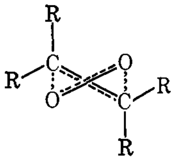
oxygen lacks the strongly electrophilic center which can be discerned in ketenes and vinyl cations,[19] it has one property that must predispose it to this mode of reaction: any peroxide structure has such a strong preference for a nonplanar conformation that the contorted transition state (**6**) for the $2_s + 2_a$ addition may bring hardly any more strain than does the dioxetane ring itself.



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Acknowledgment. This research was supported by grants from the National Science Foundation and the National Institutes of Health.

(19) Reference 9, p 847.

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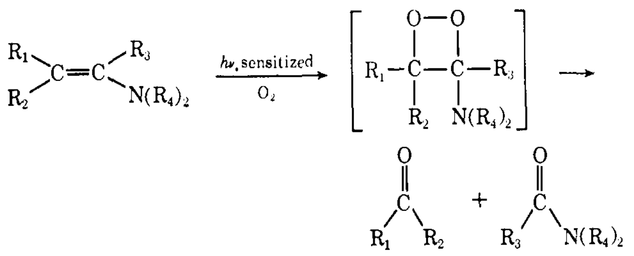
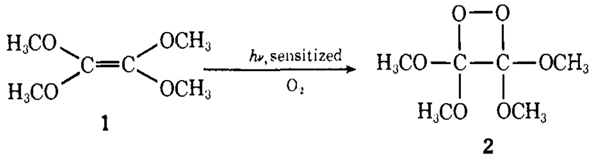
Chemistry of Singlet Oxygen. IX. A Stable Dioxetane from Photooxygenation of Tetramethoxyethylene[1]

Sir:

There has been much recent interest in 1,2-dioxetanes as possible intermediates in chemiluminescent reactions[2] and in olefin photooxygenations.[3] Electron-rich olefins are well known to undergo 1,2 cycloadditions with dienophiles,[4] and enamines were found to undergo photosensitized oxygenation[3a,d] to produce unstable intermediates which decomposed cleanly to carbonyl fragments. However, these intermediates were shown to be not solely monomeric 1,2 cycloadducts.[3a] The report by Hoffman and Häuser that the reactive olefin 1,1,2,2-tetramethoxyethylene (**1**) undergoes 1,2 cycloaddition[5] suggested that photooxygenation of this compound might produce the dioxetane 1,2-dioxa-3,3,4,4-tetramethoxycyclobutane (**2**).





Photooxygenation of **1** in ether, at −70°, sensitized by either zinc tetraphenylporphine or dinaphthalenethiophene with visible light[6] proceeded rapidly, and ceased abruptly after uptake of 1 equiv of oxygen. Both sensitizer and light were found to be essential. Evaporation of solvent (−78°) and evaporative distillation of the residue (25°) yielded a clear, pale-yellow liquid in 94% yield. This material, which contained (nmr) approximately 10% of dimethyl carbonate, was further purified by low-temperature crystallization from pentane–ether. The pure product (mp −8 to −9°) was found to be remarkably stable ($t_{1/2}$ = 102 min at 56°), although its decomposition appears to be catalyzed by zinc tetraphenylporphine.[7] The nmr spectrum (in Freon 12, 100 MHz) consisted of a single sharp resonance at 3.45 ppm at temperatures as low as −118°. The ir spectrum (neat) had principal bands at 2980 (m), 2870 (w), 1440 (m), 1345 (m), 1210 (s), 1130 (s), 1065 (s), 1020 (m), 975 (w), 910 (m), 875 (w), and 830 cm^{-1}. Elemental analysis was consistent with the formula $C_6H_{12}O_6$ (*Anal.* Calcd: C, 40.01; H, 6.71. Found: C, 40.02; H, 6.74). The molecular weight was determined to be 185 ± 6 (cryoscopic, benzene) and 198 (vapor pressure osmometry); the calculated value is 180. Iodometric determination showed 87% of one peroxidic oxygen. When the product was heated at 56° in benzene in an nmr tube, a smooth decomposition occurred, giving dimethyl carbonate (identified by ir, nmr, and vpc comparison with authentic material) as the sole product in quantitative yield.

These data are entirely consistent with dioxetane structure **2**. Although alternate structures **3** and **4** can be envisioned, they may be discounted on the following grounds. Structure **3** would be expected to show two nonequivalent methoxyl resonances in the nmr (assuming oxygen inversion would be slow on the nmr time scale at −118°, the lowest temperature so far investigated).[8] The equilibrium **4a** ⇄ **4b**, even if it were rapid enough to result in a single methoxyl resonance, should produce an averaged chemical shift considerably downfield from the observed position.[9]

One of the most intriguing aspects of structure **2** is its close relationship to the CO_2 dimer (**5**), which has been implicated as the key intermediate in the chemiluminescent reaction of oxalyl halides and esters with H_2O_2,[10] and to the suggested dioxetane interme-

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(1) Contribution No. 2544; supported by HEW-NAPCA Grant No. AP-00681 and NSF Grant No. GP-8293. Paper VIII: C. S. Foote and M. Brenner, *Tetrahedron Lett.*, 6941 (1968).

(2) (a) F. McCapra, *Quart. Rev., Chem. Soc.*, 20, 485 (1966); (b) F. McCapra, *Chem. Commun.*, 155 (1968); (c) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969); (d) E. H. White, J. Wiecko, and D. R. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969).

(3) (a) C. S. Foote and J. W.-P. Lin, *Tetrahedron Lett.*, 3267 (1968); (b) D. R. Kearns, *J. Amer. Chem. Soc.*, **91**, 6554 (1969); (c) W. Fenical, D. R. Kearns, and P. Radlick, *ibid.*, **91**, 3396, 7771 (1969); (d) J. Huber, *Tetrahedron Lett.*, 3271 (1968).

(4) Reviews: R. Gompper, *Angew. Chem. Int. Ed. Engl.*, **8**, 312 (1969); R. W. Hoffman, *ibid.*, 7, 754 (1968).

(5) R. W. Hoffman and H. Häuser, *ibid.*, 3, 380 (1964).

(6) See C. S. Foote, S. Wexler, W. Ando, and R. Higgins (*J. Amer. Chem. Soc.*, 90, 975 (1968)) for details of the technique.

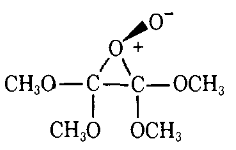
(7) The dioxetane reported by Kopecky[2c] appears to be comparably stable, but no evidence for its structure or molecular weight has so far been published.

(7a) Note Added in Proof. The dioxetane has been characterized (E. H. White, J. Wiecko, and C. C. Wei, *J. Amer. Chem. Soc.*, **92**, 2167 (1970)).

(8) An approximate analogy may be found in the inversion rate of O-isopropylethyleneoxonium fluoroborate, for which the coalescence temperature is −50°: J. B. Lambert, *ibid.*, **90**, 1349 (1968).

(9) The average of the methoxyl shifts of trimethyl orthoformate (3.23 ppm) and of the dimethoxycarbonium ion $[HC(OCH_3)_2]^+$ (4.64 ppm: see R. I. Borch, *ibid.*, **90**, 5303 (1968)) would be 3.93 ppm whereas the observed value is 3.45 ppm.

(10) M. M. Rauhut, *Accounts Chem. Res.*, **2**, 80 (1969); H. F. Cordes, H. P. Richter, and C. A. Heller, *J. Amer. Chem. Soc.*, **91**, 7209 (1969).



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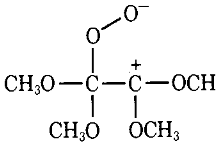
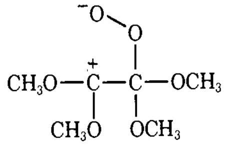
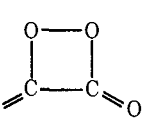


4a



4b

diate (6) in the chemiluminescent oxidation of tetrakis(dimethylamino)ethylene.[11]



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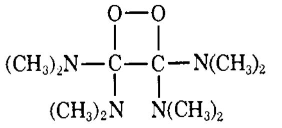

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When **2** was heated to 80° in dilute benzene solution with several different fluorescent hydrocarbons, distinct luminescence was observed; the color corresponded to the hydrocarbon fluorescence.

This represents the first preparation of a 1,2-dioxetane by photooxygenation[12] but by no means requires that 1,2 cycloaddition of singlet oxygen be concerted;[3b] in particular, dipolar ions such as **4** may well be intermediate.[4] Furthermore, these experiments do not provide evidence either for or against the assertion[3c] that dioxetanes may be intermediate in the formation of allylic hydroperoxides in the ene-type photooxygenation.

Acknowledgment. Miss Heather King carried out microanalyses; Dr. Gwendolyn Chmurny recorded the 100-MHz nmr spectra.

[11] J. P. Paris, *Photochem. Photobiol.*, **4**, 1059 (1965).

[12] See P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, **92**, 3223 (1970), for similar results. We thank Professor Bartlett for communicating these results, reported in part at the International Conference on Singlet Oxygen, New York, N. Y., Oct 1969 (*Ann. N. Y. Acad. Sci.*, in press).

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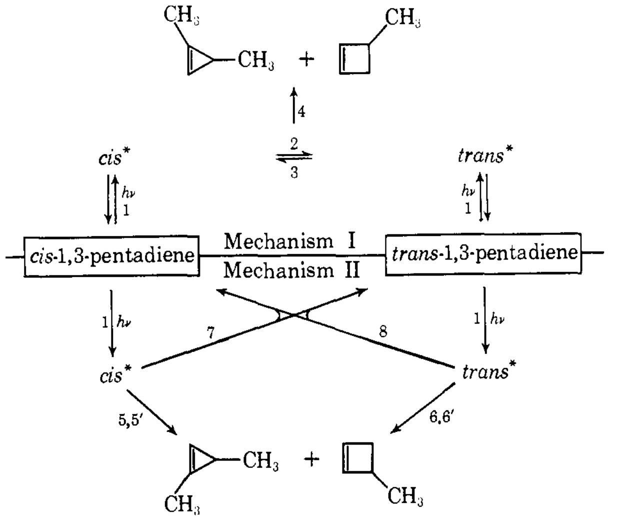
Differences in Reactivity between Excited States of *cis*- and *trans*-1,3-Pentadiene

Sir:

We have observed that 1,3-pentadiene can photoisomerize to 1,3-dimethylcyclopropene in solution, on direct irradiation, in a reaction similar to that previously observed[1] in the gas phase on sensitization by Hg($^3P_1$) atoms. The reaction offers a unique probe into the nature of the electronically excited states that are formed from the *cis* and trans isomers. The photoisomerization of 1,3-pentadiene to 3-methylcyclobutene[2] is observed only on direct irradiation in solution and thus can serve the same purpose in a more limited way.[3]

Two mechanisms may be visualized to explain the possible reactions when one of the stereoisomers of 1,3-pentadiene is irradiated. In the first one (steps 1–4) the electronically excited states of *cis* and *trans* are assumed to come into rapid equilibrium while the cyclization reactions (4) are relatively slow. In the second scheme (steps 1, 5, and 6) there is little or no equilibration between the *excited* states of *cis*- and *trans*-1,3-pentadiene; as a result, the rates of cyclization of each of these stereoisomers to products should be distinctly different. Steps 7 and 8 are internal conversion processes which are postulated to result in partial stereoisomerization; these steps are necessary to explain the experimental observation that stereoisomerization is considerably faster than any of the cyclizations under all irradiation conditions.



We have obtained quantum yields for the cyclization and stereoisomerization reactions of pure *cis*- and *trans*-1,3-pentadienes in solution (solvent cyclohexane; ambient room temperature) at a series of concentrations when irradiated at 253.7 nm. Corrections were applied for the progressive increase in the concentration of the stereoisomer that is formed as a product in any given instance. The actual quantum yields are given in Table I, the values extrapolated to infinite dilution being indicated in dark print. In discussing these results, the contribution of bimolecular (*e.g.*, dimerization) processes to the overall reaction of the excited states can be disregarded if the quantum yield values at zero concentration are considered.

The data in Table I show that the excited states of *cis*- and *trans*-1,3-pentadiene yield 3-methylcyclobutene as well as 1,3-dimethylcyclopropene at distinctly different rates, which is compatible only with the second mechanism. Further, the quantum yield for *cis* → *trans* or *trans* → *cis* isomerization is no more than 10%. These data suggest that the singlet excited states of *cis*- and *trans*-1,3-pentadiene are (i) chemically distinct species[4] and (ii) undergo interconversion with none of

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[1] R. Srinivasan and S. Boué, *Tetrahedron Lett.*, 203 (1970).

[2] R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 4141 (1962).

[3] In the vapor phase, direct irradiation of 1,3-pentadiene yields 1,4-pentadiene as the major product along with many other minor products, including 1,3-dimethylcyclopropene.

[4] On sensitization to the triplet state by Hg($^3P_1$) atoms, we found no detectable difference between *cis* and *trans* isomers in the rate of forma-