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HYDRIDE TRANSFER REACTIONS IN THE SERIES OF 1-BORAADAMANTANE "ATE"-COMPLEXES *

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Summary

Lithium 1-alkyl-1-boraadamantanates, obtained from lithium alkyls and the tetrahydrofuran complex of 1-boraadamantane, afford 7-methylene-3-alkyl-3-borabicyclo[3.3.1]nonanes when treated with acetyl chloride. With the use of selectively deuterated lithium [7-D]-1,3,5-trimethyl-1-boraadamantanate, it is shown that the reaction involves the elimination of deuteride ion from the β-carbon atom.

Lithium tetraalkylboranates, $R_3R'BLi$, obtained from trialkylboranes and lithiumalkyls, react with acyl halides at 25°C to give the corresponding ketones [1,2].

The tetraalkylboranates are also able to react with alkyl halides, reducing them to hydrocarbons. In this process, the transfer of the α-hydride ion to the electrophile, with simultaneous intra-molecular displacement of R from the boron atom to the α-carbon, leads to formation of the rearranged trialkylborane. Thus lithium tetra-n-butylboranate reduces benzyl chloride to toluene (84%) at 100—120°C and forms 4-octyldibutylborane which decomposes under the reaction conditions affording octenes (51%) [3]. The tetraalkylboranate reducing ability is greatly increased if it contains a secondary alkyl group, e.g. sec-$Bu_3B^-BuLi^+$ reduces benzyl chloride to toluene at 20°C [4]. Even more active reagents with respect to different substances are the "ate"-complexes of 9-alkyl-9-borabicyclo[3.3.1]nonanes with tertiary hydrogen atoms situated at the α-position with respect to the boron atom. These boranates readily reduce tert-alkyl, benzyl, and allyl halides at 20°C to hydrocarbons [4], and ketones to alcohols [5]. Under the same conditions, acyl halides are

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* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.
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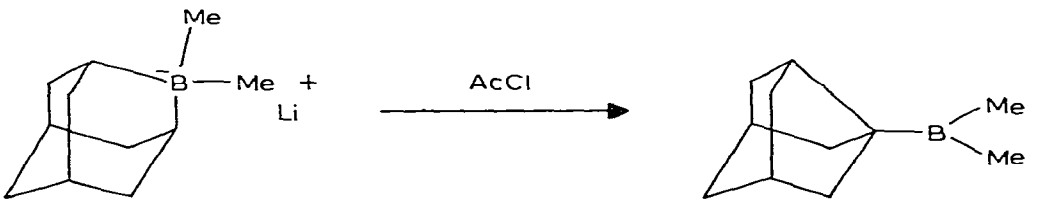
reduced to corresponding esters [6]. It should be noted that, eliminating hydride ion from the α-position, "ate"-complexes undergo an intra-molecular rearrangement to *cis*-bicyclo[3.3.0]oct-1-yl-dialkylboranes, this fact being highly interesting from the synthetic viewpoint.

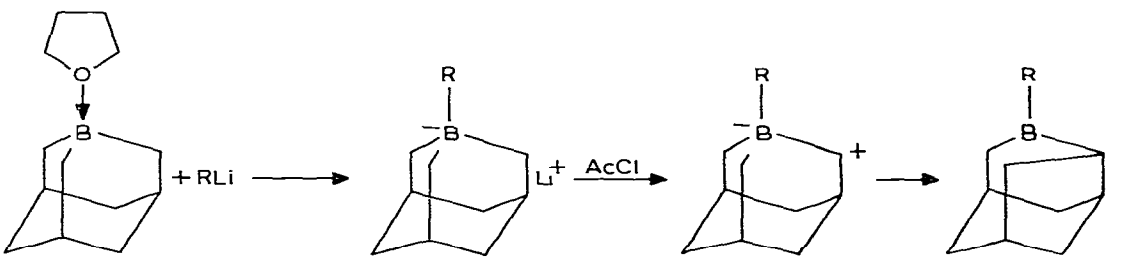
It has been recently found that lithium 2,2-dimethyl-2-boraadamantanate (I) obtained by interaction between 2-methyl-2-boraadamantane and lithium methyl reacts with acetyl chloride (AcCl) also eliminating hydride ion from the α-carbon atom, the reaction being accompanied by a rearrangement of the 2-boraadamantane skeleton to that of noradamantane resulting in 3-noradamantyldimethylborane (II) [7]. Thus a transition from bicyclo[3.3.1]nona-3,6-diene, from which 2-boraadamantane is obtained [8], to the noradamantane series compounds was effected.



(I) (II)

In connection with above-stated, a study of the conversions of "ate"-complexes of 1-boraadamantane by acetyl chloride appeared to be worthwhile. Objects of this study were lithium methyl-, n-butyl-, and 1-phenylboraadamantanates (IV) prepared by reaction of THF-1-boraadamantane (III) [9—11] with the corresponding organolithium compounds.

It was hoped that on reaction of IV with AcCl, the hydride ion would also eliminate from the α-position activated by the adjacent boron atom. This process, followed by an intramolecular rearrangement, was expected to lead to 4-substituted derivatives of 4-boraprotoadamantane (VI) according to the scheme below, in which the zwitter-ion (V) represents the transition state, with a view to clarifying the mechanism of the reaction.

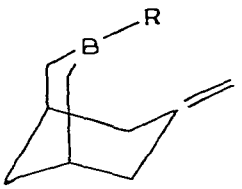


(III) (IV) (V) (VI)

R = Me, n — Bu, Ph

However it turned out that the 3-substituted derivatives of 7-methylene-3-borabicyclo[3.3.1]nonane (VII) were formed instead of VI.

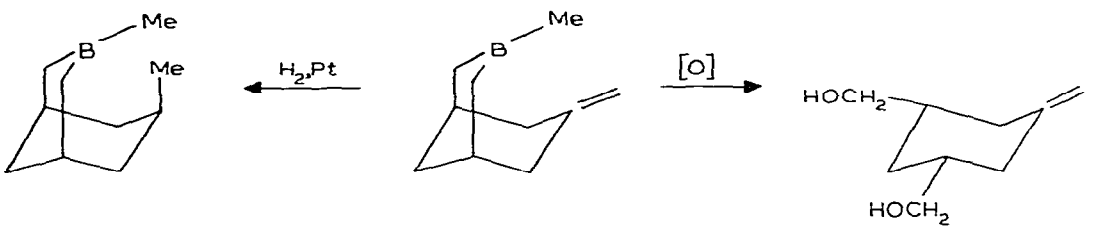
The structure of compound VII was determined by physical and chemical



(VIIa, R = Me;
VIIb, R = n-Bu;
VIIc, R = Ph)

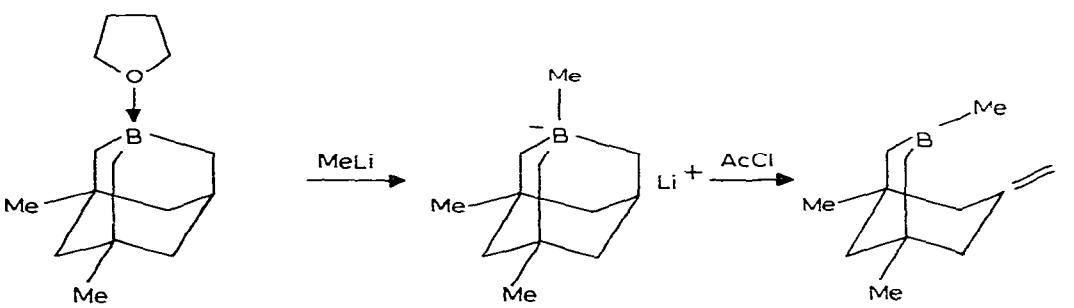
means. The IR spectrum of VIIa contains absorption bands at 899, 1642, and 3079 cm^{-1} characteristic of the exo-cyclic CH_2 = group. The PMR spectrum of the compound shows signals at 4.66 (CH_2=C) and 0.65 ppm (CH_3—B). ^{13}C NMR spectra of the compounds obtained are listed in Table 1. These data, namely downfield values of the C(9) and C(1,5) chemical shifts, evidence a predominate chair-chair conformation [12].

Hydrogenation of VII (R = Me) over Pt-black led to the known 3,7-dimethyl-3-borabicyclo[3.3.1]nonane (VIII) [13] while oxidation with alkaline hydrogen peroxide afforded *cis*-3,5-dihydroxymethyl-1-methylenecyclohexane (IX):



(VII) (VIIa) (IX)

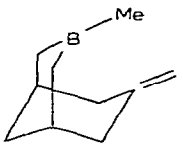
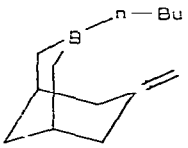
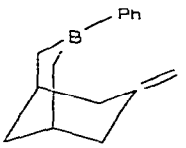
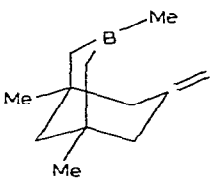
The reaction of AcCl with lithium 1,3,5-trimethyl-1-boraadamantanate (XI), obtained from THF-3,5-dimethyl-1-boraadamantane (X) [14] and MeLi, was next studied. This reaction was found to proceed in a manner analogous to that with IV, i.e. to form 7-methylene-1,3,5-trimethyl-3-borabicyclo[3.3.1]nonane (XII) and not 1,4,6-trimethyl-4-boraprotoadamantane:



(X) (XI) (XII)

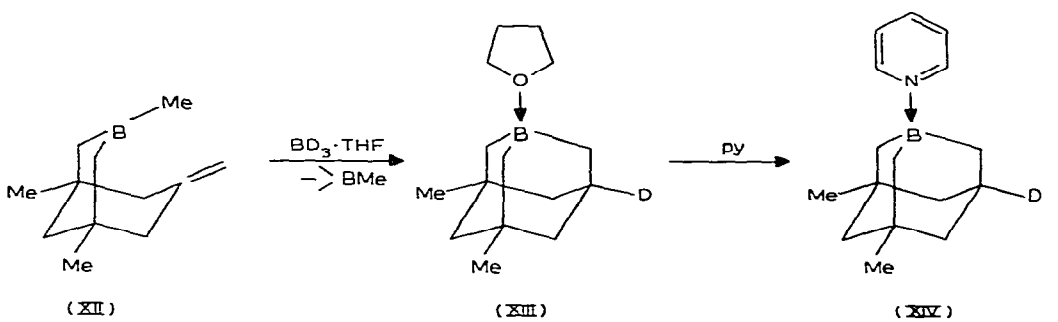
TABLE 1

^{13}C NMR CHEMICAL SHIFTS (ppm) OF 3-SUBSTITUTED DERIVATIVES OF 7-METHYLENE-3-BORABICYCLO[3.3.1]NONANE

Compound		C(1,5)	C(2,4)	C(6,8)	C(7)	C(9)	CH_2=C	remainder
	[a]	34.4	33.75	43.7	147.2	34.6	114.1	11.5 (B—Me)
	[a]	34.5	31.7	43.8	147.2	35.1	113.6	—
	[a]	35.6	29.6	43.8	147.95	35.0	115.5	133.9, 131.4, 127.85 (C_6H_5)
		34.8	41.3	50.1	148.5	50.0	112.7	32.9 (*Me*—C)

[a] Spectrum was recorded at —80°C.

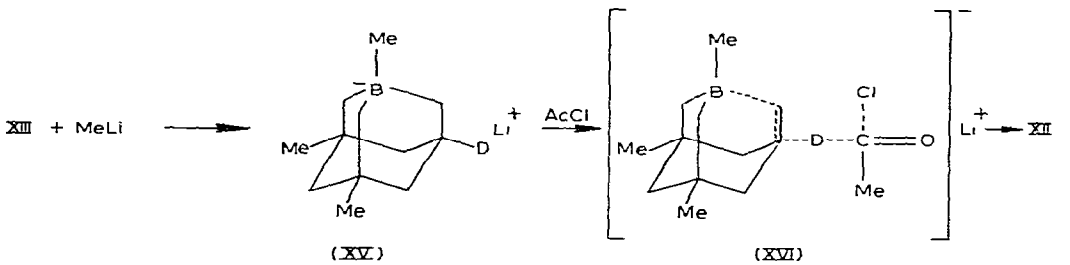
Formation of compounds VII and XII might be explained by scission of the B—C bond in V and transfer of H^- from C(3) to C(2), however, such an interpretation appeared to be rather ambiguous since the reaction of IV with AcCl has to be a synchronous process. Hence the question arose whether the α-hydride ion transfer takes place in the reaction or β-hydride ion migrates instead. In order to solve the problem it was necessary to study the behaviour of AcCl with respect to the "ate"-complexe of 1-boradamantane, in which two bridgehead hydrogens are replaced by alkyl groups and the third by deuterium. A compound of this sort, namely lithium [7-D]-1,3,5-trimethyl-1-boraadamantanate (XV) was prepared according to the following method. Deuteration of XII in THF gave tetrahydrofuran (XIII) and pyridine (XIV) complexes of [7-D]-3,5-dimethyl-1-boraadamantane:



(XII) (XIII) (XIV)

Both the presence and the position of the deuterium in the complexes XIII and XIV were determined with the aid of ^1H and ^{13}C NMR spectroscopy, as well as by mass-spectrometry (for XIV). PMR spectra of complexes XIII and XIV contain no signal of the proton at C(7). Their ^{13}C NMR spectra do not show the line of C(7) due to splitting by the D atom. Furthermore, in the mass-spectrum of the pyridinate XIV the parent ion is characterized by the mass 242.

The action of MeLi on complex XIII gave XV which reacted with AcCl to afford XII, i.e. the compound not containing the deuterium atom, this fact being confirmed by ^1H, ^{13}C, and mass-spectral data.



The process probably proceeds via a transition state (XVI) characteristic of synchronous elimination reactions with the bimolecular mechanism E_2.

Thus, unlike the 2-boraadamantane "ate"-complexes, those of the 1-boraadamantane series react with AcCl through β-hydride ion transfer. Hence it appears that the effect of the negatively charged boron atom on hydride mobility of the hydrogen at the α-carbon is less than that of electronic effects at the bridgehead carbon atom.

The effect of the polarization degree of C(2)—H and C(3)—H bonds in 1-boraadamantane "ate"-complexes, may be judged by data from X-ray analysis of 1-boraadamantane pyridinate having an analogous structure [15]. In this compound, the s-character of the bridgehead carbon orbital towards hydrogen is less than that of C(2) of the C—H bond. So the degree of polarization of the C(3)—H bond, conditioned by the smaller electronegativity of the C(3) orbital, is less than that of C(2)—H bond. Therefore elimination of both the hydride ion and H atom occurs more readily from C(3) than C(2).

It is possible to draw a parallel between the discussed reactions of 1-boraadamantane "ate"-complexes and ionic bromination reactions of adamantane [16,17]as well as its free-radical reactions [18] accompanied by elimination of H^- or $H^\cdot$ from the bridgehead carbon atom. Both hydride and hydrogen atom mobilities in adamantane are in line with the smaller degree of polarization of the C(1)—H bond as compared with the C(2)—H bond; the s-character of carbon orbital in these bonds is determined to be equal to 0.244 and 0.256, respectively, on the basis of the geometrical parameters of adamantane [19].

Experimental

All manipulations with organoboron compounds were carried out under a stream of dry argon. IR spectra were recorded on a UR-20 spectrometer. ^1H

NMR spectra were recorded on a BS-497 instrument (100 MHz) and ^{13}C NMR spectra on Bruker WP-60 (15.08 MHz for carbon) and Bruker XHE-90 spectrometers. Assignment of spectral lines was carried out with the use of the off-resonance method and by comparison of chemical shifts of a number of related compounds.

A solution of $BD_3 \cdot THF$ in THF was prepared by interaction of $NaBD_4$ and $BF_3 \cdot OEt_2$.

7-Methylene-3-methyl-3-borabicyclo[3.3.1]nonane (VIIa)

To a solution of 12.49 g (60.5 mmol) of THF-1-boraadamantane (III) [11] in 40 ml of ether there was added 38 ml of an ethereal solution of MeLi (1.6 *N*) at —60°C, the mixture was then allowed to warm up to 20°C and stirred for 30 min. The major part of the ether was removed in vacuo and 60 ml of pentane was added. The mixture was cooled to 0°C and 4.3 ml of freshly distilled (over CaH_2) AcCl was added with the aid of a syringe via rubber septum keeping the temperature at 0—5°C. After stirring for 3 h at 20°C the organic layer was decanted and the precipitate washed with 30 ml of pentane. After removing the solvent the remainder was vacuum distilled to give 6.7 g (75%) of VIIa as a low-melting crystalline substance. B.p. 77—80°C (21 torr). Found: C, 80.58; H, 11.49; B, 6.91. $C_{10}H_{17}B$ calcd.: C, 81.12; H, 11.57; B 7.31%. ^1H NMR spectrum (δ, ppm): 4.66 (CH_2=), 2.37—0.77 (signals of aliphatic protons), 0.65 s (CH_3B). IR spectrum (cm^{-1}): 899, 1642, 3079 (CH_2=).

7-Methylene-3-n-butyl-3-borabicyclo[3.3.1]nonane (VIIb)

To a solution of 12.1 g (60 mmol) of III in 40 ml of pentane was added dropwise at —60°C 28 ml of n-BuLi (2.08 *N*). The mixture was warmed up to 20°C, stirred for 1 h and refluxed for a further 0.5 h, thereupon 4.3 ml of AcCl was added from a syringe at 0—5°C with subsequent stirring during 2 h. The mixture was filtered and the filtrate evaporated. Double distillation of the residue gave 8 g (65%) of VIIb. B.p. 69—70°C (3.5 torr), n_D^{20} 1.4865. Found: C, 80.97; H, 12.25; B, 5.59. $C_{13}H_{23}B$ calcd: C, 82.11; H, 12.20; B, 5.69%. ^1H NMR spectrum (δ, ppm): 4.63 (CH_2=C), 2.38—0.74 (multiplets of aliphatic protons), IR spectrum (cm^{-1}): 895, 1646, 3072 (CH_2=C).

3-Phenyl-7-methylene-3-borabicyclo[3.3.1]nonane (VIIc)

In an analogous manner, from 10.12 g (49 mmol) of III, 46 ml of ethereal solution of PhLi (1.08 *N*), and 3.55 ml of AcCl 2.8 g of VIIc (27%) was obtained. B.p. 112—114°C (2 torr), n_D^{20} 1.5688. Found: C, 85.53; H, 9.06; B, 4.92. $C_{15}H_{19}B$ calcd: C, 85.73; H, 9.11; B, 5.15%. ^1H NMR spectrum (δ, ppm): 7.72 and 7.32 (C_6H_5), 4.50 (CH_2=C), 2.55—1.0 (bicycle protons signals). IR spectrum (cm^{-1}): 700, 745, 1600, 3015, 3028, 3040, 3055 (C_6H_5), 900, 1650, 3080 (CH_2=C).

7-Methylene-1,3,5-trimethyl-3-borabicyclo[3.3.1]nonane (XII)

To 13.89 g (59 mmol) of X [14] in 30 ml of ether was added dropwise at —60°C 34.1 ml of ethereal solution of MeLi (1.73 *N*); the mixture was then heated to 20°C and stirred for 1 h. After removing most of the ether in vacuo 30 ml of pentane was added and then, at 0°C, 4.63 g of AcCl. The solution ob-

tained was decanted and the remainder washed several times with pentane. After removing the solvent, distillation gave 6.53 g (63%) of XII as a colourless liquid, b.p. 50—51°C (4 torr), n_D^{20}1.4750. Found: C, 81.17; H, 12.03; B, 6.05. $C_{12}H_{21}B$ calcd: C, 81.84; H. 12.02; B, 6.14%. ^{1}H NMR spectrum (δ, ppm): 4.59 (CH_2=), 1.77 m (CH_2—C), 1.37 m (C—CH_2—C), 1.04 (CH_3—C), 0.63 s (CH_3—B), two doublets at 1.15 and 0.52 (AB-spectrum, J = 18 Hz, CH_2B). IR spectrum (cm^{-1}): 898, 1643, 3075 (CH_2=C).

3,7-Dimethyl-3-borabicyclo[3.3.1]nonane (VIII)

A solution of 3.02 g of VIIa in 20 ml of isopentane was hydrogenated over Pt-black (0.1 g). After the calculated amount of hydrogen was taken up the catalyst was filtered, solvent evaporated, and the residue distilled to give 2.2 g (75%) of VIII. B.p. 79—80°C (19 torr), n_D^{20} 1.4779 [13]. IR and ^{1}H NMR spectra were identical with the standard [13].

1-Methylene-3,5-dihydroxymethylcyclohexane (IX)

To a solution of 3.4 g (15.5 mmol) of VIIa in 10 ml of ether there was added a solution of 0.85 g NaOH in 5 ml H_2O. Then 5 ml of 30% H_2O_2 was added dropwise at 0—5°C and the mixture stirred for 4 h at 20°C. The aqueous layer was extracted with ether (3 × 20 ml). After removing ether the residue was recrystallized from ether to afford 2.5 g (70%) of IX. M.p. 73—75°C. Found: C, 69.02 H, 10.43. $C_9H_{16}O_2$ calcd.: C, 69.16; H 10.32%. ^{1}H NMR spectrum ($CHCl_3$, δ, ppm): 4.69 (CH_2=), 3.5 d (CH_2O), 2.5—0.85 (complex spectrum of cyclohexane ring protons). ^{13}C NMR spectrum (δ, ppm): 148.5 (CH_2=*C*), 108.2 (*C*H_2=C), 68.05 (CH_2O), 42.25 (CH), 38.9 (*C*H_2—C=), 33.0 (CH—*C*H_2—CH). IR spectrum (cm^{-1}): 1652, 3080, (CH_2=), 3630 (free OH).

Tetrahydrofuran-[7-D]-3,5-dimethyl-1-boraadamantane (XIII)

To 5.3 g (30 mmol) of XII in 5 ml of THF was added dropwise 28 ml of a solution of BD_3 in THF (1.29 *N*). After removing the solvent under vacuum the residue was distilled to give 6.12 g (86%) of XIII. B.p. 73—74°C (1 torr), n_D^{20} 1.5071. Found: C, 76.73; H, 11.10; D, 0.85; B, 4.93. $C_{15}H_{26}BDO$ calcd.: C, 76.60; H, 11.14; D, 0.85; B, 4.60%. ^{1}H NMR spectrum (δ, ppm): 3.93 m (CH_2O), 1.96 m (CH_2, THF), 1.16 m (CH_2—CD—CH_2), 0.98 (C—CH_2—C), 0.85 (CH_3), 0.5 (B—CH_2—CD), 0.34 (CH_2BCH_2). ^{13}C NMR spectrum (δ, ppm): 68.6 (CH_2O) 53.75 (C(4)), 45.8 (C(6, 10)), 36.5 (C(3, 5)), 35.8 (C(2, 9)), 34.8 (CH_3), 26.9 (C(8)), 24.4 (CH_2, THF).

Pyridine-[7-D]-3,5-dimethyl-1-boraadamantane (XIV)

To 0.42 g (1.7 mmol) of XIII in 5 ml of pentane was added 0.14 ml of pyridine. The solvent was removed and the residue was purified by low-temperature recrystallization from pentane affording 0.3 g (70%) of XIV, m.p. 56—57°C. *m/e* 242 (M^+). Found: C, 79.47; H, 9.60; D, 0.79; B, 4.41. $C_{16}H_{23}BDN$. calcd.: C, 79.35; H, 9.57; D, 0.80; B 4.47%. ^{1}H NMR spectrum (δ, ppm): 7.87 m and 7.48 m (C_5H_5N), 1.23 (CH_2CDCH_2), 1.03 (C—CH_2—C), 0.84 (CH_3), 0.52 (B—CH_2—CD), 0.37 (CH_2BCH_2). ^{13}C NMR spectrum (δ, ppm): 144.4, 138.8, 125.0 (C_5H_5N), 53.4 (C(4)), 45.7 (C(6, 10)), 39.4 (C(2, 9)), 35.3 (CH_3), 34.7 (C(3, 5)), 30.5 (C(8)).

Reaction of lithium [7-D]-1,3,5-trimethyl-1-boraadamantanate with acetyl chloride

To 5.04 g (22 mmol) of XIII in 25 ml of ether was added dropwise at —60° C 14.26 ml of a solution of MeLi in ether (1.52 *N*). The reaction mixture was then heated to 20° C and left for 1 h at room temperature. After removing ether under vacuum (oil pump) 25 ml of pentane were added to the residue and (at 0° C) 1.68 of AcCl. The precipitate was separated and rinsed several times with pentane. After removing the solvent, distillation gave 2.82 g (74%) of XII. B.p. 51—52° C (4 torr), n_D^{20} 1.4745. *m/e* 176 (M^+). Found: C, 81.61; H, 12.02; B, 5.98. $C_{12}H_{21}B$ calcd.: C, 81.84; H, 12.02; B, 6.14%. ^1H, ^{13}C NMR, and IR spectra unequivocally confirm the structure of the compound obtained.

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