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EVIDENCE FOR AN INTERMEDIATE IN THE REACTION OF SINGLET OXYGEN WITH A SILYLENOL ETHER

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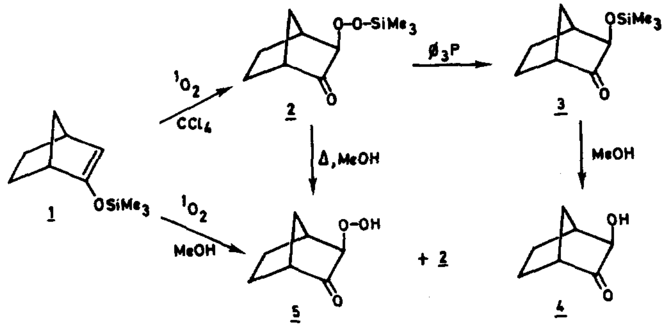
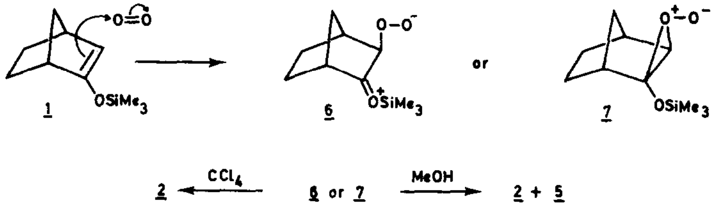
The mechanisms by which singlet oxygen reacts with olefins have been the subject of much controversy. When a hydroperoxide or a dioxetane is formed from an appropriate olefin, the crucial question is to know whether the reaction is fully concerted or does it pass through an intermediate.[1] In the case of hindered olefins, typified by biadamantylidene, the production of epoxide is now considered insufficient evidence for a perepoxide intermediate.[2] Nevertheless, a perepoxide precursor could still be a realistic alternative to the concerted [2+2] cyclo-addition for formation of dioxetane. The essence of the problem lies in devising a suitable trapping experiment. Norbornene, originally reported to be inert, was thought to yield the perepoxide reversibly.[3] However, it has now been shown to behave similarly to biadamantylidene in reacting sluggishly with singlet oxygen to give norbornene epoxide and *cis*-cyclopentane-1,3-dicarboxaldehyde. Unfortunately, attempts to characterize either the dioxetane or its hypothetical perepoxide precursor proved unavailing.[4] In this paper we describe the behaviour of 2-trimethylsilyloxynorbornene (1) which, unlike norbornene, reacts rapidly with singlet oxygen in a variety of solvents.[5] Moreover, unmistakable evidence is found for the intermediacy of a polar peroxy species.

Photo-oxygenation of 1 in aprotic solvents such as chloroform, carbon tetrachloride or acetonitrile using *meso*-tetraphenylporphin or methylene blue as sensitizer proceeds readily at temperatures of 0 to -20°.[6] One mole of oxygen is consumed within two minutes and by inspection of the NMR and IR spectra, only one product is detected, namely the silylperoxy ketone 2, isolated in 95% yield by distillation (b.p. 51° at 0.025 Torr).[8] Its structure follows by its reduction with triphenylphosphine to the corresponding siloxy ketone 3 and thence by hydrolysis in neutral aqueous methanol to the known *exo* ketol 4.



When 1 is oxidized in methanol using methylene blue or rose bengal as sensitizer at temperatures between 0 and -78°, oxygen uptake once again is found to be quantitative within three to five minutes. Under these conditions, a second product is formed, in addition to 2, the hydroperoxy ketone 5 in 15% yield. What is significant is that the silylperoxy ketone 2 is completely stable not only under the reaction conditions (at -20°), whether in the presence or not of singlet oxygen, but also for periods of 30 minutes. Nevertheless, 2 at 36° in methanol has a half-life of 32 minutes and undergoes conversion to the hydroperoxide 5. Similar results are obtained in deuteromethanol.

Therefore, the provenance of hydroperoxide 5 on photo-oxygenation must be sought elsewhere. As a concerted "ene" reaction is not possible, a two-step process becomes necessary. Singlet oxygen could undergo electrophilic addition to the double bond in 1 to give either the ionic intermediate 6 or its perepoxide tautomer 7. Naturally, in aprotic solvents 6 or 7 can only undergo formal 1,5 silatropic shift to give 2.[10] However, in methanol proton abstraction competes to give the desilated product 5.



Such incorporation of solvent is unknown for dioxetanes[11] and is only encountered in one other case, that of N-methylindole, where a similar polar peroxide has been proposed.[12] These findings to our mind reinforce the theoretical predictions of Dewar[13] and Fueno[14] who have suggested that photo-oxygenation of enol ethers proceeds by initial formation of a zwitterionic species which can cyclize to a dioxetane or to a perepoxide, the latter rearranging subsequently to the "ene" product.

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5) Compound 1 was prepared in 67% yield from norbornanone by treating it with lithium diisopropylamide and trimethylchlorosilane (H.O. House, L.J. Czuba, M. Gall & H.D. Olmstead, *J. Org. Chem.* 34, 234 (1969)).

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