Chiral Ketone Catalysts Derived from D-Fructose

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Introduction

In 1996, a new chiral ketone 1 (1,2;4,5-di-isopropylidene-D-erythro-2,3-hexodioiuoro-2,6-pyranose), derived from inexpensive D-fructose, was reported by Shi and co-workers as a highly active asymmetric epoxidation catalyst. This rapidly developed into a new class of highly efficient catalysts for the asymmetric epoxidation of a wide range of olefins.

Preparation

Ketones 1, 2 and 3 were prepared from D-fructose in excellent yields. Ketone 4 was prepared from D-glucose.

Abstract

(A) Ketone 1 is an efficient epoxidation catalyst for trans-disubstituted and trisubstituted olefins with potassium peroxomonosulfate (Oxone) as the oxidant. Cheap dilute 30% H₂O₂, a green oxidant, shows an enantioselectivity comparable to that of Oxone.

(B) Hydroxyalkenes can be asymmetrically epoxidized by chiral ketone 1 with Oxone or H₂O₂. As shown, asymmetric epoxidation of trans-β-hydroxymethylstyrene can be achieved in 98% ee and 85% yield.

(C) A highly effective and mild asymmetric monoepoxidation of conjugated dienes with chiral ketone 1 and Oxone presents an efficient approach to prepare enantiomerically enriched vinyl epoxides. The enantiomeric excess for the major monoepoxides ranges from 89% to 97%.

(D) For the asymmetric epoxidation of conjugated enynes using chiral ketone 1 as the catalyst and Oxone or H₂O₂ as the oxidant, a high ee up to 95% is obtained. Double bonds in conjugated enynes can also be selectively epoxidized by ketone 2 and Oxone.
Chiral oxy-substituted epoxides or hydroxy ketones can be synthesized through the enantioselective epoxidation of chiral silyl enol ethers or enol esters catalyzed by ketone 1 and Oxone.\textsuperscript{13}

Through the asymmetric epoxidation of 2,2-disubstituted vinylsilanes, chiral 2,2-disubstituted $\alpha,\beta$-epoxysilanes can be synthesized.\textsuperscript{14} Upon desilylation, the corresponding 1,1-disubstituted enol ethers or enol esters catalyzed by ketone synthesized through the enantioselective epoxidation of chiral silyl (E) Chiral oxy-substituted epoxides or hydroxy ketones can be synthesized. \textsuperscript{15} Upon desilylation, the corresponding 1,1-disubstituted enol ethers or enol esters catalyzed by ketone synthesized through the enantioselective epoxidation of chiral silyl (F) The kinetic resolution of racemic 1,3- and 1,6-disubstituted cyclohexene via chiral ketone has been achieved.\textsuperscript{15}

Asymmetric epoxidation of several trans-disubstituted and trisubstituted $\alpha,\beta$-unsaturated esters was achieved with high yields and ee values, using a system consisting of ketone 2 and oxone. $\text{CO}_2\text{Et}$

For the asymmetric epoxidation of terminal olefins, ketone 1 shows a similar reactivity to ketone 4, but a much lower enantioselectivity.\textsuperscript{16}

Ketone 1 shows both a lower reactivity and a lower enantioselectivity than ketone 4 for the asymmetric epoxidation of cis-disubstituted olefins.\textsuperscript{17}

The enantioselectivity obtained with ketone 3 is very similar to that of ketone 1 in the asymmetric epoxidation of trans-disubstituted and trisubstituted olefins, hydroxalkenones and chiral enol esters. However, the catalyst consumption is greatly decreased from 20–30 mol% for ketone 1 to 1–5 mol% for ketone 3.\textsuperscript{5}

References