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Photochemistry of Substituted Dibenzothiophene Oxides: The Effect of Trapping Groups[1]

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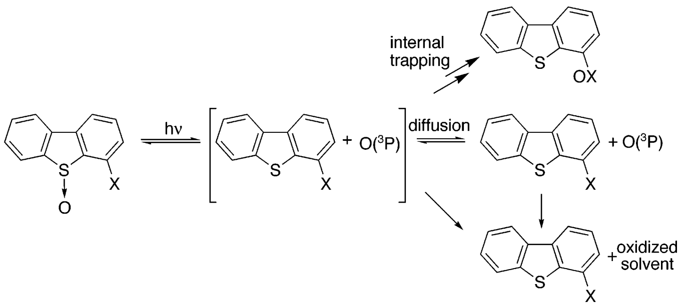

Photolyses of dibenzothiophene sulfoxides (DBTOs) with intramolecular trapping functionalities attached in the 4-position show higher quantum yields of deoxygenation. Deoxygenation quantum yields are also less solvent dependent for the substituted DBTOs. Product analysis shows a detectable amount of intramolecular O-trapped products and suggests that solvent effects observed in previous studies of DBTO derive at least mainly from the reactivity between the oxidizing species that is released, presumably $O(^3P)$, and the solvent, rather than from other macroscopic solvent parameters.

Introduction

Along with C−S homolysis and stereomutation, one of the fundamental photochemical reactions of aromatic sulfoxides is deoxygenation to form the corresponding sulfide.[2−17] Direct photolysis of dibenzothiophene oxide (DBTO) provides a nearly quantitative yield of dibenzothiophene (DBT).[7,15,16] Mechanistic evidence strongly favors a unimolecular mechanism for deoxygenation, and several experiments point to formation of $O(^3P)$. For example, while direct evidence for formation of this active oxygen species is lacking, the oxidation pattern of various substrates is quite consistent with expectations for it.[9,10,15]

It has already been reported that the quantum yield of DBT formation is higher in tetrahydrothiophene, cyclohexene, and DMSO than in many other solvents.[15] This could be explained by supposing that these three were better oxygen atom acceptors than other solvents (e.g., THF, isopropyl alcohol) and that the nascent sulfide (DBT) competes with the solvent as an acceptor of the oxygen atom, as shown in Scheme 1. It would be expected that these solvents, which react most rapidly with $O(^3P)$, would produce net deoxygenation quantum yields closer to the quantum yield of the initial cleavage event itself, though the latter number has not been established.

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(1) Photochemistry and Photophysics of Aromatic Sulfoxides. 23. For paper 22 in the series, see ref 45.

(2) Still, I. W. J.; Thomas, M. T. *Tetrahedron Lett.* **1970**, 4225−4228.

(3) Still, I. W. J.; Cauhan, M. S.; Thomas, M. T. *Tetrahedron Lett.* **1973**, 1311−1314.

(4) Still, I. W. J.; Arora, P. C.; Chauhan, M. S.; Kwan, M.-H.; Thomas, M. T. *Can. J. Chem.* **1976**, *54*, 455−470.

(5) Still, I. W. J.; Arora, P. C.; Hasan, S. K.; Kutney, G. W.; Lo, L. Y. T.; Turnbull, K. *Can. J. Chem.* **1981**, *59*, 199−209.

(6) Still, I. W. J. In *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappaport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons, Ltd.: New York, 1988; pp 873−887.

(7) Gurria, G. M.; Posner, G. H. *J. Org. Chem.* **1973**, *38*, 2419−2420.

(8) Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 217−228.

(9) Lucien, E.; Greer, A. *J. Org. Chem.* **2001**, *66*, 4576−4579.

(10) Thomas, K. B.; Greer, A. *J. Org. Chem.* **2003**, *68*, 1886−1891.

(11) Kumazoea, K.; Arima, K.; Mataka, S.; Walton, D. J.; Thiemann, T. *J. Chem. Res., Synop.* **2003**, 60−61.

(12) Thiemann, T.; Dongol, K. G. *J. Chem. Res., Synop.* **2002**, *2002*, 303−308.

(13) Thiemann, T.; Ohira, D.; Arima, K.; Sawada, T.; Mataka, S.; Marken, F.; Compton, R. G.; Bull, S.; Davies, S. G. *J. Phys. Org. Chem.* **2000**, *13*, 648−653.

(14) Thiemann, T.; Kumazoe, K.; Arima, K.; Mataka, S. *Kyushu Daigaku Kino Busshitsu Kagaku Kenkyusho Hokoku* **2001**, *15*, 63−71.

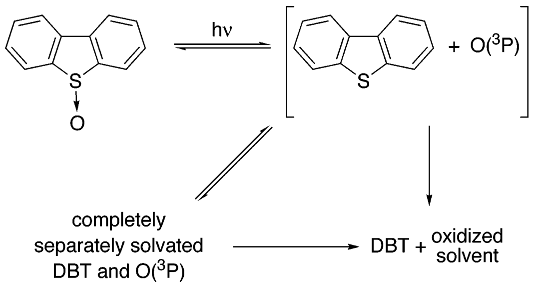
(15) Gregory, D. D.; Wan, Z.; Jenks, W. S. *J. Am. Chem. Soc.* **1997**, *119*, 94−102.

(16) Wan, Z.; Jenks, W. S. *J. Am. Chem. Soc.* **1995**, *117*, 2667−2668.

(17) Jenks, W. S.; Gregory, D. D.; Guo, Y.; Lee, W.; Tetzlaff, T. In *Organic Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 1997; Vol. 1, pp 1−56.

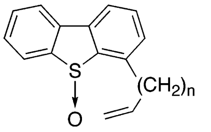
10.1021/jo047995e CCC: $30.25

SCHEME 1. Quantum Yield of DBTO Deoxygenation Is Higher When the Solvent Competes More Effectively for the Oxygen Atom

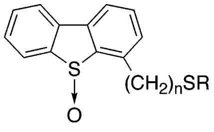


This explanation points to a new series of experiments. Substituents can be appended to the 4-position of DBTO that should themselves act as chemical traps for O(^{3}P) without affecting the bulk solvent parameters such as polarity or hydrogen bonding capability. A DBTO derivative with an appropriate functionality could yield the internally trapped products and be considerably less sensitive to solvent effects. A higher overall quantum yield might be expected for such a molecule (than is observed for DBTO) in solvents that are among the low Φ group for DBTO itself, e.g., acetonitrile. The identity of the functional group is obviously of key importance. However, it should also be expected that the chain length between the trapping functionality and the DBTO nucleus will affect the efficiency of trapping and the relative effect of solvent on the observed quantum yields.

The most straightforward choices for trapping functionalities are alkenes and sulfides. These derive from the solvents that had higher quantum yields in our previous work,[15] and the molecules had very high rate constants in a kinetic study of Bucher and Scaiano.[18,19] We now report the preparation and photochemistry of sulfoxides **1a**–**c** and **2a**–**d** and show that their photochemistry supports the hypothesis laid out in Scheme 1, though the results are more complex than most simply implied by the above analysis.



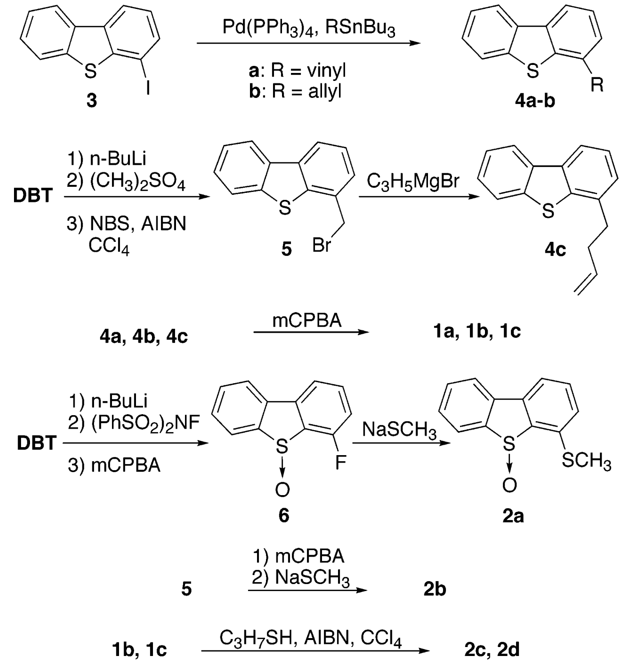
1 **a**: n = 0
b: n = 1
c: n = 2



2 **a**: n = 0, R = CH_3
b: n = 1, R = CH_3
c: n = 2, R = C_3H_7
d: n = 3, R = C_3H_7

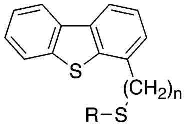
Results

SCHEME 2. Preparation of Sulfoxides

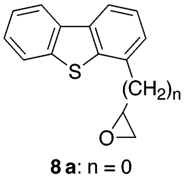


Preparation of Sulfoxides 1a–c and 2a–d. The preparations of the sulfoxides are outlined in Scheme 2, while full synthetic details are given in Supporting Information. 4-Iododibenzothiophene[20] was converted to the corresponding vinyl or allyl DBT derivative via Stille coupling.[21–25] This was followed by selective oxidation of the sulfur using *m*CPBA.[26,27] For preparation of **1c**, methylation in the 4-position was followed by benzylic bromination.[28,29] An allyl group was then coupled by way of Grignard chemistry,[30] and oxidation was carried out.[27]

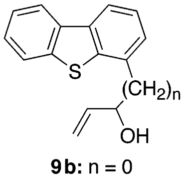
DBTO derivatives with a sulfide appendage could not be prepared from the corresponding precursors **7** with oxidation as the final step because the oxidation of DBT is sluggish relative to that of other sulfides. Instead, the functionality must be introduced to the preoxidized DBTO derivative. Sulfoxide **2a** was prepared by nucleophilic substitution of the corresponding fluoro-substituted DBTO **6**.[31] Sulfoxide **2b** was prepared via intermediate **5** by oxidation and substitution. Compounds **2c** and **2d**



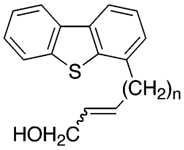
7a: n = 0, R = CH_3
b: n = 1, R = CH_3
c: n = 2, R = C_3H_7
d: n = 3, R = C_3H_7



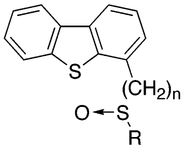
8 **a**: n = 0
b: n = 1
c: n = 2
d: n = 3



9 **b**: n = 0
c: n = 1



10b: n = 0
c: n = 1



11a: n = 0, R = CH_3
b: n = 1, R = CH_3
c: n = 2, R = C_3H_7
d: n = 3, R = C_3H_7

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(18) Bucher, G.; Scaiano, J. C. *J. Phys. Chem.* **1994**, *98*, 12471–12473.

(19) This study used pyridine-*N*-oxide, for which deoxygenation is a minor photochemical process, as a precursor.

(20) Katritzky, A. R.; Perumal, S. *Magn. Reson. Chem.* **1990**, *28*, 914–17.

(21) Crisp, G. T.; Papadopoulos, S. *Aust. J. Chem.* **1988**, *41*, 1.

were prepared with SC_3H_7 groups rather than SCH_3 because the method of preparation involved radical addition of the thiol to the corresponding sulfoxides **1b** and **1c**.[32] The propyl group served to make the thiol easier to handle than methanethiol.

Photoproducts. The method of choice for identification and quantification of products in this study was GC-MS. It was anticipated that compounds **1a**−**c** might, respectively, produce epoxides **8a**−**c** and/or allylic alcohols **9b**,**c** or **10b**,**c** as intramolecular trapping products.[15,33] Preliminary photolyses of **1b** gave GC-MS peaks that had the same mass as **1b** but different retention times, consistent with this idea. As such, it was desirable to prepare the potential photoproducts independently for comparison of their chromatographic and mass spectral behavior.

Attempts to produce products **8b**−**d**, however, were not successful. For example, the preparation of **8b** was attempted by the coupling of 4-lithiodibenzothiophene to epichlorohydrin using CuCN as a catalyst[34] and by dihydroxylation[35] of **4b**, which would eventually give **8b** by dehydrative ring closure; neither of these pathways were fruitful. Instead, then, for compounds **8**−**10**, assignments of GC-MS peaks to structures were based on the fragmentation patterns observed in the EI mass spectra, which were compared to functional group analogues using benzene as the aromatic nucleus instead of dibenzothiophene. (For example, styrene oxide was used as the analogue of **8a**.) In contrast to the internally trapped products from **1a**−**c**, deoxygenated sulfides **4a**−**c** were already available from the preparation of the sulfoxides.

The potential photoproducts from **2a**−**d** were straightforward to prepare. Deoxygenated sulfoxides **7a**−**d** were obtained by routes analogous to the preparations of **2a**−**d**, save that the dibenzothiophene nucleus was not oxidized. Sulfoxides **11a**−**d** were then obtained by oxidation of the compounds in the **7** series.

General Photolysis Conditions. Photolyses of compounds **1** and **2** were done in Ar-flushed solvents using a Xe arc lamp coupled to a monochromator set to 320 nm (±12 nm linear dispersion), which is near their first absorption maxima. Initial concentrations were in the range of 5 mM. Product distributions and quantum yields are quoted at low conversion (ca. 10%) unless otherwise noted. All solvents were spectro-grade when available. Cyclohexene was refluxed under Ar over Na for several hours and then distilled immediately before use. Photolyses carried out in cyclohexene (only) were done after 3−5 freeze−pump−thaw cycles in addition to the Ar flushing to eliminate as much O_2 as possible. All quantum yields were measured using valerophenone as an actinometer.[36]

TABLE 1. Results of Photolysis of 1a−c and 2a−d in Several Solvents

compd	solvent	product(s)	Φ_{total}
DBTO[a]	acetonitrile	DBT	0.0026
	benzene	DBT	0.0029
	cyclohexene	DBT	0.0100
	DMSO	DBT	0.0079
1a	acetonitrile	**4a**	0.0018
	benzene	**4a** (75%), **8a** (25%)	0.0020
	cyclohexene	**4a**	0.010
1b	acetonitrile	**4b** (85%), **8b** (15%)	0.0074
	benzene	**4b** (75%), **8b** (25%)	0.0068
	cyclohexene	**4b**	0.0126
	DMSO	**4b**	0.0078
1c	acetonitrile	**4c**	0.0085
	benzene	**4c** (75%), **8c** (25%)	0.0096
2a	acetonitrile	**7a**	0.0038
	benzene	**7a** (55%), **11a** (45%)	0.0058
	cyclohexene	**7a**	0.0114
2b[b]	acetonitrile	**7b** and **12**[b]	0.0048
2c	acetonitrile	**7c**	0.0028
	benzene	**7c**	0.0050
2d[c]	acetonitrile		~0

[a] Literature value.[15] [b] Secondary photolysis of **7b** leads to **12**. The reported quantum yield has a larger error associated with it, because it is only to about 3% conversion, to avoid excessive secondary photolysis. [c] Extended photolysis did not lead to observable photochemical reaction.

Photolysis of Olefin-Labeled Sulfoxides 1a−**c.** Photolysis of 4-vinyl DBTO **1a** to low conversion in acetonitrile provided only the deoxygenated product **4a** in apparently quantitative yield. In benzene, the sulfur-containing products were a mixture of **4a** and epoxide **8a** in a 3:1 ratio, again in quantitative yield with respect to consumed starting material. The assignment of the new product to **8a** was based on a comparison of its EI-MS fragmentation pattern to those of styrene oxide, acetophenone, and phenylacetaldehyde, i.e., the benzene analogues of the reasonable side chain-oxidized isomers of **1a**. The major peaks in the observed spectra were $(M - 17)^+$, $(M - 31)^+$, and $(M - 43)^+$, which corresponded well to styrene oxide; the other compounds had much different fragmentation patterns. The quantum yields for deoxygenation in these two solvents are both near 0.002, as reported in Table 1.

1a **4a** **8a**

Photolysis of **1b** and **1c** gave similar results. The allyl sulfoxide yielded mainly the deoxygenation product **4b**,

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(22) Agharahimi, M. R.; LeBel, N. A. *J. Org. Chem.* **1995**, *60*, 1856−1863.

(23) Larhed, M.; Hoshino, M.; Sabine, H.; Curran, D. P.; Hallberg, A. *J. Org. Chem.* **1997**, *62*, 5583−5587.

(24) Han, X.; Soltz, B. M.; Corey, E. J. *J. Am. Chem. Soc.* **1999**, *121*, 7600−7605.

(25) Schubert, U. R.; Eschbaumer, C.; Heller, M. *Org. Lett.* **2000**, *2*, 3372−3376.

(26) Nag, M.; Jenks, W. S. *J. Org. Chem.* **2004**, *69*, 8177−8182.

(27) Mata, E. G. *Phosphorus, Sulfur, Silicon* **1996**, *117*, 231−286.

(28) Katritzky, A. R.; Perumal, S. *J. Heterocycl. Chem.* **1990**, *27*, 1737−1740.

(29) Blanchard, P.; Svenstrup, N.; Rault-Berthlot, J.; Riou, A.; Becher, J. *Eur. J. Org. Chem.* **1998**, 1743−1757.

(30) Hirato, T.; Misu, D.; Yao, K.; Agawa, T. *Tetrahedron Lett.* **1996**, 929−932.

(31) Padwa, A.; Gasdaska, J. R. *Tetrahedron* **1988**, 4147−4156.

(32) Bakuzis, P.; Bakuzis, M. L. F.; Fortes, C. C.; Santos, R. *J. Org. Chem.* **1976**, *41*, 2769−2776.

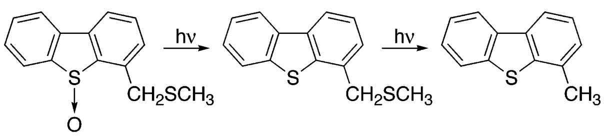
(33) We shall refer to all compounds that formally may be formed by oxygen atom transfer from the DBTO nucleus to the side chain as "internal trapping products."

(34) Takano, S.; Yanase, M.; Ogasawara, K. *Heterocycles* **1989**, *29*, 1825−1828.

(35) Raunkjaer, M.; Olsen, C. E.; Wengel, J. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2543−2551.

with 15 and 25% yields of **8b** in acetonitrile and benzene, respectively. Homoallyl-substituted sulfoxide **1c** did not provide detectable **8c** in acetonitrile but provided both the deoxygenation (**4c**) and trapped product (**8c**) in benzene, as shown in Table 1. Quantum yields are higher for both of these compounds. Again, the assignments of the structures of the observed GC-MS peaks to **8b** and **8c** were done by comparison of the fragmentation to the benzene analogues of structures **8**−**10**.

The results among the thio-substituted DBTOs were less uniform. Sulfoxide **2a** behaved largely as the olefins had. An apparently quantitative yield of **7a** was obtained in acetonitrile, while a 55:45 mixture of **7a** and **11a** was obtained in acetonitrile. Compound **2b**, however, had a more complex behavior. In acetonitrile, at low conversion (ca. 10%), a 2:1 mixture of **7b** and 4-methyldibenzothiophene **12** was observed. As the reaction proceeded, the ratio dropped until all the **7b** was converted to **12**. The apparent explanation that photolysis of **7b** yields a benzylic-type homolysis reaction that gives **12** was confirmed by independent photolysis of **7b**. The quoted quantum yield (Table 1) of 0.0048 is subject to a greater error than the others because we attempted to extrapolate the data more closely to zero conversion to get around the secondary photolysis problem.



2b **7b** **12**

We cannot rule out that a certain amount of **12** is produced on direct photolysis of **2b** but do not believe this to be the case. We also cannot rule out that photolysis of **2b** produces some of the internally trapped sulfoxide **11b**, which in turn is photolyzed to **12** in high quantum yield, but **11b** was not ever detected in any of the reaction mixtures.

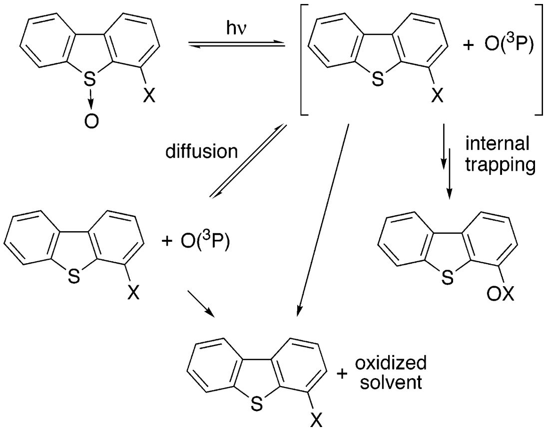
Photolysis of **2c** resulted only in formation of **7c**, with a quantum yield of 0.0050 or 0.0028, depending on the solvent. Photolyses of **2d** were carried out in benzene and acetonitrile. In neither solvent was any new product observed; the starting material remained unchanged.

As reported in Table 1, **1a**, **1b**, and **2a** were also photolyzed in cyclohexene. These were the starting materials that showed significant internal trapping products in the other solvents. In each case, the only sulfur-containing product was that of deoxygenation, i.e., **4a, 4b**, and **7a**, respectively. Also, the samples were checked for oxidized solvent products. Cyclohexene oxide and 2-cyclohexenol were observed in ratios of 1:2, 1:2, and 1:1.4 for the three cases.

Discussion

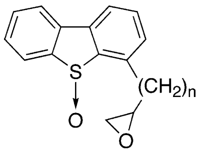
In our 1997 paper on the photodeoxygenation of DBTO, we reported the quantum yield obtained with 320 nm irradiation for deoxygenation in 13 solvents. The value was 0.0030 ± 0.0004 for the great majority of these: acetonitrile, benzene, 2-propanol, tetrahydrofuran, toluene, and four different alkane solvents. Only cyclohexene, DMSO, and tetrahydrothiophene stood out, with values of 0.0100, 0.0079, and 0.0085, respectively. For purposes of further discussion, we will refer to these two sets as the "low quantum yield solvents" and the "high quantum yield solvents," respectively.

SCHEME 3. Expanded Reaction Scheme, Accounting for Internal Trapping by the Pendant Functionality



Given the structural diversity of the solvents in both groups, we asserted that the variation in quantum yield had mainly to do with specific functionality of the high quantum yield solvents, rather than a bulk property such as polarity.[15] As implied in Scheme 1, those solvents that reacted with O(^{3}P) more rapidly than the others showed a higher quantum yield because of the competitive back-reaction of the oxygen atom with DBT. The experiments here address this attribution by expanding this notion to that in Scheme 3, where the explicit functionality in the pendant group X is designed to model that of the high quantum yield solvent. Then, the substrate can be examined in multiple solvents, both among the high and low quantum yield groups. The effect of its X group and the concomitant high effective local concentration of what we pose to be the trapping functionality can be examined. In the event, it turns out that the results do not lead to a black and white conclusion, but we believe that we may draw speculative interpretations that are consistent with Scheme 3 and the explanation of the solvent effect that we advanced previously.

We first consider the results for the series **1a**−**c** with Scheme 3 in mind. In none of the experiments was a product observed such as **13**, which corresponds to an *intermolecular* trapping product from **1a**. Because of the lack of any such "M + 16" product in all the photolyses, we assume that all the trapped products come from unimolecular chemistry.



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It is immediately notable that the quantum yields for deoxygenation for compounds **1b** and **1c** are in the range that would have been in (or at least quite near) the high quantum yield solvent group for DBTO. These are also

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(36) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506−7512.

two cases in which internally trapped products are observed, consistent with the hypothesis in Scheme 3. When the photolyses are carried out in the most efficient externally trapping solvent, i.e., cyclohexene, the quantum yield is near 0.01 for both of them. This value is still higher than the quantum yield in benzene or acetonitrile, and the internally trapped products disappear. This is entirely consistent with the idea that the principal quality of cyclohexene that makes it a high quantum yield solvent is its ability to trap the nascent O(^{3}P). It also suggests that 0.01 is near the quantum yield limit that would be obtained for 100% trapping of the oxygen atom for DBTO derivatives whose substituents do not have a substantial effect on the excited states or their dynamics.

It is, however, considerably less obvious why no internally trapped product is observed for **1a** and **1c** when photolysis is carried out in acetonitrile. According to Scaiano's data,[18] O(^{3}P) reacts about 300 times more rapidly with benzene than with acetonitrile. (It is thought that the major reaction channel in acetonitrile is formation of the nitrile oxide, but we did not specifically examine any of the reaction mixtures for products of solvent oxidation.) Thus, one might expect that a greater fraction of the photolyzed material might be expected to end up as the internally trapped product in CH_3CN. It may be speculated that the lower viscosity acetonitrile might be more conducive to diffusive separation of O(^{3}P) from the DBT derivative; however, this should lead to a greater quantum yield for DBTO as well, and this is not observed.

However, the greater polarity of acetonitrile might also be more conducive to separation of O from the DBT nucleus if the pathway to their formation involves significant charge separation. Greer has made the argument that charge separation is involved in the related (and also spin-forbidden) oxidation of sulfides by O(^{3}P) in solution,[9,10] and it has been widely noted that there is a correlation between substrates' low ionization potentials and high gas-phase reaction rate constants with O(^{3}P).[37−42] Though not strictly a case of microscopic reversibility, it is reasonable to infer that the same charge separation may also occur as S−O dissociation begins on an excited-state energy surface. (The logical limit of a mechanism along these lines involves DBTO* forming a transient ion pair $DBT^{\bullet+}/O^{\bullet-}$, which forms DBT and O(^{3}P) by back electron transfer.) This "looser" transition state in acetonitrile might easily lead to lower trapping efficiency for entropic reasons.

A second point in this series about which we can only speculate is the data set for **1a**, a compound that shows trapping products in benzene but not an elevated Φ. The observed quantum yield for **1a**, approximately 0.002 regardless of the solvent, is lower than for the other two in the series and is comparable to that of DBTO. Here, we speculate in hindsight that the direct attachment of the vinyl group to the aromatic ring provides unpredictable results on the basis of the possibility of cis−trans isomerization as a mechanism for excited state deactivation. In retrospect, it could easily have been the case that the vinyl group coupled to the aromatic moiety of DBTO in such a way as to completely eliminate the deoxygenation process; in any case, the vinyl substituent should decrease the observed deoxygenation quantum yield because of this to some degree. That the cis−trans isomerization deactivation is relatively *inefficient* is evidenced both by the observation of the internally trapped products in benzene and the observation of a quantum yield of 0.01 in cyclohexene. Nonetheless, this issue does muddy the comparison of **1a** to DBTO and the rest of the series.

The series of compounds with sulfanyl labels **2a**−**d** behaves less uniformly than the series **1a**−**c**, but the "misbehavior" is straightforward to rationalize. Again, none of the quantum yields qualitatively exceeds 0.01, consistent with this being the approximate upper limit for a conventional DBTO nucleus. Trapping products are observed for **2a** in benzene but not in acetonitrile, as above. With a CH_2SCH_3 appendage, no trapping products were observed in acetonitrile, but secondary photolysis led to methyl-substituted dibenzothiophene **12**. As a result of this complication, we chose not to pursue the photolysis of this compound extensively. When the facile benzylic homolysis is removed by homologation to **2c**, still no trapping products are observed, and the quantum yields are comparable to those for DBTO. This simply implies that the best geometry for internal trapping before dissociation (including the unfavorable entropic issues involved with the flexible linker) is best achieved with compound **2a**.

The simplest interpretation of these data for the photoinert **2d** is that the pendant sulfide is poised at a particular length that quenches the reactive excited state much more efficiently than the other analogues. This idea has precedent, for example, in β-phenylvalerophenone, which is a uniquely unreactive phenyl ketone toward internal hydrogen abstraction.[43] In analogy to that example, the mechanism for quenching by the side chain of **2d** is most likely reversible charge transfer from the side chain sulfur to the easily reduced[44] DBTO nucleus.

An alternative interpretive framework with substantial merit has been offered by a referee. It was suggested that the initially populated excited state, rather than bifurcating into a reactive channel that generates O(^{3}P) and one or more nonreactive channels (e.g., formation of the low-energy T_1 state), undergoes a trifurcation. In addition to the two channels described previously, it is hypothesized that a particular excited state, perhaps T_2, acts as a second oxygen transfer agent if an appropriate receptor is available. Under this framework, the quantum yield of O(^{3}P) formation is universally about 0.003, and the maximum additional oxygen transfer quantum yield is about 0.007. It is entirely reasonable to suggest that such a mechanism, which would not entail any diffusible intermediates, would have a distinct dependence on the

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[37] Klaning, U. K.; Sehested, K.; Wolff, T. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 2969.

[38] Cvetanovic, R. J. *Adv. Photochem.* **1963**, *1*, 115−182.

[39] Cvetanovic, R. J.; Singleton, D. L.; Irwin, R. S. *J. Am. Chem. Soc.* **1981**, *103*, 3530−9.

[40] Cvetanovic, R. J. *J. Phys. Chem. Ref. Data* **1987**, *16*, 261−326.

[41] Nip, W. S.; Singleton, D. L.; Cvetanovic, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 3526−30.

[42] Singleton, D. L.; Cvetanovic, R. J. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1377−437.

[43] Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; Haug, A.; Graber, D. R. *Mol. Photochem.* **1970**, *2*, 81−85.

[44] Cubbage, J. W.; Tetzlaff, T. A.; Groundwater, H.; McCulla, R. D.; Nag, M.; Jenks, W. S. *J. Org. Chem.* **2001**, *66*, 8621−8628.

chain lengths between the S−O bond and the trapping functionality because of a limited range of transition-state geometries that could effect the oxygen transfer. The fact that trapped products are favored in benzene, relative to acetonitrile, would then depend on a differential solvent effect on the two channels that did not affect the total reaction quantum yield much but did deflect more of the compound to the O(^{3}P) channel. The same basic arguments we presented above in favor of O(^{3}P) formation could be invoked here.

In our 1997 paper,[15] we reported that the quantum yield of DBTO deoxygenation is dependent on the wavelength of irradiation such that irradiation into S_2, rather than S_1, increased the deoxygen efficiency. This clearly indicates that there are multiple channels of reactivity, i.e., reactivity out of S_1 and some other excited state such as an upper triplet or upper singlet. While this observation is clearly consistent with the hypothesis that an upper excited state might react as a direct oxygen transfer reagent, while the other reacts as an O(^{3}P) donor, it is also consistent with two states leading to the common diffusible intermediate with different quantum yields. We thus cannot distinguish between the two hypotheses on the basis of the current data.

However, one thing we will address in a separate publication is the possibility that the two hypotheses could be distinguished by an "oxidation fingerprinting" method, as was used to argue that dibenzoselenophene-*Se*-oxide and DBTO produce a common oxidizing species.[45] The two different oxidizing species postulated above ought to show different selectivities among substrates. This same approach is being taken for a study of various sensitized DBTO deoxygenations, and a report that will include an exploration of the wavelength effect will be forthcoming from these laboratories.

Conclusion

Ultimately, while the results of this study are not entirely satisfying, they are at least consistent with the hypothesis advanced that it is largely the specific functionality of some of the solvents that leads to more efficient photochemical deoxygenation, rather than other macroscopic parameters. However, the results also reduce what might usually be the conclusions of a work to interpretations.

The members of the two series were chosen on the basis of the unpredictability of how many methylenes would be ideal for trapping. Assuming the basic hypothesis was correct, there was the expectation that there might be some sort of smooth curve of results in which the efficiency of internal trapping would be maximized at a particular chain length. We suggest that the behaviors of **1a**, **2b**, and **2d** are "exceptional" because of the unintended alternate reactivity induced by their functionalities. For overall trapping efficiency, it is **1b** that comes out ahead among the olefin series and **2a** among the sulfanyl series. The alternate reactivity of **2b** due to benzylic-type cleavage doomed this compound from the ability to show whether the additional methylene would increase trapping efficiency in that series.

Furthermore, on the basis of the internal trapping effects, our initial assumption that benzene and acetonitrile would be effectively identical solvents for deoxygenation appears to have been false. Again, this can be interpreted in reasonable terms, i.e., that the transition state for deoxygenation involves some charge separation that acetonitrile can help solvate, but proof awaits further work. An alternative hypothesis that involves multiple excited states and at least two distinct mechanisms of deoxygenation also cannot be eliminated. Experimental and computational efforts are underway to address these and related issues.

Experimental Section

General. Routine gas chromatography and quantification were performed on an instrument with a flame ionization detector, and it was assumed that the response factors for isomeric compounds would be identical. GC-MS analyses were done with either an EI/CI-quadrupole MS or a benchtop instrument with an ion trap. All analyses were done using a 30 m 5% phenyl column.

Photolyses. Experiments were carried out closely following previous procedures.[15] Photolyses were done in spectro-grade solvents, as indicated with initial concentrations in the range of 1−5 mM. Cyclohexene was treated by refluxing under Ar and over Na immediately before use. Dodecane was used as an internal standard for all photoreactions. Valerophenone was used as an actinometer for quantum yield measurements. Irradiations were carried out with a 75 Xe arc lamp from PTI, coupled to a matching monochromator. All the settings of the monochromator were kept constant during the measurements. Actinometry was repeated frequently to avoid any effect on quantum yield measurement due to any drift of the light flux. Some preliminary reactions were done using a minireactor with broadly emitting 300 nm fluorescent tubes.

Preparation of compounds and analytical procedures are given in detail in Supporting Information.

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Supporting Information Available: Synthetic details and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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[45] McCulla, R. D.; Jenks, W. S. *J. Am. Chem. Soc.* **2004**, *126*, 16058−16065.