

degradation is possibly due to its known ability to photoionize [6] coupled with the relatively long $O_2(^1\Delta_g)$ lifetime. No such effects were observed using the T4MPP sensitizer.

Other solvents investigated were ethylene glycol, characterized by increased viscosity and correspondingly lengthened triplet transfer times, 1-octanol, with similar behavior but with a significantly longer $O_2(^1\Delta_g)$ decay time, glacial acetic acid and formamide.

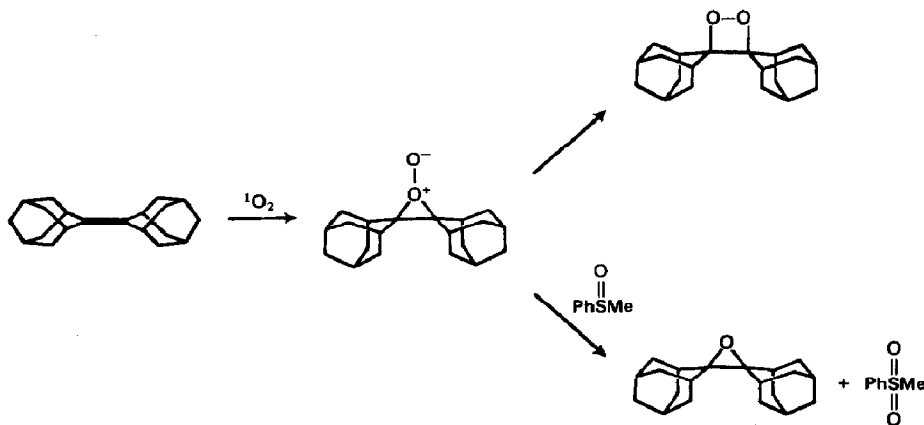
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Nucleophilic oxygen atom transfer from a perepoxide intermediate to sulfoxides†

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1O_2 reacts with adamantylideneadamantane to form an unusually stable 1,2-dioxetane. We have recently obtained evidence for a trappable intermediate in this 1,2-cycloaddition reaction of 1O_2 . This species, which we propose is the perepoxide, can be quantitatively trapped by nucleophilic oxygen atom transfer to sulfoxides to yield sulfones and the epoxide:



The ratio of epoxide to dioxetane is found to be a function of the concentration of the sulfoxide.

Additional evidence for the proposed mechanism is provided by a study of substituent effects on the trapping reaction. A series of competition experiments with substituted

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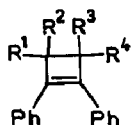
phenylmethyl sulfoxides gave a Hammett plot with a ρ value of +0.52. These results are consistent with the proposed nucleophilic character of the intermediate. Solvent effects on this reaction have also been investigated.

Sensitized photo-oxidation of methyl-substituted cyclobutenes[†]

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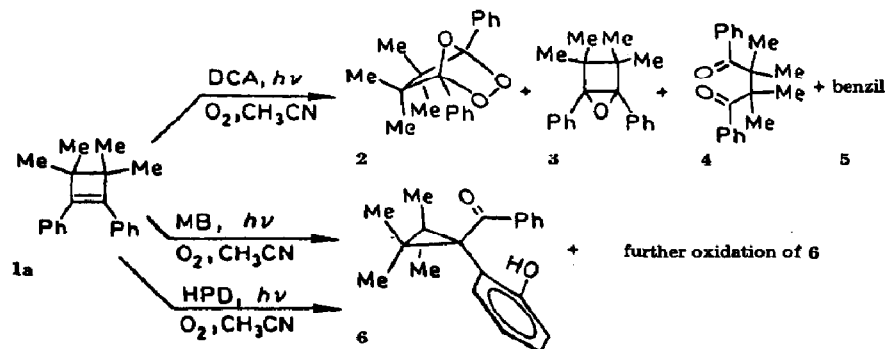
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The series of methyl-substituted 1,2-diphenylcyclobutenes **1** (1a, $R^1 = R^2 = R^3 = R^4 = \text{Me}$; 1b, $R^1 = R^2 = R^3 = \text{Me}$, $R^4 = \text{H}$; 1c, $R^1 = R^3 = \text{Me}$, $R^2 = R^4 = \text{H}$ (*trans*); 1d, $R^1 = \text{Me}$, $R^2 = R^3 = R^4 = \text{H}$) (Me = methyl; Ph = phenyl)



were subjected to photo-oxidation in the presence of sensitizers including methylene blue (MB) and Rose Bengal (RB).

Sensitized photo-oxidations of **1a** with MB and RB lead to formation of the ring-contracted product **6** presumably by initial [4 + 2] addition of singlet oxygen to the styryl diene moiety of the substrate (DCA, 9,10-dicyanoanthracene; HPD, hematoporphyrin derivative):



When the electron transfer sensitizer 9,10-dicyanoanthracene is used, the reactions of **1** take a markedly different course. For example, **1a** is rapidly photo-oxidized in CH_3CN to give the spectrum of products **2** - **5** through a mechanism in which superoxide radical anion is implicated. Thus tetramethylcyclobutene **1a** may be employed to differentiate between photo-oxygenations involving singlet oxygen and superoxide ion. The selectivity exhibited by this substrate has been used to probe the identity of the cytotoxic agent responsible for the dramatic cancer cures observed with HPD as a phototherapeutic agent. Our preliminary data using HPD as a sensitizer *in vitro* support Dougherty's contention that singlet oxygen is involved although his conclusion was based on trapping experiments with 1,3-diphenylisobenzofuran, an assay which must now be considered questionable.

[†] Abstract of a paper presented at the COSMO 84 Conference on Singlet Molecular Oxygen, Clearwater Beach, FL, U.S.A., January 4 - 7, 1984.