BULLETIN

OF THE KOREAN CHEMICAL SOCIETY

VOLUME 11, NUMBER 6
DECEMBER 20, 1990

BKCS 11(6) 471-588
ISSN 0253-2964

Communications

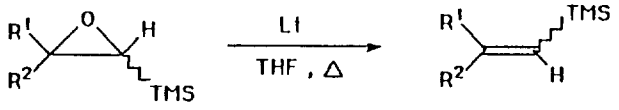
Deoxygenation of α,β-Epoxy Silanes by Lithium to Vinylsilanes

Kyung-Tae Kang*, Young Doo Choi, and Chun Yi Park

Department of Chemical Education, Pusan National University, Pusan 609-735

Received May 23, 1990

α,β-Epoxy silanes have become one of the most valuable organosilicon compounds because of its availability and facile transformation into various types of compounds.[1] Recently, Y. Ito and coworkers have reported that α,β-epoxy silanes having one or two alkoxy groups on silicon produce the vinylsilanes through the deoxygenation reactions with copper-catalyzed Grignard reagent while α,β-epoxy trimethylsilane does afford only the normal ring opening product.[2] However, in this study, we want to report that α,β-epoxy trimethylsilanes can undergo the deoxygenation reaction with lithium instead of copper-catalyzed Grignard reagent to give vinylsilanes stereoselectively. This reaction is quite simple and attractive compared to the method reported by Y. Ito because trimethylsilyl derivatives are readily more available than alkoxysilyl ones.

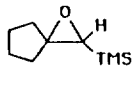
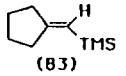
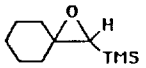
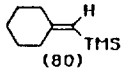
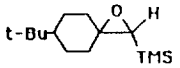
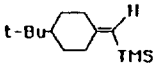
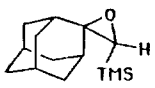
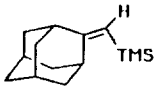
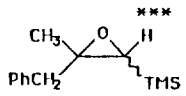
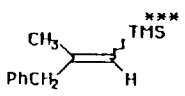
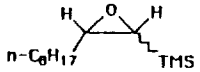
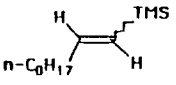
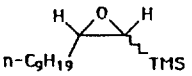
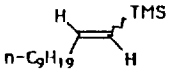
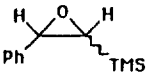
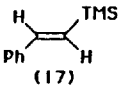
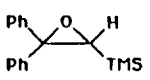
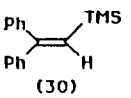


1 2

A typical procedure is as following. A THF (4 ml) solution of cyclopentan-1-oxiran-2-ylmethyltrimethylsilane, **1a** (0.309g, 1.82 mmol) was added to lithium powder (0.04g, 5.7 mmol) washed free of mineral oil with THF, and heated at 80°C for 12 hrs under argon. The mixture was cooled, poured into cold aq NH_4Cl solution, and extracted with ether (3×15 ml). The combined extracts were dried (Na_2SO_4) and concentrated. Preparative thin layer chromatography on silica gel (hexane) afforded the vinylsilane, **2a** (0.232g, 83%).

Using the procedure described above, various α,β-

Table 1.

Entry	Epoxysilane (Z/E)**	Vinylsilane (%)*(Z/E)**
a		 (83)
b		 (80)
c		 (85)
d		 (84)
e	 (50/50)	 (66) (5/95)
f	 (77/23)	 (80) (5/95)
g	 (86/14)	 (95) (9/91)
h		 (17)
i		 (30)

*Isolated yields after chromatography on a silica gel. **The ratio of isomers was determined by ^1H NMR and/or capillary G.L.C. ***See ref. 8.

epoxy silanes were deoxygenated to afford vinylsilanes. The results are shown in Table 1. As shown in the table, this method is quite general for the synthesis of vinylisilanes except epoxy silanes containing phenyl group (entries h and i).[3]

It is interesting to note that the mixture of E and Z isomers of α,β-epoxysilanes which were prepared by the Magnus method,[4] afforded vinylsilanes having an (E)-configuaration in >90% (entries e-h). From these results we can assume that E-vinylsilanes are obtained predominantly (over Z-isomers) regardless of the stereochemistry of epoxy silanes. The stereoselectivity observed in our study is quite similar to the results reported by Ito[2] and Barluenga.[5]

The greater electron transfer ability of lithium over alkylcopper species may responsible for the deoxygenation reaction of α,β-epoxy silanes which do not have any alkoxy groups on silicon atom.[6]

Acknowledgements. We thank the Korea Science and Engineering Foundation for financial support.

References

1. (a) E. Colvin, "*Silicon in Organic Synthesis*", Butterworths, London 83 (1981); (b) Y. Ukaji, A. Yoshida, and T. Fusisawa, *Chem. Lett.*, 157 (1990) and references cited therein.
2. K. Tamao, E. Nakajo, and Y. Ito, *J. Org. Chem.*, **53**, 414 (1988).
3. The lower yields are owing to the further reactions of aromatic unsaturated compounds with alkali metals; V. Kalyaneraman and M. V. George, *J. Organomet. Chem.*, **47**, 225 (1973).
4. C. Burford, F. Cooke, G. Roy, and P. Magnus, *Tetrahedron*, **39**, 867 (1983).
5. J. Barluenga, J. L. Fernandez-Simon, J. M. Concellon, and M. Yus, *Synthesis*, 234 (1988).
6. An electron transfer mechanism for the deoxygenation of epoxides or α,β-epoxysilanes has been proposed[2,7].
7. K. N. Gurudutt and B. Ravindranath, *Tetrahedron Lett.*, **21**, 1173 (1980).
8. **1e** was prepared from phenylacetone by the Magnus method[4]. **1e** : 73% yield; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.11 and 0.17 (two s, 9H total, 1/1 ratio), 1.20 (s, 3H), 2.14 and 2.17 (two s, 1H total) 2.70-2.93 (m, 2H) and 7.2-7.4 (m, 5H). **2e** (E isomer): ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.10 (9H, s), 1.72 (3H, s), 3.27 (2H, s), 5.28 (1H, s), 7.1-7.3 (5H, m). **2e** (Z isomer): ^{1}H-NMR ($CDCl_3$, 270MHz) δ 0.15 (9H, s), 1.69 (3H, s), 3.47 (2H, s), 5.41 (1H, s), 7.1-7.3 (5H, m).

Enzyme Resolution of 1-formyl-trimethylenemethane-iron-Tricarbonyl with Horse Liver Alcohol Dehydrogenase in Microemulsion

Kang Min Lee*, Daniel Martina†, Chung Ung Park, and Jean-Francois Biellmann‡

Department of Molecular Biology, Chonbuk National University, Chonju 560-756

†*Laboratoire de Chimie Organique Synthetique, ERA-687 Institut de Chimie, Université Louis Pasteur, 1 Rue Blaise Pascal, 67008 Strasbourg, France*

‡*Laboratoire de Chimie Organique Biologique, UA-31, Institut de Chimie, Université Louis Pasteur, 1 Rue Blaise Pascal, 67008 Strasbourg, France*

Received May 31, 1990

The use of enzymes in organic synthesis is limited by the low water solubility of many substrates and by the high sensitivity of enzymes toward organic solvent[1-3]. To overcome these problems, much attention has been paid to the solubilisation of hydrophilic enzymes in organic solvents in presence of a small amount of water with help of surfactant. For instance we studied cholesterol oxidase in microemulsion where cholesterol is highly soluble and extended this study to the preparative conversion of cholesterol to Δ^4-cholestenone[4-6]. The stability and the kinetics of horse liver alcohol dehydrogenase (HLADH, EC.1.1.1.1)[7], have been studied in microemulsion[8-10]. The cosurfactant of in the microemulsion, 1-butanol, is also a substrate of the enzyme and can be used to regenerate coenzyme NAD^+ to NADH[8]. We have studied the kinetics of the reduction of cinnamaldehyde in buffer and in microemulsion. Cinnamaldehyde shows substrate inhibition. In microemulsion, through the partitioning of the substrate between the organic phase and the buffer, the concentration at which substrate inhibition occurred was so increased that a concentration of preparative significance was attained[8].

The resolution of (±) formyl-trimethylenemethane iron tricarbonyl **1**[11-13] through derivatives, has been hampered by partial racemisation during regeneration of the aldehyde **1**[13]. (±) Aldehyde **1** is a substrate of HLADH (Michaelis constant 0.23 mM and maximum velocity 2.9 mmol min^{-1} mg^{-1} in 50 mM TES buffer, pH 7.5) showing substrate inhibition at a concentration above 0.45 mM. Hydroxymethylferrocene has been shown to be a substrate for this enzyme[14]. For some unknown reasons, the kinetics of the reduction of aldehyde **1** by NADH with HLADH could not be determined in microemulsion made with t-butanol as cosurfactant[8] since the reduction rate was not constant at what should have been the steady state.

We undertook the preparative reduction of the (±) aldehyde **1** (1.1 g; 4.9 mmol) in a microemulsion (5 m*l*: *cyclo*hexane 60 g; 1-butanol 11 g; cetyltrimethyl ammonium bromide 11 g; 50 mM TES buffer pH 7.5, 18 g) containing the enzyme (HLADH 50 mg) and NAD^+ (800 mg)[15]. After three days at 4°, the volatile solvents were removed under partial vacuum. The oily residue was treated with methylene chloride and filtrated on a porous glass filter. The solvent was evaporated and the crude material chromatographed on silica gel (30 g; hexane-ether). Aldehyde **1** (0.53 g) was eluted first and alcohol **2** second (0.50 g). The ee of the aldehyde was determined by ^{1}H-NMR analysis with a chiral agent; Tris (d,d-dicampholylmethanato) europium III[16]. The ee of the unreacted aldehyde was 68%. In order to determine the ee of the alcohol (0.5 g), its oxidation to the aldehyde **1** with manganese dioxide (2 g) in benzene (30 m*l*) for 3 hrs with a yield of 80% was performed. Using the NMR chiral