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Chiral (OC)Ru(salen)-catalyzed tandem sulfimidation and [2,3]sigmatropic rearrangement: asymmetric C–N bond formation

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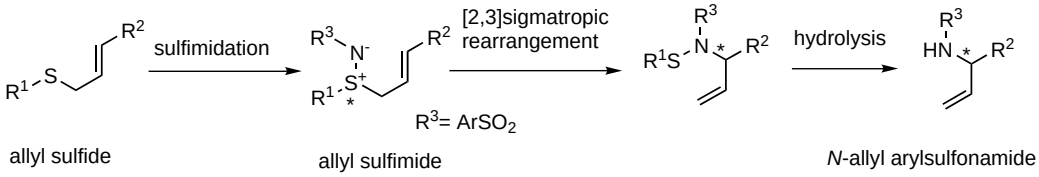
Abstract—Asymmetric C–N bond formation was achieved in a highly enantioselective manner by using (OC)Ru(salen)-catalyzed sulfimidation and the subsequent [2,3]sigmatropic rearrangement: treatment of allyl aryl sulfides with *p*-toluenesulfonyl azide in the presence of a catalytic amount of (OC)Ru(salen) followed by hydrolysis of the resulting *N*-allyl-*N*-arylthio toluenesulfonamides provided *N*-allyl toluenesulfonamides of high enantiomeric excess.

Optically active allyl amines are useful chiral building blocks for the synthesis of various amino compounds. Thus, a variety of synthetic methods of optically active allyl amines have been developed.[1] Among them, nucleophilic substitution of allyl-substituted materials such as allyl alcohols and allyl acetates with amine or amide anion derivatives is the most conventional one. This method generally requires optically active starting materials, though highly enantioselective allylic substitution reactions of prochiral and racemic substrates have recently been developed.[2] Another useful method is C–N bond formation via [2,3]sigmatropic rearrangement, in particular, the rearrangement of allyl sulfimides because their synthetic precursors, allyl sulfides, are readily available (Scheme 1).

The first example of this type of reaction was reported by Greenwood et al.[3] Subsequent to this, Kresze et al.[4] and Sharpless et al.[5] independently reported [2,3]sigmatropic rearrangement of the related sulfinamidines. Recently, Bach et al. reported Fe(II)-catalyzed imidation of allyl sulfides and subsequent [2,3]sigmatropic rearrangement to synthesize *N*-Boc-protected *N*-allylamines.[6] On the other hand, it had been reported that allyl sulfoxides, oxygen equivalents of sulfimides, rearrange to the corresponding allyl sulfenates stereospecifically.[7] Thus, it was expected that optically active allyl amine derivatives would be obtained from allyl sulfides if their sulfimidation occurs in an enantioselective manner. Indeed, Uemura et al. developed catalytic enantioselective sulfimidation using a copper–bis(oxazoline) complex as the catalyst[8] and successfully applied it to the synthesis of *N*-allyl toluenesulfonamide derivatives via the allylsulfimides, though enantioselectivity was moderate.[9] Recently, we found highly enantioselective sulfimidation of alkyl aryl sulfides with (OC)Ru(salen) complex **1** as the catalyst (Scheme 2).[10] On the basis of this result, we examined enantioselective sulfimidation of allyl aryl sulfides using **1** as the catalyst.

We first examined the reaction of *E*-crotyl aryl sulfides[11] with arylsulfonyl azides in the presence of (OC)Ru(salen) **1** as the catalyst (Table 1). Enantioselectivity of the reactions was determined by HPLC analysis after the resulting chiral *N*-allyl-*N*-arylthio



Scheme 1.

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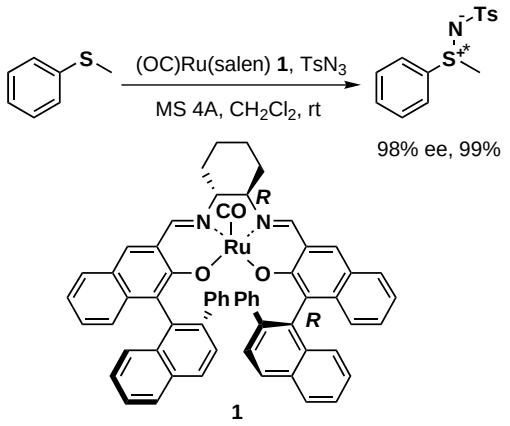


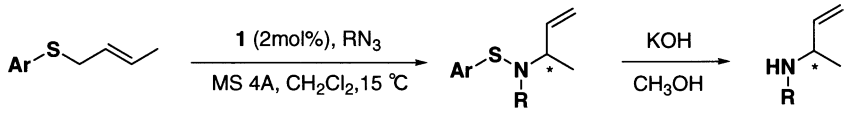
Scheme 2.

arylsulfonamides were hydrolyzed to *N*-allyl arylsulfonamides. The reaction of *E*-crotyl phenyl sulfide[11] with *p*-toluenesulfonyl azide at room temperature proceeded with good enantioselectivity of 78% ee. The enantioselectivity was enhanced as reaction temperature was decreased, but the reaction became slow at 0°C. The acceptable result in terms of enantioselectivity and chemical yield was obtained at 15°C (entry 2). Thus, the following experiments were carried out at 15°C. Among the reactions of *E*-crotyl aryl sulfides examined, that of *E*-crotyl phenyl sulfide showed the highest enantioselectivity (entries 2–8): introduction of either an electron-withdrawing or -donating group into the aryl group (Ar) slightly reduced enantioselectivity (entries 4–7). Effect of the arylsulfonyl group of azide was also examined, but all arylsulfonyl azides used showed a similar level of enantioselectivity. No electronic effect on enantioselectivity was observed (entries 9 and 10).

Under the optimized conditions, we examined the reactions of various other allyl phenyl sulfides with complex **1** as the catalyst in the presence of *p*-toluenesulfonyl azide (Table 2). The reactions of *E*-allyl phenyl sulfides showed enantioselectivity similar to the reaction of *E*-crotyl phenyl sulfide (entries 1–3). The reaction of *Z*-pentenyl phenyl sulfide also proceeded with high enantioselectivity (entry 4). It is, however, noteworthy that the main enantiomer of the reaction was identical with the main enantiomer obtained in the reaction of *E*-pentenyl phenyl sulfide. Since it is reasonable to consider that the sense of asymmetric induction in the reaction of *Z*-pentenyl phenyl sulfide is identical with that in the reaction of the corresponding *E*-substrate, the above results suggest that the transition state conformation in [2,3]sigmatropic rearrangement of the *Z*-sulfimide intermediate is different from that of the *E*-sulfimide intermediate.[13] The poor enantioselectivity observed in the reaction of geranyl phenyl sulfide that bears *E*- and *Z*- substituents suggests that plural transition states participate in the rearrangement process (entry 5).

Typical experimental procedure was exemplified by the reaction of *E*-crotyl phenyl sulfide and *p*-toluenesulfonyl azide using **1** as the catalyst (Table 1, entry 2): complex **1** (1.9 mg, 2.0 μmol) was dissolved in dry toluene (0.5 ml), concentrated azeotropically in vacuo and re-dissolved in dichloromethane (0.5 ml). To this solution were added *E*-crotyl phenyl sulfide (16.4 μl, 0.1 mmol) and 4 Å MS (20 mg), and the resulting suspension was stirred for half an hour at 15°C. To this suspension was added *p*-toluenesulfonyl azide (19.7 μl, 0.13 mmol) and the whole mixture was stirred for another 24 h at the temperature. The mixture was evaporated and the resulting residue was treated with methanolic 0.5N potassium hydroxide solution (1 ml). The mixture was stirred for 6 h and filtered through a

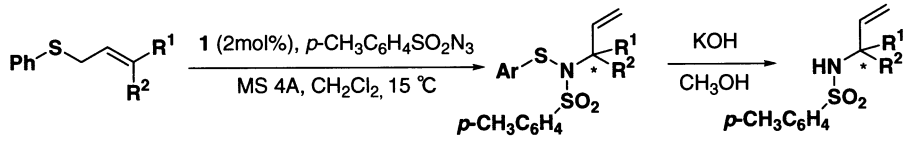
Table 1. Asymmetric conversion of *E*-crotyl aryl sulfide into *N*-allyl arylsulfonamide using **1** as the catalyst



Entry	Ar	R	*E*/*Z*[a]	Yield (%)[b]	% ee[c]	Config.[d]
1	C_6H_5[e]	*p*-$CH_3C_6H_4SO_2$	81/19	82	78	*R*
2	C_6H_5	*p*-$CH_3C_6H_4SO_2$	81/19	65	84	*R*
3	C_6H_5[f]	*p*-$CH_3C_6H_4SO_2$	81/19	16	86	*R*
4	*p*-$(O_2N)C_6H_4$	*p*-$CH_3C_6H_4SO_2$	76/24	47	81	*R*
5	*p*-$CH_3OC_6H_4$	*p*-$CH_3C_6H_4SO_2$	85/15	79	80	*R*
6	*p*-BrC_6H_4	*p*-$CH_3C_6H_4SO_2$	83/17	79	82	*R*
7	*o*-BrC_6H_4	*p*-$CH_3C_6H_4SO_2$	85/15	22	81	*R*
8	2-$C_{10}H_7$	*p*-$CH_3C_6H_4SO_2$	83/17	88	78	*R*
9	C_6H_5[e]	*p*-$CH_3OC_6H_4SO_2$	81/19	57	83	–
10	C_6H_5[e]	*p*-$BrC_6H_4SO_2$	81/19	69	83	–

[a] *E*/*Z*-isomer ratio of the starting material.
[b] Isolated yield.
[c] Determined by HPLC analysis using DAICEL CHIRALCEL AD-H (hexane/2-propanol = 9:1).
[d] Absolute configuration was determined by comparison of the sign of specific optical rotation with the reported one (Ref. 12).
[e] Reaction was carried out at room temperature.
[f] Reaction was carried out at 0°C

Table 2. Asymmetric conversion of various allyl phenyl sulfides into *N*-toluenesulfonylallylamine using **1** as the catalyst



Entry	R^1	R^2	E/Z[a]	Yield (%)[b]	% ee[c]
1	C_2H_5	H	90/10	48	86[d]
2	n-C_7H_{15}	H	89/11	46	85[e]
3	C_6H_5	H	100/0	40	84[d]
4	H	C_2H_5	6/94	66	82[d]
5	$(CH_3)_2C{=}CHCH_2CH_2$	Me	98/2	55	<1[e]

[a] E/Z-isomer ratio of the starting material.
[b] Isolated yield.
[c] Absolute configuration of the product has not been determined.
[d] Determined by HPLC using DAICEL CHIRALCEL AD-H (hexane/2-propanol = 9/1).
[e] Determined by HPLC using DAICEL CHIRALCEL AD-H (hexane/ethanol = 30/1).

pad of Celite. The filtrate was evaporated, treated with 1N hydrochloric acid, and extracted with ether. The organic layer was washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate. The mixture was concentrated and chromatographed on silica gel (hexane:diethyl ether = 7:3) to give *N*-(1-methyl-2-propen-1-yl) *p*-toluenesulfonamide (14.6 mg, 65% yield). The enantiomeric excess of the product was determined to be 84% by HPLC analysis using DAICEL CHIRALCEL AD-H (hexane/2-propanol = 9:1).

In conclusion, we were able to demonstrate that *N*-allyl arylsulfonamides can be prepared from allyl phenyl sulfides by using enantioselective sulfimidation with (OC)ruthenium(salen) complex **1** as the key step.

References

1. Jørgensen, K. A. In *Modern Amination Methods*; Ricci, A., Ed.; Wiley-VCH: Weinheim, 2000; Chapter 1.
2. (a) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301–6311; (b) Connell, R. D.; Rein, T.; Åkermark, B.; Helquist, P. *J. Org. Chem.* **1988**, *53*, 3845–3849; (c) Burckhardt, U.; Baumann, M.; Trabesinger, G.; Gramlich, V.; Togni, A. *Organometallics* **1997**, *16*, 5252–5259; (d) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395–422; (e) Trost, B. M.; Radinov, R. *J. Am. Chem. Soc.* **1997**, *119*, 5962–5963; (f) Evans, D. A.; Campos, K. R.; Tedrow, J. S.; Michael, F. E.; Gagné, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 7905–7920; (g) Deng, W.-P.; You, S.-L.; Hou, X.-L.; Dai, L.-X.; Yu, Y.-H.; Xia, W.; Sun, J. *J. Am. Chem. Soc.* **2001**, *123*, 6508–6519; (h) For a review of allylic amination, see: Johannsen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689–1708.
3. Ash, A. S. F.; Challenger, F.; Greenwood, D. *J. Chem. Soc.* **1951**, 1877–1882.
4. Schönberger, N.; Kresze, G. *Liebigs Ann. Chem.* **1975**, 1725–1731.
5. (a) Sharpless, K. B.; Hori, T. *J. Org. Chem.* **1976**, *41*, 176–177; (b) Sharpless, K. B.; Hori, T.; Truesdale, L. K.; Dietrich, C. O. *J. Am. Chem. Soc.* **1976**, *98*, 269–271.
6. Bach, T.; Körber, C. *J. Org. Chem.* **2000**, *65*, 2358–2367.
7. Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 563–572.
8. Miyake, Y.; Takada, H.; Ohe, K.; Uemura, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, *18*, 2373–2376.
9. (a) Takada, H.; Nishibayashi, Y.; Ohe, K.; Uemura, S. *J. Chem. Soc., Chem. Commun.* **1996**, 931–932; (b) Takada, H.; Nishibayashi, Y.; Ohe, K.; Uemura, S.; Baird, C. P.; Sparey, T. J.; Taylor, P. C. *J. Org. Chem.* **1997**, *62*, 6512–6518.
10. Murakami, M.; Uchida, T.; Katsuki, T. *Tetrahedron Lett.* **2001**, *42*, 7071–7074.
11. The starting crotyl aryl sulfides were prepared from commercial crotyl bromide (E:Z = 81:19) and used for the present reaction without separation of geometric isomers because of difficulty of their separation.
12. Moriwake, T.; Hamano, S.; Saito, S.; Kashino, S.; Torii, S. *J. Org. Chem.* **1989**, *54*, 4114–4120.
13. A similar stereochemistry was observed in the [2,3]sigmatropic rearrangement of *S*-ylides derived from allyl sulfides: the reactions of *E*- and *Z*-cinnamyl phenyl sulfides gave the same product: Fukuda, T.; Irie, R.; Katsuki, T. *Tetrahedron* **1999**, *55*, 649–664.