

Enantioselective epoxidation of 1-hexene with sugar derived hydroperoxides

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Dedicated to Prof. Dr. Berhanu M. Abegaz on the occasion of his 60th birthday

Abstract

The catalyzed asymmetric epoxidation of 1-hexene with various optically active hydroperoxides derived from sugars has been examined in the presence of an achiral molybdenum-complex. Enantioselectivities up to 53% e. e. were achieved.

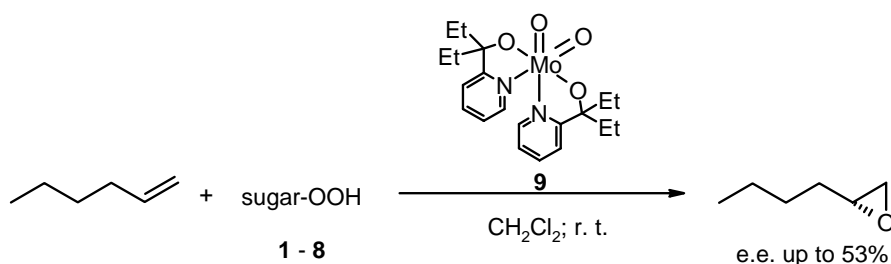
Keywords: Asymmetric Synthesis, epoxidation, hydroperoxides

Introduction

The asymmetric oxidation of unfunctionalized as well as functionalized olefins is the subject of intensive research in organic synthesis.¹ Recently we described the asymmetric epoxidation of allylic alcohols and the oxidation of sulfides to sulfoxides with optically active sugar hydroperoxides.^{2,3,4} Enantioselectivities up to 50% e. e. were observed. Because the Jacobsen method¹ using Mn-salen-complexes works highly efficient only for cis-substituted olefins the epoxidation of unfunctionalized olefins is still a great challenge in asymmetric oxidation. In order to approach this problem we investigated the epoxidation of terminal olefins with sugar derived hydroperoxides in the presence of Mo-catalyst such as MoO₂(acac)₂ or Mo(CO)₆. Unfortunately, these complexes were active only at temperatures above 80°C. Thus no significant enantioselectivity could be detected under these conditions.⁵ Recently, Herrmann et al. described new dioxo-molybdenum(VI)-complexes of the type MoO₂L₂ (L = 2`- pyridinyl alcoholate), e.g. **9** and their application as catalysts for the oxidation of terminal n-alkenes with molecular oxygen and hydroperoxides.⁶

Results and Discussion

Here we report our results in the asymmetric epoxidation of 1-hexene by optically active sugar derived hydroperoxides in the presence of such a Mo-complex **9**.⁷ 1-Hexene was epoxidized by the sugar derived hydroperoxides **1-8** in the presence of catalytic amounts of **9** in CH₂Cl₂ at r.t. according to Scheme 1.

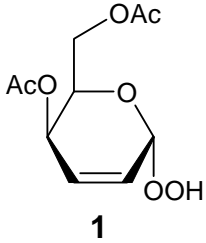
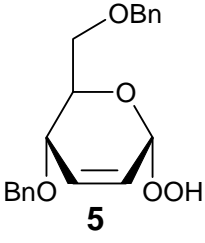
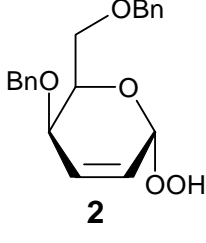
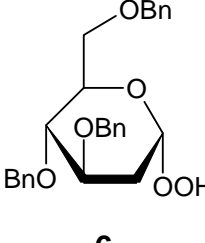
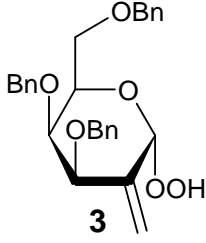
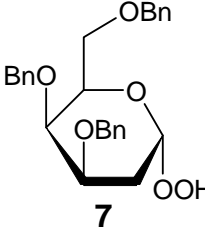
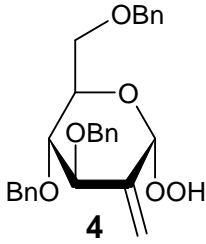
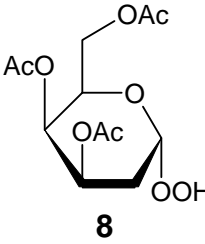


Scheme 1

The conversion of the hydroperoxides was complete within 3 days as determined by TLC. The e.e. of the epoxyhexane formed was determined in the reaction mixture by GC on cyclodextrine chiral stationary phases. The results obtained are summarized in Table 1.

In all cases the (*R*)-epoxyhexane was formed as major enantiomer. It appears that the direction of asymmetric induction is not affected by the other chiral centres at the sugar hydroperoxide but by the configuration at the anomeric carbon atom to which the hydroperoxy group is bound. The lowest e.e. (up to 30%) were detected with methylenedihydroperoxides **3** and **4** and the 2,3-unsaturated hydroperoxide **2**. Moderate enantiomeric excesses were observed using saturated hydroperoxide **6**, **7** and **8**, while the highest enantioselectivity up to 53% e.e. was achieved with compounds **1** and **5**. To the best of our knowledge this is the best outcome in asymmetric epoxidation of a terminal unfunctionalized olefin so far.

Table 1. Enantioselective epoxidation of 1-hexene with sugar derived hydroperoxides **1 - 8**

Hydroperoxide	% e.e. ^a	Hydroperoxide	% e.e. ^a
	50		53
	30		40
	20		38
	28		34

^a Determined by GC on a chiral stationary phase LIPODEX E (25 m x 0.25 mm, 40 °C, carrier gas: hydrogen, 0.3 bar) using a HP 5890 series II gas chromatograph with a split injector and FID.

Experimental Section

General Procedure. All reaction were carried out using hydroperoxide **1-8** (0.1 mmol), 1-hexene (0.1 mmol) and 10 mol % Mo-catalyst **9** in dichloromethane at r.t. After complete conversion of the hydroperoxide (detected by TLC) the e.e. of the epoxyhexane formed was estimated in the resulting reaction mixture by GLC on LIPODEX E. Peak assignment to the (*R*) and (*S*) configuration was possible by comparison with an authentic sample from ALDRICH.

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References and Notes

1. Jacobsen, E. N. In *Comprehensive Organometallic Chemistry II*, Abel, E. W.; Stone, F.G.A.; Wilkinson, G. Eds., Vol.12, pp 1097-1132, Pergamon: Oxford, 1995.
2. Hamann, H.-J.; Höft, E.; Chmielewski, M.; Maciejewski, S. *Chirality* **1993**, *5*, 338.
3. Hamann, H.-J.; Höft, E.; Mostowicz, D.; Mishnev, A.; Urbanczyk-Lipkowska, Z.; Chmielewski, M. *Tetrahedron* **1997**, *53*, 185.
4. Mostowicz, D.; Jurczak, M.; Hamann, H.-J.; Höft, E.; Chmielewski, M. *Eur J. Org. Chem.* **1998**, 2617.
5. Hamann, H.-J.; Höft, E.; "Peroxide Chemistry: Mechanistic and Preparative Aspects of Oxygen Transfer", Meeting of the Deutsche Forschungsgemeinschaft, Freyburg/Unstrut, Germany, 20-22 September 1995.
6. Herrmann, W. A.; Lomaier, G. M.; Priermeier, T.; Mattner, M. R.; Scharbert, B. *J. Mol. Catal.* **1997**, *117*, 455.
7. Hamann, H.-J.; Höft, E.; "Peroxide Chemistry: Mechanistic and Preparative Aspects of Oxygen Transfer", Meeting of the Deutsche Forschungsgemeinschaft, Köln, Germany, 28-30 September 1997.