

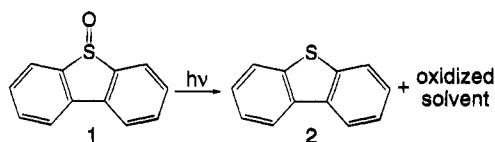
# Oxenoid Reactivity Observed on the Photolysis of Certain Aromatic Sulfoxides<sup>1</sup>

Zehong Wan and William S. Jenks\*

Department of Chemistry, Iowa State University  
Ames, Iowa 50011-3111

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We wish to report the efficient oxenoid functionalization of hydrocarbons which takes place as a result of photolysis of certain aromatic sulfoxides, notably dibenzothiophene sulfoxide **1**. In analogy to various metalloporphyrin models of cytochrome P-450<sup>2-9</sup> and other systems,<sup>10-16</sup> we observe hydroxylations of alkanes and epoxidations of alkenes. Additionally, we observe conversion of benzene and other aromatic compounds to the corresponding phenols<sup>17</sup> and dehydrogenation of alkanes to alkenes.



The photochemical deoxygenation of sulfoxides occurs fairly generally to a minor extent, but the sulfide is the major or exclusive photoproduct in certain cases.<sup>18-25</sup> Some time ago, it was shown<sup>22</sup> that dibenzothiophene sulfoxide (**1**) is nearly quantitatively reduced to dibenzothiophene (**2**) in a few solvents;<sup>21</sup> we have verified this and found it to be true in each solvent we have tried. We began our investigation by testing the intriguing mechanistic suggestions for the reaction made

(1) Photochemistry and Photophysics of Aromatic Sulfoxides. 2.

(2) References 3-17 are meant as leading sources, not an exhaustive list.

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Table 1. Oxidation Products Observed on Photolysis of 1




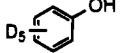


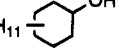
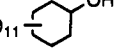


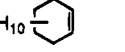
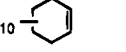


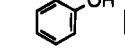
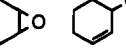
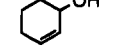


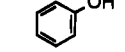
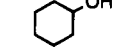


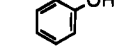
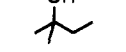
Substrate	Total Yield	Product Ratio
	0.60-0.65	
	0.55-0.60	 1.0 0.15-0.17 0.15-0.17
	0.95-1.00 <sup>a</sup>	 1.9-2.2 1.0
	0.40-0.45 <sup>b</sup>	 1.0 0.3-0.4 0.2-0.3 <sup>c</sup>
	0.45-0.50 <sup>d</sup>	 1.0 0.55-0.60 <sup>e</sup>
	0.65-0.70 <sup>f</sup>	 1.0-1.4 1.0 0.2-0.3
	0.97-1.00	 8.0-9.0 5.0-5.5 4.5-5.0 1.0

Total yields are expressed as fractions of the yield of **2**. (a) Cyclohexanone formed only in trace concentration at relatively high conversions. (b) Possible olefinic products were not measured, so the actual total yield is likely higher. (c) The two primary alcohols were not chromatographically separated. (d) Possible 3,3-dimethylbutene was not measured, so the actual total yield is likely higher. (e) Ratio of primary alcohols 3.5-4:1 in favor of 2,2-dimethylbutanol. (f) Possible cyclohexadiene not included. Neither is the cyclohexene dimer, as small quantities of it are formed on photolysis of cyclohexene in the absence of **1**.

nearly simultaneously by Shelton<sup>18</sup> and Posner.<sup>22</sup> These authors suggested that reduction proceeds by way of a sulfoxide dimer, which decomposes to two molecules of sulfide and a molecule of dioxygen (O<sub>2</sub>). The latter author suggested that singlet molecular oxygen (<sup>1</sup>O<sub>2</sub>, <sup>1</sup>Δ<sub>g</sub>) was formed in the reaction mixture, by virtue of the isolation of 2-cyclohexenol in moderate yield after photolysis of **1** in cyclohexene (with 10% AcOH added), followed by reduction with NaI. Using identical experimental conditions, we obtain an extremely similar yield of 2-cyclohexenol, but find that the *reduction step is unnecessary*. Moreover, it is now recognized that cyclohexene is not an efficient chemical quencher of singlet oxygen, and we have verified through conventional means of preparing singlet oxygen that 2-cyclohexenol is not formed to any detectable extent in neat cyclohexene under reasonable experimental conditions. This and several other mechanistic observations we have made are inconsistent with the dimer mechanism; a detailed discussion of our mechanistic hypothesis will be the subject of a forthcoming full publication.

A variety of oxidized solvent products are shown in Table 1. Cyclohexane is converted to cyclohexanol and cyclohexene. Substantial selectivity for tertiary hydroxylation is observed with branched alkanes. Reaction with cyclohexene can proceed similarly or by epoxidation. A strongly electrophilic nature of the reactive intermediate is suggested by the reactivity with benzene, which we speculate probably goes through epoxidation, followed by rearrangement to phenol. All samples were prepared with multiple cycles of freeze-pump-thaw degassing to eliminate O<sub>2</sub>. Photolyses were carried out at ambient temperature in quartz cells using either the output of "300 nm" bulbs of a Rayonet photoreactor or the light of a 150 W Xe lamp filtered through a monochromator set to 320 nm with a 24 nm total linear dispersion.<sup>26</sup> Reactions in benzene and xylene

Table 2. Competitive Oxidation of Several Substrates

Compound A	Compound B	Products <sup>a</sup>	A : B	Product Ratio	Selectivity A/B	Prediction from Scaiano's kinetic results
		 	1 : 1 1 : 3 3 : 1	1.40 : 1 0.48 : 1 4.52 : 1	1.4	0.8
		 	1 : 1 1 : 4	6.30 : 1 1.59 : 1	6.5	6.0
		 	1 : 1 1 : 4	6.10 : 1 1.55 : 1	6.2	6.0
		  	10.2 : 1 21.5 : 1	0 <sup>b</sup> : 1.3 : 1 0.9 : 1.2 : 1	0.019	0.021 <sup>c</sup>
		 	1.2 : 1	1 : 1.6	0.52 <sup>d</sup>	0.88
		 	1.3 : 1	1 : 2.6	0.4	

A:B ratio is molar. Predictions from Scaiano's kinetic results are based on ratios of quenching rate constants, which have 15–20% error limits. (a) Phenols and alcohols washed with H<sub>2</sub>O prior to analysis. (b) Too little observed to quantify. (c) Taken from Scaiano's values for benzene and cyclopentene, and adjusted by 10% for the difference between cyclopentene and cyclohexene, as determined in the gas phase.<sup>37</sup> (d) Cyclohexene was not assayed, so the absolute selectivity ratio may vary from this number.

were not particularly sensitive to O<sub>2</sub>, but in alkane solvents the presence of O<sub>2</sub> resulted in oxidized products in excess of 100%, relative to dibenzothiophene production. While catalytic oxidation is certainly an ultimate goal, it obscures the basic mechanism and the source of the oxygen in the observed products.

The hydroxylation chemistry observed with iron porphyrin complexes with iodosylbenzene or other single oxygen sources is often described as "oxenoid." In the "oxygen rebound" mechanism proposed by Groves, a (porphyrin)Fe<sup>V</sup>=O or (porphyrin<sup>+</sup>)Fe<sup>IV</sup>=O species abstracts a hydrogen atom from the substrate to produce an alkyl radical and a metal-coordinated hydroxyl radical, which rapidly recombine. The reactivity observed here mimics what one would expect if O atom (<sup>3</sup>P) or a related oxenoid species were the oxidizing agent, using a similar mechanism.

We are unaware of any clean method of producing triplet oxene in solution for use as a standard in product studies. Though there is a substantial literature on the reactivity of O atoms in the gas phase, very little data is available in condensed phases. There are three sources of data for comparison to the present oxidations. Photolysis of N<sub>2</sub>O in saturated hydrocarbons produces O(<sup>1</sup>D), which reacts with solvent largely by insertion to form alcohols.<sup>27</sup> Only a slight selectivity for tertiary hydrogens is observed for O(<sup>1</sup>D), and the high-energy photons necessary for photolysis of N<sub>2</sub>O limit its usefulness to solvents which are essentially transparent in the UV, such as alkanes. A second plausible comparison is to the photolysis of various aromatic *N*-oxides to form O(<sup>3</sup>P).<sup>28–30</sup> Indeed, photolysis of pyridine *N*-oxide in benzene provides phenol in low yield<sup>31</sup> and photolysis of pyridazine oxides causes hydroxylation of cyclohexane and benzene and epoxidation of olefins, among other products.<sup>32,33</sup> However, the cleavage of O atoms is actually a minor process, accompanied by formation of a reactive dear-

omatized oxaziridine and other rearrangements.<sup>34,35</sup> The oxaziridine is of course a strong oxidizing agent, presumably with selectivity for epoxidation over hydroxylation. Because of this interference and the observation that significant conversion of pyridine *N*-oxide is accompanied by formation of a tenacious brown tar, comparison with these product studies is also of limited value.

Quite recently Scaiano and co-workers have used flash photolysis of pyridine *N*-oxide to determine the rate constants for reaction of O(<sup>3</sup>P) with various substrates by competition with formation of acetonitrile *N*-oxide.<sup>36</sup> He points out that O(<sup>3</sup>P) is a relatively selective reagent, much more so than hydroxyl radicals. The rate constants generated by Scaiano can be used for qualitative comparisons with competition product studies, as shown in Table 2. The agreement between the rate ratios taken from Scaiano and the product ratios determined here are good, even though the product ratios are a far more indirect measure of reactivity. The isotope effects suggest that reaction with cyclohexane has H-abstraction as a primary step, but are not as diagnostic for the reaction with benzene.

In summary, photolysis of dibenzothiophene oxide results in the production of an extremely active oxidizing agent which hydroxylates alkanes and arenes. It additionally epoxidizes olefins. The product distributions and selectivity are certainly reminiscent of the expected stepwise reactivity of O(<sup>3</sup>P) or other oxenoid species, but no direct characterization of the intermediate is yet available.

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(26) Initial concentrations of **1** were approximately 1 mM, except in alkane solvents, where they were about 0.4 mM. All reported data is for 20–25% conversion of **1**, but yields and product ratios are not particularly sensitive to this parameter.

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