Asymmetric [2,3] Sigmatropic Rearrangement of Chiral Allylic Selenonium Ylides

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Quite recently, we reported that the nucleophilic substitution reaction of the chloroselenuranes **1** having allylic substituents with amides gave the chiral allylic amines **3** with up to 93% enantiomeric excess (ee) (Scheme 1).[1] The result indicates that the nucleophilic substitution reaction of **1** with amides selectively proceeds with retention of configuration to generate the chiral allylic selenimides **2** *in situ*, which undergo the [2,3] sigmatropic rearrangement highly selectively when the substituent (R′) on nitrogen is sufficiently bulky. If the nucleophilic substitution reaction of **1** with carbon nucleophiles generated chiral selenonium ylides **4**, and the [2,3] sigmatropic rearrangement of **4** proceeded stereoselectively, this rearrangement would be a new method for carbon−carbon bond formation with chiral induction at the C(3) stereocenter. We have already reported that the nucleophilic substitution reaction of the chloroselenurane with active methylene compounds as a carbon nucleophile proceeds in a highly stereoselective manner with retention of configuration to give selenonium ylides.[2] Little is known about the stereochemisty of the [2,3] sigmatropic rearrangement of the selenonium ylide, and to the best of our knowledge, there has been only one example of the asymmetric [2,3] sigmatropic rearrangement using a chiral allylic selenonium ylide by Uemura and co-workers.[3] In this case, both the chemical yield and the selectivity of the rearrangement were low. We report here the first successful example of the asymmetric [2,3] sigmatropic rearrangement of the chiral allylic selenonium ylides **4** generated by the nucleophilic substitution reaction of the chloroselenuranes **1** with (phenylsulfonyl)acetonitrile.

We examined the [2,3] sigmatropic rearrangement of the allylic selenonium ylides as follows. To the solution of **1a**−**e** in CH_2Cl_2 were added Et_3N (1 equiv) and (phenylsulfonyl)acetonitrile (1 equiv) at −20 °C. Reaction time and isolated yield of **5a**−**e** are shown in Table 1. When **1a** was used, we obtained homoallylic selenide **5a** in 78% isolated yield along with its minor diastereomers[4] and diastereomeric deselenenyl compounds **6a** (entry 1). In the same manner, treatment of **1b**−**e** with (phenylsulfonyl)acetonitrile gave **5b**−**e** (30−87% yield) as a single diastereomer (entries 2−5).[5] These results indicate that the [2,3] sigmatropic rearrangement of the resulting allylic selenonium ylides **4** proceeds in a highly stereoselective manner to yield homoallylic selenides **5**.

Scheme 1

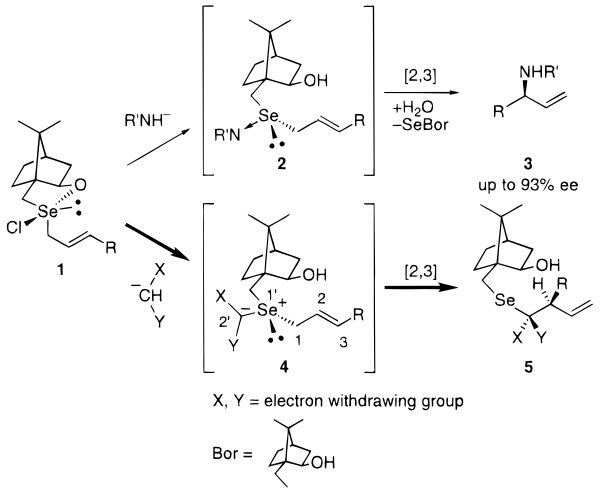
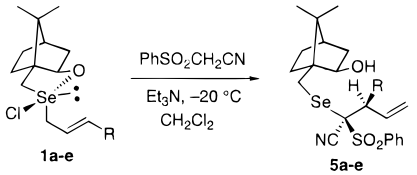


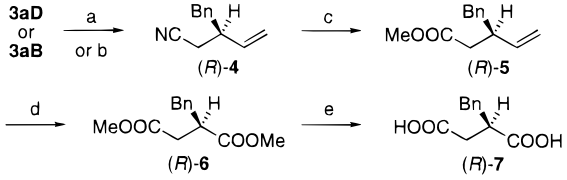
Table 1. Asymmetric [2,3] Sigmatropic Rearrangement of Chiral Selenonium Ylides



entry	R	time (h)	product	yield (%)
1	Bn	0.5	**5a**	78
2	Me[b]	1	**5b**	87
3	*n*-Pr	1	**5c**	83
4	*n*-Hex	1	**5d**	85
5	Ph	0.5	**5e**	30

[a] Isolated yield of the major isomer. [b] E:Z = 83:17.

Scheme 2[a]



[a] Key: (a) Na(Hg), Na_2HPO4, MeOH, 88% (from **3aD**); (b) Zn, HCl, THF, then NaCl, H_2O, DMSO, 160 °C, 88% (from **3aB**); (c) HCl, MeOH, 75% (from **3aD** and **3aB**); (d) $RuCl_3$, $NaIO_4$, H_2O-CH_3CN-CCl_4, then CH_2N_2, 82%; (e) 1 N NaOH, MeOH, 73%.

In order to determine the absolute configuration of the allylic C(3) position of the diastereomer **5a**, we converted **5a** into 2-benzylbutanedioic acid **10** (Scheme 2). The product mixture from **1a** was treated with 5% Na(Hg)[6] to give **7** (88% yield from **1a**). Methanolysis of **7** afforded **8** (76% yield and 88% ee). The ee of **8** was determined by HPLC using a Daicel Chiralcel OJ column (hexane/*i*-PrOH = 95/5). Reaction of **8** with $RuCl_3 \cdot nH_2O$ and

(1) Kurose, N.; Takahashi, T.; Koizumi, T. *J. Org. Chem.* **1996**, *61*, 2932.

(2) Takahashi, T.; Kurose, N.; Kawanami, S.; Nojiri, A.; Arai, Y.; Koizumi, T.; Shiro, M. *Chem. Lett.* **1995**, 379.

(3) Nishibayashi, Y.; Ohe, K.; Uemura, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1245.

(4) When **1a** was used, we obtained homoallylic selenides(*ca.* 92:5:2:1, **5a**; 78% isolated yield)[4] and diastereomeric deselenenyl compounds **6a** (4% yield). The structures and the diastereomers ratio were determined by ^1H NMR spectrum.

(5) Minor products of **5b**−**e** and **6b**−**d** could not be detected by ^1H NMR spectra. In the case of entry 5, diastereomeric deselenyl compounds **6e** were isolated in 31% yield.

(6) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, *39*, 3477.

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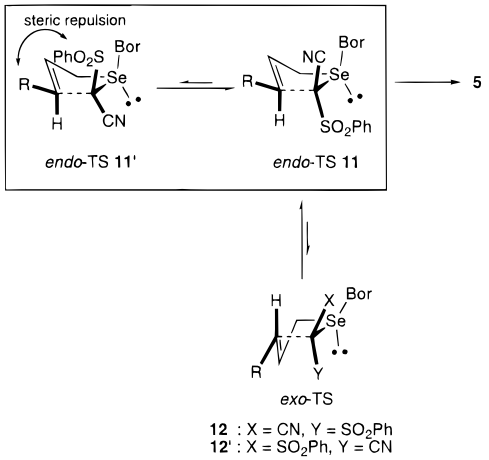
Scheme 3



$NaIO_4$[7] followed by treatment with CH_2N_2 gave (*R*)-dimethyl 2-benzylbutanedioate **9** (80% yield in two steps). Hydrolysis of (*R*)-**9** yielded (*R*)-2-benzylbutanedioic acid **10** [$[\alpha]^{25}_D$ +24.5° (*c* 1.18, AcOEt) (*R*-form: lit.[8] $[\alpha]^{25}_D$ +27° (*c* 1.5, AcOEt))] (76% yield). Accordingly, the absolute configuration at the allylic C(3) position of the diastereomer **5a** was determined to be *S*.

On the basis of these results, we propose the stereochemical course of the asymmetric [2,3] sigmatropic rearrangement of the allylic selenonium ylides shown in Scheme 3.[9] In this rearrangement, the *endo* transition states **11** and **11′** should be more stable than the *exo* transition states **12** and **12′** to yield the homoallyl compound **5a** having C(3)-(*S*) absolute configuration. Of the two *endo* transition states, the transition state **11** is much more favorable than the transition state **11′** because the steric interaction between R and $PhSO_2$ groups across the developing C(2′)−C(3) bond should be increased in the case of **11′**.[10] Therefore, the [2,3] sigmatropic rearrangement of the allylic selenonium ylides **4** should selectively progress *via* the *endo* transition state **11** to give homoallylic selenides **5**.

In conclusion, the [2,3] sigmatropic rearrangement of the allylic selenonium ylides **4** (1) affords the homoallylic selenides **5** with high diastereoselectivity and in high chemical yield and (2) provides an excellent method for carbon−carbon bond formation with chiral induction at C(3) stereocenter.

We are now investigating synthetic studies on the asymmetric [2,3] sigmatropic rearrangement of the allylic selenonium ylides **4**.

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Supporting Information Available: Experimental procedures, characterization data, and ^1H and ^{13}C NMR spectra for new compounds (7 pages).

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(7) Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, B. *J. Org. Chem.* **1981**, *46*, 3936.

(8) Cohen, S. G.; Milovanovic, A. *J. Am. Chem. Soc.* **1968**, *90*, 3495.

(9) Mechanisms of [2,3] sigmatropic rearrangement of allylic sulfonium ylides have been studied in detail: Wu, Y. D.; Houk, K. N. *J. Org. Chem.* **1991**, *56*, 5657 and references cited therein.

(10) For the [2,3] sigmatropic rearrangement of allylic sulfonium ylide: Hartley, R. C.; Richards, I. C.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1996**, 359.