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# Photochemistry of Dibenzothiophene-S,S-dioxide: Reactions of a Highly Constrained Biradical

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***Abstract:*** Photolysis of dibenzothiophene sulfoxide in isopropanol provides biphenyl in quantitative yield via two sequential photochemical reactions. Mechanistic aspects of the reaction are discussed, including the unusual observation that isoprene increases the quantum yield of loss of starting material.

In this communication, we report the quantitative photochemical transformation of dibenzothiophene sulfone (1) to biphenyl (7) in isopropanol. This sequential, two photon hydrodesulfonation is unprecedented to the best of our knowledge, but we propose a mechanism consistent with known sulfone photochemistry. The critical intermediate is the 1,5-biradical 2, which has only two rotational degrees of freedom. Our results show that conditions need to be finely tuned in order to carry out the conversion, an observation that we attribute to the reactivity of the intermediates. The proposed reaction sequence is shown in figure 1.

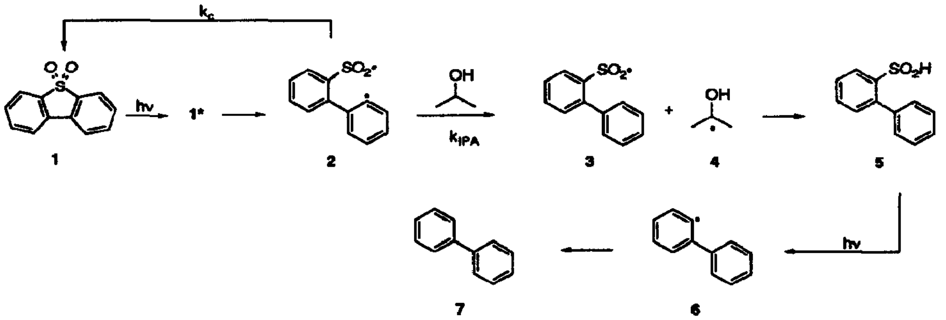
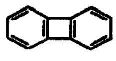


**Figure 1.** Proposed mechanism for the photohydrodesulfonation of dibenzothiophene sulfone.

Direct irradiation of dilute solutions (*ca.* 0.5 mM) of dibenzothiophene sulfone (1) in deoxygenated isopropanol held in borosilicate test tubes using the output of the "300 nm" bulbs of a Rayonet RMR-600 photoreactor[1] results in quantitative conversion to biphenyl. Photolyses were monitored by GC. Verification that the extra hydrogen atoms come from solvent was provided by photolysis of 1 in isopropanol-$d_8$, which gave biphenyl-$d_2$, as determined by mass spectral analysis. Although quantitative photoconversion of 1 to 7 is essentially limited to isopropanol solvent in our experience, in several other hydrogen-donating solvents (*e.g.*, methanol, THF) complete loss of starting material is accompanied by partial conversion to biphenyl in more complex reaction mixtures. Under no GC conditions was 5 detected, but as shown in figure 2, the apparent mass balance dipped and rose again in a manner completely consistent with the formation of a stable



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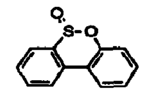

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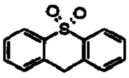

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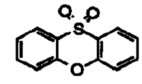

**11**

intermediate which did not survive the GC analysis.[2] Quantitative mass balance was reproducibly reachieved on extended photolysis. The quantum yield for loss of **1** in isopropanol was found to be 0.003.[3] Support for the mechanism in figure 1 was provided by the photolysis of the known **5**,[4] which results in **7**. In no case was biphenylene (**8**) or the sultine **9**[5] observed; both were shown to be stable to the analysis conditions. Photolysis of **9** in isopropanol yields 2-phenylphenol, which was also not observed.

Large scale photoreactions are also successful. Photolysis of well stirred suspensions of 0.5 g of **1** in 300 ml isopropanol under Ar using the output of a 450 W Hanovia lamp filtered through Vycor, followed by addition of *ca.* 1 g silica, evaporation of the solvent, and washing of the silica with hexane provides biphenyl in 75% yield and 98% purity.

Dibenzothiophene sulfone is essentially photoinert in solvents which are poor hydrogen atom donors (*e.g.*, benzene, acetonitrile). Photolysis of the neat solid led to no products detectable by GC and no macroscopic degradation was apparent. Attempts to extend the hydrodesulfonation to molecules **10** and **11** were unsuccessful. At which stage the hydrodesulfonation fails cannot yet be determined, but these compounds are photoactive.

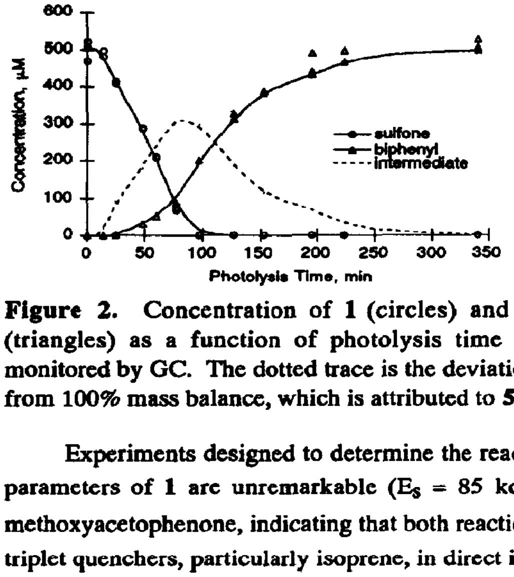

Figure 2. Concentration of **1** (circles) and **7** (triangles) as a function of photolysis time as monitored by GC. The dotted trace is the deviation from 100% mass balance, which is attributed to **5**.

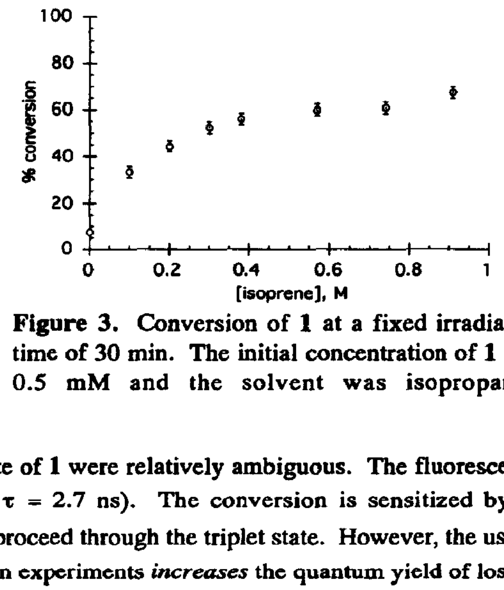

Figure 3. Conversion of **1** at a fixed irradiation time of 30 min. The initial concentration of **1** was 0.5 mM and the solvent was isopropanol.

Experiments designed to determine the reactive state of **1** were relatively ambiguous. The fluorescence parameters of **1** are unremarkable ($E_S$ = 85 kcal/mol, $\tau$ = 2.7 ns). The conversion is sensitized by *p*-methoxyacetophenone, indicating that both reactions can proceed through the triplet state. However, the use of triplet quenchers, particularly isoprene, in direct irradiation experiments *increases* the quantum yield of loss of **1**. In parallel fashion, the yield of biphenyl falls to zero with added isoprene, showing that at least one of the intermediates is diverted from the path outlined in figure 1. Figure 3 shows a typical plot of loss of **1** versus isoprene concentration after a fixed period of irradiation of otherwise identical samples. The quantum yield of loss of **1** leveled off (within experimental error) at approximately 0.053 for irradiations in isoprene/benzene mixtures that contained at least 50% isoprene.

Postulation of the intermediate **2** is, we believe, entirely reasonable. It has long been known that irradiation of acyclic diaryl sulfones leads to the formation of aryl radicals. Their subsequent reactions with benzene solvent lead to the formation of biphenyls derived from solvent and substrate.[6-8] Loss of $SO_2$ from the arylsulfonyl radicals is not a major process, but recovery of sulfinic acids or discovery of any of their alternate fates is problematic. By contrast, photolysis of cyclic dialkyl sulfones or bisbenzylic acyclic sulfones in unreactive solvents does lead to products representing the net extrusion of $SO_2$, as desulfonylation of alkylsulfonyl radicals is much more rapid.[9-15] In a few instances, the isomerization of cyclic sulfones to sultines (cyclic sulfinic esters), has been observed, and this is presumed to go through a biradical intermediate analogous to **2**.[11,16,17] Even in the cases of some unsaturated sulfones whose chemistry is complicated by electrocyclic sulfene formation, carbon-sulfur bond rupture is still one of the major processes.[17-20]

It has been shown for diphenyl sulfone that cleavage derives from both singlet and triplet states.[21,22] The same is likely true here. While it is tempting to suggest that singlet cleavage of **1** is irrelevant because of very rapid reclosure of $^{1}$**2**, we have no evidence that proves this. Moreover, isoprene should be an efficient triplet quencher of **1**.[23] Traditionally, the role of isoprene in photochemical reactions is as a triplet quencher which lowers the efficiency of reactions that proceed through long lived triplets. The increased efficiency observed here demands another explanation. We propose that (1) isoprene is an ineffective quencher due only to a short lifetime for $^{3}$**1**, and that (2) isoprene acts as a substrate for radical-molecule reactions which compete with $k_c$.[24] We cannot rule out that isoprene is simultaneously quenching $^{3}$**1**, but we take 0.053 to be a reasonable estimate of the efficiency for the formation of trappable **2**, since this is the highest quantum yield for decomposition of **1** we could obtain. While the rate constant $k_{IPA}$ is not known, a reasonable upper limit may be taken from the rate of reaction between phenyl radical and isopropanol ($4.1 \pm 0.1 \times 10^5$ $M^{-1}s^{-1}$).[25] Given these data and the quantum yield for loss in neat isopropanol (0.003), an order of magnitude estimate of the lifetime of **2** of 10 ns can be made. Such a lifetime is at least consistent with the known rate constant for addition of phenyl to pentadiene (*ca.* $10^8$ $M^{-1}s^{-1}$ at 60 °C)[26,27] and our quantum yield results.[28]

The chemistry we observe here is particularly sensitive to the nature of the hydrogen atom donor, most likely because a number of reactions are available at several stages, and the system must be tuned to steer toward formation of **7**. Biradical **2** is a highly constrained system. Only rotations of the bond connecting the phenyl rings and the remaining C-S bond are available, and one would expect that intramolecular closure to **1** or the unobserved **9** would dominate the chemistry. In fact, that is the case, as **1** is "inert" in solvents such as benzene and acetonitrile. Even in neat isopropanol, no more than about 6% of the biradicals **2** are intercepted before returning to **1**.

In summary, we have uncovered the remarkable, quantitative two-stage photochemical transformation from dibenzothiophene sulfone to biphenyl in isopropanol. Although simple enough in appearance, this transformation is relatively complex, as evidenced by the strong dependence on solvent and the sulfone-containing ring size. Elucidation of further details and spectroscopic characterization of the intermediates await our further efforts.

## ACKNOWLEDGMENT

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## REFERENCES AND NOTES

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2. Preliminary HPLC measurements showed a broad peak which grew in and disappeared in parallel with the mass balance depression in the GC analysis.
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