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ANODIC OXIDATION OF 2-ALKYL 2 TRIALKYLSILYL-1, 3 DITHIANES A FACILE PREPARATION OF ACYLSILANES

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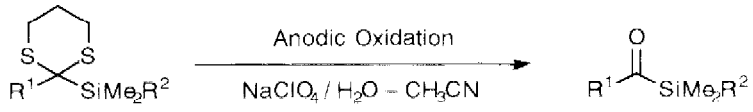
Abstract: Acylsilanes can easily be prepared by the anodic oxidation of 2-alkyl-2 trialkylsilyl-1, 3-dithianes with a platinum anode in wet acetonitrile. This electrochemical reaction provides a general and convenient access to aroyl, saturated and α, β-unsaturated acylsilanes.

Acylsilanes are interesting class of compounds with unique reactivities and have recently been accepted as valuable intermediates in synthetic organic chemistry.[1] Although several synthetic methods have been developed for acylsilanes,[1, 2] the methods with facility and generality are very much limited. Among these methodologies, "dithiane route", originally proposed by Seebach and Corey and by Brook, is known to be one of the most general access to aroyl and saturated acylsilanes.[1, 3] However, this route is unfavorable for the synthesis of α, β-unsaturated acylsilanes.[1, 4] We wish to report here the anodic oxidation of 2-alkyl-2-trialkylsilyl-1, 3-dithianes (**1**) to give acylsilanes (**2**) in excellent yields under very mild conditions (Scheme 1).[5, 6] This electrochemical transformation of **1** to **2** can easily be applied to the synthesis of aroyl, saturated and α, β-unsaturated acylsilanes.



1 **2**

Scheme 1

Substrates **1** were obtained by silylation of 2-alkyl-1, 3-dithianes.[7] General procedure for the electrochemical preparation of **2** is as follows: A solution of **1** (3 mmol) in 40 ml of wet acetonitrile (5 v/v % of H_2O) containing $NaClO_4$ (0.25 M) was placed in an undivided electrolysis cell equipped with a platinum plate anode and a platinum plate cathode. The system was subjected to a constant current electrolysis (300 mA; current density, *ca.* 20 mA/cm^2) at ambient temperature. After 4 faradays per mol of **1** had been consumed, the electrolyzed solution was poured into water (50 ml) and extracted with CH_2Cl_2 (30 ml × 3). The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica-gel to afford **2**. The results are summarized in Table 1.

The electrolysis of **1a**, **1b**, **1c** and **1d** gave saturated acylsilanes **2a**, **2b**, **2c** and aroyl acylsilane **2d**, respectively, in high yields. Acylsilane **2e** having a terminal olefin was also prepared easily from **1e**. Under the same conditions described above, the electrolyses of 3-methy-2-butenal derivative, **1f**, and (*E*)-nonenal derivative,

(*E*)-**1g**, afforded α, β-unsaturated acylsilanes **2f** and (*E*)-**2g**, respectively, in good yields. On the electrolysis of (*E*)-**1g**, (*E*)-**2g** was the only isomer isolated and no corresponding *Z* isomer could be detected in the ^{1}H-NMR spectrum of the crude reaction products.[8] Thus, the stereochemistry of the starting aldehyde is kept over all the processes. Recently, it has been reported that electrochemical oxidation of organosilicon compounds bearing a silicon and a heteroatom or a π-system on the same carbon brings about the carbon–silicon bond cleavage and introduction of oxygen or nitrogen nucleophiles into the carbon.[9] In the anodic oxidation of **1**, however, no such a product was obtained under the experimental conditions.

It is interesting to note that the formation of **2** is affected by the anode materials used. For example, the electrolysis of **1a** with a platinum plate anode gave **2a** in 95 % yield, while with a glassy carbon plate the yield of **2a** decreased to 25 %. The detailed mechanism and further applications of the electrochemical transformation of **1** to **2** are now under investigation.

Table 1 Electrochemical Preparation of 2

	Acysilanes (2)	Yields (%)[a]		Acylsilanes (2)	Yields (%)[a]
a	$Me_3SiCO(CH_2)_2Ph$	95	**e**	$Me_3SiCO(CH_2)_8CH{=}CH_2$	73
b	t-$BuMe_2SiCOCH_3$	76	**f**	$Me_3SiCOCH{=}CMe_2$	70
c	$Me_3SiCO(CH_2)_8CH_3$	88	**g**	$Me_3SiCOCH{=}CH(CH_2)_5CH_3$ ((*E*)-isomer)	84
d	$Me_3SiCOPh$	96			

[a] Isolated yields based on **1**.

References and Notes

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3. (a) Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431. (b) Corey, E. J.; Seebach, D.; Freedman, R. *Ibid.* **1967**, *89*, 434.
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5. A portion of this work has been presented at the 110th Annual Meeting of the Pharmaceutical Society of Japan, Sapporo, August, 1990.
6. Electrochemical deprotection of 1, 3-dithioacetals has been reported: (a) Martre, A. M.; Mousset, G. *Tetrahedron Lett.* **1990**, *31*, 2599; (b) Platen, M.; Steckhan, E. *Tetrahedron Lett.* **1980**, *21*, 511; and references cited therein.
7. 2-Alkyl-1, 3-dithianes are generally prepared by the following two routes: Protection of aldehydes with 1, 3-propanedithiol (Marshall, J. L.; Belletive, J. L. *Tetrahedron Lett.* **1971**, 871) and alkylation of the anion of 1, 3-dithiane (Page, P. C. B.; Niel, M. B.; Prodger, J. C. *Tetrahedron* **1989**, *45*, 7643 and references cited therein).
8. The configuration of the double bond in compound **2f** was established by comparison of its ^{1}H-NMR data with that of the related compound, *viz.*, (*E*)-(2-undecenoyl)trimethylsilane, reported in ref. 2 (a).
   2f: IR (neat) 1580 cm^{-1} (C=O); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.23 (s, 9 H), 0.84 – 0.89 (m, 3 H), 1.27 – 1.46 (m, 8 H), 2.18 – 2.26 (m, 2 H), 6.18 (dt, J = 16.2 and 1.3 Hz, 1 H), 6.74 (dt, J = 16.2 and 6.9 Hz, 1 H).
9. (a) Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962; (b) Koizumi, T.; Fuchigami, T.; Nonaka, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 219; and references cited therein.

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