N-NITROHYDRAZINES AND THEIR SALTS

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A method was developed for the synthesis of functionally substituted N-nitrohydrazines by nonacid nitration of the respective silylhydrazines. It was shown that the stability of these compounds increases with increase in the number of electronegative substituents. The first representative of N,N'-dinitrohydrazines, i.e., N,N'-dinitro-N,N'-diacetylhydrazine, was synthesized. Some of the obtained N-nitrohydrazines are characterized by dissociation with the formation of diazenes. The action of nucleophilic reagents on functionally N,N'-disubstituted N-methyl-N'-nitrohydrazines gave the salts of N-nitrohydrazines.

In spite of numerous attempts at the synthesis of N-nitrohydrazines (NH) [1-11], the only reliable representative of this type of compound is 1,1,2-tristrifluoromethyl-2-nitrohydrazine [1, 2]. The previously postulated formation of other nitrohydrazines was not proved [11]. In our opinion, one of the possible reasons for the lack of success in the synthesis of nitrohydrazines is the instability of the nitrohydrazines in the acidic media in which they were usually obtained. It is known that N-nitro compounds are as a rule unstable in media with high acidity, and we therefore used nonacidic nitration of trimethylsilylhydrazines not containing NH fragments for the synthesis of nitrohydrazines.

Earlier the successful nitration of N–Si derivatives was described for the synthesis of N-nitro-substituted azoles [12, 13] and carbodiimides [14]. The reactions were realized under very mild conditions by the action of N_2O_5 or nitronium salts on the silylated substrates in aprotic media, and the process was monitored by NMR. As starting compounds in the synthesis of the nitrohydrazines we used trimethylsilylhydrazines (TSH) $RR'N–NR''SiMe_3$ (Ia-j), the synthesis of which was described in [15-17] (Table 1). As nitrating agent we used N_2O_5:*

$$\underset{(Ia-g)}{RR'N–NR''SiMe_3} + N_2O_5 \rightarrow \underset{(IIa-g)}{RR'N–NR''NO_2} + Me_3SiONO_2 \qquad (1)$$

It was shown by special tests that the Me_3SiONO_2 formed in reaction (1) is inert toward the initial TSH and is easily removed from the reaction mixture at 0°C (0.5 mm Hg). The reaction (1) was monitored by PMR by means of the signals of the Me_3Si group in the initial TSH and the obtained Me_3SiONO_2.

Reaction (1) takes place fairly smoothly at ≤20°C and is greatly accelerated with the addition of a catalytic amount of anhydrous $SnCl_4$.†

Data on the nitration of TSH are given in Table 1.

Earlier we showed that trimethylsilylhydrazines with the N–NCO fragment exist in solutions as an equilibrium mixture of structural and stereochemical isomers.

*The nitration of TSH by nitronium salts [NO_2BF_4 or $(NO_2)_2SiF_6$] is ineffective, since the released Lewis acids (BF_3 or SiF_4) react with the initial TSH.

†The addition of an equimolar amount of $SnCl_4$ leads to the formation of unidentified products.

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TABLE 1. Conditions for the Nitration of Trimethylsilylhydrazines

R	R′	R″	TSH	NH	Reaction temperature, °C (time, min)	Catalyst $SnCl_4$, mole %	Yield, %	T, °C*	Method of evidence†
Me	CO_2Me	CO_2Me	(Ia)	(IIa)	+10(180)	0	65 ‡	10	B, C
			(Ia)	(IIa)	−20(50)	3,5	85	10	»
Me	Ac	Ac	(Ib)	(IIb)	0(15)	0	85	10	»
Me	Ac	CO_2Me	(Ic)	(IIc)	−15(90)	3,5	85	10	»
Me	CO_2Et	Ac	(Id)	(IId)	−20(30)	3,5	85	10	»
Ac	CO_2Me	CO_2Me	(Ie)	(IIe)	+20(600)	0	80	70	A, B
			(Ie)	(IIe)	0(90)	3,5	85	70	»
Ac	Ac	Ac	(If)	(IIf)	0(600)	0	90	70	A, B
			(If)	(IIf)	0(60)	3,5	80	70	»
$SiMe_3$	CO_2Me	CO_2Me	(Ig)	(IIg)	+13(540)	0	95	25	B
			(Ig)	(IIg)	−20(120)	7	80	25	»
$SiMe_3$	Ac	Ac	(Ih)	(IIh)	−20(60)	0	0 **	10	»
NO_2	Ac	Ac		(IIk)			65	10	»
H	Ac	Ac		(IIℓ)			5	10	»
NO	Ac	Ac		(IIm)			30	10	»
Me	Me	Ac	(Ii)	(IIi)	−20(5)	3,5	0 ††	–	–
$SiMe_3$	CO_2Et	Me	(Ij)	(IIj)	−20(120)	7	60	10	B

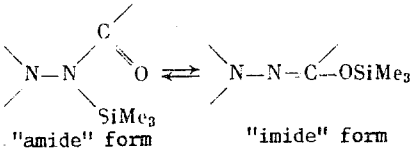
*The temperature at which the NH decomposes in less than 24 h.

†A = elemental analysis, B = spectroscopic method; C = salt production.

‡Yield of $MeONO_2$ 30% (in the distillate), see Eq. (3).

**The ratio of the reaction products according to data from the PMR spectrum is given.

††Yield of $MeONO_2$ 13% (in the distillate).



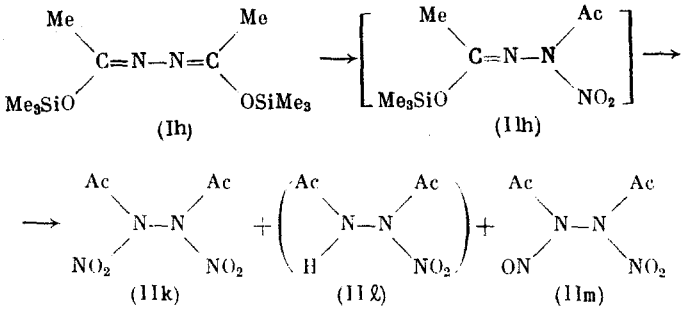
"amide" form (A) "imide" form (B)

The "amide" form predominates for the N-alkoxycarbonyl-substituted compounds, and the "imide" form predominates for the N-acetyl-substituted compounds [17, 18]. However, these features of the trimethylsilylhydrazines only affect the specific characteristics of nitration but not the final products, the structural evidence for which is of separate interest and is discussed below.

It is seen from Table 1 that the N-nitration of the "amide" fragment (A), characteristic of the alkoxycarbonyl derivatives, is realized more slowly than for the "imide" fragment (B) in the acetyl-substituted derivatives. This is evidently due to the electron and steric factors. During the nitration of the "imide" fragment and also of the cyclic trimethylsilyl derivative of trisacetylhydrazine [16] the nitronium cation attacks the molecule at the sterically accessible N atom with transfer of the reaction center. In the "amide" form the approach to the N atom is sterically hindered, and the presence of the electron-withdrawing alkoxycarbonyl group reduces its nucleophilicity.

The introduction of electron-donating substituents at the nitrogen atom adjacent to the reaction center facilitates nitration [cf. (Ia) and (Ie)], while electron-withdrawing substituents hinder it. On account of this, evidently, we were unable to nitrate at the N–Si bond (IIg, j).

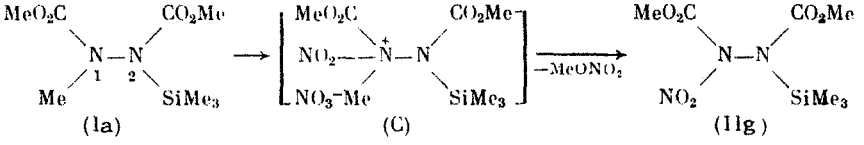
Unlike (Ig), (Ih) reacts with N_2O_5 extremely quickly (the effect of the "imide" form), but we were unable to isolate or detect the intermediate mononitrohydrazine (IIh). In the reaction mixture we identified the product from substitutive nitration of two trimethylsilyl groups (IIk) and also the nitrohydrazine (IIℓ, m):



(2)

The presence of the NH (IIℓ) is clearly due to protolysis of the initial TSH (Ih) or the intermediate mononitrohydrazine (IIh). The proportion of (IIℓ) in the reaction mixture is small, varies from experiment to experiment, and can be minimized. The mechanism of the formation of (IIm) is not clear at the present time. Its yield does not decrease after special purification of the initial N_2O_5, and it can therefore hardly be due to nitrosation of the TSH (Ih) or the intermediate NH (IIh) by the N_2O_4 impurity.

Interesting data were obtained during the nitration of TSH (Ia) by N_2O_5 at temperatures above 0°C without the $SnCl_4$ catalyst. In the reaction products by PMR and GLC, in addition to the NH (IIa) and the corresponding "side" nitration product (trimethylsilyl nitrate) we identified methyl nitrate (30%) and the NH (IIg), which corresponded to authentic (IIg) in its PMR spectrum. The formation of the latter can be explained by nitration at the N–Me bond.

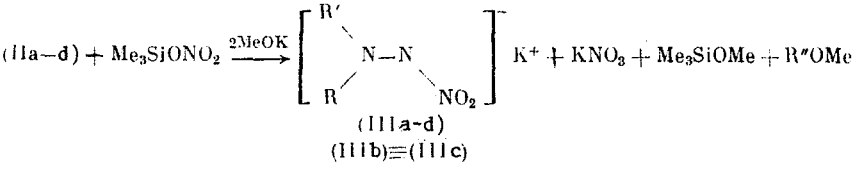


(3)

On account of the higher nucleophilicity and of the steric accessibility of this nitrogen atom in the TSH (Ia) nucleophilic attack on the carbon of the Me group by the NO_3^- anion by the S_N2 mechanism can occur in the intermediate C.* It is interesting that the nitration of the TSH $MeN(SiMe_3)N(SiMe_3)CO_2Et$ (Ij) by N_2O_5, which takes place predominantly in the $N(Me)SiMe_3$ fragment, is also accompanied by the formation of methyl nitrate (13%).

The unsuccessful attempt at the synthesis of the NH (IIi) is evidently explained by preferential attack by the nitrating agent on the initial TSH at the most basic "amide" nitrogen atom and not at the silylated amide system.

The action of potassium methoxide (MeOK) on the NH (IIa-d) gave the corresponding NH salts (IIIa-d). Here it is not necessary to isolate the NH from the reaction mixture. After treatment with two equivalents of potassium methoxide the obtained compounds (IIIa-d) are easily separated from the potassium nitrate, since the latter (unlike the required salts) is practically insoluble in alcohol:



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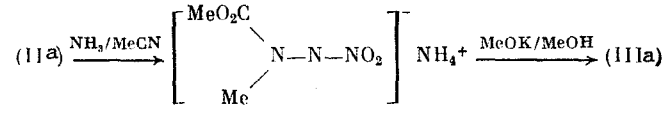
Ammonia acts in the same way as potassium methoxide:

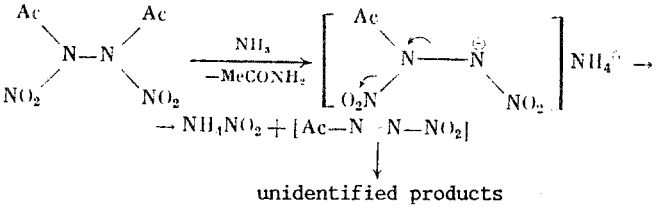


(5)

*At the same time S_N2 substitution by the NO_3^- anion at the CO fragment of the MeOCO group is impossible, while S_N1 substitution is unfavorable in the nonpolar aprotic solvent.

In the reaction of the NH with MeOK the functional group (Ac or MeOCO) attached to the amide and not the amine fragment is attacked. In (IIa-d) the reaction takes place exclusively at the $N(NO_2)R''$ fragment with the formation of the corresponding NH salts. In (IIe, f) attack can be realized not only at $N(NO_2)R''$, but also at the NRR' fragment containing two electron-withdrawing groups. In the products from the reaction of (IIe) with MeOK, for example, we detected equal amounts of AcOMe (attack at the Ac group) and $(MeO)_2CO$ (attack at one of the MeOCO groups). Here the residue after distillation of the volatile compounds, starting both from (IIe) and from (IIf), contained complex mixtures, in which it was only possible to identify KNO_3, KNO_2, and AcK, instead of the expected salts.*

During treatment of a solution of the NH (IIk) with ammonia only NH_4NO_2, formed evidently according to the following scheme



(6)

was isolated from the reaction mixture instead of the ammonium salt of the nitrohydrazine.

The structure of the NH salts (IIIa-d) was confirmed by the data from elemental analysis and spectroscopy (Table 2), and the structure of (IIIa) was confirmed by x-ray crystallographic analysis, which will be described separately. In the UV spectra of the salts a characteristic maximum is observed at λ = 235 nm. The NMR data confirm the presence of the main structural fragments and also show that in contrast to the initial N-nitrohydrazines the signals of only one conformer are observed in the spectra of the salts. In chemical shifts the NO_2 groups of the NH salts correspond to those in the salts of N-nitroamides and differ significantly from those of the salts of N-nitroamines. Like the upfield shift of the ^{13}C signal of the CO group, this fact indicates appreciable interaction between the π system of the R fragment and the anionic center of the NH salts.

The salts (IIIa-d) are stable in the solid form under normal conditions. For example, the temperature of the beginning of strong decomposition of the salt (IIIa) is ~155°C (DTA data). However, to judge from the rapid disappearance of the maximum with λ = 235 nm in the UV spectra of the solutions, these salts decompose fairly rapidly in protic solvents and are also unstable in the melt.

To obtain evidence for the structure of the NH (II) is a separate difficult problem. It is the lack of suitable methods for the identification of the nitrohydrazines in conjunction with their lability which gives rise to the subsequently unsupported reports on the synthesis of compounds of this type [3-11].

As seen from Tables 1 and 2, our obtained nitrohydrazines can be divided into groups: 1) Stable at ~20°C; 2) unstable at ~20°C and giving salts; 3) unstable at ~20°C and not giving salts.

The molecular formula for the nitrohydrazines stable at ~20°C was confirmed by elemental analysis, while the choice between the structures of the nitrohydrazines and the isomeric nitrate ($>N-N=\overset{|}{C}-ONO_2$) was made on the basis of data from heteronuclear magnetic resonance.

The conclusion about the production of NH of the second group was reached on the basis of their conversion into salts. The structure of the third group was confirmed reliably by spectral methods.†

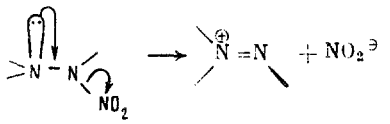
*The mixtures exhibit enhanced sensitivity to impact.
†For the results from study of the NH (II) by heteronuclear NMR, see the next publication.

TABLE 2. Characteristics of the N-Nitrohydrazine Salts

Compound	Yield, %	Mp, °C	λ, nm (ε) water	IR spectrum, cm^{-1}		NMR (D_2O)				Found/Calculated, %				Empirical formula
				NO_2	CO	PMR (δ, ppm)			^{14}N NMR (δ, ppm) (half-width, Hz)	C	H	N	K	
						$N-CH_3$	$O-CH_3$	$C-CH_3$						
(IIIa) *	70	152	235 (5900)	1310, 1370	1680	2,90	3,60	–	−6,5 (85)	19,38 19,25	3,24 3,23	22,60 22,45		$C_3H_6N_3O_4K$
(IIIb, c)	72 (79)	135	**237 (6800)**	1300, 1370	1650	3,05	–	1,95	−6,5 (130)	21,53 21,04	3,76 3,53		22,73 22,83	$C_3H_6N_3O_3K$
(IIId)	83	168	**235 (5700)**	1300, 1370	1690	3,07	†			23,81 23,87	3,85 4,00	20,86 20,92		$C_4H_8N_3O_4K$
(IVa) ‡	50	135	**235**	1310, 1370	1680–1760	2,95	3,60	–	−2,3 (70) −357,6 (41)					

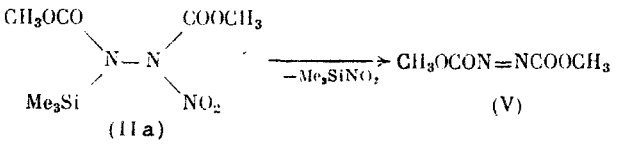
*^{13}C NMR spectrum at 60°C in methanol (δ, ppm): 33.4 (NMe), 52.1 (OMe), 157.7 (CO).
†For the $MeCH_2$ fragment, PMR spectrum (δ, ppm): 1.16 t (Me), 4.02 q (CH_2).
‡The salt could not be brought to analytical purity.

In our opinion, the instability of the NH is due to the nucleophilicity of the nitrogen atom attached to the N-nitro fragment.



A similar dissociation mechanism was proposed earlier for 6-nitro-2,9-dioxa-1-azabicyclo[4.3.0]nonane [19] and was used to explain the instability of N-chloro-substituted hydrazines [20]. The presence of electron-withdrawing substituents at the nitrogen atom attached to the N-nitro fragment leads to delocalization of the unshared electron pair (UEP) and stabilization of the NH. Effective interaction between the UEP and the NO_2 group is only possible in their trans-antiparallel arrangement. Therefore, stabilization of the NH can take place not only by delocalization of the UEP but also by the transition to structures in which this pair is fixed in a position differing from trans-antiparallel in relation to the NO_2 group.*

In certain cases during the dissociation of the NH we established reliably the formation of diazenes:



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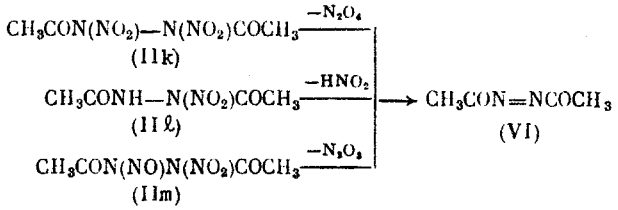

(8)

Thermal dissociation of (IIa) occurs completely in 24 h at ~20°C. The diazene (V) was isolated in the free form and was used in the synthesis of the NH (Ie) labeled with the ^{15}N atom.

Thermal dissociation of the mixture (IIk, ℓ) takes place at temperatures above 0°C. The process was studied on nitrohydrazines containing the ^{15}N label both in the NO_2 group and in the nitrogen atoms of the hydrazine fragment. According to the ^{15}N NMR spectra of the reaction mixture, the gradual disappearance of the signals of the original NH and the appearance of the signals of the diazene (VI) (at about 178 ppm) are observed.† The diazene (VI) could not be isolated from the reaction mixture, but the intensity of the signal assigned to it decreases with time. Gaseous products, which to judge from the color contain nitrogen oxides, are also formed during the thermolysis of the NH (IIk, ℓ).

EXPERIMENTAL

All the work with the trimethylsilylhydrazines (Ia-j) was conducted without access to moisture in an atmosphere of dry argon and in dry solvents. Compounds (Ia-j) were synthesized according to [15-17]. The N_2O_5 was obtained from concentrated nitric acid and phosphorus pentoxide [22]. The PMR spectra were recorded on Perkin-Elmer R-12 and Bruker WP-60 spectrometers at 60 MHz. The IR spectra were obtained on a UR-10 spectrometer. The GLC

*For our obtained 7-nitro-1,7-diazabicyclo[2.2.1]heptane the temperature of the beginning of intensive decomposition is higher than 150°C (details in subsequent publications). Such stabilization must be observed to an even greater degree with quaternization of the nitrogen attached to the N-nitro fragment, as occurs in R_3NNNO_2 [21].

†During the thermal dissociation of the NH (IIk-m) (not containing the ^{15}N label in the hydrazine fragment) the signal at 178 ppm does not appear.

was conducted on an LKhM-81 chromatograph with a katharometer as detector (carrier gas helium, ℓ = 2 m, Reoplex 400, 10% on Chromosorb P). For preparative TLC we used silica gel LSL_{254M} 5/40 with a luminescent indicator (+40% of gypsum) (Chemapol).

General Procedure for the Nitration of Trimethylsilylhydrazines (Ia-j). a. Production of Nitrohydrazines (IIa, b, e-m) without a Catalyst. To a solution of 5 mmoles of (a,b, e-h) in 2 ml of methylene chloride, while stirring at −45°C, we added 5.2 mmoles of N_2O_5 (for each Me_3Si group). After the temperature rise and the corresponding holding time the volatile products were distilled into a cooled receiver at 0°C under the vacuum of an oil pump and were then analyzed by PMR with cyclohexane as internal standard. The composition of the residue was determined by NMR spectroscopy [19]. The stable nitrohydrazines (IIe, f) were purified by preparative TLC with ethyl acetate as eluant. The elemental analyses of these nitrohydrazines agreed with the calculated data. The reaction temperatures, holding times, and yields for (IIa, b, e-h, k-m) are given in Table 1. The obtained nitrohydrazines were treated with potassium methoxide to produce the salts (III).

b. Production of Nitrohydrazines (IIa, c-g, i, j) in the Presence of $SnCl_4$. The reaction was conducted by analogy with method a with the same materials. Stannic chloride was added at −45°C before the temperature began to rise. Even in an excess of N_2O_5 the nitration of (Ig, j) only took place at one N—Si bond. The nitration conditions are given in Table 1.

Potassium Salt of N-Nitrohydrazines (III). To the reaction mixture produced in the nitration of 5 mmoles of (Ia-d) at −40°C with stirring we added dropwise 4 ml of a 2.4 N solution of potassium methoxide in methanol. After holding for 30 min the temperature was raised to ~20°C, the volatile substances were distilled into a cooled receiver under the vacuum of an oil pump at ~20°C, and the product was then analyzed by PMR spectroscopy. The residue was dissolved in methanol, and the potassium nitrate precipitate was filtered off (≈100%). When necessary, the solution was purified with active charcoal, the methanol was evaporated under the vacuum of a water-jet pump, and the residue was recrystallized from methanol. The yields and characteristics of the obtained salts (IIIa-d) are given in Table 2.

Ammonium Salt of N-Methoxycarbonyl-N-methyl-N-Nitrohydrazine (IVa). A 1.5-g sample of (IIa), obtained by method b (a double load), in 2.5 ml of methylene chloride and cooled to −10°C was added at −40°C with stirring to a solution of 1.7 g of liquid ammonia in 13 ml of acetonitrile. The mixture was kept at −30°C for 15 min, 50 ml of toluene was added, and the mixture was evaporated to a total volume of 20 ml under vacuum. The solution was decanted, and the remaining oil was rubbed with acetonitrile until a white powder had formed (Table 2). The action of an equivalent amount of a solution of potassium methoxide in methanol on (IVa) gave compound (IIIa).

Decomposition of (Ig). A 0.65-g sample of (Ig), obtained by method a, was left in 2 ml of methylene chloride at 25°C for 3 days, after which the total decomposition of the mixture into (V) (PMR spectrum, δ, ppm, 4.12) and HMDS was detected by means of the PMR data. The HMDS and methylene chloride were removed under the vacuum of a water-jet pump, and compound (V) was distilled at 90°C (15 mm Hg). The yield was 75%. The product was converted by the action of 1 g of acetaldehyde over 24 h into compound (Ie) with a yield of 88%.

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