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Preliminary communication

Electrochemical oxidation of organosilicon compounds

V *. Electrochemical oxidation of α-silylethers. Remarkable effect of silicon on oxidation potentials and reaction pathways

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Abstract

Substitution of a silyl group for hydrogen at the α-position of ethers caused a significant decrease in their oxidation potentials. This effect is attributed to an interaction of the carbon–silicon σ-bond with the lone pair of the oxygen atom. The preparative anodic oxidation of α-silylethers proceeded smoothly in methanol and the carbon–silicon bond was selectively cleaved to give the corresponding acetals.

The effect of silicon on various properties of carbon species has been studied extensively [1]. For example, substitution of a silyl group for hydrogen at the allylic position raised the HOMO of the olefin. Up to now, however, only a few studies on the effect of silicon on the properties of heteroatoms such as oxygen have been reported [2]. During a systematic study on electrochemical oxidation of organosilicon compounds [3] we found that replacement of a silyl group at the α-position of ethers caused a significant decrease in their oxidation potentials and that electrochemical oxidation of α-silylethers resulted in facile cleavage of the carbon–silicon bond.

Direct electrochemical oxidation of aliphatic ethers is difficult because of their high oxidation potentials (> 2.5 V vs. Ag/AgCl) [4]. 1-Dimethylphenylsilyloctyl methyl ether, however, exhibited an anodic wave with peak potential of 1.60 V vs. Ag/AgCl (Table 1). This potential is also much less than that required for the organosilicon compound without ether functionality [5] (octyldimethylphenylsilane: 2.25 V). This significant effect of silicon seems to be universal. The trimethylsilyl group is also effective as the silyl group. Substitution of a silyl group at the α

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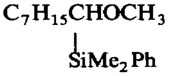
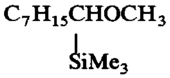
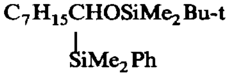
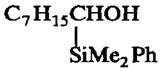
* For part IV see ref. 3d.

Table 1

Oxidation potentials of α-silylethers [a]

Compound	E_p (V)	Compound	E_p (V)
 $C_7H_{15}\underset{\overset{\mid}{SiMe_2Ph}}{C}HOCH_3$	1.60		2.15
 $C_7H_{15}\underset{\overset{\mid}{SiMe_3}}{C}HOCH_3$	1.72		1.67
 $C_7H_{15}\underset{\overset{\mid}{SiMe_2Ph}}{C}HOSiMe_2Bu\text{-}t$	1.95		2.08
 $C_7H_{15}\underset{\overset{\mid}{SiMe_2Ph}}{C}HOH$	1.70	$C_8H_{17}OCH_3$	> 2.5 [b]
$C_8H_{17}SiMe_2Ph$	2.25	$C_8H_{17}OH$	> 2.5 [b]

[a] Cyclic voltammetry was carried out with a glassy carbon working electrode and a platinum wire counter electrode in 0.1 *M* $LiClO_4/CH_3CN$. Sweep rate was 50 mV/sec. Ag/AgCl was used as reference electrode. [b] A clear anodic peak was not observed.

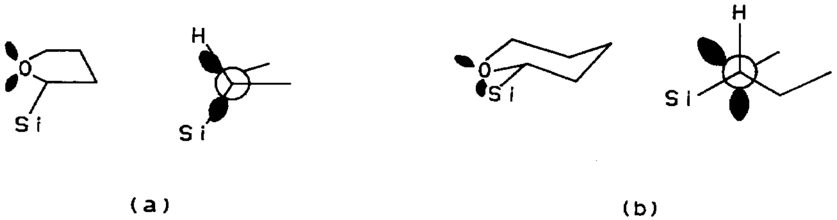


Fig. 1.

position of alcohols as well as ethers also resulted in a significant decrease in their oxidation potentials.

These phenomena can be attributed to the interaction between the C–Si σ-bond and the lone pair of the oxygen atom both in the neutral molecule and in the intermediate cation radical. Overlap with the C–Si σ-bond may increase the energy level of the lone pair of the oxygen, and facilitate the one-electron transfer from the oxygen atom. The cation radical thus produced may be stabilized by the interaction of the half vacant MO of the oxygen with the C–Si σ-bond *. However, only a little experimental evidence for such interaction has been published [2]. Since the fixed geometry of the ring system may enable the evaluation of such interaction, the oxidation potentials of some cyclic α-silylethers were examined. An α-silyltetrahydrofuran exhibited an anodic peak at 1.67 V, whereas the oxidation potential of α-silyltetrahydropyran (2.08 V) was much greater. These facts can be explained in terms of the favorable geometry of the five-membered ring in which one of the lone pairs of the oxygen can overlap with the C-Si σ-bond (Fig. 1a). In the case of the six-membered ring, however, the geometry seems to be less favorable

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* Interaction between the C–Si bond and a vacant MO of the β-carbocation is well known.

Table 2
Electrochemical oxidation of α-silylethers [a]

Run	Substrate	Electricity (F/mol)	Product	Yield [b] (%)
1	$\underset{\mathrm{SiMe_2Ph}}{\mathrm{C_9H_{19}CHOMe}}$	2.02	$C_9H_{19}CH(OMe)_2$	95
2	$\underset{\mathrm{SiMe_2Ph}}{\mathrm{C_7H_{15}CHOMe}}$	2.31	$C_7H_{15}CH(OMe)_2$	68
3	$\underset{\mathrm{SiMe_3}}{\mathrm{C_9H_{19}CHOMe}}$	2.01	$C_9H_{19}CH(OMe)_2$	86
4	$\underset{\mathrm{SiMe_3}}{\mathrm{C_7H_{15}CHOMe}}$	2.00	$C_7H_{15}CH(OMe)_2$	79 [c]
5	$\mathrm{C_9H_{19}}\underset{\mathrm{SiMe_3}}{\mathrm{CH}}\mathrm{OCH_2CH{=}CH_2}$	11.00	$\mathrm{C_9H_{19}}\underset{\mathrm{OMe}}{\mathrm{CH}}\mathrm{OCH_2CH{=}CH_2}$	87 [d]
6	$\underset{\mathrm{SiMe_3}}{\mathrm{C_9H_{19}CHOH}}$	2.60	$C_9H_{19}CHO$	99 [d]
7	$\mathrm{C_7H_{15}}\overset{\mathrm{OH}}{\mathrm{CH}}\underset{\mathrm{SiMe_2Ph}}{\mathrm{CH}}\mathrm{OMe}$	2.49	$\mathrm{C_7H_{15}}\overset{\mathrm{OH}}{\mathrm{CH}}\mathrm{CH(OMe)_2}$	74

[a] Constant current electrolyses (10 mA) were normally carried out with 1.0 mmol of the substrate in 0.2 *M* Et_4NOTs/MeOH (10 ml) (Ts = tosyl) in an undivided cell equipped with two carbon rod electrodes (Ø 6 mm). [b] Isolated yields determined by flash chromatography unless otherwise stated. [c] Isolated yields determined by bulb-to-bulb distillation. [d] The reaction was carried out in the presence of a small amount of pyridine (0.10 ml) to avoid acid-catalyzed acetal exchange or acetal formation.

for such interaction (Fig. 1b). Thus the remarkable "stereoelectronic effect" [6] observed here strongly supports the crucial role played by the interaction between the carbon–silicon bond and the lone pair of the oxygen atom *.

Substitution of a silyl group at the α-position of sulfides and carbamates also caused a decrease in their oxidation potentials, but to a much lesser extent [3c,3d]. The energy level of the oxygen lone pair presumably is lower than that of sulfur and nitrogen, and is closer to the energy level of the carbon–silicon σ-bond. Better overlap between the lone pair and C–Si σ-bond thus is attained and a greater decrease in oxidation potentials was observed in the case of the oxygen compounds.

Preparative electrolysis of α-silylethers proceeded smoothly in methanol to give the methoxylated compounds in high yields (Table 2). The corresponding aldehyde was obtained in the case of an α-silylalcohol (run 6). The reaction seems to proceed by a mechanism proposed similar to that for α-silylsulfides and α-silylcarbamates

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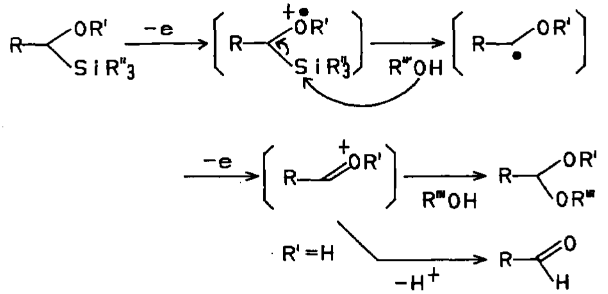
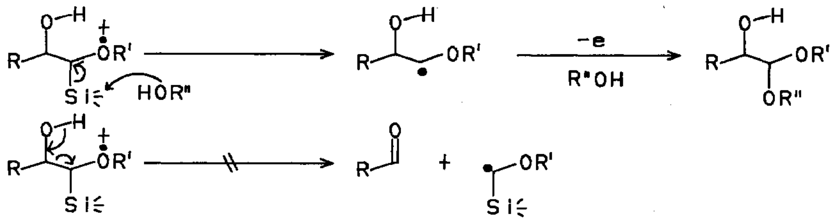
* The difference in oxidation potential between the five-membered ring and the six-membered ring cannot be attributed to that between the parent compounds. Although it is difficult to determine the electrochemical oxidation potentials of the parent cyclic ethers, (> 2.5 V vs. Ag/AgCl), vertical ionization potential of tetrahydrofuran is reported to be greater than that of tetrahydropyran [9]. In the silylated analogue the order of the oxidation potential is reversed. In the case of the three-membered ring the ionization potential of the parent compound, ethylene oxide, is greater than that of the other cyclic ethers [9], and therefore it is difficult to elucidate the effect of silicon in the epoxysilane.

(Scheme 1). The initial one-electron transfer produces the intermediate cation radical and nucleophilic attack of methanol on silicon cleaves the carbon–silicon bond. The resulting radical is further oxidized to a cationic species which is trapped by methanol to give the methoxylated product. In the case of the α-silylalcohol elimination of proton takes place at the cationic intermediate to give the aldehyde. A mechanism involving one-electron transfer from the carbon–silicon bond rather than the lone pair of the oxygen atom is also a possible candidate, but it is difficult to distinguish between these two mechanisms experimentally at present.



It is noteworthy that the carbon–silicon bond was cleaved selectively without affecting other carbon–hydrogen bonds at the α-position even in the presence of the allylic hydrogen (run 5). Electrochemical oxidation of a β-hydroxyether is known to give the carbon–carbon bond cleavage product [7]. However, the α-silylated analogue [8] did not give such a type of product. The compound derived from the cleavage of the carbon–silicon bond was obtained as a sole product (run 7) (Scheme 2).



A propensity for nucleophilic attack on silicon in the cation radical intermediate seems to be responsible for the high product selectivity of the present reaction. Thus, silicon controls the pathways of the reaction as well as activating ethers so that they can undergo electrochemical oxidation.

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