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Homogeneous redox catalysed reduction of chloromethyldimethylchlorosilane

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Abstract

The electrochemical reduction of chloromethyldimethylchlorosilane, affording 1,1,3,3-tetramethyl-1,3-disilacyclobutane, involves a dissociative electron transfer to the LUMO which contains the predominant contribution of the Si-Cl orbitals, and results in the C-Cl bond cleavage. The reduction of trimethylchlorosilane occurs through the dissociative Si-Cl bond rupture. In the course of the reduction of chloromethyltrimethylsilane, the α -silicon stabilisation of the negative charge makes an individual anion radical to appear on the reaction coordinate. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Cathodic reduction of organic chlorosilanes, bearing at least one Si-Cl bond in the molecule, is widely used in preparative electrochemistry for obtaining symmetrical and unsymmetrical disilanes [1–6] as well as tri- [4,5,7], tetra- [7] and polysilanes [6,8–10]. A number of processes of cathodic silylation of unsaturated compounds [11–14], using the chlorosilanes as starting compounds, is also described. All these processes suggest a reductive cleavage of the Si-Cl bond.

On the other side, it has been reported that the electrochemical reduction of C-X (X = Cl, Br, I) bond containing compounds in the presence of difficult to reduce chlorosilanes leads to the formation of a carbon-silicon bond by nucleophilic substitution of chlorine by the electrogenerated carbanion [15–22].

A problem which rises in the cathodic electrosynthesis of organosilicon compounds from organohalides

and organosilanes, is which one of these compounds is first reduced and what is the mechanism of formation of the final products. This question is particularly important when considering the electroreduction of bifunctional compounds simultaneously carrying both electrochemically active centres, C-Cl and Si-Cl. For example two cyclic carbosilanes 1,2- and 1,3-disilacyclobutanes, which are promising precursors of polycarbosilanes [23], have been obtained in the course of the electrochemical reduction of bis-(chlorodimethylsilyl)ethane and chloromethyldimethylchlorosilane [24,25], respectively. While the 1,2-isomer cannot be obtained otherwise than by reductive cleavage of the Si-Cl bond of bis-(chlorodimethylsilyl)ethane, the mechanism of formation of 1,3-derivative is not yet clear because of the presence in the starting molecule of two potentially electrochemically active centres one C-Cl and one Si-Cl bonds. Thus, the questions which rise are which of these two bonds is first reduced and consequently what is the electrogenerated nucleophile? The study of the second question about the relative

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