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Electrochemical Oxidation of 1-Phenylthio-1-trimethylsilylalkanes[1]

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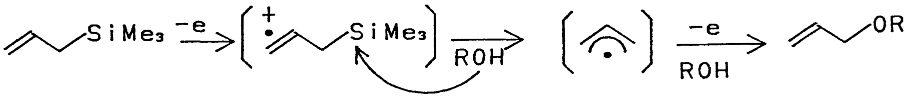
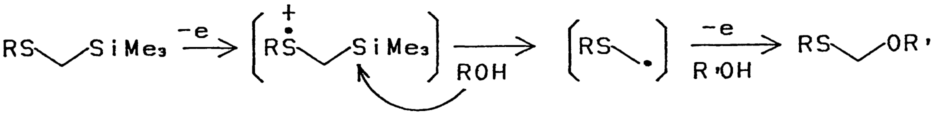
Electrochemical oxidation of 1-phenylthio-1-trimethylsilylalkanes in the presence of alcohol resulted in facile cleavage of the carbon-silicon bond and formation of the corresponding acetals.

Recently Nonaka[2] and we[3] have reported that electrochemical oxidation of allyltrimethylsilanes and benzyltrimethylsilanes resulted in selective cleavage of the carbon-silicon bond and facile introduction of oxygen nucleophiles into the organic moiety. Presumably the initial one-electron transfer from the π-system affords the cation radical species and attack of oxygen nucleophile on silicon cleaves the carbon-silicon bond to generate the radical species[4] (Scheme 1).



Scheme 1.

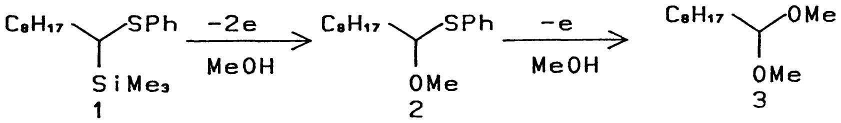
As an extension of this concept we have been interested in electrochemical oxidation of organosilicon compounds substituted by the heteroatom at the carbon bearing the silicon. One electron-transfer from the heteroatom is expected to generate a cation radical and the carbon-silicon bond in such species may be cleaved smoothly by nucleophilic attack on silicon [5](Scheme 2).



Scheme 2.

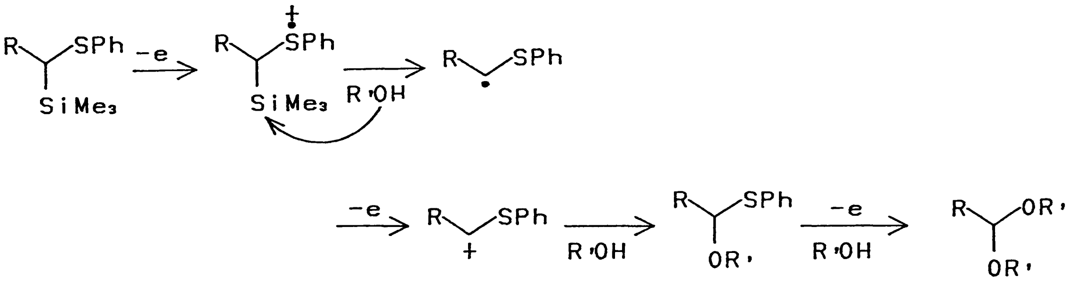
In the present study we focused on sulfur as the heteroatom and examined electrochemical oxidation of 1-phenylthio-1-trimethylsilylalkanes.[6] First, cyclic voltammetry was performed using glassy carbon electrode in $LiClO_4$/acetonitrile. 1-Phenylthio-1-trimethylsilylnonane exhibited the first oxidation wave at the peak potential of 1.25 V vs. Ag/AgCl. This potential was only slightly less anodic than the oxidation potential of sulfides which do not have the silyl group at the adjacent carbon such as 1-phenythiooctane (1.35 V vs. Ag/AgCl). Therefore trimethylsilyl group does not seem to activate the sulfur atom so much toward the electrochemical oxidation in contrast with significant activation of the π-system in allyl- and benzylsilanes.[7]

Preparative electrolysis of 1-phenylthio-1-trimethylsilylnonane (**1**) in the presence of methanol took place smoothly to give the corresponding acetal (**3**) in good yield (Eq 1).



(1)

Constant current (10 mA) was passed through a solution of **1** in 0.2 M Et_4NOTs/methanol in an undivided cell using carbon rod electrodes (Φ 2 mm × 15 mm). Monitoring the reaction by vapor-phase chromatography indicated that 1-methoxy-1-phenylthiononane (**2**) was initially formed which underwent further reaction under the electrolysis conditions to give the corresponding dimethylacetal, 1,1-dimethoxynonane (**3**). After consumption of 4.13 F/mol of electricity, the amount of thioacetal (**2**) was negligibly small and acetal (**3**) was obtained in 84% yield (flash chromatography). A possible reaction mechanism is as follows (Scheme 3):



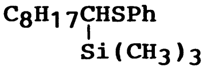
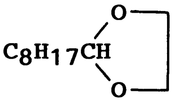
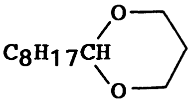
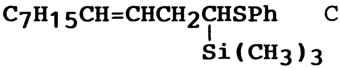
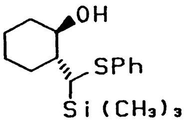
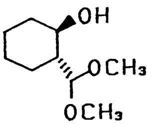
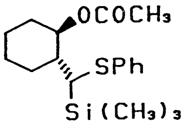
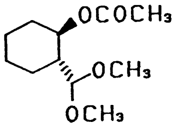
Scheme 3.

The initial one-electron oxidation produced the cation radical species. Nucleophilic attack of methanol on silicon cleaved the carbon-silicon bond to generate the radical species which was further oxidized at the anode to afford the cationic species.[5] Trapping of this cation by methanol gave the 1-methoxy-1-phenylthioalkane. Then cleavage of the carbon-sulfur bond took place under the electrochemical conditions to give the acetal. As a matter of fact, a separate experiment revealed that a mixture of **2** (63% yield) and **3** (16%) was obtained after 2.0 F/mol of electricity were passed.[8] Further electrochemical oxidation of this mixture (2.28 F/mol of electricity based on **2**) resulted in consumption of **2** and increase in the amount of **3** (85% yield based on **2**). This fact indicated that the carbon-sulfur bond in **2** was cleaved by electrochemical oxidation.[9]

The reaction can be applied to other 1-phenylthio-1-trimethylsilylalkanes as shown in Table 1. Functional groups such as free hydroxyl, ester, and carbon-carbon double bond tolerated under the reaction conditions. Similar reactions also proceeded in the presence of diol such as 1,2-dihydroxyethane and 1,3-dihydroxypropane to give the cyclic acetals.

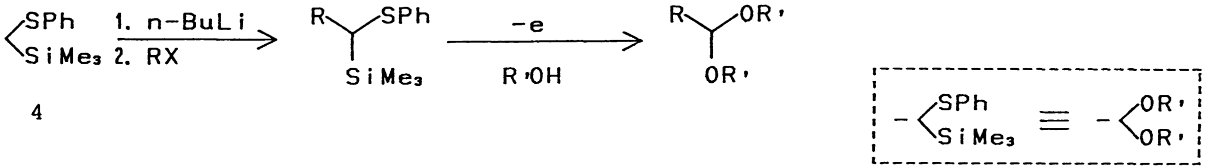
The present reaction is also interesting from a synthetic point of view, because 1-phenylthio-1-trimethylsilylalkanes were easily prepared by the alkylation of phenylthiotrimethylsilylmethyllithium.[10] Thus 1-phenylthio-1-

Table 1. Electrochemical Oxidation of 1-Phenylthio-1-trimethylsilylalkanes [a]

Substrate	Alcohol	Electricity (F/mol)	Product	Yield/% [b]
 $C_8H_{17}\underset{\mid \atop Si(CH_3)_3}{C}HSPh$ 1	CH_3OH	4.13	$C_8H_{17}CH(OCH_3)_2$ 3	84
	$HO(CH_2)_2OH$ [c]	4.16		60
	$HO(CH_2)_3OH$ [d]	4.61		46
 $C_7H_{15}CH{=}CHCH_2\underset{\mid \atop Si(CH_3)_3}{C}HSPh$	CH_3OH	4.21	$C_7H_{15}CH{=}CHCH_2CH(OCH_3)_2$	64
	CH_3OH	3.96		81
	CH_3OH	3.59		81

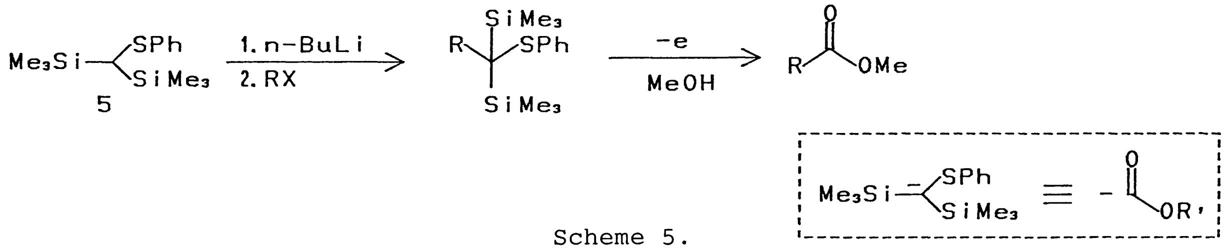
a) Reactions were usually carried out with 0.3-0.5 mmol of 1-phenylthio-1-trimethylsilylalkanes in 1.5 ml of 0.2 M Et_4NOTs/CH_3OH at room temperature. b) Isolated yields. c) 18.5 equiv. of 1,2-dihydroxyethane was used in 1.5 ml of 0.2 M Et_4NOTs/CH_3CN. d) 14.2 equiv. of 1,3-dihydroxypropane was used in 1.5 ml of 0.2 M Et_4NOTS/CH_3CN.

trimethylsilylmethane (**4**) was lithiated with n-butyllithium/tetramethylethylenediamine (TMEDA) in hexane at 0 °C and thus generated anion was allowed to react with alkyl halides or epoxides. The combination of this alkylation reaction with the present electrochemical oxidation provides a synthetic equivalent of the anion of 1,1-dialkoxymethane (Scheme 4).



Scheme 4.

Success of the present reaction prompted us to examine the electrochemical oxidation of sulfides having two trimethylsilyl groups at the carbon bearing sulfur. Thus 1-phenylthio-1,1-bis(trimethylsilyl)methane (**5**), prepared by lithiation of **4** followed by trapping with chlorotrimethylsilane, was treated with n-butyllithium/TMEDA in hexane at 0 °C and the resulting anion was trapped with alkyl halides (RX) to give the corresponding 1-phenylthio-1,1-bis(trimethylsilyl)alkanes (RX = $C_{12}H_{25}Br$, 55%; RX = $C_8H_{17}Br$, 73%). Electrochemical oxidation of thus obtained 1-phenylthio-1,1-bis(trimethylsilyl)alkanes proceeded smoothly in methanol to give the corresponding methyl esters (R = $C_{12}H_{25}$, 11.5 F/mol, 81%; R= C_8H_{17}, 9.83 F/mol, 72%). Therefore **5** provides a synthon of the anion of $C(=O)OCH_3$ (Scheme 5).



Scheme 5.

References

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2) T. Koizumi, T. Fuchigami, and T. Nonaka, Chem. Express, 1, 355 (1986).

3) J. Yoshida, T. Murata, and S. Isoe, Tetrahedron Lett., 27, 3373 (1986).

4) M. Kira, H. Nakazawa, and H. Sakurai, Chem. Lett., 1985, 1845.

5) M. A. Brumfield, S. L. Quillen, U. C. Yoon, and P. S. Mariano, J. Am. Chem. Soc., 106, 6855 (1984); M. Kira, H. Nakazawa, and H. Sakurai, Chem. Lett., 1986, 497.

6) α-Acetoxylation of organic sulfides by electrochemical oxidation has been reported: J. Nokami, M. Hatate, S. Wakabayashi, and R. Okawara, Tetrahedron Lett., 21, 2557 (1980). See also, T. Fuchigami, Y. Nakagawa, and T. Nonaka, ibid., 27, 3869 (1986).

7) The oxidation potential of allylsilanes are lower by 0.5-0.6 V than those of the parent π-system, see Refs. 2 and 3.

8) A small amount of the starting material (**1**) remained unchanged.

9) Cleavage of the carbon-sulfur bond catalyzed by electrogenerated acid seems to be less likely, because passing of a catalytic amount of electricity (ca. 0.4 F/mol based upon **2**) followed by standing overnight resulted in only a small increase in the amount of **3**. Most of **2** remained unchanged. Electrochemical cleavage of carbon-sulfur bond has been reported by Uneyama and Torii: K. Uneyama and S. Torii, Tetrahedron Lett., 1971, 329.

10) D. J. Ager and R. C. Cookson, Tetrahedron Lett., 21, 1677 (1980); P. J. Kocienski, ibid., 21, 1559 (1980).

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