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Visible light-induced photodeoxygenation of polycyclic selenophene *Se*-oxides

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Abstract

Photodeoxygenation of dibenzothiophene *S*-oxide (DBTO) is believed to produce ground-state atomic oxygen [O(^{3}P)] in solution. Compared with other reactive oxygen species (ROS), O(^{3}P) is a unique oxidant as it is potent and selective. Derivatives of DBTO have been used as O(^{3}P)-precursors to oxidize variety of molecules, including plasmid DNA, proteins, lipids, thiols, and other small organic molecules. Unfortunately, the photodeoxygenation of DBTO requires ultraviolet irradiation, which is not an ideal wavelength range for biological systems, and has a low quantum yield of approximately 0.003. In this work, benzo[*b*]naphtho[1,2-*d*]selenophene *Se*-oxide, benzo[*b*]naphtho[2,1-*d*]selenophene *Se*-oxide, dinaphtho[2,3-*b*:2',3'-*d*]selenophene *Se*-oxide, and perylo[1,12-*b,c,d*]selenophene *Se*-oxide were synthesized, and their ability to utilize visible light for generating O(^{3}P) was interrogated. Benzo[*b*]-naphtho[1,2-*d*]selenophene *Se*-oxide produces O(^{3}P) upon irradiation centered at 420 nm. Additionally, benzo[*b*]naphtho[1,2-*d*]selenophene *Se*-oxide, benzo[*b*]naphtho[2,1-*d*]selenophene *Se*-oxide, and dinaphtho[2,3-*b*:2',3'-*d*]selenophene *Se*-oxide produce O(^{3}P) when irradiated with UVA light and have quantum yields of photodeoxygenation ranging from 0.009 to 0.33. This work increases the utility of photodeoxygenation by extending the range of wavelengths that can be used to generate O(^{3}P) in solution.

KEYWORDS

photooxidation, photodeoxygenation, selenoxide

1 | INTRODUCTION

Ground-state atomic oxygen [O(^{3}P)] is an important oxidant because of its selective reactivity and strong oxidative properties.[1–7] The reactivity of O(^{3}P) has been investigated extensively in the gas phase due to its importance in industrial and environmental chemistries.[8–10] The widely used methods for producing O(^{3}P) in gas phase are decomposition of N_2O by mercury photosensitization, photolysis of liquid CO_2 by γ-rays, and microwave discharge of a helium and molecular oxygen mixture.[9,11–13] In contrast to the gas phase, the reactivity of O(^{3}P) in the condensed phase is yet to be thoroughly explored due to the dearth of clean and efficient methods of generating O(^{3}P) in the condensed phase.

Photodeoxygenation of certain aryl sulfoxides is the most commonly used method for generating O(^{3}P) in solution.[4,5,14,15] Other sources of O(^{3}P) in the condensed phase include photodeoxygenation of dibenzoselenophene *Se*-oxide (DBSeO), pyridine *N*-oxide, and oxo-anions.[1,5,6] Irradiation of pyridine *N*-oxide at 308-nm light yields 95% oxaziridine and only 5% O(^{3}P) and pyridine.[1] Photodeoxygenation of DBSeO generates O(^{3}P) and dibenzoselenophene (DBSe) but also yields the undesired selenic ester as shown in Figure 1.[6] Photolysis of oxo-anions produces O(^{3}P) but requires 193 nm, 248.5 nm, or 308 nm light and generates ozone as a byproduct.[16] Photodeoxygenation of dibenzothiophene *S*-oxide (DBTO) is a clean source of O(^{3}P) as it produces solely O(^{3}P) and dibenzothiophene (DBT).[5] However, this method requires high-energy UVA irradiation and has a low quantum yield of photodeoxygenation of 0.003.[5]

In the condensed phase, O(^{3}P) has been shown to cause deoxyribonucleic acid (DNA) strand scission in plasmid DNA and selectively oxidize cysteine residues of adenosine-5′-phosphosulfate kinase (APSK).[17,18] The oxidation of low-density lipoprotein (LDL) by O(^{3}P) yielded primarily fatty aldehydes.[19] Additionally, O(^{3}P) selectively oxidizes the tertiary carbon of 2-methylbutane to the corresponding alcohol and benzene to phenol.[4] These results show that O(^{3}P) could be a potential oxidant in organic synthesis and be used to probe oxidative stress-induced biological pathways.

Despite the advantages of utilizing O(^{3}P), the necessity of UVA light combined with low photodeoxygenation quantum yields of currently available O(^{3}P)-precursors have hindered the application of O(^{3}P) in organic synthesis, biochemistry, and microbiology. Previously, photodeoxygenation of 2,8-dihydroxymethyldibenzothiophene *S*-oxide, which is presumed to generate O(^{3}P), has been used to study the effect of O(^{3}P) in RAW 264.7 cells.[19] However, UVA is not a preferable range of wavelengths to use with biomolecules and cells as it causes degradation of biomolecules, and longer exposure of UVA can lead to cell death.[20–24] In this work, O(^{3}P)-precursors that are expected to deoxygenate upon irradiation with visible light and have high quantum yields of photodeoxygenation are investigated.

One strategy to develop an O(^{3}P)-precursor that deoxygenates upon irradiation with visible light is to modify the structure of DBTO. Previously, the DBTO structure has been modified in various ways depending on the objective of the particular research. For example, DBTO derivatives that are water-soluble, lipophilic, photodeoxygenate more quickly, or absorb visible wavelength light have been synthesized to suit the required experimental conditions.[3,25,26] Sulfonic acids and hydroxymethyl groups have been added to DBTO to improve water solubility and to allow generation of O(^{3}P) in water.[3,18,25] Alkyl groups have been substituted on the DBTO structure to enhance its lipophilicity.[26] When a higher quantum yield of photodeoxygenation was required, sulfur in the structure of DBTO was replaced with selenium.[6,27] The change of sulfur to selenium in the DBTO structure improved the quantum yield of photodeoxygenation to approximately 0.1.[6] To extend the ultraviolet-visible (UV-Vis) absorption into the visible wavelength range, benzannulation of the DBTO structure has been employed.[14,28] However, benzannulated DBTO derivatives displayed other photodeoxygenation mechanisms in addition to the unimolecular S—O bond scission mechanism that yields O(^{3}P), and none appeared to generate O(^{3}P) upon visible light irradiation.[28,29] The combination of creating selenium containing analogs with *π*-extended chromophores was postulated to create O(^{3}P)-precursors that have a high quantum yield of photodeoxygenation upon irradiation with visible light. To examine this hypothesis, polycyclic aryl selenoxides **1** to **4** were synthesized, and their photodeoxygenation processes were studied (Figure 2).

2 | EXPERIMENTAL SECTION

2.1 | Materials

All chemicals were purchased from Sigma Aldrich, Fisher, Arctom Chemicals, Oakwood chemicals, or Ark Pharm and used without further purification except as specified. Anhydrous *N*-Methyl-2-pyrrolidone (NMP) obtained from Sigma Aldrich was further dried using 3-Å molecular sieves. HPLC-grade toluene, benzene, and acetonitrile were used for common intermediate experiments. Selenides **1Se** to **4Se** and **DBSe** except for **2Se** were synthesized according to the literature.[28,30–37] Compounds **1** to **4**, DBSeO, diphenyl selenoxide, and DBTO were synthesized by oxidizing **1Se** to **4Se**, DBSe,

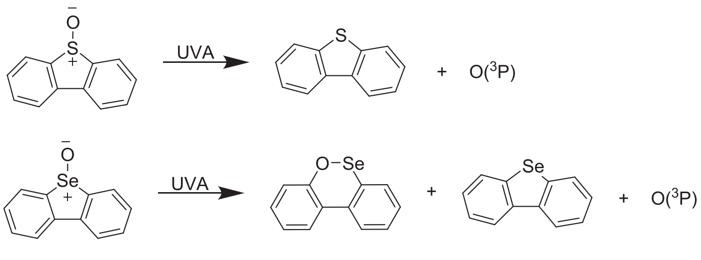


FIGURE 1 Photodeoxygenation of dibenzothiophene *S*-oxide (DBTO) and dibenzoselenophene *Se*-oxide (DBSeO)

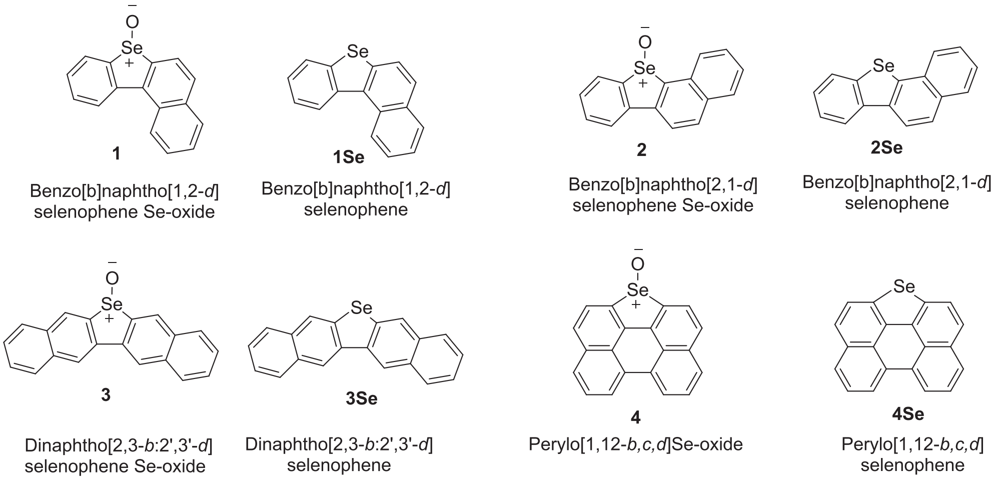


FIGURE 2 Aryl selenoxides and selenides used in this study

diphenyl selenide, and DBT, respectively. Selenoxide **3** used for all the experiments that had less than 10% isomer content. All the information about the synthesis of **1** to **4** are provided below in this section.

2.2 | General methods

Shimadzu GC-2010 Plus was used for GC-FID analysis. Absorption spectra were obtained using a Shimadzu UV-1800 UV spectrophotometer. A Bruker DRX-400 NMR was used to obtain NMR spectra of compounds **1** to **4**. HPLC analysis was conducted using an Agilent 1200 Series HPLC with a quaternary pump, diode-array detector, and a Higgins Analytical CLIPEUS C18 column (5 μm, 150 × 4.6 4.6 mm). A Shimadzu GCMS equipped with QP2010S was used for gas chromatography-mass spectrometry (GC-MS) analysis.

2.3 | Photodeoxygenation quantum yield determination

One- to five-millimolar solutions of compounds **1** to **4** were prepared in HPLC grade acetonitrile or ethanol for determining the quantum yields of photodeoxygenation below 390 nm. Saturated solutions of **1** and **3** in ethanol were used for determining the quantum yields of photodeoxygenation at 400 ± 3 nm. The optical densities of the prepared solutions were ensured to be greater than 2 at the desired wavelength for photolysis. Four milliliters of prepared samples in quartz cuvettes (1 cm × 1 cm) cells with long stem were degassed with argon for 10 min. The degassed solutions in quartz cuvettes were irradiated using a 75W Xenon lamp focused on a monochromator (Photon Technologies International). The reactions were carried out to low conversions (<20%). HPLC was used to analyze the solutions before and after photolysis. Photorearrangement of azoxybenzene to 2-hydroxyazobenzene was used as an actinometer for wavelengths less than 390 nm, and for wavelengths above 390 nm, K[Cr $(NH_3)_2(NCS)_4$] was used.[38,39]

2.4 | Common intermediate experiments

One- to 10-millimolar solutions of DBTO and compounds **1** to **4** were prepared. The solutions were sparged with argon in quartz cuvettes (1 cm × 1 cm) with long stems. The degassed solutions were irradiated with either UVA bulbs (Luzchem LZC-UVA bulbs centered at 350 nm) or bulbs centered at 420 nm (Luzchem LZC-420 nm). The common intermediate experiments with 420 nm irradiation were also performed in glass test tubes. The changes in the concentrations of products were analyzed using GC-FID, and changes in the concentration of DBT and corresponding selenides of **1** to **4** were analyzed using HPLC. Dodecane was used as an internal standard.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis of compounds 1 to 4

Compounds **1Se** and **4Se** were synthesized according to previously reported procedures.[30–33] Compounds **1** and **4** were prepared by oxidation of **1Se** and **4Se**, respectively, with 3-chloroperoxybenzoic acid (mCPBA) in dichloromethane (DCM). For selenide **4Se**, the reported procedure yielded product, only if anhydrous NMP was used as the solvent.

The previously reported method for synthesis of DBSe has multiple steps.[6] In this work, DBSe was prepared using a similar procedure to **3Se**, which is a one-pot, two-steps process, as shown in Scheme 1.[40] The synthesis of DBSe involved the reaction of 2,2′-dibromo-1,1′-biphenyl with *tert*-butyllithium (*t*-BuLi) at −78°C in anhydrous tetrahydrofuran (THF) followed by addition of prepared $SeCl_2$, which was prepared by addition of selenium to SO_2Cl_2. DBSeO was obtained by oxidation of DBSe with mCPBA.

Selenoxide **2** was synthesized in four steps as shown in Scheme 2. The first step involved selenobromination of phenyl acetylene using HBr, SeO_2, and cyclohexene in 1,4-dioxane to yield 3-bromo-benzo[*b*]selenophene (**2A**).[30] A Suzuki-Miyaura reaction was utilized in the second step for coupling *trans*-2-phenylvinylboronic acid with **2A** to yield 3-(2-phenylethenyl)-benzo[*b*] selenophene (**2B**). Selenide, **2Se**, was prepared by photocyclization of **2B** in the presence of iodine and propylene oxide under UVA irradiation. This method to synthesize **2Se** has been previously used to prepare dinaphthothiophenes and benzonaphthothiophenes.[28,34–36] The final step was oxidation of **2Se** by mCPBA in DCM.

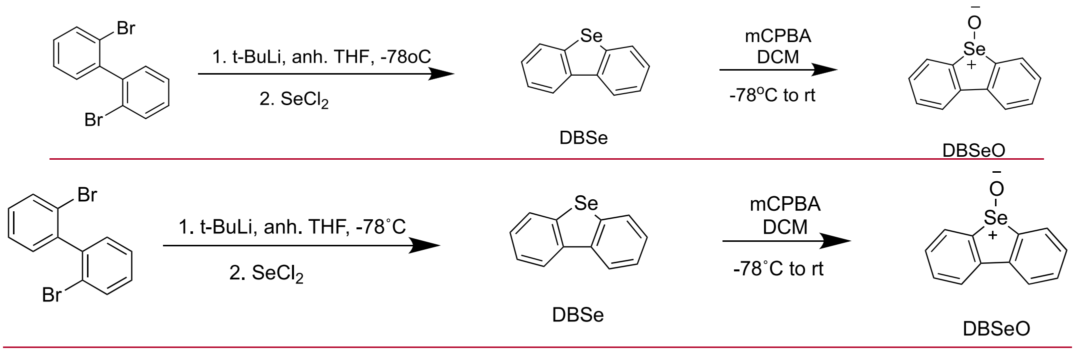
Selenoxide **3** was prepared by slightly modifying the reported synthetic procedure.[37,40] The modified procedure is shown in Scheme 3. The synthesis of selenide **3Se** yielded approximately 90% selenide **3Se** and 10% of an isomer, which had the same molecular mass as **3Se**. After purification using column chromatography, recrystallization of **3Se** in 17% DCM in hexanes eliminated the unidentified isomer. However, the isolated yield after recrystallization was low (~10%). Therefore, to prepare selenoxide **3**, selenide **3Se** containing 10% isomer, or less, was used. Selenoxide **3** prepared by oxidation of **3Se** using mCPBA had less than 10% isomer.

3.2 | UV-Vis spectra of compounds 1 to 4

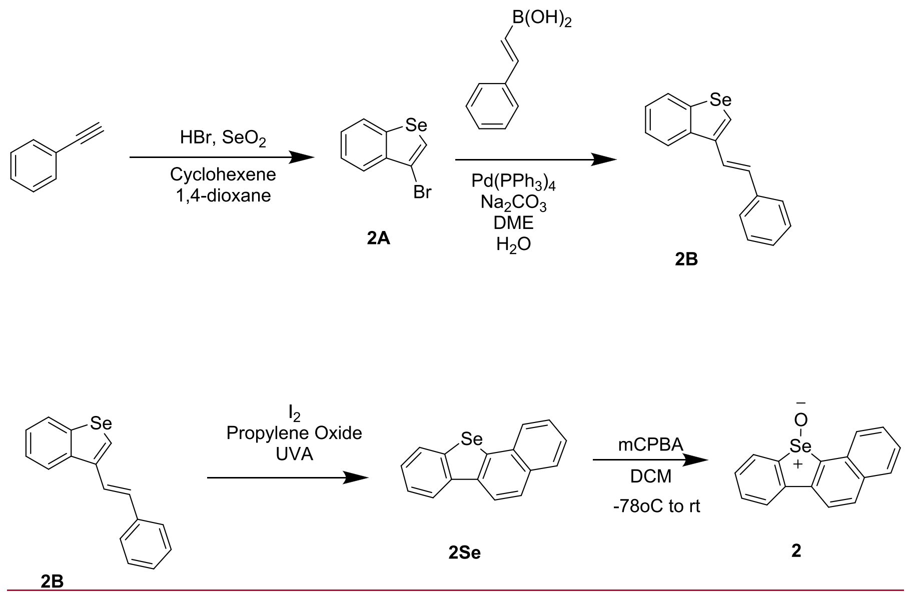
The currently available O(^{3}P)-precursors require UV light irradiation for producing O(^{3}P). One of the objectives of this work is to prepare O(^{3}P)-precursors that absorb and photodeoxygenate in the visible wavelength region. The UV-Vis spectra of compounds **1** to **4** were obtained to determine if visible light was absorbed by **1** to **4**. Compounds **1** to **4** had cutoff wavelengths ($\varepsilon < 50$) that are significantly higher than DBTO (365 nm) and DBSeO (354 nm). Compounds **1** and **2** had cutoff wavelengths of 400 nm and 376 nm, respectively, and selenoxides **3** and **4** absorptions extend above 400 nm with cutoff wavelengths of 433 nm and 533 nm, respectively (Figure 3).

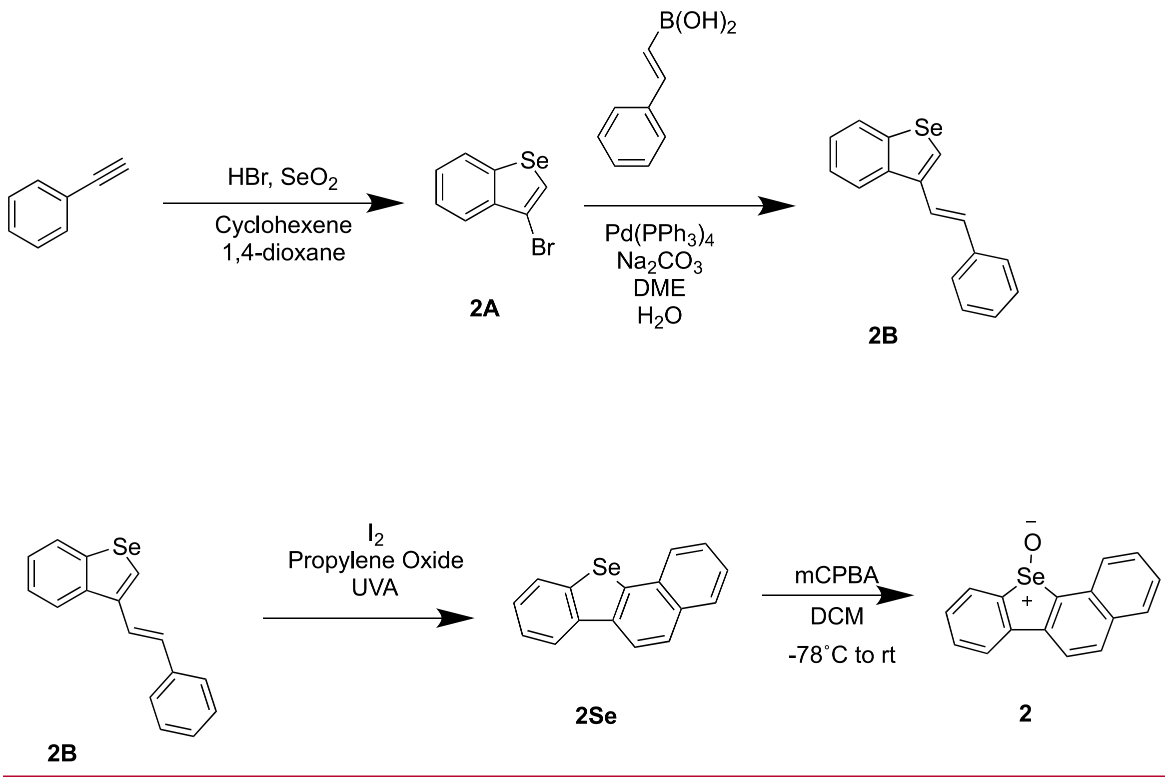
3.3 | Quantum yield of photodeoxygenation

The photodeoxygenation of DBTO is the most commonly used clean source of O(^{3}P) in the condensed phase. However, it suffers from low quantum yield of photodeoxygenation. The selenoxides **1** to **4** were synthesized to improve the quantum yield of photodeoxygenation and therefore make the generation of O(^{3}P) more efficient. To verify whether **1** to **4** undergo photodeoxygenation more efficiently, the quantum yields of photodeoxygenation of compounds **1** to **4** were measured upon UV irradiation. These experiments were performed in ethanol and acetonitrile. For individual selenoxides, the wavelength with maximum absorbance above 320 nm in the UV-Vis spectrum was used for irradiation. The quantum yields of photodeoxygenation were calculated based on the increase in the selenide concentration and are listed in Table 1. The values ranged from 0.009 to 0.33. Among the compounds tested, selenoxide **2** had the highest quantum yield of photodeoxygenation, which was 0.33, and selenoxide **4** had the lowest quantum yield of 0.009. The quantum yield of photodeoxygenation of compound **4** was only obtained in ethanol, as it had poor solubility in acetonitrile. HPLC analysis was used to determine the increase in the selenide concentration used for calculating the quantum yield of photodeoxygenation. Since irradiation



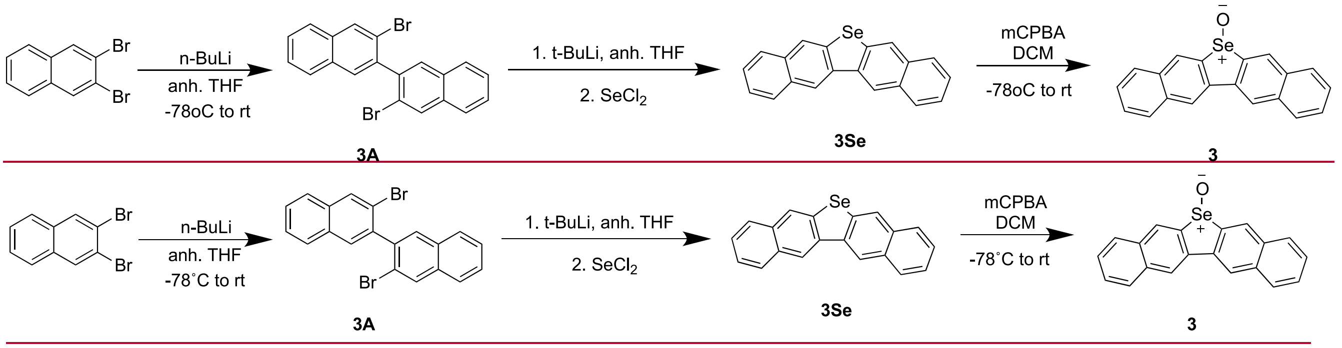
SCHEME 1 Synthesis of compound dibenzoselenophene *Se*-oxide (DBSeO)





SCHEME 2 Synthesis of compound **2**

of DBSeO leads to DBSe and ring expansion to a selenic ester as shown in Figure 1, multiple products were possible upon irradiation of **1** to **4**. However, no other significant products were observed in HPLC analysis after photolysis of **1**, **3**, and **4** other than their corresponding selenides. This is surprising as photodeoxygenation of DBSeO yields DBSe and a ring-expanded selenic ester product, and thus, it was anticipated that selenic esters might form for **1** to **4**. Photolysis of **2** yielded corresponding selenide **2Se** and a new compound **2X**. The ^{1}H NMR of purified compound **2X**, which is included in the Supporting Information, had peaks with chemical shifts in the aromatic region and resembled a polymer. To measure the light flux of the lamp used, photorearrangement of azoxybenzene to 2-hydroxyazobenzene was used as the actinometer.[38]



SCHEME 3 Synthesis of compound **3**

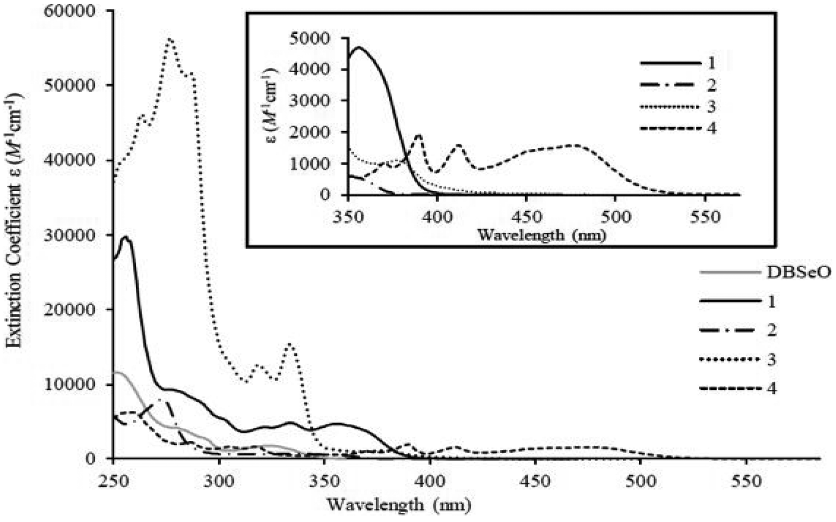


FIGURE 3 Ultraviolet-visible (UV-Vis) absorption spectra of dibenzoselenophene *Se*-oxide (DBSeO) and **1** to **4**

TABLE 1 Quantum yields of photodeoxygenation of DBSeO and **1** to **4**

		Quantum yield[b] $\Phi_{+selenide}$		
Entry	**Compound**	**Acetonitrile**	**Ethanol**	**Wavelength (nm)**
1	**DBSeO**	-	0.13 ± 0.01[a]	320 ± 12
2	**1**	0.14 ± 0.03	0.21 ± 0.01	356 ± 6
3	**2**	0.25 ± 0.01	0.33 ± 0.15	340 ± 6
4	**3**	0.23 ± 0.04	0.19 ± 0.02	330 ± 6
5	**4**	-	0.009 ± 0.006	320 ± 6

Abbreviation: DBSeO, dibenzoselenophene *Se*-oxide.

[a] Quantum yield of photodeoxygenation of DBSeO from McCulla and Jenks.[6]

[b] Quantum yields reported are within 95% confidence intervals and were calculated by increase in selenide concentration.

3.4 | Photochemistry upon UVA irradiation

A number of substrates such as toluene, benzene, styrene, and 1-octene have been oxidized using O(^{3}P) produced by the photodeoxygenation of DBTO.[2,4,5] These substrates yield multiple products upon reaction with O(^{3}P). For instance, oxidation of toluene by O(^{3}P) yields benzyl alcohol, *o*-cresol, *m*-cresol, and *p*-cresol in a specific ratio.[5,6,14,27,28] Two different chemical reactions can be shown to share a common intermediate if the reactions yield the same product distribution. Therefore, if the oxidation of substrates by the photodeoxygenation of **1** to **4** produces the same distribution of products as DBTO, then **1** to **4** are considered to produce O(^{3}P) on photodeoxygenation. Three different common intermediate experiments were conducted to verify if selenoxides **1** to **4** produce O(^{3}P) on photodeoxygenation. Toluene, benzene, and 1-octene were used as substrates in these common intermediate experiments for **1** to **3**. Since compound **4** is not soluble in toluene or benzene, oxidation of toluene or benzene common intermediate experiments were not conducted for **4**. However, the 1-octene common intermediate experiment of **4** was performed in ethanol as the solubility of **4** in acetonitrile was very low.

3.5 | Common intermediate experiments

The oxidation of toluene has been used as a common intermediate experiment to verify if the oxidant that formed during the photodeoxygenation of sulfoxides and selenoxides is the same and likely $O(^3P)$.[6,27,28,41] However, the results must be carefully analyzed since the ratio of the oxidized products is sensitive to the amount of dissolved molecular oxygen.[27,28,41] This sensitivity arises from the ability of dissolved molecular oxygen to oxidize toluene upon UVA irradiation. Irradiation of toluene for 4 h, which was degassed using argon sparging, with UVA light yielded mainly benzaldehyde and benzyl alcohol and some cresols in a 10:1 CH_3:ring ratio of oxidation products. As shown in Figure 4, when toluene was degassed by argon sparging, the oxidation of toluene by the photodeoxygenation of DBTO yielded 1:3 CH_3:ring ratio (Table 2, entry 1) upon 4 h of UVA irradiation.[29] However, when the freeze-pump-thaw technique, which is a superior technique for removing dissolved oxygen, was used to degas toluene, the amount of benzaldehyde obtained was negligible and the ratio of CH_3:ring obtained was 1:17 (Table 2, entry 2). It should also be noted that the head space for all of the argon sparged samples was the same, which has been shown to effect the ratio of oxidized products.[41]

Unlike DBTO, the CH_3:ring ratio obtained for the oxidation of toluene by photodeoxygenation of DBSeO was 1:26 (Table 2, entry 3) when degassed by argon sparging. This was due to the higher quantum yield of photodeoxygenation of DBSeO compared with DBTO, which results in a difference in the photolysis time of DBTO and DBSeO. When 14 Luzchem UVA bulbs (LZC-UVA) were used for irradiation, the photolysis time for DBTO was 4 h to yield approximately 0.5 mM DBT whereas DBSeO was photolyzed for only 10 min to yield approximately 0.5 mM DBSe. Thus, the longer irradiation time for DBTO affected the CH_3:ring ratio for argon-sparged samples due to the background oxidation of toluene by the residual dissolved molecular oxygen. The product ratio obtained for DBSeO when degassed using argon sparging was similar to the product ratio obtained for DBTO when freeze-pump-thaw technique was used to remove oxygen. Therefore, as the quantum yields of photodeoxygenation of selenoxides **1** to **3** are closer to DBSeO, argon sparging was used to degas the photolysis samples. The ratio obtained for DBSeO was considered as the reference ratio.

Oxidation of toluene by the photodeoxygenation of DBTO, DBSeO, and **1** to **3** produced more cresols than

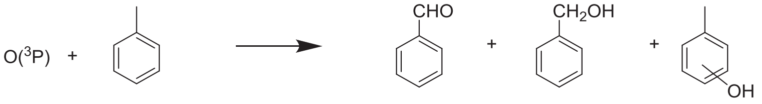


FIGURE 4 Oxidation of toluene by $O(^3P)$

TABLE 2 Product distribution and yields of toluene oxidation by photolysis of DBTO, DBSeO, and **1** to **3**

		Percentage product yield (%)[a]					
Entry	**Compound**	**Benzaldehyde**	**Benzyl alcohol**	**o-cresol**	**m/p-cresol**[b]	**Total oxidation product yield (%)**	**CH_3:ring** [c]
1	**DBTO**[d]	5 ± 3	6 ± 3	17.6 ± 0.9	13 ± 1	42 ± 4	1: 3
2	**DBTO**[e]	0.5 ± 0.7	1.3 ± 0.7	21 ± 1	10 ± 3	33 ± 5	1: 17
3	**DBSeO**	1.2 ± 0.2	0.0 ± 0.2	18 ± 3	13 ± 3	32 ± 7	1: 26
4	**1**	0.2 ± 0.2	0.4 ± 0.1	9 ± 3	7 ± 1	17 ± 4	1: 27
5	**2**	0.5 ± 0.9	0.2 ± 0.4	11.6 ± 0.5	6.1 ± 0.1	18.4 ± 0.9	1: 25
6	**3**	0.3 ± 0.4	0.5 ± 0.5	6 ± 3	3 ± 2	10 ± 2	1: 11

Abbreviations: DBSeO, dibenzoselenophene *Se*-oxide; DBTO, dibenzothiophene *S*-oxide.

[a] Percentage yields of toluene oxidation products are calculated with respective to formation of selenide/DBT and are within 95% CI.

[b] Calculated as one peak.

[c] Ratio of sum of yields of PhCHO and benzyl alcohol to combined yields of cresols.

[d] From Petroff et al.[41]

[e] Photolysis samples were degassed using freeze pump thaw technique.

benzaldehyde and benzyl alcohol after photolysis. No other toluene oxidation products for DBTO, DBSeO, and **1** to **3** were observed in GC-FID analysis after photolysis. The product yields of DBSeO and **1** to **3** were calculated relative to the formation of selenide. For DBTO, the product yields were calculated relative to the formation of DBT. HPLC analysis was used to determine the increase in the selenide and DBT concentration. The photolysis time for **1** to **3** and DBSeO was approximately 10 min, while for DBTO, it was 4 h. The total product yields obtained for DBTO when toluene was degassed by argon sparging and freeze pump thaw were 42 ± 4% and 33 ± 5%, respectively. The total product yield obtained for DBSeO was 32 ± 7%, which is within the limits of the experimental error of the yields obtained for DBTO. Compound **1** had a similar CH_3:ring oxidation ratio of 1:27 compared with DBSeO. The total product yield obtained for **1** was 17 ± 4 %, which is lower than the total product yield obtained for DBSeO. Similar to **1**, compound **2** had 1: 25 CH_3:ring oxidation, which is similar to DBSeO. However, the total product yield obtained for **2**, 18.4 ± 0.9%, is also lower than that of DBSeO. For selenoxide **3**, the CH_3:ring oxidation ratio obtained was 1:11, which is slightly lower than DBSeO in terms of amount of ring oxidation. However, the CH_3:ring oxidation ratio can be considered as nearly 0:1 because the errors obtained for the yields of benzaldehyde and benzyl alcohol are high. Although these results suggest that compounds **1** to **3** produce the same oxidant as DBTO and DBSeO, namely $O(^3P)$, the oxygen sensitivity makes the oxidation of toluene a less robust approach to make this conclusion.

As the oxidation of toluene common intermediate experiment is oxygen-sensitive, other common intermediate experiments were explored. Oxidation of benzene is another common intermediate experiment that has been used to support if $O(^3P)$ is the intermediate of photodeoxygenation of sulfoxides and selenoxides.[5,6,14] Oxidation of benzene by $O(^3P)$ predominantly produces phenol along with some biphenyl, as shown in Figure 5. The product distribution of this test is not oxygen-sensitive since irradiation of benzene with UVA did not yield any benzene oxidation products even when the solution was not degassed. Hence, the product distribution of the oxidation of benzene should not be affected due to a difference in irradiation times.

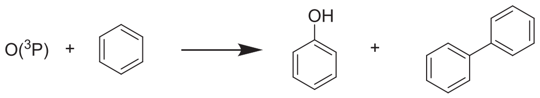


FIGURE 5 Oxidation of benzene by $O(^3P)$

Oxidation of benzene as a common intermediate experiment was conducted for DBTO, DBSeO, and **1** to **3**. The photolysis time for **1**, **2**, and DBSeO was 3 min and for **DBTO** and **3** were 60 min and 5 min, respectively. The product distribution and total product yields of DBTO, DBSeO, and **1** to **3** are listed in Table 3. Photolysis of DBTO, DBSeO, and **1** to **3** primarily yielded phenol with biphenyl as the minor product. No other benzene oxidation products were observed in GC-FID analysis after photolysis. Compounds **1** to **3** had similar product distribution as obtained for DBSeO and DBTO, but the total product yields obtained were lower. For compound **1**, the total product yield obtained, 18.4 ± 0.1%, is lower than the total product yield obtained for DBSeO (32 ± 6%) and DBTO (33 ± 2%). Similar to **1**, the total product yield of **2**, 17.9 ± 0.9%, was lower compared with DBTO and DBSeO. Compound **3** had the lowest total product yield of 7.7 ± 0.2% compared with all the other entries in Table 3. The similar product ratio implies that **1** to **3** produce $O(^3P)$ upon photodeoxygenation. However, as the total product yields of **1** to **3** are lower than the total product yields of DBSeO and DBTO, **1** to **3** might also undergo photodeoxygenation through an alternate pathway which does not result in the oxidation of benzene.

The oxidation of 1-octene common intermediate experiment was also performed to provide further support that photodeoxygenation of **1** to **3** produced $O(^3P)$. The reaction of 1-octene and $O(^3P)$ gives 1,2-epoxyoctane and 1-octanal as products, as shown in Figure 6. Similar to the oxidation of benzene common intermediate experiment, the product distribution of this common intermediate experiment was not oxygen sensitive as no 1-octene oxidation products were obtained by the irradiationof 1-octene (500 mM) with UVA light in acetonitrile when the solution was not degassed.

Compounds **1** to **3** along with DBTO and DBSeO were used to oxidize 1-octene in acetonitrile. The photolysis time for DBTO was approximately 4 h and for DBSeO and **1** to **3** was approximately 5 min. The results of the 1-octene oxidation test are listed in Table 4. The product distributions obtained for DBTO, DBSeO, and **1** to **3** were alike. The ratios of 1-octanal to 1,2-epoxyoctane obtained for DBTO, DBSeO, and **1** to **3** were around 1:1.3. The total product yield obtained for DBTO was 59 ± 6% which is significantly higher than the total product yield of DBSeO which was 25.4 ± 0.7%. Compound **1** had a total product yield of 13.0 ± 0.3%, which is lower than both DBTO (59 ± 6%) and DBSeO (25.4 ± 0.7%). The total product yields of **2** and **3** are 8 ± 1% and 11 ± 3%, respectively. Again, the similar product ratio suggests that compounds **1** to **3** generate $O(^3P)$ upon irradiation like DBTO. However, the lower yields for **1** to **3**, which

TABLE 3 Product distribution and yields of benzene oxidation by photolysis of DBTO, DBSeO, and **1** to **3**

		Percentage product yields(%)[a]		
Entry	**Compound**	**Phenol**	**Biphenyl**	**Total oxidation product yield (%)**
1	**DBTO**	32 ± 2	1.0 ± 0.1	33 ± 2
2	**DBSeO**	31 ± 6	0.8 ± 0.5	32 ± 6
3	**1**	17.40 ± 0.03	1.0 ± 0.1	18.4 ± 0.1
4	**2**	17.5 ± 0.7	0.40 ± 0.01	17.9 ± 0.9
5	**3**	7.4 ± 0.2	0.30 ± 0.01	7.7 ± 0.2

Abbreviations: DBSeO, dibenzoselenophene *Se*-oxide; DBTO, dibenzothiophene *S*-oxide.

[a] Percentage yields of benzene oxidation products are calculated with respective to formation of selenide/DBT and are within 95% CI.

FIGURE 6 Oxidation of 1-octene by $O(^3P)$

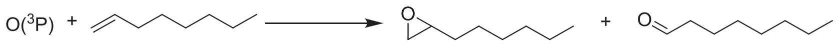


TABLE 4 Product distribution and yields of 1-octene oxidation by photolysis of DBTO, DBSeO, and **1** to **3**

		Percentage product yield (%)[a]			
Entry	**Compound**	**1-octanal**	**1,2-epoxyoctane**	**Total oxidation product yield (%)**	**1-octanal: 1,2-epoxy octane**[b]
1	**DBTO**	24 ± 2	35 ± 3	59 ± 6	1: 1.4
2	**DBSeO**	11.0 ± 0.2	14.4 ± 0.9	25.4 ± 0.7	1: 1.3
3	**1**	5.9 ± 0.4	7.00 ± 0.04	13.0 ± 0.3	1: 1.2
4	**2**	3.4 ± 0.6	4.9 ± 0.5	8 ± 1	1: 1.4
5	**3**	5 ± 1	7 ± 2	11 ± 3	1: 1.3

Abbreviations: DBSeO, dibenzoselenophene *Se*-oxide; DBTO, dibenzothiophene *S*-oxide.

[a] Percentage yields of 1-octene oxidation products are calculated with respective to formation of selenide/DBT and are within 95% CI.

[b] Ratio of yield of 1-octanal to yield of 1,2-epoxyoctane.

were also observed in the tests with toluene and benzene, suggest other deoxygenation mechanisms that do not produce $O(^3P)$ could be operative.

As previously mentioned, common intermediate experiments for **4** were not possible due to low solubility in acetonitrile, which is required to obtain significant oxidation of toluene or benzene. However, the oxidation of 1-octene as a common intermediate experiment could be performed in ethanol. Since ethanol is more reactive with $O(^3P)$ than acetonitrile, a lower yield of 1-octanol and 1,2-epoxyoctane was expected.[1,42] When DBSeO was irradiated in ethanol with 500 mM 1-octene, the total product yield of 1-octanal and 1,2-epoxyoctane dropped to 4%. Irradiation of **4** in ethanol with 500 mM 1-octene with UVA light resulted in **4Se**; however, GC-FID analysis showed neither a 1-octanal nor a 1,2-epoxyoctane peak. Given that the detection limit of 1-octanal and 1,2-epoxyoctane was 3.0 μM, **4** produces less than half the $O(^3P)$ of that of DBSeO or possibly none at all. The concentrations of DBSeO and **4** in ethanol used for 1-octene oxidation were both 1.1 mM.

The total product yields obtained for DBTO and DBSeO in the oxidation of toluene and oxidation of benzene common intermediate experiments were similar. However, the total product yield obtained for DBSeO for the 1-octene oxidation common intermediate experiment was much lower than the total product yield obtained for DBTO. To examine if solvent effects influenced these oxidations, DBTO and DBSeO were photolyzed individually with 1-octene in dichloromethane. No significant change in the total product yields was observed when the solvent was changed to dichloromethane from acetonitrile for both DBTO and DBSeO. The total product yields of oxidation of 1-octene by photodeoxygenation of DBTO and DBSeO in dichloromethane were 70 ± 8% and 29 ± 3%. Therefore, the lower total product yield for DBSeO was not due to different solvent effects for DBSeO and DBTO. A similar observation was reported previously when a mixture of benzene and cyclohexane, in the ratio of 3:1 (*v*/v), was oxidized in dichloromethane individually by photolysis of DBTO and DBSeO.[27] Both DBTO and DBSeO yielded product ratios which were approximately 1:3 phenol:cyclohexanol. However, the total product yield obtained for DBSeO, 6.2 ± 0.8 %, was significantly lower compared with the total product yield, 42 ± 5.1%, obtained for DBTO.[27] The reason for the lower product yields of 1-octene oxidation by DBSeO compared with DBTO was not investigated.

3.6 | Mechanistic studies

Various mechanisms have been proposed to explain the photodeoxygenation of aryl sulfoxides.[5,7,14,15,27,43–45] The first proposed mechanism postulated that the photodeoxygenation of aryl sulfoxides proceeds by a bimolecular process.[15] However, common intermediate experiments, results of photolysis at low temperature (77 K), and ^{18}O-labeling studies refuted the bimolecular mechanism.[5,14] Currently, the accepted mechanism of photodeoxygenation by direct irradiation of aryl sulfoxides to yield $O(^3P)$ is unimolecular scission of the S—O bond.[5,27] In addition to $O(^3P)$ formation, photodeoxygenation of aryl sulfoxides also occurs through other pathways such as photoinduced electron transfer and triplet sensitization.[27,43,44] Specifically for DBTO, deoxygenation through the T_1 triplet state reached by photosensitization did not yield $O(^3P)$.[27] Similarly, photoinduced deoxygenation of DBTO derivatives at high pH was the result of electron transfer from hydroxide ion to the sulfoxide, which results in deoxygenation to yield the corresponding sulfides and no $O(^3P)$.[44] Fewer mechanistic studies have been done to explain the process of photodeoxygenation of aryl selenoxides. The limited studies that have been done show photodeoxygenation of aryl selenoxides occurs by unimolecular and bimolecular pathways. Photodeoxygenation of diphenyl and dibenzyl selenoxides by irradiation with a high-pressure mercury lamp yielded their corresponding selenides through a bimolecular mechanism.[46] However, photodeoxygenation of DBSeO to DBSe occurs by a unimolecular mechanism producing $O(^3P)$.[6,27]

Since the product ratios for all the three common intermediate experiments of selenoxides **1** to **3** were similar to DBTO, the photodeoxygenation of selenoxides **1** to **3**, DBSeO, and DBTO likely have $O(^3P)$ as a common intermediate. However, the total product yields of **1** to **3** were lower than to that of DBTO and DBSeO. One explanation for the lower yields observed for **1** to **3** is that they deoxygenate through other additional pathways that do not produce $O(^3P)$. To test this hypothesis, mechanistic studies for **1** to **3** were conducted. Selenoxides **1** to **3** were individually dissolved in EPA glass (ether:pentane:ethyl alcohol = 5:5:2) at low concentration at 77 K and photolyzed by UVA irradiation. HPLC analysis after the photolysis showed increase in the corresponding selenide concentration. This indicatesthat a plausible unimolecular mechanism for photodeoxygenation of **1** to **3** is operable, which is the posited mechanism for $O(^3P)$ release. However, this result does not rule out an additional bimolecular photoreduction mechanism accounting for some of the photodeoxygenation in solution.

Photodeoxygenation by a bimolecular mechanism could potentially occur by electron transfer, energy transfer, or the formation of a bimolecular exciplex between two selenoxides that undergoes deoxygenation to release a “dioxygen” oxidant.[43,46] The potential for a bimolecular exciplex was tested for selenoxide **1**. Direct irradiation of selenoxide **1** dissolved in acetonitrile with 390 ± 3 nm light in the presence of DBSeO yielded **1Se** and DBSe. The UV-Vis cut-off wavelength of DBSeO is 352 nm. Thus, the observed deoxygenation of both DBSeO and **1** in these conditions implied either a bimolecular exciplex or energy transfer from excited **1** to DBSeO, which both would be expected to result in **1Se** and DBSe. To differentiate them, selenoxide **1** was irradiated with 390 ± 3 nm light at variable concentrations of DBSeO and 500 mM of 1-octene. Acetonitrile was used as the solvent for these experiments, and the results of these experiments are shown in the Table 5.

TABLE 5 Product distribution and yields of 1-octene oxidation by direct irradiation of **1** in the presence of DBSeO

	Initial concentration (mM)			
Entry	**Selenoxide 1**	**DBSeO**	**Total oxidation product yield (%)**[a]	**1-octanal:1,2-epoxy octane**[b]
1	1.7	0.0	15 ± 2	1:1.5
2	1.7	0.4	13 ± 2	1:1.4
3	1.7	0.8	14 ± 2	1:1.4
4	1.7	1.6	11.1 ± 0.1	1:1.4
5	1.7	3.2	12 ± 2	1:1.4

Abbreviations: DBSeO, dibenzoselenophene *Se*-oxide.

[a] Percentage yields of 1-octene oxidation products are calculated with respective to formation of **1Se** and DBSe and are within 95% CI.

[b] Ratio of yields of 1-octanal to yield of 1,2-epoxyoctane.

The product ratio 1-octanal:1,2-epoxyoctane was approximately 1:1.4 for all the experiments. The total product yields for all the experiments were within the limits of the experimental error. If a bimolecular complex was the reason for the lower yields of oxidized product, the total product yields should decrease with increase in the concentration of DBSeO. Therefore, these results indicated photodeoxygenation of DBSeO occurred by energy transfer from the excited state of **1** to DBSeO rather than through a bimolecular exciplex that dissociates to deoxygenated products.

Direct irradiation of **1** in methanol with 390 ± 3 nm in the presence of diphenyl selenoxide was performed to provide more evidence that **1** does not undergo deoxygenation through a bimolecular exciplex. As selenoxide **1** and diphenyl selenoxide had higher solubility in methanol compared with acetonitrile, methanol was used for this reaction. This reaction did not yield any diphenyl selenide after the reaction. Similarly, direct irradiation of **2** and **3** individually in methanol in the presence of diphenyl selenoxide did not yield any diphenyl selenide for either reaction. The wavelengths used for irradiation of **2** and **3** were 350 ± 3 nm and 390 ± 3 nm, respectively.

As a bimolecular exciplex was ruled out, another possible mechanism that was investigated was electron transfer. As the selenides **1Se** to **3Se** are produced during the photodeoxygenation of **1** to **3**, photoinduced electron transfer from the selenide to the selenoxide could result in deoxygenation without the release of $O(^3P)$.[43] This hypothesis was tested by obtaining the total product yields of 1-octene oxidation by photodeoxygenation of **2** at different reaction time points. The total product yields of 1-octene oxidation at all the reaction time points were in the range of 8 ± 4%, which is similar to the total product yield reported in Table 4. In another experiment, **2Se** was added to the solution containing **2**, 1-octene, and acetonitrile. The concentrations of **2** and **2Se** were both 2 mM. This solution was irradiated, and the total yield of the 1-octene oxidation products was obtained. The obtained total oxidation product yield was in the same range as reported in Table 4. These results indicate no electron transfer from **2Se** to **2** during the photolysis process. Similar results were expected for **1** and **3**.

The possibility of a unimolecular mechanism that does not produce $O(^3P)$, which would result in lower total product yields, was investigated. Photodeoxygenation of DBTO to DBT and $O(^3P)$ occurs from the T_2 triplet state of DBTO.[27,47] However, the T_1 state of DBTO accessed by triplet sensitization was shown to cause photodeoxygenation to produce DBT, but this process does not yield $O(^3P)$.[27] In contrast, photodeoxygenation of DBSeO occurs through both T_1 and T_2 triplet states to produce DBSe and $O(^3P)$.[27,47] The total product yields of the common intermediate experiments of **1** to **3** would be lower if the selenoxides **1** to **3** deoxygenated through both T_1 and T_2 but only produced $O(^3P)$ from the T_2 state as with DBTO. Photosensitization of selenoxides **1** to **3** to the T_1 state could be used to test this hypothesis. The energies of T_1 triplet states of **1** to **3** were obtained computationally using a HSEH1PBE/6-311G(d,p) level of theory.[48–50] The T_1 triplet states energies of **1** to **3** are shown in Table 6.

Acridine orange was chosen as the sensitizer because its triplet energy of 50.2 kcal/mol was close to the calculated triplet energies of **1** to **3**.[51] Hence, the T_1 triplet state of acridine orange has enough energy to promote **1** to **3** to their corresponding T_1 triplet states. However, acridine orange could also act as an electron donor in its excited state as its halfwave oxidation potential is closer to aniline, which is a good electron donor.[52,53] Therefore, both mechanisms have to be considered while using acridine orange to sensitize **1** to **3**.

Selenoxides **1** to **3** dissolved in acetonitrile were excited by sensitization using acridine orange in the presence of 1-octene, as shown in Figure 7. HPLC analysis after the experiment showed that triplet sensitization resulted in photodeoxygenation of **1** to **1Se**. However, GC-FID analysis showed no formation of 1-octene oxidation products. Similarly, sensitization of selenoxide **3** yielded **3Se**, but no 1-octene oxidation products were obtained. Interestingly, sensitization of **2** produced only **2Se** and no **2X**, which was the other product obtained when **2** was directly irradiated with UVA light. GC-FID analysis of this reaction showed that 1-octene was oxidized to 1-octanal and 1-octanol in low yields of 6% and 5%, respectively. However, as 1,2-epoxyoctane was not obtained, it can be concluded that $O(^3P)$ was not produced during photosensitization of **2**. In another experiment, sensitization by acridine orange was carried out in benzene; however, no oxidation products were observed.

The photosensitization of **1** to **3** by acridine orange could have occurred by energy transfer from the T_1 triplet state of acridine orange to T_1 triplet state of **1** to **3** or by electron transfer from excited state of acridine orange to the ground state of **1** to **3** or by both mechanisms. If the deoxygenation of **1** to **3** occurred through energy transfer, it suggests that T_1 triplet state of **1** to **3** did not produce $O(^3P)$. However, if the deoxygenation occurred by

TABLE 6 Triplet energies of selenoxides **1** to **3**

Entry	Selenoxide	T_1 energy (kcal./mol.)
1	**1**	46.8
2	**2**	39.8
3	**3**	49.2

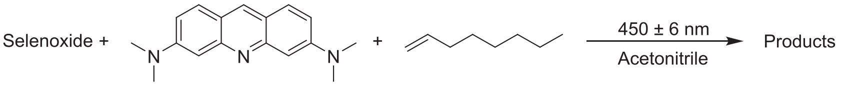


FIGURE 7 Oxidation of 1-octene by sensitized photolysis of **1** to **3**

electron transfer, it would lead to the reduction of **1** to **3** to their corresponding selenide and nothing can be concluded about the deoxygenation of **1** to **3** in their T_1 triplet state.[43,44] To determine if the halfwave oxidation potential of acridine orange made electron transfer feasible, perylene, which has much lower triplet state energy but similar halfwave oxidation potential, was used as the photosensitizer to induce electron transfer. The triplet-state energy and halfwave oxidation potential of perylene are 36.1 kcal/mol. and 0.85 V versus saturated calomel electrode (SCE) (Table 7), respectively. Selenoxide **1** was chosen for this experiment, as the calculated T_1 triplet state energy of **1** was higher than that of perylene and **1** had a UV-Vis cutoff wavelength lower than that of perylene. Therefore, only the electron transfer mechanism is possible in this case. Perylene (1.3 mM) was excited using 435 ± 3 nm in the presence of selenoxide **1** (3.8 mM), 1-octene (500 mM), and dodecane (0.125 mM) in acetonitrile. GC-FID and HPLC analyses showed formation of **1Se** (0.23 mM) but no 1-octene oxidation products. These results imply that 0.85 V versus SCE halfwave oxidation potential is sufficient for an electron transfer mechanism. However, as the calculated T_1 triplet-state energy of acridine orange is higher than that of **1** to **3**, an energy transfer mechanism cannot be ruled out. Additional studies to selectively perform energy transfer using a photosensitizer to selenoxides **1** to **3** were not conducted due to limitations in readily available photosensitizers with properties that would facilitate only energy transfer and not electron transfer.

Therefore, deoxygenation of **1** to **3** by photosensitization using acridine orange could have occurred by an energy transfer mechanism or electron transfer mechanism or by both these mechanisms. Hence, it is inconclusive whether the T_1 energy state of **1–3** produces $O(^3P)$. Other photosensitizers with high halfwave oxidation potential could not be used for these experiments, as they had lower UV-Vis cutoff wavelengths than **1** to **3**.

TABLE 7 Halfwave oxidation potentials and triplet state energies of acridine orange and perylene

Photosensitizer	$E_{1/2}^{ox}$/V vs. SCE in acetonitrile	T_1 energy (kcal./mol.)
Acridine orange	0.82[53]	50.2[51]
Perylene	0.85[54]	36.1[55]

Abbreviation: SCE, standard calomel electrode.

All the above mechanistic studies suggest that photodeoxygenation of **1** to **3** is a unimolecular process and not bimolecular. However, the efforts to identify a photoinduced deoxygenation mechanism that would account for the lower total oxidation product yields observed in the common intermediate experiments were not successful.

3.7 | Photochemistry of 1 and 3 with visible light irradiation

The primary goal of this work was to prepare photoactivatable $O(^3P)$-precursors that generate $O(^3P)$ using visible light irradiation. Therefore, compounds which absorb in visible light, **1** and **3**, were tested with a common intermediate experiment. 1-octene was used as the substrate, and acetonitrile was used as the solvent. Bulbs centered at 420 nm (Luzchem LZC-420 nm, 14 bulbs) were used for irradiation. The use of glass or quartz test tube had no effect on the observed products or yields. Selenoxides **1** and **3** were photolyzed for 1 and 4 h, respectively. The product yields of 1-octene oxidation by the irradiation of **1** at 420-nm light are shown in Figure 8. Upon irradiation, **1** yielded 1,2-epoxyoctane and 1-octanal upon irradiation in a ratio 1:1.2. The total product yield obtained was 13 ± 2%, which was similar to the total product yield of 1-octene oxidation obtained by UVA irradiation of **1**. The product ratio is similar to the product ratio of DBSeO listed in Table 5. The product distribution and total product yield of **1** are similar to that of the 1-octene oxidation common intermediate experiment performed by using bulbs centered at 350 nm. The implication of these results is that the photodeoxygenation of **1** produces $O(^3P)$ upon irradiation with visible light.

Irradiation of **3** with visible light resulted in the photodeoxygenation of **3**. However, unlike **1**, the oxidation of 1-octene common intermediate test of **3** did not yield any detectable amounts of 1-octanal or

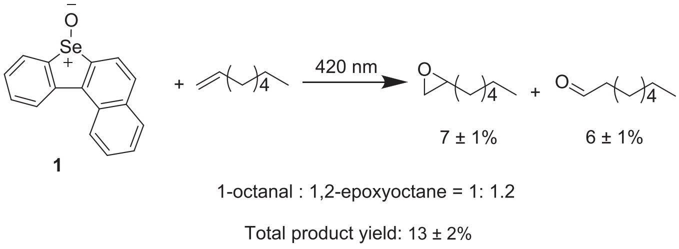


FIGURE 8 Oxidation of 1-octene by **1** using bulbs centered at 420 nm

TABLE 8 Quantum yields of photodeoxygenation of **1** and **3** at 400 nm

Entry	Compound	Quantum yield $\Phi_{+\text{selenide}}$[a]
1	**1**	0.13 ± 0.03
2	**3**	0.37 ± 0.03

[a] Quantum yields reported are within 95% confidence intervals and calculated based on the increase in selenide concentration. 400 ± 3 nm wavelength light was used for photolysis and ethanol was used as the solvent.

1,2-epoxyoctane. This indicates that the photodeoxygenation of **3** induced by visible light irradiation produces considerably less or no O(^{3}P) compared with irradiation with UVA light. The reason for this wavelength dependence was not investigated.

3.8 | Determination of quantum yield of photodeoxygenation at 400 nm

The UV-Vis cutoff wavelengths ($\varepsilon < 50$) for **1** and **3** are 400 nm and 433 nm. The quantum yields of photodeoxygenation of **1** and **3** are obtained in ethanol at wavelength range 400 ± 3 nm and are listed in Table 8. Saturated solutions of **1** and **3** in ethanol had optical densities greater than 2. $K[Cr(NH_3)_2(NCS)_4]$ was used as the actinometer.[39] The quantum yields of photodeoxygenation of **1** and **3** were 0.13 ± 0.03 and 0.37 ± 0.03, respectively.

4 | CONCLUSION

Selenoxides **1** to **3** have shown to generate O(^{3}P) in condensed phase when irradiated by UV light. Selenoxides **1**to **4** have higher UV-Vis absorption wavelength cutoffs than DBTO and DBSeO, with **1**, **3**, and **4** having the cutoff wavelength equal to or above 400 nm. Photodeoxygenation of compound **4** to corresponding selenide **4Se** had a lower quantum yield compared with **1** to **3**. Although photodeoxygenation of **3** occurs upon visible light irradiation, it did not produce O(^{3}P). Most importantly, the photodeoxygenation of selenoxide **1** induced by 420-nm light generated O(^{3}P). The quantum yields of photodeoxygenation of **1** to **3** are higher than all the O(^{3}P)-precursors reported till date.

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