

CHEMISTRY OF BORANES. XXXIII.*
 THE SYNTHESIS
 OF 8-BROMO-1,2-DICARBA-*closo*-DODECABORANE(12)

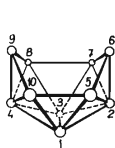
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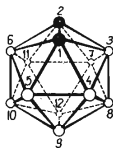
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Contrary to the data in the literature, the reaction of 2-bromodecaborane(14) (*Ia*) or 2-bromo-6,9-bis(diethylsulphide)decaborane(12) (*Ila*) with acetylene does not give a single product, but yields a mixture of bromo-1,2-dicarba-*closo*-dodecaboranes *IIIa-d*, substituted on the boron atoms.

In the presence of a Lewis base, acetylene reacts with decaborane(14) (*I*) or 6,9-diligand-decaborane(12) (*II*) to give 1,2-dicarba-*closo*-dodecaborane(12) (*III*). The reaction consists in the insertion of an acetylene molecule between atoms 6 and 9 of decaborane, perpendicularly to an imaginary line connecting these two atoms. Consequently, a monosubstituted decaborane (14) should afford only monosubstituted 1,2-dicarba-*closo*-dodecaborane(12). In agreement with this theory the reaction of 2-bromodecaborane (*Ia*) with acetylene in acetonitrile was reported^{1,2} to yield only 8-bromo-1,2-dicarba-*closo*-dodecaborane(12) (*IIIc*). Contrary to these reports we have found, however, that even when the starting 2-bromodecaborane(14) was the pure isomer *Ia*, its reaction with acetylene in acetonitrile gave not only the expected derivative *IIIc*, but also the compounds *III*, *IIIa*, *IIIb* and *III d*. Since the bromine atom may have migrated during the formation of the ligand derivative (postulated



Skeleton I



Skeleton III



IIIa = 3-Br-

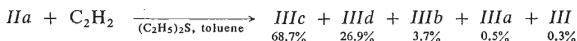
IIIb = 4-Br-

IIIc = 8-Br-

III d = 9-Br-

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intermediate) we investigated the reaction of acetylene with chromatographically pure 2-bromo-6,9-bis(diethylsulphide)decaborane(12). The result of the reaction is expressed by the following equation



This experiment is a convincing proof that the bromine atom does not migrate until after the reaction of 2-bromodecaborane(14) with the Lewis base. Further experiments revealed that migration of the bromine atom bound at position 8 of the molecule of 1,2-dicarba-*closo*-dodecaborane does not take place even under much more drastic conditions than those in the reaction with acetylene or in the working-up of the reaction mixture. These two limitations suggest that the rearrangement of the bromine atom probably occurs on the unstable addition product of acetylene and the ligand derivative of bromodecaborane in the dehydrogenation step or before.

EXPERIMENTAL

The melting points (in sealed capillaries) were not corrected. The IR spectra were read on a double beam spectrophotometer Beckman, model IR-20. Analyses were performed on a gas chromatograph Chrom-3 with a stainless steel column, 2400 mm long and 6 mm in diameter, packed with 3% QF 1 on Chromosorb W. Preparative chromatography was carried out on an apparatus (Carlo Erba Fractovap, model P), on a stainless steel column, 2000 mm long and 25 mm in diameter, packed with silanized chromosorb W (mesh 60–80) coated with 20% QF-1; the carrier was nitrogen, column temperature 180°C. The mass spectra were measured with an apparatus Gaschromatograph Mass Spectrometer LKB 9000.

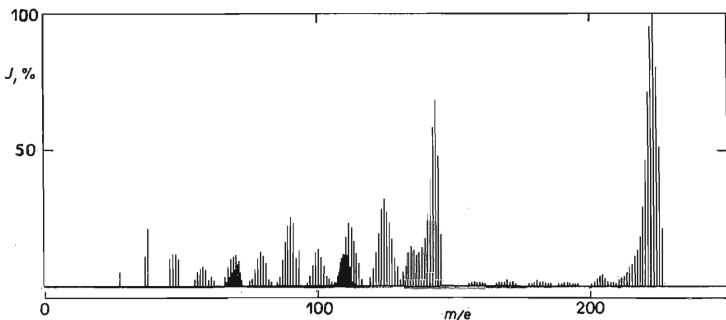


FIG. 1

The Mass Spectrum of 8-Bromo-1,2-dicarba-*closo*-dodecaborane(12) (IIIc)

Synthesis of Reference Compounds for Gas-Liquid Chromatography

Compound *IIla* was obtained according to the literature³ by the reaction of boron bromide with the dilithium salt of $C_2B_9H_{11}^{2-}$ in diethyl ether; m.p. 122–123°C (hexane), the IR spectra agreed with the reported ones³. In addition to this product there was also formed 3-ethoxy-1,2-dicarba-*closo*-dodecaborane(12). Compounds *IIlb* (ref.⁴) and *IIId* (ref.⁵) were prepared according to the literature. After resublimation and five crystallizations from heptane *IIId* had a m.p. of 191.5°C.

2-Bromodecaborane(14) was obtained according to a reported procedure^{6,7}. After four crystallizations from hexane it melted at 106–106.5°C; its purity was checked by gas-liquid chromatography (thermal-conductivity detector, hydrogen as carrier, column temperature 150°C, V_g 67; cf.⁸)

6,9-Diethylsulphide-2-bromodecaborane(12) (*IIa*). A solution of 2-bromodecaborane(14) in benzene was covered with an excess of diethyl sulphide and the system was left standing under nitrogen for 48 h at 20°C. The mixture was then heated to 40–50°C for 8 h, after which time the excess of diethyl sulphide and benzene were distilled off and the product was dried *in vacuo* at room temperature. It was then dissolved in dichloromethane and covered with a layer of diethyl ether. The separated crystals were collected on a filter under a nitrogen atmosphere. After three crystallizations the product (*IIa*) had a m.p. of 101.5–102°C and IR spectra identical with the reported ones⁹.

Reaction of Compound *II* with Acetylene

Purified acetylene was introduced into a solution of *IIa* (25.2 g) in toluene (150 ml) under nitrogen. After one hour the reaction temperature was slowly elevated to 90°C and maintained at this value for 19 h, with stirring. On cooling, the solution was concentrated under reduced pressure. The oily residue was shaken with dilute aqueous NaOH, water, 10% hydrochloric acid and water; then it was dissolved in methanol, stirred 3 h at room temperature and concentrated *in vacuo*. An aliquot portion of the reaction mixture was chromatographed on a column of silica gel. The first fractions, eluted with hexane, were successively compounds *III*, *IIla* and *IIlb* (checked for purity by gas-liquid chromatography and thin-layer chromatography on Silufol^{10,11}), whose mixed melting points with authentic compounds were undepressed. The remaining mixture of the isomers *IIlc* and *IIId* was eluted with benzene and separated by preparative gas-liquid chromatography. We obtained 1.2 g of the 8-bromo derivative (*IIlc*), which after crystallization from heptane and drying (0.03 Torr/20°C) had a m.p. of 184.5 to 185°C and purity >99%; its dipole moment is 5.48 D (ref.¹²). For $C_2B_{10}H_{11}Br$ (223.2) calculated: 48.45% B, 35.82% Br, 10.76% C, 4.96% H; found: 48.44% B, 35.99% Br, 10.87% C, 5.20% H. The IR spectrum (0.26 mm NaCl cell, 2.3% solution in tetrachloromethane) exhibited bands 605 w, 635 w, 715 s, 883 vs, 850 s, 880 w, 900 w, 917 m, 935 m, 938 m, 950 shw, 985 m, 997 m, 1030 m, 1040 shw, 1045 shw, 1135 m, 1147 s, 1210 m, 1260 vw, 2600 vs, 3070 s, cm^{-1} , which is in agreement with the literature¹³. The mass spectrum is shown in Fig. 1. The compound was heated *a*) in a sealed ampoule under nitrogen to 100°C for 10 h, *b*) in toluene to 100°C for 10 h. No change was detected by gas-liquid chromatography.

Preparative gas-liquid chromatography afforded 0.5 g of the compound *IIId*; after crystallization from heptane and drying *in vacuo* it had a m.p. of 191.5°C. The mixed m.p. with an authentic compound was not depressed. The reported¹² dipole moment is 5.98 D. The IR spectrum (0.09 mm NaCl cell, 5% solution in tetrachloromethane) had bands 608 w, 630 m, 730 s, 858 vs, 875 m, 885 shm, 895 shw, 920 m, 950 w, 973 m, 990 m, 1010 s, 1035 w, 1055 w, 1145 m, 1215 m, 2620 vs, 3090 s; these data agree with the reported ones¹³.

Reaction of 2-Bromodecaborane(14) with Acetylene in the Presence of Acetonitrile

A solution of 1.0 g of 2-bromodecaborane(14) in 20 ml of toluene and 0.5 ml of acetonitrile was heated under nitrogen for 2 h to 40°C and 2 h to 80°C. Purified acetylene was then introduced into the stirred mixture for 8 h. There was formed a mixture of products, in which compounds *III* (1.0), *IIIa* (1.30), *IIIb* (2.22), *IIIc* (4.18) and *IIId* (4.58) were identified by gas-liquid chromatography (flame-ionization detector, column temperature 188°C, nitrogen as carrier); the numbers in parentheses give the relative retention times.

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