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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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 [1] from the dioxetane-forming olefins during Rose Bengal (RB)-sensitized photooxygenation reactions, we have already shown the intermediacy of dioxetanes by ^{18}O-labelling experiments [2] as well as low-temperature detection with the NMR spectroscopy. [3] 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. [1] Therefore, we intended to isolate the diol-free samples of the dioxetanes (**1** and **2**) from thujopsene (**3**)[4] and the Diels-Alder dimer (**4**)[5] 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. [6] 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. [7] 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 [4] 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

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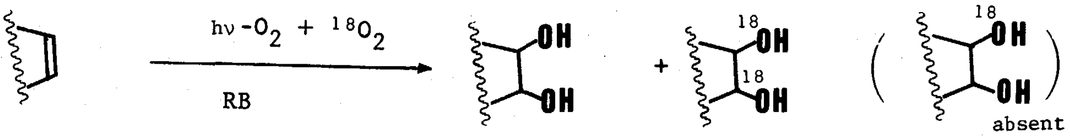
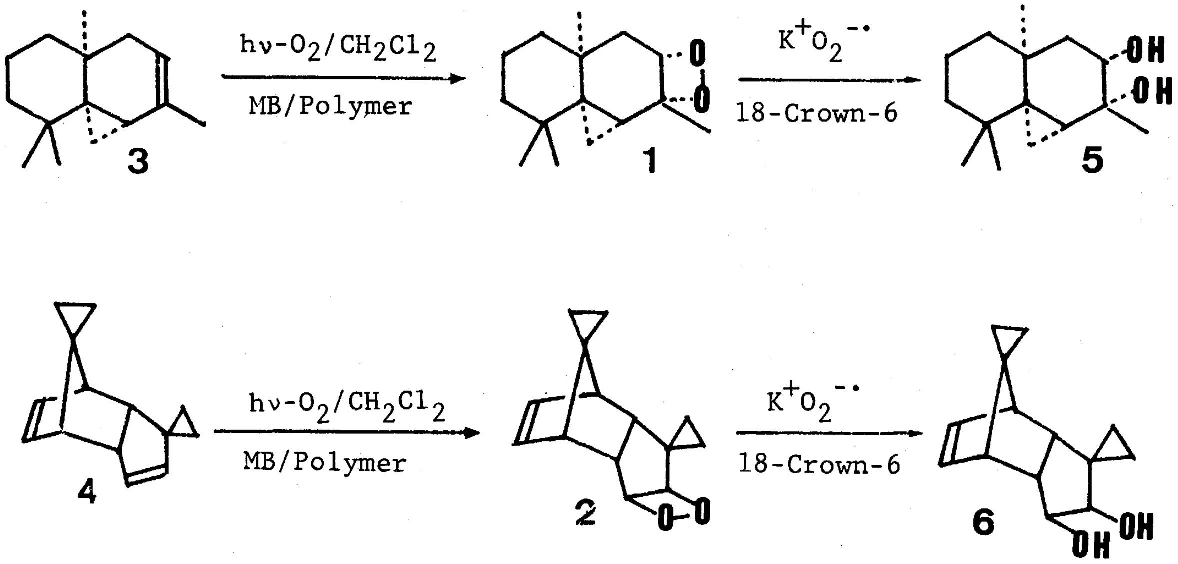


Scheme 1



Scheme 2

of SO.[8]

Then, the sensitizer was filtered off, and to the filtrate, potassium superoxide (KO_2) and dibenzo-18-crown-6 (CE) were added and stirred at −40 to 0°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°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°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.[9]

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6) This was prepared from IRA 120B, a kind of cation exchange resin of poly(styrenesulfonate) type, and an excess of MB. Cf., J. R. Williams, G. Orton, and L. R. Unger, *Tetrahedron Lett.*, **1973**, 4603; E. C. Blossey, D. C. Neckers, A. C. Thayer, and P. A. Schaap, *J. Am. Chem. Soc.*, **95**, 5820 (1973).

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 recoreded in literature as D.T. Sawyer and M.J. Gibian (*Tetrahedron*, **35**, 1471 1979)) has determined the rate constants:

$\mathrm{SO+SO+H^{+}}$ ——— $\mathrm{O_2+HOO^{-}}$ $k_1=1.0\ \mathrm{dm^{3}\ mol^{-1}\ sec^{-1}}$

$\mathrm{SO+HOO^{\bullet}}$ ——— $\mathrm{{}^{T}O_2+HOO^{-}}$ $k_2=8.5\times10^{7}\ \mathrm{dm^{3}\ mol^{-1}\ sec^{-1}}$

9) Second step of the reduction must be very rapid: 8)

$\mathrm{SO+HO^{\bullet}}$ ——— $\mathrm{{}^{T}O_2+OH^{-}}$ $k_3=10^{10}\ \mathrm{dm^{3}\ mol^{-1}\ sec^{-1}}$.