

COSENSITIZATION BY 9,10-DICYANOANTHRACENE AND BIPHENYL OF THE ELECTRON-TRANSFER

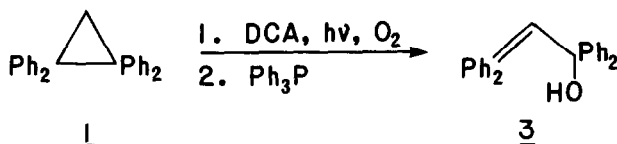
PHOTOOXYGENATION OF 1,1,2,2-TETRAPHENYLCYCLOPROPANE¹

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Summary: Electron-transfer photooxygenation of 1,1,2,2-tetraphenylcyclopropane with 9,10-dicyanoanthracene in oxygen-saturated acetonitrile yields 1,1,3,3-tetraphenyl-2-propen-1-ol after reduction of the intermediate hydroperoxide. The rate of reaction is significantly increased by the addition of biphenyl as a cosensitizer.

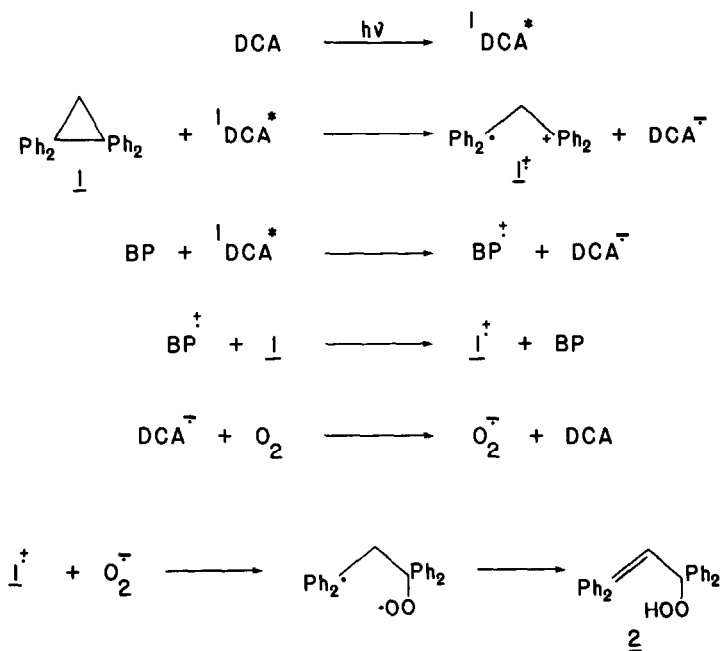
Electron-transfer photooxygenation has received considerable attention recently.² Olefins, acetylenes, and sulfides are oxidized upon irradiation in oxygen-saturated polar solvents in the presence of electron-deficient sensitizers. We now report the first example of the photooxygenation of a cyclopropane with the formation of a ring-opened hydroperoxide.³ The use of a non-light-absorbing, chemically unreactive aromatic hydrocarbon as a cosensitizer to accelerate the reaction is also described.



Photooxygenation of 1,1,2,2-tetraphenylcyclopropane (1) was carried out in dry acetonitrile with 6×10^{-3} M 1 and 6×10^{-4} M 9,10-dicyanoanthracene (DCA). The solution was irradiated at 10°C under oxygen with a 450-W medium-pressure mercury lamp using a CuSO_4 -filter solution.⁴ The reaction was monitored by hplc and judged complete in 19 h. Treatment of the reaction mixture with 1 equivalent of Ph_3P to reduce the hydroperoxide and chromatography over silica gel with hexane as elutant gave 1,1,3,3-tetraphenyl-2-propen-1-ol (3)⁵ in 60% yield. Benzophenone (4) was also identified as a reaction product.⁷

Arnold⁸ and Roth⁹ have shown that photo-induced electron-transfer reactions of aryl-substituted cyclopropanes result in the formation of radical cations with C-C bond cleavage. A plausible mechanism for the conversion of 1 to hydroperoxide 2, therefore, involves electron-transfer fluorescence quenching of singlet excited DCA by 1 with generation of radical cation 1⁺. Reaction of 1⁺ with superoxide forms an intermediate biradical which subsequently abstracts hydrogen to yield 2.¹⁰ Control experiments have shown that one source of 4 is the photooxidative cleavage of hydroperoxide 2.¹¹ Further, cyclopropane 1 was not oxidized upon irradiation for 38 h with a 400-W high-pressure sodium lamp in an oxygen-saturated acetonitrile solution containing Rose Bengal, indicating that singlet oxygen is not involved in the reaction.

We have recently observed that the rate of DCA-sensitized photooxygenation of tetraphenyl-oxirane to produce the corresponding ozonide can be dramatically enhanced by the addition of biphenyl (BP) as a cosensitizer.¹² Similarly, we have found that the oxidation of 1 can be accelerated by BP. In the presence of 6×10^{-3} M BP, the reaction is complete in 1.5 h. Analysis by hplc indicated that the BP is not appreciably consumed during the reaction.¹³ No reaction occurs in the absence of DCA.



We have previously reported that the rate of DCA-sensitized photooxygenation of 2,3-bis(p-methoxyphenyl)-1,4-dioxene ($E_{1/2}^{\text{ox}} = 0.73$ V vs. SCE, in MeCN) was increased in the presence of 2,3-bis(p-methylphenyl)-1,4-dioxene ($E_{1/2}^{\text{ox}} = 0.84$ V vs. SCE, in MeCN).^{2k} Similar results have recently been described by Foote for the photooxygenation of tetraphenylethylene in the presence of trans-stilbene.^{14,15} In both of these reactions, the olefins quench $^1\text{DCA}^*$ at diffusion-controlled rates and the enhanced reactivity of the more easily oxidized olefin results from electron exchange of that olefin with the radical cation of the more difficultly oxidized olefin. In present case the cosensitizer BP ($E_p^{\text{ox}} = 1.85$ V vs. SCE, in MeCN)¹⁸ has a higher oxidation potential than the substrate 1 ($E_p^{\text{ox}} = 1.38$ V vs. SCE, in MeCN). As a result, BP ($k_q = 3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) is a less effective quencher of $^1\text{DCA}^*$ than 1 ($k_q = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).¹⁹ Nevertheless, an equimolar concentration of BP is able to greatly enhance the rate of oxidation of 1. This result would seem to suggest that in $^1\text{DCA}^*$ quenching the efficiency for the formation of cage-escaped BP^+ is significantly greater than for 1^+ in spite of the lower oxidation potential of 1. Cyclopropane 1 is subsequently oxidized in an exothermic electron-transfer step by BP^+ .

Although the mechanism of catalysis is not fully delineated, cosensitization by electron-deficient sensitizers and aromatic hydrocarbons may prove to be generally useful for the oxidation of a variety of substrates. Research is continuing in our laboratory on this problem.

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References and Notes

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- (3) Dr. K. Mizuno, Osaka Prefecture University, Japan, has isolated 1,2-dioxolanes from the DCA-sensitized photooxygenation of methoxyphenyl-substituted cyclopropanes. We thank Dr. Mizuno for communicating these results to us.
- (4) The 1-cm path-length filter solution was prepared from 27 g of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, 30 g of NaNO_2 and 50 mL of conc. NH_4OH diluted with water to 1000 mL.
- (5) The mp (138–139°C) and spectral properties of the isolated alcohol 3 were identical to those of an authentic sample of 3.⁶
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- (7) Preliminary evidence has been obtained for the formation of minor amounts of 3,3,5,5-tetraphenyl-1,2-dioxolane.
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- (10) Alternatively, ground-state oxygen could add to 1⁺ with subsequent reduction of the peroxy radical cation by $\text{O}_2^{\cdot-}$, DCA⁻, 1 or BP. Arnold⁸ has shown that 1,1,3,3-tetraphenylpropene (5) is formed by 1,4-dicyanonaphthalene-sensitized irradiation of 1 in deoxygenated acetonitrile. However, we do not observe the formation of 5 under our reaction conditions. Control experiments with authentic 5 have shown that this olefin is significantly less reactive than 1.
- (11) Photooxygenation of 2 in MeCN with DCA and BP gives a solution which produces chemiluminescence upon heating with concomitant formation of 4. These results are evidence for an intermediate 1,2-dioxetane. The other product of the decomposition is presently being identified.
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