ORGANOBORON COMPOUNDS.

377. SYNTHESIS OF 3-BORAHOMOADAMANTANE COMPLEXES

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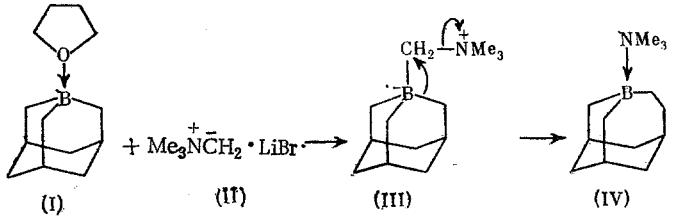
One of the properties of organoboron compounds is their ability to react with the methylides of phosphorus [1], nitrogen [2-4], sulfur [5, 6], and arsenic [7], as a result of which the chain of the radical on the boron atom is enriched by a methylene group. It seemed of interest to apply this reaction to 1-boraadamantane [8-12], in which the trivalent B atom is found in a tetrahedral valence state. It could be expected that 3-borahomoadamantane is obtained when a CH_2 group is inserted into the 1-boraadamantane molecule, whose study would lead to an expansion of the chemistry of strained boron-containing polyhedral systems.

For this purpose we studied the reaction of the tetrahydrofuran complex of 1-boraadamantane (I) [11] with trimethylammonium methylide (II) [3, 13], and here the trimethylamine complex of 3-boratricyclo[4.3.1.1^{3,8}]undecane (trimethylamine-3-borahomoadamantane) (IV) is actually formed in 60% yield.



The unstable adduct of the ylide with 1-boraadamantane (III) is initially formed in the reaction, as can be seen from the PMR spectra: the spectrum of the reaction mixture, obtained after treatment with water to remove the unreacted (II), has, together with the proton signals of (IV) and the secondarily formed (6%) trimethylamine-1-boraadamantane (V), the proton signals of (III), (δ, ppm): 2.91 $(CH_3N)^+$, 1.61 $(CH_2CC\overline{B})$, 0.40 $(CH_2\overline{B})$, which disappear with time. The crystalline (IV) complex is heat stable and does not dissociate when vacuum-distilled.

The ratio of (IV) and (V) in the reaction products was established by mass spectrometry. In the mass spectra the most characteristic are the peaks of the ions with m/e 207, 193, 148, and 134. The first and second are the peaks of the molecular ions $[M]^+$ of complexes (IV) and (V), while the third and fourth are the peaks of the ions of the free $[M - \text{ligand}]^+$ of 3-borahomoadamantane (VI) and 1-boraadamantane (VII). In the mass spectrum of the pure (V) the M^+ peak (193) is much more intense than the peak of the (VII) ion (134). The reverse ratio in the intensities of the peaks of M^+ (207) and ion (VI) (148) is characteristic for (IV), which attests that (IV) is less stable than (V). For analytical purposes we prepared mixtures of (IV) and (V) with a variable ratio of the components. A study of the mass spectra of these mixtures disclosed that the ratio of the components approximated the ratio of the intensities of the peaks of the (VI) (148) and (V) (193) ions. The ratio of the intensities of the peaks with masses 148 and 193 in the spectra of the same mixture's sample remained practically unchanged in the range 20-80°C.

The ratio of (IV) and (V) in the reaction product could also be judged by analyzing the compounds obtained by its acidolysis. Thus, the reaction of (IV) (containing ~6% of (V), based on the mass spectral data) with stearic acid, with heating (1.5 h, 250-260°) in vacuo (120 torr), gave in 59% yield cis-5-ethyl-1,3-dimethylcyclohexane (VIII), contaminated

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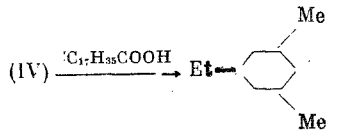
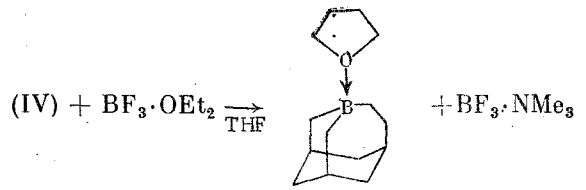
with ∿5.5% of cis-1,3,5-trimethylcyclohexane (GLC). The purity of the (VIII) isolated by preparative GLC was 99%.



(VIII)

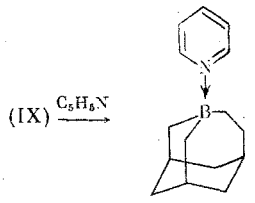
The stable (IV) could be converted to the less stable THF complex of 3-borahomoadamantane (IX) by treating (IV) with BF_3 etherate in THF. Here the BF_3 etherate is converted to trimethylamine·BF_3, while the formed 3-borahomoadamantane gives (IX):



(IX)

Complex (IX), obtained in 72% yield, contained 11% of (I), since the starting (IV) was contaminated with (V). After a double recrystallization from isopentane the amount of (I) dropped to 4%.* Complex (IX) represents colorless crystals that are unstable in the air.

Similar to compound (I) [12], (IX) when treated with pyridine is converted to pyridine-3-borahomoadamantane (X), which, in contrast to (IV), gradually decomposes in air.



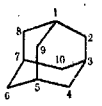
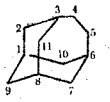
(X)

The ^{13}C NMR spectral data confirm the structure of (IV), (IX), and (X) (Table 1). In the spectrum of (IV), containing ∿6% of (V), together with the signals, characteristic for (IV), were present weak signals of the carbon atoms of (V). As followed from the ^{13}C NMR and mass spectral data, the ratio of (IV) and (V) in the sample after its recrystallization did not essentially change. In the spectra of (IX) and (X), respectively containing below 4% of (I) and pyridine-1-boraadamantane (XI), the signals of these impurities were not detected. The assignment of the signals in the ^{13}C NMR spectra of (IV), (IX), and (X), given in Table 1, was based on the character of the multiplicity of the spectral lines, obtained under the conditions of a partial suppression of the ^{13}C—^{1}H spin—spin couplings (SSC), taking into account the integral intensity of the signals, and comparing the ^{13}C chemical shifts (CS) in the spectra of (IV), (IX), and (X) with the values of the shifts in the spectra of adamantane [14], homoadamantane [15], (V), (I) [16], and (XI). The signals of the C atoms, attached to the B atom ($C^{2,4,11}$), are very diffuse under the conditions of measuring the spectra (30°) and are not given in Table 1. For comparison, we have given the CS values of the β- and γ-carbons of the 1-boraadamantane complexes and the analogous C atoms of adamantane and homoadamantane.

In the spectrum of (IV), measured under the conditions of a partial suppression of the ^{13}C—^{1}H SSC, the signal at 39.5 ppm (3C), representing a triplet, was assigned to $C^{7,10}$ and C^{9}, the doublet at 29.6 ppm (2C) was assigned to $C^{1,8}$, and the signals at 32.6 ppm (1C, d) and 39.2 ppm (1C, t) were respectively assigned to C^{6} and C^{5}. The quartet at 47.7 ppm (3C) was caused by the C atoms in NMe_3. In the spectrum of (IX) the signal at 38.7 ppm (3C), representing a triplet, was assigned to $C^{7,10}$ and C^{9}, the triplet at 29.3 ppm (1C) was assigned to C^{5}, and the doublets at 29.3 ppm (1C) and 32.6 ppm (1C) were respectively assigned to $C^{1,8}$ and C^{6}. The triplets at 67.9 ppm (2C) and 25.0 ppm (2C) were caused by the

*To determine the amount of (I) in (IX) the recrystallized product was treated with trimethylamine, and then the mixture of obtained (IV) and (V) was analyzed via the mass spectra.

TABLE 1. ^{13}C Chemical Shifts (δ, ppm) in Spectra of Complexes of 1-Boradamantane and 3-Borahomoadamantane

Compound	$C^{3,5,7}$	$C^{4,6,10}$	Ligand C	Compound	$C^{1,8}$	C^{2}	$C^{7,10}$	C^{9}	C^{5}	Ligand C
	28,5	37,8	–		27,7	32,1	38,4	36,5	34,0	–
Trimethylamine-1-boraadamantane (V)	32,9	40,3	47,3	(IV)	29,6	32,6	39,5	39,5 *	39,2 *	47,7
(I)	33,9	40,0	68,5(α) 24,5(β)	(IX)	29,6	32,6	38,7	38,7	29,3	67,9(α) 25,0(β)
Pyridine-1-boraadamantane (XI)	32,9	40,2	144,7(α) 124,8(β) 138,3(γ)	(X)	29,9	33,4 †	39,5	39,0	33,5†	144,7(α) 124,8(β) 138,3(γ)

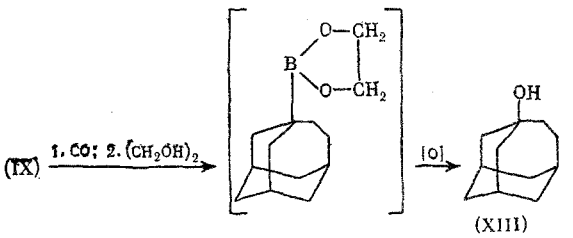
*, †The CS can be transposed in places.

carbon atoms of THF. In the spectrum of (X) the signals at 39.5 ppm (2C) and 39.0 ppm (1C) (triplets) were assigned to $C^{7,10}$ and C^9, and the signal at 29.9 ppm (2C) (doublet) was assigned to $C^{1,8}$. The two close signals at 33.4 ppm (1C) and 33.5 ppm (1C) were respectively assigned to C^6 and C^5. In the 120-150 ppm region, characteristic for the signals of aromatic hydrocarbons, are observed the signals of the pyridine C atoms.

The made assignment of the signals makes it possible to estimate the effect of the $>B\leftarrow L$ fragment on the value of the ^{13}C CS and the character of the changes when going from adamantane and homoadamantane to the complexes of their boron-containing analogs.

From the data in Table 1 it follows that in the spectra of the 1-boraadamantane complexes the observed signals of the C atoms are shifted downfield relative to the corresponding signals in the spectrum of adamantane ($\Delta\delta CH$ = 4.4; 5.4; 4.4 ppm; $\Delta\delta CH_2$ = 2.5; 2.2; 2.4 ppm). A shift in the same direction, but to a lesser degree, is experienced by the signals of the C atoms of the corresponding methine $C^{1,8}$ and methylene $C^{7,10}$ groups of (IV), (IX), and (X) relative to the position of the signals of these atoms in the spectrum of homoadamantane. The C^6 and C^9 signals in the spectra of (IV), (IX), and (X) are also shifted downfield when compared with the signals of these atoms in homoadamantane. Mention should be made of the sharp change in the value of the C^5 CS when going from (IV) to (X) and (IX), and also of the closeness or coinciding of the $C^{7,10}$ and C^9 CS values, whereas the position of the $C^{7,10}$ and C^9 signals in the spectra of a homoadamantane [15] with substituents in the 3 position [15, 17] is noticeably different. As can be seen from Table 1, the transition from the adamantane to the homoadamantane structure is characterized in general by the same direction in the changes of the ^{13}C CS values in both the hydrocarbons and the complexes of their boron-containing analogs.

It is known [8-10] that (I) by carbonylation with CO and subsequent oxidation is converted to 1-adamantanol (XII). Compound (IX) was converted by this method to 3-homoadamantanol (XIII), which after purification contained 2.3% of (XII).



(XIII)

The ^{13}C NMR (identical with the literature data [17]) and mass spectral data confirm the structure of (XIII).

EXPERIMENTAL

All of the reactions with the organoboron compounds were run in an argon atmosphere. Tetrahydrofuran-1-boraadamantane (I) was synthesized according to [11], and trimethylamine-1-boraadamantane (V) and pyridine-1-boraadamantane (XI) were synthesized according to [12]. cis-1,3,5-Trimethylcyclohexane was obtained by the methanolysis and subsequent acidolysis of (I). The PMR spectra were measured on a Tesla BS-497 spectrometer (100 MHz) relative to TMS. The ^{13}C NMR spectra were measured on a Bruker WP-60 spectrometer (15.08 MHz) relative to TMS. The solvent was $CHCl_3$, and in the case of (IX) it was CCl_4. The mass spectra were measured on a Varian CH-6 spectrometer. The GLC was run on a Chrom-3 chromatograph.

Complex of Trimethylammonium Methylide with LiBr (II) [3, 13]. A mixture of 19.3 g (125 mmoles) of dry Me_4NBr powder in 260 ml of a 1.0 N ether solution of PhLi was shaken vigorously with beads in a sealed ampul for 42 h. The solution was decanted and the residue was washed with ether (3 × 30 ml). We obtained 22.6 g of a colorless powdery product, which, based on acidimetric titration, contained 14.2 g (89 mmoles) of (II). Yield 71%.

Trimethylamine-3-borahomoadamantane (IV). With stirring and cooling to −65°, to 6.4 g (40 mmoles) of (II) was added in 20 min a solution of 7 g (34 mmoles) of (I) in 55 ml of THF. The mixture was stirred for 4 h with gradual elevation of the temperature to 20° and then left standing overnight. The solvent was vacuum-distilled, and 30 ml each of H_2O and CH_2Cl_2 were added to the residue. The organic layer was separated, washed with 15 ml of

H_2O, and dried over Na_2SO_4. The solvent was distilled off, and the residue was dissolved in 20 ml of monoglyme and refluxed for 2.5 h. The monoglyme was vacuum-distilled, while the residue was distilled at 2 mm to give 4.2 g (60%) of (IV), contaminated with ∿6% of (V), mp 150-156° (from alcohol). PMR spectrum (δ, ppm, $CHCl_3$): 0.43-0.68 m (CH_2B), 2.23-2.11 m (remaining H atoms of 3-borahomoadamantane), 2.34 s (CH_3N). Found: C 74.96; H 12.61; B 5.30%. $C_{13}H_{26}BN$. Calculated: C 75.36; H 12.65; B 5.22%.

Tetrahydrofuran-3-borahomoadamantane (IX). With stirring and cooling to −60°, to 9.6 g (60 mmoles) of (II) was added in 20 min a solution of 10.3 g (50 mmoles) of (I) in 75 ml of THF. The mixture was stirred for 4 h with gradual elevation of the temperature to 20° and then left standingovernight. The solvent was vacuum-distilled, 30 ml of H_2O and 40 ml of CH_2Cl_2 were added to the residue, and the organic layer was separated, washed with 20 ml of H_2O, and dried over Na_2SO_4. The solvent was distilled off and the residue was refluxed with 25 ml of monoglyme for 2.5 h. The monoglyme was vacuum-distilled to give as residue 11.4 g of yellow crystalline (IV), contaminated with 11% of (V) (mass spectrometry). The substance was dissolved in 20 ml of THF, and8.1 g (57 mmoles) of $BF_3 \cdot OEt_2$, distilled over CaH_2, was added to the solution. After 3 h the solvent and excess $BF_3 \cdot OEt_2$ were evaporated in vacuo. Extraction of the residue with hexane (4 × 20 ml) gave 8.3 g (72%) of (IX) (contaminated with 11% of (I)). A double recrystallization from isopentane gave (IX) as colorless crystals (containing less than 4% of (I)), mp 55-70°. Found: C 75.30; H 11.27; B 5.38%. $C_{14}H_{25}BO$. Calculated: C 76.36; H 11.45; B 4.91%.

Pyridine-3-borahomoadamantane (X). To a solution of 0.75 g (3.4 mmoles) of (IX) (less than 4% of (I) as impurity) in 3 ml of THF was added a solution of 0.3 g (3.8 mmoles) of pyridine in 3 ml of THF. The solvent and excess pyridine were evaporated in vacuo. We obtained 0.77 g (99%) of (X) with mp 104-107° (from alcohol). Mass spectrum: 227 $[M]^+$, 148 $[M - \text{ligand}]^+$. Found: C 79.01; H 9.73; B 4.87%. $C_{15}H_{22}BN$. Calculated: C 79.31; H 9.65; B 4.58%.

cis-5-Ethyl-1,3-dimethylcyclohexane (VIII). To 30 g of stearic acid was added 3.8 g (18.5 mmoles) of (IV) (contaminated with ∿6% of (V)) in 10 ml of THF, the solvent was distilled off, and the residue was heated in vacuo (120 torr) to 180°, and here the Me_3N was collected in a trap, cooled in an acetone–dry ice mixture, and subsequently isolated as the methiodide (14.5 mmoles). Then the mixutre was heated to 250° and kept at this temperature for 1.5 h. Here the liquid that distilled into the receiver was washed in succession with 20% NaOH solution and H_2O, dried over Na_2SO_4, and distilled. We obtained 1.53 g (59%) of a mixture of (VIII) (94.5%) and cis-1,3,5-trimethylcyclohexane (5.5%) (GLC). The pure (VIII), containing less than 1% of impurity, was isolated by preparative GLC. Bp 167-168°, n_D^{20} 1.4349. ^{13}C NMR spectrum (δ, ppm, the numbering of the carbons is given in parentheses): 32.7 (1), 44.7 (2), 41.9 (4), 39.6 (5), 22.8 (1'), 30.3 (1"'), 11.5 (2"'). Mass spectrum: 140 $[M]^+$. Found: C 85.43; H 14.71%. $C_{10}H_{20}$. Calculated: C 85.63; H 14.37%.

3-Homoadamantanol (XIII). Into a 150-ml autoclave was charged 30 ml of THF solution, which contained 6.20 g (46 mmoles) of (IX) contaminated with ∿15% of (I). CO was fed into the rotated autoclave under a pressure of 80 atm and the mixture was heated for 1 h at 120°. Then it was cooled, 2 ml of ethylene glycol was added, CO was passed in at 30 atm, and the mixture was heated to 120°. After cooling, the mixture was evaporated in vacuo to dryness, and to the residue were added 10 ml each of ether and THF, and12 ml of 10% NaOH solution. With vigorous stirring, to the mixture, cooled to 10°, was added 12 ml of 30% H_2O_2 solution, and the mixture was refluxed for 20 min. K_2CO_3 was added until the aqueous layer was saturated, the organic layer was separated, and the aqueous layer was extracted twice with ether, dried over Na_2SO_4, and evaporated in vacuo. We obtained 3.31 g of a yellow crystalline substance. After sublimation in vacuo (100-120°, 1.5 torr) and chromatographing an ether solution on a SiO_2 column we obtained 2.42 g (51.5%) of a colorless crystalline substance, which represented a mixture of 86% of (XIII) and 14% of (XII) (GLC). After repeated recrystallization from 40% isopropanol we isolated (XIII) contaminated with 2.3% of (XII); mp 272-275° (cf. 274.5-275.5° [18]). ^{13}C NMR spectrum (δ, ppm, $CDCl_3$, the numbering of the carbons is given in parentheses): 27.8 (1.8), 47.2 (2.11), 41.8 (4), 73.3 (3), 29.9 (5), 31.8 (6), 37.6 (7.10), 35.8 (9). Mass spectrum: 166 $[M]^+$.

CONCLUSIONS

1. 3-Borahomoadamantane was obtained from tetrahydrofuran-1-boraadamantane and trimethylammonium methylide as the complex with trimethylamine, tetrahydrofuran, and pyridine.

2. The acidolysis of trimethylamine-3-borahomoadamantane gave cis-5-ethyl-1,3-dimethylcyclohexane.

3. 3-Homoadamantanol was synthesized by the carbonylation of tetrahydrofuran-3-borahomoadamantane with CO.

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SYNTHESIS AND STERIC STRUCTURE OF 5-PHENYL-1,3,5-DIOXAPHOSPHORINANE AND ITS DERIVATIVES

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At the present time it may be considered as established that a Ph on the P atom in phosphorinanes is found preferably in the equatorial orientation. It was shown that in the equilibrium of the conformers of 1-phenylphosphorinane [1] at −80°C and 1-phenyl-4-tert-butylphosphorinane [2] at 140° the equatorial orientation of the Ph predominates (respectively 65 and 55%). These data also testify that the dependence of the position of the equilibrium on the temperature is negligible. As in the case of substituted cyclohexane and 5-substituted 1,3-dioxanes, in phosphorinanes the orientation of a Ph on the P atom is determined by the enthalpy factor. Analogous results were obtained when the 1-phenylphosphorinan-4-ones [3, 4] and their oxides and sulfides [3, 5] were studied.

The determining effect of the enthalpy factor on the orientation of substituents on the C and P atoms in six-membered rings made it possible to propose that when going from 1-phenylphosphorinane to 5-phenyl-1,3,5-dioxaphosphorinane the same effect will be observed as when going from phenylcyclohexane to 5-phenyl-1,3-dioxane [6]. To check this assumption

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