Tetrahedron Letters No. 21, pp. 1757-1760, 1971. Pergamon Press. Printed in Great Britain.

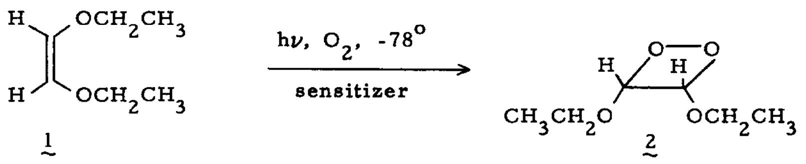
FORMATION OF STABLE BICYCLIC 1,2-DIOXETANES FROM THE ADDITION OF SINGLET OXYGEN TO *p*-DIOXENE AND 1,3-DIOXOLE[1a]

A. Paul Schaap
Department of Chemistry, Harvard University, Cambridge, Massachusetts and
Department of Chemistry, Wayne State University, Detroit, Michigan 48202 [1b]

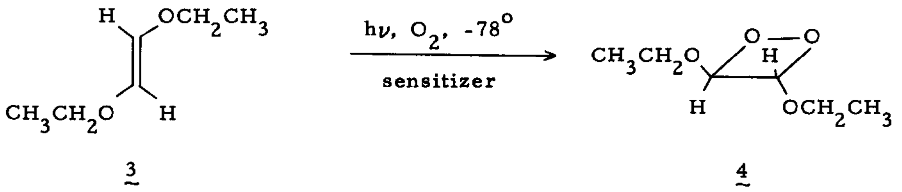
(Received in USA 8 April 1971; received in UK for publication 14 April 1971)

We would like to report the first preparation of two surprisingly stable *bicyclic* dioxetanes *via* the addition of singlet molecular oxygen to cyclic olefins. Also described is the isolation of the diformate of methanediol (**11**), a simple, highly oxygenated compound which to our knowledge was previously unknown.

Singlet oxygen adds stereospecifically to *cis*- and *trans*-diethoxyethylene (**1** and **3**) to give the 1,2-dioxetanes **2** and **4**, respectively.[2a-c] *cis*-Diethoxydioxetane (**2**) was isolated from the photooxidation of **1** at -78° in trichlorofluoromethane with tetraphenylporphin sensitization. Mazur and Foote have isolated tetramethoxydioxetane (**5**) from the photooxidation of tetramethoxyethylene.[3] On heating to 50-70°, dioxetanes **2**, **4** and **5** were found to decompose quantitatively to 2 moles of the carbonyl containing products; in the presence of a fluorescent hydrocarbon, the decompositions were attended with chemiluminescence.[2,3] The chemiluminescent results are in accord with the properties of trimethyldioxetane as reported by Kopecky and Mumford.[4] 1,2-Dioxetanes have also been discussed as possible intermediates in the photooxidation of other olefins: enamines,[5,6] aryl-substituted olefins,[7,8] and vinyl ethers.[2c,9]



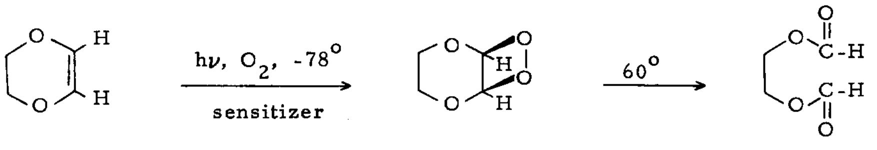
(1)



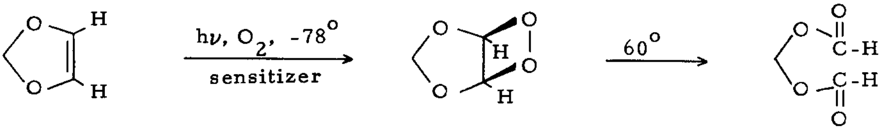
(2)

The isolation of ethylene diformate (**8**) in quantitative yields from the photooxidative cleavage of *p*-dioxene (**6**) has previously been described by us[2b, c] and by Kearns.[10]

Evidence has now been obtained for the intermediacy of dioxetane 7. The addition of singlet oxygen to cyclic vinylene diethers, *p*-dioxene (6) and 1,3-dioxole (9), yields the relatively stable bicyclic dioxetanes, *cis*-1,4,5,6-tetraoxabicyclo[4.2.0]octane (7) (*p*-dioxene dioxetane) and *cis*-1,3,4,5-tetraoxabicyclo[3.2.0]heptane (10) (1,3-dioxole dioxetane), respectively. Thermal decomposition of 7 and 10 yields the carbonyl cleavage products, ethylene diformate (8) and the diformate of methanediol (11), a heretofore unreported compound.



6 7 8 (3)



9 10 11 (4)

The photooxidation at -78° of a 0.1*M* solution of 6 in deuterioacetone with Rose Bengal sensitization was monitored by nmr.[11a] The irradiation was continued for 150-200 min until all of the starting olefin 6 had been consumed as indicated by the disappearance of the singlet nmr absorptions of 6 (δ5.99, 2H; δ4.06, 4H). The nmr spectrum of the *p*-dioxene dioxetane (7) was obtained (Fig. 1) with a two-proton sharp singlet at δ6.22 (dioxetane ring protons) and 2 two-proton AA' BB' multiplets centered at δ4.10 and 4.56 (methylene protons of 7,

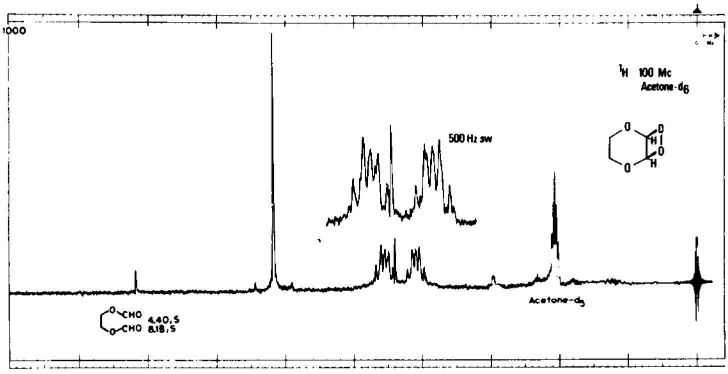


Figure 1. 100 MHz NMR Spectrum of *p*-Dioxene Dioxetane (7).[11b]

two of which are *exo* and two of which are *endo* to the bicyclic system).[12-14] The spectrum also showed small singlets at δ4.40 and 8.18 indicating the presence of 7% of the cleavage product 8. This amount of 8 formed at -78°, at which temperature 7 is completely stable, arises through photosensitized decomposition of 7 by the excited dye. Indeed, when the photooxidation is carried out over extended periods of time, increasing amounts of 8 are observed. This result was also obtained in the photooxidation of *cis*-diethoxyethylene.[2b,c] Heating the photooxidation solution containing 7 to 60° for approximately 20 min decomposed the dioxetane 7 so that the nmr spectrum became only that of 8. Decomposition of 7 at 60° in the presence of a fluorescent hydrocarbon such as 9, 10-dibromoanthracene (DBA) produced chemiluminescence of the color of the DBA fluorescence.

The photooxidation of 1, 3-dioxole (9) was carried out under the same conditions as employed for 6. After irradiation at -78° for 60 min, the nmr spectrum taken at ambient temperature indicated the complete consumption of 9 with the disappearance of the singlet absorptions at δ6.52 and 5.51; the spectrum showed absorptions at δ6.68 (s, 2H, ring protons), 5.78 (s, 1H) and 5.70 (s, 1H) for the dioxetane 10. Singlet absorptions of equal intensity at δ8.25 (formate protons) and 5.91 (methylene protons) were also observed in the spectrum indicating the presence of the cleavage product 11. The geminal coupling constant of 10 is apparently zero within the limits of the resolution of the spectrometer (0.5 Hz). Cookson and coworkers have reported that geminal coupling constants in the methylene groups of 1, 3-dioxolanes are characteristically 0 to ± 2 Hz.[15]

On heating the solution containing 10 to 60° for 0.5 hr, the spectrum became only that of the cleavage product 11. Thermal decomposition of 10 in the presence of DBA produced chemiluminescence.

Methylene diformate (11) has been isolated by the following procedure. Photooxidation of 0.11 g (1.5 mmol) of 9 in 4 ml of $CFCl_3$ at -78° with tetraphenylporphin sensitization in the presence of 10 mg of 2, 6-di-*t*-butyl-*p*-cresol, a free radical inhibitor, for 150 min produced a solution containing 55% 10 and 45% 11 by nmr. This solution was warmed to room temperature and the $CFCl_3$ removed under vacuum. The residue was bulb to bulb distilled at room temperature under vacuum to yield a clear, colorless liquid with a pungent odor. This material was greater than 98% pure by nmr with 1:1 singlet absorptions in $CDCl_3$ at δ8.03 and 5.90. An infrared spectrum of the compound showed intense absorptions at 1755, 1170 and 1085 cm^{-1}. Gas-liquid chromatography of this material at 100° over 20% carbowax 20 M on chromosorb W in a Teflon column showed only one peak.[16]

The relative rates of reaction of vinylene diethers, 1, 6 and 9 with singlet oxygen have been determined at 8° in acetone from a series of competitive photooxidations: 6 (1.00), 9 (10), and 1 (151). Preliminary kinetic results indicate that bicyclic dioxetanes 7 and 10 are not significantly different from acylic dioxetane 2 in thermal stability.[17]

Acknowledgments: The author wishes to express his gratitude to Professor Paul D. Bartlett of Harvard University, in whose laboratory this work was begun and to Professor Morton Raban of this department for helpful discussions concerning the nmr spectra of the dioxetanes. Support from the National Science Foundation and the Petroleum Research Fund (PRF 2031 - G) as administered by the American Chemical Society is gratefully acknowledged.

REFERENCES

1. a) Presented at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March, 1971; b) Present address.
2. a) P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, **92**, 3223 (1970); b) P. D. Bartlett, paper presented at the International Symposium on Singlet Oxygen, New York Academy of Sciences, New York, N.Y., Oct. 23, 1969; c) P. D. Bartlett, G. D. Mendenhall and A. P. Schaap, *Ann. N. Y. Acad. Sci.*, **171**, 79 (1970).
3. S. Mazur and C. S. Foote, *J. Amer. Chem. Soc.*, **92**, 3225 (1970).
4. K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969).
5. C. S. Foote and J. W.-P. Lin, *Tetrahedron Lett.*, **29**, 3267 (1968).
6. J. Huber, *ibid.*, **29**, 3271 (1968).
7. W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 7771 (1969).
8. G. Rio and J. Berthelot, *Bull. Soc. Chim. Fr.*, **10**, 3609 (1969).
9. R. S. Atkinson, *Chem. Commun.*, 177 (1970).
10. D. R. Kearns, paper presented at the International Symposium on Singlet Oxygen, New York Academy of Sciences, New York, N.Y., Oct. 23, 1969.
11. a) The photooxidation conditions were the same as previously employed for the addition of singlet oxygen to *cis*- and *trans*-diethoxyethylene;[2a] the solution was held in an acetone-dry ice bath at -78° in a Dewar with Pyrex windows and irradiated through a Corning uv filter with a 500-W quartz-iodide lamp. b) A. P. Schaap, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1970, p. 96.
12. The nmr spectrum of **7** was unchanged from -78° to ambient temperature.
13. For a discussion of nmr spectra of four-proton AA' BB' systems, see J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, New York, N.Y., 1965, pp. 399-423.
14. Dioxetane **7** has also been produced by reaction at -78° of triphenylphosphite ozonide with **6**: A. P. Schaap and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 6055 (1970).
15. R. C. Cookson, T. A. Crabb, J. J. Frankel and J. Hudec, *Tetrahedron Suppl.*, **7**, 355 (1966).
16. Further characterization of **11** is in progress.
17. The activation energy for the decomposition of **2** is 24 kcal/mole: T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, **93**, 0000 (1971).