Efficient synthesis of (carboranylmethyl)siloxanes from carboranylcopper and chloromethylsiloxanes

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A preparative synthesis of (carboranylmethyl)siloxanes from carboranylcopper and chloromethylsiloxanes was developed.

Key words: (carboranylmethyl)siloxanes, synthesis; carboranylcopper, chloromethylsiloxanes.

The interest in the study of (carboranylmethyl)siloxanes is caused by their high thermal stability[1] and the stability of the Si—CH_2—$CB_{10}H_{10}C$— bond system against the action of aggressive reagents.[2—5] Condensation of (carboranylmethyl)hydroxysilane with α,ω-bis(*N*,*N*-dimethylamino)siloxanes[1] and hydrolytic polycondensation of (carboranylmethyl)chlorosilanes[3] and -alkoxysilanes[5—7] are the main methods for the synthesis of these compounds.

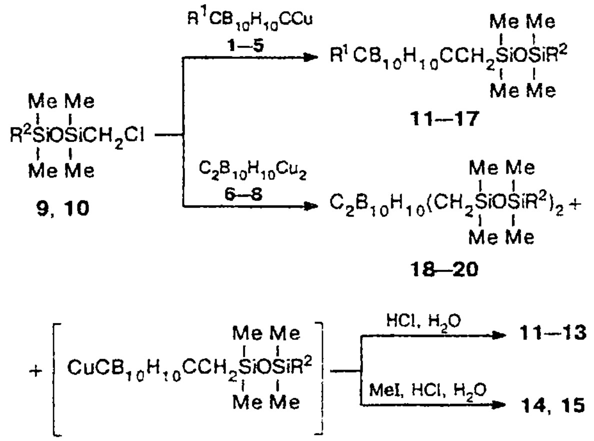
Previously, the reaction of carboranyllithium with chloromethylsiloxanes has also been studied in a work aimed at the synthesis of (carboranylmethyl)siloxanes.[8] A considerable drawback of this reaction is that the synthesis of (carboranylmethyl)siloxanes is accompanied by competitive siloxane cleavage by carboranyllithium and lithium silanolates formed in this reaction. The fraction of products resulting from cleavage of the siloxane bond may be as high as 20%.

It is known[9] that carboranylcopper is superior to carboranyllithium in reactions of halogen substitution in halohydrocarbons. In addition, neither organocopper compounds nor copper chlorides cause the cleavage of the siloxane bond.[10] We assumed that the use of carboranylcopper in reactions with chloromethylsiloxanes would eliminate side processes and increase the yield of (carboranylmethyl)siloxanes.

In the present work, we describe the results of a study of the reactions of chloromethylsiloxanes with carboranylcopper derivatives (**1—8**) readily obtained from the corresponding lithium carboranides.

It was found that the reaction of compounds **1—5** with 1-chloromethyl-1,1,3,3,3-pentamethyldisiloxane (**9**) and 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane (**10**) in an Et_2O—C_6H_{14}—THF mixture results in the expected products (**11—17**) (Scheme 1).

Scheme 1



R^1 = H, *o*- (**1**), *m*- (**2**), *p*- (**3**); R^1 = Me, *o*- (**4**), *m*- (**5**); 1,2-*o*- (**6**), 1,7-*m*- (**7**), 1,12-*p*- (**8**); R^2 = Me (**9**), CH_2Cl (**10**); R^1 = H, R^2 = Me, [*o*- (**11**, **18**), *m*- (**12**, **19**), *p*- (**13**, **20**)]; R^1 = R^2 = Me, *o*- (**14**), *m*- (**15**); R^1 = Me, R^2 = CH_2Cl, *o*- (**16**), *m*- (**17**)

No cleavage of the Si—O bond, either in the starting compounds (**9**, **10**) or in the products (**11—17**), was observed under these conditions.

Similarly, reactions of chloromethyldisiloxane **9** with dicopper 1,2-*o*-, 1,7-*m*-, and 1,12-*p*-carboranides (**6—8**) followed by hydrolysis gave siloxane derivatives **11—13** and **18—20**. The fraction of polysubstituted products **18—20** is 23%. Products of addition of only one disiloxane molecule, *i.e.*, compounds **11—13**, are mainly formed.

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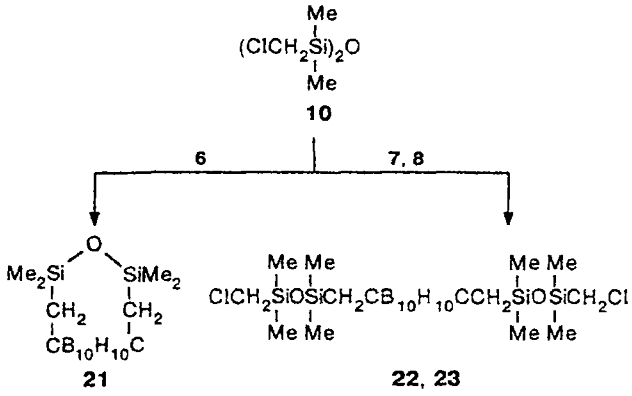
The action of methyl iodide on the product mixture obtained by the reaction of chloromethyldisiloxane **9** with compounds **6** and **7** also gives *C*-methylation products **14** and **15**.

It was expected that because of the *cis*-arrangement of copper atoms in *ortho*-derivative **6**,[11] its reaction with disiloxane **10** could give a cyclic product. In fact, when a fourfold molar excess of disiloxane **10** is used, the reaction quantitatively gives 1,2-(*o*-carborano)-4,4,6,6-tetramethyl-5-oxa-4,6-disilacycloheptane (**21**) (Scheme 2), whose structure was confirmed[12] by X-ray diffraction analysis. Compound **21** has been obtained previously by hydrolytic polycondensation of (carboranylmethyl)chlorosilanes.[7]

The reaction of dicopper 1,7-*m*- and 1,12-*p*-carboranides **7** ans **8** with disiloxane **10** was interesting as a possible way to the synthesis of oligomeric carboranylmethylsiloxanes. It was found that when an equimolar ratio of the reagents is used, oligomeric products, which contain from one to four 1,7(12)-bis(dimethylsilylmethyl)-*m*(*p*)-carboranediyl units, are formed. Reactions of compounds **7**, **8** with a fourfold molar excess of disiloxane **10** give compounds **22** and **23** (see Scheme 2).

Thus, the reaction of carboranylcopper with chloromethylsiloxanes occurs by replacement of chlorine atoms in chloromethyl groups by carborane residues to give (carboranylmethyl)siloxanes in high yields.

Scheme 2



21: 1,2-*o*; **22**: 1,7-*m*; **23**: 1,12-*p*

The yields, physicochemical constants, and results of elemental analyses of compounds **11**—**23** are presented in Table 1. The IR and ^{1}H NMR spectroscopic data for these compounds are shown in Table 2.

Table 1. Physicochemical constants, yields, and elemental analysis data for compounds **11**—**23**

Compound	Yield (%)	B.p.* /°C (m.p./°C)	n_D^{20}	Found/Calculated (%) C	H	B	Cl	Si	M_w	Molecular formula
11	76	126—127 (30)	—	31.55 32.31	9.27 8.95	35.49 38.20	—	18.44 16.84	304.6 350.0	$C_8H_{28}B_{10}OSi_2$
12	80	118—119	1.4910	31.55 31.87	9.27 9.31	35.49 34.82	—	18.44 18.67	304.6 332.0	$C_8H_{28}B_{10}OSi_2$
13	80	100—101	1.4895	31.55 31.75	9.27 9.25	35.49 34.50	—	18.44 18.72	304.6 330.0	$C_8H_{28}B_{10}OSi_2$
14	82	142—144	1.5125	33.92 34.15	9.49 9.55	33.92 34.51	—	17.62 17.51	318.6 325.0	$C_9H_{30}B_{10}OSi_2$
15	83	138—139	1.5105	33.92 34.08	9.49 9.58	33.92 34.60	—	17.62 17.38	318.6 323.0	$C_9H_{30}B_{10}OSi_2$
16	80	169—170	1.5178	30.61 30.42	8.28 8.30	30.62 30.23	10.04 9.91	15.90 15.87	353.0 360.0	$C_9H_{29}B_{10}OClSi_2$
17	83	150—152	1.5066	30.61 30.83	8.28 7.83	30.62 30.56	10.04 10.10	15.90 15.75	353.0 360.0	$C_9H_{29}B_{10}OClSi_2$
18	23	167—168	1.4816	36.17 36.52	9.54 9.10	23.25 23.75	—	24.14 24.25	464.8 475.0	$C_{14}H_{44}B_{10}O_2Si_4$
19	23	162—164	1.4811	36.17 36.47	9.54 9.12	23.25 23.65	—	24.14 24.30	464.8 470.0	$C_{14}H_{44}B_{10}O_2Si_4$
20	23	155—157	1.4798	36.17 36.48	9.54 9.15	23.25 23.58	—	24.14 24.20	464.8 470.0	$C_{14}H_{44}B_{10}O_2Si_4$
21	90	(172.6)	—	31.75 32.06	8.66 8.79	35.73 36.12	—	18.56 18.19	303.0 304.0	$C_8H_{26}B_{10}OSi_2$
22	38	215—217	1.5202	37.50 37.70	7.93 7.87	20.25 20.18	13.28 13.00	21.02 21.00	533.0 540.0	$C_{14}H_{42}B_{10}O_2Cl_2Si_4$
23	38	208—210	1.5193	37.50 37.00	7.93 7.90	20.25 20.07	13.28 13.01	21.02 20.95	533.0 540.0	$C_{14}H_{42}B_{10}O_2Cl_2Si_4$

* *p* = 1 Torr.

Table 2. IR and ^{1}H NMR spectroscopic data for compounds **11—23**

Compound	IR, ν/cm^{-1}			^{1}H NMR, δ		
	H—CB	B—H	SiOSi (C—Cl)	MeSi	CH_2 (CH_2Cl)	MeCB (H—CB)
11	3080	2600	1120—1030	0.16	1.72	(3.67)
12	3070	2600	1130—1080	0.23	1.40	(2.93)
13	3070	2600	1130—1080	0.23	1.38	(2.65)
14	3080	2600	1120—1035	0.27, 0.33	1.70	2.07
15	3070	2600	1130—1080	0.18, 0.23	1.54	1.70
16	3080	2600	1120—1035 (850—800)	0.32, 0.40	1.73 (2.77)	2.10
17	3070	2600	1130—1080 (850—800)	0.23, 0.30	1.57 (2.93)	1.73
18	—	2600	1120—1030	1.16	1.72	—
19	—	2600	1130—1080	0.20, 0.17	1.52	—
20	—	2600	1130—1080	0.20	1.52	—
21	—	2600	1120—1030	0.43	2.15	—
22	—	2600	1130—1080 (850—800)	0.30	1.57 (2.93)	—
23	—	2600	1130—1080 (850—800)	0.30	1.57 (2.90)	—

Experimental

Chromatographic analysis was performed on an LKhM-8MD (model 5) chromatograph using 2 m × 3 mm columns with SE-30 organosilicon liquid on Chromaton H, a katharometer as the detector, and helium (30 mL min^{-1}) as the carrier gas; the column temperature was 220—280 °C.

Thin-layer chromatography was carried out on plates with Al_2O_3 in petroleum ether using iodine vapor for visualization.

^{1}H NMR spectra were recorded on a Varian T 60A instrument (60 MHz, CCl_4) using $CHCl_3$ as the internal standard.

IR spectra were obtained on a UR-20 spectrometer (KBr, NaCl, and LiF pellets) in the 400—4000 cm^{-1} region.

Molecular masses were determined by ebullioscopy in acetone. Crystalline compounds were recrystallized from heptane.

1-*o*-, *m*-, *p*-Carboranylcopper (1—3) and 2-methyl-*o*(*m*)-carboranylcopper (4, 5). BuLi (0.02 mol) in hexane (17 mL, 1.18 mol L^{-1}) was added at 0—5 °C with stirring in an N_2 atmosphere to a solution of *o*-, *m*-, or *p*-carborane (2.88 g, 0.02 mol) or 1-methyl-*o*(*m*)-carborane (3.16 g, 0.02 mol) in dry ether (30 mL). Cooling was discontinued, and the mixture was brought to boiling and cooled (−10 to −20 °C). Anhydrous CuCl (2.47 g, 0.025 mol) and dry THF (50 mL) were added with stirring in a stream of N_2 (as a result, the temperature increased to 0 °C). Cooling was stopped, and the mixture was stirred for 2 h and kept for 10 min at 40 °C. The resulting dark-brown suspension of carboranylcopper was used in the reactions without isolation.

Dicopper 1,2-*o*-, -1,7-*m*-, and -1,12-*p*-carboranides (6—8) were obtained in a similar way from *o*-, *m*-, or *p*-carborane (2.88 g, 0.02 mol) in dry ether (50 mL), BuLi (0.04 mol) in hexane (34 mL, 1.18 mol L^{-1}), anhydrous CuCl (4.94 g, 0.05 mol), and dry THF (50 mL).

1,1,3,3,3-Pentamethyldisiloxanylmethyl-*o*(*m,p*)- (11—13), 1-methyl-2(7)-(1,1,3,3,3-pentamethyldisiloxanylmethyl)-*o*(*m*)-(14, 15), and 1-methyl-2(7)-(1,1,3,3-tetramethyl-3-chloromethyldisiloxanylmethyl)-*o*(*m*)-carboranes (16, 17). 1-Chloromethyl-1,1,3,3,3-pentamethyldisiloxane **9** (9.83 g, 0.05 mol) or 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane **10** (11.55 g, 0.05 mol) was added with stirring to a suspension of 1-*o*(*m,p*)-carboranylcopper (**1—3**) or 2-methyl-*o*(*m*)-carboranylcopper (**4, 5**) prepared as described above from *o*(*m,p*)-carborane (5.77 g, 0.04 mol) or 1-methyl-*o*(*m*)-carborane (6.32 g, 0.04 mol) in dry ether (60 mL), BuLi (0.04 mol) in hexane (37.4 mL, 1.07 mol L^{-1}), anhydrous CuCl (5.0 g, 0.05 mol), and dry THF (100 mL) in an N_2 atmosphere at 20 °C. The mixture was stirred for 1 h at 20 °C, refluxed for 2 h, and cooled to 0 °C. A ~5% solution of HCl was added with stirring. The mixture was extracted with ether, and the extract was washed with ~5% HCl and water to pH 7 and dried with Na_2SO_4 or $MgSO_4$. The ether was distilled off. Distillation of the residue *in vacuo* followed by recrystallization gave compounds **11—17**.

1,2(7,12)-Bis(1,1,3,3,3-pentamethyldisiloxanylmethyl)-*o*(*m*, *p*)-carboranes (18—20), 1,2-(*o*-carborano)-4,4,6,6-tetramethyl-5-oxa-4,6-disilacycloheptane (21), 1,7(12)-bis(3-chloromethyl-1,1,3,3-tetramethyldisiloxanylmethyl)-*m*(*p*)-carboranes (22, 23). Compounds **6—8** were obtained similarly to compounds **1—5** from *o*(*m,p*)-carborane (5.77 g, 0.04 mol) in dry ether (100 mL), BuLi (0.08 mol) in hexane (74.8 mL, 1.07 mol L^{-1}), anhydrous CuCl (10 g, 0.1 mol), and THF (100 mL).

Compounds **11—13** and **18—20** were synthesized from compounds **6—8** and 1-chloromethyl-1,1,3,3-pentamethyldisiloxane **9** (10 g, 0.1 mol), and compounds **21—23** were obtained from compounds **6—8** and 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane **10** (36.97 g, 0.16 mol). All products were purified by distillation *in vacuo* followed by recrystallization. The mixtures obtained from compounds **6**, **7**, and **9** were cooled to 0 °C, MeI (5.68 g, 0.04 mol) was added with stirring, and the mixture was then stirred for 1 h at 20 °C, refluxed for 1 h, and cooled to 0 °C. HCl (~5%) was added, and the mixture was extracted with ether. The extract was washed with ~5% HCl and water to pH 7 and dried with Na_2SO_4 or $MgSO_4$. The ether was distilled off, and the residue was distilled *in vacuo* to give compounds **14**, **15** and **18**, **19**.

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