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Substitution for a nitro group in 1,3,5-trinitrobenzene under the action of NH-azoles

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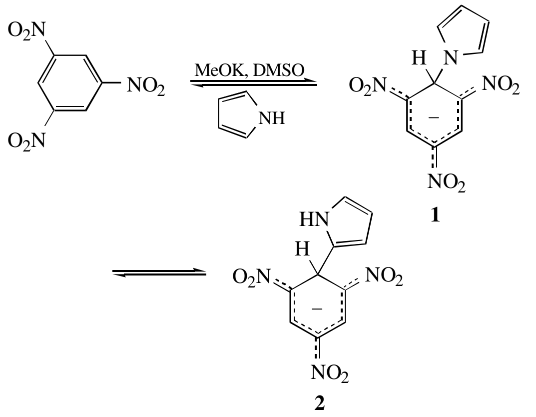
Conditions under which a nitro group in 1,3,5-trinitrobenzene is replaced under the action of NH-azoles were found.

As a continuation of our studies[1,2] devoted to the conversion of aromatic explosives, we examined the reaction of 1,3,5-trinitrobenzene with NH-azoles.

By now, the formation of stable anionic σ-complexes as a result of reactions between nitrogen-containing heterocycles such as pyrrole, indole and imidazole with 1,3,5-trinitrobenzene (TNB) is well known.[3–5] The kinetics of formation of these adducts was thoroughly studied. Initially, N-σ-complex **1** is rapidly formed; next, it undergoes rearrangement to more stable C-σ-complex **2** (Scheme 1). Some of these intermediates can be isolated as pure compounds. The products with replaced nitro groups were not reported.



Scheme 1

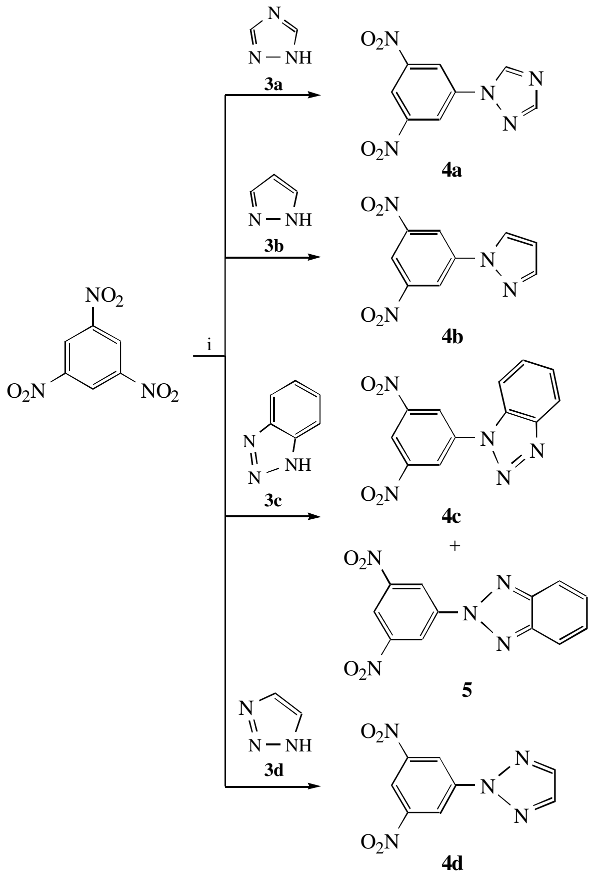
On the other hand, it was found[2,6–8] that, in principle, a nitro group in TNB can be replaced under the action of O- anf S-anionic nucleophiles with good yields.

We decided on compounds containing the =N–N(H)– unit, in particular, pyrazole, 1,2,3-triazole, 1,2,4-triazole and benzotriazole, as NH-azoles. The reactions of these heterocycles (**3a**–**d**) with TNB were examined under various conditions. The products of substitution for a nitro group were formed on heating in amide dipolar aprotic solvents (such as DMF and *N*-methyl-2-pyrrolidone) in the presence of K_2CO_3 (Scheme 2, Table 1).[†]

The lowest yield and the longest reaction time were observed in the case of pyrazole. In the case of benzotriazole, two products **4c** and **5** were formed in overall yield 96%. Recrystallization from DMF gave rise to isomer **5**. Mother liquor was evaporated, and the residue was recrystallised from dioxane to give isomer **4c**. Using ^1H NMR spectroscopy, we found the **4c**/**5** ratio between these isomers to be equal to 2/3 and characterised the structure of these compounds. The ^1H NMR spectrum of compound **5** exhibits two multiplets with the integral intensity 2H in the region 7–9 ppm, which correspond to a symmetrically substituted benzotriazole. The protons of the benzene ring in asymmetrically substituted benzotriazole **4c** form an ABCD spin system and appear as two doublets and two triplets (a doublet of doublets) in the ^1H NMR spectrum.[†] The NOE interaction with a doublet at 8.25 ppm was observed on irradiation of H(2′) and H(6′) protons. On this basis, we concluded that this signal is ascribed to H(7) proton. Next, the other protons of the benzotriazole nucleus were identified using a double resonance technique. The predominance of an isomer substituted at the 2-position of the benzotriazole ring is not typical of the arylation of benzotriazole, and it probably results from the electrophilic properties of TNB. In the case of 1,2,3-triazole, only compound **4d**, which is the product of substitution at the 2-position of the triazole nucleus, was formed.

Table 1 Reaction of **3a**–**d** with TNB.

Product	Reaction time/h	Yield (%)	mp/°C	Solvent for recrystallization
4a	30	20	112–114	$CHCl_3$
4b	6	75	131–133	$CHCl_3$
4c	4	10	184–186	Dioxane
5	4	45	213–214	DMF
4d	2.5	71	126–128	EtOH



Scheme 2 *Reagents and conditions:* i, N–MP, 80 °C, K_2CO_3.

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[†] ^{1}H and ^{13}C NMR spectra were measured on a Bruker AM-300 instrument using [$^2H_6$]DMSO as a solvent and TMS as a standard. Peaks due to molecular ions ($M^{+\cdot}$) were present in the mass spectra of all compounds synthesised. The spectra were obtained on an MS-30 (Kratos) (EI, 70 eV) spectrometer. The structure of products were confirmed by elemental analysis.

General procedure for the reaction of NH-azoles with 1,3,5-trinitrobenzene. A mixture of TNB (0.01 mol), an NH-azole (0.01 mol) in 20 ml of *N*-methyl-2-pyrrolidone was heated at 80 °C for the time specified in Table 1 (until the disappearance of TNB). After completion of the reaction, the mixture was poured into water. The precipitate formed was washed several times with dilute hydrochloric acid and dried. The compounds were purified by recrystallization.

1-(3,5-Dinitrophenyl)-1,2,4-triazole **4a**: ^{1}H NMR, δ: 9.70 (s, 1H, H-5), 9.05 (d, 2H, H-2′,6′, ^4J 2.0 Hz), 8.81 (s, 1H, H-4′, ^4J 2.0 Hz), 8.33 (s, 1H, H-3). ^{13}C NMR, δ: 116.6 [s, C(4′)], 119.2 [s, C(2′)], 138.0 [s, C(1′)], 143.8 [s, C(5)], 148.8 [s, C(3′)], 153.1 [s, C(3)].

1-(3,5-Dinitrophenyl)pyrazole **4b**: ^{1}H NMR, δ: 9.05 (d, 2H, H-2′,6′, ^4J 2.0 Hz), 8.95 (d, 1H, H-3, ^3J 2.7 Hz), 8.71 (t, 1H, H-4′, ^4J 1.9 Hz), 7.89 (d, 1H, H-5, ^3J 1.7 Hz), 6.72 (t, 1H, H-4, ^3J 2.8 Hz). ^{13}C NMR, δ: 109.6 [s, C(4)], 114.8 [s, C(4′)], 117.7 [s, C(2′)], 129.3 [s, C(5)], 140.8 [s, C(1′)], 143.0 [s, C(3)], 148.8 [s, C(3′)].

1-(3,5-Dinitrophenyl)benzotriazole **4c**: ^{1}H NMR, δ: 9.05 (d, 2H, H-2′,6′, ^4J 1.9 Hz), 8.95 (t, 1H, H-4′, ^4J 1.9 Hz), 8.25 (d, 1H, H-7, ^3J 7.9 Hz), 8.10 (d, 1H, H-4, ^3J 7.7 Hz), 7.81 (t, 1H, H-5, ^3J 8.1 Hz), 7.62 (t, 1H, H-6, ^3J 8.0 Hz). ^{13}C NMR, δ: 111.0 [s, C(7)], 117.9 [s, C(4′)], 120.1 [s, C(4)], 123.2 [s, C(2′)], 125.5 [s, C(5)], 129.7 [s, C(6)], 131.9 [s, C(3a)], 137.6 [s, C(1′)], 145.9 [s, C(7a)], 148.9 [s, C(3′)].

2-(3,5-Dinitrophenyl)benzotriazole **5**: ^{1}H NMR, δ: 9.25 (d, 2H, H-2′,6′, ^4J 2.0 Hz), 8.92 (t, 1H, H-4′, ^4J 2.0 Hz), 8.05 (dd, 2H, H-4,7, ^3J 6.6 Hz, ^3J 7.3 Hz), 7.58 (dd, 2H, H-5,6, ^3J 6.6 Hz, ^3J 7.3 Hz). ^{13}C NMR, δ: 118.2 [s, C(4′)], 118.5 [s, C(4)], 120.0 [s, C(2′)], 129.1 [s, C(5)], 140.3 [s, C(1′)], 145.1 [s, C(3a)], 148.9 [s, C(3′)].

2-(3,5-Dinitrophenyl)-1,2,3-triazole **4d**: ^{1}H NMR, δ: 8.98 (d, 2H, H-2′,6′, ^4J 1.9 Hz), 8.82 (t, 1H, H-4′, ^4J 1.9 Hz), 8.33 (s, 2H, H-4,5). ^{13}C NMR, δ: 149.4 [s, C(3′)], 140.3 [s, C(1′)], 139.0 [s, C(4)], 118.6 [s, C(2′)], 117.1 [s, C(4′)].