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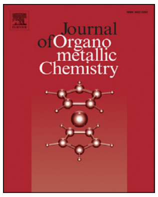

The efficient method for the preparation of alkenylsilanes from organoaluminums

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ABSTRACT

Silyl esters of sulfonic acids are convenient and efficient silylating agents for β,β- and β-substituted 1-alkenylaluminums. The reaction proceeds at room temperature in CH_2Cl_2 or hexane for 18 h to give corresponding alkenylsilanes in high yield. At the same time, α,β-disubstituted and α,β,β-trisubstituted 1-alkenylaluminums were inert in the reaction under study. The reaction with aluminacyclopen-2-enes and aluminacyclopentanes takes place on the less sterically hindered reaction center. Using electron-donating solvents (diethyl ether, THF) inhibits the reaction. A new convenient procedure of silylation was developed, which consists in obtaining the silyl tosylate by the reaction of chlorosilanes with anhydrous sodium tosylate in toluene solution. The resulting reaction mixture was reacted with organoaluminum compounds without isolation of silyl tosylate.

Introduction

The reaction of organometallic compounds with chlorosilanes is one of the general methods of formation of carbon–silicon bond [1,2]. Despite the fact that the first organosilicon compounds were prepared by Friedel and Crafts by the reaction of dialkylzinc with tetrachlorosilane [3], nowadays the organolithium and magnesium compounds are more widely used in the synthesis of substituted silanes. Recently it was found that silver [4], copper [5] and zinc [6] salts catalyze the reaction of chlorosilanes with aryl- and alkenyl Grignard reagents. Organic derivatives of sodium and of aluminum are used to a much lesser extent. For example, it is known that sodium reacts with halogenated aromatic compounds and chlorosilanes in a manner analogous to the Wurtz–Fittig reaction [7]. The reaction of aluminum alkyl halides with $SiCl_4$ at a temperature of 350–450 °C gives the alkyl substituted silanes [8]. At the same time, very few examples of the alkylation of halogenated silanes with organoaluminum compounds are known. Me_3SiCl was obtained in 88% yield by the treatment of Me_2SiCl_2 with Me_3Al at 60 °C [9]. The alkylation of SiF_4 by lower alkylaluminums at 325–375°°C and a pressure of 250 psi was described [10]. There is an example of silylation of *trans*-3,4-dialkylsubstituted aluminacyclopentanes by dichloro(methyl)vinylsilane which gives substituted silacyclopentanes with 50–60% yield [11]. Thus, the preparative methods for the conversion of organoaluminum compounds into alkenylsilanes are missing and very few examples of the silylation of higher alkylaluminums are known. It is noteworthy that alkenyl derivatives of aluminum can be obtained by hydro-, carbo- and cycloalumination of alkynes and some transformations are easily feasible only in the case of the organoaluminum compounds.

Results and discussion

Negishi methylalumination is one of the most useful transformations of alkynes [12]. However we have found that alkenylaluminums prepared in this way [13] do not react with chlorosilanes. Carrying out the reaction at 50 °C for 18 h did not result in the formation of expected alkenylsilanes. Earlier we have demonstrated the efficiency of the use of alkyl esters of sulfonic acids for the alkylation of cyclic alkenylaluminums (aluminacyclopen-2-enes) [14,15]. High yields of the resulting cyclopropanes and selectivity of the transformation called our attention to the prospects of using the derivatives of sulfonic acids for the functionalization of organoaluminum compounds. It is possible that esters of sulfonic acids react with organoaluminum compounds through the formation of a less strained six-membered transition state. Moreover, silyl esters of sulfonic acids are stronger electrophilic agents than TMSCl. The global electrophilicity index [16], calculated using 6-31G(d), is decreasing in the series: TfOTMS (0.47) > $(TMSO)_2SO_2$ (0.34) > MsOTMS (0.33) > TMSCl (0.30). From the above, we assumed that the organosilicon

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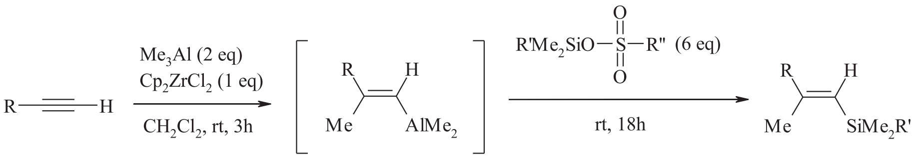


1a: R= n-C_6H_{13}; R'=Me;
R"=Me (82 %); Me_3SiO (80 %);
n-Tol (85 %), Ph (86 %), CF_3 (94 %)
1b: R= n-C_8H_{17}; R'=Me; R"=Me (93 %)
1c: R= Ph; R'=Me; R"=Me (88 %)
1d: R= n-C_6H_{13}; R'=Ph; R"=Me (86 %)

Scheme 1. The reaction of β,β-disubstituted 1-alkenylaluminums with silyl esters of sulfonic acids.

derivatives of sulfonic acids may be effective agents for silylation of organoaluminium compounds. Thus, in order to develop effective method for the synthesis of alkenylsilanes, we have studied the reactions of acyclic and cyclic alkenylaluminums with $(TMSO)_2SO_2$, MsOTMS, TsOTMS, TfOTMS and $MsOSiMe_2Ph$.

We have found that Zr-catalyzed methylalumination of terminal alkynes (1-octyne, 1-decyne, phenylacetylene) [13] followed by treatment with 6 equivalents of MsOTMS in CH_2Cl_2 solution at room temperature for 18 h afforded substituted 1-alkenylsilanes **1a**–**c** with *E*-configuration of the double bond in high yield (82–93%) (Scheme 1). Using electron-donating solvents (diethyl ether, THF) inhibits the reaction.

The addition of trimethylsilyl group takes place with preservation of the configuration of the double bond that was confirmed by the presence of cross-peaks between the hydrogen atom at the double bond and the α-hydrogen atoms of n-C_6H_{13} and n-C_8H_{17} groups in NOESY spectra of **1a**, **b**. It should be noted that all aluminum–carbon bonds of organoaluminum compounds (including unreacted in first stage Me_3Al) were involved in the silylation reaction, so 6 equivalents of silylating agent was required to complete the conversion. A number of silyl esters of sulfonic acids were tested. The yields of compound **1a** using $(TMSO)_2SO_2$, TsOTMS, $PhSO_2OTMS$ and TfOTMS as silylating agents are 80–94%, which are close to the result obtained in the case of MsOTMS. The reaction with $MsOSiMe_2Ph$ gave alkenylsilane **1d** in 86% yield.

Due to the simplicity of the procedure and the efficiency of silyl esters of sulfonic acids as silylating agents, we examined this methodology for the functionalization of alkenylaluminums of different structure. Alkyl substituted terminal alkynes can be readily converted to β-substituted 1-alkenylaluminums under the action of DIBAL-H [17]. Further reaction of resulting organoaluminum compounds with one equivalent of silyl esters of methanesulfonic acid (MsOTMS, $MsOSiMe_2Ph$) gave the corresponding alkenylsilanes **2a**, **b** in high yields (88, 81%) (Scheme 2). Note that it is enough to use only one equivalent of silylating agent to complete the conversion. Presumably, *iso*-butyl group at aluminum atom is less reactive toward silyl esters of sulfonic acids. Phenylacetylene reacts with DIBAL-H to yield mainly alkynylaluminum formed by metalation of the terminal alkyne [18]. The addition of one equivalent of MsOTMS produces trimethyl(2-phenylethynyl)silane in 66% yield.

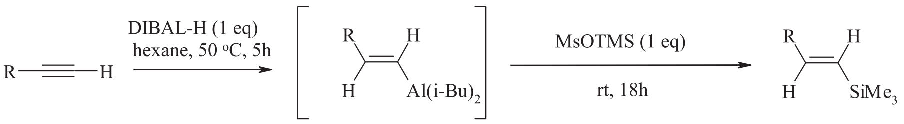
Ti-catalyzed hydroalumination [19] and the Zr-catalyzed methylalumination of 5-decyne [13] gives α,β-disubstituted, and α,β,β-trisubstituted 1-alkenylaluminums which were inert towards to MsOTMS (Scheme 3). Obviously the steric factor plays an important role in the reaction under investigation. Bulk trimethylsilyl group is experiencing considerable steric hindrance to the approach to the reaction center due to the interaction with α-positioned n-butyl substituent of alkenylaluminum.

Zr-Catalyzed reaction of disubstituted alkynes with Et_3Al gives aluminacyclopent-2-enes which are a particular case of α,β,β-substituted 1-alkenylaluminums [20]. As expected, the reaction of 2,3-dialkyl substituted aluminacyclopent-2-enes with 3 equivalents of silyl esters of methanesulfonic acid (MsOTMS, $MsOSiMe_2Ph$) involves only Al–C(sp^3) bond of metallacycle to give organosilicon alkenes **3a**–**c** with 84–89% yield after deuterolysis (Scheme 4). Apparently, the low reactivity of the Al–C(sp^2) bond of aluminacyclopent-2-enes caused by the same factors that have prevented the formation of alkenylsilanes in the case of α,β-disubstituted and α,β,β-trisubstituted 1-alkenylaluminums on Scheme 3.

As the functionalization of aluminacyclopent-2-enes involved only Al–C(sp^3) bond of metallacycle, it was interesting to examine aluminacyclopentanes in the reaction under study. Zr-catalyzed cycloalumination of 1-octene and styrene [21] followed by subsequent treatment with silyl esters of methylsulfonic acid (MsOTMS, $MsOSiMe_2Ph$) gave compounds **4a**, **b** with high yield after quenching with H_2O or D_2O (Scheme 5). Only less hindered Al–C bond of aluminacycle was involved in the reaction that allows the further functionalization of the other Al–C bonds. For example, sequential treatment of 2-ethyl-3-n-hexylaluminacyclopentane with MsOTMS and O_2 yielded 2-[2-(trimethylsilyl)ethyl]-1-octanol **5** in 85% yield.

In order to simplify the silylation procedure, we have developed a new method, which consists in obtaining the silyl tosylate by the reaction of chlorosilanes with sodium tosylate in toluene solution. The resulting reaction mixture was reacted with organoaluminum compounds without isolation of silyl tosylate. The first stage of the procedure takes only 5 min at 110 °C. When used one and a half-fold excess of chlorosilanes, the product yields were almost similar to those observed with isolated silyl esters.

The developed method provides some benefits in the preparation of tetraorganosilanes. While β-substituted silanes can be prepared in



2a: R= n-C_6H_{13} (88 %);
2b: R= n-C_8H_{17} (81 %)

Scheme 2. The reaction of β-substituted 1-alkenylaluminums with MsOTMS.