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ELECTROCHEMICAL OXIDATION OF ORGANOSILICON COMPOUNDS I. OXIDATIVE CLEAVAGE OF CARBON-SILICON BOND IN ALLYLSILANES AND BENZYLSILANES

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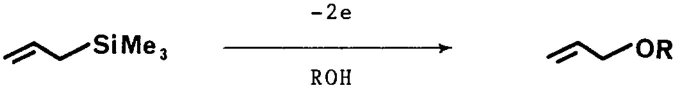
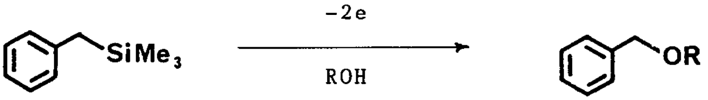
Summary: Electrochemical oxidation of allylsilanes and benzylsilanes in the presence of alcohol, carboxylic acid, or water resulted in cleavage of the carbon-silicon bond and formation of the corresponding ether, ester, or alcohol, respectively.

The purpose of this letter is to disclose our observations on the electrochemical oxidation of two types of organosilicon compounds, i.e. allyl- and benzyltrialkylsilanes. The basic ideas behind this work were as follows. (1) Both theoretical[1] and experimental[2] works suggest the definite electron donating effect of β-silyl group toward the π-system. Therefore such π-systems having β-silyl group seem to be quite susceptible toward electrochemical oxidation[3] compared with the parent system. (2) Electrochemical oxidation of olefins is suggested to proceed via the cation radical intermediate which, in some cases, looses an allylic proton to give the allyl radical.[4] If trimethylsilyl group is substituted for the allylic proton, the silyl group is expected to act as a "super proton"[5] giving rise to selective cleavage of the carbon-silicon bond.[6,7] For benzylic cases a similar effect is also expected. (3) Thus produced radical species is expected to be further oxidized to the cation under the conditions. Introduction of nucleophiles into such cationic species[8] will provide a useful method for "umpolung" of organosilicon compounds.[9]

The reaction does indeed occur exactly as expected (eqs 1 and 2).

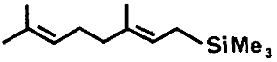
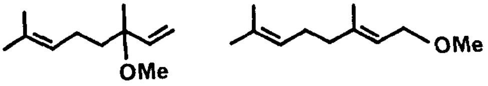
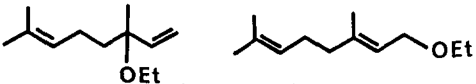
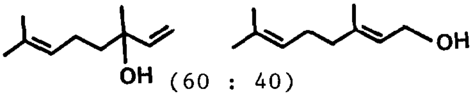
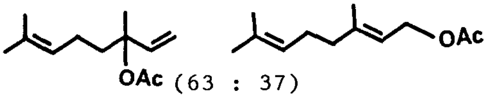
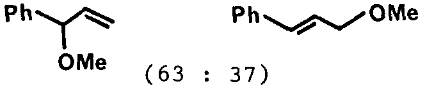
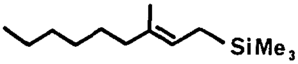
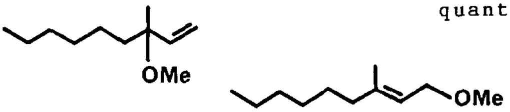
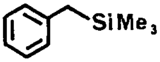
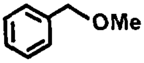
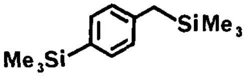
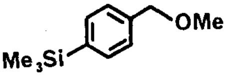
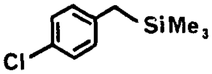
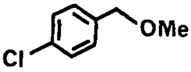
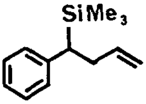
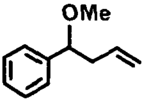


(1)



(2)

Table I. Electrochemical Oxidation of Allylsilanes and Benzylsilanes[a]

$RSiMe_3$	R'OH	method	product	yield (%)[b]
	MeOH	A	 (68 : 32)	69
	EtOH	B	 (63 : 37)	56
	H_2O	B	 (60 : 40)	62
	AcOH	B	 (63 : 37)	26[c]
	MeOH	B	 (63 : 37)	(76)
	MeOH	A	 (61 : 39)	quantitative
	MeOH	A		(91)
	MeOH	A		quantitative
	MeOH	A		72
	MeOH	A		69

[a] Reactions were normally carried out with an organosilicon compound (1.0 mmol) in 0.2 M $Et_4NOTs/MeOH$ (method A) or in 0.2 M $Et_4NOTs/MeCN$ in the presence of an alcohol, water, or acetic acid (25 mmol) (method B) using carbon rod electrodes. Passed electricity was normally 2.1 F/mol. [b] Isolated yields. Yields in parentheses were determined by VPC. [c] A mixture of linalool and geraniol was also produced in 31% yield.

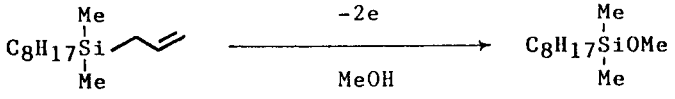
A typical procedure for the electrochemical oxidation of allylsilanes is as follows. Geranyltrimethylsilane (1.0 mmol) dissolved in 0.2 M solution of tetraethylammonium p-toluenesulfonate in methanol (10 ml) was placed in an undivided cell equipped with two carbon rod electrodes. After 2.1 F/mol of electricity was passed (constant current, 10 mA), aqueous work-up followed by bulb-to-bulb distillation afforded a 68 : 32 mixture of linaloyl methyl ether and geranyl methyl ether in 69% yield (Method A). The reaction was also carried out in acetonitrile as solvent in the presence of 25 equiv of an alcohol to obtain the corresponding ether. In a similar fashion the reaction in the presence of water or acetic acid afforded the corresponding alcohols or esters, respectively (Method B). Table I summarizes the results obtained for several allylsilanes.

It should be noted that the simple carbon-carbon double bond in geranylsilane was not affected. Only allylsilane moiety was oxidized under the conditions. This observation is in accord with the suggested electron donating ability of β-silyl group.[10] Another important feature to note is that the allyl carbon-silicon bond was selectively cleaved in the presence of several allyl carbon-hydrogen bonds, indicating much higher reactivity of the former than the latter.

The oxygen nucleophile was introduced to the both ends of the allyl moiety in consistent with allyl cation intermediate.[11] The regioselectivity does not seem to depend on the nature of the nucleophile employed. Methoxyl, ethoxyl, hydroxyl, and acetoxyl groups were introduced to the both ends of the allyl moiety of geranylsilane in approximately 6 : 4 ratio. The attack on the more substituted carbon was predominant. A similar regioselectivity was observed for other allylsilanes.

Benzyltrimethylsilanes were also oxidized by the electrochemical method under similar conditions. The oxygen nucleophile was introduced onto the benzylic position exclusively and no products derived from attack on aromatic nucleus was detected. High chemoselectivity observed for the reaction of p-(trimethylsilyl)benzyltrimethylsilane is interesting. Only the benzyl carbon-silicon bond was cleaved without affecting the aromatic carbon-silicon bond.

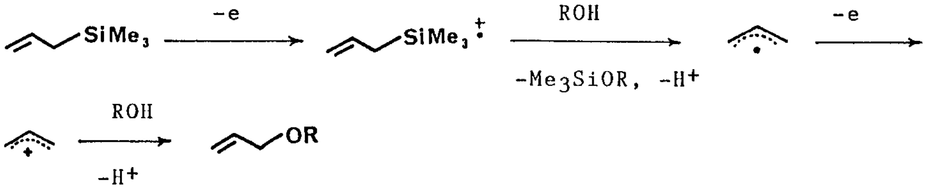
In order to get a deeper insight into the reaction mechanism the fate of the silyl moiety was investigated. Thus allyldimethyloctylsilane was electrolyzed in methanol to obtain methoxydimethyloctylsilane in 82 % yield (eq 3),[12] implying that the carbon-silicon bond cleavage was induced by the attack of the alcohol on silicon.



$$\mathrm{C_8H_{17}\overset{Me}{\underset{Me}{Si}}CH_2CH{=}CH_2} \xrightarrow[\mathrm{MeOH}]{-2e} \mathrm{C_8H_{17}\overset{Me}{\underset{Me}{Si}}OMe} \qquad (3)$$

Although more data should be accumulated before elucidation of the mechanism, the following scheme (Scheme I) seems to be reasonable at present. Initial electron transfer from the allyl- or benzylsilane produces cation radical intermediate. Selective attack of the oxygen nucleophile on silicon cleaves the carbon-silicon bond to give the allyl- or benzyl radical. Further oxidation gave the corresponding cation which reacts with another molecule of the oxygen nucleophile to produce the final product.

Scheme I



Further studies in progress may hopefully delineate the full scope and the detailed mechanism of this reaction.

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(6) Oxidative cleavage of carbon-silicon bond, see: (a) Tamao, K.; Kakui, T.: Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. Tetrahedron **1983**, 39, 983. (b) Tamao, K. in "Organosilicon and Bioorganosilicon Chemistry", Sakurai, H. Ed. Ellis Horwood: Chichester, 1985, and references cited therein.

(7) Electrochemical cleavage of metal-carbon bonds, see: C. J. Pickett in "The Chemistry of the Metal-Carbon Bond", Hartley, F. R.; Patai, S. Ed. Wiley: Chichester, 1985.

(8) Reactions of organosilicon compounds with electrophiles are well known, for example, see:(a) Weber, W. P. "Silicon Reagents for Organic Synthesis", Springer-Verlag, Berlin, 1983. (b) Colvin, E. W. "Silicon in Organic Synthesis", Butterworths, London, 1981.

(9) Ochiai, M.; Arimoto, M.; Fujita, E. Tetrahedron Lett. **1981**, 22, 4491.

(10) Oxidation potential of geranyltrimethylsilane (Ep = 1.30 V vs. Ag/AgCl) is much less anodic than those of trisubstituted olefins such as 2-methyl-2-butene (Ep = 1.85 V vs. Ag/AgCl) under the conditions employed in the present reaction.

(11) DeWolfe, R. H.; Young, W. G. Chem. Rev. **1956**, 56, 753.

(12) From a synthetic point of view this reaction is interesting, since it provides a convenient method for conversion of allylsilanes to alkoxysilanes under neutral conditions. Organic synthesis using alkoxysilanes, see ref 6b and references cited therein.

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