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TRIMETHYLSILYL AND DIETHYLBORON DERIVATIVES OF ETHYL N-NITROCARBAMATE

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UDC 542.91:547.1'128:547.1'127:547.495.1

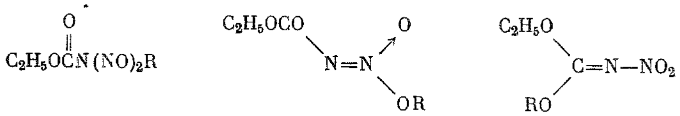
The reaction between the Ag or NH_4 ethyl N-nitrocarbamate salts and trimethylsilyl or diethylboron chloride in inert aprotic solvents gives the corresponding trimethylsilyl or diethylboron ethyl N-nitrocarbamate derivatives.

$$[C_2H_5OCON(NO_2)]M + RCl \xrightarrow{CH_2Cl_2 \text{ or ether}} [C_2H_5OCON(NO_2)]R$$

where, if R is $(CH_3)_3Si$, M is Ag (I), the yield is nearly 100% at 20°; if R is $(C_2H_5)_2B$, M is NH_4 (II), the yield is 80% at −30°. Compounds (I) and (II) are sensitive to hydrolysis and react rapidly with aerial moisture. Compound (I) decomposes at 90-100°C, or as a result of a prolonged keeping at 20° to give nitrogen oxide and some other products. Compound (II) decomposes above 0°.

The presence of $C_2H_5OCON(NO_2)$ and $Si(CH_3)_3$ (the product I only) groups has been confirmed by treating (I) and (II) with the alkali metal alcoholates or with alkali alcoholic solutions giving the corresponding salt of the starting ethyl N-nitrocarbamate and trimethylalkoxysilane. Compound (II) reacts with pyridine at a low temperature to give the crystalline $C_2H_5OCON(NO_2)B(C_2H_5)_2 \cdot NC_5H_5$ (III) complex. The structure of this complex is discussed below.

Previous NMR studies showed that the trimethylsilyl and diethylboron alkylnitramine derivatives undergo a rapid 1,3 migration of the organometallic fragments between the nitro group oxygen and the "amine" nitrogen [1, 2]. In the case of nitrourethane derivatives, the migration of the organometallic fragment to the CO group oxygen must also be considered, since it was shown earlier [3], that the trialkylsilyl group in N-alkylurethanes is always connected to N. Therefore, the organometallic nitrourethane derivatives can exist as either the O, N, or the imide isomers.



N-isomer O-isomer Imide isomer

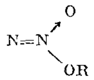
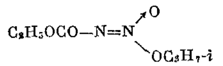
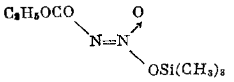
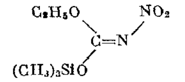
R — organometallic group

Each of the above isomers can form stereoisomers due to the restricted rotation round the $\overset{O}{\overset{/\!\!/}{C}}{-}N$, N=N, and C=N bonds. In (II), the tendency of the boron atom towards the coordination bond formation has to be considered. At present, the only way to determine the structures of (I)-(III) is to use complex physicochemical methods.

The compounds (I)-(III) were therefore studied using the IR and the ^1H, ^{13}C, ^{11}B, ^{14}N, and ^{15}N NMR (at various temperatures) spectroscopical techniques. Some IR spectra and also the NMR ^{15}N spectra were recorded.

N. D. Zelinskii Organic Chemistry Institute. Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2547-2557, November, 1976. Original article submitted August 27, 1975.

TABLE 1. IR Spectra of Compounds (I) and (III)-(VI) in CH_2Cl_2

Compound		ν, cm⁻¹ *							
		NO_2 (s)	NO_2 (as)	 $N{=}N(\rightarrow O)OR$				C=O	C=N
$C_2H_5OCONHNO_2$ (IV)		1330 m (10) [0]	1623 s (30) [0]					1795 s (0) [0]	~3380 broad (NH)
$C_2H_5OCON(NO_2)C_3H_7$-i	(VI)	1310 m	1580 s					1770 s	
 $C_2H_5OCO{-}N{=}N(\rightarrow O)OC_3H_7$-i	(V)			1230 s (10) [0]	1280 s (10) [0]	1560 s (23) [0]	1605 m (30) [5]	1770 s (0) [0]	
$C_2H_5OCON(NO_2)Si(CH_3)_3$	†	1310 s (18) [3]	1565—1570 s (25—35) [5]					1765 w (0) [0]	
 $C_2H_5OCO{-}N{=}N(\rightarrow O)OSi(CH_3)_3$	(I)			1230 m (5) [0]	1565—1570 s (25—35) [5]			1765 w (0) [0]	
 $C_2H_5O(({CH_3})_3SiO)C{=}N{-}NO_2$		1310 s (18) [0]	1565—1570 s (25—35) [5]						1627 s (0) [18]
$C_2H_5OCON(NO_2)B(C_2H_5)_2 \cdot \ddot{N}C_5H_5$	(III)	1340 m (15) [0]	1510 s (40) [0]					1760 s (0) [0]	

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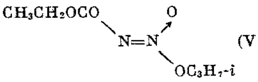
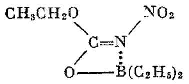
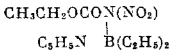
* The isotope shifts due to $^{15}NO_2$ are given in round brackets; the shifts due to ^{15}N are given in square brackets.

† The line intensity is given as for the tautomeric mixture.

TABLE 2. NMR Spectra of Compounds (II)- (VI)

Compound	Solvent	T, °C	δ, ppm (TMS standard)				(J, Hz)
			OCH₂	CH₃	CH	(CH₃)₂	
$CH_3CH_2OCON(NO_2)C_3H$-i (VI)	CCl_4	36	4,25	1,25	4,57 broad	1,30	$J_{CH_2CH_3} = 7$ $J_{CHCH_3} = 6,5$
 (V)	CCl_4	36	4,35	1,35	5,18	1,35	$J_{CH_2CH_3} = 7$ $J_{CHCH_3} = 6$
 (II)	CH_2Cl_2†	—48	4,60	1,49			$J_{CH_2CH_3} = 7$ $B(CH_2CH_3)_2$ gives a multiplet at 0.4-0.9 ppm
 $CH_3CH_2OCON(NO_2)$ $C_5H_5N\ B(C_2H_5)_2$ (III)	CH_2Cl_2	36	4,25	1,30			$J_{CH_2-CH_3} = 7$ $B(CH_2CH_3)_2$ broad signal at 0.67 ppm; Pyridine, multiplets at 7.60, 8.01, and 8.68 ppm.

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* The integrated intensity of all signals does not differ from the calculated value by more than ± 10%.

† With ether added.

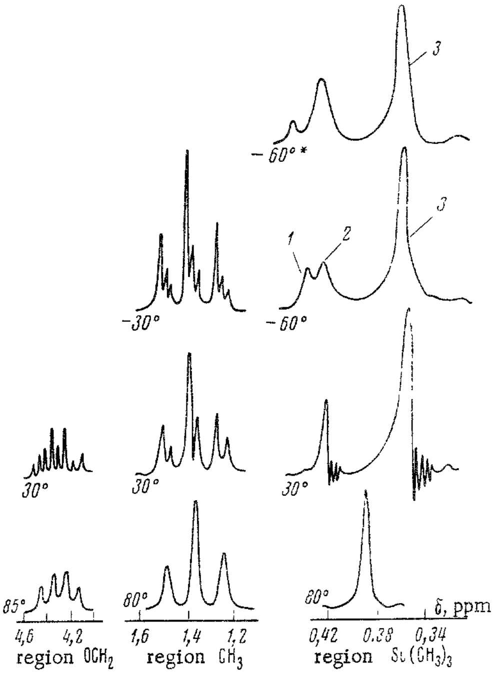

Fig. 1. NMR spectrum of (I) in CH_2Cl_2 (recorded at various amplifications); *) NMR spectrum of $[EtOCO^{15}N(NO_2)]Si(CH_3)_3$ (cf. experimental).

using samples enriched with ^{14}N or ^{15}N or both. The spectral line positions were determined using ethyl N-nitrocarbamate (IV), its O-isopropyl derivative (V) and O-ethyl-N-nitro-N-isopropylurethane (VI) as standards. When necessary, the ^{15}N-labelled (IV)-(VI) compounds were also used. The experimental data are given in Tables 1-4.

The observed changes of the NMR spectrum of (I) with temperature show that the compound can exist as a mixture of up to three isomers. Two processes can take place at different rates: $1 \rightleftharpoons 2$ and, more slowly, $[1; 2] \rightleftharpoons 3$* (see Fig. 1). The ^{13}C NMR spectrum of (I) can also be interpreted in terms of an equilibrium be-

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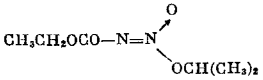
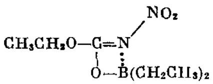
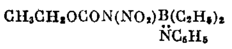
* The $[1; 2] \rightleftharpoons 3$ process can take the form of $1 \rightleftharpoons 3$ or $2 \rightleftharpoons 3$ processes.

TABLE 3. ^{13}C NMR Spectra of Compounds (I)-(VI) in CH_2Cl_2

Compound	T., °C	δ, ppm (TMS standard)*									Note
		OCH_2	CH_3	C=O	C=N	$Si(CH_3)_3$	CH	$(CH_3)_2$	BCH_2	BCH_2CH_3	
$CH_3CH_2OCONHNO_2$ (IV)	20	63,97	13,48	148,50							With introduction of two ^{15}N, $J_{^{13}CO-^{15}N}$ = 22.1 Hz.
$CH_3CH_2OCON(NO_2)CH(CH_3)_2$ (VI)	20	64,36	13,55	150,90			53,38	18,87			
 $CH_3CH_2OCO-N{=}N(\rightarrow O)OCH(CH_3)_2$ (V)	20	64,03	13,61	155,32			76,57	19,72			
(I)	20	64,03 66,95	13,61		157,34	—0,62 —1,14					
(I)	—40	63,12 63,84 66,70	13,29	151,75† 155,00	156,95	—0,84 —1,19 —1,59					The presence of C=O in (IV) is apparent.
$[CH_3CH_2OCO^{15}N(^{15}NO_2)]Si(CH_3)_3$ (I)	—40	63,12 63,97 67,30	13,29	152,50 155,19	157,08	—1,85 —2,30					For signals with δ 152.2, J = 17.6 Hz for δ 157.08, J = 4.4 Hz.
 $CH_3CH_2O-C(=N-NO_2)-O-B(CH_2CH_3)_2$ (II)	—30	68,51	13,42		165,78				9,91 broad	6,37	
 $CH_3CH_2OCON(NO_2)B(C_2H_5)_2\cdot NC_5H_5$ (III)	20	63,64	13,48	154,02					broad	8,35	Pyridine; 125,63; 141,22; 144,34

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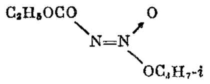
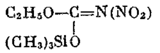
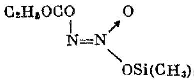
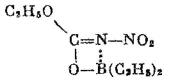
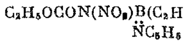
* The chemical shifts expressed are relative to CH_2Cl_2 internal standard, having the chemical shift 53.7 ppm.

† A secondary constituent signal at 148.07 ppm has $J_{^{13}C-^{15}N}$ = 21.9 Hz; the integrated ratio of signals 63.12; 63.97; and 67.30 ppm is 1.2 : 1 : 2.4.

TABLE 4. ^{14}N, ^{15}N, and ^{11}B NMR Spectra of Compounds (I)-(VI) in CH_2Cl_2

Compound	δ, ppm* ^{14}N and ^{15}N							Note (J, Hz)	Chemical shift of ^{11}B, ppm from $(C_2H_5)_2OBF_3$ (δ scale)
	NO_2	$^{15}NO_2$†	$-N(\rightarrow O)-OR$	$-^{15}N(\rightarrow O)-OR$	$-^{15}N<$	$^{15}N=N(\rightarrow O)-OR$	$C=^{15}N$		
$C_2H_5OCONH(NO_2)$ (IV)	−39±1 20 Hz	−41,7 (−42,6)			−186 (184,5)			$J_{^{15}N-H} = 93$	
$C_2H_5OCON(NO_2)C_3H_7\text{-}i$ (VI)	−39,0±1 20 Hz								
 (V)			−48,0±2,5 150 Hz	−45,0		−98,8			
$C_2H_5OCON(NO_2)Si(CH_3)_3$		−32,4 (−35,2)			−167,0 (−167,4)			$J_{^{15}N-^{15}N} = 6,7$**	
 $C_2H_5O-C(=N(NO_2))-OSi(CH_3)_3$	−19,8±1 25 Hz	−16,2 (−17,0)					−113,0 (−114,6)	$J_{^{15}N-^{15}N} = 14$	
 (I)			−46,5±2‡	−46,3 (−42,0)		−93,7 (−94,0)			
 (II)	−29,0±1 at 0°	−24,1 (−30°)					−127,3 (−20°)		20±3 (−25°)
 $C_2H_5OCON(NO_2)B(C_2H_5)_2 \cdot NC_5H_5$ (III)	−28,0±1 20 Hz	−24,0			−160				3,1±1

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*Unless indicated otherwise, the determination was carried out at 20°, the standard for ^{14}N was nitromethane, for $^{15}N-Na^{15}NO_3$; at a low temperature the NO_2 group of (I), having the chemical shift of −41.5 ppm from $Na^{15}NO_3$, was used.

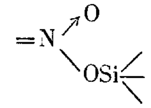
† The chemical shifts of compounds having two labelled nitrogens are given in brackets.

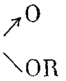
‡ Measured in CCl_4.

** The spectra recorded at −30° for one ^{15}N atom, and at −20° for two ^{15}N atoms.

tween three isomers. All the analytical data indicate that, at equilibrium, all three isomers are present with the signals 1, 2, and 3 corresponding to the N-, O-, and the imide structure isomer, respectively.

A more detailed discussion of this conclusion is given below.

The NMR spectrum of (I) enriched with the ^{15}N "amino" nitrogen shows only the signal 1, split into a doublet with $J_{^{15}N-Si-C-H} = 0.9 \pm 0.1$ Hz, corresponding roughly to the value of J in ^{15}N-trialkylsilylamide derivatives (0.8-1.1 Hz) [4]. Therefore, the signal 1 can be assigned to the N-isomer since only this structure can give rise to $J_{^{15}N-Si-C-H}$. Furthermore, the corresponding IR spectrum indicates the presence of the "imide" isomer in the equilibrium mixture of (I). The intensity of the $\nu_{C=O}$ band in (I) is considerably lower than that in the compounds used as standards; this absorption is, of course, missing in the "imide" isomer. Furthermore, the IR spectrum of (I) contains an intensive band at 1627 cm^{-1} which, judging from the isotope shift, is not due to the  $=N(\rightarrow O)OSi\lessdot$ or NO_2 but rather to $\nu_{C=N}$ vibrations. Its position also agrees well with the position of similar bands in the N-nitrimines (V) IR spectra. The intensity of the 1627-cm^{-1} band and also the intensity of the ^{13}C, ^{14}N, and ^{15}N NMR spectra "imide" form signals suggest that the "imide" isomer predominates in the equilibrium mixture and, therefore, the signal 3 in the NMR spectrum of (I) can be assigned as being due to the "imide" isomer.

The signal 2 can be assigned either to the O-isomer, or to the thermodynamically less likely "imide" stereoisomer.* The first assumption seems more likely, since the IR spectrum of (I) contains the 1230-cm^{-1} band that appears in other O-derivatives (V) and, at the same time, is missing in the IR spectra of the other standards. In CCl_4, the total intensity of the 1 + 2 NMR signals of (I) increases relative to the signal 3; correspondingly, the intensity of the 1230-cm^{-1} band in the IR spectrum of (I) in CCl_4 increases. Interestingly, under the same conditions, the ^{14}N NMR spectrum of (I) shows a broad signal at 46.5 ppm, similar to the  $=N(\rightarrow O)OR$ signal in (V). The ^{15}N low-temperature NMR spectrum of (I) also contains weak signals corresponding to the signals in (V) and their disappearance at higher temperatures can be explained by their broadening due to the $1 \rightleftharpoons 2$ process. One of the two OCH_2 signals in the ^{13}C NMR spectrum of (I), having 63.12 and 63.84 ppm chemical shifts, should then be due to the third isomer. The difference between the position of these two signals and the "imide" OCH_2 signal is 3-4 ppm, and it is, therefore, not likely that either of the signals is due to the "imide" cis-isomer, especially since $(C_2H_5O)_2C=NCl$ [6] exhibits two OCH_2 group signals different only by 0.33 ppm (65.07 and 65.40 ppm relative to TMS).

The spectral analysis data given in Tables 1-4 further confirm the suggested structure of (I). A detailed discussion is not necessary here. Note that the relative ratio of signals can be expressed either as $J_{^{15}N-^{15}N}$ or as $J_{^{13}C-^{15}N}$ constants. Furthermore, the 1565-1570 and 1765 cm^{-1} bands in the IR spectrum of (I) are multiplets as has been confirmed by IR spectra of CH_2Cl_2 solutions at low temperatures.

The above study of (I) is the first ever-reported case of a tautomeric process accompnaied by migration of a radical R to the functional group directly connected to a nitro group-bearing atom. Furthermore, first-ever observation of a tautomeric 1,3-migration of the $Si(CH_3)_3$ group from O to N in urethane was made.

As a quantitative investigation of tautomerism in (I) is difficult, a qualitative analysis only was attempted. Also, the effect of various factors on the coalescence temperature of $Si(CH_3)_3$ group signals was studied (Table 5). The low-temperature $1 \rightleftharpoons 2$ process could not be studied in detail – however, it was established that the coalescence temperature of 1 and 2 signals does not depend on concentration and is only little influenced by the nature of the solvent. It can thus be concluded that this monomolecular process takes place via a multicenter ring-type transition state and, apparently coincides with the trialkylsilyl group 1,3 migration in the trialkylsilyl nitramine derivatives [7].

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*Apparently, the formation of the cis-isomer is thermodynamically less likely.

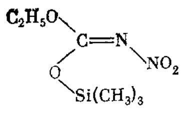


TABLE 5. Coalescence Temperature of the $Si(CH_3)_3$ Group NMR Spectra Signals for the Structural Isomers of (I) in Various Solvents

Solvent	Coalescence temperature, °C			Difference in chemical shifts, Hz*	
	process				
	$1 \rightleftarrows 2$	$1,2 \rightleftarrows 3$	$1,2 \rightleftharpoons 3$ at 5-fold dilution	$\Delta\nu_{1-2}$	$\Delta\nu_{(1+2)-3}$
CH_2Cl_2†	—31	70	70	~0,8(—60°)	3,5 (0°)
CCl_4‡		80	80		3,3 (0°)
Acetone	~—30	—4,5	—	—	3,5 (—14°)
THF		27,6	44	—	3,6 (—19°)
CH_3CN		—0,5	—9,5		3,8 —(24°)

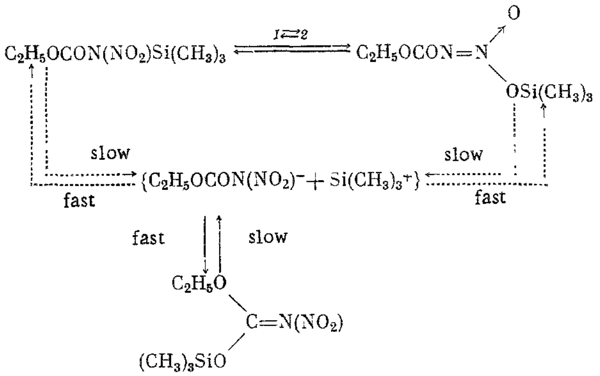
* The temperature of the $\Delta\nu$ determination is given in brackets.

† The coalescence temperature for the CH_3 group $1 \rightleftharpoons 2$ triplets is $-5°$. The difference in chemical shifts at $-60°$ is 1.7 Hz.

‡ The coalescence temperature of CH_3 group triplets for $1 \rightleftharpoons 2$ at 10°, the difference in chemical shifts being 1.5 Hz at $-10°$.

From the observed data (cf. Table 5) one can assume that the $[1; 2] \rightleftharpoons 3$ is a monomolecular process, particularly in CH_2Cl_2, CCl_4, and CH_3CN.* In THF, however, some contribution from an intermolecular process cannot be excluded.

From the changes of the coalescence temperature it appears that polar solvents increase the rate of the $[1; 2] \rightleftharpoons 3$ process by more than two orders of magnitude. Obviously, the species involved in the transition state of the process are more polar than the ground states of the isomers. The following scheme fully corresponds to such a situation:



The scheme adequately explains the experimental data. For example, the substitution of the NO_2 group by an N-alkyl should decrease the stability of the anion and, consequently, the stability of the ion pair should also decrease. This indicates that the migration via an ionic mechanism is inhibited. Similarly, the stability of the anion is low in the case of the trialkylsilyl-N-alkylnitramines that undergo the 1,3 migration of the trialkylsilyl group via a ring-type transition state [7]. Furthermore, if the isomerization follows an ionic mechanism, then the more thermodynamically stable 'imide' stereosiomer should prevail in the equilibrium mixture. This is indeed the case. At present we cannot state which of the two possible isomers (N or O) forms the ion pair, therefore, a dotted line has been used to connect the two products and the possible transition compound. This corresponds to the $[1; 2] \rightleftharpoons 3$ process although in principle both $1 \rightleftharpoons 3$ and $2 \rightleftharpoons 3$ processes are possible.

According to our data (see Tables 2-4), the compound (II) is a single isomer containing a tetracoordinated boron atom. The ^{13}C, ^{14}N, and ^{15}N NMR spectra are very similar to the corresponding spectra of (I) in its "imide" form. The differences are apparently caused by the presence of the boron atom coordinated to the free elec-

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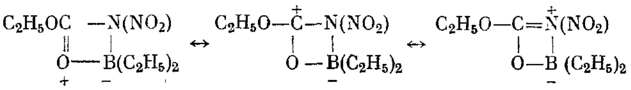
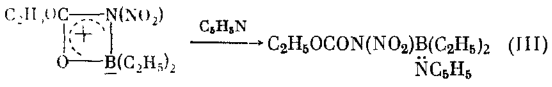
* The decrease of coalescence temperature in CH_3CN is, apparently, due to the solvent effect.

tron pair of the "imide" nitrogen. As a result, the positive charge is redistributed round all the atoms of the O−C−N[*] group.



The reaction of (II) with pyridine cleaves the B−O bond and a neutral N-complex is formed. Its structure has been unequivocally confirmed by physicochemical methods.[†]



(II)

(III)

$$C_2H_5OCON(NO_2)B(C_2H_5)_2 \cdot NC_5H_5$$

The low temperature ^1H, ^{13}C, and ^{15}N NMR spectra of (III) showed an absence of any rapid exchange and thus confirmed that the equilibrium is fully shifted towards the N-product formation. These results agree with the reported behavior of diethylboron methylnitramine [2] but disagree with the results obtained for diethylboron N-nitro-p-toluenesulphonamide for which only the O-product formation was reported [9].

EXPERIMENTAL[‡]

IR spectra were recorded on a UR-10 spectrometer from CH_2Cl_2 or CCl_4 solutions using 0.02 mm KBr cells. UV spectra were recorded on a Unicam SP-800 spectrophotometer. ^1H NMR were measured on Perkin−Elmer R-12 60 MHz spectrometer at 36°. The low- and high-temperature NMR spectra were recorded on PC 60/15 60 MHz spectrometer. The $J_{^{15}N-Si-C-H}$ and the coalescence temperature values of signals 1, 2, and 3 (Fig. 1) were determined from the chemical shifts measured to ± 0.02-Hz accuracy (the values were calculated from the peak maxima using the digital frequency generator G-3-49). The half-width of the signals were determined to ± 0.06-Hz accuracy, and the temperature was maintained to ± 0.05°.

The sample values (signal position, chemical shift relative to TMS, Hz) [the half-width value (in Hz) is given in brackets] were as follows: $C_2H_5OCON(NO_2)Si(CH_3)_3$ (0.09 ml in 0.7 ml CH_2Cl_2 + a few drops of TMS), 1, 26.38 (0.63); 2, 25.71 (0.75); 3, 21.62 (0.63); $C_2H_5OCO^{15}N(NO_2)Si(CH_3)_3$ (under the same conditions), 1d, a shoulder at 26.83 (not measured); 2, 25.77 (0.63); 3, 21.61 (0.71).

The ^{13}C NMR spectra were recorded on a Bruker HX-90 spectrometer at 22.63 MHz using the repeated scanning technique. The chemical shifts were determined with ± 0.1-ppm accuracy. The ^{14}N and ^{15}N NMR spectra were recorded on a Bruker SXP 4-100 spectrometer at 6.05 MHz for ^{14}N, and at 9.12 MHz for ^{15}N, in an impulse regime, again using the signal accumulation technique. The ^{15}N chemical shifts were determined to ± 0.4 ppm accuracy. The ^{11}B NMR spectra were recorded on PC-56/19 spectrometer having the working frequency of 19.27 MHz.

All the experiments with (I)-(III) compounds were carried out under Ar in anhydrous solvents (containing $\leq 0.005\%$ of water). Previously published methods were employed to obtain urethane (IV) [10], its Ag-salt [11] and also (IV) and its Ag-salt (IV) containing ^{15}N label. $C_2H_5OCON^{15}HNO_2$ was obtained according to [12] using $^{15}NH_4NO_3$ (the degree of enrichment $\geq 91\%$). Ag-salt (IV) (3.15 g) in ether (30 ml) was reacted with $i\text{-}C_3H_7Br$ (6 ml) for 20 h with stirring, the mixture was filtered and the solvent was evaporated under vacuum to give (V) (1.86 g, 81%) (cf. Tables 1-4).

^{15}N-Labelled (V) was prepared as follows: Ethyl-N-isopropylcarbamate (3.5 g) was added dropwise to the HNO_3 (2 ml, sp.g. 1.5) and Ac_2O (5.8 g) mixture at 20-30°, cooled to 0° and then poured into ice-cold water (20 ml). The organic layer was separated and the aqueous layer was extracted with ether; the organic layer and the extract were combined to give (VI) (2 g, 43%), bp 88° (11 mm); n_D^{20} 1.4371 (cf. Tables 1-4).

$(CH_3)_3SiCl$ (5.5 ml) in CH_2Cl_2 (10 ml) was added dropwise with stirring to Ag salt (IV) (10 g) in CH_2Cl_2 (40 ml). The mixture was kept for 1 h at 20°, AgCl was filtered off (near 100% of AgCl were recovered) and the residue was evaporated under vacuum (starting at 10 and finishing at 1 mm) to give 90-95% pure (according to NMR) (I) in near 100% yield (8.6 g). Compound (I) solidifies at −60° and distills (with partial decomposition) at 70° (0.9 mm).

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[*] An intermolecular coordination of the boron atom is also possible.

[†] It was reported previously that borates only were isolated after the reaction between pyridine and diethylboron nitro derivatives [8, 9].

[‡] With contributions from V. F. Pyaterikov.

The labelled Ag-salt (IV) was used to prepare ^{15}N-labelled (I). CH_3OH (0.47 g) was added to (I) (1.2 g) in 4 ml CCl_4. According to GLC (2 m × 5 mm column, 10% Reoplex 400 on Chromosorb, 48°, He flow rate 40 ml/min) and NMR, within 10 min the mixture contained $CH_3OSi(CH_3)_3$, nitrourethane (IV) and a small amount of hexamethyldisiloxane. The solvents were evaporated under vacuum to give the urethane (IV) (0.7 g, 91%), bp 62° (does not depress the melting point). Diethylboron chloride (0.65 g) was added dropwise to the NH_4 salt (IV) (1 g) in ether or CH_2Cl_2 (15 ml) with stirring at −30 to −40°, the mixture was kept at this temperature for 1 h, filtered (at −40°) to remove NH_4Cl, and the solvents were evaporated at −30° (1 mm) to give (II) (crystalline at −20°, decomposes > 0°). To (II) in ether (25 ml) at −40° was added dropwise with stirring a solution of KOH (0.32 g) in CH_3OH (6 ml), the mixture was stirred for a further 20 min at −40° and then heated to 20°, and the K salt (IV) was then filtered off (0.84 g, 80%), mp 187-188°. UV spectrum in water: 258 nm (log ε 4.03); (cf. [13]).

Pyridine (1.33 g) was added with stirring to (II) (1.7 g) in CH_2Cl_2 (20 ml) at −30°, the mixture was kept for about 20 min at this temperature and then heated to 20° and stirred for a further 30 min. About a third of the solvent was evaporated under vacuum, and the residue was precipitated into hexane or ether. The precipitate was filtered to give (III) (1.7 g, 72%), mp 75-80° (as determined by a capillary method). Found: C 51.10; H 7.30; B 3.82; N 14.97%. $C_{12}H_{20}BN_3O_4$. Calculated: C 51.24; H 7.11; B 3.91; N 14.94%.

Data on (II) and (III) are summarized in Tables 1-4.

We are grateful to N. O. Cherskaya for recording the low-temperature IR spectra of (I) and to N. I. Shlykova and O. A. Luk'yanov for their help in preparing (V).

CONCLUSIONS

The trimethylsilyl and diethylboron derivatives of ethyl-N-nitrocarbamate were prepared.

The former compound was found to exist as an equilibrium mixture of three stereoisomers, i.e., the N- and O-derivatives together with the previously unknown "imide" isomer. A mechanism of the tautomeric rearrangements in the system, involving both the charged ring intramolecular and the dissociative migration of the $Si(CH_3)_3$ group is suggested.

The latter compound appears to exist in its "imide" form in which the boron atom is coordinated to the carbonyl group oxygen. The pyridine complex of this derivative has the N-isomer structure.

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