ORGANOBORON COMPOUNDS

COMMUNICATION 203. REACTION OF TRIALLYLBORANE WITH PROPYNE*

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Heating of triallylborane with acetylene [1, 2] and with propyne [2] leads to derivatives of 3-borabicyclo[3.3.1]non-6-ene. We have recently discovered three successive stages of the reaction of triallylborane with an alkylacetylene. The first stage consists in the cis addition of triallylborane at the triple bond of the 1-alkyne, which results in the formation of the (2-alkyl-1,4-pentadienyl)diallylborane (I). In the second stage the addition product (I) is cyclized into the 5-alkyl-1,3-diallyl-1,2,3,4-tetrahydroborin (II). The third stage of the process consists in the isomerization of the cyclic compound (II) into the 7-alkyl-3-allyl-3borabicyclo[3.3.1]non-6-ene (III)



This paper is concerned with the study of the intermediate stages of the reaction of triallylborane with propyne.

Unlike acetylene [1, 2], propyne reacts with triallylborane at room temperature. The compound (I) formed in the first stage is converted, slowly at room temperature and more rapidly with gentle heating (40-60°), into the monocyclic compound (II). Therefore, if the reaction products, which consist mainly of (I), are distilled the only substance which can be isolated is 1,3-diallyl-1,2,3,4-tetrahydro-5-methylborin (II); previously [2, 3] we did not observe that this occurred, and we erroneously took the cyclic compound (II) to be the addition product (I). Although we were unable to isolate diallyl(2-methyl-1,4-pentadienyl)-borane (I) in a homogeneous state, its formation was proved fairly reliably. Thus, as a result of the oxidation of the products of the reaction (6 days, 20°) of triallylborane with propyne (without their distillation) by means of hydrogen peroxide in an acid medium we obtained 2-methyl-4-pentenal (IV), which was identified as its 2,4-dinitrophenylhydrazone. We found that with time the yield of the hydrazone diminishes, which must be attributed to the gradual conversion of the linear compound (I) into the cyclic compound (II) at 20°C.



*This article is published in accordance with a resolution of the Conference of Editors-in-Chief of the Journals of the Academy of Sciences of the USSR, held July 12, 1962, as a dissertation paper by S. I. Fro-lov.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No.9, pp.1996-2004, September, 1969. Original article submitted April 4, 1969.

When the undistilled reaction products were treated with methanol we obtained not only 3-allyl-1,2, 3, 4-tetrahydro-1-methoxy-5-methylborin (V), but also dimethyl 2-methyl-1,4-pentadiene-1-boronate (VI) in 10-20% yield. * When oxidized with hydrogen peroxide in an acid medium, the linear compound (VI) also gives 2-methyl-4-pentenal (IV). The formation of an aldehyde in the oxidation of (I) and (VI) indicates that the boron atom in these compounds is linked to a vinyl group B-CH = C [4]. The IR spectrum of (VI) contains a strong absorption band at 1628 cm⁻¹ due to the double bond of B-CH = C and bands characterizing the group $-CH = CH_2$ (915, 997, 1643, 3075 cm⁻¹). The PMR spectrum contains: a signal at 1.77 ppm (= C $-CH_3$); a doublet ($I_{CH_2-CH} = 6.5$ Hz) with its center at 3.04 ppm (= $C-CH_2-C=$); a singlet at 3.48 ppm (B $-OCH_3$); a multiplet in the range 4.65-5.33 ppm (terminal C = CH₂ protons and a singlet from the vinyl proton of B-CH = C at 5.25 ppm); multiplet from a methine proton in the range 5.37-6.11 ppm (-C-CH = C). The integral-intensity ratio for the signals of these groups of protons is 3:2:6:3:1. Some linear derivatives of types (I) and (VI) prepared from monosubstituted acetylenes $(C_4H_9C \equiv CH, C_2H_5OC \equiv CH, and (CH_3)_3Si - C$ \equiv CH) have been described by us previously [5]. 1,3-Diallyl-1,2,3,4-tetrahydro-5-methylborin (II) is more stable thermally than the linear compound (I) and can be obtained in about 70% yield by distilling the reaction products. The structure of (II) was proved by a series of chemical transformations, leading finally to the known 2,4-dimethylheptane (XIII)



In the action of methanol (20-30°) on (II) an exothermic reaction led to the liberation of one molecular proportion of propene and the formation of 3-allyl-1,2,3,4-tetrahydro-1-methoxy-5-methylborin (V); at the same time the compound (VII) was also formed in about 3% yield. The IR spectra of (II) and (V) contain very strong absorption bands due to the double band of B-CH=C [1600 cm⁻¹ in the case of (II) and 1615 cm⁻¹ in the case of (V)], and also bands characterizing the group $-CH = CH_2$ (915, 1000, 1640, 3075 cm⁻¹). The PMR spectrum of (II) contains: a multiplet due to aliphatic protons ($CH_2-CH-CH_2$) in the range 0.22-2.35 ppm, which includes a singlet at 1.88 ppm ($C = C - CH_3$) and a doublet ($I_{CH_2}-CH = 8$ Hz) with its center at 2.02 ppm ($B-CH_2$); a multiplet in the range 4.55-5.15 ppm ($-C = CH_2$); a multiplet due to the methine protons of two allyl groups (-C-CH = C) in the range 5.35-6.28 ppm, which is superimposed on the singlet of the vinyl proton (B-CH=C) in the range 0.13-2.82 ppm, which includes a singlet at 1.88 ppm ($C = C - CH_3$) and a doublet ($I_{CH_2}-CH = 6.5$ Hz) with its center at 1.95 ppm (probably $B-CH_2$); a singlet at 3.6 2 ppm ($B-OCH_3$); a multiplet in the range 4.62-5.15 ppm ($-C = CH_2$); a singlet at 3.6 2 ppm ($B-OCH_3$); a multiplet in the range 4.62-5.15 ppm ($-C = CH_2$); a singlet at 3.6 2 ppm ($B-OCH_3$); a multiplet in the range 0.13-2.82 ppm, which includes a singlet at 1.88 ppm ($C = C - CH_3$) and a doublet ($I_{CH_2}-CH = 6.5$ Hz) with its center at 1.95 ppm (probably $B-CH_2$); a singlet at 3.6 2 ppm ($B-OCH_3$); a multiplet in the range 4.62-5.15 ppm ($-C = CH_2$); and a multiplet due to a methine proton (-C - CH = C) in the range 5.38-6.22 ppm, which is superimposed on the singlet of the vinyl proton (B-CH = C) at 5.52 ppm. The integral-intensity ratios for these groups of protons are: for (II), 12:4:2; for (VI), 10:3:2:2.

Prolonged boiling of (V) with methanol leads to the protolytic cleavage of the B-vinyl bond with formation of dimethyl 2-allyl-4-methyl-4-pentene-1-boronate (VII). (V) is decyclized much more rapidly when it is heated (80°) with a mixture of methanol and acetic acid. In this case the product is a mixture of

^{*} When liquid 1-alkynes are used, the yields of compounds of type (VI) are considerably higher, for the exothermic reaction of these alkynes with triallylborane is easier to control than the reaction with gaseous propyne (in a hydrogenation flask).

the ester (VII) and 2-allyl-4-methyl-4-pentene-1-boronic anhydride trimer (VIII), or only the trimeric anhydride (VIII) if after the cleavage the mixture is left for 1 day at room temperature. The completeness of the protolytic cleavage of the B-vinyl bond in (V) was checked from the disappearance of the absorption band at 1615 cm⁻¹. Under the action of glacial acetic acid the opening of the ring in (V) goes only after prolonged heating (100°); the trimeric anhydride (VIII) and methyl acetate are then formed



As a result of the oxidation of the ester (VII) and the anhydride (VIII) with hydrogen peroxide in an alkaline medium 2-allyl-4-methyl-4-penten-1-ol (IX) was obtained in about 90% yield. The most convenient method for the synthesis of the alcohol (IX) is provided by the oxidation of the crude product of the acid -alcohol cleavage of (V). By the action of p-toluenesulfonyl chloride on the alcohol (IX) in pyridine we obtained the tosylate (X), which without isolation was reduced with lithium tetrahydroaluminate to 2,4-dimethyl-1,6-heptadiene (XI). When hydrogenated over PtO2, the dienic hydrocarbon (XI) absorbs two molecules of hydrogen with formation of 2,4-dimethylheptane (XIII). The physicochemical properties and retention time (GLC) of the hydrocarbon obtained agreed with these properties of the 2,4-dimethylheptane synthesized by Nazarov's method [6]. The formation of 2,4-dimethylheptane (XIII) confirms the structure of the carbon skeleton of the 1-substituted 3-allyl-1,2,3,4-tetrahydro-5-methylborins (II) and (V). Further proof of their structure was obtained as follows. In the hydrogenation of 3-allyl-1,2,3,4-tetrahydro-1-methoxy-5-methylborin (V) over platinum two molecules of hydrogen are absorbed (two double bonds) with formation of 1methoxy-3-methyl-5-propylborinane (XII), which when heated with stearic acid also gives 2,4-dimethylheptane (XIII). The IR and PMR spectra of (VII)-(XI) confirm the proposed structures (see Experimental). At 125-140° 1,3-diallyl-1,2,3,4-tetrahydro-5-methylborin (II) is isomerized quantitatively with liberation of heat into 3-allyl-7-methyl-3-borabicyclo[3.3.1]non-6-ene (III). We prepared the latter previously in 83.5% yield by the reaction of triallylborane with propyne at 130° [2].

As we now have additional data on the structure of the intermediate products, in particular (II), we can improve the accuracy of the mechanism proposed earlier [2] for the reactions of triallylborane with acetylenic compounds. In the first stage of the reaction there occurs the addition of the allyl and diallyl-boryl groups of the triallylborane molecule to the triple bond of the acetylenic compound with formation of a diallyl(2-substituted 1,4-pentadienyl)borane (I). Such addition is probably preceded by the formation of a π -complex. The conversion of the latter into the vinyl compound goes with allyl rearrangement through a six-membered transition state (A):



The ability of (I) to be cyclized into the substituted 1,2,3,4-tetrahydroborin (II) indicates that the allyl group and the boron atom at the double bond in [1] are in cis positions relative to each other, i.e., that the allylboration of the triple bond in acetylene derivatives goes by cis addition. The second stage of the condensation is the cyclization of (I) into (II). This process amounts to the addition of the 3-borylpropene fragment to the terminal double bond of the 1,4-pentadienyl group. It should be noted that, according to our data, triallylborane is able to add at an activated double bond, e.g., in vinyl ethers, with subsequent elimination of 1,4-pentadiene. The third stage of the reaction – the conversion of the monocyclic compound (II) into the bicyclic compound (III) – is explained by the intramolecular addition of the fragment $B - C^2$ to the terminal double bond $C^8 - C^9$. Here the boron atom adds at the terminal carbon atom (C^9), while the carbon atom (C^2) adds at the nonterminal carbon atom C^8 .

It should be noted that, when heated, the methoxy compound (V) does not form a bicyclic compound. According to our results, which will be published shortly, a necessary condition for the conversion of a 3-allyl-1,2,3, 4-tetrahydroborin into a bicyclic compound of the type (III) is the presence of certain substituents on the boron atom in the borin system.

EXPERIMENTAL

All operations with organoboron compounds were conducted in an atmosphere of dry argon. The chromatographic analysis of hydrocarbons was conducted on a Khrom-2 instrument with a 50-m capillary column, stationary phase triethylene glycol dibutyrate; for alcohols Tween 20 was used as stationary phase.

The IR spectra were determined on the undiluted substances with a UR-10 instrument. PMR spectra were determined with an RS-60 [7] or Varian DA-60-IL instrument with hexamethyldisiloxane as internal standard. The chemical shifts given in the text are expressed relative to tetramethylsilane. The integral intensities of signals of groups of protons in the PMR spectra given below correspond to the theoretical values. Propyne was prepared from 1,2-dibromopropane [8] and purified from allene via the sodium derivative [9]. For the preparation of 2,4-dinitrophenylhydrazones (2,4-DNPH) we used a solution of the following composition: 10 g of 2,4-dinitrophenylhydrazine (DNPH), 100 ml of conc. H_2SO_4 , 400 ml of methanol, and 200 ml of water (1 g of DNPH is contained in about 85 ml of the solution).

<u>Reaction of Triallylborane with Propyne.</u> A hydrogenation flask was charged with 56.7 g of triallylborane. Propyne, which passed to the flask from a gas holder under a pressure of about 50 mm of water, was dried by passage over soda-lime and P_2O_5 . The flask was shaken for 6 days at 20°, and in this time 9.5 liters of propyne was absorbed. A 1-ml sample of the reaction product was taken for the preparation of the 2,4-DNPH (see below). After 12 days the reaction mixture was transferred to a distilling flask and dissolved in 160 ml of isopentane; 30 ml of methanol was added dropwise with stirring. When no more propene came off, the mixture was fractionally distilled. We obtained: 1) 4 g (6%) of dimethyl 2-methyl-1,4-pentadiene-1-boronate (VI), bp 61-61.5° (18 mm); n_D^{20} 1.4418; d_4^{20} 0.879. Found: C 62.65; H 10.03; B 7.11%. $C_8H_{15}BO_2$. Calculated: C 62.38; H 9.82; B 7.02%. 2) 44 g (63.5%) of 3-allyl-1,2,3,4-tetrahydro-1-methoxy-5-methylborin (V), bp 93-95° (18 mm). The sample analyzed had bp 91-92° (15 mm); n_D^{20} 1.4722; d_4^{20} 0.889. Found: C 73.22; H 10.65; B 6.36%. $C_{10}H_{17}BO$. Calculated C 73.20; H 10.44; B 6.60%.

(V) and (VI) are colorless mobile liquids, readily soluble in carbon tetrachloride, chloroform, benzene, and other organic solvents; in air they are oxidized and hydrolyzed.

We condensed 18.6 g of propyne in a glass ampoule at -80°, and a solution of 62 g of triallylborane in 160 ml of isopentane which had been cooled to -80° was added. The ampoule was sealed and left for 4 days at 20°. The mixture was then treated with 40 ml of methanol and distilled. We isolated 12 g (17%) of (VI), bp 61-62° (18 mm) and n_D^{20} 1.4415, and 15 g (19%) of the methoxy derivative (V), bp 94.5-95.5° (19 mm); n_D^{20} 1.4719.

<u>2-Methyl-4-pentenal 2,4-Dinitrophenylhydrazone</u>. Oxidation of Reaction Mixture. Methanol (2 ml) was added at -70° to 1 ml of the undistilled product of the reaction (20°, 6 days) of triallylborane with propyne, and at a residual pressure of 2 mm low-boiling substances were distilled off with gradual warming of the contents of the flask to 20°. The residue was cooled (-70°), 80 ml of DNPH solution was added, and then 8 ml of 30% H₂O₂ was added. The mixture was shaken vigorously with gradual warming to room temperature. The precipitate formed was filtered off (0.6 g; mp 97-98°). After chromatography on alumina and crystallization from methanol we obtained 0.4 g of 2-methyl-4-pentenal 2,4-DNPH, mp 99.5-100° ([10] gives mp 98°; [11] gives mp 104-105°). Found: C 51.78; H 4.90%. C₁₂H₁₄N₄O₄. Calculated: C 51.79; H 5.07%.

Oxidation of Dimethyl 2-Methyl-1,4-pentadiene-1-boronate (VI). To a mixture of 0.68 g of (VI) and 90 ml of DNPH solution cooled to -30° we added 2.5 ml of 30% H₂O₂, and with shaking the temperature was gradually raised to 20°. The mixture was stirred for 2 h at room temperature, and then 2-methyl-4-pentenal 2,4-DNPH was filtered off and recrystallized from 100 ml of methanol; we isolated 0.9 g (74%), mp 102-103° (corr.).

<u>1,3-Diallyl-1,2,3,4-tetrahydro-5-methylborin (II)</u>. In the course of 6 days at 20° with shaking in a hydrogenation flask 37.5 g of triallylborane absorbed 6.5 liters of propyne. The reaction mixture was kept at 20° for 2 months. By distillation we isolated 35 g (70%) of (II), bp 54-55° (1 mm); n_D^{20} 1.4879; d_4^{20} 0.844. Found: C 82.91; H 10.99; B 6.17%. C₁₂H₁₉B. Calculated C 82.78; H 11.00; B 6.21%. The allyl derivative (II) is a clear mobile liquid which fumes in air; it is readily soluble in benzene and other solvents.

<u>3-Allyl-1,2,3,4-tetrahydro-1-methoxy-5-methylborin (V)</u>. To a solution of 12 g of (II) 10 ml of methanol was added dropwise. Heat was liberated, and 1.65 liters of propene came off. Distillation gave 9.2 g (90%) of (V), bp 90-91° (14 mm); n_D^{20} 1.4720; d_4^{20} 0.886.

Dimethyl 2-Allyl-4-methyl-4-pentene-1-boronate (VII) and 2-Allyl-4-methyl-4-pentene-1-boronic Anhydride Trimer (VIII). To 31.3 g of (V) we added 77 ml of methanol and 77 ml of glacial acetic acid, and the mixture was boiled (78°) for 3.5 h. Volatile products were removed at a residual pressure of 8 mm, and by distillation we obtained: 1) 14 g (41%) of (VII), bp 81.5-82° (8 mm); n_D^{20} 1.4425; d_4^{20} 0.8742. Found: C 67.50; H 11.08; B 5.34%. C₁₁H₂₁BO₂. Calculated: C 67.37; H 10.80; B 5.51%.

IR spectrum (ν , cm⁻¹): 895, 915, 1000, 1640, 3075 (C = CH₂ and - CH = CH₂). PMR spectrum (δ , ppm): singlet 1.68 (= C-CH₃), singlet 3.48 (-B(OCH₃)₂), complex signal at 0.68 (probably B-CH₂); multiplets: 1.85-2.23 (-CH₂-CH-CH₂-); 4.58-5.15 (-C = CH₂ and C = CH₂); 5.43-6.03 (-CH = C). 2) 11.8 g (41.1%) of the trimer (VIII), bp 155-157° (0.03 mm); n_D²⁰ 1.4737; d₄²⁰ 0.9097. Found: C 72.08; H 10.07; B 7.19%. C₂₇H₄₅B₃ \cdot O₃. Calculated: C 73.05; H 10.08; B 7.21%.

IR spectrum $(\nu, \text{ cm}^{-1})$: 895, 920, 1000, 1640, 3075 (C = CH₂ and -HC = CH₂), 1380 (B-O). PMR spectrum (δ , ppm): signal at 0.82 (B-CH₂), singlet at 1.65 (= C-CH₃), multiplets at 1.35-2.48 (-CH₂-CH-CH₂), 4.58-5.15 (-C = CH₂ and C = CH₂), 5.43-6.03 (-CH = C).

The anhydride (VIII) is a colorless rather viscous liquid, soluble in organic solvents; it is more stable to atmospheric oxygen and mositure than the ester (VII). If a mixture of (V), methanol, and acetic acid is boiled and then left for 1 day at room temperature, only the trimetric anhydride is obtained. The same anhydride is formed also by the action of glacial acetic acid. Heating of a mixture of 19 g of (V) and 28 ml of glacial acetic acid for 8 h at 98° led to the disappearance of the band at 1615 cm⁻¹ in the IR spectrum. Volatile products were vacuum-distilled off (9 g of propyne and excess of acetic acid), and the residue, ac-cording to the IR and PMR spectra, was the trimeric anhydride (VIII).

<u>2-Allyl-4-methyl-4-penten-1-ol (IX)</u>. To 12 g of (VII) we added 60 ml of 20% NaOH. To the white precipitate formed 11 ml of 30% H_2O_2 was added dropwise at 0-5° and the mixture was left overnight. The reaction product was extracted with four 50-ml portions of ether, and the extract was dried over Na₂SO₄. Distillation gave 7.7 g (83.3%) of (IX), bp 48-48.5° (2 mm); n_D^{20} 1.4614; d_4^{20} 0.8684. Found: C 77.20; H 11.30%. $C_9H_{16}O$. Calculated: C 77.09; H 11.50%.

IR spectrum $(\nu, \text{ cm}^{-1})$: 895, 915, 995, 1640, 1825, 3000, 3075 (C = CH₂ and -HC = CH₂), 3360 (OH). PMR spectrum (δ , ppm): singlet 1.68 (= C-CH₃), singlet 2.9 (OH), doublet with its center at 3.46 (I_{CH₂}-CH = 5 Hz) (-CH₂O); multiplets: 1.45-2.25 (-CH₂-CH-CH₂-), 4.54-5.20 (C = CH₂ and -C = CH₂), 5.44-6.07 (-C-CH = C). According to GLC, the alcohol obtained was a homogeneous compound.

Under analogous conditions by the oxidation of 9 g of the anhydride (VIII) we obtained 5.2 g (92%) of the alcohol (IX), bp 88-89° (13 mm); n_D^{20} 1.4613.

A mixture of 18.3 g of (V), 38 ml of methanol, and 38 ml of acetic acid was boiled for 3 h. Low-boiling substances were removed in a vacuum, 80 ml of 20% NaOH was added to the residue, and then at 0-5° 19 ml of 30% H_2O_2 was added. By procedure similar to that described above we isolated 13.9 g (89%) of (IX), bp 86-87.5° (12 mm).

<u>2,4-Dimethyl-1,6-heptadiene (XI)</u>. A solution of 16.4 g of p-toluenesulfonyl chloride in 30 ml of pyridine was added dropwise at 10-15° to a solution of 11.4 g of (IX) in 20 ml of pyridine. The mixture was stirred for 3 h at 20°. The contents of the flask were then poured into a mixture of 150 g of ice and 50 ml of conc. HCl. The precipitated oil was extracted with benzene, and the extract was washed with 2 N HCl, neutralized with sodium carbonate solution, and dried with potassium carbonate. Solvent was vacuum-distilled off, the liquid tosylate (X) then obtained was dissolved in 100 ml of ether, and at -70° a solution of 9 g of LiAlH₄ in 100 ml of ether was added. At room temperature a vigorous reaction occurred. The mixture was boiled for 2 h and then treated with water. The precipitate formed was filtered off and washed with ether. The ethereal solution was dried with K_2CO_3 . As a result of distillation over sodium we isolated 8 g (81%) of the diene (XI), bp 65-65.5° (71 mm); n_D^{20} 1.4300; d_4^{20} 0.7501. Found: C 87.08; H 12.90%.

IR spectrum $(\nu, \text{ cm}^{-1})$: 895, 915, 996, 1645, 3075 (-HC = CH₂ and C = CH₂). PMR spectrum (δ , ppm): singlet 1.66 (= C-CH₃), doublet (I_{CH₃-CH} = 6 Hz) with its center at 0.83 (C-CH₃); multiplets: 1.35-2.31 (-CH₂-CH-CH₂-), 4.44-5.22 (C = CH₂ and -C = CH₂), and 5.38-6.12 (C-CH = C).

<u>1-Methoxy-3-methyl-5-propylborinane (XII)</u>. In the hydrogenation of 8.9 g of (V) dissolved in 20 ml of hexane over platinum black (0.15 g) for 5 h 2.47 liters of hydrogen was absorbed. After filtration and removal of solvent the residue was distilled. We obtained 8.44 g (94%) of (XII), bp 69;69.5 (4 mm); n_D^{20} 1.4430; d_4^{20} 0.8532. Found: C 71.33; H 12.60; B 6.40%. C₁₀H₂₁BO. Calculated: C 71.45; H 12.59; B 6.44%.

The compound (XII) is more sensitive to atmospheric oxygen than its unhydrogenated analog (catches fire in air).

<u>2,4-Dimethylheptane (XIII).</u> Hydrogenation of 2,4-Dimethyl-1,6-heptadiene (XI). A mixture of 4 g of (XI), 0.1 g of PtO₂, and 15 ml of glacial acetic acid was shaken with hydrogen in a hydrogenation flask, and 1.4 liters of hydrogen was absorbed. After the neutralization of acid with 20% NaOH, the hydrocarbon was extracted with ether. The extract was dried with Na₂SO₄. By distillation over sodium we isolated 3.72 g (91%) of (XIII), bp 64.5-65° (74 mm); n_D^{20} 1.4022; d_4^{20} 0.7131 ([6] gives: n_D^{20} 1.4021; d_4^{20} 0.7130). Found: C 84.43; H 15.49%. C₉H₂₀. Calculated: C 84.28; H 15.72%. According to GLC (XIII) was free from impurity; the retention time of the compound obtained was the same as that of 2,4-dimethylheptane synthesized as described in [6].

<u>Cleavage of (XII) with Stearic Acid.</u> A Favorskii flask was charged with 6.7 g of (XII) and 34 g of stearic acid. The mixture was heated (bath temperature 290-350°), and 4.5 g of crude hydrocarbon, bp 129-130°, distilled off. The hydrocarbon was washed with 20% NaOH and water and then distilled over sodium. We isolated 4 g (80%) of (XIII), bp 130-130.5° (748 mm); n_D^{20} 1.4040; d_4^{20} 0.7175. According to GLC the substance contained about 0.5% of unidentified impurity.

<u>Thermal Isomerization of 1,3-Diallyl-1,2,3,4-tetrahydro-5-methylborin (II) into 3-Allyl-7-methyl-3-borabicyclo[3,3,1]non-6-ene (III)</u>. The compound (II) (16 g) was heated to 135°, after which the temperature rose spontaneously to 150°; it was then kept at 140° for 4 h (the product had n_D^{20} 1,4930). Distillation gave 14.1 g (88%) of (III), bp 97-98° (12 mm); n_D^{20} 1,4930. The compound (III) was prepared by us previously, and it then had bp 88-89° (10 mm); n_D^{20} 1,4930.

We thank V. G. Kiselev for constant assistance in the chromatographic investigations and V. S. Bogdanov and I. P. Yakovlev for valuable advice in the examination of the spectral data.

CONCLUSIONS

1. It was shown that there are three successive stages in the reaction of triallylborane with a 1-alkyne: a) the addition of triallylborane at the triple bond of the alkyne with formation of a (2-alkyl-1,4-pentadienyl)diallylborane; b) the cyclization of the (2-alkyl-1,4-pentadienyl)diallylborane into a 5-alkyl-1,3-diallyl-1,2, 3,4-tetrahydroborin; c) the thermal isomerization of the 5-alkyl-1,3-diallyl-1,2,3,4-tetrahydroborin into a 7-alkyl-3-allyl-3-borabicyclo[3.3.1]non-6-ene.

2. Some chemical properties of the intermediate reaction products were investigated.

LITERATURE CITED

- 1. B. M. Mikhailov and Yu. N. Bubnov, Izv. Akad. Nauk SSSR, Ser. Khim., 1310 (1965).
- 2. B. M. Mikhailov, Yu. N. Bubnov, and S. I. Frolov, Izv. Akad. Nauk SSSR, Ser. Khim., 2290 (1967).
- 3. V. S. Bogdanov, Yu. N. Bubnov, S. I. Frolov, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 307 (1968).
- 4. M. F. Hawthorne, J. Am. Chem. Soc., 83, 2541 (1961).
- 5. B. M. Mikhailov, Yu. N. Bubnov, S. A. Korobeinikova, and S. I. Frolov, Izv. Akad. Nauk SSSR, Ser. Khim., 1923 (1968).
- 6. I. N. Nazarov and A. I. Kakhniashvili, in: Collection of Papers on Organic Chemistry [in Russian], Vol.2 (1953), p.925.
- 7. A. N. Lyubimov, A. F. Varenik, and A. V. Kesseinikh, Zh. Strukt. Khim., 7, 694 (1966).
- 8. J. E. Douglas and B. S. Rabinovitch, J. Am. Chem. Soc., 74, 2486 (1952).
- 9. C. D. Hurd, R. N. Meinert, and L. U. Spence, J. Am. Chem. Soc., 52, 1138 (1930).
- 10. A. T. Babayan, M. G. Indzhikyan, and L. R. Tumanyan, Dokl. Akad. Nauk ArmSSR, 36, 95 (1965).
- 11. F. Weiss, A. Lantz, and A. Isard, Bull. Soc. Chim. France, (11), 3215 (1965).