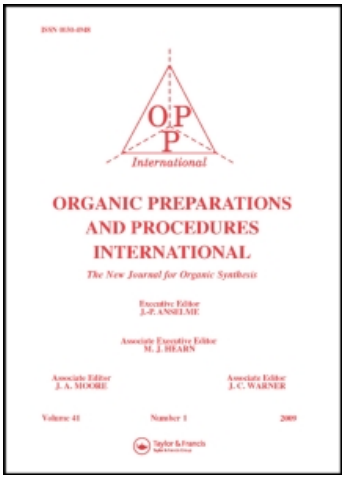

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Toshio Shimizu[a]; Nobumasa Kamigata[a]
[a] Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo, JAPAN

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OPTICALLY ACTIVE SELENIUM AND TELLURIUM COMPOUNDS. SYNTHESIS AND APPLICATION FOR ASYMMETRIC SYNTHESIS. A REVIEW

Toshio Shimizu and Nobumasa Kamigata*

Department of Chemistry, Graduate School of Science
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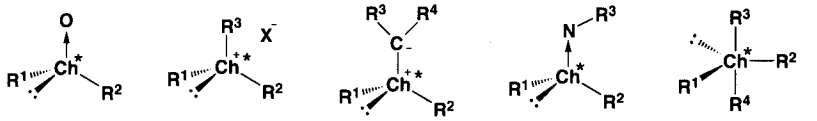
INTRODUCTION

A number of optically active tricoordinate organosulfur compounds, such as sulfoxides, sulfonium salts, sulfonium ylides, and sulfilimines, have already been synthesized, and their properties and reactivities have been studied in detail.[1] It is widely known that many organoselenium and tellurium compounds have structures similar to those of the corresponding organosulfur compounds since selenium and tellurium are homologous with sulfur. However, studies on the synthesis and stereochemistry of organoselenium and tellurium compounds have been limited[2] in contrast to those of organosulfur compounds. Recently, some optically active tricoordinate selenium and tellurium compounds, such as selenoxides and telluroxides (**I**), selenonium salts and telluronium salts (**II**), selenonium ylides and telluronium ylides (**III**), and selenonium imides (**IV**), were synthesized, and their stereochemistry was studied.[3] Moreover, optically active tetracoordinate selenium and tellurium compounds (**V**), namely selenurane and tellurane, which correspond to the sulfur analogue, sulfurane, were also synthesized recently.



I **II** **III** **IV** **V**

Ch = Se, Te

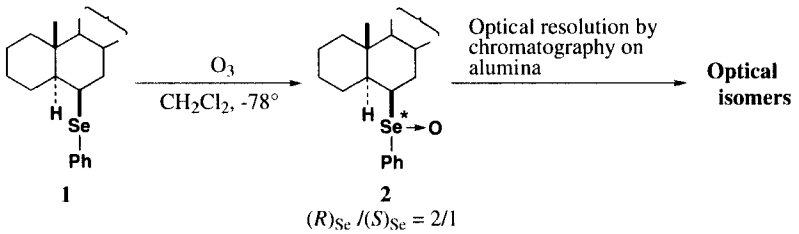
With the progress of studies on synthesis and stereochemistry of these compounds, optically active selenium and tellurium compounds have been utilized for asymmetric reactions. This review will focus on the synthesis and synthetic application for asymmetric synthesis of optically active tri- and tetracoordinate organoselenium and tellurium compounds.

I. SYNTHESIS OF OPTICALLY ACTIVE TRICOORDINATE SELENIUM AND TELLURIUM COMPOUNDS

1. Selenoxides

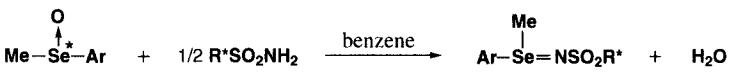
Many reports have appeared concerning optically active sulfoxides.[1] Several synthetic methods for the synthesis of optically active sulfoxides have been developed, and numerous papers have been also reported on the asymmetric synthesis utilizing the chiral sulfoxides as a chiral source. Selenoxides were also presumed to have a pyramidal structure, as do sulfoxides, by studies of the mixed crystal[4] and by NMR spectroscopy.[5] Therefore, it is possible that optically active selenoxides could be synthesized similarly to sulfoxides. However, optically active selenoxides had not been isolated as a stable form until recently. A rapid inversion of the configuration on the selenium atom of a selenoxide (racemization) has been considered because it was difficult to isolate the optically active selenoxides.[6,7] Racemization *via* an achiral hydrate, formed from selenoxide and water, was considered to be a reason for the configurational instability.[5,6,8-10]

An optically active selenoxide possessing a steroid frame was obtained for the first time by Jones and co-workers in 1970.[11] Oxidation of 6β-phenylselenenyl-5α-cholestane **1** with ozone at -78° afforded a mixture of the $(R)_{Se}$- and $(S)_{Se}$-6β-phenylselenoxides **2** in the ratio 2:1 (*Eq. 1*). The mixture could be optically resolved by column chromatography on alumina at -50°. The diastereomeric selenoxides were configurationally stable at temperature between -78° and 25° in solution either in the absence or presence of water, and decomposed at room temperature through β-elimination of the selenoxides.



(1)

In 1983, selenoxides of enantiomeric excess possessing the chiral center only on the selenium atom were obtained by Davis and co-workers.[12] Optically active methyl phenyl selenoxide **3a** and methyl 2,4,6-triisopropylphenyl selenoxide **3b** were obtained by kinetic resolution in the reaction of the racemic selenoxides with a chiral sulfonamide (*Eq. 2*). Enantiomeric excess of the remaining



(2)

R* = (+)-10-camphor

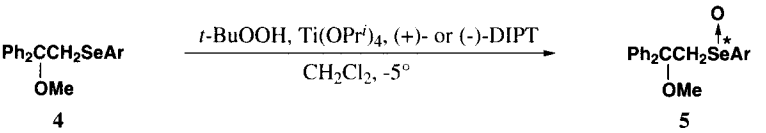
	Ar	ee(%) of remaining **3**	(Config.)	yield(%)
a:	Ph	10	(*S*)	48
b:	2,4,6-triisopropylphenyl	9	(*R*)	50

selenoxides **3a** and **3b** were 10 and 9% ee, respectively, and configurational stability of the selenoxides in the presence of water was increased by the presence of bulky substituent.

Many other optically active diastereomeric and enantiomeric selenoxides have been isolated to date. Two methods, asymmetric oxidation of prochiral selenides and optical resolution of diastereomeric or enantiomeric mixtures were widely used for isolating the optically active selenoxides.[13]

a. Asymmetric Oxidation of Selenides

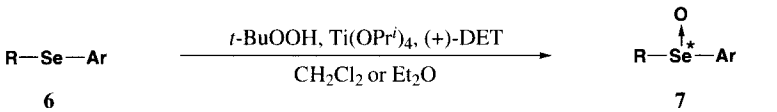
Some methods have been reported for asymmetric oxidation of prochiral alkyl aryl selenides.[13,14] Asymmetric oxidation of alkyl aryl selenides under Sharpless oxidation conditions were reported by Tiecco *et al.*[15] and ourselves.[16,17] Oxidation of 1,1-diphenyl-1-methoxy-2-arylselenylethanes **4** by *t*-butyl hydroperoxide in the presence of titanium tetraisopropoxide and (+)- or (-)-diisopropyltartrate (Sharpless-Katsuki reagents) afforded corresponding optically active selenoxides **5** with moderate optical yields (*Eq. 3*).[15] Oxidation of alkyl aryl selenides **6**, possessing bulky



4 **5** (3)

Ar	Tartrate	ee(%)	(Config.)	yield(%)
Ph	(-)-DIPT	20	(*R*)	75
o-$MeOC_6H_4$	(+)-DIPT	40	(*S*)	72

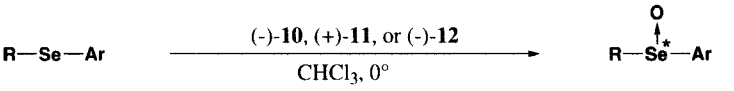
substituents for preventing the racemization, under Sharpless oxidation conditions also yielded corresponding optically active selenoxides **7** after chemical purification by means of chromatography on alumina at room temperature (*Eq. 4*).[16,17]



6 **7** (4)

R	Ar	Conditions	ee(%)	(Config.)	yield(%)
Me	2,4,6-triisopropylphenyl	CH_2Cl_2 -15°	28	(*R*)	58
Me	2,4,6-tri-*t*-butylphenyl	Et_2O -15°	33	(*S*)	12
Me_3CCH_2	2,4,6-tri-*t*-butylphenyl	Et_2O 25°	11	(*R*)	30
Bn	2,4,6-tri-*t*-butylphenyl	CH_2Cl_2 25°	7	(*R*)	22
o-MeOBn	2,4,6-tri-*t*-butylphenyl	CH_2Cl_2 25°	17	(*R*)	19

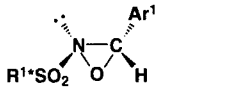
Davis and co-workers reported asymmetric oxidation of alkyl aryl selenides **8** with some optically active oxaziridines such as (-)-**10**,[18] (+)-**11**,[19] and (-)-**12**[19,20] as the oxidizing reagents (*Eq. 5*). In some cases, over 95% ee were obtained for the corresponding selenoxides **9**. Low %ee obtained in the case of oxidation of methyl phenyl selenide with (-)-**12** was considered to be caused by the racemization during the chemical purification.



8 9 (5)

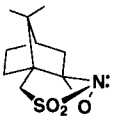
R	Ar	Oxaziridine	ee(%)[b]	(Config.)	yield(%)
Me	Ph	(-)-**10**[a]	9	(*S*)	20
Me	Ph	(+)-**11**	0 (10)[c]	(*S*)	68
Me	Ph	(-)-**12**	15 (>95)	(*S*)	70
Me	2,4,6-triisopropylphenyl	(+)-**11**	70 (84)	(*S*)	72
Me	2,4,6-triisopropylphenyl	(-)-**12**	85 (>95)	(*S*)	85
Et	2,4,6-triisopropylphenyl	(+)-**11**	54 (68)	(*S*)	74
Et	2,4,6-triisopropylphenyl	(-)-**12**	86 (91)	(*S*)	68
p-MeOBn	2,4,6-triisopropylphenyl	(+)-**11**	68 (72)	(*S*)	65
p-MeOBn	2,4,6-triisopropylphenyl	(-)-**12**	87 (95)	(*S*)	60

a) At 25°. b) Isolated %ee. c) In parentheses are %ee by NMR.

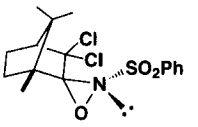


Ar^1 = 2-chloro-5-nitrophenyl
R^1* = *d*-10-camphor

(-)-**10**

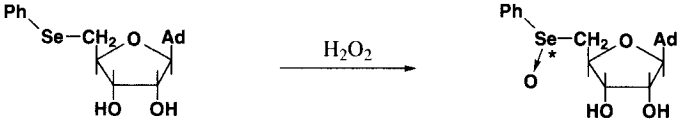


(+)-**11**



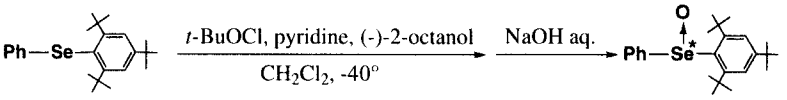
(-)-**12**

Zylber and co-workers reported the oxidation of alkyl aryl selenide substituted by deoxyadenosine in the course of their synthetic study of nucleosides.[21] Oxidation of 5'-phenylseleno-5'-deoxyadenosine **13**, prepared *in situ*, with hydrogen peroxide gave a single diastereomer **14** as a stable crystalline solid (*Eq. 6*).



13 **14** (6)

Asymmetric oxidation of diaryl selenides was reported only by us though the enantiomeric excess of the resulting selenoxide was very low.[22] Oxidation of phenyl 2,4,6-tri-*t*-butylphenyl selenide **15** with *t*-butyl hypochlorite in the presence of pyridine and (-)-2-octanol followed by hydrolysis afforded corresponding optically active selenoxide **16** (ee ≈ 1%) (*Eq. 7*).



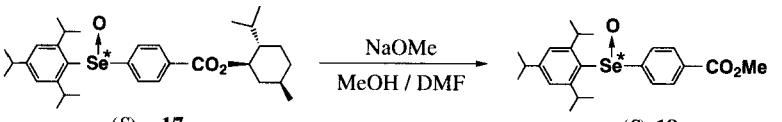
15 **16** (7)

b. Optical Resolution of Selenoxides

Fractional recrystallization of diastereomeric selenoxides, chromatographic separation using a chiral stationary phase, and separation by complexation with chiral compounds are available for

optical resolution of asymmetric selenoxides.

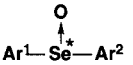
We succeeded in isolating configurationally stable diastereomerically pure selenoxide $(S)_{Se}$-**17** for the first time by repeated recrystallization of the diastereomeric mixture from methanol.[23] Another diastereoisomer $(R)_{Se}$-**17** also was obtained from the mother liquid in 75% ee. Removal of the chiral menthyl group of $(S)_{Se}$-**17** by transesterification with sodium methoxide afforded enantiomerically pure 4-(methoxycarbonyl)phenyl 2,4,6-triisopropylphenyl selenoxide (*S*)-**18** without loss of optical purity, which is the first example of isolation of an enantiomerically pure selenoxide (*Eq. 8*).[24]



$(S)_{Se}$-**17** (*S*)-**18** (8)

Enantiomarically pure

We also reported chromatographic separation of asymmetric selenoxides.[25,26] Several asymmetric diaryl selenoxides **19** were optically resolved by medium-pressure column chromatography on an optically active column packed with DNBPG/aminopropylsilica, and their optical purities were determined by high-performance liquid chromatography on a same type of column or ^{1}H-NMR spectroscopy using an optically active shift reagent. Although optically pure selenoxide was not obtained as shown in table, in the practice the purity of the selenoxides obtained depends on the amount of substrates and the size of column. In fact, small portions of rapidly eluted selenoxides were optically pure.



19

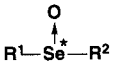
Ar^1	Ar^2	fast eluted **19** ee(%)	(Config.)	slow eluted **19** ee(%)	(Config.)
Ph	mesityl	12	(*S*)	16	(*R*)
Ph	2,4,6-triethylphenyl	12	(*S*)	4	(*R*)
Ph	2,4,6-triisopropylphenyl	66	(*S*)	24	(*R*)
Ph	2,4,6-tri-*t*-butylphenyl	49	(*R*)	33	(*S*)
p-tolyl	mesityl	14	(*R*)	14	(*S*)
p-tolyl	2,4,6-triisopropylphenyl	63	(*R*)	36	(*S*)
o-$MeOC_6H_4$	2,4,6-triisopropylphenyl	56	(*S*)[a]	41	(*R*)[a]

a) Tentative.

The above two methods, fractional recrystallization and chromatographic separation, are useful to obtain optically active diaryl selenoxides because a suitable asymmetric oxidation method for prochiral diaryl selenides has not yet been developed.

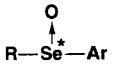
Toda and Mori reported optical resolution of selenoxides by complexation with optically active compounds.[27] Some dialkyl and alkyl aryl selenoxides **20** and **21** were optically resolved by complexation with optically active 2,2'-dihydroxy-1,1'-binaphthol or 1,6-di(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol. In some cases, optically pure selenoxides were obtained as

complexes in yields of greater than 50% by enantiomerization through equilibration. However, optical purities of selenoxides were determined for the complexes since the free optically active selenoxides racemized quite easily.



20

R^1	R^2
Me	*n*-pentyl
Et	*n*-butyl
Et	*n*-pentyl

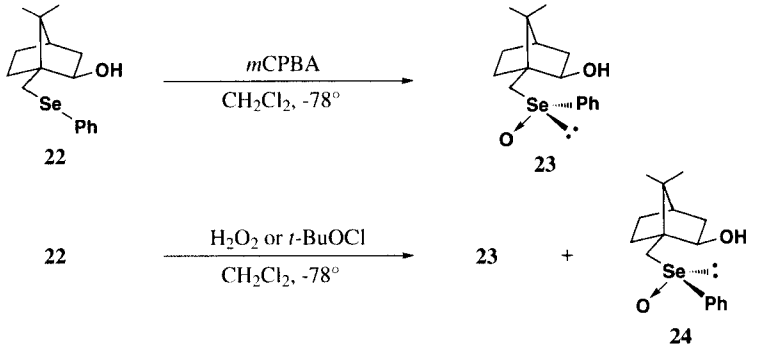


21

R	Ar
Me	Ph
Me	*o*-tolyl
Me	*m*-tolyl
Et	Ph
Et	*o*-tolyl
Et	*m*-tolyl
Et	*p*-tolyl

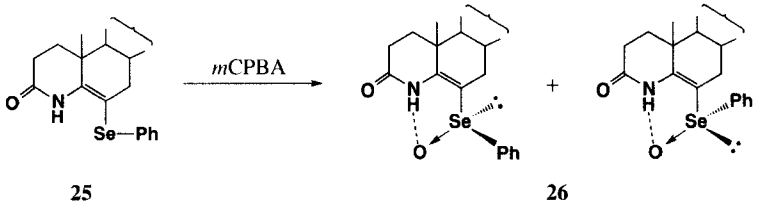
c. Miscellaneous Methods

An interesting study was reported by Koizumi and co-workers.[28] Oxidation of selenide **22** with *m*-chloroperbenzoic acid yielded a single diastereomeric selenoxide **23** in 96% yield (*Eq. 9*). On the other hand, oxidation of **22** with hydrogen peroxide or *t*-butyl hypochlorite gave a mixture of diastereomers **23** and **24**. However, a mixture of the selenoxides **23** and **24** changed into **23** upon treatment with silica gel column chromatography of the reaction mixture. Therefore, selenoxide **23** is the result of this operation. Selenoxide **23** was stable at room temperature in the solid state. It was mentioned that the configurational stability of **23** seems to reflect stabilization by an intramolecular hydrogen bond between the seleninyl oxygen and the secondary hydroxy group.



(9)

Back and co-workers reported oxidation of a selenide which possesses an azasteroid skeleton.[29,30] Oxidation of selenide **25** with *m*-chloroperbenzoic acid gave a 2:1 mixture of selenoxide diastereomers **26** (*Eq. 10*). The major isomer could be separated by equilibration and precipitation from aqueous potassium carbonate solution.

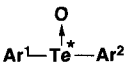


(10)

Racemization of optically active selenoxides *via* achiral hydrates, which is a most important problem for isolating the optically active isomers, has been kinetically studied using optically active diaryl selenoxides, and the mechanism involving the hydrate as the key intermediate has also been clarified by a tracer experiment with $H_2{}^{18}O$.[31] Pyramidal inversion, which is important as the mechanism for racemization of optically active tricoordinate chalcogen compounds, of selenoxides has also been studied theoretically by *ab initio* MO calculations.[32]

2. Telluroxides

Telluroxides are more hygroscopic than the corresponding selenoxides and easily form hydrates.[33-36] Thus, an optically active telluroxide had not been isolated until recently when we succeeded in obtaining optically active diaryl telluroxides with bulky substituents which prevent racemization *via* the achiral hydrate.[37] Optically active phenyl 2,4,6-tri-*t*-butylphenyl telluroxide **27a** and mesityl 2,4,6-tri-*t*-butylphenyl telluroxide **27b** were obtained by means of medium-pressure liquid chromatography using an optically active column packed with amylose carbamate derivative/silica gel. Optically active telluroxide **27b** was found to be configurationally stable, and the optically pure isomer (*R*)-**27b** was isolated, while the telluroxide **27a** was still configurationally unstable for the isolation in an optically pure form. The mechanism for the racemization *via* an achiral hydrate was clarified by kinetic and tracer studies. The pyramidal inversion energy for dimethyl telluroxide was estimated to be about 64 kcal mol^{-1} based on *ab initio* MO study. This result also indicates that the mechanism involving achiral hydrate is of greater importance than pyramidal inversion for racemization of telluroxides in the presence of water.



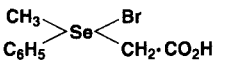
27

	Ar^1	Ar^2
a:	Ph	2,4,6-tri-*t*-butylphenyl
b:	mesityl	2,4,6-tri-*t*-butylphenyl

3. Selenonium Salts

There are few reports on synthesis of optically active selenonium salts although an optically active selenonium salt had been obtained in the early twentieth century for the first time by Pope and Neville.[38] All reports are based on optical resolution of the diastereomeric mixture of selenonium salts with a chiral counter anion for obtaining the optical isomers.

Fractional recrystallization of diastereomeric mixtures of phenylmethylselenetine *d*-bromocamphorsulfonate (the authors report the name like this and the structure as **28**), prepared from silver *d*-bromocamphorsulfonate and phenylmethylselenetine bromide, gave optically active *d*-phenylmethylselenetine *d*-bromocamphorsulfonate as colorless crystals.[38] Moreover, repeated recrystallization of the compounds remaining in the mother liquid from water yielded *l*-phenylmethylselenetine *d*-bromocamphorsulfonate. Addition of a cold alcohol solution of platinic chloride to an alcohol solution of the *d*-bromocamphorsulfonate containing a little hydrochloric acid afforded the corresponding optically active platinichloride **29** as a microcrystalline compound.



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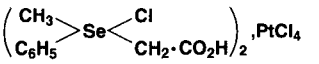
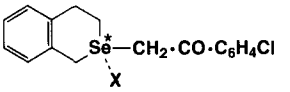


29

Isolation of optically active selenoisochromanium salts were reported by Holliman and Mann.[39] Repeated recrystallization of 2-*p*-chlorophenacylselenoisochromanium *d*-bromocamphorsulfonate **30a** from alcohol afforded the optically pure *l*-selenonium *d*-bromocamphorsulfonate. A *d*-selenonium salt was also obtained similarly by using *l*- bromocamphorsulfonate as a counter anion. Enantiomeric *l*-selenonium salts **30b** and **30c** could be obtained by suitable anion exchange reactions of the *l*-selenonium *d*-bromocamphorsulfonate. In the above two reports, the mutarotation of the selenonium salts were examined.

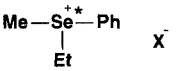
Simpler optically active selenonium salts, (*S*)-(+)-ethylmethylphenylselenonium (*1S*)-(+)-camphor-10-sulfonate and the (*R*)-(-)-isomer **31a** were obtained by means of fractional recrystallization of the diastereomeric mixture from methanol-acetone-ether.[40] These optically active selenonium salts were also converted into their enantiomeric perchlorate **31b** by the anion exchange reactions.



30

X

a: *d*-bromocamphorsulfonate
b: picrate
c: mercury triiodide



31

X

a: (*1S*)-(+)-camphor-10-sulfonate
b: perchlorate

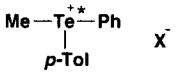
4. Telluronium Salts

Optical resolution of asymmetric telluronium salts were reported by Lowry and Gilbert for the first time.[41] Fractional recrystallization of methylphenyl-*p*-tolyltelluronium *d*-bromocamphor-π-sulfonate **32a** from acetone-ethyl acetate-ether yielded the l_{Te}-isomer, and the recrystallization of the diastereomeric *d*-camphor-β-sulfonate **32b** gave the d_{Te}-isomer. Anion exchange reactions of the diastereomeric isomers **32a** and **32b** with potassium iodide followed by precipitation afforded enantiomeric *l*-telluronium and *d*-telluronium iodides **32c**, respectively. It was also reported that mutarotation took place when the optically active salts were dissolved in solvent.

Optically active *l*-2-*p*-chlorophenacyltelluroisochromanium *d*-bromocamphorsulfonate **33a** was also obtained by Holliman and Mann by means of recrystallization of the diastereomeric mixture from ethanol-ether, similarly in the case of corresponding selenonium salt.[39] The corresponding *d*-isomer remained in the solution. Methanol solution of optically active salts **33a** caused mutarotation even at 15°. Treatment of the *l*-telluronium and *d*-telluronium *d*-bromocamphorsulfonates **33a** with picric acid in methanol gave corresponding *l*-telluronium and *d*-telluronium picrates **33b**, respectively.

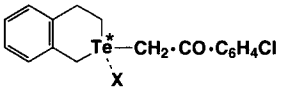
More recently, we also isolated optically pure telluronium salts.[42,43] $(R)_{Te}$-$(+)_{Te(MeOH)}$-Ethylmethylphenyltelluronium (*1S*)-(+)-camphor-10-sulfonate **34a** was obtained as optically pure crystals by repeated recrystallization of the diastereomeric mixture from acetone-ether-hexane. The $(S)_{Te}$-$(-)_{Te(MeOH)}$-isomer was also given in optically pure form by recrystallization from acetone-ether of the telluronium salt, obtained from the mother solution. Sign and magnitude of the specific rotations were strongly influenced by the solvents and concentrations employed for the measurement.

Enantiomerically pure (*R*)-telluronium salts **34b-34g** were obtained by successful anion exchange reactions of the $(R)_{Te}$-$(+)_{Te(MeoH)}$-isomer of **34a**. (*R*)-**34b** was stable toward pyramidal inversion, and no racemization took place even in refluxing methanol after 3 days. Anion-cation interaction of optically active telluronium salts in solution was also examined,[43] and the interaction in crystalline state of the selenonium and telluronium salts were also discussed.[44]



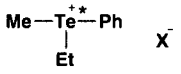
32

X	
a:	*d*-bromocamphor-π-sulfonate
b:	*d*-camphor-β-sulfonate
c:	iodide



33

X	
a:	*d*-bromocamphorsulfonate
b:	picrate

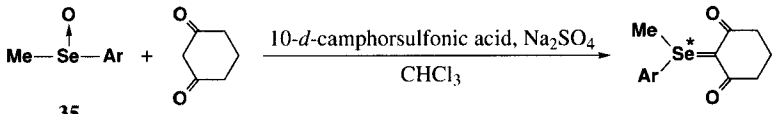


34

X	
a:	(*1S*)-(+)-camphor-10-sulfonate
b:	perchlorate
c:	tetrafluoroborate
d:	*p*-chlorobenzenesulfonate
e:	bornane-10-sulfonate
f:	tetraphenylborate
g:	picrylsulfonate

5. Selenonium Ylides

Optically active selenonium ylides were obtained in 1976 for the first time by Sakaki and Oae.[45] Reactions of methyl aryl selenoxides **35** with 1,3-cyclohexanedione in the presence of 10-*d*-camphorsulfonic acid and anhydrous sodium sulfate afforded optically active selenonium ylides **36**, however, the enantiomeric excesses were unknown (*Eq. 11*).

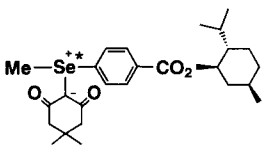


(11)

35 **36**

Ar	yield(%)
Ph	54
o-$MeOC_6H_4$	97
α-naphthyl	89
mesityl	26

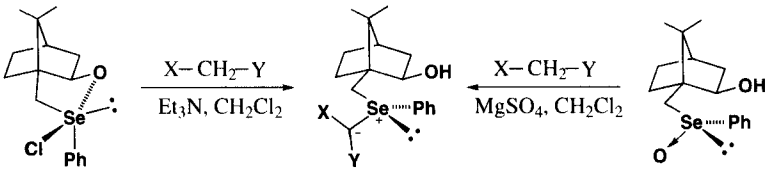
An optically pure selenonium ylide was obtained for the first time in 1991 by means of optical resolution of a diastereomeric mixture.[46,47] Fractional recrystallization of diastereomeric selenonium ylide **37** from hexane-ether gave the optically pure isomer $(R)_{Se}$-**37** as stable crystals. Another diastereomeric isomer $(S)_{Se}$-**37** was also obtained from the mother liquor in 27% de. However, attempts to isolate an enantiomerically pure selenonium ylide by transesterification under several conditions have failed because of chemical instability of the ylide structure.



37

Recently, Koizumi and co-workers also reported the preparation of optically active selenonium ylides.[48] Reactions of optically active $(R)_{Se}$-chloroselenurane $(R)_{Se}$-**38** (which will be mentioned

later, Chap. II 1) or $(R)_{Se}$-selenoxide $(R)_{Se}$-**39** with active methylene compounds proceeded with retention of the configuration to give $(S)_{Se}$-selenonium ylides $(S)_{Se}$-**40** in high optical yields (de >99%) and chemical yields (up to 100%) (*Eq. 12*).



(12)

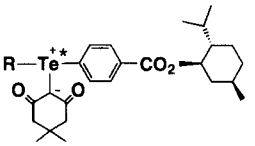
$(R)_{Se}$-**38** $(S)_{Se}$-**40** $(R)_{Se}$-**39**

de(%)	yield(%)	X–CH_2–Y	de(%)	yield(%)
>99	93	dimedone	>99	99
>99	100	methyl acetoacetate	>99	88
>99	96	ethyl cyanoacetate	>99	93
>99	94	acetylacetone	>99	84
>99	70[a]	Meldrum's acid	>99	82

a) Lithium hydride was used as a base.

6. Telluronium Ylides

We reported the only example of the isolation of optically active telluronium ylides.[49] Optical resolution of diastereomeric telluronium ylides **41a** and **41b** by means of fractional recrystallization from hexane-dichloromethane afforded optically active $(R)_{Te}$-**41a** and $(+)_{Te}$-**41b**, respectively, though the optical purities were not high, 30 and 25% de, respectively. $(S)_{Te}$-**41a** and $(-)_{Te}$-**41b** were also obtained from corresponding mother liquids.



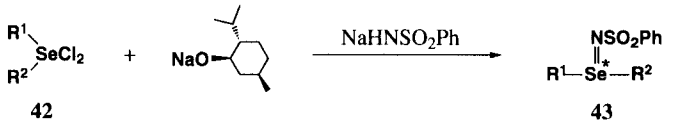
41

R	
a:	Me
b:	2,4,6-triisopropylphenyl

Activation energies for pyramidal inversion, which is one of plausible pathway for racemization of sulfonium, selenonium and telluronium ylides, were also studied on basis of *ab initio* MO calculations.[50]

7. Selenonium Imides

Optically active selenonium imides were prepared for the first time in 1981 by Krasnov and co-workers.[51] Alkyl aryl and asymmetric diaryl selenium dichlorides **42** reacted with sodium benzenesulfone amide in the presence of sodium (-)-menthyloxide to give the optically active selenonium imides **43**, though the enantiomeric excesses were unknown (*Eq. 13*).

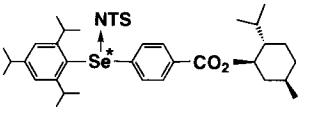


(13)

42 **43**

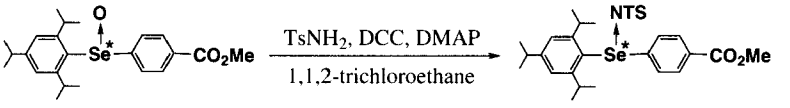
R^1	R^2	yield (%)
Me	Ph	25
Me	*p*-BrC_6H_4	38
o-tolyl	Ph	20

Optically pure selenonium imide was obtained by us by means of optical resolution of the diastereomeric mixture.[52] Optical resolution by fractional recrystallization of diastereomeric selenonium imide **44** from methanol gave optically pure $(S)_{Se}$-selenonium imide $(S)_{Se}$-**44** as crystals. The isomer $(R)_{Se}$-**44** was also obtained from the mother liquid in 40% de. However, transesterification of **44** to prepare the enantiomeric selenonium imide failed. Kinetics for mutarotation of **44** was also studied.[53]



44

The reaction of optically pure selenoxide (*S*)-**45** with *p*-toluenesulfonamide in the presence of dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) afforded enantiomeric selenonium imide (*S*)-**46** in 80% optical purity with a retention of stereochemistry (*Eq. 14*).[54]

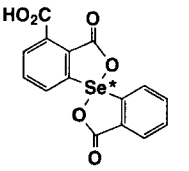


(*S*)-**45** (*S*)-**46** (14)

II. SYNTHESIS OF OPTICALLY ACTIVE TETRACOORDINATE SELENIUM AND TELLURIUM COMPOUNDS

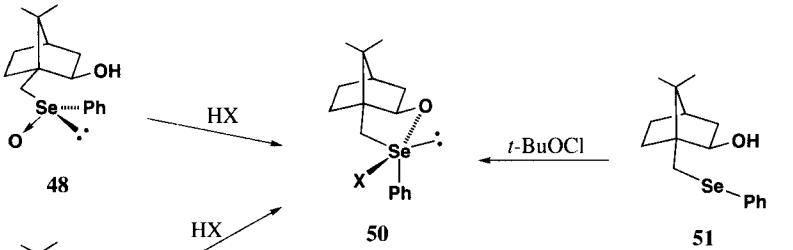
1. Selenuranes

Lindgren reported partial resolution of chiral selenurane in 1972.[55] A quinine salt of the selenurane **47**, obtained by recrystallization from ethyl acetate-methanol, gave optically active free acid (-)-**47**. The another isomer (+)-**47** was also obtained from the mother liquor.



47

Optically pure haloselenuranes were synthesized by Koizumi and co-workers.[28] Treatment of optically active selenoxide **48** with HCl afforded chloroselenurane **50a** in quantitative yield (*Eq. 15*). Diastereomeric mixture of selenoxides **48** and **49** also gave selenurane **50a** as a single diastereomer (96%) by treatment with HCl. In a similar manner, bromoselenurane **50b** was obtained by treatment of **48** with HBr. Oxidation of selenide **51** with



48 **50** **51** **49**

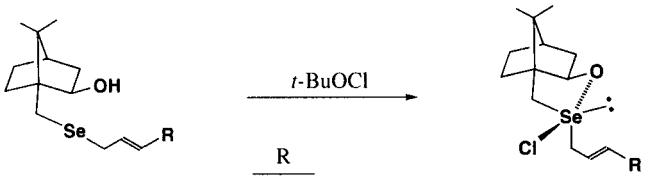
X

a: Cl
b: Br
c: 3,5-dinitrobenzoyloxy
d: *p*-TolSO$_3$
e: F

(15)

t-butyl hypochlorite also afforded selenurane **50a**, quantitatively. Selenuranes **50c** and **50d** was prepared by the reaction of **48** with 3,5-dinitrobenzoic acid (88%) and *p*-toluenesulfonic acid (91%) in the presence of $MgSO_4$, respectively. No selenurane, epimeric at selenium atom, was formed in these reactions. Formation of the selenurane with opposite configuration of **50** might be unfavorable due to the steric repulsion. Halogen exchange reactions among the haloselenuranes **50a**, **50b**, and **50e** were possible by using sodium halides or silver halides.

Chloroselenuranes **53** were also obtained by treatment of the corresponding allylic selenides **52** with *t*-butyl hypochlorite (*Eq. 16*).[56]



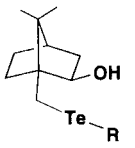
52 53

R
Ph
i-Pr

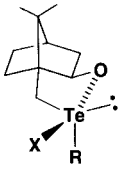
(16)

2. Telluranes

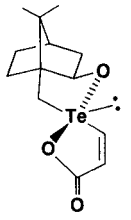
Very recently, optically active Te-chiral-10-Te-4 organotellurium species, namely tellurane were also reported by Koizumi and co-workers.[57] Treatment of tellurides **54a-54f** with *t*-butyl hypochlorite at 0° afforded chlorotelluranes **55a-55f** as exclusive products (86-97%). Bromotellurane **55g** was also obtained as a single diastereomer by the reaction of telluride **54e** with *N*-bromosuccinimide (NBS). Halotelluranes **55a-55g** were stable even in air at room temperature. Halogen exchange reactions of halotelluranes were also available similar to corresponding selenuranes described above. Reaction of chlorotellurane **55e** with NaBr gave bromotellurane **55g** in 96% yield, and **55g** also yielded iodotellurane **55h** (98%) by treatment with NaI. Treatment of **55e** with AgF gave fluorotellurane **55i** (85%). Chlorotellurane (*Z*)-**55f** reacted with aqueous $NaHCO_3$ to give spirotellurane **56** in 62% yield.



54



55



56

	R	X
a:	Me	Cl
b:	Et	Cl
c:	*i*-Pr	Cl
d:	*n*-Hex	Cl
e:	Ph	Cl
f:	HC=C-CO_2Me	Cl
g:	Ph	Br
h:	Ph	I
i:	Ph	F

III. SYNTHETIC APPLICATION OF OPTICALLY ACTIVE SELENIUM AND TELLURIUM COMPOUNDS FOR ASYMMETRIC SYNTHESIS

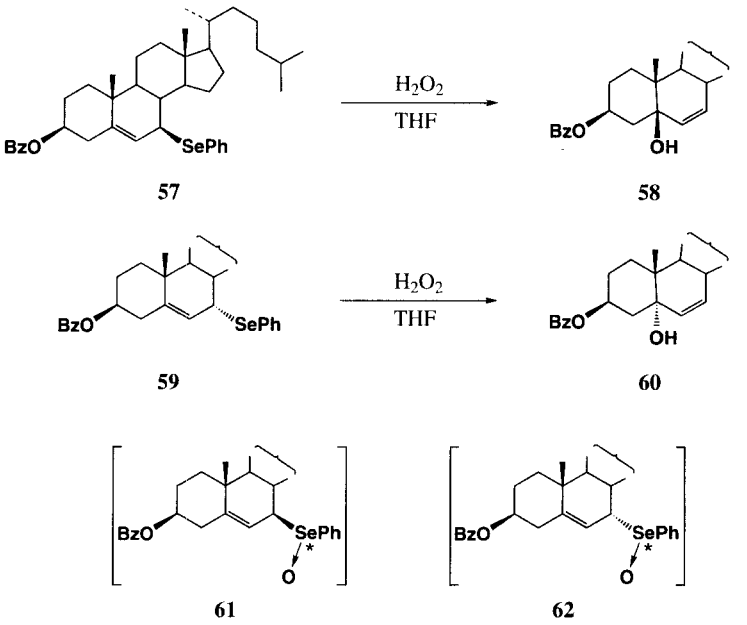
With the progress of studies on synthesis and stereochemistry of optically active organoselenium and tellurium compounds, some synthetic applications by using optically active organoselenium and tellurium compounds for asymmetric synthesis have been attempted.[3,13,58]

1. via Selenoxides and Telluroxides

It is well known that selenoxides possessing β-hydrogen easily decompose to give olefins.[10,11] Allylic selenoxides are also known to undergo [2,3] sigmatropic rearrangement to yield allylic alcohols after hydrolysis.[59] Recently, some asymmetric reactions *via* optically active selenoxides and telluroxides as key intermediates have been developed.

a. [2,3] Sigmatropic Rearrangement of Optically Active Allylic Selenoxides and Telluroxides

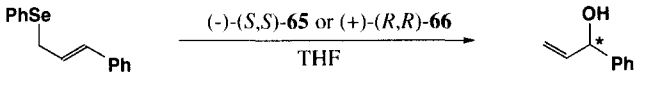
Salmond and co-workers reported asymmetric reaction of selenoxides attached to steroidal system in 1977.[60] Oxidation of 7β-phenylselenocholesteryl benzoate **57** with 90% hydrogen peroxide at 0° to -5° followed by conventional workup afforded 3-benzoate of coprost-6-en-3β,5-diol **58** in 45% yield *via* [2,3] sigmatropic rearrangement of the selenoxide **61**, together with 7-dehydrocholesteryl benzoate (45%) which was formed by β-elimination of the selenoxide (*Eq. 17*). In contrast, oxidation of the 7α-phenylseleno derivative **59** led to the 3-benzoate of cholest-6-en-3β,5α-diol **60** in 94% yield *via* **62** under similar conditions.



(17)

Davis and co-workers also reported [2,3] sigmatropic rearrangement of chiral selenoxide.[18] Asymmetric oxidation of (*E*)-phenyl cinnamyl selenide **63** with chiral oxaziridines (*S,S*)-**65** and (*R,R*)-

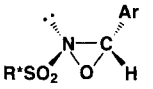
66 yielded optically active 1-phenyl allyl alcohol **64** *via* concerted [2,3] sigmatropic rearrangement of optically active selenoxides formed by oxidation of the selenide (*Eq. 18*).



(18)

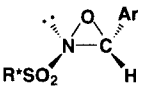
63 **64**

Oxaziridine	Conditions	ee(%)	(Config.)	yield(%)
(-)-(*S*,*S*)-**65**	-37°	8.8	(*S*)	63
(+)-(*R*,*R*)-**66**	0 - 5°	12.8	(*R*)	51



Ar = 2-chloro-5-nitrophenyl
R* = *d*-10-camphor

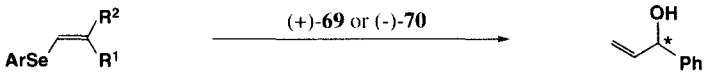
(-)-(*S*,*S*)-**65**



Ar = 2-chloro-5-nitrophenyl
R* = *d*-α-bromo-π-camphor

(+)-(*R*,*R*)-**66**

Asymmetric oxidations of cinnamyl selenides **67** with oxaziridines (+)-**69** and (-)-**70** were also reported by Davis *et al.*[19] Asymmetric oxidations of (*E*)- and (*Z*)-aryl cinnamyl selenides **67** with oxaziridine (+)-**69** or (-)-**70** afforded optically active 1-phenyl allyl alcohol **68** *via* a concerted [2,3] sigmatropic selenoxide-selenenate rearrangement (*Eq. 19*).

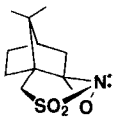


(19)

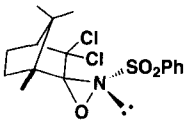
67 **68**

Ar	R^1	R^2	Oxaziridine	Method[a]	ee(%)	(Config.)	Yield (%)
Ph	H	Ph	(+)-**69**	A	4	(*R*)	65
Ph	H	Ph	(-)-**70**	A	35	(*R*)	62
2,4,6-triisopropylphenyl	H	Ph	(+)-**69**	A	25	(*S*)	44
2,4,6-triisopropylphenyl	H	Ph	(+)-**69**	B	31	(*S*)	56
2,4,6-triisopropylphenyl	H	Ph	(-)-**70**	A	36	(*S*)	41
2,4,6-triisopropylphenyl	H	Ph	(-)-**70**	B	40	(*S*)	55
Ph	Ph	H	(+)-**69**	B	9	(*R*)	35
Ph	Ph	H	(-)-**70**	B	40	(*R*)	55
2,4,6-triisopropylphenyl	Ph	H	(+)-**69**	B	42	(*R*)	43
2,4,6-triisopropylphenyl	Ph	H	(-)-**70**	B	60	(*R*)	46

a) Method A. After the oxidation was complete, the reaction was quenched with water and pyridine. Method B. Pyridine was added prior to oxidation.

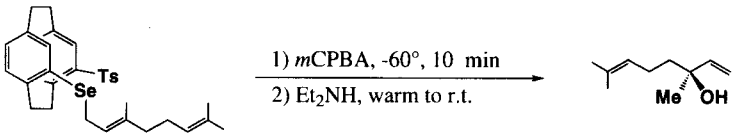


(+)-**69**



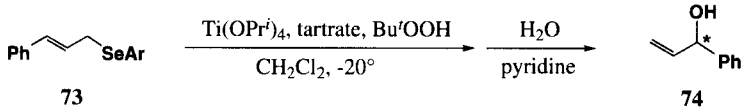
(-)-**70**

Preparation of linalool through the rearrangement of intermediate chiral selenoxide was reported by Reich and Yelm.[61] Oxidation of selenide **71** with *m*-chloroperbenzoic acid followed by addition of diethylamine (to avoid any undesired side reactions) gave an optically active linalool (*S*)-**72**, a naturally occurring alcohol for which the absolute configuration is known, through the [2,3] sigmatropic rearrangement of the optically active $(S)_{Se}$-selenoxide intermediate (*Eq. 20*).



71 **72** *S* / *R* = 5 / 1 (20)

Synthesis of optically active alcohol based on asymmetric oxidation of achiral selenide under Sharpless oxidation conditions were reported by Uemura and co-workers.[62] Oxidation of aryl cinnamyl selenides **73** with *t*-butyl hydroperoxide in the presence of titanium tetraisopropoxide and tartrate afforded a chiral 1-phenyl-2-propen-1-ol **74** *via* asymmetric [2,3] sigmatropic rearrangement in a moderate to high enantiomeric excess (up to 92% ee) (*Eq. 21*).

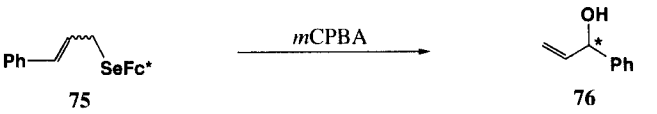


73 **74** (21)

Ar	Tartrate	ee(%)	(Config.)	yield(%)
o-$NO_2C_6H_4$	(+)-DIPT	92	(*R*)	42
o-$NO_2C_6H_4$	(+)-DCHT	61	(*R*)	35
o-$NO_2C_6H_4$	(+)-DET	41	(*R*)	43
Ph	(+)-DIPT	69	(*R*)	41
Ph	(+)-DIPT	42	(*R*)	21
Ph	(-)-DIPT	61	(*S*)	65
Ph	(+)-DCHT	43	(*R*)	42
Ph	(+)-DET	10	(*R*)	46
Ph	(+)-BINOL[a]	7	(*S*)	16
2-pyridyl	(+)-DIPT	31	(*R*)	10
ferrocenyl	(+)-DIPT	25	(*R*)	10

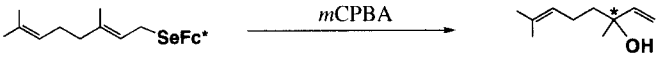
a) Two eq. of (+)-binaphthol was used instead of tartrate.

Asymmetric [2,3] sigmatropic rearrangement of diastereomeric selenoxides was also reported by Uemura and co-workers.[63] Treatment of chiral cinnamyl ferrocenyl selenides **75** and chiral geranyl (*trans*-3,7-dimethyl-2,6-octadienyl) ferrocenyl selenides **77** with *m*-chloroperbenzoic acid yielded chiral 1-phenyl-2-propen-1-ol **76** and linalool **78** up to 89 and 83% ee, respectively (*Eq. 22 and 23*).



75 76 (22)

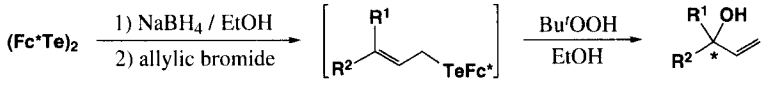
Config. of olefin	Config. of Fc*	Solvent	ee(%)	(Config.)	Yield(%)
E	*R,S*	MeOH	89	(*R*)	60
E	*R,S*	CH_2Cl_2	65	(*R*)	39
E	*R,S*	Et_2O	68	(*R*)	58
E	*R,S*	CCl_4	87	(*R*)	16
E	*R,S*	MeOH	88	(*R*)	38
E	*R,S*	CH_2Cl_2	89	(*R*)	30
E	*R,S*	Et_2O	76	(*R*)	44
E	*R,S*	toluene	76	(*R*)	28
E	*S,R*	MeOH	72	(*S*)	83
Z	*R,S*	MeOH	84	(*R*)	37
Z	*S,R*	MeOH	67	(*S*)	56



77 78 (23)

Config. of Fc*	Solvent	ee(%)	(Config.)	Yield(%)
R,S	MeOH	83	(*S*)	45
S,R	MeOH	77	(*R*)	51

Only one example on asymmetric [2,3] sigmatropic rearrangement of optically active telluroxides was reported by Uemura and co-workers.[64] *t*-Butyl hydroperoxide or air oxidation of allylic chiral ferrocenyl tellurides **79**, prepared from chiral ferrocenyltellurium anions and corresponding allylic bromides, afforded the corresponding chiral allylic alcohols **80** by chirality transfer *via* [2,3] sigmatropic rearrangement of the intermediate allylic telluroxides (*Eq. 24*).



79 80 (24)

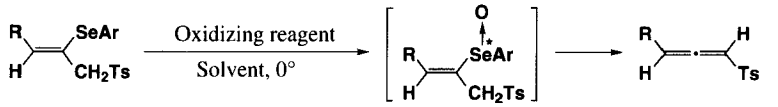
R^1	R^2	Config. of Fc*	ee(%)	(Config.)	Yield(%)
Me		*S,R*	19	(*S*)	46
Me		*S,R*	14[a]	(*S*)	13
Me		*S,R*	21	(*S*)	51
Me		*R,S*	22	(*R*)	39
	Me	*S,R*	14	(*S*)	30
H	Ph	*S,R*	21	(*R*)	26
H	Ph	*S,R*	20[a]	(*R*)	12

a) Without *t*-butyl hydroperoxide.

b. β-Elimination of Optically Active Selenoxides

Uemura and co-workers reported the synthesis of optically active allenes and cyclohexylidenemethyl ketones by asymmetric selenoxide elimination.

The oxidations of aryl vinyl selenides **81** under Sharpless oxidation conditions or with chiral oxaziridines (Davis oxidant) afforded chiral allenes **82** *via* asymmetric selenoxide elimination though the reactions were very slow (18-19 days, 0°) (*Eq. 25*).[65,66]

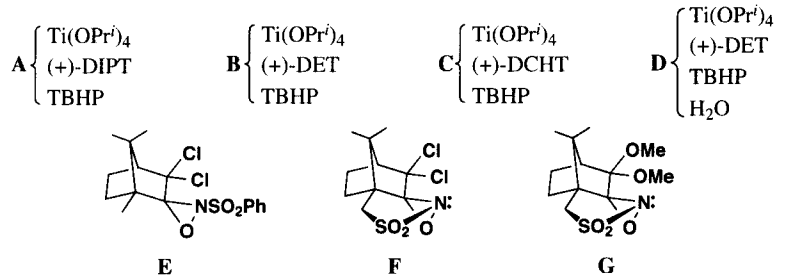


(25)

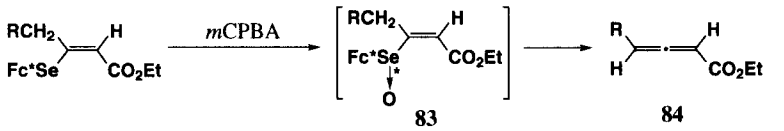
Ar = *o*-$NO_2C_6H_4$ **81** **82**

R	Oxidant	Solvent	ee(%)	(Config.)	Yield(%)
n-C_3H_7	A	CH_2Cl_2	38	(*R*)	43
n-C_3H_7	A	$ClCH_2CH_2Cl$	38	(*R*)	58
n-C_3H_7	B[a]	CH_2Cl_2	25	(*S*)	55
n-C_3H_7	C	CH_2Cl_2	42	(*R*)	85
n-C_3H_7	D	CH_2Cl_2	1	(*S*)	42
n-C_3H_7[b]	E	CH_2Cl_2	28	(*R*)	41
n-C_3H_7[b]	F	CH_2Cl_2	23	(*R*)	26
n-C_3H_7[b]	G	CH_2Cl_2	15	(*S*)	9
n-C_7H_{15}	A	CH_2Cl_2	38	(*R*)	59
n-C_7H_{15}	B	toluene	20	(*R*)	69
n-C_7H_{15}[b]	E	CH_2Cl_2[d]	24	(*R*)	*c*
n-C_7H_{15}[b]	F	CH_2Cl_2	23	(*R*)	16
n-C_7H_{15}[b]	G	CH_2Cl_2	17	(*S*)	16
Cl	A	CH_2Cl_2	5	(*R*)	41
Cl	B	CH_2Cl_2	10	(*S*)	78
Cl	D	CH_2Cl_2	16	(*R*)	32[e]

a) (-)-Tartrate was used. b) At r.t. c) The imide derivative from oxaziridine was contaminated. d) Treated with K_2CO_3 before use. e) The values for crude product.



Chiral ferrocenyl vinyl selenoxides **83**, formed by the oxidation of corresponding selenides with *m*-chloroperbenzoic acid, gave optically active allenes **84** up to 89% ee by the asymmetric selenoxide elimination (*Eq. 26*).[63,67]

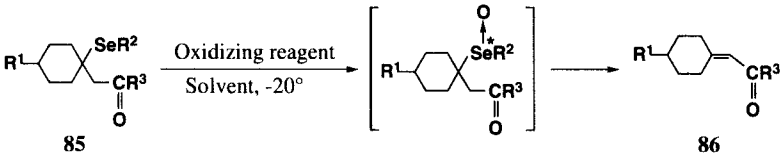


83 84 (26)

R	Config. of Fc*	Solvent	ee(%)	(Config.)	Yield(%)
Me	*R,S*	CH_2Cl_2[a]	83	(*R*)	47
Et	*R,S*	CH_2Cl_2[a]	75	(*R*)	38
n-C_3H_7	*R,S*	CH_2Cl_2[a]	79	(*R*)	45
Me	*S,R*	MeOH	30	(*S*)	35
Me	*S,R*	CH_2Cl_2	43	(*S*)	33
Me	*S,R*	Et_2O	16	(*S*)	21
Me	*S,R*	CH_2Cl_2	70	(*S*)	48
Me	*S,R*	CH_2Cl_2[a]	89	(*S*)	43
Et	*S,R*	CH_2Cl_2[a]	82	(*S*)	59
n-C_3H_7	*S,R*	CH_2Cl_2[a]	85	(*S*)	52

a) In the presence of molecular sieves 4A (powder).

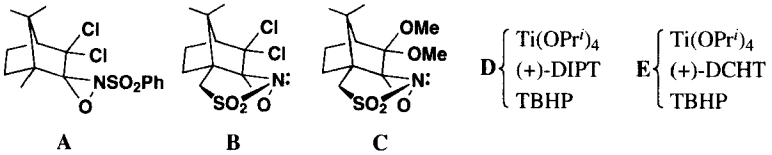
Axially chiral alkyl and aryl cyclohexylidenemethyl ketones **86** were given by asymmetric oxidation of a single isomer of cyclohexyl selenides **85** (*Z*-config., tentative) in high enantiomeric excesses (up to 83% ee) *via* the asymmetric selenoxide elimination (*Eq. 27*).[68]



85 86 (27)

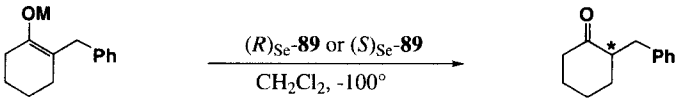
R^1	R^2	R^3	Oxidant	Solvent	ee(%)	(Config.)	Yield(%)
Ph	Me	Ph	A	CH_2Cl_2	74	(*R*)	92
t-Bu	Me	Ph	A	$CHCl_3$[a]	83	(*R*)	96
t-Bu	Me	Ph	A	CCl_4	82	(*R*)	100
t-Bu	Me	Ph	B	CCl_4	24	(*S*)	56
t-Bu	Me	Ph	C	CCl_4	6	(*R*)	95
t-Bu	Me	Ph	D	CH_2Cl_2[a]	2	(*S*)	100
t-Bu	Me	*t*-Bu	A	$CHCl_3$[a]	82	(*R*)	70
t-Bu	Me	Me	A	$CHCl_3$[a]	74	(*R*)	97
t-Bu	Ph	Ph	A	CH_2Cl_2	7	(*R*)	66
t-Bu	Ph	Ph	D	CH_2Cl_2	0	–	64
t-Bu	Ph	Ph	E	CH_2Cl_2	1	(*S*)	71
Me	Me	Ph	A	CH_2Cl_2	81	(*R*)	91

a) Treated with anhydrous K_2CO_3 prior to use.



c. Enantioselective Protonation of Enolates with Optically Active Selenoxides

Very recently, enantioselective protonation of prochiral enolates with chiral γ-hydroxyselenoxides was performed by Koizumi and co-workers.[69] Reaction of enolates **87** with chiral selenoxides **89** gave optically active 2-benzylcyclohexanone **88** with high enantioselectivity (*Eq. 28*).

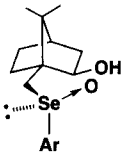


(28)

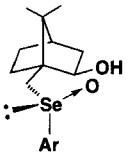
87 **88**

M	Config. of **89**	Ar	ee(%)	(Config.)	Yield(%)
Li	$(R)_{Se}$	Ph	29	(*R*)	51
Li	$(R)_{Se}$	4-FC_6H_4	0	–	68
Li	$(R)_{Se}$	4-$MeOC_6H_4$	64	(*S*)	47
Li	$(S)_{Se}$[a]	4-$MeOC_6H_4$	62	(*S*)	35
ZnBr	$(R)_{Se}$[b]	4-$MeOC_6H_4$	62	(*S*)	82
ZnBr	$(S)_{Se}$[c]	4-$MeOC_6H_4$	89	(*S*)	81

a) $(R)_{Se}$: $(S)_{Se}$ = 5 :95. b) $(R)_{Se}$: $(S)_{Se}$ = 95 :5. c) $(R)_{Se}$: $(S)_{Se}$ = 3 :97.



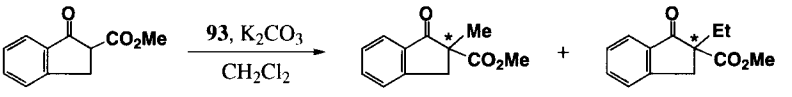
$(R)_{Se}$-**89**



$(S)_{Se}$-**89**

2. via Selenonium Salts

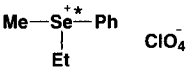
We reported asymmetric alkylation with chiral selenonium salts.[40] Alkylation of enolate anion of 2-methoxycarbonyl-1-indanone **90** with optically active ethylmethylphenyl selenonium salts **93** resulted in the formation of optically active C-alkylated compounds **91** and **92** with opposite configuration, though the enantiomeric excesses were low (*Eq. 29*).



(29)

90 **91** **92**

Config. of **93**	**91** ee(%)	(Config.)	Yield(%)	**92** ee(%)	(Config.)	Yield(%)
(*S*)	2.4	(*S*)	41	6.2	(*R*)	36
(*R*)	0.6	(*R*)	39	7.0	(*S*)	35

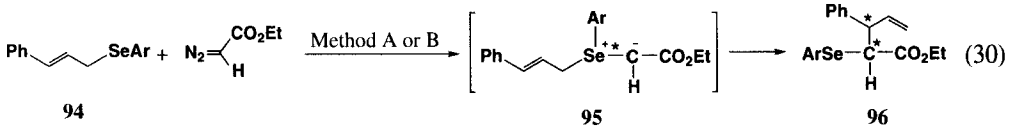


93

3. via Selenonium Ylides

In the presence of catalytic amount of chiral copper (I) or rhodium (II) compounds, the enantioselective addition of a carbenoid to selenium atoms of aryl cinnamyl selenides **94** afforded a

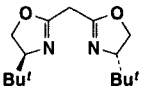
diastereomeric mixture of ethyl 2-arylseleno-3-phenylpent-4-enoates **96** *via* [2,3] sigmatropic rearrangement of the intermediate selenonium ylide **95** with up to 41% ee (*Eq. 30*).[70]



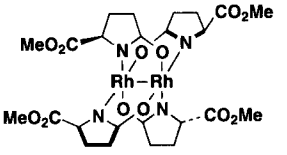
94 95 96 (30)

Ar	Method	Solvent	Diastereoisomeric ratio	(ee%)	Yield(%)
Ph	A[a]	$CHCl_3$	66 : 34	(22, 32)	71
o-$NO_2C_6H_4$	A	$CHCl_3$	53 : 47	(13, 34)	55
o-$CF_3C_6H_4$	A	$CHCl_3$	69 : 31	(8, 30)	35
Ph	B[b]	CH_2Cl_2	58 : 42	(25, 41)	65

a) Method A: CuOTf (5 mol%) and bisoxa zoline **97** (5 mol%) were used. b) Method B: Rh_2(5*S*-MEPY)$_4$ **98** (1 mol%) was used.



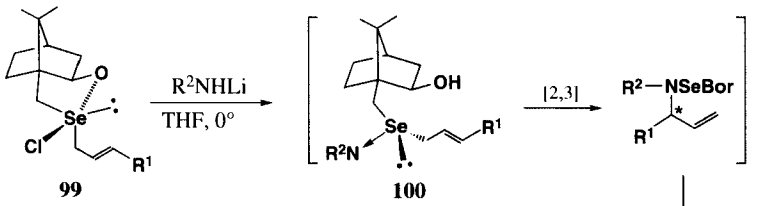
97: bisoxazoline



98: Rh_2(5*S*-MEPY)$_4$

4. via Selenonium and Telluronium Imides

Asymmetric [2,3] sigmatropic rearrangement of chiral allylic selenimides was reported by Koizumi and co-workers.[56] Nucleophilic reaction of chloroselenuranes **99** with lithium *N*-protected amides afforded chiral allylic selenimides **100** as intermediate with retention of configuration. A [2,3] sigmatropic rearrangement of **100** yielded chiral *N*-protected allylic amides **101** up to 93% ee (*Eq. 31*).

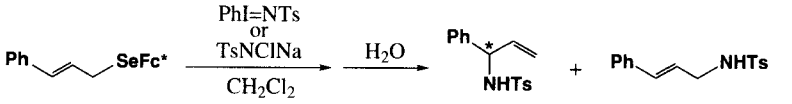


99 **100** **101** (31)

R^1	R^2	ee(%)	(Config.)	Yield(%)
Ph	Cbz	24	–	67
i-Pr	Cbz	67	(*S*)	57
Ph	Boc	7	–	74
i-Pr	Boc	73	(*S*)	63
Ph	*p*-Ts	90	(*R*)	57
Ph	*p*-Ts	93	(*S*)	74
i-Pr	*p*-Ts	93	(*S*)	86
Ph	$Ph_2P(O)$	92	(*R*)	53
i-Pr	$Ph_2P(O)$	93	(*S*)	69

Asymmetric [2,3] sigmatropic rearrangement of chiral selenimides and tellurimides were reported by Uemura and co-workers. The imination of chiral cinnamyl 2-(1-dimethylaminoethyl)-

ferrocenyl selenides **102** with [*N*-(toluene-*p*-sulfonyl)imino]phenyliodinane or chloramine-T afforded the corresponding chiral allylic amines **103** *via* [2,3] sigmatropic rearrangement of the selenimide intermediates with up to 87% ee (*Eq. 32*).[71]



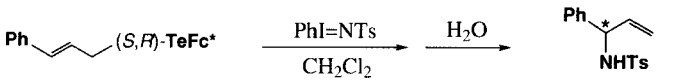
(32)

102 **103** **104**

Config. of Fc*	Reagent	T/° (t/h)	**103** ee(%)	**103** Yield(%)	**104** Yield(%)
R,S	TsNClNa	25 (1)	13	29	23
R,S	TsNClNa	0 (20)	45	13	27
S,R	TsNClNa	0-25 (22)	13	17	24
S,R	PhI=NTs	25 (1)	49	52	0
S,R	PhI=NTs	0 (20)	80	52	0
S,R	PhI=NTs	-20 (72)	–	0	0
R,S	PhI=NTs	0 (20)	87	42	0
S,R	PhI=NTs	0 (20)[a]	77	49	0

a) (*Z*)-Cinnamyl selenide was used.

Similarly, imination of chiral cinnamyl 2-(1-dimethylaminoethyl)ferrocenyl telluride **105** with [*N*-(toluene-*p*-sulfonyl)imino]phenyliodinane gave the corresponding chiral allylic amine **106** in 93% ee (*Eq. 33*).[72]



(33)

105 **106**

93% ee, Y. 45%

IV. CONCLUSIONS

Recently, many optically active tricoordinate organoselenium and tellurium compounds have been synthesized. Some optically active tetracoordinate chalcogen compounds have also been isolated. However, optically active penta- or hexacoordinate selenium or tellurium compounds have not yet been synthesized. With the progress in the preparation of optically active selenium and tellurium compounds, some synthetic applications *via* chiral chalcogen compounds have been reported. However, the application is limited except selenoxides. Hereafter, development of the application of other chiral chalcogen compounds for asymmetric synthesis is expected.

This review has surveyed the isolation and the versatile synthetic utilization of optically active organoselenium and tellurium compounds. However, for details of the chemistry, such as properties of the optically active compounds, determination of the absolute configuration, chirality recognition, conditions of the reactions, and reaction mechanisms, the original papers should be consulted.

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