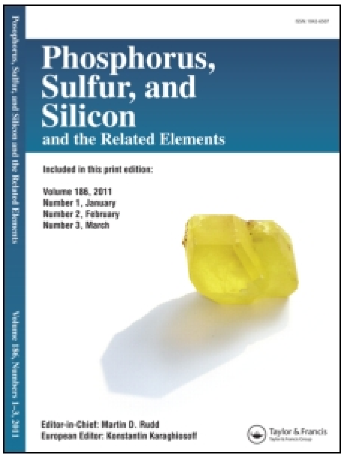

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# Sulfimide-mediated Asymmetric Synthesis

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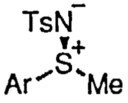
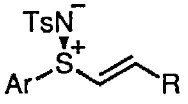
Enantiomerically enriched sulfimides are used to prepare enantiomerically enriched epoxides, aziridines and substituted tetrahydro-furans and -pyrans. A new 'asymmetric sulfimidation' procedure is described.

The enantiomerically pure chiral sulfimide **1** is a useful asymmetric methylidene transfer reagent, which can also be condensed with aldehydes to provide chiral Michael-type acceptors **2**.

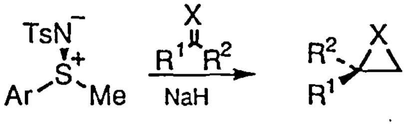


**1**



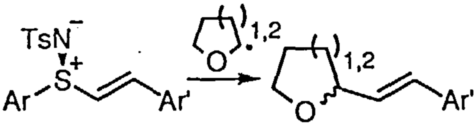
**2**

Sulfimide **1** was found to act as an asymmetric methylidene transfer agent to carbon-heteroatom double bonds to yield chiral three-membered heterocycles (Scheme 1). For X = O, a range of chiral epoxides was prepared in 60-64% yield and 20-70% ee. For X = NAr, chiral aziridines were the products, formed in 73-79% yield and 18-38% ee.



*Scheme 1*

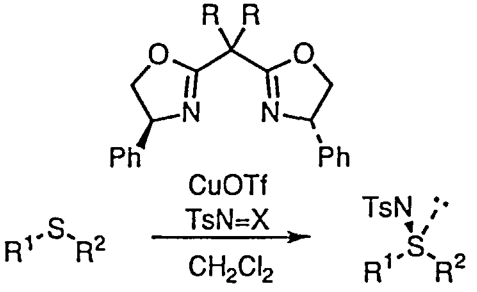
Vinyl sulfimides **2**, prepared by an *in situ* Wittig-Horner-type reaction,[2] were found to react with tetrahydrofuran (thf) and tetrahydropyran (thp) radicals, *via* α-addition and subsequent elimination, to yield new chiral vinyl compounds (Scheme 2).[2]



*Scheme 2*

Ring expansion of the substituted thf and thp products, using Taylor's adaptation of the Malherbe-Bellus rearrangement,[3] led to 9- and 10- membered chiral lactones.

As chiral sulfimides appear to hold a good deal of promise in asymmetric synthesis, we decided to attempt their asymmetric synthesis by an 'asymmetric sulfimidation' reaction, using conditions similar to those used by Evans for the analogous asymmetric aziridination procedure.[4]



5 mol % Cu + ligand

*Scheme 3*

The results of a number of asymmetric sulfimidation reactions are shown in the Table. Two main conclusions can be drawn:

1. High ees are observed only when both the ligand is bulky (R = Me) and both substituents on sulfur ($R^1$ and $R^2$) are bulky. Japanese colleagues have also observed this phenomenon.[5] This has led us to propose the existence of a possible zero asymmetric induction approach of sulfide to the nitrenoid intermediate when a $C_2$-symmetric ligand is used.
2. Chloramine T (TsNClNa) is potentially a replacement for TsN=IPh as a nitrene source, but ees are reduced by the presence of sodium chloride as a by-product. This was demonstrated by adding 5 mol % of NaCl to the standard TsN=IPh reaction.

|  |  | R = H | R = Me |  |  |
|---|---|---|---|---|---|
| $R^1$ | $R^2$ | X = IPh | X = IPh | X = NaCl | X = IPh (NaCl added) |
| Ph | Bn | <5 | 74 | <5 | 10 |
| Bn | Me | <5 | 15 | <5 | 5 |
| tol | Me | <5 | 14 | <5 | 4 |

Table of enantiomeric excesses for asymmetric sulfimidation reactions, varying sulfide, chiral ligand and nitrene source.[6]

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