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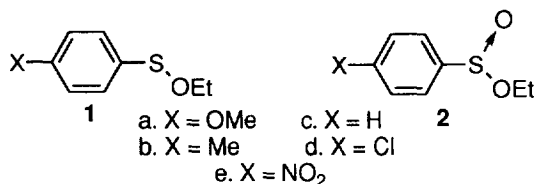
New Potent Trapping Agents for the Peroxidic Intermediates Formed in the Reactions of Singlet Oxygen.

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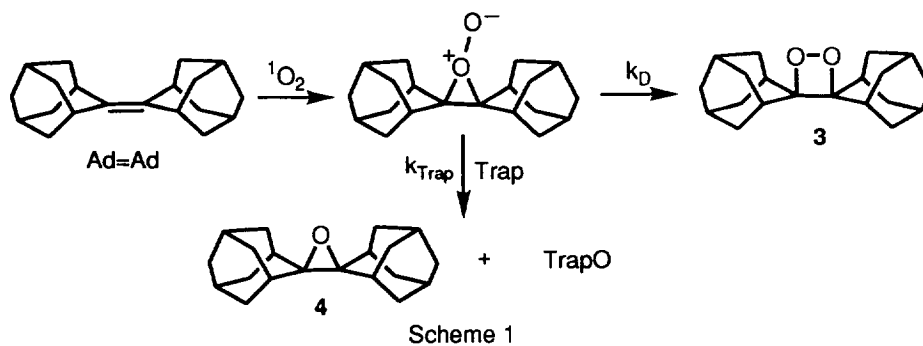
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Abstract: The ability of sulfenate and sulfinate esters to trap the perepoxide intermediate formed in the photooxidation of adamantylideneadamantane has been explored. The results demonstrate that these compounds are the most potent trapping agents for peroxidic intermediates yet reported. The electrophilic character of the trapping event was also demonstrated with a series of substituted sulfenate esters. Copyright © 1996 Elsevier Science Ltd

A variety of metastable intermediates including diradicals, exciplexes, ion pairs, perepoxides, persulfenates, persulfoxides, thiadioxiranes, and zwitterions have been implicated in singlet oxygen reactions.¹ In most cases the presence of these intermediates on the reaction surface have only been indirectly inferred from the effects of experimental parameters on the regiochemistry or kinetics of the reaction. In a limited number of cases trapping agents such as alcohols,² olefins, phosphites,^{3,4} sulfoxides, and sulfides,⁵ have successfully intercepted peroxidic intermediates.¹ The successful trapping agent must be unreactive towards the substrate, product, and singlet oxygen, but at the same time be reactive enough with the intermediate to prevent its often facile interconversion to product.



We have discovered that sulfenate, **1**, and sulfinate esters, **2**, meet these stringent requirements for trapping agents. *In addition these compounds are the most reactive electrophilic trapping agents yet reported.* To demonstrate their efficiency and electronic character we have examined their ability to trap the perepoxide formed in the reaction of adamantylideneadamantane (Ad=Ad).(Scheme 1) The results of these studies are reported below.



The reaction of singlet oxygen with Ad=Ad gives a remarkably stable dioxetane, **3**, and under some conditions a trace amount of epoxide, **4**. Schaap and coworkers⁶ demonstrated that sulfoxides (Trap in Scheme 1) could intercept the peroxide intermediate and divert it totally to the epoxide product. The dioxetane/epoxide ratio, **3/4**, is consequently given by equation 1 and examination of the k_D/k_{Trap} values for different trapping agents allows a direct comparison of their trapping efficiencies.

$$\frac{[\text{Dioxetane}]}{[\text{Epoxide}]} = \frac{[\mathbf{3}]}{[\mathbf{4}]} = \frac{k_D}{k_{\text{Trap}} [\text{Trapping Agent}]} \quad 1$$

The study was conducted by taking oxygen saturated benzene solutions each consisting of 0.10 M Ad=Ad, 1×10^{-3} M biphenyl as the internal standard, 4×10^{-5} M tetraphenyl porphyrin (TPP) as the sensitizer, and 0.02 - 0.002 M **1e** and irradiating on a merry-go-round with a 450 W medium pressure Hanovia lamp through a 12 M sodium nitrite filter solution. Under these rigorously controlled conditions $k_T[\text{Ad=Ad}] \gg k_T[\mathbf{1e}]$ guaranteeing that singlet oxygen reacted exclusively with Ad=Ad.⁷ After irradiation, all the samples were analyzed on a Perkin-Elmer Autosystem capillary gas chromatograph equipped with a HP-5 30 m x 0.25 mm x 0.25 μm (length x inside diameter x film thickness) capillary column. The dioxetane, **3**, quantitatively cleaved under the GC conditions to adamantanone and its concentration and that of the epoxide **4** were determined by reference to recently constructed calibration curves. The concentrations of **4** were corrected for epoxide formed in the absence of **1e** and for that formed by adventitious trapping by the sulfinate ester product, **2e**.⁸ In addition, control reactions demonstrated that reduction of **3** to form **4**, a process which is known to occur with trialkylphosphites⁹ does not occur in the presence of the sulfinate esters. Diphenyl sulfide, on the other hand, has been successfully used to intercept elusive dioxetanes.¹⁰ A value of 1.1×10^{-4} M for k_D/k_{Trap} was derived from the slope of a plot of the resulting data according to equation 1. (Figure 1a)

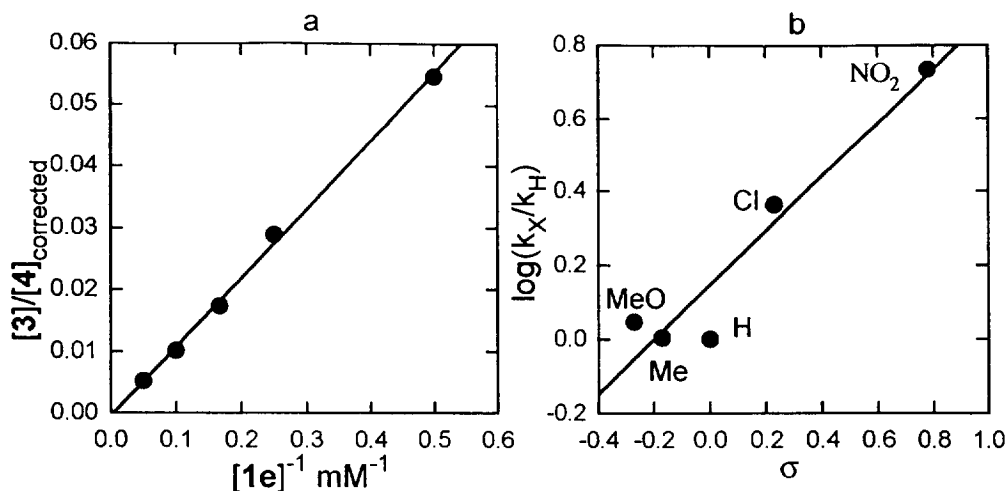


Figure 1. a. Dioxetane/epoxide ratio as a function of $1/[1e]$. Slope = 0.11 mM; $r = 0.998835$. b. Hammett Plot for the Trapping of Adamantylideneadamantane Perepoxyde by Sulfenate Esters

Similar trapping studies with sulfenate ester **1c** and sulfinate ester **2e** were also conducted. The data from these studies are presented in Table 1 along with the data for **1e** and $(\text{PhO})_3\text{P}$ for comparison. Examination of the data reveals that the p-nitro substituted compounds in particular are significantly better trapping agents than $(\text{PhO})_3\text{P}$. Stratakis and coworkers⁴ have previously reported that $(\text{PhO})_3\text{P}$ and diphenylsulfoxide (Ph_2SO) are similar in their trapping ability and are approximately three times more efficient than trimethylphosphite.

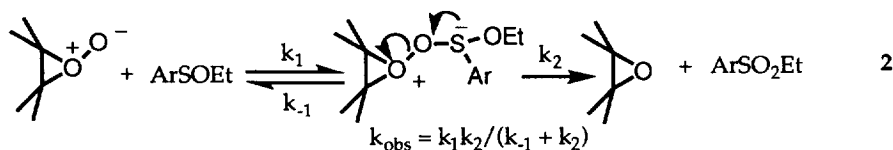
Table 1. Kinetic Data for Trapping of Adamantylideneadamantane Perepoxyde.^a

Compound	k_D/k_{Trap}	$k_{\text{Trap}}(\text{rel})^b$	Compound	k_D/k_{Trap}	$k_{\text{Trap}}(\text{rel})^b$
1c	5.2×10^{-4}	3.26	1e	1.11×10^{-4}	15.3
$(\text{PhO})_3\text{P}^c$	1.7×10^{-3}	1.0	2e	8.94×10^{-5}	19.0

a. In benzene. b. Trapping ability relative to $(\text{PhO})_3\text{P}$. c. Reference 4.

The electronic character of the trapping reaction with sulfenate esters was explored by allowing **1a** - **1e** to compete for adamantylideneadamantane perepoxyde. A Hammett plot (Figure 1b) gave $\rho = +0.73$ ($r = 0.9579$) indicative of nucleophilic transfer of oxygen to the sulfenate ester.

A possible mechanism for the nucleophilic oxygen transfer is shown in equation 2. It is tempting to suggest that the apparent insensitivity to electron donating substituents ($X = \text{Me}$, and MeO in Figure 1b) reflects a near cancellation of opposing substituent effects on k_1 and $k_2/(k_1 + k_2)$. Unfortunately, the difficulty associated with handling sulfonate esters with electron donating groups currently precludes testing of this possibility.



The utilization of these new trapping agents in other singlet oxygen reactions will be reported in the near future.¹¹

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- k_t is the total rate of removal of singlet oxygen by the substrate and is equal to $3.49 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ for Ad=Ad, $5.58 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ for PhSOEt, and $< 5 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ for pNO₂PhSOEt.
- The amount of **4** formed by adventitious trapping with **2e** was set equal to the amount of sulfonate ester (p-NO₂PhSO₃Et) formed in the reaction.
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