ORGANOBORON COMPOUNDS. 400 . BORON-CONTAINING HETEROCYCLES FROM VINYLAMINODIALKYLBORANES AND ISONITRILES

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Abstract - Vinylaminodialkylboranes react with isonitriles to give the (4+1) cycloadducts (5). These adducts undergo thermal anionotropic rearrangements producing the derivatives of 2-amino-1,2-azaboroline (7), for which the reactions of splintering the exo-cyclic B-N bond are characteristic. On action of alcohol-aqueous solution of HCl, the heterocycles (7) turn into their oxygenous analogues - the 2-alkoxy-3H-1,2 -oxaborol derivatives (10).

Vinylaminodialkylboranes (VADAB) are valuable starting reagents for the synthesis of boron-containing heterocyclic compounds. VADAB were formerly shown to form the (4+2) cycloadducts with nitriles [1,2], phenyl isocyanate, and phenyl isothiocyanate [3]. Now we report an interaction between VADAB and isonitriles which results in the five-membered boron-nitrogenous heterocycles (see a preliminary report [4]).

The well-known reactions of isonitriles with some boronic compounds: diborane, triorganylboranes, and organylmercaptodiethylboranes, are classified as reactions of inserting isonitriles into the B-E bond (E= H,C,S) [5]. As a plausible exclusion, one can envisage the addition of isonitriles to the dialkylboryl derivatives of N,N'-disubstituted amidines affording the (4+1) cycloadducts,[6] however it is impossible, in this case, to exclude the possibility of proceeding the reaction by way of isonitrile insertion into the B-N bond too.

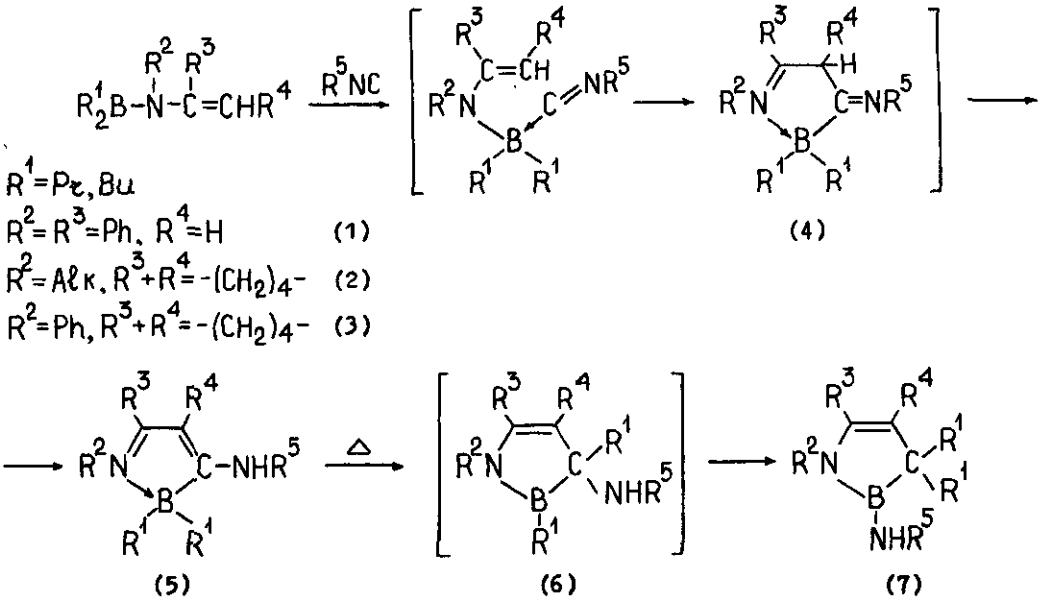
It has turned out that isonitriles add to VADAB at the 1,4-position though. Depending on the reagents structures and reaction conditions, there are formed either five-membered cyclic compounds of the four-coordinated boron or the products of rearrangement of the latter compounds - heterocycles with the trivalent

boron atom.

As initial reagents, we have chosen VADAB with partially alkylated β-C atom of the vinyl group: easily available (α-styryl)phenylaminodialkylboranes (1) and (cyclohexenyl)organylaminodialkylboranes (2,3) [2,7].

On addition of isonitriles to (1-3), an exothermal reaction occurs which, in most cases, leads to the 2-amino-1,2-azaboroline derivatives (7), but with the use of t-BuNC and (1) or (2) the reaction terminates in the stage of 3-amino-1-azonia-2-borata-3,5-cyclopentadiene derivatives (5) formation. The latter compounds isomerize into corresponding (7) only on heating. In general terms, conversions of VADAB with isonitriles can be symbolized as follows (Scheme 1).

Scheme 1



The reaction begins, probably, with the electrophilic attack by VADAB on the C atom of isonitrile. The complex thus formed undergoes cyclization to turn into the compound (4) which formally is the product of (4+1) cycloaddition. Though complex compounds of VADAB with isonitriles were not detectable, it should be noted that the complexes Et_2BSR with R'NC were earlier described [5]. The intermediate compounds (4) were not identified because of fast conversion into (5) by way of the prototropic 1,3(C→N) rearrangement.

The heterocycles (5) represent a novel type of boron heterocyclic compounds, in which the five-membered boron-containing ring is isoelectronic with cyclopentadiene. The presence of amino group at the α-C atom in (5), as well as conju-

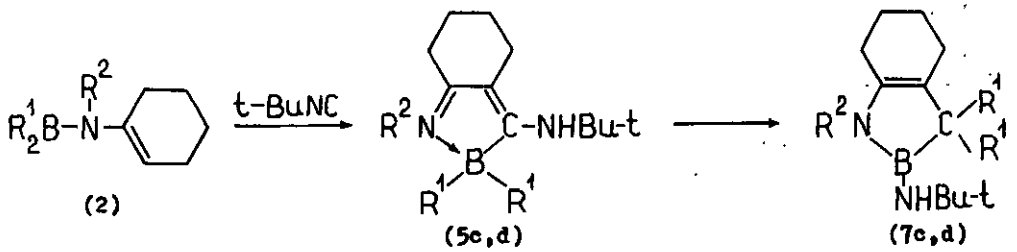
gated double bonds in the ring, stipulates the possibility of anionotropic rearrangements. In the beginning, the alkyl group R^1 migrates from the four-coordinated B atom to the adjacent C atom in the cycle with simultaneous reorganizing the ring bonds and formation, in the end, of the cyclic compound (6) with the trivalent B atom. Neither isolation of (6) nor its detection by physico-chemical methods worked well because of fast further rearrangement consisting in migration of the amino group to the B atom and the second alkyl group R^1 - to the α-C atom to produce (7). Rearrangement of such kind, proceeding on interaction between isonitriles and triorganylboranes, are well known [5].

Crystalline (5a,b) (see Table 1), obtained from corresponding (1) and t-BuNC in 86-89% yield, are stable in air, they are not decomposed by water, alcohols, and acetic acid. The intra-complex structures of these compounds are confirmed by the ^{11}B NMR data (upfield signals). An alternative structure (4) should be rejected as the IR spectra of (5a,b) contain the NH absorption band in the region 3400 cm^{-1}, and the ^1H NMR spectra thereof reveal the vinyl proton signal (δ 5.52-5.57 ppm).

Isomerization of (5a,b) proceeds smoothly at 130-140°C, i.e. even on distillation in vacuum.

Mixing t-BuNC with (2) leads to formation of the bicyclic compounds (5c,d), which is confirmed by appearance of the absorption bands at 3375 (NH), 1520, and 1570 cm^{-1} (C=C-C=N) in the IR spectrum of the reaction mixture, and the signal with δ=4.83 ppm in the ^1H NMR spectrum. It is necessary to heat the mixture for completing the reaction, however even at 40-50°C the rearrangement of (5c,d) into (7c,d) sets in, so isolation of (5c,d) in pure state is impossible. The formation of (7c,d) rapidly occurs at 100-110°C (Scheme 2).

Scheme 2



(2) (5c,d) (7c,d)

R^1=Bu, R^2=i-Bu (c); R^1=Bu, R^2=i-Am (d)

Table 1. The boron-nitrogenous heterocycles from VADAB and isonitriles

Compound	R^1	R^2	R^3	R^4	R^5	Yield %	B.p.°C/torr	^{11}B NMR, ppm (solvent, °C)	Formula
5a	Bu	Ph	Ph	H	t-Bu	86	a)	-3 e) (THF, 70)	$C_{27}H_{39}BN_2$
5b	Pr	Ph	Ph	H	t-Bu	89	b)	-	$C_{25}H_{35}BN_2$
7a	Bu	Ph	Ph	H	t-Bu	79	161-163/1	36 e) (THF, 80)	$C_{27}H_{39}BN_2$
7b	Pr	Ph	Ph	H	t-Bu	76	154-156/0.8 c)	-	$C_{25}H_{35}BN_2$
7c	Bu	i-Bu	$-(CH_2)_4-$		t-Bu	77	152-153/1	-	$C_{23}H_{45}BN_2$
7d	Bu	i-Am	$-(CH_2)_4-$		t-Bu	81	153-154/1	39 (THF, 80)	$C_{24}H_{47}BN_2$
7e	Bu	Ph	$-(CH_2)_4-$		t-Bu	85	145/0.7	41 e) (THF, 80)	$C_{25}H_{41}BN_2$
7f	Pr	Ph	$-(CH_2)_4-$		n-Bu	69	153-155/1	-	$C_{23}H_{37}BN_2$
7g	Pr	i-Bu	$-(CH_2)_4-$		Ph	88	160-162/1.5	36 (THF, 70)	$C_{23}H_{37}BN_2$
7h	Bu	i-Bu	$-(CH_2)_4-$		Ph	78	172-174/1	36 (THF, 70)	$C_{25}H_{41}BN_2$
7i	Pr	Ph	$-(CH_2)_4-$		Ph	83	190-191/1.5	-	$C_{25}H_{33}BN_2$
7j	Bu	Ph	$-(CH_2)_4-$		Ph	80	185-187/0.5	39 (toluene, 80)	$C_{27}H_{37}BN_2$
7k	Bu	Ph	Ph	H	Ph	79	205-207/1	42 (THF, 80)	$C_{29}H_{35}BN_2$
7l	Pr	Ph	Ph	H	n-Bu	67	178-180/1 d)	-	$C_{24}H_{35}BN_2$

Footnotes:

a) M.p. 54-56°C, b) M.p. 50-54°C, c) M.p. 75-77°C (CH_3OH), d) M.p.48-50°C,
e) ^{1}H NMR (CCl_4, δ, ppm): 7.1 m (C_6H_5), 5.52 s (CH=C), 5.23 broad. s (NH), 1.33 s (CMe_3) (5a); 6.92 m (C_6H_5), 4.68 s (CH=C), 3.46 broad. s (NH), 1.33 s (CMe_3) (7a); 7.0 m (C_6H_5), 2.98 s (NH), 1.03 s (CMe_3) (7e).

The 2-amino-1,2-azaboroline derivatives (7e-l) were obtained directly from isonitriles and VADAB. The heterocycles (7) are colourless liquids distilling in vacuum without decomposition (only (7b,l) are crystalline substances). Their ^{11}B NMR spectra contain signals in the region 36-42 ppm, therefore, being based only on these data, one cannot exclude the alternative structure (6). Thus, 2-isobutylamino-1-butyl-1,2-azaborolidine, which is a saturated analogue of (7) shows the upfield signal (34 ppm) like the compounds of the $RB(NR_2)_2$ series (32-34 ppm) [8]. However, the ^{13}C NMR data allow to draw an unambigous conclusion in favour of (7) as they demonstrate the alkyl groups R^1 to be equivalent and the C atom connected with the B atom to be the tertiary one. Thus, in the spectrum of (7j) four signals (δ =35.6, 28.2, 23.35, and 14.0 ppm) from two groups C_4H_9 are observed, and the broadened signal with chemical shift (CS) 41.1 ppm should be assigned to the tertiary C atom connected with the B one because the broadened resonance signal of the CH_2 group in (6) would be observed in higher field (δ 30 ppm) [9].

In the IR spectra of (7), the NH absorption band is observed over a range 3370-3410 cm^{-1} , the stretching vibration band of the C=C bond is at 1625-1630 (7a-d) or 1665-1680 cm^{-1} (7e-l). Intense absorption at 1500 cm^{-1} is also characteristic of (7), which is probably conditioned by the B-N vibrations.

In the mass-spectra of (7), the parent ions peaks are observed, the main direction of decomposition of these ions being elimination of one of the alkyl groups R^1 in the shape of the radical.

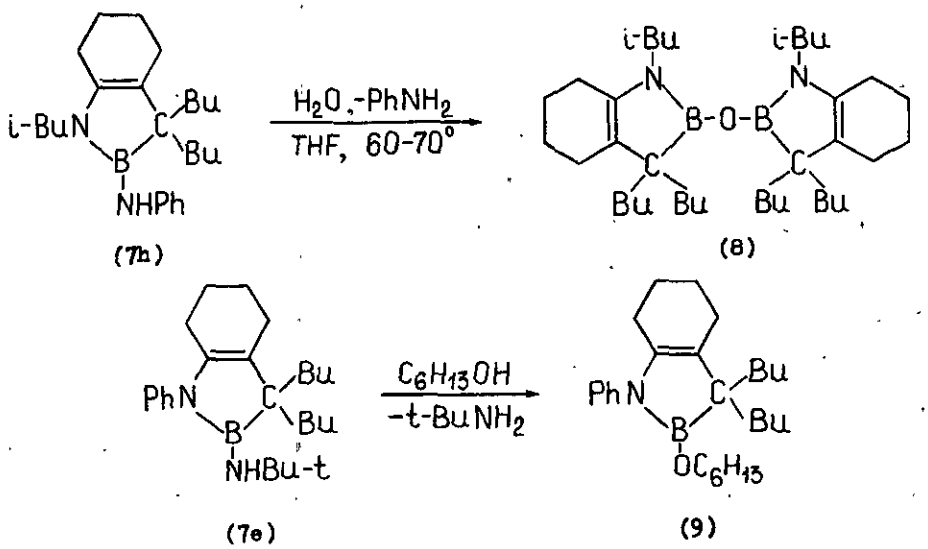
The heterocycles (7) do not change on heating up to 150-160°C (^{11}B NMR spectroscopy). The reactions proceeding with splitting the exo-cyclic B-N bond are most characteristic of these compounds, e.g. hydrolysis of (7h) in boiling aqueous THF and reaction of (7e) with 1-hexanol which occurs at 150-160°C (Scheme 3). The heterocycles (9) are formed at 20°C if alcoholysis of (7e) is carried out with hexanol in the presence of ethereal solution of HCl.

In the series of the 2-amino-1,2-azaboroline derivatives, it is possible to effect a transamination reaction, e.g. (7j) was obtained by interaction between (7e) and aniline (Scheme 4).

It is of interest that carrying out alcoholysis and transamination requires more hard conditions than those usually applied in the case of simple aminoboranes. Probably, it is accounted for by sterical hindrance in the nucleophilic attack by alcohol or amine on the B atom. An influence of the sterical factors on the

hydrolysis and transamination was demonstrated previously [10].

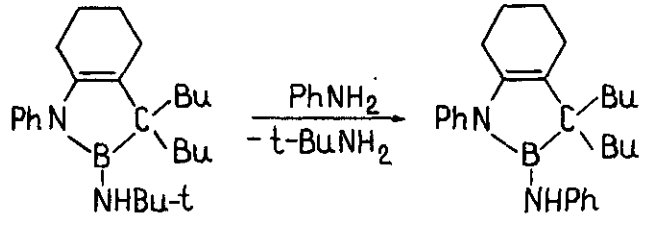
Scheme 3



(7h) (8)

(7e) (9)

Scheme 4



(7e) (7j)

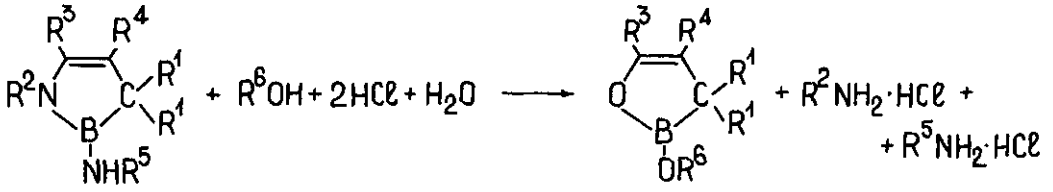
We used the heterocycles (7) for the synthesis of their oxygenous analogues - the 2-hydroxy-3H-1,2-oxaborol derivatives (10). The conversion of (7) into (10) was accomplished by action of alcohol-aqueous solution of HCl on (7). Thus, the compounds (10a-c) were prepared in 54-78% yield from (7c,j,k) (Scheme 5).

In acidic medium, there occure apparently an opening of the cycle in (7) and hydrolysis of the enamine to lead to the ketone, which enolic form takes part in consequent recyclization producing (10) (Scheme 6).

The compounds (10a-c) are colourless liquids which are distilled in vacuum without decomposition. Their ^{11}B NMR spectra reveal signals in the region 36-38 ppm. The alkyl groups R^1 in the ^{13}C NMR spectra are equivalent, and the signal of the

C atom connected with the B atom has CS that is characteristic of the tertiary C atom in five-membered ring (δ =37.7 ppm, for 10b). In the mass-spectra of these heterocycles, the largest masses conform to the parent ions peaks, while 40-60% of full ionic current falls to the share of the $(M-R^1)^+$ ions. The absorption band of the C=C bond in the IR spectra is at 1690 (10a,b) and 1630 cm^{-1} (10c). An intense absorption in the region 1350-1370 cm^{-1} is related to the B-O stretching vibrations.

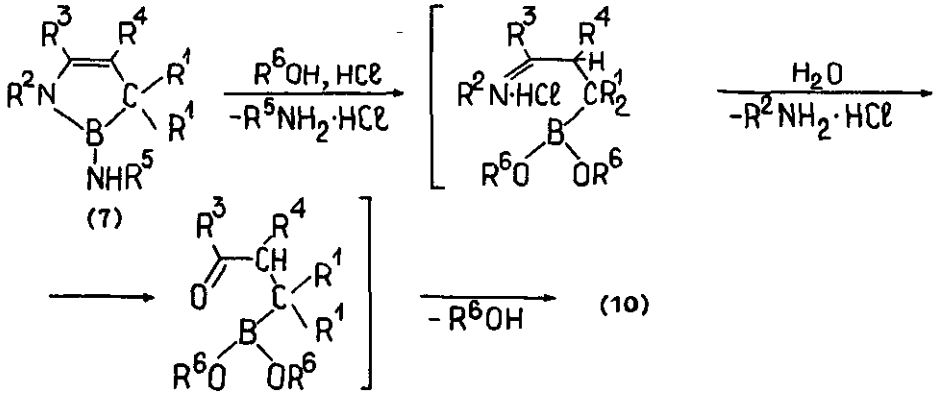
Scheme 5



(7) (10)

$R^1=R^6=Bu$, $R^3+R^4=-(CH_2)_4-$ (10a)
$R^1=Bu$, $R^3+R^4=-(CH_2)_4-$, $R^6=C_6H_{13}$ (10b)
$R^1=R^6=Bu$, $R^3=Ph$, $R^4=H$ (10c)

Scheme 6

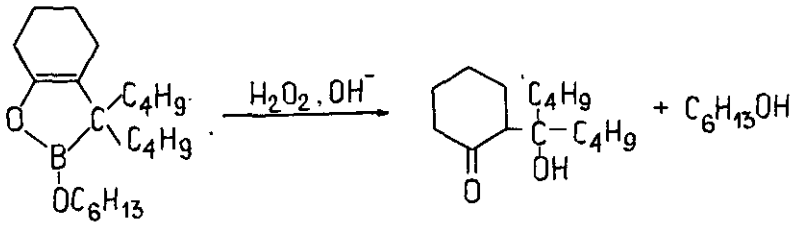


Oxidation of (10b) with H_2O_2 in alkaline medium yielded 2-(5-hydroxynonyl)cyclohexanone (11) and n-hexanol (Scheme 7).

Only two dehydroborol derivatives were previously described, these pertain to the 2-alkyl-3H-1,2-oxaborol series. The two compounds were obtained in low yield by reactions of the carboxylic acids chloroanhydrides with sodium 1-propynyltri-

ethylboranate [11].

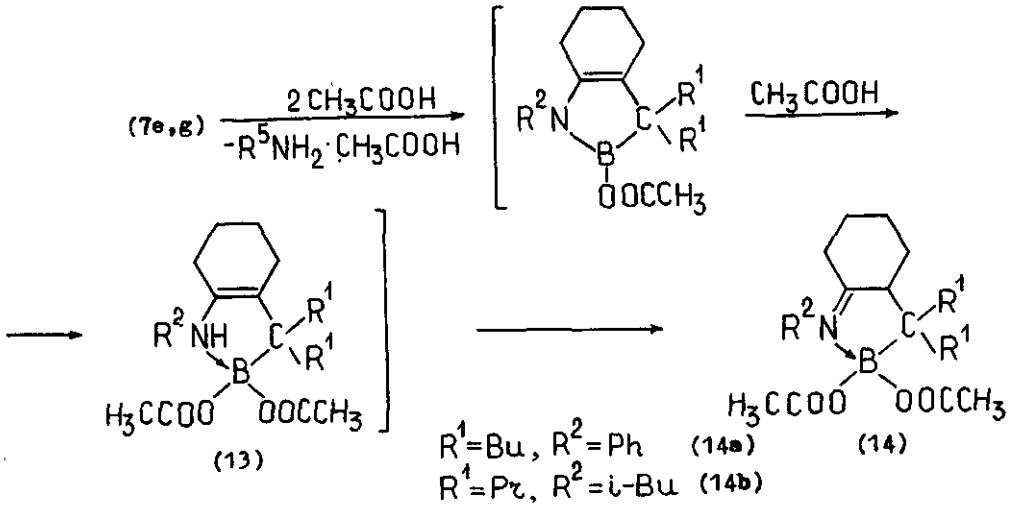
Scheme 7



(10b) (11)

One more example of using 2-amino-1,2-azaboroline derivatives for synthesis of other heterocyclic boron compounds is the reaction of (7e,g) with CH_3COOH leading to the derivatives of 1-azonia-2-borata-5-cyclopentene (14a,b) (Scheme 8).

Scheme 8



(13)

R^1=Bu, R^2=Ph (14a)
R^1=Pr, R^2=i-Bu (14b)

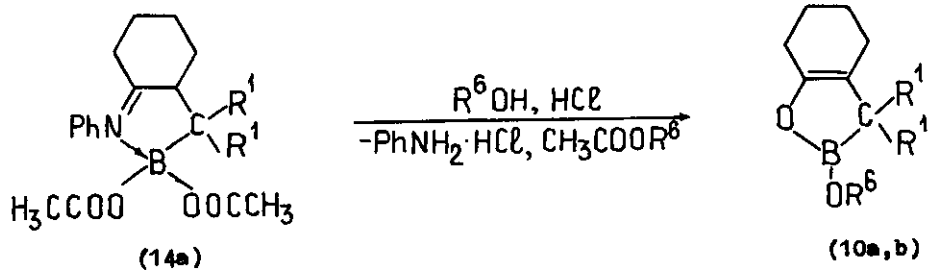
(14)

Formation of (14a,b) probably is the result of the following successive transformations: replacement of the exo-cyclic amino group in corresponding (7) by the acetoxy one, addition of the second CH_3COOH molecule to the intermediate azaboroline (12), and isomerization of the adduct (13) into its tautomer (14). (One mole of CH_3COOH is required for binding the amine formed). Thus, of the heterocycles with the tetra-coordinated boron obtained, the imine structure (14) proves to be more advantageous from energetical viewpoint than the enamine structure (13), which is in full conformity with the results of the study on products of addition of CH_3COOH, H_2O, alcohols, and HCl to 1-cyclohexenyl-2-butyl-

azaborolidine [12].

The compounds (14a,b) are crystalline substances which are hydrolized in air. Heating these compounds with a solution of HCl in BuOH or $C_6H_{13}OH$ produces corresponding (10) (Scheme 9).

Scheme 9



(14a) (10a,b)

The ability of (7) for entering addition reactions, however, is expressed to a less extent than that of 1,2-azaborolidines [11-14]. All attempts to obtain the four-coordinated boron compounds by action of water and alcohols on (7) failed as the reaction stops in the stage of formation of (8) and (9).

Experimental

All operations with organoboron compounds were carried out in dry argon atmosphere. ^{11}B NMR spectra were recorded on a "Bruker SXP 4-100" spectrometer (positive shifts at low field relative to $Et_2O{\cdot}BF_3$), ^1H NMR - on a "Varian DA-60-IL" instrument, ^{13}C NMR - on a "Varian WP-60" spectrometer. IR spectra were recorded on a UR-20 spectrometer. Mass-spectra were obtained on a "Varian CH-6" instrument with the use of direct inlet of the samples into ionic source. Vinylaminodialkylboranes were synthesized according to the methods described[1,2]. All compounds herein prepared had exellent elemental analyses.

3-t-Butylamino-1,5-diphenyl-2,2-dibutyl-1-azonia-2-borata-3,5-cyclopentadiene (5a). To 7.9 g of (1, R^1=Bu) was added dropwise 2.4 g of fresh-distilled t-BuNC (strong warming-up is observed). After distilling off excess isonitrile the residue was allowed to stay until crystallization was completed. The crystals were filtered and rinsed with cooled methanol. 8.5 g (86%) of (5a) was obtained. ^{11}B NMR (THF, 70°C): -3 ppm. IR (CCl_4,ν, cm^{-1}): 1520, 1540 (C=C-C=N), 3400 (NH). ^1H NMR (CCl_4,δ, ppm): 7.1 m (C_6H_5), 5.52 s (CH=C), 5.23 broad.s (NH), 1.33 s (CMe_3). Mass-spectrum (MS) (m/z): 345 $(M-C_4H_9)^+$. UV-Spectrum (hexane): λ_{max} 375 nm (ε 16400).

3-t-Butylamino-1,5-diphenyl-2,2-dipropyl-1-azonia-2-borata-3,5-cyclopentadiene (5b). This was prepared in a similar manner in 89% yield. ^{1}H NMR (CCl_4,δ, ppm): 7.1 m (C_6H_5), 5.57 s (CH=C), 5.30 broad.s (NH), 1.33 s (CMe_3). MS (m/z): 331 $(M-C_3H_7)^+$.

Reaction of t-BuNC with (N-isobutyl)cyclohexenylaminodibutylborane. A mixture of 5.8 g of (2, R^1=n-Bu, R^2=i-Bu) and 3.6 ml of t-BuNC was heated at 70-90°C for 20 min, then excess isonitrile was distilled off in vacuum to give viscous liquid residue - 3-t-butylamino-1-isobutyl-2,2-dibutyl-4,5-tetramethylene-1-azonia-2-borata-3,5-cyclopentadiene (5c) together with small amounts of initial (2) and 2-t-butylamino-1-isobutyl-3,3-dibutyl-4,5-tetramethylene-1,2-azaboroline (7c). IR (CCl_4,ν, cm^{-1}): 1520, 1570 (C=C-C=N), 3395 (NH). ^{1}H NMR (CCl_4,δ, ppm): 4.83 broad.s (NH). MS (m/z): 303 $(M-C_4H_9)^+$.

2-Organylamino-1,3,3,4,5-pentaorganyl-1,2-azaborolines (7a-l). To 0.03-0.05 mole of VADAB was added dropwise 0.036-0.056 mole of fresh-distilled isonitrile (warming-up). The mixture was kept at room temp. for several hours and distilled to afford (7) (see Table 1).

Thermal isomerization of (5a) into 2-t-butylamino-1,5-diphenyl-3,3-dibutyl-1,2-azaboroline (7a). 6.7 g of (5a) was heated at 130-140°C during 15 min, the conversion having been checked quantitatively by IR and ^{1}H NMR spectra. Distillation gave 5.73 g (94%) of (7a), b.p. 150-161°C (1 torr), n_D^{20} 1.5477. ^{1}H NMR (CCl_4,δ, ppm): 4.68 s (CH=C), 3.44 broad.s (NH). IR (CCl_4,ν, cm^{-1}): 1632 (C=C), 3370 (NH).

Thermal isomerization of (5b) into 2-t-butylamino-1,5-diphenyl-3,3-dipropyl-1,2-azaboroline (7b). Analogously, from (5b) was obtained (7b) in 91% yield, b.p. 154-156°C (0.8 torr). ^{1}H NMR (CCl_4,δ, ppm): 4.68 s (CH=C), 3.46 broad.s (NH). IR (CCl_4,ν, cm^{-1}): 1630 (C=C), 3375 (NH).

Transamination of 2-t-butylamino-1-phenyl-3,3-dibutyl-4,5-tetramethylene-1,2-azaboroline (7e) with aniline. A mixture of 5.7 g of (7e) and 4.05 g of aniline was heated at 130-160°C distilling off t-$BuNH_2$ (1.2 ml). The residue was distilled to give 5.4 g (96%) of 2-anilino-1-phenyl-3,3-dibutyl-4,5-tetramethylene-1,2-azaboroline (7j), b.p. 180-185°C (1 torr), n_D^{20} 1.5610.

Hydrolysis of 2-anilino-3,3-dibutyl-1-isobutyl-4,5-tetramethylene-1,2-azaboroline (7h). To a solution of 9.1 g of (7h) in 22 ml of THF was added 1 ml of water, then the mixture was refluxed for 1 h. Removing the solvent and distilla-

tion afforded 3.6 g (75%) of the anhydride (8), b.p. 240-242°C (2 torr), n_D^{20} 1.5392. IR (CCl_4,ν, cm^{-1}): 1350-1370 (B-O), 1662 (C=C). MS (m/z): 592 ($M^{+\cdot}$).

2-Hexyloxy-1-phenyl-3,3-dibutyl-4,5-tetramethylene-1,2-azaboroline (9). A mixture of 5.8 g of (7e) and 5 ml of abs. $C_6H_{13}OH$ was heated at 150-160°C distilling off t-$BuNH_2$ (1 ml). Distillation of the residue gave 5.8 g (93%) of (9), b.p. 202-204°C (2 torr), n_D^{20} 1.5081. ^{11}B NMR (THF, 80°C): 39.4 ppm. ^1H NMR (CCl_4,δ, ppm): 6.96 m (C_6H_5), 3.83 t (OCH_2). IR (CCl_4,ν, cm^{-1}): 1350-1370 (B-O), 1670 (C=C).

2-Butoxy-3,3-dibutyl-4,5-tetramethylene-3H-1,2-oxaborol (10a). To 8.0 g of (7c) in 10 ml of BuOH was added dropwise 10 ml of 4.2 N solution of HCl in BuOH (warming-up), then 1 ml of water was added and the mixture refluxed for 1.5 h. After cooling to 20°C, 20 ml of hexane was added, and amines salts were filtered(5.46 g). The filtrate was evaporated and distilled to give 9.7 g (58%) of (10a), b.p. 130-132°C (1.5 torr), n_D^{20} 1.4610. ^{11}B NMR (THF, 70°C): 37.3 ppm. IR (CCl_4,ν, cm^{-1}): 1350-1370 (B-O), 1690 (C=C). MS (m/z): 306 ($M^{+\cdot}$).

2-Hexyloxy-3,3-dibutyl-4,5-tetramethylene-3H-1,2-oxaborol (10b). Similarly to (10a), the compound (10b) was obtained in 78% yield, b.p. 132-134°C (1 torr), n_D^{20} 1.4674. ^{11}B NMR (THF, 80°C): 37.9 ppm. MS (m/z): 334 ($M^{+\cdot}$).

2-Butoxy-5-phenyl-3,3-dibutyl-3H-1,2-oxaborol (10c). In a similar manner, the compound (10c) was prepared in 54% yield, b.p. 167-169°C (3 torr), n_D^{20} 1.4993. ^{11}B NMR (THF, 80°C): 38.6 ppm. ^1H NMR (CCl_4,δ, ppm): 7.25 m (2 C_6H_5), 5.33 s (CH=C$\langle$), 4.00 m (OCH_2).

2-(5-Hydroxynonyl)cyclohexanone (11). 7.8 g of (10b) in 20 ml of ether was oxidized with alkaline H_2O_2 at +5°C. Routine work-up and distillation gave 1.3 g (36%) of (11), b.p. 114-119°C (2 torr), n_D^{20} 1.4688. IR (CCl_4,ν, cm^{-1}): 1700 (C=O), 3530 (OH).

2,2-Diacetoxy-1-phenyl-3,3-dibutyl-4,5-tetramethylene-1-azonia-2-borata-5-cyclopentene (14a). To 8.5 g of (7e) in 10 ml of hexane was added in parts 4 g of MeCOOH (warming-up). Crystalline t-$BuNH_2$ (2.47 g) was filtered and washed with ether. The filtrate was evaporated, and the solid crystallized from hexane yielding 5.6 g (59%) of (14a), m.p. 85-87°C. ^{11}B NMR (MeCOOH, 120°C): 9.3 ppm. IR (CCl_4,ν, cm^{-1}): 1640 (C=N), 1668, 1700 (C=O). MS (m/z): 427 ($M^{+\cdot}$), 367 $(M-MeCOOH)^+$.

2,2-Diacetoxy-1-isobutyl-3,3-dipropyl-4,5-tetramethylene-1-azonia-2-borata-

5-cyclopentene (14b). This was prepared in a similar way in 58% yield, m.p. 105-108°C (hexane). ^{1}H NMR (CCl_4, δ, ppm): 3.41 d (N-CH_2), 2.45 m (-$\overset{|}{C}$H), 1.87 s (OCOMe).

Action of HCl in BuOH on (14a). To 4.2 g of (14a) in 15 ml of BuOH was added in portions 4.15 ml of 8 N HCl in BuOH. After refluxing for 1 h and removing butanol, 20 ml of hexane was added to the residue. $PhNH_2 \cdot HCl$ (1.2 g) was filtered, and the filtrate was evaporated. Distillation of the residue gave 2.2 g (74%) of the oxaborol (10a), b.p. 123-127°C (1 torr), n_D^{20} 1.4630.

Action of HCl in $C_6H_{13}OH$ on (14a). According to the above procedure, the compound (10b) was obtained in 85% yield, b.p. 132-134°C (1 torr), n_D^{20} 1.4662.

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