5. Demoncour, 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× 4.6 mm I.D., 5 μm, 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

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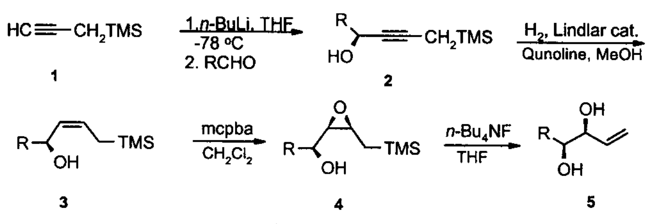
Stereoselective synthesis of 1,2-diols and 1,3-diols[1] has been well utilized by synthetic chemists who are interested in polyoxygenated natural products. As part of our efforts to develop methods for the stereoselective synthesis of 1,2-diols, we describe herein a simple approach to *syn*-1,2-diols *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.

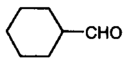
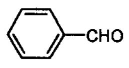
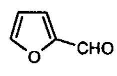
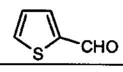
In our synthetic route, first of all, the carbanion of 3-(trimethylsily)-1-propyne (**1**) was reacted with aldehyde to give compound **2**. Subsequently **2** was partially hydrogenated to *cis*-allylic alcohol **3**[3] utilizing Lindlar catalyst. Then, compound **3** was converted to *threo*-epoxide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



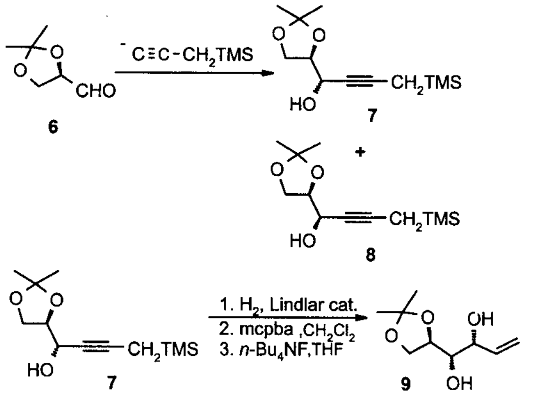
Scheme 1

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*-butylhydroperoxide[4] for the expoxidation 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 (%)	*syn* : *anti*[a]
1	C_2H_5CHO	92	97:3
2	C_3H_7CHO	90	96:4
3		81	96:4
4		92	94:6
5		98	100:0
6		92	95:5

[a] The ratios were determined with both GC separations and ^1H NMR data of the acetonide of diols.[5]



$[\alpha]^{18}_D = +31.4°$ (c=6.86, $CHCl_3$)

scope of this reaction for synthesis of natural products, we performed the reaction with (*R*)-glyceraldehye **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.

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References

1. (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.
2. Matsumoto, T.; Kitano, Y.; Sato, F. *Tetrahedron Lett.* **1988**, *29*, 5685.
3. Angoh, A. G.; Clive, D. L. *J. Chem. Soc., Chem. Commun.* **1984**, 534.
4. Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136.
5. The stereochemistry of ring opening reaction was determined by ^{1}H 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[†]

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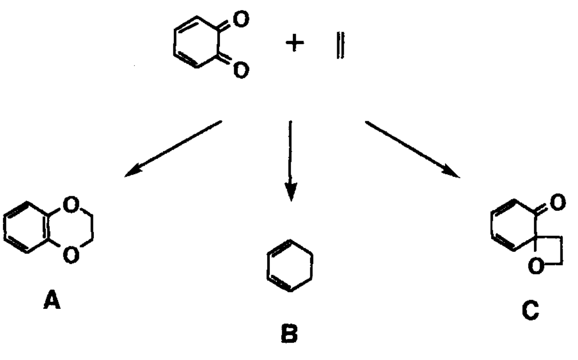
Quinones are an important class of compounds in organic synthesis, in industry, and in nature. Due to their various spectroscopic properties, the photochemistry of quinones has been a subject of extensive investigations in many areas.[1,2] It has been known that photoaddition of *o*-quinones to olefins 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 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.