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Fluoride ion mediated reactions of disubstituted acetylenes $Me_3SiC{\equiv}CMMe_3$ (M = C, Si, Ge, Sn) with terminal acetylenes

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Dedicated to Professor M.G. Voronkov on the occasion of his 80th birthday

Abstract

The CsF–18-crown-6 mediated reactions of disubstituted acetylenes $Me_3SiC{\equiv}CMMe_3$ (M = C, Si, Ge, Sn) with phenylacetylene and 2-methyl-5-pyridylacetylene in benzene have been studied. The first step of the reaction is the deprotonation of aryl acetylene by F^--ion. The carbanion formed interacts with the disubstituted acetylene. The silylated, germylated and stannylated acetylenes were formed in yields 26–91%. Quantum chemical calculations of trimethylsilyl and trimethylgermyl group transfer have been performed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 1-*tert*-Butyl-2-trimethylsilyl-, bis(trimethylsilyl)-, 1-trimethylgermyl-2-trimethylsilyl-, and 1-trimethylstannyl-2-trimethylsilylacetylenes; Phenylacetylene and 2-methyl-5-pyridylacetylene; Fluoride ion mediated; Quantum chemical calculations

1. Introduction

Aryl and hetaryl trimethylsilylacetylenes are usually prepared by the reactions of aryl(hetaryl)acetylene with BuLi–Me_3SiCl or EtMgBr–Me_3SiCl [1], ArCu with trimethylsilyliodoacetylene [2], as well as by the Pd catalyzed alkynylation of aryl triflates [3] or halides [4]. Phenyltrimethylsilylacetylene is also obtained from phenylacetylene by the reaction with ethyl trimethylsilylacetate in the presence of Bu_4NF [5] or trimethylsilylacetylene in the presence of KF-Al_2O_3 [6]. According to the literature data germyl and stannyl substituted acetylenes were obtained using the three general methods: interaction of germyl(stannyl)halogenides with ethynylmagnesium bromides [1,7–11] or lithium derivatives of the corresponding acetylenes [12–15], reaction of triorganosubstituted germyl(stannyl) amines with acetylenes R–C≡CH [16]. The reactions of Group 14 element containing compounds catalyzed with nucleophiles have also been studied extensively [17,18].

Recently we have studied the CsF–18-crown-6 mediated trimethylsilyl group transfer from trimethylsilylacetylene to an aryl or hetaryl acetylene [19]. In the present paper we are reporting the results of the investigations of the cesium fluoride mediated metallation of phenylacetylene and 2-methyl-5-pyridylacetylene with $Me_3SiC{\equiv}CMMe_3$ (M = C, Si, Ge, Sn) to compare the influence of Group 14 elements on this substitution reaction. Semiempirical AM1 calculations were used to describe the mechanism of the reaction. MS and ^1H-NMR spectroscopy confirmed the structure of the final products.

2. Results and discussion

Phenylacetylene (**1**) and 2-methyl-5-pyridylacetylene (**2**) have been chosen as model substances for investigating the cesium fluoride mediated metallation of aromatic and heteroaromatic acetylenes (Scheme 1).

The synthesis of Group 14 element substituted arylacetylenes **3a**–**c** and **4a**–**c** was carried out in the presence of catalytic amount of CsF as the fluoride ion source and 18-crown-6 in benzene (Table 1). The two

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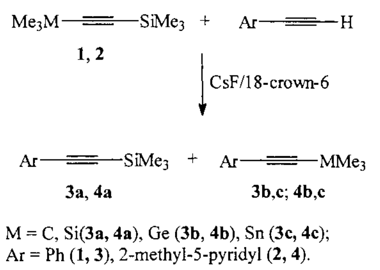


Scheme 1.

fold excess of cesium fluoride to 18-crown-6 was used because of possible side reactions, e.g. $\mathrm{Me_3SiF}$ formation or HF evolution. The Molar ratio of $\mathrm{ArC{\equiv}CH{-}Me_3SiC{\equiv}CMMe_3{-}CsF{-}18\text{-}crown\text{-}6}$, 1:1:0.2:0.1 appeared to be optimal [19].

It has been found that the interaction of 1-*tert*-butyl-2-trimethylsilylacetylene with arylacetylenes **1** and **2** affords silylated acetylenes **3a** (34%) and **4a** (27%). The conversion of the phenylacetylene **1** did not exceed 34%, and was not influenced by the increase in the base (CsF) amount up to 1.5 equivalents and a rise in temperature from 25 to 50 °C.

On the contrary, bis(trimethylsilyl)acetylene reacted with arylacetylenes giving the desired products $\mathrm{ArC{\equiv}CSiMe_3}$ **3a** and **4a** at room temperature with excellent yields (90–91%). We tried to decrease the ratio of bis(trimethylsilyl)acetylene to **1** or **2** from 1:1 to 0.5:1.0 taking into account the presence of two trimethylsilyl groups in $\mathrm{Me_3SiC{\equiv}CSiMe_3}$, but the process stopped at the 50% yield of silylated product and trimethylsilylacetylene. The silylation of terminal acetylenes with $\mathrm{Me_3SiC{\equiv}CH}$ needs activation and occurs only at 50 °C [19].

The interaction of arylacetylenes with the 1-trimethylsilyl-2-trimethylgermylacetylene occurred smoothly and gave the mixture of silylated and germylated arylacetylenes **3a**,**b** and **4a**,**b**, respectively. The 30–40% excess of trimethylgermyl derivatives (**3b**, **4b**) was observed in both cases.

Transmetallation of stannyl substituted acetylenes has been described in Ref. [21]. We have found that 1-trimethylsilyl-2-trimethylstannylacetylene in the CsF–18-crown-6–benzene system at room temperature forms symmetrical bis(trimethylsilyl)- and bis(trimethylstannyl)acetylenes. The latter is inactive under the described phase transfer catalysis conditions (GCMS data). Therefore, the aryl trimethylsilylacetylenes **3a** and **4a** were formed in 30–60% excess relative to the corresponding trimethylstannyl derivatives **3c** and **4c** (Table 1).

The ^{1}H-NMR and mass spectroscopic data of acetylenes **3a**–**c**, **4a**–**c** are shown in Tables 2 and 3.

Semiempirical methods like AM1 provide a quite effective compromise between the accuracy of the results and the expense of computer time required. Calculations performed with AM1 reflect the experimental results as effectively as ab initio calculations using a small basis set [22]. Reactions of bis(trimethylsilyl)acetylene and 1-trimethylsilyl-2-trimethylgermylacetylene with phenylacetylene have been chosen as models for the calculations due to their smooth running.

The $\mathrm{Cs^+}$–crown ether complex formation leads to 'organic masking' of the metal and $\mathrm{F^-}$-ion solubilisation. Such systems have been described as involving the 'reaction of naked anions' [23].

At the beginning we supposed that the first step of the fluoride ion mediated reactions of silicon containing

Table 1
Reactions of disubstituted acetylenes $\mathrm{Me_3SiC{\equiv}CMMe_3}$ (M = C, Si, Ge, Sn) with terminal acetylenes (molar ratio $\mathrm{ArC{\equiv}CH{-}Me_3SiC{\equiv}CMMe_3{-}CsF{-}18\text{-}crown\text{-}6}$, 1:1:0.2:0.1)

Starting acetylene	Ar	M	Reaction time (h)	Reaction product [a]	Yield (%)
1	Ph	C	5	**3a** [b]	34
1	Ph	Si	6	**3a**	91
1	Ph	Ge	5	**3a**	31
				3b	45
1	Ph	Sn	5	**3a**	38
				3c [c]	29
2	2-Me-5-pyridyl	C	7	**4a** [b]	27
2	2-Me-5-pyridyl	Si	6	**4a**	90
2	2-Me-5-pyridyl	Ge	5	**4a**	36
				4b	46
2	2-Me-5-pyridyl	Sn	5	**4a**	41
				4c [c]	26

[a] Reaction products were described: **3a**, **3b** [13]; **3c** [20]; **4a** [19].

[b] The conversion of the phenylacetylene 1 did not exceed 34%.

[c] It was detected that 16–20% of the 1-trimethylsilyl-2-trimethylstannylacetylene was converted to the symmetrical bis(trimethylstannyl)acetylene.

Table 2
^{1}H-NMR spectroscopic data of acetylenes **3a–c**, **4a–c**

$ArC{\equiv}CMMe_3$	M	δ (ppm), J (Hz)		
		MMe_3 (s)	2-Me (s)	Ring protons (m)
3a	Si	0.25	–	7.28 and 7.47
3b	Ge	0.43	–	7.28 and 7.46
3c	Sn	0.36 ($J_{^{117,119}Sn-H}$ = 60, 53 and 59.27)	–	7.28 and 7.47
4a	Si	0.25	2.54	7.05 (H-3), 7.59 (H-4), 8.61 (H-6)
4b	Ge	0.48	2.58	7.10 (H-3), 7.66 (H-4), 8.62(H-6)
4c	Sn	0.36 ($J_{^{117,119}Sn-H}$ = 60, 53 and 59.27)	2.57	7.09 (H-3), 7.63 (H-4), 8.57 (H-6)

compounds could be the F^- attack at the silicon with the formation of pentacoordinated species. The calculations showed that two mechanisms of fluoride ion interaction with bis(trimethylsilyl)acetylene are possible. The pentacoordinated silicon formation could take place only if the starting position $F{\cdots}Si\text{-}C \equiv C$ was strongly linear. All others fluoride ion steric positions led to the elimination of the proton from the methyl group and HF formation. Due to the low probability of the sterical position necessary for the pentacoordinated silicon formation, we had to find another possible reaction route.

Deprotonation of phenylacetylene **1** with fluoride ion turned out to be more advantageous under PTC conditions. The reaction heat is -73.3 kcal mol^{-1} (Fig. 1a and b). Thus, it can be concluded that the first step of the process is deprotonation of the starting arylacetylene. In favour of this mechanism is the fact that alkynes with less acidic terminal proton (propargyl ethers, for example) did not react under the described conditions.

The interaction of the arylacetylene carbanion with bis(trimethylsilyl)acetylene is the next reaction step (Fig. 2). The calculation starting state is shown in Fig. 2a.

During the anion approach the tetrahedral configuration of silicon was changed and turned to the bipyramidal in the equilibrium state (Fig. 2b). The heat of the intermediate formation is -27.5 kcal mol^{-1}.

It is natural to assume that the negatively charged intermediate interacts with the counterion. The lithium ion was used as a counterion, because the cesium ion parameters are absent in the MOPAC6 program. The biggest negative charge of the intermediate is localised at the β-carbon atom of the C≡C bond. That is why we suppose that Li^+ would attack the Si–C bond (Fig. 3). The starting state of this process is shown in Fig. 3a. The change in the linearity caused by the interaction with the lithium ion is shown in Fig. 3b. The C–Si bond cleavage and $PhC{\equiv}CSiMe_3$ (**3a**) formation are shown in Fig. 3c. The heat of the reaction is -159.6 kcal mol^{-1}. All the steps of the reaction studied occur without activation energy.

The quantum-chemical calculations and computer visualisation of the process allow proposing the following reaction mechanism (Scheme 2).

The interaction of phenylacetylene **1** with 1-trimethylsilyl-2-trimethylgermylacetylene was calculated

Table 3
Mass spectra data for acetylenes **3a–c**, **4a–c**

$ArC{\equiv}CMMe_3$	m/z (I, %)
3a	174(M^+, 17), 160(16), 159(M^+-Me, 100), 143(4), 131(4), 129(9), 105(8), 53(6), 43(10)
3b	220(M^+, 11), 207(21), 206(12), 205(M^+-Me, 100), 204(33), 203(76), 201(56), 175(31), 174(10), 173(23), 171(17), 115(13), 89(11)
3c	266(M^+, 8), 255(18), 253(14), 252(11), 251(M^+-Me, 100), 250(36), 249(76), 248(31), 247(44), 225(11), 221(62), 220(23), 219(46), 218(19), 217(29), 145(17), 143(12), 120(23), 118(17), 116(12), 115(12)
4a	189(M^+, 18), 175(16), 174(M^+-Me, 100), 144(5), 77(5), 53(5), 43(7)
4b	235(M^+, 12), 233(9), 222(21), 221(11), 220(M^+-Me, 100), 219(32), 218(76), 216(58), 190(21), 188(17), 186(13), 163(5), 123(6), 87(6)
4c	281(M^+, 8), 270(18), 268(14), 267(11), 266(M^+-Me, 100), 265(37), 264(78), 263(30), 262(45), 236(51), 235(19), 234(40), 233(16), 232(24), 169(11), 135(11), 133(10), 120(32), 119(12), 118(30), 117(15), 116(18)

Fig. 1. (a) F^- attack at the C–H bond; (b) proton elimination.

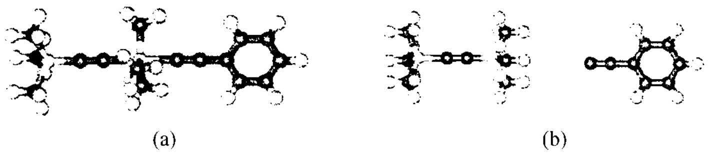


Fig. 2. (a) Starting state; (b) equilibrium state.

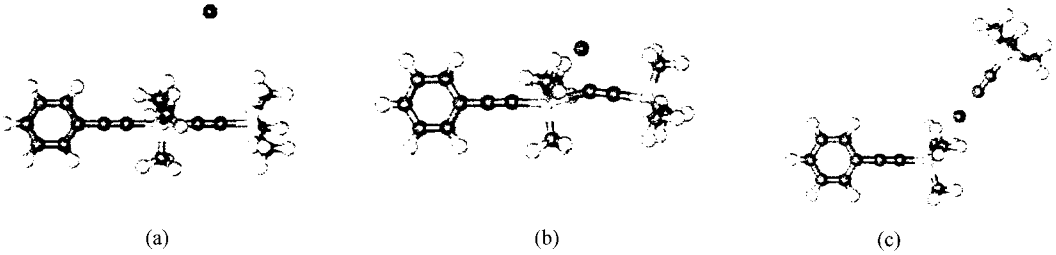
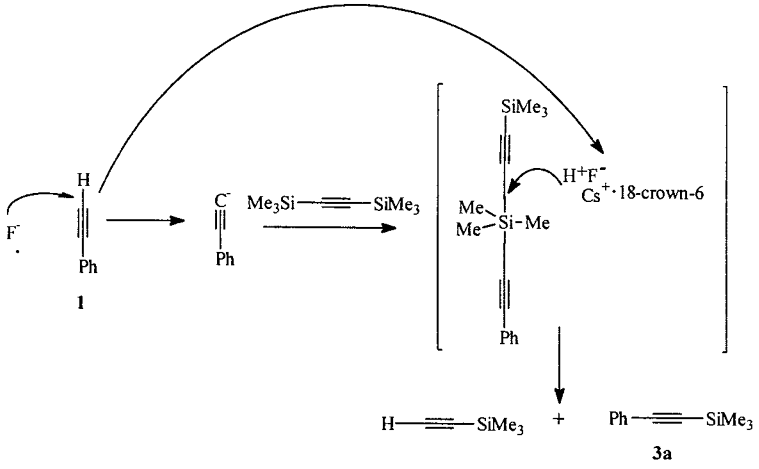


Fig. 3. (a) Starting state; (b) Li^+ attack at the Si–C bond; (c) Si–C bond cleavage.



Scheme 2.

Fig. 4. (a) Starting state; (b) PhC≡C–Ge containing intermediate.

in a similar way. The first step of the reaction was the deprotonation of the starting arylacetylene. There are two competing reaction centres for aryl carbanion attack in the 1-trimethylsilyl-2-trimethylgermylacetylene molecule. The PhC≡**C**–**Si** bond formation had the heat of -25.5 kcal mol^{-1}, but the formation of PhC≡**C**–**Ge** bond was characterised by the reaction heat of -43.6 kcal mol^{-1} (Fig. 4). The PhC≡C–Ge containing intermediate destruction leads to the 1-trimethylgermyl-2-phenylacetylene **3b** and trimethylsilylacetylene formation. The latter does not react with phenylacetylene at room temperature [19]. However, it was shown that the reaction of 1-trimethylsilyl-2-trimethylgermylacetylene with phenylacetylene gave not only 1-trimethylgermyl-2-phenylacetylene **3b** but also 1-trimethylsilyl-2-phenylacetylene **3a**. Thus, it can be concluded that both the competing reactions were observed. As the heat of PhC≡**C**–**Si** bond formation (-25.5 kcal mol^{-1}) is lower than that of PhC≡**C**–**Ge** (-43.6 kcal mol^{-1}) the germylacetylene **3b** yield (45%) is higher than the yield of the corresponding silyl analogue **3a** (31%).

3. Materials and methods

3.1. Instrumental

^{1}H-NMR spectra were recorded on a Varian 200 Mercury spectrometer (200 MHz) using $CDCl_3$ as the solvent. Mass spectra were registered on a GCMS HP 6890 (70 eV) apparatus. GC analysis was performed on a Chrom-5 instrument equipped with a flame-ionisation detector using a glass column packed with 5% OV-101/Chromosorb W-HP (80–100 mesh, 1.2 m × 3 mm). Bis(trimethylsilyl)acetylene (Aldrich) was used without purification. 1-*tert*-Butyl-2-trimethylsilylacetylene, 1-trimethylsilyl-2-trimethylgermylacetylene and 1-trimethylsilyl-2-trimethylstannylacetylene were prepared and characterised as outlined in Refs. [21], [24–26]. CsF was calcinated at ca. 200 °C during 1 h. Benzene was distilled over CaH_2 and kept over molecular sieves of 4 Å.

3.2. General procedure for the synthesis of acetylenes ***3a–c***, ***4a–c***

Freshly calcinated CsF (0.03 g, 0.2 mmol) was added to a mixture of 1 or 2 (1 mmol) and 18-crown-6 (0.026 g, 0.1 mmol) in 1.5 ml of dry benzene under argon atmosphere. After 5 min of stirring the corresponding acetylene (1 mmol) was added. The reaction was carried out for 5–7 h at room temperature (r.t.) to achieve the substrate disappearance (GC control, 120–250 °C). The reaction mixture was filtered over a thin layer of silica gel or Al_2O_3 and evaporated under reduced pressure.

3.3. Theoretical calculations

All calculations were carried out using the semiempirical AM1 [27] method as implemented in MOPAC6 [28]. The equilibrium geometries were obtained with complete optimisation at the PRECISE level. The frequencies analysis has shown that all optimum structures present the minimum points on the potential energy surface. A keyword PARASOK was applied in the calculations of the lithium cation containing structures [29]. To obtain the data on the change in geometry during the optimisation process, calculations were performed using a keyword FLEPO. Post-processing animation was carried out with XMOL [30] and JMOL [31] programs.

Supporting Information is available from the authors on request. The multi-structure XYZ files describing the geometry changes of the molecular systems during the optimisation process are available from the author (M.F.) at misha@osi.lv.

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