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LETTERS

Zeolite (H-ZSM 5) Catalysed Regio and Stereoselective Reduction of 2,3-Epoxy Alcohols to 1,2-Diols and Vinylic Epoxides to Homoallylic Alcohols with Sodium Cyanoborohydride[1]

Anuradha Gupta and Yashwant D. Vankar*

Department of Chemistry, Indian Institute of Technology, Kanpur -208 016, India
(Fax: 0512-590007; E mail: vankar@iitk.ernet.in)

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Abstract: A variety of 2,3-epoxy alcohols and vinylic epoxides (having the epoxide moieties at the terminal positions) undergo reduction with zeolite H-ZSM 5/$NaCNBH_3$ combination of reagent system in refluxing dichloroethane to give 1,2-diols and homoallylic alcohols in moderate to good yields. Under these conditions acid sensitive groups such as an acetal and a THP ether are not affected which indicates the mildness of the reaction conditions. © 1999 Elsevier Science Ltd. All rights reserved.

The importance of 2,3-epoxy alcohols in contemporary organic synthesis is well documented in the literature[2] particularly after the discovery of the Sharpless epoxidation.[3] Among many reactions, the regio-selective reduction of 2,3-epoxy alcohols into 1,2 or 1,3-diols has, therefore, become very useful[4] in the synthesis of polyhydroxy compounds and other natural products. As a result, several reducing agents such as RedAl,[5] $LiAlH_4$,[6] DIBAL-H,[6] $LiBH_4$,[7] and $NaCNBH_3/BF_3.Et_2O$[8] have been introduced for this purpose. The regioselectivity of the reduction producing 1,2 or 1,3-diols is dependent on the reagent employed. An indirect method includes conversion of 2,3-epoxy alcohols into 1-iodo-2,3-diols via their rearrangement followed by deiodination using n-Bu_3SnH to obtain 1,2-diols.[9]

Recently we introduced[10] a new reagent system comprising of zeolite H-ZSM 5/$NaCNBH_3$ for the efficient reduction of conjugated nitroalkenes into the corresponding nitroalkanes. In an effort to explore the potential of such a reducing system, we have found that 2,3-epoxy alcohols undergo regioselective reduction[11] to 1,2-diols in good yields. Although, zeolite H-ZSM 5 permits isomerisation of glycidic esters into α-hydroxy-β,γ-unsaturated esters, as reported by us,[12] in the present case no isomerisation of the epoxide was found to take place. It appears that the reduction of the epoxide occurs in an S_N2 fashion at the end of the epoxide away from the hydroxy group, leading to 1,2-diols as the major products. This is substantiated by the observation that 2,3-epoxy alcohols derived from geraniol and nerol, obtained via the Sharpless epoxidation, give 1,2-diols with inversion of configurations (cf. entries 5 and 6 Table 1) at the reducing centres (cf. footnotes Table 1). We had earlier observed that the $NaCNBH_3$/H-ZSM 5 combination in methanol has a pH of 6.5 and consequently acid sensitive groups such as acetals were found to be stable. Although in the present case the reaction proceeded best in refluxing dichloroethane and not in methanol, acid sensitive groups such as an acetal and a THP ether were found to be unaffected.[13] Likewise, a ketone was not affected[13] under these conditions unless it was placed immediately next to the epoxide moiety[14] (cf. entry 8). Further, simple epoxides, such as cyclohexene oxide, do not undergo reduction with this reagent system.

In an effort to explore further the potential of the present reagent system we have found that vinylic epoxides bearing the epoxide moieties at the terminal positions only are cleanly reduced to homoallylic

0040-4039/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
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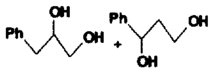
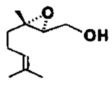
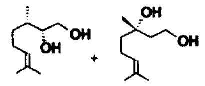
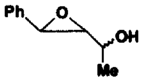
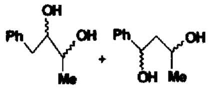
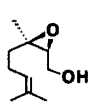
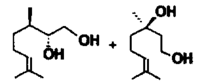
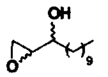
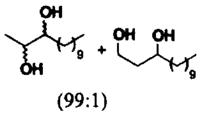
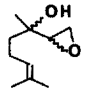
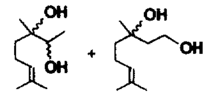
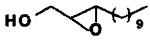
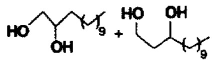
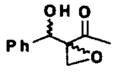
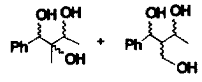
Table 1. Zeolite (H-ZSM 5) Catalysed Reduction of 2,3-Epoxy Alcohols

Entry	2,3-Epoxy Alcohol	Diols Ratio (1,2:1,3)	Yield (%)/ Time (hr)	Entry	2,3-Epoxy Alcohol	Diols Ratio (1,2:1,3)	Yield (%)/ Time (hr)
1		 (98:2)	76/6	5	 #	 (97:3)	75/8
2		 (97:3)	74/6	6	 #	 (99:1)	70/8
3		 (99:1)	76/6	7		 (98:2) *	74/6
4		 (99:1)	78/6	8		 (70:30) $	70/10

The epoxide (2*S*,3*S*)-3,7-dimethyl-2,3-epoxy-6-octen-1-ol derived from geraniol was prepared using (+)-diethyl tartarate which gave the diol[8] having (2*R*,3*S*) configuration and specific rotation as $[\alpha]^{25}_D = +8°$ (C 0.5, $CHCl_3$). The epoxide (2*S*,3*R*)-3,7-di-methyl-2,3-epoxy-6-octen-1-ol derived from nerol was also prepared using (+)-diethyl tartarate which resulted into the diol having (2*R*,3*R*) configuration and specific rotation as $[\alpha]^{25}_D = +5°$ (C 1.5, $CHCl_3$). The stereochemistry of this diol has been assigned as exactly opposite to that reported by Taber and Houze[8] who reduced the corresponding epoxy alcohol, obtained from nerol by the Sharpless epoxidation using (-)-diethyl tartarate instead of (+)-diethyl tartarate. Since we have prepared the corresponding epoxy alcohol using (+)-diethyl tartarate, it is expected that the rotation value of the major diol obtained by us is exactly opposite to that obtained {$[\alpha]^{25}_D = -4.36°$ (in abs. EtOH) } by Taber and Houze.[8] The spectroscopic data of the diols match with the reported ones.[8]

* The stereochemistry of neither the epoxide, prepared by m-chloroperbenzoic acid epoxidation of (±)-linalool, nor the diols have been determined. Monoacetate of the major 1,2-diol: IR (neat): 3400, 2920, 1720 cm^{-1} . ^1H NMR (CCl_4): δ 1.09 (d, 3H, J = 6 Hz), 1.49 (t, 2H, J = 7 Hz), 1.2 (s, 3H), 1.68, 1.7 (2s, 6H), 2.0 (s, 3H), 1.85-2.12 (m, 2H), 3.89 (s, 1H), 4.45-4.75 (m, 1H), 4.76-5.3 (m, 1H). MS m/z: 215 $(M+1)^+$, 197, 137, 43. Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.29; H, 10.35. Found: C, 67.34; H, 10.47%.

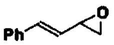
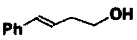
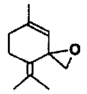
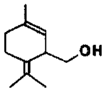
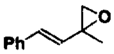
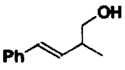
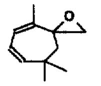
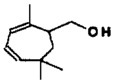
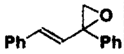
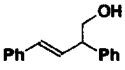
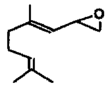
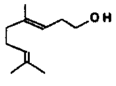
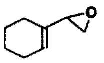
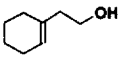
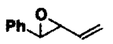
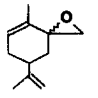
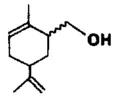
$ The stereochemistry of neither the epoxide, prepared by H_2O_2/NaOH epoxidation, nor the diols have been determined.
Diacetate of the major triol i.e 1-phenyl-1,3-diacetoxy-2-methyl butan-2-ol: IR (CCl_4): 3400, 1720 cm^{-1}. ^1H NMR (CCl_4): δ 0.96 (s, 3H), 1.32 (d, 3H, J = 8 Hz), 2.0 (s, 6H), 2.19 (br s, 1H), 4.75-5.15 (m, 1H), 5.72 (br s, 1H), 7.32 (s, 5H). MS m/z: 281 $(M+1)^+$, 221, 203. Anal. Calcd. for: $C_{15}H_{20}O_5$: C,64.29; H,7.19. Found: C, 64.51; H, 7.46%.

alcohols in fair yields. Our results are summarised in Table 2. Vinylic epoxides having non-terminal epoxides (cf. entry 9) did not undergo reduction indicating the selectivities associated with this method. It is noteworthy that 1,3-cylooctadiene monoepoxide is reported to be reduced to the corresponding allylic alcohol as the major product with $NaCNBH_3/BF_3.Et_2O$ reagent system[15] whereas the present reagent system does not react with this epoxide. Vinylic epoxides are a useful class of compounds having many applications in organic synthesis.[16] The importance of vinylic epoxides is further augmented by the fact that these molecules are available in optically pure form and more new methods for improving enantioselectivities are being discovered.[16(i),17] Reagents which allow the reduction of vinylic epoxides into allylic alcohols include $LiEt_3BH$,[18] $LiAlH_4$,[18] Ca/Liq. NH_3,[19] DIBAL-H,[19] diborane,[20] $NaCNBH_3/BF_3.Et_2O$[15] and more recently Cp_2TiCl_2.[21] On the other hand, their reduction into homoallylic alcohols has been rather scarcely reported and only in some instances $LiAlH_4$[22] and DIBAL-H[23] have been reported to produce homoallylic alcohols. However, these reducing agents do not distinguish between vinylic epoxides bearing terminal or non-terminal epoxy moieties. In view of the importance[24] of homoallylic alcohols in organic synthesis and recent efforts to obtain vinylic epoxides in optically pure form it appears that there is a need to develop newer reagents/reagent systems for the reduction of vinylic epoxides into homoallylic alcohols. In this regard the present methodology is useful especially since it provides distinct chemo and regioselectivities.

Due to the increasing awareness of environmental hazards,[25] the importance of zeolites in organic synthesis has gained recognition[26] in recent years. Further, due to the defined pore size, the zeolites permit selective reactions with molecules having the correct shape and size.[27] Also, since zeolites are heterogeneous in nature, reactions involving them require mere filtration of the catalyst which could also be recycled. These advantages, coupled with the regioselectivity and tolerance of acid sensitive groups, make the present method a useful one. We are hopeful that these methodologies will find use in organic synthesis.

In a typical experiment, a solution of an epoxy alcohol or a vinylic epoxide (2 mmol) in 5ml dry dichloroethane was treated with zeolite H-ZSM 5 (weight equivalent) and $NaCNBH_3$ (2.4 mmol) and the

Table 2. Reduction of Vinylic Epoxides into Homoallylic Alcohols

Entry	Vinylic Epoxide	Homoallylic Alcohol	Time (h)	% Yield	Entry	Vinylic Epoxide	Homoallylic Alcohol	Time (h)	% Yield
1			6	60	6			6	60
2			7	55	7			7	65
3			8	58	8			6	58
4			5	59	9		No Reaction	--	--
5			5	59					

reaction mixture refluxed for the time indicated in the Tables. At the end of the reaction (TLC monitoring), the mixture was filtered through a pad of celite and washed with ethyl acetate (2 x 10 ml). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the crude product by column chromatography gave the pure diol which was characterised by spectroscopic means and compared with the literature data.

Acknowledgement: One of us (A.G.) thanks the University Grants Commission, New Delhi for a Senior Research Fellowship.

References and Notes:

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