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LOW-TEMPERATURE CHARACTERIZATION OF A DIOXETANE PRODUCED IN THE SENSITIZED PHOTOOXYGENATION OF A VINYLCYCLOPROPANE, 3,10-DISPIROCYCLOPROPYLTRICYCLO[5.2.1.$0^{2,6}$]DECA-4,8-DIENE

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The sensitized photooxidation of the title olefin at -80°C was, contrary to the results of the reaction at room temperature, shown to afford only the dioxetane and its cleavage product, regardless of the sensitizers and the solvent used. Low-temperature characterization of the product by means of ^{1}H- and ^{13}C-NMR as well as some chemical transformations confirmed the occurrence of the $(2+2)\pi$ cycloaddition mode in the singlet oxygen oxidation of vinylcyclopropanes.

Recently, we have demonstrated that cis-1,2-glycols obtained by Rose Bengal (RB)-sensitized photooxygenation of vinylcyclopropanes have been derived from corresponding dioxetanes.[1,2] Although some dioxetanes are shown to be quite stable during the usual work up, intensive efforts to isolate these particular dioxetanes from vinylcyclopropanes were unsuccessful. The ^{1}H- and ^{13}C-NMR spectral characterization of such dioxetane will be described herein for the first time together with the results of both chemical and photochemical reductions.

When a dichloromethane-d_2 solution of Methylene Blue (MB) and 3,10-dispirocyclopropyltricyclo[5.2.1.0^{2,6}]deca-4,8-diene (1, 3–10 mg for each run) was irradiated by a tungsten lamp at -80°C (Runs 1 and 2), a formation of only two products was identified on thin-layer chromatograms. The major product (2) gradually changed into the minor product which was identified to be the previously characterized diol (3).3) Therefore, 2 must be the dioxetane. According to the NMR spectrometry, the ratio of 2 : 3 immediately after the reaction was *ca.* 8 : 1, and the ^{1}H-NMR signals of 2 were compatible to the formulation; especially, a pair of doublets [$\delta^{CD_2Cl_2}$: 4.76(1H, d, J=5 Hz) and 5.42(1H, d, J=5 Hz)] should be a firm evidence. The ^{13}C-NMR [δ4) : 5.9, 7.9, 11.3, 15.3, 30.0, 46.4, 49.9, 51.9, 57.2, 58.1, 90.0, 98.4, 133.2 and 138.3] also supported the dioxetane structure.5) Fig. 1 is disclosing a quantitative conversion of 2 to 3.

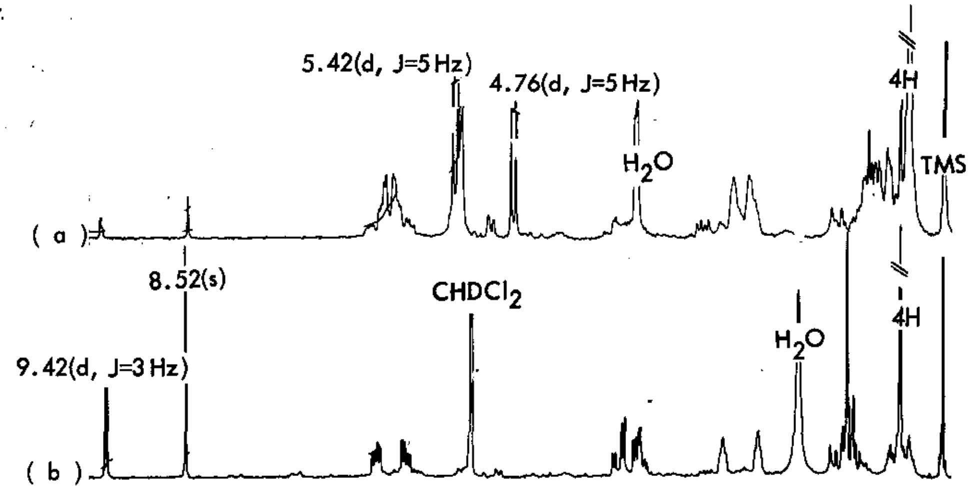


Fig. 1. The ^{1}H-NMR spectra of the reaction mixture of run 2. (a) at -62°C, and (b) at 25°C after 2 h.

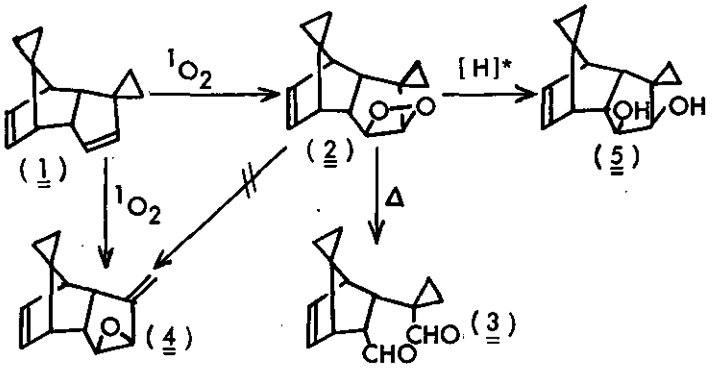
This conversion was very rapid; more than 30 % of 2 changed to 3 within 20 min by a gradual warm up of the dichloromethane-d_2 solution to 0°C.

When 1 was oxygenated in dichloromethane-d_2 and pyridine-d_5 (1 : 1) at -80°C (Run 3), the products were 2 and 3 (*ca.* 1 : 1). At 25°C, the product in pyridine was solely a vinyloxirane, 4.3) This temperature dependence for formation of 4 is remarkable, and the lower limit of temperature to form 4 was below -40°C (Runs 4, 7, 8 and 9). But, 2 must not be a precursor of 4 because additions of aliquots of pyridine-d_5 at various temperatures (-80° to 25°C) into solutions of 2, which was obtained by Run 1, resulted in an exclusive formation of 3 in each time. The conversion of 2 to 3 was accelerated by pyridine (Runs 3, 7 and 9). In addition, when 1 was photooxygenated with RB in a hydroxylic solvent, methanol-d_4, at -30°C, the cis-glycol (5)[1] was formed in nearly quantitative yield (Run 6). Improvement of the yield at low temperature should be due to an increase of stability of 2. Table I shows the product distributions of the oxygenation.

Table I. The Product Distributions of Low Temperature Photooxygenation of 1.

Runs	Sensitizers	Temperature (°C)	Solvents	% of Products			
				2	3	4	5
1	MB	-80	CD_2Cl_2	85	15		
2	MB	-80	CD_2Cl_2	88	12		
3	RB*)	-80	$C_5D_5N : CD_2Cl_2$ (1 : 1)	50	50		
4	MB	-40	$CDCl_3$	65	22	13	
5	MB	-40	$CD_3OD : CDCl_3$ (3 : 1)	83	17		
6	RB	-30	CD_3OD				100
7	RB	-30	C_5D_5N	+	25	75	
8	MB	0	$CDCl_3$	45	30	25	
9	RB	0	C_5D_5N		5	95	

*) 18-Crown-6 was added to dissolve the sensitizer.



Reduction of **2** to **5** was also accessible by chemical means. When **2** (obtained by Run 2) was kept with an excess of thiourea6) in a mixed solution of dichloromethane-d_2 and methanol-d_4 for overnight at -30° to -10°C, **5** (10 %) was obtained together with isomerized **3** (90 %). On the other hand, the reduction by dimethyl sulfide yielded very complicated mixture, from which, only **5** (20 %) was isolated by silica gel chromatography. The reduction by diphenyl sulfide was again complicated one; **5** (less than 5 %) and **3** (70 %) were only the isolated products after repeated chromatography.

In conclusion, present results constitute the first direct evidence for occurrence of a $(2+2)\pi$ cycloaddition in the reaction of singlet oxygen with vinylcyclopropanes. This type of olefins can be now regarded as one of the simplest dioxetane-forming substrates, which may even possess an allylic hydrogen capable for the ene-reaction.7)

References and Notes

1) H. Takeshita and T. Hatsui, J Org. Chem., **43**, 3080 (1978).

2) H. Takeshita, T. Hatsui, and I. Shimooda; Tetrahedron Lett., 2889 (1978).

3) H. Takeshita, T. Hatsui, and H. Kanamori, Tetrahedron Lett., 1697 (1973).

4) This was measured in a mixed solution of $CDCl_3$ and CD_3OD (3 : 2) at -40°C.

5) K. R. Kopecky, J. E. Filvy, C. Mumford, P. A. Lockwood, and J. -Y. Ding, Can. J. Chem., **53**, 1103 (1975).

6) C. Kaneko, A Sugimoto, and S. Tanaka, Synthesis, 867 (1974).

7) Most of the hitherto examined tetrasubstituted cage olefins, the other dioxetane-forming alicyclic olefins, lack the hydrogen capable for the ene-reaction. In this respect, 2-bornylidene-2-bornanes (H. Takeshita, T. Hatsui, and O. Jinnai, Chemistry Lett., 1059 (1976)) are rare exceptions.

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