**SYNLETT Spotlight 97**

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

**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-hexodiuro-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.³,⁴,⁵ Ketone 4 was prepared from D-glucose.³,⁶

**Abstract**

(A) Ketone 1 is an efficient epoxidation catalyst for trans-disubstituted and trisubstituted olefins with potassium peroxomonosulfate (Oxone) as the oxidant.¹,³,⁵ 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

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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. Upon desilylation, the corresponding 1,1-disubstituted terminal epoxides are obtained without any loss in enantioselectivity.

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.

For the asymmetric epoxidation of terminal olefins, ketone 1 shows both a lower reactivity and a lower enantioselectivity than ketone 4 for the asymmetric epoxidation of cis-disubstituted olefins.

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.

**References**

9. Oxone or H2O2/CH3CN was used as the oxidant; while Y1, Y3 or Y4 stands for the yield and ee values when ketone 1, 3 or 4 is used as catalyist.