Reaction of Singlet Oxygen with Hindered Olefins: Evidence for a Perepoxide Intermediate

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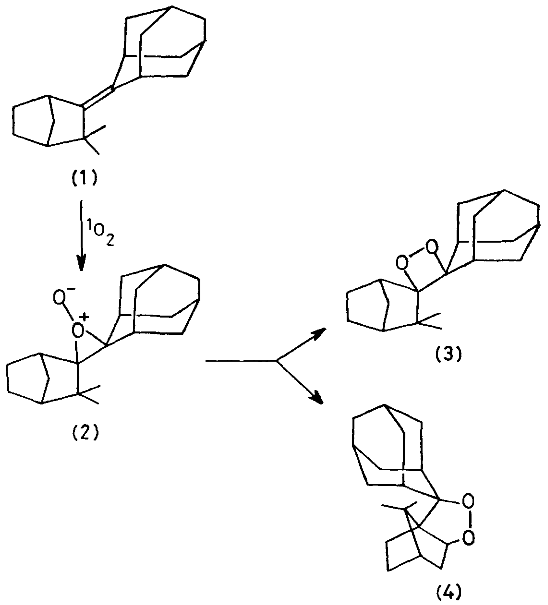
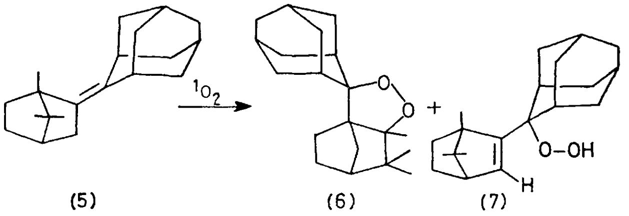
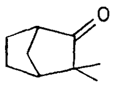
Summary Isolation, along with expected product, of 1,2-dioxolans of rearranged skeleton from the reaction of singlet oxygen with certain hindered alkenes suggest the intermediacy of a dipolar species such as a perepoxide.

THE addition of singlet oxygen to mono-olefins normally produces two primary products, an allylic hydroperoxide and a dioxetan.[1] Recent calculations[2] suggest that the initial adduct should be a perepoxide (peroxiran) which would rearrange to the observed products. However, a large body of evidence indicates that the allylic hydroperoxide is formed from unhindered olefins without significant development of charge.[1,3,4] It has also been shown[5] that the isolation[6] of epoxides from trapping experiments is not diagnostic of a perepoxide intermediate in that the epoxide appears to arise from a reaction of oxygen with the sensitiser, although not all singlet oxygen reactions which form epoxides may be open to this objection.[2,7] It is known that the dioxetan is not a precursor of the allylic hydroperoxide, so that the perepoxide could well be an intermediate in dioxetan formation, with the ene reaction occurring competitively. The situation may resemble that of the related ozonolysis reaction of sterically hindered double bonds where, in addition to the normal trioxolan formation, a charged three-membered ring complex is inferred[8] from the presence of the epoxide in the products. In that case we would expect that the oxidation of hindered olefins would give products resulting from the formation of a perepoxide. By suitable choice of olefin we have obtained evidence for this perepoxide or a closely related intermediate with strong carbonium ion character.

Singlet oxygen, in spite of its reactivity and relatively small bulk, failed to react with fenchylidene-fenchane and gave only traces of peroxide with camphenylidene-camphenilane.[9] However, oxidation of camphenylidene-adamantane (**1**) using a variety of sensitisers and solvents (see Table) gave two very stable isomeric crystalline peroxides in high yield. Satisfactory analyses and spectral data were obtained for both compounds. One of the peroxides was assumed to be the expected dioxetan on the basis of the similarity in its chemiluminescent light yield, products, spectra, and other properties to those of the dioxetan derived from adamantylidene-adamantane.[10] The quantum yield (ϕ) on decomposition was 2×10^{-5} with an activation energy (E_a) of $30{\cdot}3 \pm 1{\cdot}3$ kcal mol^{-1} (log A 12·0). The second peroxide had E_a 35·2 kcal mol^{-1} (log A 14·3), and emitted considerably less light ($\phi = 2{\cdot}0 \times 10^{-7}$). Its structure (**4**) was determined by X-ray crystallography.[11] It is clearly a rearrangement product and could be assumed to arise from an intermediate carbonium ion. The dioxolan (**4**) is not formed from the dioxetan as shown by the stability of the latter under irradiation in the presence of a variety of sensitisers and solvents. The corresponding epoxide was formed in amounts varying with the sensitiser used as expected,[5] but the ratio of dioxetan to dioxolan was not dependent on the nature of the sensitiser.







(8)

There was a solvent effect (Table) on this ratio. Such effects have been noted before in the reactions of singlet oxygen but in no case is there a straightforward relationship with polarity.[12] Addition of the singlet oxygen quencher DABCO (diazabicyclo-octane) inhibited formation of both

TABLE. Oxidation of (**1**) in different solvents.

Solvent	Ratio of (**3**) : (**4**)[c]
CH_2Cl_2[a]	7:3
MeCN[a]	3:7
Me_2CO[a]	1:9
Me_2CO[b]	1:9
MeOH[a]..	1:9
MeOH–30%H_2O[a] ..	1:9

[a] Methylene Blue as sensitiser, irradiation with 500 W lamp.
[b] Rose Bengal as sensitiser, irradiation with 500 W lamp.
[c] Yields were determined by t.l.c. and by light emission using the pure compounds to calibrate the detection system.

isomers, but the free radical inhibitor, di-t-butyl-*p*-cresol (at 0·1M concentration), did not significantly affect the formation of either.

Adamantylidene-camphane (**5**) which can undergo the ene reaction in addition to rearrangement and dioxetan formation gave only two products; one of these is clearly identifiable as the hydroperoxide (**7**) [δ 6·15 (d, J 2·0 Hz) and 6·58 (s, –O–OH)]. The other compound appears to be dioxolan (**6**) rather than a dioxetan, as shown by its low light yield, decomposition products, and mass spectrum. Attempts to confirm this structure are in hand.

In contrast, no rearrangement is observed in unhindered olefins of the norbornene type, only products of the ene reaction being found.[4] Our conclusion is that in hindered olefins rearrangement and dioxetan formation both derive from the perepoxide (**2**) (or equivalent charged species) whereas the hydroperoxide is expected to form by a concerted mechanism.

Another goal of this work was the synthesis of a chiral dioxetan, perhaps producing chiral ketones in the excited state so that we could study the decomposition by the emission of circularly polarised light. Optically active camphenilone (**8**) was synthesised *via* isoborneol phenylurethane by an established route,[13] and converted into the chiral dioxetan (**3**), $[\alpha]_D + 155{\cdot}3°$. We were unable to detect polarised emission, but in view of the success recently reported with another dioxetan,[14] we will re-investigate this reaction in more detail. We expect that the degree of polarisation in the emission could be diagnostic of energy transfer processes in a solvent cage during decomposition and our investigations will be reported later.

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