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Synthesis of *B*-silylmethyl substituted *o*- and *m*-carboranes

Boris A. Izmaylov, Valerii A. Vasnev and Galy D. Markova*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5085; e-mail: mgaly@yandex.ru

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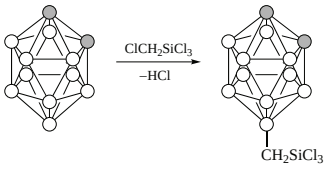
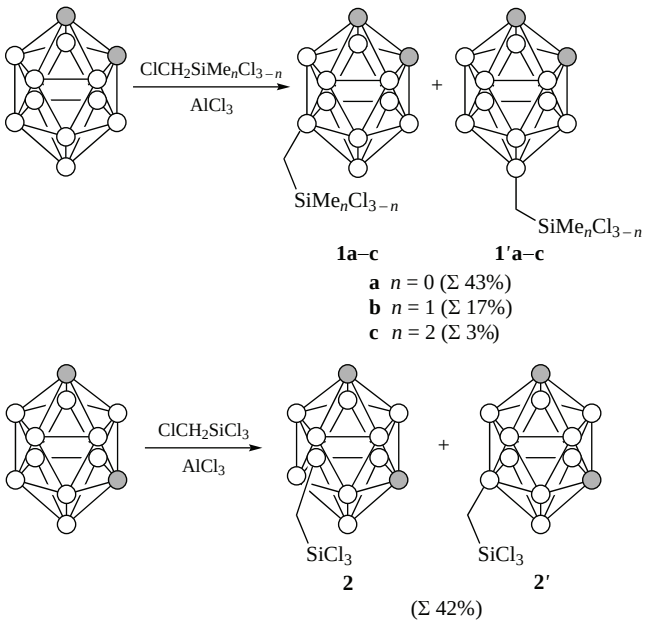
Monosubstituted *B*-chloro(organyl)silylmethyl-*o*- and *m*-carboranes have been synthesized by the reaction of *o*(*m*)-carboranes with chloro(chloromethyl)organylsilanes in the presence of $AlCl_3$ at 200–250 °C under a pressure of 20–25 atm.



Keywords: *o*(*m*)-carborane, chloro(chloromethyl)organylsilanes, *B*-chloro(organo)silyl-*o*(*m*)-carboranes, Fridel–Crafts reaction, organosilicon compounds.

Numerous works on the synthesis and application of C-derivatives of carboranes have been reported.[1–6] In particular, carborane derivatives are used in boron neutron capture therapy.[7,8] It was documented[9,10] that (trichloro)vinyl- and dichloro(methyl)vinylsilanes in the presence of aluminum chloride reacted with *o*-, *m*- and *p*-carboranes to give new *B*-(chlorosilylethyl)carborane derivatives.

In this work, we prepared similar lower homologues, namely, *B*-[chloro(organyl)silylmethyl]-substituted *o*(*m*)-carboranes, from chloro(chloromethyl)organylsilanes and *o*(*m*)-carboranes in the presence of catalytic amounts of aluminum chloride. We found that the reaction started only at temperature higher than 200 °C and pressure of 20 atm, and only monosubstituted carboranes **1a**–**c** + **1′a**–**c** and **2** + **2′** were formed (Scheme 1), which conformed with the data of elemental analysis and cryoscopy results for molecular weights. All the substances obtained appeared as colourless transparent high-boiling liquids.



Scheme 1 *Reagents and conditions*: heat, 250 °C, 20–25 atm, 6–16 h.

The Friedel–Crafts methylation of carboranes is known to occur at the B–H bond.[1,2,11] Due to the shift of electron density in the carborane core, the carbon atoms C (+0.25) and C′ (+0.25) are the most electropositive in *o*-carborane and C (+0.15) and C′ (+0.15) in *m*-carborane. The negative charge on the boron atoms in *o*-carborane increases in the following order: C(1,2) < B(3,6) < < B(4,5,7,11) < B(8,10) < B(9,12), while for *m*-carborane this order is C(1,7) < B(2,3) < B(5,12) < B(4,6,8,11) < B(9,10).[11] In accordance with this sequence, the electrophilic silylmethylation should proceed first at the 9/12-positioned boron atoms of *o*-carborane and the 9/10-positioned boron atoms of *m*-carborane, *i.e.*, at the boron atoms most remote from the carbon ones.

However, ^{1}H and ^{13}C NMR data for the products indicated formation of regioisomeric pairs **1** + **1′** or **2** + **2′** in each experiment (see Scheme 1). The ^{1}H NMR spectrum of product **1a** + **1′a** shows a singlet at 3.56 ppm typical for Ccb–H groups (Ccb is carborane), which indicates the retention of these groups in the reaction products. Furthermore, the spectrum displays two singlets of equal intensity for CH_2 groups at 0.23 and 1.06 ppm, the sum of integral intensities of two these signals equals to the integral intensity of the Ccb–H singlet. Chemical shifts of these groups in substances **1b** + **1′b** and **1c** + **1′c** are similar to those of **1a** + **1′a** pair. The ^{1}H NMR spectrum of **2** + **2′** pair also contains a singlet at 2.90 ppm (Ccb–H) and two singlets of equal intensity for CH_2 groups at 0.39 and 1.19 ppm. Additionally, ^{13}C NMR spectra contain, along with the Ccb–H signal (54.48 ppm for **1a** + **1′a** and 55.17 ppm for **2** + **2′**), two singlets of equal intensity from the CH_2 groups (1.27 and 12.67 ppm for **1a** + **1′a** and 1.3 and 12.45 ppm for **2** + **2′**). We believe that, in accordance with the values of negative charges on boron atoms, the isomers comprise the 9/12 atoms in the case of *o*-carborane (**1a**–**c**/**1′a**–**c**), and the 9/10 atoms for *m*-carborane (**2** + **2′**). The values of integrated intensities of signals for CH_2 groups in ^{13}C NMR spectra indicate that the isomers are formed in approximately equal amounts.

We have found that the optimal ratio between carborane and chloro(chloromethyl)silane is 1 : 3.5, and the molar amount of $AlCl_3$ relative to carborane is 0.1. When the temperature is raised from 200 to 250 °C, the pressure in the autoclave grows from 20 to 25 atm whereas the yield of products **1a** + **1′a** is improved from 30 to 43%. At 250 °C, the yields of substances **1b** + **1′b**, **1c** + **1′c** and **2** + **2′** are 17, 3 and 42%, respectively.†

In summary, the Friedel–Crafts silylmethylation of *o*- and *m*-carboranes with $ClCH_2SiMe_nCl_{3-n}$ proceeds in the presence of $AlCl_3$ at 200–250 °C and 20–25 atm with the formation of monosubstitution products being isomeric *B*-(silylmethyl)-*o*(*m*)-carboranes.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.01.042.

† *Synthesis of compounds* **1a** + **1′a** *(typical procedure)*. A stainless steel autoclave was charged with *o*-carborane (25.0 g, 0.173 mol), trichloro(chloromethyl)silane (105.0 g, 0.570 mol) and $AlCl_3$ (2.6 g, 0.0187 mol). The mixture was heated up to 250 °C and kept with stirring under pressure of 25 atm for 12 h. The autoclave was then cooled, the resulting mixture was dissolved in heptane (300 ml) and treated with $POCl_3$ (3.4 g) to quench aluminum chloride. The solid product was filtered off on a glass filter, the volatiles were distilled off from the filtrate, and the residue was distilled *in vacuo* to collect fraction with 136–138 °C (1 Torr), yield 21.7 g (43%).

For details and syntheses of other compounds, see Online Supplementary Materials.

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