of unfavourable 7- or 8-membered rings in the intramolecular addition. The 6,8-dioxabicyclo[3.2.1]octane system is a structural feature of several natural products,[8] and our results suggest that the peroxide-based approach which was successful in the synthesis of frontalin[4] may have more general application.

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