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A Simple Route to Enantiomerically Enriched Oxazolidin-2-ones

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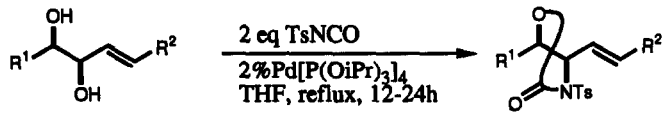
Abstract: *The reaction of ene diols, which are readily available through catalytic asymmetric dihydroxylation of conjugated dienes, with p-tosylisocynate catalyzed by Pd(0) gave enantiomerically enriched oxazolidin-2-ones in high yields.*

We have recently shown that catalytic asymmetric dihydroxylation (AD) of conjugated dienes affords the corresponding ene diols with excellent enantiomeric excesses.[1] The contiguous functionality of ene diols, coupled with the variety of known allylic transformations, provides them with great potential for use in organic synthesis. We report here a one step Pd(0) catalyzed transformation of these ene diols to the corresponding oxazolindin-2-ones.

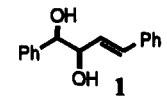
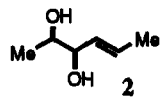
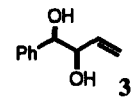
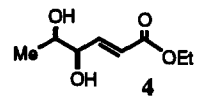
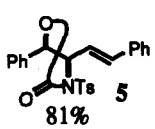
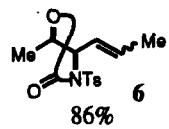
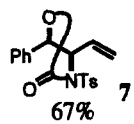
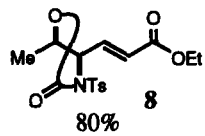
Trost and co-workers reported that an unsaturated 1,4-bis-urethane, derived from the corresponding 1,4-diol, underwent Pd(0) catalyzed cyclization to form the oxazolidin-2-one.[2] An asymmetric version of this transformation was subsequently invented by the same authors, and up to 88% ee was achieved under optimal conditions.[2b] The involvement of an intermediate π-allyl Pd complex indicated that this type of cyclization would also be applicable to 1,2-ene diols. Using the reported protocol,[2] treatment of an ene diol[1,3] with two equivalents of p-tosylisocyanate in the presence of a catalytic amount of Pd(0) in refluxing THF indeed afforded the corresponding oxazolidin-2-one (eq 1).[4] The course of the reaction was followed by TLC and was normally complete in 12 to 24 hours. As shown in Table I, the oxazolidin-2-ones were obtained in good yields from different types of ene diols. Reaction of the hex-4-ene-2,3-diol **2** gave a mixture of two isomers in a ratio of 6:1. The major isomer was assigned from ^{1}H NMR spectrum to be the *trans* isomer (J = 15.1 Hz for the vinylic protons vs. 10.2 Hz for the minor isomer).[4] Interestingly, double bond isomerization was not observed for substrates **1** and **4**. One significant feature of this transformation is that the configuration of both stereogenic centers is retained.

The easy access to a variety of enantiopure ene diols should make this approach a viable alternative for preparation of optically active oxazolidin-2-ones which can be converted to the synthetically useful amino alcohols.[5] Further manipulations of the remaining double bond should also enrich the possible applications which arise for these synthetic sequences.



(eq 1)

Table I

ene diol[a]	 1	 2	 3	 4
product[b]	 5	 6	 7	 8
yield[c]	81%	86% (*trans:cis* = 6:1)	67%	80%

a) See references 1 and 3. b) All products are fully characterized. See reference 4. c) Isolated yield.

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References and Notes:

1. Xu, D.; Crispino, G; Sharpless,K. B. *J. Am. Chem. Soc.* **1992**, *114*, 7570.
2. (a) Trost, B. M.; Van Vranken, D. L. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 228. (b) Trost, B. M.; Van Vranken, D. L. *J. Am. Chem. Soc.* **1991**, *113*, 6317.
3. The preparation of ene diols **1**, **2**, **4** have been reported in reference 1. 1-phenyl-3-butene-1,2-diol (**3**) together with 4-phenyl-3-buten-1,2-diol were prepared in 50% and 23% yield, respectively, from 1-phenyl 1,3-butadiene. The ee value of **3** was 98% which was determined by direct analysis of the hydrogenated ene diol on a HPLC Chiralcel OF column.
4. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR and the elemental compositions were established by high-resolution mass spectroscopy. Spectroscopic data of ^{1}H NMR ($CDCl_3$, 400 MHz) of the products **5** - **8** are as followings: **5**: δ: 7.86 (2H, d, *J* = 8.4 Hz), 7.33-7.41 (8H, m), 7.24-7.29 (4H, m), 6.72 (1H, d, *J* = 15.7 Hz), 6.14 (1H, dd, *J* = 15.7, 8.9 Hz), 5.20 (1H, d, *J* = 4.1 Hz), 4.90 (1H, dd, *J* = 8.9, 4.0 Hz), 2.43 (3H, s). **6**: major isomer, δ: 7.89 (2H, d, *J* = 8.4 Hz), 7.33 (2H, d, *J* = 8.4 Hz), 5.90 (1H, dq, *J* = 15.1, 6.6 Hz), 5.36 (1H, ddq, *J* = 15.1, 8.8, 1.6 Hz), 4.37 (1H, dd, *J* = 8.8, 4.1 Hz), 4.24 (1H, qd, *J* = 6.3, 4.1 Hz), 2.45 (3H, s), 1.76 (3H, dd, *J* = 6.6, 1.6 Hz), 1.40 (3H, d, *J* = 6.3 Hz); minor isomer, δ: 7.91 (2H, d, *J* = 8.6 Hz), 7.31 (2H, d, *J* = 8.6 Hz), 5.87-5.91 (1H, m), 5.20 (1H, dd, *J* = 9.5, 6.4 Hz), 5.18 (1H, qq, *J* = 10.2, 1.7 Hz), 4.79 (1H, pseudo quintet, *J* = 6.5 Hz), 2.44 (3H, s), 1.82 (3H, dd, *J* = 6.9, 1.7 Hz), 1.24 (3H, d, *J* = 6.5 Hz). **7**: δ: 7.89 (2H, d, *J* = 6.7 Hz), 7.32-7.38 (6H,m), 7.19-7.21 (2H,m), 5.91-6.00 (1H, m), 5.46 (1H, s), 5.42 (1H, d, *J* = 6.8 Hz), 4.68 (1H, dd, *J* = 8.2, 4.6 Hz), 2.46 (3H,s). **8**: δ: 7.90 (2H, d, *J* = 8.4 Hz), 7.35 (2H, d, *J* = 8.4 Hz), 6.79 (1H, dd, *J* = 15.6, 8.2 Hz), 6.12 (1H, dd, *J* = 15.6, 0.6 Hz), 4.52 (1H, ddd, *J* = 8.2, 4.7, 0.6 Hz), 4.33 (1H, qd, *J* = 6.3, 4.7 Hz), 4.24 (1H, q, *J* = 7.1 Hz), 2.46 (3H, s), 1.43 (3H, d, *J* = 6.3 Hz), 1.32 (3H, d, *J* = 7.1 Hz).
5. Synthesis of optically active α-amino alcohols from enantiomerically enriched vicinal diols via cyclic sulphates or cyclic sulfites has been reported: a) Lohray, B. B.; Gao, Y.; Sharpless, K. B. *Tetrahedron Lett.* **1989**, *30*, 2623. b) Lohray, B. B.; Ahuja, J. R. *J. Chem. Soc., Chem. Commun.* **1991**, 95.

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