Mechanism of nitration of nitrogen-containing heterocyclic *N*-acetonyl derivatives. General approach to the synthesis of *N*-dinitromethylazoles

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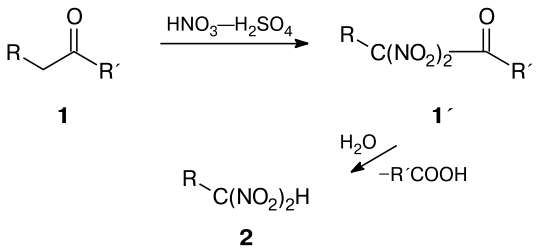
A general synthetic procedure for the synthesis of *N*-dinitromethyl derivatives of nitrogen-containing heterocycles has been developed. The procedure includes the destructive nitration of heterocyclic *N*-acetonyl derivatives of tetrazoles, 1,2,4- and 1,2,3-triazoles, pyrazoles, imidazoles and their bicyclic analogs, as well as imides of carboxylic and sulfonic acids and substituted hydrazines with mixtures of sulfuric and nitric acids. The kinetic study of the reaction mechanism was performed using UV and NMR spectroscopy. It was found that the NO_2 groups were sequentially introduced into the methylene fragment by the addition of the nitronium ion to multiple bonds of intermediate enols followed by hydrolysis of the acetyl moiety. The rate and direction of the enolization (due to the CH_2 and CH_3 groups) of the *N*-acetonyl compounds in sulfuric acid solutions were determined by the study of the deuterium exchange kinetics. The synthesis of the *N*-dinitromethyl compounds is complicated by side reactions, such as the decomposition of intermediate α-nitroketone, the nitration of the methyl group in the acetonyl moiety, and the nitration of the dinitromethyl products to trinitromethyl derivatives.

Key words: nitration, kinetics, enolization, nitronium ion, *N*-acetonylazoles, *N*-dinitromethylazoles, *N*-trinitromethylazoles, tetrazoles, triazoles, pyrazoles, imidazoles.

Nitration with acidic nitrating mixtures of the active methylene moiety of carbonyl structures (**1**) to form dinitromethyl compounds (destructive nitration) was studied.[1] It can be assumed that the process proceeds through the formation of dinitromethylene derivatives of carbonyl compounds (**1´**), whose hydrolysis affords dinitromethyl compounds (**2**) (Scheme 1).

Scheme 1



In these works, the nitration conditions were selected empirically without revealing regularities of the reaction and its mechanism, which impedes the optimization of synthesis of dinitromethyl compounds.

In the present work, in order to detail processes of destructive nitration of active methylene compounds,[2—9] we studied the mechanism, kinetics, and conditions of this reaction using easily accessible *N*-acetonylazoles[10] as an example.

Results and Discussion

We have earlier[11] studied by ^{13}C NMR spectroscopy the state of *N*-acetonylazoles in an H_2SO_4 solution for the lowest-basicity tetrazole derivatives. It turned out that on going from solutions in neutral solvents to solutions in concentrated H_2SO_4 the direct spin-spin coupling (SSC) constants ($^1J_{C,H}$) for the $N—CH_2$ group and CH cycle increase by 4—5 and 16—18 Hz for 1- and 2-acetonyltetrazoles and 5-methyltetrazole analogs, respectively. The same increase in $^1J_{C,H}$ in neutral media is characteristic of *N*-acetonyltetrazolium salts **4** compared to non-quaternized *N*-acetonyltetrazoles **3**: these constants for the carbon atoms in the $N—CH_2$, N—Me, and C—Me fragments increase by 4—5 Hz, whereas for the C_5 cycle they increase by 15—20 Hz.[11] It follows from this that the *N*-acetonyl derivatives of tetrazole and 5-methyltetrazole in concentrated H_2SO_4 are protonated to the nitrogen atom of the cycle.[12] Even in the case of low-basicity nitrotetrazole ($pK_{BH^+} = -9.26$),[13] the corresponding ketone is protonated, most likely, to a considerable extent: the ^{13}C NMR spectrum exhibits a noticeable increase in the direct SSC constants in the CH_2 (by 1.5 Hz) and Me (by 1.8 Hz) groups.

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Therefore, the nitrating mixtures (conc. HNO_3 + conc. H_2SO_4) should nitrate *N*-acetonylazole cations **3´** (Scheme 2, route *b*), as they nitrate salts **4**, from which imidazolium, triazolium, tetrazolium, pyridinium, and pyridazinium *N*-dinitromethylides **5** have been obtained previously (Scheme 2, route *a*).[4]

In the present study, we used analogous conditions for the synthesis of *N*-dinitromethyl structures with the uncharged cycle. In all cases, the nitration of various *N*-acetonylazoles in sulfuric—nitric acid mixtures containing a noticeable amount of water gave *N*-dinitromethylazoles, *viz.*, derivatives of pyrazoles, imidazoles, 1,2,4-triazoles, 1,2,3-triazoles, and tetrazoles (see Scheme 2, structures **6a—t**).*

In the most cases, the yields of *N*-dinitromethyl compounds pass a maximum in time and then decrease. Therefore, to develop the preparative method for synthesis of *N*-dinitromethyl derivatives, regularities of their accumulation and disappearance in sulfuric—nitric acid mixtures should be studied.

Interaction of *N*-dinitromethylazoles with sulfuric—nitric acid mixtures. All *N*-dinitromethylazoles in conc. H_2SO_4 at room temperature do not decompose for at least 24 h, but have different stability in sulfuric—nitric acid mixtures. For instance, it is known that 1,2,4-triazole derivatives are nitrated to stable trinitromethyl derivatives **7h**,[7,8] whose presence was monitored by TLC and the amount was determined by UV spectroscopy (by an increase in the absorption maximum of the dinitrocarbanionic fragment upon the addition of KI and $Na_2S_2O_3$). According to our data,[15] *N*-trinitromethyltetrazoles **7a—g** are unstable and decompose even at 0 °C to form *N*-trinitromethylnitrile imines and N_2.

The kinetics of disappearance of *N*-dinitromethylazoles in 89.2% H_2SO_4 containing KNO_3 (1.15 mol L^{-1}) was studied by UV spectroscopy at 20 °C. The concentration of *N*-dinitromethylazoles (0.02—0.03 mol L^{-1}) was considerably lower, which made it possible to use a first-order equation for the calculation of the kinetics of their decomposition. The logarithmic anamorphoses of the kinetic curves of disappearance of *N*-dinitromethyltetrazoles (**6a**,**c**,**d**) and -1,2,4-triazoles (**6h**,**j**) represent straight lines (the equations are given in Table 1), indicating the disappearance of *N*-dinitromethylazoles in the reaction of the pseudo-first order. The apparent rate constants for the disappearance of other *N*-dinitromethylazoles were calculated similarly (Table 2).

As follows from Table 2, the compounds with low CH-acidity, *viz.*, *N*-dinitromethyl derivatives of imidazole **6s** and pyrazoles **6p**,**q**, are stable in this medium for 1 day. Tetrazole derivatives **6a**,**c**,**d** react with nitronium ions more rapidly than triazole analogs **6h**,**m**, which is due to the higher acidity of the dinitromethyl group in **6a**,**c**,**d**.

* For the preliminary publication, see Ref. 14.

Table 1. Parameters in the equations of the linear anamorphoses ($\ln C_0/C = Kt + A$) of the disappearance of *N*-dinitromethylimidazoles (0.02 mol L^{-1}) in H_2SO_4—KNO_3 solutions (1.15 mol L^{-1}) and correlation coefficients (*R*)

N-Dinitromethylazole	Volume ratio H_2SO_4 : H_2O	$K \cdot 10^5/s^{-1}$	*A*	*R*
6a	5% oleum	0.60±0.1	0.029±0.011	0.918
	12 : 0	1.73±0.4	0.019±0.013	0.998
	12 : 1	1.35±0.04	0.007±0.011	0.998
6d	12 : 1	9.00±0.1	0.001±0.019	0.999
6c	12 : 1	2.40±0.5	0.018±0.051	0.951
6h	12 : 1	0.36±0.06	0.060±0.021	0.933

The results on nitration of 2-dinitromethyl-5-nitrotetrazole **6a** in media of various acidity (Fig. 1) indicate the formation of *N*-trinitromethylazoles *via* the mechanism of direct proton substitution for nitronium ions, as in the case of trinitromethane and dinitroacetonitrile.[16—18] In concentrated H_2SO_4 (mixture 12 : 0) the apparent rate constant for the disappearance of **6a** is fivefold higher than that in 5% oleum, as for the nitration of trinitromethane and dinitroacetonitrile.[16—18]

As the acid is diluted, K_{app} decreases as the concentration of nitronium ions decreases (mixture 12 : 1 v/v, 87.5% H_2SO_4), whereas in 76% H_2SO_4 (mixture 12 : 5) compound **6a** does not undergo nitration.

Thus, when optimizing the synthesis of *N*-dinitromethylazoles, one can find such conditions under which the formation of *N*-trinitromethyl derivatives would be reduced to minimum.

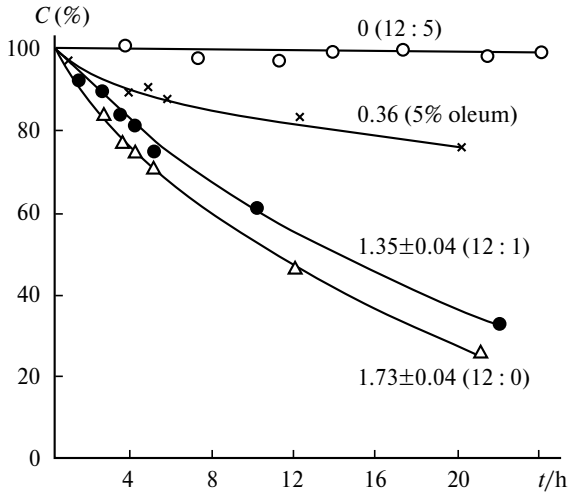
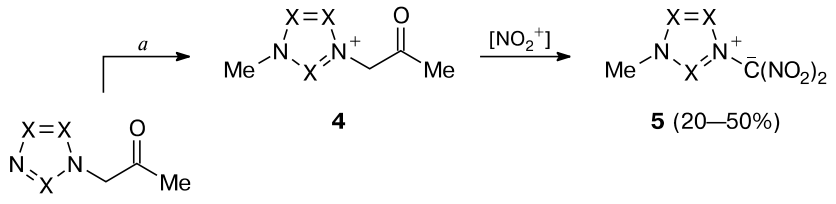
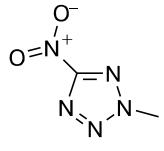


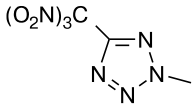
Fig. 1. Kinetic curves of the conversion of 2-dinitromethyl-5-nitrotetrazole **6a** in H_2SO_4 solutions by the action of nitronium ions. The initial concentrations of **6a** and KNO_3 are 0.02 and 1.15 mol L^{-1}, respectively. The numbers on the curves are $K_{app} \cdot 10^5$ (s^{-1}); the volume ratios H_2SO_4 : H_2O in the nitrating mixtures are given in parentheses, and *C* is the conversion.

Scheme 2

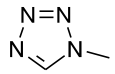




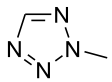
6a, 78% (−1.7)



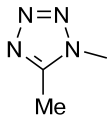
6b, 50% (−1.7)



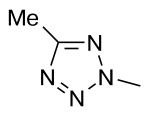
6c, 42% (−0.15)



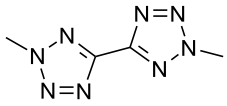
6d, 52% (−0.3)



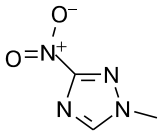
6e, 13% (−1.3)



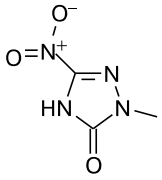
6f, 9% (+0.1)



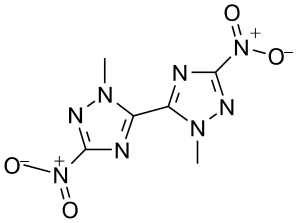
6g, 50% (−1.2; 0.0)



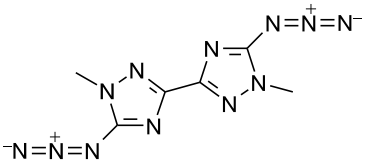
6h, 70% (+0.1)



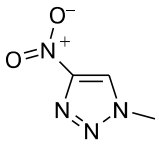
6i, 51% (+1.25)



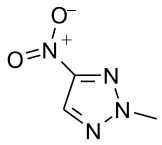
6j, 55% (−1.75)



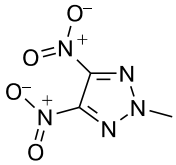
6k, 6%



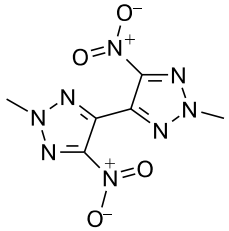
6l, 34% (−0.05)



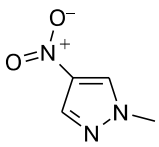
6m, 65% (+0.2)



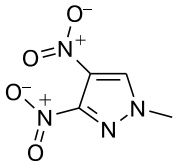
6n, 35% (−2.4)



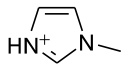
6o, 51% (−1.7; +0.25)



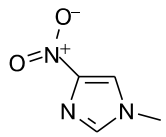
6p, 35%



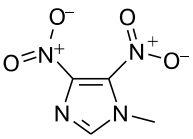
6q, 62% (+0.25)



6r, 35% (+0.05)



6s, 33% (+1.2)



6t, 55% (−1.7)

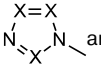
Note. The azolyl fragments  are shown, the pK_a values are given in parentheses.

Table 2. Apparent rate constants for the disappearance of *N*-dinitromethylazoles in an H_2SO_4—H_2O (12 : 1, vol.)—KNO_3 (1.15 mol L^{-1}) mixture, 20 °C

Compound	$K_{app} \cdot 10^6/s^{-1}$
2-Dinitromethyltetrazole (**6d**)	90.0±1
1-Dinitromethyltetrazole (**6c**)	24.0±5
2-Dinitromethyl-5-nitrotetrazole (**6a**)	13.5±0.4
Bis(1-dinitromethyl-3-nitro-1,2,4-triazol-5-yl) (**6j**)	11.0±1
1-Dinitromethyl-3-nitro-1,2,4-triazole (**6h**)	3.6±0.6
2-Dinitromethyl-4-nitro-1,2,3-triazole (**6m**)	0.6±0.01
1-Dinitromethyl-4-nitropyrazole (**6p**)	No nitration for 3—4 days
1-Dinitromethyl-3,4-dinitropyrazole (**6q**)	No nitration for 3—4 days
1-Dinitromethyl-4-nitroimidazole (**6s**)	No nitration for 3—4 days
Pyridinium dinitromethylide	No nitration for 3—4 days

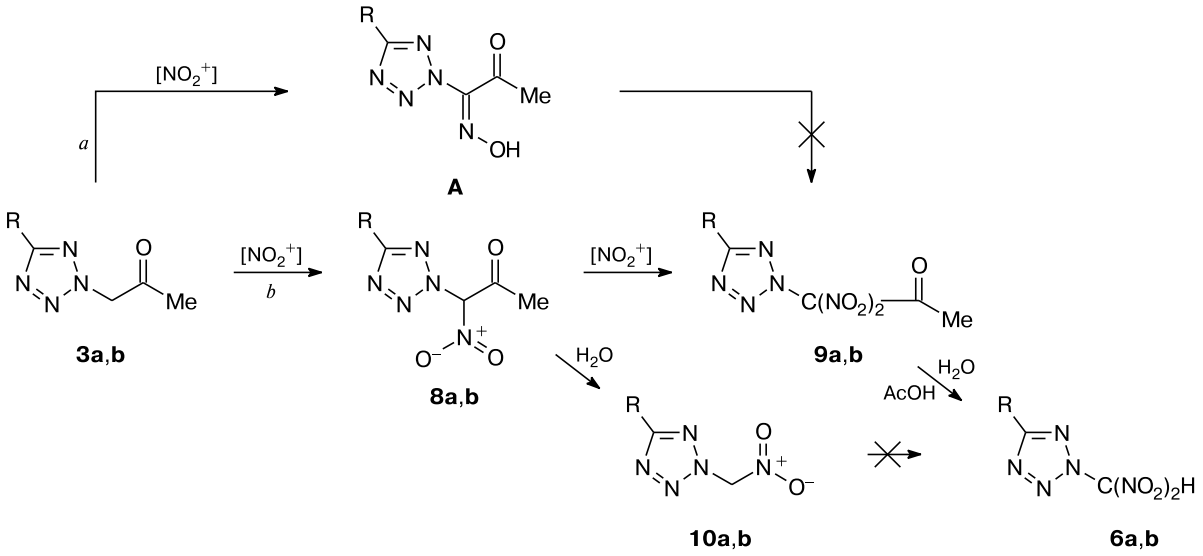
Isolation of intermediate nitration products. The study of the nitration of *N*-acetonyl derivatives **3a**,**b** (Scheme 3) showed that in a mixture of sulfuric and nitric acids the nitration of the CH_2 moiety does not proceed through the preliminary nitrosation to form compound **A** (route *a*), as it is accepted for the formation of α,α′-nitroketones (5—7% yields) in the aliphatic series.[1c,d,g] For example, we found for the nitration of *N*-acetonylpyridinium and 2-acetonyl-5-nitrotetrazole **3a** in sulfuric—nitric acid mixtures that the absence of nitrosating agents in the reaction mixture exerts no effect on the course and result of nitration, which was shown for the reaction with freshly purified KNO_3 instead of HNO_3 and in the presence of an excess removing nitrogen oxides (urea, hydrazine, or sulfaminic acid).

At the same time, the introduction of nitrosating agents (nitrogen oxides or $NaNO_2$) into the reaction does not change the accumulation rate and the yield of *N*-dinitromethyl compounds.

In the case of nitration of **3a**,**b**, nitro groups are introduced sequentially (route *b*), which is favored by the isolation in a series of nitrating mixtures of intermediate mononitro products (**8b** and **10a**,**b**) in high yields.

Hydrolysis with the removal of the acetyl group occurs only after the second nitro group was introduced, because the mononitromethyl derivatives (**10a**,**b**), which are the hydrolysis products in the first step, are incapable of transforming into *N*-dinitromethyl compounds under the nitration conditions. In other examples of nitration of *N*-acetonylazoles (in aliquots of reaction mixtures 100—1000-fold diluted with water) the formation of mononitroketones can be detected in the first steps by UV spectroscopy. For example, in the case of 1-acetonyl-4-nitroimidazole and 1-acetonyl-4-nitropyrazole, the corre-

Scheme 3



R = NO_2 (**3a**, **6a**, **8a**, **9a**, **10a**), $C(NO_2)_3$ (**3b**, **6b**, **8b**, **9b**, **10b**)

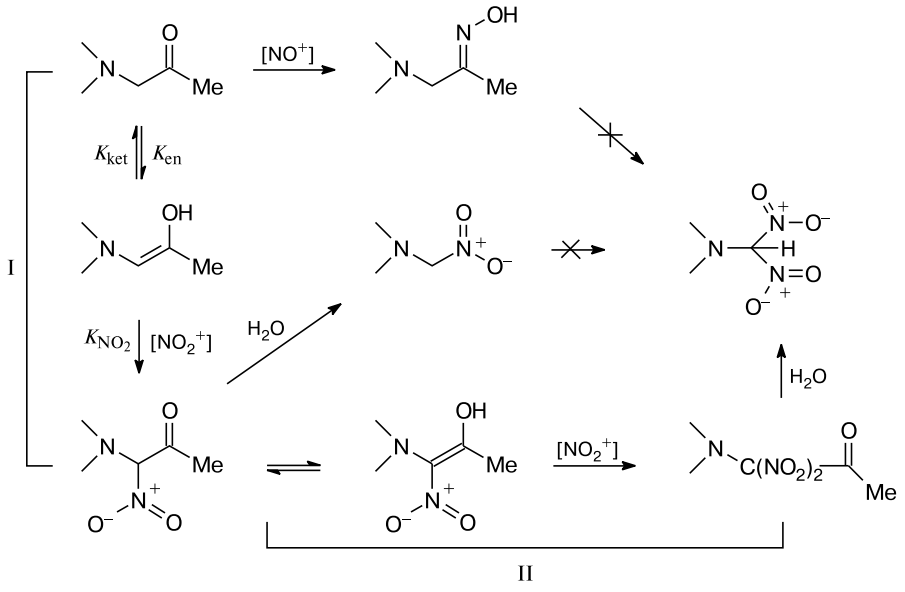
sponding mononitroketones have lower electron-withdrawing ability of the cycles and, hence, undergo hydrolysis more slowly than the tetrazole analogs. The UV spectra of these mononitroketone anions exhibit characteristic intense maxima at 310—320 nm, whose intensity decreases during the detection of the UV spectra due to the transformation of these nitroketones into the mononitromethyl derivatives (analogs **10a**,**b**) and, possibly, as a result of other side processes related to the destruction of the nitro group.[19—21]

The kinetic data obtained by UV spectroscopy, namely, the rate of absorbance increase in the absorption maxima of *N*-dinitromethylazole anions (330—350 nm upon the dilution of reaction solutions with water), indicate that the accumulation of the *N*-dinitromethyl compounds occurs very rapidly, which confirms the assumption about the involvement of highly reactive enol forms of *N*-acetonyl derivatives and intermediate α-nitroketones in the process. It is clear from this why poorly enolized structures, such as analogous derivatives of acetic acid N—CH_2CO_2R, cannot be transformed into *N*-dinitromethyl compounds.

Enolization of *N*-acetonylazoles. Since the enolization rate and the relative content of enols in various ketones can substantially affect the formation rate of the *N*-dinitromethyl derivatives, we had to study the enolization ability of these ketones in media, whose acidity coincides with that in nitrating mixtures. It is known[22] that for aliphatic ketones the enolization rate increases with an increase in the acidity of the medium according to the equation $V = [K_{en}][Ket][H^+]$, where K_{en} is the enolization rate constant; [Ket] and $[H^+]$ are the concentrations of ketone and H^+, respectively. However, in highly concentrated acids (beginning from ~85% H_2SO_4) the enolization rate decreases again (10—30-fold decrease in the 85—90% range) and is described by another equation.[23]

According to the general kinetic equation, the formation of the *N*-dinitromethyl compounds (Scheme 4) is affected by the enolization rate and also by the keto—enol tautomeric equilibrium constant $K_t = K_{en}/K_{ket}$. However, no enol form is observed in the ^1H NMR spectra of all *N*-acetonylazoles synthesized. Therefore, with allowance for the accuracy of the method K_t does not exceed 0.01.

Scheme 4



$$V = \frac{K_{en} K_{NO_2} [Ket][NO_2^+]}{K_{ket} + K_{NO_2}[NO_2^+]}$$

$V_1 = K_{en}[Ket]$

$K_{en} << K_{NO_2}[NO_2^+]$

(I)

$V_2 = (K_{en}/K_{ket})[Ket][NO_2^+]$

$K_{en} >> K_{NO_2}[NO_2^+]$

(II)

$V_1/V_2 = 10—15$

Therefore, the enol form in these ketones is determined by indirect methods.[24] At the same time, the qualitative change in the enol content as a function of the change in the withdrawing properties of the cycle can be estimated by the easily measurable enolization rate.

Indeed, the K_t constant changes according to a change in the ratio of rates of the rate-determining steps of enolization and ketonization.[22]

In the whole series of *N*-acetonylazoles, steric conditions for proton elimination in the rate-determining step (approach of a base to the protonated form of ketone) remain almost unchanged. However, with an enhancement of the withdrawing properties of the cycle the proton elimination rate should inrease and the rate of the inverse step should decrease, and as a result, K_t increases.

We studied the enolization of the *N*-acetonyl compounds in D_2SO_4 solutions by ^1H NMR spectroscopy from the rate of proton deuteriosubstitution,[25,26] which is determined by the enolization rate. The kinetic equations for butan-2-one deuteration in acidic media[26] were used for the calculation of the enolization rate constant by the H/D-substitution constant value. The enolization rate constants are related to the rate constants of H/D-substitution K_{obs} observed in the ^1H NMR spectra by the following equations:

$$K_{en}(CH_2) = -2K_{obs}(CH_2), \qquad K_{en}(Me) = -3K_{obs}(Me).$$

Our experimental data on the decrease in the signals of the methyl and methylene groups in time correspond to the H/D-substitution rate according to the pseudo-first-order equation. The logarithmic anamorphoses $\ln[H_0]/[H] = kt$ according to the results of deuteriosubstitution in 2-acetonyl-5-nitrotetrazole **3a** are shown in Fig. 2.

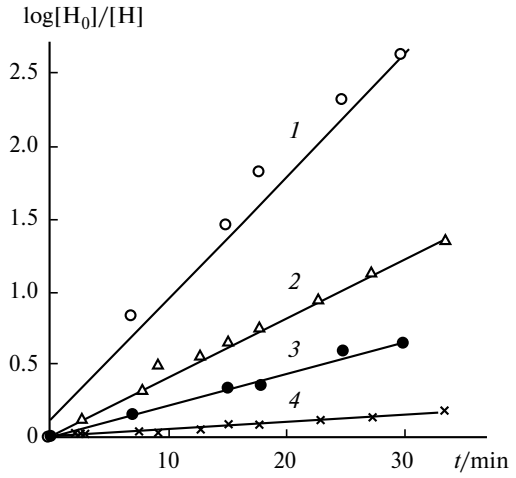


Fig. 2. Logarithmic anamorphoses of the kinetics of deuteriosubstitution of methylene (*1*, *2*) and methyl groups (*3*, *4*) in 2-acetonyl-5-nitrotetrazole **3a** (initial concentration 0.35 mol L^{-1}) in D_2SO_4 solutions. Volume ratios of D_2SO_4 to D_2O: 12 : 1 (*1*, *3*) and 12 : 5 (*2*, *4*).

For other objects (**3r**,**s**), which differ strongly in the electron-withdrawing ability of the cycle and in the transformation rate into *N*-dinitromethylazoles, analogous linear dependences were obtained (Scheme 5, Tables 3 and 4). It was found that these ketones are enolized not only due to the CH_2 moiety but also (with rather high rates) due to the Me group.

In 89.2% H_2SO_4 Me-enolization is almost the same for all ketones, whereas CH_2-enolization is accelerated with the enhancement of the withdrawing properties of the nitrous substituent, which results in an increase in the relative fraction of CH_2-enol (K_D). Unlike the azole derivatives, acetonyltrimethylammonium is enolized predominantly due to the Me group, which is associated, most likely, with unsuccessful attempts to nitrate acetonyltrimethylammonium to the *N*-dinitromethyl compound with a sulfuric—nitric acid mixture.

On going to 76.7% D_2SO_4, the enolization rates due to the Me and CH_2 groups decrease nonproportionally and, as a result, the fraction of CH_2-enols increases sharply. In the more concentrated (93.6%) acid the enolization rate and the relative content of enols remain unchanged compared to those in 89.2% D_2SO_4.

As shown above, the determined enolization rates are in essence the enolization rates of the corresponding

Scheme 5

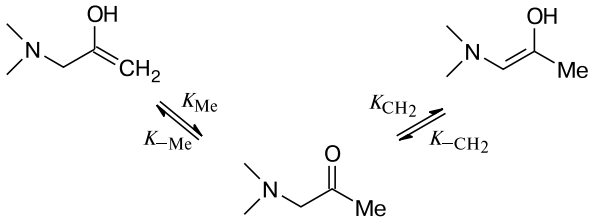


Table 3. Rate constants for enolization of the *N*-acetonyl derivatives in D_2SO_4

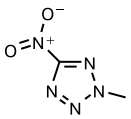
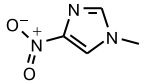
N—	$[D_2SO_4]$ (%)	$K_{Me} \cdot 10^4$	$K_{CH_2} \cdot 10^4$	$K_D = K_{CH_2}/K_{Me}$
	89.2	10.80	28.6	2.7
	76.7	2.49	13.4	5.4
	89.2	8.70	22.2	2.5
	76.7	0.48	2.68	6.0
	89.2	10.80	21.0	1.9
	89.2	9.60	7.2	0.8

Table 4. Parameters of equations of the logarithmic anamosphoses ($\ln(H_0/H) = Kt + A$) of deuterioexchange in the *N*-acetonyl derivatives (0.35 mol L^{-1}) and correlation coefficients (*R*)

N-Acetonyl derivative	Me Group				CH_2 Group		
	$D_2SO_4 : D_2O$ (vol.)	$K \cdot 10^4/s^{-1}$	*A*	*R*	$K \cdot 10^4/s^{-1}$	*A*	*R*
5-Nitrotetrazole (**3a**)	12 : 5	0.83±0.07	−0.006±0.070	0.970	6.70±0.2	0.019±0.026	0.994
	12 : 1	3.60±0.2	0.007±0.024	0.993	14.30±0.9	0.140±0.093	0.993
	12 : 0	3.60±0.4	0.038±0.017	0.971	14.90±0.8	0.086±0.033	0.993
4-Nitroimidazole (**3s**)	12 : 5	0.16±0.04	0.029±0.012	0.829	1.34±0.04	0.020±0.015	0.996
	12 : 1	2.90±0.2	0.011±0.017	0.991	11.10±0.4	0.017±0.031	0.998
Imidazole (**3r**)	12 : 1	3.60±0.07	0.007±0.001	0.999	10.50±0.5	−0.003±0.045	0.995
Trimethylammonium	12 : 1	3.20±0.07	0.007±0.006	0.999	3.60±0.3	−0.028±0.028	0.986

N-acetonylcycloimmonium salts. It should be mentioned that in a neutral medium (D_2O and CD_3OD) the deuterioexchange of the methylene moiety in *N*-acetonyltetrazoles is substantially slower than that in the corresponding *N*-acetonyltetrazolium salts.[11] This also indicates the higher enolization rates of ketones with protonated cycles.

The study of the kinetics of destructive nitration of the *N*-acetonyl functional group by UV spectroscopy and ^{1}H NMR spectroscopy showed (see below) that this process consisted of two consecutive irreversible reactions: the introduction of the first and second nitro groups, each of which consists, in turn, of two steps, namely, the reversible enolization of ketone and the irreversible addition of the nitronium ion to the double bond of enol. The rate of this reaction, which occurs in the quasi-stationary regime, is described in the general form by the equation presented in Scheme 4. At the low enolization rate (compared to the nitration rate) this equation is reduced to Eq. (I), whereas at the high rate is reduced to Eq. (II).

Kinetics of nitration of 2-acetonyl-5-nitrotetrazole. The detailed study of the nitration kinetics was carried out for 2-acetonyl-5-nitrotetrazole **3a**, because easily identified products are formed in this case and the reaction is rather selective. The kinetics of accumulation of mononitroketone **8a** in 89.2% H_2SO_4 was studied at room temperature by UV spectroscopy according to the change in the concentration of 2-nitromethyl-5-nitrotetrazole anion **10a** (λ =312 nm, ε = 8500), which is the product of hydrolysis of nitroketone **8a** (see Scheme 3).

At low KNO_3 concentrations only one hydrogen atom in the methylene unit is substituted for the NO_2 group even under the conditions of the twofold molar amount of KNO_3. At the maximum yield of nitroketone **8a** (76% in 45 min) the yield of 2-dinitromethyl-5-nitrotetrazole **6a** is 3—4%. After 17 h the yield of dinitromethyl derivative **6a** achieves only 6%, whereas the yield of nitroketone **8a** decreases to 25—30% because of side decomposition reactions.[19—21]

In acidic media nitroketone **8a** is not quite stable. For example, in a weakly acidic medium (pH = 4) nitroketone **8a** dissociates to form the corresponding anion. The intensity of the absorption maximum of this anion (λ = 311.5 nm) decreases gradually (by ~30% within 30 min) because of hydrolysis to 2-nitromethyl-5-nitrotetrazole **10a**. The position of the absorption maximum of compound **8a** remains unchanged upon the acidification of the medium to pH = 1; however, its intensity decreases in time much more rapidly than at pH = 4, indicating that **8a** decomposes *via* another direction, because the rate of hydrolysis to nitromethyltetrazole **10a** in an acidic medium should be retarded. In addition, if an aliquot of the reaction mixture is poured at once into a solution of Na_2CO_3, anion **10a** is formed in larger amounts than in the case when the aliquot is poured first into water and then the medium is alkalized (to pH = 10). Therefore, in an acidic medium before alkalization a portion of nitroketone **10a** has time to decompose, but not due to hydrolysis. The decomposition of **8a** in the reaction medium is also indicated by the decrease in the yield of 2-dinitromethyl-5-nitrotetrazole **6a** with the retardation of the rate of transformation of nitroketone **8a** into **6a**, *i.e.*, when KNO_3 is added not at once but in portions during several hours.

For the kinetic curves of accumulation of **8a** (Fig. 3, curves *1*—*3*), the logarithmic anamorphoses at the equimolar (*1′*) and double (*2′*) amount of KNO_3 represent straight lines only in the initial regions, *i.e.*, the concentration of KNO_3 remains yet almost unchanged. Then their slope decreases, indicating the dependence of the reaction rate on the KNO_3 concentration, *i.e.*, the overall reaction order exceeds 1. The apparent rate constant calculated in the initial region increases twofold with a twofold increase in the KNO_3 concentration, indicating the first order with respect to potassium nitrate. For the fourfold increase in the amount of KNO_3 the logarithmic anamorphosis (curve *3′*) is a straight line in the whole region, which is usually observed in the case of bimolecular reactions carried out under the pseudo-first-order conditions. It is important that in this case K_{app} increases only threefold instead of the fourfold increase, *i.e.*, the order with respect to the nitronium ion decreases.

The maximum yield (82%) of mononitroketone **10a** from this mixture (see Fig. 3, curve *3*) is achieved 20 min

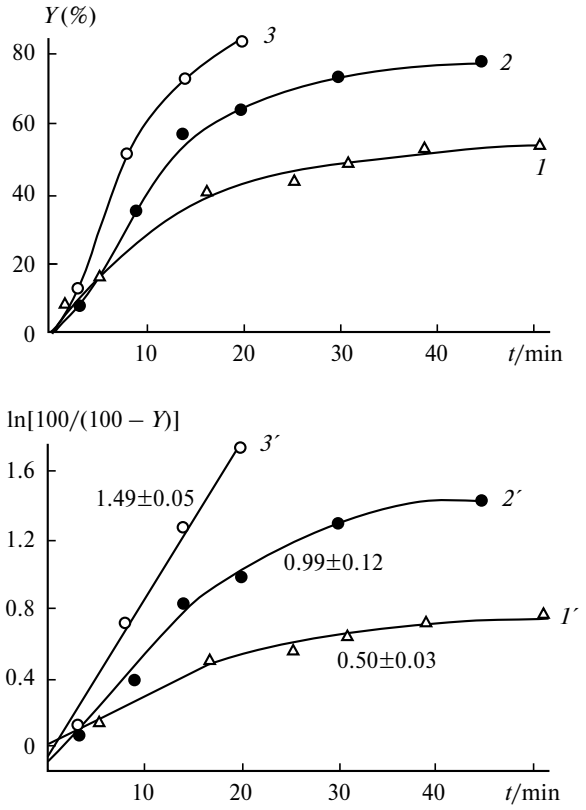


Fig. 3. Kinetic curves of accumulation (*1*—*3*) of 2-acetonyl-(1′-nitro)-5-nitrotetrazole **8a** and the corresponding logarithmic anamorphoses of disappearance (*1′*—*3′*) of 2-acetonyl-5-nitrotetrazole **3a** in 89.2% H_2SO_4 ($H_2SO_4 : H_2O = 12 : 1$, vol.) at different initial concentrations of KNO_3: 0.058 (*1*, *1′*), 0.116 (*2*, *2′*), and 0.232 mol L^{-1} (*3*, *3′*). The initial concentration of **3a** is 0.058 mol L^{-1}. Figures on the anamorphoses are the values of $K_{app} \cdot 10^3$ (s^{-1}); *Y* is the yield of the product.

after the beginning of the reaction, and the yield of dinitro derivative **6a** is 4—5% at this moment. After 7—8 h the largest amount of **6a** is formed: 37%.

The values of the rate constants for the formation of mononitroketone **8a** indicate that the replacement of the proton of the methylene moiety in **3a** by the nitro group does not proceed *via* the mechanism of concerted attack of $[NO_2^+]$ to the carbon atom with the simultaneous attack of a base (H_2O or HSO_4) to the hydrogen atom.[17,18] Indeed, the mobility of the CH_2 proton in **3a** ($pK_a > 7$) is significantly lower than that of the $CH(NO_2)_2$ proton in **6a** ($pK_a = -1.7$). Hence, according to this mechanism, the nitration of the CH_2 moiety should occur much more slowly than nitration at the dinitromethyl group or should not occur at all (as, *e.g.*, in the case of *gem*-dinitroethane, $pK_a = +5.30$).

However, the experimental K_{app} value of the rate of nitro group introduction into the methylene moiety of **3a** ($1.49 \cdot 10^{-3}$ s^{-1}) is two orders of magnitude higher than K_{app} for the nitration of **6a** to the trinitromethyl derivative even in the case of a higher KNO_3 concentration. At the same time, this value is comparable with the rate of enolization of **3a** in this medium ($2.8 \cdot 10^{-3}$ s^{-1}).

The high rate constant for the nitration of the methylene moiety in **3a** indicates that another, more reactive form (enol form) is nitrated. Since the apparent rate constant for the accumulation of nitroketone **8a** depends on the concentration of nitronium ions, the reaction rate is determined by the overall kinetic equation (see Scheme 4), *i.e.*, the nitration of the enol form is the rate-determining step. At a low concentration of nitronium ions, the rate of addition of $[NO_2^+]$ is lower than the enolization rate and the whole process depends on the concentration of nitronium ions. At the high concentration $[NO_2^+]$ (>0.3—0.4 mol L^{-1}), the addition rate of nitronium ions is equal to the enolization rate and is independent of the concentration $[NO_2^+]$, *i.e.*, it is described by Eq. (I).

The apparent rate constant for the disappearance of ketone **3a** in 89.2% H_2SO_4 at the high KNO_3 concentration (1.15 mol L^{-1}) was estimated by ^1H NMR spectroscopy from a decrease in the intensity of signals of protons of the CH_2 moiety. The values of this constant range from $1.7 \cdot 10^{-3}$ to $2.7 \cdot 10^{-3}$ s^{-1}, *i.e.*, almost coincide with the enolization rate constant ($2.8 \cdot 10^{-3}$ s^{-1}) in this medium.

Thus, at the stage of introduction of the first nitro group into the methylene moiety, the enolization rate and the rate of addition of the nitronium ion to the double bond have close values: at the high concentration $[NO_2^+]$ (>0.36 mol L^{-1}) the enolization is the rate-determining step, whereas at the low concentration (<0.14 mol L^{-1}) the rate is determined by the addition of the nitronium ion.

Kinetics of accumulation of 2-dinitromethyl-5-nitrotetrazole (6a) was studied at 24 °C in 89.2% H_2SO_4 containing KNO_3 in a high concentration (1.15 mol L^{-1}) using UV spectroscopy. The change in the absorbance of the reaction mixture samples diluted with water was studied at the absorption wavelength of anion **6a** (336 nm, $\varepsilon = 17500$). The concentration of the starting ketone **3a** (0.058 mol L^{-1}) should be 20-fold lower than the concentration of KNO_3 for the reaction to be pseudo-monomolecular with respect to the starting ketone **3a**. The kinetics of accumulation of **6a** (Fig. 4) is described by the S-like curve with the inflection point in the initial region, which is characteristic of consecutive reactions. An analysis of the kinetic equations of these reactions shows that if the rate of one step is considerably lower than the rates of other steps, then after some time interval the kinetic curve of this process is well described by an equation of the first order.[27]

At the high KNO_3 concentration, the rate of formation of intermediate product **8a** will be equal to the enolization rate ($K_{app} = 2.8 \cdot 10^{-3}$ s^{-1}). It can easily be calculated that already 11 min after nitroketone **8a** is formed in 84% yield. At the same time, according to the experimental data, at this moment (the second experimental point in curve *2*) the final product **6a** is formed in 8% yield, *i.e.*, the

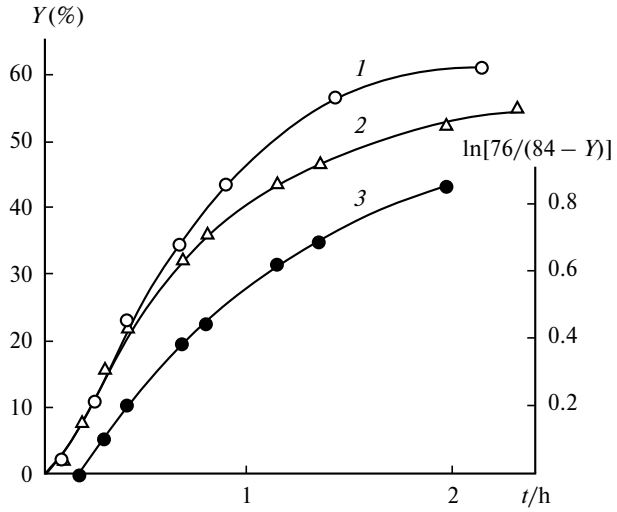


Fig. 4. Kinetic curves of accumulation of compound **6a** for the nitration of ketone **3a**: *1*, $D_2SO_4 + D_2O$ (12 : 1, vol.); *2*, $H_2SO_4 +$ $+ H_2O$ (12 : 1, vol.); *3*, logarithmic anamorphosis of curve *2* (*i.e.*, disappearance of nitroketone **8a** after an autoacceleration period of 11 min). The initial concentrations of KNO_3 and **6a** are 1.15 and 0.058 mol L^{-1}, respectively.

true amount of **8a** is 84 – 8 = 76% due to its further transformation into **6a** (the amount of **8a** at later moments is calculated similarly). Beginning from this moment, the kinetic curve of accumulation of **6a** corresponds to the transformation of nitroketone **8a** into **6a** and should obey an equation of the first order. In fact, the logarithmic anamorphosis (*3*) for the disappearance of nitroketone **8a** plotted after the induction period (11 min) represents a straight line with the correlation coefficient 0.99 until 2-dinitromethyl-5-nitrotetrazole is formed in 35% yield. Then the slope of the anamorphosis decreases gradually because of the increasing error of the calculation of unreacted nitroketone **8a** due to its side decomposition and an increase in the decomposition rate of accumulated 2-dinitromethyl-5-nitrotetrazole **6a** ($K_{app} = 1.35 \cdot 10^{-5}$ s^{-1} in the same mixture). The apparent rate constant for the disappearance of nitroketone **8a** (*i.e.*, the introduction of the second group, $K_{app} = 1.9 \cdot 10^{-4}$ s^{-1}) is 15-fold lower than the rate constant of its accumulation, which is equal to the enolization rate of the starting *N*-acetonyltetrazole **3a** in this mixture (see above). Analogous K_{app} values at other initial concentrations of **3a** (0.02 and 0.08 mol L^{-1}) confirm the first order of the reaction with respect to the starting ketone.

The kinetic curve of accumulation **6a** in D_2SO_4 in the region of formation coincides up to 30% with the curve in the non-deuterated acid, and then K_{app} in D_2SO_4 decreases somewhat more slowly than in H_2SO_4. It is most likely that the nitration of **6a** to the trinitromethyl derivative in D_2SO_4 occurs more slowly, which is consistent with the known mechanism of nitration of the dinitromethyl group.[16—18]

Thus, the rate constant for the introduction of the first nitro group is considerably higher (10—15-fold) than that for the second nitro group, while the latter is an order of magnitude higher than the rate constant of nitration of **6a** to the trinitromethyl derivative, which excludes the nitration of mononitroketone **8a** according to the mechanism of direct electrophilic substitution (see above). In addition, the absence of the kinetic isotope effect during nitration of **3a** in D_2SO_4 indicates that the proton transfer is not a rate-determining step of the reaction, as it takes place in the case of nitration of the dinitromethyl compounds according to the concerted mechanism.[17,18]

As follows from the data on the rate of accumulation of **6a** (Fig. 5), the nitration is accelerated with an increase in the H_2SO_4 concentration (in the 76—91.6% range), whereas in the range of 91.6—5% oleum the rate remains almost unchanged (see Fig. 5). Although *via* the mechanism of concerted substitution[17,18] the nitration rate should decrease with an increase in the H_2SO_4 concentration, while in 100% H_2SO_4 no nitration occurs. When the influence of the concentration of nitronium ions on the rate of final product formation was studied, in essence this was the study of the kinetics of nitration of intermediate nitroketone, because this step is substantially slower than the first step. The concentration $[NO_2^+]$ was changed both at the constant H_2SO_4 concentration and by the variation of the acidity of the medium at the constant amount of KNO_3. The reaction rates were determined after the induction periods (5—10 min) and were compared only for the curves with high yields of **6a** (~60%). According to Ref. 28, the concentration $[NO_2^+]$ increases sharply (from 0 to 98%) in the range of H_2SO_4 concentrations 81—93%. The rate of formation of **6a** increases strongly in the same interval (Fig. 6).

Since the rate of transformation of HNO_3 to NO_2^+ in this media ($K_{NO_2} = 10^2$—10^3 s^{-1})[28] is six—seven orders of magnitude higher than the rate of introduction of both the first and second nitro groups, the apparent concentration $[NO_2^+]$ can be accepted constant during the reaction, because the KNO_3 concentration is 10—20-fold higher than the concentration of ketone **3a**.

In 89.2% H_2SO_4 at a twofold increase in the KNO_3 concentration, the effective concentration of nitronium ions increases only 1.24-fold due to some decrease in the acidity of the medium. The same increase, namely, 1.27-fold, is characteristic of the apparent rate constant for the formation of **6a** (see Fig. 5, curves *3* and *4*).

If the concentration of nitronium ions increases due to the threefold increase in the acidity of the medium without changing the amount of KNO_3 (see Fig. 5, curves *1* and *3*), then K_{app} of formation of **6a** increases considerably (2.6-fold), although the rate of enolization of **3a** in these mixtures is the same. The $K_{app}/[NO_2^+]$ ratio remains constant, *i.e.*, the rate of introduction of the second nitro group depends linearly on the concentration of nitronium ions.

Thus, at the stage of introduction of the second nitro group, the reaction has approximately the first order with respect to the nitronium ion and the overall second order within the experimental error. The rate of this reaction depends on the keto—enol equilibrium constant K_t and the concentration of nitronium ions $[NO_2^+]$ rather than

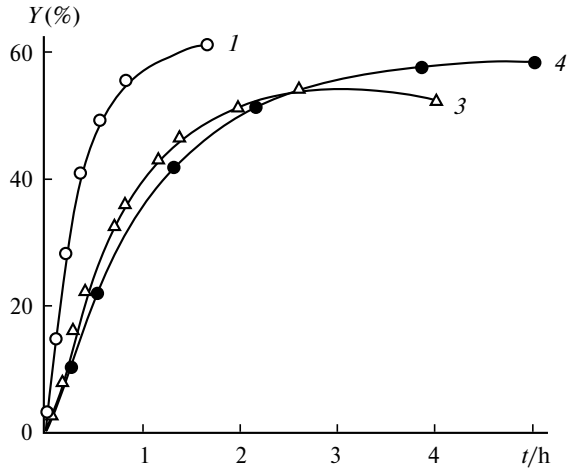


Fig. 5. Kinetic curves of accumulation of compound **6a** for the nitration of ketone **3a** (0.058 mol L^{-1}) in H_2SO_4—KNO_3 mixtures at different effective concentrations of nitronium ions. The apparent rate constants (K_{app}) for the introduction of the second nitro group after 10-min induction periods:

Curve	Volume ratio $H_2SO_4 : H_2O$	$[H_2SO_4]$ (%)	$[KNO_3]_0$ (mol L^{-1})	$[NO_2^+]_{eff}$ (mol L^{-1})	$K_{app} \cdot 10^4$ /s^{-1}	$K = K_{app} \cdot 10^4/[NO_2^+]$ /mol L^{-1} s^{-1}
1	12 : 0	93.64	1.15	1.08	4.9±0.1	4.5
3	12 : 1	89.23	1.15	0.36	1.9±0.2	5.3
4	12 : 1	89.23	0.575	0.29	1.5±0.1	5.2

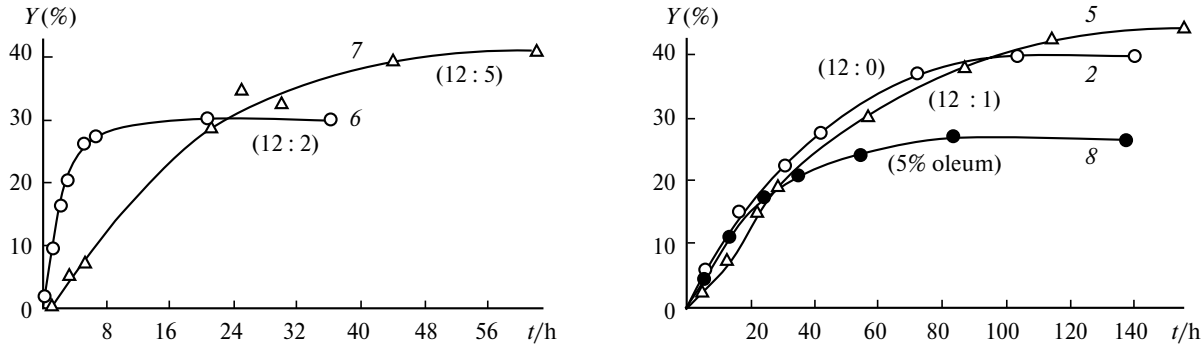


Fig. 6. Kinetic curves of accumulation of compound **6a** for the nitration of ketone **3a** (0.058 mol L^{-1}) in H_2SO_4—KNO_3 mixtures at different effective concentrations of nitronium ions. The apparent rate constants (K_{app}) for the introduction of the second nitro group after induction periods: after 12 min (*5*) and 1 h (*7*) by the first five points; after 5 min by the first four points (*8*):

Curve	Volume ratio $H_2SO_4 : H_2O$	$[H_2SO_4]$ (%)	$[KNO_3]_0$ (mol L^{-1})	$[NO_2^+]_{eff}$ (mol L^{-1})	$K_{app} \cdot 10^4$ /s^{-1}
2	12 : 0	93.64	0.575	0.56	—
5	12 : 1	89.23	2.3	0.31	1.1+0.2
6	12 : 2	89.23	1.15	0.10	—
7	12 : 5	76.77	0.575	0.00	0.05+0.1
8	5% oleum	—	1.15	1.15	1.8+0.2

on the enolization rate. The addition of nitronium ions is much slower than the formation of the enol form of intermediate nitroketone, and the reaction rate is described by Eq. (II). In the general case, the rate of introduction of the second nitro group is 1—1.5 times of magnitude lower than the rate of introduction of the first group.

The absence of the kinetic isotope effect also confirms that the enolization rate does not determine the nitration rate in the second step. Note that the introduction of the nitro group into the CH_2 moiety of *N*-acetonylazoles should increase the keto—enol equilibrium constant K_t, as, *e.g.*, in the case of acetoacetic and nitroacetoacetic esters.[29] Therefore, the significant difference in the rates of introduction of the first and second groups is due only to the slower addition of the nitronium ion to nitroenol than to the starting enol.

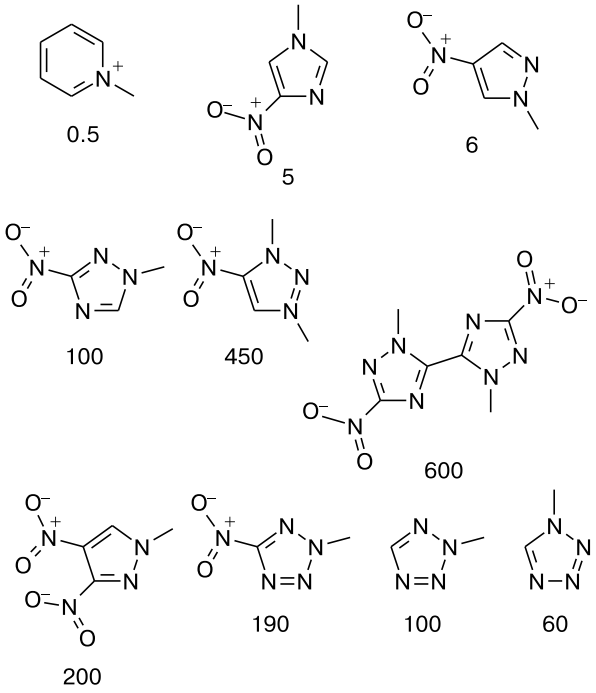
Compound **6a** is formed rather rapidly in 5% oleum as well ($K_{app} = 1.8 \cdot 10^{-4}$ s^{-1}). However, side processes related to the decomposition of intermediate nitroketone **8a** and cycle destruction occur rapidly in the medium considered, which is indicated by appreciable gas release. The yield of **6a** does not exceed 25%, although this substance is relatively stable in the medium considered.

In the general case, the yield of **6a** increases under the conditions when the nitration rate of nitroketone **8a** exceeds the decomposition rate. As a rule, with an increase in the KNO_3 concentration, the yield of **6a** increases but to a certain limit. For instance, at the very high concentration of KNO_3 (2.3 mol L^{-1}) the effective concentration of nitronium ions decreases due to a decrease in the acidity of the medium, resulting in a decrease in the nitration rate and in the yield of **6a** (see Figs 5, 6; curves *3* and *5*). At the same time, an increase in the effective concentration [NO_2^+] due to an increase in the acidity of the medium (89.2—93.6% H_2SO_4) increases the fraction of Me-enol ($K_D = 2.7$, see Table 3), favoring the side nitration of the Me group (see below).

Rather high yield (42%) of compound **6a** in dilute H_2SO_4 (76.77%, see Fig. 6, curve *7*) should be noted, in spite of the low nitration rate and concentration [NO_2^+]. The final product **6a** and, most likely, intermediate nitroketone **8a** are most stable just in this medium. In addition, at this acidity the favorable ratio of CH_2- and Me-enols equal to 5.4 is observed (see Table 3). As can be seen from Fig. 6, the yield of **6a** in dilute H_2SO_4 (12 : 5) is higher than that in the more concentrated acid (12 : 2), although in the latter mixture the effective concentration of nitronium ions and the rate of formation of compound **6a** are substantially higher.

Kinetics of accumulation of *N*-dinitromethylazoles 6 was studied similarly. The induction periods were 10—60 min, depending on the rate of formation of the final products.

The $K_{app} \cdot 10^6$ (s^{-1}) values of the accumulation of *N*-dinitromethylazoles **6** for the nitration of *N*-acetonylazoles **3** obtained by UV spectroscopy in an H_2SO_4—KNO_3 solution (mixture *3*, see caption to Fig. 5) at 24 °C (the azolyl fragments are shown) are given below.



The rates of introduction of the first nitro group into the methylene moiety are close in all examples, because they are determined by the enolization rates, which differ slightly for various heterocycles ($K_{en} = (2—2.9) \cdot 10^{-3}$ s^{-1}). Therefore, the difference in the accumulation rates of the *N*-dinitromethyl derivatives depends on the rate of introduction of the second nitro group. This rate is one to three orders of magnitude and depends on the amount of nitroenol in the mixture, *i.e.*, on K_t. For *N*-acetonylazoles. the enolization rate K_{en} and the percent content of enol K_t increase with the enhancement of the withdrawing properties of the cycle. It is most likely that K_t for mononitroacetonylazoles will change in the same order and, hence, for the more enolized objects the *N*-dinitromethyl derivatives are formed more rapidly. For instance, 2-acetonyl-5-nitrotetrazole **3a** is more rapidly transformed into the *N*-dinitromethyl derivative than 1-acetonylimidazole **3r** and 1-acetonyl-4-nitroimidazole **3s**, because its enolization is higher (see Table 3) and, therefore, the percent content of enol for the corresponding nitroketone is also higher. At the same time, acetonyltrimethylammonium nitrate is not transformed into the *N*-dinitromethyl derivative, because it is enolized much more slowly than acetonylazoles, and its enolization proceeds predominantly due to the Me group.

In the general case, the apparent rate constants for the accumulation of the *N*-dinitromethyl structures increase with an increase in the number of nitro groups and nitrogen atoms in the cycle.

The studies performed made it possible to reduce side processes to minimum and to direct the reaction in the required direction.

On the one hand, according to the kinetics of formation of the *N*-dinitromethyl group, one should attain high concentrations of nitronium ions and increase the amount of HNO_3. At the same time, it is undesirable to take a high amount of HNO_3 over H_2SO_4 during the work in concentrated nitrating mixtures, because this decreases the acidity of the medium and, hence, the effective concentration of nitronium ions. The optimal volume ratio H_2SO_4 : HNO_3 ranges from 10 : 1 to 10 : 4.

On the other hand, as solutions of H_2SO_4 are diluted, the fraction of CH_2-enol increases compared to that of Me-enol in the *N*-acetonyl derivatives. Therefore, the nitration with sulfuric—nitric acid mixture occurs better in the presence of a large amount of water, although the effective concentration of nitronium ions decreases. This is especially important for the lowly nitrated cycles and those containing a small number of nitrogen atoms, namely, pyridine, imidazole, pyrazole, and their mononitro derivatives. In concentrated media their K_D value, *i.e.*, the ratio CH_2-enol/Me-enol, is lower than in *N*-acetonylazoles with electron-withdrawing cycles of the 5-nitrotetrazole type.

Nitrating mixtures diluted with water should also be used in the case of formation of *N*-dinitromethyl compounds that are readily nitrated further to undesirable trinitromethyl derivatives (for example, tetrazoles and nitrotriazoles). The decrease in the general acidity of the medium upon the addition of water also favors the enhancement of stability of intermediate nitroketones. However, the rate of their transformation into dinitroketones decreases because of a decrease in the effective concentration of nitronium ions.

As a whole, for the reasons indicated, the optimal degree of dilution can differ for different types of compounds. In several cases, the poor solubility of *N*-acetonylazoles and intermediate acetonylazoles in nitrating mixtures should be taken into account. For instance, in the presence of a large amount of water in the nitration of the acetonyl derivatives of 5-trinitromethyltetrazole **3b** and bis(3-nitro-1,2,4-triazol-5-yl) **3j**, the reaction ceases at the step of formation of mononitroketones precipitating from the reaction mixtures. When selecting the nitration conditions, it is important to take into account the ability to enolization determining the rate of the whole process. The latter can be qualitatively evaluated by the chemical shift (δ) of the CH_2 protons: the weaker the field δ, the faster the nitration.

Optimal methods for synthesis of the *N*-dinitromethyl compounds. The maximally diluted nitrating mixture H_2SO_4—HNO_3—H_2O (12 : 5 : 5 v/v) was chosen experimentally. This is the "standard nitrating mixture" in which the reaction of destructive nitration can occur. At the same time, the maximum 100% conversion of HNO_3 to the NO_2^+ ion and the highest enolization rate are observed in 93—94% H_2SO_4 and further do not increase. Therefore, it is unreasonable to use more concentrated media. In addition, intermediate α-nitroketone decomposes more rapidly in these media. The yields of *N*-dinitromethylazoles presented in Scheme 2 were optimized not in all cases, and there are opportunities to increasing them.

The methods for synthesis of some structures have been developed in more detail. For example, in the "standard" mixture 2-dinitromethyl-5-nitrotetrazole **6a** was obtained in 70—78% yield at 30—35 °C for 8 h, whereas at 20 °C this yield was achieved for 2—3 days. The nitration of 2-acetonyl-5-(trinitromethyl)tetrazole **3b** in the "standard" mixture ceases at the step of formation of mononitroketone **8b** (76% yield), which precipitates from the reaction mixture.

However, in more concentrated mixtures compound **8b** is nitrated further to *N*-dinitromethyltetrazole **6b**, which can also be obtained, under these conditions, in one step from the corresponding *N*-acetonyltetrazole **3b**.

The most complicated case is the nitration of bis(2-acetonyl-3-nitro-1,2,4-triazol-5-yl) **3j**, which is insoluble in the "standard" mixture. In anhydrous mixtures in which **3j** is soluble, the bis(2-dinitromethyl-3-nitro-1,2,4-triazol-5-yl) **6j** that formed is easily nitrated to the trinitromethyl derivative. Nevertheless, in an H_2SO_4 solution containing small amounts of HNO_3 and water in a ratio of 12 : 1 : 1, the starting ketone **3j** is rather soluble and the undesirable formation of the trinitromethyl derivative is not too fast. Therefore, the target product **6j** can be obtained in 50% yield accompanied by rigid spectrophotometric monitoring almost without admixture of trinitromethyl compound.

Bis(2-dinitromethyl-4-nitro-1,2,3-triazol-5-yl) **6o** was obtained in 50% yield in a mixture of concentrated H_2SO_4—HNO_3 (1 : 1), because this compound is much difficultly nitrated to the trinitromethyl derivative and the use of concentrated acids accelerates the process and increases the solubility of the starting acetonylazole.

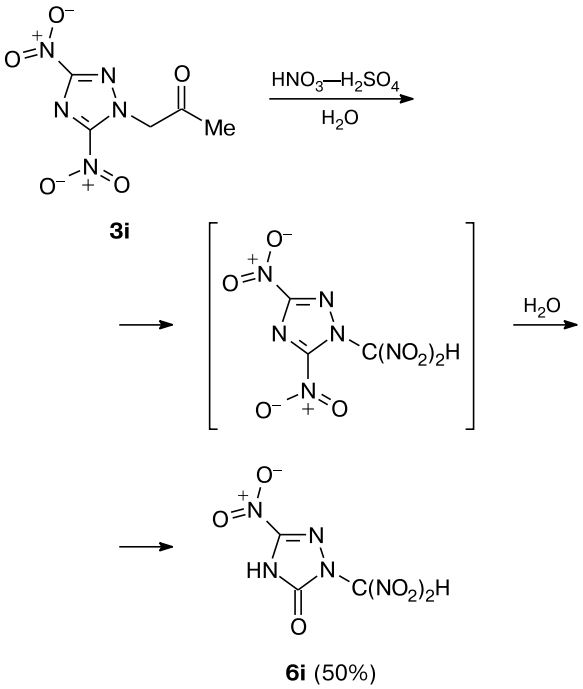
The characteristic property of the strongly nitrated azoles is the capability of easy nucleophilic substituting of the NO_2 group, which manifests itself in the nitration of *N*-acetonyl-3,5-dinitro-1,2,4-triazole **3i** and results in the substitution of the NO_2 group for OH to form triazolone **6i** (Scheme 6).

Attempts to nitrate the *N*-acetonyl derivatives of 2,4,5-trinitroimidazole and bis(4,5-imidazol-2-yl) and 1,2-isomers of bis(acetonyl-3-nitro-1,2,4-triazol-5-yl) failed for the same reason.

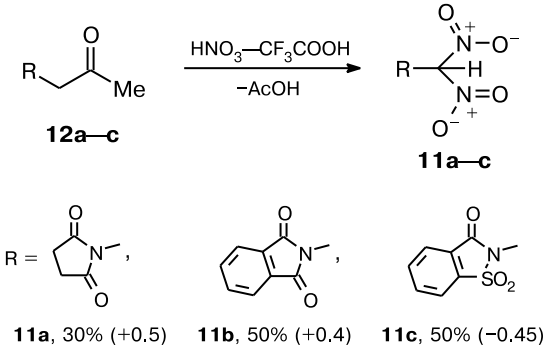
***N*-Dinitromethylimides of carboxylic and sulfonic acids 11a—c.** To prevent destruction processes, milder nitrating mixtures CF_3COOH—HNO_3 (3 : 2 v/v) with lower acidity and hydrolytic activity were used (Scheme 7).

The principal possibility for the destructive nitration of β-dicarbonyl compounds was shown using the synthesis

Scheme 6



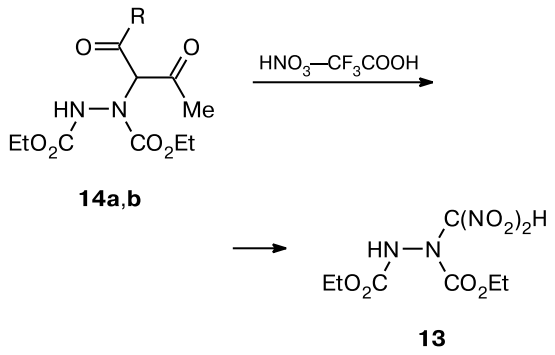
Scheme 7



of substituted *N*-dinitromethylhydrazine **13** as an example (Scheme 8). According to our data, the starting 2-hydrazinyl-substituted β-diketones **14a**,**b** (see Ref. 30) exist in the enol form by 66% for R = Me and by 100% for R = CO_2Et in a $CDCl_3$ solution, whereas in sulfuric acid solutions the content of enols is higher. Therefore, they are rapidly transformed into substituted *N*-dinitromethylhydrazine **13**, probably, through the consecutive steps of nitration, removal of the acetyl group, and introduction of the second nitro group.

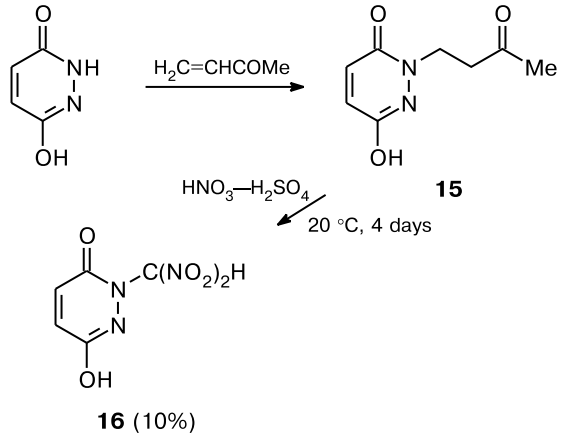
The synthesis of *N*-dinitromethylhydrazines under the conditions of destructive nitration with sulfuric—nitric acid mixtures was shown for the oxobutyl derivative **15** (see Ref. 31). In this case, the reaction proceeds, most likely, according to the mechanism of successive elimination—addition[7,8,32,33] (Scheme 9).

Scheme 8



R = Me (**13** (48%), **14a**), OEt (**13** (26%), **14b**)

Scheme 9



Structure of *N*-dinitromethyl compounds. The structure of *N*-dinitromethyl compounds was proved by a complex of spectral methods.

In the ^1H and ^{13}C NMR spectra, the total set of signals and SSC constants in the heterocycle remain almost unchanged when the *N*-acetonyl group is replaced by the *N*-dinitromethyl one (Table 5).

The presented parameters of the *N*-dinitromethyl and *N*-dinitrocarbanionic moieties correspond to their position at the electronegative group, in this case, at the nitrogen atom of the heterocycle. The tendency of shifting ν_{as} to the high-frequency region on going to more electron-withdrawing cycles is observed. The UV spectra of aqueous solutions of all *N*-dinitrocarbanionic structures contain an intense absorption maximum at 330—350 nm, being shorter-wavelength than that of the dinitromethane anion (362.5 nm),[34] which corresponds to its binding with the electron-withdrawing group.[34]

In the general case, an increase in the electron-withdrawing ability of the cycle results in the hypsochromic shift of the absorption maximum. The high molar absorption coefficients indicate the planar (at ε = 17 000) or

Table 5. Main spectral parameters of the dinitromethyl and dinitrocarbanionic fragments at the nitrogen atom of the heterocycle

Fragment	IR, ν/cm^{-1}		UV		NMR, δ (J/Hz)		
	ν_s	ν_{as}	λ_{max}/nm	ε	^1H	^{13}C	^{15}N (relative to $MeNO_2$)
$N-CH(NO_2)_2$	1300—1500	1580—1620	—	—	8.2—8.8	102—110 ($^1J_{C,H}$ = = 188—190)	−(28—29) ($^1J_{N,C}$ = 13—14)
$N-C(NO_2)_2^-$	1230—1280	1460—1505	330—350	15000—19000	—	125—137	−(27—30) ($^1J_{N,C}$ = 28—30)

close to planar structure of the dinitrocarbanionic moiety. It was also concluded on the basis of the regular change in the chemical shift of these groups in the ^{13}C NMR spectra and the SSC constants ($J_{C,N}$) that the carbon atom changes its tetrahedral configuration to the trigonal (planar) one.

According to the X-ray diffraction analysis data for potassium salt **6a** (Fig. 7), the aromatic nitro group in position 5 is almost coplanar to the tetrazole cycle plane and, hence, is conjugated with it. The dinitrocarbanionic moiety is planar and unfolded relative to the ring by 80.6°, due to which no conjugation between them is observed.

The acidity of the *N*-dinitromethyl groups was determined in $H_2SO_4-H_2O$ solutions by the spectrophotometric method using the Boyd acidity functions[35] H_- similarly to the procedure described.[36] The obtained pK_a values (see Scheme 2) show that *N*-dinitromethylazoles are strong CH-acids exceeding trinitromethane ($pK_a = 0.06$).[37]

The structures bearing a substituent in the *ortho*-position to the dinitromethyl group have anomalously high CH-acidity, *i.e.*, they manifest the *ortho*-effect, indicating a considerable turn of the planar $C(NO_2)_2$ moiety relative to the heterocycle plane.[38]

General regularities. The following conclusions can be drawn on the basis of the obtained results.

1. During the nitration of *N*-acetonylazoles, the nitro groups are introduced directly into the methylene moiety,

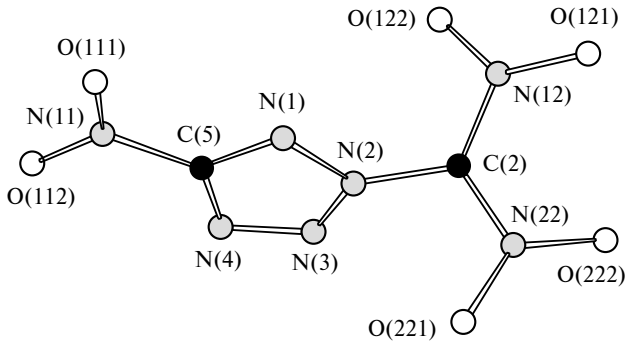


Fig. 7. Projection of the anion of 2-dinitromethyl-5-nitrotetrazole potassium salt K-**6a** on the plane passing through the N(2), C(2), N(12), and N(22).

and the hydrolysis with the acetyl moiety removal occurs only after the introduction of two nitro groups.

2. The reaction occurs by the addition of nitronium ions to the double bond of the enol forms of *N*-acetonylazoles and intermediate nitroketones.

3. The introduction of nitrosating agents exerts no effect on the yields of *N*-dinitromethylazoles.

4. The introduction of the first nitro group proceeds with the rate close to the enolization rate of *N*-acetonylazole. At the low concentration $[NO_2^+]$, the rate of addition of nitronium ions is lower than the enolization rate and the whole process depends on the concentration $[NO_2^+]$. At the higher concentration $[NO_2^+]$ (>0.3—0.4 mol L^{-1}), the rate of addition of nitronium ions is equal to the enolization rate and the process is independent of the concentration $[NO_2^+]$.

5. The rate of addition of the second nitro group is 1—1.5 orders of magnitude lower than that of the first group; it depends on the amount of the enol form and concentration $[NO_2^+]$ but is independent of the enolization rate. In this case, the addition of nitronium ions is much slower than the formation of the enol form of intermediate nitroketone.

6. The role of the heterocycle in the destructive nitration is related to its influence on the enolization step. In the series of structurally related ketone, the CH_2-enolization rate increases with an increase in the withdrawing properties of the cycle. According to the known mechanism of the enolization—ketonization process, the keto—enol equilibrium constant increases ($K_t = K_{en}/K_{ket} =$ = [En]/[Ket] (%)). The K_t value in mononitroacetonylazoles should increase similarly. Therefore, the formation of the *N*-dinitromethyl derivatives is faster in the case of substances with high enolization rates.

7. For the nitration of various *N*-acetonyl derivatives, the first nitro group is rapidly introduced into almost all CH_2 moieties and the difference in the rates of formation of the *N*-dinitromethyl compounds is mainly related to the step of introduction of the second nitro group.

8. For the nitration of *N*-acetonylazoles, the protonation of the nitrogen atom of the heterocycle favors the acceleration of enolization and increases the content of enol in the mixture (increasing K_t). That is why, probably,

the protonated forms, *i.e.*, cycloimmonium salts, are nitrated. In the case of the most withdrawing cycles, the yields of *N*-dinitromethylazoles are higher, as a rule, because the content of CH_2-enol in them is higher compared to that of Me-enol.

9. The formation of *N*-dinitromethylazoles is deteriorated by the following side processes (Scheme 10). *A*. The decomposition of intermediate nitroketones was confirmed kinetically and chemically; this process is accelerated with an increase in the acidity of the medium and is due, most likely, to the elimination of an acetic acid molecule to form nitrile oxide.[19—21] *B*. Since the enolization of the acetonyl compounds occurs due to the Me group, the nitration also occurs at this group to form polynitro derivatives of methane and *N*-heterylacetic acids, which cannot transform into *N*-dinitromethyl compounds under the nitration conditions. In an experiment on the nitration of acetone, we pioneered to isolate dinitromethane in 5% yield, which was also detected spectrophotometrically upon the nitration of 2-acetonyl-5-nitrotetrazole **3a**. *C*. In several cases, derivatives of electron-withdrawing cycles are characterized by the nitration of *N*-dinitromethylazoles to trinitromethyl compounds. The kinetic studies showed that this process occurs one—two orders of magnitude more slowly than the accumulation of *N*-dinitromethylazoles, while in the presence of significant amounts of water at the volume ratio $H_2SO_4 : H_2O = 12 : 5$ the process does not occur.

Experimental

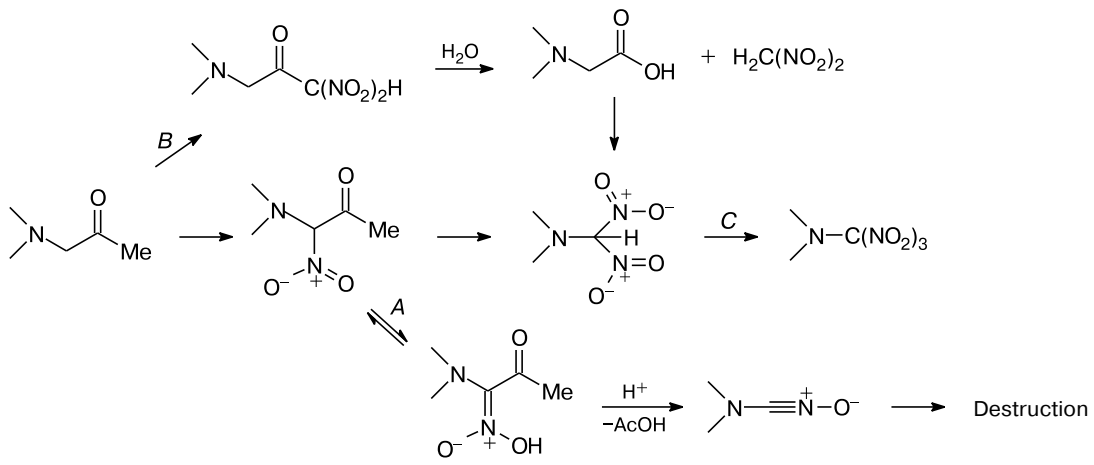
^1H, ^{13}C, and ^{15}N NMR spectra were recorded on a Bruker AM-300 instrument with the working frequencies 300.13 (^1H), 75.47 (^{13}C), and 21.68 MHz (^{15}N). The chemical shift values are given in ppm, and the SSC constant values are expressed in Hz. The standards were Me_4Si (internal) and CF_3COOH (^{19}F) and $MeNO_2$ (^{15}N) (external). The NMR spectra in D_2O, D_2SO_4, and H_2SO_4 solutions were detected with $Me_4N^+ClO_4^-$ as the internal standard, whose chemical shift in these solvents has a constant value of 3.10 ppm relative to Me_4Si.[39] This standard is not deuterated in D_2SO_4 for at least several hours. IR spectra were obtained on a UR-20 instrument (KBr pellts), and UV spectra were measured on a Specord UV—Vis spectrometer. Mass spectra were recorded on a Kratos MS-30 instrument (70 eV) with direct sample injection into the source at the temperature of the ionization chamber 250 °C.

The starting *N*-acetonylazoles were obtained according to known procedures.[10]

Synthesis of *N*-dinitromethylazoles 6 (general procedure). Nitric acid (d = 1.5 g cm^{-3}) (1—5 mL) was added dropwise to a solution of *N*-acetonylazole **3** (2 g) in H_2SO_4 (10—12 mL) (76.8—93.6%) with ice cooling (5—10 °C) The ratio $H_2O : H_2SO_4$ (d = 1.83 g cm^{-3}) for the preparation of sulfuric acid solutions of indicated concentrations and the temperature and duration of storage of the reaction mixtures are given below in examples. *N*-Dinitromethylazoles insoluble in sulfuric—nitric acid mixtures were isolated by filtration. In other cases, the reaction mixture was poured into 50 g of finely divided ice with vigorous stirring, urea was added to remove nitrogen oxides, and the mixture was extracted with ether, ethyl acetate, or dichloromethane (3×10 mL). To obtain aqueous solutions of *N*-dinitromethylazoles, water was added to ethereal solutions, and the ether was evaporated on a rotary evaporator. A saturated solution of potassium acetate in methanol or water was added to a solution of *N*-dinitromethylazole **6** in an organic solvent or water until the precipitate of poorly soluble *N*-dinitromethylazole potassium salt stopped to form. Analytically pure potassium salts of *N*-dinitromethylazoles were obtained after recrystallization from water. The analytically pure compounds with high CH-acidity ($pK_a < 0$) can be obtained using a KI solution in water. The yields and pK_a values are indicated in Scheme 2.

2-Dinitromethyl-5-nitrotetrazole (6a). Water (10 mL) was added dropwise with ice cooling to a solution of 2-acetonyl-5-nitrotetrazole **3a** (5 g) in H_2SO_4 (d = 1.83 g cm^{-3}) (24 mL), then HNO_3 (d = 1.5 g cm^{-3}) (10 mL) was added, and the reaction mixture was stored for 3 days (or heated for 5 h at 40 °C). The precipitate that formed was filtered off, washed with trifluoroacetic acid, and dried in a vacuum desiccator over P_2O_5. Tech-

Scheme 10



nical **6a** (5 g) was obtained, which contains (according to the UV analysis data) 4.6 g (72%) of the major substance. Compound **6a** can be used without purification for further syntheses. Found (%): C, 10.97; H, 0.38; N, 45.04. $C_2HN_7O_6$. Calculated (%): C, 10.96; H, 0.46; N, 44.76. ^{1}H NMR (CF_3COOH), δ: 8.47 (s, CH). IR, ν/cm^{-1}: 1320, 1596, 1620 ($CH(NO_2)_2$); 1373, 1570 (NO_2 arom.). pK_a (H_2O—H_2SO_4) −1.7.

Potassium salt K-6a. A saturated aqueous solution of potassium acetate (1 mL) was added to a solution of compound **6a** (1 g). The precipitate that formed was filtered off, washed with methanol and ether, and dried in air. The analytically pure salt was obtained in a yield of 1 g (85%). ^{13}C NMR (DMSO-d_6), δ: 131.5 ($C(NO_2)_2^-$, $J_{C,N}$ = 30.0 Hz), 166.2 (C(5)). UV (H_2O), λ/nm (ε): 336 (18000). IR, ν/cm^{-1}: 1260, 1300, 1493 ($C(NO_2)_2^-$); 1350, 1587 (NO_2 arom.). According to the UV spectroscopic data, the mother liquor contains 0.22 g (18%) of 2-dinitromethyl-5-nitrotetrazole **6a**.

2-Nitromethyl-5-nitrotetrazole (10a). Ketone **3a** (1 g) was dissolved in an HNO_3—H_2SO_4—H_2O (5 : 12 : 5, vol.) nitrating mixture (11 mL), and the reaction mixture was stored for 2 h at 20 °C and poured into 50 g of ice. The precipitate that formed was filtered off, washed with water, and dried in air. Compound **10a** was obtained in a yield of 0.14 g (14%), m.p. 138—139 °C (MeOH—H_2O). Found (%): C, 13.71; H, 0.95; N, 47.93. $C_2H_2N_6O_4$. Calculated (%): C, 13.80; H, 1.16; N, 48.28. ^{1}H NMR (CD_3CN), δ: 7.64 (s, CH_2). UV (H_2O, pH = 8), λ/nm (ε): 312 (8600). IR, ν/cm^{-1}: 1305, 1560, 1590 (NO_2 group).

2-Dinitromethyl-5-trinitromethyltetrazole (6b). Nitration conditions: HNO_3—H_2SO_4—H_2O (12 : 12 : 1, vol.), 20 °C, 3 h. M.p. 58—59 °C ($CHCl_3$—hexane). UV (H_2O), λ/nm (ε): 336 (16500). Found (%): C, 11.22; H, 0.38; N, 39.12. $C_3HN_9O_{10}$. Calculated (%): C, 11.15; H, 0.31; N, 39.02.

Potassium salt K-6b crystallizes from water. M.p. 148 °C (with decomp.). UV (H_2O), λ/nm (ε): 336 (16 800). ^{13}C NMR (DMSO-d_6), δ: 120.8 ($C(NO_2)_3$); 131.0 ($C(NO_2)_2^-$); 152.6 (C(5)).

2,5-Bis(dinitromethyltetrazole) dipotassium salt. A solution of KOH (0.48 g, 7.6 mmol) in methanol (8 mL) was added dropwise with stirring at 0—5 °C to a solution of hydroxylamine hydrochloride (0.11 g, 1.5 mmol). Compound **6b** (0.32 g, 1 mmol) in methanol (5 mL) was added to the resulting solution. The reaction mixture was stored for 1 h at 10 °C, and the precipitate that formed was filtered off, washed with water and methanol, and dried in air. Salt 2K-**6b** was obtained in a yield of 0.34 g (91%). The decomposition temperature was 146 °C (H_2O). Found (%): C, 10.27; K, 22.02; N, 31.83. $C_3K_2N_8O_8$. Calculated (%): C, 10.17; K, 22.07; N, 31.63. UV (H_2O), λ/nm (ε): 343 (28 800). ^{13}C NMR (DMSO-d_6), δ: 123.76 ($CC(NO_2)_2^-$); 131.04 ($NC(NO_2)_2^-$); 158.85 (C(5)). IR, ν/cm^{-1}: 1280, 1500, 1550 ($C(NO_2)_2^-$).

2-(1′-Nitro)acetonyl-5-trinitromethyltetrazole (8b). Ketone **3b** (1 g) was added with mixing to an HNO_3—H_2SO_4—H_2O (5 : 12 : 5, vol.) nitrating mixture (11 mL), and the mixture was stored at 20 °C for 20 h. The precipitate that formed was filtered off, washed with CF_3COOH, and dried in a vacuum desiccator over P_2O_5. Compound **8b** was obtained in a yield of 0.88 g (76%) as white crystals, m.p. 86 °C (from CF_3COOH). Found (%): C, 18.63; H 1.12; N, 34.91. $C_5H_4N_8O_9$. Calculated (%): C, 18.76; H, 1.76; N, 35.00. ^{1}H NMR (CD_3CN), δ: 2.48 (s, Me); 8.22 (s, CH). ^{13}C NMR (CD_3CN), δ: 27.12 (Me, $J_{C,H}$ = 131 Hz); 95.26 (CH, $J_{C,H}$ = 169 Hz); 120.4 ($C(NO_2)_3$); 153.9 (C(5)); 187.31 (C=O). IR, ν/cm^{-1}: 1365, 1610, 1590 ($C(NO_2)_3$; 1280, 1590 (NO_2 at CH); 1760 (C=O).

2-Nitromethyl-5-trinitromethyltetrazole (10b). A solution of nitroketone **8b** (1 g) in methanol (8 mL) was heated to 60 °C, water (8 mL) was added, and the mixture was stored for 14 h at 20 °C. The precipitate that formed was filtered off, washed with water, and dried in air. Compound **10b** was obtained in a yield of 0.83 g (96%) as colorless crystals, m.p. 83 °C (from $CHCl_3$). Found (%): C, 13.01; H, 0.87; N, 40.38. $C_3H_2N_8O_8$. Calculated (%): C, 12.95; H, 0.72; N, 40.29. UV (H_2O), λ/nm (ε): 313 (6600). IR, ν/cm^{-1}: 1360, 1605, 1620 ($C(NO_2)_3$); 1280, 1585 (NO_2 at CH); 1760 (C=O). ^{1}H NMR (CD_3CN), δ: 7.6 (s, CH_2). ^{13}C NMR (CD_3CN), δ: 81.49 (CH_2, $J_{C,H}$ = 169 Hz); 120.5 ($C(NO_2)_3$); 153.52 (C(5)). IR, ν/cm^{-1}: 1360, 1605, 1620 ($C(NO_2)_3$); 1280, 1585 (NO_2 at CH_2).

Bis(1-dinitromethyl-3-nitro-1,2,4-triazol-5-yl) (6j). A solution prepared from HNO_3 (d = 1.5 g cm^{-3}) (10 mL) and water (10 mL) was added dropwise with stirring to a solution of diketone **3j** (10 g) in H_2SO_4 (d = 1.83 g cm^{-3}) (120 mL) at 10 °C. The reaction mixture was stored for 1 h at 40 °C and for 1 h more at 20 °C. The precipitate that formed was filtered off and washed 2—3 times with a small amount of water. According to the UV spectroscopic data, the wet product contains 25% of the major substance **6j**. The yield based on the pure product was 48—55%.

Bis(1-dinitromethyl-3-nitro-1,2,4-triazol-5-yl) dipotassium salt (2K-6j). Sodium bicarbonate was carefully added with stirring to a suspension of non-purified compound **6j** (3 g) in water (30 mL) to pH of the medium 6—7. A hot solution of KCl (1 g) in water (5 mL) was added at 80 °C to the obtained solution of disodium salt **6j** filtered from undissolved admixtures. Analytically pure dipotassium salt **2K-6j** crystallized during slow cooling. The yield was 2.8 g (80%). The decomposition temperature was 254 °C (decomp. onset 221 °C). UV (H_2O), λ/nm (ε): 338 (33 600). IR, ν/cm^{-1}: 1240, 1287, 1488 ($C(NO_2)_2^-$); 1351, 1361, 1581 (NO_2 arom.). ^{13}C NMR (DMSO-d_6), δ: 130.7 ($C(NO_2)_2^-$), 144.7 (C(5)), 162.3 (C(3)).

Analytically pure bis(1-dinitromethyl-3-nitro-1,2,4-triazol-5-yl) (6j). Salt **2K-6j** (3 g) was added with stirring to H_2SO_4 (d = 1.83 g cm^{-1}) (15 mL), and the mixture was stored for 30 min at ~20 °C, during which the yellowish salt transformed into a colorless precipitate. The precipitate was filtered off, washed with CF_3COOH, and dried in air. Compound **6j** was obtained in a yield of 2 g (78%). Found (%): C, 16.69; H, 0.56; N, 38.90. $C_6H_2N_{12}O_{12}$. Calculated (%): C, 16.60; H, 0.46; N, 38.71. M.p. 164—165 °C (decomp., CF_3COOH). UV (H_2O), λ/nm (ε): 338 (33 400). IR, ν/cm^{-1}: 1315, 1590, 1615 ($CH(NO_2)_2$); 1357, 1570 (NO_2 arom.).

Bis(2-dinitromethyl-4-nitro-1,2,3-triazol-5-yl) (6o). Diketone **3o** (2.38 g) was dissolved in a mixture of 12 mL of HNO_3 (d = 1.5 g cm^{-1}) and 12 mL of H_2SO_4 (d = 1.83 g cm^{-1}), and the mixture was stored for 1 h with stirring for 20 °C, preventing the temperature increase. Then the reaction mixture was poured into 250 mL of a mixture of ice with water, washed 2—3 times (10 mL at once) of cool water, and dried for 10 min on the filter. According to the UV analysis data, the wet product contains 25—35% of the major substance **6o**. The yield based on the pure product was 55—75%. Pure **6o** (51%) was isolated through the dipotassium salt.

Analytically pure compound 6o was obtained similarly to compound **6j** through the corresponding dipotassium salt. Found (%): C, 16.71; H, 0.49; N, 38.84. $C_6H_2N_{12}O_{12}$. Calculated (%):

C, 16.60; H, 0.46; N, 38.71. UV (H_2O), λ/nm (ε): 339 (34 000). IR, ν/cm^{-1}: 1315, 1600, 1620 ($CH(NO_2)_2$); 1355, 1567 (NO_2 arom.). ^{13}C NMR (CD_3CN), δ: 107.2 ($CH(NO_2)_2$), 134.3 (C(5)), 154.2 (C(4)).

Bis(2-dinitromethyl-4-nitro-1,2,3-triazol-5-yl) dipotassium salt (2K-6o) was obtained similarly to compound **2K-6j**. The decomposition temperature was 172 °C (decomp. onset 152 °C). UV (H_2O), λ/nm (ε): 339 (34 000). IR, ν/cm^{-1}: 1258, 1485, 1508 ($C(NO_2)_2^-$; 1370, 1565 (NO_2 arom.). ^{13}C NMR (DMSO-d_6), δ: 134.4 ($C(NO_2)_2^-$), 132.0 (C(5)), 151.5 (C(4)).

1-Dinitromethyltetrazole (6c). Nitration conditions: HNO_3—H_2SO_4—H_2O (1 : 12 : 1), 20 °C, 4 h. Found (%): C, 13.75; H, 1.05; N, 48.36. $C_2H_2N_6O_4$. Calculated (%): C, 13.80; H, 1.16; N, 48.28.

Potassium salt K-6c. The decomposition temperature was 151 °C (decomp. onset 127 °C). UV (H_2O), λ/nm (ε): 344 (17 200). IR, ν/cm^{-1}: 1259, 1277, 1485, ($C(NO_2)_2^-$). ^{1}H NMR (DMSO-d_6), δ: 9.72 (s, 1 H). ^{13}C NMR (DMSO-d_6), δ: 127.6 ($C(NO_2)_2^-$), 147.3 (C(5), $J_{C,H}$ = 222 Hz).

2-Dinitromethyltetrazole (6d). Nitration conditions: HNO_3—H_2SO_4—H_2O (5 : 12 : 5), 40 °C, 1 h. Found (%): C, 13.72; H, 1.08; N, 48.21. $C_2H_2N_6O_4$. Calculated (%): C, 13.80; H, 1.16; N, 48.28.

Potassium salt K-6d. The decomposition temperature was 184 °C (decomp. onset 160 °C). UV (H_2O), λ/nm (ε): 341 (17 700). IR, ν/cm^{-1}: 1265, 1290, 1502 ($C(NO_2)_2^-$). ^{1}H NMR (DMSO-d_6), δ: 9.22, (s, 1 H). ^{13}C NMR (DMSO-d_6), δ: 130.6 ($C(NO_2)_2^-$), 153.5 (C(5), $J_{C,H}$ = 216 Hz).

1-Dinitromethyl-5-methyltetrazole (6e). Nitration conditions: HNO_3—H_2SO_4—H_2O (5 : 12 : 5), 55 °C, 40 min. Found (%): C, 19.22; H, 2.22, N, 44,76. $C_3H_4N_6O_4$. Calculated (%): C, 19.16; H, 2.14; N, 44.68.

Potassium salt K-6e. The decomposition temperature was 162 °C (decomp. onset 136 °C). UV (H_2O), λ/nm (ε): 345.5 (17 000). IR, ν/cm^{-1}: 1220, 1240, 1462, 1505 ($C(NO_2)_2^-$). ^{1}H NMR (DMSO-d_6), δ: 2.37 (s, 3 H). ^{13}C NMR (DMSO-d_6), δ: 8.1 (Me), 127.0 ($C(NO_2)_2^-$), 156.0 (C(5)).

2-Dinitromethyl-5-methyltetrazole (6f). Nitrating agent HNO_3 (d = 1.5 g cm^{-3}), 20 °C, 3.5 h. Found (%): C, 19.28; H, 2.03, N, 44.55. $C_3H_4N_6O_4$. Calculated (%): C, 19.16; H, 2.14; N, 44.68.

Potassium salt K-6f. The decomposition temperature was 174 °C (decomp. onset 154 °C). UV (H_2O), λ/nm (ε): 341 (17 300). IR, ν/cm^{-1}: 1225, 1268, 1495 ($C(NO_2)_2^-$). ^{1}H NMR (DMSO-d_6), δ: 2.75 (s, 3 H). ^{13}C NMR (DMSO-d_6), δ: 10.4 (Me), 130.6 ($C(NO_2)_2^-$), 162.5 (C(5)).

Bis(2-dinitromethyltetrazol-5-yl) (6g). Nitration conditions: HNO_3—H_2SO_4—H_2O (10 : 12 : 0), 35 °C, 2 h. UV (H_2O), λ/nm (ε): 338 (33 200). Found (%): C, 13.93; H, 0.54; N, 48.63. $C_4H_2N_{12}O_8$. Calculated (%): C, 13.88; H, 0.58; N, 48.56.

Dipotassium salt 2K-6g. The decomposition temperature was 210 °C (decomp. onset 140 °C). UV (H_2O), λ/nm (ε): 338 (33 400). IR, ν/cm^{-1}: 1260, 1505 ($C(NO_2)_2^-$). ^{13}C NMR (DMSO-d_6), δ: 131.0 ($C(NO_2)_2^-$), 155.6 (C(5)).

1-Dinitromethyl-3-nitro-1,2,4-triazole (6h).[7] Nitration conditions: HNO_3—H_2SO_4—H_2O (5 : 12 : 5), 40 °C, 1.5 ч. Found (%): C, 16.59; H, 0.88; N, 38.41. $C_3H_2N_6O_6$. Calculated (%): C, 16.52; H, 0.92; N, 38.54. UV (H_2O), λ/nm (ε): 344 (17 600).

Potassium salt K-6h. The decomposition temperature was 206 °C (decomp. onset 193 °C). UV (H_2O), λ/nm (ε): 344 (17 700). IR, ν/cm^{-1}: 1235, 1495 ($C(NO_2)_2^-$); 1308, 1370, 1578 (NO_2 arom.). ^{13}C NMR (DMSO-d_6), δ: 130.4 ($C(NO_2)_2^-$), 151.6 (C(5)); 162.7 (C(3)).

2-Dinitromethyl-5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one (6i). An HNO_3—H_2SO_4—H_2O (5 : 12 : 5) mixture, 20 °C, 72 h. M.p. 135 °C ($CHCl_3$). Found (%): C, 15.50; H, 0.93; N, 35.97. $C_3H_2N_6O_7$. Calculated (%): C, 15.39; H, 0.86; N, 35.90. UV (H_2O), λ/nm (ε): 350 (19 700). IR, ν/cm^{-1}: 1320, 1350, 1390, 1597 ($CH(NO_2)_2$); 1568 (NO_2 arom.). ^{13}C NMR (CH_3NO_2), δ: 103.5 ($CH(NO_2)_2$), 151.7 (C=O), 149.1 (C(3)).

Dipotassium salt 2K-6i. The decomposition temperature was 338 °C (decomp. onset 225 °C). UV (H_2O), λ/nm (ε): 350 (19 900). IR, ν/cm^{-1}: 1342, 1495 ($C(NO_2)_2^-$); 1318, 1522 (NO_2 arom.). ^{13}C NMR (DMSO-d_6), δ: 132.0 ($C(NO_2)_2^-$), $J_{C,N}$ = 28.4); 160.9 (C=O); 163.0 (C(5)).

Bis(5-azido-1-dinitromethyl-1,2,4-triazol-3-yl) (6k). Nitration conditions: HNO_3—H_2SO_4—H_2O (5 : 12 : 5), 20 °C, 24 h. Found (%): C, 16.84; H, 0.52; N, 52.65. $C_6H_2N_{16}O_8$. Calculated (%): C, 16.91; H, 0.47; N, 52.58. UV (H_2O), λ/nm (ε): 342 (32800). IR, ν/cm^{-1}: 1314, 1591, 1610 ($CH(NO_2)_2$), 2164 (N(3)).

Dipotassium salt 2K-6k. The decomposition temperature was 120—121 °C (decomp.). UV (H_2O), λ/nm (ε): 342 (32 800). IR, ν/cm^{-1}: 1240, 1260, 1487 ($C(NO_2)_2^-$); 2125 (N(3)).

1-Dinitromethyl-4-nitro-1,2,3-triazole (6l). Nitration conditions: HNO_3—H_2SO_4—H_2O (10 : 10 : 0), 20 °C, 40 min. UV (H_2O), λ/nm (ε): 345 (19 200). IR, ν/cm^{-1}: 1320, 1610, 1625 ($CH(NO_2)_2$); 1350, 1565 (NO_2 arom.). ^{1}H NMR (CD_3CN), δ: 8.75 (s, $CH(NO_2)_2$); 9.33 (s, 1 H, C(5)H). ^{13}C NMR (CD_3CN), δ: 105.3 ($CH(NO_2)_2$), $J_{C,H}$ = 187.7 Hz); 126.6 (C(5), $J_{C,H}$ = = 214.5 Hz); 154.0 (C(4)).

Potassium salt K-6l. The decomposition temperature was 178 °C (decomp. onset 165 °C). Found (%): C, 14.20; H, 0.36; K, 15.237; N, 32.92. $C_3HKN_6O_6$. Calculated (%): C, 14.07; H, 0.39; K, 15.26; N, 32.81. UV (H_2O), λ/nm (ε): 345 (19 300). IR, ν/cm^{-1}: 1225, 1465 ($C(NO_2)_2^-$); 1318, 1385, 1570 (NO_2 arom.). ^{1}H NMR (DMSO-d_6), δ: 9.82 (s, 1 H, C(5)H). ^{13}C NMR (DMSO-d_6), δ: 130.7 ($C(NO_2)_2^-$), 129.7 (C(5), $J_{C,H}$ = 210.8 Hz); 152.8 (C(4), $J_{C,H}$ = 7.4 Hz). ^{15}N NMR (DMSO-d_6), δ: 135.2 (N(1), $J_{N(1),H(5)}$ = 4.2 Hz); 7.2 (N(2)); 32.2 (N(3)); 25.6 (NO_2 arom.); 29.0 (NO_2 aliphat.).

2-Dinitromethyl-4-nitro-1,2,3-triazole (6m). Nitration conditions: HNO_3—H_2SO_4—H_2O (1 : 12 : 1), 20 °C, 2 h. UV (H_2O), λ/nm (ε): 342 (18 800). IR, ν/cm^{-1}: 1318, 1595, 1615 ($CH(NO_2)_2$); 1358, 1565 (NO_2 arom.). ^{1}H NMR (CD_3CN), δ: 8.76 (s, $CH(NO_2)_2$); 8.73 (s, 1 H, C(5)H). ^{13}C NMR (H_2SO_4), δ: 105.6 ($CH(NO_2)_2$), $J_{C,H}$ = 187.7 Hz); 134.0 (C(5), $J_{C,H}$ = = 212.7 Hz); 154.4 (C(4), $J_{C,H}$ = 9.2 Hz).

Potassium salt K-6m. The decomposition temperature was 229 °C (decomp. onset 222 °C). Found (%): C, 14.17; H, 0.45; K, 15.35; N, 32.74. $C_3HKN_6O_6$. Calculated (%): C, 14.07; H, 0.39; K, 15.26; N, 32.81. UV (H_2O), λ/nm (ε): 342 (19 000). IR, ν/cm^{-1}: 1255, 1292, 1490, 1510 ($C(NO_2)_2^-$); 1355, 1550 (NO_2 arom.). ^{1}H NMR (DMSO-d_6), δ: 9.67 (s, 1 H, C(5)H). ^{13}C NMR (DMSO-d_6), δ: 134.6 ($C(NO_2)_2^-$); 132.8 (C(5), $J_{C,H}$ = 207.2 Hz); 154.2 (C(4), $J_{C,H}$ = 8.3 Hz). ^{15}N NMR (DMSO-d_6), δ: 29.5 (N(1), $J_{N(1),H(5)}$ = 11.9 Hz); 136.8 (N(2)); 44.5 (N(3)); 26.8 (NO_2 arom.); 28.1 (NO_2 aliphat.).

2-Dinitromethyl-4,5-dinitro-1,2,3-triazole (6n). Nitration conditions: HNO_3—H_2SO_4—H_2O (10 : 10 : 0), 10 °C, 4 h. UV (H_2O), λ/nm (ε): 337 (17 400).

Potassium salt K-6n. The decomposition temperature was 191 °C (decomp. onset 177 °C). UV (H_2O), λ/nm (ε): 337

(17 500). Found (%): C, 11.88; K, 12.86; N, 32.73. $C_3KN_7O_8$. Calculated (%): C, 11.96; K, 12.98; N, 32.56. IR, ν/cm^{-1}: 1260, 1290, 1485, 1516 ($C(NO_2)_2^-$); 1360, 1558, 1577 (NO_2 arom.). ^{1}H NMR (DMSO-d_6), δ: 134.4 ($C(NO_2)_2^-$); 144.8 (C(4), C(5)).

1-Dinitromethyl-4-nitropyrazole (6p). Nitration conditions: HNO_3—H_2SO_4—H_2O (5 : 12 : 5), 20 °C, 20 h. UV (H_2O), λ/nm (ε): 347 (17 550). ^{13}C NMR (H_2SO_4), δ: 103.9 (d, $(CH(NO_2)_2)$, $J_{C,H}$ = 189.6 Hz); 137.3 (d, C(4), $J_{C,H}$ = 212.5 Hz); 137.2 (C(5)); 138.9 (C(3)).

Potassium salt K-6p. The decomposition temperature was 165 °C (decomp. onset 192 °C). Found (%): C, 18.92; H, 0.87; K, 15.48; N, 27.55. $C_4H_2KN_5O_6$. Calculated (%): C, 18.83; H, 0.79; K, 15.32; N, 27.44. UV (H_2O), λ/nm (ε): 347 (17 700). IR, ν/cm^{-1}: 1252, 1462, ($C(NO_2)_2^-$); 1329, 1520 (NO_2 arom.). ^{1}H NMR (DMSO-d_6), δ: 8.75 (s, 1 H, C(3)H); 9.28 (s, 1 H, C(5)H). ^{13}C NMR (DMSO-d_6), δ: 133.8 ($C(NO_2)_2^-$); 135.9 (C(5), $J_{C,H}$ = 201.6); 136.1 (dd, C(4), $J_{C,H}$ = 5.5 Hz, $J_{C,H}$ = 6.5 Hz); 137.1 (dd, C(3), $J_{C,H}$ = 197.9 Hz, $J_{C,H}$ = 6.5 Hz).

1-Dinitromethyl-3,4-dinitropyrazole (6q). Nitration conditions: HNO_3—H_2SO_4—H_2O (5 : 12 : 5), 20 °C, 20 h. UV (H_2O), λ/nm (ε): 343 (17 800). ^{1}H NMR ($CDCl_3$), δ: 8.75 (s, 1 H, $(CH(NO_2)_2)$; 9.2 (s, 1 H, C(5)H)). ^{13}C NMR (H_2SO_4), δ: 106.4 (d, $CH(NO_2)_2$, $J_{C,H}$ = 187.7 Hz); 129.4 (d, C(4), $J_{C,H}$ = 3.7 Hz); 136.6 (d, C(5), $J_{C,H}$ = 210.8 Hz); 149.5 (C(3)).

Potassium salt K-6q. The decomposition temperature was 200 °C (decomp. onset 170 °C). Found (%): C, 16.07; H, 0.42; K, 13.22; N, 27.90. $C_4HKN_6O_8$. Calculated (%): C, 16.00; H, 0.34; K, 13.02; N, 28.00. UV (H_2O), λ/nm (ε): 343 (17 900). IR, ν/cm^{-1}: 1215, 1500, ($C(NO_2)_2^-$); 1338, 1380, 1543, 1560, 1520 (NO_2 arom.). ^{1}H NMR (DMSO-d_6), δ: 9.82 (s, 1 H, C(5)H). ^{13}C NMR (DMSO-d_6), δ: 133.0 ($C(NO_2)_2^-$); 126.8 (d, C(4), $J_{C,H}$ = 4.6 Hz); 139.1 (d, C(5), $J_{C,H}$ = 207.1 Hz); 148.3 (d, C(3), $J_{C,H}$ = 7.4 5 Hz).

1-Dinitromethylimidazole (6r). Nitration conditions: HNO_3—H_2SO_4—H_2O (5 : 12 : 5, vol.), 60—70 °C, 1.5 h. The decomposition temperature was 133 °C (decomp. onset 90 °C). Found (%): C, 27.82; H, 2.45; N, 32.46. $C_4H_4N_4O_4$. Calculated (%): C, 27.92; H, 2.34; N, 32.55. UV (H_2O), λ/nm (ε): 347 (13 700). IR, ν/cm^{-1}: 1220, 1260, 1495 ($C(NO_2)_2^-$).

Potassium salt K-6r. Found (%): C, 27.82; H, 2.45; N, 32.46. $C_4H_4N_4O_4$. Calculated (%): C, 27.92; H, 2.34; N, 32.55. UV (H_2O), λ/nm (ε): 358 (13 700). IR, ν/cm^{-1}: 1210, 1240, 1470 ($C(NO_2)_2^-$).

1-Dinitromethyl-4-nitroimidazole (6s). Nitration conditions: HNO_3—H_2SO_4—H_2O (5 : 12 : 5), 50 °C, 2 h. Found (%): C, 22.15; H, 1.29; N, 32.23. $C_4H_3N_5O_6$. Calculated (%): C, 22.13; H, 1.39; N, 32.26. UV (H_2O), λ/nm (ε): 351 (16 700).

Potassium salt K-6s. The decomposition temperature was 193 °C (decomp. onset 169 °C). UV (H_2O), λ/nm (ε): 351 (16800). IR, ν/cm^{-1}: 1210, 1477 ($C(NO_2)_2^-$); 1355, 1566 (NO_2 arom.). ^{1}H NMR (DMSO-d_6), δ: 8.12 (s, 1 H); 8.70 (s, 1 H).

1-Dinitromethyl-4,5-dinitroimidazole (6t). Nitration conditions: HNO_3—H_2SO_4—H_2O (5 : 12 : 5), 50 °C, 2 h. Found (%): C, 16.04; H, 0.42; K, 12.93; N, 27.91. $C_4HKN_6O_8$. Calculated (%): C, 16.00; H, 0.34; K, 13.02; N, 28.00. UV (H_2O), λ/nm (ε): 347 (15 500).

Potassium salt K-6t. The decomposition temperature was 138 °C (decomp. onset 103 °C). UV (H_2O), λ/nm (ε): 347 (15700). IR, ν/cm^{-1}: 1249, 1479 ($C(NO_2)_2^-$); 1350, 1550 (NO_2 arom.).

***N*-(Acetonyl)succinimide (12a).** A solution of KOH (14 g) in MeOH (100 mL) was added to a solution of succinimide (25 g, 0.25 mol) in methanol (200 mL), and the mixture was stirred for 10 min and cooled to 20 °C, and bromoacetone (25 mL, 0.3 mol) was added for 30 min, maintaining the temperature at 20—25 °C. The reaction mixture was stored at this temperature for 30 min more, and KBr that precipitated was filtered off. The solution was evaporated *in vacuo*, acetone (200 mL) was added, and precipitated KBr was filtered off. The solvent was evaporated, ether (100 mL) was added to the semicrystalline mixture that formed, and the precipitate was filtered off, washed with ether, and recrystallized from MeOH—CCl_4 (1 : 3). Compound **12a** was obtained in a yield of 22 g (56%), m.p. 72—73 °C. Found (%): C, 54.30; H, 5.94; N, 9.12. $C_7H_9NO_3$. Calculated (%): (C); 54.19; H, 5.85; N, 9.03. ^{1}H NMR ($CDCl_3$), δ: 2.2 (s, 3 H); 2.78 (s, 4 H); 4.3 (s, 2 H).

***N*-(Acetonyl)phthalimide (12b).** Bromoacetone (21 mL, 0.25 mol) was added to potassium phthalimide (37 g, 0.2 mol) in DMF (200 mL), maintaining the temperature at 20—25 °C. The reaction mixture was stored at this temperature for 1 h and poured into water. The precipitate that formed was filtered off and recrystallized from MeOH—CCl_4 (1 : 3). Compound **12b** was obtained in a yield of 0.31 g (76%), m.p. 120 °C (*cf.* Ref. 40: m.p. 118 °C).

***o*-Sulfobenzoic acid *N*-(acetonyl)imide (12c).** Bromoacetone (10 mL, 0.12 mol) was added to a suspension of saccharine sodium salt (20.5 g, 0.1 mol) in MeOH (400 mL), and the mixture was heated to 60 °C and stirred to a homogeneous solution. The reaction mixture was cooled and evaporated, acetone (400 mL) was added, and precipitated NaBr was filtered off. Acetone was removed *in vacuo*, and the residue was recrystallized from $CHCl_3$—MeOH (10 : 1). Compound **12c** was obtained in a yield of 18 g (75%) m.p. 142 °C (*cf.* Ref. 41: m.p. 143 °C).

Synthesis of *N*-dinitromethylimides of acids 11a—c (general procedure). *N*-Acetonyl derivative **12a—c** (1 g) was dissolved in a mixture of CF_3COOH (6 mL) and HNO_3 (d = 1.51 g cm^{-1}, 4 mL). The reaction mixture was stored for 24—90 h at ~20 °C and poured into ice. The precipitate formed was filtered off, washed with water, and dried over P_2O_5. *N*-Dinitromethylimide potassium salts were obtained by the treatment of solutions of *N*-dinitromethylimides in nitromethane or acetonitrile with potassium acetate in methanol. The yields were 80—90%.

***N*-Dinitromethylsuccinimide (11a).** Synthesis conditions: 20—25 °C, 70 h. M.p. 154—155 °C (MeOH). Found (%): C, 29.48; H, 2.41; N, 20,38. $C_8H_4KN_3O_7S$. Calculated (%): C, 29.57; H, 2.48; N, 20.69. UV (H_2O), λ/nm (ε): 353 (15 700). IR, ν/cm^{-1}: 1329, 1370, 1587, 1612 ($CH(NO_2)_2$); 1742 (C=O). ^{1}H NMR (DMSO-d_6), δ: 3.05 (s, 4 H); 8.08 (s, 1 H). ^{13}C NMR (DMSO-d_6), δ: 29.6 (CH_2); 104.9 ($CH(NO_2)_2$); 175.5 (C=O).

Potassium salt K-11a. UV (H_2O), λ/nm (ε): 353 (15 700). IR, ν/cm^{-1}: 1235, 1500 ($C(NO_2)_2^-$); 1728 (C=O). ^{13}C NMR (DMSO-d_6), δ: 29.2 (CH_2); 126.1 ($C(NO_2)_2^-$); 177.0 (C=O).

***N*-Dinitromethylphthalimide (11b).** Synthesis conditions: 20—25 °C, 90 h. M.p. 135—137 °C (MeOH). Found (%): C, 43.15; H, 2.13; N, 16.66. $C_9H_5N_3O_6$. Calculated (%): C, 43.04; H, 2.01; N, 16.73. UV (H_2O), λ/nm (ε): 352 (15 200). IR, ν/cm^{-1}: 1309, 1320, 1580, 1602 ($CH(NO_2)_2$); 1742 (C=O). ^{1}H NMR (DMSO-d_6), δ: 7.88 (s, 4 H); 8.02 (m, 4 H). ^{13}C NMR (DMSO-d_6), δ: 109.5 ($CH(NO_2)_2$); 124.9, 130.7, 136.4, 164.7 (C=O).

Potassium salt K-11b. UV (H_2O), λ/nm (ε): 352 (15 200). IR, ν/cm^{-1}: 1215, 1482 ($C(NO_2)_2^-$); 1721 (C=O). ^{13}C NMR (DMSO-d_6), δ: 124.5 ($C(NO_2)_2^-$); 124.0, 131.1, 135.5, 166.1 (C=O).

***o*-Sulfobenzoic acid *N*-(dinitromethyl)imide (11c).** Synthesis conditions: 20—25 °C, 24 h. M.p. 120—122 °C (MeOH). UV (H_2O), λ/nm (ε): 349 (15 000). IR, ν/cm^{-1}: 1580, 1607 ($CH(NO_2)_2$); 1760 (C=O). ^{1}H NMR (DMSO-d_6), δ: 8.04 (s, 1 H); 8.16 (m, 4 H). ^{13}C NMR (DMSO-d_6), δ: 102.7 ($CH(NO_2)_2$); 156.8 (C=O).

Potassium salt K-11c. Found (%): C, 29.65; H, 1.32; K, 12.13; N, 12.84; S, 9.95. $C_8H_4KN_3O_7S$. Calculated (%): C, 29.54; H, 1.24; K, 12.02; N, 12.92; S, 9.86. UV (H_2O), λ/nm (ε): 349 (15 000). IR, ν/cm^{-1}: 1221, 1480 ($C(NO_2)_2^-$); 1726, 1750 (C=O).

1-Dinitromethyl-1,2-dicarboethoxyhydrazine potassium salt (K-13). ***A.*** Diketone **14a** (see Ref. 30) (1 g) was added with stirring for 5 min at 0—5 °C to a mixture of 6 mL of CF_3COOH and 4 mL of HNO_3 (d = 1.5 g cm^{-3}). Thirty minutes after the dissolution of the all amount of the substance, the cooling bath was removed and the reaction mixture was stored for 17 h at ~20 °C. An aliquot of the reaction mixture (0.5 mL) was diluted with water to 250 mL, potassium acetate (0.5—1 g) was added, and the amount of compound **13** was determined spectrophotometrically. The yield was 48%. The reaction mixture was poured into 50 g of ice-cold water, and the mixture was extracted with ether (2×20 mL). Water (2 mL) was added to the extract, ether was evaporated, and the extract was neutralized with potash to pH = 8. After cooling, crystals of salt **K-13** precipitated from the obtained solution were filtered off, washed with ice-cold water, and recrystallized from water. Found (%): C, 26.52; H, 3.57; K, 12.40; N, 17.51. $C_7H_{11}KN_4O_8$. Calculated (%): C, 26.42; H, 3.48; K, 12.28; N, 17.60. UV (H_2O), λ/nm (ε): 359 (14 800). IR, ν/cm^{-1}: 1190, 1220, 1250, 1485 ($C(NO_2)_2^-$); 1700 and 1743 (C=O); 3290 (NH); the IR spectrum is identical to that of the authentic sample obtained by an earlier described procedure.[42]

B. Under analogous conditions, the nitration of ketoester **14b** (see Ref. 30) affords, according to the UV analysis results, compound **13** (26%). Salt **K-13** was isolated similalrly.

Maleic acid *N*-dinitromethylhydrazide (16). Nitric acid (d = = 1.5 g cm^{-3}) (8 mL) was added dropwise with cooling (0—5 °C) and stirring to a solution of 2-(3-oxobutyl)-6-hydroxy-3(2*H*)-pyridazinone **15** (2 g) (see Ref. 43) in H_2SO_4 (d = 1.84 g cm^{-3}) (11 mL). The reaction mixture was stored for 4 days at ~20 °C, then poured into 50 g of ice-cold water, extracted with ether (5×20 mL), and evaporated. The residue was dissolved in a saturated aqueous solution of potassium acetate (2 mL). After cooling, the precipitated crystals of potassium salt **K-16** were filtered off and recrystallized from water. The yield of salt **K-16** was 0.27 g (10%). The decomposition temperature was 185 °C (decomp. onset 137 °C). Found (%): C, 23.70; H, 1.26; K, 15.43; N, 22.21. $C_5H_3KN_4O_6$. Calculated (%): C, 23.63; H, 1.19; K, 15.38; N, 22.04. IR, ν/cm^{-1}: 1247, 1290, 1470 ($C(NO_2)_2^-$); 1673 (C=O); 3515, 3635 (OH); 2550—3000 (NH amide). UV (H_2O), λ/nm (ε): 354.5 (18 000).

Procedure of determination of the acidity of *N*-dinitromethyl compounds. The equations for mono- and dibasic acids were used for the calculation.[36] An aliquot part of an aqueous solution of *N*-dinitromethylazole salt was 100-fold diluted with water, and the absorbance was measured spectrophotometrically. An analogous aliquot part was 100-fold diluted with H_2SO_4 solutions of such a concentration at which the absorbance decreases ~2-fold, and the absorbance was determined. Then the normality of this solution was determined by titration with NaOH. Based on these data, pK_a was calculated by the equations for mono- and dibasic acids,[36] having determined H_- by the Boyd table.[35] The concentrations of measured solutions ranged from 10^{-4} to 10^{-5} mol L^{-1}. The Lambert—Beer law was fulfilled.

Kinetic studies. For kinetic studies *N*-acetonylazoles were purified by successive crystallization from methanol and dichloroethane, and *N*-dinitromethylazole potassium salts were crystallized from water. Then all samples were dried *in vacuo* over P_2O_5. Potassium nitrate was prepared according to a procedure described earlier,[44] providing the purification from KNO_2. In all experiments on the deuterioexchange and nitration kinetics, the temperature was maintained at 24±0.5 °C with a thermostat. The results obtained are given in Table 1.

Dynamics of signal changing in the ^{1}H NMR spectrum in the nitration of 2-acetonyl-5-nitrotetrazole (**3a**) in 89.2% H_2SO_4 with potassium nitrate (1.15 mol L^{-1}): the signals of the MeCO (δ 2.6) and CH_2 (δ 6.03) groups disappear, while the signals of AcOH (see Ref. 45) (δ 2.2 for the non-protonated form (~5—10%) and 2.66 for the protonated form (90—95%)) and the signal of the $CH(NO_2)_2$ group (δ 8.9) appear.

In addition, 20 min after the beginning of the reaction, the total signal intensity of the protons of the Me groups in ketone **3a** and AcOH decreases by 20% due to the nitration at the Ne group to form dinitromethane. Since the latter is unstable in this mixture, its presence can indirectly be judged from the change in the absorbance of an aliquot of the reaction mixture upon the nitration of ketone **3a**: the difference in the absorbance at pH = 0—1, when compound **6a** is completely dissociated and dinitromethane is suppressed, and at pH = 6—7, when both substances are dissociated, is 10—15%.

Deuterioexchange of methyl and methylene groups in *N*-acetonylazoles occurred by 93% due to the accumulation in a medium of H^+ and retarded at the end. For this reason, the deuteriosubstitution rate constants were calculated at the deuteriosubstitution "depth" not more than 75%. The concentrations of ketones in D_2SO_4 were 0.35 mol L^{-1}. The equations of logarithmic anamorphoses of the experimental curves on the kinetics of proton deuterioexchange obtained by the least-squares processing are given in Table 4.

For studying the nitration kinetics of *N*-acetonylazoles, the reaction solutions were prepared prior to the reaction. To create a homogeneous medium, prior to the reaction the overall amount of H_2SO_4 was divided into two portions: KNO_3 was dissolved in one portion, the nitrated object was dissolved in another portion, and then both solutions were poured together.

To observe the 2-nitromethyl-5-nitrotetrazole anion **10a** in the nitration of **3a**, aliquots of the reaction mixture were poured into 200 mL of a 10% solution of Na_2CO_3. The amount of anions of 1-dinitromethyl-4-nitroimidazole **6s** and 1-dinitromethyl-4-nitropyrazole **6p** was determined spectrophotometrically upon pouring the reaction solution (0.5 mL) into 100 mL of water containing potassium acetate (2 g, pH = 3). The amount of anions of other *N*-dinitromethylazoles with higher acidity was determined upon pouring into water.

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