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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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To cite this Article Uemura, Sakae(2001) 'Application of Asymmetric Oxidation and Imidation of Organic Selenides to Organic Transformations', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 171: 1, 13 – 30

To link to this Article: DOI: 10.1080/10426500108046626

URL: <http://dx.doi.org/10.1080/10426500108046626>

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Application of Asymmetric Oxidation and Imidation of Organic Selenides to Organic Transformations

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Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan*

Our results on an enantioselective and diastereoselective oxidation (up to 89% ee) and imidation (up to 87% ee) of organic selenides to afford optically active selenoxides and selenimides, respectively, which lead to optically active organic compounds by successive selenoxide elimination or [2,3]sigmatropic rearrangement, are mainly described.

Keywords: organic selenides; selenoxides; selenimides; selenoxide elimination; [2,3]sigmatropic rearrangement; enantioselective reaction; diastereoselective reaction

Nowadays, organoselenium compounds-participated reactions are very useful in the field of synthetic organic chemistry and they are regularly employed for preparation of many organic compounds including natural products, sometimes compensating with the corresponding reactions of

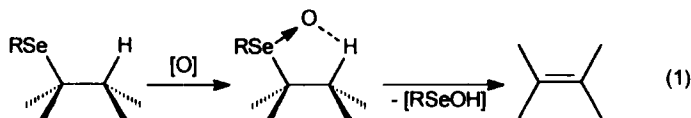
organosulfur compounds. However, their application to asymmetric organic synthesis was undeveloped until recently, in contrast to the corresponding organosulfur chemistry where the usefulness and the potentiality of the optically active organosulfur compounds has long been known for asymmetric synthesis.

We have so far made several efforts on finding preparative uses of optically active organoselenium compounds, either as isolated ones or as intermediates, for asymmetric synthesis. In this article we would like to describe mainly our results on an enantioselective and diastereoselective oxidation and imidation of organic selenides to afford the corresponding optically active selenoxides and selenimides, respectively, which lead to optically active organic compounds by successive selenoxide elimination or [2,3]sigmatropic rearrangement.^[1] The corresponding chemistry of organic tellurides is briefly described when it concerns. It is worth noting here that optically pure organic selenoxides have been prepared by the optical resolution method^[2] and also that a few corresponding organic selenimides have been prepared by either the optical resolution method or the conversion of a chiral selenoxide with TsNH_2 .^[3]

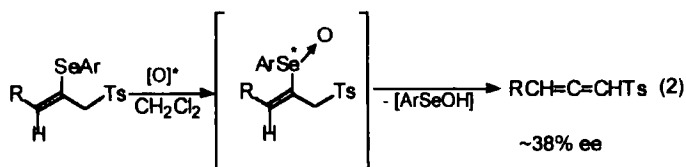
1. ENANTIOSELECTIVE SELENOXIDE ELIMINATION PRODUCING AXIALLY CHIRAL ALLENES AND CYCLOHEXYLIDENE KETONES

It is well known that organic selenides can easily be oxidized by various reagents to the corresponding organic selenoxides and, when the resulting selenoxides bear a β -hydrogen atom, syn elimination occurs

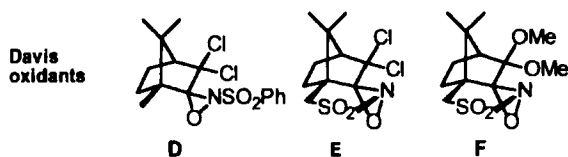
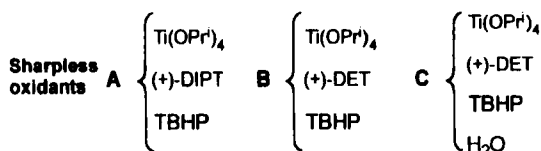
readily to give the corresponding alkene together with a selenenic acid (eq. 1).^[4]



We were successful, for the first time, in asymmetric version of this selenoxide elimination; namely, the production of optically active allenic sulfones via enantioselective oxidation of some aryl vinyl selenides using chiral Sharpless and Davis oxidants (eq. 2).^[5]



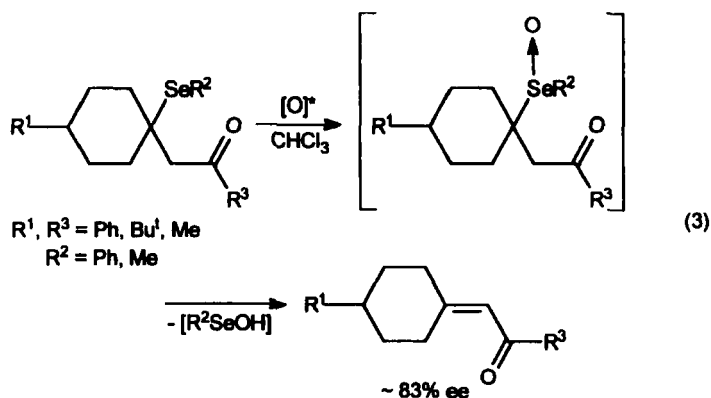
[O]*



A maximum enantioselectivity obtained so far was yet 38% ee with a product yield ranging from 43 to 59% when Ar = *o*-NO₂C₆H₄-, R = C₃H₇

or C_7H_{15} , and the Sharpless oxidant **A** were employed. The kinetic study on the effects of aryl groups indicated that the rates of both oxidation and elimination steps were accelerated by the introduction of an electron-withdrawing group at ortho-position which suppresses sterically the racemization of the intermediate chiral selenoxides to achieve a higher asymmetric induction.^[6]

As a further work, this reaction was applied to the preparation of axially chiral alkyl and aryl cyclohexylidene methyl ketones starting from the substituted-cyclohexyl methyl and phenyl selenides (eq. 3).^[7]

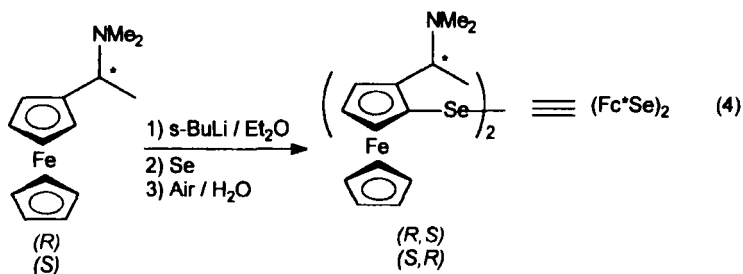


In this asymmetric induction, R^2 of the substrate and the chiral oxidant employed were revealed to show remarkable effects upon the enantioselectivity of the product. The use of Me as R^2 instead of Ph gave a higher enantioselectivity, probably due to the steric difference between the groups bonded to the selenium atom of the substrate. Davis oxidants were revealed to be much better than Sharpless oxidants and a maximum

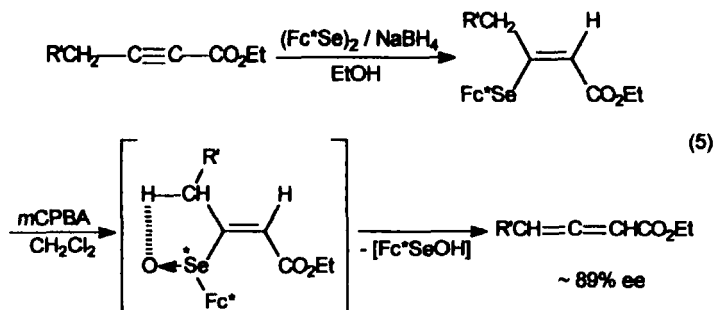
enantioselectivity was 83% ee with 96% chemical yield using the Davis oxidant **D**, the configuration of the product being *R*.

2. DIASTEREOSELECTIVE SELENOXIDE ELIMINATION PRODUCING AXIALLY CHIRAL ALLENECARBOXYLIC ESTERS

In a previous section, we described the results of enantioselective oxidation of organic selenides using chiral oxidants to give optically active selenoxides followed by facile selenoxide elimination affording axially chiral organic compounds. If the organic selenides contain some chiral centres, their oxidation with non-chiral oxidants might give optically active selenoxides diastereoselectively, resulting in the formation of optically active compounds after a similar selenoxide elimination. In fact this was the case. For this purpose, we have newly prepared optically active organic diselenides, diferrocenyl diselenides, from the corresponding chiral ferrocenes (eq. 4) and introduced thus prepared optically active ferrocenyl selenenyl group (Fc^*Se) into organic molecules to afford the alkenyl selenides as shown in eq. 5.^[8]

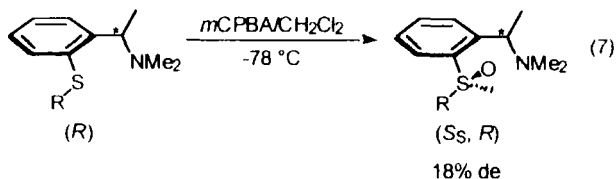
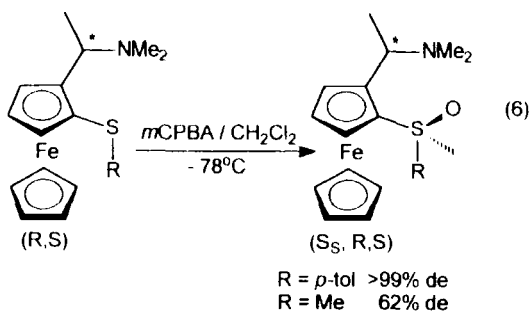


The oxidation of the alkenyl selenides with 1 molar equivalent of meta-chloroperbenzoic acid (*m*CPBA) gave the corresponding chiral selenoxides diastereoselectively which suffered in situ selenoxide elimination to afford the axially chiral allenecarboxylic esters [*R*-isomer from (*R*, *S*) and *S*-isomer from (*S*, *R*), respectively] in 38–59% yields with moderate to high enantioselectivities (39–89% ee).



The lower reaction temperature was required to suppress the racemization of the diastereomeric alkenyl selenoxide intermediates in order to obtain a high selectivity.

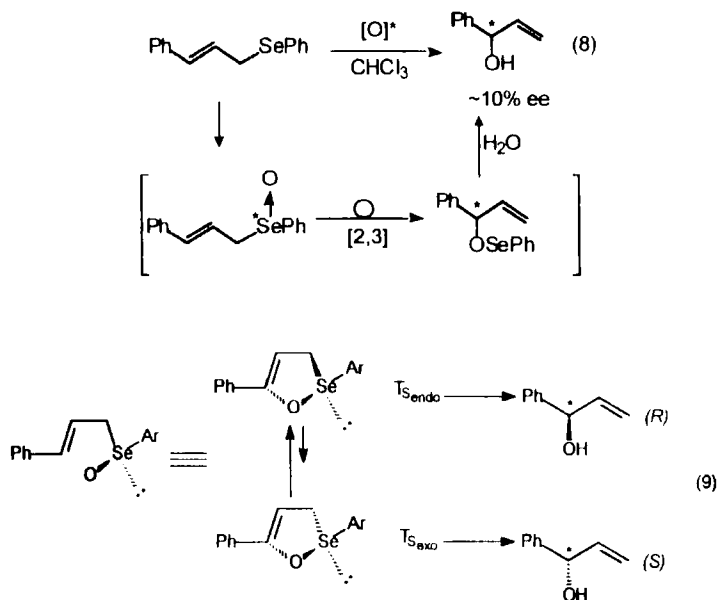
The diastereoselection in the step of oxidation of chiral ferrocenyl alkenyl selenides was supported from the fact that the oxidation of chiral *p*-tolyl or methyl ferrocenyl sulfide, instead of the selenide, with *m*CPBA occurred highly diastereoselectively to give the corresponding chiral sulfoxide (eq. 6).^[8b] On the other hand, a similar oxidation of its benzene analogue has been reported to afford the corresponding sulfoxide with low diastereoselectivity (eq. 7),^[9] suggesting that the high diastereoselectivity observed here is not due to the chirality of the substituent on the ferrocene ring, but rather to the planar chirality of the ferrocene.



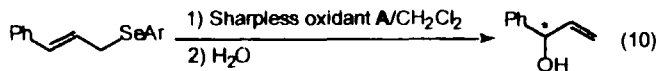
3. ENANTIOSELECTIVE [2,3]SIGMATROPIC REARRANGEMENT PRODUCING OPTICALLY ACTIVE ALLYLIC ALCOHOLS

Asymmetric [2,3]sigmatropic rearrangement via allylic selenoxides was first reported by Davis et al. in the enantioselective oxidation of cinnamyl phenyl selenide with a oxaziridine-type oxidant developed by them and the selectivity of the product, 1-phenyl-2-propen-1-ol, was up to ~10% ee (eq. 8).^[10a] Later, the selectivity was much improved (up to 60% ee) using the Davis oxidant **D** and starting from various (*E*) and (*Z*)-cinnamyl aryl selenides.^[10b] They postulated that the selectivity of the allylic alcohols produced may be dependent on the free energy difference of the two possible transition states (*endo* and *exo*) at the transformation

step from an allylic selenoxide to an allylic selenenate as shown in eq. 9.^[10b]



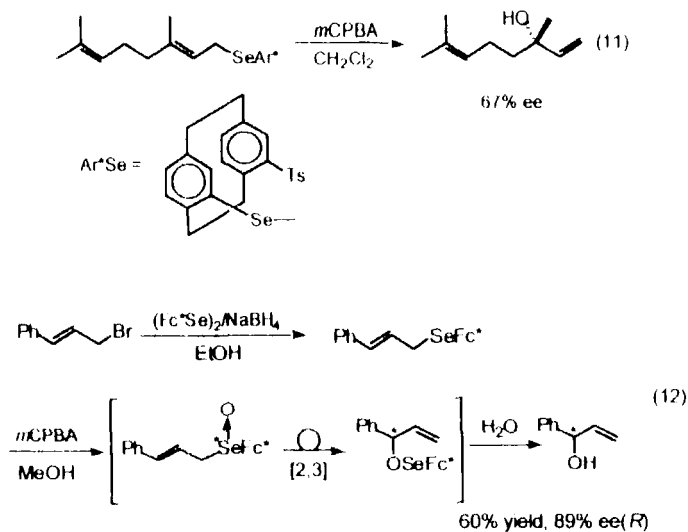
We also succeeded in the enantioselective oxidation of several aryl cinnamyl selenides using the Sharpless oxidant **A** and clarified a strong correlation between the aryl group and the ee value of the product alcohol (eq. 10).^[11] The introduction of an *o*-nitro group to a benzeneselenium moiety (Ar = *o*-nitrophenyl) remarkably enhanced the enantioselectivity. The large steric and/or electronic effects of the group to stabilize the chiral selenoxide intermediate are important for obtaining a high selectivity and also a large energy difference between the two possible transition states may be formed by introduction of the group.



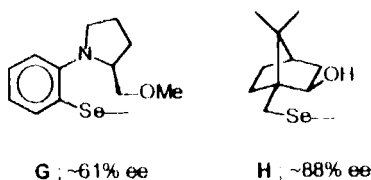
Ar	Yield(%)	ee(%)
Ph	41	69
<i>o</i> -nitrophenyl	42	92
2'-pyridyl	10	31
ferrocenyl	10	25

4. DIASTEREOSELECTIVE [2,3]SIGMATROPIC REARRANGEMENT PRODUCING OPTICALLY ACTIVE ALLYLIC ALCOHOLS

In 1991, Reich and Yelm reported the first example of the diastereoselective oxidation of the optically active geranyl [2.2]paracyclophanyl selenide with *m*CPBA to give linalol with 67% ee via [2,3]sigmatropic rearrangement of the corresponding selenoxide (eq. 11). We have applied our optically active diferrocenyl diselenide to a similar rearrangement as shown in eq. 12, both diastereoselective oxidation step and the chirality transfer step from Se to C-3 atom of the intermediate allylic selenenate being important.^[6b] The oxidation of cinnamyl and geranyl selenides bearing a chiral ferrocenyl group with *m*CPBA afforded the corresponding optically active allylic alcohols in moderate yields with a high ee (up to 89% ee and 83% ee, respectively).

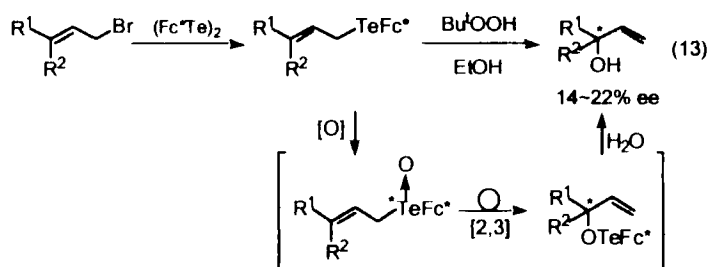


Several other chiral arylselenenyl group such as **G**^[13] and **H**^[14] were also developed for similar purpose and diastereoselective oxidation of the corresponding allyl aryl selenides has been carried out with success.



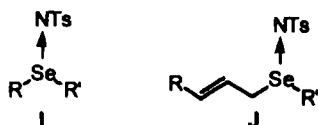
It is worth noting here that when similar diastereoselective oxidation was applied under various conditions to the optically active allylic ferrocenyttellurides, derived from allylic bromides and chiral diferrocenyl ditelluride $[(\text{Fc}^*\text{Te})_2]$ similar to the selenium analogue, the corresponding

optically active allylic alcohols were obtained in 30-50% yield with 14-22% ee (eq. 13).^[15] The lower selectivity in the tellurium case may be due to the very rapid epimerization of the intermediate chiral telluroxides through the achiral dihydrates compared with the selenium case.

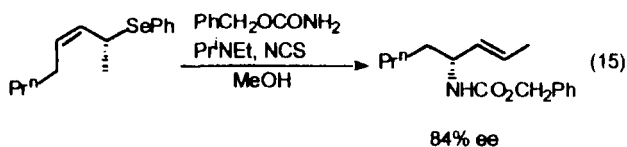
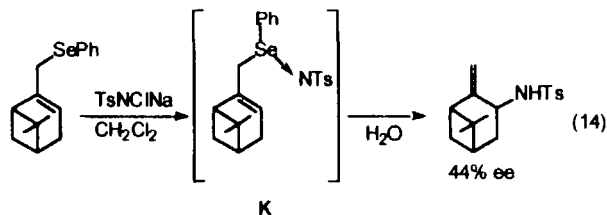


5. PREPARATION OF OPTICALLY ACTIVE SELENIMIDES AND THEIR ASYMMETRIC ORGANIC TRANSFORMATIONS

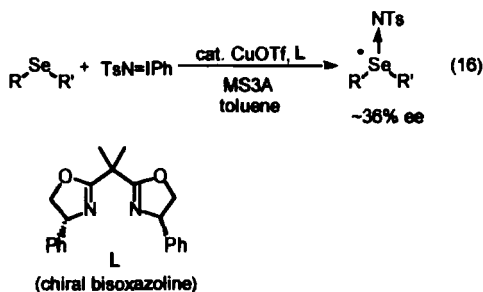
The nitrogen analogues of the selenoxides, the selenimides such as **I**, are well-known compounds, although their preparative use in organic chemistry is still quite undeveloped. Their allylic derivatives (**J**) are capable of [2,3]sigmatropic transformation and, actually, Hori and Sharpless reported such reaction to give allylic amine derivatives using Chloramine T [TsN(Cl)Na] two decades ago (eq. 14).^[16]



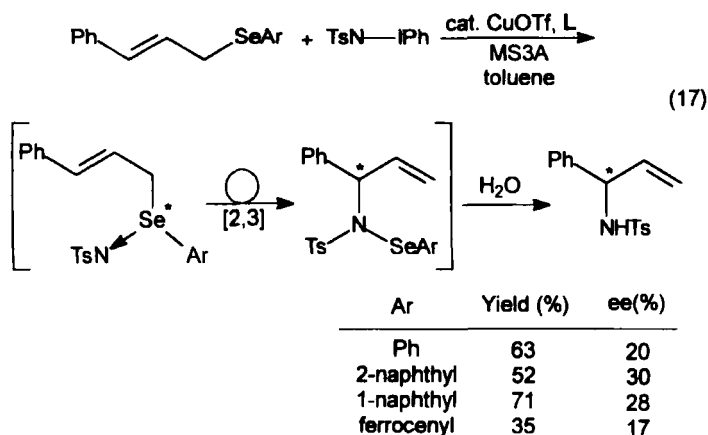
This reaction presumably proceeds by way of the corresponding allylic selenimide intermediate (K) and, later, Hopkins et al. reported several improved methods using other imidation reagents as shown in eq. 15.^[17]



We have recently found that *N*-(*p*-tolylsulfonyl)imino(phenyl)iodinane (TsN=IPh) works as a convenient imidation reagent of sulfides^[18] and selenides^[19] in the presence of a catalytic amount of CuOTf and also that the presence of a chiral bisoxazoline such as L as a ligand enabled the reaction to occur enantioselectively (eq. 16).

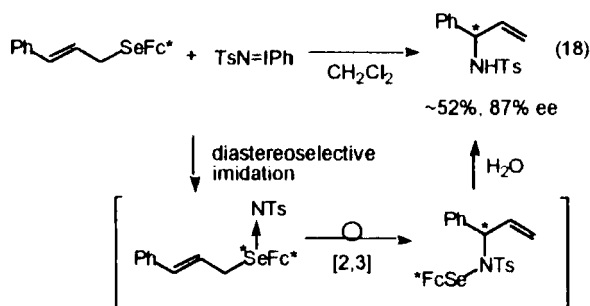


Application of this reaction to various aryl cinnamyl selenides resulted in the formation of optically active allylic amine derivatives in moderate to good yields with moderate enantioselectivities via [2,3]sigmatropic rearrangement of the intermediate allylic chiral selenimides (eq. 17). Although a maximum selectivity obtained is not yet so high (~30% ee), this is quite close to that (~36% ee) obtained by direct imidation of other prochiral selenides, indicating that the chirality is not lost in the rearrangement step.



As in the case of diastereoselective oxidation of chiral allylic selenides described in a previous section, we also carried out the corresponding imidation using similar compounds containing optically active ferrocenylselenenyl moiety and succeeded in it to obtain the optically active allylic amine derivatives in moderate yields with high enantiomeric excess (eq. 18).^[20] The result of the high ee values of the

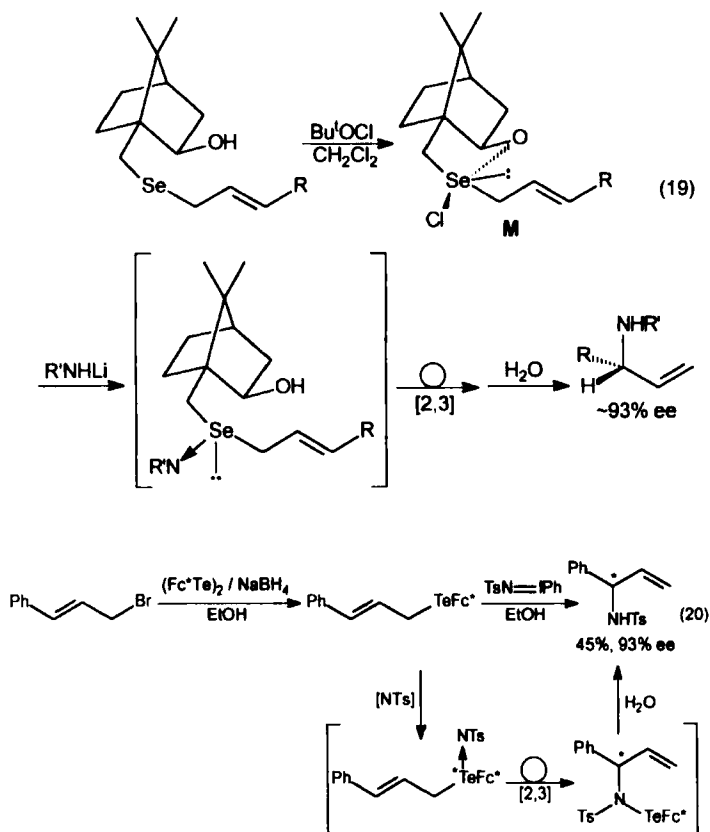
produced compounds in eqs. 12 and 18 provided the basis of the following speculations concerning the present diastereoselective reaction: 1) The initial oxidation or imidation step proceeds with high diastereoselectivity and 2) the chirality transfer via [2,3]sigmatropic rearrangement occurs almost without loss of optical purity.



It is noteworthy that Koizumi et al. used the optically active allylic chloroselenuranes bearing H group, prepared by diastereoselective chlorination of the starting selenides, to obtain optically active allylic amines. The nucleophilic reaction of the selenurane (**M**) with lithium *N*-protected amides proceeded in situ with retention of configuration to afford the optically active allylic selenimides, which migrated to give the *N*-protected allylic amines in high yields with high enantiomeric excesses (eq. 19).^[21]

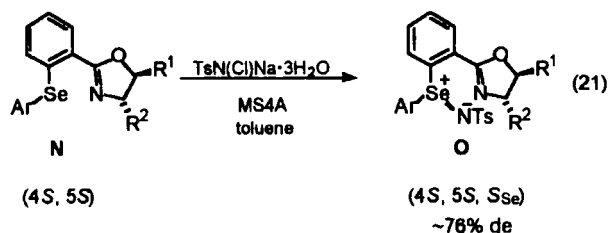
Although a detailed study has not yet been carried out, one example of the tellurium version of this diastereoselective imidation is known. This, treatment of an optically active cinnamyl ferrocenyl telluride with TsN=IPh afforded the corresponding allylic amine derivative highly selectivity (93% ee) via [2,3]sigmatropic rearrangement (eq. 20),^[22] in

sharp contrast to the result of the diastereoselective oxidation of similar compounds (eq. 13) where only low enantioselectivities were observed. This may suggest a very slow epimerization of tellurimides compared to the corresponding telluoxide analogues.

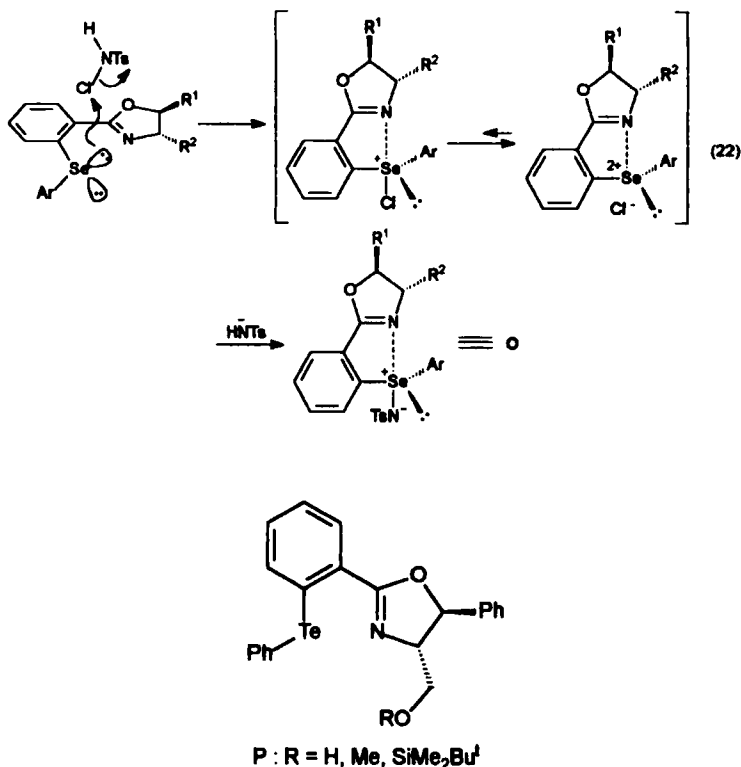


Lastly, we would like to describe our recent finding on the diastereoselective imidation of selenides having a chiral oxazolinyl moiety

(**N**) with TsN=IPh or Chloramine T trihydrate to give the corresponding optically active N-tosylselenimides (**O**) (eq. 21).^[23]



Different from similar imidation of the corresponding sulfides where a high diastereoselectivity of 99% was obtained in the presence of some Cu salts,^[24] the addition of copper salts did not give any effects on this diastereoselective selenoimidation and an ionic pathway involving a chloroselenonium ion intermediate was proposed (eq. 22). Although similar sulfimides have been revealed to work as chiral ligands for enantioselective transition metal-catalyzed allylic alkylation,^[24] the selenimides **O** obtained here, unfortunately, did not work well for that purpose and we are looking for the utility of these novel compounds. We also add here the fact that some tellurium analogues of **N**, namely **P**, could be prepared, but imidation of these compounds did not proceed well.^[25]



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