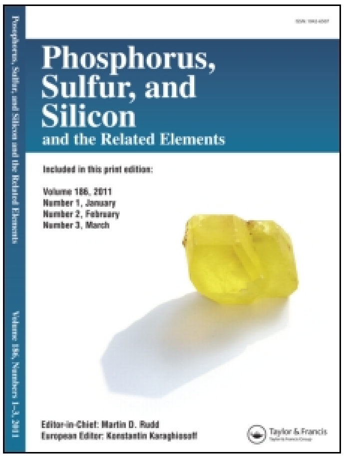

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Chiral Bis(oxazoline)-copper Catalyzed Enantioselective Imidation of Sulfides

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Prochiral sulfides reacted with PhI=NTs in the presence of a catalytic amount of Cu(I) salt together with a chiral 4,4'-disubstituted bis(oxazoline) ligand to afford the corresponding chiral sulfimides.

KEYWORDS: sulfide, sulfimide, sufenamide, bis(oxazoline) ligand

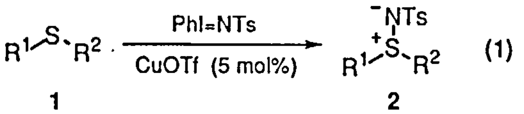
INTRODUCTION

Quite recently, chiral sulfimides were demonstrated to be useful in organic synthesis as methylidene transfer reagents to prochiral carbonyl groups, leading to optically active epoxides.[1] Despite the fact that other optically active organosulfur compounds such as sulfonium ylides and sulfoxides have many asymmetric synthetic applications, the chemistry of their nitrogen analogues, sulfimides, has been much less investigated.[2,3] We now report that the asymmetric reaction of various sulfides **1** with PhI=NTs in the presence of Cu(I) catalyst derived from CuOTf and the chiral 4,4'-disubstituted bis(oxazoline) ligand **3** produces the corresponding chiral sulfimides **2**.[4]

RESULTS AND DISCUSSION

Our initial attempts were to explore and exploit a new imidation method of sulfides **1** with PhI=NTs using Cu(I) salt as catalyst, eqn. (1). The synthesis of sulfimides was carried out by treatment of suitable sulfides with 1 equiv PhI=NTs in MeCN as solvent in the presence of 5 mol% of Cu(I) triflate (CuOTf). Representative results are summarized in Table I. Treatment of methyl *p*-tolyl sulfide with PhI=NTs at 25 °C for 26 h afforded the corresponding sulfimide in 83 % isolated yield (entry 1). Similarly, a variety of sulfides could be converted smoothly to the corresponding sulfimides.

In addition, using a chiral bis(oxazoline) ligand we applied the direct imidation of various sulfides into optically active sulfimides. Thus, in the imidation of benzyl 1-



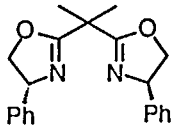


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TABLE I
Catalytic synthesis of sulfimides.

1		2
R^1	R^2	yield / %
p-Tol	Me	83
Ph	Ph	79
Ph	Bn	82
$PhCH_2CH_2$	Bn	50
$4\text{-}MeOC_6H_4$	Bn	70
1-Nap	Bn	54
$4\text{-}NO_2C_6H_4CH_2$	Ph	72

TABLE II
Synthesis of chiral sulfimides.

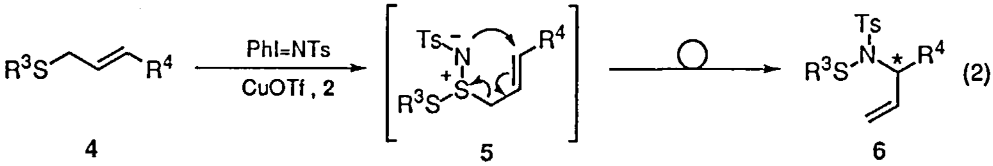
1		2	
R^1	R^2	yield / %	ee / %
1-Nap	Bn	75	71
Ph	Bn	78	64
$PhCH_2CH_2$	Bn	63	22
$4\text{-}NO_2C_6H_4CH_2$	Ph	37	25
Ph	*i*-Pr	44	23

TABLE III
Synthesis of chiral sulfenamides.

4		6	
R^3	R^4	yield / %	ee / %
Ph	Ph	40	27
$2\text{-}NO_2C_6H_4$	Bn	37	43
1-Nap	Ph	80	58
Ph	Me	30	25
1-Nap	Me	35	50

naphthyl sulfide, the best enantiomeric excess (71 % ee) was obtained when the reaction was performed in toluene in the presence of 6 mol% chiral ligand 3 and 5 mol% CuOTf at 25 °C for 48 h to afford the corresponding chiral sulfimide in 75 % isolated yield (Table II). Other results are also shown in the table.

When the reaction was applied to allylic sulfides 4, the expected aziridination to the double bond did not occur at all and, instead, the chiral allylic sulfenamides 6 were obtained selectively in good yields, Table III. This fact shows that the nitrogen attack occurred only at the sulfur atom to give the chiral allylic sulfimide intermediates 5 and the [2,3] sigmatropic rearrangement with chirality transfer followed, eqn. (2) (Table III).



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