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ORGANOBORON COMPOUNDS

CCXCIII *. SYNTHESIS OF 1-BORAADAMANTANE VIA BORON- AND SILICON-CONTAINING PROPARGYL ESTERS

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Summary

Propargyl dipropylborinate reacts with trialkylborane at room temperature to form dipropylboryloxy-1,5-diallyl-1-boracyclohex-2-ene (XI), which forms 7-dipropylboryloxy-3-allyl-3-borabicyclo[3.3.1]non-6-ene (XVI) on heating above 100°C. The latter compound undergoes an intermolecular condensation at 100—130°C in vacuum to form the bis-ester XVII. Hydroboration of the latter as well as of 3-methoxy-7-trimethylsiloxymethyl-3-borabicyclo[3.3.1]-non-6-ene (II) with $H_3B \cdot THF$ affords 1-boraadamantane.

We have previously developed a preparative method for the synthesis of 1-boraadamantane via hydroboration of 3-methoxy-7-methoxymethyl-3-borabicyclo[3.3.1]non-6-ene (I) [1—3], obtained from triallylborane and propargylmethyl ether. The method was then developed in works on the synthesis of 1-boraadamantane with the use of propargyltetrahydropyranyl ether [4] and on the synthesis of 4,6-dimethyl- [5] and 3,5-dimethyl-1-boraadamantane [6] from the related allylboranes. Previously, we had obtained 3-methoxy-7-trimethylsiloxymethyl-3-borabicyclo[3.3.1]non-6-ene (II) [7].

As found in this work, hydroboration of II with $H_3B \cdot THF$ leads to 1-boraadamantane. Apparently, the process proceeds according to the same scheme as in the synthesis of 1-boraadamantane from I [1,3] (Scheme 1).

On hydroboration, the B atom adds to the atoms C(6) and C(7) of II forming III and IV, respectively. The borane III readily (even at 0°C) isomerises in the course of the reaction to give IV. Further, compound IV undergoes β-elimination to afford 3-methoxy-7-methylene-3-borabicyclo[3.3.1]nonane (V) [8,9] (β-elimination of β-trimethylsiloxyalkylboranes at 0°C has been described

* For part CCCXCII see ref. 14.

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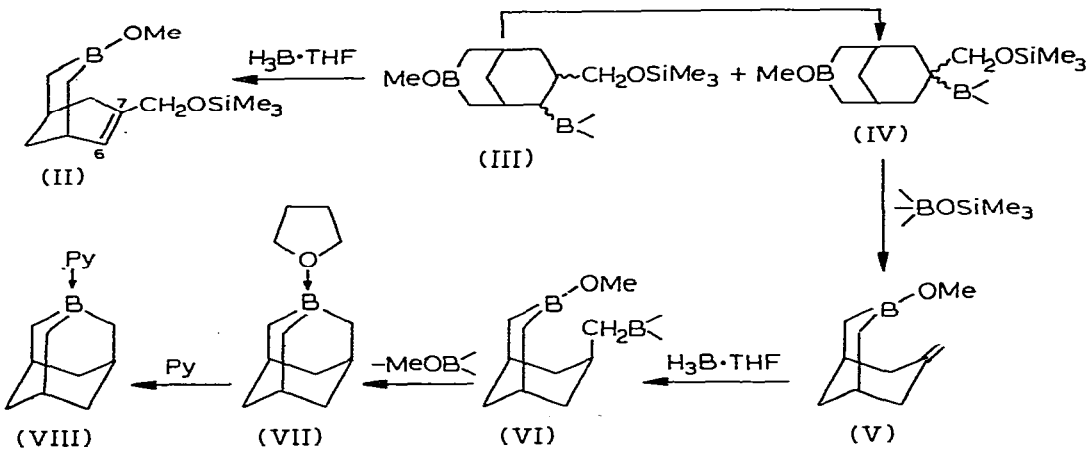
SCHEME 1



in ref. 10. On subsequent hydroboration with $H_3B \cdot THF$, compound V gives the diboron product VI which undergoes an intramolecular cyclization to yield the complex 1-boraadamantane with THF (VII). Reaction of the latter with pyridine gives the pyridinate of 1-boraadamantane (VIII) described before [3,9].

The rate of conversion of II into VII can be monitored by the amount of reacting hydride using the method described previously [3]. Data on the hydride uptake during the hydroboration of II with $H_3B \cdot THF$ at 0°C are listed in Table 1.

After 30 min, 1.25 equivalents of BH are absorbed whereas further hydride absorption proceeds considerably more slowly. After 24 h 1.91 equiv. of BH are taken up, i.e. the rate of hydride absorption is the same as in the conversion of I into VII [1,3].

At higher temperatures the formation of VII occurs considerably faster; this fact is connected with accelerated migration of the B atom from C(6) to C(7). The rate of isomerization of III to IV also increases if an excess amount of the hydroborating reagent is used, since the process occurs according to the "bridge hydrogen tautomerism" mechanism with the participation of compounds with B—H bonds [11]. Refluxing a mixture of II and $H_3B \cdot THF$ for 1.5 h with subsequent work-up of the reaction mixture with pyridine gave VIII in 55% yield.

The next subject of the study was the product of the condensation of triallylborane with propargyl dipropylborinate (IX). In studying the reaction of triallylborane with propargyloxytrimethylsilanes, interesting synthetic possibili-

TABLE 1

THE HYDRIDE UPTAKE (mol) DURING THE HYDROBORATION OF II AT 0°C

The ratio II : BH	Time						
	5 min	30 min	1 h	2 h	3 h	5 h	24 h
1 : 3	0.80	1.25	1.50	1.64	1.74	1.78	1.91

ties, based on the aptitude of the $SiMe_3$ group for elimination, were found. It might be expected that inserting a dipropylboryl group into the initial propargyl ester, i.e. a second B atom into the product of triallylborane condensation, would also affect the chemical behaviour of the latter compounds.

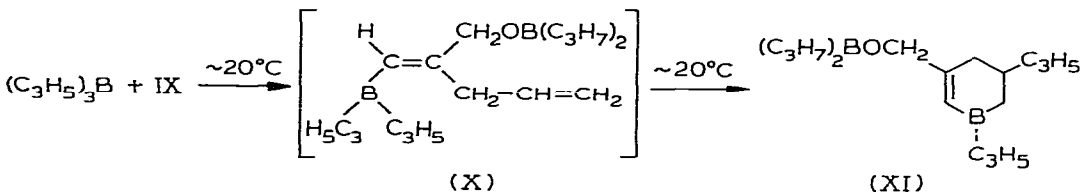
The initial ester IX was synthesized from butylmercaptodipropylborane and propargyl alcohol (eq. 2):

$$(C_3H_7)_2BSC_4H_9 + HC{\equiv}CCH_2OH \xrightarrow{\Delta} HC{\equiv}CCH_2OB(C_3H_7)_2 + C_4H_9SH \qquad (2)$$

(IX)

The reaction of triallylborane with IX proceeds according to the known scheme for the condensation of triallylborane with acetylene compounds [12,13]. Triallylborane reacts slowly (5 days) with IX at 20°C giving 3-dipropylboryloxy-1,5-diallyl-1-boracyclohex-2-ene (XI) (Scheme 2). Initially forming under the conditions given, the product of the addition of triallylborane to the C≡C bond of the propargyl ester X is not detected. After 5 days, the absorption band, at 3310 cm^{-1} (HC≡C) in the IR spectrum of the reaction mixture vanishes, and bands at 1610 (C=C—B), 1635, 3080 (CH_2=CH—CH_2), 1300—1400 cm^{-1} (B—O) are observed.

SCHEME 2



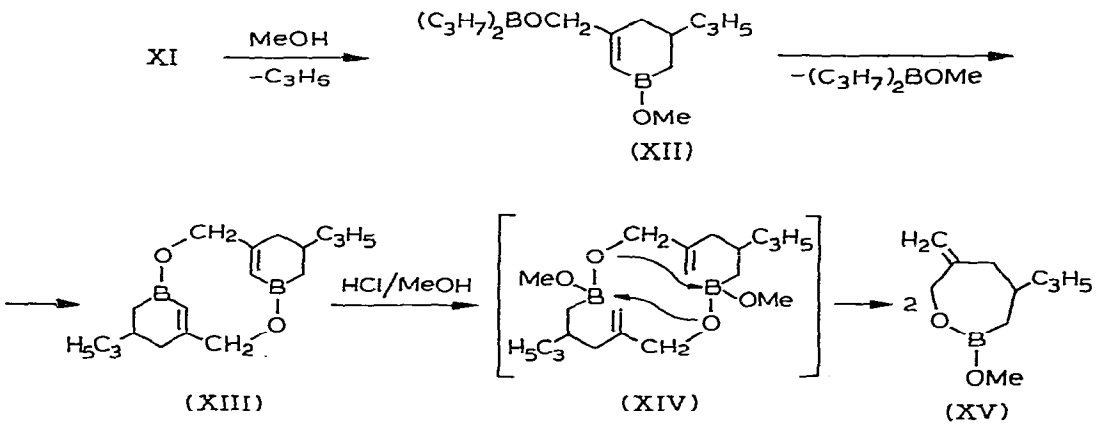
(X) (XI)

When treated with 1 mol of MeOH, XI eliminates 1 mol of propylene to form 3-dipropylboryloxy-1-methoxy-5-allyl-1-boracyclohex-2-ene (XII), which on heating to 75°C in vacuum (1 Torr) undergoes an intermolecular condensation with elimination of Pr_2BOMe to form the heterocycle XIII, previously obtained from 3-trimethylsiloxymethyl-1-methoxy-5-allyl-1-boracyclohex-2-ene [7].

As a reagent for cleaving the B—C(sp^2) bond in the boracyclohex-2-ene cycle, we formerly used with success a methanolic solution of HCl [2]. On addition of the latter to XII the B—C bond is split to give the intermediate compound XIV which, via an intramolecular exchange reaction, converts to 6-methylene-2-methoxy-4-allyl-1,2-oxaborepane (XV) in 56% yield (Scheme 3)

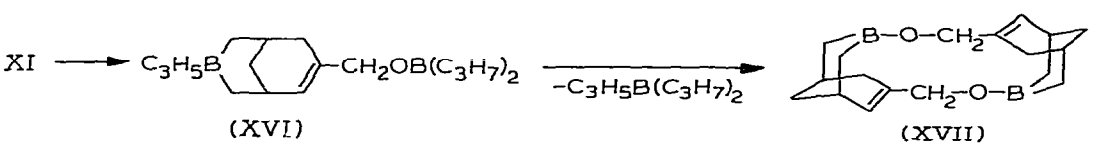
Heating XI above 100°C gives 7-dipropylboryloxy-3-allyl-3-borabicyclo[3.3.1]-non-6-ene (XVI). XVI can be prepared more conveniently by addition of XI to triallylborane heated to 130°C. The IR spectrum of XVI exhibits absorption bands at 1640, 3080 (CH_2=$CHCH_2$), 1675 and 3000 cm^{-1} (C=CH cycl.). On heating to 130°C in vacuum (1 Torr), XVI undergoes an intermolecular condensation, forming the polycyclic compound XVII, isolated in crystalline form in

SCHEME 3



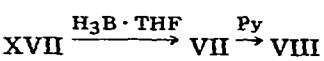
63% yield (Scheme 4). Compound XVII readily hydrolizes in air and on keeping polymerises.

SCHEME 4



On hydroboration of XVII with $H_3B \cdot THF$ (refluxing for 1.5 h) followed by work-up with pyridine VIII was obtained in 48% yield (Scheme 5).

SCHEME 5



Experimental

All manipulations with organoboron compounds were carried out under dry argon. IR spectra were recorded on a UR-20 spectrometer. ^1H NMR spectra were recorded on a Tesla BS-497 instrument (100 MHz, relative to TMS).

Hydroboration of II with $H_3B \cdot THF$ at 0°C (II : BH = 1 : 3)

1.5 ml (0.01 mol) of II were added at 0°C to a solution of BH_3 (0.1 mol) in 50.5 ml of THF. Then, using a syringe, samples of 1 ml were withdrawn to determine the BH content in the reaction mixture. For this purpose, a sample from the syringe was inserted via a rubber stopper to a two-necked flask filled with the mixture of H_2O and glycerol (1 : 1) equipped with magnetic stirrer and connected with a gas burette containing hydrogen. The results of these experiments are listed in Table 1.

Preparation of propargyl dipropylborinate (IX)

9.6 g (0.17 mol) of propargyl alcohol were added with stirring to 31.7 g (0.17 mol) of butylmercaptodipropylborane (an increase in temperature to 35°C was observed). Then the reaction mixture was heated for 1 h more (to b.p. 113°C) to give 19.1 g (74%) of IX, b.p. 70—71°C/17 Torr, n_D^{20} 1.4249. Found: C, 70.82; H, 11.22; B, 6.98. $C_9B_{17}BO$ calcd.: C, 71.09; H, 11.26; B, 7.12%. ^{1}H NMR (CCl_4): 2.23 m (1 H, CH≡), 4.4 d (2 H, OCH_2).

Reaction of triallylborane with IX at 20°C, (preparation of 3-dipropylboryloxy-1,5-diallyl-1-boracyclohex-2-ene (XI))

7.1 g (0.045 mol) of IX were added to 6.3 g (0.045 mol) of triallylborane while stirring at 20°C. After 5 days the absorption band at 3310 cm^{-1} (CH) in the IR spectrum of the reaction mixture had vanished completely. Then XI was subjected to methanolysis.

Reaction of XI with MeOH (preparation of XIII)

2.1 g of MeOH were added over a period of 15 min at 20—25°C to 11.3 g (0.04 mol) of XI. 0.95 l of propylene was evolved. The reaction mixture was kept under vacuum (1 Torr) at 75°C, the low-boiling substances being condensed in a trap. 11.7 g of XIII were obtained [7] which polymerized on storage.

Preparation of 6-methylene-2-methoxy-4-allyl-1,2-oxaborepane (XV)

1 ml of a 5 *M* methanolic solution of HCl was added to 1.7 g (0.006 mol) of XIII in 3 ml of MeOH. After heating the mixture for 15 min at 50°C, 1.2 g (56%) of XV were obtained, b.p. 55—56°C/1 Torr, n_D^{20} 1.4762. Found: C, 67.20; H, 9.64; B, 5.61. $C_{10}H_{17}BO_2$ calcd.: C, 66.71; H, 9.51; N, 6.00%. IR spectrum (cm^{-1}): 1640, 3080 (CH_2=C), 1300—1400 (B—O). ^{1}H NMR (ppm, CCl_4): 3.43s (MeO), 4.19s (CH_2O), 4.64—5.33 m (4 H, CH_2=), 5.4—6.1m (CH=).

Reaction of triallylborane with IX at 130—140°C (preparation of 7-dipropylboryloxy-3-allyl-3-borabicyclo[3.3.1]non-6-ene (XVI) and the compound XVII)

10.5 g (0.07 mol) of IX were added at 130—140°C during 30 min with stirring to 9.2 g (0.07 mol) of triallylborane. Then the mixture was kept at 130—140°C for 1 h: 19.7 g (0.07 mol) of XVI thus obtained were kept under vacuum (1Torr) at 70—130°C while simultaneous distilling off 8.9 g of a substance with b.p. 32—45°/1 Torr. To the residue (a viscous colourless liquid) were added 30 ml of isopentane. After 24 h in a refrigerator the compound crystallized to afford 6.3 g (63%) of XVII, m.p. 111—115°C. Found: C, 73.18; H, 8.75; B, 7.34. $C_{18}H_{26}B_2O_2$ (*M* 296.02) calcd.: C, 73.02; H, 8.85; B, 7.31%. M.w. 303 (cryoscopy in benzene).

Preparation of 1-boraadamantane pyridinate (VIII)

a) 35 ml of a 0.8 *M* solution of $H_3B \cdot THF$ were added with stirring to 7.0 g (0.028 mol) of II. An increase in temperature to 37°C was observed. The mixture was refluxed for 1.5 h, the low-boiling products distilling off into a trap. To the residue, dissolved in 20 ml of hexane, 2.2 g (0.028 mol) of pyridine were added. The precipitate formed was recrystallized from ethanol

to yield 3.3 g (55%) of VIII, m.p. 164—166°C [3].

b) 35 ml of a 0.8 *M* solution of $H_3B \cdot THF$ were added to 6.1 g (0.02 mol) of II. After refluxing and distilling as above, 3.2 g (0.04 mol) of pyridine were added to the residue (in 20 ml of hexane). Crystallization from ethanol gave 4.2 g (48%) of VIII, m.p. 164—167°C [3].

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