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HYDROGENATION OF 6,9-BIS(DIALKYL SULFIDE)DECABORANE TO THE PARENT DECABORANE

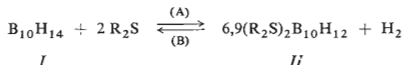
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Hydrogenation of $(R_2S)_2B_{10}H_{12}$ in the presence of BCl_3 , CH_3J , or under heating gives $B_{10}H_{14}$ in 30–68% yields. The product of deuteration is $B_{10}H_{12}D_2$ in which the D-atoms are in positions 5, 6, and μ . Unsatisfactory yields are given by hydrogenation of substituted $X-B_{10}H_{11}(SR_2)_2$ derivatives. The mechanism and the intermediates of the hydrogenation are also discussed.

The isolation of optically active (–)-5-bromo-6,9-bis(dialkyl sulfide)decaborane(12)¹ and the discovery of the reaction enabling the transformation of the anion $B_{10}H_{10}^{2-}$ to bis(diethyl sulfide)decaborane(12)² stimulated interest in the transformation of this ligand derivative to the parent decaborane, *i.e.* in the reversal of the spontaneous reaction of decaborane (*I*) with dialkyl sulfide³. On following the reaction (*A*) at laboratory temperature we observed that the rate of hydrogen evolution does not differ at starting hydrogen pressures from 0 to 100 atp. Therefore the reaction cannot be either inhibited by hydrogen pressure, or, still less, reversed. In agreement with this observation, from the experiment aiming at hydrogenation of 6,9-bis(dimethyl sulfide)decaborane(12) (*II*, $R = CH_3$) at room temperature in benzene, only the starting substance *II* was regenerated.



In a previous paper⁴ we supposed that at room temperature the decisive step for dehydrogenation is the attack of the second Lewis base molecule:



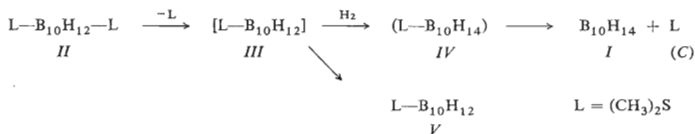
In accordance with this hypothesis we now discovered that the hydrogenation according to equation (*B*) takes place under conditions in which the splitting off of the Lewis base is preferred, *i.e.* in the presence of BCl_3 , CH_3J (binding R_2S in the form of the insoluble salt $R_3S^+J^-$) or at elevated temperature. Best yields (65–68%) were achieved on hydrogenation of pure 6,9-bis(dimethyl sulfide)deca-

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borane(12) in benzene in the presence of boron trichloride which was liberated in the solution after the pressurizing of the autoclave with hydrogen.

Boron trifluoride was an unsuitable Lewis acid, as in its presence almost no splitting off of dimethyl sulfide took place and the starting material was regenerated. Similarly aluminum trichloride is also unsuitable for this hydrogenation because in its presence monoligand derivative is formed predominantly in addition to a small amount of unidentified substances of polymeric character and a trace of decaborane. Very low yields were obtained under optimum conditions (20°C, BCl₃) also when substituted derivatives were hydrogenated, such as 5-X-6,9[(CH₃)₂S]₂ B₁₀H₁₁ (X = CH₃, J).

In a manner similar to hydrogenation, deuteration was also carried out. It gave decaborane which according to ¹¹B NMR and IR spectra is substituted by deuterium in the position 5, 6 and bridge. This fact indicates that the attachment of the deuterium takes place simultaneously on one side of the molecule, probably at the stage of the reactive fragment [L-B₁₀H₁₂] (III) which is formed after the splitting off of the dialkyl sulfide molecule. The fact that the hydrogenation takes place at room temperature only when the reagent is present which facilitates the splitting off of the ligand L, further the presence of a small amount of monoligand derivative V in the reaction mixture, and finally the result of the deuteration, lead to the supposition that hydrogenation takes place in a series of steps (C).



An easy decomposition of the supposed intermediate IV was confirmed by the reaction of the salt NaB₁₀H₁₃S(CH₃)₂ with anhydrous hydrogen chloride in ether, which we may suppose takes place *via* the intermediate IV and which affords decaborane (I) in a 90% yield.

EXPERIMENTAL

Hydrogenation of 6,9-Bis(dimethyl sulfide)decaborane(12) (II, R = CH₃)

a) *In the presence of boron trichloride:* Into a 320 ml autoclave containing 3.50 g (14.3 mmol) of substance II in 100 ml of benzene a glass ampoule containing 3.36 g (28.7 mmol) of boron trichloride was placed and the autoclave was filled with hydrogen under pressure (103 atp.). The ampoule in the autoclave was broken and hydrogenation was carried out at room temperature under vigorous stirring. The main pressure drop was observed in the course of the first 10 min. After 3 h the measured hydrogen consumption was 360 ± 50 ml (calculated value: 320 ml). The reaction mixture was washed five times with water, filtered through a filter wetted with

benzene, and the filtrate was evaporated to dryness. The light yellow viscous residue contained crystals of decaborane. It was sublimated at $70-85^{\circ}\text{C}/10^{-2}$ Torr. Repeated sublimation gave 1.2 g (68%) of decaborane. The sublimation residue contained, according to thin-layer chromatography, decaborane, monodimethyl sulfide decaborane(12) and other unidentified compounds.

b) *Under heating and in the presence of methyl iodide*: Into a solution of 3.5 g (14.3 mmol) of *II* in 100 ml of benzene, placed in a 320 ml autoclave, 8.5 g of methyl iodide (60 mmol) were added and the autoclave closed and filled with hydrogen at 101 atp. It was heated at 80°C under stirring for 16 h. Hydrogenation took place even at 20°C , but one order of magnitude slower. The separated trimethylsulfonium iodide (3.35 g, 57%) was filtered off, the solution concentrated, and decaborane sublimated. On resublimation 0.68 g, i.e. 39%, of decaborane were obtained.

c) *Deuteration at 90°C* : In an autoclave of 320 ml volume, containing 24.4 g (100 mmol) of substance *II* and 150 ml benzene deuterium was introduced under pressure until it rose to 137 atp. After 10 hours shaking at $85-95^{\circ}\text{C}$ the pressure drop was only 12 atp, which corresponded to a deuterium consumption of 30 mmol. From the benzene solution 0.72 g (6%) of $\text{B}_{10}\text{H}_{12}\text{D}_2$ was obtained after evaporation of the reaction mixture, a prolonged extraction with pentane, and sublimation. More than half of the D-atoms are bound in positions 5 and 6 (according to ^{11}B NMR spectra at 80 MHz), and the remaining D-atoms are bound according to IR spectra in bridge position. In accordance with this the IR spectrum (in CCl_4 , spectrometer UR-10, Zeiss, Jena) contained absorption bands (cm^{-1}) at 2585 s (B—H_{term} stretch.), 1931 ms (B—D_{term} stretch.), 1800 ms, sh (B—H—B stretch.), 1380 ms, sh (B—D—B stretch.), and 1150 ms (B—D—B def.).

Reaction of Decaborane with Dimethyl Sulfide

The rate of hydrogen evolution was measured on the basis of the pressure increase during the reaction of 12.2 g of decaborane in 100 ml dimethyl sulfide, placed in a 320 ml vessel provided with a manometer (accuracy of the readings was ± 0.3 atp.). In experiment A the initial hydrogen pressure was 0 atp., in experiment B it was 100 atp.

Time, h	4	8	24	48	72	100
Exp. A, Δ atp H_2	1.4	2.9	8.0	9.4	10.1	10.0
Exp. B, Δ atp H_2	1.7	3.2	8.6	9.5	9.8	9.7

After 100 hours the pressure bottles were opened, dimethyl sulfide distilled off *in vacuo*, and the remaining crystalline residu was purified by repeated extraction with ether which takes all impurities. In experiment A 19.3 g (79%) of compound *II*, and in experiment B 19.0 g (78%) of this compound were obtained.

Regeneration of $\text{B}_{10}\text{H}_{14}$ from $\text{NaB}_{10}\text{H}_{13}\text{S}(\text{CH}_3)_2$

To a suspension of 13.65 g (66 mmol) of $\text{NaB}_{10}\text{H}_{13}\text{S}(\text{CH}_3)_2$ (ref.⁵) in diethyl ether saturated HCl solution in ether (50 ml) was added dropwise over 1 h. After another hour of standing the reaction mixture according to thin-layer chromatography on silica gel contained predominantly decaborane containing traces of substances *II* and *V*. The reaction mixture was filtered and the

separated NaCl was washed with ether. After evaporation of the filtrate to dryness and sublimation of the residue at $80^{\circ}\text{C}/10^{-2}$ Torr decaborane was obtained (7.2 g; 89.5%) which was identified chromatographically.

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