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# AN UNUSUAL SOLVENT EFFECT IN THE REACTION OF SINGLET OXYGEN WITH 1,2-DIPHENYLCYCLOBUTENE

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We wish to report that the reaction of photogenerated singlet oxygen with 1,2-diphenylcyclobutene (1)[3] exhibits a dramatic solvent dependency with respect to product formation.[4] Reaction of 1 with singlet oxygen could lead to both the hydroperoxide 2 and the diketone 3. By simply varying the reaction solvent in the dye-sensitized photoöxidation of 1, we have found it possible to realize either 2 or 3 as the major reaction product.

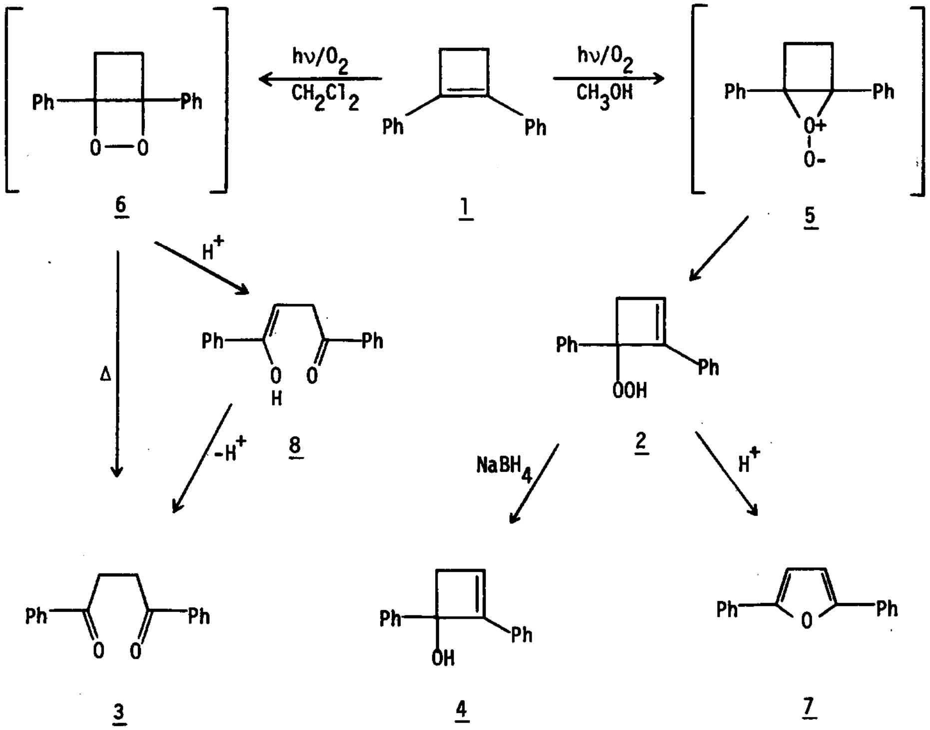
Photolysis (520 nm light) of oxygen enriched methanol solutions of 1 ($10^{-2}$ M) in the presence of methylene blue resulted in complete consumption of the hydrocarbon and gave rise to the hydroperoxide 2 (95%) as well as diketone 3 (5%).[5] High yields of the hydroperoxide (93%) were also obtained in methanol when fluorenone was used as the sensitizer.[6] Additionally, 2 was the predominate product (85%) when the reaction was carried out in acetone using either methylene blue or fluorenone.

The nmr spectrum of 2 showed a well-defined AB quartet for the methylene protons centered at 2.95 δ ($J_{AB}$ = 14.5 cps). This quartet is further split (J = 2.0 cps) by the vinyl proton which appears as a triplet (J = 2.0 cps) at 6.75 δ. The aromatic protons of 2 gave resonance as a complex multiplet between 7.20 and 7.65 δ. Sodium borohydride reduction of 2 gave rise to the alcohol 4 in 90% yield. Alcohol 4 exhibits a parent peak in the mass spectrum at m/e 222 and a strong hydroxyl absorption at 3300 $cm^{-1}$ in the infrared. The nmr spectrum of 4 showed the methylene protons as a doublet (J = 2.5 cps) centered at 2.90 δ while the vinyl proton showed resonance as a triplet (J = 2.5 cps) centered at 6.81 δ. Compound 4 also gave hydroxyl proton resonance at 2.55 δ along with aromatic proton resonance as a multiplet between 7.30 and 7.80 δ.

In marked contrast, irradiation of oxygen enriched methylene chloride solutions of 1 ($10^{-2}$M) with 520 nm light absorbed only by the sensitizer methylene blue gave diketone 3[7] in 40% yield. The remainder of the reaction mixture consisted of a polymeric material and trace amounts of hydrocarbon 1.[8] Similar results were obtained when the photoöxidation of 1 was carried out in benzene using fluorenone as the sensitizer. The polymeric material formed in methylene chloride or benzene appears to arise from the hydroperoxide 2 and not from the diketone. Diketone 3 was recovered unchanged after prolonged irradiation not only in methylene chloride or methanol using methylene blue as the sensitizer but also in benzene solution with fluorenone present. Benzene solutions of hydroperoxide 2 with fluorenone present were found stable in the dark. However, irradiation of these solutions led exclusively to polymer formation. Methylene chloride solutions of 2 with methylene blue present were moderately unstable in the dark and rapidly gave only polymeric material on photolysis.[8]

The above experiments also show that neither hydroperoxide 2 nor diketone 3 are interconvertible under the conditions in which they are formed. Thus, it seems reasonable to assume that 2 could arise from hydrocarbon 1 by an "ene" reaction possibly involving the perepoxide intermediate 5.[9] On the other hand, diketone 3 presumably would be formed by cycloaddition of singlet oxygen to 1 followed by decomposition of the resulting dioxetane intermediate 6.

In an attempt to intercept dioxetane 6, we carried out the reaction of 1 and singlet oxygen in methylene chloride with hydrogen chloride gas present. It was felt that protonation of 6 might yield the hydroperoxide 2 which in turn would suffer dehydration to give 2,5-diphenylfuran (7).[10] Brief treatment of the hydroperoxide with hydrogen chloride gas in either methylene chloride or methanol (light or dark conditions) quantitatively dehydrated 2 into the furan. Thus, if the dioxetane were intercepted in this manner by added acid the only reaction product which should form from 1 under these conditions would be furan 7. Alternatively, protonation of the dioxetane intermediate could be followed by ring opening to give enolate 8 which on deprotonation would yield diketone 3. Diketone 3 was treated with HCl gas under the appropriate conditions and found to be stable. Interestingly, when the reaction of 1 was carried out in oxygen enriched methylene chloride with added HCl gas (520 nm light, methylene blue sensitizer) only a reduction of polymer formation was observed and yields as high as 60% of the diketone could be realized. In a typical experiment carried to partial completion, diketone 3 was formed in 35% yield along with furan 7 (8%) and unreacted hydrocarbon (37%); the remaining 20% of the reaction mixture was polymer.



The surprising solvent dependency for the photoöxidation of 1 is not understood, but what has been observed must be the result of a delicate balance between two reaction paths. Thus, it is obvious that hydrocarbon 1 and derivatives of it could be useful probes into the many questions of topical interest in singlet oxygen chemistry.

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