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Favorable effect of *ortho* substituents on selenoxide *syn* elimination of *n*-alkyl aryl selenoxides

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Abstract

n-Alkyl aryl selenides with an *ortho* substituent were found to be superior to the corresponding *para* isomers as starting materials for the preparation of terminal olefins when hydrogen peroxide was used as the oxidant, because the *para* isomers afforded unwanted selenones and a primary alcohol as by-products. © 2000 Elsevier Science Ltd. All rights reserved.

Sharpless¹ and other groups^{2,3} have reported that an electron-withdrawing substituent on the benzene ring accelerated the selenoxide *syn* elimination of alkyl aryl selenoxides, and have recommended the use of *n*-alkyl *o*-nitrophenyl selenides as starting materials for the preparation of terminal olefins. However, the reason why the *o*-nitro derivatives are superior to the corresponding *p*-nitro ones has not been clearly rationalized. In order to clarify this reason, the selenoxide elimination reaction of *n*-alkyl *ortho*-substituted phenyl selenides has been compared with that of the corresponding *para*-substituted isomers using hydrogen peroxide as the oxidant. In this communication, we would like to report on the favorable effect of *ortho* substituents on the selenoxide elimination reaction.

The olefin-forming reaction by the oxidation of alkyl aryl selenides with hydrogen peroxide is a two-step reaction. First, the selenides are oxidized to selenoxides, and then a *syn* elimination reaction of the selenoxides takes place to yield olefins. In order to compare the overall reaction of *n*-alkyl *ortho*-substituted phenyl selenides with that of the *para*-substituted compounds, the progress of the reactions was followed by gas–liquid chromatography (GLC) and ¹H NMR. The reactions were conducted in tetrahydrofuran (THF) as usual, using aryl 1-dodecyl selenides **1a–1g** as the substrates and 30% hydrogen peroxide as the oxidant. In nuclear magnetic resonance (NMR) measurements, however, the reactions were performed in acetone-*d*₆ instead of THF-*d*₈, because non-deuterated THF in the solvent has resonance signals at 3.6–3.9 ppm, which overlap with the signals of the reaction products.

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First, the progress of the reactions was monitored by 270 MHz ^1H NMR. Every reaction rate in the first step (selenide to selenoxide) was not proportional to the product of the concentrations of selenides **1a–1g** and hydrogen peroxide. This is presumably because $\text{ArSe}(\text{O})\text{OOH}$, which formed gradually during the oxidation reaction, catalyzed the reaction in the first step.^{2,4–6} Therefore, the half life ($t_{1/2}$) of each selenide has been used to compare the reaction rates of the first step. The results are given in Table 1. Selenides **1a**, **1b**, **1c** and **1d** have an electron-withdrawing substituent on the benzene ring, and were oxidized to selenoxides more slowly than selenides **1e**, **1f** or **1g**. This could be explained by the fact that an electron-withdrawing substituent on the benzene ring diminishes the electron density of the lone pair of electrons on the selenium atom.^{7,8}

Table 1
Oxidation of selenide with H_2O_2 to selenoxide and its *syn* elimination to olefin in acetone- d_6 ^a

The reaction scheme shows a selenide with a benzene ring substituted with R_1 and R_2 , and a $-\text{Se}(\text{CH}_2)_{11}\text{CH}_3$ group. It reacts with H_2O_2 in acetone- d_6 to form a selenoxide intermediate with a $-\text{Se}(\text{O})(\text{CH}_2)_{11}\text{CH}_3$ group. This intermediate then undergoes *syn* elimination to form a terminal olefin 3 , which is $\text{CH}_2=\text{CH}(\text{CH}_2)_9\text{CH}_3$.

Entry	Selenide			First step	Selenoxide	Second step ^b
	R^1	R^2		$t_{1/2}$ (min)		$k_1 \times 10^3$ (min^{-1})
1	1a	NO_2	H	183	2a	9.7
2	1b	H	NO_2	80	2b	5.2
3	1c	COOCH_3	H	85	2c	7.8
4	1d	H	COOCH_3	138	2d	1.2
5	1e	CH_3	H	31	2e	3.8
6	1f	H	CH_3	10	2f	0.32
7	1g	H	H	29	2g	0.17

^a A mixture of selenide (0.015 mmol), 30% H_2O_2 (0.45 mmol), and benzene (internal standard for quantitative analysis) in acetone- d_6 (0.70 mL) was placed in an NMR tube. The progress of the reaction at 30°C was monitored by 270 MHz ^1H -NMR. ^bSee ref. 10.

According to the literature,¹ a selenide such as **1a**, which has a nitro group at the *ortho* position of the benzene ring, is expected to be the optimal compound for the preparation of terminal olefin **3**. However, this selenide was also the most resistant to oxidation to selenoxide in the first step, and its half life was approximately twice as long as that of *p*-nitro-substituted isomer **1b**. This slow reaction can be compensated by the subsequent fast step. The *syn* elimination reaction of *o*-nitro substituted selenoxide **2a** took place about 1.9 times as fast as that of the *p*-nitro-substituted compound (see below). The rate of olefin formation will be first-order in selenoxides, because *syn* elimination of selenoxides is a unimolecular reaction.⁹ Actually, first-order kinetics were observed for this second step.¹⁰ As can be seen in Table 1, the elimination rate of the selenoxides is faster (**2b** > **2d** > **2f**) if the *para* substituent on the benzene ring is more electron-withdrawing. Such a relationship can be seen in the corresponding *ortho* isomers (**2a** > **2c** > **2e**) and has been pointed out by Sharpless et al.¹

Comparing the elimination rate of each of the *ortho*-substituted selenoxides with that of the corresponding *para*-substituted isomers, the former was faster than the latter (see k_1 in Table 1):

in the case of the nitro substituent, *ortho*-substituted selenoxide **2a** decomposed to the olefin about 1.9 times as fast as *para*-substituted selenoxide **2b**. Similar results were observed both in methoxycarbonyl-substituted (**2c** versus **2d**: 6.5 times) and methyl-substituted selenoxides (**2e** versus **2f**: 12 times). The selenium atoms in the *o*-nitro-substituted and *o*-methoxycarbonyl-substituted selenoxides could be trigonal bipyramidal rather than pyramidal due to the coordination of the substituents with the selenium atoms in the *ortho* position.¹¹ These selenoxides would consequently decompose faster than the corresponding *para* isomers, since the selenoxide oxygen atom is closer to the leaving hydrogen atom in the trigonal bipyramid than in the pyramid structure. This may be the reason why **2a** and **2c** decomposed faster than **2b** and **2d**, respectively. *o*-Methyl-substituted selenoxide **2e**, in which the selenium atom is pyramidal, is sterically more hindered than the *para* isomer and hence would decompose to the products more rapidly in order to relieve the steric strain.

As can be seen in Table 2, the yields of olefin **3** are very high (98%, 97% after 18.5 h) for the oxidation of *o*-nitro- and *o*-methoxycarbonyl-substituted selenides (**1a**, **1c**), whereas in their *para* isomers (**1b**, **1d**) the yields are not as high (79%, 68% after 18.5 h) and a few percent of an unexpected alcohol (1-dodecanol) was detected as a by-product. The same alcohol was also obtained from *p*-methyl-substituted selenide **1f** as well as from unsubstituted selenide **1g**.¹² On the other hand, only trace amounts (less than 0.5%) of the alcohol were found in the reaction mixture of *ortho*-substituted selenides (**1a**, **1c**, **1e**). Eventually, dodecyl 4-tolyl selenone¹³ was isolated from the reaction mixture of selenide **1f**, and decomposed gradually to the alcohol. It is known that treatment of *n*-alkyl aryl selenones with water affords *n*-alkyl alcohols.¹⁴ The structure of the selenone was characterized by NMR and high resolution mass spectroscopy (MS) analyses. The ⁷⁷Se NMR chemical shift of the selenone (996 ppm relative to Me₂Se) was different from that of the related benzeneseleninic acid (ca. 1173 ppm)¹⁵ and close to the chemical shift of selenones (ca. 970 ppm).^{16,17} Meanwhile, in the case of aryl selenoxides with an *ortho* substituent, almost no such side reaction occurred. This is presumably because the *ortho* substituent would obstruct the approach of hydrogen peroxide or arylperseleninic acid to the central selenium atom.

Table 2
Oxidation of aryl dodecyl selenide to 1-dodecene with H₂O₂ in THF^a

	Selenide		1-Dodecene (3)	1-Dodecanol (By-product)
	R ¹	R ²	Yield ^b (Reaction Time/h)	Yield ^b (Reaction Time/h)
1a	NO ₂	H	98% (18.5), 98% (43.5)	0.2% (18.5)
1b	H	NO ₂	79% (18.5), 80% (43.5)	5.4% (18.5)
1c	COOCH ₃	H	97% (18.5), 97% (43.5)	0.5% (18.5)
1d	H	COOCH ₃	68% (18.5), 74% (43.5)	7.8% (18.5)
1e	CH ₃	H	55% (18.5), 86% (41.0)	0.5% (18.5)
1f	H	CH ₃	27% (24.0), 43% (46.0)	5.8% (24.0)
1g	H	H	45% (18.5), 61% (43.5)	8.1% (18.5)

^aA mixture of selenide (0.10 mmol), 30% H₂O₂ (2.0 mmol), and tridecane (internal standard for GLC analysis) in THF (6.0 mL) was stirred in an ice bath for 1 h and allowed to warm to room temperature (ca. 2 h), and then stirring was continued at 25°C. ^bThe yields were determined by GLC after quenching the reaction with a Na₂S₂O₃ solution.

In conclusion, *n*-alkyl aryl selenides with an electron-withdrawing *ortho* substituent on the benzene ring are more suitable compounds than the corresponding *para* isomers for the preparation of terminal olefins, because the selenoxides of the former decompose to the olefins faster than those of the latter, and hardly undergo further oxidation to selenones leading to the production of unwanted primary alcohols. Although the *o*-nitro group in *n*-alkyl aryl selenides is one of the best groups for the preparation of terminal olefins,¹⁸ the *o*-methoxycarbonyl group could also be suitable, since selenide **1c** was converted into terminal olefin **3** in a high yield of 97% after 18.5 h (see Table 2).

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