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# Novel desilylation of *alpha*-dimethylsilyl esters by electrochemically generated superoxide ion

Christos Kaimakliotis and Albert J. Fry*

*Chemistry Department, Wesleyan University, Middletown, CT 06459, USA*

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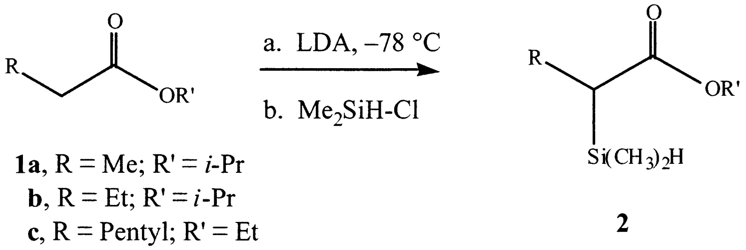
**Abstract**—Electrochemical reduction of oxygen in the presence of an *alpha*-dimethylsilyl ester results in removal of the dimethylsilyl group. The reaction presumably proceeds by a mechanism involving electrochemically-generated superoxide ion.

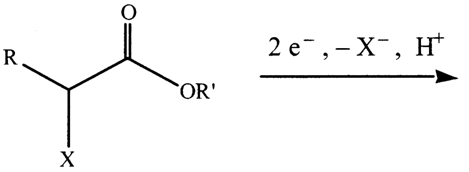
As part of a series of investigations into the electrochemical behavior of organosilanes,[1–3] we have synthesized a series of *alpha*-dimethylsilyl esters (**2**) (Eq. (1)).[4] Although our initial interest was in other facets of the chemistry of these substance, it was of interest to examine their cathodic behavior. As we have earlier pointed out,[5,6] the ease of electrochemical removal of the *alpha*-substituent of *alpha*-*X*-substituted carbonyl compounds, including esters, (Eq. (2)) is directly related to the leaving group ability of $X^-$, i.e. the acidity of HX.



**1a**, R = Me; R' = *i*-Pr
**b**, R = Et; R' = *i*-Pr
**c**, R = Pentyl; R' = Et
**d**, R = $C_6H_5CH_2$; R' = Me

**2**

(1)



**1**

(2)

In view of the highly basic nature of silyl anions,[7,8] it should not be possible to desilylate species **2** by direct cathodic cleavage of the carbon–silicon bond. Furthermore, esters themselves are reduced only at very negative potentials[6] and the electron-supplying silyl substituent should reinforce the resistance of the carbonyl group of **2** to reduction by cathodic electron transfer. Indeed, cyclic voltammograms of the *alpha*-silyl esters **2** in nitrogen-purged acetonitrile containing 0.1 M $Bu_4N^+BF_4^-$ exhibit no reduction current at any potential before solvent discharge (Fig. 1, curve **A**). A cyclic voltammogram of acetonitrile saturated with oxygen, on the other hand, exhibits the well-known[9] reversible wave due to reduction of oxygen to superoxide (curve **B**) at −1.3 V versus the $Ag/AgNO_3$ reference electrode.[10] Addition of any one of the silyl esters **2** to the solution of voltammogram **B** results in both an increase in the height of the reduction wave and elimination of the anodic wave for reoxidation of superoxide (curve **C**). We interpret this to be due to an ECE process involving reaction of superoxide with **2**. The nature of the current-consuming process was established by preparative controlled-potential or constant electrolysis in acetonitrile at the oxygen reduction potential while bubbling air through the solution. In every case, conversion to the parent ester (**1**) took place cleanly and in 95–100% yield. Although superoxide can

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* Corresponding author. Tel.: 860-685-2622; fax: 860-685-2211; e-mail: afry@wesleyan.edu

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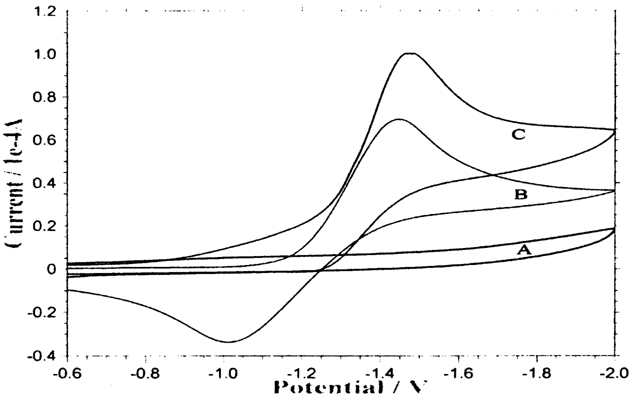


**Figure 1.** Curve A: cyclic voltammogram of 2 mM silyl ester **2a** in acetonitrile/0.1 M tetrabutylammonium tetrafluoroborate at a glassy carbon electrode versus Ag/0.1 M $AgNO_3$ (scan rate 100 mV/s). Curve B: cyclic voltammogram of oxygen-saturated acetonitrile under the conditions of curve A. Curve C: same as curve B with 2 mM **2a** added.

cleave esters,[11,12] this did not take place under our reaction conditions (acetonitrile, room temperature).[13,14]

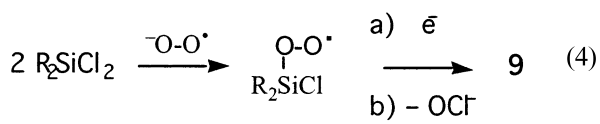
We suggest the mechanism of Scheme 1 for the conversion of **2** into **1**. In aprotic media oxygen is reduced to superoxide ion ($O_2^{-\bullet}$).[9] Addition of superoxide ion to the silicon atom of **2** would afford pentacovalent intermediate **3**. Decomposition of **3** into a silylhydroperoxy species (**4**) and enolate (**5**), followed by protonation of **5**, would lead to **2**. Reduction of **4** to the $SiMe_2HOO^-$ anion (**6**) and attack of **6** upon a second molecule of **1** would result in a second desilylation. A possible variant on this mechanism would be fragmentation of **3** into **6** and a carbonyl-substituted radical (**8**), followed by reduction of **8** to **5**.

Sufficient oxygen is available in the solution to sustain the stoichiometry of Scheme 1. The solubility of oxygen in acetonitrile at room temperature is 8.1 mM,[9] whereas the concentration of silane in the voltammetric experiment was only 2 mM. The concentration of silane was higher (62 mM) in the preparative experiment, but oxygen was continually bubbled through the solution to maintain a saturated solution throughout.

A reviewer raised the question whether *alpha*-trialkylsilyl esters would also undergo this transformation. Because there is no good synthetic route to such substances, we are unable to answer this question with certainty. We believe, however, that they would, since we do not believe that Si–H bond breakage is involved in this transformation. GC–Mass spectrometry showed that in addition to **1**, a substance whose mass and fragmentation pattern correspond to that of *bis*-[dimethylsilyl] ether (**7**) was also produced, but it was too volatile to isolate from the mixture.

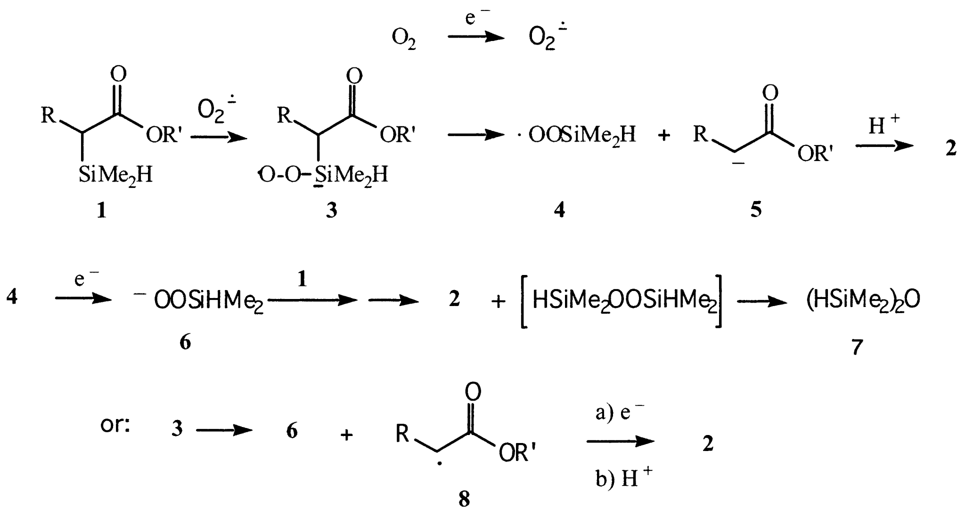
This oxygen-mediated desilylation process has no close precedent. However, Fattakhova, et al., have shown that cathodic reduction of oxygen in the presence of a dialkyldichlorosilane or diaryldichlorosilane leads to the production of cyclosiloxanes (**10**), apparently via intermediate silanones (**9**) (Eq. (3)).[15] The reaction producing **9** could also involve a pentacovalent intermediate formed by addition of superoxide ion to the central silicon atom (Eq. (4)).

$$R_2SiCl_2 \xrightarrow{e^-,\, O_2} \underset{\mathbf{9}}{\left[ R_2Si{=}O \right]} \longrightarrow \underset{\mathbf{10}}{(R_2Si{=}O)_n} \qquad (3)$$

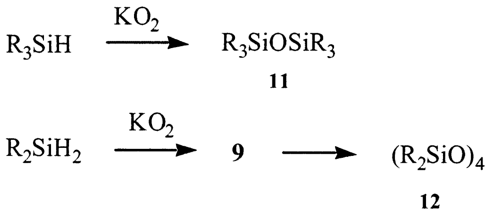


$$2\ R_2SiCl_2 \xrightarrow{^{-}O\text{-}O^{\bullet}} \underset{R_2SiCl}{\overset{O\text{-}O^{\bullet}}{|}} \xrightarrow[\text{b) } -\,OCl^-]{\text{a) } e^-} \mathbf{9} \qquad (4)$$

In an apparently related process, Park, et al., reported that reaction of trialkylsilanes with potassium superoxide in acetonitrile affords hexaalkyldisiloxanes (**11**) while dialkylsilanes were found to afford primarily tetracyclosiloxanes (**12**), presumably via silanones (**9**) (Scheme 2).[16]



**Scheme 1.**



$$R_3SiH \xrightarrow{KO_2} \underset{\textbf{11}}{R_3SiOSiR_3}$$

$$R_2SiH_2 \xrightarrow{KO_2} \textbf{9} \longrightarrow \underset{\textbf{12}}{(R_2SiO)_4}$$

**Scheme 2.**

## Acknowledgements

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13. Representative preparative electrolysis: Electrolyses were carried out in a divided electrolysis cell of standard design[14] using Union Carbide X2014 WCA grade carbon cloth anode and cathode of 4 $cm^2$ area each. The anode compartment contained 75 mL of 0.1 M 0.1 M $Bu_4N^+$ $BF_4^-$ in acetonitrile; the cathode compartment contained 50 mL of 0.1 M $Bu_4N^+BF_4^-$ in DMF above a methylcellulose gel[14] to prevent mass transfer through the coarse frit dividing the two compartments. One gram (4.63 mmol) of ester **1c** was added to the cathode compartment and electrolysis was commenced at −1.4 V versus Ag/0.1 M $AgNO_3$ (using a Bioanalytical Systems PWR-3 potentiostat) for controlled-potential electrolyses or at 100 mA (using a Kepco ATE 150-0.7M power supply) for constant current electrolyses. When the calculated current (one Faraday per mole of silyl ester) had been passed, the reaction mixture was evaporated, the residue extracted with hexane, and the hexane evaporated to afford 0. 72 gm (4.6 mmol, 99% yield) of colorless liquid. Its mass spectrum, GC retention time, and 300 MHz $^1H$ NMR spectrum were identical to those of an authentic sample of ethyl heptanoate (**1c**) prepared by esterification of heptanoic acid. Esters **1a**, **1b**, and **1d** were produced in 95, 97, and 100% yield, respectively, using the same procedure. GC-mass spectrometry also demonstrated the formation of a substance of mass 134, believed to be bis-[dimethylsilyl] ether (**7**), but this material was lost during evaporation of the electrolysis mixture.
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