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DIOXETANO-CROWN ETHERS.
STABILIZATION THROUGH COMPLEXATION WITH METAL IONS[1)]

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The first members of dioxetanocrown ethers **3** and **4** were prepared in methylene blue-sensitized photooxygenations of 9- and 18-membered stilbenocrown ethers **1** and **2**, and the activation parameters for the thermolyses of **3** and **4** were obtained. Thermal decomposition of the bis-dioxetano-18-crown-6 **4** was decelerated or accelerated in the presence of alkali metal salts depending upon the nucleophilicity of the counter anion.

We have recently reported the syntheses and cation-binding abilities of some stilbenocrown ethers.[1)] Singlet oxygenations of these unsaturated crown ethers give direct access to dioxetanocrown ethers, a new category of crown ether. In the present communication, we wish to report our preliminary results on the photooxygenations of 9- and 18-membered stilbenocrown ethers and the effects of various alkali metal salts upon stability of the dioxetanocrown ether.

Photooxygenations of 1 % solutions of stilbeno-9-crown-3(**1**) and distilbeno-18-crown-6(**2**) were performed at -78 or 0°C in dichloromethane or chloroform-d containing 1.5×10^{-4}M methylene blue(MB) as a sensitizer with continuous bubbling of oxygen gas.[2)] The irradiation of the solution for ca. 10 min led to complete consumption of the stilbenocrown ether, as shown by NMR monitoring. The formation of dioxetane **3** or **4**[3)] was proved by the appearance of an O-O stretching band around 880 cm^{-1} on IR

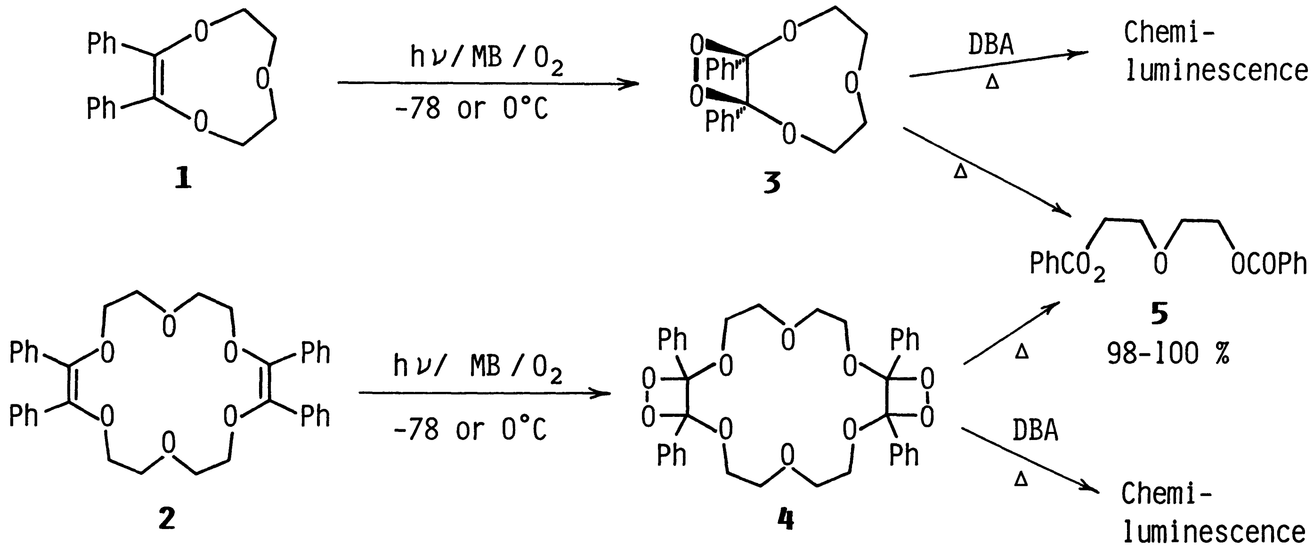


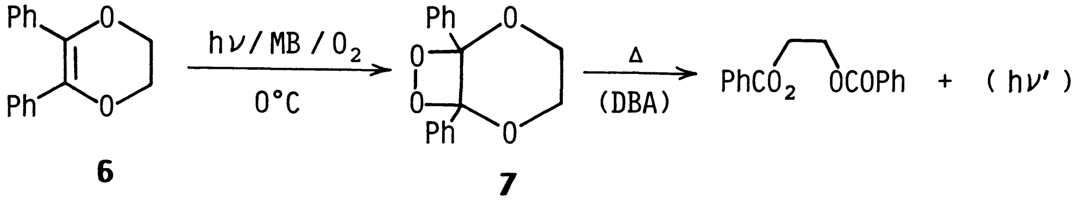
Table 1 Spectral Changes upon Photooxygenation of Stilbenocrown Ethers **1** and **2** and the Subsequent Thermolysis of the Resulting Dioxetanes **3** and **4**

	$\mathbf{1} \xrightarrow{^1O_2}$	$\mathbf{3} \xrightarrow{\Delta}$	$\mathbf{5} \xleftarrow{\Delta}$	$\mathbf{4} \xleftarrow{^1O_2}$	$\mathbf{2}$
IR(cm^{-1})	1630(C=C)	1200(C-C-O) 880(O-O)	1720(C=O)	1200(C-C-O) 870(O-O)	1620(C=C)
^1H NMR(δ) ($CDCl_3$,TMS)	7.13(s,10H)	7.0-7.5(m,10H)	8.07(m,4H) 7.47(m,6H)	7.0-7.5(m,20H)	7.15(s,20H)
	4.30(t,4H) 3.97(t,4H)	4.4-4.8(m,2H) 3.7-4.1(m,6H)	4.50(t,4H) 3.90(t,4H)	3.7-4.5(m,16H)	3.96(s,16H)

and by the drastic changes in chemical shifts of the crown-ring and phenyl protons on ^1H NMR spectra; the spectral changes during the course of reaction are shown in Table 1.

Upon heating, the dioxetanes **3** and **4** gave diethylene glycol dibenzoate **5** in quantitative yields without concomitant emission of light. Thermal decomposition of **3** or **4** in the presence of 9,10-dibromoanthracene(DBA) as an energy acceptor however produced sensitized chemiluminescence, the shape of which was exactly identical to the DBA fluorescence.4)

Thermolyses of the dioxetanes **3** and **4** were carried out at 60-85°C in toluene in order to evaluate their thermal stabilities. In these experiments, the stilbenocrown ethers **1** and **2** were photooxygenated in dichloromethane5) to the corresponding dioxetanes according to the same procedure mentioned above. The resulting dichloromethane solution of the dioxetane was passed through a very short silica-gel column at 0°C to eliminate the sensitizer methylene blue, which was shown to enhance the decomposition rate upon thermolysis. The solution thus obtained was evaporated to dryness at 0°C at a reduced pressure and the solvent toluene5) containing 1×10^{-3}M DBA was added to make ca. 1% solution of the dioxetane. The decompositions of both dioxetanes, monitored by the chemiluminescence decay at 433 nm, obeyed first-order kinetics. Arrhenius plots gave excellent straight lines ($r^2 > 0.999$) for **3** and **4**. The activation parameters obtained are presented in Table 2 along with those for the reference dioxetane, 1,6-diphenyl-2,5,7,8-tetraoxabicyclo[4.2.0]octane(**7**),6,7) prepared from 2,3-diphenyl-1,4-dioxene(**6**).8) As shown in Table 2, no evident deviations in activation parameters are seen at least for the dioxetanocrown ether **4**,9) whereas somewhat different parameters are given for **3**.



Although the above results mostly coincide with those reported previously,7,10) interesting may be how the stability of the dioxetanocrown ether **4** is affected through complexation of a cation in the crown cavity. An attempt to stabilize

Table 2 Activation Parameters for Thermolyses of Dioxetanes **3**, **4**, and **7** in toluene

Dioxetane	Ea, kcal/mol	log A	$\Delta H^{\ddagger}_{298}$, kcal/mol	$\Delta S^{\ddagger}_{298}$, cal/mol·deg	Rate const. at 25°C,[a] s^{-1}
7	24.8_5[b)] (24.8)[c)]	12.4_4[b)] (12.39)[c)]	24.2_6[b)] (24.2)[c)]	-3.6[b)] (-3.8)[c)]	1.66×10^{-6}[b)] (1.62×10^{-6})[c)]
3	24.3_2	12.9_0	23.7_3	-1.5	1.18×10^{-5}
4	24.5_0	12.3_8	23.9_1	-3.9	2.66×10^{-6}

a) Calculated from Arrhenius equation. b) Ref. 6. c) Ref. 7; the original $\Delta S^{\ddagger}$ value reported for **7**, i.e. -1.8 cal/mol·deg, must be miscalculated, since our own calculation using their data gives the different value presented here.

the dioxetane **4**, by adding finely ground potassium bromide to the toluene solution of **4**, resulted in failure; the decomposition rate was not affected by the addition probably due to the poor solubility of the salt in toluene. We finally used ethanol[5)] as a solvent and measured the decomposition rate constants of **4** and **7** at 74.4°C in the presence of excess amounts of various alkali metal salts. The results are presented in Table 3. The decomposition of the dioxetanocrown ether **4** was fairly decelerated by adding the salts with counter anions of low nucleophilic constants[11)] ($\underline{n} \leq 1.03$), while the same salts had little effect on the decomposition rates of the reference dioxetane **7**. That the magnitude of deceleration is in rough agreement with the tendency of cation extractabilities ($K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$) of the parent 18-crown-6[1)] may be taken as another support for the stabilization through complex formation. The salts with anions of $\underline{n} > 3$, on the other hand, gave rise to accelerated decompositions of both **4** and **7**, which may be ascribable to the nucleophilic attack by the anion or, more probably, to the electron-transfer interaction between the anion and the dioxetane.[12)]

Table 3 Decomposition Rate Constants ($\underline{k}_1$) in Ethanol at 74.4°C in the Presence of Alkali Metal Salts

Counter anion	Nucleophilic const. ($\underline{n}$)	$\underline{k}_1$ for **4**, $10^{-3}s^{-1}$					$\underline{k}_1$ for **7**, $10^{-3}s^{-1}$			
		Li^+	Na^+	K^+	Rb^+	Cs^+	Li^+	Na^+	K^+	Rb^+
None	-	1.01[a)]					0.79[a)]			
ClO_4^-	<0	1.10	0.59	0.62			0.79	0.85	0.78	
NO_3^-	1.03	0.94	0.74	0.69	0.65	0.84	0.97	0.78	0.83	0.88
Cl^-	3.04	5.37	1.73	1.12			1.52	1.01	0.76	
Br^-	3.89		6.29	3.21				2.38	1.54	
SCN^-	4.77			7.9					>30	
I^-	5.04		>50	16.5				16.3	24.3	

a) Rate constant in the absence of a metal salt.

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References

1) Unsaturated crown ethers. 2. For part 1, see Y. Inoue, M. Ouchi, T. Nakazato, T. Matsuda, and T. Hakushi, Chem. Lett., 1982, 781.

2) Irradiations were run through a transparent Dewar vessel using a 60-W white bulb at a distance of 2 cm.

3) The dioxetanes **3** and **4** produced in the photooxygenation usually contained a small amount (<5 %) of the dibenzoate **5**. No further attempts were made to purify the dioxetanes, since satisfactory spectral identification could be made and the presence of the benzoate did not affect the decomposition rates.

4) The chemiluminescence and fluorescence spectra were recorded on a Hitachi 650-10 spectrofluorimeter.

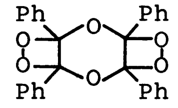
5) All the solvents used were distilled from or treated with EDTA·2Na prior to use in order to eliminate any transition metal cations which catalyze the nonchemiluminescent decomposition of dioxetanes; see, for example, H.R. Wasserman and R.W. Murray, "Singlet Oxygen," Academic Press, New York, NY, 1979, pp. 270.

6) Unpublished results of the authors.

7) K.A. Zaklika, A.L. Thayer, and A.P. Schaap, J. Am. Chem. Soc., 100, 4916(1978).

8) The dioxetane **6** was prepared in a reaction of benzoin with ethylene glycol ditosylate according to the method reported in ref. 1. Similar photooxygenation procedure gave the dioxetane **7** in an excellent yield.

9) It would be of interest whether the two dioxetane rings in **4** cleave stepwise or simultaneously in the sense of our present time scale. This question has already been posed by Adam et al. upon thermolysis of the first-prepared bisdioxetane **8**.10e) Although the answer has not yet been given, it seems quite unlikely to assume that the electronically and/or vibrationally excited monodioxetane-diester **9** can still survive from the subsequent spontaneous decomposition to allow the observation of the second cleavage as a distinct process. This speculation may be supported by the fact that the thermal behaviors of the bisdioxetane **4**, as well as **8**, are quite similar to those of the reference mono-dioxetane **7**.



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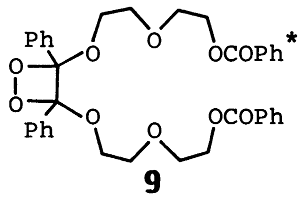

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10) a) P.D. Bartlett, G.D. Mendenhall, and A.P. Schaap, Ann. N.Y. Acad. Sci., 171, 79 (1970); b) G. Rio and J. Berthelot, Bull. Soc. Chim. France, 3555(1971); c) A.P. Schaap, Tetrahedron Lett., 1757(1971); d) W. Adam, Adv. Heterocycl. Chem., 21, 437(1977); e) W. Adam, C.-C. Cheng, O. Cueto, I. Erden, and K. Zinner, J. Am. Chem. Soc., 101, 4735(1979); f) W. Adam, O. Cueto, E. Schmidt, and K. Takayama, Angew. Chem. Int. Ed. Engl., 20, 1031(1981).

11) C.G. Swain and C.B. Scott, J. Am. Chem. Soc., 75, 141(1953).

12) Nonchemiluminescent decompositions of alkoxy or phenyl substituted dioxetanes catalyzed by nucleophiles such as amines have been well documented and attributed to electron-transfer interactions; see ref. 5, p. 270. Analogous competing nucleophilic substitution and/or one-electron transfer mechanisms have been postulated for the reactions of nucleophiles with peroxidic substrates; for the detailed discussion, see S. Videl, J. Court, and J.-M. Bonnie, J. Chem. Soc., Perkin Trans. 2, 663(1982); D.F. Church and W.A. Pryor, J. Org. Chem., 45, 2866 (1980); W.A. Pryor and W.H. Hendrickson, Jr., J. Am. Chem. Soc., 97, 1580(1975); and the references cited therein.

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