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PHOTOCHEMICAL TRANSFER OF OXYGEN FROM SELENOXIDE TO SULFIDE

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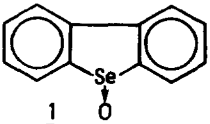
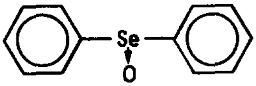
It has recently been known that oxygen liberated photochemically from the pyridine or pyridazine N-oxide is trapped by olefins or sulfide.[1,2] This type of the reaction is interesting from several points of view.[2] We wish to report the first example of photochemical transfer of oxygen from selenoxides (1 and 2) to sulfides.

When a 3:1 mixture of the selenoxide 1 and methyl phenyl sulfide in methanol was irradiated with a high pressure mercury lamp through a Pyrex filter under argon gas for 30 min., methyl phenyl sulfoxide was formed in 87% yield together with deoxygenated dibenzoselenophene (82%) (Scheme 1). Similarly, photolysis of a mixture of 1 and dibutyl or pentamethylene sulfide afforded dibutyl or pentamethylene sulfoxide in good yield, respectively. Yield of these sulfoxides was slightly higher in methanol than in methylene chloride as indicated in Table 1. Photolysis of a mixture of the selenoxide 2 and methyl phenyl sulfide also gave methyl phenyl sulfoxide along with deoxygenated diphenyl selenide (61%). The results are presented in Table 1.

It is to be noted that diphenyl sulfide was unsusceptible to the photooxidation with the selenoxides 1 and 2. In addition, sulfones were not found in any reaction run. The oxidation of methyl phenyl sulfide with the selenoxides 1 and 2 did not occur thermally (below 80°C) in methanol, methylene chlo-

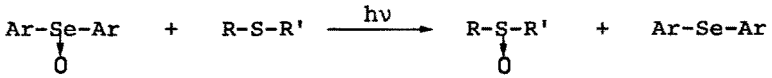


1



2

Scheme 1



$$\mathrm{Ar}-\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{Se}}-\mathrm{Ar} + \mathrm{R{-}S{-}R'} \xrightarrow{h\nu} \mathrm{R}-\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{S}}-\mathrm{R'} + \mathrm{Ar{-}Se{-}Ar}$$

Table 1. The photooxidation of sulfides to sulfoxides with selenoxides.[a]

Selenoxide	Sulfide	Selenoxide/Sulfide (mole/mole)	Solvent	Sulfoxide	Yield
1	PhSMe	3	MeOH	PhSOMe	87%
1	"	3	CH_2Cl_2	"	64%
2	"	2	"	"	40%
1	$n\text{-}Bu_2S$	3	MeOH	$n\text{-}Bu_2SO$	97%
1	"	3	CH_2Cl_2	"	77%
1	$(CH_2)_5S$	3	MeOH	$(CH_2)_5SO$	78%
1	"	3	CH_2Cl_2	"	60%

a) Sulfoxides were separated by means of Alumina TLC and identified by comparison with authentic samples.

ride, or benzene.[3] In contrast to the pyridine or pyridazine N-oxide,[1,2] the selenoxide 2 did not oxidize photochemically olefins such as cyclohexene and stylene.

Molecular oxygen ($^3O_2$ and $^1O_2$) may not be involved in the photooxidation reaction with the selenoxides, since it could not be trapped when the selenoxide 1 was irradiated in the presence of 9,10-diphenylanthracene. In addition, the photooxidation of methyl phenyl sulfide with 2 was not quenched by β-carotene. In view of these facts the following two mechanistic paths for the photochemical transfer of oxygen from the selenoxide to the sulfide may be considered: (i) atomic oxygen[1,2,4] liberated photochemically from the selenoxide reacts with the sulfide; (ii) an excited molecule of the selenoxide interacts with the sulfide to form a bimolecular intermediate which collapses to a sulfoxide and selenide. The fact that the selenoxide 2 did not oxidize photochemically the olefins suggests that atomic oxygen is not involved in the photooxidation of sulfides with the selenoxides 1 and 2.

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