

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lsyc20>

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Published online: 27 Oct 2006.

To cite this article: Suk-Ku Kang, Sung-Gyu Kim, Dong-Gyu Cho & Jae-Ho Jeon (1993) Synthesis of Optically Active Allylic Alcohols, *Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry*, 23:5, 681-684, DOI: [10.1080/00397919308009827](https://doi.org/10.1080/00397919308009827)

To link to this article: <http://dx.doi.org/10.1080/00397919308009827>

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SYNTHESIS OF OPTICALLY ACTIVE ALLYLIC ALCOHOLS

Suk-Ku Kang,* Sung-Gyu Kim, Dong-Gyu Cho, and Jae-Ho Jeon

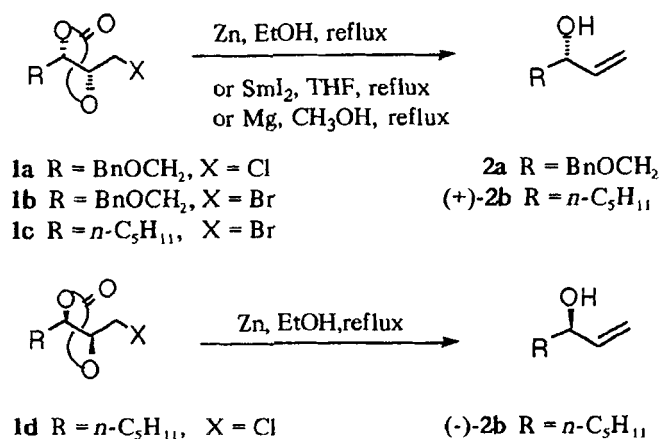
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ABSTRACT: A practical and enantiospecific method for the synthesis of optically pure allylic alcohols [(*R*)- or (*S*)-1-alken-3-ols] is described. The key reaction is the reductive cleavage of the cyclic carbonates of 1-halo-2,3-alkanediols with zinc, magnesium, or samarium diiodide.

Optically active secondary allylic alcohols, (*R*)- or (*S*)-1-alken-3-ols, have been used as versatile chiral synthons in the synthesis of natural products. Several synthetic methods for the preparation of these alcohols in chiral forms have been developed which include Sharpless kinetic resolution¹ of allylic alcohols, catalytic asymmetric addition of divinylzinc to aldehydes,² the lipase catalyzed enantioselective transesterification of vinyl laurate,³ and metal-graphite⁴ or zinc induced⁵ dealkoxyiodination. Here we wish to report an efficient method for the preparation of optically pure allylic alcohols based on the reductive cleavage of the cyclic carbonates of 1-halo-2,3-alkenediols by zinc, magnesium, or samarium diiodide (Scheme 1).

The chloride **1a** on reaction with activated zinc (10 equiv) in refluxing ethanol for 7 h underwent a facile elimination to afford (*R*)-1-benzyloxy-3-buten-2-ol⁵ (**2a**) in 78% yield (Method A, run 1, in Table 1). The bromide **1b** was more easily converted to **2a** with zinc (run 2). The reductive cleavage of **1b** was also accomplished with samarium diiodide⁷ (10 equiv) in THF (Method B, run 3) or magnesium⁸ (7 equiv) in methanol (Method C, run 4). The bromide **1c** reacted with zinc to afford (+)-(*S*)-1-octene-3-ol⁹, (+)-**2b**, [α]_D²⁵ +11.8 (c 1.02, CHCl₃), lit.^{9b} [α]_D²⁶ +8.1 (c 1.46, CHCl₃) (run 5). Also, the alcohol (+)-**2b**, was synthesized from the bromide **1c** by magnesium or samarium diiodide (runs 6 and 7). The results are summarized in Table 1. By this methodology, (-)-(*R*)-1-octene-3-ol⁹ [(-)-**2b**, matsutake alcohol], [α]_D²⁵ -11.9 (c 1.03, CHCl₃), lit.^{9b} [α]_D²⁴ -8.8 (c 1.50, CHCl₃), an important flavor compound of mushrooms was synthesized from **1d**



Scheme 1

Table 1. Preparation of optically active allylic alcohols

Run	Carbonate	Products ^a	Reaction Conditions ^b	Reaction Time(h)	Yield(%)
1	1a	2a	A	7	78
2	1b	2a	A	4	98
3	1b	2a	B	10	62
4	1b	2a	C	10	71
5	1c	(+)- 2b	A	10	89
6	1c	(+)- 2b	B	11	59
7	1c	(+)- 2b	C	11	72
8	1d	(-)- 2b	A	14	75

^a **2a**: $[\alpha]_D^{25} +4.16$ (c 2.05, CHCl₃), lit.⁵ $[\alpha]_D^{25} +6.2$ (c 1.6, CHCl₃); (+)-**2b**: $[\alpha]_D^{25} +11.8$ (c 1.02, CHCl₃), lit.^{9b} $[\alpha]_D^{26} +8.1$ (c 1.46, CHCl₃); (-)-**2b**: $[\alpha]_D^{25} -11.9$ (c 1.03), lit.^{9b} $[\alpha]_D^{24} -8.8$ (c 1.50, CHCl₃). ^b A: Zn, EtOH, reflux; B: SmI₂, THF, reflux; C: Mg, CH₃OH, reflux.

(run 8). However, the reaction of the chloride **1d** with magnesium or samarium diiodide did not give (-)-**2b**.

In summary, chiral allylic alcohols, versatile chiral building blocks for the synthesis of natural products, were synthesized.

EXPERIMENTAL

General Procedures for the Reductive Cleavage of the Carbonates:

Method A: The typical procedure is as follows. To a stirred solution of the carbonate **1a** (400 mg, 1.5 mmol) in ethanol (20 ml) was added activated zinc (1.0g, 15 mmol, 10 equiv) and stirred at reflux for 7 h. The reaction mixture was filtered and ethanol was evaporated. Then the crude product was purified by column chromatography (silica gel, eluent: hexanes-ethyl acetate 3 : 1, R_f = 0.53) to afford the allylic alcohol **2a** (210 mg, 78%).

Method B: The typical procedure is as follows. To a stirred solution of the carbonate **1b** (88 mg, 0.29 mmol) in dry THF (2 ml) was added SmI_2 solution (1 M in THF, 3 ml, 2.91 mmol, 10 equiv) and stirred at reflux for 10 h. The reaction mixture was filtered and evaporated. The crude product was purified by column chromatography (silica gel, eluent: hexanes-ethyl acetate 4 : 1, R_f = 0.20) to afford **2a** (32 mg, 62%).

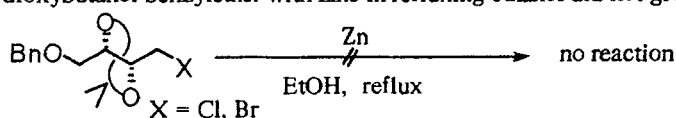
Method C: The typical procedure is as follows. To a stirred solution of the carbonate **1b** (115 mg, 0.42 mmol) in dry MeOH (5 ml) was added magnesium turnings (71 mg, 2.9 mmol, 7 equiv) and stirred at reflux for 10 h. The reaction mixture was filtered and evaporated. The crude product was purified by column chromatography (silica gel, eluent: hexanes-ethyl acetate 4 : 1, R_f = 0.20) to afford **2a** (53 mg, 71%).

Acknowledgement. We acknowledge financial support by Korea Science and Engineering Foundation (KOSEF) and the Organic Chemistry Research Center (OCRC). We also thank Dr. Chwang Siek Pak (KRICT, Korea) for helpful discussion.

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(Received in UK 22 September, 1992)