

Dedicated to the Corresponding Member of the Russian Academy of Sciences
B. V. Gidasov on occasion of his 60th anniversary

Synthesis and Some Properties of 1,2-Dinitroguanidine

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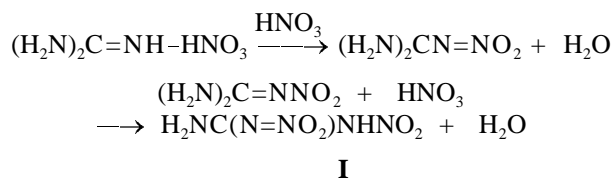
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Abstract—1,2-Dinitroguanidine is a product of nitroguanidine nitration with nitric acid and its mixtures with sulfuric acid and oleum. It is a diacid (pK_a 1.11, ~11.5) and at the same time a weak base undergoing protonation at the nitrogen of the amino group (pK_{BH^+} -5.81). The decomposition kinetics of 1,2-dinitroguanidine was studied by spectrophotometric method both in acid and alkaline media, and the mechanism of the process was assumed. In the media of high acidity ($H_0 > -8$) the 1,2-dinitroguanidine suffers reversible denitration into nitroguanidine. At lower acidity its conjugate acid or molecular form undergoes hydrolysis yielding nitrourea. Monoanion of 1,2-dinitroguanidine in a weak acid or in an alkali is hydrolyzed into *N,N'*-dinitrourea. The reaction of 1,2-dinitroguanidine with alkali in alcohol provides its salts, with nitrogen-containing bases form both salts and derivatives of 2-nitroguanidine. The treatment of 1,2-dinitroguanidine with haloalkanes results in its *N*-alkylated products.

Nitration of guanidine salts with nitric acid or its mixtures with concn. sulfuric acid is known to furnish nitroguanidine in up to 95% yield (see, e.g., [1-3]). Up till now the nitroguanidine was regarded as the final product of this reaction. We found however that dissolution of nitroguanidine in mixtures of HNO_3 with H_2SO_4 or N_2O_5 resulted in reaction yielding a compound with a spectrum quite unlike that of the initial nitroguanidine (Fig. 1). The reaction rate considerably increased with growing nitrating activity of the medium in the series 98% HNO_3 < 100% HNO_3 < 2% solution of N_2O_5 in HNO_3 .

Even after a prolonged keeping of the solution its diluting with water resulted only in precipitation of nitroguanidine. The reaction product remained in water solution and was isolated by extraction with ethyl acetate. The elemental analysis and spectral characteristics of the colorless crystalline substance obtained were fully consistent with those of 1,2-dinitroguanidine (**I**). We therefore revealed that the nitroguanidine is not the final but intermediate product of the guanidine nitration with nitric acid:



On recrystallization from alcohol or acetic acid the 1,2-dinitroguanidine is a sufficiently stable compound with mp 169°C. It is moderately soluble in water and organic solvents. For instance, the concentration of a saturated 1,2-dinitroguanidine solution in water at 20°C is 53 g l⁻¹, in ethyl acetate 86 g l⁻¹. Its solubility quickly grows at heating, both in warm water and in common organic solvents, as ethyl acetate, ethanol, acetone, acetonitrile, the 1,2-dinitroguanidine

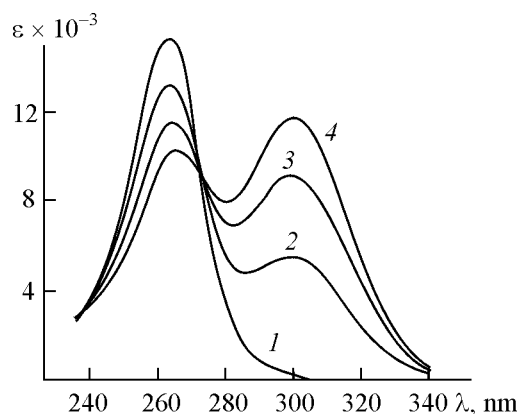
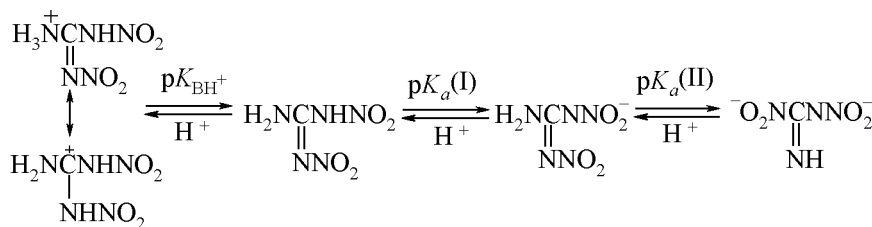


Fig. 1. Spectra of diluted aliquots of reaction mixture from nitration of 5 g of nitroguanidine in 35 ml of 2% solution of N_2O_5 in HNO_3 , -20°C. Aliquots diluted 10 000 times, pH 4-8. Time since the end of mixing, min: 0 (1), 20 (2), 70 (3), 120 (4).

dine is well soluble. At 45°C its solubility in water attains 125 g l⁻¹, and in ethyl acetate at 65°C 166 g l⁻¹. It is a lot less soluble in aromatic hydrocarbons and chloroalkanes.

In water solutions 1,2-dinitroguanidine exists as monoanion whose UV spectrum does not change in the pH range from 4 to 9. A strong absorption band of ϵ 21 000 l mol⁻¹ cm⁻¹ appears at λ_{\max} 302 nm. The analysis of dependence of the UV spectra of 1,2-dinitroguanidine solutions on the acidity in the range

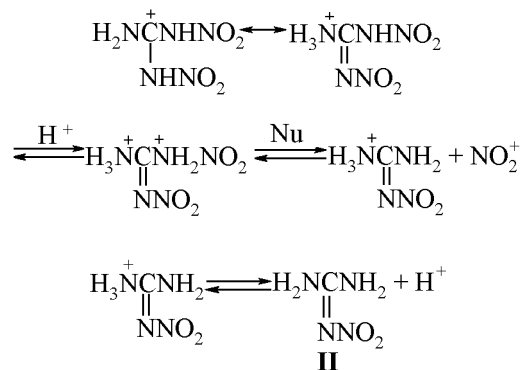
from pH 3 to H_0 -8 revealed two acid-base equilibria corresponding to protonation of 1,2-dinitroguanidine anion and to protonation of its molecular form to give its conjugate acid. The protonation of 1,2-dinitroguanidine may occur at the nitrogen atom of amino or nitrimino group for the N-protonation of the nitramino group would immediately result in the rupture either of N-C or N-N bond (see, e.g., [4]). The increasing of the medium pH to 10 and more leads to equilibrium formation of 1,2-dinitroguanidine dianion:



It was found by spectrophotometric method that the $pK_a(\text{I})$ value was 1.11, pK_{BH^+} -5.81 in the H_0 scale [5], and $pK_a(\text{II})$ ~11.5 in the H -scale [6]. These data show that unlike the nitroguanidine the 1,2-dinitroguanidine is relatively strong acid. This is quite understandable since its first dissociation step corresponds to proton cleavage from a nitramino group that is lacking in the nitroguanidine molecule. At the same time to the second step of its dissociation related to the tautomeric equilibrium in the 1,2-dinitroguanidine anion corresponds to a constant of the same order of magnitude as in the case of nitroguanidine (pK_a ~13.6 [7]) although still the 1,2-dinitroguanidine remains the stronger acid. The basicity of 1,2-dinitroguanidine is considerably lower than that of nitroguanidine (pK_{BH^+} - 0.93 [8] and -0.98 [9] respectively). This is also understandable since the basicity of nitroguanidines depends on the inductive effect of the substituents [8, 9], and in the molecule of 1,2-dinitroguanidine exists an additional electron-withdrawing substituent, NO₂ group, significantly reducing the electron density on nitrogen atoms.

At the room temperature the UV spectra of 1,2-dinitroguanidine dissolved in aqueous sulfuric acid of concentration over ~80% revealed irreversible transformations the rate of which grew with growing acidity and temperature. Since in such solutions the 1,2-dinitroguanidine is present exclusively in a monoprotinated form the increase in the reaction rate with acidity of the medium may arise only in the case when the reactive species is dication. After keeping the 1,2-dinitroguanidine in solution of concn. H₂SO₄

the reaction mixture acquired notable nitrating activity (the amount of separated HNO₃ measured by method from [10] reached over 1.9 mol per 1 mol of 1,2-dinitroguanidine). The dilution of these solutions with water always resulted in precipitation of colorless crystals that we identified as nitroguanidine (II). Thus the reaction that 1,2-dinitroguanidine underwent in media of high acidity was denitration common to N-nitro compounds containing electron-withdrawing groups attached to the nitrogen atom (see, e.g., [11]):



The second molecule of nitric acid arises at subsequent denitration of intermediately formed nitroguanidine [12].

The spectrophotometric measurement of the denitration rate of 1,2-dinitroguanidine in 83.9–90.6% H₂SO₄ revealed that the kinetic relations in this reaction are common for dinitration of N-nitro compounds. Thus the slope of the straight line of

$\log k_{\text{app}}$ vs. H_0 for 25°C (Fig. 2) amounts to -1.20 , quite close to the figure for nitroguanidine (-1.46 [13]), dinitramide (from -1.3 to -1.4 [11]), aromatic *N*-nitramines (-1.2 to -1.4 [14, 15]).

As the H_2SO_4 concentration is decreased below 80% the 1,2-dinitroguanidine decomposition is to greater extent accompanied by gas evolution. We identified the latter by the characteristic band in the IR spectrum at 596, 1300, 2277 cm^{-1} as nitrogen(I) oxide. The nitrating activity of these solution steeply decreased, and in 75% H_2SO_4 it was already absent. Diluting with water the solution of 1,2-dinitroguanidine in 75% H_2SO_4 after keeping it at 50°C resulted in precipitation of white powder that was identified by the melting point and UV spectrum as nitrourea, a product of nitramide NH_2NO_2 elimination from 1,2-dinitroguanidine. Thus its decomposition catalyzed by acids takes a similar route as that of *N*-nitramides of aromatic carboxylic and sulfonic acids [4, 10, 16, 17] where depending on the electronegativity of substituents in the aromatic ring occurs both denitration and nitramide elimination with subsequent formation of nitrogen(I) oxide. The plots of both denitration and cleavage of these nitramides at the N-C or N-S bond as a function of the medium acidity (slopes of the straight lines $\log k_{\text{app}}$ vs. H_0 equal to $-1.1\dots-1.3$) are quite similar to analogous plots corresponding to the acid-catalyzed decomposition of 1,2-dinitroguanidine. The weak dependence of the decomposition rate on acidity in relatively diluted H_2SO_4 (Fig. 2) that is also observed for decomposition of substituted benznitramides [4] and benzenesulfonitramides [17] is due to decomposition of both monoprotonated and neutral forms of 1,2-dinitroguanidine. The less is the medium acidity, the less is the dication concentration and the corresponding denitration degree, and consequently the greater becomes the relative rate of nitrourea formation from the monoprotonated and neutral forms of the 1,2-dinitroguanidine.

Nitrourea formation in the course of 1,2-dinitroguanidine decomposition in the media containing more than 20% of H_2SO_4 is easily detected in spectra of the diluted aliquots of the reaction mixture by the characteristic spectrum of anion at pH 5–7 [18]. This

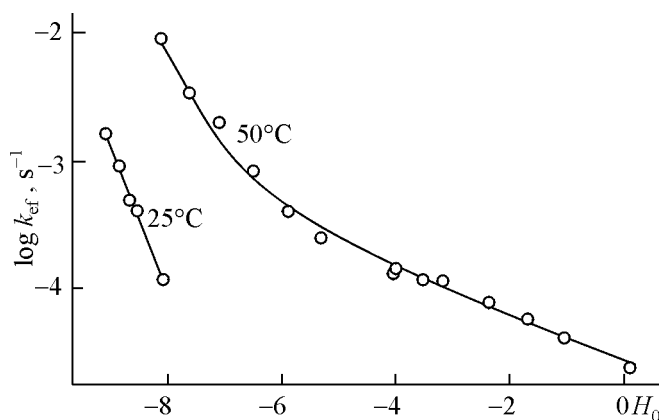
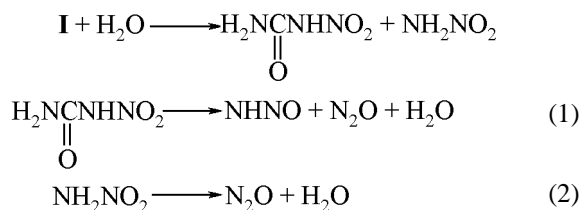


Fig. 2. Dependence of apparent first order rate constants of 1,2-dinitroguanidine decomposition in aqueous H_2SO_4 on the medium acidity. H_0 values are taken from [5].

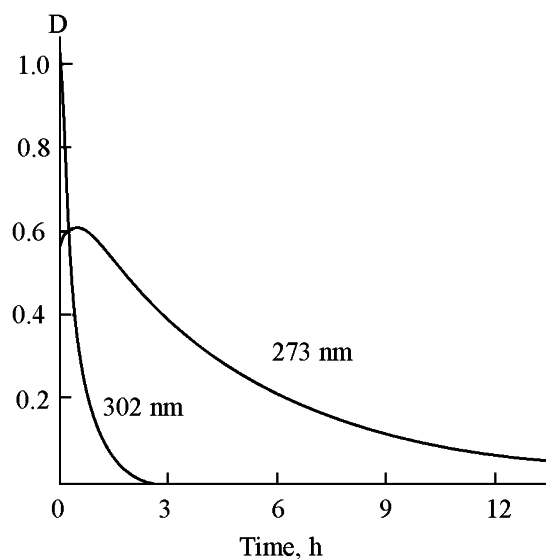


Fig. 3. Plots versus time of optical density of diluted aliquots of reaction mixtures obtained at decomposition of 5 mg of 1,2-dinitroguanidine in 30 ml of 0.011 M NaOH solution at 50°C. Aliquots are diluted 1:25, pH 4–8.

is possible for further decomposition of nitrourea in these media occurs much slower [19] and it is accumulated in the course of 1,2-dinitroguanidine decomposition. The formed nitramide and nitrourea decompose further providing nitrogen(I) oxide, cyanic acid, and water [20]:

When the acidity of the medium is decreased more, the relative amount of nitrourea becomes smaller, and in the hydrolysis products obtained from 1,2-dinitroguanidine in solutions containing less than 20% of H_2SO_4 the nitrourea is not detected spectrophotometrically. The fact means that in these media of low acidity the primary product of 1,2-dinitro-

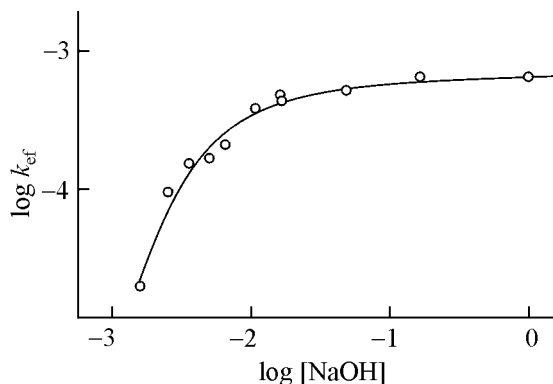
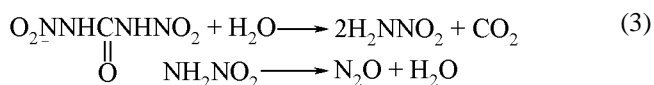
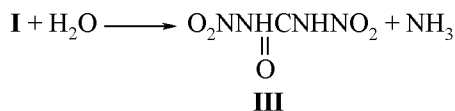


Fig. 4. Plot of first order rate constants of 1,2-dinitroguanidine decomposition in alkaline medium versus NaOH concentration. Water solutions, 50°C.

guanidine decomposition is not the nitrourea but some other compound whose degradation into simple products occurs with a higher rate than that of its formation.

The spectrophotometric measurements revealed that at pH > 2 in the reaction mixture arises a relatively stable intermediate with a strong absorption at λ_{\max} 273 nm not only in alkali as nitrourea anion, but also in weak acids (pH 1–2). For instance, it is seen from Fig. 3 that the optical density at λ 273 nm first grows and then gradually decreases indicating formation and subsequent decomposition of the intermediate product. The decrease in the optical density corresponds to first order rate of reaction with respect to the intermediate concentration. The apparent rate constant of its decomposition under these conditions is $5.90 \times 10^{-5} \text{ s}^{-1}$ whereas the corresponding value for nitrourea measured independently under the same conditions is considerably larger, $2.95 \times 10^{-4} \text{ s}^{-1}$. On the contrary, the rate constant of the intermediate product decomposition and that of authentic *N,N'*-dinitrourea measured at 50°C and NaOH concentration 0.01–0.05 M are identical within the measurement error (10–15%).

The positions of absorption maxima also coincide. The anion of *N,N'*-dinitrourea absorbs at λ_{\max} 273 nm (ϵ 13000 $\text{lmol}^{-1} \text{ cm}^{-1}$) [21] in conformity to the data for the intermediate product. These results



permit an assumption that the hydrolysis product of 1,2-dinitroguanidine in alkaline and weak acid media is *N,N'*-dinitrourea (III). Its subsequent decomposition in the aqueous medium furnished nitramide [21] and further nitrogen(I) oxide.

In order to reveal the nature of the reactive form of 1,2-dinitroguanidine in course of *N,N'*-dinitrourea formation we measured the rates of its alkaline hydrolysis. As seen from Fig. 4, the hydrolysis rate grows with alkali concentration and reaches the maximum value in the 0.05 M solution. The reaction is of the second order: first order in 1,2-dinitroguanidine and first order in hydroxide anion; the dependence of the reaction rate on alkali concentration corresponds to equation (4) if the reactive form of the 1,2-dinitroguanidine is monoanion, and to equation (5) if the reaction proceeds through dianion:

$$\log k_{\text{app}} = \log k_1 - \log(1 + a_{\text{H}^+}/K_a(\text{I}) + K_a(\text{III})/a_{\text{H}^+}) + \log[\text{OH}^-], \quad (4)$$

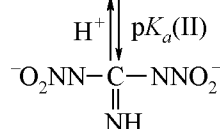
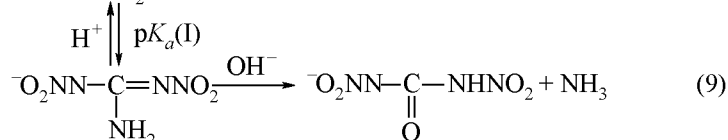
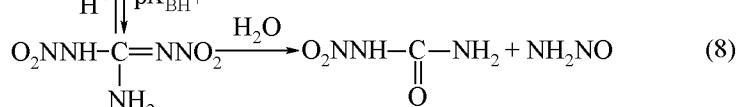
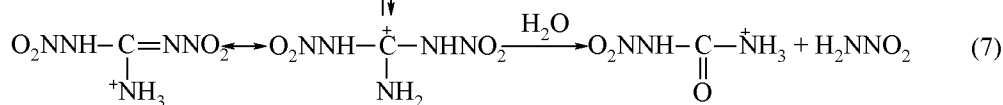
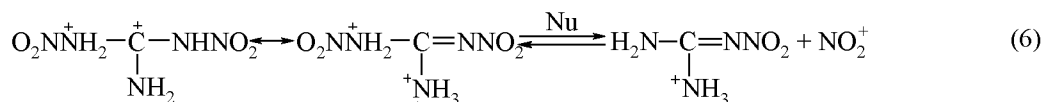
$$\log k_{\text{app}} = \log k_1 - \log[1 + a_{\text{H}^+}/K_a(\text{I}) + a_{\text{H}^+}^2/K_a(\text{I})K_a(\text{II})] + \log[\text{OH}^-]. \quad (5)$$

The analysis of equations (4) and (5) suggests that hydrolysis of 1,2-dinitroguanidine in alkaline media occurs via monoanion because only from equation (4) follows the experimentally found reaction rate independence of the alkali concentration in the range of significant dissociation of anion into dianion. Actually, in the alkaline environment where the 1,2-dinitroguanidine is completely ionized to monoanion [$a_{\text{H}^+}/K_a(\text{I}) \ll 1$] and the monoanion is already to a considerable extent dissociated [$K_a(\text{III})/a_{\text{H}^+} \gg 1$] equation (4) is simplified into:

$$\log k_{\text{app}} = \log k_1 - \log(K_a(\text{III})/a_{\text{H}^+}) + \log[\text{OH}^-] \approx \log k_1 + \text{p}K_a(\text{III}) + \log[\text{H}^+][\text{OH}^-] \approx \text{const},$$

in agreement with the experiment (Fig. 4). According to equation (5) with growing concentration of alkali the hydrolysis rate of 1,2-dinitroguanidine through dianion should only grow. Thus the dinitrourea formation in alkaline medium occurs by reaction of hydroxide anion with the monoanion of 1,2-dinitroguanidine. Its dianion is stable in the alkaline medium.

Basing on the sum of the data obtained we assumed the following overall scheme of 1,2-dinitroguanidine decomposition in water solutions of acids and alkali:



The nitramide, nitro- and *N,N'*-dinitrourea arising during the decomposition may further decompose to simpler products along reactions (2), (1), and (3).

It follows from the overall scheme that in reactions of 1,2-dinitroguanidine with water and hydroxide anion not only dissociation may occur but also nucleophilic substitution both of amino and nitramino groups along reactions (7)–(9). The study of 1,2-dinitroguanidine properties showed that neutralization of its water or alcoholic solutions with alkali resulted in formation of the corresponding metal salts (Table 1). The yield and purity of salts depended on the order of reagents mixing. For instance, the addition of 1,2-dinitroguanidine solution to alkali solution always resulted in contamination of the salt obtained with the corresponding dinitrourea salt arising along reaction (9). The attempts to purify the sample by recrystallization led only to increased content of dinitrourea salt. The best way of preparation of 1,2-dinitroguanidine salts was slow addition of one equiv. of alkali into the alcoholic solution of 1,2-dinitroguanidine. Most of the salts are insoluble in alcohol. They crystallize from the alcohol as they form and virtually do not contain dinitrourea salts. The salts soluble in alcohol, as those of methyl- and dimethylammonium, were isolated by alcohol evaporation at room temperature.

Whereas the metal salts of 1,2-dinitroguanidine acquire impurity of dinitrourea salts only at heating,

the salts of the nitrogen-containing bases are far less stable and slowly decompose in water solutions already at room temperature. The least stable is the hydrazinium salt: The rate constants of 1,2-dinitroguanidine hydrolysis in water at 25°C in the presence of 1.15 mol l⁻¹ of NaOH, NH₃, Me₂NH, and 0.05 mol l⁻¹ of N₂H₄ are respectively 0.883 × 10⁻⁴, 1.52 × 10⁻², 1.25 × 10⁻², and 4.48 × 10⁻² s⁻¹.

In contrast to reaction with the hydroxide anion (9) the reaction with ammonia resulted in substitution not of amino but nitramino group affording nitroguanidine which we isolated in a quantitative yield

Table 1. Properties of 1,2-dinitroguanidine salts [H₂NC(=NNO₂)NNO₂]⁻ Cat⁺

Cat ⁺	mp, °C	Solubility in water, 20°C, g l ⁻¹
K ⁺	183 (explosion)	–
Na ⁺	157	–
NH ₄ ⁺	205	67
1/2Ba ²⁺	187 (explosion)	9.1
1/2Sr ²⁺	258 (explosion)	82.5
MeNH ₃ ⁺	178	186
Me ₂ NH ₂ ⁺	137	200
N ₂ H ₅ ⁺	135	16
H ₂ NC(=NH)N ₂ H ₅ ⁺	180	5.0

Table 2. Stability of 1,2-dinitroguanidine (**I**) in nitrating systems based on nitric acids at 20–22°C (weight reagents ratio are presented)

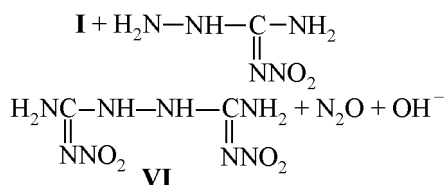
Time, h	I, %	II, %	Time, h	I, %	II, %
HNO ₃ :H ₂ O = 98:2			HNO ₃ :H ₂ SO ₄ :H ₂ O = 21.1:73.8:5.1		
0	100	0	0	100	0
1	77	21	1	63	36
2.5	58	37	2	41	61
4	46	40	3.5	29	68
5	44	40	4.5	24	77
			6	22	81
HNO ₃ :H ₂ SO ₄ :H ₂ O = 44.2:51.6:4.2					
0	100	0	0	0	100
0.5	96	4	0.5	10	90
1.5	74	27	1.5	20	81
4	50	53	2.5	21	79
5	33	61	3.5	27	73
6	31	73	4.5	28	72
8	30	72			

guanidine which we isolated in a quantitative yield after heating a solution of 1,2-dinitroguanidine in aqueous ammonia. A similar process proceeded with methylamine and hydrazine providing the corresponding 1-substituted 2-nitroguanidines:

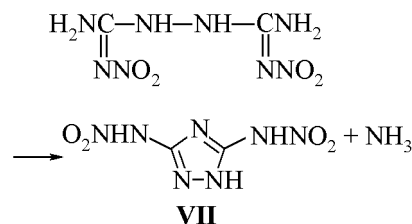


R = H (**II**), Me (**IV**), NH₂ (**V**).

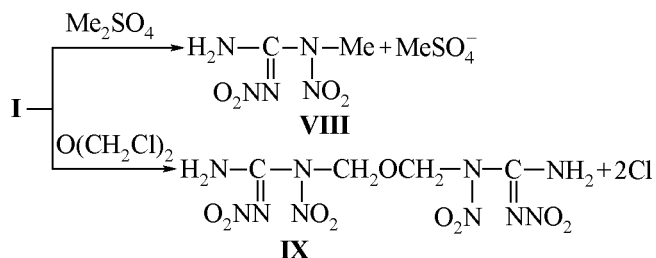
Further research revealed that depending on the reagents ratio the reaction with hydrazine afforded not only 1-amino-2-nitroguanidine (**V**) but also more complex products. For instance, 2 mol of 1,2-dinitroguanidine with 1 mol of hydrazine give rise to 2,5-dinitrobiguanidine (**IV**), a product of reaction between 1-amino-2-nitroguanidine and 1,2-dinitroguanidine anion:



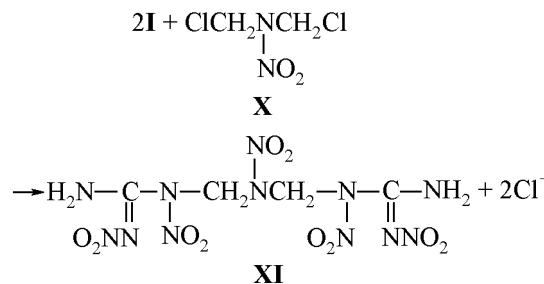
The composition and structure of compound **VI** were confirmed by elemental analysis, spectral data, and by independent synthesis from hydrazine and nitroguanidine [22]. Its structure was conclusively established by carrying out the cyclization in a water-alcoholic medium into 3,5-bis(nitramino)-1,2,4-triazole (**VII**):



Reaction of 1,2-dinitroguanidine anion with electrophilic reagents gives rise to products of substitution at the nitrogen atom of the nitramino group. For instance, the treatment of 1,2-dinitroguanidine potassium salt with dimethyl sulfate furnished 1-methyl-1,2-dinitroguanidine (**VIII**) in 85% yield, and the reaction with dichlorodimethyl ether gave the corresponding ether (**IX**) in 75% yield.



A similar N-alkylation of 1,2-dinitroguanidine was performed by treating with 2-nitro-1,3-dichloro-2-azapropene (**X**). As also with dichlorodimethyl ether the reaction is carried out in acetone in the presence of crown ether:



Interestingly enough the alkylation of dinitramide [23] and nitrocyamide [24–26] occurs to a large extent at the oxygen atom of the nitro group in contrast to the process observed with 1,2-dinitroguanidine.

The general scheme indicates that save the equilibrium with nitronium cation (6) all the other stages of 1,2-dinitroguanidine decomposition are irreversible reactions with nucleophilic reagents in the reaction mixture (water, hydroxide anion, all the other present bases sufficiently nucleophilic for this process). In order to estimate the effect of irreversible decomposition reactions on the final result of nitroguanidine nitration with the nitric acid and its mixtures with concn. H_2SO_4 we studied the stability of 1,2-dinitroguanidine in the common nitrating mixtures.

As seen from Table 2, in 98% HNO_3 which is of relatively low acidity [27] and therefore contains sufficiently much nucleophilic species (H_2O , HNO_3 , NO_3^-) the irreversible decomposition of 1,2-dinitroguanidine actually takes place. The addition of H_2SO_4 to the nitric acid increases the acidity of the medium [28] and sharply decelerates the irreversible decomposition processes of the 1,2-dinitroguanidine. The data in Table 2 also indicate that the nitrating activity of water-containing mixtures is insufficient for shifting the equilibrium of guanidine nitration to 1,2-dinitroguanidine. This conclusion follows both from the decomposition of 1,2-dinitroguanidine and from the unsuccessful results of attempts to nitrate the nitroguanidine with the mixtures of the same composition.

The high stability of 1,2-dinitroguanidine in the nitrating mixtures containing the sulfuric acid suggests the fundamental possibility of quantitative conversion of guanidine into 1,2-dinitroguanidine. The process requires application of nitrating systems of high acidity and maximum nitrating activity. The anhydrous mixtures of nitric acid with sulfuric acid and sulfur trioxide are known to fit to these requirements [29]. The first attempts of nitroguanidine nitration with mixtures of nitric acid with oleum afforded 1,2-dinitroguanidine in up to 70% yield (Table 3). The increased concentration of sulfur trioxide and nitric acid in the nitrating mixture results in higher equilibrium yield of 1,2-dinitroguanidine. Since the addition of powdered nitroguanidine into such nitrating mixture disregarding the vigorous stirring occurs with decomposition at the contact place the losses of the nitration product amount to 30%. The losses were minimal at the use of freshly prepared nitroguanidine solution in 98% nitric acid. In this case the yield obtained amounted to 90% (Table 4).

The nitroguanidine is known to be the intermediate product of nitration of guanidine salts. Therefore the most feasible way to 1,2-dinitroguanidine preparation

Table 3. Results of nitroguanidine nitration by mixtures of 98% HNO_3 with solution of SO_3 in H_2SO_4 (oleum). The composition of the nitrating mixtures is presented as g g^{-1} of nitroguanidine.

Oleum	98% HNO_3	Time, h ^a	Temperature, °C	Yield, %	
				I ^b	II ^c
4.8 ^d	6.4	6	10	40	32
4.3	7.2	3	20	59	14
5.4	7.2	3	20	57	13
4.2	5.2	2	20	64	8
4.2	5.2	4	0	72	4

^a Time sufficient for attaining the equilibrium yield.

^b With respect to nitroguanidine.

^c Percent with respect to the initial amount.

^d 20% SO_3 , in all the other cases 60% SO_3 .

would be nitration of guanidine sulfate or nitrate which are relatively readily available commercial products. As seen from Table 5, the nitration of guanidine salts to 1,2-dinitroguanidine is as successful as that of nitroguanidine.

The major part of 1,2-dinitroguanidine produced is separated from the reaction mixture by diluting it to concentration corresponding to minimum solubility of the target product. The precipitated 1,2-dinitroguanidine is isolated by filtration, and the rest is easily extracted from acid filtrates into ethyl acetate or absorbed on activated carbon. The experiments have shown that 1,2-dinitroguanidine is a lot more readily adsorbed than the nitric and sulfuric acid. Therefore when the acid solutions of 1,2-dinitroguanidine are passed through a column charged with activated carbon it is adsorbed by the carbon, and the nitric and sulfur acids pass through the column. Unlike the similar process of 5-nitraminotetrazole isolation [30] that is stable in acid solutions, with 1,2-dinitroguanidine a fractional filling of the column is required: after passing a portion of the acid solution the column should be washed with water to reduce the content of mineral acids in the carbon layer.

EXPERIMENTAL

UV spectra of solutions were recorded on spectrophotometer Specord M-40. IR spectra were measured on spectrometer Shimadzu FTIR-8400 from samples pelletized with KBr. ^1H and ^{13}C NMR spectra were registered on spectrometer Bruker AC-300 at operating frequencies 300 and 75 MHz respectively.

Table 4. Results of nitroguanidine nitration as solution in 98% HNO₃. Nitrating mixture composition and amount of HNO₃ required for nitroguanidine dissolution (g g⁻¹)

98% HNO ₃ for dissolution	Nitrating mixture			Time, h ^b	Temperature, °C	Yield, %	
	98% HNO ₃	87% SO ₃ ^a	Oleum, 60% SO ₃			I ^c	II ^d
3	3	–	6	10	10	42	56
2.8	1.2	–	5.6	3	20	85	11
2.8	1.6	–	6.6	2	20	90	4
3	3	3.2	–	3.5	0	94	4
3	3	3.2	–	1	30	75	4
1.8	2.8	2.6	–	3	–5	82	15
3	1.6	1.6	–	5	0	82	15
3	1.6	1.6	–	3	20	85	13

^a Sulfur trioxide stabilized with nitric acid.

^b Time sufficient for attaining the equilibrium yield.

^c With respect to nitroguanidine.

^d Percent with respect to the initial amount.

Elemental analysis was carried out on CHN Analyzer Hewlett Packard 185B.

Sulfuric acid for kinetic measurements was distilled in the presence of potassium bichromate. Water solutions of H₂SO₄ were prepared by dilution of the obtained sulfuric acid having ~98% concentration. The anhydrous nitric acid was prepared by distilling under reduced pressure of commercial 98% HNO₃ with a 1.5 times greater volume of concn. H₂SO₄. N₂O₅ was obtained by dehydration of the nitric acid with phosphorus pentoxide [31]. Its solutions in 100% nitric acid were prepared from weighed portions. The concentration of sulfuric and nitric acid was measured by potentiometric titration with accuracy not worse than ±0.1 rel. %.

N,N'-Dinitrourea was obtained by urea nitration along procedure in [21], nitroguanidine was prepared by guanidine nitrate nitration as in patent [1]. Nitrourea was obtained by treating urea nitrate with sulfuric acid [18].

1,2-Dinitroguanidine (I). To 35 ml of 2 % N₂O₅ solution in anhydrous nitric acid cooled to –20°C was added at vigorous stirring 5 g of fine crystalline nitroguanidine, the mixture was kept for 6 h at –20°C and then poured on 200 g of ice. The separated precipitate of unreacted nitroguanidine (0.9 g) was filtered off, the reaction product was extracted from filtrate with ethyl acetate (5 × 20 ml). The combined extracts were washed with ice water (2 × 10 ml) and dried on MgSO₄. On removing ethyl acetate in a

vacuum we obtained 4.2 g (59%) of slightly colored crystals, mp 155–159°C. On recrystallization from acetic acid mp 168–169°C. ¹H NMR spectrum, δ, ppm: 9.61 s (NH₂), 14.3 s (NH). ¹³C NMR spectrum, δ, ppm: 156.2. IR spectrum, KBr, cm⁻¹: 3430, 3330, 3100, 2900, 1655, 1625, 1520, 1420, 1300, 1250, 1140, 1045, 995, 955, 790, 710. Found, %: C 8.02; H 2.0; N 47.01. CH₃N₅O₄. Calculated, %: C 8.05; H 2.01; N 46.98.

Measurement of solubility of 1,2-dinitroguanidine and its salts. A weighed portion of 1,2-dinitroguanidine or its salt was charged into a cell whose temperature was controlled within ±0.1°C where was placed the corresponding solvent. The dispersion was stirred with magnetic stirrer, and every hour a sample of 2 ml was taken through a glass frit. The sample was diluted in a volumetric flask with distilled water to a volume of 1 l. The solution obtained was analyzed by spectrophotometry at pH 4–8.

Evaluation of acid-bas properties of 1,2-dinitroguanidine. The determination of acidity and basicity constants was performed by spectrophotometry as described in [32, pp. 141–152]. The measuring of p*K*_a(I) was carried out in aqueous sulfuric acid at 25 ± 0.1°C at λ 302 nm, ε_A⁻ 21000, ε_{AH} 3600 l mol⁻¹ cm⁻¹. The logarithm of ionization balance as a function of pH (*H*₀) is strictly linear: log *I* = -(1.02 ± 0.03) + 1.13; *r* 0.995, *s* 0.01, *n* 5. The p*K*_{BH}⁺ was measured in the similar way at λ 278 nm, ε_B 15750, ε_{BH}⁺ 2920 l mol⁻¹ cm⁻¹. The logarithm of ionization balance as a function of acidity *H*₀ [5] is as follows:

$\log I = -(1.00 \pm 0.04) - 5.81; r 0.998, s 0.02, n 7$. The $pK_a(\text{III})$ was measured at $25 \pm 0.1^\circ\text{C}$ in water solutions of alkali on $\lambda 302 \text{ nm}$, $\epsilon_A^- 21000$, $\epsilon_A^{2-} 6240 \text{ l mol}^{-1} \text{ cm}^{-1}$. Since the 1,2-dinitroguanidine suffers slow decomposition the values of optical density of solutions were extrapolated to "zero" time. Dependence of the logarithm of ionization balance on a function [6] is linear, but the slope of the plot is not equal to unity: $\log I = -(1.22 \pm 0.06) + 11.5; r 0.999, s 0.02, n 6$, therefore the $pK_a(\text{III})$ value should be regarded as approximate.

Decomposition of 1,2-dinitroguanidine in an aqueous H_2SO_4 . To vigorously stirred 35 ml of 75% sulfuric acid was added 5 g of 1,2-dinitroguanidine. The dispersion was slowly heated to 50°C at stirring till complete dissolution of the solid phase. The solution obtained was poured on 100 g of ice, and the precipitate formed was filtered off. After drying and recrystallization from chloroform we obtained 0.7 g of compound with mp 158°C . No depression of the melting point was observed in a sample mixed with an authentic nitrourea. UV spectrum in an acetate buffer solution at pH 4.5 also completely coincided with the nitrourea spectrum [18].

Kinetic measurements. All kinetic measurements were performed on spectrophotometer SF-26 in 1 cm quartz cells.

The rate constants of 1,2-dinitroguanidine decomposition in aqueous sulfuric acid were measured as follows. Into 30 ml of acid maintained at desired temperature within accuracy of $\pm 0.1^\circ\text{C}$ was added 5 mg of 1,2-dinitroguanidine. After dissolution of the weighed portion (within ~ 1 min) an aliquot of 1 ml was taken from the reaction mixture and quickly brought into a volumetric flask of 25 ml capacity containing a solution of sodium acetate of concentration sufficient to keep the pH of the final solution at 4–8. Distilled water was added to obtain exact volume 25 ml, and the optical density of the solution was measured at $\lambda 302 \text{ nm}$. The 1,2-dinitroguanidine decomposition in water solutions of alkali was studied in the same way but the aliquots were diluted with acetic acid solutions. The rate constants of an intermediate compound decomposition were measured similarly at $\lambda 273 \text{ nm}$. The rate constant of nitrourea decomposition was measured as described in [18] by decreasing optical density at $\lambda 259 \text{ nm}$. The decomposition of N,N' -dinitrourea was followed similarly at $\lambda 273 \text{ nm}$ corresponding to the maximum of the absorption band of its anion. The first order rate constants were calculated by the known formula: $k = (2.3/\tau) \log(D_0 - D_\infty/D_\tau - D_\infty)$, where D_0 ,

D_τ and D_0 are optical densities at the first measurement, at time τ since the start of reaction, and at the completion of reaction. The accuracy in the constants evaluation was no worse than 5–10 rel.%.

Preparation of 1,2-dinitroguanidine salts. To a solution of 1.49 g (0.01 mol) of 1,2-dinitroguanidine in 20 ml of ethanol was gradually added 0.01 mol of the corresponding base or carbonate. The separated precipitate was filtered off, washed with 5–10 ml of ethanol, and dried. The isolation of methylammonium and dimethylammonium salts soluble in ethanol was carried out by evaporation of ethanol at room temperature followed by washing with hexane. The yield of salts amounted to 90–98%. According to the spectrophotometric analysis the content of the main product in the salts exceeded 98%.

Nitroguanidine (II) from 1,2-dinitroguanidine ammonium salt. A solution of 1.7 g of the ammonium salt in 50 ml of water was heated for 2 h to $70\text{--}80^\circ\text{C}$. On cooling the precipitate formed was filtered off. Yield 0.92 g (86%), mp 246°C (decomp.). The product is completely identical to that obtained by guanidine nitrate nitration.

1-Methyl-2-nitroguanidine (IV). A solution of 1.9 g of 1,2-dinitroguanidine methylammonium salt in 50 ml of water was heated for 2 h to $70\text{--}80^\circ\text{C}$. On cooling the precipitate was filtered off. Yield 1.1 g (88%), mp 159°C (decomp.). The product is completely identical to that obtained by treating 1-methyl-1-nitroso-2-nitroguanidine with methylamine [33].

1-Amino-2-nitroguanidine (V). To a dispersion of 1.49 g (0.01 mol) of 1,2-dinitroguanidine in 50 ml of water was added 25% water solution of hydrazine hydrate till the neutral reaction of the mixture toward litmus. The reaction mixture was maintained at $70\text{--}80^\circ\text{C}$ for 2 h, then cooled, the separated precipitate was filtered off and recrystallized from aqueous DMF. Yield 1.07 g (90%), mp $181\text{--}182^\circ\text{C}$. The compound is identical to that obtained by nitroguanidine hydrazinolysis [34].

2,5-Dinitrobiguanidine (VI). To a solution of 3.0 g (0.02 mol) of 1,2-dinitroguanidine in 100 ml of methanol was added 25% water solution of hydrazine hydrate till the neutral reaction of the mixture toward litmus and then 1.2 g of KOH. The reaction mixture was boiled for 2 h, cooled, and the separated 2,5-dinitrobiguanidine potassium salt was filtered off. The salt was dissolved in 20 ml of warm water and acidified with concn. HCl. The precipitate formed was filtered off, washed with water, and dried. We

Table 5. Results of guanidine salts nitration as solution in 98% HNO₃. Nitrating mixture composition and amount of HNO₃ required for salts dissolution (g g⁻¹).

98% HNO ₃ for solution	Nitrating mixture			Time, h ^b	Temperature, °C	Yield, %	
	98% HNO ₃	87% SO ₃ ^a	Oleum, 60% SO ₃			I ^c	II ^d
2 ^e	2	4.8	–	4	–10	88	2
2 ^e	2	4	–	6	–10	60	38
3	2	6	–	2	–5	85	12
2.7	2.7	4	–	1.5	5	65	30
2.7	2.7	4	–	2	–10	65	35
2.4	3	4.8	–	2	5	80	12
2.4	3	4.8	–	1	20	74	14
2.4	3	4.8	–	4	–5	94	3
2.1	2.4	–	6.8	3	0	96	3
2.1	2.4	–	6.8	2	20	92	4
2.4	2.8	–	6	4	20	80	15
2	2	–	8	2	0	82	8

^a Sulfur dioxide stabilized with nitric acid.

^b Time sufficient for attaining the equilibrium yield.

^c With respect to nitroguanidine.

^d Percent with respect to the initial amount.

^e Guanidine sulfate, in all other cases guanidine nitrate.

obtained 3.1 g (88%) of colorless crystals, mp 182–194°C. ¹H NMR spectrum, δ, ppm: 8.61 s (NH₂) 10.01 s (NH). ¹³C NMR spectrum, δ, ppm: 156.8. IR spectrum, KBr, cm⁻¹: 3360, 3310, 3250, 1680, 1440, 1390, 1290. Found, %: C 11.64; H 3.01; N 54.29. C₂H₆N₈O₄. Calculated, %: C 11.65; H 2.91; N 54.37.

3,5-Bis(nitramino)-1,2,4-triazole potassium salt (VII). To a solution of 3.0 g (0.02 mol) of 1,2-dinitroguanidine in 100 ml of methanol was added 25% water solution of hydrazine hydrate till the neutral reaction of the mixture toward litmus and then 1.2 g of KOH. The reaction mixture was boiled for 2 h, 25 ml of 20% HCl was added, and the boiling was continued for 3.5 h. Then the reaction mixture was cooled and the separated precipitate was filtered off. Yield 2.3 g (91%), mp 202°C. Found, %: C 10.64; H 1.01; N 42.91. C₂H₂KN₇O₄. Calculated, %: C 10.57; H 0.88; N 43.17.

1-Methyl-1,2-dinitroguanidine (VIII). To a dispersion of 1.89 g (0.01 mol) of 1,2-dinitroguanidine potassium salt in 50–70 ml of acetone was added 1.26 g (0.01 mol) of dimethylsulfate and 50–100 mg of 18-crown-6. The reaction mixture was boiled for 3–4 h, then it was cooled, the precipitate was filtered off and washed with 10–20 ml of acetone.

The acetone solutions were evaporated, and the residue was recrystallized from 70% ethanol. We obtained 1.38 g (85%) of colorless crystals, mp 82–82.5°C identical to the product obtained by nitration of 1-methyl-2-nitroguanidine [35].

Bis(1,2-dinitroguanidinomethyl) ether (IX). To a dispersion of 3.78 g (0.02 mol) of 1,2-dinitroguanidine potassium salt in 50 ml of acetone was added 1.5 g (0.01 mol) of dichlorodimethyl ether, 50–100 mg of 18-crown-6, and 50–100 mg of NaI. The reaction mixture was boiled for 4 h, cooled, the precipitate was filtered off and washed with 10–20 ml of acetone. The acetone solutions were evaporated, and the residue was recrystallized from 70% ethanol. After drying in air we obtained 2.55 g (75%) of colorless crystals, mp 145°C. ¹H NMR spectrum, δ, ppm: 5.68 s (CH₂), 8.78 s (NH₂). IR spectrum, cm⁻¹: 3400, 3300, 1650, 1600, 1580, 1520, 1450, 1380, 1260, 1100, 1050, 960, 920. Found, %: C 14.02; H 2.12; N 41.38. C₄H₈N₁₀O₉. Calculated, %: C 14.11; H 2.35; N 41.17.

1,7-Diamino-1,7-dinitrimino-2,4,6-trinitro-2,4,6-triazaheptane (XI). To a dispersion of 3.78 g (0.02 mol) of 1,2-dinitroguanidine potassium salt in 50–70 ml of acetone was added 1.36 g (0.01 mol) of 1,3-bis(chloromethyl)nitramine (X) [36], 50–100 mg

of 18-crown-6, and 50–100 mg of NaI. The reaction mixture was boiled for 4 h, cooled, the precipitate was filtered off and washed with 10–20 ml of acetone. The acetone solutions were evaporated, and the residue was recrystallized from 70% ethanol. Yield 3.07 g (80%), mp 171°C. ^1H NMR spectrum, δ , ppm: 6.1 s (CH_2), 10.1 s (NH_2). Found, %: C 12.41; H 2.01; N 43.52. $\text{C}_4\text{H}_8\text{N}_{12}\text{O}_{10}$. Calculated, %: C 12.5; H 2.08; N 43.75.

Nitroguanidine nitration. (a) Thoroughly dried fine crystals of nitroguanidine at vigorous stirring were added by small portions to the previously prepared nitrating mixture of the desired composition. After addition was finished and the reaction mixture maintained for the required time at the required temperature an exactly weighed sample of the reaction mixture (about 1.5 g) was quantitatively transferred into a volumetric flask of 1 l capacity and diluted with distilled water to 1 l volume; 5 ml of this solution was diluted in a volumetric flask to 50 ml and optical density of this solution was measured at λ 302 and 265 nm. The concentrations of the nitro- and 1,2-dinitroguanidine were determined by Vierordt procedure [32, pp. 65–70] using the molar extinctions of 1,2-dinitroguanidine [21000 and 4700 l (mol-cm) $^{-1}$ at λ 302 and 265 nm respectively] and of nitroguanidine [15000 l (mol-cm) $^{-1}$ at λ 265 nm]. The absorption of nitroguanidine at λ 302 nm is negligible. The results of nitration are partly given in Table 3.

(b) Nitroguanidine at room temperature was dissolved in a required volume of 98% HNO_3 , and the solution thus obtained was added at vigorous stirring to the preliminary prepared nitrating mixture. After required reaction time the content of nitro- and 1,2-dinitroguanidine in the reaction mixture was determined. The nitration results are presented in Table 4.

Nitration of guanidine salts. Guanidine sulfate or nitrate was dissolved at room temperature in 98% HNO_3 , and the obtained solution was added at vigorous stirring to the preliminary prepared nitrating mixture as described above under nitroguanidine nitration. The analysis of the reaction mixture for nitro- and 1,2-dinitroguanidine content was carried out as above. The nitration results are presented in Table 5.

Synthesis of 1,2-dinitroguanidine from nitroguanidine. To a mixture of 20 ml of 98% HNO_3 and 36 ml of 60% oleum at 0–10°C was added dropwise a solution of 14 g of nitroguanidine in 20 ml of 98% nitric acid. Then 15 ml of 60% oleum and 2 ml of

98% nitric acid was added, the mixture was kept at this temperature for 1 h, and at the same temperature to the reaction mixture was added 80–90 g of ice. The separated precipitate (12 g) was filtered off and washed with trifluoroacetic acid. The filtrate was extracted with ethyl acetate (5 \times 20 ml). The extract was washed with water, dried with sodium sulfate, the solvent was distilled off, and the residue was washed with hexane. Both portions of the product were combined and recrystallized from acetic acid or acetonitrile. Yield of pure substance of mp 169°C was 16 g (80%).

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