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THE SYNTHESIS OF ISOMERIC 1,9- AND
1,12-DIBROMO-1,2-DICARBA-*closo*-DODECABORANES

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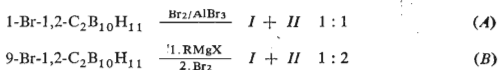
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A mixture of 1,9- and 1,12-dibromo-1,2-dicarba-*closo*-dodecaborane was obtained by direct bromination of 1-bromo derivative and by magnesylation and subsequent bromination of the 9-bromo derivative. The substances were isolated and assigned a probable structure.

Of the twenty-six possible isomeric dibromo-1,2-dicarba-*closo*-dodecaboranes only the isomers with bromine atoms in the positions 1,2- (ref.¹), 9,12- (ref.²), and 8,9- (ref.³) have been described so far. In this paper the preparation of two additional ones is described, *i.e.* 1,9-dibromo-1,2-dicarba-*closo*-dodecaborane (*I*) and 1,12-dibromo-1,2-dicarba-*closo*-dodecaborane (*II*).

As both substances were required as comparative and starting material for some studies in the carborane series^{4,5}, we chose for their synthesis two independent routes (*A*, *B*), in order to decrease the possibility of an erroneous structure:



In both cases we obtained a mixture of the isomers. The choice of starting compounds assured that one halogen atom was in the position 1- in both cases, while the second halogen atom was in the position 9- in one case, and in the position 12- in the other.

To the less soluble isomer of m.p. 180–182°C, which on thin layer chromatography moves more slowly, (substantially, the rate is indirectly proportional to the dipole moment⁴) we assign the structure of 1,12-dibromoderivative *II* while the structure of 1,9-dibromoderivative *I* is assigned to the easily soluble substance with m.p. 92–93°C, which moves more rapidly (great solubility and a low melting point, as well as a lower dipole moment are in agreement with the lower symmetry, if considered from the point of view of the positions of the heavy atoms of bromine).

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A definite solution will be given by an X-ray diffraction study carried out with a monocrystal of the isomer *II*, which is currently in process⁶.

The mutual ratio of isomers *I* and *II* in the products of syntheses (*A*) and (*B*) may be different if the first bromine atom exerts a directing effect on the second, entering the molecule. Unfortunately the two isomers cannot be separated by gas chromatography, and their quantitative representation may be judged only from the results of preparative chromatography on a silica gel column. From this it follows that in the case of route (*A*) the directing effect of the first bromine atom cannot be taken into consideration, while in the case of route (*B*) this effect is probable.

EXPERIMENTAL

Bromination of 1-bromo-1,2-dicarba-closo-dodecaborane: A mixture of 25 ml of carbon disulfide, 0.03 g of Al, and 0.8 g of bromine was shaken for 40 minutes. To the formed suspension 4.45 g (0.02 mol) of 1-bromo-1,2-dicarba-closo-dodecaborane and 1.1 ml of bromine were added. When the reaction subsided the mixture was refluxed for 1 hour, the solvent evaporated *in vacuo*, and the residue partitioned between 30 ml of dichloromethane and water. The dichloromethane layer was washed with 10 ml water and, after separation, evaporated *in vacuo*. The residue was extracted 5 times with 20 ml pentane, leaving 2.2 g of the crude isomer *II* undissolved, while the total of isomer *I* accompanied by a small portion of the isomer *II* and the unreacted starting compound passed into pentane. This extract was chromatographed on a column of silica gel with hexane, and single fractions were controlled by thin-layer chromatography on Silufol. The regenerated starting material passed into the first fractions (0.15 g), in subsequent fractions isomer *I* appeared, and eventually isomer *II*. The fractions of isomer *I* were evaporated *in vacuo* and the product sublimated at 0.01 Torr and 120°C; 1.8 g (29.6%), m.p. 92–93°C. The fractions containing isomer *II*

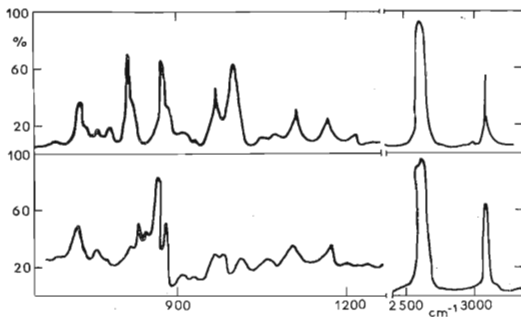


FIG. 1

IR Spectra of Compounds *I* (above) and *II* (below)

Measured in tetrachloromethane on a UR 10 (Zeiss, Jena) apparatus.

were evaporated *in vacuo*, added to the crude fraction, and sublimated together at 0.01 Torr and 135°C. After crystallisation from hexane 2.1 g (34.4%) of compound *II* were obtained, m.p. 180–182°C. On thin-layer chromatography in tetrachloromethane substance *I* has a relative rate 123 if the rate of *II* is 100. Both compounds reduce silver nitrate, in contrast to unsubstituted 1,2-dicarba-*closo*-dodecaborane. Both compounds give in their mass spectrum a molecular peak at $m/e = 306$, corresponding to the composition $C_2B_{10}H_{10}Br_2$. Their IR spectra are represented in Fig. 1. The substances are soluble in ethanol under a strong evolution of gas and spontaneous heat evolution.

Magnesylation and Bromination of 9-Bromo-1,2-dicarba-*closo*-dodecaborane

A solution of 8.9 g (0.04 mol) of 9-Br-1,2- $C_2B_{10}H_{10}$ in 200 ml of benzene was added dropwise within one hour to a solution of 0.05 mol of C_2H_5MgBr in 100 ml of tetrahydrofuran. A gas evolved slowly. After 5 hours standing the mixture was boiled for 2 hours, cooled to 10°C, and added dropwise over one hour to a solution of 8.0 g of bromine (0.05 mol) in 200 ml of benzene which was cooled in order to keep the reaction mixture constantly in a semisolid state. Bromine was decolorized practically immediately. The mixture was extracted twice with 100 ml of water and the benzene layer was evaporated *in vacuo* and the residue isolated similarly as in the preceding case. Yield, 2.4 g (19.7%) of isomer *I*, m.p. 92–93°C, and 4.8 g (39.4%) of isomer *II*, m.p. 180–182°C.

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REFERENCES

1. Leites L. A., Vinogradova L. E., Kalinin V. N., Zacharkin L. I.: *Izv. Akad. Nauk SSSR, Ser. Chim.* 1968, 1016.
2. Potenza J. A., Lipscomb W. N., Vickers G. D., Schroeder H. A.: *J. Am. Chem. Soc.* 88, 628 (1966).
3. Zacharkin L. I., Kalinin V. N.: *Izv. Akad. Nauk SSSR, Ser. Chim.* 1966, 586.
4. Plešek J., Gregor V., Heřmánek S.: *This Journal*, in press.
5. Plešek J., Gregor V., Stuchlík J., Heřmánek S.: *This Journal*, in press.
6. Šubrtová V.: Unpublished results.

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