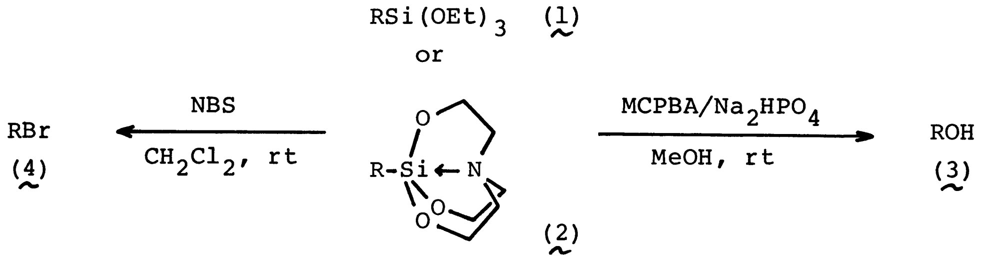
CHEMISTRY LETTERS, pp.243-246, 1981.

CARBON-SILICON BOND CLEAVAGE OF ORGANOTRIALKOXYSILANES AND ORGANOSILATRANES WITH m-CHLOROPERBENZOIC ACID AND N-BROMOSUCCINIMIDE. NEW ROUTE TO PHENOLS, PRIMARY ALCOHOLS AND BROMIDES[1]

Akira HOSOMI, Susumu IIJIMA, and Hideki SAKURAI
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

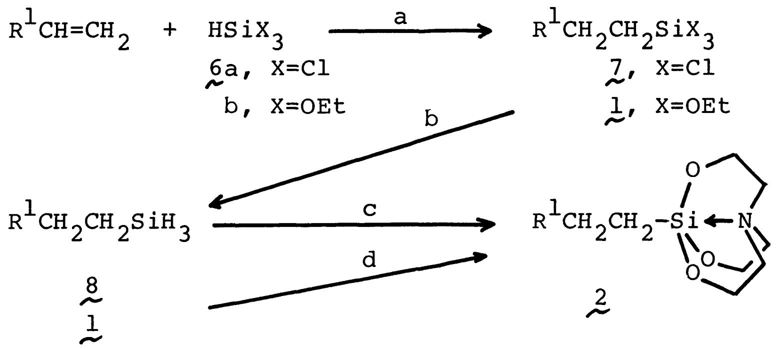
Alkyl- and aryltriethoxysilanes undergo oxidative carbon-silicon bond cleavage smoothly with m-chloroperbenzoic acid (MCPBA) to afford the corresponding alcohols. Silatranes similarly gave alcohols and bromides with MCPBA and N-bromosuccinimide, respectively.

Although numerous reports have been published on the smooth carbon-silicon bond cleavage of anionic organosilicon ate-compounds such as organopentafluorosilicates with peracid, N-bromosuccinimide (NBS) and halogens,[2,3] the use of neutral tetra- and penta-coordinate organosilanes has been rather limited. A comparison of ^{1}H and ^{29}Si NMR chemical shifts of organotrialkoxysilanes and organosilatranes[4] with those of organosilicon ate-species[5] indicates high charge densities at silicon atoms of alkoxysilanes and silatranes like those of organosilicon ate-compounds. Therefore, these alkoxysilanes and silatranes could also be attacked readily with electrophilic reagents. We report here a novel carbon-silicon bond cleavage reaction of neutral tetra- and penta-coordinate organosilanes by m-chloroperbenzoic acid (MCPBA) and NBS to give the corresponding alcohols and bromides, respectively. The reaction formally corresponds to anti-Markownikoff hydration and hydrobromination of olefins. (eq. 1)



(1)

The starting materials were prepared by the following scheme. Hydrosilylation of olefins (5) with trichlorosilane (6a) and triethoxysilane (6b) catalyzed by chloroplatinic acid gave the corresponding alkyltrichlorosilanes (7) and alkyltriethoxysilanes (1), respectively. Reduction of either 7 or 1 with lithium aluminum hydride afforded alkylsilane (8). Conversion of hydrosilane (8) to silatrane (2) catalyzed by dicobalt octacarbonyl proceeds very smoothly via dehydrogenative condensation under mild condition,[6] although direct conversion of 1 to 2 is also effective under considerably severe condition.[7] Aryltriethoxysilanes (9) were prepared by the ethanolysis of aryltrichlorosilanes, prepared by the Grignard reaction. Arylsilatranes (**10**) were similarly obtained according to the procedures mentioned above.



a. H_2PtCl_6, heat(80°-140°); b. $LiAlH_4$, ether, reflux; c. $N(CH_2CH_2OH)_3$, $Co(CO)_8$, CH_2Cl_2, rt; d. $N(CH_2CH_2OH)_3$, KOH, PhH, reflux.

Organotriethoxysilanes (**1**,**9**) thus obtained can react with MCPBA smoothly in methanol in the presence of disodium hydrogen phosphate (Na_2HPO_4) to give the corresponding alcohols.[8] The results are listed in Table 1. Phenyltrimethylsilane was intact under a similar reaction condition.

The nature of the solvent in the presence of Na_2HPO_4 plays an important role in the reaction. Methanol was the most satisfactory solvent. Other aprotic solvents such as THF, acetonitrile, dichloromethane, dimethoxyethane, and DMF were less effective than methanol to the reaction.

Similarly, silatranes as a representative five-coordinate organosilane can enter the reaction with MCPBA and NBS. The results are summarized in Table 2. In the case of silatranes the solvent effect was not very important, since methanol and dichloromethane gave products in similar yields.

In conclusion, the present reactions provide new mild procedures for preparing primary alcohols and bromides from 1-olefins via hydrosilylation. Phenols and phenyl bromides can also be prepared by similar procedures.

Preparation of n-octyl alcohol from 1-octene is typical. n-Octyltriethoxysilane (**11**) (11.4g, 41.2mmol) was prepared by the hydrosilylation of 1-octene (8.0g, 71.3mmol) with triethoxysilane (10.0g, 60.9mol) in the presence of chloroplatinic acid as catalyst at 125° for 46h in 68% yield. n-Octyltriethoxysilane (285mg, 1.0mmol) and MCPBA (80% purity) (409mg, 1.9mmol) was stirred in methanol (2ml) at room temperature for 24h in the presence of disodium hydrogen phosphate (335mg, 2.4mmol) in a flask. The resulting solution was hydrolyzed with water. The organic layer was separated and the aqueous layer was washed with ether. The combined organic layer was dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by TLC (silica gel) using hexane-ether (1/1) as an eluent to give 57.5mg (0.43mmol) of n-octyl alcohol (12) (R_f 0.5) in 43% yield.

Acknowledgement: We thank Toshiba Silicone Co., Ltd., for a gift of chlorosilanes. The work is supported in part by the Mitsubishi Foundation.

Table 1. Reactions of alkyl- and aryltriethoxysilane with m-chloroperbenzoic acid (MCPBA)[a]

Entry	Organotriethoxysilane	Solvent	Product	Yield/%[b]
1	n-$C_8H_{17}Si(OEt)_3$ (11)	MeOH	n-$C_8H_{17}OH$ (12)	43 (56)
2	11	EtOH	12	(11)
3	11	DMF	12	(10)
4	11	DME	12	(9)
5	11	CH_2Cl_2	12	(8)
6	11	THF	12	(3)
7	11	CH_3CN	12	(3)
8	n-$C_{16}H_{33}Si(OEt)_3$	MeOH	n-$C_{16}H_{33}OH$	48
9	$CH_3OCO(CH_2)_{10}Si(OEt)_3$	MeOH[c]	$CH_3OCO(CH_2)_{10}OH$	55
10	$C_6H_5Si(OEt)_3$	MeOH	C_6H_5OH	60

Table 2. Reactions of Organosilatranes with MCPBA[d]

Entry	R in organosilatrane	Electrophile	Reaction time/h	Product	Yield/%
1	n-C_8H_{17}	MCPBA	22	n-$C_8H_{17}OH$	43 (43)
2	n-C_8H_{17}	MCPBA	23[f]	n-$C_8H_{17}OH$	(41)
3	n-C_8H_{17}	NBS	78	n-$C_8H_{17}Br$	(15)
4	C_6H_5	MCPBA	18	C_6H_5OH	(18)
5	C_6H_5	NBS	13	C_6H_5Br	(55)
6	p-ClC_6H_4	MCPBA	22	p-ClC_6H_4OH	(22)
7	p-ClC_6H_4	NBS	8	p-ClC_6H_4Br	52 (77)
8	p-$CH_3OC_6H_4$	MCPBA	18	p-$CH_3OC_6H_4OH$	(17)
9	p-$CH_3OC_6H_4$	NBS	22	p-$CH_3OC_6H_4Br$	64 (71)
10	p-$CH_3C_6H_4$	MCPBA	22	p-$CH_3C_6H_4OH$	(23)

Captions to Tables (Common)

[a] Reactions of organotriethoxysilane with MCPBA were carried out at room temperature for 24h in the presence of Na_2HPO_4, unless otherwise noted. [b] Yields after isolation by TLC. Yields determined by GLC are given in parentheses. [c] The reaction time is 40h. [d] Reactions with MCPBA were carried out in CH_2Cl_2 in the presence of Na_2HPO_4 at room temperature unless otherwise noted. [e] Reactions with NBS were carried out in CH_2Cl_2 at room temperature. [f] The reaction was carried out in MeOH at room temperature.

References and Notes

(1) Chemistry of Organosilicon Compounds 144.

(2) a) K. Tamao, J. Yoshida, M. Takahashi, H. Yamamoto, T. Kakui, H. Matsumoto, A. Kurita, and M. Kumada, J. Am. Chem. Soc., 100, 290 (1978); b) K. Tamao, T. Kakui, and M. Kumada, ibid., 100, 2268 (1978); c) idem, ibid., Tetrahedron Lett., 619 (1979); d) J. Yoshida, K. Tamao, A. Kurita, M. Kumada, ibid., 1809 (1978); e) J. Yoshida, K. Tamao, M. Takahashi, and M. Kumada, ibid., 2161 (1978); f) K. Tamao, H. Matsumoto, T. Kakui, and M. Kumada, ibid., 1137 (1979); g) J. J. Moscony and A. G. MacDiarmid, Chem. Commun., 307 (1965); h) R. Müller and C. Dathe, Z. anorg. allgem. Chem., 343, 150 (1966); i) idem, ibid., 341, 49 (1965); j) idem, Ber. 99, 1609 (1966).

(3) For reviews, see a) R. Müller, Organometal. Chem. Rev., 1, 359 (1966); b) C. Eaborn and R. W. Bott, in "Organometallic Compounds of the Group IV Elements," Vol. 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N.Y., 1968, p435-437; c) K. Tamao, J. Yoshida, and M. Kumada, J. Synth. Org. Chem., 38, 769 (1980).

(4) a) R. K. Harris, J. Jones, and S. Ng, J. Magnetic Resonance, 30, 521 (1978); b) V. A. Pestunovick, S. N. Tandura, M. G. Voronkov, V. P. Baryshok, G. Z. Zelchan, V. I. Glukhikn, G. Engelhardt, and M. Witanowski, Spectroscopy Lett., 11, 339 (1978); c) G. Engerhardt, R. Radeglia, H. Jancke, E. Lippmaa, and M. Mögi, Org. Mag. Res., 5, 561 (1973); d) R. K. Harris and B. J. Kimber, ibid., 7, 460 (1975); e) H. C. Marsmann, Chemiker-Zeitung, 97, 128 (1973).

(5) a) D. Kummer and T. Seshadri, Z. anorg. allg. Chem., 428, 129 (1977); b) H. C. Marsmann and R. Löwer, Chemiker- Zeitung, 97, 660 (1973).

(6) A. Shirahata, MS Thesis, Tohoku University, p6 (1976). A typical procedure follows. n-Octylsilane (2.9g, 20mmol) was added slowly to a solution of triethanolamine (1.98g, 20mmol) in dichloromethane (30ml) in the presence of dicobalt octacarbonyl (2ml of 0.1 M solution in dichloromethane, 0.2 mmol). After the reaction mixture was stirred at reflux for 50h, the solvent was evaporated. The residue was dissolved in chloroform and the inorganic materials were removed from the reaction mixture by the filfration. Chloroform was evaporated and the residue was crystallized in carbon disulfide to give pure n-octylsilatrane (5.3g, 18.4mmol), mp 71-2°, in 92% yield.

(7) a) C. L. Frye, G. E. Vogel, and J. A. Hall, J. Am. Chem. Soc., 83, 996 (1961); b) M. G. Voronkov, Pure. Appl. Chem., 13, 35 (1966); c) A. B. Firestone, Ger. Pat., 1131681 (1963); Chem. Abstr., 58, 4598 (1963).

(8) The effect of Na_2HPO_4 is not clear. Possibly, it acts as a buffer

(Received November 15, 1980)