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-hexodioiros-2,6-pyranose), derived from inexpensive D-fructose, was reported by Shi and co-workers as a highly active asymmetric epoxidation catalyst.1 This rapidly developed into a new class of highly efficient catalysts for the asymmetric epoxidation of a wide range of olefins.2

Preparation

Ketones 1, 2 and 3 were prepared from D-fructose in excellent yields.3a,4,5 Ketone 4 was prepared from D-glucose.3c,6

Abstract

(A) Ketone 1 is an efficient epoxidation catalyst for trans-disubstituted and trisubstituted olefins with potassium peroxomonosulfate (Oxone) as the oxidant.1,3a,7 Cheap dilute 30% H2O2, a green oxidant, shows an enantioselectivity comparable to that of Oxone.8,9

(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.10

(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%.11

(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.12 Double bonds in conjugated enynes can also be selectively epoxidized by ketone 2 and Oxone.4
(E) 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.13

(F) Through the asymmetric epoxidation of 2,2-disubstituted vinylsilanes, chiral 2,2-disubstituted α,β-epoxysilanes can be synthesized.15 Upon desilylation, the corresponding 1,1-disubstituted terminal epoxides are obtained without any loss in enantioselectivity.

(G) The kinetic resolution of racemic 1,3- and 1,6-disubstituted cyclohexene via chiral ketone 1 has been demonstrated.15

(H) Asymmetric epoxidation of several trans-disubstituted and trisubstituted α,β-unsaturated esters was achieved with high yields and ee values, using a system consisting of ketone 2 and oxone.4

(I) For the asymmetric epoxidation of terminal olefins, ketone 1 shows a similar reactivity to ketone 4, but a much lower enantioselectivity.16

(J) Ketone 1 shows both a lower reactivity and a lower enantioselectivity than ketone 4 for the asymmetric epoxidation of cis-disubstituted olefins.5

(K) 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 3.5

References

(9) YOxone or YH2O2 stands for the yield when Oxone or H2O2 is used as the oxidant; while Y1 or Y2 stands for the yield when ketone 1, 3 or 4 is used as the catalyst.