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Photodeoxygenation and *α*-Cleavage Reactions of Selenoxides

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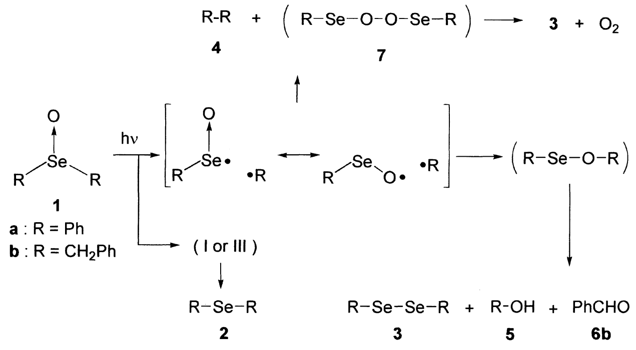
Upon UV-irradiation, diphenyl and dibenzyl selenoxides underwent deoxygenation and *α*-cleavage competitively to give selenides, and diselenides and others, respectively. A mechanism of bimolecular photodeoxygenation is proposed, since the yields of the photoproducts were dependent on the initial concentration of the selenoxides.

The photochemistry of organic sulfur compounds has been well-studied. From a mechanistic point of view, the photodeoxygenation of sulfoxides is particularly interesting,[1] since three fundamentally different mechanisms have been proposed for the deoxygenation.[2–4] The photochemical reactions of selenides[5] and diselenides[6] have been studied compared with that of the corresponding organic sulfur compounds. However, only a few papers have been reported on the photochemistry of selenoxides.[7] We report here on the photochemical behavior of selenoxides.

The irradiation of diphenyl selenoxide (**1a**, 2.1×10^{-2} mol dm^{-3}) in benzene under nitrogen with a high-pressure mercury lamp gave diphenyl selenide (**2a**), diphenyl diselenide (**3a**), biphenyl (**4a**), and phenol (**5a**) in 52, 48, 25, and 15% yields, respectively, at 6% conversion of **1a**. The irradiation of dibenzyl selenoxide (**1b**, 2.5×10^{-2} mol dm^{-3}) under similar conditions gave dibenzyl selenide (**2b**), dibenzyl diselenide (**3b**), and benzaldehyde (**6b**) in 64, 32, and 38% yields, respectively, together with a trace of 1,2-diphenylethane (**4b**) and benzyl alcohol (**5b**) at 17% conversion of **1b**. Only a trace of **4a** was formed when **1a** was irradiated in acetonitrile, while d_5-biphenyl (*m*/*e* 159) was detected when **1a** was irradiated in d_6-benzene. These results indicate that *α*-cleavage of **1a** occurs to give phenyl radicals, a great majority of which then react with benzene to yield **4a**. The recombination of *α*-cleavage fragments, the phenyl or benzyl radical and the seleninyl radical, in a solvent cage would give the selenenic ester RSeOR, as in the case of sulfenic ester formation in the photoreaction of sulfoxides,[1,8] though the selenenic ester could not be detected in TLC, GC, LC, and NMR analyses. The formation of compounds **3**, **5**, and **6** can be explained in terms of a secondary reaction of the selenenic ester.[9] The formation of the diselenide **3** can also be explained in terms of the decomposition of intermediate **7**, as shown in Scheme 1.



Scheme 1.

The formation of **2** may be explained in terms of direct elimination of the oxygen atom from **1**. If phenol is formed through the reaction of an oxygen atom with solvent benzene,[2] phenol should not be formed when **1a** is irradiated in solvents other than benzene. When **1a** was irradiated in acetonitrile, nearly the same amount of phenol as that in benzene was formed. Therefore, phenol was not produced by the oxygenation of solvent benzene, and atomic oxygen was not formed in the photodeoxygenation of **1**.

The formation of **2** may be explained in terms of the recombination of a radical pair formed through *α*-cleavage.[3] According to this mechanism, cross-coupled selenides must be formed when a mixture of two kinds of selenoxides is irradiated. However, only a small amount of cross-coupling selenides, benzyl phenyl selenides, was detected when a mixture of **1a** and **1b** was irradiated in benzene. This result indicates that *α*-cleavage is not the main process for producing **2**.

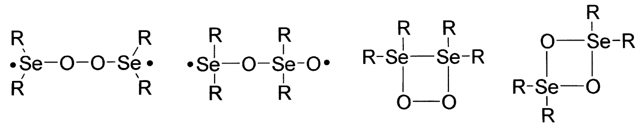
The initial concentration of the starting material shows little influence on the product distribution in unimolecular photoreactions of most organic compounds. However, the yields of the photoproducts from **1** depended on the initial concentration of **1**. The ratio of the yield of the selenide **2a** to that of the diselenide **3a**, Y_{2a}/Y_{3a}, increased along with an increase in the initial concentration of **1a** (Table 1). The variation of Y_{2a}/Y_{3a} indicates that the photodeoxygenation of the selenoxide proceeded not unimolecularly, but bimolecularly.

Four possible structures may be considered for the bimolecular intermediate produced from two molecules of **1**. However, structures II and IV (Fig. 1), which contain a Se–O–Se–O bond, are presumably excluded, because no selenones were detected in the photoreaction of the selenoxide **1**. Structure I seems to be plausible for the intermediate, though the possibil-

Table 1. Dependence of Product Yields on the Initial Concentration of **1a**

Initial concentration of **1a**/10^{-2} mol dm^{-3}	Consumption of **1a**/%	$\dfrac{Y_{2a}{}^{a)}}{Y_{3a}}$
2.1	6	1.1 (52/48)
6.2	5	1.6
10.0	8	2.6

a) The ratio of the yield of the selenide **2a** to that of the diselenide **3a**. The yields were calculated assuming that one mole of **2a** is formed from one mole of **1a** and one mole of **3a** from two moles of **1a**.



I II III IV

Fig. 1.

ity of structure III cannot be excluded. The sulfur analogue of I was proposed in a sensitized photoreaction of sulfoxide.[4c]

In conclusion, selenoxides **1** undergo photodeoxygenation competing with α-cleavage, and the photodeoxygenation proceeds through a bimolecular intermediate having a Se–O–O–Se bond.

Experimental

IR and UV spectra were recorded with JASCO IR A-3 and JASCO UV-505 spectrometers, respectively. ^{1}H and ^{13}C NMR spectra were measured with a JEOL FX90Q spectrometer using tetramethylsilane as an internal standard. GC-MS spectra were measured with a Varian Saturn 2000R. An Ushio 450 W high-pressure mercury lamp was used as an irradiation source. Selenoxides **1** were prepared according to a literature procedure.[10]

General Procedure for Irradiation of 1. A solution of selenoxide **1** in benzene or acetonitrile was irradiated for 2 h at 20 °C under nitrogen with a 450 W high-pressure mercury lamp. A potassium chromate filter solution was used to isolate the 313 nm line. The starting material **1** and products **2**–**4** and **6** were analyzed using a Gasukuro Kogyo 570B high-pressure liquid chromatograph with a Model 511 single-wave UV detector (254 nm). An Inertsil ODS-2 column (4.6 × 150 mm) was used, and a mixture of acetonitrile–water (v/v = 1/1) was used as the moving phase at a flow rate of 6 cm^{3} min^{-1}. Naphthalene was used as a calibrant for the analyses. Product **5** was determined on a Shimadzu GC-4A gas chromatograph equipped with a flame ionization detector using a 2 m column containing Apiezon Grease L on Neopak 1A. In the photolysis of a mixture of **1a** ($\lambda_{\max}^{\mathrm{MeOH}}$ 222 (ε 11850), $\varepsilon_{313}^{\mathrm{benzene}} = 24$) and **1b** ($\lambda_{\max}^{\mathrm{MeOH}}$ 232 (ε 19260), $\varepsilon_{313}^{\mathrm{benzene}} = 10$), 6.6×10^{-3} mol dm^{-3} of **1a** and 1.6×10^{-2} mol dm^{-3} of **1b** were used.

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