Oxygen–Oxygen Cleavage in Bicyclic Trialkylperoxonium Intermediates

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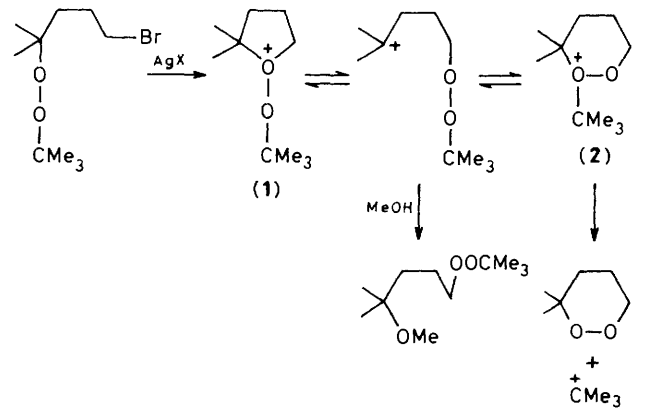
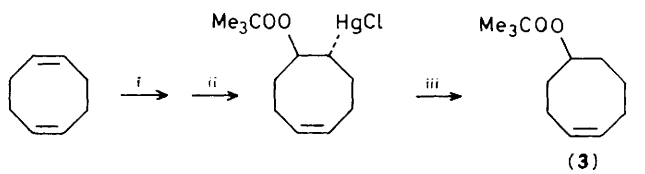
Oxygen–oxygen cleavage in bicyclic trialkylperoxonium ions can account for the mixtures of bicyclic ethers and 2-methoxypropane derivatives obtained from the reaction of 5-t-butylperoxycyclo-octene with *N*-bromosuccinimide in methanol or with bromine in carbon tetrachloride.

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 peroxymercuriation[3] of cyclo-octa-1,5-diene followed by reduction[4] 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

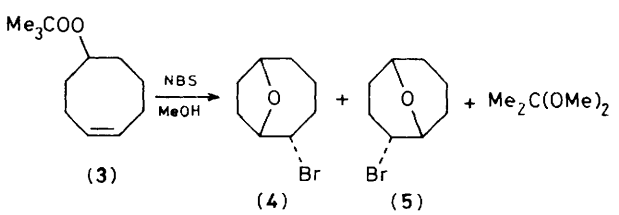


Scheme 2. *Reagents*: i, $6Me_3COOH + Hg(O_2CCF_3)_2$; ii, NaCl; iii, $(Bu_3Sn)_2O + (MeSiHO)_x$.

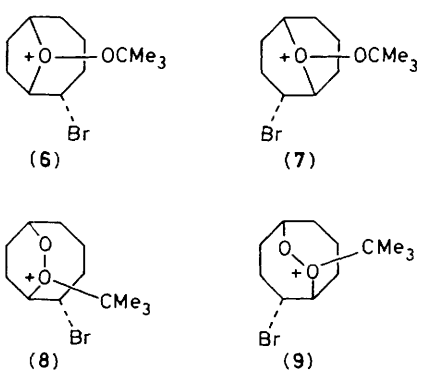
† All new compounds had satisfactory analytical and ^1H and ^{13}C n.m.r. spectral data.

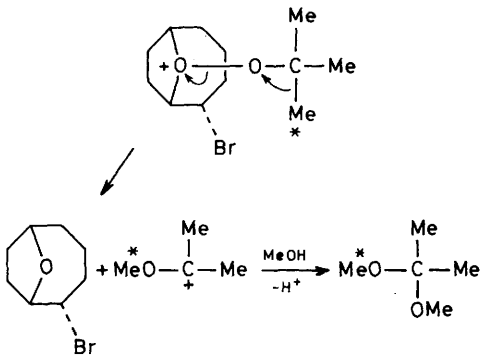
Formation of four possible bicyclic trialkylperoxonium ions (**6**)—(**9**) can be envisaged from the electrophilic attack of NBS on peroxide (**3**), but it appears that those with bicyclic ether structures, (**6**) and (**7**), are favoured under these conditions. The products may then be accounted 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 [$^2H_4$]methanol (24.4 mol) from which was isolated the expected [$^2H_3$]-2,2-dimethoxypropane [$Me_2C(OCD_3)(OMe)$], which only slowly exchanged with [$^2H_4$]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





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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