SUMMARY

1. 3-Methoxy-7-methylene-3-borabicyclo[3.3.1]nonane and 3-methoxy-1,5-dimethyl-7-methylene-3borabicyclo[3.3.1]nonane were converted by the action of diborane or tetraethyldiborane into 1-boraadamantane and 3,5-dimethyl-1-boraadamantane, respectively.

2. 1-Boraadamantane compounds possess increased complex-formingability in comparison with trialkylboranes. A series of complexes of 1-boraadamantane and 3,5-dimethyl-1-boraadamantane has been described.

3. 1-Boraadamantane and 3,5-dimethyl-1-boraadamantane on carbonylation and subsequent oxidation of the reaction products were converted into 1-hydroxyadamantane and 1-hydroxy-3,5-dimethyladamantane, respectively.

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BOROORGANIC COMPOUNDS

322. THE PREPARATION OF 1,2-OXABORINANES

AND 1,2-OXABORE PANES

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Among heterocyclic compounds containing boron and oxygen atoms in the ring (1,2-oxaboracyclanes) the most accessible are the five-membered 1,2-oxaborolanes for which several simple methods of preparation have been developed [1-4]. Higher 1,2-oxaboracyclanes are less accessible.

It was shown by us previously [3] that alkaline hydrolysis of the methyl ester of δ -bromobutyl-n-butylboronic acid (I) led to 2-n-butyl-1,2-oxaborinone (II) in ~50% yield. On more detailed investigation of the reaction it was discovered that the moderate yield of (II) was explained by the secondary formation of a highboiling compound (III) having empirical formula $C_{18}H_{40}B_2O_3$. On oxidation of this compound with H_2O_2 in alkaline medium 4-methoxy-1-butanol and n-butanol were obtained in ~1:1 ratio. Consequently, compound (III) is the anhydride of δ -methoxybutyl-n-butylboronic acid, and thus on alkaline hydrolysis of ester (I) substitution of a bromine atom both by OH and by OCH₃ had occurred although the ratio of the reaction products was

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approximately unity. It is known that esters of boroorganic acids dissolve in alkali with the formation of salts of borinic acids [6-8].

Considering the ease with which substitution of bromine by OH and OCH_3 groups occurred in ester (I) it must be proposed that this is accomplished in the boranate anion (IV) by intramolecular nucleophilic attack on the C – Br bond by OH and OCH_3 groups bonded to the boron atom.



The methyl ester of δ -hydroxybutyl-n-butylboronic acid (V), formed as an intermediate, underwent intramolecular transesterification being converted into 2-n-butyl-1,2-oxaborinane (II). Dehydration of δ -methoxybutyln-butylboronic acid (VI) into the anhydride (III) occurred in all probability on distillation in vacuum.

In the light of this mechanism it became obvious that to increase the yield of (II) it was necessary to exclude substitution of the bromine atom by OCH_3 i.e., to start from boroorganic compounds containing no OCH_3 on the boron atom. It is convenient to use δ -bromobutyl-n-butylboronic acid (VII) or its anhydride (VIII) as such a compound. The acid was readily formed on hydrolysis of ester (I) with water.

$$(I) \xrightarrow{H_1O} Br(CH_2)_4B \xrightarrow{OH} \xrightarrow{-H_1O} \frac{1}{2} \begin{bmatrix} R \\ Br(CH_2)_4B \\ (VII) \end{bmatrix}_2 O$$

In practice it was shown that alkaline hydrolysis of acid (VII) or its anhydride (VIII) led to (II) in 84.5% yield [9].

Acid (VII) may also be obtained by the hydrolysis of bromo- δ -bromobutyl-n-butylborane pyridinate (IX) formed on bromination of 1-n-butylboracyclopentane. For the purpose of preparing (II) it is more convenient to proceed from 1-n-butylboracyclopentane, without isolating intermediate reaction products, and this led to a significant increase in yield. Thus, (II) was obtained in 80.5% yield starting from 1-n-butylboracyclopentane by bromination of the pyridine complex and subsequent hydrolysis.

$$\begin{array}{c}
\begin{array}{c}
\begin{array}{c}
\end{array} BR \frac{1}{2} & Py \\
\end{array} & \begin{array}{c}
\end{array} & \begin{array}{c}
\end{array} & \begin{array}{c}
\end{array} & Br \\
\end{array} & Br \\
\end{array} & Br \\
\end{array} & \begin{array}{c}
\end{array} & H_{0}O \\
\end{array} & (VII) & \begin{array}{c}
OH^{-} \\
OH^{-} \\
\end{array} & (II) \\
\end{array}$$
(IX)

Similarly 2-n-hexyl-1,2-oxaborinane (X) was synthesized in 72.3% yield from 1-n-hexylboracyclopentane

$$(BR' \rightarrow \bigcup_{\substack{B \\ B'}} (X) \qquad R' = n - C_{g} H_{13}$$

Alkaline hydrolysis of ô-bromobutylboronic acid led to 2-hydroxy-1,2-oxaborinane (XI).

$$Br(CH_2)_{4}B(OH)_{2} \xrightarrow{OH^{-}} B \xrightarrow{BOH} B \xrightarrow{B$$

It is interesting to note that compound (XI), being a cyclic semiester of an alkylboronic acid, may be redistilled in vacuum and was obtained in analytically pure form although it also undergoes partial dehydration. The determination of the molecular weight of acid (XI) cryoscopically in benzene gave an enhanced value which was linked with association of (XI) due to the formation of intermolecular hydrogen bonds. In actual fact there was only a wide absorption band at $\sim 3400 \text{ cm}^{-1}$ in the IR spectrum of pure (XI). In CCl₄ solution a band for the free OH group appeared (3625 cm⁻¹). Depending on the dilution of (XI) the intensity of the bond at 3625 cm⁻¹ grew and the band at $\sim 3400 \text{ cm}^{-1}$ was reduced accordingly. However, even at 0.005 N solution a small amount of compound (XI) having associated OH groups was still noticeable.

2-n-Butyloxy-1,2-oxaborinane (XII) was obtained on esterification of (XI) with n-butanol. Hydrolysis of bromo-5-bromohexyl-n-hexylborane led to 7-methyl-2-n-hexyl-1,2-oxaborepane (XIII) in 73% yield.



The seven-membered 1,2-oxaborepane condensed with a benzene ring as in 2-n-butyl-6,7-benzo-1,2-oxaborepane (XIV) was obtained by the hydroboration of o-allylphenol with a mixture (1:1) of tetra-n-butyldiborane and tri-n-butylborane with subsequent cyclization on distillation of the first formed diboron compound. Cyclization was catalyzed by compounds containing > B - H groups which were present in the reaction mass.



 $R = n - C_4 H_9$

The structure of compound (XIV) was proved by oxidizing it with H_2O_2 in alkaline medium into o-(γ -hydroxy-propyl)phenol (XV) which was isolated as the diacetate derivative.

Analysis of the GLC and PMR spectral data of compound (XIV), of its oxidation products, and of their acetyl derivatives indicated that (XIV) was a single substance. Consequently, the boron atom of tetra-n-butyl-diborane added exclusively to the terminal C-atom of the double bond in allylphenol.

Another method of preparing 1,2-oxaborepanes developed by us was based on the hydroboration of 2,3dihydropyran and of its derivatives with a tetraalkyldiborane.

According to patent data [10], on reacting diborane with an excess of 2,3-dihydropyran, subsequent heating of the reaction products at 145-200° for 10 h, and hydrolysis with water 5-penten-1-ol was formed. In the opinion of the authors trialkylborane (XVI) was formed in the first step and is an unusual cyclic β -alkoxyborane.

 β -Alkoxyethylboranes are unstable and undergo thermal β -fission being converted finally into borate esters [11]. Compound (XVI) also underwent β -fission, tri-(5-pentenyl) borate (XVII) was formed in this way and was converted without isolation into 5-penten-1-ol.

$$3 \underbrace{\bigcirc}_{O} \xrightarrow{V_{3}B_{3}H_{4}} \left(\underbrace{\bigcirc}_{O} \right)_{3} B \xrightarrow{\Delta} B[O(CH_{2})_{3}CH=CH_{2}]_{3} \xrightarrow{H_{3}O} 3CH_{2}=CH(CH_{2})_{3} \cup H_{2}$$
(XV1) (XV11)

Hydroboration of borate (XVII) led to a polymeric product on hydrolysis of which tri-(5-hydroxypentyl)borane (XVIII) was formed as was demonstrated by its oxidation to 1,5-pentanediol.

$$(XVII) \xrightarrow{1. B_{2}H_{4}} B[(CH_{2})_{5}OH]_{3} \xrightarrow{H_{6}O_{6}} 3HO(CH_{2})_{5}OH$$
(XVIII)

Later it was found [12] that the β -fission was catalyzed by such Lewis acids as BF₃. In study [13] a simple method was developed for obtaining unsaturated alcohols from dihydropyrans and dihydrofurans using BF₃. It is interesting to note that if diborane instead of BF₃ is added to the product of hydroboration of 2,3-dihydropyran (XIX) then reduction of the C - O bond proceeded in addition to β -fission.



Hydroboration of 2,3-dihydropyran by the stoichiometric amount of diborane, catalytic fission of (XIX) in the

presence of BF_3 etherate, subsequent hydroboration, and oxidation led to a 9:1 mixture of 1,5- and 1,4-pentanediols [13].

It was found by us that if a tetraalkyldiborane was used as a hydroborating agent in place of diborane then the pentenyl ester of a dialkylboronic acid (XX) was formed.



Ester (XX) was converted on further hydroboration into the diboron compounds (XXI) and (XXII) which, as was shown previously [14], readily cyclized into 1,2-oxaborepanes and 1,2-oxaborinanes.



Thus on interacting equimolar amounts of tetra-n-hexyldiborane and 2,3-dihydropyran with subsequent heating of the reaction products at 120° for 2 h and distillation, 2-n-hexyl-1,2-oxaborepane (XXV) was obtained in 90% yield which according to GLC data contained \sim 7% isomeric 3-methyl-2-n-hexyl-1,2-oxaborinane (XXVI).



In the case of 6-ethoxy-2,3-dihydropyran the reaction proceeded in a more complicated manner and in place of the expected 2-n-hexyl-7-ethoxy-1,2-oxaborepane (XXIX), compound (XXV) was obtained in 70% yield containing ~10% (XXVI) according to GLC data.



Evidently at the stage of forming compound (XXVII) or (XXVIII) an unusual β -fission occurred with separation of the ethyl ester of a dialkylboronic acid (detected in the reaction products) and a pentenal or aldehyde (XXX), respectively, which were converted into (XXV) on subsequent hydroboration.

 $(XXVIII) \xrightarrow{\Delta}_{-R_{4}'BOC_{4}H_{4}} (XXV) \xrightarrow{D_{4}'(R_{4}'BH)_{4}} (XXV) \xrightarrow{D_{4}'(R_{4}'BH)_{4}} (XXV)$

It is also possible that the formation of (XXV) from 6-ethoxy-2,3-dihydropyran occurred as a result of exchange of OC_2H_5 by a hydrogen atom of the tetraalkyldiborane or some intermediate borane such as (XXXI).



A similar cleavage of a C - O bond occurred under the action of diborane in tetrahydrofuran (THF) [15]. This process takes place particularly easily if the C - O bond is weakened by coordination with a neighboring boron atom [13].

EXPERIMENTAL

All operations with boroorganic compounds were carried out in an atmosphere of dry nitrogen. 1-Alkylboracyclopentanes and the methyl esters of δ -bromobutyl-n-butylboronic and δ -bromobutylboronic acids were obtained by the methods in [16]. Tetra-n-butyl- and tetra-n-hexyldiborane were synthesized by passing diborane into an ether solution of the trialkylborane [17]. o-Allylphenol was prepared by the method in [18] and 6-ethoxy-2,3-dihydropyran was obtained from acrolein and ethyl vinyl ether according to [19].

<u>Hydrolysis of δ -Bromobutyl-n-butylboronic Acid Methyl Ester</u>. Potassium hydroxide solution (20%: 172 g) was added to δ -bromobutyl-n-butylboronic acid methyl ester (106.1 g) and the ester dissolved. The resulting solution was left overnight (reaction occurred ~75% in this time). To complete the hydrolysis the reaction mass was heated at 70-80° for ~2 h while following the course of the reaction by the formation of KBr (AgNO₃ titration). The reaction mixture was acidified with dilute H₂SO₄, extracted with isopentane, the solvent removed in vacuum, and the following were isolated from the residue * (76.6 g, n_D²⁰ 1.4350) by fractional distillation on a Hempel column with metallic packing: 1) 2-n-butyl-1,2-oxaborinane (II) (29.7 g: 47%) of bp 48-51° (9 mm), n_D²⁰ 1.4340 [5]; 2) δ -methoxybutyl-n-butylboronic acid anhydride (III) (30.8 g: 42%) of bp 135-137° (3 mm), n_D²⁰ 1.4380. Found: C 66.04; H 12.26; B 6.40%. C₁₈H₄₀B₂O₃. Calculated: C 66.28; H 12.36; B 6.63%.

<u> δ -Bromobutyl-n-butylboronic Acid Anhydride (VIII)</u>. Bromine (57.0 g) in benzene (100 ml) was added to a solution of 1-n-butylboracyclopentane (70.4 g) in benzene (100 ml) and kept overnight. The mixture was then boiled for 3 h, cooled to ~20°, and water (100 ml) and isopentane (0.5 liter) added. The organic layer was separated, washed with water, and the solvent distilled off. Compound (VIII) (59.6 g: 81%) was isolated by distillation of the residue and had bp 181-182° (4 mm); d_4^{20} 1.1672; m_D^{20} 1.4735. Found: C 45.26; H 8.11; B 5.07; Br 37.79%. C₁₆H₃₄Br₂O. Calculated: C 45.23; H 8.07; B 5.09; Br 37.61%.

<u>2-n-Butyl-1,2-oxaborinane (II).</u> a) Potassium hydroxide solution (20%: 57.0 g) was added to (VIII) (23.7 g), the mixture was heated at 70-80° for 2 h, then acidified with dilute H_2SO_4 , and extracted with isopentane. Compound (II) (13.2 g: 84.5%) was isolated from the organic layer and had bp 70-73° (24 mm); n_D^{20} 1.4345.

b) Pyridine (22.7 g) in benzene (50 ml) was added dropwise to a solution of freshly distilled 1-n-butylboracyclopentane (35.4 g) in benzene (100 ml), 1 h later bromine (47 g) in benzene (100 ml) was added, and the mixture was left overnight. On the following day the mixture was boiled for 2-3 h, cooled to ~20°, water (50 ml) was added, the organic layer was separated, the solvent was distilled off in vacuum, and 20% KOH (100 ml) was added to the residue. The solution was heated at 70-80° for 2.5 h, acidified with dilute H_2SO_4 , and extracted with isopentane. Compound (II) (32.1 g: 80.5%) was isolated by distillation and had bp 69-73° (24 mm); np^{20} 1.4345.

Hydrogen peroxide (~25%: 45 ml) was added dropwise to 0 to 5° to (II) (21.7 g) in 20% KOH (50 ml), the mixture was kept overnight, then extracted with ether, and the organic layer separated. n-Butanol (9.1 g: 82%) was isolated by distillation and had bp 116-119°, np²⁰ 1.3995. The aqueous layer was saturated with K₂ K₂CO₃ and extracted with tetrahydrofuran (THF). 1,4-Butanediol (10.9 g: 81%) was isolated from the THF extract by distillation and had bp 101-103° (3 mm); np²⁰ 1.4455.

<u>2-n-Hexyl-1,2-oxaborinane (X).</u> Compound (X) was obtained similarly to the preceding experiment b) from 1-n-hexylboracyclopentane (122 g), pyridine (65 ml), bromine (129.5 g), and 20% KOH (300 ml). It had bp 80-83° (4 mm); n_D^{20} 1.4403 [5].

<u> δ -Bromobutylboronic Acid.</u> The dimethyl ester of δ -bromobutylboronic acid (69.2 g) and water (250 ml) were shaken vigorously until formation of a white solid and the mixture was kept overnight. The resulting acid was filtered off, washed with water, and dried in vacuum. δ -Bromobutylboronic acid (52.3 g: 87%) was

*Residue (5 g) in 5 N NaOH (6.4 ml) was oxidized with 30% H₂O₂ (10 ml). The following were found by GLC in a THF solution of the oxidation products: n-butanol (2 g), 4-methoxy-1-butanol (1.41 g), and 1,4-butanediol (0.97) g). The ratio of 4-methoxybutanol to 1,4-butanediol was 56:44.

obtained having mp 84-85° (from benzene – hexane). Found: C 26.59; H 5.60; B 6.06; Br 43.70%. C₄H₁₀-BBrO₂. Calculated: C 26.56; H 5.57; B 5.98; Br 44.18%.

<u>2-Hydroxyl-1,2-oxaborinane (XI).</u> δ-Bromobutylboronic acid (54.3 g) and 10% KOH (250 g) were heated at 60-90° for 2-3 h, the mixture was acidified with dilute H_2SO_4 , extracted with ether, and the solvent removed in a water pump vacuum. Compound (XI) (28.1 g: 94.5%) was obtained in the residue as a thick liquid which may be redistilled in an oil pump vacuum but during this (XI) underwent a significant degree of dehydration being converted into the anhydride. Thus on distilling the residue through a Hempel column with glass packing (XI) (8.2 g) was obtained having bp 35-40° (3 mm); n_D^{20} 1.4455. An analytically pure specimen had bp 36-37° (3 mm); n_D^{20} 1.4460. Found C 47.56; H 8.88; B 10.62% mol. wt. 128. C₄H₉BO₂. Calculated: C 48.07; H 9.08; B 10.83%; mol. wt. 99.93. In addition the anhydride (4.4 g) of (XI) was obtained having bp 90-93° (3 mm). Found: C 52.91; H 8.76; B 11.87%. C₈H₁₉B₂O₃. Calculated: C 52.83; H 8.77; B 11.9%. On subsequent distillation (XI) was completely converted into the anhydride.

<u>2-n-Butyloxy-1,2-oxaborinane (XII)</u>. Potassium hydroxide solution (20%: 120 g) was added to δ -bromobutylboronic acid (60.2 g), the mixture was left overnight, then heated at 60-90° for 2.5 h, cooled to ~20°, acidified with dilute H₂SO₄, extracted with ether, and the ether was distilled off. n-Butyl alcohol (23.8 g) and benzene (100 ml) were added to the residue of (XI), and the water formed on esterification was separated using a Dean and Stark adapter. Compound (XII) (34.6 g: 68%) was obtained by distillation using a Hempel column with metallic packing and had bp 59-61° (8 mm); mD²⁰ 1.4307. Found: C 61.61; H 10.88; B 6.79\%. C₈H₁₇BO₂. Calculated: C 61.55; H 10.98; B 6.93\%.

<u>7-Methyl-2-n-hexyl-1,2-oxaborepane (XIII)</u>. Benzene (50 ml), pyridine (9.2 ml), and water (30 ml) were added to bromo-5-bromohexyl-n-hexylborane which had been obtained from 7-methyl-2-n-hexyl-1,2-oxaborepane (25.0 g) [14] and PBr₅ (54.5 g) at 120-130° with subsequent distillation of the POBr₃ formed. The organic layer was separated, the solvent distilled off in vacuum, 20% KOH (75 g) was added to the residue, the mixture was heated at 70-80° for 5 h, acidified with dilute H_2SO_4 , and extracted with benzene. Compound (XIII) (9.1 g: 72.8%) was isolated by distillation and had bp 66-68° (1 mm); mp²⁰ 1.4410 [14].

<u>2-n-Butyl-6,7-benzo-1,2-oxaborepane (XIV).</u> o-Allylphenol (64 g) in absolute ether (50 ml) was added at 0 to 5° over 2 h to a solution of tetra-n-butyldiborane (126.1 g) and tri-n-butylborane (91.2 g) in absolute ether (180 ml) and the mixture was left overnight. Tri-n-butylborane (175 g: 96%) was distilled off in vacuum and methanol (25 ml) was added to the residue. Compound (XIV) (86.4 g: 90%) was isolated by distillation through a Hempel column with glass packing and had bp 85-86° (1 mm); n_D^{20} 1.5042. Found: C 77.31; H 9.56; B 5.02 $\frac{7}{6}$; mol. wt. 200. C₁₃H₁₉BO. Calculated: C 77.25; H 9.47; B 5.34%; mol. wt. 202.

Hydrogen peroxide (20%: 35 ml) was added at 0 to 5° to (XIV) (15.0 g) in 3 N NaOH (28 ml) and the mixture left overnight. The following day the mixture was extracted with ether, the solvent distilled off, and to the residue [consisting of n-butyl alcohol and o-(γ -hydroxypropyl)phenol] was added pyridine (17 ml) in ether (50 ml) and AcCl (16.2 g), and the mixture was left overnight. The following day the reaction mass was boiled for 1 h and the solid filtered off. Ether and butyl acetate were distilled from the filtrate in vacuum and o-(γ -acetoxypropyl)phenyl acetate (14.1 g: 81%) was isolated having bp 128-129° (3 mm); mD²⁰ 1.4970, which according to GLC data contained practically no contamination by isomers. Found: C 66.13; H 6.84%. C₁₃H₁₆-O₄. Calculated: C 66.08; H 6.83%.

<u>2-n-Hexyl-1,2-oxaborepane (XXV) from 2,3-Dihydropyran.</u> Dihydropyran (26.0 g) was added to a solution of tetra-n-hexyldiborane (114.4 g) in absolute ether (100 ml) and the mixture was left overnight. After distilling off ether the residue was heated at 120° for 2 h. Compound (XXV) (53.7 g: 94%) was obtained by distillation on a Hempel column and had bp 66-68° (1.5 mm); mD^{20} 1.4460. Compound (XXV) was boiled for 30 min with methanol (15 ml) (to destroy impurities containing B – H bonds) and distilled once again. Compound (XXV) (50.9 g: 90%) was obtained having bp 60-62° (1 mm); mD^{20} 1.4420 which by GLC (polyethylene glycol on xylite 545, 90°) contained ~7% (XXVI). Hydrogen peroxide (~30%: 34 ml) was added at 0-5° to the obtained (XXV) (18.2 f) in 20% NaOH (20 ml). The mixture was left overnight, then saturated with K₂CO₃, and extracted with THF. A mixture (8.3 g: 80%) of 93:71,5- and 1,4-pentanediols was isolated having bp 134-136° (12 mm); mD^{20} 1.4498 (literature data for 1,5-pentanediol, bp 119-120° (10 mm), mD^{20} 1.4499 [20]).

<u>2-n-Hexyl-1,2-oxaborepane (XXV) from 6-Ethoxy-2,3-dihydropyran.</u> 6-Ethoxy-2,3-dihydropyran (20.0 g) in absolute ether (20 ml) was added to tetra-n-hexyldiborane (91.0 g) in absolute ether (50 ml) and the mixture was left overnight. Ether was distilled off and the residue was heated at 120-140° for 1.5 h. A portion (42.0 g) was withdrawn from the reaction mixture, oxidized with ~30% H_2O_2 (7 ml), and gave a 9:1 mixture (4.57 g: 75'?) of 1,5-pentanediol and 1,4-pentanediol of bp 155-156° (30 mm), np^{20} 1.4496. The remainder was distilled

through a Hempel column with metallic packing taking the fraction with bp 80-100° (3 mm) (26.4 g). This fraction was heated with absolute methanol (15 ml) and then subjected to fractional distillation. Compound (XXV) (12.4 g: 70%) was obtained having bp 62-70° (1.5 mm); n_D^{20} 1.4420, which contained ~10% (XXVI) according to GLC.

SUMMARY

1. On alkaline hydrolysis of δ -bromobutyl-n-butylboronic acid methyl ester replacement of the bromine atom both by hydroxyl and methoxyl groups took place.

2. Convenient methods have been developed for the synthesis of 1,2-oxaborinanes and 1,2-oxaborepanes based on the alkaline hydrolysis of the corresponding δ -bromobutyl- or ε -bromoalkylboronic acids or their anhydrides.

3. Hydroboration of o-allylphenol, 2,3-dihydropyran, or 6-ethoxy-2,3-dihydropyran with tetra-n-butyland tetra-n-hexyldiborane gave 2-n-butyl-6,7-benzo-1,2-oxaborepane and 2-n-hexyl-1,2-oxaborepane as appropriate.

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