Tetrahedron Letters,Vol.28,No.52,pp 6621-6624,1987
Printed in Great Britain

0040-4039/87 $3.00 + .00
Pergamon Journals Ltd.

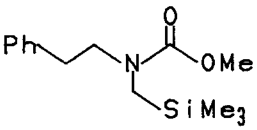
ELECTROCHEMICAL OXIDATION OF α-SILYLCARBAMATES[1]

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

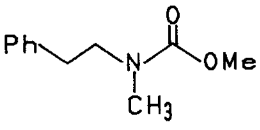
Summary: α-Silyl group activates carbamates toward electrochemical oxidation which results in facile cleavage of carbon-silicon bond and regioselective introduction of methanol at α-carbon.

Increasing attention has been paid for electron transfer reactions of organosilicon compounds especially in the field of photochemistry.[2] We have been interested in electron transfer reactions of organosilicon compounds using electrochemical method,[3] and our recent investigation in this field revealed that electrochemical oxidation of α-silylsulfides results in facile cleavage of the carbon-silicon bond and introduction of oxygen nucleophile into the carbon.[4] However, oxidation potential of such compounds did not differ from the parent sulfides so much (difference is about 0.1 V). In contrast, we found that nitrogen atom is activated significantly by introduction of α-silyl group toward electrochemical oxidation and we wish report herein preliminary results.

As a nitrogen compound substituted by a silyl group at the α-carbon we chose α-silyl carbamates because the electrochemical behavior of their parent compounds, carbamates is well established.[5] First the oxidation potential of α-silyl carbamate was examined using cyclic voltammetry. Methyl N-(phenylethyl)-N-(trimethylsilylmethyl)carbamate (**1**) exhibits the first oxidation wave at peak potential of 1.45 V vs. Ag/AgCl in $LiClO_4$/acetonitrile, whereas the peak potential of methyl N-(phenylethyl)-N-methylcarbamate (**2**) was 1.95 V vs. Ag/AgCl. Although Cooper and Owen also reported the effect of α-silyl group in aromatic amines, decrease in oxidation potential relative to the non-silylated compounds was less than 0.2 V.[6] The remarkable effect observed in α-silylcarbamates seems to be responsible for effective overlapping of lone pair of nitrogen atom of carbamates and the neighboring carbon-silicon σ bond.

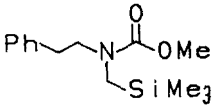
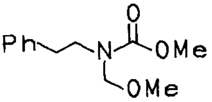
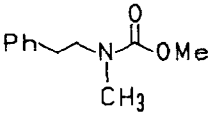
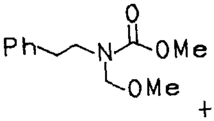
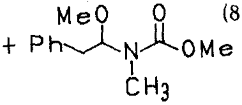
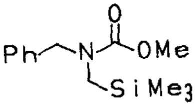
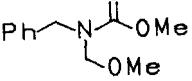
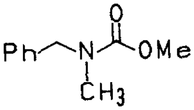
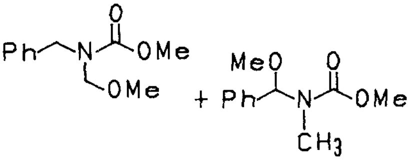
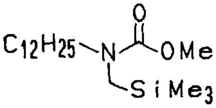
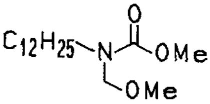
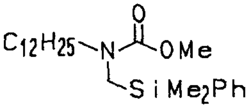
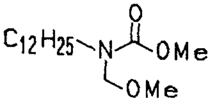
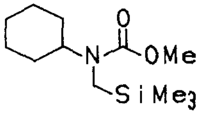
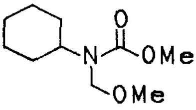
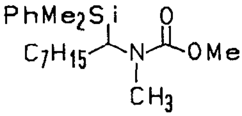
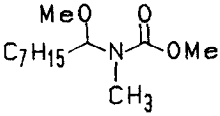


(**1**)
Ep = 1.45 V



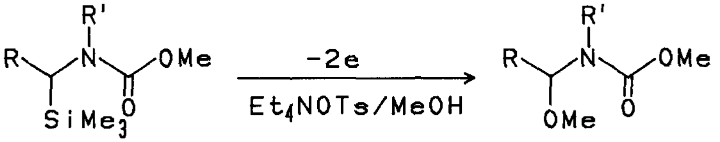
(**2**)
Ep = 1.95 V

Table 1. Electrochemical Oxidation of α-Silyl Carbamates [a]

substrate	electricity (F/mol)	product	yield [b] (%)
	2.35		95
	2.49	 	91 (82 : 18)
	2.71		97
	5.25		quantitative (65 : 35) [c]
	2.57		95
	5.55		quantitative
	2.26		68
	2.36		quantitative

[a] Reactions were normally carried out with 0.1-0.8 mmol of α-silylcarbamate or carbamate in 1.0 ml of 0.2 M $Et_4NOTs/MeOH$. Current was 10 mA. [b] Isolated yields. [c] A similar result has already been reported by Shono et al. See ref 5.

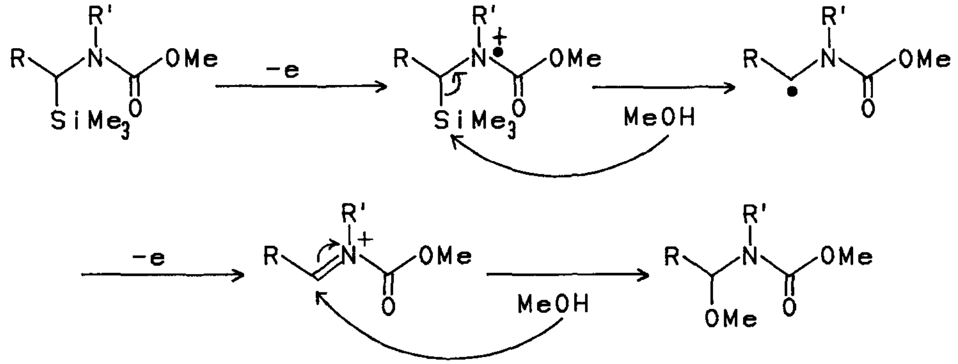
Preparative constant current electrolysis of α-trimethylsilyl substituted carbamates in an undivided cell equipped with carbon rod anode and cathode in Et_4NOTs/methanol proceeded smoothly to give the desilylated products (eq 1). Table I summarizes the results.



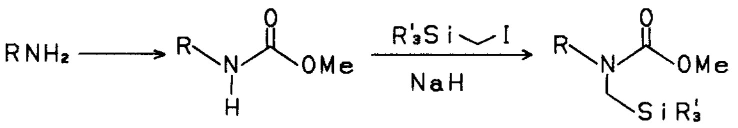
(1)

Dimethylphenylsilyl group was also effective as the silyl group. It should be noted that methanol was introduced regioselectively onto the carbon to which the silyl group had been attached. Presumably the initial one electron transfer from nitrogen atom produced the cation radical intermediate and nucleophilic attack on silicon cleaved the carbon-silicon bond.[7] Thus produced radical was further oxidized to the cation which was trapped by methanol to give the methoxylated product as a single regioisomer (Scheme I). In the case of non-silylated unsymmetrical carbamates, however, a mixture of two regioisomeric products were obtained. Thus, by introduction of a silyl group at the α-carbon of the carbamate one can completely control regiochemistry of the reaction as well as activate nitrogen atom toward electrochemical oxidation.

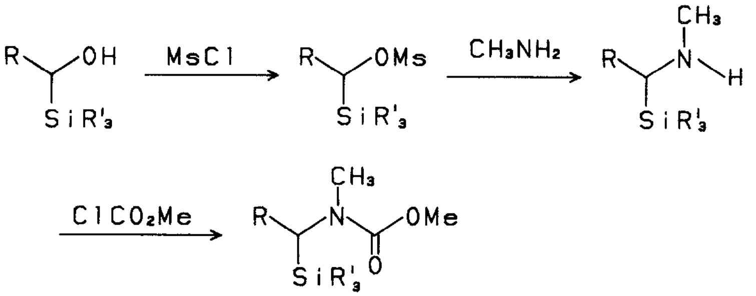
Scheme I.



α-Silyl substituted carbamates can be readily prepared by the following two methods. N-Alkyl-N-(silylmethyl)carbamates were prepared by the reaction of N-alkylcarbamates with trimethylsilylmethyl iodide or dimethylphenylsilylmethyl iodide using sodium hydride as base (eq 2). N-methyl-N-(α-silylalkyl)carbamates were prepared by the sequence of mesylation of α-silylalcohol,[8] reaction with methylamine, and N-methoxycarbonylation with methyl chloroformate (eq 3).



(2)



(3)

Since the methoxyl group can be readily replaced by various carbon nucleophiles, α-methoxylated carbamates are useful intermediates for the synthesis of nitrogen containing compounds.[5b] The present reaction enables regioselective synthesis of such α-methoxylated carbamates utilizing organosilicon chemistry and therefore it provides a useful tool in organic synthesis.

References and Notes.

(1) Electrochemical Oxidation of Organosilicon Compounds 4. Part 3, ref 4.

(2) (a) Chen, S. -F; Ullrich, J. W.; Mariano, P. S. J. Am. Chem. Soc., **1983**, 105, 6160. (b) Brumfield, M. A.; Quillen, S. L.; Yoon, U. C.; Mariano, P. S. ibid., **1984**, 106, 6855. (c) Lan, A. J. Y.;Quillen, S. L.; Heuckeroth, R. O.; Mariano, P. S. ibid., **1984**, 106, 6439. (d) Ohga, K; Yoon, U. C.; Mariano, P. S. J. Org. Chem. **1984**, 49, 213. (e) Mizuno, K.; Ikeda, M.; Otsuji, Y. Tetrahedron Lett., **1985**, 26, 461; Mizuno, K.; Terasaka, K.; Ikeda, M.; Otsuji, Y. ibid., **1985**, 26, 5819.

(3) (a) Yoshida, J.; Murata, T.; Isoe, S. Tetrahedron Lett., **1986**, 27, 3373. (b) Yoshida, J.; Murata, T.; Isoe, S. ibid., **1987**, 28, 211 and 1234. (c) Koizumi, T.; Fuchigami, T.; Nonaka, T. Chem. Express., **1986**, 1, 355. (d) Schaefer, H. J.; Hermeling, D.; Lange, K.-H.; Extended Abstracts of the Spring Meeting of the Electrochemical Society, May 6-11, 1984, Cincinnati, Ohio, p441.

(4) Yoshida, J.; Isoe, S. Chem. Lett., **1987**, 631.

(5) Extensive work on electrochemical oxidation of non-silylated carbamates has been reported. For example, (a) Shono, T.; Hamaguchi, H.; Matsumura, Y. J. Am. Chem. Soc., **1975**, 97, 4264. (b) Shono, T. "Electroorganic Chemistry as a New Tool in Organic Synthesis", Springer-Verlag: Berlin, 1984. and references cited therein.

(6) Cooper, B. E.; Owen, W. J. J. Organomet. Chem., **1971**, 29, 33.

(7) A similar mechanism has been proposed for photochemical reactions, see ref 2.

(8) α-Silylalcohols were prepared by the reaction of aldehydes with silyllithium.

(Received in Japan 28 July 1987)