Pergamon

Tetrahedron: *Asymmetry* 10 (1999) 3667–3669

TETRAHEDRON: *ASYMMETRY*

Asymmetric cyclization of *meso*-diepoxides using chiral (salen)Co(III)OAc catalyst forming optically active 1,4-anhydropentitols and 2,5-anhydrohexitols

Masatoshi Kamada,[a] Toshifumi Satoh,[a] Toyoji Kakuchi [b] and Kazuaki Yokota [a,*]

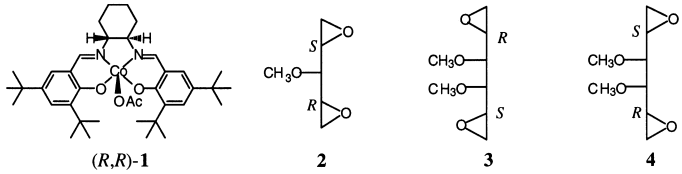
[a] *Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan*
[b] *Division of Bioscience, Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan*

Received 9 August 1999; accepted 30 August 1999

Abstract

The asymmetric hydrations of *meso*-diepoxides, 1,2:4,5-dianhydro-3-*O*-methylxylitol **2**, 1,2:5,6-dianhydro-3,4-di-*O*-methylallitol **3** and 1,2:5,6-dianhydro-3,4-di-*O*-methylgalactitol **4**, were carried out using (*R*,*R*)-**1** and (*S*,*S*)-**1**. An optically active five-membered cyclic compound was selectively produced in good yield from **2**, but a mixture of the five- and six-membered cyclic compounds was obtained in the cases of **3** and **4**. The ees of all cyclic products exceeded 90%.

The cyclopolymerization of 1,2:5,6-dianhydrohexitols corresponding to diepoxides has been developed as a novel method for producing carbohydrate polymers with regio- and stereoselective structures.[1,2] The hydration of the diepoxides afforded the five- and six-membered cyclic compounds as model compounds for the constitutional units of the polymers. Recently, Jacobsen et al. reported that the enantioselective ring-opening of *meso*-epoxides and kinetic resolution of terminal epoxides resulted in the optically active products exceeding 90% ee by asymmetric catalysis using chiral salen–metal complexes.[3–6] The method has the advantage of obtaining an optically active compound from an achiral material, so it is of great interest to investigate the stereoselective cyclization of a *meso*-diepoxide. Here we report the catalytic enantioselective reaction of *meso*-diepoxides, 1,2:4,5-dianhydro-3-*O*-methylxylitol **2**,[7] 1,2:5,6-dianhydro-3,4-di-*O*-methylallitol **3**[2] and 1,2:5,6-dianhydro-3,4-di-*O*-methylgalactitol **4**,[2] with water using chiral Co(salen) complexes (*R*,*R*)-**1** and (*S*,*S*)-**1**[8] to produce chiral cyclic compounds.



(*R*,*R*)-**1** **2** **3** **4**

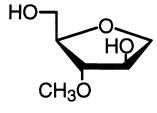
* Corresponding author. Fax: +81-11-706-6602; e-mail: yokota@poly.eng.hokudai.ac.jp

0957-4166/99/$ - see front matter
PII: S0957-4166(99)00393-6

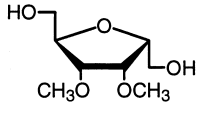
Table 1
Asymmetric hydration of *meso*-diepoxides with chiral (salen)Co(III)OAc complex

Diepoxide	Catalyst	Product	Yield(%)[d]	% ee[e]	$[\alpha]^{25}_{D}$ [f]
2[a]	(*R*,*R*)-**1**	**D-5**	78	>99	+30.1
	(*S*,*S*)-**1**	**L-5**	88	>99	- 31.0
3[b]	(*R*,*R*)-**1**	**D-6**	86	95.1	+29.2
		D-7	6	91.9	+54.9
	(*S*,*S*)-**1**	**L-6**	80	97.3	- 30.7
		L-7	12	>99	- 58.4
4[c]	(*R*,*R*)-**1**	**D-6**	27	90.4	+26.3
		D-8	26	96.0	+71.7
	(*S*,*S*)-**1**	**L-6**	25	92.2	- 27.8
		L-8	22	97.0	- 72.5

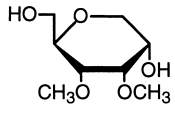
[a]Hydration of **4** was carried out at r.t. for 60 hours. [b]Hydration of **2** was carried out at r.t. for 24 hours. [c]Hydration of **3** was carried out at 35°C for 48 hours. [d]Estimated by ^{13}C NMR using the inverse gated spin decoupling technique. [e]Determined by HPLC; Chiralcel OD; hexane/IPA 8:2; 0.5mL/min. [f]Measured in chloroform (c = 1.0).



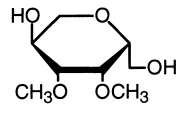
D-5



D-6



D-7

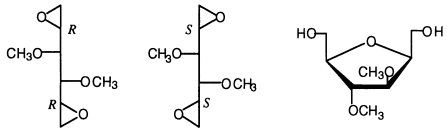


D-8

The reaction of neat **2** with 1.05 equiv. of H_2O in the presence of (*R*,*R*)-**1** (0.5 mol%) resulted in a five-membered cyclic compound after 60 h at room temperature.[9] Removal of (*R*,*R*)-**1** afforded 1,4-anhydro-3-*O*-methyl-D-arabinitol (D-**5**, >99% ee) in 78% yield. Enantiomer L-**5** was obtained by treatment of **2** with (*S*,*S*)-**1** in 88%.

Table 1 summarizes the results of the asymmetric hydration of **2**, **3** and **4** catalyzed by (*R*,*R*)-**1** and (*S*,*S*)-**1**. For the hydration of **3** with (*R*,*R*)-**1**, 2,5-anhydro-3,4-di-*O*-methyl-D-altritol (D-**6**, 91.5% ee) and 1,5-anhydro-3,4-di-*O*-methyl-D-allitol (D-**7**, 93.3% ee) were obtained in 86% and 6% yields, respectively. On the other hand, the reaction of **4** with (*R*,*R*)-**1**, which was less reactive than those of **2** and **3**, gave D-**6** and 1,5-anhydro-3,4-di-*O*-methyl-D-galactitol (D-**8**, 96.0% ee) in 27% and 26% yields, respectively, and one-half its initial amount was recovered as an unreacted material for **4**. All the cyclic products showed high enantioselectivity with the value over 90% ee, and the specific rotations were positive for the compounds produced using (*R*,*R*)-**1** and negative for those using (*S*,*S*)-**1**. This result indicates that the highly stereoselective ring-opening reaction along with cyclization was achieved in the hydrations of diepoxides using catalysts (*R*,*R*)-**1** and (*S*,*S*)-**1**.

Application of the method to 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-mannitol **9**[1] and L-iditol **10**[1] clarified the stereochemical interaction between the diepoxide and Co(salen) complex. Dianhydrohexitols **9** and **10** corresponding to (*R*,*R*)- and (*S*,*S*)-diepoxides, respectively, have been reported, on acidic hydration, to give 2,5-anhydro-3,4-di-*O*-methyl-D-glucitol **11**.[1] The hydration of **9** using (*R*,*R*)-**1** produced the five-membered cyclic compound **11**, but that using (*S*,*S*)-**1** had no product. The reaction of **10** showed the stereochemical reaction opposite to that of **9**.



9 **10** **11**

Conclusively, Co(salen) complexes (*R*,*R*)-**1** and (*S*,*S*)-**1** catalyzed the asymmetric selective cyclization of *meso*-diepoxides **2**, **3** and **4** to produce optically active cyclic compounds with enantiomeric excesses of 90%. The stereoselectivity for the hydration of **2**, **3** and **4** followed the enantioselectivity for the kinetic resolution of terminal epoxide.

References

1. Kakuchi, T.; Satoh, T.; Umeda, S.; Hashimoto, H.; Yokota, K. *Macromolecules* **1995**, *28*, 5643.
2. Kamada, M.; Satoh, T.; Yokota, K.; Kakuchi, T. *Macromolecules* **1999**, *32*, 5755.
3. Larrow, J. F.; Schaus, S. E.; Jacobsen, E. N. *J. Am. Chem. Soc*. **1996**, *118*, 7420.
4. Schaus, S. E.; Larrow, J. F.; Jacobsen, E. N. *J. Org. Chem.* **1997**, *62*, 4197.
5. Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 936.
6. Jacobsen, E. N.; Kakiuchi, F.; Konsler, R. G.; Larrow, J. F.; Tokunaga, M. *Tetrahedron Lett*. **1997**, *38*, 773.
7. The preparation of diepoxide **2** has been reported: Satoh, T.; Shibata, K.; Yokota, K.; Kakuchi, T. *Macromol. Rapid Commun*. **1999**, *20*, 55.
8. The preparations of (*R*,*R*)-**1** and (*S*,*S*)-**1** have been reported: Leung, W. H.; Chan, E. Y. Y.; Chow, E. K. F.; Williams, I. D.; Peng, S. M. *J. Chem. Soc., Dalton Trans*. **1996**, 1229.
9. General procedure for the asymmetric cyclization of *meso*-diepoxides is as follows: to **2** (0.43 g, 3.3×10^{-3} mol) and (*R*,*R*)-**1** (10 mg, 1.65×10^{-5} mol) was added water (63 μl, 3.5×10^{-3} mol) and then the mixture was stirred for 60 h occasionally checking the progress of reaction by TLC chromatogram. After the reaction mixture was diluted with water, the whole was filtered through the membrane (nitrocellulose), and the filtrate was evaporated. Repetition of these procedures a few times gave D-**5** (0.42 g, 86%) as a colorless oil.