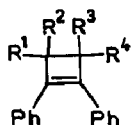


phenylmethyl sulfoxides gave a Hammett plot with a ρ value of +0.52. These results are consistent with the proposed nucleophilic character of the intermediate. Solvent effects on this reaction have also been investigated.

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

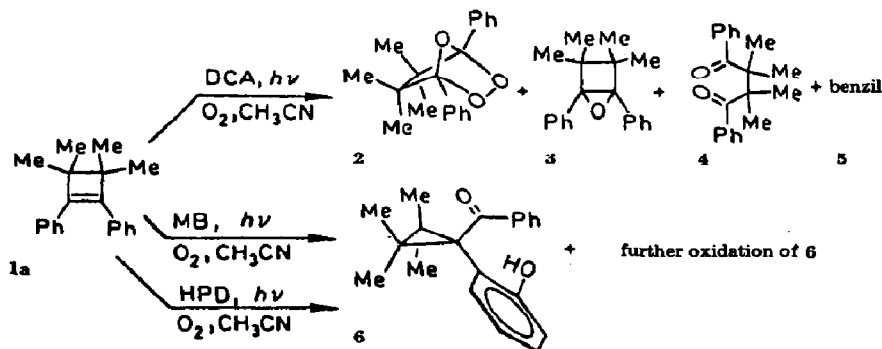
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The series of methyl-substituted 1,2-diphenylcyclobutenes **1** (1a, $R^1 \equiv R^2 \equiv R^3 \equiv R^4 \equiv \text{Me}$; 1b, $R^1 \equiv R^2 \equiv R^3 \equiv \text{Me}$, $R^4 \equiv \text{H}$; 1c, $R^1 \equiv R^3 \equiv \text{Me}$, $R^2 \equiv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