High Chirality Transfer in Chiral Selenimides *via* [2,3]Sigmatropic Rearrangement

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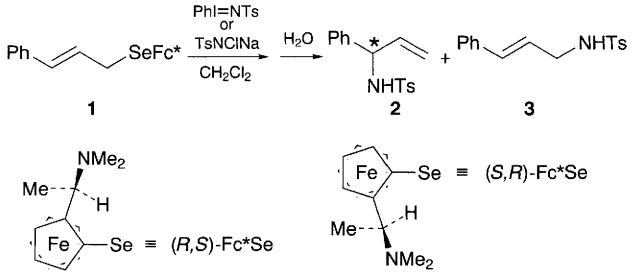
The imination of chiral cinnamyl 2-(1-dimethylaminoethyl)ferrocenyl selenides with [*N*-(toluene-*p*-sulfonyl)imino]-phenyliodinane and chloramine-T affords the corresponding chiral allylic amines *via* [2,3]sigmatropic rearrangement of the selenimide intermediates with up to 87% ee, highly diastereoselective imination of selenides and highly stereospecific [2,3]sigmatropic rearrangement being shown.

Previously we succeeded in asymmetric [2,3]sigmatropic rearrangement of the chiral selenoxides which were prepared by diastereoselective[1] and enantioselective oxidation.[2] In the former case, the chiral 2-(1-dimethylaminoethyl)ferrocenyl-selenium moiety played an important part in stereoselection. The diastereoselective oxidation of the selenide was a key step. The selenimides, nitrogen analogues of selenoxides, are known to undergo the same [2,3]sigmatropic transformation as selenoxides.[3] If the imination of selenides occurred diastereoselectively, chirality transfer should in principle occur. Compared with the well established preparation of chiral allylic alcohols,[4] the preparation of chiral allylic amines, important compounds in organic synthesis,[5] is still quite limited.[6] We present here the preliminary results of the asymmetric imination of chiral cinnamyl ferrocenyl selenides (*E* and *Z*) with [*N*-(toluene-*p*-sulfonyl)imino]phenyliodinane (PhI=NTs)[7] or chloramine-T(TsNClNa)[8] giving the corresponding chiral allylic amines.

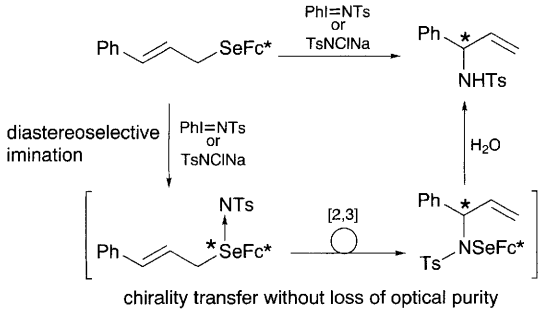


Scheme 1

Table 1 Asymmetric [2,3]sigmatropic rearrangement *via* chiral selenimides

Run[a]	Fc*	Reagent	*T*/°C (*t*/h)	Yield (%)[b] **2**	**3**	ee (%)[c]
1	(*R*,*S*)	TsNClNa	25 (1)	29	23	13
2	(*R*,*S*)	TsNClNa	0 (20)	13	27	45
3	(*S*,*R*)	TsNClNa	0–25 (22[d])	17	24	13
4	(*S*,*R*)	PhI = NTs	25 (1)	52	0	49
5	(*S*,*R*)	PhI = NTs	0 (20)	52	0	80
6	(*S*,*R*)	PhI = NTs	−20 (72)	0	0	—
7	(*R*,*S*)	PhI = NTs	0 (20)	42	0	87
8[e]	(*S*,*R*)	PhI = NTs	0 (20)	49	0	77

[a] All the reactions were carried out in 0.10 mmol scale. [b] Isolated yield. [c] The ee values of **2** were determined by HPLC. [d] The reaction was carried out at 0 °C for 2 h and then at 25 °C for 20 h. [e] (*Z*)-Cinnamyl selenide was used.



Scheme 2

Treatment of chiral (*E*)-cinnamyl (*R*,*S*)-ferrocenyl selenide [(*R*,*S*)-**1**][1a] with TsNClNa in dichloromethane at 25 °C afforded the secondary allylic amine **2**† and the primary allylic amine **3** in moderate yields with only a low enantiomeric excess (ee) of **2** (Scheme 1; Table 1, run 1). —The ee of **2** was determined by HPLC on a Daicel Chiralcel OD column. At low temperature a moderate ee was obtained but with low yield (runs 2 and 3). Surprisingly, when PhI = NTs was used as an imination reagent instead of TsNClNa, only compound **2** was produced from (*S*,*R*)-**1** in 52% yield with moderate ee (49%) at 25 °C (run 4) and with much higher ee (80%) at 0 °C (run 5). From (*R*,*S*)-**1**, a similar result (42%, 87% ee) was obtained (run 7).‡ However, at −20 °C the reaction did not proceed and the starting selenide **1** was recovered (run 6). Interestingly, even starting with the (*Z*)-cinnamyl (*S*,*R*)-ferrocenyl selenide, the same enantiomer was produced (49% yield, 77% ee) at 0 °C (run 8),§ the result being consistent with a [2,3]sigmatropic rearrangement of the corresponding selenoxides to give the chiral 1-phenylprop-2-en-1-ol.[1a]

The resulting high ee of the products gave grounds for the following speculation on the present asymmetric reaction (Scheme 2): i, the initial imination step proceeds with high diastereoselectivity; ii, the chirality transfer *via* [2,3]sigmatropic rearrangement occurs almost without loss of optical purity. Compared with the chiral selenoxide, the epimerisation of chiral selenimides did not occur under our reaction conditions.[9,10]¶ Similar to the selenoxide, the axial chirality of the ferrocene plays an important role in the stereoselective formation of the chiral selenimide. To our knowledge, this is the first clear-cut example of high chirality transfer in chiral selenimides, where selenium acts as one of the chiral centres *via* [2,3]sigmatropic rearrangement.[11–13]‖ We do not yet know the reason for the superiority of PhI = NTs over TsNClNa in both product selectivity and enantioselectivity.

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Footnotes

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† Satisfactory spectral data were obtained for racemic **2** prepared separately by the reaction of cinnamyl phenyl selenide with TsNCl.

Selected spectroscopic data for **2**, white solid, mp 97–99 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.39 (3 H, s), 4.80 (1 H, d, *J* = 6.9 Hz), 4.94 (1 H, dd, *J* = 6.9 and 5.9 Hz), 5.12 (1 H, d, *J* = 16.8 Hz), 5.14 (1 H, d, *J* = 10.6 Hz), 5.87 (1 H, ddd, *J* = 16.8, 10.6 and 5.9 Hz), 7.1–7.2 (2 H, m), 7.2–7.3 (5 H, m) and 7.63 (2 H, d, *J* = 8.4 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.5(q), 59.9(d), 116.9(t), 127.1(d), 127.2(d), 127.8(d), 128.7(d), 129.4(d), 137.1(d), 137.7(s), 139.4(s) and 143.3(s).

Selected spectroscopic data for **3**.[13] ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.42 (3 H, s), 3.76 (2 H, ddd, J = 6.4, 6.4 and 1.0 Hz), 4.47 (1 H, br), 6.02 (1 H, dt, J = 15.6 and 6.4 Hz), 6.44 (1 H, d, J = 15.6 Hz), 7.2–7.4 (7 H, m), 7.78 (2 H, d, J = 7.8 Hz).

‡ The difference of the data for runs 5 and 7 was considered to be the accumulation of errors of measurement in a pair of independent experiments.

§ The absolute configurations of the chiral allylic *N*-tosylamine **2** and the amine itself have not been reported. We are now trying to determine the absolute configuration and will report in due course. Under the conditions of analysis (10% *iso*-propanol–hexane in 0.3 cm^3 min^{-1} at 40 °C) the two enantiomers of **2** appear at 29.5 and 34.4 min, respectively. With the chiral amine **2**, prepared from the (*E*)-cinnamyl (*S*,*R*)-ferrocenyl selenide[(*R*,*S*)-**1**], the peak at 34.4 min was larger.

¶ The rate of epimerisation by pyramidal inversion of the optically active selenimide was shown to be very slow,[9] while in the selenoxide it is rather fast.[10]

‖ Oxidative rearrangement of allylic selenide by NCS in the presence of chiral amine nucleophile[11] and that of chiral allylic selenide in the presence of achiral amine nucleophile[12] provided the corresponding chiral allylic amine with up to 37% de and up to 84% ee, respectively, *via* [2,3]sigmatropic rearrangement of the selenimide intermediates. However, it is not clear in these reactions whether selenium played a role as a chiral centre.

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