ORGANOBORON COMPOUNDS COMMUNICATION 199. ALKOXYACETYLENES IN THE ALLYLBORON – ACETYLENE CONDENSATION*

S. A. Korobeinikova, Yu. N. Bubnov, and B. M. Mikhailov

The reaction of alkoxyacetylenes with triallylboranes in a 1:1 ratio at -50-20 °C leads to diallyl-(2alkoxypenta-1,4-dien-1-yl)boranes (I) in which the boron atom and the allyl group are located in a cis position at the double bond [1]. Compounds of type (I) cyclize into 3-substituted 1,5-diallyl-1-bora-2-cyclohexenes (II) [2], which in their turn are transformed upon heating into 7-substituted 3-allyl-3-boracyclo-[3.3.1]non-6-enes (III). This work is devoted to the study of cyclization of alkoxy derivatives of type (I) into 1-bora-2-cyclohexene derivatives (II) and was carried out in parallel with the investigation of condensation of triallylborane with alkylacetylenes [3]. It was found that the linear compounds, diallyl-(2-alkoxypenta-1,4-dien-1-yl)boranes (I), are thermally more stable than the corresponding 2-alkyl derivatives [3], and in contrast to them, are transformed into 3-alkoxy-1,5-diallyl-1-bora-2-cyclohexenes (II) only upon heating (120-130°C), i.e., under conditions where the condensation of triallylborane with acetylene and alkylacetylenes leads to bicyclic compounds [4]. In the case of alkoxy derivatives the further transformation (II) \rightarrow (III) is only accomplished at a still higher temperature (170-180°C). The preparation of compounds of type (II)



can be carried out by both heating the 1,4-pentadienyl derivative (I) and without its preliminary isolation. In the latter case 1 mole of the alkoxyacetylene is added initially at -50 to -30 °C to a solution of triallylborane in an inert solvent (isopentane). After removal of the solvent the residue is heated for 3-3.5 h at 120-130 °C, during which the yield of (II) reaches 80%. In certain experiments the cyclohexene compound (II) obtained in this way contains 5-10% of the bicyclic derivative (III) from NMR spectroscopic data. The structure of the 3-alkoxy-1,5-diallyl-1-bora-2-cyclohexene (II) was demonstrated by a series of chemical transformations presented above and also confirmed by spectral methods. Two types of double bonds are present in the cyclic compounds (II); a terminal allyl and a cyclic vinylboron. Their IR spectra contain intense absorption bands at 1569 (R = C₂H₅) and 1573 cm⁻¹ (R = CH₃) due to the double bond of the B - CH \sim OR

 \approx C fragment, and also absorption bands characterizing the terminal double bonds (1638, 3075 cm⁻¹).

* The paper is published on the basis of the decision of the Conference of the Chief Editors of Journals of the Academy of Sciences of the USSR of July 12, 1962, as the dissertation work of S. A. Korobeinikova.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No.10, pp.2212-2219, October, 1969. Original article submitted April 24, 1969.

©1970 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.



The PMR spectra of these compounds also confirm their structure. For example, the spectrum of (II, R = C_2H_5) contains: a multiplet of the aliphatic protons at 0.95-2.25 ppm with an expressed triplet centered at 1.22 ppm (O - C - CH₃) and a doublet (J = 8 Hz) centered at 1.95 ppm (-O - C - CH₂ and -B - CH₂); a quartet centered at 3.68 ppm (C - CH₂O); a multiplet at 4.45-5.08 ppm (C = CH₂) with an expressed singlet at 4.95 ppm (vinyl proton B - CH = C) and a multiplet at 5.25-6.20 ppm (-CH = C), with relative integral intensities of 12:2:5:2.

Only the terminal double bonds of the 1-boracyclohexene compounds (II) are hydrogenated on catalysts of the platinum group (the vinyl bond $\supset B - CH = C$ is not affected); during this 2 moles of H₂ are absorbed and 3-alkoxy-1,5-di-n-propyl-1-bora-2-cyclohexenes (IV) are obtained. Heating (2 h) the cyclohexene compound (II) with methanol leads to dimethoxy-(4-alkoxy-2-allylpent-4-en-1-yl)borane (V, R = C₂H₅), which is formed as a result of protolytic cleavage of the B – vinyl and B – allyl bonds. The reaction is accompanied by liberation of 1 mole of propylene, which indicates the presence in the compound of one allyl group on the boron atom. The 1-boracyclohexene system of compound (II) is also cleaved upon heating with ethylene glycol. Here 2-(4',4'-ethylenedioxo-2'-allyl-1'-pentyl)-1,3,2-dioxaborolane (VIII) is formed via the step (VI) \rightarrow (VII). Although the B – C bond in allyl boron compounds is cleaved very easily by alcohols [5], we unexpectedly observed in the study of alcoholysis of compounds (II) by IR spectroscopy that upon reaction with alcohols the B – vinyl bond is cleaved first, followed by the B-allyl bond. The competing cleavages of these two types of B – C bonds can be judged, on one hand, from the disappearance in the IR spectrum of the intense absorption band in the 1570 cm⁻¹ region due to the double bond of the fragment B – CH = C OR and the appearance of an absorption band at 1653 cm⁻¹ corresponding to the CH₂ = C , and, on the

other hand, from liberation of propylene. It was found that the B – vinyl bond is cleaved quite rapidly [with formation of asymmetric compounds of type (VI)] upon addition of alcohol or glycol to (II), and propylene is liberated only upon heating. The fact that upon heating (II) with ethylene glycol the 1,3,2-dioxaborolane system [compound (VII)] is formed at 20-100°C and the alkoxyvinyl group of (VII) is transformed into the ketal group of (VIII) at 100-180°C also deserves attention. Since it is known that organic ketals are stable in neutral and basic media and give ketones in the presence of acids [6], we subsequently used these properties.

Upon hydrogenation of (VIII) over Pt-black in hexane 1 mole of hydrogen is absorbed and 2-(4',4'-ethylenedioxy-2'-propyl-1'-pentyl)-1,3,2-dioxaborolane (IX) is formed. Oxidation of dioxaborolane (VII) with H₂O₂ in basic medium leads to 4,4-ethylenedioxy-2-allyl-1-pentanol (X), the ketal group of which is removed by reaction with 0.3 N phosphoric or 7% hydrochloric acid. The formed 4-ketoalcohol (XI) was hydrogenated (Pt-black, 1 mole of H₂ absorbed) into 4-oxo-2-n-propyl-1-pentanol (XII). The latter was

oxidized with CrO_3 in CH_3CO_2H to the known 2-n-propyllevulinic acid (XIII), identified in the individual state and as the semicarbazone, phenylhydrazone, and 2,4-dinitrophenylhydrazone.

The 4-hydroxyketal (XIV) was synthesized by oxidation $(H_2O_2 \text{ in basic medium})$ of the saturated organoboron ketal (IX). Hydrogenation of the unsaturated alcohol (X) with absorption of 1 mole of hydrogen also gives (XIV). In acid media compound (XIV) gives the ketoalcohol (XII), from which 2-propyllevulinic acid (XII) was also obtained by oxidation. Reduction of 4-oxo-2-n-propyl-1-pentanol (XII) with LiAlH₄ leads to diol (XV), the bis-tosylate of which (XVI) gives 4-methylheptane (XVII) upon boiling with LiAlH₄ in ether



The described series of transformations leading to the known 2-n-propyllevulinic acid (XIII) and 4methylheptane (XVII) is chemical evidence for the structure of the 3-alkoxy-1,5-diallyl-1-bora-1-cyclohexenes (II). IR and PMR spectra of compounds (IV)-(XV) confirm the presented structures and are partially presented in the experimental section.

To supplement the above, we carried out certain other reactions with the compounds obtained in the transformations (II) \rightarrow (XIII). As do other 4-ketoalcohols [7], 4-oxo-2-allyl-1-pentanol (XI) and its cyclic ketal (X) give the dihydrofuran derivative, 2-methyl-4-allyl-4,5-dihydrofuran (XVIII), upon heating (180-195°C) in the presence of a catalytic amount of phosphoric acid. The IR spectrum of (XVIII) contains absorption bands of the terminal double bond (1642, 3077 cm⁻¹) and an intense band at 1673 cm⁻¹, characteristic for analogous 2-methyl-4,5-dihydrofuran derivatives [8]. The PMR spectrum of (XVIII) is extraordinarily complex and confirms its structure



2-Allyl-1,4-pentanediol (XIX) was obtained from ketoalcohol (XI) by reaction with lithium aluminum hydride.

Earlier [3] we discussed the mechanism of transformation of the linear compound (I) into the cyclohexene derivative (II), which consisted of addition of the B – allyl fragment to the terminal double bond of the 1,4-pentadienyl system of (I). The more severe conditions necessary for the cyclization (I) \rightarrow (II) in the case of alkoxyacetylene derivatives in comparison with alkylacetylene derivatives are probably due to complex formation of the ether oxygen with the boron atom. The latter hinders formation of a π -complex between the terminal double bond of the 1,4-pentadienyl system and the boron atom, which precedes addition to it of the B – allyl fragment.

EXPERIMENTAL

All operations with organoboron compounds were carried out under an atmosphere of dry argon.

Alkoxyacetylenes were obtained from the corresponding vinyl ethers by the method of Nazarov, Krasnaya, and Vinogradov [9].

IR spectra were taken on a UR-10 instrument, and PMR spectra were taken on a Varian DA-60-IL or a RS-60 [10] instrument; hexamethyldisiloxane was used as internal standard; the scale of the spectra is presented relative to tetramethylsilane. Integral intensities of signals of groups of protons in the PMR spectra presented below correspond to the theoretical.

<u>3-Methoxy-1,5-diallyl-1-bora-2-cyclohexene (II, R = CH₃)</u>. In a three-necked flask fitted with a cold-finger condenser, thermometer, magnetic stirrer, and gas inlet was placed a solution of 25.3 g of triallyl-borane in 40 ml of isopentane. At a temperature of -50° C- -70° C to the flask was added over 2 h 10.3 g of methoxyacetylene, after which the mixture was gradually warmed to room temperature and the solvent was

distilled. The residue was heated for 3.5 h at 120-125°C. Fractional distillation yielded 19.9 g (56%) of (II) (R = CH₃) having bp 72-73°C (3 mm); n_D^{20} 1.4932; d_4^{20} 0.8989. Found: C 75.64; H 10.07; B 5.72%. C₁₂H₁₉ ·BO. Calculated: C 75.82; H 10.07; B 5.69%.

PMR spectrum (δ , ppm): multiplet in the 0.28-2.71 region with an expressed doublet (J = 7 Hz) centered at 2.05 (-O - C - CH₂ and B - CH₂); singlet at 3.48 ppm (-O - CH₃); singlet at 4.93 (B - CH = C); multiplets in the regions 4.32-5.12 (-C = CH₂) and 5.25-6.25 (-CH = C).

 $\frac{3-\text{Ethoxy-1,5-di-n-propyl-1-bora-2-cyclohexene (IV, R = C_2H_5)}{\text{placed 8.1 g of (II) (R = C_2H_5), 0.1 g of technical Pt-black, and 10 ml of hexane. Over 3 h was absorbed 1.98 liters of hydrogen, after which absorption of hydrogen stopped. We obtained 7.5 g (91.5%) of (IV) (R = C_2H_5) having bp 84-85.5°C (2 mm); n_D^{20} 1.4694, d_4^{20} 0.8901. Found: C 75.13; H 12.24; B 5.19%. C_{13}H_{25}BO. Calculated: C 75.01; H 12.20; B 5.19%.$

PMR spectrum (δ , ppm): multiplet of aliphatic protons at 0-1.40 with an expressed triplet centered at 0.90 (OC - CH₃); quartet centered at 3.81 ppm (O - CH₂C); singlet at 4.98 (B - CH = C).

 $\begin{array}{l} \underline{\text{Dimethoxy-(4-ethoxy-2-allylpent-4-en-1-yl)borane.}} \quad (V, \ R=C_2H_5). \ \text{To 3.9 g of compound (II) (R} \\ = C_2H_5) \ \text{at room temperature was added 3 ml of methanol; during this 80 ml of propylene was liberated.} \\ \hline \text{Boiling the mixture for 2 h led to liberation of 1 mole (430 ml) of gas.} \ \text{Distillation of the liquid reaction} \\ \hline \text{products yielded 2.2 g (51\%) of compound (V) (R = C_2H_5) with bp 90-92°C (4.5 mm); n_D^{20} 1.4498; d_4^{20} 0.9217.} \\ \hline \text{Found: C 63.65; H 10.38; B 5.12\%.} \ C_{12}H_{23}BO_3. \ \text{Calculated: C 63.74; H 10.25; B 4.79\%.} \end{array}$

 $\frac{2-(4'-\text{Methoxy}-2'-\text{allylpent}-4'-\text{en-1'-yl})-1,3,2-\text{dioxaborolane (VII, R = CH_3)}{\text{At 70-80°C was carefully added 2.5 ml of ethylene glycol, during which 966 ml of propylene was liberated.} Distillation in vacuum of the liquid reaction products isolated 7.0 g (77.3%) of compound (VII) (R = CH_3) having bp 79-80.5°C (2 mm); <math>n_D^{20}$ 1.4651; d_4^{20} 0.9892. Found: C 62.85; H 9.06; B 4.87%. C₁₁H₁₉BO₃. Calculated: C 62.89; H 9.12; B 5.15%.

IR spectrum (ν , cm⁻¹): intense absorption in the region 1180-1420 $\begin{pmatrix} -B \\ 0 \end{pmatrix}$; 1610; 1658 $\begin{pmatrix} \text{double bond} \\ -C = C \\ \end{pmatrix}$; 1641 (double bond C = CH₂); 3073, 3115 $\begin{pmatrix} = C \\ H \\ \end{pmatrix}$.

 $\frac{2-(4^{\prime},4^{\prime}-\text{Ethylenedioxy}-2^{\prime}-\text{allyl}-1^{\prime}-\text{pentyl})-1,3,2-\text{dioxaborolane (VIII)}.$ To 22.3 g of (II) (R = C₂H₅) at 70-80 °C in small portions was added 13.1 g of ethylene glycol during which 2.45 liters of propylene was liberated. The residue was heated over 1.5 h (170-180 °C) in a vacuum of 135 mm with simultaneous distillation of ethanol; 6.5 ml of ethanol was distilled. Distillation of the residue yielded 19.83 g (75:5%) of (VIII) having bp 87-88° (1.5 mm); n_D^{20} 1.4641; d_4^{20} 1.0319. Found C 59.98; H 8.90; B 4.39%. C₁₂H₂₁BO₄. Calculated:

C 60.02; H 8.82; B 4.51%. PMR spectrum (δ , ppm): singlet at 3.73 $\begin{pmatrix} CH_2 - 0 \\ CH_2 - 0 \end{pmatrix}$; singlet at 3.97 $\begin{pmatrix} CH_2 - 0 \\ CH_2 - 0 \end{pmatrix}$;

multiplets in the regions 4.60-5.05 ($-C = CH_2$); 5.27-5.88 (-CH = C), and 0.68-2.20 (remaining aliphatic protons) with an expressed singlet at 1.22 ppm $\begin{pmatrix} CH_3 - C \end{pmatrix}$.

PMR spectrum (δ , ppm): singlet at 1.25 $\begin{pmatrix} CH_{3}-C \\ \end{pmatrix}$ superimposed on the complex spectrum of the

aliphatic protons in the region 0.42-2.05; singlet at 3.72 $\begin{pmatrix} CH_2 \rightarrow 0 \\ CH_2 \rightarrow 0 \end{pmatrix}$; singlet at 3.98 $\begin{pmatrix} CH_2 \rightarrow 0 \\ CH_2 \rightarrow 0 \end{pmatrix}$

4,4-Ethylenedioxy-2-allyl-1-n-pentanol (X). To a mixture of 14.5 of compound (VIII) and 24 ml of 10% NaOH at 0-5°C was added 12 ml of 30% H₂O₂. After stirring for 4 h at room temperature the oxidation products were extracted three times with benzene (in 40-ml portions). The solvent was distilled and the residue was distilled in vacuum. We obtained 10.6 g (94.2%) of (X) having bp 98-99°C (3 mm); n_D²⁰ 1.4661; d₄²⁰ 1.0559. Found: C 64.50; H 10.01%. C₁₀H₁₈O₃. Calculated: C 64.49; H 9.74%.

PMR spectrum (δ , ppm); doublet (J = 5 Hz) centered at 3.45 (-CH₂ - O -); singlet at 3.68 (- O - H);

singlet at $3.92\left(\int_{CH_{-0}}^{CH_{-0}}C\right)$; multiplets in the regions 4.78-5.25 (C = CH₂), 5.42-6.15 (- C = C), and 1.1-2.37

(aliphatic protons) with an expressed singlet at 1.28 $\begin{pmatrix} CH_3 - C \end{pmatrix}$.

4,4-Ethylenedioxy-2-propyl-1-n-pentanol (XIV). In a long-necked hydrogenation flask were placed 15.3 g of (X), 0.15 g of Pt-black, and 25 ml of n-hexane. In 3 h 1.85 liters of H₂ was absorbed. Distillation yielded 13.6 g (88.5%) of compound (XIV), bp 77-78°C (2 mm); n_D^{20} 1.4528; d_4^{20} 1.007. Found: C 64.23; H 10.84%. C₁₀H₂₀O₃. Calculated: C 63.80; H 10.71%.

4-Oxo-2-allyl-1-n-pentanol (XI). A mixture of 6.5 g of alcohol (X) and 30 ml of 0.3 N phosphoric acid was stirred for 8 h at 30-40°C. The ether extract was dried with K₂CO₃. Distillation isolated 3.7 g of (XI) having bp 64-66°C (2 mm); n_D²⁰ 1.4573. Found: C 67.68; H 9.98%. C₈H₁₄O₂. Calculated: C 67.52; H 9.92%.

Intense absorption bands at 1715 (>C = O), 1641 (C = C), and a broad band at 3460 cm⁻¹ (OH) are present in the IR spectrum of (XI).

To 20.4 g of (II), ($R = C_2H_5$) was added at 20-30°C 9 ml of methanol (strong evolution of heat observed) and then 50 ml of 10% NaOH (propylene is liberated). At 0-5 $^\circ C$ was added 17 ml of 30% H_2O_2 and the mixture was left overnight. The next day the mixture was saturated with K2CO3 and extracted with ether. After distillation in vacuum of the ether and obtained allyl alcohol to the residue was added 70 ml of 10% HCl and the mixture was heated for 1 h at 70 °C. The mixture was neutralized, saturated with K_2CO_3 , and extracted with ether; the ether was dried over K₂CO₃. Distillation yielded 7 g of ketoalcohol (XI) having bp 103-105℃ $(8 \text{ mm}); n_D^{20} 1.4578.$

2-Propyllevulinic Acid (XIII). Upon hydrogenation of 2.84 g of (XI) in 20 ml of n-hexane in the presence of 0.1 g of Pt-black 480 ml of hydrogen was absorbed in 3 h. After filtration the n-hexane was distilled. The IR spectrum of the residue contained the following: an intense band at 1715 cm^{-1} (C = O) and a broad band at 3460 cm⁻¹ (OH group). The residue (2.7 g) of crude (XII) was dissolved in 100 ml of 70% CH₃COOH and with stirring and cooling (10°C) was added 12 g of CrO₃; heating up of the mixture was observed. The mixture was stirred for 1 h at 10°C and then left overnight. The next day the mixture was evaporated in vacuum to a volume of ~50 ml and diluted with water to 300 ml. The mixture was extracted with ether and dried over Na₂SO₄. We isolated 1.75 g of (XIII) having bp 134-137°C (5 mm); after a repeated distillation the material had bp 110-111°C (1.5 mm); n_D²⁰ 1.4439 (data of [11]: bp 162-163°C (15 mm), [12]: bp 165°C (20 mm)).

From 0.2 g of acid (XIII) was obtained 0.3 g of the 2,4-dinitrophenylhydrazone, which after crystallization from a mixture of benzene – hexane (1:3) had mp 173-173.5℃ (data of [12]: mp 174℃). Found: C 49.81; H 5.47%. C₁₄H₁₈N₄O₆. Calculated: C 49.70; H 5.36%.

The phenylhydrazone of acid (XIII) had mp 124-126°C (data of [13]: mp 126-128°C). From 0.29 g of acid (XIII), 0.21 g of semicarbazide hydrochloride, and 0.5 g of CH₃COONa in 2 ml of ethanol was obtained the semicarbazone, which was crystallized from ethanol, mp 161-161.3°C (data of [11]: mp 165°C). Found: C 50.46; H 7.90%. $C_{9}H_{17}N_{3}O_{3}$. Calculated: C 50.22; H 96%.

<u>2-Propyl-1,4-pentanediol (XV)</u>. Upon hydrogenation in a long-necked hydrogenation flask of a solution of 10.7 g of compound (VIII) in 21 ml of hexane in the presence of 0.1 g of Pt-black 1 liter (100%) of H₂ was absorbed. To the residue obtained after filtration and distillation of hexane was added 30 ml of 7% NaOH and then at 0-5°C 12 ml of 30% H₂O₂. The next day the mixture was heated to 60°C and after cooling extracted with ether. The ether was distilled in vacuum and the residue was heated for 20 min at 60°C with 30 ml of 7% HCl. The acid was neutralized and the solution was saturated with K₂CO₃ and extracted with ether. The ether extract was concentrated in vacuum to approximately 15 ml and to the solution was added 5 g of LiAlH₄ in 50 ml of ether. The mixture was boiled for 1 h and after normal decomposition (water and H₂SO₄ solution) extraction with ether yielded 4.01 g of 2- propyl-1,4-pentanediol (XV) having bp 105-107°C (2 mm); n_D^{20.5} 1.450°d. From 3.6 g of diol (XV) by the usual method (in pyridine) was obtained the bis-tosylate (XVI), which after crystallization from 200 ml of methanol had mp 93.5-94.5°C. Found: C 58.44; H 6.66; S 13.81%. C₂₂H₃₀O₆S₂. Calculated: C 58.12; H 6.65; S 14.11%.

<u>2-Allylpentanediol (XIX)</u>. Analogously to that described from 7.11 g of (X) (after hydrolysis and reduction with LiAlH₄) was obtained 3.65 g of diol (XIX) having bp 96-97°C (3 mm); n_D^{20} 1.4641. Found: C 67.11; H 11.20%. C₈H₁₆O₂. Calculated: C 66.63; H 11.19%. From 3 g of diol (XIX) was obtained (after crystallization from methanol) 3.65 g of the bis-tosylate having mp 78.5-79.1°C. Found: C 58.14; H 6.32%. C₂₂H₂₈O₆S₂. Calculated: C 58.38; H 6.24%.

<u>4-Methylheptane (XVII)</u>. A solution of 3.4 g of bis-tosylate (XVI) and 2 g of LiAlH₄ in 50 ml of ether was boiled for 7 h. The mixture was decomposed with 8 ml of water and after filtration the ether solution was dried over Na_2SO_4 . We obtained 0.5 g of 4-methylheptane (XVII) having bp 115-118°C, which had retention time (GLC) equal to that of an authentic sample kindly submitted by O. V. Bragin.

<u>2-Methyl-4-allyl-4,5-dihydrofuran (XVIII)</u>. The reaction was carried out by the method of Norman [7] in a slightly simplified apparatus. A mixture of 3.4 g of compound (X) and 0.04 ml of a 0.3 N solution of H_3PO_4 was heated in a Favorskii flask. At a temperature of ~190°C dehydration of the alcohol began. We isolated 1.67 g of a fraction having bp 144-157°C; the vat temperature at the end of the reaction increased to 199°C. The distillate was dried over K_2CO_3 and distilled. We obtained 1.50 g (75%) of (XVIII) having bp 47-48°C (19 mm); n_D^{20} 1.4566; d_4^{20} 0.8975. Found: C 77.06; H 9.62%. $C_8H_{22}O$. Calculated: C 77.37; H 9.74%.

PMR spectrum (δ , ppm): singlet at 1.62 (CH₃ - $\overset{[]}{C}$ - O); triplet (two doublets with equal constants)

centered at 2.05 (C - CH₂ - C =); a multiplet of the cyclic proton $\begin{pmatrix} -0 - C - CH \\ C \end{pmatrix}$ centered at 2.95; the AB

portion of the ABX spectrum of $(O - CH_2 -)$ at $\delta_A = 4.00$ and $\delta_B = 4.12$; a broadened singlet at 4.48 (cyclic proton $C = C \swarrow^N$); multiplets of the allyl protons in the regions 4.72-5.15 and 5.32-6.05.

CONCLUSIONS

1. Diallyl-(2-alkoxypenta-1,4-dien-1-yl)boranes, obtained by reaction of alkoxyacetylenes and triallylborane, cyclize upon heating to 3-alkoxy-1,5-diallyl-1-bora-2-cyclohexenes.

2. 3-Alkoxy-1,5-diallyl-1-bora-2-cyclohexenes were used as starting materials for synthesis of substituted 4-ketoalcohols, 1,4-diols, dihydrofuran derivatives, hydrocarbons, and also certain functional boron compounds.

3. The possibility was shown of using the ketal-protected carbonyl group in organoboron compounds.

LITERATURE CITED

1. B. M. Mikhailov, Yu. N. Bubnov, S. A. Korobeinikova, and S. I. Frolov, Izv. Akad. Nauk SSSR, Ser. Khim., 1923 (1968).

- 2. B. M. Mikhailov, Yu. N. Bubnov, S. I. Frolov, and S. A. Korobeinikova, Izv. Akad. Nauk SSSR, Ser. Khim., 1631 (1969).
- 3. S. I. Frolov, Yu. N. Bubnov, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 1996 (1969).
- 4. B. M. Mikhailov, Yu. N. Bubnov, and S. I. Frolov, Izv. Akad. Nauk SSSR, Ser. Khim., 2290 (1967).
- 5. B. M. Mikhailov and F. B. Tutorskaya, Dokl. Akad. Nauk SSSR, 123, 479 (1958).
- 6. J. F. McOmy, Protecting Groups, Progress in Organic Chemistry [Russian translation], Vol. 3, Mir (1966), p. 263.
- 7. H. Norman, USA Patent No. 2758118, 4.08.1956; Chem. Abstr., 51, 2870 g (1957).
- 8. L. D. Meakins, J. Chem. Soc., 4170 (1953).
- 9. I. N. Nazarov, Zh. A. Krasnaya, and V. P. Vinogradov, Zh. Obshch. Khim., 28, 460 (1958).
- 10. A. N. Lyubimov, A. F. Varenik, and A. V. Kessenikh, Zh. Strukt. Khim., 7, 694 (1966).
- 11. Huan, Bull. Soc. Chim. France [5], 5, 1341 (1938).
- 12. N. Thoai, Bull. Soc. Chim. France, 225 (1964).
- 13. H. Gutman and O. Isler, USA Patent No. 2783232, 26.02.57; Chem. Abstr., 51, 10592c (1957).