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Preliminary communication

ELECTROCHEMICAL SYNTHESIS OF ORGANOSILICON COMPOUNDS

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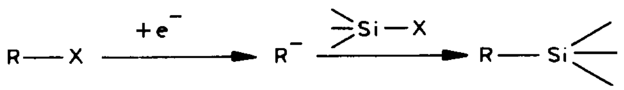
Summary

Electrochemical reduction of allyl, vinyl, and aryl halides in the presence of a silylating agent (Me_3SiCl, HMe_2SiCl, or $PhMe_2SiCl$) afforded the corresponding organosilicon compounds offering a valuable method for introduction of a silyl group into organic molecules.

The usefulness of organosilicon compounds as synthetic intermediates has been recognized by many organic chemists [1]. In searching for a general, simple, and chemoselective access to such compounds, we envisioned an electrochemical approach which involves trapping of carbanions [2], generated in cathodic reduction of organic halides, by a silylating agent (eq. 1) [3,4,5]. Although Shono et al. have reported that electrochemical reduction of some benzyl halides in the presence of trimethylchlorosilane gave benzyltrimethylsilanes [6], the generality of this concept is still uncertain*. We now wish to report that this concept works for combinations of a variety of organic halides including allyl, aryl, and vinyl halides and several silylating agents.



(1)

The reactions were simple to perform. An organic halide (1.0 mmol) was electrochemically reduced in 0.2 *M* Et_4NOTs/DMF using an H-type cell

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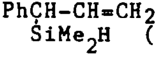
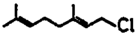
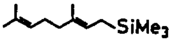
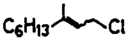
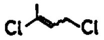
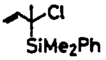
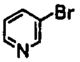
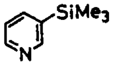
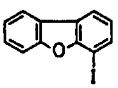
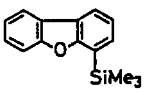
*After completion of our work Shono et al. reported that this method can be applied to allylic halides [7].

TABLE 1
ELECTROCHEMICAL SYNTHESIS OF ORGANOSILICON COMPOUNDS[a]

substrate	silylating agent	electricity[b] F/mol	product	yield[c] %
$PhCH=CHCH_2Cl$	Me_3SiCl	2.40	$PhCH=CHCH_2SiMe_3$	70
		2.85		(98)
	BSA[d]	2.85		(0)
	Me_3SiOMe	2.87		(0)
	HMe_2SiCl	2.43	$PhCH=CHCH_2SiMe_2H$ +  $PhCH(SiMe_2H)-CH=CH_2$ (1:1)	(84)
	$PhMe_2SiCl$	2.45	$PhCH=CHCH_2SiMe_2Ph$	(66)
$PhCH=CHCH_2OAc$	Me_3SiCl	2.74	$PhCH=CHCH_2SiMe_3$	50
$PhCH=CHCH_2OCOOMe$	Me_3SiCl	3.47	$PhCH=CHCH_2SiMe_3$	25
	Me_3SiCl	2.81		(59)
	Me_3SiCl	2.40		63[e]
	$PhMe_2SiCl$	3.63	  (7 : 3)	74
Ph-I	Me_3SiCl	2.29	$Ph-SiMe_3$	(70)
$p-BrC_6H_4I$	Me_3SiCl	2.62	$p-BrC_6H_4SiMe_3$	60
$p-MeOC_6H_4I$	Me_3SiCl	3.64	$p-MeOC_6H_4SiMe_3$	(53)
	Me_3SiCl	3.64		(55)
	Me_3SiCl	3.01		(89)
$C_6H_{13}CH=CHI$[f]	Me_3SiCl	3.32	$C_6H_{13}CH=CHSiMe_3$[g]	47

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[a] Normally reactions were carried out with an organic halide (1.0 mmol), a silylating agent (5.0 mmol) in a solution of Et_4NOTs in DMF (8 ml). Constant current (10 mA) was passed at room temperature. [b] Based on the organic halide. [c] Isolated yields. Yields in parentheses are determined by GLC. [d] *O,N*-Bis(trimethylsilyl)acetamide. [e] *E/Z* = 65/35. [f] >95% E. [g] *E/Z* = 57/43.

equipped with platinum electrodes in the presence of a silylating agent (5.0 mmol). After 2—4 F/mol of electricity was passed, aqueous work-up followed by flash chromatography afforded the corresponding organosilicon compounds in good yields. As shown in Table 1, the reaction can be applied to a wide range of organic halides involving allyl, vinyl, aryl and heteroaromatic halides.

Cinnamyl acetate and carbonate also served as substrates for the electrochemical silylation reaction, though yields were low. However, geranyl and linaloyl acetates were found to be inactive under these conditions.

Trimethylchlorosilane, dimethylchlorosilane, and phenyldimethylchlorosilane were effective silylating agents, but bis(trimethylsilyl)acetamide and methoxytrimethylsilane failed to react. Silicon—oxygen bonds seemed to be inactive to electrogenerated carbanions.

Regioselectivity of the reaction with allylic substrates depends on the nature of the silylating agent. In the case of cinnamyl chloride, trimethylsilyl and phenyldimethylsilyl groups were introduced to the less substituted end of the allyl group exclusively, whereas dimethylsilyl groups were introduced into both ends of the allyl group. Presumably steric factors play a major role [8]. These results suggest that regiochemistry can be controlled by changing the structure of the silylating agent.

Potentially high chemoselectivity of electroorganic reactions [9] would merit this approach. Most significantly, two types of organic halides can be easily differentiated; for example, selective monosilylation of *p*-bromoiodobenzene* was accomplished to obtain *p*-bromophenyltrimethylsilane. Thus this electrochemical reaction offers a general and versatile approach for introduction of a silyl group into organic molecules.

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*Half-wave potential of iodobenzene is reported to be —1.62 V vs. SCE, whereas that of bromobenzene is —2.32 V vs. SCE (in 75% dioxane containing $Et_4N^+ Br^-$) [9].