

METALLIZATION OF 1-SUBSTITUTED 1-BENZYL-o-CARBORANES
WITH *n*-BUTYLLITHIUM AND SOME CONVERSIONS OF
1-R-2-BENZYL-LITHIUM-o-CARBORANES

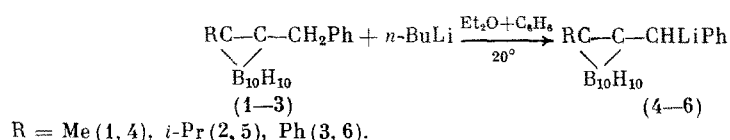
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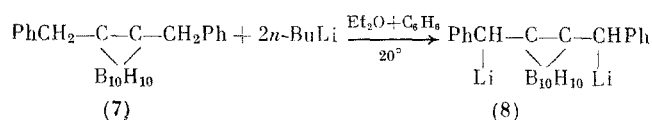
It was shown that 1-R-2-benzyl-o-carboranes (R = Me, *i*-Pr, Ph, PhCH₂) and other derivatives of o-carborane containing an ArCH₂ group in positions 1 and 2 are readily metallized by *n*-butyllithium, forming the corresponding benzyllithium derivatives, which react with electrophilic reagents like the usual organolithium compounds, permitting the synthesis of various C-substituted 1-o-carboranes.

Keywords: benzyl-o-carboranes, metallization, *n*-butyllithium.

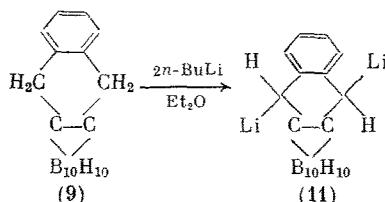
It was shown earlier that replacement of a hydrogen atom in the CH₃ group of toluene by a 1-methyl-2-o-carboranyl group leads to a substantial increase in the acidity of the benzyllithium hydrogen atoms: 1-methyl-2-benzyl-o-carborane pK 19.5, toluene pK 35 (according to the MSÉD scale) [1]. Under the action of *n*-butyllithium on 1-methyl-2-benzyl-o-carborane (1) in THF solution, 1-methyl-2-lithium-benzyl-o-carborane was readily formed; its reaction with CO₂ led to (1-methyl-o-carboranyl)phenylacetic acid. In this work we made a further study of the metallization of 1-R-2-benzyl-o-carboranes to use this reaction for synthetic purposes. It was found on the example of compound 1, 1-isopropyl-2-benzyl-o-carborane (2), and 1-phenyl-2-benzyl-o-carborane (3) that 1-R-2-benzyl-o-carboranes are readily metallized by *n*-butyllithium in ether-hexane and ether-benzene solutions at 20°C, forming the corresponding 1-R-2-benzyllithium-o-carboranes.



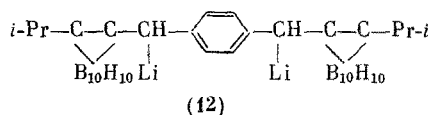
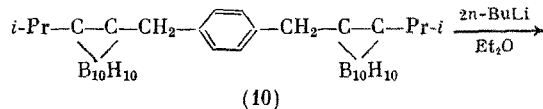
1,2-Dibenzyl-o-carborane (7) is metallized under these conditions to form 1,2-di(lithium-benzyl)-o-carborane (8):



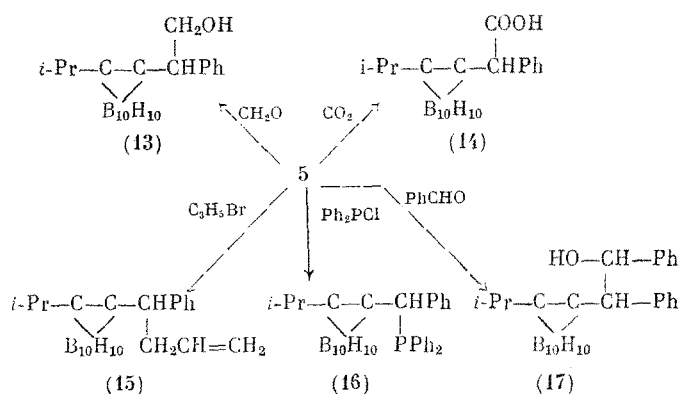
Such benzyl derivatives of o-carborane as 1,2-benzo-4,5-carboranyl-cyclohexane (9) and bis-1,4-(1-isopropyl-o-carboranylmethyl)benzene (10) also form dilithium derivatives (11) and (12), respectively, under the action of butyllithium:



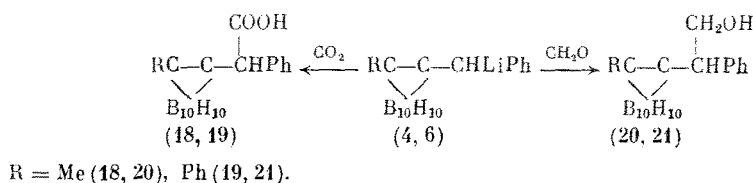
A. N. Nesmeyanov Institute of Heteroorganic Compounds, Russian Academy of Sciences, 117813 Moscow. Translated from *Izvestiya Akademii Nauk, Seriya Khimicheskaya*, No. 2, pp. 431-435, February, 1992. Original article submitted April 16, 1991.



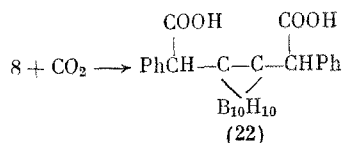
The lithium derivatives 4-6 obtained possess low solubility in ether-hexane and ether-benzene mixtures and are isolated from the solution in the form of a yellow liquid layer. The dilithium derivatives 8, 9, and 12 are isolated in the form of a red layer. The low solubility of lithium derivatives 4-6, 8, 9 and 12 and the color are evidence of a substantial degree of polarity of the C-Li bond in these compounds. The reactions of the lithium derivative 5 with CO_2 , CH_2O , PhCHO , allyl bromide, and Ph_2PCl proceed similarly to the usual reactions of organolithium compounds according to the scheme:



The reaction of lithium derivatives (4) and (6) with CO_2 and CH_2O yielded the corresponding acids (18) and (19) and carbinols 20 and 21:



The action of CO_2 on dilithium derivative 8 gives a dicarboxylic acid 22:



Under the action of butyllithium on the 1-benzyl-o-carborane 18, metallization occurs at the CH-carborane and CH_2 -benzyl groups, forming the dilithium derivative 24, which, when treated with CO_2 , gives the dicarboxylic acid 25:

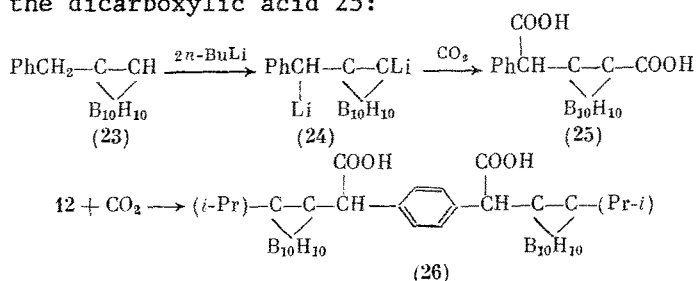


TABLE 1. Characteristics of the Compounds Obtained

Compound	Yield, %	Mp, °C	Empirical formula	Found Calculated, %		
				C	B	H
13	82	72-73	C ₁₃ H ₂₆ B ₁₀ O	51.26 50.95	8.73 8.55	35.08 35.27
14	85	208-209	C ₁₃ H ₂₄ B ₁₀ O ₂	48.53 48.72	7.43 7.54	33.82 33.73
15	79	91-92	C ₁₅ H ₂₈ B ₁₀	56.88 56.94	8.95 8.85	34.20 34.21
16	83	245-246	C ₂₄ H ₃₈ B ₁₀ P *	62.47 62.59	7.00 7.17	23.04 23.49
17	94	136-137	C ₁₉ H ₃₀ B ₁₀ O	59.50 59.66	7.80 7.85	28.22 28.29
18	81	193-194	C ₁₁ H ₂₀ B ₁₀ O ₂	44.99 45.18	6.80 6.84	36.95 37.01
19	86	219-220	C ₁₆ H ₂₂ B ₁₀ O ₂	54.45 54.22	6.30 6.21	30.34 30.53
20	82	92-93	C ₁₁ H ₂₂ B ₁₀ O	47.58 47.46	7.81 7.91	38.51 38.87
21	90	99-100	C ₁₆ H ₂₄ B ₁₀ O	56.21 56.45	6.98 7.05	32.03 31.78
22	78	199-200	C ₁₈ H ₂₄ B ₁₀ O ₄	52.37 52.41	6.09 5.86	26.77 26.20

*Found/Calculated P, %: 6.39/6.73.

TABLE 2. PMR Spectra of the Compounds Obtained

Compound	PMR spectrum, δ , ppm (J, Hz)
13	1.22 d (3H, CH ₃ , J=7), 1.29 d (3H, CH ₃ , J=7), 2.95 m (2H, CH), 3.64 m (2H, CH ₂), 4.09 (OH)
15	1.23 d (3H, CH ₃ , J=7), 1.28 d (3H, CH ₃ , J=7), 1.74 m (CH ₂), 2.78 m (2H, CH), 4.78 d (cis-H from=CH ₂ , J=6), 4.97 d (trans-H from=CH ₂ , J=13), 5.35 m (=CH), 7.03 m (Ph)
16 *	0.82 d (3H, CH ₃ , J=7), 1.14 d (3H, CH ₃ , J=7), 3.04 m (1H, CH(CH ₃) ₂), 5.04 d (1H, CH-Ph), 6.94-7.61 m (15H, Ph)
17	1.06 d (3H, CH ₃ , J=7), 1.33 d (3H, CH ₃ , J=7), 2.79 m (1H, CH(CH ₃) ₂), 3.59 (1H, OH), 4.96 d (1H, CHPh, J=4.3), 7.33 m (10H, Ph), 4.96 q (1H, CHPhOH, J=5)
25	3.74 s (1H, CH), 7.8 m (Ph)

* $\delta^{31}\text{P}$ 31.02 ppm.

The structures of the compounds were confirmed by the data of PMR spectroscopy.

Acids 14 and 19, when reduced by LiAlH₄, smoothly formed the carbinols 13 and 21, respectively. Thus, the use of metallization by n-butyllithium of 1-R-2-benzyl-o-carboranes and other o-carborane derivatives bonded in the 1- and 2-positions to Ar-CH₂ groups permits the synthesis of various C-substituted o-carboranes.

EXPERIMENTAL

The course of the reaction was monitored on Silufol plates. The PMR spectra were recorded on a Bruker WP-200SY instrument in acetone-d₆ solution. The chemical shifts of ¹H are cited relative to TMS.

Metallization of 1-R-2-Benzyl-o-carboranes by n-C₄H₉Li. To a solution of 0.01 mole of 1-R-2-benzyl-o-carborane in 15-20 ml of abs. ether, 0.01 mole of n-C₄H₉Li in hexane or benzene

was added with mixing in an atmosphere of argon at 20°C. A yellow color appeared immediately, and two layers were formed. After the addition of $n\text{-C}_4\text{H}_9\text{Li}$, the mixture was mixed for 0.5 h at 20°C and then for 10 min while boiling.

The carboxylation of 1-R-2-benzyl-lithium-o-carboranes was performed in the usual way by pouring the reaction mixture into solid CO_2 in abs. ether. The reactions with CH_2O , PhCHO , allyl bromide, and Ph_2PCl were carried out according to the usual procedures by adding the reagent to the reaction mixture at 20°C, following by heating. The yield of the compounds obtained, melting points, and data of elementary analysis are presented in Table 1, and the data of the PMR spectra in Table 2.

Reduction of 1-R-2-[CH(COOH)Ph]-o-Carboranes by LiAlH_4 to 1-R-2-[CH(CH₂OH).Ph]-o-carboranes. A solution of 5 mmoles of 1-R-2-[CH(COOH)Ph]-o-carborane in ether was added to 5 mmoles of LiAlH_4 in abs. ether with mixing, and the mixture was mixed with heating for 30 min. The excess LiAlH_4 was decomposed with methanol with cooling, then 10% HCl was added. The ether layer was removed, washed with HCl, with a dilute KOH solution, with water, and dried with Na_2SO_4 . The solvent was distilled off, and the residue was recrystallized from a benzene-hexane mixture.

Metallization of 1-Benzyl-o-carborane (23) and bis-1,4-(1-Isopropyl-o-carboranylmethyl)benzene (10). To a solution of 0.01 mole of compound 23 in 20 ml of abs. ether or compound 10 in 20 ml of abs. THF, 0.02 mole of $n\text{-C}_4\text{H}_9\text{Li}$ in benzene was added with mixing in an atmosphere of argon at 20°C. A red color appeared immediately, and two layers were formed. After the addition of $n\text{-C}_4\text{H}_9\text{Li}$ the mixture was mixed for 0.5 h at 20°C and then for 20 min at the boiling point. Carboxylation of dilithium derivatives 24 and 12 was performed by pouring the reaction mixture into solid CO_2 in abs. ether. Yield 2.5 g (78%) of the acid 25, mp 152-153°C (benzene-heptane). Found: C 41.27; H 5.68; B 34.05%. $\text{C}_{11}\text{H}_{18}\text{B}_{10}\text{O}_4$. Calculated: C 40.97; H 5.58; B 33.56%. From compound 10 4.5 g (80%) of the acid (26) was obtained, mp 254-256°C (with decomp.). Found: C 42.80; H 7.54; B 38.07%. $\text{C}_{20}\text{H}_{42}\text{B}_{20}\text{O}_4$. Calculated: C 42.68; H 7.47; B 38.45%. PMR spectrum (acetone- d_6 , δ , ppm): 1.24 d (7), (CH_3), 1.28 d (7) (CH_3), 2.03 m (CH), 3.64 s (OH), 7.72 s (Ph).

LITERATURE CITED

1. L. I. Kruglyak, É. S. Petrov, V. N. Kalinin, E. G. Rys, L. I. Zakharkin, and A. I. Shatenshtein, Zh. Obshch. Khim., 42, No. 12, 2670 (1972).