ON THE ACTION OF AMINES AND AMMONIA ON TRIALLYLBORON

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Triallylboron is highly reactive toward reagents with mobile hydrogen; contrary to trialkylborons [1], it reacts with water, alcohols [2], and mercaptans [3] at room temperature; depending on the nature of the nucleophilic reagent and the ratio of the original substances, one or two allyl radicals are split off, and the corresponding diallyl or monoallyl boron compounds are formed. The increased reactivity of triallylboron is explained by the hypothesis, that the energy of the bonds between the allyl radicals and the boron atom is much lower than that of alkyl-boron bonds, which is based on comparison of the energies of bonds between allyl and alkyls and various other atoms [4]. As we found earlier [2], the reaction of triallylboron with n-butylamine requires a higher temperature than its reactions with water, alcohols, or mercaptans; however, the process goes much more readily than with trialkylborons [3].

In order to find out the effect of the nature of the amines on the ease with which they react with triallylboron, we investigated its transformations on treatment with ethylamine, diethylamine, aniline, and ammonia. In the first stage of the reaction of triallylboron with amines, complex compounds are formed. Thus in the reaction of triallylboron and diethylamine heat is evolved and a complex (1) is formed, which splits off propylene at 100-130°, being converted to diallyl(diethylamino)boron in 93% yield.

$$(C_3H_5)_3 B + (C_2H_5)_2 NH \rightarrow (C_3H_5)_3 B \cdot NH (C_2H_5)_2 \rightarrow (C_3H_5)_2 BN (C_2H_5)_2 + C_3H_6$$

The reaction of triallylboron with ethylamine goes similarly, giving diallyl(ethylamino)boron as a final product. Triallylboron reacts more vigorously with aniline, evolving propylene on mixing of the reagents and being converted to diallyl(phenylamino)boron in 77.5% yield. With ammonia triallylboron forms a complex compound which on distillation gives a moderate yield of diallyl(amino)boron.

 $(C_3H_5)_3 B + NH_3 \rightarrow [(C_3H_5)_3 B \cdot NH_3] \rightarrow (C_3H_5)_2 BNH_2$

EXPERIMENTAL

All operations were carried out in a nitrogen atmosphere.

<u>Diethylamine-triallylboron</u>. To 6.9 g (0.0515 mole) of triallylboron, 4.1 g (0.056 mole) of diethylamine was slowly added dropwise, the mixture being stirred and cooled so that the temperature within the reaction mass was 30-35°. Then the reaction mixture, cooled to 0°, was kept in vacuo (10 mm) for 10 min. There was obtained 10.3 g (96.7%) of the triallylboron-diethylamine complex; d_{40}^{20} 0.8397; n_{20}^{20} D 1.4812. Found: C 74.60; H 12.89; B 4.08%. C₁₃H₂₅BN. Calculated: C 75.37; H 12.65; B 5.22%.

<u>Diallyl(diethylamino)boron</u>. When 8.4 g (0.405 mole) of the triallylboron-diethylamine complex was heated at 100-130°, 0.035 mole of propylene was evolved. The liquid was distilled in vacuo. There was obtained 6.2 g (92.6%) of diallyl(diethylamino)boron, b. p. 69-72° (11 mm). After redistillation diallyl(diethylamino)boron had b. p. 79-80° (20 mm); d^{20}_{4} 0.8025; n^{20} D 1.4562. Found: C 72.98, 72.69; H 12.07, 12.06; B 6.77, 6.7%. C₁₀H₂₀BN. Calculated: C 72.75; H 12.21; B 6.55%. The substance fumed in air and dissolved in organic solvents. Diallyl-(diethylamino)boron could be prepared, without isolating the complex, by adding the amine to the triallylboron and then distilling the reaction mixture.

<u>Diallyl(ethylamino)boron</u>. To 5.7 g (0.042 mole) of triallylboron, 2.7 g (0.059 mole) of ethylamine was added with stirring; the reaction mixture became quite warm, but no gas was evolved. When all the ethylamine had been added, the mixture was heated for 1 hr at 100-110°; in this case 0.035 mole of propylene was obtained.

On distillation 4.9 g (85.2%) of diallyl(ethylamino)boron, b. p. 76-80° (51 mm), was isolated. On redistillation the substance had b. p. 63-64.5° (26 mm); d_{4}^{20} 0.8394; n^{20} D 1.4686; b. p. 14-17°; it fumed in air. Found: C 69.62, 69.63; H 11.55, 11.68; B 8.29, 8.07%. C₈H₁₆BN. Calculated: C 70.11; H 11.77; B 7.90%.

<u>Diallyl(phenylamino)boron.</u> To 9.3 g (0.0696 mole) of triallylboron, 6.5 g (0.0696 mole) of aniline was added dropwise with stirring; the mixture became quite warm. Gas was vigorously evolved even on addition of the first drops of the amine. In this experiment 0.058 mole of propylene was obtained. On distillation of the liquid reaction products 9.9 g (77.4%) of diallyl(phenylamino)boron, b. p. 77-78° (2 mm), was isolated; d^{20}_{4} 0.9215; n^{20} D 1.5342. Found: C 78.09, 78.26; H 8.52, 8.55; B 6.41, 6.16%. C₁₂H₁₆BN. Calculated: C 77.87; H 8.71; B 5.84%.

<u>Diallyl(amino)boron</u>. A current of dry ammonia was passed into triallylboron (8 g, 0.0597 mole) for 30 min, the temperature of the spontaneously-heating reaction mass being kept at about 60° by external water-cooling. On distillation of the solidified reaction mixture there was obtained 3.2 g (49.3%) of diallyl(amino)boron, b. p. 50-62° (18 mm). On redistillation diallyl(amino)boron had b. p. 58-60° (23 mm); d^{20}_4 0.8686; n^{20} D 1.4902. Found: C 66.13, 66.27; H 10.79, 10.99; B 9.93, 9.97%. C₈H₁₂BN. Calculated: C 66.12; H 11.10; B 9.93%. The residue in the distilling flask (1.1 g) was a solid mass.

SUMMARY

On treatment of triallylboron with ammonia or amines, diallyl(amino)boron or N-substituted derivatives thereof are formed.

LITERATURE CITED

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.