REACTION OF DIETHYLBORON CHLORIDE WITH SALTS OF PRIMARY NITROALKANES AND SOME FUNCTIONALLY SUBSTITUTED NITRO COMPOUNDS

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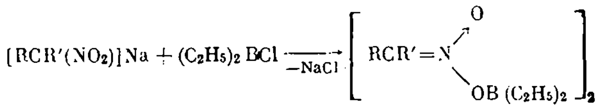
Previously it was shown [1] that the diethylboric esters of sec-alkanenitronic acids are formed when the Na and K salts of secondary nitroalkanes are reacted with diethylboron chloride. In the plan of a systematic study of the dual reactivity of nitro compounds, in the present paper we investigated the diethylborylation of the salts of primary nitroalkanes, and also of nitro compounds that contain C_6H_5, $COOCH_3$, and $CONH_2$ groups on the α-carbon atom.

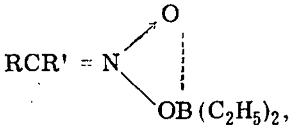
The diethylboric esters of the corresponding nitronic acids are formed when diethylboron chloride is reacted with the Na salts of either primary nitroalkanes or α-phenylnitroethane.



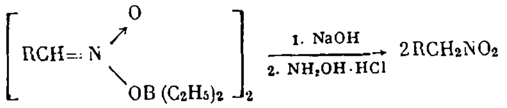
$$[RCR'(NO_2)]Na + (C_2H_5)_2BCl \xrightarrow[-NaCl]{} \left[RCR'{=}N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OB(C_2H_5)_2} \right]_2 \qquad (1)$$

(Ia — c)

$R' = H$, $R = CH_3$ (a), n-C_3H_7(b); $R' = CH_3$, $R = C_6H_5$(c)

The structure of compounds (Ia-c) was confirmed by the data of the ^1H and ^{11}B NMR spectra, and also by some chemical transformations. In the NMR spectra of the (I) esters the signals of the protons of the R' groups are shifted downfield when compared with the analogous signals in the starting nitroalkanes or their salts.* The ^{11}B NMR signals of the (I) esters are in the region that is characteristic for tetracoordinated boron [1, 2] (δ = −12 to −13 ppm).† Although the spectral data do not permit excluding the structure of the monomers  $RCR' = N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OB(C_2H_5)_2}$, for products (Ia-c), by analogy with the previously studied compounds of this type [2], we assign a dimeric structure to them [see Eq. (1)].

The corresponding nitroalkanes were isolated when the (I) esters were subjected to alkaline hydrolysis.



$$\left[RCH{=}N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OB(C_2H_5)_2} \right]_2 \xrightarrow[2.\ NH_2OH\cdot HCl]{1.\ NaOH} 2RCH_2NO_2 \qquad (2)$$

$R = CH_3$, n-C_3H_7

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* In contrast, a diamagnetic shift of the signals would have been observed if C-borylation had occurred.

† Here and subsequently the ^{11}B NMR shifts are given from $(C_2H_5)_2O \cdot BF_3$, and a + sign means an upfield shift.

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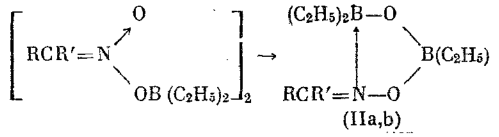
Esters (Ia-c) decompose rapidly at ~20°C. Their decomposition is evidently analogous to the thermal decomposition of the diethylboric esters of sec-alkanenitronic acids (see [1]) and leads to 2,5,5-triethyl-4-alkylidene-1,3-dioxa-4-aza-2,5-diboracyclopentanes. Compounds (IIa-b) could not be completely freed of impurities.

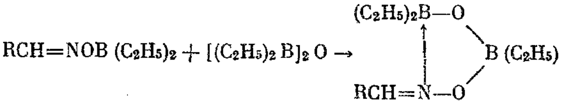


(IIa,b)

R′ = H, R = CH_3 (a), C_3H_7 (b)

(3)

They were identified via spectroscopic studies and chemical transformations. The spectral characteristics of samples (IIa-b) were compared with the corresponding data of the products obtained by counter synthesis.



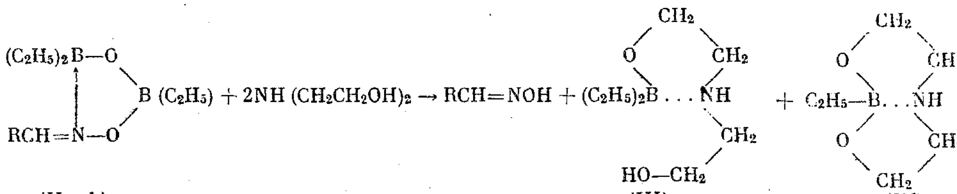
(IIa, b)

R = CH_3 (a), C_3H_7 (b)

(4)

The NMR spectrum of product (IIa), obtained by Eq. (3), has the quartet of the CH proton at the C = N bond with δ 6.80 ppm (J = 6 Hz),* the doublet of the CH_3 protons (δ 2.09 ppm), and the multiplets of the $>B(C_2H_5)$ and $-B(C_2H_5)_2$ protons (0.5-1 ppm region). A comparison of the integral intensities of the signals reveals that impurities are present in the sample. Two singlets with δ −10.1 and −30.9 ppm can be seen in the ^{11}B NMR spectrum of (IIa) (CCl_4), which correspond to tetra- and tricoordinated boron. The ^{11}B NMR spectrum of (IIa) is very close to the spectra of the decomposition products of the diethylboric esters of sec-alkanenitronic acids [1]. The ^1H and ^{11}B NMR spectra of (IIb) confirm the presence of a proton at the C = N bond (triplet with δ 6.84 ppm, J = 6 Hz), and also of tri- and tetracoordinated boron atoms (δ −11.6 and −31.9 ppm; respectively δ −13.1 and −35.5 ppm in the authentic specimen). Judging by the integral intensities of the signals in the ^1H NMR spectrum, (IIb) contains a substantial amount of impurities. The ^{11}B NMR spectrum of the product, obtained after the decomposition of ester (Ic), has two singlets at −11.5 and −33.2 ppm.

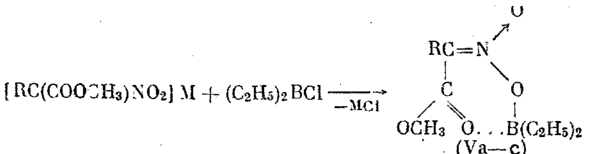
In order to identify the 2,5,5-triethyl-4-alkylidene-1,3-dioxa-2,5-diboracyclopentanes, in a previous paper [1] we used their reaction with diethanolamine. In a similar manner, the treatment of (IIa-b) with diethanolamine gave the corresponding aldoximes, and also the 2-hydroxyethylaminoethyl ester of diethylboric acid (III)† and the ester of diethanolamine with ethylboric acid (IV).



(IIa—b) (III) (IV)

(5)

The diethylboric esters of the corresponding carbomethoxymethanenitronic acids are formed when the salts of nitro compounds, which contain a carbomethoxyl group α to the nitro group, are reacted with diethylboron chloride, in which connection the boron atom in these products is connected to the oxygen of the carbonyl group of a complex bond.



(Va—c)

M = K,Na; R = H (a), CH_3 (b) $COOCH_3$ (c)

(6)

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* Here and subsequently all of the chemical shifts of the protons are given relative to HMDS on the δ scale.

† The pure (III) was isolated only from (IIa).

TABLE 1. Data of NMR Spectra (the chemical shifts are given on the δ scale, ppm)

Formula	Compound	^1H NMR (standard = HMDS)						^{13}C NMR (standard = TMS)						^{11}B NMR (standard = BF_3O-$(C_2H_5)_2$
		solvent	CH_3O	CH or CH_2	CH_3	NH_2	C_2H_5	solvent	C=N or C—N	CH_2	OCH_3	CO	C_2H_5*	
$CH(COOCH_3){=}N{<}^{\nearrow O}_{OB(C_2H_5)_2}$	(Va)	CCl_4	4,05	6,77	—	—	0,4—0,9	CCl_4	103,0	—	56,0	171,8	8,1	—15,8
$CH_3C(COOCH_3){=}N{<}^{\nearrow O}_{OB(C_2H_5)_2}$	(Vb)	CCl_4	4,00		2,05		0,4—0,9	CCl_4	111,5	10,2	55,8	170,9	8,0	—16,7
$(CH_3OOC)_2C{=}N{<}^{\nearrow O}_{OB(C_2H_5)_2}$	(Vc)	CH_2Cl_2, —30° 20°	3,7; 4,0 3,85				0,4—0,9	CCl_4, —20°	111,7		57,4 52,9	170,1 158,1		—15,9
$CH(CONH_2){=}N{<}^{\nearrow O}_{OB(C_2H_5)_2}$	(VIIa)	Acetonitrile Dioxane		6,8 6,7		7,2 7,4 and 7,9	0,3—0,9	Dioxane	105,8			168,9	8,7	—12,8
$CH_3C(CONH_2){=}N{<}^{\nearrow O}_{OB(C_2H_5)_2}$	(VIIb)	"			2,08	7,8 and 8,2	0,3—0,9		112,4	10,2		167,2	8,7	
$CH_2(NO_2)COOCH_3$		CH_2Cl_2	3,78	5,30				CH_2Cl_2	74,9		52,1	161,4		
$CH_3C(NO_2)HCOOCH_3$		CCl_4	3,75	5,1	1,7d									
$CH_2(NO_2)CONH_2$		CH_3CN		5,1		6,5 broad		Dioxane	78,8			168,7		
$CH_3CH(NO_2)CONH_2$		Deuteroacetone		5,4	1,65d	7,2 broad		Deuteroacetone	80,4	9,6		164,2		
$CH(NO_2)(COOCH_3)_2$ [3]		CH_2Cl_2	3,83	5,94					88,3		54,3	160,8		
$C(COOCH_3)_2{=}N{<}^{\nearrow O}_{OCH_3}$ [3]									110,0		52,6 53,8	159,5 158,5		

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*The CH_3 signal is observed, while the CH_2 signal is broadened due to coupling with the boron atom.

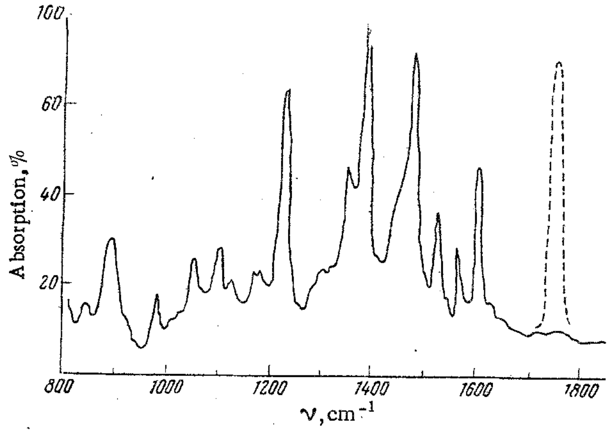


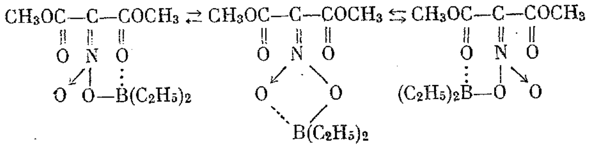
Fig. 1. Infrared spectrum of diethylboric ester of carbomethoxyethanenitronic acid (Vb) in CCl_4 (the band of the C = O group in methyl 2-nitropropionate is indicated by the dotted line).

The structure of esters (Va-c) was confirmed by the NMR method and certain chemical transformations. The NMR spectral data for (Va-c) on the ^1H, ^{13}C, and ^{11}B nuclei are given in Table 1. For comparison we have also given in Table 1 the corresponding characteristics of some other nitro derivatives. In the proton spectra of esters (Va, b), due to the formation of the C = N double bond, the signals of the R group are shifted downfield when compared with the corresponding signals in the nitro compounds. In the ^{11}B NMR spectrum the (Va-c) esters give a singlet in the —15 to —16 ppm region, which suggests the presence of a tetracoordinated boron atom.

The ^{13}C NMR spectra of esters (Va-c) testify to the presence of the C = N double bond in them (the corresponding carbon signal is shifted downfield by 10-15 ppm when compared with the signal in the starting nitroalkanes), and to complex formation between the C = O group and B. As a result of complex formation the signal of the carbon of the C = O group is shifted downfield by more than 10 ppm.

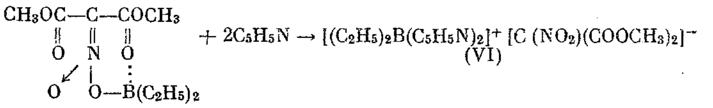
The spectral data very clearly indicate the structure of (Vc). In its ^{13}C NMR spectrum can be seen the nonequivalence of the two $COOCH_3$ ester groups, in which connection one of them in its chemical shifts is close to the ester group in the starting nitroparaffins and in the o-methyl ester of bis-carbomethoxymethanenitronic acid, while the second is close to the ester group in (Va-b). The ^1H NMR spectrum of (Vc), taken at low temperature, also displays a nonequivalence of the two OCH_3 groups, but at 35° the OCH_3 protons give one broad singlet. As a result, it is obvious that an exchange process takes place in (Vc). Employing the known method [4], we determined the coalescence point of the OCH_3 signals (20.5°), the exchange rate constant $K_{293.5°K} = 41.1$ sec^{-1}, and the free activation energy of the exchange process $\Delta G^*_{293.5°K} = 15$ kcal/mole. When the sample was diluted five-fold the parameters of the process changed but slightly (coalescence T = 289°K, K = 37.8 sec^{-1}, $\Delta G^*_{289°K} = 14.8$ kcal/mole).

These data testify to a rapid intramolecular exchange of the diethylboron group between the two carbomethoxyl fragments. This exchange probably proceeds by the scheme:



$$\underset{\substack{\| \quad \| \quad \| \\ O \quad N \quad O \\ O \quad O{-}B(C_2H_5)_2}}{CH_3OC{-}C{-}COCH_3} \rightleftarrows \underset{\substack{\| \quad \| \quad \| \\ O \quad N \quad O \\ O \qquad O \\ B(C_2H_5)_2}}{CH_3OC{-}C{-}COCH_3} \leftrightarrows \underset{\substack{\| \quad \| \quad \| \\ O \quad N \quad O \\ (C_2H_5)_2B{-}O \quad O}}{CH_3OC{-}C{-}COCH_3} \qquad (7)$$

The hydrolysis of ester (Vc) led to the isolation of dimethyl nitromalonate in 70% yield. The reaction of (Vc) with pyridine gives the corresponding boronium salt. The structure of (VI) was proved by elemental analysis and the NMR data.



$$\underset{\substack{\| \quad \| \quad \| \\ O \quad N \quad O \\ O \quad O{-}B(C_2H_5)_2}}{CH_3OC{-}C{-}COCH_3} + 2C_5H_5N \rightarrow \underset{(VI)}{[(C_2H_5)_2B(C_5H_5N)_2]^+ [C(NO_2)(COOCH_3)_2]^-} \qquad (8)$$

The ^1H NMR spectrum has multiplets at 7.2-8.5 and 0.5-0.95 ppm, which respectively belong to the complexed pyridine and the $-B(C_2H_5)_2$ group, and the singlet of OCH_3 at 3.6 ppm. The integral intensity of the signals shows that two complexed pyridine molecules correspond to two OCH_3 groups.

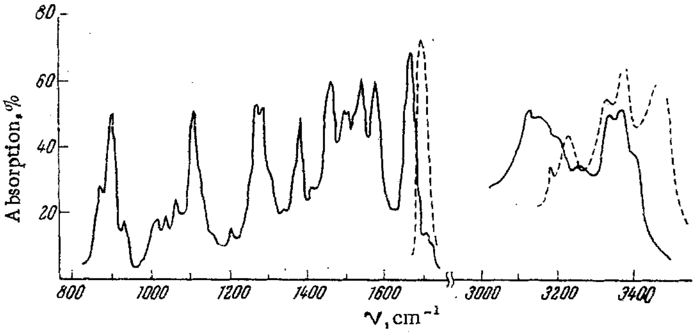
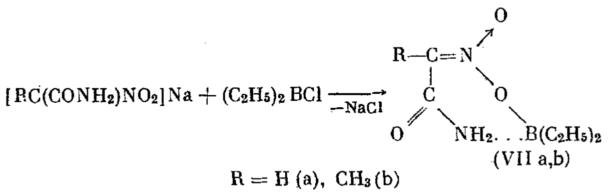


Fig. 2. Infrared spectrum of diethylboric ester of carbamidomethanenitronic acid (VIIa) in Nujol (the bands of the C = O and NH_2 groups in the amide of nitroacetic acid are designated by dotted lines).

It is interesting to mention that, in contrast to the O-methyl [5, 6] and O-trimethylsilyl [7, 8] esters of the carbomethoxymethane- and bis(carbomethoxymethane)nitronic acids, esters (Va) and (Vc) do not enter into the 1,3-dipolar cycloaddition reaction with styrene at 20-50°.*

The O-diethylboric esters of the corresponding nitronic acids are formed when the Na salts of the amides of the nitroacetic and α-nitropropionic acids are reacted with diethylboron chloride.



(9)

The structure of (VIIa, b) was proved employing NMR (see Table 1) and IR spectroscopy.

The cited data (as well as for products (Va-c)) confirms the presence of the C = N bond and tetracoordinated boron in esters (VIIa, b), but in contrast to the derivatives (Va-c), in (VIIa, b) the boron atom is connected by a complex bond to the amide group, and not to the carbonyl group. This is evidenced by the substantially smaller paramagnetic shift of the signal of the carbon of the C = O group in the ^{13}C NMR spectrum of (VIIa, b), when compared with the starting nitro compounds, than for (Va-c). In addition, a nonequivalence of the protons of the amide group can be seen in the ^{1}H NMR spectra of (VIIa, b), which is associated with a decrease in the exchange rate between these protons.

The IR spectrum of (Vb) is given in Fig. 1, while that of (VIIa) is given in Fig. 2. The bands of the corresponding starting nitro compounds are designated by dotted lines. As can be seen from Fig. 1, when the boron is complexed with the carbonyl group of (Vb) the C = O stretching vibration is shifted toward lower frequencies by more than 150 cm^{-1}. At the same time in (VIIa), when compared with the starting nitramide, the shift in the C = O stretching vibration is much smaller (~40 cm^{-1}), and here the bands of the NH_2 stretching vibrations are shifted substantially toward weaker frequencies. The cited data convincingly testifies to the fact that, in contrast to the (V) esters, complex formation in the (VII) products takes place at the nitrogen of the amide group.

EXPERIMENTAL METHOD

Nitrobutane [9], the Na salts of nitroethane and nitrobutane [10], dimethyl nitromalonate [11], the methyl esters of the nitroacetic [12] and 2-nitropropionic acids [13], the amides of the nitroacetic [14] and 2-nitropropionic acids [13], diethylboron chloride [15], triethylboron [16], and the anhydride of diethylboric acid [17] were obtained by known procedures. The Na and K salts of the functional nitro compounds were obtained from the corresponding nitro compounds and alkali metal alcoholates. All of the reactions with

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* Methyl acrylate is polymerized when (Va, c) are added to it.

diethylboron chloride and the diethylboric derivatives of the nitronic acids were run in a dry argon atmosphere using absolute solvents.

The ^1H NMR spectra were taken on Perkin—Elmer R-12, Varian DA-60, and RS-60/15 spectrometers at a frequency of 60 MHz, the ^{11}B NMR spectra were taken on an RS-56/19 spectrometer (19.27 MHz), and the ^{13}C NMR spectra were taken on a Jeol PS-100 instrument. The IR spectra were recorded on a UR-10 spectrometer, using KBr cells for (V) and (VII). The GLC analysis was run on an LCM-8 chromatograph, using a katharometer as the detector and helium as the carrier gas.

Preparation of Diethylboric Derivatives of Primary Nitroalkanes and α-Phenylnitroethane

Diethylboric Ester of Ethanenitronic Acid (Ia). To 8.3 g of the Na salt of nitroethane in 60 ml of ether was added 8.5 g of diethylboron chloride at —30 to —40°, the mixture was stirred for 1 h, the NaCl was filtered at —30°, the precipitate was washed with a little ether, 2/3 of the solvent was vacuum-distilled, and the residue was cooled to —70° and the obtained crystals were filtered at —40°. We obtained 6 g (54%) of (Ia). ^1H NMR spectrum (CH_2Cl_2, —20°, δ, ppm): 6.95 q (CH, J = 6.20 Hz), 2.00 d (CH_3), 0.1-0.7 m ($B(C_2H_5)_2$). ^{11}B NMR spectrum (CH_2Cl_2, —20°): —12.7 ppm.

Diethylboric Ester of 1-Butanenitronic Acid (Ib). In a similar manner, from 6.5 g of the Na salt of nitrobutene and 5.5 g of diethylboron chloride in 50 ml of ether we obtained 1.9 g (21%) of (Ib). ^{11}B NMR spectrum (CH_2Cl_2, —20°): —12.7 ppm.

Diethylboric Ester of Phenylmethylmethanenitronic Acid (Ic). In a similar manner, from 1 g of the Na salt of 1-phenyl-1-nitroethane and 0.61 g of diethylboron chloride in 15 ml of ether we obtained 0.53 g (42%) of (Ic) (colorless crystals at 0°). ^1H NMR spectrum (CH_2Cl_2, —30°, δ, ppm): 7.7 broad signal of (C_6H_5), 2.49 ppm broad signal* of (CH_3), 0.2-0.6 m ($B(C_2H_5)_2$).

Esters (Ia-c) are hydrolyzed by atmospheric moisture and are unstable at 20°.

Alkaline Hydrolysis of Diethylboric Esters (I)

With stirring, 0.65 g of NaOH in 5 ml of water was added at —10° to 1.93 g of (Ia) in 20 ml of ether, after which the mixture was kept at 0° for 1.5 h, heated up to 20° for 2.5 h, and the aqueous layer was separated, diluted with 25 ml of ether, 1.13 g of $NH_2OH \cdot HCl$ in 5 ml of water was added at 0-5°, and the whole was extracted with ether. Nitroethane was isolated from the ether extracts in 26% yield.

In a similar manner, from 1.22 g of (Ib) we obtained 0.32 g (44%) of 1-nitrobutane, bp 67-68° (45 mm), n_D^{20} 1.4100, see [9].†

Preparation of 2,5,5-Triethyl-4-alkylidene-1,3-dioxa-4-aza-2,5-diboracyclopentanes(II)

Alkylideniminoxydiethylboranes (VIII). A mixture of 5 g of acetaldoxime and 8.9 g of triethylboron in 20 ml of benzene was heated at 40-50° until the gas evolution ceased, and then the solvent was vacuum-distilled. We isolated 9.5 g (89%) of ethylideniminoxydiethylborane (VIIIa), mp 79-81° (sublimes). Found: C 56.64; H 11.28; B 8.77; N 10.50%. $C_6H_{14}BNO$. Calculated: C 56.70; H 11.02; B 8.66; N 11.02%. ^1H NMR spectrum (CCl_4, δ, ppm): 7.0 q (CH, J = 6 Hz). 2.0 d (CH_3), 0.3-0.5 m ($B(C_2H_5)_2$). ^{11}B NMR spectrum (in C_6H_6): —7.34 ppm.

To 5.43 g of the Na salt of butyraldehyde oxime in 50 ml of ether at —15° was added 4.33 g of diethylboron chloride, the mixture was stirred for 2 h, and the precipitate was filtered and washed with ether. From the filtrate we isolated 6.17 g (96%) of n-butylideniminoxydiethylborane (VIIIb), bp 70-72° (0.4 mm). Found: C 61.69; H 11.44; B 7.10; N 8.76%. $C_8H_{18}BNO$. Calculated: C 61.93; H 11.61; B 7.03; N 9.04%. ^1H NMR spectrum (CCl_4, δ, ppm): 6.96 t (CH, J = 6 Hz), 2.49 m (CH_2CH), 1.55 m (CH_3CH_2), 1.00 m (CH_3, J = 6.60 Hz), 0.35-0.6 m ($B(C_2H_5)_2$).

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* Gives two signals when taken on a spectrometer with an operating frequency of 100 MHz.

† Based on the GLC data (stationary phase = 10% of poly(ethylene glycol) deposited on Chromosorb W, temperature 100°), the yield of 1-nitrobutane was 50%.

Compounds (IIa, b). To 6.2 g of (VIIIa) in 25 ml of ether at 20° was added 7.6 g of diethylboric anhydride and then dry air was passed through for 4 h at reflux. After evaporation of the solvent in vacuo we obtained 5.7 g (64%) of (IIa), bp 71-72° (2mm). Found: C 53.02; H 10.43; B 11.37; N 7.87%. $C_8H_{19}B_2NO_2$. Calculated: C 52.46; H 10.38; B 12.02; N 7.65%. ^1H NMR spectrum (CCl_4, δ, ppm): 6.8 q (CH, J = 6 Hz), 2.09 d (CH_3), 0.5-0.9 m $(C_6H_5)B$ and $(C_2H_5)_2B$. ^{11}B NMR spectrum (CCl_4): −10.1 ($B(C_2H_5)_2$), −30.9 ppm ($B(C_2H_5)$).

A mixture of 3.26 g of (VIIIb) and 6.75 g of diethylboric anhydride in 10 ml of ether was refluxed for 8 h, and the solvent was vacuum-distilled. We obtained 3.59 g (81%) of (IIb), bp 60-64° (0.3 mm). Found: C 57.64; H 11.14; B 10.06, N 6.94%. $C_{10}H_{23}B_2NO_2$. Calculated: C 56.91; H 10.90; B 10.42; N 6.65%. ^1H NMR spectrum (CCl_4, δ, ppm): 6.84 t (CH, J = 6 Hz), 2.54 m (CH_2CH), 1.53 m (CH_3CH_2), ~1.1 (CH_3), 0.35-0.9 m ($B(C_2H_5)$ and $B(C_2H_5)_2$).

Decomposition of Diethylboric Derivatives of Primary Nitroalkanes

A solution of 5 g of (Ia) in 10 ml of ether was gradually heated from −30 to 20°, kept for 3 h, the solvent was vacuum-distilled and the mixture was fractionally distilled. We isolated 0.75 g of a fraction with bp 48-53° (0.4 mm), the spectral characteristics of which coincided with the characteristics of (IIa). Found: C 51.65; H 10.06; B 9.21; N 9.67%. $C_8H_{19}B_2NO_2$. Calculated: C 52.46; H 10.38; B 12.02; N 7.65%.

To 2.3 g of diethanolamine in 15 ml of chloroform at 20° was added 2 g of the fraction with bp 48-53° (0.4 mm), and the mixture was stirred at 55-60° for 4 h. Based on the GLC data (stationary phase = 10% of poly(ethylene glycol) deposited on Chromosorb W, carrier gas = helium, 100°), the aldoxime (50% yield) was recorded in the reaction mixture. The solvent was vacuum-distilled, ~2 ml of dioxane was added to the residue, and the precipitate was filtered. Employing the known procedure [1], from the precipitate we isolated 0.41 g (22%) of (III), mp 80-90°, and 1.15 g (74%) of (IV), mp 157-160° (see [1]).

In a similar manner, from ester (Ib) we obtained 1.7 g (24%) of a fraction with bp 52-55° (0.21 mm), the spectral characteristics of which are close to the spectra of the (IIb) obtained by an independent synthesis. After treatment with diethanolamine, from 1.2 g of this fraction we obtained butyraldehyde oxime (30%) and product (IV) (70% yield).

Preparation of Diethylboric Derivatives of α-Functionally Substituted Nitroparaffins (V) and (VII)

To 3.34 g of the K salt of methyl nitroacetate in 20 ml of ether (or CH_2Cl_2) at −30° was added 2 g of diethylboron chloride, the mixture was stirred for 1 h (−30°), heated up to 20°, the precipitate was filtered, washed on the filter with ether (or CH_2Cl_2), and the solvent was removed in vacuo. We obtained 2.96 g (~84%) of product (VA).*

In a similar manner, from 2.62 g of the Na salt of methyl 2-nitropropionate and 1.7 g of diethylboron chloride in 26 ml of ether we obtained 3.2 g (~97%) of (Vb).

In a similar manner, from 3.6 g of the K salt of dimethyl nitromalonate and 1.54 g of diethylboron chloride we obtained 3.1 g (~86%) of (Vc).

To 3.6 g of the Na salt of nitroacetamide in 45 ml of ether at −30° was added 2.7 g of diethylboron chloride, the mixture was stirred for 1 h, heated up to 20°, the NaCl was filtered, washed with ether, and the filtrate was evaporated in vacuo. We obtained 4.15 g (94%) of (VIIa), mp 110°. Found: C 40.18; H 7.36; B 5.7; N 17.45%. $C_6H_{13}BN_2O_3$. Calculated: C 41.86; H 7.55; B 6.4; N 16.27%.

In a similar manner, from 1.1 g of the Na salt of 2-nitropropionamide and 0.74 g of diethylboron chloride in 20 ml of ether we obtained 0.85 g (60%) of (VIIb), mp 109-115° (ether—hexane). Found: C 44.27; H 7.98; B 5.44%. $C_7H_{15}BN_2O_3$. Calculated: C 45.16; H 8.06; B 5.91%.

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* Products (Va-c) are extremely unstable hydrolytically; they are liquids at 20° and crystallize when the temperature is lowered to −30°. The given yields of (Va-c) are somewhat high, since the obtained oils contain 10-15% of the starting nitro compounds.

Reaction of Diethylboric Ester of Bis(carbomethoxy)methanenitronic Acid with Pyridine

With stirring, to 0.8 g of (Vc) in 20 ml of ether at 0° was added 0.26 g of pyridine in 2 ml of ether, after 30 min the mixture was heated up to 20°, stirred for another 1 h, and the solvent was vacuum-distilled. We obtained 0.46 g (35%) of diethylbis(pyridine)boronium dimethyl nitromalonate (VI), mp 78-80° (CH_2Cl_2—pentane). Found: C 55.37; H 6.59; B 2.70; N 10.28%. $C_{19}H_{26}BN_3O_6$. Calculated: C 56.60; H 6.44; B 2.73; N 10.40%.

CONCLUSIONS

1. The diethylboric esters of the corresponding nitronic acids, with a tetracoordinated boron atom, are formed when diethylboron chloride is reacted with either the Na or K salts of primary nitroalkanes, α-phenylnitroethane, and nitroparaffins that contain ester or amide functions α to the NO_2 group.
2. In the diethylboric esters of the carbomethoxymethane- and carbomethoxyethanenitronic acids the boron atom is coordinated at the oxygen of the carbonyl group.
3. Rapid (on the NMR scale) intramolecular transfer of the diethylboric fragment from one carbomethoxyl group to the other takes place in the diethylboric ester of bis(carbomethoxy)methanenitronic acid.
4. In the diethylboric esters of the carbamidomethane- and carbamidoethanenitronic acids the boron atom is coordinated at the nitrogen of the amide group.

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