Tetrahedron Letters,Vol.30,No.39,pp 5293-5296,1989
Printed in Great Britain

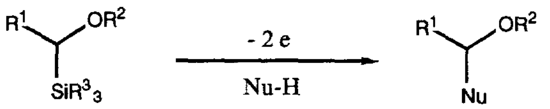
0040-4039/89 $3.00 + .00
Pergamon Press plc

ELECTROCHEMICAL OXIDATION OF ACYLSILANES [1]

Jun-ichi Yoshida,* Shin-ichiro Matsunaga, and Sachihiko Isoe*
Institute of Organic Chemistry, Faculty of Science, Osaka City University,
Sugimoto 3-3-138, Sumiyoshi, Osaka 558, Japan

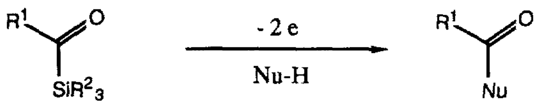
Summary: Oxidation potentials of acylsilanes were found to be much less than those of the corresponding ketones and aldehydes. Electrochemical oxidation of acylsilanes resulted in facile cleavage of the carbon-silicon bond and introduction of oxygen and nitrogen nucleophiles at the carbonyl carbon. Therefore acylsilanes serve as a synthetic equivalent of acyl cations.

We have been investigating the electrochemical oxidation of silicon substituted heteroatom compounds[2] and reported that substitution of a silyl group at the carbon adjacent to the oxygen resulted in significant decrease in oxidation potentials.[3] The electrochemical oxidation of silicon substituted ethers took place smoothly to cleave the carbon-silicon bond and nucleophiles were introduced at the carbon (eq 1).[3] On the basis of this concept new synthons of formyl anion and alkoxycarbonyl anion have been developed.[4]



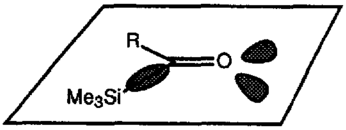
(1)

We have also been interested in electrochemical oxidation of acylsilanes because acylsilanes also have a silyl group at the carbon adjacent to the oxygen atom, although the nature of the C-O bond is different. Herein we wish to report that acylsilanes were oxidized smoothly at the anode to cleave the carbon-silicon bond (eq 2).

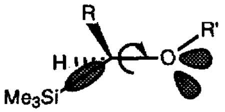


(2)

Generally, it is difficult to oxidize aldehydes and ketones electrochemically because their oxidation potentials are very high (>2.5 V).[5] We found, however, that silyl-substitution at the carbonyl carbon resulted in significant decrease in the oxidation potential. For example, undecanoyltrimethylsilane exhibited an oxidation wave at the peak potential of 1.45 V vs. Ag/AgCl. Decrease in oxidation potential is attributed to the rise of HOMO level by the interaction of the C-Si bond and the lone pair of the carbonyl oxygen.[6] In the previous work we proposed that decrease in oxidation potentials of ethers caused by silyl substitution is also ascribed to the overlap between the C-Si bond and the lone pair of the oxygen atom.[6b,7,8] In the case of silicon substituted ethers the rotation around the C-O bond is free and therefore the C-Si bond and the oxygen lone pair do not always overlap with each other. In the case of acylsilanes, however, the C-Si bond and the lone pair of the carbonyl oxygen are fixed in the same plane and therefore they can interact with each other quite effectively. Thus acylsilanes seem to be more susceptible to oxidation than the silyl-substituted ethers. This is consistent with the fact that oxidation potentials of acylsilanes are somewhat less than those of silyl substituted ethers.



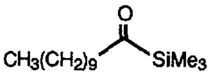
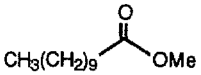
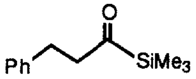
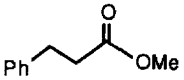
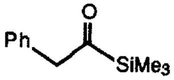
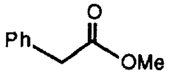
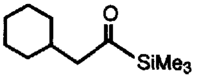
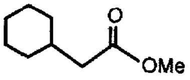
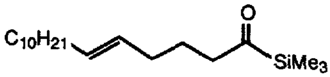
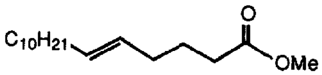
acylsilane
Ep = 1.45 V vs. Ag/AgCl
($R = C_{10}H_{21}$)



α-alkoxysilane
Ep = 1.60 V vs. Ag/AgCl
($R = C_8H_{17}$, $R' = CH_3$)

Preparative electrochemical oxidation of acylsilanes proceeded smoothly in an undivided cell equipped with carbon rod anode and cathode in 0.2 M Et_4NOTs/MeOH under constant current conditions. After usual work-up followed by flash chromatography the corresponding methyl esters were obtained in good yields and with high current efficiency as shown in Talbe I.

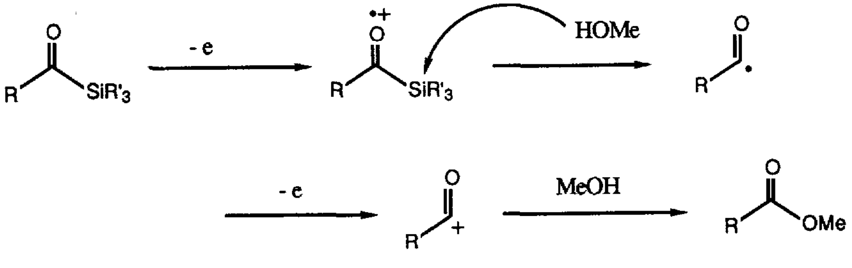
Table I. Electrochemical Oxidation of Acylsilanes in Methanol[a]

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

[a] Reactions 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. [b] Isolated yields.

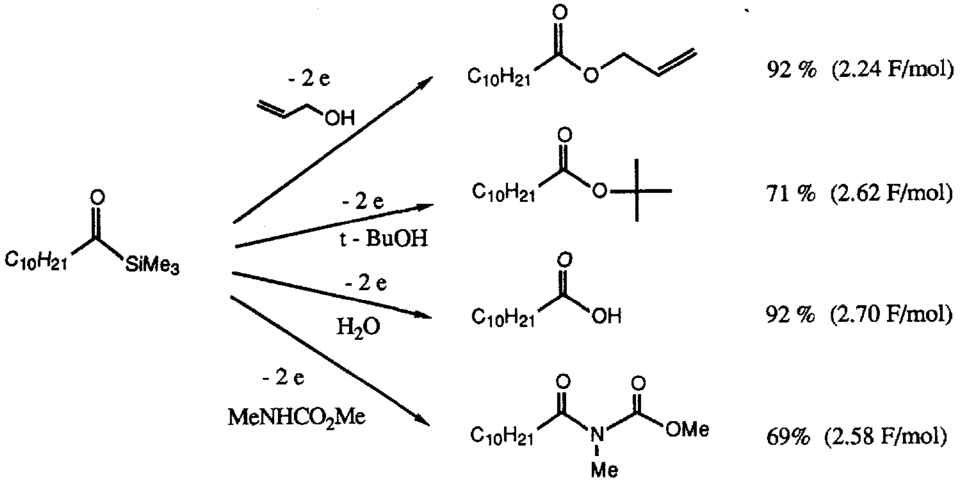
The following mechanism seems to be reasonable (Scheme I). The initial one electron oxidation of the acylsilane produces the cation radical intermediate. Attack of methanol at the silicon cleaves the carbon-silicon bond to give the acyl radical intermediate. The acyl radical is further oxidized to the acyl cation which reacts with methanol to give the corresponding methyl ester.

Scheme I.

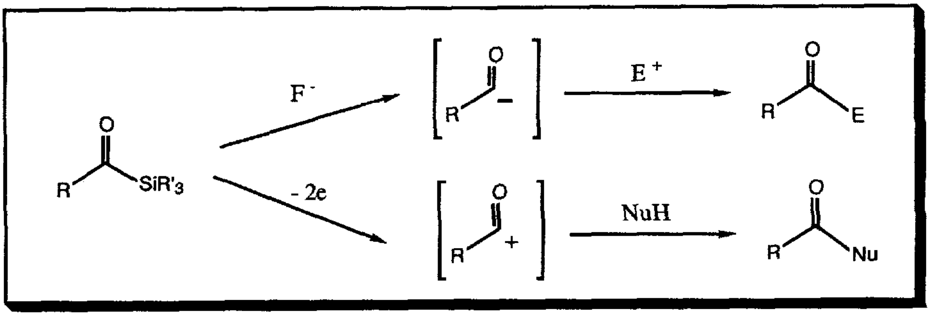


In the electrochemical reaction in methanol as solvent, methanol acted as the nucleophile to attack the carbonyl carbon. In order to introduce other nucleophiles we examined several supporting electrolyte/solvent systems and found that Bu_4NBF_4/CH_2Cl_2 system was quite effective for introduction of some oxygen and nitrogen nucleophiles at the carbonyl carbon. Electrochemical oxidation of the acylsilane in the presence of 5 - 6 equiv of allyl alcohol, t-butanol, water, and methyl N-methylcarbamate gave the corresponding substitution products in good yields (Scheme II).[9,10]

Scheme II.



Recently acylsilanes have been utilized as useful reagents in organic synthesis.[11] 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 the acylsilanes.[12] On the other hand, by using the present electrochemical method acylsilanes serve as acyl cation equivalent because a nucleophile is introduced at the carbonyl carbon. Mild reaction conditions of the electrochemical method (almost neutral, at room temperature) are also advantageous from a synthetic point of view. Since various methods have been developed for the synthesis of acylsilanes,[13] the present reaction provides a useful method for introducing ester, carboxylic acid, and amide functionalities in organic molecules.



Acknowledgment. We thank the Ministry of Education, Science, and Culture, Japan for a Grant-in-Aid for Scientific Research (No. 63540408) for partial financial support of this work.

References and Notes

(1) Electrochemical oxidation of organosilicon compounds Part 8. For part 7, submitted for publication.

(2) (a) Yoshida, J.; Isoe, S. *Chem. Lett.*, **1987**, 631; (b) Yoshida, J.; Isoe, S. *Tetrahedron Lett.*, **1987**, *28*, 6621.

(3) Yoshida, J.; Murata, T.; Isoe, S. *J. Organomet. Chem.*, **1988**, *345*, C23.

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

(5) Electrochemical reduction of aldehydes and ketones have been studied extensively. Recently we have reported that electrochemical oxidation of 1,3-diketones took place smoothly in the presence of olefins, see Yoshida, J.; Sakaguchi, K.; Isoe, S. *J. Org. Chem.* **1988**, *53*, 2525.

(6) Oxidation potential of benzoyltrimethylsilane was reported to be slightly less than the corresponding ketone: (a) Mochida, K.; Okui, S.; Ichikawa, K.; Kanakubo, O.; Tsuchiya, T.; Yamamoto, K. *Chem. Lett.* **1986**, 805. Decrease in ionization potentials of carbonyl compounds caused by silyl-substitution was also reported: (b) Ramsey, B.; Brook, A.; Bassindale, A. R.; Bock, H. *J. Organomet. Chem.* **1974,** *74*, C41; (c) Bock, H.; Alt, H.; Seidl, H. *J. Am. Chem. Soc.* **1969**, *91*, 355. See also (d) Reuter, M. J.; Damrauer, R. *J. Organomet. Chem.* **1974**, *82*, 201.

(7) Theoretical studies on the effect of silyl-substitution of ethers will be reported elsewhere.

(8) Block and Mariano also pointed out independently that there exits some interaction between the C-Si bond and the orbital of the oxygen atom of silyl substituted ethers. (a) Block, E.; Yencha, A. J.; Aslam, M.; Eswarakrishnan, V.; Luo, J.; Sano, A. *J. Am. Chem. Soc.*, **1988**, *110*, 4748. (b) Brumfield, M. A.; Quillen, S. L.; Yoon, U. C.; Mariano, P. S. *J. Am. Chem. Soc.*, **1984**, *106*, 6855. Kira and Sakurai reported the interaction of the C-Si bond and the p orbital of the oxygen atom in ESR study of the cation radical of $(CH_3)_3SiCH_2OCH_3$: (c) Kira, M.; Nakazawa, H.; Sakurai, H. *Chem. Lett.* **1986**, 497.

(9) Chemical oxidation of acylsilanes into carboxylic acids with hydrogen peroxide has been reported. (a) Miller, J. A.; Zweifel, G. *Synthesis*, **1981**, 288; (b) Miller, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1981**,*103*, 6217. Recently T. Mandai *et al* in Okayama University of Science found that MCPBA and t-BuOOH were also effective for such conversion. Unpublished results personally communicated.

(10) Carbon rod anode and platinum plate cathode were used for the reaction.

(11) For example, (a) Magnus, P.D.; Sarkar, T.; Djuric, S. in *Comprehensive Organometallic Chemistry*, Wilkinson, G. Ed., Pergamon: Oxford, Vol 7, Chapt 48, p631. (b) Colvin, E. W. *Silicon Reagents in Organic Synthesis*, Academic Press: London, 1988, p81.

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

(13) For example, (a) Mandai, T.; Yamaguchi, M.; Nakayama, Y.; Otera, J.; Kawada, M. *Tetrahedron Lett.* **1985**, *26*, 2675; (b) Linderman, R. J.; Suhr, Y. *J. Org. Chem.* **1988**, *53*, 1569 and references cited therein. We also have developed a new method for the synthesis of acylsilanes from aldehydes with one carbon elongation, which will be reported elsewhere.

(Received in Japan 9 June 1989)