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Highly enantioselective (OC)Ru(salen)-catalyzed sulfimidation using *N*-alkoxycarbonyl azide as nitrene precursor

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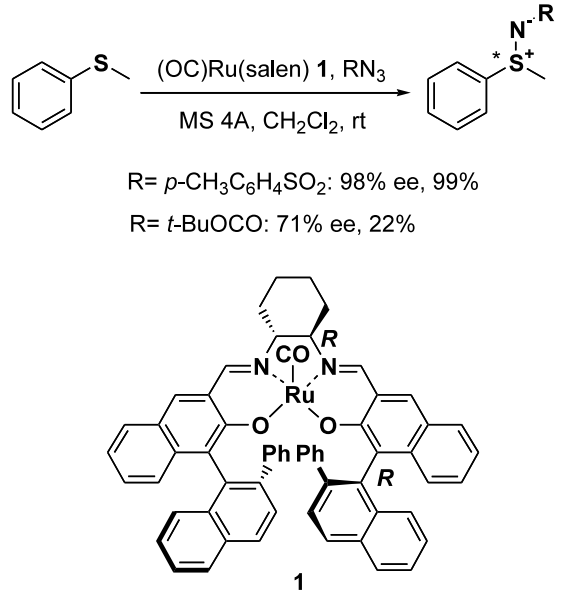
Abstract—Enantioselective imidation of alkyl aryl sulfides with *N*-alkoxycarbonyl azide as a nitrene precursor was effected by using (OC)Ru(salen) complex **1** as catalyst. The steric and electronic nature of the *N*-alkoxycarbonyl group was found to strongly affect the enantioselectivity and the reaction rate, and high enantioselectivity (up to 99% ee) and good chemical yields were achieved by using 2,2,2-trichloro-1,1-dimethylethoxycarbonyl azide as the nitrene precursor at room temperature.

Nitrene transfer reaction is the most important method for the synthesis of optically active compounds including a nitrogen functional group. Therefore, many catalysts have been developed for this reaction and high enantioselectivity has been achieved in many reactions.[1–3] However, there is still big room for improvement in the atom efficiency of the nitrene precursor, because *N*-arylsulfonyliminophenyliodinanes ($ArSO_2N=IPh$) that are low atom efficient reagents have been mostly used as nitrene precursors in those reactions. Recently, the use of azide compounds as the nitrene precursor, which produce the corresponding nitrene and the by-product nitrogen, has been examined. Jacobsen et al. reported that arylsulfonyl azide served as a nitrene precursor for asymmetric aziridination in the presence of a copper ion under photo-irradiation.[4] We found that (OC)Ru(salen) complex **1** catalyzed sulfimidation of alkyl aryl sulfides using arylsulfonyl azide as the nitrene precursor without photo-irradiation, in a highly enantioselective manner (Scheme 1).[5] However, removal of the arylsulfonyl group from the resulting nitrogen compounds usually needs harsh reaction conditions.[6]

On the other hand, Bach and Körber used *N*-*tert*-butoxycarbonyl azide as the nitrene source for $FeCl_2$-catalyzed imidation of alkyl and allyl sulfides, though in a non-asymmetric reaction.[7,8] We also examined sulfimidation using *N*-*tert*-butoxycarbonyl azide as the nitrene source in the presence of complex **1** (Scheme 1).[5] Although the reaction proceeded with moderate selectivity, the reaction was slow. In the course of this study, however, we found that the nature of the alkoxycarbonyl group affected the enantioselectivity and reaction rate of the sulfimidation to a considerable extent (Table 1).



Scheme 1.

Keywords: (OC)Ru(salen) complex; asymmetric catalysis; sulfimidation; *N*-alkoxycarbonyl azide.

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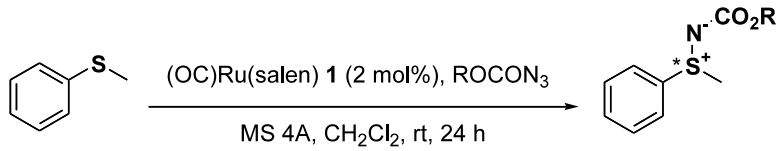
Table 1. Asymmetric imidation of methyl phenyl sulfide with various *N*-carbamoyl azide in the presence of complex **1**



Entry	R	% ee[a]	Yield (%)[b]
1	CH_3	13	21
2	n-C_4H_9	18	18
3	$C_6H_5CH_2$	36	28
4	t-C_4H_9	71	22
5	C_6H_5	8	37
6	Cl_3CCH_2	77	62
7	$Cl_3CC(CH_3)_2$	95	93

[a] Determined by HPLC analysis using DAICEL CHIRALPAK AD-H (hexane:*i*-PrOH = 9:1).
[b] Isolated yield.

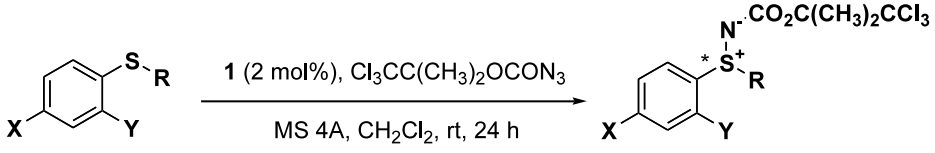
Enantioselectivity increased as the bulkiness of the alkygroup of the alkoxycarbonyl group became larger (entries 1–4). On the other hand, use of phenoxycarbonyl azide improved the chemical yield, albeit with poor enantioselectivity (entry 5). From these results, we speculated that the *N*-alkoxy- (or aryloxy)carbonyl group would affect the enantioselectivity through a steric factor and the reaction rate through an electronic factor, though some aromatic effect seemed to affect enantioselectivity adversely. Thus, we examined the reaction with trichloroethoxycarbonyl azide and found that reaction proceeded with moderate enantioselectivity and acceptable chemical yield (entry 6). Encouraged by this result, we further examined the reaction with 2,2,2-trichloro-1,1-dimethylethoxycarbonyl azide that possesses a bulky and electron-withdrawing alkyl group, and high enantioselectivity of 95% ee as well as good chemical yield of 93% was finally achieved (entry 7).

We also examined the use of other nitrene sources such as acyl azides, benzoyl and *p*-nitrobenzoyl azides, and alkyl azides, benzyl and *p*-nitrobenzyl azides, but no desired reaction occurred when these reagents were used.

We next examined imidation of various alkyl aryl sulfides using 2,2,2-trichloro-1,1-dimethylethoxycarbonyl azide in the presence of complex **1** (Table 2). The effect of a *p*-substituent on the phenyl group was first examined: introduction of an electron-donating methoxy group or of an electron-withdrawing chloro group had no influence on enantioselectivity: imidation of methyl *p*-methoxy- and *p*-chlorophenylsulfides showed enantioselectivity as high as that of methyl phenyl sulfide (entries 1 and 2). Imidation of ethyl phenyl sulfide also showed good but somewhat reduced enantioselectivity of 92% ee (entry 3). On the other hand, introduction of an *o*-substituent remarkably improved enantioselectivity (entries 4 and 5).

Typical experimental procedure for imidation of sulfides was exemplified by the reaction of methyl phenyl sulfide with **1** as the catalyst: complex **1** (1.9 μg, 2.0 μmol) was dissolved in dry toluene (1 ml), concentrated azeotropically in vacuo, and re-dissolved in

Table 2. Asymmetric imidation of alkyl aryl sulfides with 2,2,2-trichloro-1,1-dimethylethoxycarbonyl azide in the presence of complex **1**



Entry	X	Y	R	% ee[a]	%[b]
1	MeO	H	CH_3	96	91
2	Cl	H	CH_3	95	88
3	H	H	CH_3CH_2	92	87
4	H	Br	CH_3	98	74
5	H	NO_2	CH_3	99	99

[a] Determined by HPLC analysis using DAICEL CHIRALPAK AD-H (hexane:*i*-PrOH = 9:1).
[b] Isolated yield.

dichloromethane (0.5 ml). To this solution were added methyl phenyl sulfide (11.7 μl, 0.1 mmol) and MS 4 Å (20 mg), and the suspension was stirred for 0.5 h at room temperature. To this suspension was added 2,2,2-trichloro-1,1-dimethylethoxycarbonyl azide (34.0 mg, 0.13 mmol), and the whole mixture was stirred for another 24 h at the temperature. The mixture was chromatographed on silica gel (ethyl acetate) to give the product (31.9 mg, 93%). The enantiomeric excess of the product was determined to be 95% by HPLC analysis using DAICEL CHIRALPAK AD-H (hexane:*i*-PrOH = 9:1).

In conclusion, we were able to demonstrate that *N*-alkoxycarbonyl azide was successfully used as the nitrene precursor for the sulfimidation using chiral ruthenium(II)(salen) complex **1** as the catalyst, when the electronic and steric nature of the alkyl group in the azide was appropriately adjusted. Further study on the sulfimidation using *N*-alkoxycarbonyl azide as the nitrene precursor is in progress in our laboratory.

References

1. (a) Faul, M. M.; Evans, D. A. In *Asymmetric Oxidation Reaction*, *Practical Approach in Chemistry*; Katsuki, T., Ed.; Oxford University Press: Oxford, 2001; Chapter 2.7; (b) Jacobsen, E. N. In *Comprehensive Asymmetric Catalysis II*; Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H., Eds.; Springer: Berlin, 1999; Chapter 17.
2. (a) Kohmura, Y.; Katsuki, T. *Tetrahedron Lett*. **2001**, *42*, 3339–3342; (b) Liang, J.-L.; Yu, X.-Q.; Che, C.-M. *Chem. Commun*. **2002**, 124–125.
3. (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; (c) Takada, H.; Nishibayashi, Y.; Ohe, K.; Uemura, S. *Phosphorus, Sulfur Silicone Relat. Elem*. **1997**, *120 and 121*, 363–364; (d) Baird, C. P.; Clark, A. J.; Rooke, S. M.; Sparey, T. J.; Taylor, P. C. *Phosphorus, Sulfur Silicon Relat. Elem*. **1997**, *120 and 121*, 365–366; (e) Miyake, Y.; Takada, H.; Ohe, K.; Uemura, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2373–2376; (f) Nishikori, H.; Ohta, C.; Oberlin, E.; Irie, R.; Katsuki, T. *Tetrahedron* **1999**, *55*, 13937–13946.
4. Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc*. **1995**, *117*, 5889–5890.
5. Murakami, M.; Uchida, T.; Katsuki, T. *Tetrahedron Lett*. **2001**, *42*, 7071–7074.
6. *o*-Nitro- or *o*,*p*-dinitrophenylsulfonyl group has been reported to be eliminated under the milder reaction conditions: (a) Fukuyama, T.; Cheung, M.; Jow, C.-K.; Hidai, Y.; Kan, T. *Tetrahedron Lett*. **1997**, *38*, 5831–5834; (b) Hidai, Y.; Kan, T.; Fukuyama, T. *Tetrahedron Lett*. **1999**, *40*, 4711–4714.
7. (a) Bach, T.; Körber, C. *Eur. J. Org. Chem*. **1999**, 1033–1039; (b) Bach, T.; Körber, C. *J. Org. Chem*. **2000**, *65*, 2358–2367.
8. Cenini et al. also reported nitrene transfer reaction using *p*-nitrophenyl azide as the nitrene source in the presence of metalloporphyrin, but high reaction temperature was required for the reaction: Cenini, S.; Tollari, S.; Penoni, A.; Cereda, C. *J. Mol. Cat. A: Chem*. **1999**, *137*, 135–146.