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Abstract

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ORGANOBORON COMPOUNDS

HYDROBORATION OF DIMETHYL ALLYLBORONATE

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The reaction of addition of diborane to unsaturated compounds, the so-called hydroboration, is of great interest from both the preparative and the theoretical points of view. The orientation of boron addition in this reaction depends on subtle structural features of the unsaturated system and is determined by the influence of polar and steric factors. Whereas, for the reaction of diborane with olefinic hydrocarbons, considerable experimental material is available ([1]), making it possible to assess the influence of molecular structure on the order of addition, the hydroboration of functional derivatives of olefins has so far been little studied.

We undertook an investigation of the reaction between diborane and dimethyl allylboronate with the aim, first, of determining the influence of the $(RO)_2B-$ group on the order of addition of boron to the double bond of the allyl radical and, second, of clarifying the possibility of obtaining in this way compounds containing several boron atoms in the molecule. The starting dimethyl allylboronate was prepared in 78.6% yield by heating triallylborane with methyl borate.

$$(C_3H_5)_3B + 2(CH_3O)_3B \rightarrow 3C_3H_5B(OCH_3)_2 \qquad (1)$$

(I)

Experiments on hydroboration were carried out by introducing diborane into an ethereal solution of ester (I), at a reagent ratio of 1 : 6.

The order of addition was determined by oxidation of the hydroboration products with hydrogen peroxide in alkaline medium and subsequent analysis of the mixture of the propanediols formed by gas-liquid chromatography. The content in the mixture of 97% propane-1,3-diol and 3% propane-1,2-diol indicates that hydroboration of I proceeds more selectively than that of α-olefins, which add a boron atom to the terminal carbon of the double bond to the extent of 93-94% (1).

After establishing the orientation in the reaction of addition of diborane to ester I, we turned to the study of the compounds formed in this process. At the chosen reagent ratio, formation of tri-(3-dimethoxyborylpropyl)-borane (II) with a small admixture (about 3%) of isomeric compounds was to be expected. The normal course

$$3CH_2{=}CH{-}CH_2B(OCH_3)_2 + \tfrac{1}{2}B_2H_6 = B\,[CH_2CH_2CH_2B(OCH_3)_2]_3 \quad (2)$$

(II)

of the process could, however, be complicated by reactions of exchange of the hydrogen atom of borane for the methoxyl group of the starting ester (I). It turned out that, upon distillation of the solvent from the reaction mass, the residue contains a colorless microcrystalline substance impregnated with an oily impurity, which, according to elemental analysis and molecular weight, is an insufficiently pure tetraboron compound II. It is highly soluble in organic solvents, including pentane, and cannot be purified by crystallization; upon heating in vacuum it undergoes thermal decomposition.

It had earlier been shown by one of us and Yu. N. Bubnov (3) that trialkylboranes are readily cleaved by alcohols in the presence of mercaptans, with formation of esters of dialkylborinic acids and saturated hydrocarbons.

Therefore compound II, as a substituted bortrialkyl, under the action of methyl alcohol in the presence of a mercaptan should have been converted into an equimolecular mixture of 1,1,5,9,9-pentamethoxy-1,5,9-triboranonane (III) and dimethyl *n*-propylboronate.

$$B[CH_2CH_2CH_2B(OCH_3)_2]_3 \xrightarrow[C_2H_5SH]{CH_3OH} CH_3OB[CH_2CH_2CH_2B(OCH_3)_2]_2 + n\,C_3H_7B(OCH_3)_2. \quad (3)$$

Indeed, on treating compound II with a mixture of methyl borate alcohol and ethyl mercaptan, we obtained III in 83.5% yield and the dimethyl ester of propylboronic acid in 75% yield, calculated according to equation (3). In order to determine the degree of purity of compound III, it was oxidized with hydrogen peroxide in an alkaline medium, and the oxidation products were analyzed by gas-liquid chromatography. The resulting mixture of diols consisted of 99.5% propanediol-1,3 and 0.5% propanediol-1,2.

As stated above, compound II is thermally unstable. On heating in vacuo, it decomposes with formation of III and the cyclic diboron compound 1,5-dimethoxy-1,5-diboracyclooctane (IV). In this process a small amount of polymer is formed

$$2B[CH_2CH_2CH_2B(OCH_3)_2]_3 \rightarrow 2CH_3OB[CH_2CH_2CH_2B(OCH_3)_2]_2 + CH_3OB(CH_2CH_2CH_2)_2BOCH_3 \quad (4)$$

(IV)

Compound IV was somewhat contaminated, apparently by an admixture of 1,1,5,5-tetramethoxy-1,5-diborapentane, which has a similar boiling point, and therefore was re-esterified with *n*-butyl alcohol into the previously obtained 1,5-di-*n*-butoxy-1,5-diboracyclooctane (^{9}).

Experimental Part

Dimethyl ester of allylboronic acid (I). 57 g (0.42 mole) of triallylboron and 90 g (0.87 mole) of methyl borate were boiled for 10 hours, the temperature of the reaction mixture rising from 70 to 102°. Then 5 ml of methyl borate alcohol was added to the cooled mixture and it was distilled.

There were obtained 114 g (78.6%) of the dimethyl ester of allylboronic acid with b.p. 104–108°, n_D^{20} 1.4023. Literature data (^{4}): b.p. 42–43° at 60 mm, n_D^{20} 1.4021.

Determination of the orientation of diborane addition to the dimethyl ester of allylboronic acid. Into a solution of 13.8 g (0.12 mole) of the dimethyl ester of allylboronic acid in 50 ml of diethyl ether there was introduced 0.02 mole of diborane, obtained from $LiAlH_4$ and boron trifluoride etherate.

After the solvent had been distilled off, 30 ml of 10% sodium hydroxide solution was added to the residue (13.2 g), and then, with stirring and cooling with cold water, 35 ml of 29% hydrogen peroxide was added. To complete the oxidation the mixture was heated for 20 minutes on a boiling water bath and, after cooling, saturated with potassium carbonate. The oxidation products were extracted three times with 20 ml portions of *n*-propyl alcohol. After distillation of the propyl alcohol, the residue was distilled.

There were obtained 6.5 g (77%) of a mixture of propanediol-1,2 and propanediol-1,3 with b.p. 110–117° at 15 mm, n_D^{20} 1.4350.

The resulting mixture of propanediol-1,3 and propanediol-1,2 was quantitatively analyzed by gas–liquid chromatography on an SKB-system instrument of our institute. For the separation a 40-cm column was used. The stationary phase was diglycerin on brick. Helium was used as the carrier gas. Complete and rapid separation of the propanediols is achieved at 100–110°. It was found that the resulting mixture contained 97% propanediol-1,3 and 3% propanediol-1,2.

Tri-(3-dimethoxyborylpropyl)boron (II). Into a solution of 21.5 g (0.188 mole) of the dimethyl ester of allylboronic acid in 30 ml of diethyl ether there was introduced 0.029 mole of diborane, obtained from $LiAlH_4$ and boron trifluoride etherate. From the clear solution, after 30 minutes, the solvent was distilled off in vacuo. The residue (20 g) was a colorless, finely crystalline substance impregnated with oily impurities. The substance melts in the presence of traces of oxygen and is very readily soluble in benzene, ether, and pentane.

Found, %: C 51.12; 51.22; H 10.13; 10.07; B 11.80; 11.89
$C_{15}H_{36}B_4O_6$. Calculated, %: C 50.64; H 10.20; B 12.16

Determination of the molecular weight was carried out by the isothermal distillation method (^{5}). Molecular weight found 322, calculated 355.7.

Action of methyl alcohol in the presence of ethyl mercaptan on tri-(3-dimethoxyborylpropyl)borane. To a solution of 43 g (0.37 mole) of dimethyl allylboronate in 60 ml of diethyl ether, 0.06 mole of diborane was introduced. After removal of the solvent, a mixture of 10 ml of methyl alcohol and 10 ml of ethyl mercaptan was added to the residue (42 g; boron content 12.3%), and the mixture was heated for 20 minutes on a water bath at gentle boiling of the solution. Under vacuum at 5 mm the volatile reaction products were distilled into a trap (−70°). Distillation of the residue gave 27.2 g (83.5%) of 1,1,5,9,9-pentamethoxy-1,5,9-triboranonane, b.p. 99—105° at 1 mm, n_D^{20} 1.4325; literature data (^{6}): b.p. 100° at 1 mm, n_D^{20} 1.4318. Distillation of the products collected in the trap gave 10.4 g of dimethyl *n*-propylboronate with b.p. 102—106°, n_D^{20} 1.3865. Literature data (^{7}): b.p. 104°, n_D^{20} 1.3847.

Oxidation of 1,1,5,9,9-pentamethoxy-1,5,9-triboranonane. 16.0 g (0.059 mole) of 1,1,5,9,9-pentamethoxy-1,5,9-triboranonane was mixed with 30 ml of 10% sodium hydroxide solution, and, with stirring and water cooling, 35 ml of 29% hydrogen peroxide was added; the mixture was heated for 20 min on a boiling water bath. After cooling, the solution was saturated with potash, and the oxidation products were extracted three times with 20 ml portions of *n*-propyl alcohol.

Obtained was 6.4 g of a mixture of 1,2- and 1,3-propanediols with b.p. 117—125° at 18 mm, n_D^{20} 1.4360. By gas chromatography it was found that the content of 1,3-propanediol was 99.5%, and of 1,2-propanediol, 0.5%.

Pyrolysis of the product of hydroboration of dimethyl allylboronate. To a solution of 43 g (0.37 mole) of dimethyl allylboronate in 50 ml of diethyl ether, 0.06 mole of diborane was introduced. After removal of the solvent, the residue was distilled under vacuum. Obtained were 38.2 g of pyrolysis products with b.p. 40—100° at 2 mm and a solid residue in the amount of 3.4 g.

On fractionation the following fractions were isolated: 1) 5.8 g, b.p. 55—60° at 2 mm, n_D^{20} 1.4480; 2) 26.7 g, b.p. 115—120° at 2 mm, n_D^{20} 1.4320. The first fraction, after repeated distillation, had b.p. 40.5—41° at 1 mm and, according to analysis, was insufficiently pure 1,5-dimethoxy-1,5-diboracyclooctane, with an impurity, apparently, of 1,1,5,5-tetramethoxy-1,5-diborapentane, having a close boiling point (^{8}).

Found, %: C 55.09; 55.15; H 10.41; 10.53; B 13.26; 12.96
$C_8H_{18}O_2B_2$. Calculated, %: C 57.23; H 10.80; B 12.89

After transesterification with *n*-butyl alcohol, 1,5-di-*n*-butoxy-1,5-diboracyclooctane was obtained with b.p. 115—118° at 2 mm, n_D^{20} 1.4520. Literature data (^{9}): b.p. 110° at 2 mm, n_D^{20} 1.4510.

Found, %: C 66.65; 66.88; H 11.64; 12.00; B 8.65; 8.70
$C_{14}H_{30}B_2O_2$. Calculated, %: C 66.72; H 11.99; B 8.59

The second fraction is 1,1,5,9,9-pentamethoxy-1,5,9-triboranonane. Yield 78%. Literature data (^{6}): b.p. 100° at 1 mm, n_D^{20} 1.4318.

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