Asymmetric Selenoxide Elimination Leading to Chiral Allenic Sulfones

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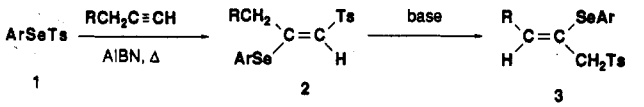
Asymmetric oxidation of some aryl vinyl selenides (**3**) with Sharpless (**A–C**), modified Sharpless (**D**) or David oxidants (**E–G**) resulted in the formation of chiral allenic sulfones **5** of up to 42% enantiomeric excess (ee) *via* double asymmetric induction, *i.e.*, asymmetric oxidation to selenoxide followed by its asymmetric elimination. The nature of aryl group of the selenides **3** showed a remarkable effect upon the ee of the product: *o*-nitrophenyl group (**a**) gave the highest ee, followed by *o,p*-dinitrophenyl (**b**), *o*-(trifluoromethyl)phenyl (**e**), and *o*-methoxyphenyl (**f**) groups, while phenyl (**c**) and 2-pyridyl (**d**) groups were not effective at all. The effects of aryl groups were kinetically analyzed by comparing the rate constants of both steps (k_1 for oxidation step and k_2 for elimination step) which were determined by ^{1}H-NMR analysis of the concentration of **3**, the intermediate selenoxides **4**, and **5**. As a result, it was disclosed that the ratio of these rate constants (k_1/k_2) was closely related to the ee of the product; the smaller the ratio is, the larger the ee becomes.

Introduction

Organoselenium methodology has already been established in the field of synthetic organic chemistry,[1] and yet its application to asymmetric synthesis is very limited.[2] Thus, although there have been many reports[2a,3] on the isolation of chiral stable selenoxides since 1983[3a] and an almost complete stereoselective oxidation of selenides to chiral selenoxides was accomplished quite recently,[4] the application of such chiral selenoxides to asymmetric induction is only limited to [2,3] sigmatropic rearrangement leading to allylic alcohols.[3b,4,5] Other examples of asymmetric synthesis involving organoselenium compounds are asymmetric selenenylations of various organic substrates such as alkenes, epoxides, and α,β-unsaturated carbonyl compounds,[2b,6] and a good stereoselectivity was achieved recently by using optically active binaphthylselenium compounds,[7] but the chemistry does not yet seem to be so practical from the viewpoint of organic synthesis. We now describe the first example of asymmetric selenoxide elimination[8] which was applied to the synthesis of chiral allenic sulfones from some aryl vinyl selenides. As to the chiral allene synthesis of current interest,[9] most of the stereochemical courses were through propargylic rearrangement; namely, the chirality of the carbon adjacent to the acetylene group was induced into the allenic skeleton. Therefore, the method of double asymmetric induction presented here, *i.e.*, asymmetric oxidation of aryl vinyl selenides followed by asymmetric selenoxide elimination, may open a new synthetic route to chiral allenes. Furthermore, our finding may add a new methodology for asymmetric elimination[10] which has so far been carried out generally by enantioselective deprotonation using chiral bases.[11]

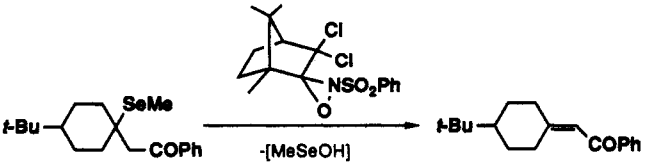
Scheme I



1 2 3

Results and Discussion

Aryl vinyl selenides **3** were synthesized by the radical addition of aryl selenosulfonates **1** to acetylenes followed by base (Et_3N or *t*-BuOK)-promoted isomerization according to the reported method (Scheme I).[12] The products were formed as nearly pure geometric isomers, and they were easily purified by flash column chroma-



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(5) Reich, H. J.; Yelm, K. E. *J. Org. Chem.* **1991**, *56*, 5672.
(6) For example: (a) Pluim, H.; Wynberg, H. *Tetrahedron Lett.* **1979**, *20*, 1251. (b) Hiroi, K.; Sato, S. *Synthesis* **1985**, 635. (c) Paulmier, C.; Outurquin, F.; Plaquevent, J.-C. *Tetrahedron Lett.* **1988**, *29*, 5889.
(7) (a) Tomoda, S.; Iwaoka, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1283; (b) *Chem. Lett.* **1988**, 1895. (c) Tomoda, S.; Fujita, K.; Iwaoka, M. *J. Chem. Soc., Chem. Commun.* **1990**, 129. (d) Fujita, K.; Iwaoka, M.; Tomoda, S. *Chem. Lett.* **1992**, 1123.
(8) Preliminary communication: Komatsu, N.; Nishibayashi, Y.; Sugita, T.; Uemura, S. *J. Chem. Soc., Chem. Commun.* **1992**, 46.
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(10) Recently we succeeded in the synthesis of axially chiral cyclohexylidene derivatives of up to 83% ee by the following Davis oxidation: Komatsu, N.; Matsunaga, S.; Sugita, T.; Uemura, S. *J. Am. Chem. Soc.*, in press.
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(12) (a) Back, T. G.; Krishna, M. V.; Muralidharan, K. R. *J. Org. Chem.* **1989**, *54*, 4146. (b) Back, T. G.; Krishna, M. V. *J. Org. Chem.* **1987**, *52*, 4265.

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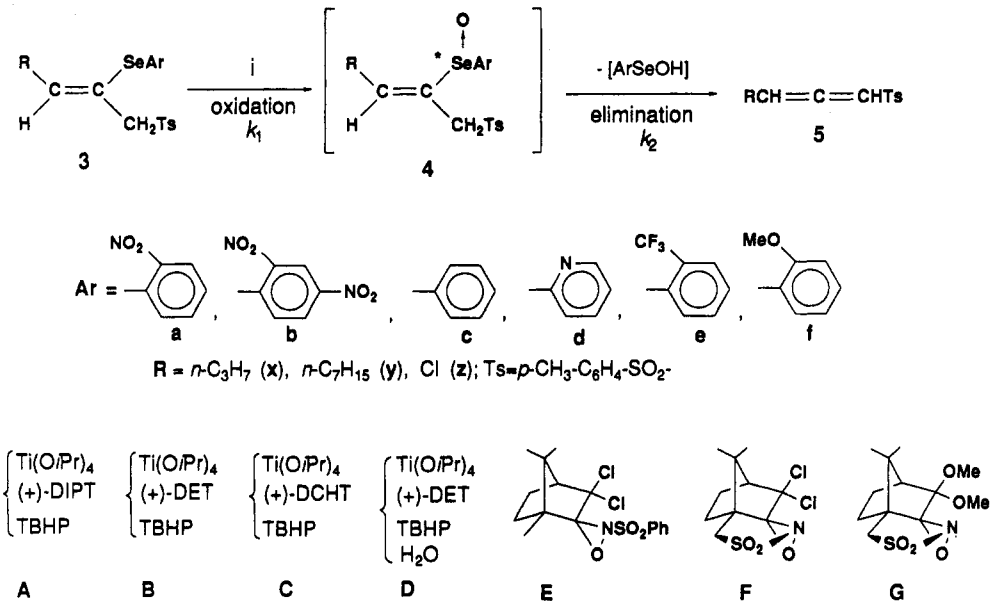
Scheme II



tography. The *Z* configuration of the major products was confirmed in comparison with the reported data of **3cx** and **3cz**.[12] All the major products except **3az** showed the ^{1}H-NMR signals attributable to the vinylic and sulfone-substituted methylene protons in the higher field than those of the minor isomers, traces of which were detected by ^{1}H-NMR. The compound **3az** showed the vinylic proton in the lower field and the methylene protons in the higher field than those of its minor isomer. Their spectral relationships were in accordance with those reported for the compounds **3cx** and **3cz**,[12] respectively. Oxidation of **3** with Sharpless (**A–C**),[13] modified Sharpless (**D**),[14] or Davis (**E–G**)[15] oxidants produced chiral allenes (**5**) in a high chemical yield with a moderate ee (up to 42%) (Scheme II). The ee of the product[16] was determined either by HPLC using a Daicel Chiralcel OF column or ^{1}H-NMR using a chiral shift reagent. The configuration was determined by optical rotation.[17] Typical results under various reaction conditions are summarized in Table I. The highest ee was obtained within our attempted experiments when 2-((*o*-nitrophenyl)seleno)-1-(*p*-toluenesulfonyl)-2-hexene (**3ax**) was oxidized by Sharpless oxidant (**C**) in CH_2Cl_2 at 0 °C (42% ee, run 10). These reactions are generally very slow (4–23 days), and the reactivity of substrates having an *ortho*-substituent in an aryl group (**a**, **b**, **e**, and **f**) was lower than that having no substituent (**c** and **d**).

The Effect of Substrate (Ar and R). Six aryl selenides (**a–f**) were examined, and the nature of a substituent on aryl groups was revealed to give a remarkable effect upon the stereochemical results. Results of runs 1, 31, 35, 38, 42, and 43 of Table I indicate that the *o*-nitrophenyl group (**a**) was most effective for this asymmetric induction, the effectiveness being followed by *o*,*p*-dinitrophenyl (**b**), *o*-(trifluoromethyl)phenyl (**e**), and *o*-methoxyphenyl (**f**) groups, while phenyl (**c**) and 2-pyridyl (**d**) groups were not effective at all. Namely, the presence of a bulky substituent at an *ortho*-position (**a**, **b**, **e**, and **f**) is essential for this asymmetric induction and, further, a strong electron-withdrawing nature of a substituent is preferable (**a**, **b** > **e** > **f**): therefore, the presence of a strong electron-withdrawing substituent at an *ortho*-position of phenyl ring is necessary to obtain a high ee value. The reason why the *o*,*p*-dinitrophenyl (**b**) group showed a less effect on the increase of the ee value than the *o*-nitrophenyl (**a**) group will be discussed later by considering the kinetic data.

This reaction involves two successive asymmetric inductions; *i.e.*, asymmetric oxidation of the vinyl selenides **3** to the chiral selenoxides **4** followed by its asymmetric elimination. The asymmetric induction from the chiral oxidant to allenic sulfones **5** is accomplished only when the following three conditions were satisfied; a stereoselective oxidation of **3** to **4**, a slow racemization of the resulted selenoxide intermediates **4**, and a stereoselective recognition of the prochiral proton in the selenoxide elimination to **5**.

A chiral selenoxide, a key intermediate in this asymmetric induction, is known to easily racemize even with a small amount of water,[2a,3b,4] and the rate of racemization is much accelerated under the acidic conditions.[2a,3d] Recently, we observed that the titanium complex of Sharpless oxidant promoted the racemization of a chiral selenoxide intermediate as a Lewis acid catalyst, and an almost racemized product was obtained in the application of asymmetric selenoxide elimination leading to cyclohexylidene derivatives.[10] Thus, in the case of Sharpless oxidant, this oxidation system may promote the racemization of the stereochemically unstable selenoxide **4** as a Lewis acid catalyst to diminish the enantioselectivity of this asymmetric induction. However, it is well-known that the bulky substituents at the *ortho*-position of the arylseleno moiety stabilize the selenoxides sterically to make the isolation of chiral selenoxides possible.[2a,4] In our oxidation system the introduction of the *o*-nitro group satisfied this condition. It might also be possible that the interaction between the oxygen of NO_2 group and the

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Table I. Asymmetric Synthesis of Allenic Sulfones from Aryl Vinyl Selenoxides

run	substrate Ar	substrate R	oxidant	solvent	condns, time (days) (temp. (°C))	yield[a] (%)	ee[b] (%)	config
1	a	x	A	CH_2Cl_2	19 (0)	43	38	*R*
2	a	x	A[c]	CH_2Cl_2	19 (0)	68	34	*S*
3	a	x	A	CH_2Cl_2[d]	20 (0)	60	37	*R*
4	a	x	A	toluene	19 (0)	55	24	*R*
5	a	x	A	$ClCH_2CH_2Cl$	18 (0)	58	38	*R*
6	a	x	A	CCl_4	18 (0)	60	17	*R*
7	a	x	B	CH_2Cl_2	16 (0)	72	21	*R*
8	a	x	B[c]	CH_2Cl_2	18 (0)	55	25	*S*
9	a	x	B	ether	16 (0)	52	21	*R*
10	a	x	C	CH_2Cl_2	19 (0)	85	42	*R*
11	a	x	D	CH_2Cl_2	19 (0), 4 (rt)	42	1	*S*
12	a	x	E	CH_2Cl_2	15 (rt)	41	28	*R*
13	a	x	F	CH_2Cl_2	15 (rt)	26	23	*R*
14	a	x	G	CH_2Cl_2	15 (rt)	9	15	*S*
15	a	y	A	CH_2Cl_2	19 (0)	59	38	*R*
16	a	y	B	CH_2Cl_2	17 (0)	72	18	*R*
17	a	y	B	toluene	18 (0)	69	20	*R*
18	a	y	B	$ClCH_2CH_2Cl$	18 (0)	53	16	*R*
19	a	y	E	CH_2Cl_2	4 (rt), 15 (30)	[e]	20	*R*
20	a	y	E	CH_2Cl_2[d]	20 (rt)	[e]	24	*R*
21	a	y	E	$ClCH_2CH_2Cl$	18 (rt)	[e]	15	*R*
22	a	y	E	CCl_4	19 (rt)	[e]	17	*R*
23	a	y	E	THF	18 (rt)	[e]	13	*R*
24	a	y	F	CH_2Cl_2	4 (rt)	16	23	*R*
25	a	y	F	CH_2Cl_2	13 (0)	28[f]	20	*R*
26	a	y	G	CH_2Cl_2	4 (rt)	16	17	*S*
27	a	y	G	CH_2Cl_2	13 (0)	44[f]	13	*S*
28	a	z	A	CH_2Cl_2	19 (0)	41	5[g]	*R*
29	a	z	B	CH_2Cl_2	18 (0)	78	10[g]	*S*
30	a	z	D	CH_2Cl_2	18 (0)	32[f]	16[g]	*R*
31	b	x	A	CH_2Cl_2	19 (0)	55	20	*R*
32	b	x	B	CH_2Cl_2	17 (0)	59	21	*R*
33	b	x	F	CH_2Cl_2	16 (rt)	16	7	*R*
34	b	x	G	CH_2Cl_2	16 (rt)	23	9	*S*
35	c	x	B	CH_2Cl_2	1 (−20), 3 (rt)	73	1	*S*
36	c	y	B	CH_2Cl_2	9 (0)	70	2	*S*
37	c	z	B	CH_2Cl_2	7 (0)	86	2[g]	*S*
38	d	x	B	CH_2Cl_2	13 (0)	52	1	*R*
39	d	x	E	CH_2Cl_2	15 (rt)	37	9	*R*
40	d	x	F	CH_2Cl_2	14 (rt)	37	4	*S*
41	d	x	G	CH_2Cl_2	14 (rt)	39	5	*S*
42	e	x	A	CH_2Cl_2	19 (0)	100	16	*R*
43	f	x	A	CH_2Cl_2	10 (0)	76	5	*S*
44	f	x	E	CH_2Cl_2	14 (rt)	74[f]	4	*R*
45	f	x	F	CH_2Cl_2	14 (rt)	87[f]	6	*S*

[a] Isolated yield. [b] Determined by HPLC using a Daicel Chiralcel OF column unless otherwise mentioned. [c] (−)-Tartrate was used instead of (+)-tartrate. [d] Treated with K_2CO_3 before use. [e] The imine derived from oxaziridine was contaminated. [f] The values for crude products. [g] Determined by ^{1}H-NMR using Eu(hfc)$_3$.

selenium of the intermediate selenoxide slows the racemization. As another example we showed recently that the introduction of the *o*-nitro group to the arylseleno moiety remarkably enhanced the enantioselectivity in the asymmetric [2,3] sigmatropic rearrangement of aryl cinnamyl selenides *via* the corresponding selenoxides to 1-phenyl-2-propen-1-ol with Sharpless oxidants.[18]

The elimination step may be considered to proceed almost without loss of ee because the high enantioselectivity (up to 83% ee) was accomplished in the asymmetric Davis oxidation of cyclohexyl methyl selenides leading to cyclohexylidene derivatives[10] and because the highest value of chiral selenoxides obtained by the Sharpless oxidation reported hitherto was 33% ee.[2a,3f]

As to the nature of the R group of the substrate, *n*-propyl (**x**) and *n*-heptyl (**y**) showed a similar property, but with Cl (**z**) the obtained ee was generally lower (runs 28–30).

The Effect of Oxidant. Among Sharpless oxidants (**A**–**C**), **A** and **C** were effective (38% ee of run 1 and 42% ee of run 10, respectively), while in the case of **B** the obtained ee value was sensitive to the type of the substrate; sometimes almost the same with **3bx** (runs 31 and 32), while ee was lower with **3ax** (runs 7 *vs* 1 and 10). The use of modified Sharpless oxidant **D**, which resulted in an almost complete asymmetric induction in the oxidation of sulfides to sulfoxides,[14] gave only a racemic product (run 11) probably because the racemization of the chiral selenoxide (**4**) *via* its hydrate is accelerated by the water added.[2a,3b] The allenic sulfones of opposite configuration were obtained by using (−)-tartrate instead of (+)-tartrate (compare run 1 with run 2 and also run 7 with run 8). These variable enantioselectivities, in the case of Sharpless oxidant, may be attributed to the variable asymmetric oxidation ability of Sharpless oxidants, its Lewis acidity to racemize the chiral selenoxide intermediate,[10] and the *ortho*-substituents of the arylseleno moiety diminishing the racemization of the selenoxide intermediate sterically and electronically.

The lower oxidation rate and yet the higher ee value of the product were reported with Davis oxidant than Sharpless oxidant in the sulfide oxidation.[4,14,15d] With Davis oxidants (**E**–**G**) in our oxidation system, however, the ee was not so high unfortunately and the reaction rate was much slower than that with Sharpless oxidants. Further, with the oxidants **E**–**G** the isolation of the product was sometimes difficult due to the contamination of the imine derived from the oxidant. These results show that Davis oxidants are less effective for this asymmetric induction. In the case of Davis oxidant, the selenoxide intermediate may not be racemized so easily as in the case of Sharpless oxidant because of its aprotic nature.[15d] Actually, Davis oxidant gave axially chiral cyclohexylidene derivatives with a high enantioselectivity (up to 83% ee), while Sharpless oxidant gave merely an almost racemized product.[10] Nevertheless, Davis oxidant did not give so high enantioselectivity as Sharpless oxidant (runs 1 *vs* 12 and 15 *vs* 20). It is probably due to the lower stereoselectivity of Davis oxidant to the selenide **3** than Sharpless oxidant. With the compound **3dx** having no substituent at the *ortho* position of arylseleno moiety, poor stereoselectivities of the range of 4–9% (runs 39–41) were obtained. This fact indicates that the chirality of selenoxides without protection by a bulky group is lost even under the anhydrous conditions during such a long reaction time as several days, although it is known that the high level of the chirality of methyl phenyl selenoxide can be kept within a short time.[4] Moreover, these results (runs 39–41), compared with the almost racemized product obtained with the Sharpless oxidation (run 38), support that Davis oxidant does not induce the racemization of the selenoxide intermediates so easily as Sharpless oxidant.

The Effect of Solvent. The effect of various solvents such as CH_2Cl_2, CCl_4, $ClCH_2CH_2Cl$, toluene, diethyl ether, and tetrahydrofuran (THF) upon the ee value was examined using **A**, **B**, and **E** as oxidants and **3ax** and **3ay** as substrates. In the case of the oxidant **A** (runs 1 and 3–6) the solvent showed a marked effect on the stereochemical results, while in the cases of oxidants **B** and **E** the obtained ee values were almost the same through the examined solvents (**B**, runs 7, 9, and 16–18; **E**, runs 19–23). Both CH_2Cl_2 (runs 1, 7, 16, and 19) and $ClCH_2CH_2Cl$ (runs 5, 18, and 21) were revealed to be the solvent of choice for this asymmetric induction. Treatment of CH_2Cl_2 with K_2CO_3[4] to remove the acid, which might accelerate

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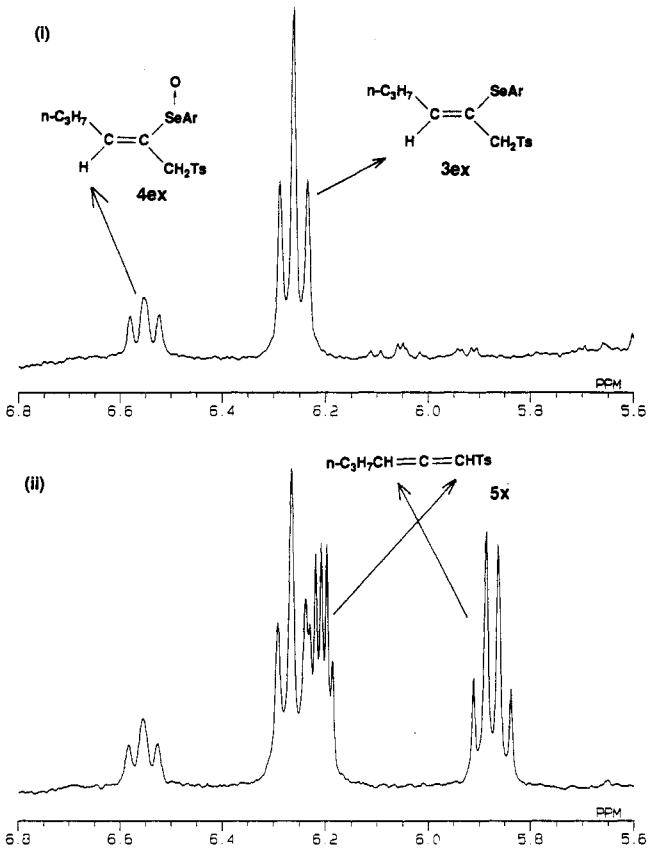

Figure 1. ^{1}H-NMR monitoring of the reaction of **3ex** with oxidant **A**: (i) after 3.5 h, (ii) after 9 days.

the racemization of the produced chiral selenoxide,[2a] did not show almost any effect in the oxidation using either **A** or **B**.

Determination of Rate Constants (k_1 and k_2). In order to clarify the effect of the nature of aryl groups (**a–f**) upon this oxidation, the rate constants of both the oxidation step (k_1) and the elimination step (k_2) were determined by monitoring the concentration of vinyl selenides **3**, selenoxides **4**, and allenic sulfones **5** by ^{1}H-NMR. Six substrates (**3ax–3fx**) were oxidized by Sharpless oxidant **A** in CD_2Cl_2 at 0 °C. The selenoxide intermediate **4ex** in the oxidation of **3ex** was recognized clearly by the appearance of the vinyl proton at δ 6.50 (t) in ^{1}H-NMR analysis, while two vinylic protons assignable to the allenic sulfone appeared at δ 5.95 (q) and 6.20 (q) as exemplified in Figure 1. The relative concentration was obtained by determining the value of the integral of specific peaks derived from each component. Figure 2 illustrates the representative time course of relative concentration of **3bx**, **4bx**, and **5x**. The rate constants k_1 and k_2 were determined from the initial slope in the log [**3bx**] *vs* reaction time plot and the slope in the log [**4bx**] *vs* reaction time plot at the later stage, respectively. The rate constants k_1 and k_2 and the ratio k_1/k_2 for each substituent are summarized in Table II. Although the values of k_1 are determined from the limited data, they are considered to be adequate as a pseudo-first-order rate constant and for relative comparisons.

If we compare the results of run 1 with run 2 and also run 3 with run 4 of Table II it is clear that k_1 becomes 2.2–2.3 times larger by the introduction of an electron-withdrawing group. Similarly, k_2 also becomes 1.7–1.8 times larger. These facts indicate that the rate of both oxidation and elimination steps were accelerated by the

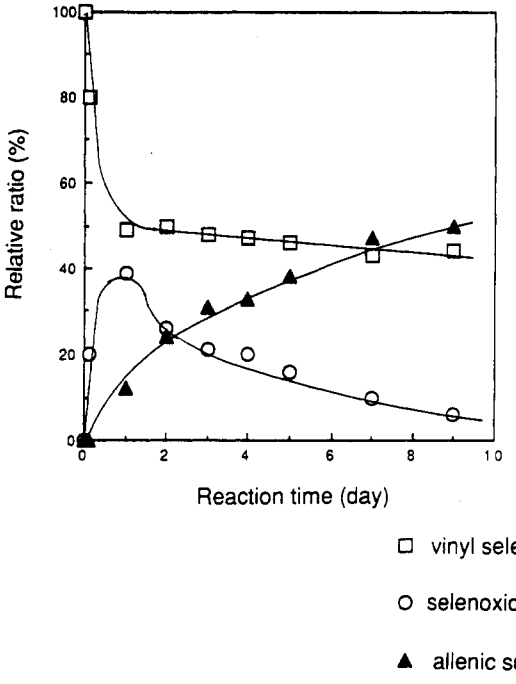

Figure 2. Relative concentration of **3bx**, **4bx**, and **5x** *vs* reaction time.

Table II. Rate Constants of the Oxidation and Elimination Steps with the Selenide 3x[a]

run	substrate Ar	k_1 (10^{-3} s^{-1})	k_2 (10^{-4} s^{-1})	k_1/k_2	ee (%)
1	**a**	0.52 (0.37)	1.0 (0.50)	5.2 (0.74)	38
2	**b**	1.2 (0.86)	1.8 (0.90)	6.7 (0.96)	20
3	**c**	1.4 (1.0)	2.0 (1.0)	7.0 (1.0)	1
4	**d**	3.1 (2.2)	3.3 (1.7)	9.4 (1.3)	1
5	**e**	0.93 (0.66)	1.1 (0.55)	8.5 (1.2)	16
6	**f**	0.84 (0.60)	0.87 (0.44)	9.7 (1.4)	5

[a] The relative values of rate constants to a phenyl selenide (**3cx**) are indicated in parentheses.

introduction of an electron-withdrawing substituent. Such acceleration has been known in the total selenoxide elimination[19a] as well as in the selenoxide elimination step of alkyl aryl selenides.[19b] On the other hand, by comparing runs 3 and 4 with runs 1, 2, 5, and 6 of Table II, both rate constants in the cases of nonsubstituted aryl groups (**c** and **d**; runs 3 and 4) are larger than those of substituted ones (**a**, **b**, **e**, and **f**; runs 1, 2, 5, and 6). Namely, the rates of both oxidation and elimination steps are suppressed sterically by the introduction of an *ortho*-substituent even of an electron-withdrawing group. The discrepancy of these results with the reported results on alkyl aryl selenides[19b] might be ascribed to the less flexibility in aryl vinyl selenides and selenoxides than alkyl aryl selenides and selenoxides. The 2-pyridyl group (run 4), which has been shown to be a better leaving group than the phenyl group in several synthetic reactions,[20] was proven kinetically for the first time to have an excellent ability of acceleration of both oxidation and elimination steps, probably due to its electron-withdrawing nature and yet the absence of sterically large substituent at the *ortho*-position.

The Relationship between Rate Constants and ee Values. The k_1/k_2 value is thought to be the index of the

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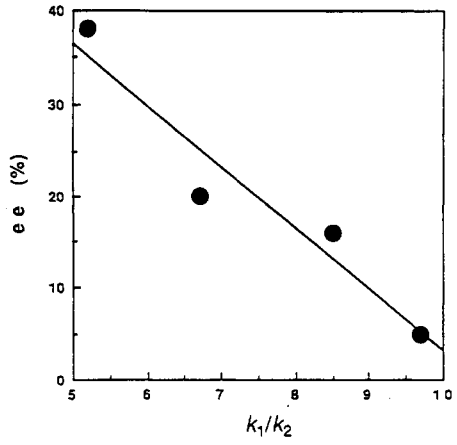

Figure 3. Ee (%) *vs* k_1/k_2 of runs 1, 2, 5, and 6 of Table II.

concentration of the intermediate selenoxide (4), a smaller value being correspondent to a lower concentration of 4. Although the titanium complex of Sharpless oxidant tends to promote the racemization of the chiral selenoxide intermediates as discussed above, the chance for the racemization resulting in a lowering of ee value should be lower in the case of smaller k_1/k_2 value. In fact, as shown in Table II, the comparison of the data of runs 1, 2, 5, and 6, where the aryl group has an *ortho*-substituent, clearly shows that the smaller the k_1/k_2 value is the larger the ee value becomes. That may be the reason why the *o,p*-dinitrophenyl group showed a less enantioselectivity than the *o*-nitrophenyl group (compare the k_1/k_2 values of runs 1 and 2). An almost linear relationship was found between the k_1/k_2 value and ee of the product allenic sulfones within the range examined in the present study as shown in Figure 3. It is also worth noting that almost similar k_1/k_2 values were obtained in runs 2 and 3 and also in runs 4–6, respectively, and yet a quite different stereochemical results were observed in each case, further racemic allenic sulfones being obtained (runs 3 and 4). This fact indicates that a bulky substituent at the *ortho*-position of an aryl group is essential for this asymmetric induction, probably because the bulky group suppresses sterically the racemization of the intermediate chiral selenoxides 4 as discussed above.

In a summary, the following points were clarified. (1) The first example of asymmetric selenoxide elimination to produce chiral allenic sulfones (up to 42% ee) was presented in the oxidation of some aryl vinyl selenides with Sharpless and Davis chiral oxidants. (2) The rate constants of each of the oxidation (k_1) and elimination (k_2) steps were determined separately by monitoring the specific protons in ^{1}H-NMR, and the marked effect of an *ortho*-substituent on aryl group was disclosed kinetically. (3) A linear relationship was found between the ratio of the above two rate constants (k_1/k_2) and the obtained ee value within the range examined in this work.

Experimental Section

General Procedures. ^{1}H (270 MHz) and ^{13}C NMR (67.5 MHz) spectra were obtained with a JEOL GSX-270 spectrometer in $CDCl_3$ with Me_4Si as an internal standard unless otherwise noted. Chemical shifts are reported in δ units downfield from the internal reference Me_4Si. The coupling constants (J) are in hertz (Hz), and those of ^{13}C-NMR were shown only in the case of C–F coupling. IR spectra were recorded on Hitachi EPI-G2 infrared spectrophotometer as KBr pellets. Melting points were determined with a Yanaco MP-J3 apparatus and were uncorrected. Optical rotations were measured on a JASCO DIP-360 polarimeter. Flash chromatography was performed by a variation of the reported method[21] with Wakogel C-300 as silica gel. Column chromatography and preparative TLC to isolate the allenic sulfone (5) were performed with Florisil 100–200 mesh (Nacalai tesque) and 20 × 20-cm silica gel 60 F_{254} PLC plates (Merck), respectively.

Materials. The chlorinated solvents and toluene were distilled from CaH_2 and stored over molecular sieves (4A) under nitrogen. The ether solvents were distilled from $LiAlH_4$ and stored similarly. *tert*-Butyl hydroperoxide (TBHP) in toluene and (+)-dicyclohexyl tartrate (DCHT) were prepared according to the reported methods.[22] $Ti(OiPr)_4$ and the other tartrates were purified by distillation and stored under nitrogen. Davis oxidants (**E–G**) were prepared according to the reported methods.[15]

Preparation of Selenosulfonates 1. All the selenosulfonates 1 were prepared by the reaction of the corresponding areneseleninic acid with commercial *p*-toluenesulfone hydrazide and purified by recrystallization from benzene–hexane.[23] The areneseleninic acids were prepared by the treatment of diaryl diselenides with H_2O_2.[24] Several new areneseleninic acids were isolated as a white solid: *o*-methoxybenzeneseleninic acid, IR 1120, 750, 640, 540 cm^{-1}; ^{1}H-NMR (in $CDCl_3$ + dimethyl sulfoxide-d_6) δ 6.85–8.20 (m, 5H), 3.93 (s, 3H); 62% yield; *o*-(trifluoromethyl)benzeneseleninic acid, mp 128–130 °C. Anal. Calcd for $C_7H_5F_3O_2Se$: C, 32.71; H, 1.96; F, 22.17. Found: C, 32.62; H, 1.80; F, 22.23. 80% yield. 2-Pyridineseleninic acid[25] and *Se*-(2-pyridyl) *p*-tolueneselenosulfonate (**1d**) were either very hygroscopic or unstable in air and immediately used after preparation for the next reaction without any purification. All the diaryl diselenides except for the commercially available diphenyl diselenide were prepared according to the reported methods; bis(*o*-nitrophenyl) diselenide,[26] bis(*o,p*-dinitrophenyl) diselenide,[26] bis(2-pyridyl) diselenide,[20b] bis(*o*-(trifluoromethyl)-phenyl) diselenide[27] and bis(*o*-methoxyphenyl) diselenide.[28]

Some physical, spectroscopic, and analytical data of bis(*o*-(trifluoromethyl)phenyl) diselenide and all the areneselenosulfonates (1) except **1c**[23] were as follows. The yield of 1 was based on the corresponding areneseleninic acid.

Bis(*o*-(trifluoromethyl)phenyl) Diselenide. The compound was prepared from *o*-(trifluoromethyl)aniline *via* *o*-(trifluoromethyl)selenocyanate:[29] mp 76–77 °C; ^{1}H-NMR δ 7.89 (2H, d, J = 7.7), 7.60–7.63 (2H, m), 7.30–7.44 (4H, m); ^{13}C-NMR δ 133.64 (d), 132.72 (d), 129.56 (q, J = 31.2), 128.58 (s), 127.51 (d), 126.61 (q, J = 6.2), 123.90 (q, J = 274.1). Anal. Calcd for $C_{14}H_8F_6Se_2$: C, 37.52; H, 1.80; F, 25.44. Found: C, 37.79; H, 1.73; F, 25.65. Yield 27% based on *o*-(trifluoromethyl)aniline.

***Se*-(*o*-Nitrophenyl) *p*-tolueneselenosulfonate (1a):** mp 152–155 °C (dec sealed tube); ^{1}H-NMR δ 8.35–8.40 (1H, m), 8.13–8.17 (1H, m), 7.64–7.74 (3H, m), 7.48–7.54 (1H, m), 7.26–7.30 (2H, m), 2.42 (3H, s); ^{13}C-NMR δ 145.68 (s), 142.29 (s), 134.44 (d), 132.33 (d), 129.91 (d), 129.10 (d), 128.10 (s), 127.18 (s), 127.18 (d), 125.84 (d), 21.71 (q). Anal. Calcd for $C_{13}H_{11}NO_4SSe$: C, 43.83; H, 3.11; N, 3.93. Found: C, 43.66; H, 3.14; N, 4.14. Yield 90%.

***Se*-(*o,p*-Dinitrophenyl) *p*-tolueneselenosulfonate (1b):** mp 114–115 °C; ^{1}H-NMR δ 9.03 (1H, d, J = 2.5), 8.69 (1H, d, J = 8.8), 8.50 (1H, dd, J = 8.8, 2.4), 7.81 (2H, d, J = 8.3), 7.36 (2H, d, 8.3), 2.45 (3H, s); ^{13}C-NMR δ 147.16 (s), 146.61 (s), 146.12 (s), 141.59 (s), 137.67 (s), 131.89 (d), 130.31 (d), 127.98 (d), 127.40 (d), 121.22 (d), 21.78 (q). Anal. Calcd for $C_{13}H_{10}N_2O_6SSe$: C, 38.91; H, 2.52; N, 6.98. Found: C, 38.86; H, 2.46; N, 7.08. Yield, 25%.

***Se*-(*o*-(Trifluoromethyl)phenyl) *p*-tolueneselenosulfonate (1e):** mp 101–102 °C; ^{1}H-NMR δ 8.00–8.03 (1H, m), 7.68–7.71 (1H, m), 7.57–7.62 (2H, m), 7.38–7.41 (2H, m), 7.17 (2H, d, J =

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8.1), 2.39 (3H, s); ^{13}C-NMR δ 145.06 (s), 142.84 (s), 140.54 (d), 133.40 (q, J = 31.1), 132.57 (d), 130.90 (d), 129.41 (d), 127.07 (s), 126.94 (d), 126.83 (d), 122.87 (q, J = 274.0), 21.62 (q). Anal. Calcd for $C_{14}H_{11}F_3O_2SSe$: C, 44.33; H, 2.93; F, 15.03. Found: C, 44.12; H, 2.75; F, 14.93. Yield, 62%.

***Se*-(*o*-Methoxyphenyl) *p*-tolueneselenosulfonate (1f)**: mp 104–105 °C; ^{1}H NMR δ 7.62–7.65 (1H, m), 7.41–7.48 (3H, m), 7.18–7.21 (2H, m), 6.93–6.99 (1H, m), 6.82–6.85 (1H, m), 3.53 (3H, s), 2.41 (3H, s); IR (KBr disk) 1120, 750, 640, 560 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_3SSe$: C, 49.27; H, 4.13. Found: C, 49.18; H, 4.12. Yield, 57%.

Preparation of Vinyl Selenides 3. All the vinyl selenides **3** were prepared according to the reported method.[12] In the cases of new compounds listed below, the crude vinyl sulfones **2** were directly isomerized into vinyl selenides **3** by the treatment with Et_3N in $CHCl_3$ at reflux temperature for 2–20 h, and the formation of the selenides was monitored with TLC and/or ^{1}H-NMR, while in the case of **3ex** *t*-BuOK and THF were used as noted below. The products consisted of an almost single isomer, but a trace of the other isomer was recognized from the ^{1}H-NMR spectral analysis. The obtained vinyl selenides **3** were purified by flash column chromatography (10–30% AcOEt/hexane as eluent) and recrystallization from $CHCl_3$–hexane. On the flash column chromatography, the minor isomer eluted faster than the major isomer in any case. The order of the elution indicated the major products to be *Z* isomers; *i.e.*, the less polar *E* isomer was eluted faster than the more polar *Z* isomer.[12] The *Z* configuration of the major products were also confirmed by their ^{1}H-NMR data as described in the text. The yield is based on the selenosulfonate **1** except for otherwise mentioned. The ^{1}H-NMR chemical shifts attributed to the vinylic and sulfone-substituted protons of the *E* isomer are added to the data of *Z* isomer listed below.

(*Z*)-2-((*o*-Nitrophenyl)seleno)-1-(*p*-toluenesulfonyl)-2-hexene (3ax): mp 114–115 °C; ^{1}H-NMR δ 7.30–8.29 (8H, m), 6.56 (1H, t, J = 7.3), 4.09 (2H, s), 2.47 (3H, s), 2.29 (2H, dt, J = 7.3, 7.7), 1.43 (2H, tq, J = 7.7, 7.3), 0.90 (3H, t, J = 7.3); ^{13}C-NMR δ 153.20 (d), 146.28 (s), 145.09 (s), 135.47 (s), 134.09 (d), 132.13 (s), 129.74 (d), 129.56 (d), 128.57 (d), 126.44 (d), 126.24 (d), 117.77 (s), 65.68 (t), 34.82 (t), 21.84 (t), 21.58 (q), 13.72 (q). Anal. Calcd for $C_{19}H_{21}NO_4SSe$: C, 52.05; H, 4.83; N, 3.19. Found: C, 52.02; H, 4.76; N, 3.08. Yield, 59%. **(*E*)-3ax**: ^{1}H-NMR δ 6.62 (1 H, t), 4.19 (2H, s).

(*Z*)-2-((*o*-Nitrophenyl)seleno)-1-(*p*-toluenesulfonyl)-2-decene (3ay): mp 83–84 °C; ^{1}H-NMR δ 7.30–8.28 (8H, m), 6.52 (1H, t, J = 7.3), 4.10 (2H, s), 2.46 (3H, s), 2.29 (2H, q, J = 7.3), 1.23–1.39 (10H, m), 0.86 (3H, m); ^{13}C-NMR δ 153.42 (d), 146.54 (s), 145.20 (s), 135.50 (s), 133.82 (d), 132.22 (s), 129.78 (d), 129.74 (d), 128.72 (d), 126.57 (d), 126.17 (d), 117.64 (s), 65.73 (t), 33.01 (t), 31.72 (t), 29.15 (t), 29.03 (t), 28.62 (t), 22.61 (t), 21.67 (q), 14.08 (q). Anal. Calcd for $C_{23}H_{29}NO_4SSe$: C, 55.85; H, 5.92; N, 2.83. Found: C, 55.56; H, 5.85; N, 2.77. Yield, 29%. **(*E*)-3ay**: ^{1}H-NMR δ 6.62 (1H, t), 4.17 (2H, s).

(*Z*)-3-Chloro-2-((*o*-nitrophenyl)seleno)-1-(*p*-toluenesulfonyl)-2-propene (3az): mp 126–129 °C; ^{1}H-NMR δ 7.30–7.69 (8H, m), 7.12 (1H, s), 4.17 (2H, s), 2.48 (3H, s); ^{13}C-NMR δ 145.78 (s), 136.60 (d), 135.13 (s), 134.77 (s), 134.06 (d), 130.23 (s), 130.13 (d), 130.02 (d), 128.64 (d), 126.78 (d), 126.55 (d), 122.10 (s), 63.60 (t), 21.71 (q). Anal. Calcd for $C_{16}H_{14}ClNO_4SSe$: C, 44.61; H, 3.28; Cl, 8.23; N, 3.25. Found: C, 44.66; H, 3.21; Cl, 8.17; N, 3.21. Yield, 55%. **(*E*)-3az**: ^{1}H-NMR δ 7.04 (1H, s), 4.38 (2H, s).

(*Z*)-2-((*o*,*p*-Dinitrophenyl)seleno)-1-(*p*-toluenesulfonyl)-2-hexene (3bx): mp 165–167 °C; ^{1}H-NMR δ 9.12 (1H, d, J = 2.4), 8.25 (1H, dd, J = 2.5, 8.8), 7.71 (2H, d, J = 8.3), 7.61 (1H, d, J = 8.8), 7.35 (2H, d, J = 8.3), 6.62 (1H, t, J = 7.3), 4.12 (2H, s), 2.48 (3H, s), 2.27 (2H, q, J = 7.3), 1.44 (2H, sext, J = 7.3), 0.90 (3H, dd, J = 7.82, 7.32); ^{13}C-NMR δ 155.14 (d), 145.79 (s), 145.68 (s), 145.55 (s), 142.08 (s), 135.48 (s), 130.72 (d), 130.02 (d), 128.63 (d), 126.96 (d), 121.93 (d), 117.02 (s), 65.77 (t), 35.15 (t), 21.84 (t), 21.71 (q), 13.79 (q). Anal. Calcd for $C_{19}H_{20}N_2O_6SSe$: C, 47.20; H, 4.18; N, 5.71. Found: C, 47.15; H, 4.10; N, 5.60. Yield, 36%. **(*E*)-3bx**: ^{1}H-NMR δ 6.72 (1H, t), 4.20 (2H, s).

(*Z*)-2-(2-Pyridylseleno)-1-(*p*-toluenesulfonyl)-2-hexene (3dx): mp 75–76 °C; ^{1}H-NMR δ 8.39 (1H, d, J = 2.9), 7.71 (2H, d, J = 8.1), 7.45 (1H, td, J = 7.7, 1.8), 7.31 (2H, d, J = 8.4), 7.18 (1H, d, J = 8.1), 7.04 (1H, dd, J = 7.3, 4.8), 6.26 (1H, t, J = 7.3), 4.25 (2H, s), 2.45 (3H, s), 2.24 (2H, q, J = 7.3), 1.36 (2H, tq, J = 7.7, 7.3), 0.86 (3H, dd, J = 7.7, 7.3); ^{13}C-NMR δ 156.02 (s), 150.34 (d), 149.05 (d), 144.74 (s), 136.51 (d), 135.70 (s), 129.65 (d), 128.86 (d), 124.83 (d), 120.71 (d), 117.26 (s), 65.73 (t), 34.95 (t), 21.97 (t), 21.67 (q), 13.75 (q). Anal. Calcd for $C_{18}H_{21}NO_2SSe$: C, 54.81; H, 5.38; N, 3.55. Found: C, 54.56; H, 5.27; N, 3.46. Yield, 26% based on dipyridyl diselenide. **(*E*)-3dx**: ^{1}H-NMR δ 6.55 (1 H, t), 4.38 (2 H, s).

(*Z*)-2-((*o*-(Trifluoromethyl)phenyl)seleno)-1-(*p*-toluenesulfonyl)-2-hexene (3ex): mp 54–56 °C; ^{1}H-NMR δ 7.60–7.71 (3H, m), 7.34 (5H, m), 6.37 (1H, dd, J = 7.1, 7.5), 3.98 (2H, s), 2.46 (3H, s), 2.27 (2H, td, J = 7.1, 7.4), 1.40 (2H, sext, J = 7.4), 0.89 (3H, dd, J = 7.1, 7.4); ^{13}C-NMR δ 149.64 (d), 144.96 (s), 135.36 (s), 132.72 (d), 132.15 (d), 130.45 (q, J = 31.1), 129.71 (d), 129.58 (s), 128.85 (d), 127.14 (q, J = 5.0), 126.88 (d), 123.73 (q, J = 274.0), 117.83 (s), 65.20 (t), 34.88 (t), 22.02 (t), 21.64 (q), 13.77 (q). Anal. Calcd for $C_{20}H_{21}F_3O_2SSe$: C, 52.05; H, 4.60; F, 12.35. Found: C, 52.14; H, 4.55; F, 12.24. Yield, 44%. **(*E*)-3ex**: ^{1}H-NMR δ 6.42 (1H, t), 4.10 (2H, s).

(*Z*)-2-((*o*-Methoxyphenyl)seleno)-1-(*p*-toluenesulfonyl)-2-hexene (3fx). The isomerization was carried out by treatment with *t*-BuOK in dry THF at −78 °C for 5 h: mp 80–82 °C; ^{1}H-NMR δ 7.68–7.71 (2H, m), 7.16–7.33 (3H, m), 7.03–7.06 (1H, m), 6.79–6.87 (2H, m), 6.22 (1H, t, J = 7.3), 4.04 (2H, s), 3.81 (3H, s), 2.45 (3H, s), 2.23 (2H, q, J = 7.3), 1.30 (2H, sext, J = 7.3), 0.86 (3H, t, J = 7.3); IR 1460, 1240, 1140 cm^{-1}. Anal. Calcd for $C_{20}H_{24}O_3SSe$: C, 56.73; H, 5.71. Found: C, 56.58; H, 5.80. Yield, 16%. **(*E*)-3fx**: ^{1}H-NMR δ 6.34 (1 H, t), 4.17 (2H, s).

Asymmetric Synthesis of Allenic Sulfones 5 from Vinyl Selenides 3. By Use of Sharpless Oxidant (run 7 in Table I). To a 10-mL two-necked round-bottomed flask containing a vinyl selenide (**3ax**) (0.22 g, 0.50 mmol), several pieces of molecular sieves (4A, pellet), and a magnetic stirring bar was introduced 5 mL of dry CH_2Cl_2 using a syringe under argon atmosphere, and then the mixture was cooled to 0 °C. To the magnetically stirred solution were introduced (+)-diethyl tartrate (0.17 mL, 1.0 mmol) and $Ti(OiPr)_4$ (0.15 mL, 0.5 mmol) using a syringe. After 0.5 h, 3.3 N *tert*-butyl hydroperoxide (TBHP) in toluene (0.32 mL) was added dropwise using a syringe at 0 °C, and the mixture was stirred at 0 °C for 16 days. The resulting mixture was directly subjected to column chromatography [AcOEt/hexane (3/7) as eluent], and the allenic sulfone (**5x**) was isolated in 72% yield. The ee was determined by HPLC [Daicel Chiralcel OF column, isopropyl alcohol/hexane (1/9) as eluent] as well as ^{1}H-NMR using a chiral shift reagent Eu(hfc)$_3$.

By Use of Davis Oxidant (run 12 in Table I). After placing a vinyl selenide (**3ax**) (44.1 mg, 0.10 mmol), Davis oxidant (**E**) (38.4 mg, 0.10 mmol), several pieces of molecular sieves (4A), and a magnetic stirring bar in a test tube sealed with septum under argon atmosphere, 2 mL of dry CH_2Cl_2 was introduced using a syringe at room temperature, and the mixture was magnetically stirred for 15 days. The produced allenic sulfone **5x** was isolated with preparative TLC [AcOEt/hexane (3/7) as eluent, 41% yield]. The ee was determined as described above.

^{1}H-NMR Monitoring of the Reaction. Each vinyl selenide (**3ax**, **3bx**, **3cx**, **3dx**, **3ex**, and **3fx**) (0.02 mmol) was oxidized with Sharpless oxidant (**A**) in CD_2Cl_2 (0.6 mL) in a ^{1}H-NMR tube sealed with septum under argon atmosphere at 0 °C in the absence of molecular sieves. Each reaction was monitored by ^{1}H-NMR, and the concentration of the three components of vinyl selenides **3**, selenoxides **4**, and allenic sulfones **5** were analyzed from the value of integral of either vinylic or allylic protons derived from each component. The k_1 was a pseudo-first-order rate constant determined from the initial slope in the log [**3**] *vs* reaction time plot, and the k_2 was a first-order rate constant determined from the slope in the log [**4**] *vs* reaction time plot at a later stage.

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