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ORGANOBORON COMPOUNDS. SYNTHESIS OF ALLYL(DIALKYL)BORANES AND DIALLYL(ALKYL)BORANES

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Summary

Highly reactive allyl(dialkyl)-, crotyl(dialkyl)-, 3,3-dimethylallyl(dialkyl)-(= prenyl(dialkyl), and diallyl(alkyl)-boranes were prepared by allylation of esters R_2BOR', $RB(OR')_2$ or thioesters R_2BSR' (R = alkyl) using allylic derivatives of aluminium, magnesium or boron in exchange reactions.

The titled compounds are stable up to 100°C and do not symmetrize even on heating at 100°C for a long time. PMR spectroscopy data show that the characteristic feature of these compounds is a permanent allyl rearrangement, the rate of which increases with an increase in temperature. For allyl(diethyl)-borane at 100°C and 125°C the rates are equal to 2500 and 5000 sec^{-1} respectively; activation energy of the rearrangement amounts to 11.8 ± 0.2 kcal mol^{-1}.

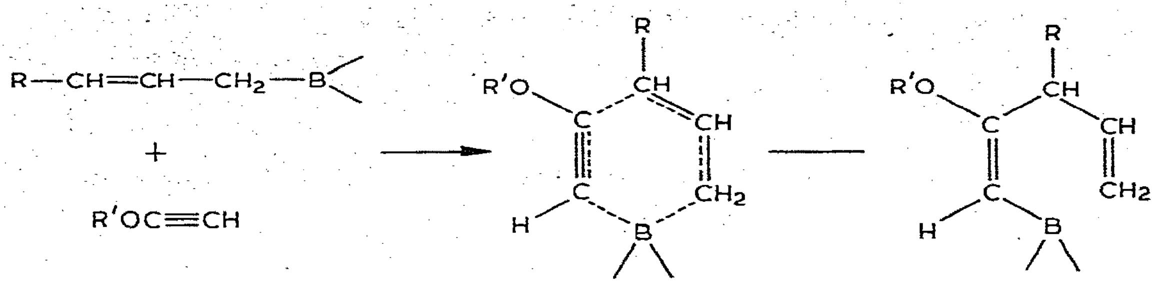
The boron—allyl bonds in unsymmetrical allyl(alkyl)boranes readily split under the action of water and alcohols, protonolysis being accompanied by allyl rearrangement, crotyl and prenyl compounds are converted into 1-butene or 3-methyl-1-butene, respectively.

Introduction

Triallylborane and its homologs are compounds of unusually high reactivity which find use in organic synthesis as allylating reagents [1—3]. The higher reactivity of these allylboranes, when compared with their alkyl analogs, is caused, firstly by a decrease in energy of B—C bond and, secondly, by their ability to undergo rearrangement of the carbon structure on reaction.

Reactions of allylboranes both with compounds containing active hydrogen (water, alcohols, amines, mercaptanes, and acids) [1—3] and with unsaturated compounds (allylboration of carbonyl compounds [4—6], nitriles [7—9], activated olefins [10—11], cyclopropenes [12—14] and acetylenes [1,2,15—17]) occur with allylic rearrangement proceeding via the cyclic electron transfer mechanism (e.g. Scheme 1).

SCHEME 1



Only four reactions of allylboranes occurring without rearrangement are known to date: oxidation with alkaline hydrogen peroxide * [18], splitting the cyclic system of cyclopropenes [13,14] and bicyclobutane [21], and allylation of diazoacetic ester [22]; it is noteworthy that trialkylboranes react similarly with these four types of reagents.

Up to now, symmetrical triallylboranes, triallylborane and tri(2-methylallyl)-borane have been used as allylborating reagents [1—3]. Unfortunately, in quite a number of reactions only one or two of the three radicals which the triallylborane molecule contains can be utilized. In this connection, unsymmetrical organoboranes with boron atom containing both allyl and alkyl radicals, allyl-(dialkyl)boranes (I) and diallyl(alkyl)boranes (II), are undoubtedly of interest.

$CH_2{=}CH{-}CH_2{-}BR_2$ (I) $(CH_2{=}CH{-}CH_2)_2BR$ (II)   (R = alkyl)

Compounds of type I and II appertain to the basic classes of organoboranes.

Before our investigation, there were no simple methods of preparing allyl-(dialkyl)boranes and diallyl(alkyl)boranes; the problems of their stability and ability to symmetrize under different conditions were also unresolved.

The first representatives of mixed organoboranes of this type, 3,3-dimethylallyl(diethyl)borane and di(3,3-dimethylallyl)ethylborane, were prepared via hydroboration of 1,1-dimethylallene with tetraethyl diborane [5]. Some authors [6,19,23] have studied hydroboration of allenes with disiamilborane or di(9-borabicyclo[3.3.1]nonane) but mixed allyl(dialkyl)boranes were not isolated in a pure state. 2-Hepten-1-yl(disiamil)borane is formed by the action of CH_3SCH_2Li and CH_3I on 1-hexenyl(disiamil)borane [20]. Allyl(diaryl)-boranes $CH_2{=}CH{-}CH_2{-}BAr_2$ (Ar = C_6H_5, *o*-, *p*-$CH_3C_6H_4$, *o*-, *p*-ClC_6H_4) were obtained by reaction of allylmagnesiumbromide and $Ar_2BOC_4H_9$ [24], *trans*-cynnamyl(diphenyl)borane was synthesized in 32% yield by reaction of *trans*-cynnamyltriphenyltin with bromodiphenylborane [25].

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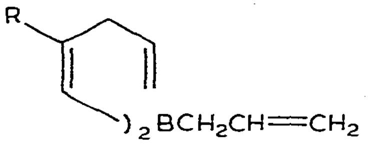
* Some authors [19,20] assert oxidation of allylboranes using the usual methods (alkaline hydrogen peroxide) to be a convenient way of preparing allyl alcohols. However, in the case of allylic boron derivatives these routes are not suited since allylboranes readily split under the alkaline conditions to give the corresponding olefinic hydrocarbons (protonolysis occurs with allylic rearrangement). Mikhailov et al. have shown [18] that allyl alcohols can be obtained in very high yields if one oxidizes the complexes of allylboranes with amines and not allylboranes themselves.

Various divinyl(allyl)boranes of type III were synthesized by addition of triallyl- or trimetallyl-borane to acetylenic compounds [1—3]. In addition cyclic IV and V and bicyclic VI compounds are mixed allyl(dialkyl)boranes [1—3]. 9-Allyl-9-borabicyclo[3.3.1]nonane (VII) was prepared by the action of lithium or magnesium allylic derivatives on 9-methoxy-9-borabicyclo[3.3.1]-nonane [26]. It should be noted, however, that VIII and its analogs are very expensive substances.



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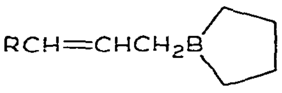

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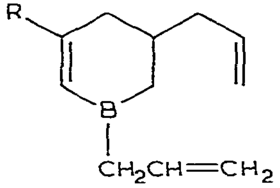

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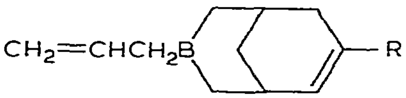

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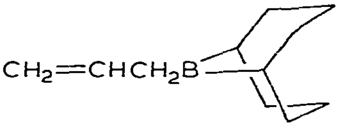

(VII)

We worked out three simple methods of preparation of allyl-, 2-methylallyl-, crotyl- and 3,3-dimethylallyl(dialkyl)boranes as well as diallyl(alkyl)boranes, and studied the properties of these compounds. Some of the data obtained have been published as a preliminary communications [27,28].

Both the first and the second routes involve the reactions of esters R_2BOR' or $RB(OR')_2$ with allyl derivatives of magnesium or aluminium. The third method is based on exchange reactions of allylboranes with esters R_2BOR' or thioesters R_2BSR'.

Results and discussion

Preparation of allyl(alkyl)boranes from alkoxy(alkyl)boranes and allylic derivatives of magnesium or aluminium

The most convenient methods of preparing allyl(dialkyl)boranes and diallyl(alkyl)boranes involve reactions of dialkylborinates or alkylboronates with allylaluminiumsesquibromide, which is obtained from aluminium and the corresponding allyl bromide (Scheme 2). Reactions are carried out by adding allyl bromide (or "crotyl bromide") * and the ester of organoboronic acid simultaneously to aluminium turnings, activated with $HgCl_2$, in a small amount of ether (20—25 ml). After completing the reaction, allyl(alkyl)boranes (I, II or VIII) are distilled from the reaction mixture under reduced pressure.

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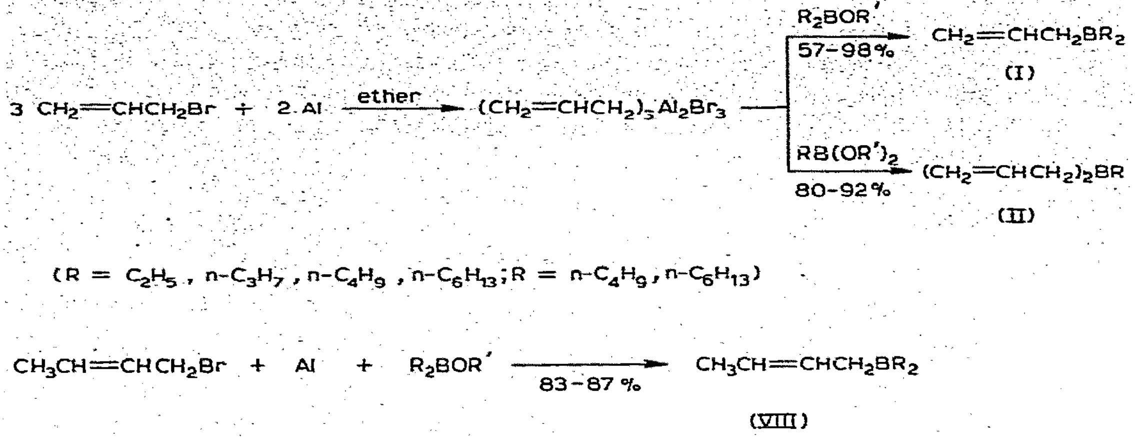
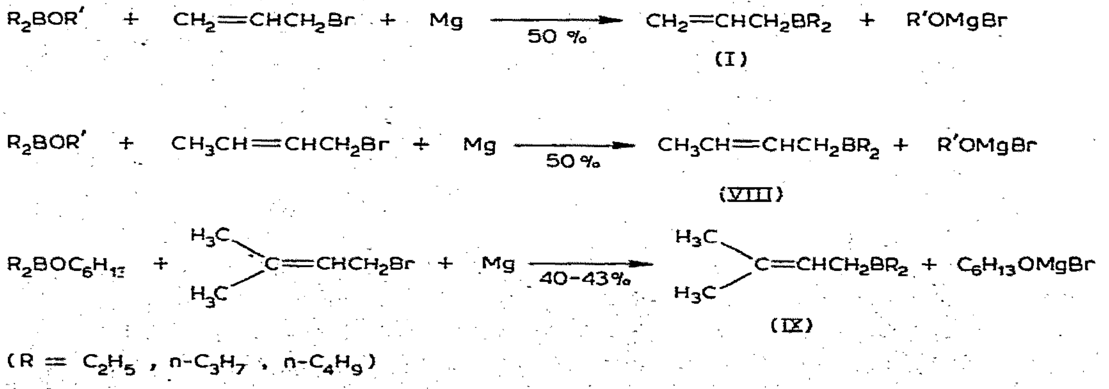
* "Crotyl bromide" and "3,3-dimethylallyl bromide" were prepared by addition of HBr to 1,3-butadiene or isoprene, respectively; for the reactions, the mixtures of isomeric allyl bromides were used since both α-methylallyl bromide and α,α-dimehtylallyl bromide convert into VIII and IX (with rearrangement).

SCHEME 2



By this method, allyl(diethyl)borane (I, R = C_2H_5), allyl(di-n-propyl)borane (I, R = n-C_3H_7), allyl(di-n-butyl)borane (I, R = n-C_4H_9), diallyl(ethyl)borane (II, R = C_2H_5), diallyl(n-propyl)borane (II, R = n-C_3H_7), diallyl(n-butyl)borane (II, R = n-C_4H_9), diallyl(n-hexyl)borane (II, R = n-C_6H_{13}), crotyl(diethyl)borane (VIII, R = C_2H_5), crotyl(di-n-propyl)borane (VIII, R = n-C_3H_7), and crotyl(di-n-butyl)borane (VIII, R = n-C_4H_9) were synthesized in 57—98% yield (see Table 1).

We elaborated another method of preparation of allyl(dialkyl)boranes, which involved reaction of dialkylborinates with the corresponding allyl derivatives of magnesium.

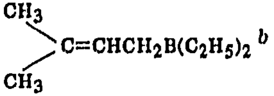
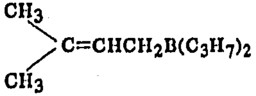


The method of isolation of products is of great importance. The reaction should be carried out as follows: to magnesium turnings in a large amount of ether, ester R_2BOR' and "crotyl"- or "3,3-dimethylallyl" bromide are added simultaneously. On completion of the reaction, ether is completely distilled off, and mixed allyl(dialkyl)borane extracted from a solid residue with hexane. After removing the solvent, pure allyl(dialkyl)borane (without the impurity R_3B) is isolated by distillation.

Using this method, allyl(di-n-butyl)borane (I, R = n-C_4H_9), crotyl(di-n-

TABLE 1

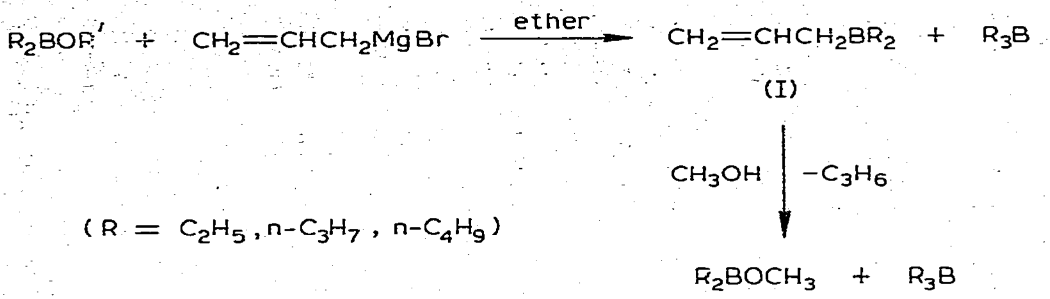
SYNTHESIS OF MIXED ALLYLBORANES FROM ALLYLIC DERIVATIVES OF Al OR Mg AND ESTERS R_2BOR' OR $RB(OR')_2$

Bornae	Metal [a]	Yield (%)	B.p. (°C) (mmHg)	n_D^{20}	^{11}B NMR (δ, ppm)	Empirical formula	Analysis (%) found (calcd.)		
							C	H	B
$CH_2{=}CHCH_2B(C_2H_5)_2$	Al	57	40—42(38)	1.4152	−83.8	$C_7H_{15}B$	76.19 (76.40)	13.67 (13.75)	9.40 (9.85)
$CH_2{=}CHCH_2B(C_3H_7)_2$	Al	85.5	48—50(12)	1.4267	−83.5	$C_9H_{19}B$	78.30 (77.79)	13.86 (13.66)	7.84 (7.76)
$CH_2{=}CHCH_2B(C_4H_9)_2$	Al	98	56—57 (2)	1.4365		$C_{11}H_{23}B$	79.03 (79.50)	13.77 (13.95)	6.54 (6.52)
	Mg	50	73—75 (10)	1.4360					
$(CH_2{=}CHCH_2)_2BC_2H_5$	Al	82.5	57—58 (48)	1.4380		$C_8H_{15}B$	78.10 (78.74)	12.10 (12.39)	8.69 (8.86)
$(CH_2{=}CHCH_2)_2BC_3H_7$	Al	80	37—38 (8)	1.4385		$C_9H_{17}B$	78.53 (79.45)	12.27 (12.59)	7.78 (7.94)
$(CH_2{=}CHCH_2)_2BC_4H_9$	Al	90.5	33—35 (4)	1.4390	−81.6	$C_{10}H_{19}B$	79.81 (80.00)	12.49 (12.78)	7.00 (7.22)
$(CH_2{=}CHCH_2)_2BC_6H_{13}$	Al	92	58—60 (2)	1.4475	−81.2	$C_{12}H_{23}B$	80.31 (80.91)	13.08 (13.01)	6.37 (6.07)
$CH_3CH{=}CHCH_2B(C_2H_5)_2$	Al	85	62—64 (50)	1.4278	−85.2	$C_8H_{17}B$	77.73 (77.48)	13.78 (13.81)	8.05 (8.71)
$CH_3CH{=}CHCH_2B(C_3H_7)_2$	Al	87	51—52 (7)	1.4317	−85.6	$C_{10}H_{21}B$	78.81 (79.00)	13.68 (13.98)	7.25 (7.11)
	Mg	50.5	35—36 (1)	1.4318					
$CH_3CH{=}CHCH_2B(C_4H_9)_2$	Al	83	58—59 (2)	1.4382	−85.9	$C_{12}H_{25}B$	79.88 (80.01)	13.85 (13.99)	6.05 (6.00)
 $(CH_3)_2C{=}CHCH_2B(C_2H_5)_2$ [b]	Mg	42.7	40—41 (7)	1.4372		$C_9H_{19}B$			
 $(CH_3)_2C{=}CHCH_2B(C_3H_7)_2$	Mg	39.5	37—38 (1)	1.4370		$C_{11}H_{23}B$	79.37 (79.53)	13.96 (13.97)	6.64 (6.51)

[a] Al - allylaluminium sesquibromodes were used; Mg - allylmagnesium halides were used. [b] Lit. b.p. 40°C/7 mmHg, n_D^{20} 1.4367 [5].

propyl)borane (VIII, R = n-C_3H_7), 3,3-dimethylallyl(diethyl)borane (IX, R = C_2H_5), and 3,3-dimethylallyl(di-n-propyl)borane (IX, R = n-C_3H_7) were obtained in 40—50% yields. All attempts to synthesize the latter two compounds using aluminium resulted in failure.

If isolation of allyl(dialkyl)boranes is carried out without extraction with hexane, i.e. by distillation under reduced pressure from solid salts, compounds I, VIII and IX are obtained in yields not exceeding 10—15%. Moreover, a mixture of allyl(dialkyl)borane: corresponding trialkylborane (1 : 4) is distilled from the solid salts, not a pure allyl(dialkyl)borane.



$$R_2BOR' + CH_2{=}CHCH_2MgBr \xrightarrow{\text{ether}} \underset{\text{(I)}}{CH_2{=}CHCH_2BR_2} + R_3B$$

$$\xrightarrow[\;]{CH_3OH,\ -C_3H_6} R_2BOCH_3 + R_3B$$

$$(R = C_2H_5, n\text{-}C_3H_7, n\text{-}C_4H_9)$$

The latter fact was ascertained on the basis of alcoholysis of distilled reaction products. Under the action of methanol, borane (I) readily and quantitatively is converted into ester R_2BOCH_3 (see below) whereas, under similar conditions, trialkylborane remains unchanged (it is well known [29] that trialkylboranes react with alcohols only at temperatures exceeding 150°C). The ratio R_3B : (I) in the products of methanolysis was estimated by means of ^{11}B NMR spectroscopy (signals at —54.5 ppm (R_2BOCH_3) and —85 ppm (R_3B) were integrated) as well as by directly determining the weights of R_2BOCH_3 and R_3B isolated.

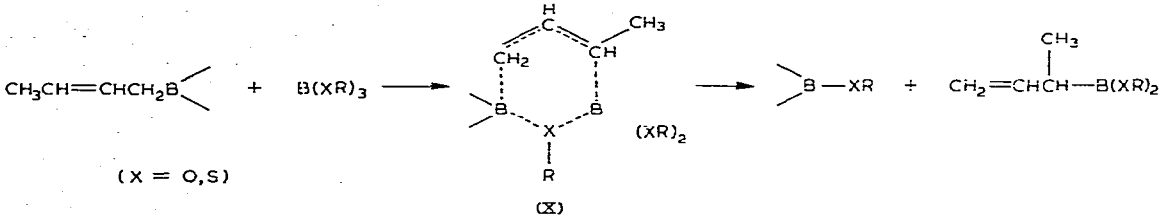
Formation of trialkylboranes can be explained by symmetrization of mixed organoboranes under the influence of magnesium compounds in ethereal medium. In some papers [30,31], allyl(dialkyl)boranes and cynnamyl(dialkyl)boranes are affirmed to be obtainable by the interaction of trialkylboranes and allyl- [30] or cynnamyl-magnesiumbromide [31]. However, this assertion is erroneous; our numerous attempts to synthesize allyl(dialkyl)boranes (I) in this way failed, and in all the cases only initial trialkylboranes were obtained from reaction mixtures.

Preparation of allyl(dialkyl)boranes by the use of exchange reactions

It has been shown previously that esters of boronic [32—34] and thioboronic acids [33,34], as well as boron halides [33,34], readily undergo exchange reactions with allylboranes, the exchange being accompanied by allylic rearrangement, according to Scheme 3.

Such reactions appertain to equilibrium ones. The exchange rate of the groups attached to the boron atom depends essentially on the structure of the boron ester $B(XR)_3$. In oxygen-containing esters the exchange proceeds relatively slowly, while triallylborane—thioester system is characterized by a very fast exchange. It is noteworthy that thioboranes catalyze intermolecular permanent allylic rearrangement, the fragment B—SR transferring allyl groups from one

SCHEME 3



boron atom to the other via a cyclic transition state of type X [33,34].

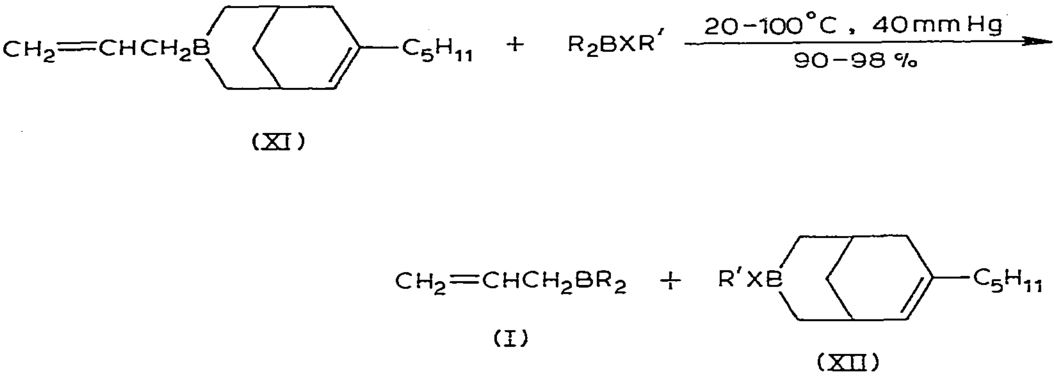
We discovered that, provided appropriate selection of reagents, one can use the exchange reaction for synthesis of allyl(dilakyl)boranes (I) [27]. Starting substances, dialkylborinates R_2BOR' and either triallyl-, tri(2-methylallyl)-borane or 3-allyl-3-borabicyclo[3.3.1]non-6-ene derivatives, were used:

$$(CH_2{=}CHCH_2)_3B + R_2BXR' \xrightarrow[83\text{—}95\%]{20\text{—}100^\circ C \; 40\,mm\,Hg} \underset{(I)}{CH_2{=}CHCH_2BR_2} + (CH_2{=}CHCH_2)_2BXR'$$

$$(R = C_2H_5;\ X = O,\ S)$$

The reaction is aided by shifting of the equilibrium to the right by distilling out the lower-boiling compounds, usuallyl allyl(dialkyl)boranes (I). For example, heating a mixture of triallylborane : diethylboronic acid hexyl ester (1/1) under reduced pressure gave allyl(diethyl)borane (I, R = C_2H_5) in 83.5% yield. The latter compound was also prepared, in 92—95% yield, by heating triallylborane with the amyl or hexyl ester of diethylthioboronic acid. The other product of this reaction, the ester of diallylthioboronic acid, symmetrizes when distilled to give thioborate $(RS)_3B$.

To prepare allyl(dialkyl)boranes (I) containing three or more carbon atoms in alkyl radical, 3-allyl-7-alkyl-3-borabicyclo[3.3.1]non-6-ene (XI) derivatives were utilized as allyl-supplying components. Since the latter have sufficiently high boiling points, isolation of mixed organoboranes is appreciably facilitated. In this way, heating, under reduced pressure (50—100 mmHg), esters of di-n-butylthioboronic acid or di-n-butylboronic acid with 3-allyl-7-n-amyl-3-borabicyclo[3.3.1]-



$(R = C_2H_5,\ n\text{-}C_4H_9;\ R' = n\text{-}C_5H_{11},\ n\text{-}C_6H_{13};\ X = O, S)$

TABLE 2

SYNTHESES OF UNSYMMETRICAL ALLYLBORANES USING EXCHANGE REACTIONS

Compound obtained	Starting components		Yield (%)	B.p. (°C) (mmHg)	n_D^{20}
	Organoboron ester	Allylborane			
$CH_2{=}CHCH_2B(C_2H_5)_2$	$(C_2H_5)_2BOC_6H_{13}$	$(CH_2{=}CHCH_2)_3B$	83.5	42—44(40)	1.4152
	$(C_2H_5)_2BOC_5H_{13}$	XI	94.5	44—46(42)	1.4154
	$(C_2H_5)_2BSC_6H_{13}$	$(CH_2{=}CHCH_2)_3B$	95	44—45(40)	1.4160
	$(C_2H_5)_2BSC_5H_{11}$	$(CH_2{=}CHCH_2)_3B$	92.5	42—43(47)	1.4165
	$(C_2H_5)_2BSC_5H_{11}$	XI	94	35—36(38)	1.4152
$CH_2{=}CHCH_2B(C_4H_9)_2$	$(C_4H_9)_2BOC_6H_{13}$	XI	92.5	86—88(12)	1.4380
	$(C_4H_9)_2BSC_5H_{11}$	XI	91	75—77(10)	1.4362
	$(C_4H_9)_2BSC_6H_{13}$	XI	98	51—52(2.5)	1.4364
$CH_2{=}\underset{\displaystyle CH_3}{\underset{\vert}{C}}CH_2B(C_2H_5)$	$(C_2H_5)_2BOC_4H_9$	$(CH_2{=}\underset{\displaystyle CH_3}{\underset{\vert}{C}}CH_2)_3B$	82	56—57(45)	1.4235
$CH_2{=}\underset{\displaystyle CH_3}{\underset{\vert}{C}}CH_2B(C_3H_7)_2$	$(C_3H_7)_2BOC_6H_{13}$	$(CH_2{=}\underset{\displaystyle CH_3}{\underset{\vert}{C}}CH_2)_3B$	65	58—59(9)	1.4315

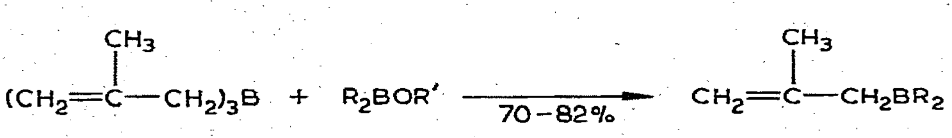
non-6-ene (prepared by condensation of triallylborane with 1-heptyne at 130—140°C [1—3]) afforded allyl(di-n-butyl)borane (I, R = n-C_4H_9) in 91—98% yield.

Reaction of bicyclic compound XI with the n-hexyl ester of diethylboronic acid led to allyl(diethyl)borane (I, R = C_2H_5). The yields and properties of allyl(dialkyl)boranes thus obtained are listed in Table 2.

Allyl(dialkyl)boranes, prepared by means of exchange reactions, are pure compounds. This fact was evidenced by alcoholysis of allyl(dialkyl)boranes; in this case scission of the boron—allyl bond is accompanied by formation of ester R_2BOCH_3 and propylene. ^{11}B NMR spectrum of the reaction mixture consists of only one signal at —54.5 ppm.

The exchange reactions described can be used to prepare 3-alkoxy- (XII, X = O) and 3-alkylthio-7-alkyl-3-borabicyclo[3.3.1]non-6-ene (XII, X = S) derivatives (see Table 3).

Heating (45 mmHg, 20—100°C) a mixture of tri(2-methylallyl)borane and diethylboronic acid butyl ester afforded, after distillation, 2-methylallyl(diethyl)-borane (XIII, R = C_2H_5). 2-Methylallyl(di-n-propyl)borane (XIII, R = n-C_3H_7) was obtained in a similar way from tri(2-methylallyl)borane and the hexyl ester of di-n-propylboronic acid.



$$(CH_2{=}\overset{\displaystyle CH_3}{\overset{\vert}{C}}{-}CH_2)_3B + R_2BOR' \xrightarrow[70-82\%]{} CH_2{=}\overset{\displaystyle CH_3}{\overset{\vert}{C}}{-}CH_2BR_2$$

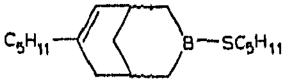
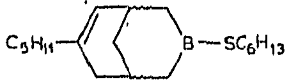
(XIII)

(R = C_2H_5 , n-C_3H_7 ; R′ = n-C_4H_9 , n-C_6H_{13})

Unlike allyl(dialkyl)boranes (I), 2-methylallyl(dialkyl)boranes (XIII) obtained

TABLE 3

ORGANOBORON ESTERS R_2BXR' (X = O, S)

Ester	Yield (%)	B.p. (°C) (mm)	n_D^{20}	^{11}B NMR (δ, ppm)	Empirical formula	Analysis (%) found (calcd.)		
						C	H	B
$(C_2H_5)_2BSC_5H_{11}$	94	69–70 (4)			$C_9H_{21}BS$	62.31 (62.79)	12.45 (12.30)	6.64 (6.29)
$(C_2H_5)_2BSC_6H_{13}$	63.5	61–62 (1)	1.4605	−71.8	$C_{10}H_{23}BS$	63.25 (64.53)	12.60 (12.45)	6.25 (5.82)
$(C_4H_9)_2BSC_5H_{11}$	93	103–104 (4)		−75.2	$C_{13}H_{29}BS$	68.03 (68.41)	12.69 (12.80)	4.81 (4.74)
$(C_4H_9)_2BSC_6H_{13}$	95	127–128 (2)	1.4618		$C_{14}H_{31}BS$	69.76 (69.40)	13.28 (12.92)	4.64 (4.46)
	95	174–176 (2.5)	1.5021	−68.7	$C_{18}H_{33}BS$	73.33 (74.00)	11.36 (11.40)	3.96 (3.71)
	96	198–200 (2)	1.5002	−70.5	$C_{19}H_{35}BS$	74.58 (74.50)	11.60 (11.50)	3.84 (3.64)
	96	159–160 (2)	1.4792	−51.5	$C_{19}H_{35}BO$	78.23 (78.50)	12.34 (12.10)	3.56 (3.73)
$(C_6H_{13}S)_3B$	70	180–181 (1)	1.5042		$C_{18}H_{39}BS_3$	59.89 (59.70)	10.87 (10.70)	3.66 (3.04)

in this way contain 10—20% of an admixture of esters R_2BOR'; ^{11}B NMR spectra of these compounds exhibit two signals at −85 and −54.5 ppm.

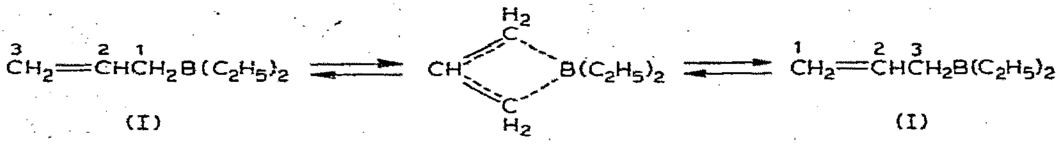
Permanent intramolecular allylic rearrangement, IR and NMR spectra

Mixed allyl(alkyl)boranes (I, II, VIII, IX, XII) are colourless liquids of low viscosity. They are stable under an atmosphere of dry argon or nitrogen but readily hydrolyze and oxidize on exposure to air; I, II and XII are capable of spontaneous inflammability.

These boranes do not symmetrize when heated up to 100°C for a long time. PMR and ^{11}B NMR spectra show symmetrization to occur only at temperatures above 120°C. So, ^{11}B NMR spectrum of methanolysis products of allyl(diethyl)-borane or allyl(di-n-butyl)borane (the borane having been preliminary heated at 100°C for 6 h) consists of only one signals, relatively: −54.1 [$(C_2H_5)_2BOCH_3$] and −54.7 ppm [$(C_4H_9)_2BOCH_3$]. However, if allyl(di-n-butyl)borane is preliminary heated at 135°C for 3 h, the ^{11}B NMR spectrum of methanolysis products consists of two signals: −54.7 ppm [$(C_4H_9)_2BOCH_3$]/−31.1 ppm (3/1) due to the ester $C_4H_9B(OCH_3)_2$, formed as the resukt of the protonolysis of $(C_3H_5)_2$-BC_4H_9. Allyl(diethyl)borane (I, R = C_2H_5) is distilled under atmospheric pressure without decomposition (b.p. 115°C).

The IR spectra of compounds I and II exhibit strong absorption bands at 1638 and 3080 cm^{-1} (vibrations of CH_2=CH moiety). The crotyl derivatives VIII show a weak broadened band at 1645 cm^{-1} (shoulder at 1660 cm^{-1}) together with intense bands at 968 and 3015 cm^{-1} (—CH=CH—). The IR spectra of 3,3-dimethylallyl(dialkyl)boranes (IX) contain bands of weak intensity at 1650, 1670 and 3020 cm^{-1}.

The ^{11}B NMR spectra of mixed allyl(alkyl)boranes show signals in the region −81.2— −86.0 ppm relative to $BF_3 \cdot O(C_2H_5)_2$ (see Table 1). The structure of PMR spectra of mixed allyl(alkyl)boranes I and II depend on the temperature, which demonstrates intramolecular permanent allylic rearrangement to proceed in these compounds as well as in symmetrical allylboranes [1—3]. PMR spectra recorded at 25—30°C, besides these due to alkyl radical protons, exhibit broadened signals at 2.10 ppm (CH_2—B), 4.85 ppm (CH_2=C), and an anomalous quintet centered at 5.85 ppm (C=CH—C). At −60 — −40°C the PMR spectrum of allyl-(diethyl)borane shows a multiplet at 0.65—1.5 ppm (C_2H_5) and an allyl group spectrum: a doublet at 2.10 ppm (*J* 7.2 Hz, —CH_2B) and multiplets at 4.74—4.95 (CH_2=C), and 5.52—6.25 ppm (=CH—C). With increasing temperatures (above 35°C), broadening of allylic CH_2 groups signals is observed, these begin to converge at 65°C and above 100°C transform into a doublet centered at 3.40 ppm; the signals due to methyne protons is in the shape of regular quintet centered at 5.85 ppm (intensity ratio 1/4/6/4/1), i.e. the spectrum due to the allyl radical is that of an AX_4 pattern. The rate of intramolecular permanent allylic rearrangement is equal to approximately 2500 sec^{-1} and 5000 sec^{-1} at 100°C and 125°C,



respectively. Activation energy of rearrangement, estimated according to ref. 35, amounts to 11.8 ± 0.2 kcal mol^{-1}.

The PMR spectrum of crotyl(diethyl)borane (VIII, R = C_2H_5), recorded at room temperature, contains a multiplet due to ethyl group protons at 0.72—1.45 ppm, a complex signal at 1.47—1.72 ppm (*cis*- and *trans*-CH_3), a broadened signal centered at 2.03 ppm (CH_2—B), and a multiplet due to methyne protons at 4.8—5.4 ppm. The PMR spectrum of 3,3-dimethylallyl(di-n-propyl)borane (IX, R = n-C_3H_7) consists of a doublet centered at 2.13 ppm (CH_2—B, *J* 8 Hz), two broadened signlets due to two methyl groups at 1.50 and 1.62 ppm, triplet due to methyne protons centered at 5.16 ppm, and a multiplet due to propyl radical protons at 0.6—1.3 ppm.

Hydrolysis and alcoholysis of mixed allyl(alkyl)boranes

The boron—allyl bond in allyl(dialkyl)boranes is readily cleaved under the action of alcohols, whereas the boron—alkyl bond remains unaffected. Protolytic cleavage at —30—+20°C is highly exothermic and gives esters of the corresponding dialkylboronic acids accompanied by evolution of one mole of propylene. The structures of esters thus prepared were determined by physical and chemical methods. It should be emphasized that the spectra of crude products of alcoholysis of allyl(dialkyl)boranes (reaction mixture) exhibit only one signal at —54.5 ppm depending on the nature of the ester R_2BOR'. The absence of the signal at —31 ± 1 ppm ($RB(OR')_2$) demonstrates the purity of allyl(dialkyl)-boranes (I) obtained.

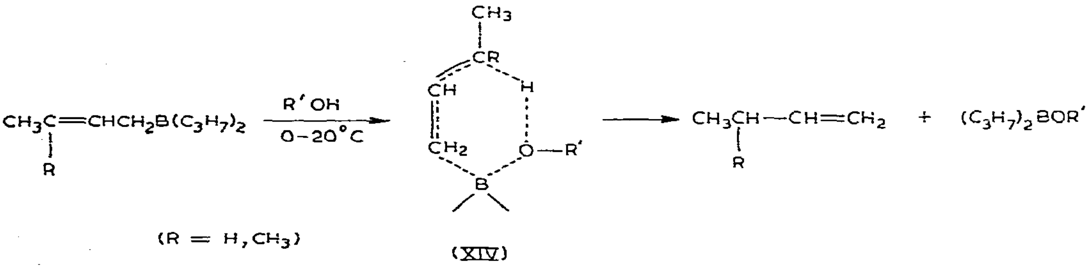
$$CH_2{=}CHCH_2BR_2 \xrightarrow[-30-20^\circ C]{R'OH} R_2BOR' + C_3H_6$$

$$(R = C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9;\ R' = CH_3,\ C_4H_9,\ C_9H_{19})$$

Alcoholysis of crotyl(di-n-propyl)borane (VIII, R = n-C_3H_7) affords 1-butene (98% purity) with an admixture of 2-butene (2%, GLC; IR spectrum: 1640 and 3082 cm^{-1}) and ester of di-n-propylboronic acid. When protolysing 3,3-dimethylallyl(di-n-propyl)borane (IX, R = n-C_3H_7) only 3-methyl-1-butene and boron ester are formed. Both these reactions are exothermic and proceeds at room temperature (Scheme 4).

These data offer additional confirmations of the fact that protolytic cleavage of allyl type boranes occurs with allylic rearrangement [1—3] via a six-member cyclic transition state of type XIV.

SCHEME 4



Both allyl radicals in diallyl(alkyl)boranes (II) eliminate exothermally under the action of alcohols to give esters of alkylboronic acids together with the two moles of propylene. The ^{11}B NMR spectrum of the reaction mixture con-

$$(CH_2{=}CHCH_2)_2BR \xrightarrow[-30\text{ to }+20^\circ C]{R'OH} 2\ C_3H_6 + RB(OR')_2$$

tains only one signal at −31 ± 1 ppm [$RB(OR')_2$], i.e. diallyl compounds II prepared in this work are individual ones.

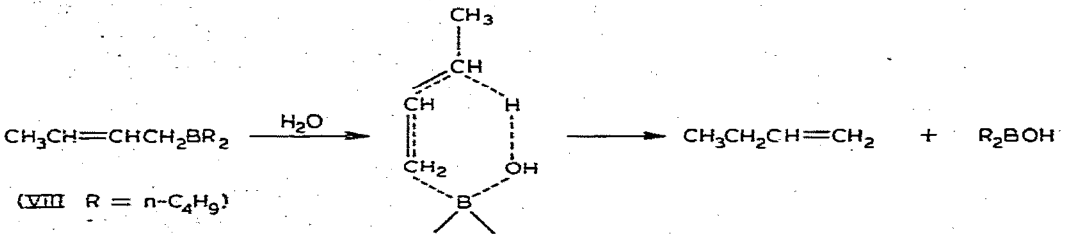
Mixed allyl(alkyl)boranes I and II react with water to give the corresponding acids or their anhydrides and one or two moles of propylene. Hydrolysis is

$$\underset{\text{(I)}}{CH_2{=}CHCH_2BR_2} \xrightarrow[0-20^\circ C]{H_2O} R_2BOH + C_3H_6$$

$$\underset{\text{(II)}}{(CH_2{=}CHCH_2)_2BR} \xrightarrow[0-20^\circ C]{H_2O} RB(OH)_2 + 2\ C_3H_6$$

highly exothermic and occurs at room temperature or on cooling. Hydrolytic cleavage of the boron—allyl bonds is accompanied by allylic rearrangement, which was confirmed by formation of 1-butene as the main gaseous product (98%) in hydrolysis of crotyl(di-n-butyl)borane (VIII, R = n-C_4H_9, Scheme 5).

SCHEME 5



Unsymmetrical allyl(alkyl)boranes react with carbonyl compounds [27] and nitriles [36] as organometallic reagents and add to the triple bonds of terminal acetylenes [27]. The reaction with carbonyl compounds leading to substituted homoallylic alcohols will be described in the following paper [51].

Experimental

General comments

All reactions of organoboron compounds were carried out under an atmosphere of dry argon or nitrogen.

IR spectra were measured on UR-20 spectrometer; PMR spectra were recorded on a DA-60-IL instrument, and all chemical shifts are relative to tetramethylsilane. ^{11}B NMR spectra were recorded on RS-56/19 spectrometer, chemical shifts are relative to $BF_3 \cdot O(C_2H_5)_2$.

Hexyl esters of dialkylboronic acids were obtained via reaction of trialkyl-

TABLE 4

ESTERS OF ORGANOBORON ACIDS

Compound	Yield (%)	B.p. (°C) (mm)	n_D^{20}	^{11}B NMR (δ, ppm)	Empirical formula	Analysis (%) found (calcd.)		
						C	H	B
$(C_2H_5)_2BOC_6H_{13}$	80	45–46 (3)	1.4160		$C_{10}H_{23}BO$	70.54 (70.61)	13.48 (13.63)	6.08 (6.36)
$(C_3H_7)_2BOC_6H_{13}$ [a]	92	100–102 (12)	1.4220		$C_{12}H_{27}BO$			
$(C_4H_9)_2BOC_6H_{13}$	92.5	88–90 (3)	1.4281	−51.6	$C_{14}H_{31}BO$	74.25 (74.33)	13.53 (13.81)	4.54 (4.78)
$C_3H_7B(OC_6H_{13})_2$ [b]	82	95–96 (3)	1.4240		$C_{15}H_{33}BO_2$			
$C_4H_9B(OC_6H_{13})_2$	85	96–98 (2)	1.4262		$C_{16}H_{35}BO_2$	72.58 (72.74)	13.86 (13.73)	5.31 (5.46)
$C_2H_5B(OC_4H_9)_2$ [c]	87	86–88 (14)	1.4060		$C_{10}H_{23}BO_2$			
$C_6H_{13}B(OC_4H_9)_2$	94.5	98–100 (3)		−29.5	$C_{14}H_{31}BO_2$	69.21 (69.42)	13.05 (12.90)	4.32 (4.46)

[a] Lit. b.p. 63–64°C/3 mmHg, n_D^{20} 1.4220 [49]. [b] Lit. b.p. 95–98°C/3.5 mmHg, n_D^{20} 1.4245 [49]. [c] Lit. b.p. 80–82°C/12 mmHg, $n_D^{20.5}$ 1.4065 [50].

boranes with hexanol in the presence of catalytic amounts of mercaptanes [37], or pivalic acid [38]. Butyl esters of ethyl- and n-hexyl-boronic acids as well as hexyl esters of n-propyl- and n-butyl-boronic acids were synthesized by reesterification of corresponding dimethyl esters that in their turn were prepared by heating mixtures of trialkylboranes and methylborate in the presence of small amounts of tetraalkyldiborane [39]. Properties of the compounds thus prepared are listed in Table 4.

Triallylborane and tri(2-methylallyl)borane were obtained from aluminium, butylborate, and allyl- or 2-methylallyl bromide, respectively [1].

Synthesis of dialkylthioborinates

n-Amyl ester of diethylthioboronic acid. This was prepared following the known method [40]. Into a flask equipped with a dropping funnel, thermometer, condenser, and a gas-removing tube was placed 40.6 g of triethylborane and some pieces of porcelain. 65.5 ml of amylmercaptane was then added at such a rate to maintain the temperature of the mixture at 50—60°C. After heating for 10 min at 110°C the mixture was distilled giving 40 g (94%) of n-amyl ester of diethylthioboronic acid.

n-Amyl ester of di-n-butylthioboronic acid, n-hexyl esters of diethyl- and di-n-butylthioboronic acids were obtained in a similar way (see Table 3).

3-Allyl-7-n-amyl-3-borabicyclo[3.3.1]non-6-ene (XI). To 37.1 g of triallylborane heated to 135—140°C was added dropwise 26.2 g of 1-heptyne over 2 h. The mixture was kept at 140°C for 1 h and distilled to afford 53.3 g (83%) of compound XI, b.p. 124—125°C/3 mmHg (Found: C, 84.40; H, 11.80; B, 4.80. $C_{16}H_{27}B$ calcd.: C, 83.50; H, 11.73; B, 4.69%).

Synthesis of allyl(alkyl)boranes I, II and VIII from allylaluminiumsesquibromides and alkylboronates or dialkylborinates

Allyl(di-n-butyl)borane (I, R = n-C_4H_9). To a three-necked flask fitted with a stirrer, a condenser, and a dropping funnel was added 10 g of aluminium turnings, 0.1 g of $HgCl_2$, and 25 ml of absolute ether. The mixture was stirred for 10 min, then 10 ml of allyl bromide was added. After the reaction was initiated, a mixture of 12 ml of allyl bromide and 44 g of n-hexyl ester of di-n-butylboronic acid was added dropwise at such a rate to maintain reflux. After completing the addition the reaction mixture was refluxed with stirring for 1 h. Distillation gave 32 g (98%) of allyl(di-n-butyl)borane (I, R = C_4H_9).

Allyl(di-n-propyl)borane (I, R = n-C_3H_7), allyl(diethyl)borane (I, R = C_2H_5), diallyl(ethyl)borane (II, R = C_2H_5), diallyl(n-propyl)borane (II, R = n-C_3H_7), diallyl(n-butyl)borane (II, R = n-C_4H_9), diallyl(n-hexyl)borane (II, R = n-C_6H_{13}), crotyl(diethyl)borane (VIII, R = C_2H_5), crotyl(di-n-propyl)borane (VIII, R = n-C_3H_7) and crotyl(di-n-butyl)borane (VIII, R = n-C_4H_9) were prepared by similar methods (see Table 1).

Synthesis of allyl(dialkyl)boranes from allylmagnesium bromides and dialkylborinates

Allyl(di-n-butyl)borane (I, R = n-C_4H_9). (a) Using hexane extraction. To a mixture of 19.5 g of n-hexyl ester of di-n-butylboronic acid, 2.1 g of magnesium turnings, and 100 ml of absolute ether was added 7.8 g of allyl bromide. The mixture was stirred until the magnesium dissolved completely, and then refluxed for 0.5 h. After the ether was distilled off, 200 ml of hexane was added to a solid residue, the mixture was heated to boiling, cooled to 20°C and the hexane solution decanted. The extraction was repeated twice. After removing the solvent by distillation 7.1 g (50%) of I ($R = n\text{-}C_4H_9$) was obtained.

Crotyl(di-n-propyl)borane (VIII, $R = n\text{-}C_3H_7$), 3,3-dimethylallyl(diethyl)borane (IX, $R = C_2H_5$) and 3,3-dimethylallyl(di-n-propyl)borane (IX, $R = n\text{-}C_3H_7$) were synthesized analogously. Properties of these boranes are listed in Table 1.

(b) Without extraction. To 13.7 of magnesium turnings in 150 ml of absolute ether was added a solution of 22 g of allyl bromide and 25.1 g of hexyl ester of di-n-butylboronic acid in 100 ml of ether. The mixture was refluxed with stirring for 1 h and both solvent and volatile compounds were distilled off under reduced pressure. Heating the residue under reduced pressure, with simultaneous removhl of the volatiles, afforded 8.15 g of a clear liquid, b.p. 60—62°C/3 mmHg. Its IR spectrum showed absorption bands at 1635 and 3080 cm^{-1} (terminal double bonds).

To 8 g of the mixture obtained, 2 ml of CH_3OH was added at 0—5°C. The mixture was heated at 50°C until evolution of propylene ceased; excess methanol was removed under reduced pressure. IR spectrum of the residue did not exhibit absorption at 1635 and 3080 cm^{-1}, ^{11}B NMR spectrum contains two signals: at —54.5 ppm [$(C_4H_9)_2BOCH_3$] and —84.6 ppm [$(C_4H_9)_3B$] with intensity ratio 1/4. Distillation afforded 1.62 g of the methyl ester of di-n-butylboronic acid, b.p. 79—80°C/24 mmHg, n_D^{20} 1.4150 (lit. see ref. 41), and 5.85 g of tributylborane, b.p. 108—110°C (24 mmHg), n_D^{20} 1.4281 (lit. see ref. 42). The content of allyl(di-n-butyl)borane (I, $R = n\text{-}C_4H_9$) in the mixture was 25%, and the total yield was equal to 9.5%.

Synthesis of allyl(dialkyl)boranes via exchange reactions

Allyl(diethyl)borane (I, $R = C_2H_5$) (a). To 13.8 g of n-hexyl ester of diethylboronic acid in a Claisen flask was added 9.15 g of triallylborane (heat evolution was observed on mixing reagents). The mixture being heated (40 mmHg) for 0.5 h; 5.65 g of allyl(diethyl)borane was distilled into a cooled trap (see Table 2).

(b). On heating a mixture of 30.5 g of triallylborane and 50 g of n-hexyl ester of diethylthioboronic acid, 29.6 g of the title compound was distilled out. Distillation of the residue gave 22.5 g of n-hexylthioborate, b.p. 180—181°C/ 1 mmHg, n_D^{20} 1.5042 (lit. see ref. 43). Constants of the compound are listed in Table 3.

(c). A mixture of 6.8 g of 3-allyl-7-n-amyl-3-borabicyclo[3.3.1]non-6-ene (XI) and 5.2 g of n-amyl ester of diethylthioboronic acid was vacuum distilled giving 3.5 g of compound I ($R = C_2H_5$). The residue gave on distillation 8.35 g of 3-n-amylthio-7-n-amyl-3-borabicyclo[3.3.1]non-6-ene (XII, $R = n\text{-}C_5H_{11}S$) (see Table 3).

(d). As described above, from 5 g of n-hexyl ester of diethylthioboronic acid and 6.7 g of 3-allyl-7-n-amyl-3-borabicyclo[3,3.1]non-6-ene (XI), 3 g of compound I ($R = C_2H_5$) and 8.3 g (96%) of 3-n-hexylthio-7-n-amyl-3-borabicyclo-[3,3.1]non-6-ene (see Table 3) was prepaped.

2-Methylallyl(di-n-propyl)borane (XIII, $R = n\text{-}C_3H_7$). This was obtained by heating under reduced pressure a mixture of 14.1 g of tri-2-methylallylborane and 19.7 g of n-hexyl ester of di-n-propylboronic acid (yield 7.4 g, see Table 2). IR spectrum: 1640 and 3080 cm^{-1} ($CH_2{=}C$). PMR spectrum (δ): 0.69—1.42 (C_3H_7), 1.67 (s, CH_3—C), broadened signals centered at 2.10 (CH_2—B) and 4.30 ppm ($CH_2{=}C$). Integrating the ^{11}B NMR spectrum shows that the compound also contains (n-$C_3H_7)_2BOC_6H_{13}$ (10%).

2-Methylallyl(diethyl)borane was synthesized in a similar way (see Table 2).

Reactions of allyl(alkyl)boranes with methanol

(a). To 3.5 g of allyl(diethyl)borane (I, R = C_2H_5) was added, with care, 1.1 g of methanol at —20 to —10°C. The reaction was accompanied by violent evolution of heat and propylene (710 ml, 100%). IR spectrum of the residue does not exhibit an absorption band at 1640 cm^{-1}; ^{11}B NMR spectrum shows only one signal, at —54.5 ppm. Distillation afforded 2.5 g (78.5%) of methoxy(diethyl)borane, b.p. 89—90°C, $n_D^{23.5}$ 1.3875 (lit. [44] b.p. 83—85°C).

(b). Propylene was evolved (1120 ml) on reaction of 6.7 g of allyl(di-n-propyl)borane (I, R = n-C_3H_7) with 4 ml of methanol. Subsequent distillation of the residue gave 5.7 g (92%) of methoxy(di-n-propyl)borane, b.p. 36—37°C/17 mmHg, n_D^{20} 1.4027 (lit. b.p. 55—56°C/44 mmHg, n_D^{20} 1.4023 [45]). ^{11}B NMR spectrum consists of only one signal, at —52.9 ppm.

(c). A similar reaction of 3.9 g of allyl(di-n-butyl)borane (I, R = n-C_4H_9) with 2.5 ml of methanol gave propylene (530 ml) and 3.4 g (93%) of methyl ester of di-n-butylboronic acid, b.p. 78—80°C/33 mmHg, n_D^{20} 1.4147. ^{11}B NMR spectrum contains but one signal, at —54.6 ppm.

(d). To 5.6 g of crotyl(di-n-propyl)borane (VIII, R = n-C_3H_7) was added 5.6 ml of methanol at 0—5°C. 1-Butene was evolved (0.8 l), and distillation gave 3.2 g (70%) of methoxy(di-n-propyl)borane, b.p. 65—67°C/85 mmHg, n_D^{20} 1.4022.

(e). To 2.3 g of 3,3-dimethylallyl(di-n-propyl)borane was added 1 ml of methanol at room temperature, the mixture was allowed to stand for 0.5 h at room temperature, then distilled to afford 0.85 g (90%) of 3-methyl-1-butene (GLC), b.p. 21—22°C (IR spectrum: 1640 and 3080 cm^{-1}) and 1.4 g (80%) of methoxy(di-n-propyl)borane, b.p. 65—66°C/80 mmHg, n_D^{20} 1.4029.

(f). To 6.15 g of diallyl(n-butyl)borane (II, R = n-C_4H_9) was added 4 ml of methanol at 0—5°C. Violent heat evolution accompanied the production of propylene (1825 ml, 99%). Distillation of the residue gave 4.05 g (91.5%) of dimethoxy(n-butyl)borane, b.p. 45—56°C/32 mmHg, n_D^{20} 1.3950 (lit. [46] b.p. 37—38°C/21 mmHg, n_D^{20} 1.3933).

Reactions of allyl(alkyl)boranes with water

(a). To 2.1 g of crotyl(di-n-propyl)borane (VIII, R = n-C_3H_7) was added 1 ml of water at room temperature. Reaction proceeds with violent evolution of heat and 300 ml of a mixture of 1-butene (98%) and 2-butene (2%). The residue gave, on distillation, 1.3 g (89%) of di-n-propylboronic acid anhydride, b.p. 75—76°C/7 mmHg, n_D^{20} 1.4160 (lit. [47] b.p. 91—92°C/10 mmHg, n_D^{20} 1.4170).

(b). To 2.4 g of diallyl(n-propyl)borane (II, R = n-C_3H_7) was added 1 ml of water, with care, at room temperature. A highly exothermic reaction occurred accompanied by evolution of propylene (780 ml). After distilling out the volatile products under reduced pressure, solid n-propylboronic acid remained. Sublima-

tion of the latter yielded 1.1 g (90%) of the pure acid, m.p. 105—106°C (lit. [48] m.p. 107°C).

References

1 B.M. Mikhailov, Usp. Khim., 45 (1976) 1102.
2 B.M. Mikhailov, Organometal. Chem. Rev. Sect. A, 8 (1972) 1.
3 B.M. Mikhailov and Yu.N. Bubnov, Organoboron Compounds in Organic Synthesis, Nauka, Moscow, 1977.
4 B.M. Mikhailov and Yu.B. Bubnov, Izv. Akad. Nauk SSSR, Ser. Khim., (1964) 1874.
5 B.M. Mikhailov, V.N. Smirnov and O.D. Riazanova, Dokl. Akad. Nauk SSSR, 204 (1972) 612.
6 I. Mehrotra and D. Devaprabhakara, J. Organometal. Chem., 51 (1973) 93.
7 Yu.N. Bubnov and B.M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., (1967) 472.
8 Yu.N. Bubnov, V.S. Bogdanov and B.M. Mikhailov, Zh. Obshch. Khim., 38 (1968) 260.
9 A. Meller and W. Gerger, Monatsh. Chem., 105 (1974) 684.
10 B.M. Mikhailov and Yu.N. Bubnov, Tetrahedron Lett., (1971) 2127.
11 B.M. Mikhailov and Yu.N. Bubnov, Zh. Obshch. Khim., 41 (1971) 2039.
12 Yu.N. Bubnov, O.A. Nesmeyanova, T.Yu. Rudashevskaya, B.M. Mikhailov and B.A. Kazansky, Tetrahedron Lett., (1971) 2153.
13 Yu.N. Bubnov, O.A. Nesmeyanova, T.Yu. Rudashevskaya, B.M. Mikhailov and B.A. Kazansky, Zh. Obshch. Khim., 43 (1973) 135.
14 B.M. Mikhailov, Yu.N. Bubnov, O.A. Nesmeyanova, T.Yu. Rudashevskaya and B.A. Kazansky, Tetrahedron Lett., (1972) 4627.
15 B.M. Mikhailov, Yu.N. Bubnov and S.A. Korobeinikova, Izv. Akad. Nauk SSSR, Ser. Khim., (1970) 2631.
16 B.M. Mikhailov, Yu.N. Bubnov, S.A. Korobeinikova and S.I. Frolov, J. Organometal. Chem., 27 (1971) 165.
17 B.M. Mikhailov, Yu.N. Bubnov and S.A. Korobeinikova, J. Prakt. Chem., 312 (1970) 998.
18 B.M. Mikhailov,and V.F. Pozdnev, Izv. Akad. Nauk SSSR, Ser. Khim., (1967) 1477.
19 L. Chevolot, J. Soulie and P. Cadiot, Tetrahedron Lett., (1974) 3435.
20 E. Negishi, T. Yoshida, A. Silveira and B.L. Chiou, J. Org. Chem., 40 (1975) 814.
21 B.A. Kazansky, Yu.N. Bubnov, S.V. Zotova, N.M. Abramova, V.G. Kiselev and B.M. Mikhailov, Tetrahedron Lett., (1974) 567.
22 B.M. Mikhailov and M.E. Gursky, Izv. Akad. Nauk SSSR, Ser. Khim., (1973) 2644.
23 D.S. Sethi, G.C. Joshi and D. Devaprabhakara, Can. J. Chem., 47 (1969) 1083.
24 Ai-Tse Po, Chia-Hsing Pan and Cheng-Heng Kao, Hua Hsueh Hsueh Pao, 30 (1964) 79; Chem. Abstr., 61 (1964) 1883.
25 Y. Tanigawa, I. Moritani and Sh. Nishida, J. Organometal. Chem., 28 (1971) 73.
26 G.W. Kramer and H.C. Brown, J. Organometal. Chem., 73 (1974) 1.
27 B.M. Mikhailov, Yu.N. Bubnov and A.V. Tsyban, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 483.
28 B.M. Mikhailov, Yu.N. Bubnov and A.V. Tsyban, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 979.
29 B.M. Mikhailov, V.A. Vaver and Yu.N. Bubnov, Dokl. Akad. Nauk SSSR, 126 (1959) 575.
30 G.E. Kacheishvili, N.I. Pirzkhalava and B.D. Dzhioshvili, Zh. Obshch. Khim., 43 (1973) 2402.
31 G.E. Kacheishvili, N.I. Pirzkhalava and B.D. Dzhioshvili, Soobshch. Akad. Nauk Grusin. SSR, 73 (1974) 69.
32 B.M. Mikhailov, G.Yu. Pek, V.S. Bogdanov and V.F. Pozdnev, Izv. Akad. Nauk SSSR, Ser. Khim., (1966) 1117.
33 B.M. Mikhailov, Yu.N. Bubnov and V.S. Bogdanov, Zh. Obshch. Khim., 45 (1975) 333.
34 B.M. Mikhailov, Yu.N. Bubnov and V.S. Bogdanov, Zh. Obshch, Khim., 45 (1975) 324.
35 J.A. Pople, W.G. Schneider and H.J. Bernstein, High Resolution Magnetic Resonance Spectra, McGraw-Hill, 1959, Ch. 10.
36 B.M. Mikhailov, Yu.N. Bubnov and A.V. Tsyban, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 2842.
37 B.M. Mikhailov and Yu.N. Bubnov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1960) 1872.
38 R. Köster, K. Amen, H. Bellut and W. Fenzl, Angew. Chem., 83 (1971) 805.
39 B.M. Mikhailov and L.S. Vasil'ev, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1962) 1756.
40 B.M. Mikhailov, Yu.N. Bubnov, Zh. Obshch. Khim., 31 (1961) 160.
41 B.M. Mikhailov, A.A. Akhnazaryan and L.S. Vasil'ev, Dokl. Akad. Nauk SSSR, 136 (1961) 828.
42 B.M. Mikhailov, Yu.N. Bubnov and V.G. Kiselev, Zh. Obshch. Khim., 36 (1966) 62.
43 J. Brault and J.M. Lalancette, Can. J. Chem., 42 (1964) 2903.
44 R. Köster, H. Bellut, G. Benedikt and E. Ziegler, Ann., 724 (1969) 34.
45 B.M. Mikhailov and Yu.N. Bubnov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1959) 172.
46 B.M. Mikhailov and T.A. Shchegoleva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1958) 777.

47 B.M. Mikhailov and T.A. Shchegoleva, Zh. Obshch. Khim., 29 (1959) 3130.
48 F. Challenger and O.V. Richards, J. Chem. Soc., (1934) 405.
49 B.M. Mikhailov and L.S. Vasil'ev, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1962) 628.
50 R.N. Sterlin, V.L. Isaev, G.M. Zakharov, B. Martin and I.L. Knunyanz, Zh. Vses. Khim. O-va., 12 (1969) 475.
51 B.M. Mikhailov, Yu.N. Bubnov, A.V. Tsyban' and M.Sh. Grigoryan, J. Organometal. Chem., 154 (1978) 131.