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Reactions of 1,4-Dinitroimidazoles with Hydrazines

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Abstract: Reaction of 2-methyl-1,4-dinitroimidazole with hydrazine results in expansion of the imidazole ring and formation of the 1,2,4-triazine derivative. Reaction of 1,4-dinitroimidazole with *N*-aminomorpholine yields 1-(*N*-morpholino)-4-nitroimidazole, by degenerative transformation of the imidazole ring. Treatment of 1,4-dinitroimidazoles with t-butoxycarbonylhydrazine results in the break down of the imidazole ring and formation of glyoxal dihydrazone derivatives. Structures of representative heterocyclic products were determined by X-ray analysis.

INTRODUCTION

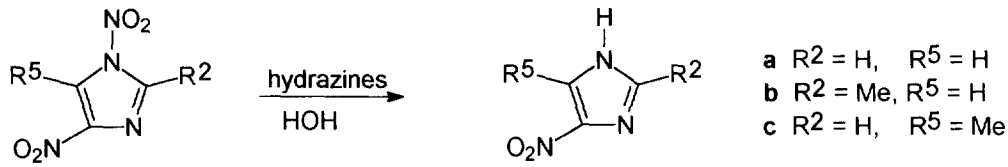
1-Amino-4-nitroimidazoles are hardly known. Only 1-amino-2-methyl-4-nitroimidazole (by the reaction of 2-methyl-4(5)-nitroimidazole sodium salt with *O*-diphenylphosphinylhydroxylamine), has been reported.[1] Attempts to aminate other 4(5)-nitroimidazoles using hydroxylamine-*O*-sulfonic acid, *O*-arenesulfonylhydroxylamines or chloramine proved unsuccessful. Chemical properties of the amino group in 1-amino-4-nitroimidazoles and in 4-amino-1,2,4-triazoles should be similar. The pK_a values of 4(5)-nitroimidazole and of 1,2,4-triazole are very similar.[2] Hence, 1-amino-4-nitroimidazoles (like 4-amino-1,2,4-triazoles) might be used as nucleophilic aminating reagents[3] or in transformations of aldehydes to nitriles. In the present work a new approach to obtain 1-amino-4-nitroimidazoles and their *N*-mono or *N,N*-disubstituted derivatives by the reaction of 1,4-dinitroimidazoles with hydrazines is presented. The work was instigated by our earlier results proving that 1,4-dinitroimidazoles react easily with several *N*-centered nucleophiles, yielding, in optimal conditions, precisely defined products in high yields.[4-11]

Very little information on the reactions of nitroimidazoles with hydrazines can be found in literature. A few examples describe the replacement of the halogen atom in halogenonitroimidazoles by hydrazines.[12,13] Furthermore, Goldman[14] proved that reaction of metronidazole or isometronidazole with hydrazine results in

imidazole ring decomposition, followed by formation of a mixture of glyoxal dihydrazone, ethanolamine nitrite and 3,5-diamino-1,2,4-triazole.

RESULTS OF THE EXPERIMENTS

The behavior of 1,4-dinitroimidazoles **1a-c** in the presence of hydrazines, in aqueous or aqueous-organic medium at 25°C was investigated. Results of the reaction depended both on the identities of substituents R^2 and R^5 and on experimental conditions. Often the 4(5)-nitroimidazoles **2a-c**, formed by 1-denitration of **1a-c**, were the only isolated compounds (Scheme 1).

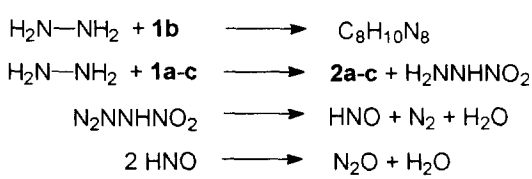


Scheme 1.

Some of the reactions led to interesting products and the mode of their formation was rationalised considering the results of the experiments presented here or cited from the literature.

Reactions of 1,4-dinitroimidazoles with hydrazine

1,4-Dinitroimidazoles **1a-c** were treated with an aqueous solution of hydrazine at 25° C, maintaining pH 7.5-8.0. From reaction of hydrazine with **1b**, a product **3b** of the formula $C_8H_{10}N_8$, was isolated in 64% yield. In other cases, formation of **2a-c** and the liberation of nitrous oxide was the major observation (Scheme 2).



Scheme 2.

Product **3b** sublimes at 250°C under 2 mm Hg. It dissolves in aqueous solutions of strong acid or alkali and is insoluble in typical organic solvents, except for hot DMSO. Product **3b** forms stable salts crystallising from concentrated aqueous solutions of strong acids (hydrochloric or *p*-toluenesulfonic acids). The UV spectrum of **3b** hydrochloride in water implies the presence of three forms of **3b**: neutral (λ_{max}=306 nm), cationic (λ_{max}=307 nm) and anionic (λ_{max}=401 nm) whereof proportions change with pH. In neutral medium, the anionic form is practically not observed. Molar absorption coefficients of each of these forms exceed 10 000; the cation absorbs most (ε_M over 16000). Due to the very poor solubility of the neutral form in water, these data are approximate. Similarly, the ^{1}H-NMR spectrum of free base **3b** recorded in DMSO-d_6

is difficult to interpret. Thus, the ^{1}H-NMR spectra of **3b** hydrochloride were recorded in perdeuterated methanol and of **3b** *p*-toluenesulfonate in DMSO-d_6. Unfortunately the analysis of these spectra did not result in definition of the **3b** structure.

Analysis of the MS spectra of free base **3b** was not conclusive. In the EI MS spectrum of **3b**, strong peaks of molecular ions of m/e 218 were observed, as well as strong peaks of ions of lower m/e (109). In addition, strong ion peaks of m/e 149 and 84 appeared. The only intensive peaks in the MS CI spectra were the ones of m/e 219 and 111, which correspond to the ion peaks 218 and 109 in the EI MS spectrum. These analyses suggested that free base **3b,** in the gaseous phase, is of a symmetrical structure, with two identical fragments of formula $C_4H_5N_4$ (weights 109) linked together by a relatively weak N-N bond.

The structure of **3b**, as its salt, was determined by subjecting a single crystal of **3b** *p*-toluenesulfonate, obtained from aqueous solution, to X-ray analysis. The salt crystallizes as the dihydrate. The results of the X-ray analysis are presented in Fig. 1 and in Tables 1- 3.

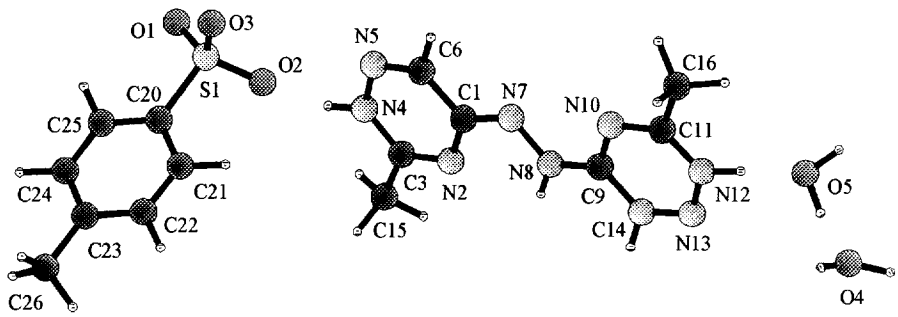


Figure 1. X-Ray projection of **3b**

Table 1. Physical Properties and Parameters for Data Collection and Refinement of **3b**.

Formula	$C_{15}H_{22}N_8O_5S$	V = 1004.5(2) Å^3, Z = 2, $D_{calc.}$ = 1.410 g/cm^3	
Color; habit	yellow cube	F(000)	448
Crystal dimensions	0.25x0.25x0.25 mm	No. of measured reflections	4373
Mol wt.	426.5	No. of independent reflections	3569
Crystal system	Triclinic	No. of observed reflections	1846
Space group	$P\bar{1}$	R	0.046
a = 7.982 (1), b= 8.401(1), c = 16.165(1) Å		R_W	0.062
α = 77.17(1), β = 82.98(1), γ = 72.19(1)°		$w^{-1} = \sigma^2(F) + 0.0008F^2$	

Table 2. Bond Lengths (Å) in Compound **3b**.

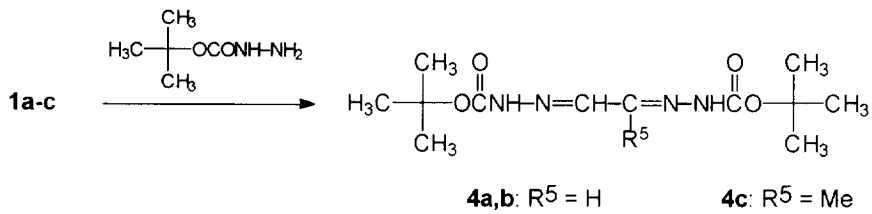
Bond	Length	Bond	Length
S(1)-O(1)	1.444(3)	S(1)-O(2)	1.453(3)
S(1)-O(3)	1.463(3)	S(1)-C(20)	1.762(5)
N(4)-N(5)	1.367(5)	N(4)-C(3)	1.336(5)
N(2)-C(1)	1.369(5)	N(2)-C(3)	1.299(5)
C(11)-N(12)	1.329(5)	C(11)-N(10)	1.325(5)
C(11)-C(16)	1.479(5)	N(7)-N(8)	1.395(4)
N(7)-C(1)	1.301(5)	N(13)-N(12)	1.349(4)
N(13)-C(14)	1.295(5)	N(8)-C(9)	1.320(5)
N(10)-C(9)	1.355(5)	N(5)-C(6)	1.275(6)
N(10)-C(9)	1.425(5)	C(1)-C(6)	1.446(5)
C(20)-C(21)	1.393(7)	C(20)-C(25)	1.385(6)
C(21)-C(22)	1.361(8)	C(25)-C(24)	1.378(8)
C(23)-C(24)	1.367(9)	C(23)-C(26)	1.509(9)
C(23)-C(22)	1.391(7)	C(3)-C(15)	1.492(6)

Table 3. Bond Angles (deg.) in Compound **3b**.

Atoms	Bond Angle	Atoms	Bond Angle
O(1)-S(1)-O(2)	113.0(2)	O(1)-S(1)-O(3)	113.2(2)
O(2)-S(1)-O(3)	111.2(2)	O(1)-S(1)-C(20)	106.4(2)
O(2)-S(1)-C(20)	106.2(2)	O(3)-S(1)-C(20)	106.2(2)
N(5)-N(4)-C(3)	123.5(3)	C(1)-N(2)-C(3)	116.4(3)
N(12)-C(11)-N(10)	122.4(3)	N(12)-C(11)-C(16)	118.4(3)
N(10)-C(11)-C(16)	119.2(3)	N(8)-N(7)-C(1)	114.0(3)
N(12)-N(13)-C(14)	116.0(3)	C(11)-N(12)-N(13)	123.7(3)
N(7)-N(8)-C(9)	118.0(3)	C(11)-N(10)-C(9)	116.0(3)
N(4)-N(5)-C(6)	114.7(3)	N(8)-C(9)-N(10)	119.4(3)
N(8)-C(9)-C(14)	120.2(3)	N(10)-C(9)-C(14)	120.4(3)
N(2)-C(1)-N(7)	124.8(3)	N(2)-C(1)-C(6)	118.4(3)
N(7)-C(1)-C(6)	116.8(3)	S(1)-C(20)-C(21)	119.5(3)
S(1)-C(20)-C(25)	121.8(4)	C(21)-C(20)-C(25)	118.7(5)
N(5)-C(6)-C(1)	123.6(4)	C(20)-C(21)-C(22)	119.8(4)
C(20)-C(25)-C(24)	119.9(5)	C(24)-C(23)-C(26)	122.1(5)
C(24)-C(23)-C(22)	117.2(5)	C(26)-C(23)-C(22)	120.7(5)
C(25)-C(24)-C(23)	122.1(5)	N(13)-C(14)-C(9)	121.4(4)
N(4)-C(3)-N(2)	123.4(4)	N(4)-C(3)-C(15)	116.3(4)
N(2)-C(3)-C(15)	120.3(3)	C(21)-C(22)-C(23)	122.2(5)

Reactions of 1,4-dinitroimidazoles with monosubstituted hydrazines

The reactions of **1a-c** with phenylhydrazine, 2-hydroxyethylhydrazine, formylhydrazine and *t*-butoxycarbonylhydrazine (*t*-BocNHNH$_2$) were investigated. In most of the reactions carried out in water, the evolution of nitrous oxide and the formation of **2a-c** were observed, and few other products were isolated. Special attention was paid to the reaction of 1,4-dinitroimidazoles with *t*-butoxycarbonylhydrazine, carried out in the aqueous-dioxane solution, which led to interesting results. We expected, that the *t*-butoxycarbonyl group would prevent the formation of triazine derivatives by lowering the nucleophilicity of nitrogen atom, but would not hinder the recyclization of the intermediate to the imidazole ring, from which it was to be easily removed by acid hydrolysis. Unexpectedly the reaction yielded the di(*t*-butoxycarbonylhydrazones) of glyoxal (65% **4a** from **1a**, 43% **4b** from **1b**) or methylglyoxal (58% **4c** from **1c**) respectively (Scheme 3).

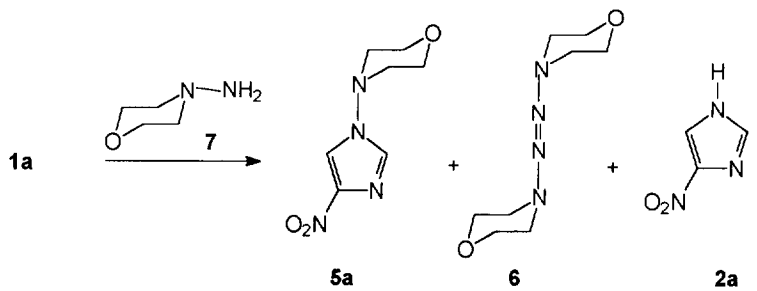


Scheme 3.

The product structures were determined by spectroscopy and confirmed by comparing the products with authentic samples.

Reactions of 1,4-dinitroimidazoles with *N,N*-disubstituted hydrazines

Reactions of **1a-c** with *N,N*-dimethylhydrazine, *N*-aminomorpholine and *N*-aminopiperidine in water solution at 25°C yielded mixtures containing considerable quantities of **2a-c**. Dinitroimidazole **1a** reacted with *N*-aminomorpholine in aqueous solution of pH 7.5-8.0 to give three products (Scheme 4).



Scheme 4.

The solid reaction products included azomorpholine (**6**, 25%), the expected 1-(*N*-morpholino)-4-nitroimidazole (**5a**, 30%) and 4(5)-nitroimidazole (**2a**, 32%). Product **5a** was subjected to elemental and spectral analyses. The ^{1}H-NMR spectrum of **5a** recorded in DMSO-d_6 consists of a multiplet (3.0-3.8 ppm)

of signals due to the morpholine ring methylene groups and of two doublets (8.00 and 8.85 ppm, J = 1.56 Hz), characteristic of the signals of imidazole protons in 1-substituted 4-nitroimidazoles. A single crystal of **5a** obtained from the aqueous solution was subjected to X-ray analysis which confirmed the proposed structure. The results of the experiments are presented in Fig. 2 and in Tables 4-6.

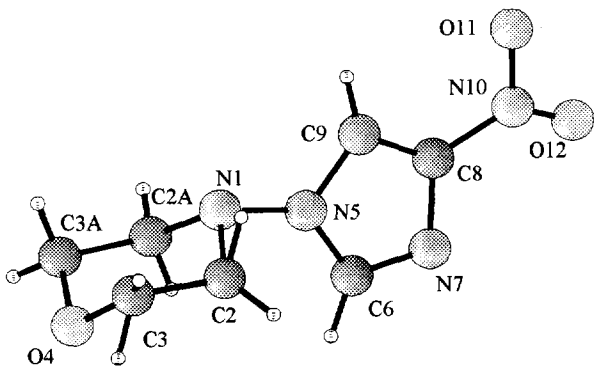


Fig. 2. X-Ray projection of 1-(*N*-morpholino)-4-nitroimidazole (**5a**)

Table 4. Physical Properties and Parameters for Data Collection and Refinement of **5a**.

Formula	$C_7H_{10}N_4O_3$	V	876.4(2) Å^3
Color, habit	Colorless rhombohedron	Z	4
Crystal dimensions	0.2x0.2x0.25 mm	$D_{calc.}$	1.502 g/cm^3
Mol. wt.	198.2	F(000)	416
Crystal system	Orthorhombic	No. of measured reflections	1910
Space group	Pnam	No. of independent reflections	1381
a	18.912(1) Å	No. of observed reflections	577 (F > 4.0σ(F))
b	6.919(1) Å	*Agreement factors*	
c	6.698(1) Å	R	0.063
		R_w	0.069
		$w^{-1}=\sigma^2(F)+0.0008F^2$	

Table 5. Bond Lengths (Å) in Compound **5a**.

Bond	Length	Bond	Length
N(1)-C(2)	1.469(4)	O(12)-N(10)	1.231(11)
N(1)-N(5)	1.439(14)	O(11)-N(10)	1.046(10)
C(2)-C(3)	1.511(5)	N(1)-C(2A)	1.469(4)
O(4)-C(3A)	1.410(5)	C(3)-O(4)	1.410(5)
C(8)-N(7)	1.411(9)	C(8)-C(9)	1.333(12)
C(8)-N(10)	1.430(12)	N(7)-C(6)	1.304(12)
C(9)-N(5)	1.371(16)	N(5)-C(6)	1.378(16)

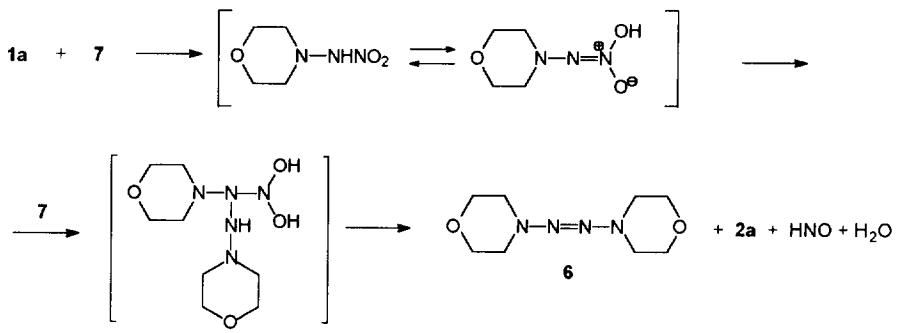
Table 6. Bond Angles (deg.) in Compound **5a**.

Atoms	Bond Angle	Atoms	Bond Angle
C(2)-N(1)-N(5)	103.6(3)	C(2)-N(1)-C(2A)	110.7(3)
N(5)-N(1)-C(2A)	103.6(3)	N(1)-C(2)-C(3)	107.3(3)
C(2)-C(3)-O(4)	111.4(4)	C(3)-O(4)-C(3A)	109.7(4)
C(9)-C(8)-N(7)	112.9(6)	N(7)-C(8)-N(10)	116.5(6)
C(9)-C(8)-N(10)	130.7(7)	C(8)-N(7)-C(6)	102.0(7)
C(8)-C(9)-N(5)	105.3(10)	C(8)-N(10)-O(11)	135.3(10)
C(8)-N(10)-O(12)	113.9(7)	N(1)-N(5)-C(9)	120.9(10)
O(12)-N(10)-O(11)	110.8(11)	N(7)-C(6)-N(5)	113.5(9)
N(1)-N(5)-C(6)	132.7(9)		

Azomorpholine or azopiperidine were also obtained from the respective hydrazines and **1b** or **1c**, but the presence of 1-(*N*-morpholino)- or 1-(*N*-piperidino)-4-nitroimidazoles in the post-reaction mixtures was deduced only from MS and ^{1}H-NMR spectra of the mixtures.

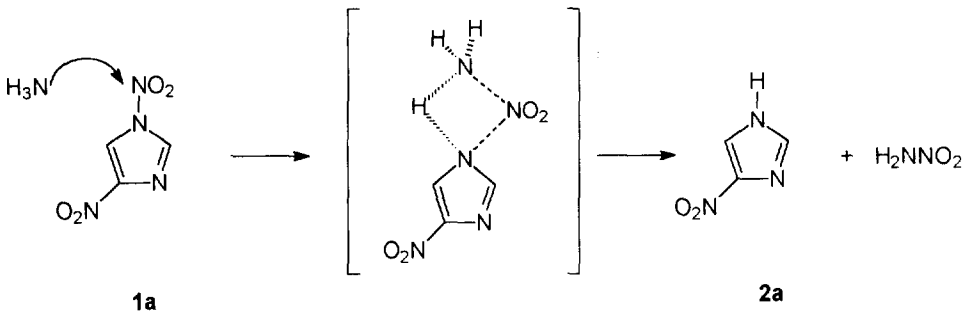
DISCUSSION OF RESULTS AND CONCLUSIONS

Two centers, susceptible to the attack of nucleophilic reagents, are present in 1,4-dinitroimidazoles: the nitrogen atom of 1-nitro group and the carbon atom 5 of the imidazole ring. It has not been possible to confirm experimentally, possible direct nucleophilic attack on carbon atom 2 in this ring. The preferred site of the attack of *N*-centered nucleophiles depends upon the reagents and the experimental conditions.[15] Low temperature and the presence of water in the medium facilitate attack on carbon atom 5 and these reactions yield *cine*[5] substitution or ring transformation products.[6-11] In aprotic organic solvents, 1-denitration usually predominates.[15] Thus, reactions of **1a-c** with hydrazines were performed in neutral aqueous medium (with possible addition of organic co-solvent), in which **1a-c** are relatively resistant to hydrolysis. Attack of hydrazine on the nitrogen atom of 1-nitro group could not be, however, be avoided. This attack yielded 4(5)-nitroimidazoles **2a-c**, azomorpholine (**6**) and also nitrous oxide. The most probable routes for the formation of these products are illustrated in Scheme 5.



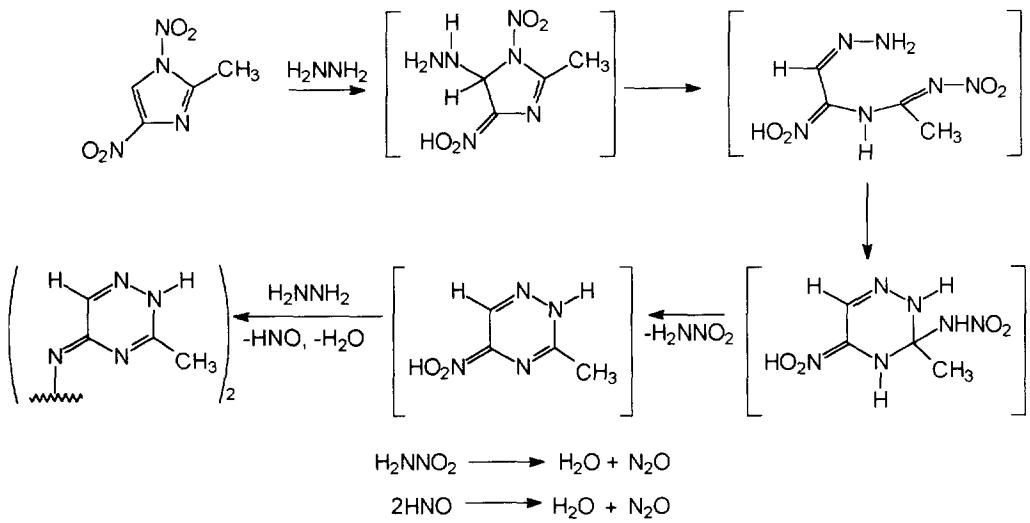
Scheme 5.

The 1-denitration mechanism was supported by quantum-chemical calculations. MNDO simulation[16] of ammonia attack on the 1-nitro group in **1a** leads to the formation of a four-center intermediate that is then decomposed into **2a** and nitroamide (Scheme 6).

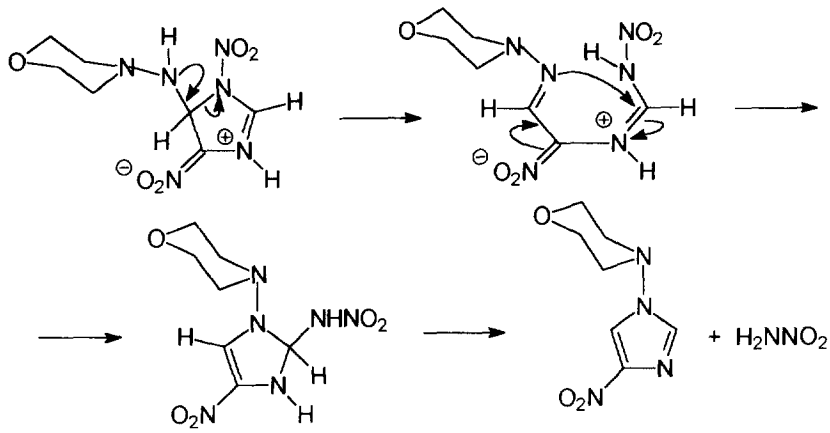


Scheme 6.

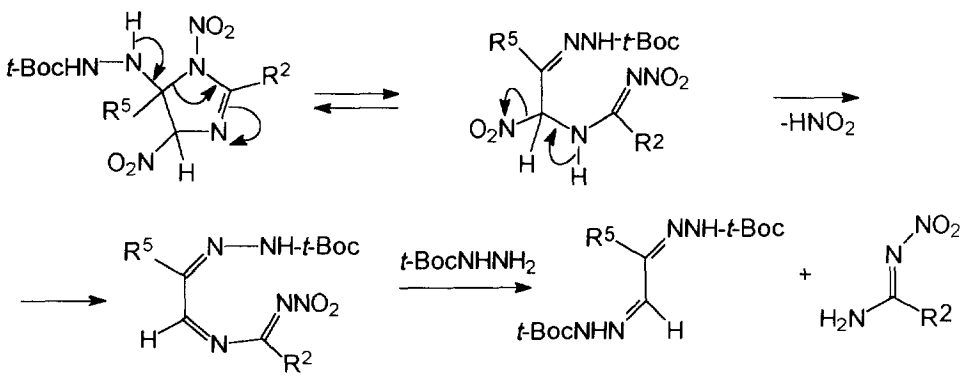
The attack of hydrazines on carbon atom 5 of the imidazole ring can yield the products of regular (triazinylhydrazine **3b**) or degenerated (morpholinonitroimidazole **5a**) transformation, as well as the products of the ring decomposition (glyoxal dihydrazones **4a-c**). Their formation is illustrated in Schemes 7, 8, and 9.



Scheme 7



Scheme 8.



Scheme 9.

Our suggested mechanisms for the imidazole ring transformations, follow from the mechanisms suggested for the reactions of 1,4-dinitroimidazoles with primary amines.[10] Our mechanism for the decomposition reaction includes the ideas of Goldman,[14] however, the direct nucleophilic replacement of 4(or 5)-nitro group, as suggested by these authors, is replaced with elimination and condensation pathways. We cannot exclude degenerative transformation of the imidazole ring, following attack of monosubstituted hydrazines on carbon atom 5 of 1,4-dinitroimidazoles, when the *t*-butoxycarbonyl group is replaced with other less bulky alkoxycarbonyl groups.

EXPERIMENTAL

General. Melting points are not corrected. ^{1}H-NMR spectra were recorded on the TESLA BS-587 spectrometer, MS(EI) spectra on SHIMADZU GC-MS 2000 and LKB-2091 (70eV) apparati, MS(CI) spectra were obtained on a SSQ 700 Finnigan MAT spectrometer.

Calculations. Semiempirical calculations were carried out using MOPAC 6.0 and the MNDO method.[16] Geometry of the system was optimized using DFP and SIGMA methods (GNORM=0.1). Geometry of the transition state was determined by the SADDLE procedure. Initial geometric data for 1,4-dinitroimidazole were taken from the X-ray analysis of this compound.[17]

Structure determination of 3b and 5a by X-ray crystallography. Diffraction data were collected using MoKα radiation (λ=0.71073 A) on a Siemens P4 diffractometer with a graphite monochromator at 301 K using a 2θ-θ scan. The structures were determined by means of direct methods (Siemens SHELXTL PLUS) and refined by the full-matrix least-squares technique. Positions of non-hydrogen atoms were determined using anisotropic thermal parameters. Positions of hydrogen atoms were located using optimized geometry.

Reaction of 2-methyl-1,4-dinitroimidazole 1b with hydrazine. To the stirred suspension of **1b** (0.01 mole) in 50 cm^3 of water, 10% aqueous solution of hydrazine hydrate was added dropwise, so that the pH did not exceed 8.0. After the pH stabilised (about 10 min), concentrated hydrochloric acid was added slowly to the resulting red solution, until the evolution of nitrous oxide stopped (GC-MS comparison with the N_2O obtained from thermal decomposition of ammonium nitrate). The post-reaction mixture was left overnight. The precipitates were filtered off, suspended in 30 cm^3 of water and heated to boiling. Concentrated hydrochloric acid was added slowly until the solids dissolved completely. The obtained solution was heated with charcoal to boiling and then filtered. To the filtrate (cooled to 25°C), 5M NaOH was added until the precipitation was complete. Crude **3b** was filtered off, washed with water and dried at 90°C for one hour to yield **3b** (0.61g). It decomposes slowly without melting from 300°C to 360°C and sublimes at 250°C under 2 mm Hg. It dissolves easily in aqueous solutions of strong acids and alkalis, and in hot DMSO; it is insoluble in typical organic solvents. EA: for $C_8H_{10}N_8$ found(calc.)%: C=43.34(44.03)%, H=4.52 (4.62)%, N=50.72 (51.35)%. MS(CI): $(M+1)^{+\cdot}$ = 219. MS(EI): $M^{+\cdot}$ = 218. ^{1}H-NMR(CD_3OD) of hydrochloride of **3b**: 2.29, 2.46, 2.55(s, Me-Triaz.), 7.63, 8.10, 8.78(s,H-Triaz.).

A sample of **3b** (0.25 g) was dissolved in a minimum volume of a concentrated aqueous solution of *p*-toluenesulfonic acid. Yellow **3b** *p*-toluenesulfonate was precipitated from the solution by means of acetone. The precipitate was filtered off, washed with water and dried. The solid (0.41 g) was recrystallized from

water to give yellow crystals, which decomposed above 270°C. EA for $C_{15}H_{22}N_8O_5S$ found(calc.)%: C=41.83(42.34)%, H=5.13 (4.98)%, N=26.03(26.35)%. MS(EI): ($M^{+\cdot}$) = 218. ^{1}H-NMR(DMSO-d_6): 2.40(s ,3H, 4-Me), 7.10-7.55 (m, 4H, C_6H_4), 2.25, 2.30 and ca. 2.50(Me-triaz.), 7.80, 8.30, 8.75(H-Triaz.). A monocrystal of this product was subjected to X-ray analysis.

The reaction of hydrazine with dinitroimidazoles **1a** or **1c** was carried out in a similar way. The obtained solids were recrystallized from a DMF-water mixture using charcoal to give **2a** (0.71g, 71%) of m.p. 309-311°C or **2c** (0.66 g, 52%) of m.p. 242-3°C.

Reactions of 1,4-dinitroimidazoles 1a-1c with t-butoxycarbonylhydrazine. *t*-Butoxycarbonylhydrazine (0.02 mole) was added to a stirred solution of **1a**, **1b** or **1c** (0.01 mole) in water-dioxane (3 : 7, 50 cm^3). After 10 minutes, white solids began to precipitate from the clear solution. After 12 hours, the solids were filtered off and recrystallized from a DMF-water mixture to yield glyoxal di(*t*-butoxycarbonylhydrazones) **4a-4c. 4a=4b:** (64% from **1a** and 43% from **1b**) of m.p 250°C (dec.), ^{1}H NMR (DMSO-d_6): 1.43(s,18H,2xt-Bu), 7.58(s,2H,2xNH), 10.89(s,2H,2xCH); MS 70eV: $M^{+\cdot}$ = 286(2), 230(11), 186(5), 174(25), 157(15), 145(9), 130(22), 129(11), 86(6), 59(14), 58(16), 57(100), 56(13), 44(15), 41(50), 29(23); 12eV: $M^{+\cdot}$ = 286(8), 186(14), 174(43), 130(55), 129(22), 86(13), 57(100). (**4c**): EA for $C_{12}H_{22}N_4O_4$ found(calc.)%: C=51.17(50.34)%, H=7.32(7.74)%, N=19.60(19.57)%. Methylglyoxal di(*t*-butoxycarbonylhydrazone) **4c** (58% from **1c**) of m.p. 238-241°C. ^{1}H-NMR (DMSO-d_6): 1.43(s,9H,*t*-Bu), 1.48(s,9H,*t*-Bu), 1.93(s,3H,Me), 7.53(s,2H,2xNH), 10.89(s,1H,CH). EA for $C_{13}H_{24}N_4O_4$ found(calc.)%: C=51.01(51.99), H=8.20(8.05), N=18.72(18.69).

Reaction of 1,4-dinitroimidazole 1a with N-aminomorpholine. To a stirred suspension of **1a** (4.2 g, 0.027 mole) in 60 cm^3 of water, *N*-aminomorpholine (2.71 g, 0.027 mole) in 5 cm^3 of water was added dropwise at the rate insuring pH 7.5-8.0. The mixture was then stirred for 0.5h; the resulting precipitate collected, stirred with aqueous 10% KOH (20 cm^3) and filtered off. Compound **2a** (0.97 g, 32%) was obtained by acidification of the filtrate. The solid product insoluble in KOH solution was collected, washed with water, dried and sublimed at 190°C to yield azomorpholine (**6**, 0.63 g, 25%) as colorless crystals of m.p. 153.5-155°C (152[18]); EA for $C_8H_{16}N_4O_2$ found(calc.)%: C=47.94(48.04)%, H=7.99(8.06)%, N=27.97(28.01)%. The residue from sublimation was recrystallized from water with charcoal, yielding colorless crystals of 1-(*N*-morpholino)-4-nitroimidazole **5a** (1.6 g, 30%) of m.p. 220-222°C. EA for $C_7H_{10}N_4O_3$ found(calc.)%: C=42.25(42.42)%, H=5.07(5.05)%, N=28.25(28.28)%. ^{1}H-NMR (DMSO-d_6): 3.11-3.80(m,8H,N(CH_2CH_2)$_2$O), 8.00(d,1H,H-Imid.,J=1.56Hz), 8.85(d,1H,H-Imid., J=1.56Hz); MS: $M^{+\cdot}$ = 198(17.2), 140(9.6), 113(9.8), 86(31.5), 57(10.4), 56(100), 55(47.4), 52(11.8). The crystals were subjected to X-ray analysis.

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