The reaction of (*tert*-Butoxysilyl)methylmagnesium chlorides with some organotin and organosilicon monochlorides

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ABSTRACT

Interaction between (*tert*-butoxysilyl)methylmagnesium chlorides of the general formula $Me_{3-n}(t\text{-}BuO)_nSiCH_2MgCl$, n = 1–3, with some organotin and organosilicon monochlorides has been studied. It has been found that the reaction of the Grignard reagents with trialkyltin chlorides readily proceeds via the methylene carbon with the formation of C-substituted products $Me_{3-n}(t\text{-}BuO)_nSiCH_2SnR_3$, R = Me, *n*-Bu in high yields. The path of this reaction with Me_3SiCl and $MePh_2SiCl$ depends on the structure of Grignard compound and chlorosilane electrophilicity. Increasing the number of the *tert*-butoxy groups in the Grignard reagent has unexpectedly been found to result in the formation of $Me_{3-n}(t\text{-}BuO)_nSiCH_2OSiMeR_2$, R = Me, Ph and decrease of the organosilylmethyl silicon compounds content in the reaction products. The structure of the compounds synthesized has been confirmed by ^{1}H, ^{13}C, ^{29}Si, [117,119]Sn NMR spectroscopy and mass spectrometry.

1. Introduction

Organosilylmethyl containing organoelement compounds with alkoxy substituents bonded to the silicon are capable of polymerization and can be used for the production of branched polysiloxanes with organoelement substituents in the side chain.

Organosilylmethyl tin derivatives are distinguished by good surface adhesion, stability toward UV irradiation and high humidity, and high biological activity exhibited in the majority of cases. The latter feature suggests their use as plant protection agents in agriculture and as components of special paints and compositions for treating vessels against biofouling [1,2], fungicides and insecticides to protect and enhance the biostability of various materials such as wood, stone, textile, paper, and leather [3].

In turn, alkoxysilylmethyl organosilicon derivatives are precursors of thermostable organosilicon polymers used in microelectronics for the creation of durable, non-cracking, chemically resistant films with high dielectric properties [4–7].

In this connection, new alkoxysilylmethyl organosilicon compounds are of considerable practical interest.

The reaction of silylmethylmagnesium chlorides with various organotin and organosilicon monochlorides is a convenient method for the synthesis of such compounds. (Trialkylsilyl)methylmagnesium chlorides have been used in the synthesis of methylenedisilicon containing compounds since the 1940s [8–10]. Later, such Grignard compounds with ethoxy and isopropoxy

substituents bonded to the silicon were used by Corriu et al. in this reaction [11,12]. Recently those containing isopropoxy groups at silicon have been employed for the synthesis of isopropoxysilylmethyl tin substances [13,14].

It should be noted that the application of Grignard reagents with the general formula $Me_{3-n}(AlkO)_nSiCH_2MgCl$, Alk = Me, Et or *i*-Pr is often limited by their low stability due to interaction with alkoxysilicon moieties [15,16].

Previously, we have reported on the synthesis of *tert*-butoxy substituted silylmethylmagnesium chlorides **3a-c** with the general formula $Me_{3-n}(t\text{-}BuO)_nSiCH_2MgCl$, n = 1–3, from the suitable chloromethylchlorosilanes **1a-c** via *tert*-butoxy substituted chloromethylsilanes **2a-c** (Scheme 1). The yields of compounds **3a-c** amounted to 90–95%. These substances were found to be stable in THF at room temperature [17,18] and their stability increased with the increasing of the number of *tert*-butoxy groups.

The reaction of these *tert*-butoxy substituted Grignard compounds with group IVa electrophiles has not been studied yet.

The purpose of the present work is the investigation of the reaction of synthesized (*tert*-butoxysilyl)methylmagnesium chlorides with some organotin and organosilicon monochlorides. Our attention was in particular focused on studying the reactivity of these reagents depending on the number of *tert*-butoxy groups bonded to the silicon and the nature of an organoelement electrophile. It was also interesting to elucidate certain structural features and spectral characteristics of these new (*tert*-butoxysilyl)methyl organoelement compounds.
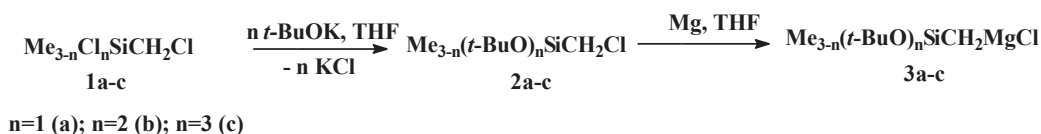
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$$\text{Me}_{3-n}\text{Cl}_n\text{SiCH}_2\text{Cl} \xrightarrow[\text{- n KCl}]{n \; t\text{-BuOK, THF}} \text{Me}_{3-n}(t\text{-BuO})_n\text{SiCH}_2\text{Cl} \xrightarrow{\text{Mg, THF}} \text{Me}_{3-n}(t\text{-BuO})_n\text{SiCH}_2\text{MgCl}$$

1a-c   **2a-c**   **3a-c**

n=1 (a); n=2 (b); n=3 (c)

Scheme 1.

2. Experimental

2.1. Material and methods

All glassware was heated at 100–120 °C in vacuum before use. All manipulations were carried out in dry solvents under dry argon. THF was boiled under argon until the formation of the deep blue color of benzophenone ketyl and distilled immediately before the experiment. Hexane was dried and distilled under phosphorus pentoxide. Potassium *tert*-butylate, a product of Acros Organics, was utilized without additional purification.

The ^{1}H (600.0 MHz), ^{13}C (150.9 MHz), ^{29}Si (119.2 MHz), ^{119}Sn (223.8 MHz), and ^{117}Sn (213.8 MHz) NMR spectra were recorded on a Bruker AVANCE 600 spectrometer at 30 °C. The proton chemical shifts (δ, ppm) were measured relative to the residual C$_6$HD$_5$ (δ 7.155 for solutions in C$_6$D$_6$) or CHCl$_3$ (δ 7.248 for solutions in CDCl$_3$). The ^{13}C chemical shifts were measured relative to C$_6$D$_6$ (δ 128.02) or CDCl$_3$ (δ 77.00). The ^{29}Si chemical shifts were measured relative to external TMS in C$_6$D$_6$ or CDCl$_3$. The ^{119}Sn and ^{117}Sn chemical shifts were measured relative to external Me$_4$Sn in C$_6$D$_6$. The HSQC (^{1}H–^{13}C) and HSQC (^{1}H–^{29}Si) spectra were recorded for assignment of ^{1}H, ^{13}C and ^{29}Si NMR signals [19,20]. Spectra processing was performed with Bruker's TopSpin software package. The $^1J_{CH}$, $^3J_{CH}$ (Hz) values and the multiplicities of the signals were obtained from the monoresonance ^{13}C spectra. Only chemical shifts are given for *t*-BuO-groups in the ^{13}C NMR, since $^1J_{CH}$ and $^3J_{CH}$ for all these groups are the same: 125.3 ÷ 125.5 and 4.0 ÷ 4.1 Hz, respectively. The $^1J_{CSi}$ and $^1J_{CSn}$ were obtained from the doublet signals of the ^{29}Si, ^{119}Sn and ^{117}Sn satellites in the ^{13}C{^{1}H} NMR spectra. Likewise, the $^1J_{SiC}$ and $^2J_{SiSn}$ were obtained from the doublet signals of ^{13}C, ^{119}Sn and ^{117}Sn satellites in the ^{29}Si{^{1}H} NMR spectra. At last, the $^nJ_{SnC}$ and $^2J_{SnSi}$ were obtained from the doublet signals of ^{13}C and ^{29}Si satellites in the ^{119}Sn{^{1}H} NMR spectra.

The mass spectra were obtained on the Agilent 240 Ion Trap GC/MS system. A VF-5 ms quartz capillary column (30 m × 0.25 mm × 0.25 μm) was used for reaction mixture separation. The volume of the probe was 1 μL and evaporator temperature was set at 300 °C. Set initially at 120 °C, the temperature of the column was raised in 1 h to 300 °C at a rate of 20 °C/min and then kept constant for 25 min. Helium was supplied at a flow rate of 1 ml/min; the stream was divided in the evaporator in the ratio 30:1.

2.2. Synthesis of tert-butoxy substituted chloromethylsilanes 2a-c

Tert-butoxy-substituted chloromethylsilanes **2a-c** were synthesized according to the abovementioned procedure with anhydrous potassium *tert*-butylate taken in an amount of 1–3 mol [17].

2.2.1. [Dimethyl(tert-butoxy)silyl]methyl chloride (2a)

Colorless liquid, yield 61%, *b.p.* 70–71 °C (28 torr), d_4^{30} 1.4517, n_D^{30} 1.4162. NMR (C$_6$D$_6$): ^{1}H δ 0.16 (s, 6H, SiMe_2, $^1J_{HC}$ = 119.2, $^2J_{HSi}$ = 6.9); 1.11 (s, 9H, Me_3CO, $^1J_{HC}$ = 125.3); 2.58 (s, 2H, CH_2Cl, $^1J_{HC}$ = 137.0); ^{13}C{^{1}H} and monoresonance δ −0.68 (s, 2C, SiMe_2, $^1J_{CH}$ = 119.2 q, $^1J_{CSi}$ = 62.4, $^3J_{CH}$ = 1.4 m, 6 lines); 31.197 (s, CH_2^{35}Cl (75%), $^1J_{CH}$ = 136.6 t, $^1J_{CSi}$ = 62.1, $^3J_{CH}$ = 1.9 m, 7 lines); 31.189 (s, CH_2^{37}Cl (25%)); 32.0 (s, 3C, Me_3CO); 72.8 (s, 1C, Me$_3$CO); ^{29}Siδ 2.4 (s, $^1J_{SiC}$ = 62.2).

2.2.2. [Methyldi(tert-butoxy)silyl]methyl chloride (2b)

Colorless liquid, yield 51%, *b.p.* 67–70 °C (1 torr), d_4^{20} 1.4897, n_d^{23} 1.4143. NMR (C$_6$D$_6$): ^{1}H δ 0.29 (s, 3H, SiMe, $^1J_{HC}$ = 119.2, $^2J_{HSi}$ = 7.3); 1.23 (s, 18H, Me_3CO); 2.62 (s, 2H, CH_2Cl, $^1J_{HC}$ = 136.5); ^{13}C{^{1}H} and

monoresonance δ −0.7 (s, 1C, SiMe, $^1J_{CH}$ = 119.3 q, $^1J_{CSi}$ = 78.5, $^3J_{CH}$ = 0.8 t); 30.78 (s, CH_2^{35}Cl (75%), $^1J_{CH}$ = 136.7 q, $^1J_{CSi}$ = 79.8, $^3J_{CH}$ = 1.0 q); 30.77 (s, CH_2^{37}Cl (25%)); 31.9 (s, 6C, Me_3CO); 73.2 (s, 2C, Me$_3$CO); ^{29}Si δ −29.0 (s).

2.2.3. [Tri(tert-butoxy)silyl]methyl chloride (2c)

Colorless liquid, yield 59%, *b.p.* 81–82 °C (5 torr), d_4^{20} 1.3210, n_D^{20} 1.4200. NMR (C$_6$D$_6$): ^{1}H δ 1.31 (s, 27H, Me_3CO); 2.61 (s, 2H, CH$_2$Cl); ^{13}C{^{1}H} δ 28.8 (s, 1C, CH$_2$Cl, $^1J_{CSi}$ = 107.8), 31.6 (s, 9C, Me_3CO), 73.2 (s, 3C, Me$_3$CO); ^{29}Si{^{1}H} and monoresonance δ −72.5 (s, $^1J_{SiC}$ = 107.6, $^2J_{SiH}$ = 5.3 t).

2.3. Synthesis of (tert-butoxysilyl)methylmagnesium chlorides 3a-c

2.3.1. [Dimethyl(tert-butoxy)silyl]methylmagnesium chloride (3a)

A solution of 25.0 mmol (4.52 g) of [dimethyl(*tert*-butoxy)silyl]methyl chloride **2a** in 50 ml of THF was added to 25.0 mmol (0.6 g) of magnesium preliminary activated with iodine in 20 ml of THF at 50 °C. After the mixture began to boil, the further process was carried out without additional heating. The chloromethylsilane was added over 1.0 h then the reaction mixture was boiled for 0.5 h until complete magnesium dissolving. The yield of the Grignard reagent **3a** according to titration by 0.1 N HCl was better than 98%.

2.3.2. [Methyldi(tert-butoxy)silyl]methylmagnesium chloride (3b)

A solution of 25.0 mmol (5.96 g) of [methyldi(*tert*-butoxy)silyl]methyl chloride **2b** in 50 ml of THF was added to 25.0 mmol (0.6 g) of magnesium preliminary activated with iodine in 20 ml of boiling THF. The chloromethylsilane was added over 1.0 h then the reaction mixture was boiled for 1.5–2 h until complete magnesium dissolving. Determined as above, the yield of the product **3b** was 95–96.5%.

2.3.3. [Tri(tert-butoxy)silyl]methylmagnesium chloride (3c)

A solution of 25.0 mmol (7.41 g) of [tri(*tert*-butoxy)silyl]methyl chloride **2c** in 50 ml of THF was added to 25.0 mmol (0.6 g) of magnesium preliminary activated with iodine in 20 ml of boiling THF. The chloromethylsilane was added over 1.0 h then the reaction mixture was boiled for 3–4 h until complete magnesium dissolving. Determined as above, the yield of the product **3c** was 92–95%.

2.4. Synthesis of (tert-butoxysilyl)methyl substituted stannanes 4a-f

A solution of 25 mmol (5.0 g) of trimethyltin chloride or 25 mmol (8.14 g) of tri(*n*-butyl)tin chloride in a fourfold volume of THF was added dropwise to a filtered solution of 25 mmol of one of the Grignard reagents **3a-c** in THF at room temperature during 0.5 h.

The temperature of the reaction mixture rose to 30–32 °C. Stirred for 1 h, the reaction mixture was then left overnight. Next day, THF was distilled off at 300 torr on a bath at 70 °C. The residue was twice extracted by a threefold volume of hexane. The precipitated residue was filtered off and washed with hexane. The hexane was removed from the combined extracts and the residue was distilled in vacuum.

2.4.1. [[Dimethyl(tert-butoxy)silyl]methyl]trimethylstannane (4a)

Colorless liquid, yield 4.71 g (61%), *b.p.* 82–84 °C (3 torr), d_4^{20} 1.5822, n_D^{20} 1.5205. NMR (C$_6$D$_6$): ^{1}H δ −0.17 (s, 2H, CH_2, $^1J_{HC}$ = 117.4, $^2J_{HSn(119/117)}$ = 72.3/69.1, $^2J_{HSi}$ = 6.6); 0.175 (s, 6H, SiMe_2, $^1J_{HC}$ = 117.7); 0.177 (s, 9H, SnMe_3, $^1J_{HC}$ = 127.8, $^2J_{HSn(119/117)}$ = 53.9/51.5); 1.20 (s, 9H, Me_3CO); ^{13}C{^{1}H} and monoresonance δ −7.9 (s, 3C, SnMe_3, $^1J_{CSn(119/117/}$

115) = 334.5/319.7/293.5, $^1J_{CH}$ = 127.7 q); −1.5 (s, 1C, CH_2, $^1J_{CSn(119/117)}$ = 244.7/233.9, $^1J_{CH}$ = 117.8 t, $^1J_{CSi}$ = 60.8); 4.2 (s, 2C, SiMe_2, $^1J_{CH}$ = 117.7 q, $^1J_{CSi}$ = 57.4, $^3J_{CSn}$ ≈ 11); 32.3 (s, 3C, Me_3CO); 72.2 (s, 1C, Me_3CO); ^{29}Si{^{1}H} δ 8.3 (s, $^1J_{SiCH2}$ = 60.9, $^1J_{SiCH3}$ = 57.4, $^2J_{SiSn(119/117)}$ = 27.8/26.6); ^{119}Sn{^{1}H} δ 4.9 (s, $^1J_{SnCH3}$ = 335.1, $^1J_{SnCH2Si}$ = 245.5, $^2J_{SnSi}$ = 27.6). Elemental analysis for $C_{10}H_{26}OSiSn$ calculated (%): C, 38.85; H, 8.48. Found (%): C, 38.78; H, 8.40.

2.4.2. [[Methyldi(tert-butoxy)silyl]methyl]trimethylstannane (4b)

Colorless liquid, yield 5.69 g (62.0%), b.p. 104–105 °C (1 torr), d_4^{25} 1.5303, n_d^{25} 1.4720. NMR (C_6D_6): ^{1}H δ −0.15 (s, 2H, CH_2, $^1J_{HC}$ = 117.8, $^2J_{HSn(119/117)}$ = 72.1/69.2, $^2J_{HSi}$ = 6.7); 0.20 (s, 3H, SiMe, $^1J_{HC}$ = 117.7, $^2J_{HSi}$ = 6.9); 0.22 (s, 9H, SnMe_3, $^1J_{HC}$ = 127.8, $^2J_{HSn(119/117)}$ = 54.3/51.8); 1.28 (s, 9H, Me_3CO); ^{13}C{^{1}H} and mono-resonance δ −7.8 (s, 3C, SnMe_3, $^1J_{CSn(119/117)}$ = 337.6/322.0, $^1J_{HC}$ = 127.8 q); −1.1 (s, 1C, CH_2, $^1J_{CSn(119/117)}$ = 239.0/228.5, $^1J_{CH}$ = 117.9 t, $^1J_{CSi}$ = 74.3); 4.7 (s, 1C, SiMe, $^1J_{CH}$ = 117.7 q, $^1J_{CSi}$ = 70.6, $^3J_{CSn}$ = 6.0); 32.3 (s, 6C, Me_3CO); 72.7 (s, 2C, Me_3CO); ^{29}Si{^{1}H} δ −17.5 (s, $^1J_{SiCH2}$ = 74.4, $^1J_{SiCH3}$ = 70.7, $^2J_{SiSn(119/117)}$ = 30.2/28.8); ^{119}Sn{^{1}H} δ 2.2 (s, $^1J_{SnCH3}$ = 337.6, $^1J_{SnCH2Si}$ = 238.6, $^2J_{SnSi}$ = 30.2). Elemental analysis for $C_{13}H_{32}O_2SiSn$ calculated (%): C, 42.52; H, 8.78. Found (%): C, 42.39; H, 8.71.

2.4.3. [[Tri(tert-butoxy)silyl]methyl]trimethylstannane (4c)

Colorless liquid, yield 6.38 g (60.0%), b.p. 87 °C (0.1 torr), d_4^{25} 1.5166, n_d^{25} 1.4445. NMR (C_6D_6): ^{1}H δ −0.14 (s, 2H, CH_2, $^1J_{HC}$ = 118.1, $^2J_{HSn(119/117)}$ = 72.0/68.9, $^2J_{HSi}$ = 7.8); 0.29 (s, 9H, SnMe_3, $^1J_{HC}$ = 128.0, $^2J_{HSn(119/117)}$ = 54.6/52.2); 1.35 (s, 27H, Me_3CO); ^{13}C{^{1}H} and monoresonance δ −7.7 (s, 3C, SnMe_3, $^1J_{CSn(119/117)}$ = 337.8/323.1, $^1J_{CH}$ = 127.8 q); −3.0 (s, 1C, CH_2, $^1J_{CSn(119/117)}$ = 242.2/231.3, $^1J_{CH}$ = 118.0 t, $^1J_{CSi}$ = 97.8); 32.0 (s, 9C, Me_3CO); 72.4 (s, 3C, Me_3CO); ^{29}Si{^{1}H} δ −57.7 (s, $^2J_{SiSn(119/117)}$ = 37.1/35.5); ^{119}Sn{^{1}H} δ 3.8 (s, $^1J_{SnCH3}$ = 337.8, $^1J_{SnCH2Si}$ = 242.2, $^2J_{SnSi}$ = 37.1). Elemental analysis for $C_{16}H_{38}O_3SiSn$ calculated (%): C, 45.19; H, 9.00. Found (%): C, 45.36; H, 8.87.

2.4.4. [[Dimethyl(tert-butoxy)silyl]methyl]tri(n-butyl)stannane (4d)

Colorless liquid, yield 9.0 g (83.0%), b.p. 83–85 °C (4 × 10^{-4} torr), d_4^{20} 1.5276, n_d^{20} 1.4745. NMR (C_6D_6): ^{1}H δ −0.13 (s, 2H, SiCH_2, $^1J_{HC}$ = 117.0, $^2J_{HSn (119/117)}$ = 66.8/64.0, $^2J_{HSi}$ = 6.6); 0.23 (s, 6H, SiMe_2, $^1J_{HC}$ = 117.7, $^2J_{HSi}$ = 6.5); 0.95 (t, 9H, $CH_2CH_2CH_2CH_3$, $^3J_{HH}$ = 7.3); 0.98 (m, 6H, $CH_2CH_2CH_2CH_3$, $^2J_{HSn(119/117)}$ = 51.1/49.0); 1.23 (s, 9H, Me_3CO); 1.40 (m, 6 lines, 6H, $CH_2CH_2CH_2CH_3$, $^3J_{HH}$ = 7.4); 1.59 (m, 6H, $CH_2CH_2CH_2CH_3$); ^{13}C{^{1}H} and monoresonance δ −4.5 (s, 1C, SiCH_2, $^1J_{CSn(119/117)}$ = 196.5/187.6, $^1J_{CH}$ = 117.2 t, $^1J_{CSi}$ = 61.6); 4.5 (s, 2C, SiMe_2, $^1J_{CH}$ = 117.6 q, $^1J_{CSi}$ = 57.1, $^3J_{CSn}$ = 9.9, $^3J_{CH}$ = 1.7 m, 6 lines); 10.7 (s, 3C, $CH_2CH_2CH_2CH_3$, $^1J_{CSn(119/117)}$ = 327.3/312.7, $^1J_{CH}$ = 126.5 t); 14.0 (s, 3C, $CH_2CH_2CH_2CH_3$, $^1J_{CH}$ = 124.5); 27.9 (s, 3C, $CH_2CH_2CH_2CH_3$, $^3J_{CSn(119/117)}$ = 58.0/55.4); 29.7 (s, 3C, $CH_2CH_2CH_2CH_3$, $^2J_{CSn(119/117)}$ = 19.8/19.0); 32.3 (s, 3C, Me_3CO); 72.2 (s, 1C, Me_3CO); ^{29}Si{^{1}H} δ 8.8 (s, $^1J_{SiCH2}$ = 61.4, $^1J_{SiCH3}$ = 57.2, $^2J_{SiSn(119/117)}$ = 24.9/23.9); ^{119}Sn{^{1}H} δ −2.4 (s, $^1J_{SnCH2CH2CH2CH3}$ = 327.3, $^1J_{SnCH2Si}$ = 196.2, $^2J_{SnSi}$ = 25.0, $^2J_{SnCH2CH2CH2CH3}$ = 20.0, $^3J_{SnCH2CH2CH2CH3}$ = 58.0).

2.4.5. [[Methyldi(tert-butoxy)silyl]methyl]tri(n-butyl)stannane (4e)

Colorless liquid, yield 10.85 g (88.0%), b.p. 103–105 °C (1 × 10^{-3} torr), d_4^{20} 1.5020, n_d^{20} 1.4655. NMR (C_6D_6): ^{1}H δ −0.13 (s, 2H, SiCH_2, $^1J_{HC}$ = 117.3, $^2J_{HSn(119/117)}$ = 66.5/64.4, $^2J_{HSi}$ = 6.5); 0.25 (s, 3H, SiMe, $^1J_{HC}$ = 117.6, $^2J_{HSi}$ = 6.7); 0.96 (t, 9H, $CH_2CH_2CH_2CH_3$, $^3J_{HH}$ = 7.3); 1.02 (m, 6H, $CH_2CH_2CH_2CH_3$); 1.31 (s, 18H, Me_3CO); 1.41 (m, 6 lines, 6H, $CH_2CH_2CH_2CH_3$, $^3J_{HH}$ = 7.4); 1.62 (m, 6H, $CH_2CH_2CH_2CH_3$); ^{13}C{^{1}H} and monoresonance δ −4.2 (s, 1C, SiCH_2, $^1J_{CSn(119/117)}$ = 190.4/181.9, $^1J_{CH}$ = 117.4 t, $^1J_{CSi}$ = 75.0); 4.9 (s, C, SiMe, $^1J_{CH}$ = 117.5 q, $^1J_{CSi}$ = 70.4, $^3J_{CSn}$ = 5.3); 10.8 (s, 3C, $CH_2CH_2CH_2CH_3$, $^1J_{CSn(119/117/115)}$ = 329.5/315.0/289.3, $^1J_{CH}$ = 126.4 t); 14.0 (s, 3C, $CH_2CH_2CH_2CH_3$, $^1J_{CH}$ = 124.4); 27.9 (s, 3C, $CH_2CH_2CH_2CH_3$); 29.7 (s, 3C, $CH_2CH_2CH_2CH_3$, $^2J_{CSn(119/117)}$ = 19.7/19.0); 32.2 (s, 6C, Me_3CO); 72.3 (s,

2C, Me_3CO); ^{29}Si{^{1}H} δ −16.8 (s, $^2J_{SiSn(119/117)}$ = 26.5/25.3); ^{119}Sn{^{1}H} δ −4.2 (s, $^1J_{SnCH2CH2CH2CH3}$ = 329.5, $^1J_{SnCH2Si}$ = 190.5, $^2J_{SnSi}$ = 26.3, $^2J_{SnCH2CH2CH2CH3}$ = 19.9, $^3J_{SnCH2CH2CH2CH3}$ = 58.6).

2.4.6. [[Tri(tert-butoxy)silyl]methyl]tri(n-butyl)stannane (4f)

Colorless liquid, yield 11.0 g (80.0%), b.p 140–145 °C (1 × 10^{-3} torr), d_4^{24} 1.5337, n_d^{24} 1.4630. NMR (C_6D_6): ^{1}H δ −0.14 (s, 2H, SiCH_2, $^1J_{HC}$ = 117.4, $^2J_{HSn(119/117/115)}$ = 66.3/63.4/58.3, $^2J_{HSi}$ = 7.9); 0.97 (t, 9H, $CH_2CH_2CH_2CH_3$, $^3J_{HH}$ = 7.3); 1.08 (m, 6H, $CH_2CH_2CH_2CH_3$, $^2J_{HSn(119/117)}$ = 52.1/49.8); 1.37 (s, 27H, Me_3CO); 1.43 (m, 6 lines, 6H, $CH_2CH_2CH_2CH_3$, $^3J_{HH}$ = 7.3); 1.65 (m, 6H, $CH_2CH_2CH_2CH_3$); ^{13}C{^{1}H} δ −6.2 (s, 1C, SiCH_2, $^1J_{CSn(119/117)}$ = 193.3/184.7, $^1J_{CSi}$ = 98.1); 10.8 (s, 3C, $CH_2CH_2CH_2CH_3$, $^1J_{CSn(119/117/115)}$ = 330.3/316.1/290.0); 14.0 (s, 3C, $CH_2CH_2CH_2CH_3$); 27.9 (s, 3H, $CH_2CH_2CH_2CH_3$, $^3J_{CSn(119/117)}$ = 58.8/56.1); 29.7 (s, 3C, $CH_2CH_2CH_2CH_3$, $^2J_{CSn(119/117)}$ = 19.7/19.0); 32.0 (s, 9C, Me_3CO); 72.5 (s, 3C, Me_3CO); ^{29}Si{^{1}H} δ −57.0 (s, $^1J_{SiC}$ = 98.2, $^2J_{SiSn(119/117)}$ = 32.1/30.7); ^{119}Sn{^{1}H} δ −3.1 (s, $^1J_{SnCH2CH2CH2CH3}$ = 330.6, $^1J_{SnCH2Si}$ = 193.3, $^2J_{SnSi}$ = 32.1, $^2J_{SnCH2CH2CH2CH3}$ = 19.8, $^3J_{SnCH2CH2CH2CH3}$ = 58.8).

2.5. (tert-Butoxysilyl)methyl substituted silanes 5a-f

The reaction was carried out according to the method described above for compounds **4a-f** using a solution of 25 mmol of one of the Grignard reagents **3a-c** in THF and 25 mmol (2.7 g) of trimethylsilicon chloride or 25 mmol (5.8 g) of methyldiphenylsilicon chloride. The reaction mixture was stirred at reflux for 1–6 h in the case of trimethylsilicon chloride and for 1–2 h when methyldiphenylsilicon chloride was taken and then left overnight. The reactions were monitored by NMR spectroscopy until the complete disappearance of the CH_2MgCl-proton signals of **3a-c**. The reaction proceeds with the formation of a complex mixture of products **5a-f**, **6a-f**, **7a-c** and **8** (part **3.4**). Substances **5a,d** were isolated by distillation in vacuum.

The ^{1}H NMR data obtained for *tert*-butoxysilylmethyl substituted silanes **5a-e** are presented in part **3.2.2**.

2.5.1. [[Dimethyl(tert-butoxy)silyl]methyl]trimethylsilane (5a)

Colorless liquid, yield 2.13 g (39.0%), b.p 74–75 °C (14 torr), n_d^{22} 1.4187. NMR (C_6D_6): ^{13}C{^{1}H} and monoresonance δ 1.5 (s, 3C, SiMe_3, $^1J_{CH}$ = 118.4 q, $^1J_{CSi}$ = 50.9, $^3J_{CH}$ = 2.1 m, 9 lines); 4.3 (s, 2C, SiMe_2, $^1J_{CH}$ = 117.7 q, $^1J_{CSi}$ = 57.4, $^3J_{CH}$ = 1.6 m, 6 lines); 7.1 (s, 1C, CH_2, $^1J_{CH}$ = 108.6 t, $^1J_{CSi}$ = 56.4, $^1J_{CSi}$ = 44.3, $^3J_{CH}$ = 1.6 m, 16 lines, only 10 visible); 32.3 (s, 3C, Me_3CO); 72.2 (s, 1C, Me_3CO); ^{29}Si{^{1}H} and monoresonance δ −0.3 (s, SiMe_3, $^1J_{SiC}$ = 50.8, $^1J_{SiC}$ = 44.2, $^2J_{SiCH2}$ = 8.8 t, $^2J_{SiCH3}$ = 6.7 m, 10 lines, only 6 visible); 6.6 (s, SiMe_2, $^1J_{SiC}$ = 57.1, $^2J_{SiCH2}$ = 8.7 t, $^2J_{SiCH3}$ = 6.6 m, 7 lines). Elemental analysis for $C_{10}H_{26}OSi_2$ calculated (%): C, 54.97; H, 12.00. Found (%): C, 54.82; H, 11.93.

2.5.2. [[Methyldi(tert-butoxy)silyl]methyl]trimethylsilane (5b)

NMR (C_6D_6): ^{13}C{^{1}H} and monoresonance δ 1.4 (s, 3C, SiMe_3, $^1J_{CH}$ = 118.4 q, $^1J_{CSi}$ = 51.1, $^3J_{CH}$ = 2.1 m, 9 lines, only 7 visible); 4.9 (s, 1C, SiMe, $^1J_{CH}$ = 117.6 q, $^1J_{CSi}$ = 70.6, $^3J_{CH}$ = 0.9 t); 7.7 (s, 1C, CH_2, $^1J_{CH}$ = 108.7 t, $^1J_{CSi}$ = 68.9, $^1J_{CSi}$ = 43.5); 32.2 (s, 6C, Me_3CO); 72.3 (s, 2C, Me_3CO); ^{29}Si{^{1}H} δ −19.9 (s, $\underline{Si}Me$), −0.6 (s, $\underline{Si}Me_3$).

2.5.3. [[Tri(tert-butoxy)silyl]methyl]trimethylsilane (5c)

NMR ($CDCl_3$): ^{13}C{^{1}H} and monoresonance δ 1.1 (s, 3C, SiMe_3, $^1J_{CH}$ = 118.6 q, $^1J_{CSi}$ = 51.3, $^3J_{CH}$ = 2.0 m, 9 lines, only 7 visible); 5.8 (s, 1C, CH_2, $^1J_{CH}$ = 108.7 t, $^1J_{CSi}$ = 90.7, $^1J_{CSi}$ = 43.6, $^3J_{CH}$ = 1.8 m, 10 lines, only 8 visible); 31.7 (s, 9C, Me_3CO); 72.6 (s, 3C, Me_3CO); ^{29}Si {^{1}H} and monoresonance δ −61.2 (s, *t*-BuOSi, $^2J_{SiCH2}$ = 10.4 t); −0.4 (s, SiMe_3, $^2J_{SiCH2}$ = 8.7 t, $^2J_{SiCH3}$ = 6.6 m, 10 lines, only 8 visible).

2.5.4. [[Dimethyl(tert-butoxy)silyl]methyl]methyldiphenylsilane (5d-I and 5d-II)

The signals of two spatial rotational isomers are observed in the

spectra: **5d-I** and **5d-II** in the integral intensity ratio 13:1. Colorless liquid, yield 5.16 g (60.3%), *b.p.* 120–125 °C (1.2 × 10^{-2} torr).

5d-I NMR (C_6D_6): $^{13}C\{^1H\}$ and monoresonance δ −1.5 (s, 1C, Si*Me*Ph$_2$, $^1J_{CH}$ = 119.9 q, $^1J_{CSi}$ = 54.1, $^3J_{CH}$ = 2.4 t); 4.34 (s, 1C, *CH$_2$*, $^1J_{CH}$ = 109.3 t, $^1J_{CSi}$ = 55.6, $^1J_{CSi}$ = 47.2, $^3J_{CH}$ = 1.5 m, 10 lines, only 8 visible); 4.37 (s, 2C, Si*Me$_2$*, $^1J_{CH}$ = 117.9 q, $^1J_{CSi}$ = 57.8, $^3J_{CH}$ = 1.6 m, 6 lines); 32.1 (s, 3C, *Me$_3$*CO); 72.4 (s, 1C, Me$_3$*C*O); 127.9 (s, 4C, *m*-Ph); 129.1 (s, 2C, *p*-Ph); 134.8 (s, 4C, *o*-Ph); 139.6 (s, 2C, *i*-Ph, $^1J_{C(ipso)Si}$ = 67.4); $^{29}Si\{^1H\}$ δ −8.1 (s, SiMePh$_2$, $^1J_{SiC(ipso)}$ = 67.3, $^1J_{SiC}$ = 54.1, $^1J_{SiC}$ = 47.0); 6.8 (s, *t*-BuOSi, $^1J_{SiC}$ = 57.8, $^1J_{SiC}$ = 55.8).

5d-II NMR (C_6D_6): $^{13}C\{^1H\}$ and monoresonance δ −1.6 (s, 1C, Si*Me*Ph$_2$, $^1J_{CH}$ = 119.8 q, $^1J_{CSi}$ = 53.8, $^3J_{CH}$ = 2.5 t); 3.5 (s, 2C, Si*Me$_2$*, $^1J_{CH}$ = 118.1 q, $^1J_{CSi}$ = 59.6, $^3J_{CH}$ = 1.6 m, 6 lines); 4.31 (s, 1C, *CH$_2$*); 32.2 (s, 3C, *Me$_3$*CO); 73.4 (s, 1C, Me$_3$*C*O); 127.6–139.6 (s, 12C, Ph); $^{29}Si\{^1H\}$ δ −8.7 (s, SiMePh$_2$); 6.9 (s, *t*-BuOSi, $^1J_{SiC}$ = 59.5).

2.5.5. [[Methyldi(tert-butoxy)silyl]methyl]methyldiphenylsilane (5e)

NMR (C_6D_6): $^{13}C\{^1H\}$ and monoresonance δ −1.6 (s, 1C, Si*Me*Ph$_2$, $^1J_{CH}$ = 120.0 q, $^1J_{CSi}$ = 54.6, $^3J_{CH}$ = 2.4 t); 4.7 (s, 1C, Si*Me*, $^1J_{CH}$ = 118.0 q, $^1J_{CSi}$ = 71.6, $^3J_{CH}$ = 1.0 t); 5.1 (s, 1C, *CH$_2$*, $^1J_{CH}$ = 109.2 t, $^1J_{CSi}$ = 67.6); 32.06 (s, 6C, *Me$_3$*CO); 72.5 (s, 2C, Me$_3$*C*O); 127.9 (s, 4C, *m*-Ph); 129.0 (s, 2C, *p*-Ph); 134.8 (s, 4C, *o*-Ph); 139.7 (s, 2C, *i*-Ph); $^{29}Si\{^1H\}$ δ −20.5 (s, *t*-BuOSi); −8.3 (s, SiMePh$_2$).

2.5.6. [[Tri(tert-butoxy)silyl]methyl]methyldiphenylsilane (5f)

NMR (C_6D_6): the ^1H and ^{13}C signals are not visible due to their overlapping with other signals; $^{29}Si\{^1H\}$ δ −64.7 (s, *t*-BuOSi), −7.4 (s, SiMePh$_2$).

2.6. (tert-Butoxysilyl)methoxy substituted silanes 6a-f

(*tert*-Butoxysilyl)methoxy substituted silanes **6a-f** were prepared according to the procedure described above in admixture with compounds **5a-f**. Substances **6c,e,f** were isolated in pure form. The ^1H NMR data (C_6D_6; δ, ppm; *J*, Hz) obtained for **6a-f** are presented in part **3.2.2**.

2.6.1. [[Dimethyl(tert-butoxy)silyl]methoxy]trimethylsilane (6a)

NMR (C_6D_6): $^{13}C\{^1H\}$ and monoresonance δ −0.7 (s, 3C, OSi*Me$_3$*, $^1J_{CH}$ = 118.1 q, $^1J_{CSi}$ = 58.9, $^3J_{CH}$ = 1.6 m, 7 lines); −0.6 (s, 2C, Si*Me$_2$*, $^1J_{CH}$ = 118.6 q, $^1J_{CSi}$ = 59.8, $^3J_{CH}$ = 1.4 m, 6 lines); 32.2 (s, 3C, *Me$_3$*CO); 55.8 (s, 1C, *CH$_2$*O, $^1J_{CH}$ = 129.2 t, $^1J_{CSi}$ = 72.3, $^3J_{CH}$ = 1.6 m, 7 lines); 72.3 (s, 1C, Me$_3$*C*O); $^{29}Si\{^1H\}$ δ 3.1 (s, SiMe$_2$, $^1J_{SiC}$ = 60.1); 18.34 (s, OSiMe$_3$, $^1J_{SiC}$ = 59.1).

2.6.2. [[Methyldi(tert-butoxy)silyl]methoxy]trimethylsilane (6b)

NMR (C_6D_6): $^{13}C\{^1H\}$ and monoresonance δ −0.7 (s, 3C, OSi*Me$_3$*, $^1J_{CH}$ = 118.1 q, $^1J_{CSi}$ = 58.8, $^3J_{CH}$ = 1.6 m, 7 lines); −0.3 (s, 1C, Si*Me*, $^1J_{CH}$ = 118.7 q, $^1J_{CSi}$ = 74.2, $^3J_{CH}$ = 0.7 t); 32.1 (s, 6C, *Me$_3$*CO); 55.3 (s, 1C, *CH$_2$*O, $^1J_{CH}$ = 129.3 t, $^1J_{CSi}$ = 89.8); 72.6 (s, 2C, Me$_3$*C*O); $^{29}Si\{^1H\}$ δ −25.7 (s, SiMe); 18.3 (s, OSiMe$_3$).

2.6.3. [[Tri(tert-butoxy)silyl]methoxy]trimethylsilane (6c)

Coloress liquid, the yield after distillation in vacuum is 2.6 g (30.0%), *b.p* 85–90 °C (50 torr). NMR (CDCl$_3$): $^{13}C\{^1H\}$ and monoresonance δ −0.9 (s, 3C, OSi*Me$_3$*, $^1J_{CH}$ = 118.1 q, $^1J_{CSi}$ = 58.8, $^3J_{CH}$ = 1.6 m, 7 lines); 31.7 (s, 9C, *Me$_3$*CO); 53.2 (s, 1C, *CH$_2$*O, $^1J_{CH}$ = 128.9 t, $^1J_{CSi}$ = 116.4); 72.5 (s, 3C, Me$_3$*C*O); $^{29}Si\{^1H\}$ and monoresonance δ −69.3 (s, *t*-BuOSi, $^2J_{SiCH2}$ = 5.8 t, $^3J_{SiCOSi}$ = 7.26); 17.8 (s, OSiMe$_3$, $^1J_{SiC}$ = 58.8, $^2J_{SiCH3}$ = 6.6 m, 10 lines, only 8 visible, $^3J_{SiOCSi}$ = 7.25, $^3J_{SiOCH2}$ = 2.3 t).

2.6.4. [[Dimethyl(tert-butoxy)silyl]methoxy]methyldiphenylsilane (6d)

NMR (C_6D_6): $^{13}C\{^1H\}$ δ −1.1 (s, 2C, Si*Me$_2$*); −0.3 (s, 1C, Si*Me*Ph$_2$); 56.6 (s, 1C, *CH$_2$*O); 127.6 ÷ 138.7 (Ph, signals overlap with product **5d** signals); $^{29}Si\{^1H\}$ δ −0.8 (s, SiMePh$_2$); 3.0 (s, *t*-BuOSi).

2.6.5. [[Methyldi(tert-butoxy)silyl]methoxy]methyldiphenylsilane (6e)

Coloress viscous liquid, the yield after distillation in vacuum is 1.04 g (10.0%), *b.p* 120–124 °C (2,5x10^{-5} torr). NMR (C_6D_6): $^{13}C\{^1H\}$ and monoresonance δ −0.1 (s, 1C, Si*Me*, $^1J_{CH}$ = 118.7 q, $^1J_{CSi}$ = 74.3, $^3J_{CH}$ = 0.8 t); −3.2 (s, 1C, Si*Me*Ph$_2$, $^1J_{CH}$ = 119.5 q, $^1J_{CSi}$ = 62.0); 32.11 (s, 6C, *Me$_3$*CO); 56.5 (s, 1C, *CH$_2$*O, $^1J_{CH}$ = 129.9 t, $^1J_{CSi}$ = 89.4); 72.7 (s, 2C, *Me$_3$*CO); 128.1 (s, 4C, *m*-Ph); 129.9 (s, 2C, *p*-Ph); 134.9 (s, 4C, *o*-Ph); 136.8 (s, 2C, *i*-Ph); $^{29}Si\{^1H\}$ δ −25.9 (s, *t*-BuOSi); −0.9 (s, SiMePh$_2$).

2.6.6. [[Tri(tert-butoxy)silyl]methoxy]methyldiphenylsilane (6f)

Colorless viscous liquid, the yield after distillation in vacuum is 2.13 g (18.0%), *b.p* 103–105 °C (4.5x10^{-5} torr). NMR (C_6D_6): $^{13}C\{^1H\}$ δ −3.1 (s, 1C, Si*Me*Ph$_2$, $^1J_{CSi}$ = 62.6); 32.0 (s, 9C, *Me$_3$*CO); 55.0 (s, 1C, *CH$_2$*O, $^1J_{CSi}$ = 116.3); 72.9 (s, 3C, Me$_3$*C*O); 128.1 (s, 4C, *m*-Ph); 129.9 (s, 2C, *p*-Ph); 135.0 (s, 4C, *o*-Ph); 136.9 (s, 2C, *i*-Ph); $^{29}Si\{^1H\}$ δ −69.7 (s, *t*-BuOSi); −1.8 (s, SiMePh$_2$).

2.7. tert-Butoxy substituted methylsilanes 7a-c

2.7.1. Trimethyl(tert-butoxy)silane (7a)

The substance was detected by ^{29}Si NMR only. The ^1H and ^{13}C signals could not be detected due to the high-intensity signals of other substances. NMR (C_6D_6): $^{29}Si\{^1H\}$ and monoresonance δ 6.8 (s, $^2J_{SiCH3}$ = 6.4 m, 10 lines, 6 visible). Literature data: ^1H δ 0.05 (s, 9H, Si*Me$_3$*); 1.23 (s, 9H, *Me$_3$*CO); $^{13}C\{^1H\}$ δ 1.4 (s, 3C, Si*Me$_3$*); 31.1 (s, 3C, *Me$_3$*CO); 71.9 (s, 1C, Me$_3$*C*O) [21–25]; ^{29}Si 6.2 [23,25].

2.7.2. Dimethyldi(tert-butoxy)silane (7b)

B.p. 57 °C (30 torr). NMR (C_6D_6): ^1H δ 0.20 (s, 6H, Si*Me$_2$*, $^1J_{HC}$ = 117.6); 1.28 (s, 18H, *Me$_3$*CO); $^{13}C\{^1H\}$ and monoresonance δ 3.1 (s, 2C, Si*Me$_2$*, $^1J_{CH}$ = 117.8 q, $^1J_{CSi}$ = 72.9, $^3J_{CH}$ = 1.0 q); 32.1 (s, 6C, *Me$_3$*CO); 72.2 (s, 2C, Me$_3$*C*O); $^{29}Si\{^1H\}$ δ −18.8 (lit. data δ −19.9 [23]).

2.7.3. Methyltri(tert-butoxy)silane (7c)

B.p. 75 °C (10 torr), n_d^{23}1.3965 (*B.p.* 90–91 °C (20 torr), n_d^{25} 1.3959, d_4^{25} 0.8493 [26], 192–5 °C, n_d^{21} 1.3972 [15]. NMR (C_6D_6): ^1H δ 0.25 (s, 3H, Si*Me*, $^1J_{HC}$ = 118.2, $^2J_{HSi}$ = 8.3); 1.35 (s, 18H, *Me$_3$*CO); $^{13}C\{^1H\}$ and monoresonance δ 1.8 (s, 1C, Si*Me*, $^1J_{CH}$ = 118.3 q, $^1J_{CSi}$ = 96.2); 31.9 (s, 9C, *Me$_3$*CO); 72.3 (s, 3C, Me$_3$*C*O); $^{29}Si\{^1H\}$ δ −59.0.

The NMR spectra obtained for compounds **7a-c** correspond to those predicted on the basis of calculation using Advanced Chemistry Development, Inc. (ACD/Labs) Software V11.01 (© 1994–2019 ACD/Labs).

2.8. THF cycle cleavage product 8

2.8.1. Trimethyl(4-iodobutoxy)silane (8)

The content of this compound in the reaction mixture amounts to 3 or 10% in the case of the reaction of Me$_3$SiCl with **3a** or **3b**, respectively. NMR (C_6D_6): ^1H δ 0.03 (s, 9H, OSi*Me$_3$*, $^2J_{HSi}$ = 6.3); ≈1.36 (m, 2H, OCH$_2$C*H$_2$*); 1.60 (m, 2H, ICH$_2$C*H$_2$*); 2.77 (t, 2H, I*CH$_2$*, $^3J_{HH}$ = 7.1); 3.32 (t, 2H, O*CH$_2$*, $^3J_{HH}$ = 6.1); $^{13}C\{^1H\}$ and monoresonance δ −0.4(s, 3C, OSi*Me$_3$*, $^1J_{CH}$ = 118.0 q, $^3J_{CH}$ = 1.6 m, 7 lines, 5 visible); 6.3 (s, 1C, I*CH$_2$*, $^1J_{CH}$ = 150.1 t, $^nJ_{CH}$ = 4.7 m, 5 lines); 30.5 (s, 1C, ICH$_2$*C*H$_2$, $^1J_{CH}$ ≈ 126 ÷ 127 tm); 33.7 (s, 1C, O*CH$_2$C*H$_2$, $^1J_{CH}$ = 126.0 t, $^3J_{CH}$ = 4.1 m, 5 lines, $^3J_{CH}$ = 2.3 t); 61.3 (s, 1C, O*C*H$_2$, $^1J_{CH}$ = 139.7 t, $^nJ_{CH}$ = 4.0 m, 5 lines); $^{29}Si\{^1H\}$ δ 16.4 (s, OSiMe$_3$).

3. Results and discussion

3.1. The reaction of (tert-butoxysilyl)methylmagnesium chlorides with trialkyltin chlorides

3.1.1. Synthesis of compounds 4a-f

It has been found, that (*tert*-butoxysilyl)methylmagnesium chlorides **3a-c** readily react with trialkyltin chlorides in THF at room temperature. The reaction proceeds on the methylene carbon giving C-substituted products **4a-f** (Scheme 2).

It should be noted, that the yields of the corresponding C-derivatives

$$\text{Me}_{3\text{-n}}(t\text{-BuO})_n\text{SiCH}_2\text{MgCl} + \text{R}_3\text{SnCl} \longrightarrow \text{Me}_{3\text{-n}}(t\text{-BuO})_n\text{SiCH}_2\text{SnR}_3 + \text{MgCl}_2$$

$$\quad\quad\quad \textbf{3a-c} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \textbf{4a-f}$$

R=Me, n=1 (a); n=2 (b); n=3 (c);

R= *n*-Bu, n=1 (d); n=2 (e); n=3 (f)

Scheme 2.

do not depend on the number of *tert*-butoxy groups bonded to the silicon. At the same time they make up about 60% for methylstannanes and reach 88% in the case of *n*-butylstannanes.

Compounds **4a-f** are stable and may be isolated by vacuum distillation in up to 88% yields.

3.1.2. NMR spectroscopic analysis of compounds 4a-f

The structures of compounds **4a-f** was confirmed by the ^{1}H, ^{13}C, ^{29}Si, [117,119]Sn NMR spectra. The assignment of the signals was carried out by analyzing the spin–spin coupling constants and chemical shifts. Characteristic doublet signals for the [119]Sn and [117]Sn magnetic isotopes with high natural abundances of 8.59 and 7.68%, respectively were observed in all the ^{1}H, ^{13}C and ^{29}Si NMR spectra of compounds **4a-f**. It was also possible to observe the satellites of the [115]Sn isotope with natural abundance of 0.34% in the ^{1}H and ^{13}C spectra for compounds **4a, 4e** and **4f**. The assignment of the ^{1}H and ^{13}C signals for *n*-BuSn-groups was performed by means of the COSY and HSQC ([1]H–[13]C, $J = 127$ Hz) spectra.

The NMR data of compounds **4a-f** are presented in **part 2.4**.

Methylene proton signals for compounds **4a-f** are observed at δ $-0.17 \div -0.13$ as singlets with two pairs of satellites due to proton interaction with [117]Sn and [119]Sn nuclei, which is typical for such compounds [27]. The $^2J_{\text{HSn}}$ coupling constants lie in the range of $66.3 \div 72.3$ Hz. The Si substitution pattern of the substances obtained has insignificant effect on methylene protons chemical shifts and coupling constants, whereas change of SnMe$_3$ to SnBu$_3$ results in a significantly lowered coupling constant.

A methylene carbon signal of compounds **4a-c** having methyl groups bonded to the tin is observed in the ^{13}C{^{1}H} spectra at δ range of $-3.0 \div -1.1$. The results obtained are in accordance with the known data [27]. This signal is shifted upfield to δ $-6.2 \div -4.2$ for sterically hindered substances **4d-f**. It is interesting to note that the substituent bonded to the tin has a pronounced effect on the $^1J_{\text{CSn}}$ for SiC*H$_2$Sn* fragment. The $^1J_{\text{CSn}}$ constants lie in the range of $238.6 \div 245.5$ Hz in the case of compounds **4a-c** and decrease to $190.5 \div 196.2$ Hz for *n*-butyl substituted derivatives **4d-f**.

The $^1J_{\text{CH}}$ constants for methyl and methylene carbons, bonded with the silicon range from 117.2 to 118.0 Hz. The influence of tin on the $^1J_{\text{CH}}$ value is negligible.

The ^{29}Si signals of C-substituted compounds **4a-f** are located in the δ range of $-57.7 \div 8.8$ depending on the number of *tert*-butoxy groups at silicon. Increasing the number of *tert*-butoxy groups gives rise to significant upfield shift of silicon signals due to rising shielding of silicon which is typical for alkoxysilanes [28]. It should be noted, however, that the alkyl chain length of the substituents bonded to the tin has no effect on the ^{29}Si chemical shifts. The $^2J_{\text{SiSn}}$ values for compounds **4a-f** are slightly different and lie in the range of $27.8 \div 37.1$ Hz in the case of substances with methyl groups at tin and in the range of $24.9 \div 32.1$ Hz in the case of products containing *n*-butyl substituents.

At the same time, the $^2J_{\text{SiSn}}$ values show a slight but systematic rise as the number of *tert*-butoxy groups increases, i.e., $27.8 < 30.2 < 37.1$ Hz and $24.9 < 26.5 < 32.1$ Hz for the series **4a–c** and **4d–f**, respectively.

In the case of ^{119}Sn NMR spectroscopy, it was found that the signals of the tin observed as singlets with three pairs of satellites caused by the interaction of [119]Sn with the [29]Si nucleus and two different ^{13}C nuclei in the regions characteristic for tetraalkyl substituted organotin compounds [1,28–31]. The tin chemical shifts for methyl substituted products **4a-c** lie in the δ range of $2.2 \div 4.9$ and shift upfield to δ $-4.2 \div -2.4$ in the case of *n*-butyl substituted derivatives **4d-f**. The coupling constants $^1J_{\text{SnC}}$ of the [119]Sn with the carbon of the alkyl substituent are in the range of $327.3 \div 337.8$ Hz, which is fully consistent with the literature data [1,29].

It is of interest to note that *n*-Bu$_3$Sn-Sn(*n*-Bu)$_3$ is also formed in amounts of up to 3% in the reaction of [(*tert*-butoxy)silyl]methylmagnesium chlorides **3a-c** with tri(*n*-butyl)tin chloride along with the target products **4d-f**. The signal of this distannane is observed in the ^{119}Sn NMR spectrum at δ -83.6. The $^1J_{(119)\text{Sn-}(117)\text{Sn}}$ direct constant is 2564.4 ± 0.5 Hz, which is determined from the doublet signals of the satellites [117]Sn of the *n*-Bu$_3$[119]Sn-[117]Sn(*n*-Bu)$_3$ isotopomer. The same constant value ($^1J_{\text{Sn}(117)\text{Sn-}(119)\text{Sn}} = 2564.9 \pm 0.6$ Hz) is observed in the [117]Sn NMR spectrum for the signal at δ -83.5. The $^1J_{(119)\text{Sn-}(119)\text{Sn}}$ value calculated according to gyromagnetic ratios is 2683 Hz. Our $^1J_{\text{SnSn}}$ data differ from those found in the literature for a distannane with *n*-Bu-groups: $^1J_{(119)\text{Sn-}(117)\text{Sn}} = 2625$ Hz [32], $^1J_{(119)\text{Sn-}(119)\text{Sn}} = 2748$ Hz (calculated) [1].

The distannane may be formed in the reaction of tri(*n*-butyl)tin chloride with (*n*-Bu)$_3$SnMgCl [33,34]. The latter could be formed as a result of the exchange process between Grignard reagent **3c** and tri(*n*-butyl)tin chloride or from the reaction of residual ultra fine magnesium and tri(*n*-butyl)tin chloride.

3.1.3. Gas chromatographic and mass spectrometric (GC/MS) analysis of compounds 4a-c

Some of the substances and reaction mixtures were investigated by GS/MS under electron ionization for an additional confirmation of the structures of the compounds obtained, wherein fragmentation routes for main compounds were determined.

Compounds **4a-c** with the general formula Me$_{3\text{-n}}$(*t*-BuO)$_n$SiCH$_2$SnMe$_3$, n = 1–3, were analyzed by GC/MS under electron ionization mode for an additional confirmation of their structures. This allows obtaining new data on fragmentation for the (*tert*-butoxysilyl) methyl tin derivatives.

The fragmentation of substances **4a-c** was investigated for the most intensive [120]Sn isotope because of its highest content in nature [35].

It was found that the molecular peaks for all these substances could not be observed using an Agilent Technologies 240 Ion Trap in the EI mode with a minimal energy of 70 eV.

For silicon and tin containing products **4a-c** splitting off one methyl group (M = 15) takes place at first giving rise to cations with m/z $[\text{M}-15]^+$. These cations undergo subsequent elimination of isobutene C$_4$H$_8$ with molecular mass 56 Da. The peaks of maximum intensity with m/z $[\text{M}-15-56n]^+$ (n = 1 ÷ 3) in the mass spectra of compounds **4a-c** prove this fact. It should be noted, that C$_4$H$_8$ fragments release for compounds **4b** with two *tert*-butoxy groups and for **4c** with three *tert*-butoxy groups goes step by step with intermediate formation of cations with m/z 297 for **4b** and m/z 355, 299 for **4c,** respectively.

Table 1
GC/MS data for compounds **4a-c** containing the ^{120}Sn isotope.

Compound	M (Da)	τ ret. (min)	m/z (I. % rel.)
4a	310	5.63	295(49) [M–CH₃]⁺; **239(100)** [295-C₄H₈]⁺; 223 (10); 209(11); 193(12); 165(7); 135(11)
4b	368	8.01	353(49) [M–CH₃]⁺; 297(17) [353-C₄H₈]⁺; **241(100)** [297- C₄H₈]⁺; 223(14); 209(14); 193(18); 165(8); 135(7)
4c	426	9.98	411(50) [M–CH₃]⁺; 355(17) [411-C₄H₈]⁺; 299(23) [355-C₄H₈]⁺; **243 (100)** [299-C₄H₈]⁺; 225(13); 195(19); 165(6); 135(6)

GC/MS data for compounds **4a-c** with ^{120}Sn isotope are given (Table 1).

Thus, it was found, that under electron ionization of compounds **4a-c** their stable cations $(HO)_nMe_{3-n}SiCH_2{}^{120}Sn^+Me_2$ with considerable signals intensity and m/z 239 (n = 1), 241 (n = 2) and 243 (n = 3) were formed due to methyl splitting off molecular ions and subsequent C_4H_8 elimination from *tert*-butoxy groups. This is an additional evidence of the compounds **4a-c** structure.

3.2. The reaction of (tert-butoxysilyl)methylmagnesium chlorides with chlorosilanes

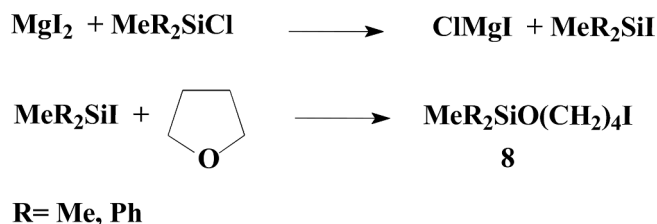#### 3.2.1. Synthesis of compounds 5-7

Unlike a similar process occurring with organotin compounds, the reaction of (*tert*-butoxysilyl)methylmagnesium chlorides **3a-c** with chlorosilanes (Me_3SiCl, $MePh_2SiCl$) runs in more severe conditions and results in three main products **5–7** (Scheme 3).

All the compounds were identified by NMR spectroscopy in their reaction mixtures after evaporation of THF. Substances **5a,d** and **6c,e,f** were isolated by distillation in vacuum.

(*tert*-Butoxysilyl)methyl silicon compounds **5a-f** with the general formula $Me_{3-n}(t\text{-}BuO)_nSiCH_2SiMeR_2$, R = Me, Ph, occur as main products of reaction (**i**) from Grignard reagent **3a** containing one only *tert*-butoxy group bonded to the silicon (n = 1). The yield of these products depends on chlorosilane electrophilicity. It amounts to about 63% for Me_3SiCl and increases up to 96% in the case of the more electrophilic $MePh_2SiCl$.

At the same time, the presence of two or three *tert*-butoxy groups in compounds **3b** and **3c** (n = 2, 3) unexpectedly leads to preferential reactions (**ii**) and (**iii**) resulting in a mixture of products, out of which substances $Me_{3-n}(t\text{-}BuO)_nSiCH_2OSiMeR_2$, R = Me, Ph **6b,c,e,f** and $Me_{4-n}Si(OBu\text{-}t)_n$ **7b,c** form predominantly.

The results we obtained differ from those reported by D.J. Brondani, R.J.P Corriu et al. [11,12] on the interaction of [tri(ethoxy)silyl]

$$MgI_2 + MeR_2SiCl \longrightarrow ClMgI + MeR_2SiI$$

$$MeR_2SiI + \overset{}{\underset{O}{\bigcirc}} \longrightarrow MeR_2SiO(CH_2)_4I$$
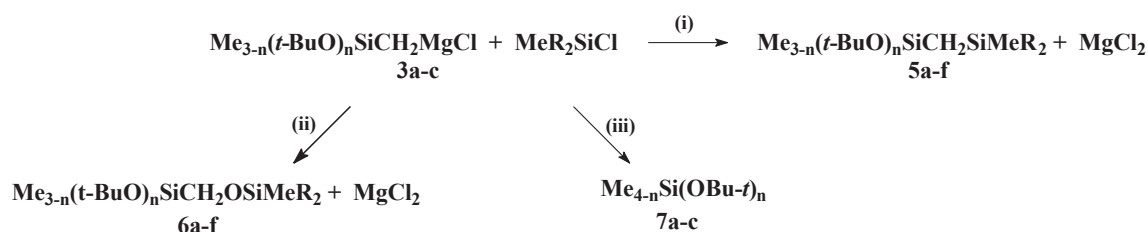**8**

$$R = Me, Ph$$

Scheme 4.

methyl- and [tri(isopropoxy)silyl]methylmagnesium chlorides with Me_3SiCl, occurring under mild conditions and resulting in the formation of [(trialkoxysilyl)methyl]trimethylsilanes as the main products with a yield of up to 82%.

The formation of compounds **6** may be explained as follows. The reaction proceeds along the path (**i**) very slowly even at severe conditions due to the poor reactivity and steric hindrance in di- and [tri(*tert*-butoxy)silyl]methylmagnesium chlorides **3b,c**. It is also known that there may take place the cleavage of THF by halosilanes during prolonged reaction mixture boiling [36,37]. This process is accelerated by iodine, which is used for magnesium activation (Scheme 4).

It should be noted, that the presence of compound **8** being the product of THF cycle cleavage was indeed confirmed by NMR spectroscopy in the case of the reactions of silylmethylmagnesium chlorides **3a,b** with Me_3SiCl.
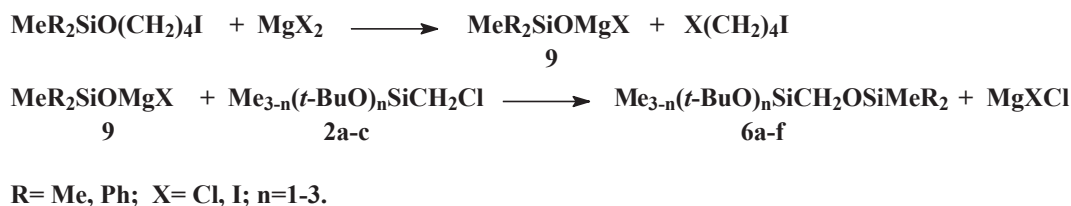
Compound **8** then interacts with magnesium halides giving magnesium silanolates-halides **9,** which react with chloromethylsilanes **2a-c** and produce substances **6a-f** (Scheme 5).

It is interesting to note, that chloromethylsilanes **2a-c** were detected in their reaction mixtures by NMR spectroscopy, although the starting Grignard reagents did not contain these substances at all. Possibly, the formation of chloromethylsilanes **2a-c** may be a result of the halogen exchange processes in the reaction mixtures.
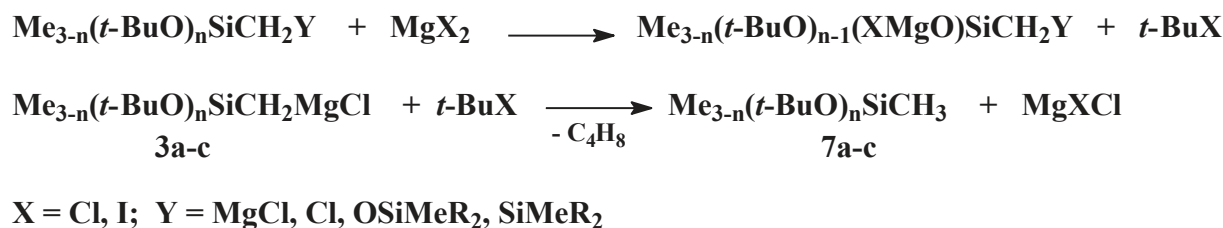

$$Me_{3-n}(t\text{-}BuO)_nSiCH_2MgCl + MeR_2SiCl \xrightarrow{(i)} Me_{3-n}(t\text{-}BuO)_nSiCH_2SiMeR_2 + MgCl_2$$
3a-c   **5a-f**

(**ii**)   (**iii**)

$$Me_{3-n}(t\text{-}BuO)_nSiCH_2OSiMeR_2 + MgCl_2 \qquad\qquad Me_{4-n}Si(OBu\text{-}t)_n$$
6a-f   **7a-c**

R=Me, n=1 (a); n=2 (b); n=3 (c);   R=Ph, n=1 (d); n=2 (e); n=3 (f);

Scheme 3.

$$MeR_2SiO(CH_2)_4I \ + \ MgX_2 \ \longrightarrow \ \underset{9}{MeR_2SiOMgX} \ + \ X(CH_2)_4I$$

$$\underset{9}{MeR_2SiOMgX} \ + \ \underset{2a\text{-}c}{Me_{3\text{-}n}(t\text{-}BuO)_nSiCH_2Cl} \ \longrightarrow \ \underset{6a\text{-}f}{Me_{3\text{-}n}(t\text{-}BuO)_nSiCH_2OSiMeR_2} \ + \ MgXCl$$

$$R= Me, Ph; \ X= Cl, I; \ n=1\text{-}3.$$

Scheme 5.

$$Me_{3\text{-}n}(t\text{-}BuO)_nSiCH_2Y \ + \ MgX_2 \ \longrightarrow \ Me_{3\text{-}n}(t\text{-}BuO)_{n\text{-}1}(XMgO)SiCH_2Y \ + \ t\text{-}BuX$$

$$\underset{3a\text{-}c}{Me_{3\text{-}n}(t\text{-}BuO)_nSiCH_2MgCl} \ + \ t\text{-}BuX \ \underset{-\ C_4H_8}{\longrightarrow} \ \underset{7a\text{-}c}{Me_{3\text{-}n}(t\text{-}BuO)_nSiCH_3} \ + \ MgXCl$$

$$X = Cl, I; \ Y = MgCl, Cl, OSiMeR_2, SiMeR_2$$

Scheme 6.

It seems that *tert*-butoxy substituted methylsilanes **7a-c** are formed owing to C–O bond splitting in the *tert*-butoxysilyl group by magnesium halide, releasing *tert*-butyl chloride and followed by dehydrochlorination of the compound by Grignard reagent **3a-c** (Scheme 6). It should be noted that no isobutene evolution was registered at this stage of research.

The relative contents of the main compounds present among the reaction products and chlorosilane conversion degrees are given (Table 2).

The data presented in Table 2 show that a severe decrease of the [methyl(*tert*-butoxy)silyl]methylsilanes **5a-f** content among the reaction products was observed as the number of *tert*-butoxy groups in the Grignard molecule increased.

We believe that the results obtained may be explained by the obstructed attack of hindered and highly THF solvated the Grignard reagents on the silicon of a chlorosilane. In this case the electrophilicity of the chlorosilane remains insufficient for the main reaction of chlorine nucleophilic substitution. It obviously runs very slowly and is outrun by side reactions.

3.2.2. NMR spectroscopic analysis of the products obtained from the reactions of 3a-c with chlorosilanes

The reactions were monitored until the complete disappearance of proton signals given by the CH_2MgCl fragment in the δ range of $-1.5 \div -1.3$.

Different substance structures were proved in reaction mixtures as a result of complete analysis of 1D- and 2D-NMR spectra. It was found that in the studied reactions O-silylated substances **6a-f** and **7a-c** are formed besides the expected C-substituted compounds **5a-f** (Scheme 3). The compounds **2a-c** and **8** are also found (Schemes 4–6).

The signals assignment of SiMe, SiMe$_2$, SiMe$_3$ and SiCH$_2$-groups for different compounds was performed on the basis of HSQC (^{1}H-^{29}Si, $J = 6.5$ Hz), HSQC (^{1}H–^{13}C, $J = 140$ and 8 Hz) correlation spectra and multiplicity of signals in monoresonance ^{13}C NMR spectra. It should be emphasized that the 2D-correlation spectra allowed us to observe cross-peaks for those substances, whose content in the mixture was 3–5%. Thus, the ^{1}H, ^{13}C and ^{29}Si signals of the compounds **5a-f**, **6a-f**, **7a-c**, **8** and **2a-c** were completely assigned, their chemical shifts and coupling constants $^1J_{HC}$, $^2J_{HSi}$, $^1J_{CH}$, $^3J_{CH}$, $^1J_{CSi}$ and $^1J_{SiC}$ were determined.

Determining the ratio of substances **2**, **5–8** in the reaction mixtures was carried out by the integration of the corresponding signals in the ^{29}Si NMR spectra without taking into account other unidentified negligible impurities.

A set of signals for *t*-BuO- and Ph-groups in the ^{1}H and ^{13}C NMR spectra was observed in various ratios for different reaction mixtures.

Chemical shifts are shown in **Part 2 (Experimental)** for those components of the mixtures whose signals were assigned. Chemical shifts for the minor substances are given as a range or omitted.

It should be noted that the highest content (96%) of the type **5** substance is observed in the reaction of **3b** with MePh$_2$SiCl. It is of interest that the structure of **5d** exists as two spatial rotational isomers (**5d-I** and **5d-II**) in a ratio of 13:1 (93% and 7%). From the 2D-correlation spectra we got the full sets ^{1}H, ^{13}C, ^{29}Si signals of both isomers. The existence of two isomers can be explained by the presence of bulky substituents (Ph$_2$- and *t*-BuO-groups) bonded to different silicon atoms in both **5d-I** and **5d-II**. The amount of isomer **5d-II** increased over time and the ratio became 3:1 (75% and 25%).

Only ^{29}Si chemical shifts for **5f** (its amount 5%) were assigned by analogy with chemical shifts of **5d** and **5e**. Assignment of ^{1}H and ^{13}C chemical shifts was not succeeded.

The formation of O-silylated compounds **6a-f** (Scheme 3) was shown unambiguously by HSQC (^{1}H-^{29}Si, $J = 6.5$ Hz) correlation spectra. For example, the proton signal at δ 3.25 (CH_2O-group of **6b**) has two cross-peaks with silicon atoms at δ -25.3 and 18.3 ($^2J_{HCSi}$ and $^3J_{HCOSi}$), which proves the presence of a SiCH$_2$OSi fragment in **6b** (Fig. 1).

We fixed the formation of Me$_3$SiO(CH$_2$)$_4$I **8** in the reaction of silylmethylmagnesium chlorides **3a,b** with Me$_3$SiCl. We fully assigned ^{1}H, ^{13}C and ^{29}Si signals by COSY, HSQC (^{1}H–^{13}C) and HSQC (^{1}H-^{29}Si) spectra and proved the structure of **8** in the case of reaction mixture of **3b** with Me$_3$SiCl, where content of compound **8** amounted to 10%. Thus, the proposed mechanism for the formation of an O-silylated substances **6a-f** was confirmed.

The NMR data of compounds **5a-f** and **6a-f** are presented in **Parts 2.5; 2.6** and Tables 3–4.

The chemical shifts (Table 3) for methylene protons of [(*tert*-butoxysilyl)methyl]trimethylsilanes **5a-c** are at δ $-0.26 \div -0.16$ and shifted downfield up to δ 0.38 $\div$ 0.45 for diphenyl substituted compounds **5d,e**. Methylene proton signals for O-silylated substances **6a-f** are located at δ 3.11 $\div$ 3.50, which is typical for alkoxysilanes [28]. Silicon connected methyl protons for all compounds **5a-e** and **6a-f** are observed at δ $-0.01 \div 0.74$ in accordance with known data for methyl substituted silanes [28,38].

The ^{13}C signals (Table 4) of methylene group for derivatives **5a-e** are located at δ 4.3 $\div$ 7.7 with two direct coupling constants $^1J_{CSi} = 43.5 \div 47.2$ and 55.6 $\div$ 90.7 Hz [39,40]. Since the value of the second constant increases significantly, it was assigned to the silicon with an attached *t*-BuO-groups.

Methyl carbon signals for **5a-e** appeared at δ 3.5 $\div$ 4.9 with $^1J_{CSi} = 57.4 \div 71.6$ Hz (SiMe$_{3\text{-}n}$), at δ 1.1 $\div$ 1.5 with $^1J_{CSi} = 50.9 \div 51.3$ Hz (SiCH_3R$_2$, R = Me) and at δ $-1.6 \div -1.5$ with

Table 2

Chlorosilane conversion degrees and the relative contents of the main compounds in the reactions of Me$_{3-n}$(t-BuO)$_n$SiCH$_2$MgCl **3a-c** with MeR$_2$SiCl, n = 1–3, R = Me, Ph.

n	R	Chlorosilane conversion (%)	Relative content (%)[a]					
			5a-f		**6a-f**		**7a-c**	
1 [b,c]	Me	84	**5a**	63	**6a**	14	**7a**	10
2 [b,c]	Me	86	**5b**	32	**6b**	40	**7b**	14
3 [b]	Me	90	**5c**	13	**6c**	72	**7c**	8
1 [d]	Ph	91	**5d** [e]	96	**6d**	4	**7a**	–
2 [d]	Ph	56	**5e**	15	**6e**	41	**7b**	37
3 [d]	Ph	64	**5f**	5	**6f**	51	**7c**	34

[a] The signals integration data in the ^{29}Si NMR spectra of the reaction mixture are shown.
[b] **2a** (10%), **2b** (4%), **2c** (7%) are formed. [c] **8** (3% for n = 1, 10% for n = 2) is formed.
[d] **2a** is not detected, **2b** (7%), **2c** (10%) are formed.
[e] **5d** is a mixture of spatial isomers **5d-I** (89%) and **5d-II** (7%).

$^1J_{CSi}$ = 53.8 ÷ 54.6 Hz (Si*C*H$_3$R$_2$, R = Ph).

Methylene carbon signals for **6a-f** are observed in ^{13}C{^{1}H} NMR spectra at δ 53.2 ÷ 56.6, which is characteristic of compounds having a C−O bond [41]. All the signals of methyl carbons bonded to silicon for **6a-f** are observed at δ −3.2 ÷ −0.1.

It can be seen that methyl carbon attached to silicon has a direct $^1J_{CH}$ = 117 ÷ 120 Hz for all compounds **5a-e** and **6a-f**. The same constant values were observed for **4a-f** (**Part 2.4**). These constants are less than normal ($^1J_{CH}$ = 125 ÷ 127 Hz) [39,42,43]. Reducing the $^1J_{CH}$ was not observed when replacing silicon by tin [39].

The appearance of a second silicon atom at methylene carbon leads to a

significant decreasing of its $^1J_{CH}$ to 108 ÷ 109 Hz for compounds **5a-e**. This constant is characteristic of the SiCH$_2$Si moiety [42]. The same decreasing of the $^1J_{CH}$ for the SiCH$_2$O moiety in substances **6a-f** has been observed. Values of $^1J_{CH}$ were 129 ÷ 130 Hz instead of $^1J_{CH}$ = 140 ÷ 143 Hz for alkoxy group in general organic compounds [42].

As for ^{29}Si signals of *tert*-butoxy substituted derivatives **5a-f** (**Part 2.5**) and **6a-f** (**Part 2.6**), they are observed in a wide range from δ −69.7 to 6.9 depending on the number of *tert*-butoxy groups. It is typical for alkoxy substituted silanes [28]. As in the case of derivatives **4a-f**, the increasing of the number of *tert*-butoxy groups in the molecule leads to a significant shielding of the silicon and shifts its signals to the upfield [28,44].

The ^{29}Si signals of trimethyl substituted silicon for compounds **5a-c** (SiCH$_2$SiMe$_3$) appear in the region of δ −0.6 ÷ −0.3, characteristic of tetraalkyl substituted silanes [28]. Significant upfield shift of ^{29}Si signals to δ −8.7 ÷ −7.4 is observed for the methyldiphenyl substituted derivatives **5d-f** compared to trimethylsilyl containing products.

The ^{29}Si signals (SiCH$_2$OSi) for compounds **6a-c** are observed in a narrow δ range of 17.8 ÷ 18.4, characteristic of trimethylalkoxysilanes [44]. They are shifted upfield to δ −1.8 ÷ −0.8 for methyldiphenyl substituted products **6d-f**.

It is of interest that we succeeded to observe a coupling constant $^3J_{Si,Si}$ for the SiCH$_2$OSi-fragment of compound **6c** with the greatest content in the reaction mixture (72%). The value of this constant for both silicon nuclei is 7.25 Hz.

3.2.3. Gas chromatographic and mass spectrometric (GC/MS) analysis of the products obtained from the reactions of 3a-c with chlorosilanes

GC/MS has proved to be a useful method for confirming the reaction paths of the Grignard reagents **3a-c** with chlorosilanes. It was studied by the example of the reaction of the Grignard reagent **3c** with Me$_3$SiCl.
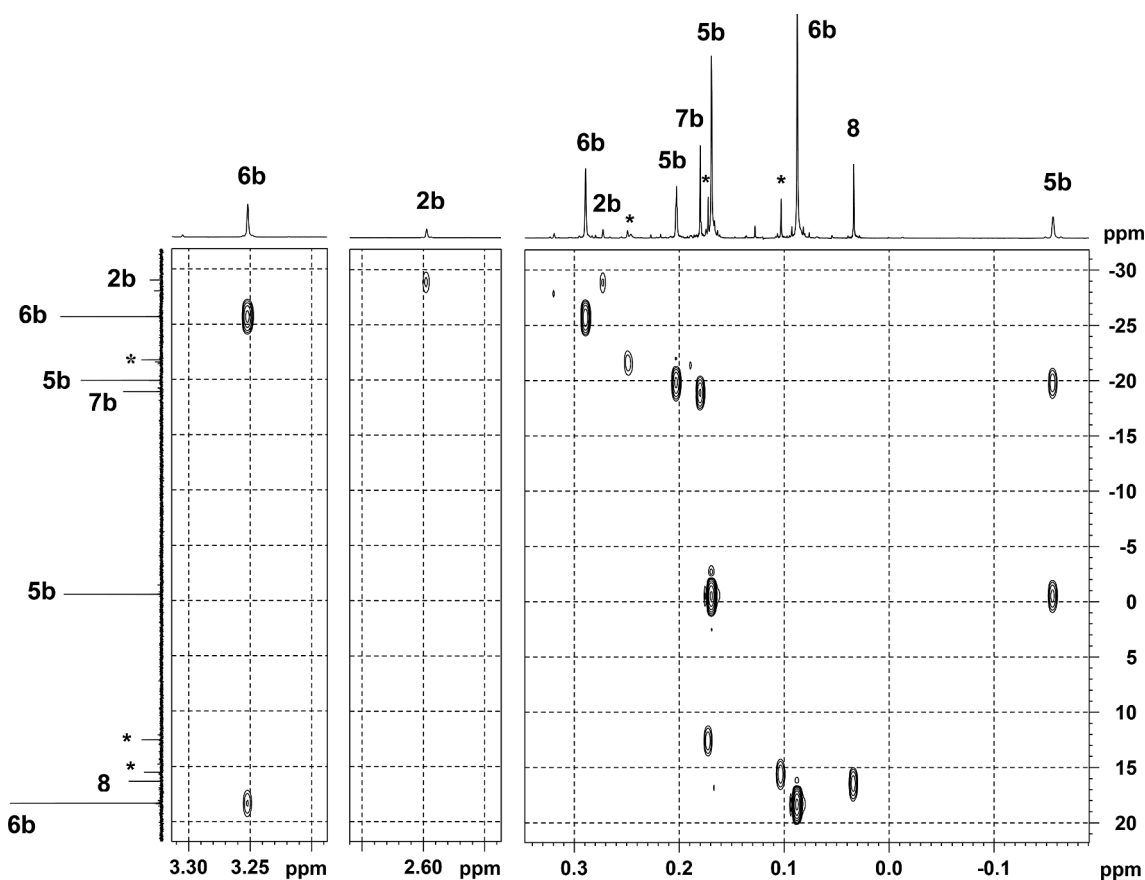

Fig. 1. HSQC (^{1}H-^{29}Si, J = 6.5 Hz) correlation spectrum of reaction mixture of **3b** with Me$_3$SiCl. **5b** - Me(t-BuO)$_2$SiCH$_2$SiMe$_3$, **6b** - Me(t-BuO)$_2$SiCH$_2$OSiMe$_3$, **7b** - Me$_2$Si(t-BuO)$_2$, **8** - Me$_3$SiO(CH$_2$)$_4$J, **2b** - Me(t-BuO)$_2$SiCH$_2$Cl, * - nonidentified signals.

Table 3
^{1}H NMR data (C$_6$D$_6$; δ, ppm; J, Hz) for Me$_{3-n}$(t-BuO)$_n$Si^{1}CH$_2$Si^{2}MeR$_2$ **5a-e** and Me$_{3-n}$(t-BuO)$_n$Si^{1}CH$_2$OSi^{2}MeR$_2$ **6a-f,** n = 1–3, R = Me, Ph.

№	n	R	Me$_{3-n}$Si^1			Si^{1}CH$_2$Si^2 (**5a-e**), Si^{1}CH$_2$OSi^2 (**6a-f**)			Si^{2}MeR$_2$		
			δ	$^1J_{HC}$	$^2J_{HSi}$	δ	$^1J_{HC}$	$^2J_{HSi}$	δ	$^1J_{HC}$	$^2J_{HSi}$
5a[a]	1	Me	0.18	117.8	6.6	−0.20	108.6	8.7	0.13	118.6	6.7
5b[a,b]	2	Me	0.20[c]	117.7	7.0	−0.16	108.8	8.9	0.17	118.5	6.6
5c[a,d]	3	Me	–	–	–	−0.26	≈109	10.3; 8.8	0.05	118.6	6.7
5d-I[a,e,f]	1	Ph	0.07	118.0	6.6	0.39	109.4	8.7	0.67	119.9	6.7
5d-II[a,e,f]	1	Ph	−0.01	118.0	6.6	0.38	[g]	[h]	0.59	[g]	6.5
5e[a,b,f]	2	Ph	0.06	117.9	7.1	0.45	[g]	9.1	0.74	120.0	6.7
6a[a]	1	Me	0.23	118.6	6.7	3.27	129.2	4.1	0.10	118.0	6.5
6b[a,b]	2	Me	0.29	118.8	7.3	3.25	129.1	4.7	0.09	118.2	6.6
6c[a,d]	3	Me	–	–	–	3.11	129.0	5.7	0.06	118.2	6.7
6d[f]	1	Ph	0.12	[g]	[h]	3.31	[g]	[h]	0.59	[g]	[h]
6e[a,b,f]	2	Ph	0.34	118.7	7.1	3.44	130.0	4.5	0.59	119.4	6.6
6f[a,b,f]	3	Ph	–	–	–	3.50	128.7	5.8	0.63	119.3	6.6

[a] δ (Me_3CO): 1.20 (**5a**); 1.27 (**5b**); 1.29 (**5c**); 1.13 (**5d-I**); 1.19 (**5d-II**); 1.21 (**5e**); 1.22 (**6a**); 1.31 (**6b**); 1.29 (**6c**); 1.29 (**6e**); 1.39 (**6f**).
[b] The reaction mixture after evaporation of the THF.
[c] $^4J_{HH}$ = 0.47 t.
[d] Solvent CDCl$_3$.
[e] Spatial rotation isomers.
[f] δ (Ph): 7.18–7.22 (*m*-Ph and *p*-Ph); 7.55–7.58 (*o*-Ph) (**5d-I**); 7.2–7.6 (**5d-II**); 7.16–7.22 (*m*- and *p*-Ph); 7.59–7.62 (*o*-Ph) (**5e**); 7.1 ÷ 7.7 (signals overlap with product **5d** signals) (**6d**); 7.18–7.23 (*m*- and *p*-Ph); 7.65–7.68 (*o*-Ph); (**6e**); 7.18–7.24 (*m*- and *p*-Ph); 7.69–7.75 (*o*-Ph); (**6f**).
[g] ^{13}C satellites were not observed due to overlapping proton signals.
[h] $^2J_{HSi}$ failed to observe.

Table 4
Some ^{13}C NMR data (C$_6$D$_6$; δ, ppm; J, Hz) for Me$_{3-n}$(t-BuO)$_n$Si^{1}CH$_2$Si^{2}MeR$_2$ **5a-e** and Me$_{3-n}$(t-BuO)$_n$Si^{1}CH$_2$OSi^{2}MeR$_2$ **6a-f,** n = 1–3, R = Me, Ph.[a]

№	n	R	Me$_{3-n}$Si^1			Si^{1}CH$_2$Si^2 (**5a-e**), Si^{1}CH$_2$OSi^2 (**6a-f**)				Si^{2}MeR$_2$		
			δ	$^1J_{CH}$	$^1J_{CSi}$	δ	$^1J_{CH}$	$^1J_{CSi}$	$^1J_{CSi}$	δ	$^1J_{CH}$	$^1J_{CSi}$
5a	1	Me	4.3	117.7	57.4	7.1	108.6	56.4	44.3	1.5	118.4	50.9
5b[b]	2	Me	4.9	117.6	70.6	7.7	108.7	68.9	43.5	1.4	118.4	51.1
5c[c]	3	Me	–	–	–	5.8	108.7	90.7	43.6	1.1	118.6	51.3
5d-I[d]	1	Ph	4.37	117.9	57.8	4.34	109.3	55.6	47.2	−1.5	119.9	54.1
5d-II[d]	1	Ph	3.5	118.1	59.6	4.31	[e]	[e]	[e]	−1.6	119.8	53.8
5e[b]	2	Ph	4.7	118.0	71.6	5.1	109.2	67.6	[e]	−1.6	120.0	54.6
6a	1	Me	−0.6	118.6	59.8	55.8	129.2	72.3	–	−0.7	118.1	58.9
6b[b]	2	Me	−0.3	118.7	74.2	55.3	129.3	89.8	–	−0.7	118.1	58.8
6c[c]	3	Me	–	–	–	53.2	128.9	116.4	–	−0.9	118.1	58.8
6d	1	Ph	−1.1	[e]	[e]	56.6	[e]	[e]	–	−0.3	[e]	[e]
6e[b]	2	Ph	−0.1	118.7	74.3	56.5	129.9	89.4	–	−3.2	119.5	62.0
6f[b]	3	Ph	–	–	–	55.0	[e]	116.3	–	−3.1	[e]	62.6

[a] $^3J_{CH}$ are shown in **Parts 2.5, 2.6**.
[b] The reaction mixture, after evaporation of the THF.
[c] Solvent CDCl$_3$.
[d] Spatial rotation isomers.
[e] $^1J_{CH}$ and $^1J_{CSi}$ failed to observe.

As mentioned above, the interaction of the Grignard reagents **3a-c** proceeds with the formation of three main compounds: **5a-f**, **6a-f** and **7a-c**. Moreover, the formation of starting chloromethylsilanes **2a-c** was detected by NMR. Indeed, it turned out that the signals of compounds **5c, 6c, 7c** and the starting tri(*tert*-butoxy)chloromethylsilane **2c** were detected in the chromatograms of the reaction products. It is known that under electron ionization methylsiloxanes easily split off the methyl group [45]. Not molecular ions [M]$^+$, but cations [M−15]$^+$ with m/z 319, 335, 247 и 281 are observed in mass spectra of compounds **5c, 6c, 7c** and **2c**, respectively.

The total ion current chromatogram for one of the distilled and enriched in [[tri(*tert*-butoxy)silyl]methyl]trimethylsilane **5c** fraction of the reaction mixture of the Grignard reagent **3c** with Me$_3$SiCl is presented (Fig. 2).

Data for the fragmentation of these substances under electron ionization are presented (Table 5). From the data in the table one can see that the signal intensity of all cations [M−15]$^+$ is low and is at the level of 10 ÷ 15% for compounds **5c** and **6c**. These cations have higher relative intensity (33 and 38%) in the case of tri(*tert*-butoxy)chloromethylsilane **2c** and methyltri(*tert*-butoxy)silane **7c**, respectively. This fact indicates a greater thermodynamic stability of these particles.

The analysis of mass-spectra for the mixture of the **5c** and **6c** has allowed an additional proving structure of these substances. Possible paths of further fragmentation of their cations [M−15]$^+$ has been proposed.

So, for C-substituted compound **5c** (M = 334 Da) after forming a cation with m/z 319 with subsequent splitting off three olefins C$_4$H$_8$, the formation of silanols takes place [46], resulting in the stable cation with m/z 151 (Scheme 7). Besides this way of fragmentation intramolecular rearrangements may take place. For example, splitting off two neutral molecules with 74 and 72 masses gives rise to cations with m/z 133 and 135 due to the charge transfer on neighboring silicon.

For O-silylated substance **6c** characteristic splitting off olefins C$_4$H$_8$ from cation with m/z 335 is observed giving rise to different structure cations with silanol groups and m/z 167, 223 (Scheme 8).
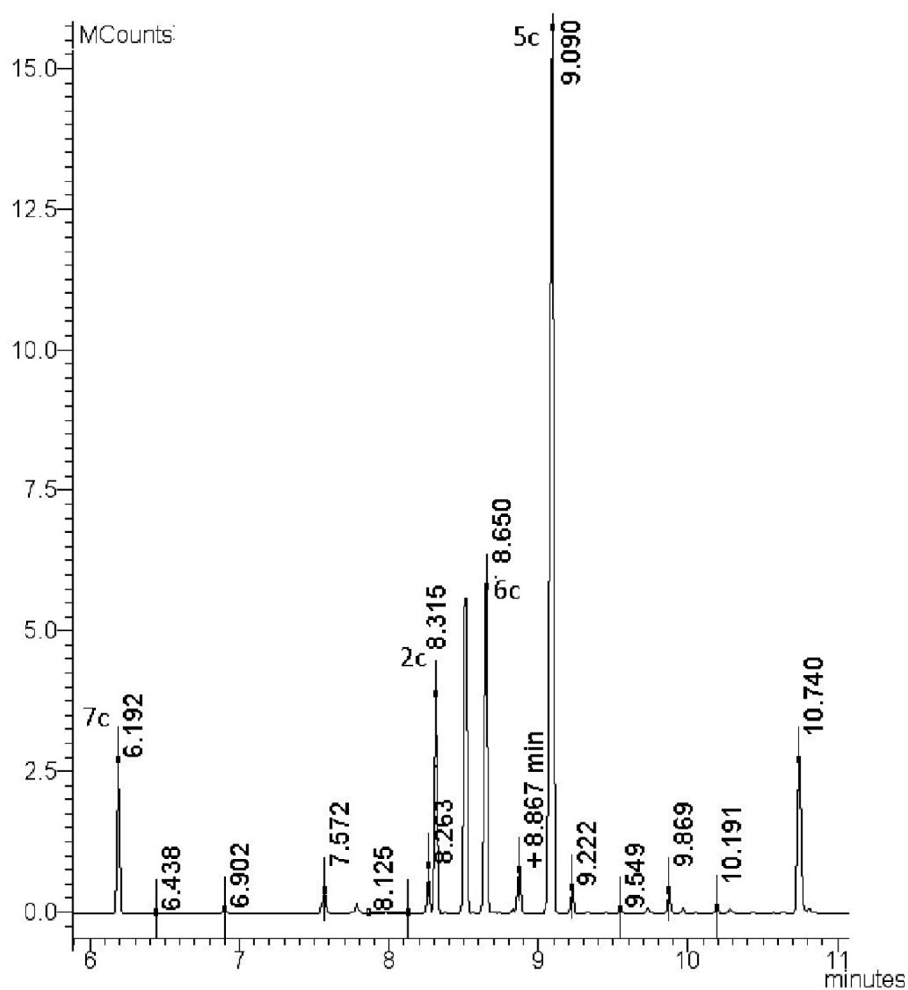
Fig. 2. The total ion current chromatogram for the reaction mixture of the Grignard reagent **3c** with Me₃SiCl.
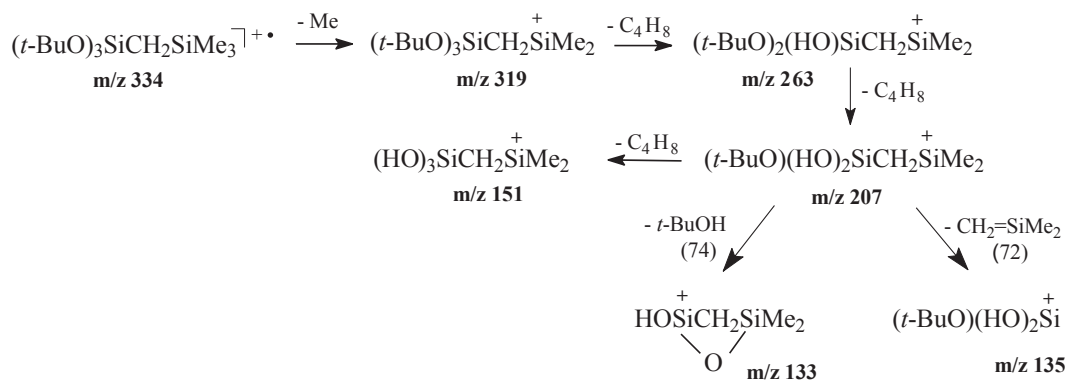
Table 5
Fragmentation data for main reaction products of the Grignard reagent **3c** with Me₃SiCl.
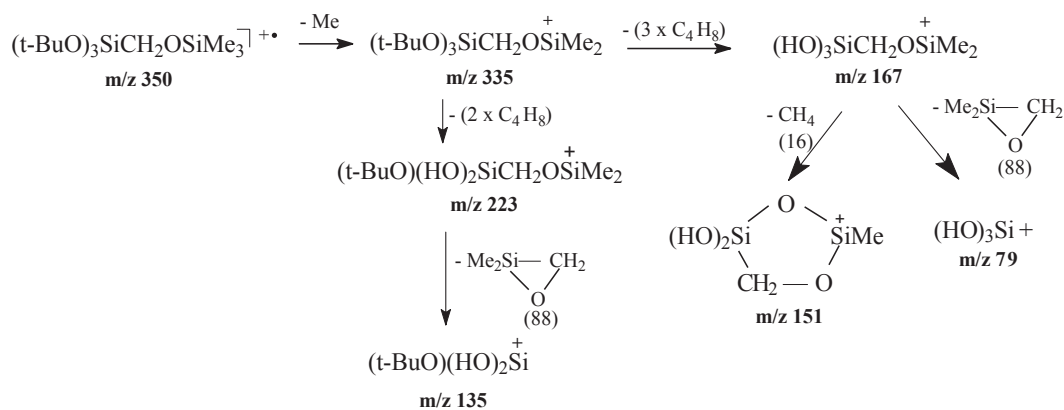
№	Formula	M, Da	τ ret., min	m/z (I, % rel.)
2c	$(t\text{-BuO})_3SiCH_2Cl$	296	8,32	283(13)[a] 281(33) 227(10)[a] 225(29) 171(35)[a] **169(100)** 135(45) 79(34)
5c	$(t\text{-BuO})_3SiCH_2SiMe_3$	334	9,09	319(15) 263(29) 207(21) **151(100)** 135(13) 133(30) 131(19)
6c	$(t\text{-BuO})_3SiCH_2OSiMe_3$	350	8,81[b]	335(10) 279(20) 223(35) 167(86) 165(44) 151(28) **135(100)** 133(22) 79(30)
7c	$(t\text{-BuO})_3SiMe$	262	6,19	247(38) 191(28) **135(100)** 117(19) 77(60)

[a] Cations with ³⁷Cl isotope.
[b] Retention time at the point of chromatographic peak rising at low concentrations coming from chromatographic column. Mass-spectrum distortion is observed in high concentration on the peak maximum (τ ret. = 8.65 min) due to ion-molecular reactions.

Scheme 7.

$(t\text{-BuO})_3SiCH_2OSiMe_3]^{+\bullet} \xrightarrow{\text{- Me}} (t\text{-BuO})_3SiCH_2O\overset{+}{Si}Me_2 \xrightarrow{- (3 \times C_4H_8)} (HO)_3SiCH_2O\overset{+}{Si}Me_2$

m/z 350   **m/z 335**   **m/z 167**

Scheme 8.

Further release of a neutral product with mass 88 from these cations, apparently extremely unstable oxasilirane [47], gives rise to hydroxyl containing cations with m/z 79 and 135. In this case, the cation with m/z 135 is the most stable, probably due to the shielding of the cationic center by the bulky *tert*-butoxy group. The formation of the cation with m/z 151 is apparently due to the splitting off methane from the cation with m/z 167 with charge transfer to the neighboring silicon.

Thus, the structure of the synthesized disilicon containing compounds was confirmed on the basis of the analysis of the fragmentation paths of reaction main products by chromatography mass spectrometry.

4. Conclusions

In summary, the reaction of (*tert*-butoxysilyl)methylmagnesium chlorides with some organotin and organosilicon monochlorides has been studied. This reaction with trialkyltin chlorides proceeds in mild conditions and leads to (*tert*-butoxysilyl)methyl organotin compounds in high yields. The reaction with chlorosilanes proceeds in more severe conditions under boiling in THF. The result of this reaction for tri-methyl- or methyldiphenyl substituted silicon chlorides depends on the Grignard reagent structure and substituents bonded to the silicon. The highest yields of (*tert*-butoxysilyl)methyl organosilanes (C-products) have been observed for the Grignard reagent with one *tert*-butoxy group at silicon and for more electrophilic methyldiphenyl silicon chloride. Increasing the number of *tert*-butoxy groups in the Grignard molecule gives rise to increasing (*tert*-butoxysilyl)methoxy silicon derivatives (O-products) as well as *tert*-butoxy substituted methylsilanes. The structure of the compounds synthesized has been determined by multinuclear NMR spectroscopy and confirmed by GC/MS.

CRediT authorship contribution statement

Evgeny A. Monin: Conceptualization, Writing - review & editing, Project administration. **Irina A. Bykova:** Investigation, Writing - original draft. **Valentina M. Nosova:** Investigation, Writing - original draft concerning NMR spectroscopy. **Alexander V. Kisin:** Project administration concerning NMR spectroscopy. **Alexander M. Philippov:** Investigation, Writing - Original Draft concerning GC/MS. **Pavel A. Storozhenko:** Supervision.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.119555.

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