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Stereochemical Investigation of Photoepoxidation of Dioxetane-forming Olefins in the Presence of Sulfur Dioxide

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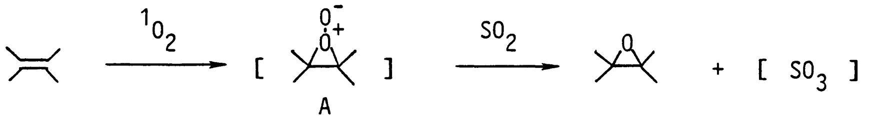
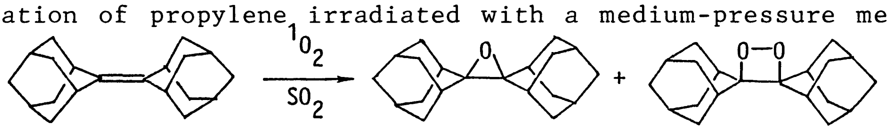
Photosensitized oxygenation of two stereoisomeric di-t-butyl-bis(bicyclo-[3.3.1]non-9-ylidenes) in the presence of sulfur dioxide afforded the corresponding epoxide stereospecifically.

Photoepoxidation of olefin is very interesting in view of reaction mechanism, but few studies have been reported in photosensitized oxygenation.[1,2] Recently we have found a novel photoepoxidation of olefin in photosensitized oxygenation of thiirane[3] in which sulfur dioxide captures efficiently an outer oxygen atom in nucleophilic perepoxide intermediate (A) (Eq. 1).[2] Presently we report a stereochemical investigation of photoepoxidation of sterically hindered olefins in the presence of sulfur dioxide.



(1)

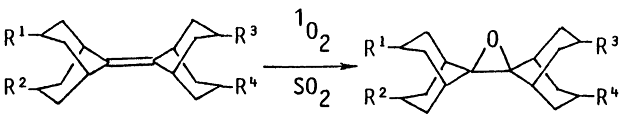
Photosensitized oxygenation of biadamantylidene (1, 3.3 x 10^{-3} mol dm^{-3}) was carried out at 15 °C in methylene chloride containing sulfur dioxide (ca. 160 equiv.) with methylene blue (MB, 1.1 x 10^{-3} mol dm^{-3}) or tetraphenylporphine (TPP) as sensitizer and use of two 500 W halogen lamps.[4] When the reaction mixture was chromatographed on silica gel, biadamantylidene epoxide 2 (98% yield) and a trace amount of biadamantylidene dioxetane 3 were obtained (Eq. 2). Very similar results were also obtained in the photooxygenation of bis(bicyclo-[3.3.1]non-9-ylidene) 4 to give epoxide 5 quantitatively (Eq. 3). Photosensitized oxygenation of vinyl ethers such as 2,3-diphenyl-1,4-dioxene[5] and 2-(methoxymethylene)adamantane,[6] however, was not trapped efficiently by sulfur dioxide to give the corresponding epoxide. Recently it has been reported that photoepoxidation of propylene irradiated with a medium-pressure mercury-arc lamp



(2)

1 2 3

4: $R^1=R^2=R^3=R^4=H$
6a: $R^1=R^4={}^tBu, R^2=R^3=H$
6s: $R^1=R^3={}^tBu, R^2=R^4=H$



(3)

5: $R^1=R^2=R^3=R^4=H$
7: $R^1=R^4={}^tBu, R^2=R^3=H$
8: $R^1=R^3={}^tBu, R^2=R^4=H$
9: $R^1=R^3=H, R^2=R^4={}^tBu$

Table 1. Photoepoxidation of 6a and 6s

Systems	Olefin	Time/h	Products and Yields a)/%		
			7	8	9
MB/hν/O_2/SO_2 b)	6a	7.5	95		
	6s	14		61	34
TPP/hν/O_2/PhSOMe c)	6a	2	78		
	6s	2		73	27

a) Isolated yields. b) This work. c) Reference 14.

(280 < λ < 500 nm) in the presence of sulfur dioxide involved an electron transfer process.7) This reaction mechanism, however, is inapplicable to the present reaction since olefin 1 and 4 were found to be inert when submitted to irradiation with halogen lamps (400 nm <) in the presence of oxygen and sulfur dioxide without sensitizer.

The reaction may not proceed by an energy transfer process because of energy difference between the excited sensitizer (E_T = 142.2 kJ mol^{-1} for MB)8) and sulfur dioxide (E_T = 309.6 kJ mol^{-1}).9) The usual tests confirmed the intermediacy of singlet oxygen as reagent.10)

The following stereochemical investigations have been done for the photosensitized oxygenation of 6a and 6s13) in the presence of sulfur dioxide and obtained the corresponding epoxide stereospecifically i.e., 7 from 6a, both 8 and 9 from 6s.14) These results are also compared with epoxidation in the presence of phenylmethyl sulfoxide (Table 1). On the basis of the preferential attack of $^1O_2$ from the less hindered face of 6s,13) it can be explained that the yields of 8 were superior to those of 9 in both systems. It might be apparent to mention that a perepoxide intermediate formed at the initial stage may transfer a nucleophilic oxygen atom to sulfur dioxide to giving sulfur trioxide15) and epoxide stereospecifically (Eq. 1).

References

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4) SO_2 (Seitetsu Chemical Co.) was used as received. Reaction time was about 1 h.
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10) Proof for singlet oxygen was obtained by testing the oxygenation in the absence of light, oxygen.11)
11) The oxidation was not inhibited by addition of DABCO, a singlet oxygen quencher,12) because of acidic system in the presence of SO_2.
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15) SO_3 was detected as dimethyl sulfate by GLC by addition of etheral diazomethane solution to the reaction mixture.

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