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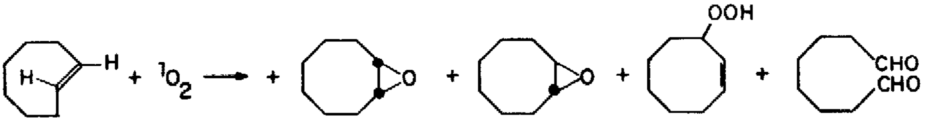
REACTION OF SINGLET OXYGEN WITH TRANS-CYCLOOCTENE. EVIDENCE FOR A 1,2-DIOXETANE INTERMEDIATE.

Y. Inoue[1] and N.J. Turro*
Chemistry Department, Columbia University
New York, New York 10027

ABSTRACT Evidence is presented that the reaction of $^1O_2$ with trans-cyclooctene yields an unstable trans-fused bicyclic dioxetane as a significant product.

INTRODUCTION. The reaction of singlet molecular oxygen ($^1O_2$) with alkenes generally yields an allylic hydroperoxide as the major product.[2] The absence of allylic hydrogens or the presence of structural constraints that inhibit abstraction of allylic hydrogens usually renders an alkene unreactive toward $^1O_2$. The reaction of "strained" alkenes with $^1O_2$ is of special interest, since the release of strain during reaction may contribute to an increased reactivity of these substrates. We report here an investigation of the reaction of $^1O_2$ with trans-cyclooctene (1-t)[3] a strained alkene that possesses abstractable allylic hydrogen atoms, and we compare the chemistry of 1-t and $^1O_2$ to that of cis-cyclooctene (1-c) with $^1O_2$.

RESULTS. Product Studies. The reaction of 1-t with $^1O_2$ (generated by methylene blue photosensitization[2], thermolysis of 1,4-dimethylnaphthalene endoperoxide[6], or thermal decomposition of triphenyl phosphite ozonide[7]) produces chemiluminescence and yields the products shown in eq. 1. Table 1 lists the product[8] ratios as a function of the method employed to produce $^1O_2$.



(1)

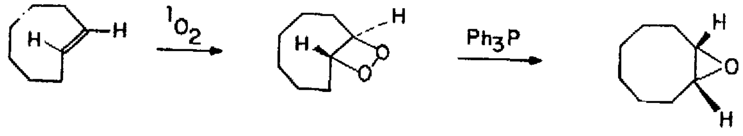
1-t 2-c 2-t 3 4

1-c was found to be completely unreactive to oxidation by 1,4-naphthalene endoperoxide[9]. Low yield of products 2 and 3 could be detected when 1-c was oxidized by methylene blue photosensitization or with triphenyl phosphite ozonide. Neither the dialdehyde 4 nor chemiluminescence was observed. Furthermore, no significant 1-t → 1-c isomerization was observed during any of the reactions studied.

Chemiluminescence Studies.[10] The chemiluminescence spectrum, determined by thermolysis of a solution of naphthalene endoperoxide and 1-t show a maximum (CH_2Cl_2 or $CHCl_3$) at ∿400 nm and was found to be experimentally indistinguishable in position and shape from the photoexcited fluorescence spectrum of 1,8-octanedial[11] (0.1 M in CH_2Cl_2 or $CHCl_3$). The decay of chemiluminescence was found to be first order in the temperature range 40° - 70°C. Activation parameters of $E_a = 23 \pm 1$ kcal/mole and $\log A = 12.5 \pm 0.5$ were derived from the decay of chemiluminescence irrespective of the method of oxidation.[12]

The observed chemiluminescence produced upon oxidation of 1-t was greatly enhanced by addition of 9,10-dibromoanthracene. 9,10-Diphenylanthracene was a less effective enhancer of chemiluminescence.[13]

DISCUSSION. The observation of 4 and of chemiluminescence upon oxidation of 1-t is consistent with the formation of a dioxetane 5 (eq. 2) as a reactive intermediate.



1-t 5 2-c (2)

In particular, the identy of the chemiluminescence spectrum and the photoexcited fluorescence of 1,8-octanedial and the activation parameters provide strong support for this conclusion.

Since 5 is strongly implicated in the reaction of 1-t with $^1O_2$, a trapping experiment which would provide both support for the intermediary of 5 and reveal the stereochemistry at the dioxetane ring fusion was attempted. The reaction of triphenylphosphine with dioxetanes is reported to yield an epoxide stereospecifically and with configurational inversion of one of the dioxetane carbons and retention of the other.[14]

1-t was subjected to methylene blue sensitized photooxidation at 0°C. The reaction mixture was then treated with triphenylphosphine. Product distribution (relative to the product distribution obtained without addition of phosphine) showed a decided increase in the yield of 2-c and a corresponding decrease in the yield of 4 (Table 2). The yield of 2-t, on the other hand, was comparable whether or not phosphite was employed in the workup. These results are consistent with a stereospecific reaction of 1-t with $^1O_2$ (eq. 2).

CONCLUSION. 1-t and 1c display a striking difference in their reactivity toward $^1O_2$. At least a portion of the reaction of 1-t with $^1O_2$ proceeds through a stereospecific [2 + 2] cycloaddition to form a trans-fused dioxetane, 5. We interpret the differing yields of allylic hydroperoxide observed to be due to oxidation pathways for 1-t that do not involve $^1O_2$.

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Table 1. Reaction of 1t with Various $^1O_2$ Sources.

$^1O_2$ Source (temp.)	[1t], M	Solvent	Product Yield, %*				
			1t	2c	2t	3	4
(a) Photooxygenation (0°C)	0.02	CH_2Cl_2	47	5.7	1.6	24	10.3
(b) 1,4-Dimethylnaphthalene endoperoxide (71°C)	0.1	CH_2Cl_2	--	7.3	0.4	1.0	2.6
	0.1	CH_3CN	81	3.7	0.3	1.2	2.6
	0.1	Freon 112	94	1.1	0.1	0.8	2.2
	0.1	MeOH	99	0.3	0	0	0
(c) $(PhO)_3PO_3$ (-17°C)	0.2	CH_2Cl_2	--	2.5	8.5	11	7.0
	0.1	CH_2Cl_2	--	2.6	8.3	4.2	4.2

*Yield based on 1t used.

Table 2. Methylene Blue Sensitized Photooxygenation in CH_2Cl_2 at 0°C and Subsequent Treatment with Triphenyl Phosphine.

[1t], M	$[Ph_3P]$, M	Product Yield, %					Chemiluminescence
		1t	2c	2t	3	4	
0.02	0	47	5.7	1.6	-	10.3	Detected
0.02	0.03*	52	8.8 +3.1	1.7	24	7.7 -2.6	None

* Triphenyl phosphine was added after the photolysis.

REFERENCES AND NOTES.

(1) Yoshida Foundation of Science and Technology Research Fellow 1978-1979; present address, Department of Applied Chemistry, Himeji Institute of Technology, Shosha 2167, Himeji, Hyogo 671-22, Japan.

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(3) Trans-cyclooctene has a higher strain energy (by 9.3 kcal/mole)[4] and lower ionization potential (by 0.29 eV, ∿7 kcal/mole)[5] than the cis-isomer; these figures may favor the initial interaction with singlet oxygen.

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(6) The concentration of the naphthalene endoperoxide was 0.032 M; for the singlet oxygen formation from the endoperoxide, see N.J. Turro and M.-F. Chow, J. Am. Chem. Soc., 101, 3701 (1979)

(7) The phosphite ozonide was prepared by the ozonolysis of triphenyl phosphite (0.034 M) in methylene chloride according to the procedures described by Murray and Kaplan; J. Am. Chem. Soc., 91, 5358 (1969).

(8) The products were analyzed and separated on vpc. All the products showed satisfactory spectroscopic data on NMR, IR, and mass spectroscopy. Compound 3 was identified directly by NMR as the corresponding alcohol after reduction by triphenylphosphine.

(9) The methylene blue sensitized photooxygenation of 1c in ethanol has been reported by Matuura et al. to give the hydroperoxide as a major product; Tetrahedron, 27, 3095 (1971).

(10) The chemiluminescence was recorded on a Hitachi MPF-3L fluorimeter and the decay of chemiluminescence at various temperatures was analyzed by single photon counting method.

(11) Synthesized by ozonolysis of cis-cyclooctene in CH_2Cl_2 at -78°C.

(12) These activation parameters are typical of 1,2-dioxetanes: W.H. Richard, M.B. Yelvington, and H.E. O'Neal, J. Am. Chem. Soc., 94, 1619 (1972); C.S. Foote and T.R. Darling, ibid., 96, 1625 (1974).

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