GEM-DINITRO COMPOUNDS IN ORGANIC SYNTHESIS. 3. SYNTHESES OF 4-NITRO-1,2,3-TRIAZOLES FROM GEM-DINITRO COMPOUNDS

A. T. Baryshnikov, V. I. Erashko, N. I. Zubanova, B. I. Ugrak, S. A. Shevelev, A. A. Fainzil'berg, A. L. Laikhter, L. G. Mel'nikova, and V. V. Semenov

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Several chemoselective syntheses have been developed for 4-nitro-1,2,3-triazoles from sodium azide and gem-dinitroethylenes prepared from readily available transformation products of dinitroacetic acid ester: N-(β,β-dinitroethyl)-N,N-dialkylamines, 2,2-dinitroethanol acetate, a mixture of dinitroacetic acid ester with aliphatic aldehydes, or 1,1,1-trinitroalkanes. Hitherto-unknown 4-nitro-5-amino- and 4,5-dinitro-1,2,3-triazoles have been synthesized via successive transformations of the CH_3 groups in 5-nitro-4-methyltriazole. Nitration of 4-nitro-1,2,3-triazole with nitronium fluoroborate or acetyl nitrate gave an unknown 2,4-dinitro-1,2,3-triazole.

Keywords: *gem-dinitro compounds, 4-nitro-1,2,3-triazoles, gem-dinitroethylenes, dinitroacetic acid ester, N-(β,β-dinitroethyl)-N,N-dialkylamines, 2,2-dinitroethanol acetate, 1,1,1-trinitroalkanes, nitration, cyclization, 2,4-dinitro-1,2,3-triazole.*

In the previous communication the cyclization of functionalized gem-dinitro compounds to nitroheterocycles was described using as an example the synthesis of 4-nitropyrazoles [1]. This approach is also promising for 4-nitro-1,2,3-triazoles, which find application as intermediate products of the synthesis of pharmaceuticals, dyes, agricultural pesticides, etc. [2, 3]. Such a line of investigation, however, is held up by the lack of convenient methods for obtaining the starting nitrotriazoles. For example, in an all-but-exhaustive review of 1,2,3-triazoles [4] no 4-nitro-5-alkyltriazoles beyond the parent 4-nitrotriazole and its 5-methyl analog were described. The methods of synthesis of the 4-nitro-1,2,3-triazole are quite unwieldy at that [5-8].

As is known, the reaction of mononitroolefins with sodium azide leads to the formation of 1,2,3-triazoles. The reaction is considered to involve the addition of the azide ion to the nitroolefin double bond with subsequent closure of the triazole ring and elimination of the nitro group as NO_2^- [9]. For β-bromo-β-nitrosterols the reaction products are 5-arylsubstituted 4-nitro-1,2,3-triazoles, i.e., here the triazole-ring formation involves the elimination of a bromide ion [1].

In contrast to the reaction with mononitrohaloolefins, which may results in nitro- or halotriazoles (the leaving group being the bromide or the nitrite ion, respectively) we have developed several chemoselective approaches to the synthesis of 4-nitro-1,2,3-triazoles from sodium azide and gem-dinitroethylenes obtained from the readily available ester of dinitroacetic acid and its transformation products [11] (Scheme 1, methods A-C) or starting from 1,1,1-trinitroalkanes (Scheme 1, method D).

The sources of 1,1-dinitroethylene, which cannot be isolated outside of the reaction, are a Mannich base (method A) and gem-dinitroethanol acetate (method B), which is readily synthesized from dinitroacetic ester via 1,1-dinitroethanol [11]. The gem-dinitroolefins may also be generated directly from an equimolar mixture of dinitroacetic ester and an aliphatic aldehyde (method C) or from 1,1,1-trinitroalkanes (method D).

By method A the reaction was best conducted in absolute methanol at 40-50°C over 1.5-2 h, the yield of 4-nitro-1,2,3-triazole (**1a**) reaching 70%. In ordinary methanol or in mixtures of it with DMSO (12:1) the yield of **1a** fell to 50-60%, while in ethanol and methylene chloride there was virtually no reaction.

The reaction of dinitroethanol acetate with sodium azide (method B) proceeded somewhat more slowly, a 70-75% yield of nitrotriazole **1a** requiring ≈5 h at 50°C.

The C variant proceeded smoothly in water (70% yield) on heating of the three-component solution and maintaining the acidity at pH 4-5. As we have previously shown [11], in the absence of sodium azide the mixture of formaldehyde and dinitroacetic acid in water forms 2,2-dinitroethanol in alkaline solutions but 1,1,3,3-tetranitropropane in neutral solutions due to the addition of dinitroethanol to dinitroethylene.

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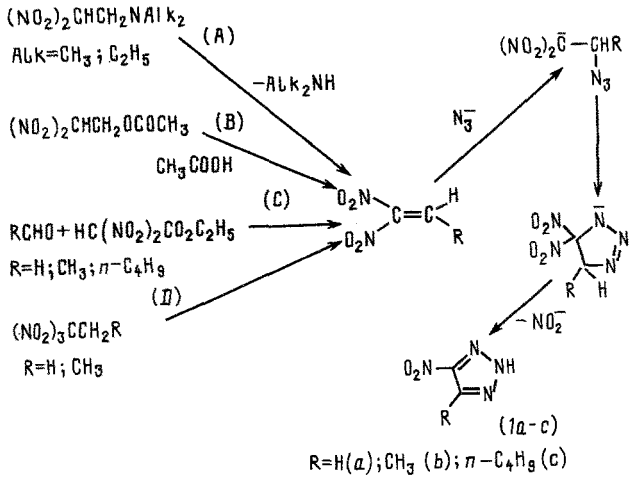
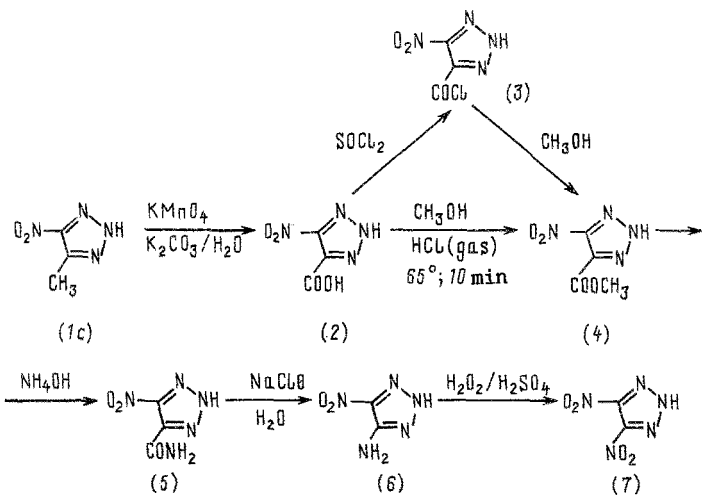
Scheme 1



In acidic solutions (pH 1-2) a more profound transformation of 2,2-dinitroethanol takes place, also via the formation of dinitroethylene, eventually yielding the N-oxide of 1,3,4-trinitropyridine [12]. For the synthesis of 4-nitro-1,2,3-triazoles, however, maintaining high acidity for more rapid generation of dinitroethylene is not possible due to the evolution of gaseous hydrazoic acid.

Among other types of precursors to 1,1-dinitroolefins — 1,1,1-trinitroalkanes [13] (method D) — we investigated 1,1,1-trinitroethane and 1,1,1-trinitropropane. The reaction of 1,1,1-trinitroethane with sodium azide in methanol at 60°C proved to give a yield of nitrotriazole **1a** no greater than 30% even after 20 h. Even slower was the formation of 5-nitro-4-methyl-1,2,3-triazole **1b** from 1,1,1-trinitropropane, giving a 3-5% yield over the same time. The substitution of methoxyethanol (methyl cellosolve) for methanol, the use of a higher temperature (100°C), and the addition of urea to destroy the forming HNO_2 sharply accelerated both reactions and greatly increased the yield of triazoles; under these conditions 1 h of reaction was sufficient to give 70-75% yields of **1a** and **1b**.

Scheme 2



The availability of vicinal 5-nitro-4-alkyltriazoles permitted their use in the synthesis of a series of difficultly accessible derivatives, among them the previously unknown 5-nitro-4-amino and 4,5-dinitro-1,2,3-triazoles, via standard successive transformations of the 4-methyl group.

Previously only their difficultly accessible substituted analogs have been described — the unstable 5-nitro-4-picrylaminotriazole [14] and the recently synthesized 2-methyl-4,5-dinitrotriazole [8].

Oxidation of the methyl group to a carboxyl was amenable to the familiar method of aromatic side-chain oxidation with potassium permanganate. Esterification of acid **2** with methanol and HCl with simultaneous removal by distillation of water gave ester **4** in 85% yield. This ester could also be obtained in overall yield of 97% via chloroanhydride **3** without intermediate isolation and purification.

TABLE 1. ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR Data for 4-Nitro-1,2,3-triazole and Its Substituted Derivatives

Compound	Solvent	^{1}H NMR, δ, ppm (J, Hz)	^{13}C NMR, δ, ppm (J, Hz)	$^{14}/^{15}N$ NMR, δ, ppm (J, Hz)
1a	DMSO-d_6	8.90 – H_5 14.50 br.s-NH a	125.50d (205.3) – C^5 153.70d (8.3) – C^4	^{15}N: –23.98 s (NO_2); –44.09 s (N^1); –52.45 s (N^3); –105.00 s (N^2)
1c	$(CD_3)_2SO$	0.92 t (7.3) – CH_3 1.40 q.t (7.3; 7.6) – CH_2^3 1.73 q (7.6) – CH_2^2 3.10 t (7.6) – CH_2^1	13.79 q (126.0) – CH_3 22.79 t (125.0) – CH_2^3 24.41 t (129.0) – CH_2^2 30.57 t (127.4) – CH_2^1 140.99 t.t (6.8; 3.9) – C–CH_2 151.20 t (2.6) – C–NO_2 131.17 s – C^4	^{14}N: –23.20 (NO_2)
2	CD_3CN	b	151.93 s – C^5 158.29 s – COOH	
4	CD_3CN	3.96 – OCH_3 a,b	53.12 q (144.0) – OCH_3 131.34 s – C^4 152.20 s – C^5 158.31 q (4.2) – COO	^{15}N: –19.21s (N^3); –22.40 (NO_2); –50.38 s (N^1); –77.30 s (N^2); –332.02 t (NH_2) (J_{N-H}=79)
5	$(CD_3)_2SO$	7.73 br.s, 7.82 br.s > NH b	134.29 s – C^4 149.61 s – C^5 158.62 s – $CONH_2$	
6	$(CD_3)_2SO$	7.44 br.s-NH_2	136.50 s – C^4–NO_2 142.80 s – C^5–NH_2	
7	CD_2Cl_2	–	144.91s – C^4, C^5	^{14}N: –33.90 s (4-, 5-NO_2)
8	$CDCl_3$	8.33 s – H^5 b,c	131.10 d (211.8) – C^5 150.60 d (8.4) – C^4	^{15}N: –30.00 s (4-NO_2)[d] –53.81 s (N^1); –54.40 s (2-NO_2) –69.70, –70.70 (N^2, N^3)

[a]In $(CD_3)_2CO$.

[b]Signals of the ring NH-protons in compounds **2-8** were absent.

[c]In $CDCl_3$.

[d]Assignment of the 4- and 2-NO_2 signals were made with ^{14}N NMR, where no ring nitrogen signals are seen.

TABLE 2. IR, UV, and Mass Spectral Characteristics of 4-Nitro-1,2,3-triazole and Its Substituted Derivatives

Compound	Mass spectrum, m/z	UV spectrum, H_2O + $NaHCO_3$), λ_{max}, nm (ε)	IR spectrum (KBr), ν, cm^{-1}
1a	114(M^+)	294 (8000)	1340, 1550 (NO_2); 3250 br (NH)
1b	128(M^+)	305 (7000)	1370, 1525, 1570 (NO_2); 3100 br (NH)
1c		307 (7600)	1375, 1530, 1600 (NO_2); 2980 br (NH)
2	158(M^+)	301 (5100)	1350, 1370, 1550, 1565 (NO_2); 1727 (C=O); 3200 br (NH)
4	172(M^+)	288 (5000)	1350, 1380, 1552 (NO_2); 1775 (C=O); 3100 br (NH)
5	157(M^+)	294 (5200)	1375, 1530 (NO_2); 1700 (C=O); 3180 (NH)
6	129(M^+)	281 (4200)	1350; 1655 (NO_2); 3200 br (NH)
8			1315, 1335, 1560 (C–NO_2); 1278, 1680 (N–NO_2)

Hofmann rearrangement of amide **5** using NaBrO gave amine **6** in 50% yield, while the use of sodium hypochlorite increased the yield to 80%.

Synthesis of amine **6** directly from acid **2** was accomplished with diphenylphosphoryl azide, a reagent successfully applied in recent years for transformation of carboxylic acids to amines with no intermediate steps [15, 16]. In our hands, however, the yield of the target aminotriazole **6** did not exceed 10%.

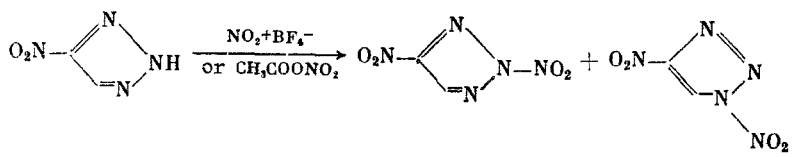
The most convenient means of oxidizing 5-nitro-4-aminotriazole **6** to dinitrotriazole **7** was a 30% mixture of hydrogen peroxide and concentrated H_2SO_4, often used to convert aromatic amines to the corresponding nitro compounds [17].

Compound **7** was a yellowish liquid under normal conditions, becoming viscous but not crystallizing with strong cooling. At 20°C it remained stable for an extended period, beginning to decompose at 100°C according to differential thermographic analysis. The structure of **7** was reliably confirmed by IR and ^{14}N NMR (NO_2 group with aromatic character, δ —33.9 ppm), and ^{13}C NMR (a single carbon signal at δ 144.9 ppm). The mass spectrum of **7** showed an intense molecular-ion peak at *m/z* 159 (Table 1).

Cautious treatment of an ether solution of 4,5-dinitrotriazole **7** with an equimolar quantity of alkali in methanol or by introduction of gaseous ammonia yielded the potassium, sodium, and ammonium salts possessing the UV maxima around 290 nm characteristic of nitro-1,2,3-triazoles (Table 2).

The crystalline derivative of dinitrotriazole, 2-acetonyl-4,5-dinitro-1,2,3-triazole, was made by alkylation of the corresponding sodium salt by bromoacetone and was described previously [18].

A shorter route to 4,5-dinitrotriazole appeared to be direct nitration of nitrotriazole **1a** by analogy with the nitration, described in [8], of 2-methyl-4-nitro-1,2,3-triazole to 2-methyl-4,5-dinitrotriazole. However, nitrotriazole **1a** could not be nitrated at 50-60°C with a mixture of concentrated HNO_3 and H_2SO_4 or fuming HNO_3, while elevation of the temperature to 90°C led to rapid destruction of the molecule due to opening of the triazole ring. In contrast, the use of such nitrating agents as $NO_2^+BF_4^-$ (in CH_3CN at 0°C or CH_2Cl_2 at 20°C) and acetyl nitrate led to N-nitration to form the previously undescribed 2,4-dinitro-1,2,3-triazole (**8**) and a compound indicated by NMR to be 1,4-dinitro-1,2,3-triazole (**8a**). The ratio of the dinitro derivatives **8** and **8a** in the reaction mixture varied from about 4:1 (for $NO_2^+BF_4^-$) to 7:1 (for CH_3COONO_2) (by PMR).



40—75%
(8) (8a)

Isomer **8a** was much less stable and could not be isolated from the product mixture. It was completely destroyed by treatment of the isomer mixture with aqueous sodium bicarbonate, while **8** remained almost unchanged. The latter could consequently be isolated and its structure unambiguously assigned.

The IR spectrum of **8** displays bands at 1315, 1335, and 1560 cm^{-1} characteristic of C—NO_2 group vibrations in nitrotriazoles [18], as well as bands at 1278 and 1680 cm^{-1} characteristic of N—NO_2 group vibrations. In the PMR spectrum the aromatic proton singlet at δ 8.33 ppm lies downfield of the CH-proton of isomer **8a** (δ 9.93 ppm). In the ^{13}C NMR spectrum both the chemical shifts of atoms C_4 (150.6 ppm) and C_5 (131.1 ppm) and the difference between them are characteristic precisely of N_2-substituted 4-nitrotriazoles [18] (Table 2).

2,4-Dinitrotriazole (**8**) is thermally unstable and by differential thermographic analysis begins to decompose at 40°C ($T_{str.decomp}$ = 114°C). Attempts to bring about its thermal rearrangement to 4,5-dinitro-1,2,3-triazole **7**, by analogy with the rearrangement of the same type described in [19] for 1,3-dinitropyrazole, were unsuccessful.

EXPERIMENTAL

IR spectra were recorded on a UR-20 in KBr disks. UV spectra were taken on a Specord UV-VIS spectrophotometer and mass spectra on a Varian MAT-CH-7.

PMR spectra were taken on a Bruker WM-250 instrument at working frequency 250.13 MHz, relative to TMS. ^{13}C, ^{14}N, and ^{15}N NMR spectra were taken on a Bruker AM-300 at working frequencies of 75.47, 21.68, and 30.42 MHz, respectively, relative to TMS (^{13}C) and CH_3NO_2 (^{14}N, ^{15}N). High-field chemical shifts in the ^{14}N and ^{15}N NMR spectra are given with minus signs.

TLC was performed with stabilized Silufol UV-254 plates using as eluents $CHCl_3$:acetone:CF_3COOH in a ratio of 50:10:1 for compounds **1a, 1b, 1c,** and **8** and 50:20:1 for products **2, 4, 5,**and **6**; and dichloroethane:CF_3COOH in a ratio of 50:1 for compound **7**.

4-Nitro-1,2,3-triazole (1a). Method A. To a suspension of 6.5 g (0.1 mole) NaN_3 in 150 ml abs. CH_3OH was added 19.1 g (0.1 mole) $(NO_2)_2CHCH_2N(C_2H_5)_2$ [20] followed by stirring 1.5 h at 45°C. The resulting solution was slowly acidified with a 20% solution of H_2SO_4 (50 ml) until gas evolution ceased, after which the methanol was removed in a rotary evaporator. The remaining aqueous solution was extracted with ether (3 × 50 ml). The combined ether extracts were washed with water, dried over $MgSO_4$, and evaporated under vacuum. The residue was stirred to 50 ml cold $CHCl_3$ and the resulting crystals filtered off, and air dried. Yield 7.85 g (70%) of **1a**, mp 161-162°C (literature data: mp 158-159 [5], 160-161°C [21]). The compound was pure by TLC and did not lower the mp of a sample synthesized as in [21].

Use of $(NO_2)_2CHCH_2N(CH_3)_2$ gave analogous results.

Method B. A mixture of 2.4 g (0.02 mole) 2,2-dinitroethanol [20], 12 ml acetyl chloride, and 0.1 ml concentrated H_2SO_4 was held 48 h at 20°C. The excess of CH_3COCl was removed in the rotary evaporator and the residue diluted with 20 ml water and extracted with ether (2 × 30 ml). The combined ether extractor were dried over $MgSO_4$ and the ether removed in the rotary evaporator. Yield 2.5 g (60%) of 2,2-dinitroethanol acetate as a light-yellow oil, which was used in the subsequent reactions without further purification. To a suspension of 0.65 g (0.01 mole) NaN_3 in 25 ml absolute CH_3OH was added 1.33 g (0.0075 mole) of 2,2-dinitroethanol acetate followed by stirring for 5 h at 50°C with subsequent workup as in method **A**. Yield 0.85 g (75%) of compound **1a** identical to the material obtained by method **A.**

Method C. With stirring and warming (30°C), 2.16 g (0.01 mole) of **9** [11] was dissolved in 20 ml water. A 27% aqueous solution of formaldehyde (0.45 g, 0.015 mole) was then added followed by 1.3 g (0.02 mole) NaN_3. The reaction mixture was acidified with a 70% solution of H_2SO_4 to pH 4 and stirred for 2 h at 80°C, then another 0.65 g (0.01 mole) NaN_3 was added and the reaction was held 2 h further at pH 4. The reaction mixture was acidified with a 20% solution of H_2SO_4 to pH 2 and heated for 1 h at 100°C, then cooled to 20%. A 20% solution of NaOH was added to pH 7-8 and the mixture, having a UV λ_{max} of 366 nm, was extracted with ether (3 × 10 ml). To the alkaline solution was added a 20% solution of H_2SO_4 to pH 2 and it was extracted with ether (3 × 20 ml). The ether extracts were dried over $MgSO_4$ and the ether was removed in the rotary evaporator. Yield 0.8 g (70%) of faintly oily product **1a**. An analytically pure sample was obtained by crystallization from ethyl acetate. Yield 0.34 g (30%) of a white crystalline substance **1a**, mp 162°C, identical to the material obtained by methods **A** and **B**.

Method D. To a solution of 1.65 g (0.61 mole) 1,1,1-trinitroethane [22] in 30 ml of methyl cellosolve was added 1.2 ml (0.02 mole)of urea and 3.3 g (0.02 mole) NaN_3. The resulting mixture was heated with stirring for ≈1 h at 100°C and chilled; then 150 ml H_2O was added and the mixture was acidified with 20% H_2SO_4 and extracted with ether (2 × 50 ml). The ether extracts were dried over $MgSO_4$ and the ether was removed in the rotary evaporator. Yield 0.8 g (70%) of compound **1a**, identical to the material obtained by the previous methods **A-C**.

5-Nitro-4-methyl-1,2,3-triazole (1b). Method C. From 2.16 g (0.01 mole) of salt **9**, 0.66 g (0.015 mole) of acetaldehyde, and 1.95 g (0.03 mole) NaN_3 was obtained 0.8 g (63%) of oily product **1b**. An analytically pure sample was obtained by recrystallization from dichloroethane. Yield 0.4 g (31%) of white crystalline substance **1b**, mp 177°C, identical to an authentic sample (literature [21]: mp 177-178°C). PMR (CD_3CN, δ, ppm): 2.66 s (3H, Me).

Method D. From 1.77 g (0.01 mole) of 1,1,1-trinitropropane [22] in 15 ml of methyl cellosolve, 1.2 g (0.02 mole) of urea, and 1.3 g (0.02 mole) NaN_3 as in the synthesis of **1a** from 1,1,1-trinitroethane (see above for **D**) using heating for 45 min at 100°C was obtained 0.96 g (75%) of compound **1b**, mp 176-177°C.

5-Nitro-4-butyl-1,2,3-triazole (1c). Method C. From 2.16 g (0.01 mole) of **9**, 0.86 g (0.01 mole)of valeraldehyde, and 1.95 g (0.03 mole) NaN_3 was obtained 1.2 g (70%) of oily product **1c**. An analytically pure sample (0.6 g, yield 35%) of a white crystalline compound **1c**, mp 92°C, was obtained by recrystallization from CCl_4. Found, %: C 42.65; H 5.82; N 32.63. $C_6H_{10}N_4O_2$. Calculated, %: C 42.35; H 5.92; N 32.93.

5-Nitro-1,2,3-triazole-4-carboxylic Acid (2). To a solution of 1.8 g (0.01 mole) of **1b** and 0.68 g (0.005 mole) K_2CO_3 in 30 ml of water was added, with stirring, 3.8 g (0.024 mole) of powdered $KMnO_4$. The reaction mixture was heated for 1.5 h at 100°C. To the cooled mixture was added with stirring 30 ml ether and 20 ml of a 40% solution of H_2SO_4, the ether layer was separated, and the aqueous layer was extracted with ether (2 × 50 ml). The combined extracts were dried over $MgSO_4$ and the ether removed in the rotary evaporator. Yield 1.52 g (96%) of a colorless crystalline product **2**, T_{decomp} 120°/150°C.*

*Data from differential thermographic analysis, heating rate 5°C/min, T_{decomp} (°C): initial/strong. The authors thank V. I. Gulevskaya [Institute of Organic Chemistry, Russian Academy of Sciences (IOKh RAN)] for these determinations.

Found, %: C 23.27; H 1.38; N 35.04. $C_3H_2N_4O_4$. Calculated, %: C 29.79; H 1.28; N 35.45. Methyl ester of 5-nitro-1,2,3-triazole-4-carboxylic acid (**4**). a) With stirring, 1 g (0.0063 mole) of acid **2** was dissolved in 5 ml absolute CH_3OH saturated with dry gaseous HCl. The reaction mixture was heated and the solvent was slowly evaporated. The solvent was removed in the rotary evaporator. Yield 0.93 g (85%) of ester **4**, mp 112°C, T_{decomp} 120°/165°C. Found, %: C 27.81; H 2.18; N 32.30. $C_4H_4N_4O_4$. Calculated, %: C 27.92; H 2.34; N 32.30. b) A mixture of 0.43 g (0.0027 mole) of 5-nitro-1,2,3-triazole-4-carboxylic acid **2** was mixed with 5 ml of thionyl chloride and heated with stirring for 1 h at 75-80°C; then the excess of $SOCl_2$ removed in the rotary evaporator. Into the remaining chloroanhydride of **3** was poured 5 ml of absolute CH_3OH followed by stirring for 2-3 h at 20°C and standing for 12 h. The methanol was removed in the rotary evaporator. Yield 0.38 g (97%) of ester **4**, completely identical (by TLC) with the product described above in a).

Amide of 5-Nitro-1,2,3-triazole-4-carboxylic Acid (5). With stirring, 1 g (0.00636 mole) of ester **4** was dissolved at 20°C in 3-4 ml of concentrated aqueous ammonia and left to stand 12 h. The excess of NH_3 was removed in the rotary evaporator and concentrated HCl was added dropwise to bring the residue to pH ≈ 1. The precipitate was filtered off, washed with cold water, and air-dried. Yield 0.82 g (92%) of light yellow amide **5**, T_{decomp} 175°/210°C. Found, %: C 23.04; H 1.88; N 44.35%. $C_3H_3N_5O_3$. Calculated, %: C 22.94; H 1.92; N 44.59.

5-Nitro-4-aminotriazole (6). a) To a solution of 3.8 g (0.0955 mole) NaOH in 30 ml of water, with stirring and cooling (0°C) was introduced 460 ml (0.019 mole) of gaseous Cl_2. To the resulting NaClO solution was added 2.5 g (0.016 mole) of amide **5** followed by stirring at 20°C until full dissolution, after which the reaction mixture was heated for 30 min at 60°C. The mixture was then cooled and concentrated HCl was added to pH ≈ 1. The precipitate was filtered off, washed with cold water (2 × 20 ml), and air-dried. Yield 2.0 g (80%) of product **6**, T_{decomp} 245°/270°C. Found, %: C 18.52; H 2.21; N 53.87. $C_2H_3N_5O_2$. Calculated, %: C 18.61; H 2.34; N 54.26. b) The reaction was conducted according to the above method with the same quantities, using bromine instead of chlorine (3.08 g, 0.019 mole). Yield 1.24 g (50%) of **6**, completely identical to the product of method a. c) A mixture of 5 g (0.032 mole) of acid **2**, 8.8 g (0.032 mole) of diphenylphosphoryl azide, 3.2 g (0.032 mole) of triethylamine, and 50 ml of absolute *tert*-butanol was refluxed for 12 h. After cooling, the reaction mixture was poured into 200 ml of water, acidified to pH 1-2 with concentrated HCl, and extracted with 50 ml of ether. The aqueous layer was concentrated in the rotary evaporator to ≈ 10 ml. The precipitate was filtered out, washed with cold water, and air-dried. Yield 0.37 g (≈ 10%) of yellow product **6**, completely identical (TLC, UV, IR) to the products of methods a and b.

4,5-Dinitro-1,2,3-triazole (7). To a mixture of 15.6 ml of 30% H_2O_2 and 30 ml concentrated H_2SO_4 was added in small portions, with stirring and cooling (10-15°C), 2 g (0.0155 mole) of 5-nitro-4-amino-1,2,3-triazole **6**, followed by standing 24 h at this temperature. The reaction mixture was then poured into 150 ml of cold water and extracted with ether (3 × 50 ml). The ether extracts were dried over $MgSO_4$ and the ether was removed in the rotary evaporator. Yield 1.5 g (60%) of product **7** as a light yellow oil. Found, %: C 15.22; H 0.75; N 43.75. $C_2HN_5O_4$. Calculated, %: C 15.10; H 0.63; N 44.03.

Compound **7** was best stored in ether solution.

To obtain the sodium and potassium salts, equimolar quantities of NaOH or KOH in methanol were added to ether solutions of **7** with cooling and the precipitated salt was then filtered off and washed with ether. Yield ≈90%.

2,4-Dinitro-1,2,3-triazole (8). a) Into 3 ml HNO_3 (d 1.5 g/cm^3) was slowly poured 3 ml of acetic anhydride, the mixture was cooled to 20°C, and 1.14 g (0.01 mole) of compound **1a** was added in portions. After standing 30 min at 20°C, the reaction mixture was poured into 10 g of crushed ice and extracted with $CHCl_3$ (2 × 15 ml). The chloroform extracts were washed with a 5% solution of $NaHCO_3$ (2 × 10 ml), then water, and dried over $MgSO_4$. The chloroform was removed in the rotary evaporator. Yield 1.25 g (78%) of product **8** as a colorless oil. T_{decomp} 40°/114°C. Found, %: C 15.32; H 0.83; N 43.55. $C_2HN_5O_4$. Calculated, %: C 15.10; H 0.63; N 44.03. b) To 0.7 g (0.0065 mole) of $NO_2^+BF_4^-$ in 5 ml absolute CH_3CN was added, with stirring and cooling (0-3°C) 0.3 g (0.0026 mole) of compound **1a**. After stirring 3.5 h more at 0°C, the mixture was poured into 30 ml of water and extracted with $CHCl_3$ (3 × 20 ml). The chloroform extracts were worked up as described in method a. Yield 0.16 g (38%) of product **8**, completely identical to the material synthesized in method a. An analogous result (yield 40%) was obtained with nitration by $NO_2^+BF_4^-$ (20°C, 2 h) in methylene chloride.

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