

Oxygen–Oxygen Cleavage in Bicyclic Trialkylperoxonium Intermediates

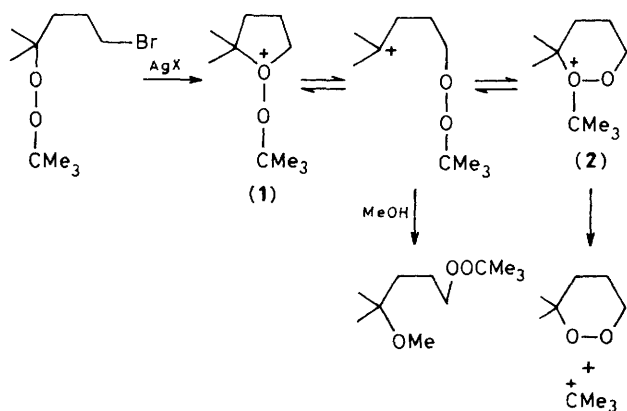
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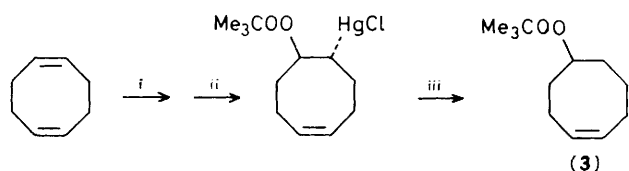
Oxygen–oxygen cleavage in bicyclic trialkylperoxonium ions can account for the mixtures of bicyclic ethers and 2-methoxypropane derivatives obtained from the reaction of 5-*t*-butylperoxycyclo-octene with *N*-bromosuccinimide in methanol or with bromine in carbon tetrachloride.

In a recent communication,¹ Porter and Mitchell postulated the intermediacy of previously unknown trialkylperoxonium salts (1) to account for the products obtained from the reaction of *t*-butyl ω -bromoalkyl peroxides with silver salts (*e.g.* Scheme 1). We now report our observations on a related system for which the isolation of products arising from novel oxygen–oxygen fission strongly suggests the formation of bicyclic trialkylperoxonium ions that contain cyclic ether groups [*i.e.* analogues of (1)].

It was envisaged that the trialkylperoxonium salts might also be formed by treating a suitable alkenyl *t*-butyl peroxide with an appropriate electrophile. Analogous dialkylperoxonium salts are presumably involved in the mercury(II) salt-induced cyclization of (cyclo)alkenyl hydroperoxides.² 5-*t*-Butylperoxycyclo-octene (3)[†] was prepared in 80% yield by *t*-butyl peroxymercuration³ of cyclo-octa-1,5-diene followed by reduction⁴ with excess of tributyltin hydride (Scheme 2). Treatment of (3) with *N*-bromosuccinimide (NBS) in methanol for 45 min afforded, in high yield, a mixture of *trans*-2-bromo-9-oxabicyclo[4.2.1]nonane (4)[†] and *trans*-2-bromo-9-oxabicyclo[3.3.1]nonane (5)[†] in the ratio 3.2:1, together with 2,2-dimethoxypropane (74%) and succinimide (Scheme 3). No other products were detected.



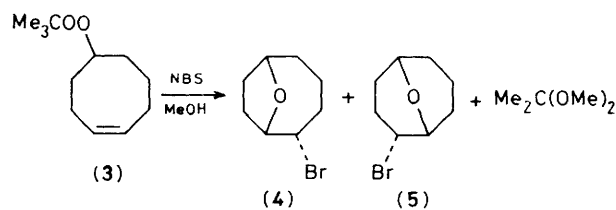
Scheme 1



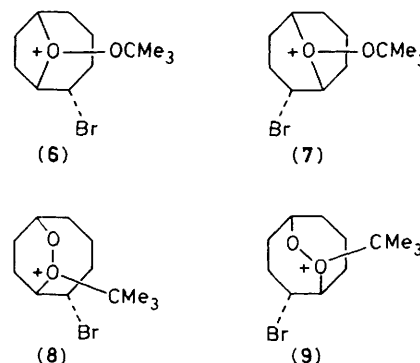
Scheme 2. Reagents: i, $6\text{Me}_3\text{COOH} + \text{Hg}(\text{O}_2\text{CCF}_3)_2$; ii, NaCl ; iii, $(\text{Bu}_3\text{Sn})_2\text{O} + (\text{MeSiHO})_x$.

Formation of four possible bicyclic trialkylperoxonium ions (6)–(9) can be envisaged from the electrophilic attack of NBS on peroxide (3), but it appears that those with bicyclic ether structures, (6) and (7), are favoured under these conditions. The products may then be accounted for by Baeyer–Villiger-type O–O cleavage with 1,2-nucleophilic migration of a methyl group (Me^*) accompanied or followed by nucleophilic attack of solvent methanol (*e.g.* Scheme 4). This mechanism was confirmed by carrying out the reaction in $[\text{}^3\text{H}_4]\text{methanol}$ (24.4 mol) from which was isolated the expected $[\text{}^3\text{H}_3]\text{-2,2-dimethoxypropane}$ $[\text{Me}_2\text{C}(\text{OCD}_3)(\text{OMe})]$, which only slowly exchanged with $[\text{}^3\text{H}_4]\text{methanol}$ to give the hexadeuteriated acetal.

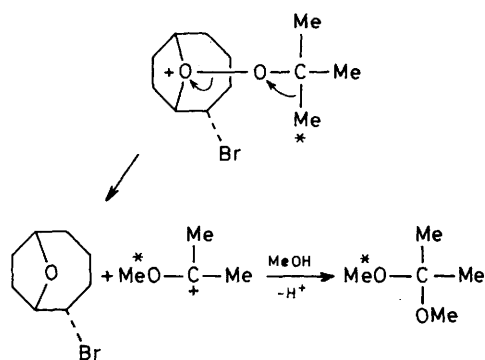
A similar peroxonium ion mechanism, with bromide ion fulfilling the role played by methanol in Scheme 4, can account for the products obtained upon treating peroxide (3) with bromine in carbon tetrachloride. In particular, the same mixture of bicyclic ethers (4) and (5) was obtained under these conditions. The anticipated product, 2-bromo-2-methoxypropane, is an unknown compound, but consistent with its formation was the appearance in the ^1H n.m.r. spectrum of the reaction mixture of singlets at δ 2.1 (6H) and 3.45 (3H). Furthermore, when the sample was exposed to atmospheric moisture, hydrogen bromide was evolved and the ^1H n.m.r. signal at δ 2.1 decayed to be replaced by one at δ 2.2, which was shown to arise from acetone by the addition of an authentic sample. These observations are consistent with the susceptibility to ready hydrolysis expected for such an α -bromo ether. About 1.5% of *t*-butyl bromide was also detected in



Scheme 3



[†] All new compounds had satisfactory analytical and ^1H and ^{13}C n.m.r. spectral data.



Scheme 4

the product mixture, which suggests that a small amount of competing formation of bicyclic peroxides *via* peroxonium intermediates (8) and/or (9) takes place.

We believe that the predisposition to form ethers, which distinguishes our reactions from those of Porter and Mitchell,¹ is a feature of having the peroxy nucleophile located on the cyclo-octene ring such that sterically favourable single oxygen-bridging can take place. Consistent with this view was the observation that the same 3:1 ratio of bicyclic ethers (4)

and (5) could be obtained by treating 5-hydroperoxycyclo-octene† with NBS in *t*-butyl alcohol or bromine in carbon tetrachloride. These results also reveal that *internal* nucleophilic attack at oxygen (Scheme 4) is not a prerequisite for O–O cleavage in bicyclic peroxonium ions. Thus it appears that 5-hydroperoxycyclo-octene represents a source of electrophilic OH which can be activated by suitable electrophiles, but it remains to be seen if this can be usefully exploited.

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References

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