

5. Démoncour, R.; Azerad, R. *J. Chromatogr.* **1987**, *410*, 355.
6. Blessington, B.; Crabb, N.; O'Sullivan, J. *J. Chromatogr.* **1987**, *396*, 177.
7. Blessington, B.; Crabb, N. *J. Chromatogr.* **1988**, *454*, 450.
8. Blessington, B.; Crabb, N. *J. Chromatogr.* **1989**, *483*, 349.
9. Muller, M. D.; Bosshardt, H.-P. *J. Assoc. Off. Anal. Chem.* **1988**, *71*, 614.
10. Lin, S. H.; Chiou, A. J.; Wu, S. H.; Wang, K. T. *Chirality* **1991**, *3*, 476.
11. Tambute, A.; Siret, L.; Caude, M.; Rosset, R. *J. Chromatogr.* **1991**, *541*, 349.
12. Bettoni, G.; Ferorelli, S.; Loiodice, F.; Tangari, N.; Tortorella, V.; Gasparrini, F.; Misiti, D.; Villani, C. *Chirality* **1992**, *4*, 193.
13. CSP 1 (β -Gem 1) and CSP 2 (Whelk-O 1) are commercially available from Regis Technologies (250 \times 4.6 mm I.D., 5 μ m, Morton Grove, Illinois).
14. Pirkle, W. H.; Lee, W.; Welch, C. J. *Enantiomer* **1997**, *2*, 423.
15. Perrin, S. R.; Pirkle, W. H. In *Chiral Separations by Liquid Chromatography*; American Chemical Society Symposium Series 471, Ahuja, S., Ed.: Washington, D. C., 1991; Chapter 3, p 43.
16. Hyun, M. H.; Kim, M. H. *J. Liq. Chromatogr.* **1990**, *13*, 3229.
17. Pirkle, W. H.; Pochapsky, T. C. *Chem. Rev.* **1989**, *89*, 347.
18. Pirkle, W. H.; McCune, J. E. *J. Chromatogr.* **1989**, *469*, 67.
19. Pirkle, W. H.; Welch, C. J.; Wilson, S. R. *Chirality* **1994**, *6*, 615.
20. McCune, J. E. *Ph. D. Dissertation*; University of Illinois, Urbana-Champaign, IL 1990.

Easy Preparation of (*Z*)- γ -Trimethylsilyl Allylic Alcohol from 3-(Trimethylsilyl)-1-propyne for the Stereoselective Synthesis of *syn*-1,2-Diols

Hyo Won Lee*, Hee Kyoon Yoon, and Ihl-Young Choi Lee†

Department of Chemistry, Chungbuk National University, Cheongju 361-763, Korea

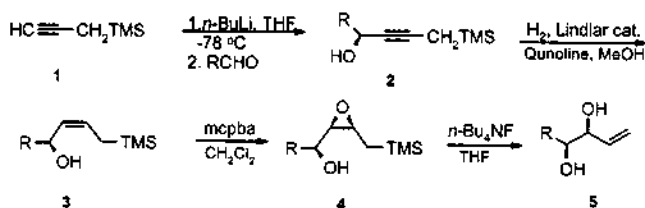
†Korea Research Institute of Chemical Technology, Taejon 305-606, Korea

Received May 25, 1998

Stereoselective synthesis of 1,2-diols and 1,3-diols¹ has been well utilized by synthetic chemists who are interested in polyoxygenated natural products. As part of our efforts to develop methods for the stereoselective synthesis of 1,2-diols, we describe herein a simple approach to *syn*-1,2-diols via (*Z*)- γ -trimethylsilyl allylic alcohols **3**.

In 1988, Matsumoto *et al.* reported the utilization of compound **3** for the synthesis of *syn*-diol **5**, which was prepared from (*Z*)- γ -allylic alcohols.² Their synthesis involved complicate sequences. In contrast, our approach in Scheme 1 is relatively concise and straightforward.

In our synthetic route, first of all, the carbanion of 3-(trimethylsilyl)-1-propyne (**1**) was reacted with aldehyde to give compound **2**. Subsequently **2** was partially hydrogenated to *cis*-allylic alcohol **3**³ utilizing Lindlar catalyst. Then, compound **3** was converted to *threo*-epoxide **4** by treating with *mcpba*. The treatment of crude **4** with tetrabutylammonium fluoride provided the desired *syn*-1,2-diol **5**.



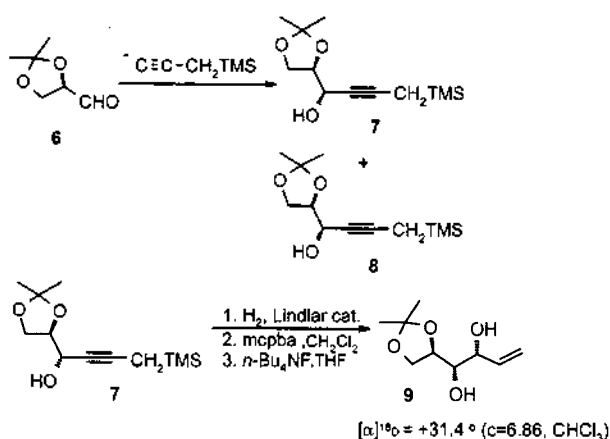
Scheme 1

We examine this reaction for several aldehydes. The results are summarized in Table 1. The yields are satisfactory and the stereoselectivities are preferentially *syn*. In a hope to change the *syn*-selectivity to *anti*-selectivity, we used VO(acac)₂ with *t*-butylhydroperoxide⁴ for the epoxidation or *t*-butyldimethylsilyl ether derivative of **3**. But the results gave predominantly *syn*-selectivity. To expand the

Table 1. The Stereoselectivity for Various Aldehydes

Entry	Aldehyde	Yield of Diol (%)	<i>syn</i> : <i>anti</i> ^a
1	C ₂ H ₅ CHO	92	97:3
2	C ₃ H ₇ CHO	90	96:4
3		81	96:4
4		92	94:6
5		98	100:0
6		92	95:5

^aThe ratios were determined with both GC separations and ¹H NMR data of the acetoneide of diols.⁵



scope of this reaction for synthesis of natural products, we performed the reaction with (*R*)-glyceraldehyde **6** (Scheme 2). The reaction of **6** with carbanion of **1** furnished products **7** and **8** (5:2) in 87% yield. Compound **7** was converted to the desired diol **9** in 65% yield in three steps.

Acknowledgment. We thank the Organic Chemistry Research Center (OCRC) for financial support.

References

- (a) Mohr, P.; Tamm, C. *Tetrahedron Lett.* **1987**, *28*, 391.

- (b) Mohr, P. *Tetrahedron Lett.* **1992**, *33*, 2455. (c) Tamao, K.; Nakajo, E.; Ito, Y. *J. Org. Chem.* **1987**, *52*, 957. (d) Cha, J. K.; Kim, N. S. *Chem. Rev.* **1995**, *95*, 1761. (e) Lipshutz, B. H.; Kozlowski, J. A. *J. Org. Chem.* **1984**, *49*, 1149. (f) Koreeda, M.; Tanaka, Y. *Tetrahedron. Lett.* **1987**, *28*, 143. (g) Keck, G. E.; Abbott, D. E.; Wiely, M. R. *Tetrahedron. Lett.* **1987**, *28*, 139. (h) Lee, A. W. M.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Walker, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 3515. (i) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483.
- Matsumoto, T.; Kitano, Y.; Sato, F. *Tetrahedron Lett.* **1988**, *29*, 5685.
- Angoh, A. G.; Clive, D. L. *J. Chem. Soc., Chem. Commun.* **1984**, 534.
- Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136.
- The stereochemistry of ring opening reaction was determined by ¹H NMR spectral data of acetonides of diols. *Syn*- and *anti*-diols were converted into corresponding *threo*- and *erythro*-isomers of acetonides, respectively.

Photochemical Formation of 1,5-Diketones from Dibenzoylmethane and *o*-Quinones[†]

Ji Ae Chang, Ae Rhan Kim, and Sung Sik Kim*

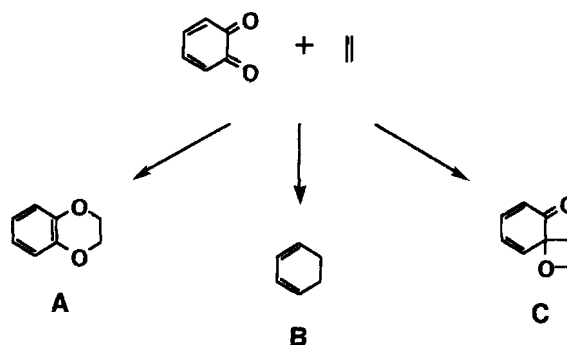
Department of Chemistry, Chonbuk National University, Chonju 561-756, Korea

Received June 8, 1998

Quinones are an important class of compounds in organic synthesis, in industry, and in nature. Due to their various spectroscopic properties, the photochemistry of quinones has been a subject of extensive investigations in many areas.^{1,2} It has been known that photoaddition of *o*-quinones to olefins gives mainly three types of products, the 1,4-dioxene (type A), 1,3-cyclohexadiene (type B) and keto-oxetane (type C), as shown in Scheme 1, along with H-abstraction products.³⁻⁹

The synthetic significance^{10,11} of the intermolecular enone-alkene photocycloaddition^{10,11} was extended by irradiating 1,3-diketones in the presence of quinones to produce 1,5-diketones. The enolic form of the 1,3-diketone, which is restricted in six-membered ring by an intramolecular hydrogen bond, is an intermediate. Photoaddition of an alkene to this enol gives a β -hydroxy ketone, which undergoes retro-aldolization to the 1,5-diketone.

Our interest in the diversity of the reactivity of excited *o*-quinones has promoted us to investigate the type of the photoproducts of *o*-quinones and 1,3-diketones. We report here, for the first time, that irradiation of *o*-quinones to 1,3-diketones leads to 1,4-dioxenes (type A) and/or keto-oxetanes (type C), in which the latter were found to give 1,



Scheme 1

[†]This paper is dedicated to Prof. Sang Chul Shim on the occasion of his 60th birthday.