Catalytic Diastereoselective Imidation of Diaryl Sulfides Bearing a Chiral Oxazolinyl Moiety with Chloramine T Trihydrate**

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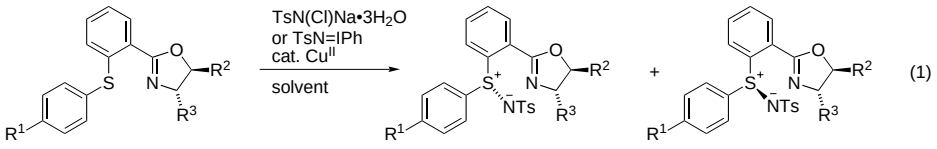
Currently, we are interested in developing a catalytic method for the enantioselective imidation of prochiral sulfides and selenides to chiral sulfimides[1, 2] and selenimides[3] using [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane (TsN=IPh)[4] in the presence of a copper salt and a chiral ligand, because these optically active products might be useful for some asymmetric reactions. Williams et al. have recently reported a highly diastereoselective oxidation of diaryl sulfides bearing a chiral oxazolinyl moiety[5] and demonstrated that the produced optically active sulfoxides are effective ligands for asymmetric palladium-catalyzed allylic substitution.[6] These interesting results prompted us to investigate the diastereoselective imidation of similar sulfides to prepare novel optically active sulfimides which might be suitable as chiral ligands and reagents.

First, imidation of diaryl sulfides **1** and **3**, bearing an enantiomerically pure 4-isopropyloxazolinyl group derived from valinol at the *ortho* position, was carried out by the procedure developed by us [Eq. (1)];[1] namely, **1** and **3** were treated with chloramine T trihydrate (*N*-chloro-*p*-toluenesulfonamide, sodium salt; $TsN(Cl)Na \cdot 3H_2O$)[7] or TsN=IPh using a copper(II) salt as catalyst in a suitable solvent. 1,6-Asymmetric induction occurred to give the corresponding optically active *N*-tosylsulfimides **2** and **4** in about 60% yield; however, the diastereoselectivity was moderate in all cases (40–48% *de*, Table 1). The use of $TsN(Cl)Na \cdot 3H_2O$ in acetonitrile gave a slightly better result than the use of TsN=IPh in toluene.[8]



(1)

1 $R^1 = R^2 = H$, $R^3 = i$Pr	**2a**	**2b**
3 $R^1 = Me$, $R^2 = H$, $R^3 = i$Pr	**4a**	**4b**
5 $R^1 = H$, $R^2 = Ph$, $R^3 = CH_2OSiMe_2t$Bu	**6a**	**6b**
7 $R^1 = H$, $R^2 = Ph$, $R^3 = CH_2OH$	**8a**	**8b**
9 $R^1 = H$, $R^2 = Ph$, $R^3 = CH_2OMe$	**10a**	**10b**
11 $R^1 = Me$, $R^2 = Ph$, $R^3 = CH_2OSiMe_2t$Bu	**12a**	**12b**
13 $R^1 = Me$, $R^2 = Ph$, $R^3 = CH_2OMe$	**14a**	**14b**

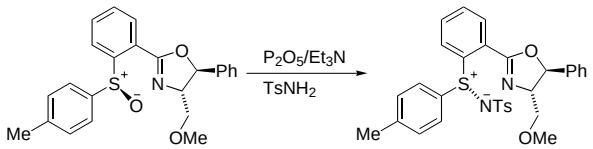
Table 1. Diastereoselective imidation of diaryl sulfides **1**, **3**, **5**, **7**, **9**, **11**, and **13**.[a]

Sulfide	NTs source	Catalyst	Solvent	Yield [%]	*de* [%][b]
1	TsN(Cl)Na	none	EtOH	29	34
1	$TsN(Cl)Na \cdot 3H_2O$	$CuCl_2$	MeCN	56	45
1	TsN=IPh	$Cu(OTf)_2$	toluene	57[c]	40
3	$TsN(Cl)Na \cdot 3H_2O$	$CuCl_2$	MeCN	63	48
5	$TsN(Cl)Na \cdot 3H_2O$	$CuCl_2$	MeCN	76	87
5	$TsN(Cl)Na \cdot 3H_2O$	$CuCl_2$	toluene	36[d]	< 10
5	$TsN(Cl)Na \cdot 3H_2O$	$Cu(OTf)_2$	MeCN	63	91
7	$TsN(Cl)Na \cdot 3H_2O$	$Cu(OTf)_2$	MeCN	67	51
9	$TsN(Cl)Na \cdot 3H_2O$	$Cu(OTf)_2$	MeCN	52	99
11	$TsN(Cl)Na \cdot 3H_2O$	$Cu(OTf)_2$	MeCN	58	74
13	$TsN(Cl)Na \cdot 3H_2O$	$Cu(OTf)_2$	MeCN	61	99

[a] Reactions were performed at 25 °C for 24 h with sulfide (0.2 mmol), NTs source (0.2 mmol), catalyst (10 mol%), and solvent (1 mL). Unless otherwise noted, the formation of a slight amount (< 5%) of the corresponding sulfoxide was observed. [b] Determined by ^1H NMR spectroscopy. [c] The formation of the corresponding sulfoxide was not observed at all. [d] The corresponding sulfoxide (12%) was also isolated.

In contrast, when diaryl sulfides **5**, **7**, **9**, **11**, and **13**, bearing an enantiomerically pure oxazolinyl group derived from (1*S*,2*S*)-(+)-2-amino-1-phenyl-1,3-propanediol, were employed as substrates, a much higher diastereoselectivity (up to 99% *de*) was observed on treatment with $TsN(Cl)Na \cdot 3H_2O$ in the presence of copper(II) salt in a suitable solvent. Here, the combination of $Cu(OTf)_2$ (OTf = trifluoromethanesulfonate) and acetonitrile was the best (Table 1). The use of TsN=IPh resulted in poor diastereoselectivity. In the present imidation, a higher stereoselectivity was observed for sulfides bearing a methoxymethyl or silyloxymethyl moiety at the 4-position of the oxazoline ring than for **1**, where an isopropyl moiety is present at the same position.

To determine the absolute configuration of the produced *N*-*p*-tosylsulfimides, the sulfoxide (4*S*,5*S*,S_S)-**15** ($[\alpha]_D^{25} = -255.2$, $c = 1.5$ in acetone), prepared by methylation of the hydroxyl group of a known compound,[5] was treated with *p*-toluenesulfonamide [Eq. (2)] since the substitution of oxygen on sulfur by the NTs moiety is known to proceed with inversion of configuration.[9] The produced *N*-tosylsulfimide **14a** ($[\alpha]_D^{25} = -136.0$, $c = 1.5$ in acetone), which is supposed to have an absolute configuration of 4*S*,5*S*,R_S, corresponded to the minor product of the present imidation.



(2)

(4*S*,5*S*,S_S)-**15** (4*S*,5*S*,R_S)-**14a**

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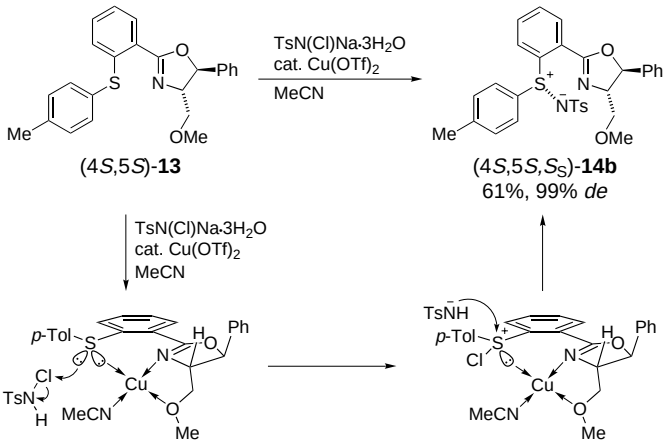
[**] The present work was supported partly by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Culture, and Sports, Japan. H.T. gratefully acknowledges a Fellowship of the Japan Society for the Promotion of Science for Japanese Junior Scientists.

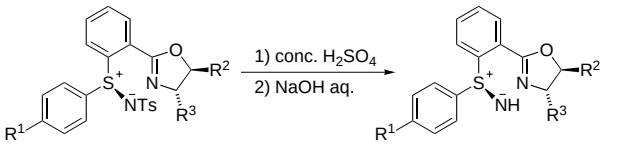
  1433-7851/99/3809-1288 $ 17.50+.50/0

The major product **14b** ($[\alpha]_D^{25} = +53.5$, $c = 1.5$ in acetone) should have the 4*S*,5*S*,S_S configuration. This evidence and the quite high diastereoselectivity observed might be explained by assuming that the reaction proceeds ionically[10] through back-side attack of the anion of *N*-*p*-tosylamine on sulfur of the chlorosulfonium ion intermediate,[11] whose lone pair interacts with Cu, which is coordinated by N, O, and a solvent molecule (Scheme 1). However, the possibility of some intervention of the nitrene transfer mechanism[12] may not be excluded.



Scheme 1. One of the possible reaction pathways for the copper-catalyzed imidation of sulfide **13**.

Additionally, hydrolysis[13] allowed *N*-*p*-tosylsulfimides **8b**, **10b**, and **14b** to be converted into the corresponding optically pure sulfimides **16**, **17**, and **18**, respectively, in high yields [Eq. (3)]. We assume that the hydrolysis proceeds without any



(3)

8b	**16** R^1 = H, R^2 = Ph, R^3 = CH_2OH (93%)
10b	**17** R^1 = H, R^2 = Ph, R^3 = CH_2OMe (96%)
14b	**18** R^1 = Me, R^2 = Ph, R^3 = CH_2OMe (68%)

change in configuration, as in the case of the hydrolysis of *N*-tosylsulfoximide.[9b]

Preliminaly results of the use of these novel, optically active sulfimides and *N*-*p*-tosylsulfimides as chiral ligands in the palladium(II)-catalyzed allylic alkylation of 1,3-diphenyl-3-acetoxy-1-propene with dimethyl malonate show that the product is obtained quantitatively. Furthermore, sulfimide **17** works more efficiently than *N*-*p*-tosylsulfimide **10** in terms of stereoselectivity (90 and 46% *ee*, respectively).[14] Further studies on the clarification of the reaction scheme as well as asymmetric reactions using these novel optically active sulfimides as chiral ligands or reagents are currently in progress.

Experimental Section

A typical experimental procedure is as follows: Acetonitrile (5.0 mL), **9** (75.5 mg, 0.20 mmol), and $Cu(OTf)_2$ (7.2 mg, 0.020 mmol) were placed in 10-mL flask. After 15 min chloramine T trihydrate (56.3 mg, 0.20 mmol) was added to this solution, and the mixture was stirred at 25 °C for 24 h. The mixture was then poured into water and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by column chromatograpy on silica gel, and the major fraction afforded 56.6 mg (52% yield) of **10b** with a diastereoselectivity of greater than 99%. A slight amount (< 3%) of the corresponding sulfoxide was also isolated. **10b**: White solid; m.p. 62–63 °C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 2.34$ (s, 3H; Me), 3.45 (s, 3H; OMe), 3.55 (dd, $J = 9.8$, 6.4 Hz, 1H; C*H*HOMe), 3.69 (dd, $J = 9.8$, 6.4 Hz, 1H, CH*H*OMe), 4.12 (m, 1H; CHN), 5.38 (d, $J = 6.4$ Hz, 1H; CHO), 6.96–8.64 (m, 18H; Ar); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 21.3$, 59.4 (CH_2O), 73.8 (OMe), 75.0 (CHN) 83.7 (CHO), 125.3, 126.2, 127.8, 128.2, 128.3, 128.7, 128.9, 129.2, 130.2, 131.2, 131.5, 132.4, 139.3, 139.8, 141.3, 141.7, 160.4 (C=N).

Received: November 4, 1998 [Z12618IE]
German version: *Angew. Chem.* **1999**, *111*, 1367–1369

Keywords: asymmetric synthesis · chiral auxiliaries · chloramine T · imidations · sulfimides

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  1433-7851/99/3809-1289 $ 17.50+.50/0