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## The Reduction of 1,2-Dioxetanes to *cis*-1,2-Diols by Superoxide. The Mechanism of the Process found in the Rose Bengal-Sensitized Photooxygenation

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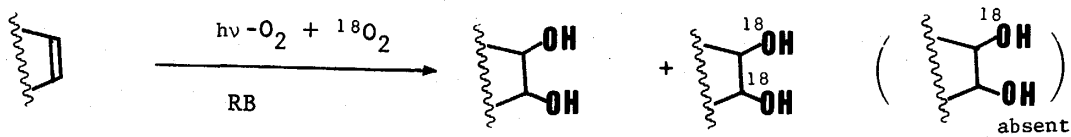
Superoxide radical anion reduced 1,2-dioxetanes to *cis*-1,2-diols by: a) visible-light irradiations under Methylene Blue-sensitized photooxygenation conditions with added sodium acetate, and b) chemical reductions with potassium superoxide and dibenzo-18-crown-6 ether in dichloromethane solutions.

For the mechanism of formation of *cis*-1,2-diols<sup>1)</sup> from the dioxetane-forming olefins during Rose Bengal (RB)-sensitized photooxygenation reactions, we have already shown the intermediacy of dioxetanes by <sup>18</sup>O-labelling experiments<sup>2)</sup> as well as low-temperature detection with the NMR spectroscopy.<sup>3)</sup> Herein, we wish to show the reducing agent to be superoxide (SO), a radical anion.

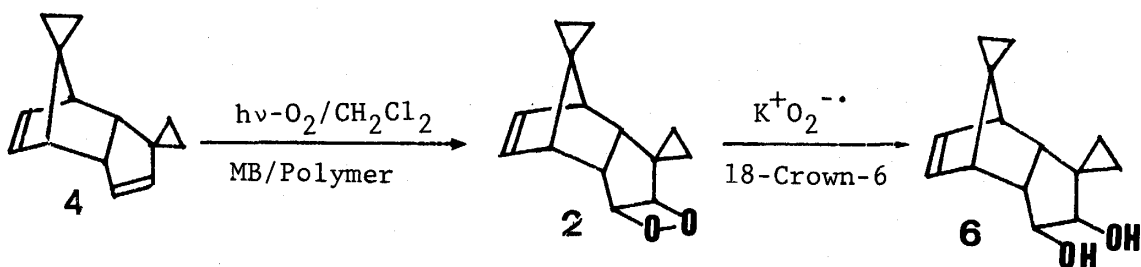
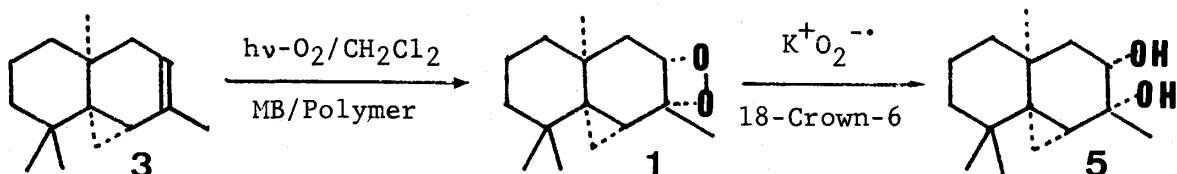
First of all, it has been noticed that only RB-sensitized photooxygenation can produce the 1,2-diols.<sup>1)</sup> Therefore, we intended to isolate the diol-free samples of the dioxetanes (**1** and **2**) from thujopsene (**3**)<sup>4)</sup> and the Diels-Alder dimer (**4**)<sup>5)</sup> of spiro[2.4]hepta-4,6-diene by a careful Methylene Blue (MB)-sensitized photooxygenation by low-temperature irradiations. However, all attempts to remove the sensitizer resulted in a quantitative cleavage of dioxetanes, and we carried out the reaction by means of polymer-bound MB in view of a convenient workup.<sup>6)</sup> Surprisingly, when **3** and **4** were respectively photooxygenated with this heterogeneous sensitizer in various solvents at -20 to -50°C, the 1,2-diols (**5** and **6**) were indeed formed in a trace amount (~1%). Thus, even MB-sensitized reaction could form 1,2-diols, and this clear-cut difference between the homogeneous and heterogeneous MB-sensitized reactions suggested that the reduction must be not sensitizer-dependent, but pH-dependent.<sup>7)</sup> Indeed, the MB-sensitized photooxygenation of **3** and **4** in methanol solution with sodium acetate, under homogeneous conditions, produced **5** (5%) and **6** (16%), respectively. Moreover, and addition of water to this methanol solution has caused a complete inhibition of the diol formation. From these findings, an involvement of an acid- and water-sensitive species in the reduction was suggested.

In this regard, SO<sup>4)</sup> is well known to be acid- and water-sensitive, and SO is, therefore, likely to be the active species, and this was indeed the case. Thus, the diol-free dioxetanes were at first prepared by polymer-bound MB-sensitized photooxygenation at -45°C in dichloromethane solution which usually contains a trace amount of hydrochloric acid to prevent an accumulation

Dioxetanes to *cis*-1,2-Glycols by Superoxide-Reduction



Scheme 1



Scheme 2

of SO.<sup>8)</sup>

Then, the sensitizer was filtered off, and to the filtrate, potassium superoxide ( $\text{KO}_2$ ) and dibenzo-18-crown-6 (CE) were added and stirred at  $-40$  to  $0^\circ\text{C}$  for 12 h. Preparative thin-layer (silica gel) chromatography of the mixture afforded **5** in 4% yield. Furthermore, when a mixture of photooxygenation products derived from **3** by means of MB in homogeneous dichloromethane solution at  $-45^\circ\text{C}$  was treated similarly with SO and CE for 12 h, **5** was obtained in 6% yield. Thus, with or without MB, SO yielded the 1,2-diol. But, without SO and CE, the photoproduct mixture afforded no **5** at all after standing for 12 h at  $-40$  to  $0^\circ\text{C}$ .

In conclusion, SO is solely responsible for the photochemical reduction of 1,2-dioxetanes to *cis*-1,2-diols, and in view of the one-electron reducing nature of SO, the reduction should be proceeded in the two-step manner, via dioxy radical anions to diols. It is already known that the reduction of hydroxy radical to hydroxide is very rapid.<sup>9)</sup>

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- 7) According to potentiometry, with Hirayama RAT-11S apparatus, following pH were obtained: 0.005M aqueous MB solution, 3.8; 0.005M MB in 0.1M aqueous NaOAc, 7.5; 0.005M aqueous RB solution, 7.5.
- 8) SO is very unstable in acidic media as recorded in literature as D.T. Sawyer and M.J. Gibian (*Tetrahedron*, **35**, 1471 1979)) has determined the rate constants:
 

$\text{SO} + \text{SO} + \text{H}^+ \longrightarrow \text{O}_2 + \text{HOO}^-$	$k_1 = 1.0 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$
$\text{SO} + \text{HOO}^\bullet \longrightarrow {}^T\text{O}_2 + \text{HOO}^-$	$k_2 = 8.5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$
- 9) Second step of the reduction must be very rapid: <sup>8)</sup>

$\text{SO} + \text{HO}^\bullet \longrightarrow {}^T\text{O}_2 + \text{OH}^-$	$k_3 = 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ .
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