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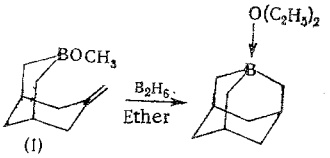
BOROORGANIC COMPOUNDS

315. THE SYNTHESIS OF 1-BORAADAMANTANE COMPOUNDS FROM TRIALLYLBORANE AND PROPARGYL CHLORIDE

B. M. Mikhailov and K. L. Cherkasova

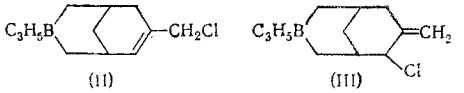
UDC 542.91:547.1'127

1-Boraadamantane is formed on hydroboration of 3-methoxy-7-methylene-3-borabicyclo[3.3.1]nonane (I) which is itself obtained from allene and triallylborane [1-3].



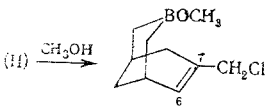
(I)

The problem arose as to the possibility of using, for the synthesis of 1-boraadamantane compounds, derivatives of 3-borabicyclo[3.3.1]nonane which were obtained from triallylborane and propargyl chloride [4, 5]. This reaction, depending on the conditions, leads to 7-chloromethyl-3-allyl-3-borabicyclo[3.3.1]non-6-ene (II) or to a mixture of (II) and 6-chloro-3-allyl-7-methylene-3-borabicyclo[3.3.1]nonane (III) in the ratio 4:1 [4, 5].



(II) (III)

Compound (III) may be converted by a simple route into 4-chloro-1-boraadamantane, but since its content in the mixture is small then our attention was first turned to compound (II) as a possible precursor of the 1-boraadamantane system. For this it was necessary to convert (II) into 3-methoxy-7-chloromethyl-3-borabicyclo-[3.3.1]non-6-ene (IV) and subject the latter to hydroboration.



(IV)

It might be expected that the boron atom will add not only to the sterically less hindered position 6 but also in some degree to position 7. The bases of this hypothesis are data on the hydroboration of 1-chloro-2-methyl-2-propene which adds the boron atom 12% at position 2 [6]. Of the two boranes (V) and (VI) able to be formed by the hydroboration of (IV), borane (VI), containing chlorine in the β position to the boron atom, must eliminate chloroborane [7-9] being converted into (I) the hydroboration of which leads as expected to 1-boraadamantane.

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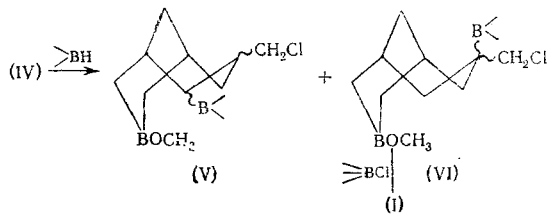


The indicated scheme of conversions failed to be achieved experimentally. Compound (II) [with a (III) content of ~5%] was obtained by keeping a mixture of triallylborane and propargyl chloride at 20° for 20 days with subsequent brief heating (~30 min) at 130°. Methanolysis of compound (II) readily gave ether (IV) [4, 5].

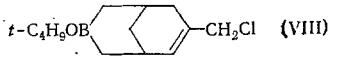
Tetraethyldiborane and diborane were used as hydroborating agents. The orientation of the addition of tetraethyldiborane was investigated first. The ratio of isomeric boranes (V) and (VI) may be assessed by the amount entering into reaction with the tetraalkyldiborane. For hydroboration 1 equivalent of hydride is required for 1 mole (IV). The consumption of hydride above this corresponds to the amount of compound (VI) formed since it is converted into (I) which consumes a further quantity of hydride on hydroboration.

The method was as follows. A solution of 15 mmole tetraethyldiborane in 50 ml tetrahydrofuran (THF) was prepared and the precise content of $R_4B_2H_2$ was determined by hydrolysis of 2-ml solution with a 1:1 mixture of H_2O + THF. The appropriate quantity (10 mmole) of compound (IV) was added to the remaining solution at 20°. In this way the initial mixture was a 0.2 N solution of olefin and a 0.6 N solution of hydride in THF. The absorption of >BH was determined by hydrolysis of an aliquot (2 ml) after a definite time interval.

It turned out (Table 1) that in the main the hydroboration of (IV) with tetraethyldiborane in THF at 20° was complete in 4 h. Further absorption of >BH went very slowly and reached a maximum (1.12-1.13 mole hydride) after 24 h. Thus, (IV) was hydroborated to 12-13% at position 7.

The orientation of the addition of diborane to (IV) was then studied. It is known that tetraalkyldiboranes possess a higher selectivity in relation to substituted double bonds than diborane and therefore in the case of diborane a large yield of compound (I) might be expected. In reality the boron atom was studied at position 7 to 27-28% on hydroboration of (IV) with diborane. The reaction was mainly complete after 4 h.

It was shown in study [10] that β elimination in boron-containing compounds was accelerated by acid catalysts such as BH_3. BF_3 also showed a catalytic action on the rate of reaction of compound (IV). BF_3 etherate at one third the amount of BH_3 accelerated the reaction so much that it was completed after 1 h. Traces of the etherate present in the diborane solution changed the reaction rate only insignificantly. It was interesting that 3-t-butoxy-7-chloromethyl-3-borabicyclo[3.3.1]non-6-ene (VIII),

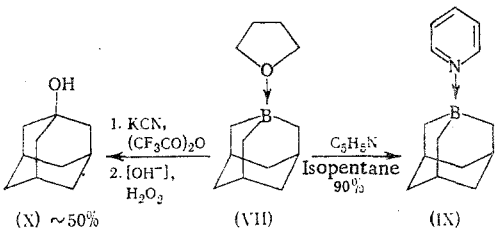


easily obtained by the action of t-C_4H_9OH on (II), reacted significantly more slowly with diborane at 20° than did (IV). After 1 h only 0.37 mole hydride was absorbed, after 6 h 0.57, after 96 h 1.00, and after 144 h 1.08 moles.

A successful method of isolating 1-boraadamantane from the reaction mixture proved to be sublimation of the complex with THF (VII) in a vacuum of 1 mm at 80-100°. In this way its yield on hydroboration with tetraethyldiborane was 9-10% and was 25-26% with diborane. The isolation of 1-boraadamantane from the reaction mixture as its tetrahydrofuran complex was effected almost quantitatively. The isolated complex of 1-boraadamantane with THF (VII) was completely identical in physicochemical properties with the compound obtained previously by another method [1-3]. The pyridinate (IX) of 1-boraadamantane was prepared by reaction of the latter with pyridine.

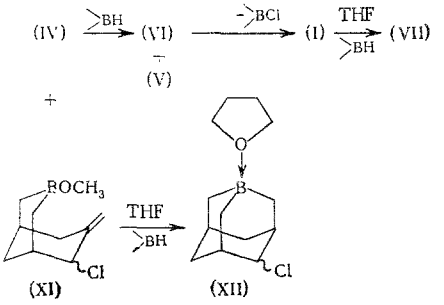
TABLE 1. Number of Moles of Hydride Consumed on Hydroboration of 1 Mole (IV) at 20°

Hydroborating agent	Time, h				
	1	2	4	20	44
$(C_2H_5)_4B_2H_2$	1,05	1,07	1,10	1,12	1,12
BH_3	1,10	1,17	1,26	1,27	1,28
$BH_3 + BF_3$ traces	1,17	1,22	1,26	1,27	1,28
$BH_3 + BF_3$ (3:1)	1,28	1,28		1,28	



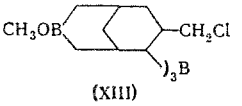
Complex (VII) was converted into 1-hydroxyadamantane which had previously been obtained by carbonylation of 1-boraadamantane with CO in ether solution in an autoclave by the method of [11, 12]. This compound was obtained by us by the method of [13] using KCN and $(CF_3CO)_2O$ in 50% yield. The physicochemical properties of compounds (IX) and (X) corresponded with the data in [1-3, 14, 15].

The results described on the hydroboration of compound (IV) made it possible to go over to a study of the hydroboration of a mixture of it with compound (XI). This mixture (in a 4:1 ratio) was obtained on adding propargyl chloride to triallylborane heated to 130° and by reacting the product with methanol [4, 5]. It might have been hoped that hydroboration of a mixture of (IV) and (XI) would lead to the formation of both 1-boraadamantane and also 4-chloro-1-boraadamantane by the following scheme. This expectation was justified.



Compounds (VII) and (XII) were successfully obtained by treatment of the mixture of (IV) and (XI) (in a 4:1 ratio) containing an equimolar amount of THF, and tetraethyl- or tetrapropyldiborane in isopentane. On cooling the THF complex of 4-chloro-1-boraadamantane (XII) was isolated, the yield of which was 17-19% [85-95% based on the isomer (XI) contained in the mixture], and from the residue the THF complex of 1-boraadamantane (VII) was obtained in 5-7% yield by sublimation in vacuum.

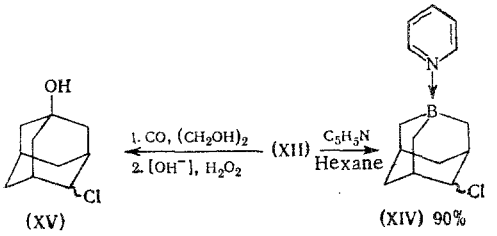
Diborane proved to be an unsuitable hydroborating agent for the preparation of 4-chloro-1-boraadamantane since the product (XIII) of addition of a boron atom at position 6 formed from (IV) was isolated from the solution in addition to (XII).



(XIII)

The complex (XII) was characterized by ^1H and ^{11}B NMR spectra and also by elemental analysis. Compound (XII) with pyridine in hexane gave 4-chloro-1-boraadamantane pyridinate (XIV) in ~90% yield. 1-Hydroxy-4-chloroadamantane (XV) was obtained in ~20% yield by the carbonylation of complex (XII) with CO.

Compounds (XIV) and (XV) were characterized by IR, PMR, and mass spectra and also by elemental analysis.



(XV)

(XIV) 90%

In contrast to the THF complex, (XIV) was fairly stable in air and could be recrystallized from methanol.

Compound (V), remaining after the isolation of the THF complex of 1-boraadamantane, was converted into (XVI) on adding $LiB(C_2H_5)_4$.

(XVI)

EXPERIMENTAL

IR spectra were taken on UR-10 and UR-20 instruments. PMR spectra were taken on a Varian DA-60-IL and ^{11}B NMR spectra on an RS-60 instrument of the Special Design Office of the Institute of Organic Chemistry of the Academy of Sciences of the USSR (IOKh AN SSSR). Mass spectra were taken on a Varian CH-6 instrument.

The solution of diborane in THF containing no trace of BF_3 was obtained by passing diborane formed by the reaction of $NaBH_4$ with $BF_3 \cdot (C_2H_5)_2O$ through 2% $NaBH_4$ in diglyme.

Propargyl chloride from Schuhardt (GFR) was washed with weak $NaHCO_3$ solution, dried with $CaCl_2$, redistilled, and stored with phenothiazine at 0°.

All operations with boroorganic compounds were carried out in an atmosphere of dry nitrogen.

7-Chloromethyl-3-allyl-3-borabicyclo[3.3.1]non-6-ene (II). Propargyl chloride (2.15 g) was added to triallylborane (3.9 g) at 20°. After 20 days highly volatile substances were distilled off in a vacuum of 2 mm. The mixture was heated for 5 min to 130° and maintained at this temperature for 30 min. PMR spectrum: singlet of CH_2Cl protons at 3.83 ppm and multiplet with center at 4.23 ppm (CHCl) in a ratio 27:1.

Hydroboration of 3-Methoxy-7-chloromethyl-3-borabicyclo[3.3.1]non-6-ene (IV). a) With tetraethyldiborane. Compound (IV) (2 ml: 10 mmole) was poured into a solution of $(C_2H_5)_4B_2H_2$ (15 mmole) in THF (50 ml) at 20°, after having taken a test portion (2 ml) for determination of BH content. After a definite time interval about 2 ml of solution was withdrawn and the content of BH groups was determined, decomposing the reaction mass with a mixture of H_2O:THF (1:1).

b) With diborane. The experiment was carried out similarly to a) above. The initial mixture was a solution containing BH_3 (10 mmole) and (IV) (10 mmole) in THF (50 ml).

c) With diborane in the presence of $Et_2O \cdot BF_3$. The initial mixture was a solution containing BH_3 (10 mmole), $Et_2O \cdot BF_3$ (3.3 mmole) and (IV) (10 mmole) in THF (50 ml). The results of these experiments are given in Table 1.

Tetrahydrofuran Complex of 1-Boraadamantane (VII). Diborane, obtained from $NaBH_4$ (1.2 g) and $Et_2O \cdot BF_3$ (5.5 ml), was passed through a solution of (IV) (95% purity, 9.8 g: 49 mmole) in absolute ether (50 ml) for 45 min at 5-12°. Next day the mixture was boiled for 30 min. All the highly volatile substances were distilled off in a vacuum of 1 mm into a trap. The Cl^- content in the trap was 13.2 mmole (26.4%). Tetrahydrofuran was added to the residue and evolution of heat was observed. By sublimation in a vacuum of 1 mm at a bath temperature up to 100° (VII) (2.73 g: 26.5%) was obtained having mp 79-83° [2]. The PMR spectrum was completely identical with the spectrum of a known specimen.

Pyridinate of 1-Boraadamantane (IX). Absolute pyridine (1 ml) was added to (VII) (2.35 g) in isopentane (15 ml). A strong evolution of heat was observed. The colorless precipitate which separated was filtered off, washed with isopentane, and dried in vacuum. Compound (IX) (2.2 g: 90%) of mp 159-162° [2] was obtained by recrystallization from methanol. The PMR and mass spectra completely reproduced the spectra of a known specimen.

1-Hydroxyadamantane (X). Potassium cyanide (96% pure, 0.95 g) was sprinkled into a solution of (VII) (2.73 g) in THF (13 ml) at 20° and the mixture was stirred at 25° for 1.5 h. Then $(CF_3CO)_2O$ (5.45 ml) was introduced at 0° with a syringe, the mixture was kept at 20° for 15 h, and at 40° for 3.5 h. Highly volatile substances were distilled off in vacuum at 10 mm, THF (5 ml) and 20% NaOH (7.6 ml) were poured on (at 5 to 10°), the mixture was cooled to 0°, and 30% H_2O_2 (12 ml) was added. After 16 h the solution was saturated with K_2CO_3 and extracted with ether. The ether extract was dried with $MgSO_4$ and the ether distilled off. Crude product (1.25 g: 62%) was obtained. Compound (X) (0.99 g: 50%) was obtained by recrystallization from hexane and subsequent sublimation. It had mp 280-282° (sealed tube), cf. [14, 15] and was identical with a known specimen (GLC).

Tetrahydrofuran Complex of 4-Chloro-1-boraadamantane (XII). Tetraethyldiborane (2.7 g: 19 mmole) was added to a 4:1 mixture of (IV) and (XI) (5.37 g: 26.7 mmole) in isopentane (5 ml) and THF (0.8 ml). Evolution of heat to 30° was observed. The mixture was kept cooled to −78° overnight. The precipitated white crystals were filtered off under cooling, washed on the filter with cold isopentane, and dried in vacuum. Compound (XII) (1.15 g: 18%) was obtained having mp 47-49°. Found: C 64.48; H 9.24; B 4.75; Cl 14.77%. $C_{13}H_{22}BClO$. Calculated: C 64.90; H 9.22; B 4.50; Cl 14.74%.

^{11}B NMR spectrum (in THF; standard was $Et_2O \cdot BF_3$): −9.8 ppm. PMR spectrum (δ, ppm in $CDCl_3$): 4.24 broad singlet (1H, >CHCl), complex signal with center at 3.80 and 1.88 (THF), 0.74 doublet (6H, >BCH_2) J = 5 Hz) and signals from the remaining adamantane protons from 0.82 to 2.5 reminiscent in character of the spectrum of 2-chloroadamantane [16].

Sublimation in a vacuum of 1 mm and bath temperature up to 100° of the combined residues from three similar experiments gave (VII) (0.95 g: 5%).

Pyridinate of 4-Chloro-1-boraadamantane (XIV). Absolute pyridine (0.11 g: 1.4 mmole) was poured into (XII) (0.3 g: 1.2 mmole) in hexane (25 ml). The reaction proceeded exothermally. The precipitated colorless solid was filtered off, dried, and recrystallized from methanol. Compound (XIV) (0.28 g: 88%) of mp 107-107.7° was obtained. Found: C 67.91; H 7.79; B 4.47; Cl 14.34%, mol. wt. 248. $C_{14}H_{19}BNCl$. Calculated: C 67.97; H 7.74; B 4.37; Cl 14.32%. ^{11}B NMR spectrum (in pyridine): 5.6 ppm. PMR spectrum (δ, ppm, in $CDCl_3$): 4.36 wide singlet (1H, >CHCl), complex signals of 14 adamantane protons with centers at 0.79 (6H, CH_2B) and 1.22-1.45; 2.06 and 3.36 (8H) and signals of the 5 pyridine protons. Mass spectrum: 4 peaks of molecular ions at 246, 247, 248, 249; 211 and 212 (M − Cl).

4-Chloro-1-hydroxyadamantane (XV). Compound (XII) (2.8 g: 12 mmole) in THF (70 ml) was put into a 100-ml autoclave. Initial CO pressure was 70 atm. After 1 h at 50° CO (10 mmole) had been absorbed. Ethylene glycol (2 ml) was added and the mixture was held at 150° for 1 h. The autoclave contents were transferred to a flask, THF (60 ml) was distilled off, and 20% NaOH (12.5 ml) and 30% H_2O_2 (10 ml) were added. The aqueous layer was saturated with K_2CO_3. The organic layer was dried with $MgSO_4$ and the solvent distilled off. Compound (XIV) (0.38 g: 18%) was separated by column chromatography (silica gel; ether) and had mp 162-164° (sublimed). Found: C 64.41; H 8.09; Cl 18.31%, mole. wt. 186. $C_{10}H_{15}OCl$. Calculated: C 64.34; H 8.10; Cl 18.99%. Mass spectrum 186 (M^+); 151 (M − Cl). PMR spectrum (in $CDCl_3$): 4.23 singlet (1H, CHCl). Signals of the remaining 14 adamantane protons at 1.36; 1.43; 1.76; 2.08, and 2.18 ppm were close in chemical shift to signals of adamantane protons in 1,4-dichloroadamantane [17]. IR spectrum (in $CHCl_3$): 3600; 3450 cm^{-1} (OH).

3-t-Butyloxy-7-chloromethyl-3-borabicyclo[3.3.1]non-6-ene (VIII). Compound (VIII) (12 g: 90%) was obtained from (II) (11.2 g) and t-C_4H_9OH (5.8 g) and had bp 101-103° (3 mm); n_D^{20} 1.4953. Found: C 65.01; H 9.31; B 4.51; Cl 14.26%. $C_{13}H_{22}BClO$. Calculated: C 64.93; H 9.20; B 4.50; Cl 14.74%. PMR spectrum (δ, ppm, in CCl_4): 3.80 singlet (2H, CH_2Cl); 1.23 singlet (9H, $(CH_3)_3C-$); 5.14 doublet (1H, >CH=); 0.86 wide doublet (4H, >BCH_2), complex signal 1.53-2.55 from the remaining six protons.

CONCLUSIONS

1. The orientation of the addition of diborane and tetraethyldiborane to 3-methoxy-7-chloromethyl-3-borabicyclo[3.3.1]non-6-ene was studied. On hydroboration with tetraethyldiborane the boron atom is added 13% at position 7 and 28% when using diborane.

2. 1-Boraadamantane was obtained by hydroboration of 3-methoxy-7-chloromethyl-3-borabicyclo[3.3.1]-non-6-ene.

3. 4-Chloro-1-boraadamantane was isolated as its complex with THF in 17-19% yield as was the THF complex of 1-boraadamantane (5-7%) on hydroboration of a mixture of 3-methoxy-7-chloromethyl-3-borabicyclo[3.3.1]non-6-ene and 6-chloro-3-methoxy-7-methylene-3-borabicyclo[3.3.1]nonane (in a 4:1 ratio) with tetraalkyldiborane.

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BOROORGANIC COMPOUNDS

316. THE HYDROCHLORINATION OF 2-(3-METHYL-1,2-BUTADIENYL)-4,4,6-TRIMETHYL-1,3,2-DIOXABORINANE

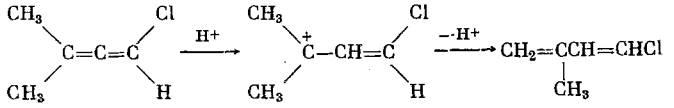
B. M. Mikhailov, M. E. Gurskii, and M. G. Gverdtsiteli

UDC 542.91:547.1'127

A characteristic peculiar to allenes is their ability to isomerize into acetylenes or 1,3-dienes [1]. 1-Chloro-3-methyl-1,2-butadiene is isomerized under the action of a solution of Cu_2Cl_2 in HCl into 1-chloro-3-methyl-1,3-butadiene [2, 3]. Substitution of chlorine by bromine facilitates the rearrangement [4, 5]. Trialkyl-substituted halogenated allenes are isomerized even more readily [6, 7].

Rearrangement of allene hydrocarbons into dienes was observed in reactions involving electrophilic addition to the allene system [8, 9]. 3-Chloro-3-methyl-1-butene and 1-chloro-3-methyl-2-butene were obtained by the action of HCl on 3-methyl-1,2-butadiene [8]. If the process is not taken to completion then ~14% isoprene was detected in the reaction products together with the indicated chlorides. From these data the conclusion may be drawn that the chlorides are formed by the addition of HCl both to 3-methyl-1,2-butadiene and to the isoprene formed as an intermediate. However, addition to the latter occurs 9-15 times more rapidly than to the initial hydrocarbon but the rearrangement of allene to diene occurs 1.5-3 times more rapidly than addition of HCl to the allene.

The most probable mechanism for these conversions is the addition of electrophile (proton) to the central atom of the allene system with subsequent splitting of a proton from the position α to the cationic center. Thus, the isomerization of 1-chloro-3-methyl-1,2-butadiene into the conjugated chloride may be represented by the scheme [10]



Interaction of the cation with nucleophile gives the addition product. It must be emphasized that the electrophilic particle is always added to the central atom of 1,1-dialkylallenes but the structure of the resulting intermediate compound depends on the nature of the electrophile. For the addition of halogens [9, 11-14],

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