Heterolytic Oxygen–Oxygen Bond Formation *via gem*-Dialkylperoxonium Ions

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Different extents of decomposition for the *cis* and *trans* isomers of 4,5-epoxycyclo-octyl hydroperoxide coupled with the formation of oxygen (identified by Raman spectroscopy) and bicyclic ethers suggest a mechanism involving the heterolytic formation of protonated alkyl hydrotrioxides by nucleophilic attack of hydroperoxide on *gem*-dialkylperoxonium ions.

There are very few established examples of heterolytic oxygen–oxygen bond formation.[1,2] The recently discovered[3] *gem*-dialkylperoxonium ions may provide a new source of electrophilic oxygen for such processes. Results which support this proposal and which point to the formation of protonated alkyl hydrotrioxides as the initial products are reported.

Treatment of cyclo-oct-4-enyl hydroperoxide with *m*-chloroperoxybenzoic acid in dichloromethane rapidly afforded a 58 : 42 mixture of *cis*- and *trans*-4,5-epoxycyclo-octyl hydroperoxide (**1c,t**) which was isolated by chromatography on neutral Brockman grade 4 alumina at −30 °C. A solution of (**1c,t**) in CD_2Cl_2 was slowly transformed (3—4 days) into a
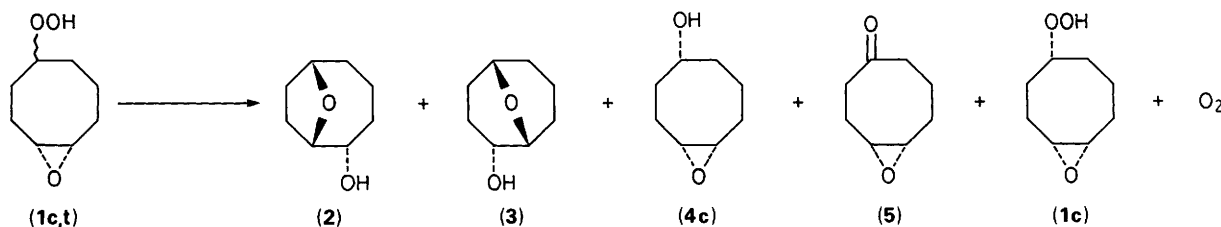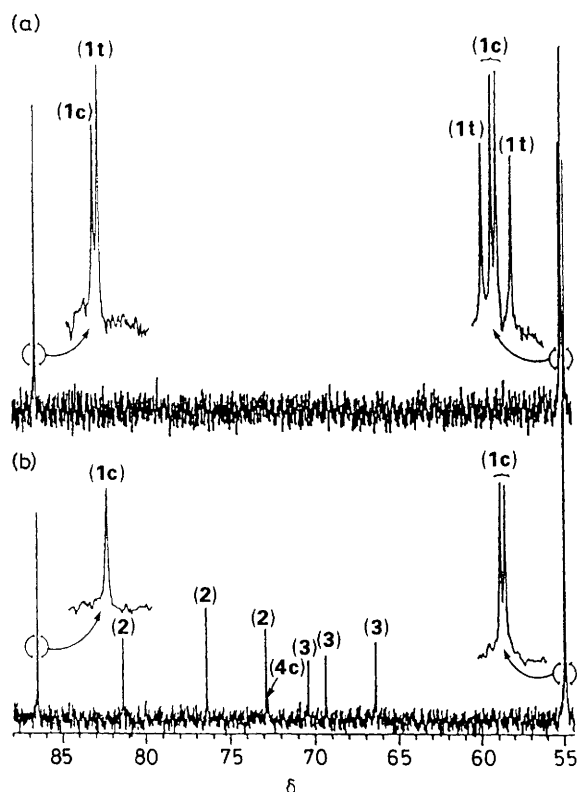

Scheme 1

Figure 1. ^{1}H-Decoupled ^{13}C NMR spectra showing the resonances of carbon atoms bonded to oxygen for a solution of (**1c,t**) in CD₂Cl₂ (a) before and (b) after reaction.

Figure 2. Raman spectra of the gas phase above a solution of (**1c,t**) in CD₂Cl₂ sealed under nitrogen (0.2 torr) (a) before and (b) after reaction.

mixture containing the following components (Scheme 1) in the molar ratio indicated, (**2**) (20%), (**3**) (15%), (**4c**) (13%), (**5**) (10%), and unchanged (**1c**) (42%). The reaction was monitored by ^{13}C NMR spectroscopy (Figure 1). The components were identified by comparison with authentic samples and the molar ratio was determined from ^{13}C NMR peak intensities for all methylene carbon nuclei. We estimate that this method provides molar fractions to an accuracy of ±5% and the spread of results over four runs fell within these limits.

The formation of oxygen (Scheme 1) was established by carrying out the reaction in a sealed NMR tube under nitrogen at *ca*. 0.2 torr and analysing the gaseous phase (Raman spectroscopy[4]). The Raman spectra recorded before and after reaction, which were correlated with the ^{13}C NMR spectra of the solution phase (Figure 1), are shown in Figure 2. By comparing the line intensities due to rotational transitions of oxygen and nitrogen in the final spectrum with those in the spectrum of air, it was possible to estimate the partial pressure of oxygen in the tube. Owing to the solubility of oxygen in the solution phase, this gives a lowest estimate of the number of moles of oxygen produced in the reaction. This was found to be about one tenth of the number of moles of (**1c,t**) consumed.

The reaction was also carried out with cyclo-oct-4-enyl hydroperoxide-[18]O₂ and the bicyclic ethers (**2**) and (**3**) were isolated by HPLC. Mass spectral analysis (18 eV) revealed that these were monolabelled, thereby confirming that the oxygen is derived from the hydroperoxyl group.

The markedly different extents of decomposition for the *cis* and *trans* isomers of the 4,5-epoxycyclo-octyl hydroperoxide argue against a mechanism involving peroxyl radicals. Furthermore, model studies suggest that 4,5-epoxycyclo-octan-
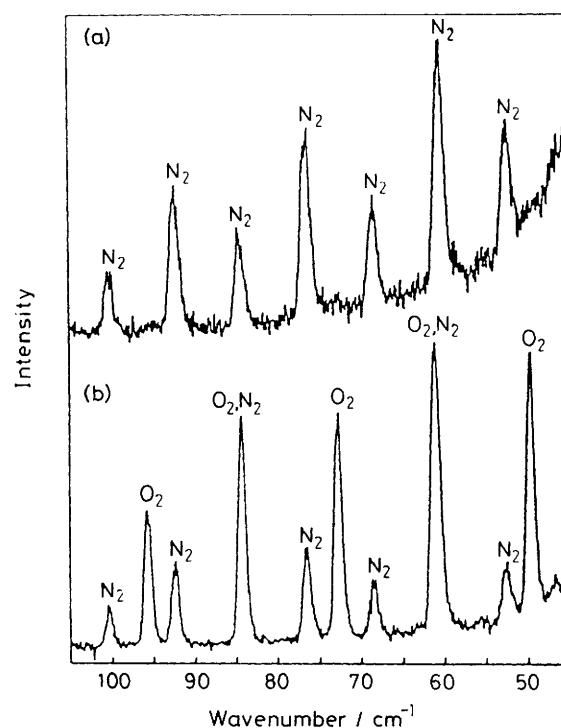
one (**5**) would be the major product under radical conditions. However, the results are explained by the polar mechanism shown in Scheme 2. Protonation of the *trans* isomer followed by intramolecular nucleophilic attack affords the isomeric *gem*-dialkylperoxonium ions (**6**) and (**7**) (step a). Intermolecular nucleophilic attack by the hydroperoxides (**1c,t**) yields the bicyclic ethers (**2**) and (**3**) and the protonated hydrotrioxides (**8c,t**) in the heterolytic O–O bond-forming step (b). A prototropic shift and unimolecular decomposition produces oxygen plus *cis*- or *trans*-4,5-epoxycyclo-octanol (**4c,t**) and regenerates the proton catalyst (step c). The *trans* alcohol (**4t**) rapidly rearranges to the bicyclic ethers (**2**) and (**3**) (step d; confirmed by an independent experiment).

The formation of peroxonium ions (**6**) or (**7**) (step a) is expected to be rate determining and, in agreement with this, no NMR signals attributable to these intermediates were detected during the course of the reaction. Assuming $k_a \ll k_b trans, k_b cis$, where k_a is the overall rate constant for step (a) and $k_b trans$ and $k_b cis$ are the rate constants for the reaction of (**1t**) and (**1c**), respectively, with peroxonium ions (**6**) or (**7**) (step b), the amount of (**1c**) remaining at the end of the reaction was calculated† for different ratios of $k_b trans$ to $k_b cis$. The observed and calculated amounts were found to agree within experimental error if $k_b trans$ is set to $2k_b cis$. We consider this small difference in the rate constants for the two isomers to be compatible with the mechanism proposed in Scheme 2.

The small yield of 4,5-epoxycyclo-octanone (**5**) may signal some concurrent radical decomposition, although an alternative mode of dissociation for the protonated hydrotrioxide (**8c,t**) could also account for this observation.

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† Using a simple model which treats the reaction as 10² to 10⁶ sequential steps; convergence occurred within 10⁴ steps.
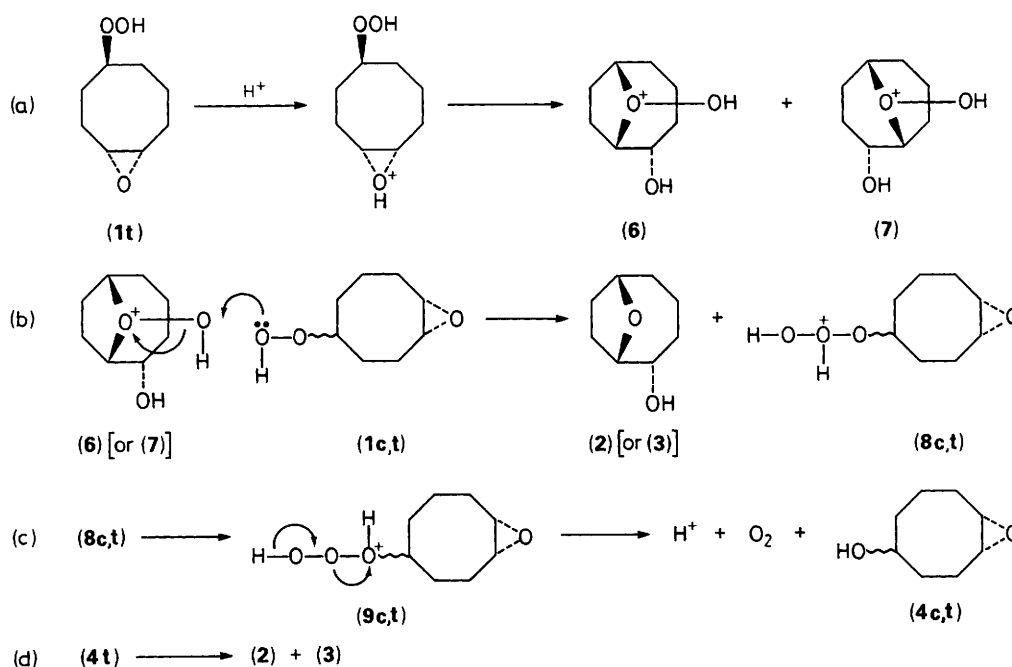
Scheme 2

The mechanism requires that the oxygen be generated in the singlet state and we attempted to detect this by adding 1,3-diphenylisobenzofuran[5] to the mixture of hydroperoxides (1c,t). A good yield of 1,2-dibenzoylbenzene was indeed obtained, but this cannot be taken as firm evidence for singlet oxygen since it was shown that the *cis* isomer (1c) [and therefore by implication also the *trans* isomer (1t)] was itself able to effect this transformation.

Alkyl hydrotrioxides are an unstable and little studied class of peroxides, but they have been reported to undergo decomposition to oxygen and alcohol and to hydrogen peroxide and ketone.[6] The only previously reported route to alkyl hydrotrioxides involves incorporation of the intact O_3 unit by ozonation.

References

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