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Unusual formation of 4-diazo-3-nitriminopyrazoles upon acid nitration of pyrazolo[3,4-*d*][1,2,3]triazoles

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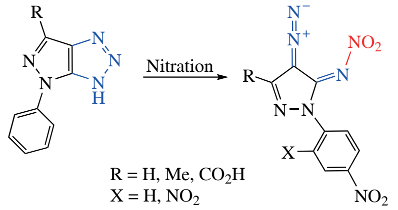
Nitration of 6-R-4-phenylpyrazolo[3,4-*d*][1,2,3]triazoles at the phenyl substituent is accompanied by the triazole ring opening to give new 3-R-4-diazo-1-(di)nitrophenylpyrazole-5-nitrimines. Chemical and physicochemical properties of the prepared compounds are reported.



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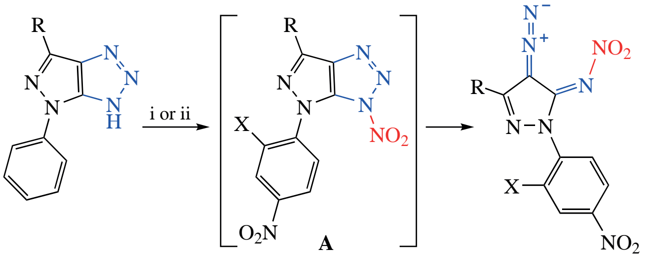
Pyrazolo[3,4-*d*][1,2,3]triazole (PT) heterocyclic framework is used to design of biologically active substances,[1–3] photographic developers[4] and luminophores.[5–7] Although the first reports of PTs date back to the beginning of 20th century,[8,9] the synthetic approaches are still in their infancy and mostly limited to the heterocyclization reactions.[1,7,10–14] To the best of our knowledge, only *N*-alkylation[1,15] and *N*-amination[16] of the triazole ring in PTs have been documented. The potential of PTs bearing nitro groups as energetic materials has been demonstrated recently.[17–21] The contemporary trend in the energetic materials design is the use of fused nitrogen-rich heterocyclic systems as a framework for the insertion of explosophoric groups (NO_2, $NHNO_2$, N_3, *etc*.).[22] Therefore, the development of new methods for the synthesis of PT nitro derivatives is topical. The main method for incorporation of a nitro group into the pyrazole ring involves the acid nitration with HNO_3 or its mixtures with inorganic or organic acids.[23,24]

To continue our studies on the synthesis of new nitro derivatives of pyrazole-containing compounds,[25–30] the acid nitration of some of the most accessible derivatives of PT **1a–c** was explored in this work. In fact, the nitration of 6-R-4-phenylpyrazolo[3,4-*d*][1,2,3]triazoles **1a–c** with fuming HNO_3 or with a mixture of fuming HNO_3 with concentrated H_2SO_4, along with the anticipated nitration of the *N*-phenyl ring, unexpectedly results in opening of the 1,2,3-triazole ring to give compounds of a previously unknown type, namely, 3-R-4-diazopyrazole-5-nitrimines **2a–c** or **3** (Scheme 1).

The opening of the N^1-substituted 1,2,3-triazole ring as a result of 1,2,3-triazole–diazo imine ring–chain tautomerism with formation of products of further transformation of *ortho*-organized diazo imines, in particular, due to reactions with nucleophiles, is not unknown.[31–34] On the other hand, the opening of the triazole ring in monocyclic triazoles and benzotriazoles under acid nitration conditions has not been reported yet. We believe that in the case of PT, the action of a nitrating agent results in *N*-nitro derivative **A** (see Scheme 1), which in the case of the strained [5 : 5] heterocyclic system of PT is unstable and irreversibly opens to deliver diazo nitrimines **2**, **3**. In the absence of nucleophiles, diazo nitrimines **2**, **3** remain stable and can be easily isolated. It should be noted that two examples of 4-diazo-5-nitroimino-1-phenyl-1,2,3-triazoles are known, but they were obtained as impurities in the acid nitration of 4-(*tert*-butyl-*NNO*-azoxy)-1-phenyl-1*H*-1,2,3-triazol-5-amine.[35]

The structure of diazo nitrimines **2b,c** was determined unambiguously by single crystal X-ray diffraction (Figure 1).[†]



1a R = H
1b R = Me
1c R = CO_2H

2a R = H, X = NO_2, 70%
2b R = Me, X = NO_2, 55%
2c R = CO_2H, X = NO_2, 42%
3 R = CO_2H, X = H, 62%

Scheme 1 *Reagents and conditions:* i, HNO_3 (100%), H_2SO_4 (93%), room temperature, 5–96 h (for **1a–c**); ii, HNO_3 (100%), 5 h (for **1c**).

[†] *Crystallographic data for* **2b**. $C_{10}H_6N_8O_6$ is monoclinic at 100 K, space group $P2_1/c$, $a = 9.8612(4)$, $b = 18.3656(7)$ and $c = 7.2762(3)$ Å, $\beta = 91.9795(14)°$, $V = 1316.98(9)$ Å^3, $Z = 4$, $M = 334.23$, $d_{cryst} = 1.686$ g cm^{-3}, $wR_2 = 0.0944$ calculated on F^2_{hkl} for all 2878 independent reflections with $2\theta < 54.0°$, [GOF = 1.061, $R = 0.0358$ calculated on F_{hkl} for 2490 reflections with $I > 2\sigma(I)$].

Crystallographic data for **2c**. $C_{10}H_4N_8O_8 \cdot 2H_2O$ is monoclinic at 100 K, space group Cc, $a = 10.4788(4)$, $b = 30.5143(12)$ and $c = 5.7829(2)$ Å, $\beta = 119.2620(10)°$, $V = 1613.14(11)$ Å^3, $Z = 4$, $M = 400.24$, $d_{cryst} = 1.648$ g cm^{-3}, $wR_2 = 0.1244$ calculated on F^2_{hkl} for all

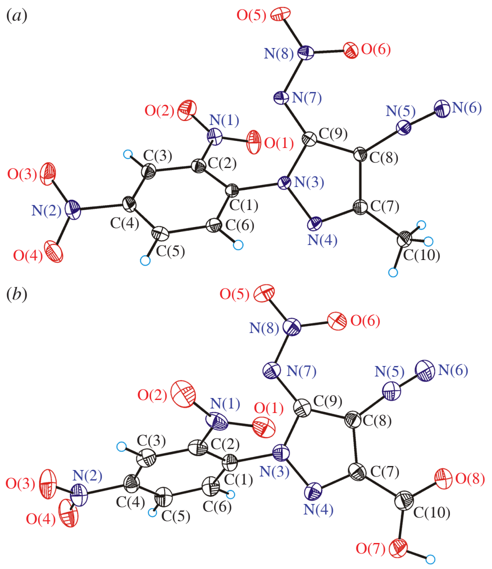
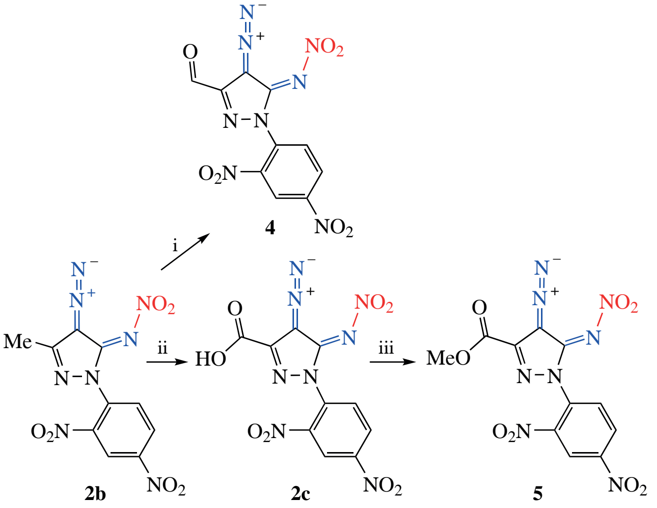


Figure 1 General view of (*a*) molecule **2b** and (*b*) molecule **2c** with the atom numbering scheme. Thermal ellipsoids are given at 50% probability level.

Both molecules have nonplanar geometry. The torsion angles defining interring mutual orientation are 62.3(2) and –65.7(5)° in compounds **2b** and **2c**, respectively. The substituents at the pyrazole and benzene rings in both molecules are nearly coplanar to the corresponding rings except for the nitro group at the C(2) atom. The distribution of bond lengths in the diazo nitrimine moiety [N(8)–N(7), 1.345(2) Å; N(7)=C(9), 1.344(2) Å; C(9)–C(8), 1.421(2) Å; C(7)–C(8), 1.432(2) Å; C(8)=N(5), 1.350(2) Å; N(5)=N(6), 1.106(2) Å for **2b** and N(8)–N(7), 1.334(4) Å; N(7)=C(9), 1.338(5) Å; C(9)–C(8), 1.419(5) Å; C(7)–C(8), 1.431(5) Å; C(8)=N(5), 1.340(5) Å; N(5)=N(6), 1.102(5) Å for **2c**] is typical of the nitrimine structure, where the lengths of C(9)=N(7) and N(7)–N(8) bonds are nearly equal, while the C(8)–C(9) bond in the pyrazole ring is only slightly shorter than the C(7)–C(8) bond, which is formally an ordinary bond. This conclusion can be supported by comparison with the nitramino form (C–N$^-$–NO$_2$) in which the C–N bond is, for instance, noticeably longer than that in nitraminofurazanyl salts.[38]

Using compound **2b** as an example, we have shown that diazo nitrimines are extremely stable under acid conditions. In fact, heating of compound **2b** in 100% H_2SO_4 in the presence of HNO_3 at 80 °C results in the oxidation of the methyl group into formyl one to produce aldehyde **4** (Scheme 2). The action of $Na_2Cr_2O_7$ in H_2SO_4 with heating results in the oxidation of this methyl group into a carboxy one leading to acid **5** whose esterification gives methyl ester **5**. The diazo nitrimine pattern was preserved in both cases. The compounds thus obtained decomposed slowly under light,[39] as this is typical of diazo compounds. Refluxing in alcohols did not cause the reduction of the diazo group. Attempts to carry out reactions with nucleophiles at one of the reaction centers resulted in resinification.



Scheme 2 *Reagents and conditions*: i, HNO_3 (100%), H_2SO_4 (100%), 80 °C, 5 h; ii, $Na_2Cr_2O_7$, H_2SO_4, 60 °C, 1 h; iii, MeOH, $SOCl_2$, 20 h, reflux.

Compounds **1a**,**c**, **2–5** were characterized by IR, ^{1}H, ^{13}C, ^{14}N NMR spectroscopy and HRMS. For compound **2b**, the ^{15}N NMR spectrum was recorded and the signals were assigned on the basis of literature data. In the ^{14}N NMR spectra of diazo nitrimines **2a**,**b** as well as **3**, **5**, a characteristic peak at ~–20 ppm for the nitrogen atom of the nitro group and a peak in the range from –120 to –155 ppm for the diazo group can be observed. In the ^{13}C NMR spectra of all diazo nitrimines **2–5**, the C^4 pyrazole signal associated with the diazo group is detected in the upfield region (~80 ppm, *cf.* ref. 37). An absorption band at 2192–2201 cm^{-1} characteristic of diazoazoles[40] is observed in the IR spectra of compounds **2–5**.

The thermal stability of diazo nitrimines **2a–c**, **3** was studied by the DSC–TGA techniques. The characteristic onset temperatures of their decomposition exotherms are in the range of 158–213 °C. The highest thermal stability is observed for compound **2b** which melts with decomposition at 213 °C and exceeds the typical primary explosive diazo dinitroquinone (DDNP). The enthalpy of formation in the gas phase was calculated for compounds **2a**,**b** by the AIQM1 method.[41] The sublimation enthalpies were estimated using the modified Trouton rule.[42] Diazo nitrimines have large enthalpies, 1.5 times higher than those of their close analogs, 3-nitro-4-diazopyrazol-5-ones (*cf.* refs. 21, 43–46) and 2 times higher than that of DDNP.[43]

The experimentally determined impact and friction sensitivities of diazo nitrimines **2a**,**b** are 3.5–5 J and 190–320 N, respectively. Based on the experimentally determined density and enthalpy of formation, the detonation performance was calculated using the PILEM[47] program (Table 1). These findings indicate that diazo nitrimines have an energetic potential comparable to that of benchmark TNT explosive. In terms of the combination of energetic parameters, thermal stability and sensitivity, the compounds of the new type, 3-R-4-diazopyrazole-5-nitrimines, are similar to previously suggested 3-nitro-4-diazopyrazol-5-ones (see Online Supplementary Materials).[21,43,44]

In conclusion, we have discovered the opening of the 1,2,3-triazole ring to yield 1,3-disustituted 4-diazopyrazole-5-nitrimines upon acid nitration of 3-R-1-phenylpyrazolo[3,4-*d*][1,2,3]triazoles. Chemical and physicochemical properties of the prepared compounds are reported, expanding our knowledge of this heterocyclic framework.

3030 independent reflections with $2\theta < 54.0°$, [GOF = 1.049, $R = 0.0474$ calculated on F_{hkl} for 2734 reflections with $I > 2\sigma(I)$].

Single crystal X-ray diffraction experiments were carried out using a SMART APEX2 CCD diffractometer [λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω-scans] at 100 K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package.[36] The structures were solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The refinement was carried out by the SHELXTL program.[37]

CCDC 2383675 (**2b**) and 2383676 (**2c**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

Table 1 Properties of diazo nitrimines **2a**,**b** compared with DDNP and TNT.

Compound	mp/°C	T_d/°C[a]	d[b]/g cm^{-3}	$\Delta_\mathrm{f}H$/kJ mol^{-1} (kJ g^{-1})[c]	D[d]/km s^{-1}	P/GPa[e]	IS/J[f]	FS/N[g]
2a	184	184	1.675[h]	577 (1.55)	7.4	27	3.6 ± 0.6	190 ± 30
2b	213	213	1.629	517 (1.79)	7.1	25	5 ± 3	320 ± 30
DDNP	159	159	1.72	125 (0.60)	7.3	26	1.8 ± 1.4	11 ± 3
TNT[48]	80	275	1.65	–62 (–0.27)	6.9	23	30	>360

[a] Decomposition onset temperature measured at a heating rate of 5 K min^{-1}. [b] Density based on X-ray analysis at room temperature. [c] Calculated enthalpy of the formation for the solid state. [d] Detonation velocity. [e] Detonation pressure. [f] Impact sensitivity (STANAG 4489). [g] Friction sensitivity (STANAG 4487). [h] Density measured using a gas pycnometer (at 25 °C).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7628.

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