## SYNTHESIS AND STRUCTURE OF TRIMETHYLSILYL AND DIETHYLBORON DERIVATIVES OF p-TOLUENE-N-NITROSULFONAMIDE

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The O-trimethylsilyl (I) and O-diethylboron (II) derivatives of p-toluene-N-nitrosulfonamide were obtained by the respective reaction of the Ag salt of the nitrosulfonamide with trimethylchlorosilane and diethylboron chloride.

 $Ag[N(NO_2)SO_2C_6H_4CH_3-p] + RCI \xrightarrow{CH_2Cl_2} p-CH_3C_6H_4SO_2N = N \xrightarrow{O} OR$   $R = Si(CH_3)_3 (I), (C_2H_5)_2B (II)$ (1)

Product (I) is also formed by the silvlation of the free p-toluene-N-nitrosulfonamide (III) with N,N'diphenyl-N-trimethyl silvlurea:

$$NH(NO_2)SO_2C_6H_4CH_{3-l'} + C_6H_5N[Si(CH_3)_2]CONHC_6H_5 \xrightarrow{-(C_6H_5NH)_2CO} (C_6H_5NH)_2CO$$

Based on the NMR data, a choice was made between the structures of the N-derivatives (A) and the O-derivatives (B) for compounds (I) and (II):

$$p-CH_{3}C_{6}H_{4}SO_{2}N(NO_{2})R$$
A
0
$$p-CH_{3}C_{6}H_{4}SO_{2}N=N$$
B
OR

The NMR spectrum of compound (I) in  $CH_2Cl_2$  has singlets at 0.33 and 2.38 ppm, which respectively belong to the protons of the Si(CH<sub>3</sub>)<sub>3</sub> and CH<sub>3</sub> groups, and also two doublets at 7.25 and 7.7 ppm (J = 9 Hz) from the  $C_6H_4$  protons. A complication of the spectra was avoided by varying the solvent, and also by cooling the samples to  $-60^{\circ}C$ . From this it is obvious that product (I) is one of the structural isomers A or B, and not their mixture. We exclude rapid exchange between A and B on the NMR scale, since for the silvl derivatives of methylnitramine this process is inhibited by cooling the samples below  $-20^{\circ}C$  [1], while the insertion of a more electronegative grouping (p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub> instead of CH<sub>3</sub>) should retard the exchange rate [2]. In the NMR spectrum of product (II) in CH<sub>2</sub>Cl<sub>2</sub> at  $-50^{\circ}C$  canbe seen a broad singlet of the (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>B protons (0.8 ppm), a singlet of the CH<sub>3</sub> group (1.45 ppm), and doublets at 7.4 and 8.0 ppm (J = 9 Hz), which belong to the C<sub>6</sub>H<sub>4</sub> protons. If a small amount of the ester is present in the reaction mixture, then it appears as a quartet at 3.7 ppm (OCH<sub>2</sub>) and a triplet at 1.25 ppm (J = 7 Hz, CH<sub>3</sub> group). Since, when compared with the literature data for the ester [3], a small paramagnetic shift of the signals is observed, the formation of an unstable complex between product (II) and the ester cannot be excluded. As a result, based on the NMR data, product (II) is apparently also one of the two possible structural isomers (A or B).

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(2)

The <sup>11</sup>B NMR spectrum of compound (II), taken at  $-10^{\circ}$ , has a broad signal with a center at + 43 ppm from BF<sub>3</sub> etherate, which testifies to the presence of a tricoordination boron atom.\* The data on the <sup>13</sup>C and <sup>14</sup>N NMR spectra of compounds (I) and (II) are given in Table 1. The spectra of nitramide (III) and its

derivatives,  $p-CH_3C_6H_4SO_2N(NO_2)CH(CH_3)_2$  (IV) and  $p-CH_3C_6H_4SO_2N = N$  (V), are also given for  $OCH(CH_3)_2$ 

comparison. Based on the <sup>13</sup>C NMR data, the same as for the <sup>1</sup>H NMR data, compounds (I) and (II) contain mainly one of the two forms (A or B). We decided between these structures on the basis of the <sup>14</sup>N NMR spectra. It is known that the NO<sub>2</sub> group usually gives a narrow signal in the <sup>14</sup>N NMR spectra, whereas the signal of the fragment  $O-N \rightarrow O$  is quite broad [1, 4]. In harmony with this, compound (III) and its Nalkylated analogs give a narrow signal of the NO<sub>2</sub> group in the -40 ppm region from nitromethane. At the same time, in the O-derivative (V) the <sup>14</sup>N signal of the  $O-N \rightarrow O$  fragment is so broad that it cannot be seen on the spectrometers using the pulse technique. Since the signal of the  $O-N \rightarrow O$  fragment is also not observed in the <sup>14</sup>N spectra of compounds (I) and (II), we assign structure B to these products. In addition, it might be mentioned that in the <sup>13</sup>C NMR spectra of compounds (I) and (V) the signals of similar fragments have the same chemical shifts.

The IR spectrum of (I) has a doublet band at  $1510-1530 \text{ cm}^{-1}$  and a broad band with a maximum at  $1262 \text{ cm}^{-1}$ . For comparison it might be mentioned that the IR spectrum of (IV) has bands at 1290 and  $1565 \text{ cm}^{-1}$ , while bands at 1240 and  $1530 \text{ cm}^{-1}$  are characteristic for compound (V). As a result, the IR spectrum of (I) is close to the IR spectrum of the O-derivative (V). It should be specially emphasized that bands are absent in the  $\nu_{\rm S}$  region of the NO<sub>2</sub> group ( $1280-1300 \text{ cm}^{-1}$ ). As our previous studies show [1, 5], the band of the NO<sub>2</sub>  $\nu_{\rm Sym}$  is not shifted substantially when the hydrogen in methylnitramine is replaced by the (CH<sub>3</sub>)<sub>3</sub>Si group. At the same time, the absence of absorption at the site of NO<sub>2</sub>  $\nu_{\rm as}$  ( $1570-1595 \text{ cm}^{-1}$ ) is not proof in support of structure B, since replacing the hydrogen in methylnitramine by the trimethylsilyl group causes the NO<sub>2</sub>  $\nu_{\rm as}$  to shift toward lower frequencies [1, 5].

The behavior of compounds (I) and (II) in certain chemical transformations confirms the presence of the principal structural fragments in these products. Primary mention should be made of the extreme hydrolytic instability of compounds (I) and (II) and their great sensitivity toward labile hydrogen. Thus, when (I) was treated with methanol we isolated (III) and trimethylmethoxysilane in nearly quantitative yield. The reaction of (II) with alcoholic KOH solution gave the K salt of product (III) in good yield.

The treatment of (II) with excess pyridine gave the corresponding boronium salt in 87% yield.



(3)

The structure of salt (VI) was confirmed by the NMR data. The signal of a tetracoordinated boron atom, with a chemical shift of 8.8 ppm, was recorded in the <sup>11</sup>B NMR spectrum of (VI) at 60°. The NMR spectrum of (VI) contains the signals of the  $(C_2H_5)_2B$  (multiplets with centers at 0.46 and 0.9 ppm), CH<sub>3</sub> (singlet at 2.3 ppm), and C<sub>6</sub>H<sub>4</sub> (doublets at 7.2 and 7.9 ppm, J = 8 Hz) groups, and also the signals of the coordinated pyridine protons (characteristic multiplets with centers at 7.7, 8.2, and 8.5 ppm). The integral intensity of the signals shows that one molecule of the complexed pyridine corresponds to each CH<sub>3</sub> group. Compound (VI) is hydrolytically very unstable and is quickly decomposed by atmospheric moisture.

Product (II) decomposes rapidly, with the liberation of nitrogen oxides, when the temperature is raised above 0°. Product (I) is stable at  $\sim 20^{\circ}$ , but it decomposes above 100°. †

$$p-CH_{3}C_{6}H_{4}SO_{2}N = N \xrightarrow{\uparrow} p-CH_{3}C_{6}H_{4}SO_{3}Si(CH_{3})_{3} + N_{2}O$$

$$(VII) \qquad (VII)$$

$$(4)$$

<sup>\*</sup>In estimating the chemical shifts the + sign always designates a shift of the signal downfield from the standard.

<sup>&</sup>lt;sup>†</sup>The decomposition of (I) is accompanied by marked tarring of the reaction mixture, from which p-toluenesulfonic acid was isolated.

TABLE 1. Chemical Shifts in <sup>13</sup>C and <sup>14</sup>N Spectra of Compounds  $[p-CH_3 \stackrel{1}{\longrightarrow} \stackrel{4}{\longrightarrow} SO_2N(NO_2)]R$  (R = H, CH-(CH<sub>3</sub>)<sub>2</sub>, Si(CH<sub>3</sub>)<sub>3</sub>, B(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)

	<sup>13</sup> C chemical shifts, ppm, from TMS									
Formula	CH3	C1	C² and C3	C4	СН	$(CH_3)_2$	BCH 2	BC₂ <u>CH</u> ₃	SI(CH <sub>3</sub> )3	<sup>14</sup> N of ONO frag- ment from CH <sub>3</sub> NO <sub>2</sub>
$[p-CH_3C_6H_4SO_2N(NO_2)]Si(CH_3)_3 *$ (1) in CH_2Cl_2	21,53	146,42	129,85 129.64	132,77					-1,14	Broad
$[p-CH_{3}C_{6}H_{4}SO_{2}N(NO_{2})]B(C_{2}H_{5})_{2}^{\dagger}$ (11) at -20° in CH <sub>2</sub> Cl <sub>2</sub>	21,60	147,33	129,71	130,95			10,82, broad	6,85	-	Broad at 0°
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> NH(NO <sub>2</sub> ) (III) in acetone CH <sub>2</sub> Cl <sub>2</sub>	20,90	146,73	<b>13</b> 0,11 129,14	133,38	—	-			_	-41,2 (55±5 Hz)
<i>p</i> -CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> N(NO <sub>2</sub> )CH(CH <sub>3</sub> ) <sub>2</sub> (IV) в CH <sub>2</sub> Cl <sub>2</sub>	21,60	146,67	129,44 129,55	134,72	54,87	19,91	-	-		$-39.8 (60 \pm 10 \text{ Hz})$
$0$ $p-CH_{3}C_{6}H_{4}SO_{2}N = N$ $OCH(CH_{3})_{2}$ $(V) in CH_{2}Cl_{2}$	21,54	146,42	129,85 129,64	132,70	78,65	19,71			_	Broad

\*The <sup>13</sup>C NMR spectrum has a weak signal at + 0.35 ppm, which we attribute to HMDS.

<sup>†</sup>The <sup>13</sup>C NMR spectrum of product (II) has weak signals at 129.3 and 7.15 ppm, which apparently belong to the  $C^4$  and BCH<sub>2</sub>CH<sub>3</sub> of an unidentified impurity, possibly the N-form (II).

The presence of  $N_2O$  in the decomposition products was confirmed by the IR spectral data (band at 2230 cm<sup>-1</sup>, cf. [6]). The structure of the hydrolytically unstable (VII) was confirmed via NMR [(CH<sub>3</sub>)<sub>3</sub>Si singlet at 0.3 ppm, CH<sub>3</sub> singlet at 2.45 ppm, and C<sub>6</sub>H<sub>4</sub> doublets at 7.4 and 7.95 ppm (J = 9 Hz), ratio of signals close to 3:1:1.35] and by hydrolysis to p-toluenesulfonic acid.

## EXPERIMENTAL METHOD

Amide (III) and its Ag salt were obtained in known manner [7]. All of the experiments on the preparation and transformations of products (I) and (II) were run in a dry argon atmosphere, employing solvents that contained less than 0.005% moisture. The <sup>1</sup>H NMR spectra were taken at low temperatures on Perkin -Elmer R-12 and PC-60/15 spectrometers at an operating frequency of 60 MHz; HMDS was used as the standard. Cyclohexane was usually used as the internal standard for the quantitative measurements. The <sup>11</sup>B NMR spectra were taken on a PC-56 instrument (19.87 MHz), using BF<sub>3</sub> etherate as the standard. The <sup>14</sup>N NMR spectra were taken on a Bruker SXP-4-100 spectrometer (6.05 MHz) under pulse conditions. The accumulation of the free induction signal and the Fourier transform of the spectra were run on a POP-8 computer. The accuracy of determining the chemical shifts was ± 0.1 ppm. The <sup>13</sup>C NMR spectra were taken on a "Bruker HX-90" instrument (22.63 MHz) under pulse conditions with accumulation of the signal. The accuracy of determining the chemical shifts was ± 0.1 ppm. The <sup>13</sup>C NMR spectra were taken on a "Bruker HX-90" instrument (22.63 MHz) under pulse conditions with accumulation of the signal. The accuracy of determining the chemical shifts was 0.1 ppm. The IR spectra were taken on a UR-10 spectrometer in 0.02-mm thick KBr cells. The UV spectra were taken on a Unicam SP-800 spectrometer. The GLC analysis was run on a LCM-8M chromatograph equipped with a katharometer; helium was the carrier gas.

Preparation and Properties of O-Trimethylsilyl Derivative of N-Nitro-p-toluenesulfonamide (1). a) With stirring, to a suspension of 2.5 g of the Ag salt of (III) in 10 ml of  $CH_2Cl_2$  at ~ 20° was added 0.84 g of  $(CH_3)_3SiCl$ , and after 1 h the AgCl was filtered (~ 100% yield), while the solvent was evaporated in vacuo. We obtained 2.1 g (95%) of product (1).

b) With stirring, to 1.08 g of N, N'-diphenyl-N-trimethylsilylurea in 6 ml of  $CH_2Cl_2$  was added 0.82 g of (III) in 9 ml of  $CH_2Cl_2$ , the mixture was kept at 20° for 2 h, and filtration gave 0.75 g (94%) of N, N'-diphenylurea. Based on the NMR data, using an internal standard, the yield of product (I) was 1 g (92%). The IR and NMR spectral data for (I) are given in the general part. Product (I) is a viscous oil that is stable at 20°C.

A solution of 2.15 g of (I) in 20 ml of xylene was refluxed for 2 h, and the volatile products were condensed in  $CH_2Cl_2$  contained in a cooled trap. (The IR spectrum of the condensate has a band at 2230 cm<sup>-1</sup>.) which is characteristic for  $N_2O$  [6]). The xylene was removed in vacuo. The residue weighed 1.7 g. Vibration bands, characteristic for (I), are absent in the IR spectrum in  $CH_2Cl_2$ . The product was vacuum-distilled, and here we isolated (VII), bp 110° (0.47 mm). When treated with methanol or allowed to stand in the air, (VII) changes to p-toluenesulfonic acid with mp 92° (the mixed melting point with an authetic specimen was not depressed). An additional amount of p-toluenesulfonic acid, bp 160° (0.47-0.9 mm) and mp 92°, was isolated from the residue.

To 2.16 g of compound (I) was added 1.5 ml of  $CH_3OH$ , and all of the volatile products were vacuumdistilled into a trap cooled to -60°. The residue was treated with a 1:2 benzene-hexane mixture, and filtration gave 1.56 g of amide (III), mp 110-111° (the mixed melting point with an authentic specimen was not depressed). Based on the GLC data (10% Rheoplex-400 deposited on Chromsorb P, column length 2 m, 48°, and flow rate of carrier gas = 40 ml/min) the condensate contains  $CH_3OSi(CH_3)_3$ , methanol,  $CH_2Cl_2$ , and a small amount of HMDS as impurity. The  $CH_3OSi(CH_3)_3$  was identified in the NMR spectrum of the condensate by the protrait method.

Preparation and Properties of O-Diethylboron Derivative of N-Nitro-p-toluenesulfonamide (II). With vigorous stirring, 0.3 g of diethylboron chloride was added to 1 g of the Ag salt of (III) in 8 ml of  $CH_2Cl_2$  at  $-30^\circ$ , after which the mixture was stirred at  $-30^\circ$  for 1 h, and the AgCl was filtered at the same temperature. Based on the NMR data ( $-20^\circ$ , standard =  $0.7 \cdot 10^{-3}$  mole of HMDS, and integration of  $B(C_2H_5)_2$  singlet relative to HMDS) the yield of product (II) is close to 100%. After distilling off the solvents in vacuo at  $-30^\circ$ , (II) was isolated as crystals that decompose above  $0^\circ$  with gas evolution. Similar results were obtained when the  $CH_2Cl_2$  was replaced by ether. To 0.81 g of product (II) in  $CH_2Cl_2$  at  $-30^\circ$  was added 0.16 g of KOH in 4 ml of  $CH_3OH$ , the mixture was stirred for 15 min, the temperature was raised to  $20^\circ C$ , and filtration gave 0.43 g (60%) of the K salt of amide (III), mp 279-280°C (the mixed melting point with an authentic specimen was not depressed). Ultraviolet spectrum (in water):  $\lambda_{max} 224$  ( $\varepsilon 15,750$ ) and 251 nm ( $\varepsilon 11, 500$ ).

To 0.81 g of product (II) in  $CH_2Cl_2$  at -30 to  $-40^\circ$  was added 0.45 g of pyridine in 2 ml of  $CH_2Cl_2$ , the mixture was kept at this temperature for 15 min, heated to 20°, stirred for 30 min, half of the solvent was evaporated in vacuo, and precipitation with ether gave 1.1 g (87% yield) of the boronium salt (VI), mp 83-87°C (ether- $CH_2Cl_2$ ).

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## CONCLUSIONS

1. The silylation of the Ag salt of N-nitro-p-toluenesulfonamide with trimethylchlorosilane, or of the free N-nitro-p-toluenesulfonamide with N,N'-diphenyl-N-trimethylurea, gave the O-trimethylsilyl derivative of N-nitro-p-toluenesulfonamide.

2. The reaction of the Ag salt of N-nitro-p-toluenesulfonamide with diethylboron chloride gave the O-diethylboron derivative of N-nitro-p-toluenesulfonamide. Treatment of the derivative with pyridine gave the bis(pyridyldiethylboronium) salt of N-nitro-p-toluenesulfonamide.

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