Tetrahedron Letters, Vol.27, No.1, pp 75-76, 1986
Printed in Great Britain

0040-4039/86 $3.00 + .00

OXIDATIVE CLEAVAGE OF SILICON-CARBON BOND WITH TRIMETHYLAMINE-N-OXIDE. NEW ACCESS TO PRIMARY ALCOHOLS AND ALDEHYDES FROM TERMINAL ALKENES AND ALKYNES1)

Hideki Sakurai,* Masatomo Ando, Nobuo Kawada
Kazuhiko Sato and Akira Hosomi*,†
Department of Chemistry, Tohoku University, Sendai 980, Japan

Summary: Oxidative cleavage of carbon-silicon bond of organosilanes with trimethylamine-N-oxide is achieved under mild conditions. The reaction occurs chemoselectively irrespective of the presence of amino and thio groups to give formally anti-Markovnikov hydration products of 1-alkenes and 1-alkynes via hydrosilylation.

Functional group transformations by C-Si bond cleavage of organosilicon compounds are important in organic synthesis.2) The smooth oxidative cleavage of a C-Si bond by peracid and peroxide has attracted much attention recently.3) We have previously reported that organoalkoxysilanes and organosilatranes undergo oxidative cleavage with m-chloroperbenzoic acid to give the corresponding alcohols.4) However, the use of peracid or peroxide is rather limited to the substrates with functional groups insensitive to such oxidizing reagents. We report herein a novel C-Si bond cleavage reaction of organosilanes (1) with trimethylamine-N-oxide (3)5) to afford alcohols (2) stereospecifically. (eq. 1)

$$\underset{\mathbf{1}}{RSiMe(OEt)_2} \xrightarrow[KF\cdot HF]{Me_3NO\ (\mathbf{3})} \underset{\mathbf{2}}{R\text{-}OH} \qquad (1)$$

A typical experimental procedure is as follows: A mixture of octylsilane (1a) (1 mmol) and trimethylamine oxide (2.5 mmol) was stirred in DMF (5 ml) in the presence of KHF_2 (3 mmol) at 70 °C for 36 h and hydrolyzed with water. Work-up (ether extraction, drying and solvent evaporation) and purification by TLC on silica gel gave 1-octanol (2a) (108 mg, 0.83 mmol) in 83% yield.

Representative results are summarized in Table 1. The general features of the reaction are as follows: (1) $KHCO_3$ and KF can be used as the additive instead of KHF_2. (2) Functional groups such as OR, halogen, NR_2, and RS are not affected under the reaction conditions which are sensitive to peracid and peroxide. (3) The stereochemistry is retained with respect to the alkyl group of 1. (4) Aldehyde

---

† Present address: Faculty of Pharmacentical Sciences, Nagasaki University, Nagasaki 852

Table 1. Oxidative cleavage of Si-C bond of organosilanes (**1**) with trimethylamine N-oxide in DMF

	R-SiMe(OEt)$_2$ **1**		R-OH (or R'CHO) **2**	
Entry	R in **1**	Conditions[a]	Product (**2**)	% Yield[b]
1	n-C_8H_{17} (**1a**)	70 °C, 36 h	n-$C_8H_{17}OH$ (**2a**)	83
2	**1a**	140 °C, 5 h	**2a**	96[c]
3	$MeO_2C(CH_2)_{10}$ (**1b**)	80 °C, 8 h	$MeO_2C(CH_2)_{10}OH$ (**2b**)	76
4	**1b**	130 °C, 15 h	**2b**	79
5	**1b**	80 °C, 8 h[d]	**2b**	76
6	**1b**	80 °C, 12 h[e]	**2b**	65
7	$PhO(CH_2)_3$ (**1c**)	70 °C, 10 h	$PhO(CH_2)_3OH$ (**2c**)	79
8	$Cl(CH_2)_5$ (**1d**)	70 °C, 4 h	$Cl(CH_2)_5OH$ (**2d**)	71
9	$PhMeN(CH_2)_3$ (**1e**)	80 °C, 5 h	$PhMeN(CH_2)_3OH$ (**2e**)	72
10	$PhS(CH_2)_3$ (**1f**)	80 °C, 7 h	$PhS(CH_2)_3OH$ (**2f**)	46
11	endo-Nornonyl (**1g**)[f]	80 °C, 8 h	endo-Norbornol (**2g**)[g]	60
12	n-$C_6H_{13}CH{=}CH$ (**1h**)	130 °C, 5 h	n-$C_7H_{15}CHO$ (**2h**)	68

a) KHF_2 was used, unless otherwise noted. b) Yields after isolation by TLC. c) Determined by GLC. d) KF (4 equiv.) was used. e) $KHCO_3$ (1 equiv.) was used. f) Triethoxysilane (endo/exo = 63/37) was used instead of methyldiethoxysilane. g) Endo/exo = 80/20.

(**2h**) can be obtained from 1-alkenylsilane (**1h**).

The new reaction corresponds to the alcohol synthesis by the anti-Markovnikov hydration in one pot operation since the starting organosilanes (**1**) can be readily prepared from 1-alkenes and 1-alkynes by the transition metal-catalyzed hydrosilylation. (eq. 2)

$$\underset{\textbf{1b}}{MeO_2C(CH_2)_8CH{=}CH_2} \xrightarrow[RhCl(PPh_3)_3]{HSiMe(OEt)_2} \xrightarrow[KHF_2/DMF]{Me_3NO} \underset{\textbf{2b},\ 72\%}{MeO_2C(CH_2)_{10}OH} \qquad (2)$$

We thank Professor J. A. Soderquist for helpful discussions and informations of his results prior to publication.

References

1) Chemistry of Organosilicon Compounds 208.
2) For reviews, see W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, 1983; E. W. Colvin, "Silicon in Organic Synthesis," Butterworth, 1981.
3) Recent works in this area can be traced in the following references. K. Tamao, T. Kakui, M. Akita, T. Iwahara, R. Kanatani, J. Yoshida, and M. Kumada, Tetrahedron, 39, 983 (1983); K. Tamao, N. Ishida, T. Tanaka, and M. Kumada, Organometallics, 2, 1694 (1983); K. Tamao, M. Kumada, and K. Maeda, Tetrahedron Lett., 25, 321 (1984); K. Tamao and N. Ishida, ibid., 25, 4245 (1984); Idem, J. Organomet. Chem., 269, C37 (1984).
4) A. Hosomi, S. Iijima, and H. Sakurai, Chem. Lett., 1981, 243.
5) For Si-Si bond cleavage with amine N-oxide, see H. Sakurai, M. Kira, and M. Kumada, Bull. Chem. Soc. Japan, 44, 1167 (1971).

(Received in Japan 19 October 1985)