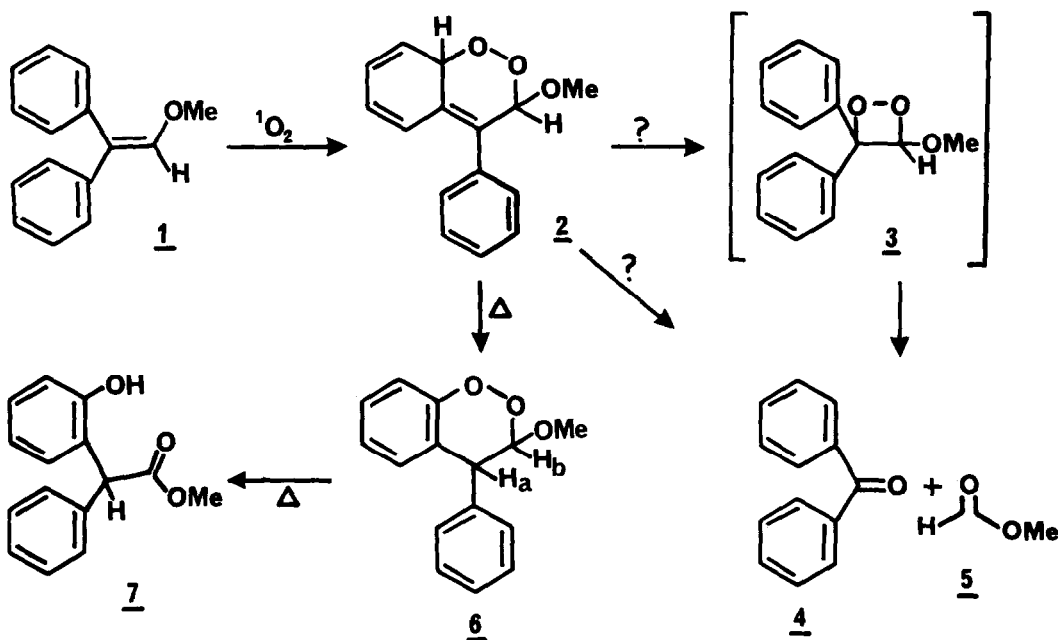


CHEMISTRY OF SINGLET OXYGEN. XXXIII. NEW PRODUCTS
FROM SENSITIZED PHOTOXYGENATION OF
1,1-DIPHENYL-2-METHOXY-ETHYLENE¹

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SUMMARY: Further investigation into the photooxygenation of 1,1-diphenyl-2-methoxyethylene (1) has yielded several products not previously reported and requires reassignment of the structure of one previously reported compound. All products derive from the decomposition of the initial endoperoxide 2.

Foote and Mazur reported² that singlet oxygen gave 1,4 cycloaddition to 1 to yield an unstable endoperoxide, 2, which decomposed on warming to give the products shown below.



Matsumoto and Kuroda recently reported³ the isolation of some novel products from the photooxygenation of β -methoxy-styrene which they suggested to be derived from a quinone methide intermediate. We now report that similar products are derived from the photooxygenation of *1*. New evidence also requires reassignment of the structure of compound *6*.

A solution of *1* and Rose Bengal in acetonitrile was irradiated at room temperature with a 650 W tungsten-halogen lamp for four hours. The solvent was removed under reduced pressure and the remaining oil was separated via medium pressure liquid chromatography. Products *4*⁴, *7*⁵, *8*⁶, *9*⁶, and *10*⁸ were isolated and identified by their spectral data and/or independent synthesis.

The spectra of the lactol *10* match those previously reported for the rearranged endo-peroxide *6*. We have reassigned its structure based on the following evidence. *10* did not free I_2 from acidified KI; compound *6* was reported to have given a positive KI test for peroxides²; however, it appears that this may have been caused by contamination of the sample by unrearranged *2*. *10* also has a weak sharp OH band at 3490 cm^{-1} , overlooked in previous spectra. This band shows no change on dilution, suggesting that it is due to an intramolecularly H-bonded OH.

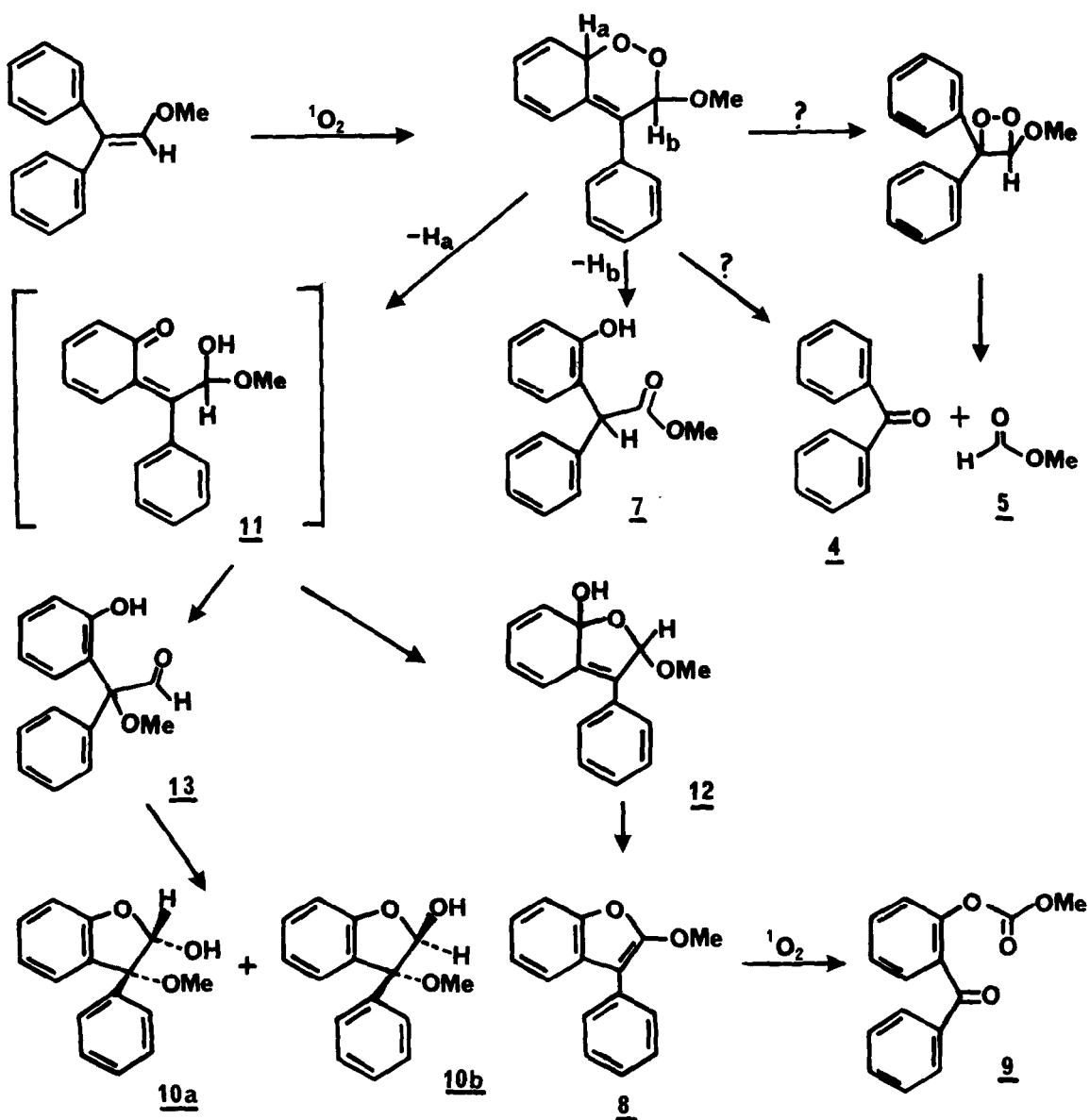
Addition of a drop of D_2O to an NMR tube containing *10* resulted in the disappearance of the 4.91 δ doublet and the collapse of the 5.53 δ doublet to a singlet. These resonances, which were previously assigned to H_a and H_b in *6*, must therefore be reassigned to a $-C-OH$ grouping with an unusually large (12.5 Hz) coupling.

Two isomers of *10* (*a* and *b*) are in fact detectable in the spectrum under all conditions; *10b* is a minor component under most conditions, but can be concentrated to become the major component by crystallization of the mixture. However, solutions of this mixture revert over several hours to a mixture in which *10a* predominates, consistent with the expected ready isomerization. The major isomer is assigned the *cis* stereochemistry, since hydrogen bonding of the OH to the *cis* OCH_3 should give the *anti* arrangement necessary for the large HO-C-H coupling and is consistent with the low frequency of the OH band. The other isomer has an OH resonance at 5.76 ppm (broad s); the C-H resonance appears at 5.73 ppm.* Its OCH_3 resonance is at slightly higher field than that of *10a*, again consistent with the hydrogen bonding present in *10a* but not in *10b*.

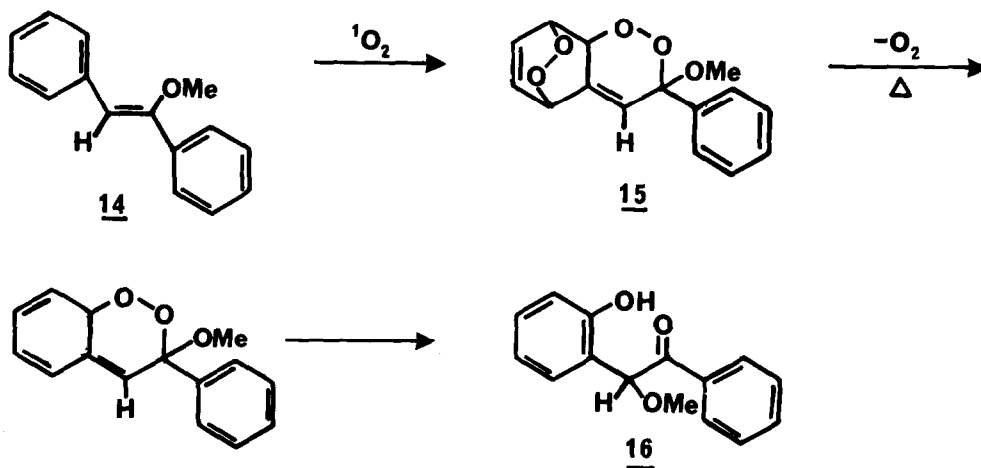
Matsumoto's mechanism³ can be modified to account for all products by allowing hemiacetal *11* to partition between two pathways, either to form product *8* or the lactols derived from aldehyde *13*. The photooxygenation of *8* to *9* has been previously reported.⁷ The transfer of the OMe group is, surprisingly, *intramolecular*, since using 20% v/v EtOH or CD_3OD in benzene as a solvent† gave no incorporation of the external alcohol in the lactol. Low temperature photolysis gave only *2* (spectra identical to those previously reported)²; warming the solution gave a mixture of all the observed products, confirming that *2* is their precursor.

* These assignments were also confirmed by D_2O addition.

† Benzene was the cosolvent in these reactions because of the higher yield of the lactol in non-polar solvents.



We have also observed a similar type of endoperoxide decomposition in the photooxygenation of 1,2-diphenyl-1-methoxy ethylene 14. The product of the low temperature photooxidation is the diendoperoxide (15), based on the NMR of the crude reaction mixture.⁹ However, the major product isolated from the photooxygenation after workup is 16¹⁰ which indicates that a rearrangement similar to that observed for 2 occurs following loss of O_2 (O_2 evolution on warming was observed in some runs). If the workup was carried out in EtOH/ C_6H_6 (1:4, v:v) a small fraction (< 20%) of the product incorporated ethanol.



References

1. Paper XXXII. J. D. Boyd and C. S. Foote, *J. Amer. Chem. Soc.*, submitted. Supported by Public Health Service grant No. GM 20080 and National Science Foundation grant No. CHE77-21560. Bruker NMR purchased from funds provided by National Science Foundation grant No. CHE76-05926.
2. C. S. Foote, P. A. Burns, S. Mazur, and D. Lerdal, *J. Amer. Chem. Soc.*, *95*, 586 (1973).
3. M. Matsumoto and K. Kuroda, *Tetrahedron Lett.*, 1607 (1979).
4. Spectra of compound 4 matched those of benzophenone.
5. Spectra of compound 7 matched those of a sample of methyl 1-(*o*-hydroxyphenyl)-1-phenyl acetate prepared by the method of S. Mazur, Ph.D. Thesis, University of California, Los Angeles (1971).
6. Spectra of compounds 8 and 9 match those of samples prepared by the method of ref. 7.
7. A. Padwa, D. Dehm, T. Oine, and G. A. Lee, *J. Amer. Chem. Soc.*, *97*, 1837 (1975).
8. NMR (ppm relative to TMS, CDCl_3), 6.7 - 7.5 (m, 9H), 5.53 (d, 1H, $J = 12.5$ Hz), 4.91 (d, 1H, $J = 12.5$ Hz), 3.21 (s, 3H); IR (CHCl_3 , 01 mm), 3490, 3080, 3000, 2900, 1615, 1470, 1460, 1450, 1120, 1080, 1010, 970, 920, 910, 850, 695 cm^{-1} ; MS (M/e , 70 eV), 242 M^+ , 210 181; high resolution MS shows the $M-32$ peak corresponds to loss of MeOH.
9. NMR (ppm relative to TMS, CD_2Cl_2), 7.3 - 7.7 (m, 5H), 6.7 - 6.9 (m, 2H), 6.1 (s, 1H), 5.15 (d, 1H, $J = 4.6$ Hz), 4.98 (d, 1H, $J = 5.3$ Hz), 3.41 (s, 3H). This spectrum is almost identical to the spectrum observed for the diendoperoxide of *trans*-stilbene. J. D. Boyd and C. S. Foote, reference 1.
10. NMR (ppm relative to TMS, CDCl_3), 7.0 - 8.2 (m, 9H), 5.81 (s, 1H), 3.5 (s, 3H); IR (CHCl_3 , 0.1 mm), 3500, 3100, 2900, 1690, 1605, 1595, 1495, 1445, 1275, 1235, 1090, 867, 690 cm^{-1} ; MS (M/e , 70 eV) 242 M^+ , 212, 211, 210, 181, 137, 121, 105, 77.

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