

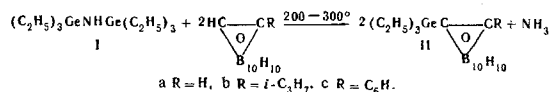
REACTION OF DIGERMAZANES WITH o-CARBORANES

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o-Carborane derivatives containing germanium can be obtained either through organometallic derivatives of carborane [1, 2] or by the hydrogermylation of alkenylcarboranes [3]. We have found a new route to the germylation of the o-carboranes. The carboranes, like monosubstituted acetylenes [4] and other compounds containing a strongly-activated hydrogen atom [5], decompose digermazane with the formation of a Ge—C bond



1-Triethylgermyl-o-carborane (IIa). A mixture of 4.32 g of carborane and 10.1 g of hexaethyldigermazane (I) was heated under reflux for 14 hr, the temperature being raised gradually from 200 to 300° C. Then another 1 g of hexaethyldigermazane was added and the mixture was heated at 300° C for another 12 hr. Then it was treated with methanol, and the low-boiling products were distilled off at 100° C (15 mm). The pure product IIa was isolated by chromatography on a column of alumina of activity grade II. The eluant was hexane: R_f of carborane 0.25; R_f of IIa 0.62. The yield of 1-triethylgermylcarborane IIa with d_4^{20} 1.0940, n_D^{20} 1.5483, was 4.51 g (50.0%). Found, %: C 31.59; H 8.60; B 8.60; Ge 22.90. Mol. wt. 318. Calculated for $\text{C}_8\text{H}_{26}\text{B}_{10}\text{Ge}$, %: C 35.7; H 8.59; B 35.70; Ge 23.95; mol. wt. 302.8.

1-Isopropyl-2-triethylgermylcarborane (IIb). A mixture of 10.29 g of 1-isopropylcarborane and 9.25 g of I was heated at 245° C for 17 hr. Distillation of the reaction mixture at 1-1.5 mm gave 5.15 g (27.0%) of unpurified IIb with bp above 150° C. It was purified further as in the preceding case. R_f of 1-isopropylcarborane 0.56; R_f of IIb 0.7; n_D^{20} 1.5506. Found, %: C 39.01; H 9.50; B 31.12; Ge 20.93; mol. wt. 356. Calculated for $\text{C}_{11}\text{H}_{32}\text{B}_{10}\text{Ge}$, %: C 38.39; H 9.25; B 31.25; Ge 21.05; mol. wt. 344.6.

1-Phenyl-2-triethylgermylcarborane (IIc). Similarly, heating a mixture of 10.5 g of 1-phenylcarborane and 7.99 g of I at 270-275° C for 28 hr yielded 4 g (22.5%) of crude IIc; R_f of phenylcarborane 0.41; R_f of IIc 0.62; n_D^{20} 1.5882. Found, %: C 44.10; H 8.31; B 28.75; Ge 19.65; mol. wt. 369. Calculated for $\text{C}_{14}\text{H}_{30}\text{B}_{10}\text{Ge}$, %: C 44.40; H 7.92; B 28.53; Ge 19.14; mol. wt. 378.8.

REFERENCES

1. L. I. Zakharkin, V. I. Bregadze, O. Yu. Okhlobystin, J. Organometal. Chem., 4, 211, 1965.
2. H. Schroeder, S. Papetti, R. P. Alexander, J. F. Sieckhaus, and T. L. Heying, U. S. Tech. Inform., AD 652379; C. A., 68, 13463, 1958.
3. T. K. Gar, V. N. Siryatskaya, A. F. Zhigach, and V. F. Mironov, KhGS [Chemistry of Heterocyclic Compounds], 5, 379, 1969.
4. V. F. Mironov, E. S. Sobolev, and L. M. Antipin, ZhOKh, 37, 1707, 1966.
5. V. F. Mironov, E. S. Sobolev, and L. M. Antipin, ZhOKh, 37, 2573, 1966.

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