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Edited by R. A. Klein
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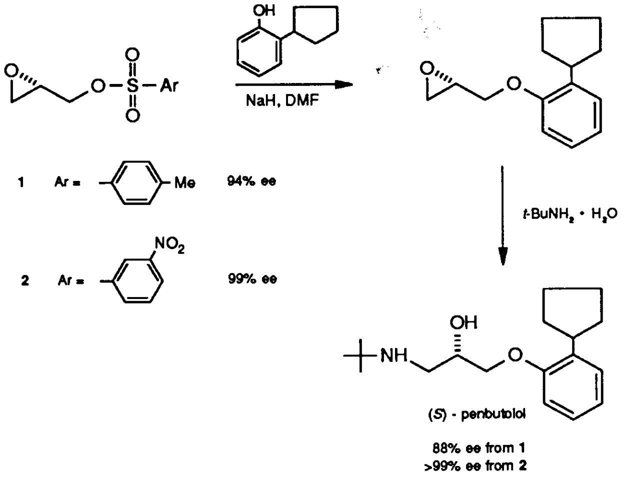
The Sharpless Asymmetric Epoxidation
"Everything you ever wanted to know . . ."

If you are planning to run an asymmetric epoxidation (AE) you should read and probably commit to memory the recent publication from the Sharpless research group at MIT.[1] This meticulously crafted paper presents the first full account of the group's work on catalytic AE[2] (*i.e.,* epoxidation with 5-10 mole % Ti-tartrate in the presence of molecular sieves), nicely contrasting results from a variety of substrate allylic alcohols with the stoichiometric protocol.[3,4] The paper also provides the real "do's and dont's" of this reaction with an in-depth discussion of important factors that influence the rate and enantioselectivity of the process, namely, catalyst stoichiometry, substrate concentration, catalyst aging, the use of molecular sieves, and the choice of oxidant and oxidation solvent. For example, Professor Sharpless now recommends the use of anhydrous isooctane (2,2,4-trimethylpentane) solutions of ***tert*-butyl hydroperoxide** (TBHP), which we offer in 3.0*M* and 5.5*M* concentrations,[5] over the traditional dichloromethane or toluene solutions. Everything you ever wanted to know about catalytic asymmetric epoxidation is contained in the text, experimental section and footnotes of this paper!

A significant advantage to using catalytic AE is that the low catalyst concentration makes *in situ* derivatization of the epoxy alcohol products by sulfonylation or acylation preparatively feasible. Thus, low-molecular-weight epoxy alcohols can now be isolated in greatly improved yields as crystalline sulfonate and p-nitrobenzoate (PNB) esters, which can be enantiomerically enriched by recrystallization. As indicated below, these derivatized epoxy alcohols are important chiral building blocks (*e.g.,* β-blocker synthons). Noteworthy in this scheme is the use of the new glycidyl sulfonate 2 which, unlike tosylate 1, can be recrystallized to >99% ee and shows greatly improved rate and selectivity in the aryl oxide displacement step providing the eutomer of penbutolol in >99% ee.[6,7]



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Glycidyl sulfonates

30,051-9	**(2*R*)-(-)-Glycidyl tosylate,* 99%**	**1g $16.45**
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30,576-6	**(2*S*)-(+)-2-Methylglycidyl 4-nitrobenzoate, 98%**	**1g $19.00**
30,045-4	**(2*R*,3*R*)-(+)-3-Methylglycidyl 4-nitrobenzoate, 98%**	**1g $15.50**
30,046-2	**(2*S*,3*S*)-(-)-3-Methylglycidyl 4-nitrobenzoate, 98%**	**1g $15.50**
30,053-5	**(2*R*)-(+)-3,3-Dimethylglycidyl 4-nitrobenzoate, 98%**	**1g $14.80**
30,054-3	**(2*S*)-(-)-3,3-Dimethylglycidyl 4-nitrobenzoate, 98%**	**1g $14.80**

These products are licensed under U.S. Patent 4,471,130.

Reagents for catalytic AE

NEW **31,037-9**	***tert*-Butyl hydroperoxide**, anhydrous, 3.0*M* solution in 2,2,4-trimethylpentane	**25g $8.30** **100g $19.90; 500g $68.20**
NEW **33,127-9**	***tert*-Butyl hydroperoxide**, anhydrous, 5.5*M* solution in 2,2,4-trimethylpentane	**25g $17.50; 100g $49.00**
20,527-3	**Titanium(IV) isopropoxide**	**100g $13.05;** **500g $17.05; 2kg $51.75**
22,780-3	**Diisopropyl D-tartrate**, 99%	**10g $16.45** **50g $54.20**
22,918-0	**Diisopropyl L-tartrate**, 99%	**25g $13.75** **100g $36.70**
23,364-1	**Molecular sieves, 3A**, powder, undried	**500g $14.00; 1kg $22.90; 2.5kg $45.25**
23,366-8	**Molecular sieves, 4A**, activated powder	**500g $15.00; 1kg $24.50; 2.5kg $48.55**
23,367-6	**Molecular sieves, 5A**, powder, undried	**500g $15.10; 1kg $24.60; 2.5kg $48.65**

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