ORGANIC AND BIOLOGICAL CHEMISTRY

ORGANOBORON COMPOUNDS

COMMUNICATION 227.* REACTION OF TRIALLYLBORANE WITH PHENYLACETYLENE

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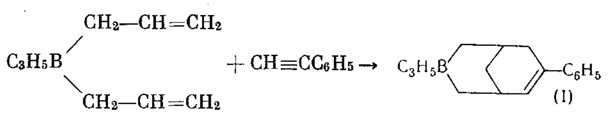
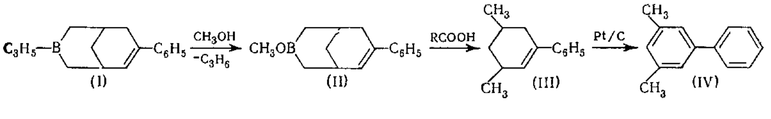
Triallylborane reacts with acetylene and its homologs to form the bicyclic system 3-allyl-3-borabicyclo[3,3,1]-6-nonene, in which the alkyl group occupies the 7-position when 1-alkynes are used [3-7].

A study of the reaction of triallylborane with phenylacetylene disclosed that replacing the alkyl group by phenyl in the acetylenic hydrocarbon fails to change the orientation of the condensation reaction, since 3-allyl-7-phenyl-3-borabicyclo[3,3,1]-6-nonene (I) is obtained



The reaction proceeds at room temperature with the spontaneous evolution of heat, and compound (I) is obtained in up to 96% yield when the reaction mass is distilled. The structure of compound (I) was proved chemically and was corroborated by the IR and NMR spectra. One mole of propylene is liberated when compound (I) is reacted with methanol and 3-methoxy-7-phenyl-3-borabicyclo[3,3,1]-6-nonene (II) is formed



Compound (II) is converted to 3,5-dimethyl-1-phenyl-1-cyclohexene (III) when subjected to acidolysis with butyric acid, which when dehydrogenated on Pt/C gives the known 3,5-dimethylbiphenyl (IV) [8]. In the UV spectrum of hydrocarbon (IV) the absorption minimum and maximum are respectively found at 231 cm^{-1} (ε = 6850) and 251.5 cm^{-1} (ε = 16,100), which is in harmony with the literature data for 3,5-dimethylbiphenyl. The oxidation of hydrocarbon (IV) with potassium permanganate in alkaline medium leads to the known 3,5-biphenyldicarboxylic acid (V). The IR spectrum of acid (V) proved to be identical with the spectrum of the 3,5-biphenyldicarboxylic acid that was obtained by us using the literature procedure [9].

In the IR spectrum of compound (I) the absorption band at 1638 cm^{-1} corresponds to the stretching vibrations of the C=C bond of the allyl radical. The absorption band at 1642 cm^{-1} in the IR spectrum of compound (II) must be assigned to the stretching vibrations of the ring C=C bond. The NMR spectra show that in compound (I) are present one allyl radical, phenyl and a proton at the double bond in the ring, corresponding to a doublet δ = 5.85 ppm (J = 5 Hz) (standard = tetramethylsilane). The signal from the allyl protons is absent in the spectrum of compound (II), and a signal is observed from the OCH_3 group (δ = 3.40 ppm). In the NMR spectra of compounds (I) and (II) the signals from the protons of the cyclic double bond have the shape of a doublet, from which it follows that the double bond in the ring is found in the 6-7 position, while the phenyl group is found in the 7-position.

In contrast to 3-methoxy-7-methyl-3-borabicyclo[3,3,1]-6-6-none [4], compound (II) does not hydrogenate in an autoclave over Raney nickel, but it smoothly adds hydrogen in the presence of palladium deposited on strontium carbonate at room temperature. Here, with the absorption of one mole of hydrogen,

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*See [1, 2] for Communications 221 and 226.

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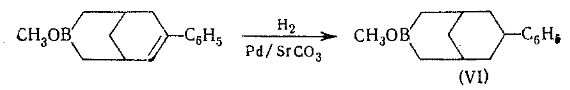
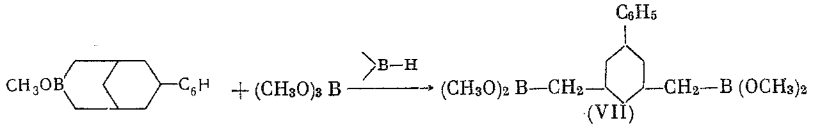
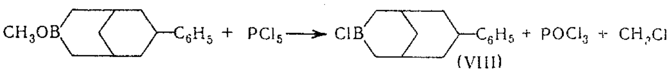
3-methoxy-7-phenyl-3-borobicylo[3,3,1]nonane (VI) is formed



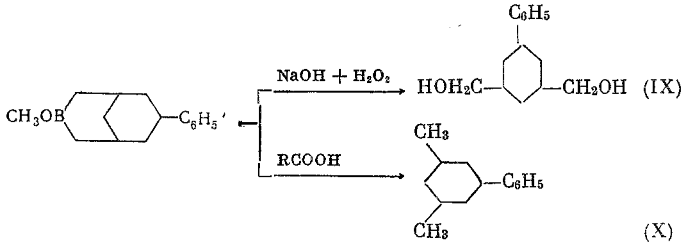
Cleavage of the boron-containing ring occurs when (VI) is refluxed for a long time with methyl borate in the presence of tetrapropyldiborane and 1,3-bis(dimethoxyborylmethyl)-5-phenylcyclohexane (VII) is formed



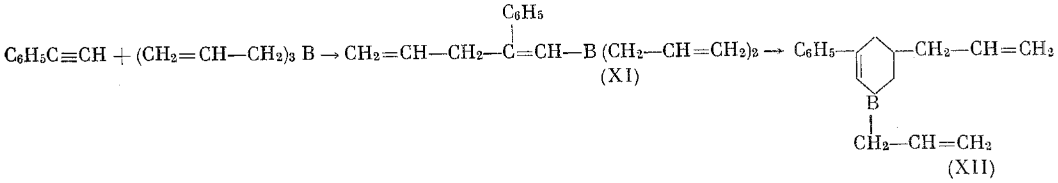
The reaction proceeds much more slowly than with the analogous monocyclic compounds [10]. Compound (VI), similar to the esters of dialkylboronic acids [11], reacts with phosphorus pentachloride to give 3-chloro-7-phenyl-3-borabicyclo[3,3,1]nonane (VIII)



The oxidation of compound (VI) with hydrogen peroxide in alkaline medium gives the crystalline diol cis-1,3-dihydroxymethyl-5-phenylcyclohexane (IX), while cis-1,3-dimethyl-5-phenylcyclohexane (X) is formed when cleavage is with stearic acid



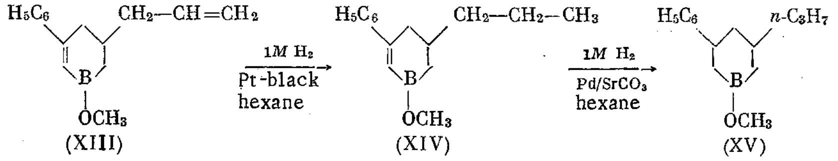
Compound (I) is the product of the thermal transformation of the substances (in the distillation process) that are initially formed during the reaction of triallylborane with phenylacetylene. Based on the data of the NMR spectrum, the reaction mass that is obtained when the reaction is run at 10-15°C does not contain compound (I). In the spectrum of the reaction mixture is absent the doublet with $\delta = 5.85$ ppm, which is characteristic for compound (I), instead there are present a singlet with $\delta = 6.39$ ppm and the signal from the protons of the two allyl groups



By analogy with the reaction of triallylborane with methyl- and butylacetylene [5, 6], it is possible to assume that also in the given case the triallylborane adds to the triple bond in the first step of the reaction, and then the formed diallyl-(2-phenyl-1,4-pentadien-1-yl)-borane (XI) is cyclized to 1,5-diallyl-3-phenyl-1-bora-2-cyclohexene (XII). Compound (XII) could not be isolated in the pure state, since during distillation it undergoes cyclization to compound (I). Compound (XII) was identified as the methoxyl derivative, namely 1-methoxy-5-allyl-3-phenylbora-2-cyclohexene (XIII), which was formed by the action of methanol on the crude reaction product as the result of replacing the allyl radical attached to the boron atom by the methoxyl group, similar to what occurs in the series of the alkyl analogs [5, 6].

The NMR spectrum indicates that compound (XIII) contains one methoxyl group ($\delta = 3.62$ ppm), one allyl group ($\delta_{CH_2} = 4.83$-5.1, $\delta_{CH} = 5.45$-6 ppm), and one vinyl proton ($\delta = 6.13$ ppm). In the IR spectrum of compounds (XII) and (XIII) are present the intense absorption bands of the bonds of $-C=C\langle$ fragment $\rangle B-C=C\langle$ (respectively 1566 and 1575 cm^{-1}).

The stepwise hydrogenation of the double bonds in compound (XIII) can be accomplished in hexane solution. The allyl double bond is the first to hydrogenate on platinum black, and then the reaction rate drops sharply. Then the hydrogenation of the vinyl double bond of 1-methoxy-5-n-propyl-3-phenylbora-2-cyclohexene (XIV) proceeds on 30% palladium deposited on strontium carbonate, as a result of which 1-methoxy-5-n-propyl-3-phenylboracyclohexane (XV) is obtained



The absorption band with ν 1638 cm^{-1} ($-CH=CH_2$) is absent in the IR spectrum of compound (XIV).

In the NMR spectrum are absent the multiplets from the methylene and methine protons of the allyl radical, and there are present a singlet from the vinyl proton (δ = 6.13 ppm), a singlet from the methoxyl protons (δ = 3.64 ppm), and a multiplet from the phenyl protons (δ = 7.14-7.54 ppm). The absorption band with ν 1570 cm^{-1} ($\rangle B-C=C\langle$) is absent in the IR spectrum of compound (XV), while the signal from the vinyl proton is absent in the NMR spectrum.

EXPERIMENTAL METHOD

All of the operations with the organoboron compounds were carried out in a dry N_2 atmosphere. The phenylacetylene was obtained as described in [12].

3-Allyl-7-phenyl-3-borobicyclo[3,3,1]-6-nonene (I). With stirring and cooling with water, to 15 g of triallylborane was added 11.5 g of phenylacetylene at such a rate that the temperature of the reaction mixture remained below 35°. The reaction mixture was stirred for 2 h at 20° and for 1 h at 80°. Distillation gave 25.5 g (96%) of (I) as a colorless liquid with bp 131-132° (1.5 mm); n_D^{20} 1.5662; d_4^{20} 0.9894. Found: C 86.58; H 8.82; B 4.53%. $C_{17}H_{21}B$. Calculated: C 86.45; H 8.96; B 4.58%.

3-Methoxy-7-phenyl-3-borabicyclo[3,3,1]-6-nonene (II). To 13.7 g of (I) was added 5 ml of methanol in 20 min. Marked heating up was observed, accompanied by the evolution of a gas. Then the mixture was heated at reflux for 15 min. A total of 1.3 liters of propylene was evolved. Distillation gave 11.7 g (89.5%) of (II) with bp 114-115° (1 mm); n_D^{20} 1.5650; d_4^{20} 1.0513. Found: C 76.69; H 8.38; B 4.74%. $C_{15}H_{19}BO$. Calculated 79.67; H 8.47; B 4.78%.

3,5-Dimethyl-1-phenyl-1-cyclohexene (III). A mixture of 15.8 g of (II) and 20 ml of butyric acid was refluxed for 9 h. Distillation gave 5 g of $CH_3(CH_2)_2COOCH_3$ and 9.5 g (71%) of (III) with bp 110-112° (4.5 mm); n_D^{20} 1.5496; d_4^{20} 0.9505. Found: C 89.90; H 9.87%; mol. wt. 178. $C_{14}H_{18}$. Calculated: C 90.26; H 9.74%; mol. wt. 186. An absorption band at 1635 cm^{-1} (stretching vibrations of $\rangle C=C\langle$).

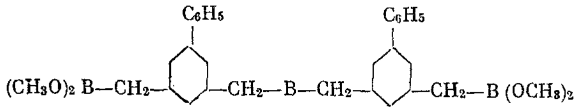
3,5-Dimethylbiphenyl (IV). A mixture of 8.6 g of compound (III) and 0.2 of 20% Pt/C was refluxed for 5 h (260-285°); here 1.95 liters of H_2 was evolved. Distillation gave 6.37 g (80.4%) of 3,5-dimethylbiphenyl with bp 118-119.5° (2 mm); n_D^{20} 1.5942; d_4^{20} 0.9980. Found: C 91.90; H 7.83%. $C_{14}H_{14}$. Calculated: C 92.26; h 7.74%. The following absorption bands are present in the IR spectrum: 843 cm^{-1} (vibrations of phenyl ring with 1,3,5-substitution), 697 and 771 cm^{-1} (vibrations of monosubstituted phenyl ring).

3,5-Biphenyldicarboxylic Acid (V). To an emulsion of 0.5 g of (IV) in 23 ml of 0.6% NaOH solution was added 1.31 g of $KMnO_4$ in four portions, at intervals of 20 min. Then the stirred mixture was heated at 90-98° until decolorization of the solution occurred (18.5 h). The MnO_2 was filtered, and washed on the filter with hot water; the filtrate under cooling was acidified with HCl. The white flocculent precipitate was filtered and dried. We obtained 0.32 g (48.4%) of (V). After recrystallization from glacial acetic acid the substance decomposes around 320°. According to the data given in [9], the melting point of the acid is above 311°.

3-Methoxy-7-phenyl-3-borabicyclo[3,3,1]nonane (VI). In a hydrogenation vessel were placed 18.2 g of (II), 0.67 g of 30% $Pd/SrCO_3$ [13] and 10 ml of methanol. The amount of H_2 absorbed in 4 h was 1.8 liters. The catalyst was filtered, and the solvent was distilled off. Distillation of the residue gave 15.8 g (86%) of

(VI) with bp 122-122.5° (0.5 mm); n_D^{20}1.5435; d_4^{20}1.0455. Found: C 78.67; H 9.15; B 4.38%; mol. wt. 227. $C_{15}H_{21}BO$. Calculated: C 78.96; H 9.28; B 4.74%; mol. wt. 228.1.

1,3-bis-(Dimethoxyborylmethyl)-5-phenylcyclohexane (VII). A mixture of 28 g of 3-methoxy-7-phenyl-3-borabicyclo[3,3,1]nonane (X), 13 ml of methyl borate and 1.28 g of tetrapropyldiborane was refluxed for 24 h. Here the temperature rose from 82 up to 105°. Then new portions of methyl borate were gradually added until the boiling point of the mixture ceased to rise when the next portion was added. A total of 9 ml of methyl borate was added. The compound, containing $>$B−H bonds, was decomposed with methanol. A colorless viscous liquid remained in the flask after distilling off 13.2 g of substance with bp 140-160° (0.2 mm), which is apparently the triboron compound



(found mol. wt. 570.1; calc. mol. wt. 590). The additional refluxing of this liquid with methyl borate in the presence of tetrapropyldiborane for five days gave an additional 15.2 g (a total of 28.46 g, 70%) of substance with bp 149-155° (0.08 mm). When subjected to fractional redistillation the substance boiled at 130-132° (0.04 mm). Found: C 65.63; H 9.07; B 6.58%. $C_{18}H_{30}B_2O_4$. Calculated: C 65.10; H 9.11; B 6.51%.

3-Chloro-7-phenyl-3-borabicyclo[3,3,1]nonane (VIII). To 15.5 g of compound (III), placed in a Favorskii flask, was added 14.7 g of PCl_5 in portions. The reaction proceeded with the evolution of heat. Distillation gave 3.6 g of CH_3Cl, 7 g of $POCl_3$, and 9 g (57%) of (VIII) as a colorless liquid, which crystallized on standing. Compound (VIII) has bp 126-128° (1.5 mm) and mp 49-50°. Found: C 72.44; H 7.78; B 4.48; Cl 14.85%. $C_{14}H_{18}BCl$. Calculated: C 72.30; H 7.80; B 4.65; Cl 15.25%.

cis-1,3-Dimethyl-5-phenylcyclohexane (X). A mixture of 7 g of (VI) and 31 g of stearic acid was heated in a Favorskii flask in vacuo (10 mm). At a temperature of 190-200° in the flask the amount of distilled (X) was 5 g (81.5%). The hydrocarbon was washed with 20% NaOH solution, then with water, and was dried over $CaCl_2$; bp 116.5-118.5° (9 mm); n_D^{20} 1.5098; d_4^{20} 0.9171. GLC indicates the absence of impurities. Found: C 89.46; H 10.40%; mol. wt. 186.6. $C_{14}H_{20}$. Calculated: C 89.30; H 10.70%; mol. wt. 188.

cis-1,3-Dihydroxymethyl-5-phenylcyclohexane (IX). To a mixture of 9.2 g of (VI) and 23 ml of 20% NaOH solution, with cooling at 0 to 5°, was added 13 ml of 30% H_2O_2 solution and themixture was allowed to stand overnight. The obtained white precipitate was filtered, washed with water, and dried.

We obtained 8.11 g (91.2%) of (IX). The substance crystallizes from a mixture of ethanol and water as colorless prisms with mp 100.5-101.8°. Found: C 76.56; H 9.07%. $C_{14}H_{20}O_2$. Calculated: C 76.32; H 9.15%.

1-Methoxy-5-allyl-3-phenyl-1-bora-2-cyclohexene (XIII). To 8.90 g of triallylborane, with stirring and cooling with an ice-water mixture, was added 6.77 g of phenylacetylene at such a rate that the temperature of the reaction mixture remained below 10°. Then the reaction mixture was allowed to stand at 10-17° until reaction was complete (disappearance of the 3300 cm^{-1} band in the IR spectrum) (10 h). To the reaction mass, with stirring and cooling in an ice-water mixture, was gradually added 5.4 ml of methanol at such a rate that the temperature in the flask remained below 17°. Here 1.46 liters of propylene was evolved. Distillation gave 10.32 g (66%) of (XIII) with bp 106.5-107.5° (2 mm); n_D^{21} 1.5610; d_4^{20} 0.9978. Found: C 79.62; H 8.72; B 4.62%. $C_{15}H_{19}BO$. Calculated: C 79.67; H 8.47; B 4.78%.

1-Methoxy-5-propyl-3-phenyl-1-bora-2-cyclohexene (XIV). A solution of 10.15 g of (XIII) in absolute hexane was hydrogenated in a hydrogenation vessel over Pt black. One liter of H_2 was absorbed in 2 h. Distillation gave 7.66 g (74.8%) of (XIV) with bp 113° (3 mm); $n_D^{15.5}$ 1.5490; d_4^{20} 0.9857. Found: C 78.74; H 9.11; B 5.00%. $C_{15}H_{21}BO$. Calculated: C 78.96; H 9.28; B 4.74%.

1-Methoxy-5-propyl-3-phenyl-1-boracyclohexane (XV). A solution of 3.55 g of (XIV) in absolute hexane was hydrogenated in a hydrogenation vessel over 30% $Pd/SrCO_3$. The amount of H_2 absorbed in 50 min was 350 ml. Distillation gave 2.75 g (77.5%) of (XV) with bp 110-111° (3 mm); n_D^{18} 1.5125; d_4^{20} 0.9604. Found: C 78.86; H 10.27; B 4.67%. $C_{15}H_{23}BO$. Calculated: C 78.28; H 10.07; B 4.70%.

CONCLUSIONS

1. Triallylborane reacts with phenylacetylene at 7-10° to give 1,5-diallyl-3-phenylbora-2-cyclohexene, which when heated is converted to 3-allyl-7-phenyl-3-borabicyclo[3,3,1]-6-nonene.

2. The transition from derivatives of 7-phenyl-3-borabicyclo[3,3,1]-6-nonene to the 3,5-derivatives of phenylcyclohexene and biphenyl was accomplished.

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