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Acyclic Epoxidations (II)

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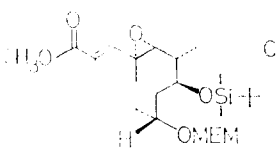
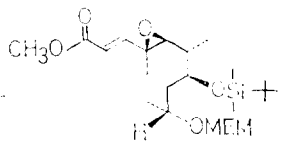
Abstract □ Conversion of vinylogous glycidic ester 1 to 2 by a stereoselective acyclic allylic epoxidation will be presented

Keywords □ Stereoselective epoxidation, Acyclic alcohol, Reductive opening of vinylogous glycidic ester

In this paper we wish to describe a stereoselective scheme for the conversion of vinylogous glycidic ester **1** to **2**.

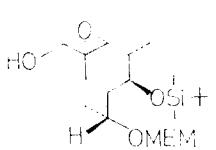


1



2

The vinylogous glycidic ester **1**, prepared from the allylic alcohol **3**[1] in three steps in 55% overall yield (m-CPBA, CH_2Cl_2, −20°C PCC, NaOAc, r.t.; methyl triphenylphosphoranylidene acetate, benzene), was reduced with Zn/HOAc in refluxing ether to give the allylic alcohol **4**, which was almost homogeneous by tlc, nmr, cmr.



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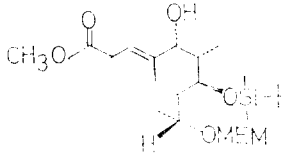
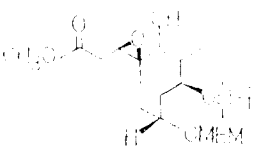


4

Epoxidation of **4** with t-BuOOH/$VO(acac)_2$ in toluene at −20°C a 4 : 1 mixture of the desired β-epoxide **5** and the undesired α-epoxide **6**. Remarkably, m-CPBA epoxidation of the allylic alcohol **4** in CH_2Cl_2 at room temperature showed completely reversed selectivity (α : β=4 : 1).[2]



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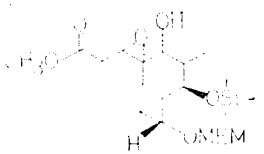
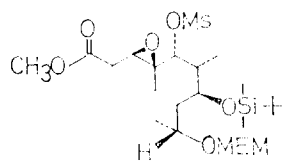


6

Treatment of the alcohol **5** with methanesulfonyl chloride in pyridine produced mesylate **7** which was smoothly converted to the vinylogous glycidic ester **2** by the treatment with K_2CO_3 in methanol at room temperature. The ester **2** was identical to the vinylogous glycidic ester prepared from the epoxide **8**.



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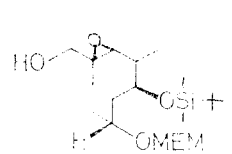

8

Thus, the desired ester **2** could be obtained from **1** in 62% overall yield.

LITERATURE CITED

1) See the previous paper.

2) Sharpless, K.B. and Michaelson, R.C., High stereo- and regioselectivities in the transition metal

catalyzed epoxidation of olefinic alcohols by tert-butyl hydroperoxide. *J. Am. Chem. Soc.*, **95**, 6136 (1973); Mahelich, E.D., Vanadium-catalyzed epoxidations I. A new selectivity pattern for acyclic allylic alcohols. *Tetrahedron Lett.*, 4729(1979); Sharpless, K.B., Rossiter, B.E. and Verhoeven, T.R., Stereoselective epoxidation of acyclic allylic alcohols. A correction of our previous work, *Tetrahedron Lett.*, 4733(1979).