Catalytic asymmetric imidation of selenides into selenimides
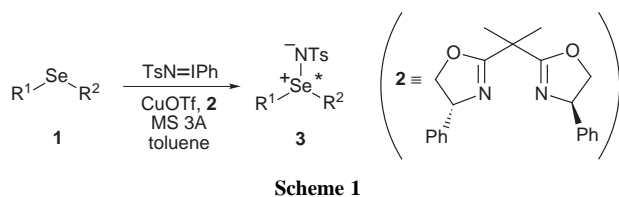
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The direct catalytic imidation of various prochiral selenides with TsN=IPh in the presence of CuOTf using chiral 4,4′-disubstituted 2,2′-bis(oxazoline) ligand afforded the corresponding chiral selenimides (~ 36% ee).

The synthesis and the synthetic application of optically active organosulfur compounds have been widely studied.[1] Recently, we succeeded in developing direct catalytic sulfimidation of prochiral sulfides to chiral sulfimides with *N*-(*p*-tolylsulfonyl)-imino(phenyl)-λ³-iodane (TsN=IPh)[2] in the presence of CuOTf and the chiral ligands, 4,4′-disubstituted bis(oxazoline).[3] In contrast, the asymmetric synthesis of analogous organoselenium compounds, selenimides, has been much less studied.[4–6] In 1981, Krasnov *et al.* reported the first synthesis of the optically active selenimides by starting from dialkyl- and diaryl-selenium dichlorides,[4] but the scope of this reaction has not been fully developed probably because of low yields of the products as well as their quite low optical activity. Recently, Kamigata and co-workers have shown an example of conversion of a chiral selenoxide obtained by optical resolution of a diastereomeric mixture[7] into the corresponding enantiomerically pure selenimide, ascertaining the detailed stereochemistry of the compound.[6] We have already demonstrated the diastereoselective imidation of chiral allylic selenides using TsN=IPh or chloramine-T (TsNClNa) as an imidation reagent.[8] We report here a first example of the direct catalytic enantioselective imidation of simple selenides into the corresponding selenimides (Scheme 1).

As described above, a direct catalytic imidation of prochiral sulfides to chiral sulfimides proceeded with TsN=IPh in the presence of CuOTf and bis(oxazoline) in various solvents. We first looked for the solvent in which imidation of prochiral

Scheme 2

selenide **1** with TsN=IPh did not proceed in the absence of CuOTf. Treatment of benzyl phenyl selenide with TsN=IPh in MeCN and CH_2Cl_2 at 25 °C for 24 h afforded benzyl phenyl selenimide in 46% and in a trace amount, respectively, but in toluene no reaction occurred. Therefore, we chose toluene as solvent[9] and carried out imidation of benzyl phenyl selenide with TsN=IPh in the presence of CuOTf (10 mol%) and the optically active bis(oxazoline) **2** (12 mol%) at 25 °C for 24 h under N_2 (Scheme 1).[10] Benzyl phenyl selenimide was formed in 40% yield, but no asymmetric induction occurred. Fortunately, further studies revealed that the reaction proceeded enantioselectively when molecular sieves were added (compare entry 1 in Table 1). This is probably due to the interference of the rapid selenimide–selenoxide equilibrium[11] (Scheme 2) by removal of water present in the reaction mixture. A rapid racemization of the selenoxide is well known.[12] At a lower temperature the reaction was slower (entry 3). The reaction also proceeded with several other aryl benzyl selenides, but the selenide having bulky substitutents on an aryl ring such as benzyl 2,4,6-tri-*tert*-butylphenyl selenide (**1e**) did not react at all. Typical results are shown in Table 1. The desired product was isolated in moderate yield without racemization by removal of the precipitate through Celite and purification of the residue by column chromatography (SiO_2). When this reaction was applied to various aryl cinnamyl selenides **4**, the expected chiral allylic amides (~ 30% ee) were obtained selectively in moderate to good yield *via* [2,3] sigmatropic rearrangement of the

Scheme 1

Table 1 Catalytic asymmetric imidation of selenides **1**[a]

Entry	Selenide	T/°C	Product	Yield (%)	Ee (%)[b]
1[c]	PhSeBn	25	**3a**	40	0
2	PhSeBn	25	**3a**	53	32
3	PhSeBn	0	**3a**	18	33
4	4-MeOC₆H₄SeBn	25	**3b**	37	20
5	1-NaphthylSeBn	25	**3c**	23	29
6[d]	2-NaphthylSeBn	25	**3d**[e]	64	36
7	2,4,6-Buᵗ₃C₆H₂SeBn	25	**3e**	nr	—

[a] All the reactions were performed in toluene (0.02 M) in the presence of 12 mol% chiral ligand **2** and 10 mol% CuOTf for 24 h unless otherwise noted. [b] Enantiomeric excesses were determined by HPLC using suitable chiral columns. [c] The reaction was performed without MS 3A. [d] MS 4A, for 48 h. [e] See footnote §.

Scheme 3

Table 2 Catalytic asymmetric imidation of cinnamyl selenides **4**[a]

Entry	R¹	Product	Yield (%)	Ee (%)[b]
1	Ph	**6a**	63	20
2	1-Naphthyl	**6b**	71	28
3	2-Naphthyl	**6c**	52	30
4	Ferrocenyl	**6d**	35	17
5	2-NO₂C₆H₄	**6e**	Trace	—

[a] All the reactions were performed in toluene (0.02 M) in the presence of 12 mol% chiral ligand **2** and 10 mol% CuOTf for 24 h. [b] Enantiomeric excesses were determined by HPLC using suitable chiral columns.

intermediate chiral allylic selenimide (Scheme 3, Table 2), clearly showing that the chirality transfer occurred at the rearrangement step.

Although the enantioselectivity obtained here is not yet satisfactory (~ 36% ee) and lower than the corresponding sulfur case,[3] the finding presented here is the first example of the direct catalytic enantioselective imidation of organic selenides into the corresponding selenimides.

Notes and References

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‡ Representative procedure for the imidation of selenide: to a solution of MS 3A (*ca.* 300 mg), CuOTf (0.010 mmol, 0.10 equiv.) and chiral 2,2′-bis(oxazoline) **2** (0.012 mmol, 0.12 equiv., Aldrich) in 5.0 ml of toluene were added first TsN=IPh (0.10 mmol, 1.0 equiv.) and then the selenide (0.20 mmol, 2.0 equiv.)[10] and the resulting mixture was stirred under nitrogen at 25 °C for 24 h. Removal of the precipitate through Celite and evaporation of the solvent gave a crude product. Purification by silica gel column chromatography gave a pure chiral selenimide.

§ *Selected data* for **3d**: white solid; 64% yield; 36% ee by Daicel chiralcel OD column with 25% Pr^{i}OH–hexane; eluent AcOEt; mp 156.0–157.0 °C; ν_{max}(KBr)/cm^{-1} 1264, 1161, 1132, 1084, 946, 937, 814, 697; δ_H(CDCl$_3$, 270 MHz) 2.27 (s, 3 H), 4.26 (d, *J* 11.3, 1 H), 4.58 (d, *J* 11.3, 1 H), 6.94–7.92 (m, 16 H); δ_C(CDCl$_3$, 67.8 MHz) 21.2, 57.2, 122.7, 125.9, 127.5, 128.0, 128.3, 128.4, 128.5, 128.8, 129.1, 129.21, 129.22, 129.9, 130.4, 132.8, 134.6, 141.0, 142.7; *m/z* (FAB LRMS) 468; FAB HRMS: calc. for C$_{24}$H$_{22}$O$_2$NSSe (M + H)$^+$: 468.0537. Found: 468.0535.

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