REACTION OF ALLYLAMINE WITH TETRAALKYLDIBORANES

B. M. Mikhailov, V. A. Dorokhov and N. V. Mostovoi

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As is well known, diborane and its derivatives can add to unsaturated compounds and can exchange hydrogen atoms for various groups as a result of the action of nucleophilic agents containing an active hydrogen (alcohols, mercaptans, amines, etc.). It appeared very interesting to study the behavior of tetraalkyldiboranes toward allylamine, a compound containing a double bond and a functional group with an active hydrogen atom.

Investigation disclosed that addition of 1M tetra-n-butyldiborane to a 2M ether solution of allylamine followed by boiling of the reaction mixture results in the evolution of hydrogen and the formation of allylaminodi-nbutylboron (I). A higher boiling substance corresponding to (3-aminopropyl)-di-n-butylboron according to the analytical data is formed together with (I). In the IR spectra of this substance the absorption bands corresponding to the stretching vibration of the NH_2 group are shifted to the longer wavelength region (3292 and 3350 cm⁻¹), as is usually observed in compounds with a coordinate B-N bond. The spectral data in conjunction with the unusual stability to disproportionation for unsymmetrical trialkylboranes allow the assignment of an inner complex structure (II) to (3-aminopropyl)-di-n-butylboron. Thus, the reaction of tetra-n-butyldiborane with allylamine proceeds in accordance with the following scheme:

$$(n-C_{4}H_{9})_{2}BNHCH_{2}CH = CH_{2} + H_{2}$$

$$(n-C_{4}H_{9})_{2}BNHCH_{2}CH = CH_{2} + H_{2}$$

$$(1)$$

$$NH_{2} - CH_{2}$$

$$(n-C_{4}H_{9})_{2}B$$

$$CH_{2} - CH_{2}$$

$$(II)$$

On mixing the reactants in the order indicated above the yield of (3-aminopropyl)-di-n-butylboron is two times smaller than the yield of allylaminodi-n-butylboron (I). Carrying out the reaction in triethylamine without a solvent at 50° leaves this ratio almost unchanged. It was found, however, that on reversing the order of mixing of the reactants, i.e. on adding allylamine to tetra-n-butyldiborane, (3-aminopropyl)-di-n-butylboron (II) is formed predominately (in 65% yield) whereas allylaminodi-n-butylboron is obtained in an insignificant amount.

A similar result is observed on reacting allylamine with tetra-n-propyldiborane. On adding tetra-n-propyldiborane to a solution of allylamine in triethylamine the chief reaction product is allylaminodi-n-propylboron (III) (70% yield); when allylamine is added to an ether solution of tetra-n-propyldiborane (3-aminopropyl)-di-n-propylboron (IV) is obtained predominately (60%).

$$(n \cdot C_3 H_7)_2 BNHCH_2 CH = CH_2 \qquad (1 \cdot C_3 H_7)_2 B \bigvee_{CH_2 - CH_2} CH_2 - CH_2$$
(111)
(111)

We consider as probable the following explanation of the course of the process proceeding predominately in one or the other direction, depending on the order of mixing of the reactants. On adding tetraalkyldiborane to allylamine, i.e. in the presence of an excess of the latter, a complex (V) of dialkylborane with allylamine is formed in the first step of the process, as is generally the case on reacting amines with alkylboranes. Apparently, complex (V) should dissociate on heating with evolution of hydrogen and formation of allylaminodialkylboron

$$\begin{array}{l} \mathrm{R_{2}BH}\cdot\mathrm{NH_{2}CH_{2}CH}=\mathrm{CH_{2}}\rightarrow\mathrm{R_{2}BNHCH_{2}CH}=\mathrm{CH_{2}}+\mathrm{H_{2}}.\\ (\mathrm{V})\end{array}$$

In fact, as our experiments demonstrated, the main volume of hydrogen is evolved only in the process of heating the reaction mixture. From the results of the experiments it follows that the direct hydroboration of allylamine by the tetraalkyldiborane, resulting in the formation of (3-aminopropyl)-dialkylboron, can occur simultaneously but to a smaller extent. On reversing the order of mixing of the reactants, i.e. when the tetraalkyldiborane is present in excess, the latter adds to the complex (V) formed initially and yields compound (VI)

$$\begin{array}{c} R_2BH \cdot NH_2CH_2CH = CH_2 + \frac{1}{2} (R_2BH)_2 \rightarrow R_2BH \cdot NH_2CH_2CH_2CH_2BR_2 \\ (V) \qquad (V1) \end{array}$$

Apparently compound (VI) reacts with the original amine and subsequently splits up into the energetically stable inner complex (3-aminopropyl)-dialkylboron and dialkylborane.

$$R_{2}BH \cdot NH_{3}CH_{4}CH_{4}CH_{4}CH_{2}BR_{3} \xrightarrow{C_{0}H_{5}NH_{2}} R_{2}B \xrightarrow{\swarrow} H_{2}H + R_{2}BH \cdot NH_{3}C_{3}H_{5}.$$

A similar mechanism of formation of (3-aminopropyl)-dialkylboron is also possible in the presence of an excess of allylamine in the reaction mixture, but it would be less likely under these conditions.

Thus, in experiments in which allylamine is added to the tetraalkyldiborane (3-aminopropyl)-dialkylboron is obtained almost exclusively.

The structure of the allylaminodialkylborons synthesized by us is confirmed by IR spectra in which the maximum absorption of the N-H bond occurs at 3410 cm⁻¹ and the absorption maximum of C=C occurs at 1640 cm⁻¹. A counter synthesis similar to the preparation of isobutylaminodi-n-propylboron [1] was also carried out for allylaminodi-n-butylboron from butylmercaptodi-n-butylboron and allylamine. In addition to the N-H absorption band mentioned above, in the IR spectra of (3-aminopropyl)-dialkylborons there is a sharp band in the 1590 cm⁻¹ region corresponding to the deformation vibration of the NH₂ group. (3-Aminopropyl)-dialkylborons are not affected noticeably in the air and are also stable on heating to 200°.

EXPERIMENTAL

All operations were conducted in an argon atmosphere. Tetrabutylborane was prepared from tributylboron and diborane [2].

Allylaminodi-n-Butylboron and (3-Aminopropyl)-di-n-Butylboron. Into a three-necked flask equipped with a stirrer, a reflux condenser and a dropping funnel and connected to a gasometer was placed 23.0 g of allylamine in 70 ml of absolute ether and 50.8 g of tetra-n-butyldiborane was added dropwise with stirring during which evolution of heat took place. The mixture was then boiled for two hours on a water bath. 6500 ml of hydrogen was collected in the gasometer. The following were separated by fractional distillation of the reaction products: 1) Allylaminodi-n-butylboron (37.5 g) (52% yield), m. p. 76-78° (5 mm); n_D^{20} 1,4408; d_4^{20} 0,7886. Found: N 7.62; 7.79%. $C_{11}H_{24}BN$. Calculated: N 7, 74%. The allylaminodi-n-butylboron prepared from butylmercaptodi-n-butylboron and allylamine had an m. p. of 76-79° (5 mm); n_D^{20} 1,4409. 2) (3-Aminopropyl)-di-n-butylboron (20.6 g, 28% yield), m. p. 94-98° (1 mm); n_D^{20} 1,4671; d_4^{20} 0,8396. Found: C 72.72; 72.97; H 14.80; 14.71; B 6.10; 6.35; N 7.33; 7.55%; mol. wt. 172, 179. $C_{10}H_{22}BN$. Calculated: C 72.13; H 14.31; B 5.92; N 7.64%; mol. wt. 183.

Allylamine (7.3 g) was slowly added dropwise with constant stirring to a solution of 16.2 g of tetra-n-butyldiborane in 60 ml of ether cooled in ice water. The reaction mixture was then allowed to warm up to room temperature and was boiled for 30 min. In all, 400 ml of hydrogen was evolved. On fractional distillation 15.2 g (65%) of (3-aminopropyl)-di-n-butylboron with a b.p. of 105-110° (1.5 mm); n_D^{20} 1,4679, as well as a small amount (less than 1 g) of allylaminodi-n-butylboron were obtained. Allylaminodi-n-Propylboron and (3-Aminopropyl)-di-n-Propylboron. Similar to the previous experiment, by the addition of tetra-n-propyldiborane to allylamine in triethylamine allylaminodi-n-propylboron was obtained in 70% yield; m. p. 59-62° (10 mm); n_D^{20} 1,4340; d_4^{20} 0,7787. Found: C 70.72; H 13.06; 12.90; B 6.92; 7.35%. C₉H₂₀BN. Calculated: C 70.61; H 13.17; B 7.07%.

On adding allylamine to tetra-n-propyldiborane (3-aminopropyl)-di-n-propylboron was isolated in 60% yield; m. p. 82-84° (1 mm); n_D^{20} 1,4680; d_4^{20} 0,8367. Found: C 69.78; 69.30; H 14.20; 14.15; B 6.85; 7.04; N 9.07; 9.13%. C₉H₂₂BN. Calculated: C 69.69; H 14.30; B 6.98; N 9.03%.

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SUMMARY

On reacting tetraalkyldiboranes with allylamine, depending on the order of mixing of the reactants, either allylaminodialkylboron or (3-aminopropyl)-dialkylboron, possessing an inner complex structure, was formed predominately.

LITERATURE CITED

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