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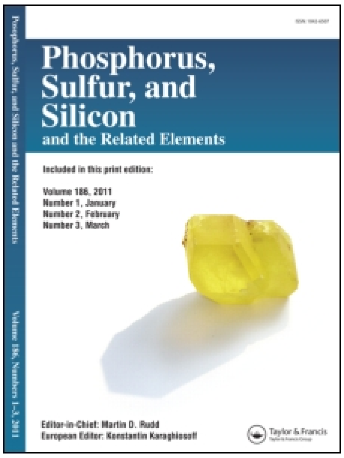

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Stereospecific Transformations of Chiral Compounds Using Anchimeric Assistance of Arylthio and Arylseleno Group

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Stereospecific Transformations of Chiral Compounds Using Anchimeric Assistance of Arylthio and Arylseleno Group

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A new chiral pool method is developed starting from readily available chiral oxiranes, the key step being the substitution reaction through the anchimeric assistance of the arylthio and arylseleno group. The overall transformation is the introduction of nucleopiles into the chiral carbon of the oxiranes with retention of the configuration.

KEY WORDS: chiral oxirane, anchimeric assistance, phenylthio group, 2,4,6-tri-*tert*-butylphenylseleno group

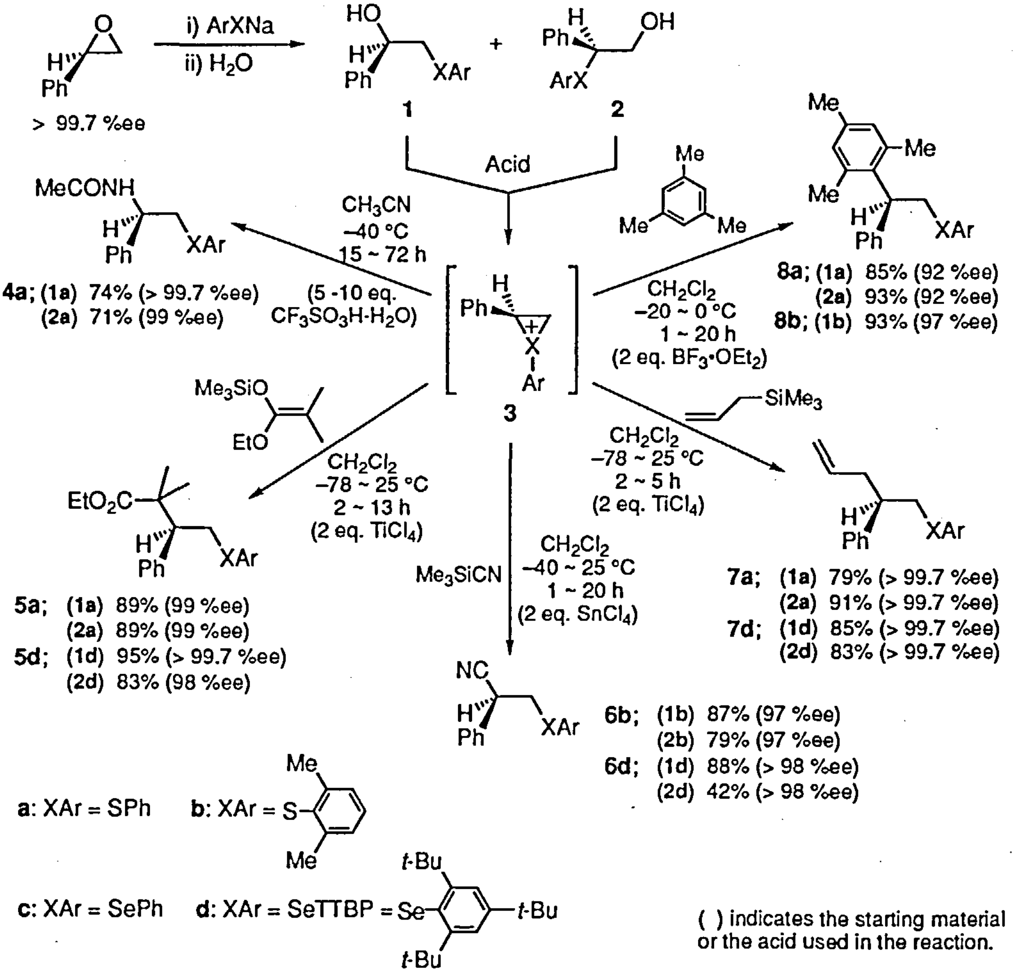
Typical examples of our method are summarized in Scheme 1 using (*R*)-phenyloxirane. The first step of our procedure is the ring-opening of the chiral oxirane by arenethiolate or areneselenolate to afford the mixture of the regioisomers of the alcohols **1** and **2** bearing an arylthio or arylseleno group on the β carbon atom. In the second step, an acid induces the intramolecular substitution of the hydroxy group by the chalcogen atom to form the cationic three-membered cyclic intermediates **3** which are trapped by various nucleophiles to afford the substitution products **4–8**. Out of two cyclic carbon atoms in **3**, the nucleophiles were introduced selectively into the benzylic carbon atom to afford the single product.

It was confirmed that the regioisomeric alcohols **1** and **2** afford the same product with the same enantiomeric purities, indicating that both isomers are useful in the transformation of the chiral oxiranes.

As for the episulfonium ion bearing phenyl group on the sulfur atom **3a**, the chiral carbon hardly racemizes during the reaction and the carbon nucleophiles do not attack the sulfur atom to afford the carbon–carbon bond formation products selectively.[1] In some cases, however, it was necessary to employ the participation of the 2,6-xylylthio group (**3b**) to improve the chemical and optical yields.

As for the analogous episelenonium ion bearing phenyl group on the slenium atom **3c**, on the other hand, the chiral carbon racemizes quite easily during the reaction[2] and carbon nucleophiles attack the selenium atom selectively rather than the carbon atom to afford no carbon–carbon bond formation products.[3] These drawbacks of the episelenonium ion are both overcome by the steric protection of the selenium atom by the 2,4,6-tri-*tert*-butylphenyl (TTBP) group (3d).[4]

Scheme 1



REFERENCES

1. A. Toshimitsu, C. Hirosawa, and K. Tamao, *Tetrahedron*, **50**, 8997(1994).
A. Toshimitsu, H. Abe, C. Hirosawa, and K. Tamao, *J. Chem. Soc., Perkin Trans. 1*, **1994**, 3465.
A. Toshimitsu, C. Hirosawa, and K. Tamao, *Synlett.*, **1996**, 465.
2. A. Toshimitsu, M. Ito, and S. Uemura, *J. Chem. Soc., Chem. Commun.*, **1989**, 530.
3. R. P. Alexander and I. Paterson, *Tetrahedron Lett.*, **24**, 5911(1983).
4. A. Toshimitsu, K. Nakano, T. Mukai, and K. Tamao, *J. Am. Chem. Soc.*, **118**, 2756(1996).