Formation of stable carbenoid α-methoxyorganolithium compounds, 1-alkyl-2-lithiummethoxymethyl-*o*-carboranes, by metalation of 1-alkyl-2-methoxymethyl-*o*-carboranes with *n*-butyllithium

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1-Alkyl-2-methoxymethyl-*o*-carboranes are easily metalated with *n*-butyllithium in an ether—benzene solution to form carbenoid 1-alkyl-2-lithiummethoxymethyl-*o*-carboranes, which are stable at room temperature. Under the action of H_2O, CO_2, and PhCHO these lithium carboranes yield the starting compounds, carboxylic acids, and benzyl alcohols, respectively.

Key words: 1-alkyl-2-lithiummethoxymethyl-*o*-carboranes, metalation; carbenoids.

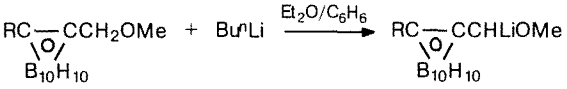
Recently, organolithium compounds containing electron-withdrawing substituents in the α-position have been of great interest among synthetic chemists.[1–3] The electron-withdrawing substituents in these compounds are divided into two groups: the typical acceptors, which efficiently stabilize the negative charge on the carbon atom (COR, SO_2R, SR, SiR_3, CN, NO_2, NC, $P(O)(OR)_2$, *etc.*), and carbenoid substituents (F, Cl, Br, I, and OR), which lead to carbenoid structures (carbenoids).[4]

Unlike organolithium compounds containing the typical acceptor substituents, α-halo- and α-alkoxyorganolithium derivatives are stable only at low temperatures (−70 to −110 °C).[5]

Previously we showed that substitution of the hydrogen atom in the methyl group of toluene with an *o*-carboranyl moiety results in a great increase in acidity of the protons of benzyl groups: 1-methyl-2-benzyl-*o*-carborane has pK_a 19.5, whereas the pK_a of toluene is 35 (according to the MSED scale).[6] 1-Benzyl-*o*-carboranes are easily metalated by Bu^nLi at room temperature in an ether—benzene mixture to give 1-lithiumbenzyl-*o*-carboranes. It is noteworthy that metalation of 1,2-dimethyl-*o*-carborane with *n*-butyllithium in an ether—benzene mixture does not occur even with boiling.[7]

Recently we have found that 1-methyl-2-chloromethyl-*o*-carborane is readily metalated with *n*-butyllithium in an ether—benzene solution at 15 °C with the formation of carbenoid 2-lithiumchloromethyl-1-methyl-*o*-carborane, which is stable at room temperature.[8] It is well known that metalation of MeOMe under the action of Bu^nLi occurs at 40 °C over a period of 7 days,[9] and it takes 100 h to metalate $MeOBu^n$ with *n*-butyllithium at 55 °C.[10]

In this work we have found that *n*-butyllithium easily metalates 1-alkyl-2-methoxymethyl-*o*-carboranes **1** and **2** in an ether—benzene solution at 20 °C to yield carbenoid 1-alkyl-2-lithiummethoxymethyl-*o*-carboranes.



1, 2 **3, 4**

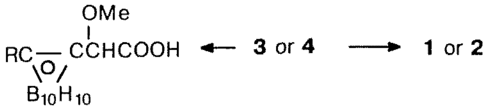
R = Me (**1, 3**); Pr^i (**2, 4**)

When a benzene solution of Bu^nLi is added to an ether solution of compound **1** (or **2**) at 15 °C the rapid metalation of the $MeOCH_2$ group occurs to form two liquid layers. The lower layer (which is orange in color) contains solvated product **3** (**4**), which remains unchanged at 20—25 °C for 2—3 h. The poor solubility of compound **3** (**4**) in an ether—benzene mixture points to its significant polarity, and the color of the solvated product **3** (**4**), is likely to be attributed by a certain delocalization of the negative charge in *o*-carborane moiety. Unlike most carbenoid α-methoxyorganolithium compounds of RCHLiOMe type which are stable only at low temperatures (<−70 °C), 1-alkyl-2-lithiummethoxy-*o*-carboranes **3** and **4** are stable at room temperature.

When water and CO_2 react with compounds **3** (or **4**) the starting carboranes **1** (**2**) and carboxylic acids **5** (**6**) are formed. The reaction of compound **4** with PhCHO leads to benzyl alcohol **7**.

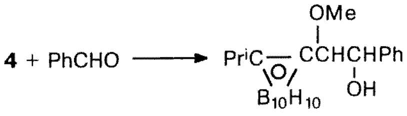
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 243—245, January, 1996.

1066-5285/96/4501-0235 $15.00



5, 6

R = Me (**5**); Pr^i (**6**)



7

The structures of compounds **5** and **7** are supported by the elemental analysis, and the ^1H NMR and IR spectra.

The higher stability of carbenoids **3** and **4** compared to the common α-methoxyorganolithium compounds is likely to be attributed to the strong electron-withdrawing effect of the 1-*o*-carbonyl group and delocalization of the negative charge into an *o*-carborane moiety similar to that occurring in the 1-phenyl-2-carboranyloxide-anion.[11]

Experimental

The course of reaction was monitored by TLC on Silufol plates. ^1H NMR spectra were recorded on a Bruker WP-200SY spectrometer in acetone-d_6 with $SiMe_4$ as the internal standard.

1-Methyl-2-methoxymethyl-*o*-carborane (1). To a solution of 1-methyl-*o*-carborane (3.2 g, 0.02 mol) in 25 mL of dry ether Bu^nLi (0.025 mol) in benzene was added at 10—15 °C with stirring under an argon atmosphere. The reaction mixture was stirred for 1 h at 20 °C, and then it was boiled for 10 min. After cooling to 10 °C a solution of chloromethyl ether (1.6 g, 0.02 mol) in 5 mL of dry ether was added to the reaction mixture, and it was stirred for 2 h at 20 °C. After completing the reaction, the mixture was poured into water, and the organic layer was separated, washed with water, and dried over Na_2SO_4. The solvent was distilled off *in vacuo* to give compound **1** (3.7 g, 92 %), m.p. 42—43 °C (from pentane). Found (%): C, 29.53; H, 8.89; B, 53.56. $C_5H_{18}B_{10}O$. Calculated (%): C, 29.70; H, 8.91; B, 53.46. ^1H NMR, δ: 1.19 (s, 3 H, CH_3); 3.35 (s, 3 H, OCH_3); 4.12 (s, 2 H, CH_2).

1-Isopropyl-2-methoxymethyl-*o*-carborane (2). Compound **2** was synthesized similarly to product **1** from 3.72 g (0.02 mol) of 1-isopropyl-*o*-carborane and 0.02 mol of Bu^nLi in 25 mL of dry ether. Compound 2 (4.1 g, 90 %) was obtained, m.p. 34 °C (from pentane). Found (%): C, 36.31; H, 9.48; B, 47.08. $C_7H_{22}B_{10}O$. Calculated (%): C, 36.52; H, 9.56; B, 46.96. ^1H NMR, δ: 1.17 (s, 3 H, CH_3); 1.21 (s, 3 H, CH_3); 2.45 (m, 1 H, CH); 3.37 (s, 3 H, OCH_3); 4.03 (s, 2 H, CH_2).

Metalation of 1-R-2-methoxymethyl-*o*-carboranes (general procedure). To a solution of 1-R-2-methoxymethyl-*o*-carborane (0.01 mol) in 15 mL of dry ether Bu^nLi (0.01 mol) in benzene was added at 10—15 °C with stirring under an argon atmosphere. The solution became yellow and was divided in two liquid layers, the lower layer gradually became orange. After the whole amount of Bu^nLi was added, the reaction mixture was stirred for 2 h at 20 °C.

1-Methylcarboranylmethoxyacetic acid (5). An ether—benzene mixture of compound **3**, obtained from 2 g (0.01 mol) of carborane **1** and Bu^nLi (0.012 mol) was poured into crashed solid CO_2 in dry ether. After evaporating the excess of CO_2 at 10 °C, 30 mL of ether was added, and the reaction mixture was treated with a 10 % solution of HCl. The organic layer was separated, the aqueous layer was extracted with ether, the ether extracts were washed with water and dried over Na_2SO_4. The ether was distilled off, and crystallization of the residue yielded acid **5** (2.2 g, 89 %), m.p. 97—98 °C (from hexane). Found (%): C, 29.39; H, 7.44; B, 43.79. $C_6H_{18}B_{10}O_3$. Calculated (%): C, 29.27; H, 7.32; B, 43.90. ^1H NMR, δ: 2.16 (s, 3 H, CH_3); 3.41 (s, 3 H, OCH_3); 4.36 (s, 1 H, CH); 6.75 (br.s, 1 H, OH).

1-Isopropylcarboranylmethoxyacetic acid (6). Acid **6** was synthesized similarly to acid **5** from 0.01 mol of lithium derivative **4**. Acid **6** was obtained (2.3 g, 83 %), m.p. 153—154 °C (from a benzene—hexane mixture). Found (%): C, 35.26; H, 8.10; B, 39.24. $C_8H_{22}B_{10}O_3$. Calculated (%): C, 35.04; H, 8.03; B, 39.42. IR, ν/cm^{-1}: 1700 (CO); 2600 (BH); 3450 (OH).

1-Isopropyl-2-(1′-methoxy-2′-hydroxy-2′-phenyl)ethyl-*o*-carborane (7). Benzaldehyde (1.1 g, 0.01 mol) in 5 mL of dry ether was added to an ether—benzene mixture of lithium derivative **4**, obtained from 0.02 mol of compound **2** and 0.012 mol of Bu^nLi, at 15—20 °C with stirring. The reaction mixture was stirred for 2 h at 20 °C; then it was boiled for 0.5 h, cooled, and poured into 30 mL of a cooled 10 % solution of HCl. The organic layer was separated, the aqueous layer was extracted with ether; the extracts were combined, washed with water, and dried over Na_2SO_4. The solvent was distilled off, and crystallization of the residue yielded compound **7** (2.7 g, 81 %), m.p. 93 °C (from hexane). IR, ν/cm^{-1}: 2600 (BH); 3320—3430 (OH). Found (%): C, 50.31; H, 8.43; B, 32.00. $C_{14}H_{28}B_{10}O_2$. Calculated (%): C, 50.00; H, 8.33; B, 32.14.

This work was financially supported by the International Science Foundation (Grant MSE 000).

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Received July 11, 1995

Synthesis of bisalkenyl ethers by the reaction of 1,1,2,2-tetracyanoethane with α-alkylacroleins in isopropyl alcohol

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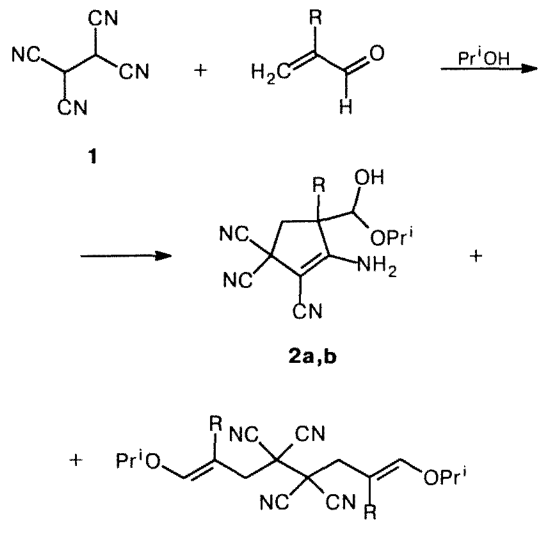
The reaction of 1,1,2,2-tetracyanoethane (**1**) with α–alkylacroleins in isopropyl alcohol affords 3-alkyl-2-amino-3-(isopropoxy)hydroxymethyl-1,5,5-tricyanocyclopentenes (**2a**,**b**) and 2,7-dialkyl-1,8-diisopropoxy-4,4,5,5-tetracyanoocta-1,7-dienes (**3a**,**b**). The structure of molecule **3b** has been established by X-ray structural analysis.

Key words: 1,1,2,2-tetracyanoethane, α–alkylacroleins, reaction; bisalkenyl ethers.

Previously[1] we have demonstrated that reactions of 1,1,2,2-tetracyanoethane (**1**) with α-alkylacroleins in alcohols afford stable hemiacetals, 3-alkyl-2-amino-3-(alkoxyhydroxymethyl)-1,5,5-tricyanocyclopentenes (in yields of up to 40 %). According to the regioselectivity of condensation of 1,1,2,2-tetracyanoethane with α,β-unsaturated carbonyl compounds, which we proposed,[2] the formation of adducts of composition 1 : 2 would be expected. Actually, 2,7-dialkyl-1,8-diisopropoxy-4,4,5,5-tetracyanoocta-1,7-dienes (**3a**,**b**) were isolated from the mixture of products of the reaction of cyanide **1** with 2-methyl- and 2-ethylacrolein in isopropyl alcohol in low yields and in addition to the known[1] 3-alkyl-2-amino-3-(isopropoxy)hydroxymethyl-1,5,5-tricyanocyclopentenes (**2a**,**b**) (the yield was 30—35 %). The structure of molecule **3b** has been established by X-ray structural analysis (Fig. 1).



R = Me (**a**), Et (**b**)

Apparently, the formation of bisalkenyl ethers **3** is associated with the possibility of additional stabilization of the alkoxyalkenyl fragments. Apparently, the main stabilizing factor is the coordination of the nucleophilic C(2) and C(2a) atoms to the electrophilic C(42) and C(42a) atoms (see Fig. 1), as evidenced by the data of X-ray structural analysis (the C(2) · · · C(42) distance is 2.927(7) Å).

[†] Deceased in 1995.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 246—247, January, 1996.