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Electrochemical synthesis of cyclic alkylsilanes

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Abstract

The electrochemical reduction of aliphatic α,ω-dibromides in the presence of polychlorosilanes of the formula R_nSiCl_{4-n} ($n = 0, 2$) was shown to afford heterocyclic silicon compounds in good yield (up to 91%). In contrast to non-electrochemical methods of synthesis of silacycloalkanes, based on the ring closure of terminal unsaturated compounds, the electrochemical route does not produce α-methylated byproducts and the heterocycle formation occurs quite selectively. The yield of cyclic organosilicon compounds goes through a maximum for 1,1-dimethyl-1-silacyclopentane (91%) and roughly decreases for 1,1-dimethyl-1-silacyclobutane (18%) and 1,1-dimethyl-1-silacycloheptane (57%). The formation of 5-silaspiro[4,4] nonane by the electrochemical process occurs with high selectivity despite the multitude of possible reaction pathways and the high probability of polymer formation due to the high functionality of the silicon. The relatively high selectivity of the electrochemical ring closure is suggested to be due to the orientating effect of an electrode in the course of an irreversible reduction of a C–Hal bond in the monosilylated intermediate. A possible mechanism for the process is discussed.

Keywords: Silicon; Electrochemistry; Electrochemical synthesis

1. Introduction

Usually, the heterocyclic organosilicon compounds are obtained by processes that involve intramolecular hydrosilylation, e.g. by ring closure reactions upon addition of dialkylsilanes to 1,5-hexadiene [1], by cyclization of compounds bearing terminal $CH_2=CH-$ and $\equiv Si-H$ groups in the presence of hexachloroplatinic acid or by heating the reaction mixture without a catalyst under pressure [2–6]. Reaction of dichlorosilanes with terminal di-Grignard or alkyldilithium reagents has also been reported [7,8]. The procedure is based on hydrosilylation of unsaturated compounds usually gives a mixture of cyclic products with n and $n-1$ C atoms in the cycle, as a consequence of the presence of two potential centres in the double bond [1,3,5].

Bicyclic silaspiro compounds have also been prepared by the reaction of unsaturated compounds with $SiCl_4$ (in a stepwise manner) or with $(RO)_2SiCl_2$ in a one-pot process [9,10]. The synthesis of silaspiranes by use of a pentacoordinated silicon complex obtained by depolymerization of silica has also been described [11].

In the past decade the electrochemical reduction of halogen derivatives in the presence of chlorosilanes has been shown to be quite an efficient way of preparing carbosilanes bearing a new Si–C bond [12–18]. In the course of electroreduction of some mixed organosilicon dihalogenides such as $ClCH_2(CH_3)_2SiCl$ and $Cl(CH_3)_2SiCH_2CH_2Si(CH_3)_2Cl$ the formation was observed, along with silicon-containing acyclic products, of mono- [19,20], di- [15,18,20] and polysilylated [15,17] silicon heterocycles.

We have reported previously the electrochemical preparation of 1,1-dimethyl-1-silacyclopentane [21] and because of the interest in new methods of making of silicon containing heterocycles we have now studied their formation under electrolytic conditions.

2. Results and discussion

It is known that the two-electron electrochemical reduction of compounds bearing $\equiv C-X$ or $\equiv Si-X$ (X = halogen) bonds gives the corresponding $\equiv C^-$ and $\equiv Si^-$ anions in appropriate aprotic solvents. These

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