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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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

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

SYNTHETIC COMMUNICATIONS, 23(5), 681-684 (1993)

SYNTHESIS OF OPTICALLY ACTIVE ALLYLIC ALCOHOLS

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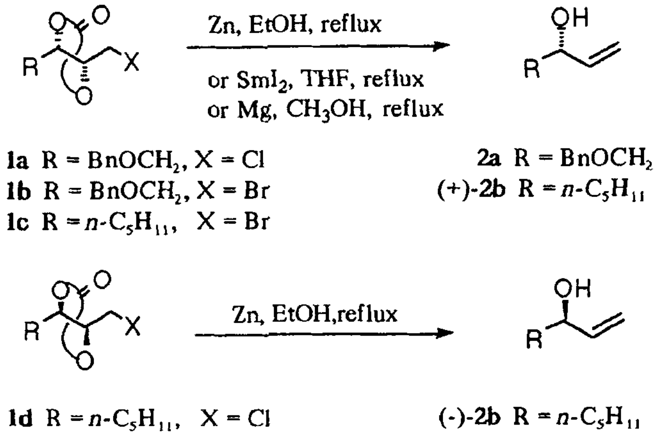
ABSTRACT: A practical and enantiospecific method for the synthesis of optically pure allylic alcohols [(*R*)- or (*S*)-1-alken-3-ols] is described. The key reaction is the reductive cleavage of the cyclic carbonates of 1-halo-2,3-alkanediols with zinc, magnesium, or samarium diiodide.

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 resolution[1] of allylic alcohols, catalytic asymmetric addition of divinylzinc to aldehydes,[2] the lipase catalyzed enantioselective transesterfication of vinyl laurate,[3] and metal-graphite[4] or zinc induced[5] 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-ol[5] (**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 diiodide[7] (10 equiv) in THF(Method B, run 3) or magnesium[8] (7 equiv) in methanol (Method C, run 4). The bromide **1c** reacted with zinc to afford (+)-*(S)*-1-octene-3-ol[9], (+)-**2b**, $[\alpha]_D^{25}$ +11.8 (*c* 1.02, $CHCl_3$), lit.[9b] $[\alpha]_D^{26}$ +8.1 (*c* 1.46, $CHCl_3$) (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-ol[9] [(-)-**2b**, matsutake alcohol], $[\alpha]_D^{25}$ -11.9 (*c* 1.03, $CHCl_3$), lit.[9b] $[\alpha]_D^{24}$ -8.8 (*c* 1.50, $CHCl_3$), 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, $CHCl_3$), lit.[5] $[\alpha]_D^{25}$ +6.2 (*c* 1.6, $CHCl_3$); (+)-**2b**: $[\alpha]_D^{25}$ +11.8 (*c* 1.02, $CHCl_3$), lit.[9b] $[\alpha]_D^{26}$ +8.1 (*c* 1.46, $CHCl_3$); (-)-**2b**: $[\alpha]_D^{25}$ -11.9 (*c* 1.03), lit.[9b] $[\alpha]_D^{24}$ -8.8(*c* 1.50, $CHCl_3$). [b] A: Zn, EtOH, reflux; B: SmI_2, THF, reflux; C: Mg, CH_3OH, 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 Proceduree s 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 evaperated. 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%).

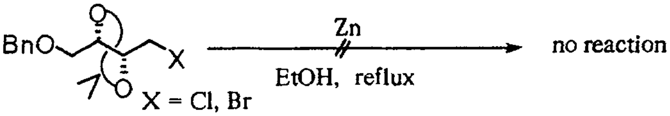
Method C: The typical procedure is as follows. To a stirred solution of the carbonate **1b** (115 mg, 0.42 mmol) in dry MeOH (5 ml) was added magnesium turnings (71 mg, 2.9 mmol, 7 equiv) and stirred at reflux for 10 h. The reaction mixture was filtered and evaporated. The crude product was purified 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.

REFERENCES AND NOTES

1. (a) Gao,Y.; Hanson, R. M.; Klunder, J.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765, and references therein.
2. (a) Review: Noyori, R.; Kitamura, M. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 49.
3. Jeromin, G. E.; Scheidt, A. *Tetraheron Lett.* **1991**, *33*, 7021.
4. Fursttner, A. *Tetrahedron Lett.* **1988**, *29*, 5645

5. Rao, A. V. R.; Reddy, E. R.; Josshi, B. V.; Yadav, J. S. *Tetrahedron Lett.* **1987**, *28*, 6497.
6. In our hands, treatment of 1-chloro or 1-bromo-2,3-isopropylidene dioxybutanol benzylether with zinc in refluxing ethanol did not give **2a**.



7. Molander, G. A.; La Belle, B. E.; Hahn, G. *J.Org. Chem.* **1986**, *51*, 5259.
8. Yoon, I. K.;Yon, G. H.; Pak, C. H. *Tetrahedron Lett.* **1986**, *27*, 4209.
9. (a) Helmchen, G.; Ihing, K.; Schinder, H. *Tetrahedron Lett.* **1987**, *28*, 183. (b) Takano, S.; Yanase, M.; Takahashi, M.; Ogasawara, K. *Chem. Lett.* **1987**, 2017.

(Received in UK 22 September, 1992)