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Thermal ring-opening reaction of *N*-polynitromethyl tetrazoles: facile generation of nitrilimines and their reactivity

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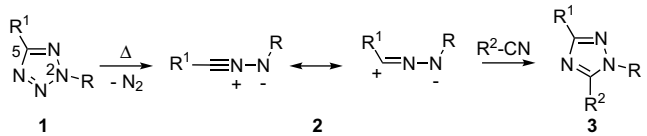
ABSTRACT

Thermal ring-opening reaction of *N*-(R-dinitromethyl)-5-nitrotetrazoles (R=NO_2, F, Cl) yielded highly reactive *N*-(R-dinitromethyl)-nitrilimine intermediates under mild conditions. These species underwent facile and regiospecific reaction with nitriles and acetylenes to afford the corresponding nitrotriazoles and nitropyrazoles in 50–90% yields. Treatment of *N*-(chlorodinitromethyl)-5-nitrotetrazole with the excess of azide led to a unique compound with the molecular formula C_2N_{14}. Based on the analytical data, it was assigned a structure of diazidomethylenecarbonohydrazonic diazide.

1. Introduction

Polynitrated azoles continue to attract considerable amount of interest as building blocks for the synthesis of a high-energy materials.[1] Elevated acidity of these substances,[2] as exemplified by tetranitropyrrole, 2,4,5-trinitroimidazole, 3,5-dinitro-1,2,4-triazole, 4,5-dinitro-1,2,3-triazole, and 5-nitrotetrazole historically limited their practical utility. This issue has been somewhat addressed by the modification of the acidic proton at the heterocyclic pyrrole (*N*-H) with the polynitromethyl moiety.[3–8] In the course of our studies on polynitrated aromatics, we have developed the synthesis of *N*-(polynitromethyl)tetrazoles and studied their thermal stability.

Literature data suggest that 2-substituted tetrazoles **1** feature facile elimination of N_2 under a variety of experimental conditions to yield highly reactive nitrilimine intermediates **2**. These species undergo 1,3-dipolar cycloaddition reaction with dipolarophiles to yield diverse heterocyclic scaffolds[9,10] (e.g., 1,2,4-triazoles, **3**) as exemplified on the Scheme 1 for nitriles.[11]



Scheme 1.

Electron-deficient substituents in position 2 of the tetrazole ring were shown to lead to accelerated rates of this thermally induced ring-opening step, while electron-donating moieties slowed it down.[12,13] For instance, 2-acyl-5-aryltetrazoles were reported to eliminate N_2 at 70 °C,[10] whereas 2-phenyl-5-aryl- and 2-alkyl-5-aryltetrazoles underwent this reaction at 140–160 °C[9,10,13,14] and 220 °C, respectively.[10] Notably, the influence of the functionality in the position 5 of tetrazole was reciprocal, namely electron-donating groups facilitated the process. The overall effect of a 2-substituent on the rate of formation of nitrilimines was more profound than that of a 5-group.[12,13]

2. Results and discussion

The desired *N*-dinitromethyl derivatives have been prepared by nitration of the easily available *N*-acetonyl-5-nitrotetrazole **4**[2] (Scheme 2). Considering our prior experience with this reaction,[3] we carried out the nitration of **4** in 75–80% H_2SO_4 in order to both enhance enolization of the acidic CH_2 group and to reduce the amounts of side products.[3] A similar strategy has been reported in the synthesis of *N*-dinitromethylylides[3] and other *N*-polynitromethylheterocycles.[4–8] Under the reaction conditions described in our earlier studies,[3] we observed a stepwise introduction of NO_2 at CH_2 of the *N*-acetonyl group. This was in contrast to the previously suggested mechanism involving initial formation of a nitroso derivative followed by its oxidative nitration to the respective dinitroketones.[15–18] Water quench of the nitration reaction after shorter reaction times (e.g., 2–3 h vs 72 h) afforded both 2-dinitro (**7a**, UV_{max}=336 nm) and 2-nitro (**8**, UV_{max}=312 nm at pH=8)

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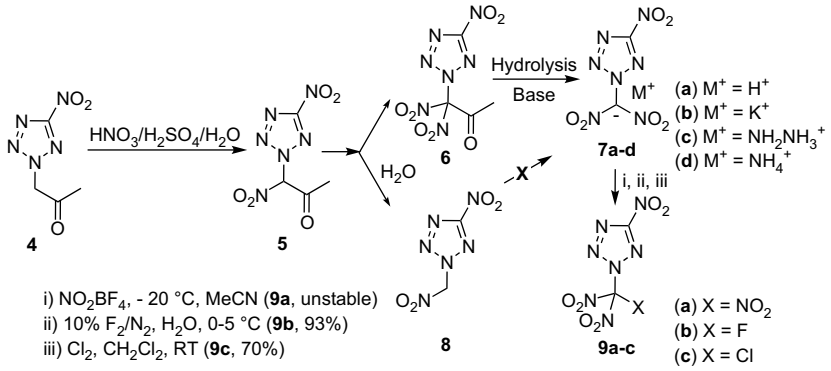
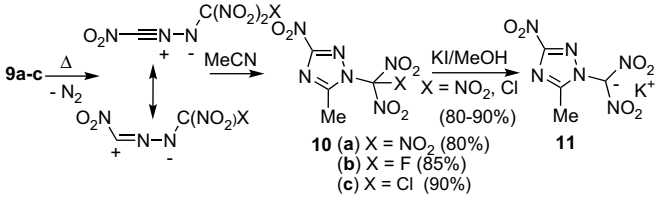


Scheme 2.

methyltetrazoles in ca. 45% overall yield and 2:1 ratio, respectively. Product **8** likely resulted from the hydrolysis of unstable mononitroketone intermediate **5**. Monitoring of the reaction course by UV spectroscopy suggested that **8** was not a direct precursor to **7a**. Moreover, we were not able to convert analytically pure **8** into **7a** under a variety of experimental conditions including direct addition of **8** to the nitrating mixture described above. Based on these observations, we concluded that the nitration at CH_2 position of **4** proceeded sequentially, hydrolysis of the acetyl group occurring at the respective dinitro derivative **6** stage.

Neither addition nor removal of nitric oxides with urea, hydrazine or sulfaminic acid affected the reaction course. A quantitative acid–base equilibrium of **7** in H_2SO_4 was easily monitored using UV spectroscopy (UV_{max}=336 nM). As evidenced from the absorption maximum, protonation of $C(NO_2)_2$ moiety versus basic N of the tetrazole ring was the initial step at all pH values evaluated. The respective pK_a=−1.7 measured at 20 °C was comparable to that of a strong mineral acid. In the course of our studies, we have prepared K^+, NH_4^+, and $NH_2NH_3^+$ salts **7b–d** (50–85% yields). Salts **7b** and **7d** were subsequently converted to 2-trinitro- (**9a**), 2-(fluorodinitro)- (**9b**, 93% yield), and 2-(chlorodinitro)- (**9c**, 70% yield) tetrazoles by the treatment with NO_2BF_4, 10% F_2/N_2 and Cl_2, respectively. In our hands **9a** was unstable at the temperatures greater than −20 °C and was used for further transformations in situ.

We were interested in the thermal behavior of **9a–c**. In our hands, these molecules underwent thermal decomposition in MeCN to afford the corresponding products of dipolar cycloaddition of the intermediate nitrilimines, 1-polynitromethyl-3-nitro-5-methyl-1,2,4-triazoles (**10a–c**) in 80–90% isolated yields and high purity (Scheme 3). Triazoles **10a** and **10c** were further converted to the dinitromethyl salt **11** using KI/MeOH (80% and 90% yields, respectively).[19]



Scheme 3.

We observed a direct link between the thermolysis temperature required to generate the reactive nitrilimine intermediate and the electron withdrawing effect of a polynitroalkyl substituent in **9** (σ^*, Table 1). For example, both **9b** (X=F) and **9c** (X=Cl) were relatively stable in both solid state and in solution compared to **9a** (X=NO_2).

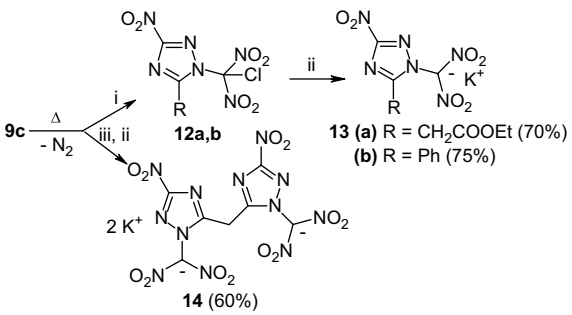
Table 1
Correlation of thermal stability and electron withdrawing nature (σ^*) of the polynitro substituent X for **9a–c**

Compound	**9a**, X=NO_2	**9b** X=F	**9c**, X=Cl
Temperature of thermolysis, °C	−20	25–30	60–65
σ^*	4.54[20]	4.4[20]	4.2[21]

In contrast, diarylnitrilimines available via thermolysis of the respective diaryl tetrazoles were reported to be considerably less reactive. For example, yields of the triazole products were ca. 15%, decomposition being the main reaction course.[11]

As evidenced from both chromatographic and NMR spectroscopic analyses, the reaction was regiospecific. It afforded a single product, namely 1,2,4-triazole derivative **10a–c**. This outcome was in accordance with data reported in the literature.[11,13] Structures of **10a–c** have been confirmed by elemental analysis, IR, ^{1}H, and ^{13}C NMR spectroscopy. For example, ^{1}H and ^{13}C NMR spectra of derivative **10b** (X=F) featured relatively large spin–spin interaction constants J (CH_3–F coupling)=3 Hz and J (CH_3–F coupling)=5 Hz, respectively, presumably due to the proximity of Me and $C(NO_2)F$ groups in the molecule. In addition, both derivatives **10a** and **10c** afforded the same salt **11** when treated with KI/MeOH.[19]

Under the conditions described above, **9c** reacted with other nitriles to furnish the targeted triazole derivatives. Specifically, **12a** (R=CH_2COOEt) and **12b** (R=Ph) were formed in quantitative yields and, without further purification converted to the dinitromethyl derivatives **13a** and **13b** (Scheme 4, 70% and 75% yields for two steps). In a similar fashion, thermally induced reaction of **9c** with malononitrile in dichloroethane (DCE) afforded bicyclic triazole **14** in a 60% yield.



Scheme 4. Conditions: (i) R-CN, DCE, 60 °C; (ii) KI/MeOH, rt; (iii) $CH_2(CN)_2$, DCE, 60 °C.

Tetrazoles **9a–c** reacted with acetylenes in dichloroethane (DCE) at the temperatures summarized in Table 1 to led to 3-nitropyrazoles **15a–c**. Products **15a–c** were converted to the respective 1-(dinitromethyl)-3-nitro-5-R pyrazoles **16a–c** by treatment with KI/MeOH (Scheme 4). Similar to the reaction of **9a–c** with nitriles, the process was regiospecific.[14]

We conducted thermolysis of **9c** in the presence of an equimolar mixture of benzonitrile and phenyl acetylene (10-fold molar excess each, Scheme 5). Upon completion of the thermolysis step, the reaction mixture was treated with KI/MeOH. ^{1}H NMR spectroscopic analysis of the crude reaction mixture revealed the presence of both pyrazole **16a** and triazole **13b** in a 3:1 ratio and ca. 70% overall yield. This outcome suggests higher reactivity of the intermediate nitrilimine toward phenyl acetylene versus benzonitrile.

In our further investigations, we heated **9c** in a mixture of organic solvent (MeOH, *n*BuOH, acetone) and water (2–30%). The only detectable product in the reaction mixture was the hydrazone of chloronitroformaldehyde **18** (52% yield) presumably formed via the intermediate formation of hydrate **17** (Scheme 6). To the best of our knowledge, this molecule is unattainable by alternative chemical procedures.[22]

Reaction of **9c** with NaN_3 (6–9 M excess) in anhydrous MeOH at rt followed by the water quench of the reaction mixture and organic extraction of aqueous phase yielded an unstable crystalline compound. An IR spectrum of the molecule featured azide group band (2160 cm^{-1}) along with strong bands at 1295, 1343, 1445, 1535, and 1600 cm^{-1} corresponding to vibrations of imine bonds. Notably, the same reaction with **9c** labeled with ^{15}N at the $C(NO_2)_2Cl$ moiety yielded unlabeled compound with identical IR spectrum. The compound did not contain Cl. HRMS analysis of the sample afforded the exact mass of 220.0430±0.0002 corresponding to the molecular formula of C_2N_{14}. Electron impact mass spectrum (70 eV; *m*/*z*, *I*, %) featured peaks corresponding to fragments composed of C and N atoms only, namely: 220 [M^+, 9%], 68 [CN_4, 57%], 54 [CN_3, 42%], 52 [C_2N_2, 9%], and 40 [CN_2, 100%]. *The molecule was found to be extremely sensitive to both mechanical and thermal stimuli.* Based on the evidence listed above, we have assigned it the structure of diazidomethylenecarbonohydrazonic diazide **22**. The suggested mechanism of this transformation involves the initial nucleophilic displacement of 5-NO_2 group in the tetrazole ring with azide to furnish unstable 5-azidotetrazole **19**. Thermally induced ring-opening reaction of **19** followed by the sequential replacement of Cl atoms with N_3 groups affords the key azidoimine intermediates **20** and **21** (observed in the UV spectrum only, UV_{max} (MeOH)=284 nm) leading to the final molecule **22**.[22–25]

In conclusion, we have shown that thermal ring-opening reaction of *N*-(R-dinitromethyl)-5-nitrotetrazoles yielded highly reactive *N*-(R-dinitromethyl)-nitronitrilimine intermediates under mild conditions. These species underwent facile regiospecific reaction with nitriles and acetylenes to yield the corresponding nitro triazoles and pyrazoles in good to excellent yields. Heating of *N*-(chlorodinitromethyl)-5-nitro tetrazole in aqueous organic solvents furnished the hydrazide of chloronitroformaldehyde (52% yield). Ring-opening reaction of the same substrate with an excess of azide anion afforded highly unstable diazidomethylenecarbonohydrazonic diazide (23% yield).

3. Experimental

3.1. General

NMR data were collected on a Bruker AM-300 instrument (working frequencies of 300.13 MHz (^{1}H) and 75.47 (^{13}C)). Mass-spectra were collected on a Finningan MAT/INCOS 50 instrument (70 eV) using direct probe injection. HRMS data were collected on a KRATOS instrument (42 eV, source temperature 150 °C). IR spectra were collected on a UR-20 instrument. UV spectra were collected on a SPECORD UV–vis instrument.

*3.1.1. 2-Dinitromethyl-5-nitrotetrazole (**7a**)*

Yield: 72%, white solid, mp 105–106 °C. Water (10 mL) followed by HNO_3 (10 mL, *d*=1.5) was added to a cooled (ice bath) solution of 5 g (29.2 mmol) of 2-acetonyl-5-nitrotetrazole **4**[2] in 24 mL of H_2SO_4 (*d*=1.83). The reaction mixture was warmed and left at 40 °C for 5 h. The resulting precipitate was filtered, washed with CF_3COOH, and dried in vacuo over P_2O_5 to yield the targeted compound (5 g). ^{1}H NMR (CF_3COOH): 8.47 (s, CH). IR (KBr, cm^{-1}): 1320, 1596, 1620 ($CH(NO_2)_2$), 1373, 1570 (aromatic NO_2). p*K*a (H_2O–H_2SO_4): −1.7. Anal. Calcd for $C_2H_1N_7O_6$: C, 10.96; H, 0.46; N, 44.76. Found: C, 10.97; H, 0.38; N, 45.04.

*3.1.2. Potassium salt (**7b**)*

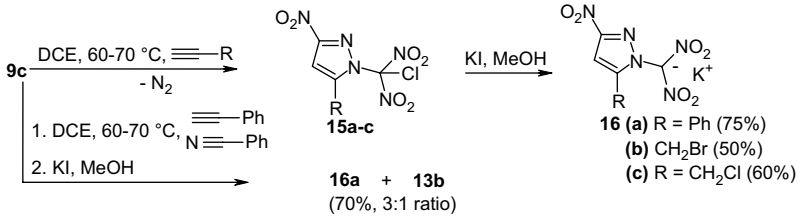
Yield: 85%, yellow crystals, mp 164 °C (decomp.), *d*=2.042 g/cm^3: Reaction of **7a** (1 g) with saturated KOAc in water (1 mL) followed by treatment of the resulting precipitate with water and ether furnished the respective analytically pure potassium salt (1 g). ^{13}C NMR (DMSO-d_6): 131.5 ($J_{13C-15N}$=30.0 Hz), 166.2 (C5). UV_{max} (H_2O)=336 nm (ε=18,000). IR (KBr, cm^{-1}): 1260, 1300, 1493 ($C(NO_2)_2^-$), 1350, 1587 (aromatic NO_2). Anal. Calcd for $C_2KN_7O_6$: C, 9.34; K, 15.20; N, 38.13. Found: C, 9.45; K, 15.11; N, 38.20.

*3.1.3. Hydrazinium salt (**7c**)*

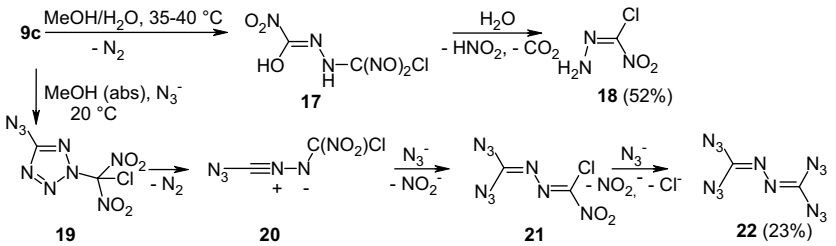
Yield: 54%, yellow crystals, mp 130–140 °C (decomp.), *d*=1.818 g/cm^3. To a cooled solution (ice bath) of **7a** (10 g, 46 mmol) in water (25 mL) was added aqueous NH_2NH_2 (85% solution, 4 mL, 100 mmol) followed by of acetic acid (5.3 mL, 84 mmol) in water (4 mL). The resulting mixture was kept at 0–5 °C for 1 h, and then filtered. The resulting precipitate was washed with ice-cold water (5 mL) and recrystallized from water (25 mL) to afford 6.2 g of the corresponding hydrazinium salts. UV_{max} (H_2O)=336 nm (ε=18,000). IR (KBr, cm^{-1}): 1300, 1365, 1375, 1380, 1493, 1520 ($C(NO_2)_2^-$), 1585 (aromatic NO_2), 3000–3250 (br, $NH_2NH_3^+$). Anal. Calcd for $C_2H_5N_9O_6$: C, 9.56; H, 1.99; N, 50.20. Found: C, 9.66; H, 1.88; N, 50.47.

*3.1.4. Ammonium salt (**7d**)*

Yield: 50%, yellow crystals, mp 130–140 °C (decomp.), *d*=1.78 g/cm^3. A solution of **7a** (1 g, 4.56 mmol) in ^{i}PrOH (3 mL) was treated with solution of NH_4OAc in MeOH (2 mL). The resulting precipitate



Scheme 5.



Scheme 6.

was filtered, washed with ^{i}PrOH, ether, and dried in vacuo to yield 0.54 g of the targeted salt. It was further dissolved in acetone (5 mL) and triturated with ether to afford analytically pure material. UV_{max} (H_2O)=336 nm (ε=18,000). Anal. Calcd for $C_2H_4N_8O_6$: C, 10.17; H, 1.71; N, 47.46. Found: C, 10.22; H, 1.83; N, 47.58.

*3.1.5. 2-Nitromethyl-5-nitrotetrazole (**8**)*

Yield: 14%, white crystals, mp 138–139 °C. *N*-Acetonyl-5-nitrotetrazole **4** (1 g, 5.84 mmol) was dissolved in a vigorously stirred mixture of HNO_3–H_2SO_4–H_2O=5:12:5 by volume (11 mL) at rt for 2 h. The reaction was poured into ca. 50 g of crushed ice. The resulting precipitate was filtered, washed with water, recrystallized from MeOH/H_2O (1:1) and dried in vacuo to yield **8** (0.14 g). ^{1}H NMR (CD_3CN), 7.64 (s, CH_2). UV_{max} (H_2O, pH 8)=312 nM (ε=8600). IR (KBr, cm^{-1}): 1305, 1560, 1590 (NO_2). Anal. Calcd for $C_2H_2N_6O_4$: C, 13.80; H, 1.16; N, 48.28. Found: C, 13.71; H, 0.95; N, 47.93.

*3.1.6. 2-(Trinitromethyl)-5-nitrotetrazole (**9a**)*

Unstable at temperatures greater than −20 °C; **9a** was prepared and used in situ for the synthesis of respective triazole **10a** (vide supra).

*3.1.7. 2-(Fluorodinitromethyl)-5-nitrotetrazole (**9b**)*

Yield: 93%, white crystals, mp 21–22 °C. A solution of **7b** (the procedure was repeated several times at 5.1–12.9 g scale, 20–50 mmol) in H_2O (250 mL) was treated with F_2 (10% in N_2) at 0–5 °C (ice bath). Reaction completion was determined by UV (disappearance of the absorption band at 336 nm). The resulting white precipitate was filtered dried and recrystallized from CCl_4–hexanes (1:1) to furnish the targeted **9b** (4.4–11 g). ^{19}F NMR (CH_2Cl_2): +9.8 (F). IR (KBr, cm^{-1}): 1280, 1615 ($CF(NO_2)_2$), 1360, 1570 (aromatic NO_2). Anal. Calcd for $C_2FN_7O_6$: C, 10.13; N, 41.36. Found: C, 10.01; N, 41.59.

*3.1.8. 2-(Chlorodinitromethyl)-5-nitrotetrazole (**9c**)*

Yield: 70%, white crystals, mp 65 °C (decomp.). A suspension of 1 g of **7b** in CH_2Cl_2 (30 mL) was treated with Cl_2 at rt until yellow solid was replaced with colorless precipitate of KCl (5–10 min). The precipitate was filtered, mother liquor was concentrated in vacuo at 20 °C and the residue was recrystallized from CCl_4 at 50 °C to afford analytically pure **9c** (0.69 g). IR (KBr, cm^{-1}): 1275, 1300, 1610 ($CCl(NO_2)_2$), 1340, 1560 (aromatic NO_2). Anal. Calcd for $C_2ClN_7O_6$: C, 9.48; N, 38.68. Found: C, 9.41; N, 38.18. Both formation and purity of **9c** were further confirmed by the treatment with KI/MeOH (20 mL solution) followed by titration of I_2 with $Na_2S_2O_3$.

3.2. General procedure for the thermal ring-opening reaction of 2-(polynitromethyl)-5-nitrotetrazoles (9a–c)

Tetrazole (2 mmol) was dissolved in absolute MeCN (10 mL). The resulting solution was kept at the temperatures summarized in Table 1 for 15–20 min until N_2 evolution stopped. The resulting mixture was concentrated in vacuo at rt and recrystallized from CCl_4 to afford **10a–c** as analytically pure compound.

*3.2.1. 1-Trinitromethyl-3-nitro-5-methyl-1,2,4-triazole (**10a**)*

Yield: 85%, white crystals, mp 55–57 °C. A suspension of **7d** (1.18 g, 5 mmol) in absolute MeCN (20 mL) was treated with NO_2BF_4 (0.95 g, 7 mmol) at −20 °C under Ar. The reaction mixture was stirred at this temperature for 15–20 min, diluted with CH_2Cl_2 and filtered to remove inorganic salts. Organic phase was concentrated at rt and the residue was recrystallized from CCl_4 to afford 1.2 g of **10a**. ^{1}H NMR ($CDCl_3$): 2.67 (s, Me). ^{13}C NMR ($CDCl_3$): 14.7 (Me), 117.9 ($C(NO_2)_3$), 161.4 (C_5), 161.8 (C_3). IR (KBr, cm^{-1}): 1310, 1621 ($C(NO_2)_3$), 1298, 1580 (aromatic NO_2). Anal. Calcd for $C_4H_3N_7O_8$: C, 17.34; H, 1.09; N, 35.38. Found: C, 17.08; H, 1.01; N, 35.53.

Reaction conducted at 20 °C furnished the targeted 1-fluorodinitromethyl-3-nitro-5-methyl-1,2,4-triazole (**10b**). Yield: 90% (1.13 g), white crystals, mp 55–57 °C. ^{1}H NMR ($CDCl_3$): 2.74 (d, J_{1H-19F}=3.0 Hz, Me). ^{13}C NMR ($CDCl_3$): 13.8 ($J_{13C-19F}$=5 Hz, Me), 113.5 ($J_{13C-19F}$=300.0 Hz, $CF(NO_2)_2$), 159.8 (C_5), 162.1 (C_3). ^{19}F NMR (CH_2Cl_2): +8.86 (F). IR (KBr, cm^{-1}): 1275, 1600, 1630 ($CF(NO_2)_2$), 1310, 1570 (aromatic NO_2). Anal. Calcd for $C_4H_3FN_6O_6$: C, 19.21; H, 1.21; N, 33.60; F, 7.60. Found: C, 19.02; H, 1.03; N, 33.72; F, 7.36.

Reaction conducted at 60–70 °C furnished the targeted 1-chlorodinitromethyl-3-nitro-5-methyl-1,2,4-triazole (**10c**). Yield: 85% (1.13 g), white crystals, mp 109–111 °C. ^{1}H NMR ($CDCl_3$): 2.72 (s, Me). IR (KBr, cm^{-1}): 1310, 1612, 1625 ($CCl(NO_2)_2$), 1360, 1570 (aromatic NO_2). Anal. Calcd for $C_4H_3ClN_6O_6$: C, 18.02; H, 1.13; N, 31.53; Cl, 13.30. Found: C, 18.19; H, 1.21; N, 31.58; Cl, 13.27.

*3.2.2. Potassium salt of 1-dinitromethyl-3-nitro-5-methyl-1,2,4-triazole (**11**)*

Yield: 80% (1.22 g from **10a**), 91% (1.23 g, from **10c**), yellow crystals, mp 182–190 °C (decomp.). Triazole (**10a** or **10c**, 2 mmol) was dissolved in MeOH (5 mL) and treated with solution of KI (0.664 g, 4 mmol) in MeOH (5 mL) at rt. The resulting mixture was stirred at rt for 40 min and triturated with 10 mL of Et_2O. Precipitate was collected, washed with ice-cold water, recrystallized from water and washed with EtOH followed by Et_2O to afford **11**. ^{1}H NMR (DMSO-d_6): 2.38 (s, Me). ^{13}C NMR (DMSO-d_6): 11.6 (Me), 129.6 ($C(NO_2)_2^-$), 160.4 (C_5), 162.1 (C_3). UV_{max} (H_2O)=343 nm (ε=16,400). IR (KBr, cm^{-1}): 1230, 1475 ($C(NO_2)_2^-$), 1540, 1562 (aromatic NO_2). Anal. Calcd for $C_4H_3KN_6O_6$: C, 17.78; H, 1.12; N, 31.10. Found: C, 17.92; H, 1.20; N, 31.29.

*3.2.3. Potassium salt of 1-dinitromethyl-3-nitro-5-carbethoxymethyl-1,2,4-triazole (**13a**)*

Yield: 70%, yellow crystals, decompose upon heating. Ethyl ester of cyanoacetic acid (5.65 g, 50 mmol) was added to solution of **1d** (1.28 g, 5 mmol) in 10 mL of dichloroethane (DCE). The reaction mixture was heated to 60–65 °C for 15 min until N_2 evolution stopped. Vigorously stirred mixture was brought to rt and treated

dropwise with solution of KI (1.66 g, 10 mmol) in MeOH (10 mL) followed by CH_2Cl_2 (30 mL). The resulting precipitate was collected, washed with ice-cold water, MeOH, and Et_2O to furnish 1.13 g of **13a**. ^{1}H NMR (DMSO-d_6): 1.18 (t, J=7.2 Hz, Me), 3.86 (s, CH_2), 4.1 (q, J=7.2 Hz, CH_2). UV_{max} (H_2O)=341 nm (ε=16,700). IR (KBr, cm^{-1}): 1235, 1480 ($C(NO_2)_2^-$), 1568 (aromatic NO_2), 1731 (C=O). Anal. Calcd for $C_7H_7KN_6O_8$: C, 24.56; H, 2.06; N, 24.55. Found: C, 24.69; H, 2.18; N, 24.71.

*3.2.4. Potassium salt of 1-dinitromethyl-3-nitro-5-phenyl-1,2,4-triazole (**13b**)*

Yield: 75% (1.25 g), yellow crystals, decompose upon heating. ^{1}H NMR (DMSO-d_6): 7.95 (m, Ph). ^{13}C NMR (DMSO-d_6): 125.3 (C-Triazole-C_5), 127.6 (*m*-C), 129.4 (*o*-C), 131.1 ($C(NO_2)_2^-$), 132.2 (*p*-C), 159.7 (Triazole-C_5), 162.4 (Triazole-C_3). UV_{max} (H_2O)=345 nm (ε=16,200). IR (KBr, cm^{-1}): 1230, 1490 ($C(NO_2)_2^-$), 1572 (aromatic NO_2). Anal. Calcd for $C_9H_5KN_6O_6$: C, 32.53; H, 1.52; N, 25.29. Found: C, 32.70; H, 1.61; N, 25.39.

*3.2.5. Bis-potassium salt of bis-(1-dinitromethyl-3-nitro1,2,4-triazolyl-5)methane (**14**)*

Yield: 60% (0.79 g), yellow crystals, decompose upon heating. ^{1}H NMR (DMSO-d_6): 4.90 (s, CH_2). ^{13}C NMR (DMSO-d_6): 16.0 (CH_2), 129.0 ($C(NO_2)_2^-$), 154.2 (Triazole-C_5), 161.9 (Triazole-C_3). UV_{max} (H_2O)=341 nm (ε=29,900). IR (KBr, cm^{-1}): 1240, 1492 ($C(NO_2)_2^-$), 1580 (aromatic NO_2). Anal. Calcd for $C_7H_2KN_{12}O_{12}$: C, 16.03; H, 0.38; N, 32.05. Found: C, 16.23; H, 0.41; N, 32.24.

3.3. Synthesis of 1-(dinitromethyl)-pyrazoles 16a–c via the 1,3-dipolar cycloaddition reaction of nitrilamines to acetylenes. Representative protocol

*3.3.1. Potassium salt of 1-(dinitromethyl)-3-nitro-5-chloromethyl pyrazole (**16c**)*

Yield: 60%, yellow crystals, decompose upon heating. Propargyl chloride (3 mL, 41 mmol) was added to a solution of 2-(chlorodinitromethyl)-5-nitrotetrazole (1.014 g, 4 mmol) in DCE (10 mL) in a Teflon tube. The tube was sealed and heated at 70 °C for 15 min (water bath). The reaction mixture was brought to rt and transferred to a 100 mL glass flask. Ether (20 mL) followed by suspension of KI (1.33 g, 8 mmol) in MeOH (10 mL) was added to a vigorously stirred mixture. After 20 min the solid residue was filtered and recrystallized from water to yield the targeted **16c** (0.64 g). ^{1}H NMR (DMSO-d_6): 4.73 (s, 2H), 7.62 (s, 1H). ^{13}C NMR (DMSO-d_6): 33.8 (t, J=152.6 Hz, CH_2Cl), 103.2 (d, J_{13C-1H}=188.6 Hz, C_4), 130.7 ($C(NO_2)_2^-$), 145.9 (C_5), 155.9 (C_3). UV_{max} (H_2O)=345 nm (ε=16,300). IR (KBr, cm^{-1}): 1221, 1483 ($C(NO_2)_2^-$), 1549 (aromatic NO_2). Anal. Calcd for $C_5H_3ClKN_5O_6$: C, 19.78; H, 1.00; N, 23.06. Found: C, 19.82; H, 1.11; N, 23.17.

*3.3.2. Potassium salt of 1-dinitromethyl-3-nitro-5-phenyl-pyrazole (**16a**)*

Yield: 75% (0.99 g), yellow crystals, decompose upon heating. ^{1}H NMR (DMSO-d_6): 7.73 (s, 1H), 7.77 (m, 5H). ^{13}C NMR (DMSO-d_6): 103.2 (d, J_{13C-1H}=186.6 Hz, C_4), 126.2 (Pyrazole-C_5), 127.5 (*m*-C), 129.1 (*o*-C), 131.8 (*p*-C), 132.8 ($C(NO_2)_2^-$), 146.2 (C_5), 156.0 (C_3). UV_{max} (H_2O)=348 nm (ε=16,500). IR (KBr, cm^{-1}): 1222, 1270, 1492 ($C(NO_2)_2^-$), 1559 (aromatic NO_2). Anal. Calcd for $C_5H_4KN_5O_6$: C, 22.32; H, 1.50; N, 26.01. Found: C, 22.45; H, 1.61; N, 26.22.

*3.3.3. Potassium salt of 1-dinitromethyl-3-nitro-5-bromomethyl-pyrazole (**16b**)*

Yield: 50% (0.70 g), yellow crystals, decompose upon heating. ^{1}H NMR (DMSO-d_6): 4.83 (s, 2H), 7.60 (s, 1H). ^{13}C NMR (DMSO-d_6): 19.1 (CH_2Br), 103.2 (d, J_{13C-1H}=186.0 Hz, C_4), 130.8 ($C(NO_2)_2^-$), 146.6 (C_5), 156.0 (C_3). UV_{max} (H_2O)=346 nm (ε=16,200). IR (KBr, cm^{-1}): 1228, 1285, 1478 ($C(NO_2)_2^-$), 1540, 1568 (aromatic NO_2). Anal. Calcd for $C_5H_3BrKN_5O_6$: C, 17.25; H, 0.87; N, 20.12. Found: C, 17.14; H, 0.91; N, 20.32.

3.4. Synthesis of hydrazones from 2-(chloronitromethyl)-5-nitrotetrazole (9c)

*3.4.1. Chloronitroformaldehyde hydrazone (**18**)*

Yield: 52%, yellow solid, mp 50 °C (decomp.). A solution of **9c** (2 g, 7.9 mmol) in MeOH (40 mL) was heated at 45 °C for 4 h until disappearance of the starting material. The reaction mixture was concentrated in vacuo at rt, the residue was redissolved in water (5 mL) at 50 °C. The resultant mixture was filtered, cooled to 0–5 °C, the resultant crystals were collected and dried to furnish **18** (0.51 g). UV_{max} (H_2O)=314.5 nm (ε=10,200). IR (KBr, cm^{-1}): 1235, 1258, 1300, 1520 (NO_2), 1560, 1620 (N=C), 3220, 3280, 3420 (NH_2). EIMS (70 eV, 20 °C) (*m*/*z*, *I*, %): 125 [M^+, 3], 79 [33]. Anal. Calcd for $CH_2N_3ClO_2$: C, 9.73; H, 1.63; N, 34.02; Cl, 28.71. Found: C, 9.60; H, 1.83; N, 33.86; Cl, 29.07.

*3.4.2. Diazidomethylenecarbonohydrazonic diazide (**22**)*

Caution! The molecule easily decomposes upon mechanical treatment when completely dry. Yield: 22%, white needles, 76–77 °C (decomp.). Dry NaN_3 (0.6 g, 9.23 mmol) was cannulated portionwise (8–10) to a vigorously stirred solution of **9c** (0.3 g, 1.18 mmol) in absolute MeOH (10 mL). In 3 h the reaction mixture was treated with 5 mL of water, concentrated in vacuo at rt to 3–4 mL, and extracted with Et_2O (3×20 mL). Organic extract was concentrated in vacuo at rt, cooled to −30 °C (water–ethylene glycol–dry ice bath) and the resulting crystals were expeditiously filtered to yield **22** (0.06 g). HRMS (42 eV), calcd for C_2N_{14}: 220.0434, found: 220.0430±0.0002. EIMS (70 eV) (*m*/*z*, *I*, %): 220 [M^+, 9], 68 [CN_4, 57], 54 [CN_3, 42], 52 [C_2N_2, 9], 40 [CN_2, 100]. IR ($CHCl_3$, cm^{-1}): 1295, 1343, 1445, 1535, 1587, 1600, 1612 (conjugated C=N), 2160 (N_3).

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