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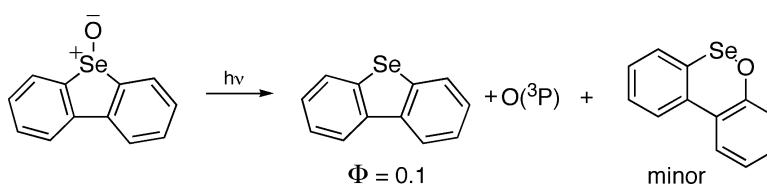
Deoxygenation and Other Photochemical Reactions of Aromatic Selenoxides

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Deoxygenation and Other Photochemical Reactions of Aromatic Selenoxides[1]

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Abstract: Atomic oxygen O(^{3}P) is a potent oxidant that has been well-studied in the gas phase. However, exploration of its reactivity in the condensed organic phase has been hampered by the lack of an appropriate source. Dibenzothiophene-*S*-oxide (DBTO) and related derivatives have been promoted as photochemical O(^{3}P) sources but suffer from low quantum yields. Photolysis of dibenzoselenophene-*Se*-oxide (DBSeO) results in the formation of dibenzoselenophene and oxidized solvent in significantly higher quantum yields, ca. 0.1. The oxidation product ratios from toluene obtained from the photolysis of dibenzothiophene-*S*-oxide and the corresponding selenoxide are the same, strongly suggesting a common oxidizing intermediate, which is taken to be O(^{3}P). An additional product, proposed to be the corresponding selenenic ester, is also observed under deoxygenated conditions. The photochemistry of diphenyl selenoxide includes a minor portion of oxidant-forming deoxygenation, in contrast to previous conclusions (Yamazaki, Y.; Tsuchiya, T.; Hasegawa, T. *Bull. Chem. Soc. Jpn.* **2003**, 201−202).

Introduction

Direct photolysis of dibenzothiophene-*S*-oxide (DBTO) has been suggested as a source of atomic oxygen O(^{3}P) in solution.[3−6] This assertion is based on the observation that it produces dibenzothiophene (DBT) and solvent oxidation products consistent with expectations for O(^{3}P) along with experiments that demonstrate the reaction is unimolecular in sulfoxide and has a low activation barrier. While deoxygenation is a relatively common process in the photochemistry of aromatic sulfoxides, in most cases the sulfide is only a minor component of the product mixture.[6−17] However, with DBTO and some related thiophene derivatives, the oxidation products and DBT can be obtained in high chemical yield.[3−5,18−21] Substantial evidence points toward a unimolecular mechanism for sulfoxide deoxygenation, but establishment of O(^{3}P) as the principal reactive intermediate has not been definitively achieved, due largely to the lack of direct detection. This paper concerns the extension of this chemistry to the selenium analogue, describing the greatly enhanced photochemical efficiency of the process and evidence for a reaction pathway parallel to that of the sulfoxide.
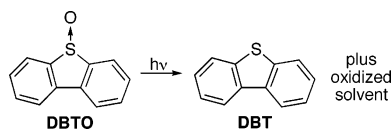
In the gas phase, the rate of reaction between O(^{3}P) and various substrates has been the subject of many studies.[22] However, in organic solution, the literature on O(^{3}P) reactivity is sparse.[3,4,23,24] Absolute rate constant ratios for O(^{3}P) oxidation of various substrates, generated by the photolysis of pyridine-*N*-oxide,[25] correlate well with product yields from competition experiments reported for DBTO.[3,23] Moreover, Greer has found a strong correlation between the relative rates of substrate

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(25) The photochemistry of pyridine oxides is complex. Unfortunately, only a small percentage of the material undergoes deoxygenation.

oxidation during DBTO photolysis and the ionization potentials of substrates,[4] consistent with expectations for an electrophilic oxene intermediate.

Alternate deoxygenation mechanisms have been proposed, but may be dismissed due to more recent evidence.[3] A "dimer mechanism" relies on formation of a transient O−O bonded intermediate, based on the reaction between excited-state DBTO and a ground-state substrate molecule; the fate of the oxygen atom is thus formation of O_2.[6,13,18] This has been eliminated on the basis of the lack of diphenyl sulfide formation on photolysis of mixed solutions of DBTO and Ph_2SO and other results.[3] Another mechanism relies on the transfer of an oxygen atom from a sulfinyl radical (RSO•) to the various subtrates,[16,17] but it can be eliminated on the basis of better understood energetics of the sulfinyl radical.[3,26]

The quantum yield for the photochemical deoxygenation of DBTO is low (<0.01). DBTO's lowest spectroscopic triplet energy ($\sim$61 kcal/mol)[27] is lower than its S−O bond dissociation energy ($\sim$75−77 kcal/mol), which is, in turn, lower than the fluorescence energy of DBTO, about 82 kcal/mol.[28] One mechanistic hypothesis accepts direct S−O scission as the basis of the reaction. It rationalizes the low quantum yield by asserting that the deoxygenation proceeds by a mechanism in which S−O bond stretching must be accompanied by intersystem crossing at some point before complete bond scission. (The logical limit to this mechanism is dissociation to the DBT•⁺/O•⁻ ion pair, followed by intersystem crossing and back-electron transfer to ground-state products.)

A more efficient substrate for the production of O(^{3}P) is desirable for mechanistic studies relying on flash photolysis and for enhancement of synthetic utility. An attractive approach to increase the quantum yield is to use the heavy atom effect on intersystem crossing (ISC) to help increase the probability of spin conversion coupled with bond scission. However, it should also be recognized that overly efficient intersystem crossing without the accompanying S−O bond stretching could lead to low quantum yields again, because S−O scission from the phosphorescent state is endothermic. We recently reported[29] a modest increase in the quantum yield of deoxygenation for bromo- and iodo-substituted DBTOs. We rationalized that a heavy atom substitution at the point of bond scission might be more effective than the halogenation of arene positions and were thus attracted to the notion that the Se analogues to DBTO could be worthwhile substrates. Moreover, an older nonmechanistic study by Tezuka et al.[30] reported the photochemical transfer of oxygen from certain selenoxides to sulfides. Thus, a natural selection to test the S−O scission hypothesis and increase the quantum yield of O(^{3}P) formation was dibenzoselenophene-*Se*-oxide (DBSeO), the selenium analogue of DBTO.

Also, a more recent and extensive report of the photochemistry of diphenyl selenoxide (Ph_2SeO) has appeared.[2] Photolysis of Ph_2SeO in benzene resulted in the deoxygenation product Ph_2Se and several additional products that were consistent with C−Se photocleavage. However, the authors suggested that deoxygenation went by way of a dimer mechanism. We thought
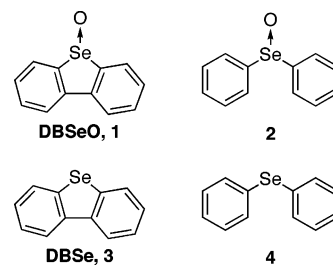
this had been discredited in the sulfoxide case,[3] so it naturally drew our attention.

Here, we report on the photochemistry of DBSeO and Ph_2-SeO. Many parallels are observed to the reported sulfoxide chemistry, but the quantum yields are indeed considerably higher; the differences between the photochemistry of DBSeO and that recently reported[2] for Ph_2SeO are cleanly rationalized.

Experimental Section

Materials. Commercial materials were obtained from Aldrich or Fisher and used without modification, except as noted. Peroxides were removed from cyclohexene. It was washed with 10% $NaHSO_3$(aq), followed by 5% NaOH(aq), and finally with water. The remaining cyclohexene was dried with anhydrous $MgSO_4$ and then distilled from Na metal under Ar. Except when combined with cyclohexene, ethanol (99%, anhydrous, Aldrich) was distilled from CaH_2 under Ar immediately before use. Dimethyldioxirane[31] (DMD) and dibenzothiophene-*S*-oxide[3] were prepared according to described procedures with only slight modifications. Dibenzoselenophene (3) was prepared by a slight modification of the procedure of McCullough.[32] The selenoxides 1 and 2 were prepared by oxidation of the corresponding selenides with *m*-CPBA; the corresponding selenone 5 was prepared by oxidation with excess DMD.[31] Synthetic details and spectral information are given in the Supporting Information.

General Methods. NMR spectra were either taken on a Bruker DRX-400 or a Varian VXR-300. Mass spectra were acquired using a Finnigan TSQ700. Solutions of 1 left in room light for 24 h decomposed significantly. Thus, solutions were made daily before use, and wrapped in aluminum foil to shield them from light. Phosphorescence spectra and quantum yields were measured using an Edinburgh FL-900 spectrometer as described previously.[27] A Hewlett-Packard 1050 HPLC, fitted with a quaternary pump and a diode detector array, was used for HPLC chromatographs. LC-MS analyses were done on a Thermo-Finnigan LCQ Advantage. A Discovery HS C18 reverse phase column was used for all liquid chromatography separations. A HP 5890 series II GC using a ZB-5 column with a flame detector was used for GC analysis. GC-MS analysis was carried out with a Finnigan benchtop Magnum instrument, which uses ion trap detection and a DB-5 column for separations. Degassing was done either by Ar-purging for at least 10 min or by a sequence of five freeze−pump−thaw (FPT) cycles.

Irradiations. A 75 W Xe lamp (Photon Technologies, Inc.), focused directly on a monochromator, was used in most experiments. It was set at wavelengths noted in the text for each experiment. The slit widths allowed ±12 nm linear dispersion from the given wavelength. Samples in 1 cm square optical cells were put in a permanently mounted cell holder in such a way that all the exiting light hits the sample cell without further focusing.

Photolysis of valerophenone to yield acetophenone was used as an actinometer for reactions at 313 and 320 nm.[33] For shorter wavelength experiments, azoxybenzene was used as the actinometer.[34] Routine

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photolyses of DBSeO were carried out at 320 nm, though a few quantum yield runs were done at 313 nm to ensure validity of the actinometer. Photolyses of Ph$_2$SeO were carried out at 254, 265, or 290 nm, as noted in the text.

All quantum yields were carried out at a concentration high enough to reach an optical density >2 at the quoted wavelength and were carried out to low conversion (<30%). For DBSeO, the range of concentrations was 1−6 mM, and no significant variation in the results was noted. For Ph$_2$SeO, the concentrations are listed in the Results.

After fixed periods of irradiation, small samples were removed by syringe and subjected to HPLC or GC analysis. For detection of all of the Se-containing compounds, HPLC was required because attempted GC analysis resulted in extensive decomposition and multiple unidentified small peaks. Routine HPLC runs were done with diode-array UV/vis detection. For quantification of oxidized solvents, GC was used, either with FID or MS detection. Dodecane was used as an internal standard.

A single Se-containing minor product was observed in photolyses of DBSeO carried out after Ar-purging. An initial mass spectrum was obtained by LC-MS. To obtain a sample of this compound (called **X** in the text), an Ar-flushed 3 mL sample of DBSeO in ethanol at 2.5 mM initial concentration was photolyzed to near completion. The ethanol was removed in vacuo, and the residue was separated by preparatory thin-layer chromatography (TLC) on silica (1:1 EtOAc: CH$_2$Cl$_2$). The minor product was identified by its HPLC retention time and UV spectrum. It had a TLC R_f of 0.43. The sub-milligram quantity of this compound was subjected to NMR analysis.

With FPT degassing, a different single Se-containing minor product was observed. This compound (referred to as **Y**) was isolated by using the same procedure as above, save that the preparative TLC was eluted with 1:1 hexane:CH$_2$Cl$_2$. The R_f of the isolated compound, again identified by HPLC and UV, was 0.16. The mass spectrum was obtained by direct infusion of the CD$_3$CN solution used for NMR using negative ion detection in EI mode.

As described in the Results, photolyses of these two Se-containing compounds were also carried out. Because of the small quantities, it was difficult to be quantitative, but the initial concentrations were approximately 1 mM. Photolyses were carried out in a 2 mm by 10 mm square quartz cell, using the same lamp setup described previously. Purging with Ar or O$_2$ was carried out prior to photolysis, as described in the text. Analysis of the resulting solutions was done by HPLC.

A set of photolyses of DBSeO was carried out in EPA (ether/pentane/ethyl alcohol = 5:5:2) at 77 K. The initial concentration of DBSeO was 26 µM, and the sample was deoxygenated by Ar purging. The sample, contained in a quartz NMR tube, was quick-frozen by immersion into liquid nitrogen. A transparent Suprasil Dewar designed for photolyses and use with the fluorometer was used. Irradiation was carried out using a Rayonet minireactor from Southern New England Ultraviolet using the broadly emitting 300 nm fluorescent bulbs. Before and after 3 min of photolysis, the sample, continuously held frozen in the Dewar, was transferred to the fluorometer and spectra were obtained. Afterward, the sample was melted and subjected to HPLC analysis. The conversion was about 40%, and DBSe was quantitatively formed, within the limits of detection.

Results

Photochemistry of DBSeO. To determine if DBSeO (**1**) has potential as an O(^{3}P) producer, quantum yields for its disappearance and appearance of DBSe (**3**) were determined, as shown in Table 1. DBSeO is not very soluble in many standard organic solvents, which limited the choice of solvents that could be used. Measurements were made in a limited concentration range of 1−6 mM. This range was set by the need for sufficient

Table 1. Photolysis Quantum Yields for Conversion of DBSeO to DBSe^a

solvent	degassing	Φ_{-DBSeO}	Φ_{+DBSe}
EtOH−toluene	Ar bubbling	0.30 ± 0.12	0.10 ± 0.02
EtOH	Ar bubbling	0.34 ± 0.05	0.13 ± 0.02
EtOH	FPT^c	0.15 ± 0.05	0.09 ± 0.02
CH$_2$Cl$_2$	Ar bubbling	0.26 ± 0.02	0.10 ± 0.01
CH$_2$Cl$_2$	FPT	0.23 ± 0.02	0.11 ± 0.01

^{a} All quantum yields reported for conversion under 30%. ^{b} Standard deviation. ^{c} Freeze−pump−thaw cycles.

optical density (>2) at the exciting wavelength (320 nm) on the low end and solubility on the high end. Little if any variation in products or quantum yields was noted within this limited range. The difference between the two reported quantum yields for each set of conditions reflects the formation of other products besides DBSe. Control experiments showed that DBSe was photostable under all reaction conditions.

A consistent feature of the direct photolysis of DBSeO was the appearance of two Se-containing products, as detected by HPLC analysis. The major product was always DBSe. However, the identity of the minor product depended upon the method of oxygen removal. Both minor products were less prevalent in dichloromethane than in EtOH.[35] While it was difficult to get large quantities of the minor products for analysis due to the low solubility of DBSeO, small quantities of both minor products were isolated from reaction mixtures by preparative TLC.

The first minor product, which we shall refer to as **X**, was only observed in the reaction mixtures of samples that were treated with Ar flushing to remove O$_2$, which has been our routine deoxygenation protocol. Control experiments showed that, at low conversion, the formation of **X** was several times faster if the solution remained open to air, rather than sealed tightly after sparging. It was not formed at all if the sample was freeze−pump−thaw degassed. The apparent quantum yield for formation of **X** in Ar-flushed samples was not very reproducible, probably because it derived from adventitious molecular oxygen. However, in most solvents, after Ar-flushing, an average value of about 0.07 was typical.

A mass spectrum of **X** had a m/z 264 parent peak, which is the molecular weight of DBSeO plus oxygen. There are four likely products with a mass of 264. The first is dibenzoselenophene dioxide (DBSeO$_2$, **5**). Compound **6** would be the product of a net O(^{3}P) C−H insertion, analogous to formation of phenol from benzene.[3] If oxygen were inserted between the arenes in the biphenyl moiety, the selenoxide **7** would be formed. Finally, net C−Se insertion leads to the seleninic ester **8**. Such esters, albeit made by very different means, have been reported previously.[36]

DBSeO$_2$ was prepared independently by dimethyldioxirane oxidation of DBSe. It was eliminated as the identity of **X**, in that it had a different HPLC retention time and UV absorption spectrum than **X**. A sub-milligram quantity of **X** was isolated by preparative TLC after exhaustive photolysis of **1**. The ^{1}H NMR spectrum of the isolated product showed eight inequivalent aromatic hydrogens, thus eliminating compounds **6** and **7** as candidate structures and confirming the elimination of **5**.[37]

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5   **6**   **7**   **8**
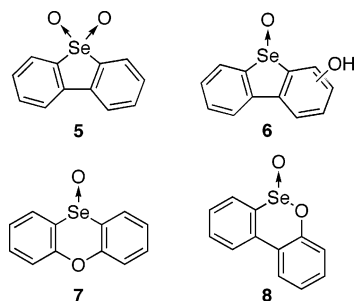
Thus, **X** was tentatively identified as **8** by process of elimination. In further support of this assignment, the S-analogue of **8**, which has been identified by preparation of an authentic sample, is observed as a minor product in the photolysis of DBTO in a few solvents.[38]

The second minor product, dubbed **Y**, was only observed in samples that had been degassed by Ar flushing, followed by five freeze−pump−thaw degassing cycles, which we considered a more rigorous method of O_2 elimination. The quantum yield for its formation was reasonably constant across the tested solvents (save dichloromethane), at about 0.05. Note that, in ethanol, the sum of quantum yields for it and for DBSe formation is within experimental error of that for loss of DBSeO. The parent mass in GC-MS analysis of **Y** is 248, the same mass as DBSeO. Plausible isomers of DBSeO include the cyclic selenenic ester **9**, hydroxylated DBSe **10**, and the symmetric heterocycle **11**. Again, ^{1}H NMR[39] of a small quantity of the isolated compound showed eight inequivalent aromatic protons. Among the compounds shown below, only **9** is reasonable.

9   **10**   **11**
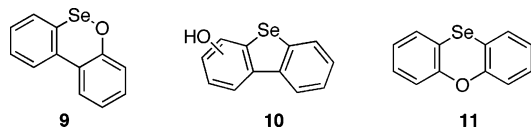
The photolyses were repeated at 77 K in EPA glass at low concentration (26 μM). Aggregation should be minimized at this concentration in the hydroxylic solvent mixture, which was quick-frozen by immersion in liquid nitrogen. Furthermore, diffusion after photon absorption at 77 K is certainly insignificant. DBSeO does not phosphoresce significantly under these conditions, but control experiments showed DBSe has a strong signal (quantum yield, 0.25) with bands at 420, 455, and 490 nm. After 3 min of photolysis with 300 nm light, the DBSeO samples showed a strong phosphorescence signal corresponding to formation of DBSe, as shown in Figure 1. After the luminescence was recorded, the glass was melted and room-temperature analysis of the mixture by HPLC showed only **1** and **3**; i.e., neither **X**, **Y**, nor any other Se-containing side product was formed in significant yield. The experiment was repeated with a higher initial concentration of 330 μM to ensure that the lack of **X** or **Y** was not due to the detection limit at the lower concentration, but neither was observed.

In parallel with experiments reported for DBTO,[3] DBSeO was photolyzed in the presence of Ph$_2$SeO. If a transient dimer that leads to O_2 is formed, deoxygenation of both selenoxides should occur, even if light is only absorbed by DBSeO. An
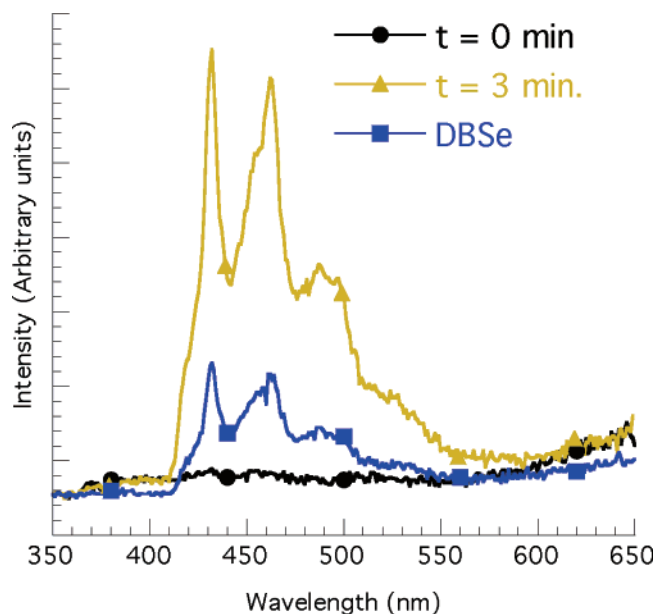
(37) The spectrum is given in the Supporting Information.
(38) Unpublished work by Zehong Wan, Mrinmoy Nag, and William Jenks.
(39) The spectrum is given in the Supporting Information.

Figure 1. Phosphorescence spectra of of DBSe (squares) and DBSeO before (circles) and after (triangles) photolysis for 3 min at 77 K in EPA.

Table 2. Formation of Oxidized Products during Photolysis of DBTO and DBSeO

product	% yield, relative to DBT formation	% yield, relative to DBSe formation
benzaldehyde	14 ± 3[a]	13 ± 3
benzyl alcohol	10 ± 1	8 ± 2
o-cresol	25 ± 3	29 ± 3
m- and *p*-cresol[b]	24 ± 6	29 ± 9

[a] Standard deviation. [b] Detected as overlapping GC peaks.

ethanol solution of DBSeO (2.4 mM) and Ph$_2$SeO (12.0 mM) was photolzyed at 320 nm, where only the former absorbs. After 50% conversion of DBSeO to DBSe, neither degradation of Ph$_2$SeO nor appearance Ph$_2$Se was observed.

Photolysis of DBSeO in benzene produces hydroxylated solvent, as with DBTO. Photolysis mixtures that were run in benzene-d_6 were subjected to GC/MS analysis. This showed only the d_5 isotopologue of phenol, indicating the phenol derives from oxidation of solvent. To probe for the possibility of a common intermediate in the photolysis of DBTO and DBSeO− e.g., O(^{3}P)−independent photolyses of the two were carried out in toluene. The observed oxidized products in both cases were benzyl alcohol, benzaldehyde, and the three possible cresols. The amounts of each of these oxidized toluene products per millimolar sulfide or selenide formed are listed in Table 2. The table indicates products from Ar-flushed solutions; no benzaldehyde was observed if FPT degassing was used.
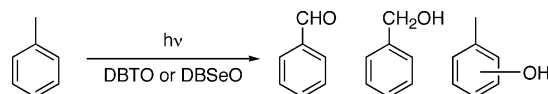
Quantum yields of direct photolysis of **1** were collect in the presence of the known O(^{3}P) trap cyclohexene, as shown in Table 3.[3] Due to the low solubility of DBSeO in cyclohexene, ethanol and dichloromethane were used as cosolvents. The concentration of cyclohexene was varied from 1.0 to 4.0 M, but no significant change in the quantum yields were observed over that range. As above, results differed somewhat with Ar-

Table 3. Quantum Yields for Photolysis of DBSeO in the Presence of Cyclohexene in Dichloromethane

degassing	Φ_{-DBSeO}	Φ_{+DBSe}	$\Phi_{+cyclohexene\ oxide}$	$\Phi_{+2-cyclohexenol}$
FPT	0.30 ± 0.04^a	0.078 ± 0.012	0.022 ± 0.004	
Ar bubbling	0.28 ± 0.16	0.07 ± 0.02	0.038 ± 0.011	0.007 ± 0.003

[a] Standard deviation.

flushed and FPT-degassed samples, with the latter having greater reproducibility, as reflected in the smaller standard deviations. In all cases, the mass balances are relatively poor, possibly due to radical chain reactions. No oxidized cyclohexene products were observed in samples using ethanol as a cosolvent. However, in agreement with results for DBTO, oxidized cyclohexene was observed when dichloromethane was used.

Photolysis of the sulfur analogue of **8** (10-oxa-9-thiaphenanthrene-9-oxide) in good proton donating solvents results in formation of 2-phenylphenol.[40] By analogy, a small quantity of **X/8** was rephotolyzed at 300 nm in 2-propanol. Trace quantities of 2-phenylphenol accompanied a nearly quantitative yield of **Y/9**.

To determine if **X/8** derives from oxidation of **Y/9** during the photolysis of DBSeO, an authentic sample of **Y/9** at a concentration of about 1 mM ethanol was photolyzed at 320 nm, in the presence of 14 mM DBSe. The sample was Ar-purged as described previously. Under these conditions, virtually all the light is absorbed by DBSe, which might act as a sensitizer. Within 50 min, 70% of the **Y/9** had been consumed, but unidentifiable materials were produced, rather than **X/8**. Even after exhaustive photolysis, **X/8** was not detected. The photolysis was repeated under identical conditions, save that no DBSe was added. Under these conditions of direct irradiation of **Y/9**, no conversion was observed, even after 15 h.

Finally, a third experiment was run, using Eosin Y as a singlet oxygen sensitizer. An O_2-saturated ethanol solution containing **Y/9** (ca. 1 mM) and Eosin Y was photolyzed. After as long as 21 h of photolysis, no **X/8** was observed, and only a small fraction of **Y/9** had decomposed.

Photochemistry of Ph$_2$SeO. In a recent report on the photolysis of phenyl selenoxide (Ph$_2$SeO, **2**) in benzene, Hasegawa isolated several photoproducts.[2] Though product distributions were concentration-dependent, the following is representative: Ph$_2$Se (52%), PhSeSePh (48%), Ph–Ph (25%), and PhOH (15%). Photolysis of Ph$_2$SeO in benzene-d_6 showed the biphenyl derived from attack of a phenyl radical on solvent, consistent with α-cleavage chemistry of sulfoxides. The phenol was attributed to the decomposition of a selenenic ester (R–Se–O–R'), the analogue of the sulfenic ester known from related sulfoxide photochemistry.[12,41] Because the yield of selenide was similar in benzene and acetonitrile, it was assumed that no unimolecular deoxygenation occurred.[2] A mechanism for deoxygenation of **2** involving the formation of a transient O–O dimer (and O_2 formation) was proposed. Unnoted was the fact that irradiation at 254 nm in acetonitrile is direct irradiation, while that in benzene is sensitized, because of the absorption of the light by the solvent. Given that we had excluded the O–O dimer mechanism for the sulfoxide case, and also found a different bimolecular mechanism of sulfoxide photoreduction,[42] this report drew our attention.

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Table 4. Apparent Quantum Yields for Photolysis of Ph$_2$SeO^a

initial concn (mM)	λ (nm)	solvent	Φ_{+Ph_2Se}	$\Phi_{+(PhSe)_2}$	Φ_{+PhOH}	$\Phi_{+PhOH-d_5}$	Φ_{+PhPh}
3.0	265	EtOH	0.12	0.050	0.06		0
11.2	290	C_6D_6	$0.016(3)^b$	0.022(2)	0.044(8)	0.011(4)	0.028(4)
2.1	254	C_6D_6	0.0024	0.0020	0.0057	0.0003	0.0028
1.9	254	C_6H_6	0.0040	0.0045	0.013		0.0060
4.5	254	C_6H_6	0.0058	0.0052	0.020		0.0078

[a] All reactions run to low conversion (<20%). [b] Standard deviation of multiple runs, indicated as uncertainty in the final significant digit.

We prepared Ph$_2$SeO and photolyzed it in benzene using 254 nm light at millimolar concentration, as reported by the previous authors. Under these conditions, our results were in good qualitative agreement with theirs, though we detected a greater yield of phenol and biphenyl than they reported. Like Hasegawa, we observed a concentration dependence on product yields. This implies that at least one product has a bimolecular mechanism for formation, as must be true for the diselenide, for example. Nonetheless, a representative product distribution is given by way of the apparent quantum yields reported in Table 4.

To examine the hypothesis that phenyl selenoxide does not produce atomic oxygen, direct photolysis was carried out in benzene-d_6 by using 290 nm excitation, which is sufficiently to the red of the benzene absorption that the great majority of the light is now absorbed by the tail of the Ph$_2$SeO band. In agreement with Hasegawa's sensitized experiment, GC-MS analysis revealed that the resulting biphenyl contained five deuteria. The phenol was also examined, and about 20% of it was the d_5 isotopologue. The data in Table 4 indicate that most of the Ph$_2$Se formed under these conditions is accounted for by solvent oxidation, but the existence of a parallel reduction mechanism cannot be ruled out.

Results from a sensitized reaction (irradiation at 254 nm) showed that about 4% of the phenol being formed was similarly deuterated, i.e., derived from oxidized solvent. Thus, for both sensitized and direct photolysis, most of the phenol is being formed by an α-cleavage mechanism, but some is formed by oxidation of the solvent. Thus, Hasegawa's conclusion that the phenol derived from α-cleavage seems to be correct for the most part, but the corollary that deoxygenation does not proceed by way of a unimolecular mechanism does not. However, given the small fraction of phenol deriving directly from oxygenation of solvent when irradiation is done at 254 nm, only an experiment such as the present one would have revealed this new mechanistic information.

It is also appears that there is a second deoxygenation mechanism at work in the sensitized photolysis. This is evidenced by the fact that the ratio of phenol to Ph$_2$Se is much smaller in the sensitized photolysis than in the direct irradiation. Again, Hasegawa's conclusion may have been largely correct in the sensitized conditions in benzene, but the current results at 290 nm point out a deoxygenation parallel to the DBTO and DBSeO mechanism.

Similar photolyses of Ph$_2$SeO were carried out in ethanol, where all irradiations are direct, and the results of all experiments are shown in Table 4. The total quantum yield for conversion of Ph$_2$SeO is higher than in benzene.[43] Such a large difference is somewhat surprising, but both the solvent and

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excitation wavelength was varied; significant wavelength dependences of quantum yields have been noted for related sulfoxides.[3]

Discussion

Clearly, the most salient practical result of this study is the observation that DBSeO is an oxygen atom donor with many advantageous properties of DBTO and a photochemical efficiency approximately 40 times higher. These studies suggest a common intermediate, likely to be $O(^3P)$. If the simple scission hypothesis stands up to the rigorous examination it deserves, the quantum yield of approximately 0.1 for formation of DBSe implies that DBSeO may be significantly more useful than DBTO for studies of $O(^3P)$ chemistry in solution.

We may speculate that two factors contribute to the higher quantum yield. First, Se is one row further down on the periodic table from S, and a heavy atom effect is expected to contribute to the probability of all intersystem crossing events. For the parent DBTO, it is clear that there is insufficient energy in the spectroscopic triplet for efficient S—O scission, leading to DBT and $O(^3P)$. This has led us to suggest a mechanism in which elongation of the S—O bond begins from the excited singlet and that intersystem crossing is somehow coupled to that event. One could imagine a direct spin-surface crossing along the elongation pathway. Alternatively, the logical limit of this mechanism is an initial step that forms an ion pair (consisting of $DBT^{\bullet+}$ and O^-) is followed by back-electron transfer, yielding ground-state DBT and $O(^3P)$. In either event, the substitution of Se for S might very well increase the probability of its occurrence, either by a heavy atom effect or a lower ionization potential. (The difference in IP between DBT and DBSe is only 0.08 eV, about 1.7 kcal/mol, but DBSe has the lower one.[44]) In related work,[29] it was shown that remote substitution of a Br or I on the DBTO benzene nuclei resulted in a modest increase in the quantum yield for deoxygenation, which was interpreted as a heavy atom effect. These results are consistent with that interpretation, but the ease of ionization of the aromatic nucleus and small differences in excitation energy cannot be ruled out.

The other obvious reason the cleavage may be more efficient comes from the expectation that the selenoxide bond should be somewhat lower in energy than the sulfoxide bond, while the electronic excitation energies are taken to be similar. The lack of phosphorescence from DBSeO makes determination of a triplet energy difficult, but there is little reason to think it will vary much from the DBTO value of about 61 kcal/mol, especially since neither the SO nor SeO is involved in the aromatic system for those compounds.[45] (The triplet energies of DBSe and DBT are within 1 kcal/mol.[46]) We have begun a study aimed at estimating the Se—O bond energy that will be reported separately. However, we can report that the Se—O bond energy calculated[47] for $(CH_3)_2SeO$ is about 12 kcal/mol lower

than that calculated for $(CH_3)_2SO$ at the G3 level of theory.[48–50] If that trend holds through the dibenzothiophene/selenophene series, the deoxygenation may very well be nearly thermoneutral from the lowest triplet of DBSeO.

The available evidence suggests that there is a common deoxygenation mechanism in the photolyses of DBTO and DBSeO. In particular, the product distributions for toluene oxidation represent a common oxidation fingerprint, which may be attributable to a common intermediate, taken to be $O(^3P)$. Furthermore, the result that mixed photolyses using DBSeO and Ph_2SeO forms only DBSe strongly argues against the necessity of dimer formation for deoxygenation, in direct analogy to DBTO.[3] The lack of observation of any isomer of $DBSeO_2$ when FPT degassing is used shows that the mechanism does not involve direct disproportionation. The observation of photochemistry at 77 K argues similarly against bimolecular intervention, but even more convincingly, shows that no strongly activated step is required for deoxygenation to occur from the relevant excited state.

The disparity between Φ_{-DBSeO} and Φ_{+DBSe} indicates that chemistry other than simple deoxygenation is occurring. Secondary photochemistry of DBSe was ruled out by control experiments, so it must be concluded that there are parallel paths taken by DBSeO*. We assume that FPT degassing is more effective in eliminating all O_2 from the samples than is Ar flushing, and thus take those results as the O_2-free standard. In the absence of oxygen, the quantum yield for the formation of **Y** is 0.05, while that for formation of DBSe is about 0.09, meaning that in ethanol most, if not all, of the loss of DBSeO is accounted for ($\Phi_{-DBSeO} \sim 0.15$). In dichloromethane, it appears that another pathway remains competitive.

The quantum yield for loss of DBSeO with Ar flushing was considerably higher than with FPT degassing. We may speculate that this comes about because the adventitious O_2 that remains after Ar flushing reacts (either directly or indirectly through a chain mechanism) with a transient intermediate. One plausible possibility is the biradical **12** resulting from α-cleavage, as illustrated in Scheme 1.[51,52] Both the results from Ph_2SeO and precedent within sulfoxide chemistry support the suggestion that cleavage occurs in parallel with deoxygenation.

The observed byproduct **Y**, observed under freeze–pump–thaw degassing conditions, is tentatively identified as the selenenic ester **9**, based on it having eight inequivalent, nonexchangeable ${}^1H$ signals in the aromatic region. The notation **9/Y** is used to indicate that the assignment of the structure **9** to **Y** is, while reasonable on many counts, not definitively established. The structure of **9**, however, is consistent with a plausible competition between deoxygenation and α-cleavage as primary photochemical mechanisms. After C—Se cleavage, the so-obtained biradical **12** ought to reclose unimolecularly but may close on either the Se (path A) or the O atom (path B), in analogy to sulfinyl radical chemistry.[12,41,53–56] The sulfenic ester

(43) We also note that the apparent quantum yield is somewhat lower in deuterated benzene than in ordinary benzene. We attribute this to a low level of quenching impurities in the deuterated solvent, which is not subject to the same level of purification as the "spectrograde" ordinary benzene we ordinarily use.

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Scheme 1. Suggested Pathways for Formation of **8** and **9**

Scheme 2. Proposed Reaction Pathway Matrix for the Photochemistry of DBSeO
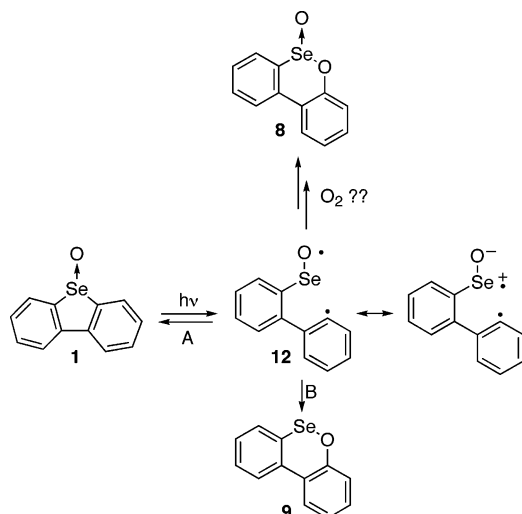

has only been observed directly in acyclic sulfoxides,[41] but a greater structural analogy exists between DBSeO and various (cyclic) thiophene sulfoxides. Indirect evidence also exists for the sulfenic ester in the reactions of some of these. Photolysis of 2,5-di-*tert*-butylthiophene-*S*-oxide results in formation of the corresponding *furan*, rather than thiophene,[57,58] a process that strongly implies the intermediacy of the cyclic sulfenic ester.

Most sulfenic esters (R−S−O−R′) are difficult to isolate without decomposition, and it would be somewhat surprising for the selenenic esters to be considerably different in this regard. Indeed, Hasegawa could not detect them in the photolysis of Ph₂SeO or (PhCH₂)SeO.[2] However, **9** may be more stable due to its cyclic nature. Direct observation of a closely analogous cyclic sulfenic ester was reported as early as 1970.[59]

The fact that **9/Y** is not formed at 77 K implies that either there is a nonnegligible activation barrier along the pathway or that nontrivial geometry changes inconsistent with the solid matrix are required. We tend to favor the former explanation on the thought that isomerization from **12** to **9** should not require a lot of new space in a solid matrix.

α-Cleavage may also be behind the formation of the major side product in the Ar-flushed cases. Again, the assignment of the structure to the seleninic ester **8** as compound **X** is based on the ¹H NMR spectrum. Isolation of **9** indicates that it is not trivially oxidized by air, and the independent photolyses of **9/Y** strongly suggest that it is not a direct precursor to **8**. The lack of its formation at 77 K is not surprising, though, given the requirement for a bimolecular mechanism.

This result suggests that **X** and **Y** derive from a common intermediate that is partitioned away from **9** to **8** by the presence of O₂. Biradical **12** is a reasonable candidate, in that either terminus of **12** might react directly with O₂ (again in analogy to sulfinyl radicals). Alternatively, one might expect that **8** is
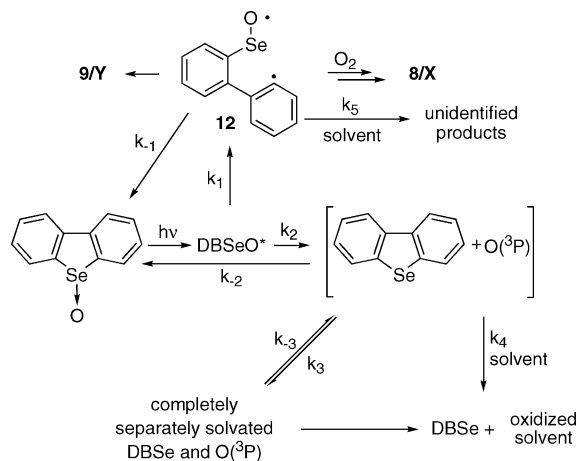
formed by ¹O₂ (from adventitious O₂ being sensitized by DBSe or DBSeO) reacting with DBSeO. However, it is known that selenoxides are not oxidized by singlet oxygen,[60] so this can be eliminated. (Selenides are oxidized by ¹O₂ to selenoxides.[61]) Also, our experiments show that **Y/9** is not a precursor of **X/8**. Unfortunately, thus, the details of formation of **8/X** must remain a matter of speculation.

The addition of good O(³P) traps such as cyclohexene was expected to increase Φ_{+DBSe} on photolysis of **1** in analogy to observations for DBTO. This was not observed. The initial partition between C−Se and Se−O cleavage is represented by effective rate constants k_1 and k_2 in the proposed pathways illustrated in Scheme 2. Once O(³P) is formed in an initial solvent cage with DBSe, several processes may occur. If recombination to form DBSeO (k_{-2}) is competitive with diffusive separation and/or direct reaction of O(³P) with a solvent trap in the solvent cage, then changing the identity of the solvent will affect the observed quantum yield for deoxygenation, as is the case for DBTO.[3] (The rate of reaction with solvent is given as the pseudo-first-order rate constant k_4.) One possibility to explain the invariance of Φ_{+DBSe} to the addition of cyclohexene is that the recombination (i.e., k_{-2}) is much faster for DBSe than for DBT. In that case, it is possible that only k_{-2} and k_3 compete, and addition of cyclohexene does not significantly affect the branching ratio for reactivity of O(³P). Because of the expected heavy atom effect and easier oxidation of DBSe, relative to DBT, this explanation is more plausible than the converse, i.e., that competition between k_{-2} and k_4 is not observed because DBSe is *less* reactive with O(³P) than is DBT and $k_{-2} \ll (k_3 + k_4)$.

However, Φ_{-DBSeO} does increase when cyclohexene is added. This is interpreted in terms of the additional reaction pathways for **12** due to reaction with the olefin that leads to unidentified, possibly polymeric, products, i.e., pseudo-first-order rate constant k_5. This affects the fraction of **12** that returns to starting material. Reaction of aryl radicals with olefins is, of course, common. (See, for example, ref 62.) Supporting this idea is the coincidence of the Φ_{-DBSeO} values in FPT-degassed cyclohexene and Ar-flushed other solvents and the quenching of formation

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of **8/X** by addition of cyclohexene to Ar-flushed solutions. All of these results are consistent with a relatively long-lived **12** that allows near-quantitative trapping in the presence of appropriate substrates.

The photochemistry of Ph_2SeO is probably rather analogous to that of diphenyl sulfoxide. As we reported,[53,54] Ph_2SO is a less than ideal sulfoxide substrate for α-cleavage, in that phenyl radicals are the necessary product, yet the process clearly occurs. A modest quantity of Ph_2S is also observed.[6,41] Though the comparison between Ph_2SeO and Ph_2SO is ultimately not quantitative, it would appear that both α-cleavage and deoxygenation occur on direct irradiation of Ph_2SeO as well. Both cases, however, lead to complex chemistry that is simplified with substituents better chosen to optimize particular primary processes. For example, while C−Se cleavage is clearly shown in the formation of biphenyl-d_5 and deoxygenation through formation of an oxidizing agent is demonstrated in the formation of phenol-d_5, the former process would be favored by substituting a more favorable radical-forming group, such as *t*-Bu or $PhCH_2$.[2,53] Deoxygenation is favored by use of structure **1**, though it is possible that other related compounds might further optimize the deoxygenation yield or suppress C−Se cleavage further.

Thus, Ph_2SeO is not a particularly attractive substrate for $O(^3P)$ study, regardless, because of the competing chemistry and because its absorption spectrum is blue-shifted, relative to DBSeO. It does not absorb to any measurable extent at the convenient laser line at 355 nm and is at only a very low extinction coefficient tailing even at 308 nm.

In recent years, there has been an increase in the study of reductive methodologies for aryl selenoxides. These include deoxygenation of selenoxides to selenide by sodium ascorbate,[63] nickel boride,[64] titanocene methylidenes,[65] and triaryl phosphites.[66] In limited instances, when products from α-cleavage are

hindered, photochemical deoxygenation of aryl selenoxides may also provide a facile way to reduce selenoxides. Bimolecular photochemical reduction of selenoxides, which has precedent from sulfoxide photochemistry,[42,67] remains to be investigated.

Conclusions

The photolyses of DBSeO and Ph_2SeO each result in the competition between C−Se and Se−O cleavage. In the former case, deoxygenation is the major process, while, in the latter case, the pattern is reversed. For DBSeO, the C−Se process must be inferred from an isomerization reaction, but for Ph_2SeO, products clearly deriving from phenyl radicals are obtained.

Because of its higher deoxygenation quantum yield (ca. 0.1), DBSeO should be an attractive choice for the generation of $O(^3P)$ in organic solution. While $O(^3P)$ has not been detected directly, the pattern of products obtained on toluene oxidation is the same for DBSeO as it is for DBTO. This and other experiments in which the deoxygenation of DBSeO mirrors that of DBTO lead us to suggest that the same oxidizer, which we presume to be $O(^3P)$, is produced.

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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