

SYNLETT Spotlight 97

Chiral Ketone Catalysts Derived from D-Fructose

H.-Q. Ge



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

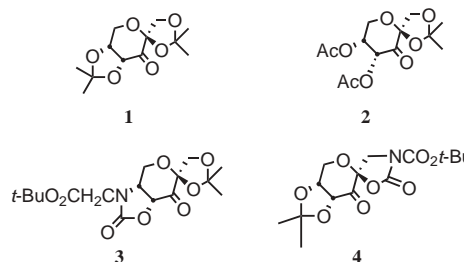
H.-Q. Ge was born in Hubei (China) in 1977. He achieved his Bachelor degree from the School of Chemistry and Material Science, Hubei University, China. He is currently in the second year of his Master-PhD through-train studies, working on the asymmetric epoxidation of olefins on organic-inorganic hybrid catalysts, under the supervision of Professors Q.-H. Xia and C.-P. Ye.

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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

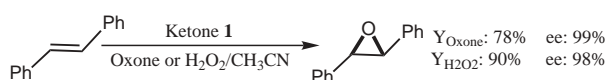


Preparation

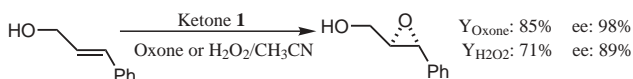
Ketones **1**, **2** and **3** were prepared from D-fructose in excellent yields.^{3a,4,5} Ketone **4** was prepared from D-glucose.^{3c,6}

Abstract

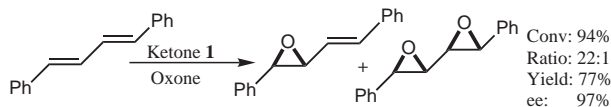
(A) Ketone **1** is an efficient epoxidation catalyst for *trans*-disubstituted and trisubstituted olefins with potassium peroxomonosulfate (Oxone) as the oxidant.^{1,3a,7} Cheap dilute 30% H₂O₂, a green oxidant, shows an enantioselectivity comparable to that of Oxone.^{8,9}



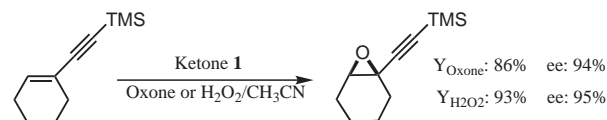
(B) Hydroxyalkenes can be asymmetrically epoxidized by chiral ketone **1** with Oxone or H₂O₂. As shown, asymmetric epoxidation of *trans*-β-hydroxymethylstyrene can be achieved in 98% ee and 85% yield.¹⁰



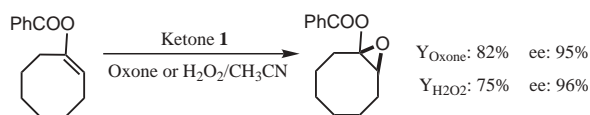
(C) A highly effective and mild asymmetric monoepoxidation of conjugated dienes with chiral ketone **1** and Oxone presents an efficient approach to prepare enantiomerically enriched vinyl epoxides. The enantiomeric excess for the major monoepoxides ranges from 89% to 97%.¹¹



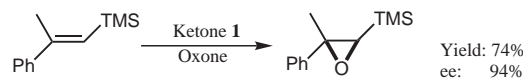
(D) For the asymmetric epoxidation of conjugated enynes using chiral ketone **1** as the catalyst and Oxone or H₂O₂ as the oxidant, a high ee up to 95% is obtained.¹² Double bonds in conjugated enynes can also be selectively epoxidized by ketone **2** and Oxone.⁴



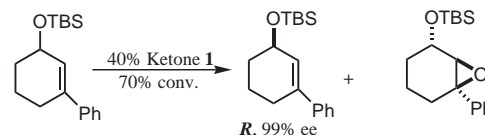
(E) Chiral oxy-substituted epoxides or hydroxy ketones can be synthesized through the enantioselective epoxidation of chiral silyl enol ethers or enol esters catalyzed by ketone **1** and Oxone.¹³



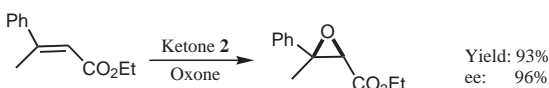
(F) Through the asymmetric epoxidation of 2,2-disubstituted vinylsilanes, chiral 2,2-disubstituted α,β -epoxysilanes can be synthesized.¹⁴ Upon desilylation, the corresponding 1,1-disubstituted terminal epoxides are obtained without any loss in enantioselectivity.



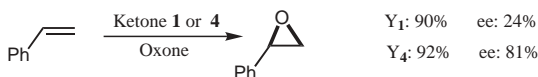
(G) The kinetic resolution of racemic 1,3- and 1,6-disubstituted cyclohexene via chiral ketone **1** has been demonstrated.¹⁵



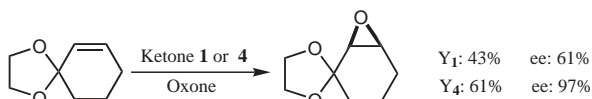
(H) Asymmetric epoxidation of several *trans*-disubstituted and trisubstituted α,β -unsaturated esters was achieved with high yields and ee values, using a system consisting of ketone **2** and oxone.⁴



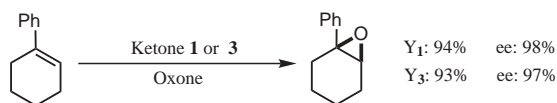
(I) For the asymmetric epoxidation of terminal olefins, ketone **1** shows a similar reactivity to ketone **4**, but a much lower enantioselectivity.¹⁶



(J) Ketone **1** shows both a lower reactivity and a lower enantioselectivity than ketone **4** for the asymmetric epoxidation of *cis*-disubstituted olefins.³



(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, hydroxyalkenes 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

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- (9) Y_{oxone} or $Y_{\text{H}_2\text{O}_2}$ stands for the yield when Oxone or H_2O_2 is used as the oxidant; while Y_1, Y_3 or Y_4 stands for the yield when ketone **1, 3** or **4** is used as the catalyst.
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