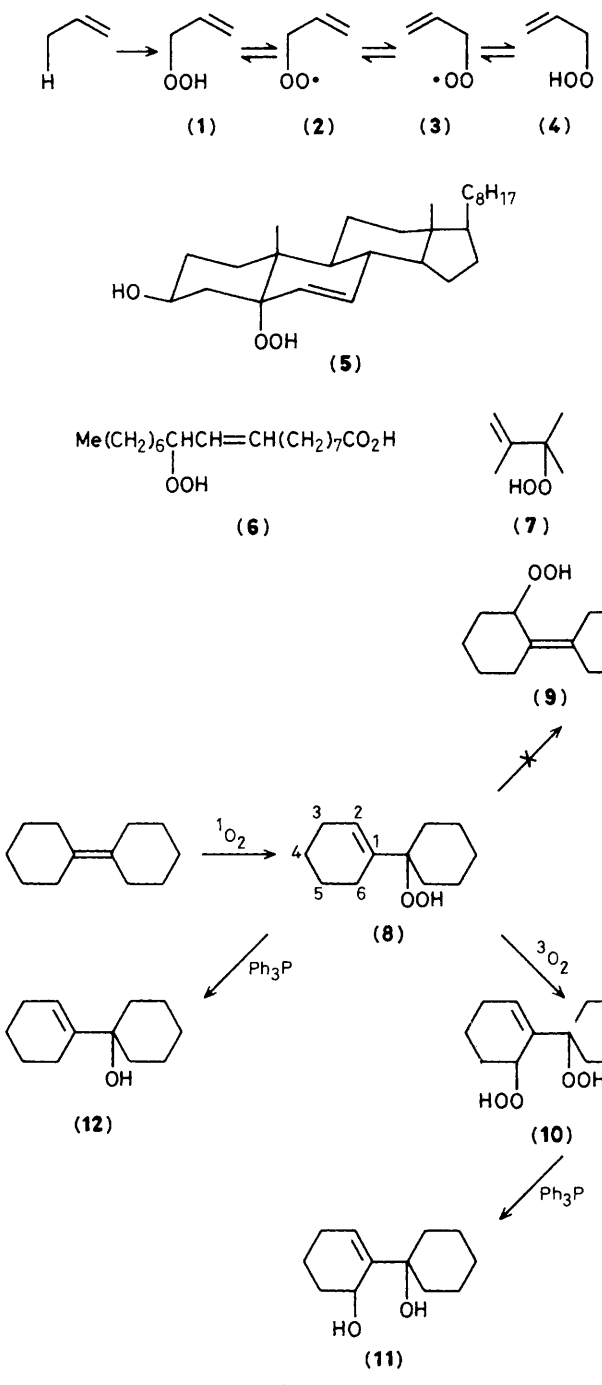
1-(Cyclohex-1-enyl)cyclohexyl Hydroperoxide: Intramolecular Propagation of Autoxidation as an Alternative Reaction to Allylic Rearrangement

Alwyn G. Davies,* Ian G. E. Davison, and Carl H. Schiesser

Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

The allylperoxyl radical derived from 1-(cyclohex-1-enyl)cyclohexyl hydroperoxide does not undergo allylic rearrangement, but in the presence of oxygen it undergoes autoxidation with an intramolecular propagation step, leading to the formation of 1-(6-hydroperoxycyclohex-1-enyl)cyclohexyl hydroperoxide.

Allylic hydroperoxides (**1**) are widespread compounds which are formed when alkenes are exposed to triplet (aerobic) or singlet oxygen, and which play important roles in many industrial and biological processes. In non-polar solvents they undergo rearrangement to the isomeric allylic hydroperoxides (**1**) → (**4**) *via* the corresponding allylperoxyl radicals (**2**) and (**3**).[1—3] In the case of the 5α-hydroperoxide (**5**) derived from cholesterol, the rearrangement occurs suprafacially.[1] This, together with the fact that neither (**5**)[4] nor the hydroperoxides [*e.g.* (**6**)] derived from oleic acid[5] incorporate labelled oxygen

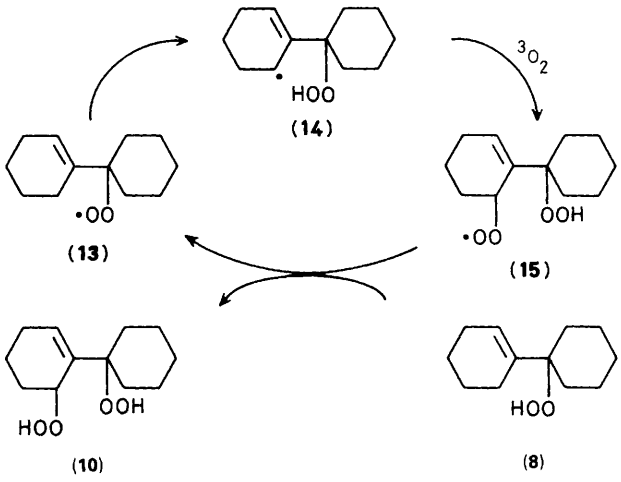


Scheme 1

when the rearrangements are carried out under an atmosphere of $^{18}O_2$, suggests that the rearrangement follows a non-dissociative sigmatropic mechanism.

The rates of the rearrangements of the hydroperoxides show a surprising dependence on structure. For example, the self-initiated rearrangement of (**5**) in deuteriochloroform at 30 °C shows a half-life of about 7 h,[4] but 2,3-dimethylbut-3-en-2-yl hydroperoxide (**7**) is reported to be resistant to rearrangement under similar conditions.[6]

In an attempt to elucidate the factors which control the rates of these rearrangements, we have examined the properties of the title compound (**8**) and have identified an alternative reaction which can occur to the exclusion of the rearrangement.



Scheme 2

The hydroperoxide (**8**) is readily prepared by the reaction of cyclohexylidenecyclohexane with singlet oxygen.[7] When (**8**) in deuteriochloroform in the absence of oxygen was kept at room temperature for two months, or 40 °C for 97 h (conditions under which rearrangements have been observed with other allylic hydroperoxides[4,8,9]), no rearrangement to the allylic isomer (**9**) could be detected (400 MHz n.m.r.). During 3 h at 80 °C, the hydroperoxide (**8**) appeared to decompose, to give a mixture of unidentified products (Scheme 1).

However, ^{1}H n.m.r. spectroscopy showed that under air or oxygen, (**8**) in chloroform was converted into a dihydroperoxide with the probable structure (**10**).† This was confirmed by a single crystal *X*-ray diffraction study of the diol (**11**)[10] which was prepared by the reduction of (**10**) with triphenylphosphine.

It appeared surprising on steric and electronic grounds, however, that hydrogen abstraction should occur intermolecularly from the methylene group at position 6, rather than position 3 in the propagation step of the chain autoxidation.[11]

We therefore propose that intramolecular abstraction of hydrogen by the peroxyl radical at the sterically accessible 6-CH_2 group [(**13**) → (**14**)] is the dominant allyl radical-forming process in this autoxidation, as depicted in Scheme 2. The allylic radical (**14**) then reacts with oxygen to give the secondary peroxyl radical (**15**) which does not abstract allylic hydrogen either inter- or intra-molecularly (else abstraction from the 3-CH_2 would be expected to occur). Instead it abstracts the hydroperoxylic hydrogen from the parent hydroperoxide (**8**) to give the dihydroperoxide (**10**) and the chain-propagating tertiary peroxyl radical (**13**). The overall reaction occurs rapidly, as peroxyl radicals abstract hydrogen about 100 times more rapidly from a hydroperoxyl than an allylic methylene group;[12] the tertiary peroxyl radical (**13**) will terminate the chain less readily than the secondary peroxyl radical (**15**),[12] and the intramolecular hydrogen transfer is favoured for steric and entropic reasons.

As supporting evidence for our proposal, a mixture of the hydroperoxide (**8**) and the corresponding alcohol (**12**) was kept under oxygen and the progress of the reaction monitored by ^{1}H n.m.r. spectroscopy. The hydroperoxide (**8**) was again converted into the dihydroperoxide (**10**), whereas the alcohol (**12**) was unchanged.

† Compound (**10**) has two distinct hydroperoxyl protons at δ 8.98 and 9.12 (which exchange with D_2O) in the ^{1}H n.m.r. The conversion of (**8**) to (**10**) is quantitative (by n.m.r.).

The autoxidation is therefore accelerated by fast intra- and inter-molecular propagation steps. We are not aware of any previous recognition of this phenomenon.

We acknowledge support by the S.E.R.C. and the award of a Ramsay Memorial Fellowship to C. H. S.

Received, 31st January 1989; Com. 9/00484J

References

1 G. O. Schenck, O. A. Neumüller, and W. Eisfeld, *Liebigs Ann. Chem.*, 1958, **618**, 202.
2 W. F. Brill, *J. Am. Chem. Soc.*, 1965, **87**, 3286; *J. Chem. Soc., Perkin Trans. 2*, 1984, 621.
3 A. A. Frimer, *Chem. Rev.*, 1979, **79**, 359.
4 A. L. J. Beckwith, A. G. Davies, I. G. E. Davison, A. Maccoll, and M. H. Mruzek, *J. Chem. Soc., Chem. Commun.*, 1988, 475; *J. Chem. Soc., Perkin Trans. 2,* in the press.
5 N. A. Porter and J. S. Wujek, *J. Org. Chem.*, 1987, **52**, 5085.
6 R. Hiatt and T. McCarrick, *J. Am. Chem. Soc.*, 1975, **97**, 5234; I. G. E. Davison, Ph.D. Thesis, University of London, 1988.
7 G. O. Schenck and K. H. Schulte-Elte, *Liebigs Ann. Chem.*, 1958, **618**, 185.
8 D. V. Avila, A. G. Davies, and I. G. E. Davison, *J. Chem. Soc., Perkin Trans. 2,* 1988, 1847.
9 A. G. Davies and W. Kinart, *J. Chem. Res. (S)*, 1989, 22.
10 Full details will be published elsewhere: A. G. Davies, I. G. E. Davison, D. C. Povey, C. H. Schiesser, and G. W. Smith, *Acta. Crystallogr.*, submitted for publication.
11 L. C. Bateman, *Quart. Rev. Chem. Soc.*, 1954, **8**, 147.
12 Landolt Börnstein, Numerical Data and Fundamental Relationships in Science and Technology, Springer Verlag, West Berlin, 1979, Vol. 9, Part C 2.