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REACTIONS OF BIS- AND MONO-LIGAND DERIVATIVES  
OF DECABORANE WITH HYDROGEN HALIDES

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The effect of the size of dialkyl sulfide and of temperature on the ratio of 5- and 6-halogenodecaboranes(14) formed in the reaction of 6,9-bis(dialkylsulfido)decaboranes(12) with hydrogen halides and a new method of preparation of 5- and 6-halogenodecaboranes(14), *i.e.* the reaction of dimethylsulfidodecaborane(12) with hydrogen halides, is described.

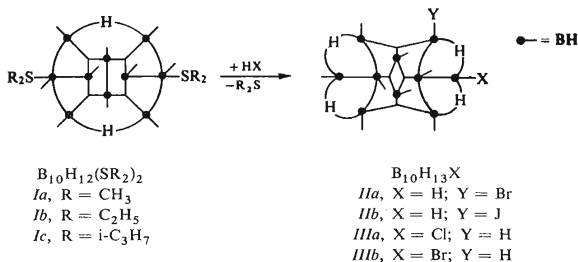
In previous communications<sup>1,2</sup> we described the reaction of 6,9-bis(diethylsulfido)decaborane(12) with hydrogen halides, which takes place at 20°C, in benzene under formation of 5-halogeno derivatives of decaborane(14), with the exception of hydrogen chloride which affords 6-chlorodecaborane(14). The fact that in these reactions formation of 5-derivatives takes place in three cases, while only in one the 6-isomer is formed, shows that the reaction course is probably affected by two factors – a thermodynamical one (preferential attachment of halogen to the position 6) and a steric one (shielding of the position 6 by a co-ordinatively bound dialkyl sulfide, *i.e.* an increase in the amount of the isomer 5). In this paper attention is paid to the effect of the size of the departing dialkyl sulfide, the size of approaching halogen in HX, and the temperature, on the total yield and mainly on the ratio of 5- and 6-isomers in the halogenodecaborane(14) formed.

Hydrogen chloride reacts with bis(dialkylsulfido)decaborane(12) *Ia–c* exclusively under formation of 6-chlorodecaborane(14) (in 69, 60, and 62% yields; the starting substance was taken as the basis of calculation) (Scheme 1). From this series it follows that the size of the departing dialkyl sulfide does not affect either the yield of the reaction or the distinct shielding of the position 6 which would cause the entry of the chlorine atom into the position 5. The effect of a still larger ligand, *i.e.* ditert-butyl sulfide, was not studied because of the inaccessibility of the corresponding diligandodecaborane. In an attempt at the preparation of 6,9-bis(ditert-butylsulfido)decaborane(12) we observed that ditert-butyl sulfide does not react with decaborane even at elevated temperatures. In contrast to hydrogen chloride the more bulky hydrogen bromide

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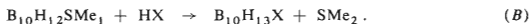
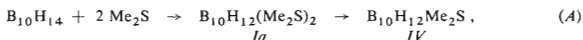
in the reaction with bis(dialkylsulfido)decaborane displays a distinct steric effect. The compound *Ib* in which diethyl sulfide is a ligand affords predominantly 5-bromo isomer *IIa*, while the compound *Ia*, where dimethyl sulfide functions as a ligand, reacts under formation of a mixture of 5- and 6-isomers in a 6 : 1 ratio and a total yield of 73%. The large effective volume of hydrogen iodide became apparent already in the reaction with 6,9-bis(dimethylsulfido)decaborane *Ia* in which 4% of 5-iodo-decaborane *IIb* were formed in addition to 57% of the prevailing 5-iodo-6,9-bis(dimethylsulfido)decaborane which was formed by a rapid subsequent reaction of 5-iodo-decaborane with the split off dimethyl sulfide. The fact that the 6-isomer is not formed indicated that a ligand as small as dimethyl sulfide displays a sufficiently strong shielding effect in the presence of the iodine atom, to prevent the formation of the 6-isomer. The increase in temperature to boiling point of the reaction mixture in benzene does not substantially affect the ratio of 5- to 6-isomers during the reaction with hydrogen iodide, while in the case of hydrogen chloride the 6-isomer is formed again. However, the shift of the equilibrium in favour of the 6-isomer is quite clear at elevated temperature when the reaction is carried out with hydrogen bromide. It increased from the original 14% at 20°C to 55% at 80°C. Simultaneously the reaction yield also increased with the temperature.

All the mentioned results are in good agreement with the view of the course of the reaction of bis(dialkylsulfido)decaboranes *I* with hydrogen halides expressed in our previous paper<sup>2</sup>. The increase in the yield of the reactions carried out at elevated temperatures led to the hypothesis that under these conditions the reaction at least partly goes *via* dimethylsulfidodecaborane(12) (*IV*) which is formed by heating the substance *Ia* at elevated temperature<sup>3</sup>. For the preparation of the starting substance *IV* we made use of a new method -- heating of decaborane or compound *Ia* in excess dimethyl sulfide at 120°C (equation (A)). In the first reaction stage with decaborane compound *Ia* is formed which loses a molecule of dimethyl sulfide at a higher temperature. The advantage of the mentioned method is that during the reaction



SCHEME 1

no undesirable polymeric products are formed, in contrast to the reaction described earlier<sup>3</sup>. The reaction of hydrogen halides with the compound *IV* takes place very easily and in good yield in benzene at 20°C, under formation of 5- and 6-substituted halogenodecaboranes (equation (B)). An exceptionally high yield (61%), when compared with the reactions with bis-dialkylsulfido derivatives, was observed in the case of the reaction of hydrogen iodide. The ratio of the product formed is approximately identical to that in the reaction of substance *Ia* with hydrogen halides at boiling point in benzene.



## EXPERIMENTAL

The utilized 6,9-bis(dimethylsulfido)decaborane(12) and 6,9-bis(diisopropylsulfido)decaborane(12) were prepared from decaborane and corresponding dialkyl sulfide<sup>4</sup>. Melting points were determined in sealed capillaries under nitrogen and they are uncorrected. The IR spectra were measured on a UR-10 spectrophotometer in 5% CS<sub>2</sub> solution. All operations connected with the isolation of the products were carried out in the standard vacuum apparatus, unless stated otherwise<sup>5</sup>.

### Reaction of 6,9-Bis(dimethylsulfido)decaborane(12) (*Ia*) with Hydrogen Halides at 20°C

a) *With hydrogen chloride*: A suspension of 26.1 g (0.165 mol) of substance *Ia* in 250 ml of benzene was saturated with anhydrous HCl for 3 h. The mixture was allowed to stand overnight under a small overpressure of HCl. After evaporation of benzene under reduced pressure the residue was extracted with pentane and the yellow oil remaining after evaporation of pentane was distilled at 40–50°C/10<sup>-2</sup> Torr. Thus, 8.6 g (52%, i.e. 69% per the reacted starting material) of 6-chlorodecaborane of m.p. 31–32°C were isolated. Its IR spectrum was identical with that of an authentic compound (*IIIa*). The fraction insoluble in pentane was extracted with ether and the residue dissolved in methylene chloride. From the solution 6.4 g (24.6%) of the starting material *Ia* separated after dilution with a double amount of ether, which was identified by thin-layer chromatography on silica gel.

b) *With hydrogen bromide*: A solution of 26.5 g (0.183 mol) of compound *Ia* in 250 ml of benzene was saturated with anhydrous HBr for 2 h and the mixture was allowed to stand for 3 h under HBr atmosphere. Benzene was evaporated *in vacuo* and the residue extracted with pentane. The fraction soluble in pentane was dissolved in 250 ml of benzene, saturated with excess hydrogen bromide, and allowed to stand overnight. After evaporation of benzene and extraction of the residue with pentane the oily residue obtained by evaporation of combined pentane extracts was distilled at 90–100°C/10<sup>-2</sup> Torr. A liquid mixture of isomers *IIa* and *IIIb* (total 15.9 g; 72.9%) was obtained which was separated chromatographically on a silica gel column, pre-treated with acetic acid<sup>6</sup>. The mixture contained 86% of compound *IIa* and 14% of compound *IIIb*. The purity of the fractions was checked by thin-layer chromatography on silica gel in benzene-hexane 1 : 5, with addition of 5% of acetic acid (*R<sub>F</sub>* 0.36, 0.52). After chromatography the pure fractions were evaporated to dryness and sublimated at 20°C/10<sup>-1</sup> Torr. 5-Bromodecaborane isolated in this manner had m.p. 48–49°C, 6-bromodecaborane had m.p. 32–34°C. The fractions which remained undissolved after extraction with pentane were extracted with ether and dichloromethane. From the dichloromethane extract 2.8 g (8%) of 5-bromo-6,9-bis(dimethylsulfido)decaborane(12) separated. For B<sub>10</sub>BrH<sub>11</sub>[S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (323.5) calculated: 14.85% C,

7.17% H, 24.70% Br, 33.45% B, 19.82% S; found: 14.58% C, 7.16% H, 24.31% Br, 33.85% B, 19.60% S.

c) *With hydrogen iodide*: A solution of 16.45 g (0.067 mol) of substance *Ia* was saturated at room temperature with hydrogen iodide. After one hour standing hydrogen started to escape from the reaction mixture. After standing overnight crystals separated which were filtered off under suction, washed with benzene, and extracted in a continuous extractor with dichloromethane. From the extract 14.2 g (57%) of 5-iodo-6,9-bis(dimethylsulphido)decaborane(12) separated, m.p. 163–165°C (decomp.). For  $B_{10}H_{11}I[S(CH_3)_2]_2$  (370.5) calculated: 12.97% C, 6.26% H, 29.21% B, 34.26% I, 17.28% S; found: 12.51% C, 6.68% H, 29.32% B, 33.62% I, 16.80% S. The benzene solution after filtration off of the product was evaporated and the residue extracted with pentane. The fraction remaining after evaporation of pentane was sublimated at 60°C/10<sup>-4</sup> Torr on a glass finger cooled at -78°C. Yield 0.7 g (4.2) of crude 5-iododecaborane which contained traces of an impurity, probably the 6-isomer (on thin-layer chromatography on silica gel in benzene-hexane 1 : 5 + 5% acetic acid the spot had  $R_F$  0.5), which was eliminated by double crystallisation from pentane at -40°C and repeated sublimation. The identity with substance *Iib* was confirmed by IR spectroscopy.

#### Reaction of 6,9-Bis(diisopropylsulphido)decaborane(12) with Hydrogen Chloride

A solution of 10.15 g (0.0285 mol) of compound *Ic* in 150 ml of benzene was saturated with anhydrous hydrogen chloride and allowed to stand overnight. After evaporation of benzene and working up as under a) 2.75 g (61.7%) of compound *IIIa* were obtained the identity of which with the authentic sample was proved by IR spectra and thin-layer chromatography.

#### Reaction of 6,9-Bis(dimethylsulphido)decaborane(12) with Hydrogen Halides at Benzene Boiling Point

A solution of 10 g (0.041 mol) of compound *Ia* in 150 ml of benzene was heated to boiling point. Hydrogen halide (approx. 0.4 mol) was then bubbled through the reaction mixture under simultaneous distillation off of the mixture of benzene and the liberated dimethyl sulfide. The amount of the condensate was restituted by dropwise addition of benzene during the reaction. The excess hydrogen halide was led off through a bubbler containing paraffin oil and out of the apparatus. When the reaction was over, the reaction mixture was evaporated to dryness and the residue was extracted with pentane and further purified as in the preceding cases. The mixture of 5- and 6-bromodecaborane was separated by column chromatography according to a procedure described earlier<sup>6</sup>. The reaction with hydrogen chloride gave 55.4% of the 6-isomer. Hydrogen bromide afforded 97.5% of a mixture of 5- and 6-isomer, composed of 45% of the 5-isomer and 55% of the 6-derivative. Hydrogen iodide reacted under formation of 4.5% of 5-iododecaborane containing a trace of the 6-isomer as an impurity. The identification of the pure products was carried out by IR spectroscopy and chromatography.

#### Dimethylsulphidodecaborane(12) (IV)

A solution of 10.3 g (0.084 mol) of decaborane in 50 ml of dimethyl sulfide was heated at 110 to 120°C for 2.5 g in a sealed pressure vessel. After cooling down to room temperature the reaction mixture was evaporated to dryness and the residue was extracted with ether. Insoluble crystals of substance *Ia* were filtered off under suction and washed with the condensate. The ethereal extract was preserved for further work-up. The substance *Ia* obtained (11.4 g) was reheated with 50 ml of dimethyl sulfide at 120°C for 4 h. The reaction mixture was evaporated to dryness

and the residue extracted with ether. The insoluble part (regenerated substance *Ia*) was returned into the reaction with 30 ml of dimethyl sulfide at 120°C for 4 h. After extraction with ether as in the preceding operations all ethereal extracts were combined, evaporated to dryness at 20°C (15 Torr), and the residue extracted with boiling pentane in a continuous extractor. From the pentane extract 6.6 g (43%) of compound *IV* were obtained which was identified by thin-layer chromatography on silica gel in benzene ( $R_F$  0.6), using an authentic sample as standard.

#### Reaction of Dimethylsulfidodecaborane(12) with Hydrogen Halides

A solution of 3.65 g (0.02 ml) of compound *IV* in 50 ml of benzene was saturated with excess hydrogen halide for one hour and then allowed to stand for another hour under a mild overpressure. The volatile components were evaporated and the residue extracted several times with pentane. The crude product obtained by evaporation of pentane was sublimated at 20–60°C/ $10^{-4}$  Torr on a sublimation finger cooled at 0°C. The isolated 6-chlorodecaborane (58.2%) and 5-iododecaborane (61%) were purified by crystallisation from pentane at –50°C and repeated sublimation. The mixture of 5- and 6-bromodecaborane, obtained (70.6%) was separated by column chromatography in the usual manner<sup>6</sup>. It contained 58% of the 5- and 42% of the 6-isomer. The identification of the purified products was carried out by IR spectroscopy and thin-layer chromatography on silica gel.

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