

SOLVENT DEPENDENT
 REACTIONS OF SINGLET OXYGEN WITH PHENYLCYCLOPROPENES¹

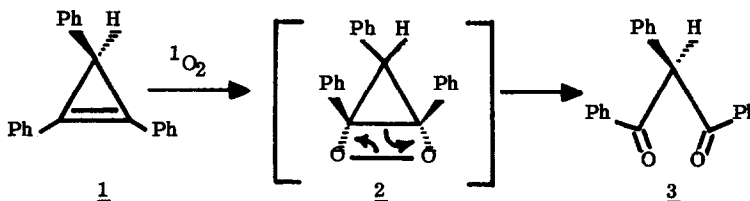
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Broad precedent exists for the intervention of dioxetanes as intermediates in reactions of singlet oxygen with alkenes² and in fact isolation of these species has been achieved in certain cases.³ We have examined the reactions of photogenerated singlet oxygen with 1,2,3-triphenylcyclopropene 1 and tetraphenylcyclopropene 4 in order to assess the effect of strain on the 2+2 addition process and the generation of electronically excited products upon subsequent thermolysis of the resulting dioxetanes.⁴

A 0.5 g (1.6×10^{-3} mole) sample of 1,2,3-triphenylcyclopropene 1⁵ in methylene chloride (350 ml) was irradiated for two hrs at $10-15^{\circ}$ in the presence of methylene blue while oxygen was introduced.⁶ The

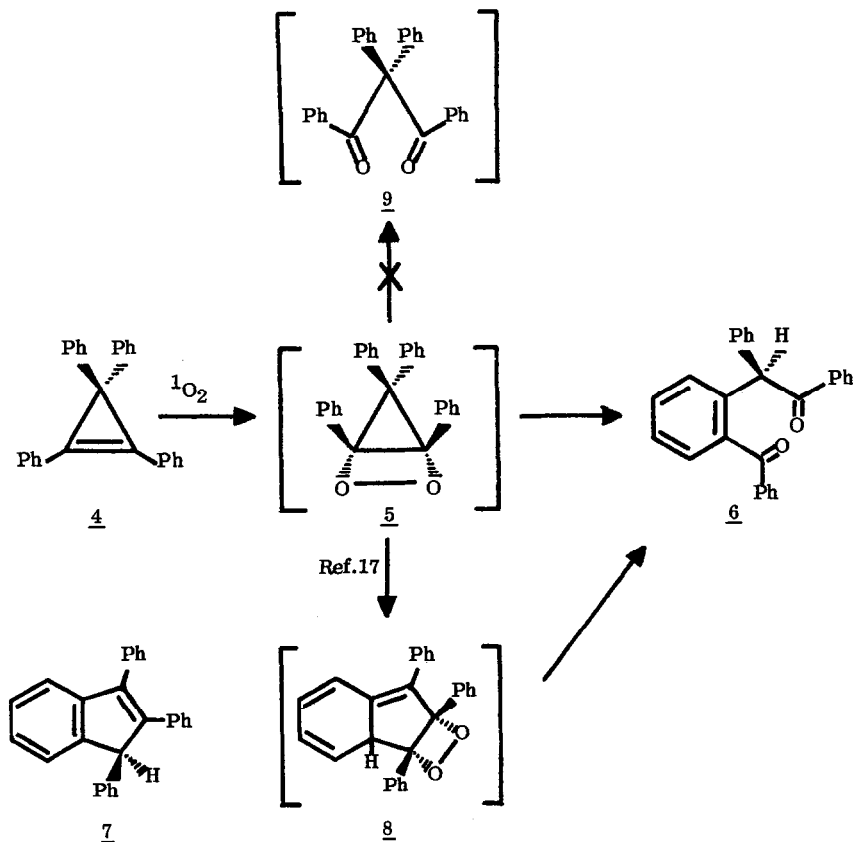


crude products were separated by thick layer chromatography and the major product 3 [40%, mp 148° (ethanol)] was found to be identical to an authentic sample of 1,2,3-triphenyl-1,3-propanedione prepared by an independent route.⁷

It is noteworthy that the complexity of the reaction products obtained from 1 with singlet oxygen increases when acetone or methanol-benzene is employed in place of methylene chloride as a solvent. In acetone, the formation of an intractable, dark, tarry mixture was observed, while in methanol-benzene, the reaction proceeds to give two major products, which were isolated and purified. One of these products was shown to be isomeric with, but not identical to, 3, while the molecular formula of the other indicates incorporation

of the elements of oxygen and methanol into 1.⁸ The dramatic effect exerted by solvent is not without precedent among reactions of singlet oxygen,^{2c, 9} and considerable current interest has been expressed in solvent dependent photooxidations of this type.¹⁰

A major reaction product which proved to be the diketone 6 was obtained upon treatment of tetraphenylcyclopropene 4¹¹ under similar conditions with singlet oxygen⁶ for two hrs in methylene chloride at 10-15°. This product was isolated by thick layer chromatography as well as by liquid chromatography¹² and its nmr spectrum is characterized by a distinctive singlet at δ 6.8 (CDCl₃) in addition to signals for the aromatic protons. The infrared spectrum exhibits strong bands at 1660 and 1685 cm⁻¹ (CHCl₃), respectively, and the structural assignment 6 was deduced from these data as well as satisfactory mass spectral⁸ and elemental analyses. A product identical in all respects to 6 was obtained upon subjecting 1, 2, 3-triphenylindene 7¹³ to oxidation under sensitized conditions⁶ in methanol-benzene solvent at 10-15°. It should be noted that previous reports of indene cleavage by singlet oxygen to give diketones have appeared.¹⁴ Whereas ozonolysis of 1, 2, 3-triphenylindene also gives 6 the singlet oxygen reaction proceeds more efficiently and with fewer by-products.



Tetraphenylcyclopropene 4 is known to undergo thermal¹⁵ and photoinduced¹⁶ rearrangement to 1,2,3-triphenylindene 7; however, prior isomerization of 4 to 7 may be excluded as a possible reaction pathway for conversion of 4 to 6 since tetraphenylcyclopropene is not converted to the triphenylindene 7 upon illumination in the absence of oxygen and/or sensitizer under otherwise identical conditions. It is possible that the dioxetane 5 rearranges by prior C-C bond cleavage to give the dioxetane 8 which would undergo thermal cleavage accompanied by a protic shift to give 6. The stabilization afforded by an additional phenyl substituent may be advanced to explain the divergent results obtained with 1 and 4.¹⁷ Attempts to detect the diketone 9 and/or its anticipated cleavage product, diphenylacetophenone, among the reaction products proved unrewarding.

It is noteworthy that unlike 1 no solvent effect was apparent with 4 and the diketone 6 was also obtained when the singlet oxygen reaction was conducted in methanol-benzene. This was verified by liquid chromatography¹² which showed the methanol-benzene and methylene dichloride reaction product mixtures to be identical. The peak corresponding to diketone 6 in the liquid chromatogram was collected in each case and a mixture of this product from both sources was prepared. A five-fold recycle on a liquid chromatograph showed retention of single peak integrity. Similarly, mixtures were prepared of the diketone 6 obtained from the singlet oxygen reactions on tetraphenylcyclopropene in methanol-benzene and methylene dichloride with the diketone 6 obtained by ozonolysis of the indene 7. Again, repetitive recycling failed to reveal any resolution of these materials.

We are presently attempting to characterize the unknown product obtained from 1 and singlet oxygen in methanol-benzene. This may provide information on the origin of the differences in the effect of solvent composition on the sensitized oxidation of the cyclopropenes 1 and 4.

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- (17) It is inviting to propose that dipolar intermediates such as 10, 11, and 12 are implicated in the conversion of 4 to 8 which in turn undergoes concerted cleavage and aromatization via proton transfer to 6.

