

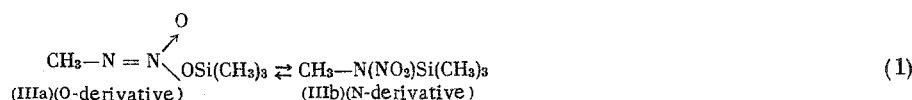
# SILYLATION OF METHYLNITRAMINE

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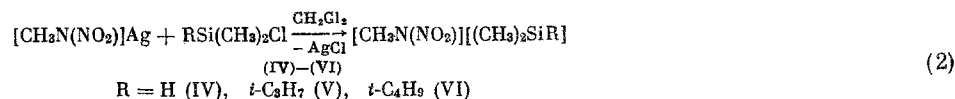
There is hardly any information in the literature on the covalently constructed heteroorganic derivatives of nitramines. A number of organotin derivatives of alkylnitramines was obtained in [1], and it was shown that they are all compounds in which the tin is pentavalent, is attached to the nitrogen by a covalent bond, and is coordinated at the oxygen atom of the NO<sub>2</sub> group. The silyl derivatives of nitramines (SDN) are not described.

We found that the silylation of methylnitramine using (CH<sub>3</sub>)<sub>3</sub>SiNHCH<sub>3</sub>, CH<sub>3</sub>C[OSi(CH<sub>3</sub>)<sub>3</sub>] = NSi(CH<sub>3</sub>)<sub>3</sub> (B. S. A.) or N,N'-diphenyl-N-trimethylsilylurea\* (I), or the silylation of the Ag salt of methylnitramine (II) with (CH<sub>3</sub>)<sub>3</sub>SiCl, leads to the same tautomeric mixture (III).



The existence of (III) as a tautomeric mixture was confirmed by us previously by the data of NMR spectroscopy [2] and the IR spectra (Fig. 1). It should be mentioned that replacing the hydrogen in CH<sub>3</sub>NHNO<sub>2</sub> by the Si(CH<sub>3</sub>)<sub>3</sub> group shifts the band of the antisymmetric vibration of the NO<sub>2</sub> group by nearly 80 cm<sup>-1</sup> toward lower frequencies.

In order to ascertain the effect of the character of the substituents attached to the Si atom on the position of equilibrium (1) we studied the reaction of salt (II) with silanes of general formula RSi(CH<sub>3</sub>)<sub>2</sub>Cl. The SDN were also isolated here.



Compounds (III)-(VI) were characterized by the elemental analysis, and by the NMR and IR spectra. Similar to compound (III), they represent tautomeric mixtures of the corresponding O- and N-derivatives, in which connection the amount of O-derivative in the equilibrium mixture increases with increase both in the temperature and in R: H < CH<sub>3</sub> < isopropyl << tert-butyl.

Compounds (III)-(IV) are easily hydrolyzed by atmospheric moisture, and they react with water and alcohols to give methylnitramine and the corresponding silyl derivatives.† While they are stable at -60°, they decompose at 20° in several days, with the formation of siloxanes and unidentified products. The reaction of the alkali metal alcoholates with compounds (III)-(VI) gives the corresponding methylnitramine salt and alkoxy silanes.

\* At the same time, methylnitramine cannot be silylated with dimethyltrimethylsilylamine.

† Apparently, compound (VI) is a convenient silylating agent for alcohols and reacts with them more rapidly than does dimethyl-tert-butylchlorosilane [3].

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TABLE 1

Compound No.	Bp, °C (p. mm of Hg)	Yield, %	Empirical formula	Found, %				Calculated, %				NMR data (chemical shifts)	
				C	H	N	Si	C	H	N	Si	R	Si(CH <sub>3</sub> ) <sub>2</sub>
(III)	56(17)	96	C <sub>4</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> Si	32.10	7.74	18.81	17.45	32.43	8.10	18.91	18.91	0.29	0.29
(IV)	58(20)	100	C <sub>5</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> Si	27.40	7.84	21.39	21.38	26.86	7.46	20.90	20.90	4.6 g	0.28
(V)	65(7)	81	C <sub>6</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> Si	41.44	8.90	15.87	15.31	40.91	9.10	15.9	15.9	0.9 m	0.25
(VI)	65(6)	57	C <sub>7</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> Si	44.71	9.45	14.53	14.91	44.24	9.42	14.73	14.73	0.95	0.3

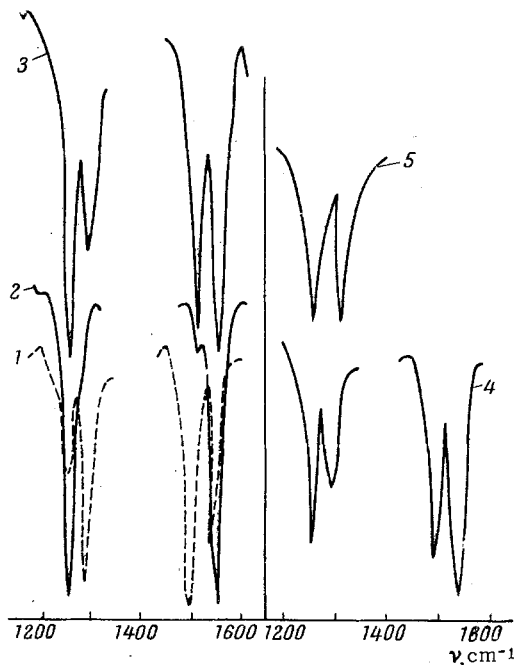


Fig. 1. Infrared spectra of compounds (III)-(VI) at 25°C: 1) (IV); 2) (VI); 3) (V); 4) (III); 5) (III) at -20°.

The reaction of salt (II) with CH<sub>3</sub>SiH<sub>2</sub>Br and (CH<sub>3</sub>)<sub>2</sub>-SiCl<sub>2</sub> gives unidentified compounds that decompose rapidly.

#### EXPERIMENTAL METHOD\*

CH<sub>3</sub>NHNO<sub>2</sub> [4], its salt (II) [5], and the silylating agents: (I) [6], (CH<sub>3</sub>)<sub>2</sub>SiCl (i-C<sub>3</sub>H<sub>7</sub>) [3], (CH<sub>3</sub>)<sub>2</sub>SiCl (t-C<sub>4</sub>H<sub>9</sub>) [3], and B.S.A. [7], were obtained by known procedures. The experiments on the synthesis and transformations of products (III)-(VI) were run in a dry argon atmosphere. The NMR spectra† were taken on a Perkin-Elmer R-12 instrument (60 MHz), using cyclohexane (δ 1.4 ppm) as the internal standard. Below are enumerated the chemical shifts of the principal fragments encountered in the study: for CH<sub>3</sub>NHNO<sub>2</sub>, CH<sub>3</sub> 3.1; CH<sub>3</sub>N(NO<sub>2</sub>)Si(CH<sub>3</sub>)<sub>2</sub>R, CH<sub>3</sub> 3.05; (CH<sub>3</sub>)<sub>3</sub>SiCl, CH<sub>3</sub> 0.35; (CH<sub>3</sub>)<sub>2</sub>SiHCl, CH<sub>3</sub> 0.35 d (J ~ 4 Hz); H = 4.8 m; (CH<sub>3</sub>)<sub>2</sub>Si(i-C<sub>3</sub>H<sub>7</sub>)Cl, (CH<sub>3</sub>)<sub>2</sub> 0.28; i-C<sub>3</sub>H<sub>7</sub> 1.0 m; (CH<sub>3</sub>)<sub>2</sub>Si(t-C<sub>4</sub>H<sub>9</sub>)Cl, (CH<sub>3</sub>)<sub>2</sub> 0.3; t-C<sub>4</sub>H<sub>9</sub> 0.95.

The IR spectra of compounds (III)-(VI) were taken in 0.02 mm cells, in CH<sub>2</sub>Cl<sub>2</sub> solution, on a UR-10 instrument.

General Procedure for Silylation of Salt (II) with R(CH<sub>3</sub>)<sub>2</sub>SiCl. To 0.04 mole of (II) in 30 ml of CH<sub>2</sub>Cl<sub>2</sub> at 20° was added 0.04 mole of R(CH<sub>3</sub>)<sub>2</sub>SiCl (R = CH<sub>3</sub>, CH(CH<sub>3</sub>)<sub>2</sub>, H) in 10 ml of CH<sub>2</sub>Cl<sub>2</sub>, and the mixture was stirred for 20 min (for R = C(CH<sub>3</sub>)<sub>3</sub> at 70° for ~4 h), filtered, the solvent was

removed in vacuo, and the residue was distilled. The principal properties of compounds (III)-(VI) are given in Table 1.

Reactions of Methylnitramine. a) With CH<sub>3</sub>NHSi(CH<sub>3</sub>)<sub>3</sub>. To a stirred solution of CH<sub>3</sub>NHSi(CH<sub>3</sub>)<sub>3</sub> in 4 ml of CH<sub>2</sub>Cl<sub>2</sub> was added 2.58 g of CH<sub>3</sub>NHNO<sub>2</sub>, the oil was separated (1.2 g), the CH<sub>2</sub>Cl<sub>2</sub> was removed in vacuo, and (III) was distilled (the yield, when based on the NMR data using an internal standard, was 45%). Ether was added to the oil and the whole was acidified; the CH<sub>3</sub>NH<sub>2</sub>·HCl was isolated from the aqueous layer. From the ether we obtained CH<sub>3</sub>NHNO<sub>2</sub> with mp 30° [4] (does not give a depression with an authentic sample).

b) With B.S.A. To 1 g of CH<sub>3</sub>NHNO<sub>2</sub> in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> at 20° was added 2.66 g of B.S.A. in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> and the mixture was stirred for 15 min. Based on the NMR data, the yield of product (III) is quantitative.

c) With Compound (I). To 1.87 g of (I) in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> at 20° was added 0.5 g of CH<sub>3</sub>NHNO<sub>2</sub> in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> and the mixture was stirred at 20° for 15 min, filtered, and the CH<sub>2</sub>Cl<sub>2</sub> was removed in vacuo. Based on the NMR data using an internal standard, the yield of (III) was 75%, bp 56° (17 mm).

Reaction of (VI) with Methanol. To 1.12 g of (VI) in 1 ml of CH<sub>2</sub>Cl<sub>2</sub> was added 0.38 g of absolute CH<sub>3</sub>OH, the mixture was stirred at 20° for 6 h, the solvent was removed, and distillation gave 0.24 g of dimethyl-tert-butylmethoxysilane with bp 56° (95 mm). NMR spectrum (in CH<sub>2</sub>Cl<sub>2</sub>): OCH<sub>3</sub> 3.3, C(CH<sub>3</sub>)<sub>3</sub> 0.85, (CH<sub>3</sub>)<sub>2</sub>Si 0 (ratio of signals 1:3:2). Based on the GLC data (74°, 10% Apiezon deposited on Chromosorb), the compound is pure. The residue contained 0.19 g of CH<sub>3</sub>NHNO<sub>2</sub>, mp 36-38° (does not give a depression with an authentic sample).

\*I. A. Maslina participated in the work.

† All the chemical shifts are given in ppm using HMDS as the standard.

Reaction of (II) with KOCH<sub>3</sub>. To 0.21 g of K in 10 ml of absolute CH<sub>3</sub>OH at 20° was added 0.87 g (III) in 4 ml of CH<sub>2</sub>Cl<sub>2</sub>, the mixture was stirred for 10 min, diluted with 25 ml of absolute ether, and filtration gave 0.41 g of the K salt of methylnitramine, mp 220° (from absolute alcohol) [8]. The NMR spectrum has a singlet at 1.8 upfield from D<sub>2</sub>O. The IR spectrum is identical with the IR spectrum of an authentic sample.

#### CONCLUSIONS

The silylation of methylnitramine with B.S.A. or N,N'-diphenyl-N-trimethylsilylurea, or of its Ag salt with silanes of general formula (CH<sub>3</sub>)<sub>2</sub>RSiCl, gives a tautomeric mixture of the corresponding O- and N-derivatives of methylnitramine. The amount of the O-derivative in the tautomeric mixture increases with increase both in the temperature and in R: H < CH<sub>3</sub> < CH(CH<sub>3</sub>)<sub>2</sub> << C(CH<sub>3</sub>)<sub>3</sub>.

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