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Acyclic Epoxidations (I)

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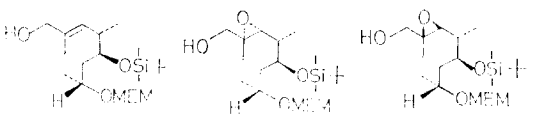
Abstract □ Some examples of stereoselective epoxidation of acyclic allylic and homoallylic systems will be presented.

Keywords □ Stereoselective epoxidation, Acyclic allylic and homoallylic alcohols, Structure determination of acyclic system

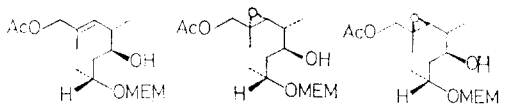
In this and following paper we wish to report some examples of steroselective acyclic allylic and homoallylic epoxidation which were observed in connection with our studies on macrocyclic anticancer agents.

Epoxidation of the allylic alcohol **1**[1] with m-CPBA in CH_2Cl_2 at $-20°C$ gave only the epoxide **2**.[2] Meanwhile, epoxidation of **1** with t-BuOOH/VO(acac)$_2$ in toluene at $-20°C$ yielded a 3 : 5 mixture of the epoxides **2** and **3**.



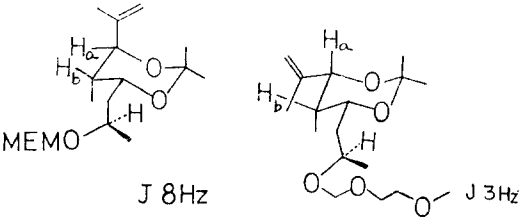
1 **2** **3**

Epoxidation of the homoallylic alcohol **4** with *m*-CPBA in CH_2Cl_2 at room temperature produced a 2 : 1 mixture of the epoxides **5** and **6**. However, epoxidation of **4** with t-BuOOH/VO (acac)$_2$ in refluxing benzene gave only the epoxide **5**.



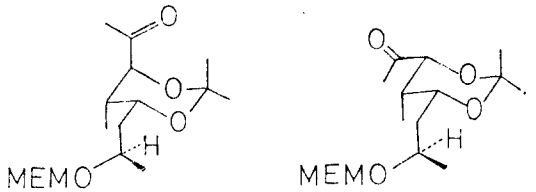
4 **5** **6**

The stereochemistry of epoxides **2** and **3** was determined by converting them to the acetonide **7** and **8**, respectively, by a straightforward five step sequence (TsCl, pyr.; NaI, acetone; Zn, HOAc, ether; $(n\text{-}Bu)_4$ NF, THF; 2,2-dimethoxypropane, PPTS).



7 **8**

It was possible to determine the coupling constants of the protons H_a and H_b in the acetonides **7** and **8**, as indicated above, by addition of Eu(fod)$_3$, which apparently complexes with the methoxyethoxymethyl group. These values are in good agreement with data known in the literature. More convincingly, the acetyl compound **9**, prepared from the acetonide **7** by the treatment with $NaIO_4$-



9 **10**

OsO_4, underwent epimerization on exposure to K_2CO_3 in methanol at room temperature to the more stable **10**, which was identical with the acetyl compound similarly prepared from **8**.

LITERATURE CITED

1) Synthesis of this allylic alcohol will be described in detail elsewhere.

2) Johnson, M.R. and Kishi, Y., Cooperative effect by a hydroxy and ether oxygen in epoxidation by a peracid. *Tetrahedron Lett.*, 4347 (1979).

3) Sharpless, K.B. and Michaelson, R.C., High stereo- and regio-selectivities in the transition metal catalyzed epoxidation of olefinic alcohols by tert-butyl hydroperoxide. *J. Am. Chem. Soc.*, **95**, 6136(1973)