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# THE ROLE OF TRIMETHYLSILYL GROUP IN HIGHLY STEREOSELECTIVE EPOXIDATION OF ALLYLIC ALCOHOLS

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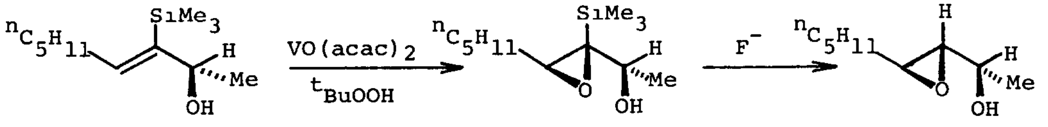
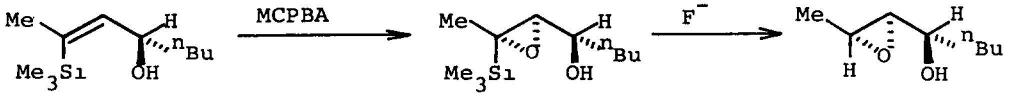
Abstract: The epoxidation of allylic alcohols carrying $Me_3Si$ group on the double bonds with $VO(acac)_2$-$^{t}BuOOH$ or MCPBA provides erythro or threo epoxy alcohols, respectively with high stereoselectivity.

Extensive studies have been devoted for the stereoselective epoxidation of secondary allylic alcohols.[1] The stereochemical outcome as listed in Table 1 heavily depends on the substitution pattern of the double bond. The rather low selectivities have been obtained in the epoxidation of the compounds such as Ia and IIIa with both peracid and metal-catalyzed epoxidation. Moreover, a single stereoisomer is produced with high stereoselectivity (~95%) in the case of IIa and IVa.[2] We now report that the substitution of appropriate hydrogen on the double bond by $Me_3Si$ group induces the production of both erythro and threo-isomer with high stereoselectivity for mono- (Ia) and di-substituted allylic alcohols (IIa, IIIa, and IVa). The silyl group can, of course, be removed easily after epoxidation.

The vanadium-catalyzed epoxidation of allylic alcohol substrate IIIb gives the erythro isomer of the corresponding epoxy alcohol, whereas the MCPBA oxidation of the substrate IIIc produces the threo isomer stereoselectively. The observed selectivity is explained by means of the steric bulk of the $Me_3Si$ group[3] and the generality of the reaction is shown by data incorporated in Table 1.

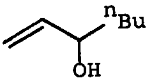
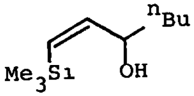
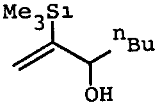
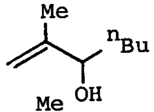
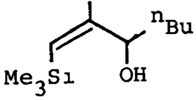
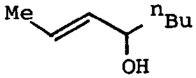
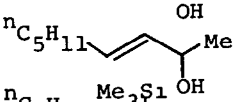
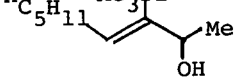
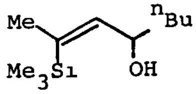
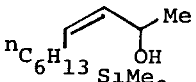
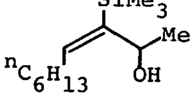


IIIb Vb erythro VI



IIIc threo

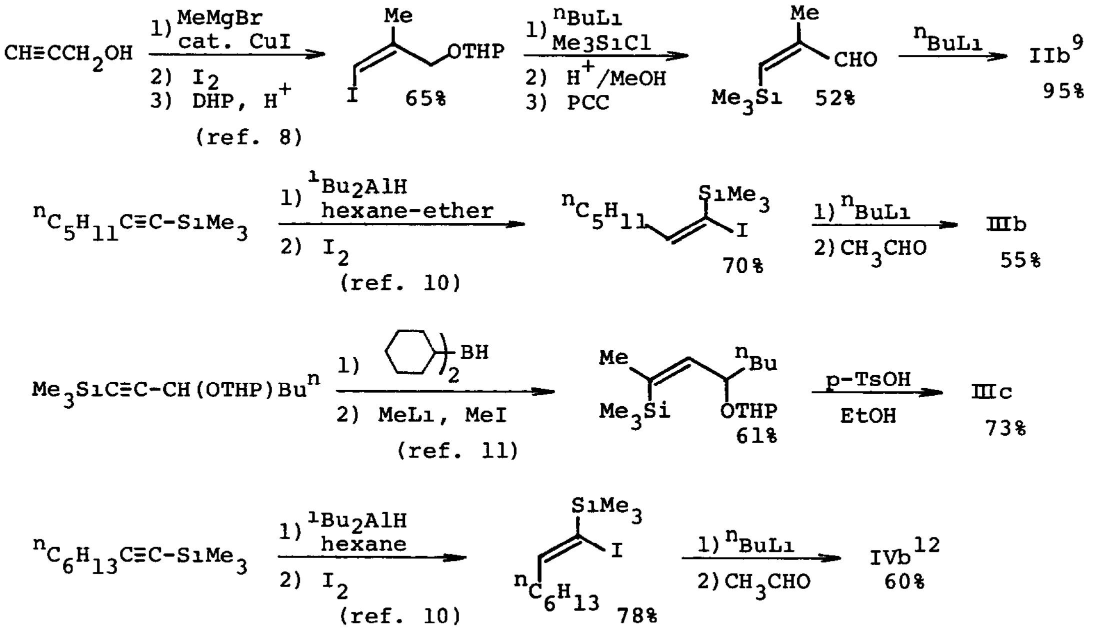
Table 1. Stereoselective epoxidation of trimethylsilyl substituted allylic alcohols

| Substrate | | VO(acac)$_2$-$^t$BuOOH | | MCPBA | |
|---|---|---|---|---|---|
| | | Yield[a] (%) | ratio of threo : erythro[b] | Yield[a] (%) | ratio of threo : erythro[b] |
|  | Ia | 85 | 22 : 78 | 85 | 58 : 42 |
|  | Ib | 74 | 92 : 8 | 70 | 87 : 13 |
|  | Ic | 84 | 1 : 99 | 92 | 39 : 61 |
|  | IIa | — | 2 : 98[c] | — | 41 : 59[c] |
|  | IIb | 84 | 74 : 26 | 84 | 91 : 9 |
|  | IIIa | 89 | 29 : 71 | 90 | 61 : 39 |
|  | IIIa' | 83 | 25 : 75 | 87 | 61 : 39 |
|  | IIIb | 70 | 1 : 99 | 65 | 15 : 85 |
|  | IIIc | 93 | 99 : 1 | 81 | 99 : 1 |
|  | IVa | 86 | 80 : 20 | 88 | 95 : 5 |
|  | IVb | 86 | 7 : 93 | 80 | 81 : 19 |

[a] Isolated yields. Two steps (epoxidation, desilylation or epoxidation, acetylation) or three steps (epoxidation, desilylation, and acetylation) overall yields. [b] The resulting mixtures of epoxy alcohols or epoxy acetates were analyzed by glpc on 2 m columns packed with 3% Silicon OV-17 on Uniport HP (for epoxy acetates derived from Ia, IIIa, IIIa', and epoxy alcohol derived from IIa) or 20% PEG 6000 on Celite 545 (for epoxy acetate derived from IVa). [c] Cited from ref. 1a.

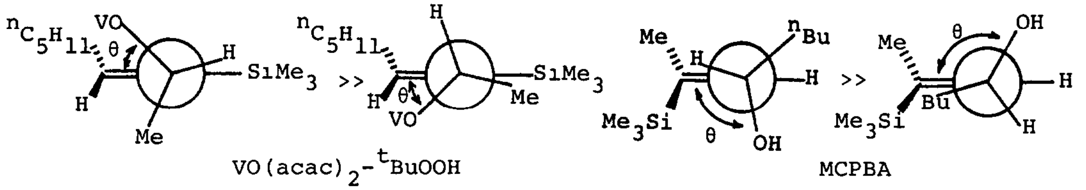
Cesium fluoride[4] has been found to be as effective as tetrabutylammonium fluoride[5] for the removal of Me$_3$Si group from α,β-epoxy alcohol. For instance, treatment of α,β-epoxysilane Vb (0.12 g, 0.5 mmol) derived from VO(acac)$_2$-$^t$BuOOH oxidation of IIIb with CsF (0.38 g, 2.5 mmol) in DMSO at 25°C for 2 h provided epoxy alcohol VI (71 mg) in 90% yield.[6]

The following scheme shows the preparation of the silylated allylic alcohols required in the epoxidation.[7,13]



## References and Notes

1. a) B. E. Rossiter, T. R. Verhoeven, and K. B. Sharpless, *Tetrahedron Lett* , 1979, 4733. b) E. D. Mihelich, *ibid.*, 1979, 4729. c) K. Takai, K. Oshima, and H. Nozaki, *ibid.*, 21, 1657 (1980). d) V. S. Martin, S. S. Woodard, T. Katsuki, Y. Yamada, M. Ikeda, and K. B. Sharpless, *J. Am. Chem. Soc.*, 103, 6237 (1981).
2. I. Hasan and Y. Kishi, *Tetrahedron Lett.*, 21, 4229 (1980). Erythro-epoxy alcohols have been prepared in high stereoselectivity by zinc borohydride reduction of α,β-epoxy ketones. T. Nakata, T. Tanaka, and T. Oishi, *Tetrahedron Lett.*, 22, 4723 (1981).
3. Assuming that O-C-C=C dihedral angles (θ) are ~50° for vanadium catalyzed oxidation and ~120° for MCPBA epoxidation,[1a] we can conclude the preference of conformations shown below.



4. For the desilylation with CsF, see the following reports. Y. Ito, S. Miyata, M. Nakatsuka, and T. Saegusa, *J. Am. Chem Soc*, 103, 5250 (1981); E. Vedejs and G. R. Martinez, *ibid*, 101, 6452 (1979).
5. T. H. Chan, P. W. K. Lau, and M. P. Li, *Tetrahedron Lett.*, 1976, 2667.
6. The desilylation of epoxysilane proceeded with retention of configuration at the oxiranyl carbon similarly as $Bu_4N^+F^-$-induced reaction.[5] Exposure of Vb to CsF gave erythro epoxy alcohol VI as a single isomer and treatment of a mixture of Vb and its threo isomer (1:2 by glpc, 3% Silicon OV-17 on Uniport HP, 2 m, 130°C) gave a mixture of erythro and threo epoxy alcohol in 1:2 ratio (by glpc after acetylation of hydroxy group).
7. Other allylic alcohols were prepared as follows. Ib: Hydrogenation ($PtO_2$, $H_2$, 1 atm) of 1-trimethylsilyl-1-heptyn-3-ol. Ic: Reaction of Grignard reagent obtained from 1-bromoethenyltrimethylsilane (A. Ottolenghi, M. Fridkin, and A. Zilkha, *Can J Chem*, 41, 2977 (1963)) and valeraldehyde.
8. J. G. Duboudin, B. Jousseaume, and A. Bonakdar, *J. Organomet. Chem.*, 168, 227 (1979).
9. (*Z*)-3-Trimethylsilyl-2-methyl-2-propenal was contaminated by *E*-isomer (*Z*/*E* = 8/2) which could not be removed after PCC oxidation. Pure compound IIb was prepared by a sequence: (1) oxidation of crude IIb, (2) separation of corresponding (*Z*)- and (*E*)-1-trimethylsilyl-2-methyl-1-hepten-3-one, and (3) $^{i}Bu_2AlH$ reduction of pure (*Z*)-isomer. IIb: bp 98-103°C (bath temp)/1 Torr; IR (neat) 3370, 1620, 1256, 1142, 836 cm$^{-1}$; NMR ($CCl_4$, $CHCl_3$ as an internal standard) $\delta$ 0.14 (s, 9H), 0.91 (t, $J$ = 6.3 Hz, 3H), 1.15-1.57 (m, 6H), 1.76 (d, $J$ = 1.5 Hz, 3H), 4.08-4.28 (m, 1H), 5.21 (q, $J$ = 1.5 Hz, 1H); MS *m/e*(%) 200 ($M^+$, 14), 143 (49), 127 (22), 75 (100). Found: C, 65.77; H, 12.32%. Calcd for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07%.
10. K. Uchida, K. Utimoto, and H. Nozaki, *J Org. Chem*, 41, 2215 (1976).
11. K. Uchida, K. Utimoto, and H. Nozaki, *Tetrahedron*, 33, 2987 (1977).
12. IVb: bp 154-156°C (bath temp)/0.5 Torr; IR (neat) 3385, 1614, 1060, 834 cm$^{-1}$; NMR ($CCl_4$, $CHCl_3$ as an internal standard) $\delta$ 0.10 (s, 9H), 0.86 (t, $J$ = 6.5 Hz, 3H), 1.17 (d, $J$ = 6.2 Hz, 3H), 1.10-1.47 (m, 8H), 1.83-2.15 (m, 2H), 4.76 (dq, $J$ = 1.5 and 6.2 Hz, 1H), 5.53 (dt, $J$ = 1.5 and 7.2 Hz, 1H). Found: C, 68.31; H, 12.44%. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35%.
13. We thank the Asahi Glass Foundation for financial support.

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