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Abstract

Full Text

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CYCLIC BORON COMPOUNDS FORMED IN THE HYDROBORATION OF 1,3-BUTADIENE

(Presented by Academician B. A. Kazanskii, 29 X 1963)

In the action of diborane on 1,3-butadiene, Köster (^1) obtained a product with b.p. 55° at 0.1 mm, to which he assigned the structure di-1,4-(1-boracyclopentyl)butane (I).

$$\text{(1-boracyclopentyl)} - \mathrm{B{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}B} - \text{(1-boracyclopentyl)} \quad \text{(I)}$$

Following Köster, and accepting this product as an individual compound, we used it for certain synthetic purposes (^2). Subsequently, however, we came to doubt the purity of the initial compound (I), since in the hydroboration of 1,3-butadiene the boron atoms add at different positions of the diene system (^3), and therefore the formation should be expected of various isomeric bicyclic compounds (I–IV), differing in the structure of the aliphatic chain,

$$\text{(1-boracyclopentyl)} - \mathrm{B{-}CH(CH_3){-}CH_2{-}CH_2{-}B} - \text{(1-boracyclopentyl)} \quad \text{(II)}$$

$$\text{(1-boracyclopentyl)} - \mathrm{B{-}CH(C_2H_5){-}CH_2{-}B} - \text{(1-boracyclopentyl)} \quad \text{(III)}$$

$$\text{(1-boracyclopentyl)} - \mathrm{B{-}CH(CH_3){-}CH(CH_3){-}B} - \text{(1-boracyclopentyl)} \quad \text{(IV)}$$

In this connection we investigated the structure of the organoboron compounds formed in the action of diborane on 1,3-butadiene. The reaction was carried out in an ether medium with a butadiene-to-diborane ratio of 5 : 1. After removal of the solvent, the reaction products were fractionated. Two fractions were obtained. The first fraction (11.5%, calculated on boron), with b.p. 61.5–66.5° at 40 mm, had the elemental composition $C_8H_{15}B$, which corresponded to isomeric 1-boracyclopentylbutenes (V–VII).

$$\text{(1-boracyclopentyl)} - \mathrm{B{-}CH_2{-}CH_2{-}CH{=}CH_2} \qquad \text{(V)}$$

$$\text{(1-boracyclopentyl)} - \mathrm{B{-}CH_2{-}CH{=}CH{-}CH_3} \qquad \text{(VI)}$$

$$\text{(1-boracyclopentyl)} - \mathrm{B{-}CH(CH_3){-}CH{=}CH_2} \qquad \text{(VII)}$$

The second fraction (70%), with b.p. 75.5–81° at 2 mm, corresponded in elemental composition and physical properties to the product described by Köster as di-1,4-(1-boracyclopentyl)butane (I). On standing it turns into a glassy mass, which liquefies again upon slight heating.

Both fractions were subjected to oxidation with hydrogen peroxide in alkaline medium. Oxidation of the main (second) fraction gave a mixture of butanediols (86%) consisting of 85% 1,4-butanediol, 13% 1,3-butanediol, and 2% 1,2-butanediol. In addition, *n*-butanol (about 5% of the theoretically possible amount) was detected in the oxidation products, indicating hydrolytic cleavage of boron-carbon bonds during the alkaline oxidation. The *n*-butyl radical arising at the boron atom gives an alcohol on oxidation. If this fraction were the pure compound (I), then its oxidation should have yielded only 1,4-butanediol. Since oxidation of the boron-containing ring leads to 1,4-butanediol, the presence of isomeric butanediols is explained by isomeric

with the structure of a bridged hydrocarbon chain. From the ratio of the isomeric butanediols it follows that the fraction under study contains 55% di-1,4-(1-boracyclopentyl)butane (I), 39% di-1,3-(1-boracyclopentyl)butane (II), and 6% di-1,2-(1-boracyclopentyl)butane (III). As will be seen below, di-2,3-(1-boracyclopentyl)butane (IV) is also present in the mixture, but in such a small amount that it is not detected in the analysis.

On oxidation of the first fraction (12 g), 7.5 g of butane-1,4-diol, 1.1 g of alcohols, and 1790 ml of gaseous products were obtained. As is to be expected, in accordance with structures (V–VII), no isomeric butanediols were obtained. The alcohol fraction consisted mainly of *n*-butyl alcohol with a small admixture of isomeric butenols. The gaseous hydrocarbons obtained consisted of butene-1 (88%), cis-butene-2 (10%), and trans-butene-2 (2%). The formation of butenes indicates that the side chain in compounds (V–VII) also partially undergoes cleavage under the oxidation conditions. Hydrolytic cleavage of the side chains in compounds (VI) and (VII) should occur especially readily, since they contain allylic boron-carbon bonds (4). The ratio of cis- and trans-butene-2 indicates that compound (VI) predominantly has the cis configuration.

Various pathways for the formation of compounds (V–VII) may be envisaged. One of them consists in cyclization of the initially formed butenylborane (VIII) to boracyclopentane (IX),

$$C_4H_6 + BH_3 \longrightarrow C{=}C{-}C{-}C{-}BH_2 \longrightarrow \overset{\text{boracyclopentane ring}}{BH}$$

(VIII) (IX)

which then adds in various positions to butadiene. Since, however, boracyclopentane (its dimer) reacts with olefins only at elevated temperature (^{5}), this mechanism appears unlikely. Preference should therefore be given to another mechanism, consisting in the addition of two diene molecules to diborane and subsequent cyclization of dibutenylboranes (X, XI) into compounds (V) or (VII). The formation of compound (VI) is apparently explained by the fact that diborane adds to butadiene not only in the 1,2-, but also in the 1,4-position, giving butenylborane (XII). Such an order of addition is spatially more favorable for the cis form of butadiene-1,3. Butenylborane (XII) is then converted into dibutenylborane (XIII), which cyclizes to (VI). The latter compound, in accordance with the cis configuration of (XII), is predominantly the cis isomer, as noted above. Compounds (V—VII) are intermediates in the formation of (I—IV).

$$\mathrm{VIII} + C_4H_6 \begin{cases} \longrightarrow (\mathrm{X}) \longrightarrow (\mathrm{V}) \\ \longrightarrow (\mathrm{XI}) \longrightarrow (\mathrm{VII}) \end{cases}$$

$$C{-}C{=}C{-}C{-}BH_2 \longrightarrow \begin{matrix} C{=}C{-}C{-}C \\ C{-}C{=}C{-}C \end{matrix} > BH \longrightarrow \mathrm{VI}$$

(XII) (XIII)

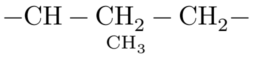
The presence of isomeric bridges in compounds (I—IV) is manifested in their reaction with methyl borate. As we have previously shown (^{2}), at a reagent ratio of 1 : 1, 1-methoxyboracyclopentane (XIV) is formed

$$\text{boracyclopentane ring}B{-}OCH_3 \qquad (\mathrm{XIV})$$

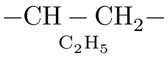
and a higher fraction (composition $C_{10}H_{22}B_2O_2$, b.p. 68—71° at 3 mm).

[[reaction scheme showing compounds (V), (VI), and (VII) forming diboracyclic compounds (I)-(IV)]]

Upon oxidation of this fraction (0.055 mole), a mixture of butanediols was obtained (yield 47%), containing 69% butane-1,3-diol, 21% butane-1,2-diol, 9.6% butane-1,4-diol, and 0.4% butane-2,3-diol, as well as *n*-butanol (0.039 mole). These data indicate that the fraction under investigation is a mixture of dimethoxy derivatives of diborocyclic compounds including the following fragments:

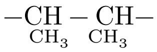


$$-\underset{CH_3}{CH}-CH_2-CH_2-$$



$$-\underset{C_2H_5}{CH}-CH_2-$$

$$-CH_2-CH_2-CH_2-CH_2-$$



$$-\underset{CH_3}{CH}-\underset{CH_3}{CH}-$$

Most probably, these cyclic compounds have a symmetrical structure:

$$CH_3O-B\left(\begin{array}{c}CH(CH_3)-CH_2-CH_2\\CH_2-CH_2-CH(CH_3)\end{array}\right)B-OCH_3$$

(XV)

$$CH_3O-B\left(\begin{array}{c}CH(C_2H_5)-CH_2\\CH_2-CH(C_2H_5)\end{array}\right)B-OCH_3$$

(XVI)

$$CH_3O-B\left(\begin{array}{c}CH_2-CH_2-CH_2-CH_2\\CH_2-CH_2-CH_2-CH_2\end{array}\right)B-OCH_3$$

(XVII)

$$CH_3O-B\left(\begin{array}{c}CH(CH_3)-CH(CH_3)\\CH(CH_3)-CH(CH_3)\end{array}\right)B-OCH_3$$

(XVIII)

The presence of butane-2,3-diol, which is obtained from 2,3,5,6-tetramethyl-1,4-dimethoxy-(1,4-diboracyclohexane) (XVIII), indicates that the mixture of bicyclic compounds (I-IV) contains traces of di-2,3-(1-boracyclopentyl)butane (IV). The formation of *n*-butyl alcohol should be explained by the fact that, during oxidation, the diboracyclic compounds undergo hydrolytic cleavage of the boron–carbon bond to a considerable extent.

Under the action of an excess of methyl borate on (I-IV), a mixture of tetramethyl esters of isomeric butanediboronic acids must inevitably be formed. In physical properties this mixture differs little from the individual ester of butane-1,4-diboronic acid obtained by the action of excess me-

tilborate to 1-methoxyboracyclopentane (XIV) (2). It may be assumed that the reaction of the mixture of bicyclic compounds (I—V) with boron trichloride also leads not to the individual 1,4-bis(dichloroboryl)butane (6), but to a mixture of isomeric tetrachlorides.

It should be pointed out that, for the analysis of butanediols with a high content of the 1,2- and 1,3-isomers, the usual method of isolating them from an aqueous solution saturated with potassium carbonate is unsuitable, since these isomers partially form cyclic complex compounds with boric acid in the presence of alkali (7), and therefore are not completely extracted by organic solvents. We therefore developed a method by which the complex compounds of the diols were destroyed with mannitol. This method of isolating the diols was used by us in all analyses.

Experimental Part

Hydroboration of butadiene-1,3. Diborane (1 mole), prepared from 87 g of sodium borohydride and 285 g of boron trifluoride etherate in 400 ml of ether, is passed into a solution of 260 g (4.8 moles) of butadiene-1,3 in 500 ml of ether at a temperature of −20°–(−30°). After the reaction is complete, the mixture is left at room temperature until the next day. Then the excess butadiene-1,3 and the solvent are distilled off, and the residue is fractionated in vacuo. Obtained: 1) 27.9 g with b.p. 59–70° at 40 mm. After repeated distillation the fraction had b.p. 61.5–66.5° at 40 mm, d_4^{20} 0.8208; n_D^{20} 1.4700.

Found, %: C 78.41; 78.14; H 12.36, 12.52; B 8.50, 8.64
$C_8H_{15}B$. Calculated, %: C 78.74; H 12.39; B 8.87

2) 129.7 g with b.p. 75.5–81° at 2 mm, n_D^{20} 1.4870.

The second fraction is a mixture of di-(1-boracyclopentyl)butanes.

Oxidation procedure. To the substance under investigation, placed in a flask connected through a reflux condenser to a gasometer, a 3 N solution of sodium hydroxide is gradually added, calculated as 1 mole per 1 g-atom of boron. After gas evolution has ceased, if it occurs, 30% hydrogen peroxide is added dropwise to the mixture in an amount of 1.1–1.2 moles per B–C bond. The temperature of the mixture is maintained within 0°–(−5°). After the addition of peroxide is complete, the mixture is left for 12–15 h at room temperature, and then mannitol is added in an amount of 1 mole per 1 g-atom of boron. After dissolution of the mannitol, water and monohydric alcohols are distilled off under a mild vacuum (50–100 mm). The residue is extracted with boiling ethanol, in portions of 40–50 ml (4–5 times). The solvent is distilled off from the extract; the residue, containing some mannitol, is dissolved in 10–20 ml of absolute ethyl alcohol, and the mannitol is precipitated with 80–100 ml of absolute ether; the precipitate is then filtered off and washed with ether. The solvents are distilled off from the filtrate, and the mixture of diols is distilled in vacuo. The distilled aqueous solution of monohydric alcohols is saturated with potassium carbonate and extracted several times with ether. Gaseous hydrocarbons, monohydric alcohols, and diols are then analyzed by methods of gas-liquid chromatography.

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Note: Figure translations are in progress. See original paper for figures.