ORGANOBORON COMPOUNDS.

366. THE SYNTHESIS AND SOME PROPERTIES OF 4,4-DIMETHYL-1-BORAADAMANTANE

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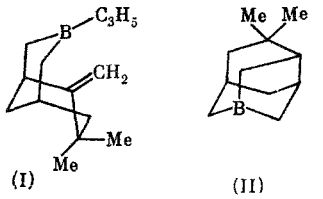
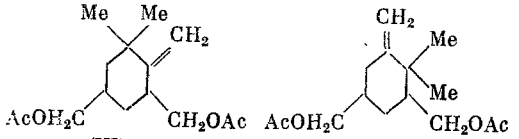
The reaction of 3-methyl-1,2-butadiene with triallylborane was previously used to yield a borabicyclic compound which was assigned the structure 3-allyl-6-methylene-7,7-dimethyl-3-borabicyclo[3.3.1]nonane (I) and the tricyclic compound obtained from (I), 4,4-dimethyl-1-boratricyclo[4.2.$0^{3,8}$]decane (4,4-dimethyl-1-boraprotoadamantane) (II) [1-3]



(I) (II)

which was based, in particular, on the structure of the diacetoxy derivative obtained by the oxidation of the borabicyclic compound with subsequent acetylation of the diol. The diacetate may be ascribed structure (III) or (IV) [1]



(III) (IV)

The 60-MHz PMR spectrum of the diacetate was used to assign structure (III) and structure (I) to the borabicyclic compound. However, subsequent study of the physical and chemical properties of the boratricyclic compound showed that it did not have the 4,4-dimethyl-1-boraprotoadamantane structure (II), but rather the 4,4-dimethyl-1-boraadamantane structure (X). Thus, we returned to the study of the diacetate which was initially assigned structure (III).

The PMR spectra of the diacetate were taken on a spectrometer with operating frequency 270 MHz since the data obtained on a 60-MHz spectrometer were not absolutely unequivocal because the protons of this compound give a poorly resolved spectrum. All the ring proton lines are rather well resolved in the spectrum obtained. The assignment of the lines in the spectrum was accomplished using the consecutive application of double proton–proton resonance. The chemical shifts and coupling constants are given in Table 1.

As seen from Table 1, the difference in the chemical shifts of protons H^4 and H^{10} is 130 Hz (0.48 ppm). This permits the confident use of our previous method [1] and shows that the diacetate has structure (IV).

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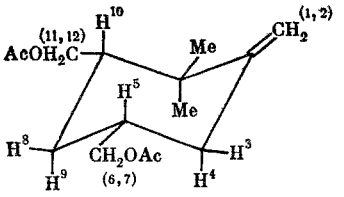
TABLE 1. PMR Spectra Parameters of Compound (IV)

Chemical shifts, δ, ppm													
H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^8	H^9	H^{10}	H^{11}	H^{12}	CH_3	CH_3CO
4,67	4,72	2,17	1,96	1,64	3,83	3,89	1,74	1,11	1,48	3,78	4,21	0,9; 1,16	1,91; 1,93

Spin–spin coupling constants,* Hz														
$J_{1,2}$	$J_{3,4}$	$J_{3,5}$	$J_{3,8}$	$J_{4,5}$	$J_{5,6}$	$J_{5,7}$	$J_{6,7}$	$J_{8,9}$	$J_{8,10}$	$J_{8,5}$	$J_{9,10}$	$J_{9,5}$	$J_{10,11}$	$J_{10,12}$	$J_{11,12}$
1,3	12,7	4,2	2,1	12,7	5,7	5,7	10,1	12,5	4,1	4,1	12,5	12,5	4,3	8,1	11,2

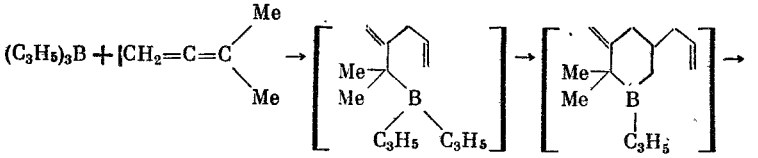
*Error ±0.3 Hz.



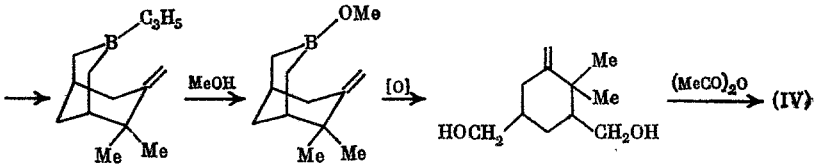
(IV)

Indeed, the allyl coupling observed for the $=CH_2$ group is lost upon suppression of the H^4 proton resonance frequency and is retained if the H^{10} proton frequency is suppressed. The reverse effect should have been observed in the case of structure (III).

Hence, the product of the reaction of 3-methyl-1,2-butadiene with triallylborane should, in contrast to the conclusions of our previous work [1], be given the structure 3-allyl-7-methylene-6,6-dimethyl-3-borabicyclo[3.3.1]nonane (VII). It is possible that the diallylborane group adds to the substituted ring carbon atom in the first reaction step, while the allyl group adds to the central carbon atom of the allene system (VI).

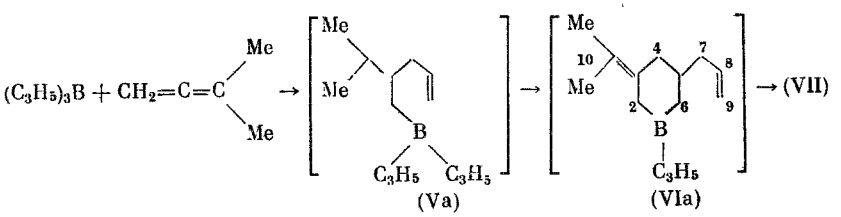


(V) (VI)



(VII) (VIII)

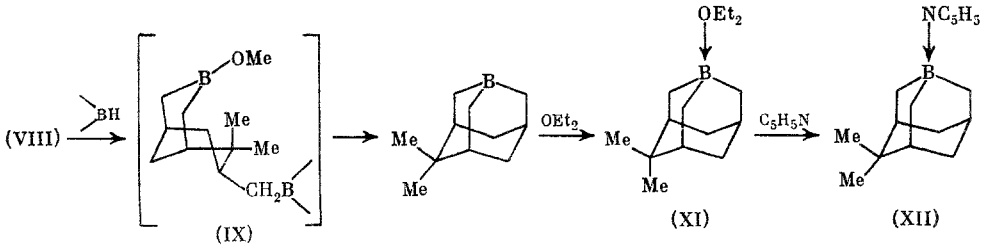
However, another reaction mechanism may be postulated by assuming that boron adds to the terminal unsubstituted carbon atom, while the allyl group adds to the central carbon atom, i.e., the reaction proceeds similar to the reaction of triallylborane or trimetallylborane with allene [1, 4]. Then, (Va) cyclizes to (VIa) accompanied by allyl rearrangement leading to the addition of C^2, and not C^{10}, to C^8.



(Va) (VIa)

A similar orientation is observed in the addition of tetraalkyldiborane to 3-methyl-1,2-butadiene [5].

The derivatives of 3-borabicyclo[3.3.1]nonane with a methylene group in the 7 position may be converted by hydroboration to 1-boraadamantane compounds [6]. In the reaction of diborane or tetraborane on (VIII) in ether, the diboron compound (IX) is formed which, by eliminating methoxyborane, is converted into the etherate of 4,4-dimethyl-1-boraadamantane (XI).

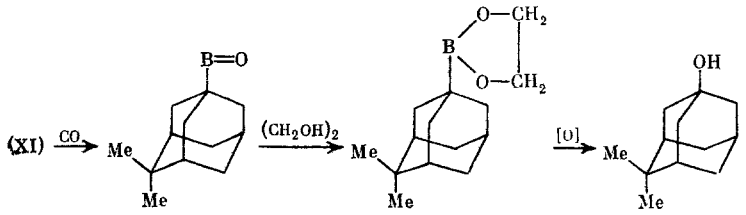


(IX) (XI) (XII)

4,4-Dimethyl-1-boraadamantane (X) was isolated upon the hydroboration of (VIII) using tetraethyldiborane in hydrocarbon solvents and vacuum distillation of the reaction mass.

Compound (XI) readily yields complexes with ligands having donor capacity greater relative to ether upon simplex mixing of the reagents. Thus, a stable complex with pyridine (XII) was obtained. There are 11 signals in the ^{13}C NMR spectrum of (XII) (the signals of the carbon atoms attached to the boron atom are broadened due to interaction with the ^{11}B nuclei), indicating the presence of planar symmetry characteristic for 4,4-disubstituted 1-boraadamantane.

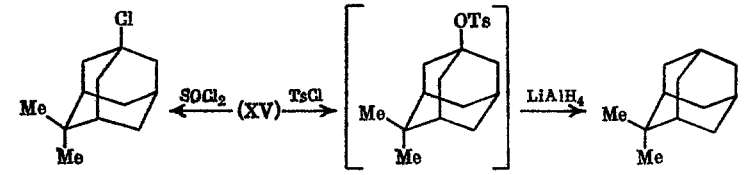
Trialkylboranes are converted to trialkylcarbinols upon the action of CO and subsequent oxidation of the carbonylation products [7, 8]. A similar transformation is undergone by 1-boraadamantanes [6]. Etherate (XI) at 20°C slowly reacts with CO to form 4,4-dimethyladamantyl-1-boric acid anhydride (XIII) in 23% yield.



(XIII) (XIV) (XV)

The carbonylation of (XI) at 50-60 atm and 100°C proceeds with higher yield. The ethylene glycol ester of 4,4-dimethyladamantyl-1-boric acid (XIV) was obtained in 49% upon the subsequent addition of $(CH_2OH)_2$. The oxidation of (XIV) by an alkaline solution of H_2O_2 leads to 1-hydroxy-4,4-dimethyladamantane (XV) with 158-160°C. According to Buss et al. [9], alcohol (XV) obtained by the oxidation of 2-spirocyclopropyladamantane and subsequent hydrogenation of the cyclopropane ring has mp 98-99°C. The observed discrepancy was one of the assumptions for our incorrect conclusion concerning the structure of the boratricyclic compound. However, further NMR study of alcohol (XV) obtained by a carbonylation reaction showed that it indeed has structure (XV). Thus, nine groups of signals (four doublets and five singlets) appeared in the PMR spectrum of (XV) upon the addition of paramagnetic shift reagents [$Eu(dpm)_3$, $Eu(fod)_3$, and $Pr(fod)_3$]. Examination of molecular models shows that such a spectrum may correspond only to a symmetrical structure. In the ^{13}C NMR spectrum of (XV), there are nine signals, which also indicates a plane of symmetry, while such symmetry is lacking in the protodamantane structure. The ^{13}C NMR chemical shifts are given in Table 2.

The reaction of (XV) with $SOCl_2$ yields 1-chloro-4,4-dimethyladamantane (XVI) (mp 70-72°C). According to Buss [9], (XVI) has mp 61-62°C.



(XVI) (XVII) (XVIII)

The reduction of tosylate (XVII) by $LiAlH_4$ leads to the isolation of 2,2-dimethyladamantane (XVIII), mp 148-150°C; according to Buss [9], (XVIII) has mp 141-142°C. The PMR spectrum coincides with that described by Buss [9].

TABLE 2. ^{13}C NMR Chemical Shifts of 1-Hydroxy-4,4-dimethyladamantane (XV)

C^1	C^8	C^2, C^9	C^3, C^5	C^4	C^6, C^{10}	C^7	CH_3
68,25	47,00	41,08	40,04	34,45	31,98	29,97	27,87; 26,78

EXPERIMENTAL

3-Allyl-7-methylene-6,6-dimethyl-3-borabicyclo[3.3.1]nonane (VII). A mixture of 20.1 g (150 mmoles) triallylborane and 13.6 g (200 mmoles) 3-methyl-1,2-butadiene was heated for 6 h in an autoclave at 140°C. Distillation of the reaction mixture yields 19.8 g (66%) (VII), bp 57-61°C (1 mm Hg), n_D^{20} 1.5025. Found, %: C 83.01; H 11.41; B 5.49. $C_{14}H_{23}B$. Calculated, %: C 83.18; H 11.47; B 5.35.

3-Methoxy-7-methylene-6,6-dimethyl-3-borabicyclo[3.3.1]nonane (VIII). To 19.8 g (VII), 5 ml methanol was added dropwise. The reaction proceeds with the evolution of heat and liberation of propylene. Distillation yielded 16.6 g (88%) (VIII), bp 54-56°C (1 mm Hg), n_D^{20} 1.4886. Found, %: C 75.25; H 10.89; B 5.69. $C_{12}H_{21}BO$. Calculated, %: C 75.05; H 10.92; B 5.73.

Etherate of 4,4-Dimethyl-1-boraadamantane (XI). To a solution of 3.1 g (17 mmoles) (VIII) in 30 ml ether, 1.15 g (8.2 mmoles) tetraethyldiborane was added dropwise. The reaction proceeds with the evolution of heat. At the completion of the reaction, the volatile products were removed in vacuum. The residue (3.7 g) was a colorless, viscous liquid which, according to ^1H and ^{11}B NMR data, is (XI). PMR spectrum (CCl_4, δ, ppm): 0.84 and 0.95 s (Me), 1.17 t (MeCO, J = 7 Hz), 3.77 q (OCH_2, J = 7 Hz). ^{11}B NMR spectrum (in ether): −15.0 ppm.

Pyridine-4,4-dimethyl-1-boraadamantane (XII). To a solution of 7.9 g (34 mmoles) (XI) in 20 ml petroleum ether, 3 ml pyridine was added dropwise with stirring. The colorless, crystalline precipitate was filtered off and washed with petroleum ether. A total of 6.5 g (77%) (XII) was obtained with mp 81-87°C or 87-89°C (from ethanol). ^{11}B NMR spectrum ($CHCl_3$, δ, ppm): 4.1. Found, %: C 79.32; H 10.00; B 4.45; N 5.73. $C_{16}H_{24}BN$. Calculated, %: C 79.67; H 10.03 B 4.49; N 5.81.

4,4-Dimethyl-1-boraadamantane (X). To 3.4 g (18 mmoles) (VIII) in 10 ml petroleum ether, 1.4 g (10 mmoles) $Et_4B_2H_2$ was added dropwise with stirring. Then, the reaction mixture was evaporated in vacuum to yield 1.7 g (58%) (X), bp 73-78°C (1 mm Hg). ^{11}B NMR ($CHCl_3$, δ, ppm): −83.5. The action of 0.5 g pyridine on 1.6 g (X) produces 1.9 g (91%) (XII), mp 87-89°C.

4,4-Dimethyladamantyl-1-boric Acid Anhydride (XIII). To a solution of 10.1 g (53 mmoles) (VIII) in 50 ml ether, a 10% excess of diborane was introduced. After vacuum distillation of the volatile components, the residue was dissolved in 20 ml hexane and placed in a long-necked flask and carbonylation was carried out for 15 h at 20°C with the absorption of 540 ml CO (theoretical 1250 ml). Upon cooling the solution to −70°C, colorless crystals were precipitated. A total of 2.28 g (22.8%) (XIII) was obtained with mp > 300°C. Found, %: C 75.05; H 10.08; B 5.66. $C_{12}H_{19}BO$. Calculated, %: C 75.02; H 10.07; B 5.69.

Ethylene Glycol Ester of 4,4-Dimethyladamantyl-1-boric Acid (XIV). To a solution 12.8 g (67 mmoles) (VII) in 70 ml ether, a 10% excess of diborane was introduced. After vacuum distillation of the volatile components, the residue was dissolved in 30 ml ether, placed in an autoclave, CO was introduced to give a pressure of 55 atm, and the solution was heated for 2 h at 100°C. Then, 5 ml $(CH_2OH)_2$ was added and the solution was again heated for 1 h at 150°C. At the completion of the reaction, the ethereal layer was separated, the solvent was distilled off, and the residue was distilled in vacuum to yield 7.4 g (49%) (XIV), bp 89-93°C (1 mm Hg). PMR spectrum ($CHCl_3$, δ, ppm): 1.0 s (2Me), 4.16 s (OCH_2). ^{11}B NMR ($CHCl_3$, δ, ppm): −33.9. Found, %: C 71.15; H 9.71; B 4.77. $C_{14}H_{23}BO_2$. Calculated, %: C 71.81; H 9.96; B 4.62.

1-Hydroxy-1,4-dimethyladamantane (XV). To a solution of 3.9 g (20 mmoles) (VIII) in 15 ml ether, 1.5 g (11 mmoles) $Et_4B_2H_2$ was added dropwise. The reaction proceeds with the evolution of heat. After evaporation in vacuum of the volatile components, the residue (4.3 g) was dissolved in 10 ml ether and placed in an autoclave. The carbonylation reaction was carried out under the conditions for the preparation of (XIV). At the completion of the reaction, the contents of the autoclave were subjected to oxidation using 30% H_2O_2 (3 ml) in 10 ml 20% NaOH. After evaporation of the solvent, the oily residue was distilled in vacuum to yield 2.3 g (64%) (XV), mp 122-130°C or 158-160°C (from pentane); according to Buss [9], mp 98-99°C. ^{13}C NMR spectrum (see Table 2) was obtained on an HX-90E spectrometer at 22.625 MHz in $CDCl_3$ with TMS internal standard, 15° pulse, 1000 accumulations, pulse repetition frequency 0.71 sec. Found, %: C 79.60; H 10.95%. $C_{12}H_{20}O$. Calculated, %: C 79.94; H 11.18.

1-Chloro-4,4-dimethyladamantane (XVI). To 1.5 g (8.3 mmoles) (XV), 1.0 g (8.6 mmoles) $SOCl_2$ was added and the mixture was heated for 3 h at 80°C. Distillation yielded 1.2 g (60%) (XVI), bp 98° (1 mm Hg), mp 70-72°C (from petroleum ether): according to Buss [9], mp 61-62°C. Found, %: C 72.69; H 9.61; Cl 17.60. $C_{12}H_{19}Cl$. Calculated, %: C 72.52; H 9.63; Cl 17.85.

2,2-Dimethyladamantane (XVIII). To a solution of 2.7 g (15 mmoles) (XV) in 100 ml ether, 12 ml 1.25 M BuLi in hexane was added. After 30 min, a solution of 2.86 g (15 mmoles) TsCl in 50 ml ether was added to the alcoholate precipitate. The reaction mass was stirred for 24 h, and then treated with 1 N HCl, $NaHCO_3$, and dried with $MgSO_4$. Then, 2 g $LiAlH_4$ in 50 ml ether was added to an ethereal solution of tosylate (XVII) at −70°C and then, the temperature was brought to ∿20°C and the reaction solution heated at reflux for 1 h. The reaction solution was neutralized with 1 N HCl. The organic layer was separated, washed with water, and dried over $MgSO_4$. After the evaporation of ether, the residue was distilled in vacuum to yield 1.05 g crystalline product with mp 95-105°C which, according to GLC analysis, consisted of ∿10% (XVI) and (XV). After separation on a preparative chromatograph, (XVIII) had 148-150°C, according to Buss [9], mp 141-142°C. PMR spectrum (300 MHz, CCl_4, δ, ppm): 1.02 s (Me), 1.31 s (α-CH), 1.51 d (β-CH, J = 12 Hz), 1.63 s (δ-CH_2), 1.77 s (δ-CH), 2.04 d (β-CH, J = 12 Hz).

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CONCLUSIONS

1. 3-Allyl-7-methylene-6,6-dimethyl-3-borabicyclo[3.3.1]nonane was obtained in the reaction of triallylborane with 3-methyl-1,2-butadiene.

2. 3-Methoxy-7-methylene-6,6-dimethyl-3-borabicyclo[3.3.1]nonane is converted by the action of diborane or tetraethyldiborane to 4,4-dimethyl-1-boraadamantane.

3. 4,4-Dimethyl-1-boraadamantane is carbonylated with CO to 1-hydroxy-4,4-dimethyladamantane, from which 1-chloro-4,4-dimethyladamantane and 2,2-dimethyladamantane were synthesized.

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