

Rhodium-Catalyzed Ring-Opening Silylformylation of Epoxides Leading to β -Siloxy Aldehydes

Yoshiya Fukumoto, Naoto Chatani, and Shinji Murai*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Received April 26, 1993

Summary: In the presence of $[\text{RhCl}(\text{CO})_2]_2$ and 1-methylpyrazole, the reaction of epoxides with a hydrosilane and carbon monoxide resulted in ring-opening silylformylation leading to β -siloxy aldehydes.

The carbonylative ring opening of epoxides has been of long-standing interest not only because of its synthetic potential but also because of the related interest in homogeneous catalysis.¹ Ring-opening esterifications,² carboxylations,³ aminocarbonylations,⁴ and formylations⁵ of epoxides of varying efficiencies have been reported. In 1977, we reported that the $\text{Co}_2(\text{CO})_8$ -catalyzed reaction of epoxides with a hydrosilane and carbon monoxide resulted in ring-opening silylformylations⁶ yielding β -siloxy aldehydes.⁷ In this reaction, however, the desire to prevent the product aldehydes from undergoing further reactions, such as formylations,⁸ hydrosilylations,⁹ and dehydrogenative silylations,¹⁰ required us to use excess amounts of the starting epoxides. We now wish to report that the use of Rh-amine catalysts enables the conversion of epoxides to β -siloxy aldehydes without causing further reactions of the product aldehydes.¹¹

Early in this study, we carried out the reaction of cyclohexene oxide (1) (2.5 mmol) with HSiEt_2Me (7.5 mmol) and CO (50 atm initial pressure at 25 °C) in the presence of $[\text{RhCl}(\text{CO})_2]_2$ (0.1 mmol) in C_6H_6 (5 mL) at 100 °C for 20 h. Only cyclohexanol silyl ether was obtained

Table I. Rhodium-Catalyzed Ring-Opening Silylformylation of Epoxides with HSiMe_2Ph and CO^a

entry	epoxide	product	yield, ^b %
1			82
2			66
3			72
4 ^c			60 (77 : 23)
5 ^c			65
6 ^c			70
7 ^c			55

^a Reaction conditions: epoxide (2.5 mmol), HSiMe_2Ph (3 mmol), $[\text{RhCl}(\text{CO})_2]_2$ (0.05 mmol), 1-methylpyrazole (1 mmol), CO (50 atm initial pressure at 25 °C), CH_2Cl_2 (5 mL), 50 °C, 20 h. ^b GC yields based on the epoxide. ^c 1-Methylpyrazole (2 mmol) was used.

in 21% yield, without the formation of any carbonylation products. An examination of the effects of various additives to this reaction revealed that Et_3N (1 mmol) promotes ring-opening silylformylation. Thus, *trans*-2-(diethylmethylsiloxy)cyclohexanecarbaldehyde (2a) was obtained in 75% yield (eq 1).¹² The ring opening of 1 occurred predominantly in a *trans* manner. To our

(1) For leading reviews of carbonylation, see: Wender, I.; Pino, P. *Organic Syntheses via Metal Carbonyls*; Wiley Interscience: New York, 1975; Vol. 2. Falbe, J. *New Syntheses with Carbon Monoxide*; Springer-Verlag: New York, 1980. Tkatchenko, I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, pp 101-223. Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation: Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991.

(2) Eisenmann, J.; Yamartino, R. L.; Howard, J. F. *J. Org. Chem.* 1961, 26, 2102. Heck, R. F. *J. Am. Chem. Soc.* 1963, 85, 1460. McClure, J. D. *J. Org. Chem.* 1967, 32, 3888. Takegami, Y.; Watanabe, Y.; Mitsudo, T.; Masada, H. *Bull. Chem. Soc. Jpn.* 1969, 42, 202.

(3) McRae, W. A.; Eisenmann, J. L. U.S. Patent 3024275, 1962; *Chem. Abstr.* 1962, 57, 2077.

(4) Tsuji, Y.; Kobayashi, M.; Okuda, F.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* 1989, 1253.

(5) Yokokawa, C.; Watanabe, Y.; Takegami, Y. *Bull. Chem. Soc. Jpn.* 1964, 37, 677. Takegami, Y.; Yokokawa, C.; Watanabe, Y. *Bull. Chem. Soc. Jpn.* 1964, 37, 935. Roos, L.; Goetz, R. W.; Orchin, M. *J. Org. Chem.* 1965, 30, 3023. Rosenthal, A.; Kan, G. *Tetrahedron Lett.* 1967, 477.

(6) The catalytic silylformylation of acetylenes and aldehydes by a hydrosilane and carbon monoxide has been recently reported. Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* 1989, 111, 2332. Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* 1991, 10, 38. Doyle, M. P.; Shanklin, M. S. *Organometallics* 1993, 12, 11. Wright, M. E.; Cochran, B. B. *J. Am. Chem. Soc.* 1993, 115, 2059.

(7) Seki, Y.; Murai, S.; Yamamoto, I.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 789.

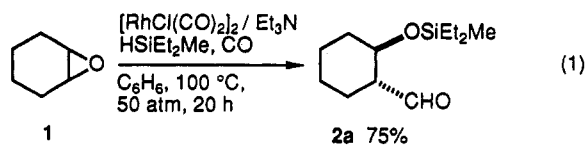
(8) Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 393.

(9) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Part 2, pp 1479-1526.

(10) Seki, Y.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* 1978, 17, 199.

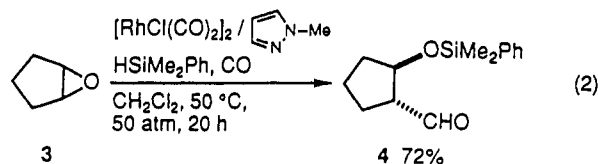
(11) For our recent results on the transition metal-catalyzed reaction with hydrosilanes and carbon monoxide, see: Chatani, N.; Ikeda, S.; Ohe, K.; Murai, S. *J. Am. Chem. Soc.* 1992, 114, 9710. Ikeda, S.; Chatani, N.; Murai, S. *Organometallics* 1992, 11, 3494. Ikeda, S.; Chatani, N.; Kajikawa, Y.; Ohe, K.; Murai, S. *J. Org. Chem.* 1992, 57, 2.

(12) All new compounds were characterized by NMR, IR, and mass spectral data and by elemental analyses or high-resolution mass spectra. *trans*-2-(Diethylmethylsiloxy)cyclohexanecarbaldehyde (2a). ¹H NMR (CDCl_3): δ 0.05 (s, 3H, SiCH_3), 0.55 (q, $J = 7.3$ Hz, 4H, SiCH_2), 0.91 (t, $J = 7.3$ Hz, 6H, SiCCH_3), 1.19-1.39 (c, 4H, CH_2), 1.67-1.93 (c, 4H, CH_2), 2.23 (m, 1H, CH), 3.80 (td, $J = 9.7, 4.1$ Hz, 1H, CHOSi), 9.74 (d, $J = 2.7$ Hz, 1H, CHO); ¹³C NMR (CDCl_3): δ -4.20 (SiCH_3), 6.71 (SiCH_2), 6.99 (SiCCH_3), 24.10, 24.16, 24.90, 35.38 (CH_2), 57.84 (CH), 70.98 (CHOSi), 205.02 (CHO); IR (neat) 2498 s, 2884 s, 2712 w, 1732 s, 1454 m, 1418 m, 1366 m, 1254 s, 1102 s, 1014 s, 966 m, 870 s, 816 s, 766 s, 695 cm^{-1} ; MS (70 eV) m/z (relative intensity) 213 (2, $\text{M}^+ - \text{CH}_3$), 200 (10), 199 (63, $\text{M}^+ - \text{C}_2\text{H}_5$), 171 (11), 169 (31), 131 (10), 103 (19), 101 (13), 93 (12), 91 (19), 89 (98), 79 (11), 75 (14), 73 (34), 67 (10), 61 (100). Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{O}_2\text{Si}$: C, 63.10; H, 10.59. Found: C, 63.21; H, 10.73.



surprise, the addition of Et_3N did not give a similar result with other epoxides, including cyclopentene oxide (3), 1-butene oxide, and styrene oxide. For example the reaction of 3 gave the corresponding formylation product in only 8% yield.

The prudent choice of both an additive and a hydrosilane is crucial to the effective silylformylation of 3. Among additives examined, 1-methylpyrazole¹³ was found to be the additive of choice. Others such as PPh_3 , Et_3N , TMEDA, morpholine, pyridine, pyrrole, and DBU were not effective. The optimized conditions for the reaction of 3 are as follows: 3 (2.5 mmol) is treated with HSiMe_2Ph (3 mmol) and CO (50 atm initial pressure at 25 °C) in the presence of $[\text{RhCl}(\text{CO})_2]_2$ (0.05 mmol) and 1-methylpyrazole (1 mmol) in CH_2Cl_2 (5 mL) at 50 °C for 20 h to give *trans*-2-(dimethylphenylsilyloxy)cyclopentanecarbaldehyde (4) in 72% yield (eq 2). While $\text{RhCl}(\text{PPh}_3)_3$ was



not effective, $[\text{RhCl}(1,5\text{-hexadiene})]_2$ (72%), $[\text{RhCl}(\text{COD})]_2$ (72%), $\text{Rh}(\text{CO})_2(\text{acac})$ (70%) and $\text{Rh}_6(\text{CO})_6$

(13) Esteruelas, M. A.; García, M. P.; López, A. M.; Oro, L. A.; Ruiz, N.; Schlünken, C.; Valero, C.; Werner, H. *Inorg. Chem.* 1992, 31, 5580.

(20%) exhibited catalytic activity when used in combination with 1-methylpyrazole.

The results of these reaction conditions on several epoxides are summarized in Table I. The reaction of 1 afforded 2b in 82% yield (entry 1). An olefin remained intact under these reaction conditions (entry 2). The reaction of cycloheptene oxide gave a silylformylation product in 15% yield, along with a 42% yield of 1-(dimethylphenylsilyloxy)cycloheptene (not shown in Table I).¹⁴ The ring opening of 1-butene oxide occurred preferentially at the primary carbon to give a 77:23 mixture of 3-(dimethylphenylsilyloxy)pentanal (5) and 2-[(dimethylphenylsilyloxy)methyl]butanal (6) in a combined yield of 60% (entry 4). An epoxide having a bulky substituent underwent a completely regioselective silylformylation (entry 5). The stereospecificity of the ring opening is demonstrated in acyclic systems by entries 6 and 7.

Although it is obvious that much remains to be done to fully discern the synthetic and mechanistic aspects of the present reaction, the present study clearly presents a solution to a long-standing problem in carbonylation chemistry.

Acknowledgment. We thank the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for the use of their facilities. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan.

Supplementary Material Available: General procedure and compound characterization data (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(14) In the case of cyclooctene oxide, 1-silyloxycyclooctene was the sole product, in 45% yield.