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Electrochemical Oxidation of Acylsilanes and Their Tosylhydrazones

Jun-ichi Yoshida,* Masanori Itoh, Shin-ichiro Matsunaga, and Sachihiko Isoe*

Institute of Organic Chemistry, Faculty of Science, Osaka City University, Sugimoto 3-3-138, Sumiyoshi, Osaka 558, Japan

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Oxidation potentials of acylsilanes were found to be much less positive than those of ketones and aldehydes. The effect of silicon is attributed to the rise of the HOMO level by the interaction between the C–Si σ orbital and the nonbonding p orbital of the carbonyl oxygen which in turn favors the electron transfer. Preparative electrochemical oxidation of acylsilanes proceeded smoothly, giving rise to facile cleavage of the C–Si bond and the introduction of nucleophiles such as alcohols, water, and carbamates onto the carbonyl carbon. Electrochemical properties of tosylhydrazones of acylsilanes were also investigated. A decrease in oxidation potential of tosylhydrazones caused by silyl substitution was found to be smaller than that for carbonyl compounds. Preparative electrochemical oxidation of tosylhydrazones of acylsilanes gave the corresponding nitriles with consumption of a catalytic amount of electricity.

Introduction

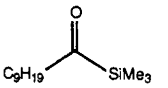
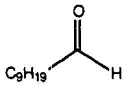
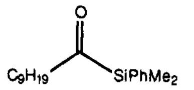
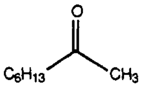
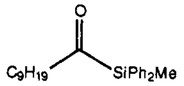
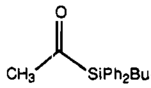
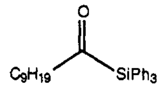
Since Brook reported that carbonyl compounds having a silyl group at the carbonyl carbon exhibit unusual reactivity,[1] increasing attention has been paid to the chemistry of acylsilanes.[2] Because of their unique reactivity, acylsilanes have recently been utilized as useful intermediates in organic synthesis.[3]

Acylsilanes exhibit interesting ultraviolet and visible spectroscopic behavior.[4] The n → π^* excitation of alkyl acylsilanes occurs around 370 nm, a shift of about 100 nm to longer wave length compared with the analogous ketones. According to the study of ionization potentials and molecular orbital calculations, this large shift can be explained in terms of the high energy of the n level.[5]

Recently, silicon has been found to promote the electron-transfer reactions from a heteroatom such as oxygen at the β position.[6] This β-effect of silicon is mainly attributed to the interaction of the carbon–silicon σ orbital and nonbonding p orbital of the heteroatom which in turn raises the HOMO level. On the basis of this concept, several new synthetically useful reactions of silyl-substituted ethers have been developed.[7]

Since acylsilanes also have a heteroatom β to silicon, we envisioned that the concept of the silicon β-effects in electron-transfer reactions is also applicable to acylsilanes. This is indeed the case. The preliminary report from this laboratory disclosed that oxidation potentials of acylsilanes are much less than those of the corresponding ketones and aldehydes. Silicon promotes the electron transfer from the carbonyl oxygen. We also found that the electrochemical oxidation gave rise to facile cleavage of the carbon–silicon bond and introduction of a nucleophile onto the carbonyl carbon.[8] We now report herein the full details of electrochemical oxidation of acylsilanes. We have also investigated the electrochemical behavior of acylsilane tosylhydrazones which have a nitrogen atom β to silicon.

Table I. Oxidation Potentials of Acylsilanes and Related Compounds[a]

compd	E_d[b]	$E_{1/2}$	compd	E_d[b]	$E_{1/2}$
	1.23	1.37		> 2.0	–[c]
	1.24	1.38		> 2.0	–[c]
	1.27	1.40		1.60	–[c]
	1.35	1.46			

[a] Determined by rotating-disk-electrode voltammetry in 0.1 M $LiClO_4/CH_3CN$. Glassy carbon electrode was used as the working electrode. Ag/AgCl electrode was used as the reference electrode. Sweep rate was 10 mV/s. [b] Decomposition potential. [c] It was impossible to determine $E_{1/2}$.

Results and Discussion

Oxidation Potentials. Pioneering work on oxidation potentials of acylsilanes has been carried out by Mochida and Yamamoto et al.[9] They reported that benzoyltrimethylsilane exhibits an oxidation wave at a peak potential of 1.88 V vs Ag/AgCl, which is slightly less than the peak potential of phenyl *tert*-butyl ketone (1.96 V). Contrary to very the small effects of silicon in aromatic system, we found that oxidation potentials of aliphatic carbonyl compounds decreased significantly by silyl substitution (Table I). For example, the half-wave potential for oxidation of decanoyltrimethylsilane was found to be 1.37 V vs Ag/AgCl, whereas decanal and 2-octanone did not show oxidation peaks at potentials less than 2.0 V.

It is interesting to note that the silicon effect in acylsilanes is larger than that in silyl-substituted ethers in which the C–Si σ orbital can also interact significantly with the lone pair of the oxygen. In the case of silyl-substituted ethers, the rotation around the C–O bond is free, and therefore, the C–Si bond and the oxygen lone pair do not

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(1) Brook, A. G. *J. Am. Chem. Soc.* **1957**, *79*, 4373–4375.

(2) Reviews: (a) Page, P. C. B.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147–195. (b) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77–84.

(3) Review: Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647–660.

(4) (a) Brook, A. G.; Quigley, M. A.; Peddle, G. J. D.; Schwartz, N. V.; Warner, C. M. *J. Am. Chem. Soc.* **1960**, *82*, 5102–5106. (b) Harnish, D. F.; West R. *Inorg. Chem.* **1963**, *2*, 1082–1084.

(5) (a) Bock, H.; Alt, H.; Seidl, H. *J. Am. Chem. Soc.* **1969**, *91*, 355–361. (b) Ramsey, B. G.; Brook, A.; Bassindale, A. R.; Bock, H. *J. Organomet. Chem.* **1974**, *74*, C41–C45.

(6) Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962–1970 and references cited therein.

(7) Yoshida, J.; Matsunaga, S.; Murata, T.; Isoe, S. *Tetrahedron* **1991**, *47*, 615–624 and references cited therein.

(8) Yoshida, J.; Matsunaga, S.; Isoe, S. *Tetrahedron Lett.* **1989**, *30*, 5293–5296.

(9) Mochida K.; Okui, S.; Ichikawa, K.; Kanakubo, O.; Tsuchiya, T.; Yamamoto, K.; *Chem. Lett.* **1986**, 805–808.

0022-3263/92/1957-4877$03.00/0

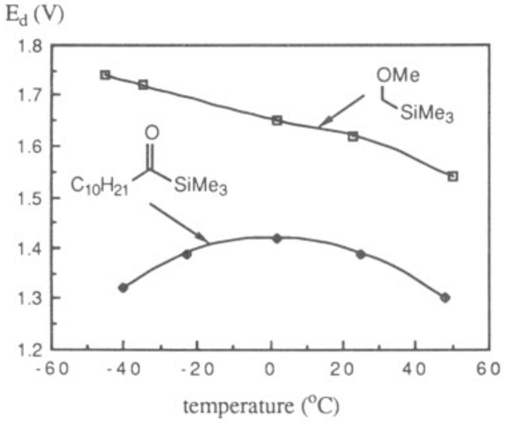


Figure 1. Temperature dependence of oxidation potentials (E_d, decomposition potentials) of methoxy(trimethylsilyl)methane and undecanoyltrimethylsilane.

always overlap effectively. In the case of acylsilanes, however, the C–Si bond and the oxygen lone pair are fixed in the same plane, and therefore, they can always interact quite effectively. Thus, acylsilanes are more susceptible to oxidation than are silyl-substituted ethers.

Substituents on silicon have some effect on oxidation potentials. Substitution of a methyl group by a phenyl group causes a small increase in oxidation potential.[10] Effects of substitution by a *tert*-butyl group are remarkable. The electron-donating effect of the *tert*-butyl group does not seem to account for this effect. Presumably the *tert*-butyl group retards the nucleophilic attack on silicon in the cation radical intermediate (vide infra). Since the oxidation potentials of irreversible systems are known to be a function of the rates of subsequent chemical reactions, a slower rate of the C–Si bond cleavage seems to be responsible for the increase of the electrochemical oxidation potential of the *tert*-butyl-substituted acylsilane.

Since significant temperature dependence was observed for the oxidation potentials of silyl-substituted ethers,[6] the temperature dependence of oxidation potentials of acylsilanes was studied. The oxidation potentials of silyl-substituted ethers decrease with increasing temperature. In contrast, the temperature dependence of the oxidation potentials of acylsilanes is complicated. The oxidation potential increases with temperature below 0 °C and then decreases with temperature above 0 °C. In the case of silyl-substituted ethers, the energy barrier of rotation around the C–O bond is relatively low. Therefore, at the higher temperatures the electron transfer takes place at the conformer which is suitable for electron transfer whereas at the low temperatures the molecule is fixed to the most stable conformation which is not suitable for electron transfer (the C–Si bond and the oxygen lone pair are in perpendicular orientation). Thus, the oxidation potential decreases with increasing temperature. In the case of acylsilanes, however, the conformation with respect to rotation around the C–O double bond seems to be fixed at any temperature we studied, because the rotational barrier of the C–O double bond is very large. So other factors seem to be responsible for this interesting behavior. Entropy effects and the rates of subsequent chemical reactions might be candidates but we are not able to get clear insight of this interesting phenomenon.

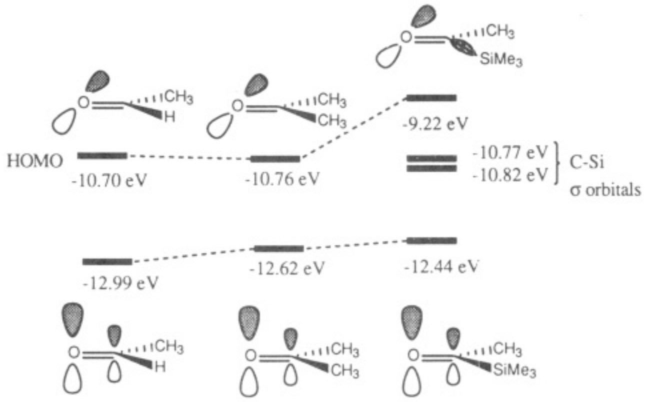


Figure 2. Energy-level diagrams of HOMO of acetaldehyde, acetone, and acetyltrimethylsilane obtained by PM3 calculations. The contributions from CH_3 parts are omitted.

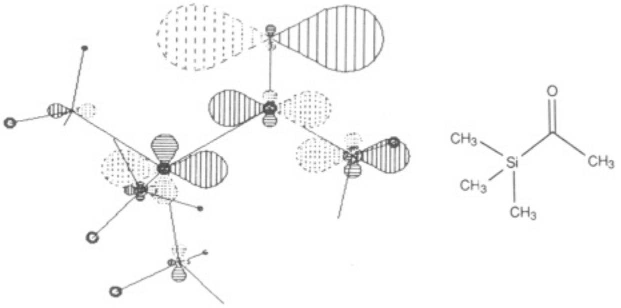
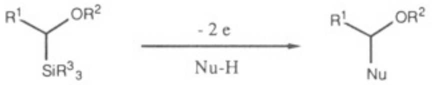


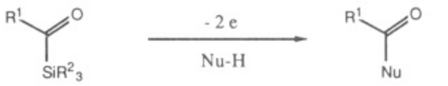
Figure 3. MOLMOL[14] display of HOMO of $CH_3COSiMe_3$ obtained by the PM3 calculation.

Molecular Orbitals. Since HOMO levels and ionization potentials can be corelated with electrochemical oxidation potentials,[11] we have carried out molecular-orbital calculations of acylsilanes.[12] The energy-level diagram of the HOMO of acylsilanes and related compounds obtained by the PM3 method[13] is shown in Figure 2. In the case of the aliphatic carbonyl system, silyl substitution causes a significant increase in the energy of HOMO. It is also noteworthy that the HOMO of acylsilane is no longer localized on the lone pair of the oxygen but is delocalized to the C–Si bond (Figure 3). This result is consistent with the results obtained by CNDO calculations and photoelectron spectroscopic studies reported in the literature.[5b] Therefore, the decrease in oxidation potential observed for aliphatic acylsilanes is attributed to the rise of the HOMO level by the interaction of the C–Si bond and the lone pair of the carbonyl oxygen.

Preparative Electrolysis. Electrochemical oxidation of silyl-substituted ethers results in the facile cleavage of the carbon–silicon bond and the introduction of a nucleophile such as methanol onto the carbon (eq 1). The present study of oxidation potentials of acylsilanes revealed



(1)



(2)

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[10] Substitution of a methyl group on germanium of acylgermanes by a phenyl group also causes a increase in oxidation potentials.[9]

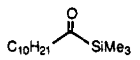
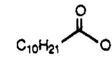
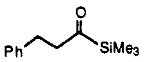
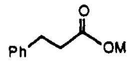
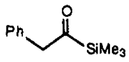
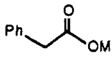
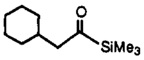
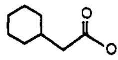
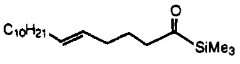
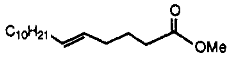
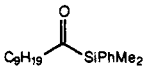
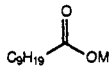
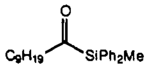
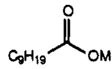
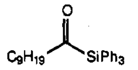
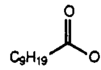
[11] (a) Gardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 1855–1865. (b) Mochida, K.; Itani, A.; Yokoyama, M.; Tsuchiya, T.; Worley, S. D.; Kochi, J. K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2149–2150.

[12] Molecular-orbital calculations of acylsilanes at various levels have been reported. For example: Nadler, E. B.; Rappoport, Z.; Arad, D.; Apeloig, Y. *J. Am. Chem. Soc.* **1987**, *109*, 7873–7875. See also ref 5.

[13] MOPAC Ver. 5, Stewart, J. J. P., QCPE No. 455. Revised as Ver. 5.01 by Tsuneo Hirano, University of Tokyo, for HITAC and Unix machines, *JCPE Newsletter*, **1989**, *1*, 36. Revised as Ver. 5.02 by Jun-ichi Yoshida, Osaka City University, for NDP Fortran.

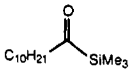
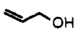
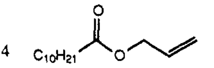
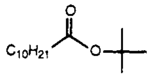
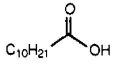
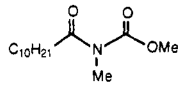
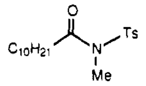
[14] MOLMOL, Tsueneo Hirano, University of Tokyo, JCPE Newsletter.

Table II. Electrochemical Oxidation of Acylsilanes in Methanol[a]

acylsilane	product	quantity of electricity (F/mol)	yield[b] (%)
		2.1	90
		2.2	80
		2.3	83
		2.0	76
		2.1	80
		2.4	76
		2.4	77
		2.4	87

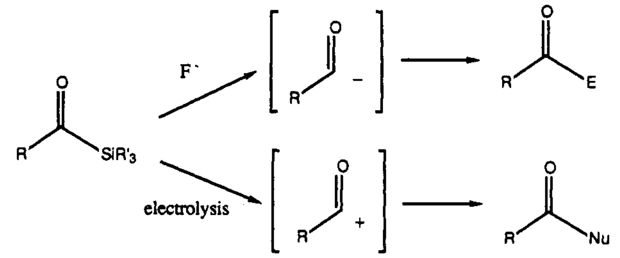
[a] Electrolyses were normally carried out with 0.5–0.6 mmol of an acylsilane in 2 mL of Et_4NOTs/MeOH (0.2 M) in an undivided cell equipped with carbon rod anode and cathode at room temperature (method A). [b] Isolated yields.

Table III. Electrochemical Oxidation of Acylsilanes in the Presence of Various Nucleophiles in Dichloromethane[a]

acylsilane	nucleophile	method	quantity of electricity (F/mol)	product	yield[b] (%)
		C	2.24		92
	t-BuOH	C	2.62		71
	H_2O	B	2.70		92
	$MeNHCO_2Me$	C	2.58		69
	MeNHTs	C	2.70		72

[a] Electrolyses were normally carried out with 0.5–0.6 mmol of a acylsilane with 5–6 equiv of a nucleophile in 0.2 M Bu_4NBF_4/CH_2Cl_2 in an undivided cell equipped with a carbon rod anode and a platinum plate cathode in the absence of molecular sieves 4A (method B) or in the presence of molecular sieves 4A (method C). [b] Isolated yields.

Scheme I



that acylsilanes were quite susceptible to anodic oxidation, whereas the corresponding aldehydes and ketones were relatively inactive under such conditions. Thus, we examined preparative electrochemical oxidation of acylsilanes. The reaction was carried out in an undivided cell equipped with a carbon rod anode and a carbon rod cathode. Tetraethylammonium *p*-toluenesulfonate was used as supporting electrolyte, and methanol was used as solvent (method A). The reaction took place smoothly, the carbon–silicon bond was cleaved, and methanol was introduced onto the carbonyl carbon. As shown in Table II, the corresponding methyl esters were obtained in high yields and high current efficiency. Phenyl group and olefinic carbon–carbon double bonds were not affected under the conditions.

The following mechanism seems reasonable. Initial one-electron oxidation of the acylsilane produces the cation radical intermediate. Attack of methanol at the silicon cleaves the carbon–silicon bond to give the acyl radical intermediate. The acyl radical is further oxidized to the acyl cation which reacts with methanol to give the corresponding methyl ester. Another explanation to be considered is as follows. In the cation radical intermediate the nucleophile attacks the carbonyl carbon rather than the silicon to give the alkoxy radical intermediate. The alkoxy radical then oxidized anodically to give the cation species β to silicon which undergoes elimination of silicon to give the final product.

In the electrochemical reaction in methanol, methanol was introduced onto the carbonyl carbon. Other nucleophiles were also found to be effective. Thus, the electrochemical reactions were carried out in the presence of allyl alcohols, 2-methyl-2-propanol, water, methyl *N*-methylcarbamate, and *N*-methyl *N*-*p*-toluenesulfonamide in a non-nucleophilic solvent, dichloromethane (methods B and C). The corresponding esters, carboxylic acids, and amide derivatives were obtained in good yields (Table III). Less hygroscopic tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) was used as the supporting electrolyte, and the reactions were usually carried out in the presence of molecular sieves 4A (method C), because a trace amount of water in the reaction medium would also act as a nucleophile.

Recently, acylsilanes have been utilized as useful reagents in organic synthesis.[3] For example, treatment of acylsilanes with fluoride ion generates the corresponding acyl anions which react with electrophiles, although there are some limitations with respect to the structure of acylsilanes.[15] On the other hand, in the present electrochemical method, acylsilanes serve as acyl cation equivalents because nucleophiles are introduced onto the carbonyl carbon.

Acylsilanes also serve as acyl cation equivalents for carbon nucleophiles. For example, the reaction of undecanoyltrimethylsilane with butyllithium gave the addition product, the α-hydroxysilane. Electrochemical oxidation of the α-hydroxysilane proceeded smoothly in methanol to give the corresponding ketone in high yields. Oxidation of silyl-substituted alcohols to the corresponding ketones can also be accomplished by PDC oxidation.[16] α-Hydroxysilanes can also be protected as α-methoxysilanes by alkylation if one employs sodium hydride and methyl iodide. α-Methoxysilanes are usually stable to acidic and basic conditions, and also chemical oxidations such as

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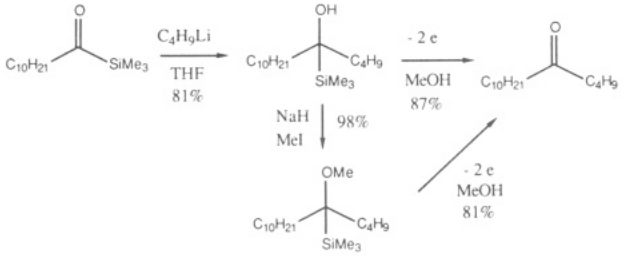
(15) (a) Page, P. C. B.; Rosenthal, S.; Williams, R. V. *Tetrahedron Lett.* **1987**, *28*, 4455–4456. (b) Schinizer, D.; heathcock, C. H. *Tetrahedron Lett.* **1981**, *22*, 1881–1884. (c) Degl'Innocenti, A.; Pike, S.; Walton, D. R. M.; Seconi, G.; Ricci, A.; Fiorenza, M. *J. Chem. Soc., Chem. Commun.* **1980**, 1201–1202.

(16) Trost, B. M.; Yoshida, J. *Tetrahedron Lett.* **1983**, *24*, 4895–4898.

Scheme II



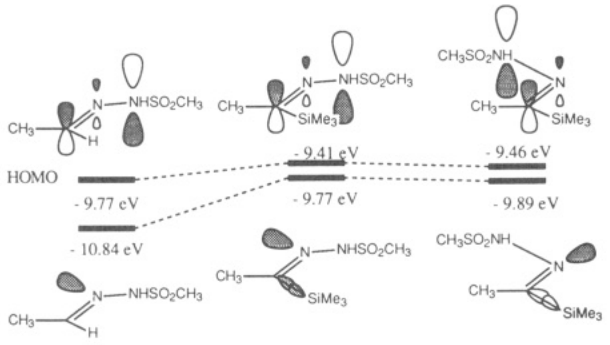


Figure 4. Energy-level diagram for mesylhydrazone and mesylhydrazones of acylsilanes.

Swern oxidation, but they readily converted to the corresponding carbonyl compounds by the electrochemical oxidation.[17] Therefore, acylsilanes serve as useful acyl cation equivalents for carbon nucleophiles. Since various methods for the synthesis of acylsilanes have been developed so far,[18] acylsilanes serve as useful acyl cation equivalents in the electrochemical oxidation.

Electrochemical Oxidation of Acylsilane Tosylhydrazones. Since silicon is also known to promote electron transfer from the nitrogen atom at the β position, as demonstrated by the facile electrochemical oxidation of silyl-substituted carbamates,[19] we investigated the electrochemical behavior of tosylhydrazones of acylsilanes which have a nitrogen atom β to silicon.

Tosylhydrazones of acylsilanes were readily prepared by the reaction of acylsilanes with tosylhydrazide in the presence of a catalytic amount of hydrochloric acid in ethanol.[20] Oxidation potentials of tosylhydrazones of acylsilanes were determined by means of rotating-disk-electrode voltammetry ($C_9H_{19}C(=NNHTs)SiMe_3$: E_d = 1.52 V vs Ag/AgCl) and were found to be more positive than those of the parent acylsilanes (Table I) and less positive than those of the tosylhydrazones of the corresponding aldehydes ($C_9H_{19}C(=NNHTs)H$: E_d = 1.72 V vs Ag/AgCl). Since oxidation potentials of tosylhydrazones of the aldehydes are much less than those of the parent aldehydes, silicon effects for tosylhydrazones are much smaller than those for the carbonyl compounds. These results are consistent with the fact that silicon β-effects for silyl-substituted ethers are greater than those for silyl-substituted amines and carbamates.[6]

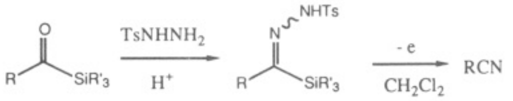
Molecular-orbital calculations are consistent with the experimental results. Methanesulfonylhydrazones of acetaldehyde and methanesulfonylhydrazones of acetyltrimethylsilane were chosen as models of tosylhydrazones and tosylhydrazones of acylsilanes, respectively. PM3 calculations[13] indicated that silyl substitution causes a relatively small decrease in ionization potentials as shown in Figure 4. The small silicon effect for hydrazones can be explained as follows. The HOMO of the hydrazone is mainly the linear combination of p_z orbitals of the carbonyl carbon and the two nitrogen atoms which are perpendicular to the C–Si bond;[21] therefore, silyl substitution causes little effect on the HOMO level.[22]

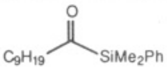
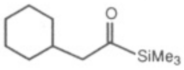
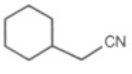
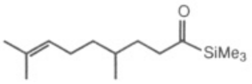
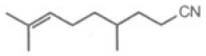
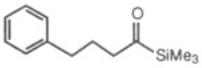
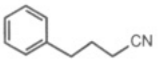
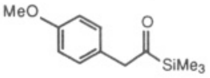
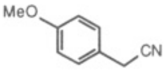
Table IV. Electrochemical Oxidation of Tosylhydrazone of Decanoylphenyldimethylsilane

condns	quantity of electricity (F/mol)	yield (%)
2 equiv of $MeOH/CH_2Cl_2$	3.2	45[b]
CH_2Cl_2	4.0	29
CH_2Cl_2 divided cell	1.8	90
THF	4.4	19

[a] Electrolyses were normally carried out in an undivided cell equipped with a carbon rod anode and a platinum plate cathode unless otherwise stated. [b] Methyl decanoate was also obtained in 11% yield.

Table V. Synthesis of Nitriles from Acylsilanes by Electrochemical Oxidation[a]



acylsilane	quantity of electricity (F/mol)	product	yield (%)
	0.26	$C_9H_{19}CN$	84
	0.80		81
	0.73		81
	0.63		72
	0.49		55

[a] The electrochemical reactions were carried out in a divided cell equipped with a carbon rod anode and a platinum plate cathode in Bu_4NBF_4/CH_2Cl_2.

Preparative electrochemical oxidation of tosylhydrazones of acylsilanes was studied (Table IV). The anodic oxi-

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(17) Yoshida, J.; Matsunaga, S.; Isoe, S. *Tetrahedron Lett.* **1989**, *30*, 219–222.

(18) Yoshida, J.; Matsunaga, S.; Ishichi, Y.; Maekawa, T.; Isoe, S. *J. Org. Chem.* **1991**, *56*, 1307–1309 and references cited therein. See also refs 1 and 3.

(19) Yoshida, J.; Isoe, S. *Tetrahedron Lett.* **1987**, *28*, 6621–6624.

(20) Brook, A. G.; Jones, P. F.; *Can. J. Chem.* **1969**, *47*, 4353–4358.

(21) Although ketones have a HOMO constructed largely from an unshared pair of oxygen (for example: Isaacs, N. S *Physical Organic Chemistry*, Longman Scientific & Technical: Essex, 1987; p 21), hydrazones have a HOMO constructed largely from three p orbitals, two of which form the C=N bond and the third contains the lone pair of electron of the amine nitrogen (Pacansky, J.; McLean, A. D.; Miller, M. D. *J. Phys. Chem.* **1990**, *94*, 90–98). The situation seems to be the same for silyl-substituted ketones (acylsilanes) and silyl-substituted hydrazones.

(22) The effect of the silyl substitution on the HOMO-1 orbital which is the in-plane lone pair of nitrogen should be noted. The orbital interaction of the C–Si σ bond and the in-plane lone pair of nitrogen increases the HOMO-1 level significantly. This effect is quite similar to the effect on the HOMO of acylsilanes which is the in-plane lone pair of the oxygen. The effect of silyl substitution is somewhat larger for oxygen than for nitrogen.

dation in dichloromethane in the presence of 2 equiv of methanol in an undivided cell equipped with a carbon anode and a platinum cathode afforded the corresponding nitrile and a small amount of the methyl ester. In the absence of methanol only the nitrile was obtained although the yield was low. The use of a divided cell resulted in a significant increase in the yield of the nitrile. In this case only a catalytic amount of electricity was required for completion of the reaction, suggesting a mechanism that is different from the mechanism for acylsilanes, although its detail has not been clearified as yet.

Tosylhydrazones of acylsilanes are relatively unstable and sometimes decompose during the purification. Therefore, we carried out the electrochemical oxidation of tosylhydrazones of acylsilanes immediately after their preparation without purification. This procedure worked well, and the corresponding nitriles were obtained in good yields from acylsilanes (Table V).

Bartoli et al. reported the conversion of acylsilanes to the corresponding nitriles by treatment with phenylhydrazine followed by reaction with PCl_3.[23] Mandai also found that reaction of acylsilanes with Ac_2O/pyridine gave the corresponding nitriles.[24] The present electrochemical method provides a useful alternative for such transformations.

Experimental Section

General Comments. Glass-support precoated (Merk silica gel 60 F_{254}, 0.25 mm) plates were employed for analytical TLC. Vapor-phase chromatography (VPC) was performed on a Shimadzu gas chromatograph equipped with a 2-m × 3-mm column packed with Silicone OV-1 (2%) on Chromosorb WAM DMCS. Proton NMR spectra were determined on a Hitachi R-90H spectrometer (90 MHz) or a JEOL JNM-GX-400 spectrometer (400 MHz). Carbon NMR spectra were determined on a JEOL JNM-GX-400 spectrometer. Infrared (IR) spectra were determined on a JASCO A-102 diffraction grating spectrophotometer. Mass spectra were obtained on a JEOL JMS-AX500 spectrometer; the ionization potential was 70 eV.

Preparation of Acylsilanes. Undecanoyltrimethylsilane was prepared by the reaction of decanal with the anion of methoxybis(trimethylsilyl)methane, followed by acid-catalyzed hydrolysis.[18] Decanoyltrimethylsilane, decanoylphenyldimethylsilane, decanoyldiphenylmethylsilane, and decanoyltriphenylsilane were prepared by the reaction of decanal with the corresponding silyllithium followed by Swern oxidation.[25] Acetyl-*tert*-butyldiphenylsilane was prepared by the reaction of ethyl vinyl ether with *tert*-butylchlorodiphenylsilane followed by acid-catalyzed hydrolysis.[26]

Rotating-Disk-Electrode Voltammetry. Rotating-disk-electrode voltammetry was carried out with a Nikko Keisoku RRDE-1 which was partially modified by ourselves and a Hokuto Potentiostat/Galvanostat HA-301 connected to a function generator Hokuto HB-104 with a Graphtec WX1000 X-Y plotter. We used an undivided cell equipped with a glassy carbon disk anode and a platinum wire cathode in 0.1 M $LiClO_4/CH_3CN$; a Ag/AgCl (saturated aqueous KCl) electrode was used as the reference electrode (−0.04 V vs SCE). The sweep rate was 10 mV/s.

Electrochemical Oxidation of Acylsilanes in Methanol. Method A. In an undivided cell equipped with a carbon rod anode and a carbon rod cathode were placed an acylsilane (0.3–0.7 mmol) and a 0.2 M solution of Et_4NOTs in methanol (2 mL). The reaction was carried out under constant-current conditions (10 mA). After most of the starting material was consumed, the reaction mixture was partitioned between brine and ether. The organic phase was separated, and the aqueous phase was extracted with ether several times. The combined organic phase and extracts were dried ($MgSO_4$). After removal of the solvent under reduced pressure, the crude product was purified via flash chromatography to obtain the corresponding methyl ester.

The electrochemical oxidation of decanoyltriphenylsilane was carried out in a mixture of MeOH and CH_2Cl_2(3:2) because the substrate did not dissolve in MeOH.

Method B. In an undivided cell equipped with a carbon rod anode and a platinum plate cathode were placed an acylsilane (0.3–0.7 mmol), a 0.2 M solution of Bu_4NBF_4 in dry dichloromethane, and a nucleophile (5–6 equiv). The reaction was carried out under constant-current conditions (10 mA) with rigorous protection from moisture (argon balloon). After most of the starting material was consumed, similar workup followed by flash chromatography afforded the corresponding product.

Method C. The same procedure as method B was used except that the reaction was carried out in the presence of molecular sieves 4A.

Spectral data for some products of the electrochemical oxidation of acylsilanes are given below. Other products were identified by comparison with their spectral data with those of authentic samples.

Methyl 5-hexadecenoate: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 3 H), 1.23–1.36 (m, 16 H), 1.69 (quint, J = 7.3 Hz, 2 H), 1.94–2.10 (m, 4 H), 2.30 (t, J = 7.3 Hz, 2 H), 3.66 (s, 3 H), 5.34 (dt, J = 15.3 and 6.7 Hz, 1 H), 5.42 (dt, J = 15.3 and 6.7 Hz, 1 H); IR (neat) 2930 (s), 2860 (s), 1740 (s), 1460 (m), 1440 (m), 1370 (w), 1310 (w), 1250 (w), 1200 (w), 1170 (m), 970 (m), 720 (w) cm^{-1}; low-resolution MS m/e 268 (M$^+$, 12), 236 (37), 194 (35), 152 (25), 96 (64), 84 (54), 74 (100), 69 (39), 55 (42); high-resolution MS calcd for $C_{17}H_{32}O_2$ 268.2402, found 268.2392.

***N*-(Methoxycarbonyl)-*N*-methylundecanamide**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.70–0.99 (br t, 3 H), 1.02–1.80 (m, 16 H), 2.88 (t, J = 7.5 Hz, 2 H), 3.17 (s, 3 H), 3.78 (s, 3 H); IR (neat) 2900 (s), 2850 (m), 1740 (s), 1700 (s), 1440 (m), 1320 (s), 1190 (m), 1150 (s), 1080 (w), 1010 (w), 920 (w), 780 (m) cm^{-1}; low-resolution MS m/e 257 (M$^+$, 1), 169 (7), 144 (36), 131 (100), 90 (19), 57 (14); high-resolution MS calcd for $C_{14}H_{27}NO_3$ 257.1991, found 257.1998.

***N*-(*p*-Toluenesulfonyl)-*N*-methylundecanamide**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 3 H), 1.21–1.33 (m, 14 H), 1.53–1.60 (m, 2 H), 2.44 (s, 3 H), 2.64 (t, J = 7.3 Hz, 2 H), 3.30 (s, 3 H), 7.34 (d, J = 8 Hz, 2 H), 7.77 (d, J = 8 Hz, 2 H); IR (neat) 2930 (s), 2860 (s), 1700 (s), 1600 (m), 1500 (w), 1460 (m), 1410 (w), 1360 (s), 1200 (w), 1160 (s), 1120 (w), 1090 (m), 1020 (w), 990 (w), 920 (m), 860 (w), 320 (m), 710 (w), 670 (m) cm^{-1}; low-resolution MS m/e 354 (M$^+$ + 1, 0.4), 352 (M$^+$ − 1, 0.3), 289 (1), 240 (2), 182 (100), 163 (5), 155 (5), 121 (6), 106 (8), 91 (8), 91 (8), 57 (11); high-resolution MS calcd for $C_{19}H_{32}NO_2S$ (M$^+$ + 1) 354.2103, found 354.2074; calcd for $C_{19}H_{30}NO_2S$ (M$^+$ − 1) 352.1946, found 352.1963.

5-Hydroxy-5-(trimethylsilyl)pentadecane. To a solution of undecanoyltrimethylsilane (356 mg, 2.71 mmol) in THF (10 mL) was added butyllithium/hexane (1.6 M, 2.0 mL, 3.2 mmol) at −78 °C. The mixture was stirred at −78 °C for 5 min, and methanol (2.0 mL) was added at the same temperature. After being warmed to room temperature, the mixture was partitioned between saturated aqueous NH_4Cl and ether. The organic phase was separated, and the aqueous phase was extracted with ether several times. The combined organic phase and extracts were dried ($MgSO_4$). After evaporation of the solvent, the crude product was purified via flash chromatography (hexane:ethyl acetate = 19:1) to obtain the title compound (0.659 g, 81%): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.05 (s, 9 H), 0.75–1.03 (m, 6 H), 1.12–1.68 (m, 24 H), 3.30 (br, 1 H); IR (neat) 3350 (br), 2920 (s), 2850 (m), 1640 (w), 1460 (w), 1250 (m), 840 (s), 750 (w) cm^{-1}; low-resolution MS m/e 300 (M$^+$, 0.2), 267 (4), 227 (22), 111 (37), 97 (80), 91 (71), 83 (100), 73 (98), 69 (84), 56 (57); high-resolution MS calcd for $C_{18}H_{40}OSi$ 300.2849, found 300.2870.

5-Methoxy-5-(trimethylsilyl)pentadecane. To a solution of sodium hydride (60% in oil, 62 mg, 1.55 mmol) in dry THF (3 mL) was added 5-hydroxy-5-(trimethylsilyl)pentadecane (273 mg, 0.908 mmol). Iodomethane (1.0 mL, 1.56 mmol) was added, and the mixture was stirred at reflux overnight. The mixture was partitioned between brine and ether. The organic phase was separated, and the aqueous phase was extracted with ether several times. The combined organic phase and extracts were dried

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[23] Bartoli, G.; Bosco, M.; Dalpozzo, R.; Marcantoni, E. *Tetrahedron Lett.* **1990**, *31*, 6935–6936.

[24] Mandai, T. Personal communication.

[25] Danheiser, R. L.; Fink, D. M.; Okano, K.; Tsai, Y.-M.; Szczepanski, S. W. *J. Org. Chem.* **1985**, *50*, 5393–5396.

[26] Dexheimer, E. M.; Spialter, L. *J. Organomet. Chem.* **1976**, 107, 229–233.

($MgSO_4$). After removal of the solvent under reduced pressure, the crude product was purified via flash chromatography (hexane:ethyl acetate = 39:1) to obtain the title compound (281 mg, 98%): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.09 (s, 9 H), 0.73–1.72 (m, 30 H), 3.20 (s, 3 H); IR (neat) 2920 (s), 2850 (m), 1460 (w), 1250 (m), 1090 (w), 1050 (w), 840 (m), 750 (w) cm^{-1}; low-resolution MS *m/e* 299 ($M^+ - CH_3$, 100), 89 (25), 73 (49); high-resolution MS calcd for $C_{18}H_{39}OSi$ ($M^+ - CH_3$) 299.2768, found 299.2751.

5-Pentadecanone. Electrochemical oxidation of 5-hydroxy-5-(trimethylsilyl)pentadecane and of 5-methoxy-5-(trimethylsilyl)pentadecane were carried out using method A to obtain the title compound in 87% and 81% yields, respectively: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.73–1.01 (m, 6 H), 1.03–1.72 (m, 20 H), 2.38 (t, J = 7.2 Hz, 4 H); IR (neat) 2990 (s), 1710 (m), 1460 (m), 1370 (w), 1120 (w), 720 (w) cm^{-1}; low-resolution MS *m/e* 226 (M^+, 6), 197 (4), 184 (10), 169 (42), 113 (18), 100 (38), 85 (74), 71 (310), 57 (100); high-resolution MS calcd for $C_{15}H_{30}O$ 226.2296, found 226.2326.

Decanoylphenyldimethylsilane Tosylhydrazone. To a mixture of decanoylphenyldimethylsilane (295 mg, 1.0 mmol) and tosylhydrazide (227 mg, 1.2 mmol) in 10 mL of ethanol was added concentrated hydrochloric acid (0.5 mL), and the mixture was stirred at room temperature for 10 min. The mixture was partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was separated, and the aqueous phase was extracted with ether several times. The combined organic phase and extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (hexane:ethyl acetate = 19:1) to obtain the title compound (318 mg, 69% yield): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.40 (s, 6 H), 0.73–1.43 (m, 17 H), 1.90–2.26 (m, 2 H), 2.43 (s, 3 H), 7.06–7.90 (m, 9 H), 8.07 (s br, 1 H); IR ($CHCl_3$) 2920 (s), 2850 (s), 1600 (w), 1460 (w), 1430 (w), 1370 (m), 1330 (w), 1250 (w), 1160 (s), 1110 (m), 1090 (w), 840 (w), 700 (w) cm^{-1}; low-resolution MS *m/e* 458 (M^+, 1), 443 (3), 346 (7), 323 (5), 303 (27), 290 (34), 259 (17), 228 (29), 150 (56), 135 (100), 121 (38), 91 (53); high-resolution MS calcd for $C_{25}H_{38}N_2O_2SSi$ 458.2423, found 458.2409.

Decanonitrile. Typical Procedure for the Electrochemical Oxidation of Tosylhydrazones of Acylsilanes. In the anode chamber of an H-type cell equipped with a carbon rod anode and a platinum plate cathode was placed a solution of decanoylphenyldimethylsilane tosylhydrazone (208 mg, 0.45 mmol) in 0.2 M Bu_4NBF_4/CH_2Cl_2 (7.5 mL). In the cathode chamber was placed 0.2 M Bu_4NBF_4/CH_2Cl_2 (7.5 mL). The electrolysis was carried out under constant-current conditions (10 mA). After the passage of 0.26 F/mol based upon the tosylhydrazone, most of the hydrazone was consumed. The solution in the anode chamber was partitioned between ether and saturated aqueous NaCl, and the organic phase was separated. The aqueous phase was extracted with ether several times. The combined organic phase and extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (hexane:ethyl acetate = 39:1) to obtain the title compound (62 mg, 90% yield). Spectral data for the product are described in the following section.

Decanonitrile. Typical Procedure for the Direct Conversion of Acylsilanes to Nitriles. To a mixture of decanoylphenyldimethylsilane (147 mg, 0.51 mmol) and tosylhydrazide (95 mg, 0.51 mmol) in ethanol (1.0 mL) was added concentrated hydrochloric acid (0.1 mL), and the mixture was stirred at room temperature for 10 min. The mixture was then partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was separated, and the aqueous phase was extracted with ether several times. The combined organic phase and extracts were dried ($MgSO_4$), and solvent was removed under reduced pressure. The crude tosylhydrazone thus obtained was placed in the anode chamber of an H-type cell equipped with a carbon rod anode and platinum plate cathode. Bu_4NBF_4/CH_2Cl_2 (0.2 M, 7.5 mL) was added to the anode chamber. In the cathode chamber was placed Bu_4NBF_4/CH_2Cl_2 (7.5 mL). The electrolysis was carried out under constant-current conditions (10 mA). After the passage of 0.26 F/mol based upon the tosylhydrazone, most of the hydrazone was consumed. The solution in the anode chamber was partitioned between ether and saturated aqueous NaCl, and the organic phase was separated. The aqueous phase was extracted with ether several times. The combined organic phase and extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (hexane:ethyl acetate = 39:1) to obtain the title compound (65 mg, 84% yield): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.70–1.83 (m, 17 H), 2.20–2.43 (m, 2 H); IR (neat) 2920 (s), 2850 (s), 2240 (m), 1460 (m), 1420 (m), 1380 m), 1120 (w), 890 (w), 720 (w) cm^{-1}; low-resolution MS *m/e* 152 ($M^+ - H$, 5), 138 (7), 124 (41), 110 (89), 97 (100), 96 (90), 83 (79), 82 (77), 69 (65), 57 (58), 54 (57); high-resolution MS calcd for $C_8H_{14}N$ ($M^+ - C_2H_5$) 124.1126, found 124.1130.

Cyclohexylacetonitrile (51 mg, 81%): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.60–2.05 (m, 11 H), 2.23 (d, J = 5.9 Hz, 2 H); IR (neat) 2920 (s), 2850 (s), 2240 (m), 1450 (s), 1420 (m), 1370 (w), 1320 (w), 1260 (w), 1070 (w), 970 (w), 930 (w), 910 (w), 890 (w), 840 (w) cm^{-1}; low-resolution MS *m/e* 123 (M^+, 1), 122 (2), 108 (2), 95 (3), 94 (3), 84 (8), 83 (100), 81 (8), 80 (11), 67 (4), 53 (63); high-resolution MS calcd for $C_8H_{13}N$ 123.1048, found 123.1048.

4,8-Dimethylnon-7-enonitrile (70 mg, 81%): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.92 (d, J = 5.9 Hz, 3 H), 1.00–2.16 (m, 7 H), 1.60 (s, 3 H), 1.69 (s, 3 H), 2.33 (t, J = 6.9 Hz, 2 H), 5.08 (t, J = 7.0 Hz, 1 H); IR (neat) 2950 (s), 2900 (s), 2850 (s), 2230 (m), 1460 (s), 1450 (s), 1430 (s), 1380 (s), 1260 (w), 1210 (w), 1110 (w), 1080 (w), 1020 (w), 990 (w), 930 (w), 830 (m), 810 (m), 760 (w), 740 (w) cm^{-1}; low-resolution MS *m/e* 165 (M^+, 16), 150 (41), 136 (9), 122 (30), 108 (27), 96 (6), 94 (6), 83 (13), 69 (100), 55 (38); high-resolution MS calcd for $C_{11}H_{19}N$ 165.1517, found 165.1514.

4-Phenylbutyronitrile (52 mg, 72%): ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.80–2.40 (m, 4 H), 2.77 (t, J = 7.0 Hz, 2 H), 6.96–7.40 (m, 5 H); IR (neat) 3050 (m), 3020 (m), 2920 (s), 2850 (m), 2240 (m), 1600 (m), 1500 (s), 1450 (s), 1420 (m), 1350 (w), 1320 (w), 1150 (w), 1080 (m), 1030 (m), 910 (w), 840 (w), 800 (w), 750 (s), 700 (s) cm^{-1}; low-resolution MS *m/e* 145 (M^+, 44), 105 (25), 104 (27), 92 (21), 91 (100), 79 (2), 78 (2), 77 (2), 65 (5), 54 (4). Anal. Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.63; N, 9.65. Found: C, 82.54; H, 7.77; N, 9.31.

***p*-Methoxyphenylacetonitrile** (44 mg, 55%): ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.64 (s, 2 H), 3.77 (s, 3 H), 6.75–7.30 (m, 4 H); IR (neat) 3000 (m), 2950 (m), 2830 (m), 2240 (m), 1610 (s), 1590 (m), 1510 (m), 1460 (m), 1440 (w), 1420 (m), 1340 (w), 1280 (w), 1250 (s), 1180 (s), 1110 (m), 1030 (s), 950 (w), 910 (m), 810 (s), 750 (m), 700 (w) cm^{-1}; low-resolution MS *m/e* 147 (M^+, 100), 146 (32), 132 (22), 116 (13), 107 (19), 104 (10), 91 (7), 77 (20), 51 (3); high-resolution MS calcd for C_9H_8NO ($M^+ - CH_3$) 132.0450, found 132.0432.

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Supplementary Material Available: ^{1}H NMR spectra (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.