Tetrahedron Letters,Vol.24,No.4,pp 395-398,1983 0040-4039/83/040395-04$03.00/0
Printed in Great Britain

EPOXIDATION OF ALLYL AND HOMOALLYL TRIMETHYLSILYL ETHERS WITH t-BUTYLDIOXYTRIMETHYLSILANE AND SILICON LEWIS ACID/VANADIUM CATALYST

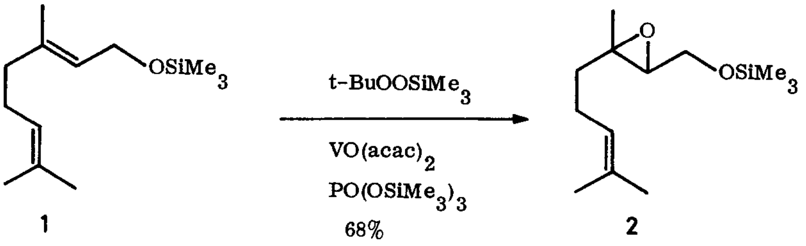
Tamejiro Hiyama* and Michio Obayashi

Sagami Chemical Research Center, 4-4-1 Nishiohnuma, Sagamihara, Kanagawa 229, Japan

Trimethylsilyl ethers of allyl and homoallyl alcohols are epoxidized with t-butyldioxytrimethylsilane and a catalyst system consisting of vanadyl acetoacetate and tris(trimethylsilyl)phosphate. Stereoselectivities of the oxidation are compared with the epoxidation of allyl alcohols with t-BuOOH/V catalyst and with m-chloroperbenzoic acid.

The trialkylsilyl group is frequently utilized for protection of hydroxyl and amino groups as well as active methylenes and methines.[1] Recent studies indicate that the trialkylsilyl group itself may exhibit similar behaviour to that of a proton.[2] Based on this supposition we have carried out reactions catalyzed by trimethylsilyl esters of inorganic acids[3] and now find that allyl and homoallyl trimethylsilyl ethers are epoxidized with t-butyldioxytrimethylsilane (BDOTMS) in the presence of tris(trimethylsilyl) phosphate (TMSP) cocatalyst in the same way as the Sharpless oxidation.[4,5,6]

Whereas, as anticipated, geranyl trimethylsilyl ether (**1**) did not undergo epoxidation with t-butylhydroperoxide and vanadium catalyst under the standard conditions,[4] oxidation was effected by means of the title reagent system to give the epoxide **2**. Typically, a mixture of **1** (1.0 mmol), BDOTMS (1.1 mmol), vanadyl acetoacetate (0.05 mmol), and TMSP (0.05 mmol) dissolved in dichloromethane (2 ml) was stirred at room temperature for 24 h. The product **2** was compared with an authentic specimen prepared by trimethylsilylation (Me_3SiCl, pyridine, r.t.) of the corresponding epoxy alcohol.[4] The yield of **2** estimated by GLC was 68%. Noteworthy is that the other trisubstituted ethene moiety of **2** is completely unaffected, as recorded by Sharpless and his coworkers.[4] In the absence of the TMSP



cocatalyst the epoxidation did not take place to any measurable extent. Trimethylsilyl esters of stronger acids such as trifluoroacetic acid and sulfuric acid induced the decomposition of **2**.[7]

Epoxidation of allyl trimethylsilyl ethers having a trisubstituted ethene moiety such as neryl trimethylsilyl ether (**3**) and the silyl ether **5** (Table 1) as well as the 1,2-disubstituted olefin **7** proceeded effectively, but the oxidation of silyl ether **9**, a 1,1-disubstituted ethene type, was somewhat sluggish. 5-Phenyl-3-trimethylsilyloxy-1-pentene was recovered unchanged, and the trimethylsilyl ethers of 2-cyclohexenol and 2-cyclooctenol produced intractable mixture of products.

3 **4**

Stereochemical aspects of the reactions of allyl trimethylsilyl ethers **5**, **7**, and **9**, and homoallyl ethers **11** and **13** are listed in Table 1. Epoxidation of **5** gave **6a** and **6b** in a ratio of 87:13 (^{1}H NMR) or 90:10 (GLC and ^{1}H NMR after desilylation). Similarly, **7** and **9** gave **8a**/**8b** (46:54) and **10a**/**10b** (35:65) mixtures. The products ratios fall roughly between those of the oxidation of allyl alcohols with t-butylhydroperoxide/V catalyst and those of m-chloroperbenzoic acid (MCPBA) oxidation (see footnotes of Table 1). Based on the proposed transition state of the vanadium catalyzed epoxidation,[4] the dihedral angle (α) is critical for the stereoselectivity of the epoxidation: $\alpha \cong 50°$ for the oxidation with t-BuOOH/V catalyst and $\alpha \cong 120°$ for MCPBA oxidation. The selectivitiy observed herein may be understood in terms of the dihedral angle of $50° < \alpha < 120°$ ascribed to the increased bulkiness of the vanadium ligand in comparison with the oxidation by t-BuOOH/V catalyst. A possible candidate for such a ligand would be the OSiMe$_3$ group generated by trimethylsilylation of O=V.[8] The TMSP cocatalyst may accelerate the transfer of trimethylsilyl group from the substrate or the oxidizing reagent to the vanadium catalyst and vice versa.

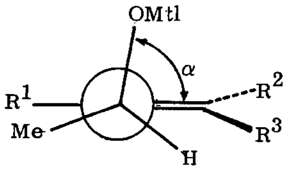
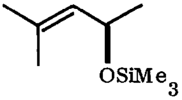
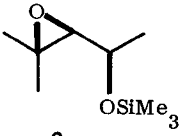
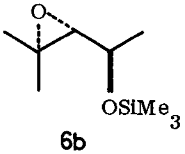
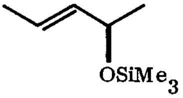
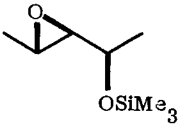
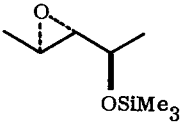
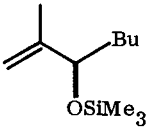
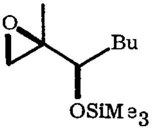
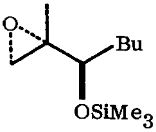
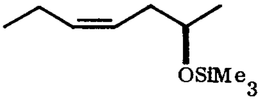
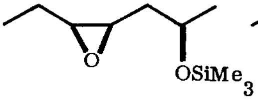
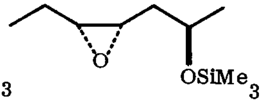
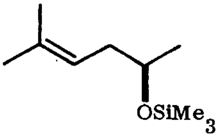
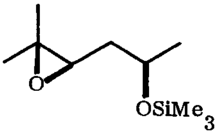
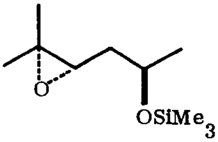


Table 1 Epoxidation of Allyl (or Homoallyl) Trimethylsilyl Ethers[a]

Ally (or Homoallyl) Trimethylsilyl Ether	% Yield[b]	Epoxide(s) (Ratio)[b]	
 **5**	85	 **6a** 87-90 :	 **6b** 10-13[c]
 **7**	78	 **8a** 46 :	 **8b** 54[d]
 **9**	21	 **10a** 35 :	 **10b** 65[e]
 **11**	60	 **12a** 87 :	 **12b** 13[f]
 **13**	56	 **14a** 89 :	 **14b** 11[g]

footnotes of Table 1

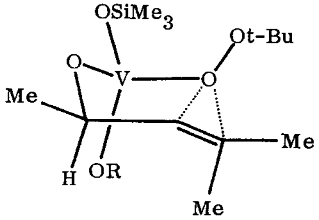
(a) The reaction was carried out usually by stirring a mixture of the silyl ether (1 mmol), BDOTMS (1.1 mmol), vanadium catalyst (0.05 mmol), and TMSP (0.05 mmol) in dichloromethane (2 ml) at room temperature. Products were characterized by comparing the GLC retention times of authentic samples as well as ^{1}H NMR spectra. (b) Estimated by GLC (ethylene glycol adipate, 2%, on Uniport B, 2 m). (c) Selectivities observed in the epoxidation of the allyl alcohol of **5** to produce the epoxy alcohols corresponding to **6a** and **6b** are given in the order of oxidant, ratio: t-BuOOH/V cat, 86:14; t-BuOOH/Mo cat, 95:5; MCPBA, 95:5; t-BuOOH/Al cat, >99.5:0.5. The values for the oxidation with t-BuOOH/V- or Mo-cat and MCPBA are cited from ref 4; the data for the oxidation with t-BuOOH/Al cat, from ref 6. (d) Reported selectivities for the epoxidation of the allyl alcohol of **7**: t-BuOOH/V cat, 29:71; t-BuOOH/Mo cat, 62:38; MCPBA, 64:36; t-BuOOH/Al cat, 64:36. (e) Reported selectivities in the epoxidation of the alcohol of **9**: t-BuOOH/V cat, 2:98; t-BuOOH/Mo cat, 16:84; MCPBA, 41:59; t-BuOOH/Al cat, 13:87. (f) Reported selectivity of the epoxidation of the alcohol of **11** with t-BuOOH/V cat is 92:8 (ref 5). (g) Epoxidation of the alcohol of **13** with t-BuOOH/V cat was 90:10 (58% isolated yield).

Homoallyl alcohol trimethylsilyl ethers **11** and **13** exhibit similar selectivity to the epoxidation of the corresponding homoallyl alcohols with t-BuOOH/V catalyst.

Further synthetic studies using esters of inorganic acids are in progress in our laboratories.

References and Notes

1. (a) "Protective Groups in Organic Chemistry," Ed. by McOmie, J. F. W. Plenum Press, London, 1973. (b) Greene, T. W. "Protective Groups in Organic Synthesis," John Wiley and Sons, New York, 1981.
2. Noyori, R.; Murata, S.; Suzuki, M. Tetrahedron, **1981**, 37, 3899.
3. (a) Morizawa, Y.; Hiyama, T.; Nozaki, H. Tetrahedron Lett. **1981**, 22, 2297. (b) Morizawa, Y.; Mori, I.; Hiyama, T.; Nozaki, H. Synthesis, **1981**, 899.
4. (a) Sharpless, K. B.; Verhoeven, T. R. Aldrichimica Acta **1979**, 12, 63. (b) Rossiter, B. E.; Verhoeven, T. R.; Sharpless, K. B. Tetrahedron Lett., **1979**, 4733.
5. (a) Mihelich, E. D. Tetrahedron Lett. **1979**, 4729. (b) Mihelich, E. D.; Daniels, K.; Eickhoff, D. J. J. Am. Chem. Soc. **1981**, 103, 7690.
6. Takai, K.; Oshima, K.; Nozaki, H. Tetrahedron Lett. **1980**, 21, 1657.
7. Trimethylsilyl trifluoromethanesulphonate readily opens epoxide ring to give 1,2-diol mono-trifluoromethanefulphonate mono-trimethylsilyl ethers. See ref 2.
8. Taking account of the transition state proposed by Mihelich (ref 5), we may propose following transition state for the epoxidation of, e.g., **5**.



(Received in Japan 16 October 1982)