

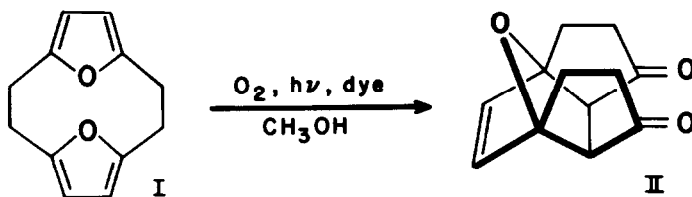
A NOVEL SOLVENT EFFECT IN THE DYE-SENSITIZED
PHOTOOXIDATION OF [2.2](2,5)FURANOPHANE

H.H. Wasserman and R. Kitzing

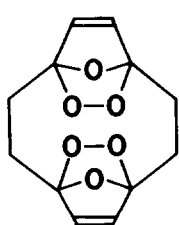
Department of Chemistry, Yale University
New Haven, Connecticut 06520

(Received in the UK 20 November 1969; accepted for publication 28 November 1969)

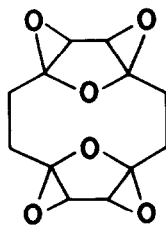
In a previous investigation¹ we have reported that the dye-sensitized photooxidation of [2.2](2,5)furanophane (I) in methanol leads to an oxygenated intermediate which undergoes an intramolecular Diels-Alder reaction forming the diketone (II)².



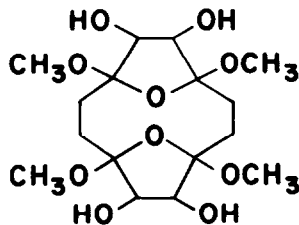
We have now observed that this oxidation reaction takes a different course when the solvent is changed from methanol to methylene chloride.* Thus, when I is irradiated in freshly distilled methylene chloride (150 watt photoflood lamp, methylene blue) for 16 hr. while oxygen is bubbled through the solution, a new product (75%) gradually precipitates. This product, showing no carbonyl or hydroxyl absorption in the infrared, melts at 181-182° with vigorous decomposition, and exhibits a parent peak in the mass spectrum at m/e 252. Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{O}_6$: C, 57.20; H, 4.66. Found: C, 57.24; H, 4.89.



IV



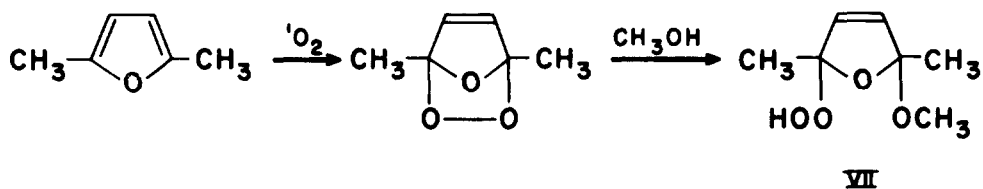
V



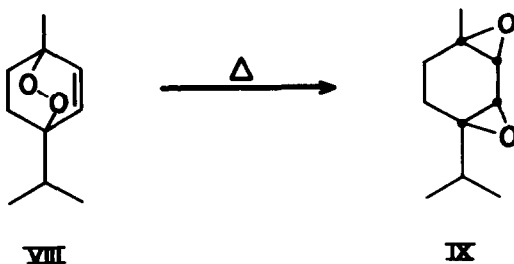
VI

The above data are in accord with either of two structures, IV or V, for the oxidation product. Owing to the lack of solubility of the material in most solvents, it was not possible to use conventional nmr methods to distinguish between these alternatives. However, the reaction of the photooxidation product with hot methanol provided strong evidence favoring structure V.

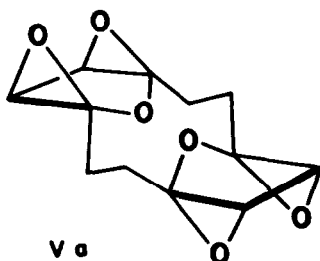
The methanol addition product formulated as VI (m.p. 161-162°, Anal. Calcd. for $C_{16}H_{28}O_{10}$: C, 50.52; H, 7.42. Found: C, 50.43; H, 7.41) has a composition corresponding to the addition of four molecules of methanol. The nmr spectrum ($CDCl_3$) shows peaks at τ 5.75 (q, 4H), 6.7 (s, 12H), 6.9 (q, 4H) and 7.5-8.5 (m, 8H). Formation of the tetramethoxy tetrahydroxy system (VI) from V is consistent with the assigned structures since V should undergo ready epoxide ring opening with the incorporation of four molecules of methanol. On the other hand, one would expect compound IV to add only two molecules of methanol since it has generally been found that endoperoxides of 2,5-disubstituted furans react with alcohols to yield alkoxy hydroperoxides corresponding to VII³.



Structure V is thus in accord with all of the spectroscopic and chemical evidence. It is formed, most probably, by rearrangement of the intermediate endoperoxide IV. Related reactions have previously been reported in studies on the photooxidation of tetraphenylcyclopentadiene⁴ and tetraphenylfuran⁵. Moreover, the thermal rearrangement of ascaridole (VIII) to the isomeric 1,2,3,4-diepoxy-p-menthane (IX) has been established⁶.



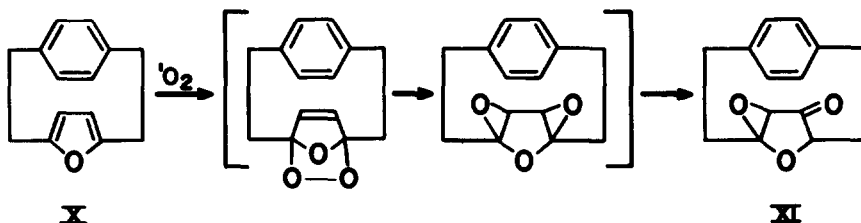
The fact that compound VI shows only one peak due to methoxyl protons in both CDCl_3 and DMSO-d_6 suggests that both VI and the tetraepoxide (V) are symmetrical molecules. This has led us to favor the symmetrical configuration shown in Va. Recently an X-ray crystallographic analysis of the oxidation product has been completed by Dr. Albert Fratini of the University of Dayton. Dr. Fratini's results, to be reported separately, confirm the above structural assignments and establish the configuration of the tetraepoxide as Va.



Acknowledgements:

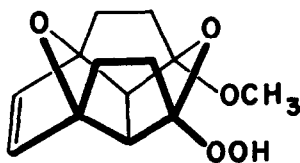
This work was supported by Grant GM-13854 from the National Institutes of Health. We thank Dr. Walter McMurray for help in determining the mass spectrum.

* We have also investigated the effect of solvent in the reaction of the [2.2](2,5)-furanocyclophane (X) with singlet oxygen. The product formed in methylene chloride ($\text{C}_{14}\text{H}_{14}\text{O}_3$, m.p. 93-94°) differs from those previously observed in the methanol photooxidation⁷, and has tentatively been assigned the structure (XI).



References

1. H.H. Wasserman and A.R. Doumaux, Jr., J. Amer. Chem. Soc., 84, 4611 (1962).
2. Our earlier communication did not deal with the stereochemistry of II. The configuration shown was determined by an analysis of the nmr spectrum of II compared with model compounds. (A.R. Doumaux, unpublished work, Ph.D. dissertation, Yale University, 1967). The same conclusions were independently reported by T. Katz, V. Balogh, and J. Schulman, J. Amer. Chem. Soc., 90, 734 (1968). These authors were also able to isolate a side-product from the photooxidation of I in methanol which appears to be III.



III

3. C.S. Foote, M.T. Wuesthoff, S. Wexler, I.G. Burstain, R. Denny, G.O. Schenck and K.H. Schulte-Elte, Tetrahedron, 23, 2583 (1967).
4. C. Dufraisse, G. Rio, and J.J. Basselier, Compt. Rend., 246, 1640 (1958).
5. R.E. Lutz, W.J. Welstead, Jr., R.G. Bass and J.I. Dale, J. Org. Chem., 27, 1111 (1962).
6. J. Boche and O. Runquist, J. Org. Chem., 33, 4285 (1968) and earlier references.
7. H.H. Wasserman, A.R. Doumaux, Jr., and R.E. Davis, J. Amer. Chem. Soc., 88, 4517 (1966).