The Reactions of Sulfoxides with Dimethyldioxirane. A Question of Mechanism

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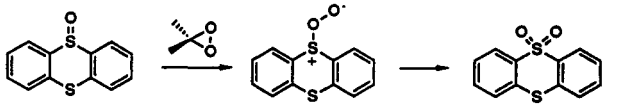
The successful isolation of an acetone solution of dimethyldioxirane (DMD) by Murray and Jeyaraman[1] has created a flurry of activity designed to examine the oxidative character of this unique small ring peroxide. It has been demonstrated that it functions as a versatile, yet remarkably mild,[2,3] oxidizing agent capable of epoxidations, insertions, and heteroatom oxidations.[4-6]

In the vast majority of its reactions DMD appears to function as an electrophilic oxidant giving negative Hammett ρ values of -0.90, -0.77, and -0.78 in its reactions with substituted styrenes,[7] sulfides,[8] and sulfoxides,[8] respectively. In contrast to these electrophilic oxidations, Adam and co-workers[9,10] reported that the reaction of thianthrene-5-oxide occurred predominantly at the sulfinyl (SO) rather than at the sulfenyl (S) sulfur. This regiochemical outcome was suggested to reflect the dominant nucleophilic character of DMD.

In order to reconcile these contrasting results Murray[5] made the very reasonable suggestion that oxidation of a sulfoxide might be initiated by attack of DMD on the oxygen rather than at the sulfur of the sulfinyl group (eq 1).



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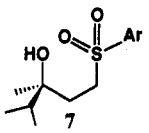
McDouall,[11] however, was unable to locate an ab initio transition state for the transfer of oxygen. All attempts to bring the dioxirane close to the sulfoxide oxygen resulted in a destabilizing repulsive interaction. Transitions states, however, for attack at sulfur in both a sulfide and sulfoxide were located, and it was shown that the activation barrier for sulfide oxidation (24.4 kcal mol^{-1}) was significantly higher than for sulfoxide oxidation (9.6 kcal mol^{-1}). McDouall also pointed out that these are gas phase results and that the sulfide transition state has a larger dipole moment than the sulfoxide transition state and consequently should experience the greater stabilization on transfer to a polar solvent.

In order to experimentally explore the feasibility of the mechanism presented in eq 1 we have examined the reaction of sulfoxide 1 with DMD. The persulfoxide intermediate 3, which would be produced by attack at oxygen has been previously been synthesized by singlet oxygen oxidation of sulfide 2[12-14] and has been shown to decompose by a unique oxidative elimination pathway to give olefins 4, 5, and 6 (Figure 1). The formation of these same olefins during the reaction of DMD with 1 can therefore serve as a fingerprint identifying the involvement of persulfoxide 3 in the reaction.

The reactions of sulfoxide 1 were conducted by additions of 1 equiv of a 5.2×10^{-2} M acetone solution of DMD to 2.2×10^{-4} and 4.4×10^{-3} M acetone solutions of 1 at room temperature. Examination of the reaction mixtures by NMR revealed that sulfone 7 was the sole product of the



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reactions at both the high and low concentrations. Similar results were obtained using 2.0×10^{-4} M solutions of 1 at -80 °C. These results appear to rule out the mechanism depicted in eq 1, however, it is not clear that 3 produced in the singlet oxygen and in the DMD reaction will behave the same. In the early stages of the reaction of DMD with 1, persulfoxide 3 is produced in the presence of a large amount of sulfoxide. In contrast, in the early stages of the reaction of 2 with singlet oxygen, 3 is produced in the presence of a large excess of sulfide. It is conceivable that olefin formation could be quenched in the DMD reaction by efficient trapping of 3 with 1.[15]

In order to determine if 1 could competitively inhibit olefin formation under the reaction conditions, the photooxidation of 2 at -80 °C was followed by proton NMR. A plot of product yields versus the % conversion of 2 is depicted in Figure 2. The arrow in Figure 2 corresponds to the point in the photooxidation where the yield of sulfoxide 1 reaches a concentration of 2.6×10^{-3} M which is a factor of 13 times higher than that used in the DMD reaction at -80 °C. *At this large concentration of 1 the olefins continue to form!* Clearly, inhibition of olefin formation cannot occur under the DMD reaction conditions and consequently the formation of sulfone 7 *is not* initiated by attack of DMD at the sulfinyl oxygen of sulfoxide 1.[16]

Experimental Section

Proton and carbon NMR were obtained on a JEOL GX270 at 269.7 and 67.8 MHz, respectively, and on a GX400 at 399.78 and

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(16) The possibility that sulfoxide 1, by virtue of the internal hydrogen bond donor, is unique and that other sulfoxides will react at the sulfinyl oxygen cannot be rigorously excluded. A referee also pointed out that hydrogen bonding to the incoming DMD could also affect the oxygen transfer behavior. We point out, however, that the solvent can also act as a hydrogen bond acceptor to disrupt the intramolecular hydrogen bond and will also compete with hydrogen bonding to DMD.
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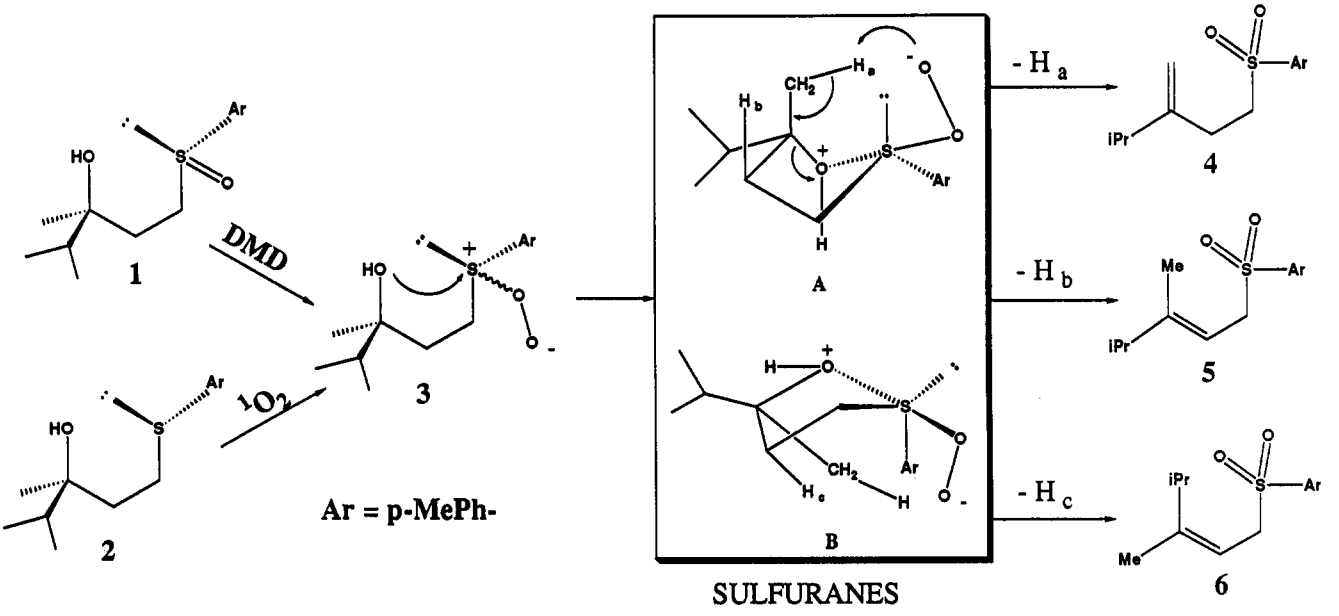

Figure 1.

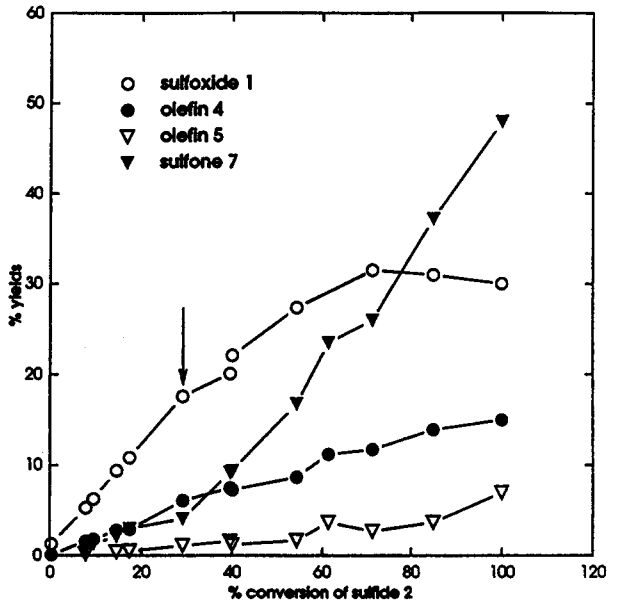

Figure 2. Reaction profile for the photooxidation of sulfide 2 as a function of % conversion of 2.

100.53 MHz, respectively. Chemical shifts were referenced to internal TMS. Sulfoxide 1 and sulfide 2 were synthesized as previously reported and 4–7 were directly compared to previously isolated samples.[14] "Oxone" was obtained from Aldrich Chemical Co. and used as received. Dimethyl dioxirane was synthesized by the method of Adam[17] and its concentration measured by oxidation of methyl *p*-methylphenyl sulfide.

Reaction of 1 with DMD. One equivalent of freshly prepared dimethyldioxirane (5.2×10^{-2} M) in acetone was added dropwise to acetone solutions of 1 and allowed to stir for 5 h at room temperature. Acetone was then removed by vacuum distillation, the residue dissolved in acetone-d_6, and the proton NMR recorded.

Photooxidations. The photooxidations of 2 were carried out at −80 °C by irradiation of a acetone-d_6 solution containing 1.5–2.0×10^{-5} M Rose Bengal as the photosensitizer through a 1 cm 0.5% aqueous $K_2Cr_2O_7$ filter. The sulfide concentration was adjusted to 1.5–2.9×10^{-2} M in each case. The product yields were measured by cutting and weighing the expanded portions of the proton NMR spectra.

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