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Studies on substitution of nitro groups in 1,3,5-trinitrobenzene with NH-azoles*

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Conditions were found under which NH-azoles (benzotriazole and its derivatives, 1,2,3- and 1,2,4-triazoles, pyrazole and its derivatives) replace one nitro group in 1,3,5-trinitrobenzene (TNB) to form the corresponding *N*-(3,5-dinitrophenyl)azoles in the presence of inorganic bases in aprotic dipolar solvents. The reaction pathway was found to depend on the structure of the starting azole. The benzotriazolyl and 1,2,4-triazolyl fragments activate the replacement of the *meta*-nitro group to virtually the same extent as the nitro group in TNB, which made it possible to successively replace all three nitro groups in TNB.

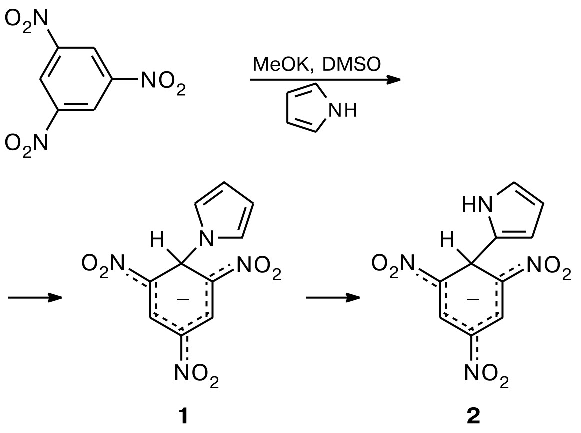
Key words: 1,3,5-trinitrobenzene, NH-azoles, nucleophilic substitution of a nitro group, *N*-(3,5-dinitrophenyl)azoles, bis- and tris-azolylbenzenes.

1,3,5-Trinitrobenzene (TNB) serves as a convenient model for studying the competition between the nucleophilic substitution of an aromatic nitro group and the addition of nucleophiles to the aromatic ring. Actually, the characteristic feature of TNB is its ability to add nucleophiles at the *ortho* position with respect to the nitro group to form stable anionic σ-complexes.[3—6] However, conditions under which certain anionic O- and S-nucleophiles can replace one or two nitro groups in TNB have been found in recent years (see, for example, Refs. 7—11). It should be emphasized that all types of products prepared by the replacement of the nitro groups in TNB have previously been inaccessible. Therefore, investigations into nucleophilic substitution in TNB are also of preparative interest.

The reactions of TNB with NH-azoles, such as pyrrole, indole, and imidazole, studied earlier[12—14] afforded stable anionic σ-complexes as the only products (Scheme 1). The kinetics of the formation of these adducts was investigated in detail. The first step of the reaction involves the formation of *N*-σ-complex **1**, which is rearranged into more stable *C*-σ-complex **2**. Some of these compounds can be isolated in the individual form. In the cited studies, no substitution products of the nitro groups were documented.

We chose benzotriazole (BT) as the first NH-azole to examine the possibility of the substitution of nitro groups in TNB. One of the reasons for this choice is that this compound is devoid of CH fragments adjacent to the nitrogen atoms, which prevents formation of complexes of type **2**. In addition, an analysis of publications devoted to the substitution of the nitro groups in TNB with phenols[7] and polyfluorinated alcohols[8] shows that the acidity of the starting nucleophile plays a significant role in this process. Generally, the acidity $\mathrm{p}K_{\mathrm{a(H_2O)}} \approx 8—12.5$ is required. Benzotriazole satisfies this requirement ($\mathrm{p}K_{\mathrm{a(H_2O)}} = 8.2$).

Scheme 1



We found that benzotriazole (or its K salt (K-BT)[15]) replaces one nitro group in TNB in dipolar aprotic solvents (DMF, *N*-methylpyrrolidone (*N*-MP), DMSO, or MeCN) in the presence of alkalis or alkali metal carbonates at 80 °C. In the absence of bases, no reaction occurs. Solid K_2CO_3 in *N*-MP is a reagent of choice from both the viewpoint of the yields of the target products (Table 1) and the ease of their isolation. Analysis of the ^{1}H NMR

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* For preliminary communications, see Refs. 1 and 2.

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Table 1. Influence of the reaction conditions on the reaction rate and yields of products for the reaction of BT with TNB in the presence of bases (1 : 1 : 1) at 80 °C

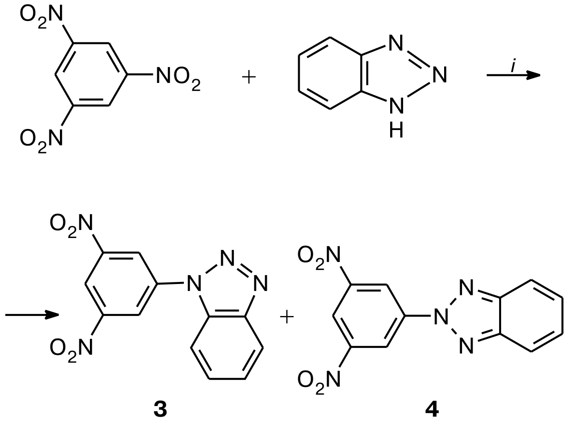
Base	Solvent	τ*/h	Yield of a mixture of isomers **3** and **4** (%)	Isomer ratio (**3**/**4**)
K_2CO_3	*N*-MP	4	96	40/60
K_2CO_3	DMF	3	85	44/56
K_2CO_3	DMSO	6	81	40/60
K_2CO_3	MeCN	5	78	42/58
K-BT**	*N*-MP	3	92	40/60
Na_2CO_3	*N*-MP	4	90	40/60
Cs_2CO_3	*N*-MP	7	77	42/58
Li_2CO_3	*N*-MP	16	75	46/54
KOH	*N*-MP	8	76	39/61
K_2CO_3	EtOH		No reaction	
K_2CO_3	Dioxane		No reaction	

* The conversion time of TNB.

** K salt of BT.

spectra of the reaction products demonstrated that the reactions always afforded isomeric 1- and 2-(3,5-dinitrophenyl)benzotriazoles **3** and **4** in a ratio of ≈2 : 3 (Scheme 2, see Table 1).

Scheme 2



i. *N*-MP, 80 °C, K_2CO_3.

Our results differ substantially from those obtained earlier in the studies of arylation of benzotriazoles with halonitrobenzenes,[16,17] including arylation with the use of Pd- and Cu-containing catalysts,[18,19] where *N*(1) isomers always predominated.

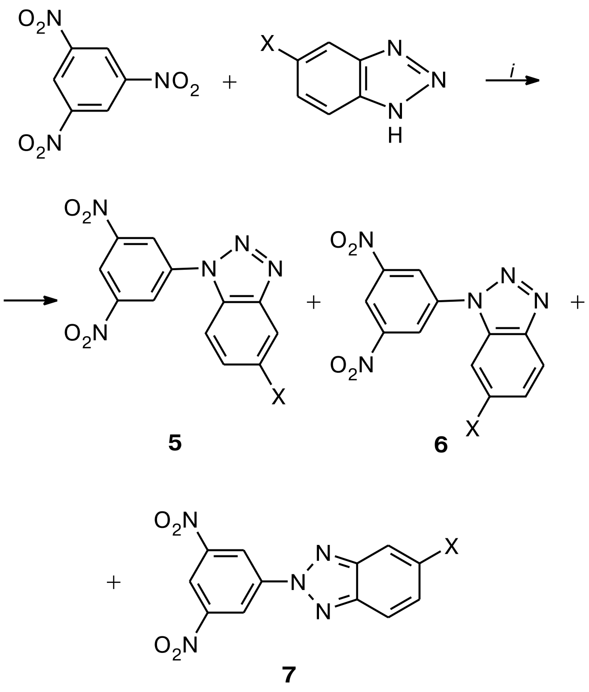
Isomers **3** and **4** were separated by either column chromatography or crystallization from DMF or DMSO, the solubility of isomer **3** being much higher than that of **4**. The structures of the isomers were established by ^1H NMR spectroscopy. The spectrum of compound **4** has two doublets of doublets at δ 7.6—8.2 with integral intensities of 2 H each. In non-symmetrically substituted benzotriazole **3**, the protons of the benzene ring form an ABCD spin system and are observed in the ^1H NMR spectrum as two doublets and two triplets (doublets of doublets). Irradiation of the H(2´) and H(6´) protons results in the NOE effect with a doublet at δ 8.25, which indicates that this proton is located at position 7. The signals for other protons of the benzotriazole moiety were assigned using the double resonance technique. The mass spectrum of compound **3** has the characteristic peak $[M - 28]^+$ associated with the elimination of the nitrogen molecule.

Earlier, compound **3** has been prepared by the addition of 3,5-dinitrophenylazide to dehydrobenzene.[20] However, the melting point of the reaction product reported in the cited study is 14 °C lower than that determined in our investigation.

We also studied the nucleophilic substitution of nitro groups in TNB under the action of 5-substituted benzotriazoles (5-X-BT). We chose 5-substituted benzotriazoles with the aim of excluding the influence of steric factors on the isomer ratio.

The reaction was carried out under the conditions analogous to those used in the reaction with benzotriazole, *viz*., heating in *N*-MP at 80 °C in the presence of an equimolar amount of potassium carbonate (Scheme 3). Water-insoluble reaction products prepared in the analytically pure form were studied by ^1H NMR spectroscopy. These spectra were compared with those of com-

Scheme 3



X = Cl (**a**), Br (**b**), CF_3 (**c**), OMe (**d**)

i. *N*-MP, 80 °C, K_2CO_3.

Table 2. Reaction of 5-X-BT with TNB in the presence of K_2CO_3 (1 : 1 : 1) in *N*-MP at 80 °C

X	τ*/h	Yield (%)	Isomer ratio (**5**+**6**)/**7**
Cl	2.5	90	31/69
Br	4.5	94	33/67
CF_3	5	93	20/80
OMe	8	83	30/70

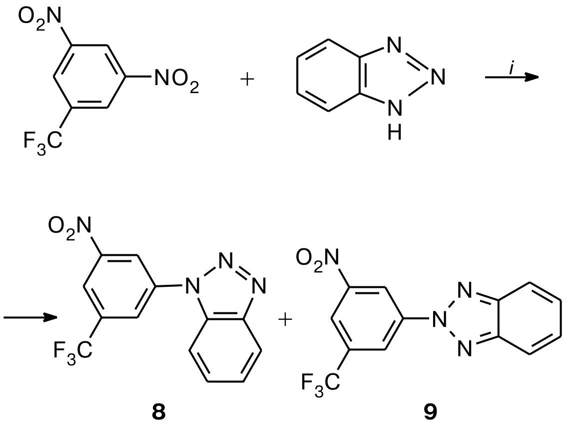
* The conversion time of TNB.

pounds **3** and **4**. A set of signals for the protons of the benzotriazole moiety in the ^{1}H NMR spectra is indicative of the formation of isomers **5**—**7**. Two groups of signals of the dinitrophenyl fragment of the molecule are evidence for the formation of *N*(1)- and *N*(2)-substitution products, which allowed us to determine the ratios between these products (see Table 2). In all cases, product **7** was isolated in the pure form. The results are given in Table 2.

The introduction of a substituent into benzotriazole leads to an increase in the percentage of the *N*(2) isomer, which is most pronounced for the CF_3 group.

The possibility of the substitution of the nitro group in TNB analogs under the action of benzotriazole was examined using the reaction of 1,3-dinitro-5-trifluoromethylbenzene in *N*-MP in the presence of an equimolar amount of K_2CO_3 (Scheme 4).

Scheme 4



8 **9**

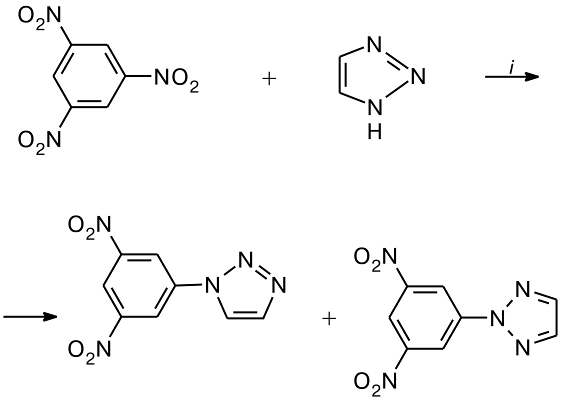
i. *N*-MP, 80 °C, K_2CO_3.

As expected, the reaction afforded two isomers, **8** and **9**, in a ratio of 45 : 55 (judging from the ^{1}H NMR spectroscopic data for the crude product).

It was of interest to compare the behavior of benzotriazole and 1,2,3-triazole, which would allow us to reveal the influence of the annelated benzene ring on the process under study.

Under the conditions optimum for the reaction of benzotriazole with TNB (heating in *N*-MP at 80 °C in the presence of an equimolar amount of K_2CO_3), 1,2,3-triazole gave two products. Judging from the presence, in the mixture, of two types of signals in the ^{1}H NMR spectral region typical of the dinitrophenyl group, the reaction produced isomeric compounds **10** and **11** in a ratio of 1 : 9 (the conversion time of TNB was 2.5 h)* (Scheme 5). The major isomer was isolated by crystallization from ethanol. The ^{1}H NMR spectrum of this compound has a singlet with a double intensity corresponding to the equivalent protons of the 1,2,3-triazole ring. The mass spectrum of this compound does not show a peak at *m/z* [M – 28] characteristic of *N*(1)-arylated 1,2,3-triazoles, which confirms its structure as 2-(3,5-dinitrophenyl)-1,2,3-triazole **11**. Therefore, the percentage of the 3,5-dinitrophenylation product at position 2 of the triazole ring sharply increases on going to 1,2,3-triazole from its benzoannelated analog.

Scheme 5



10 **11**

i. *N*-MP, 80 °C, K_2CO_3.

The results of our study demonstrate that a high degree of *N*(2)-arylation of benzotriazoles and 1,2,3-triazole is a specific feature of TNB as an electrophile.

1,2,4-Triazole also substitutes a nitro group in TNB on heating in *N*-MP at 80 °C in the presence of an equimolar amount of K_2CO_3 to give exclusively isomer **12** (the yield was 75%, the conversion time of TNB was 6 h) (Scheme 6).

The observed direction of 3,5-dinitrophenylation of 1,2,4-triazole at position 1 is consistent with the published data on arylation of 1,2,4-triazole.

Unsubstituted pyrazole exhibits lower reactivity in the reaction with TNB (Scheme 7). Thus the reactions with benzotriazole, 1,2,3-triazole, and 1,2,4-triazole were completed in 4—8 h (the time of complete conversion of

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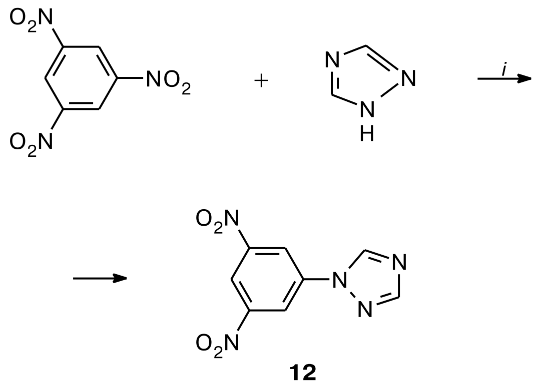
* In all cases, equal concentrations of reactants were used to compare different experiments with regard to the conversion times of the starting material.

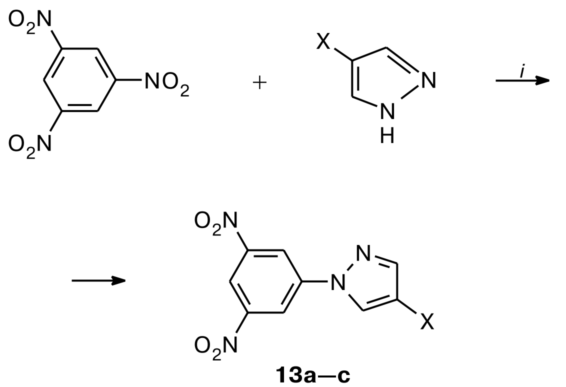
Scheme 6



i. *N*-MP, 80 °C, K_2CO_3.

TNB) to give products of replacement of a nitro group in yields of ≥70%, whereas the time of complete conversion of TNB in the reaction with pyrazole under the same conditions was 30 h, and the yield of compound **13a** was 20%.

Scheme 7



X = H (**a**), Cl (**b**), Br (**c**)

i. *N*-MP, 80—100 °C, K_2CO_3.

In our opinion, this is associated with low NH-acidity of unsubstituted pyrazole ($pK_{a(H_2O)}$ = 14.1). Studies on the kinetics of the formation of stable nucleophile—TNB adducts (Meisenheimer σ-complexes) demonstrated that the higher is the basicity of the anion formed by a nucleophile, *i.e.*, the higher is pK_a of its conjugated acid (NuH), the more stable is the Meisenheimer complex[3,5] of this nucleophile with TNB. The stability of a σ-complex is directly related to the equilibrium concentration of TNB in solution, and the latter, in turn, determines apparently the rate of substitution of a nitro group. From this it follows that the more stable the σ-complex, the lower the rate of substitution of a nitro group. This accounts for a slow rate of the reaction of TNB with pyrazole. The low yield of the product of this reaction can be rationalized considering possible thermal decomposition of the complex at the reaction temperature, like that of any salt of an alicyclic nitro compound.

Actually, the reactions of TNB with 4-bromopyrazole ($pK_{a(H_2O)}$ = 12.69) and 4-chloropyrazole (possessing similar $pK_{a(H_2O)}$) afforded substitution products **13b,c** in yields above 70%, and the reaction time was no longer than 6 h.

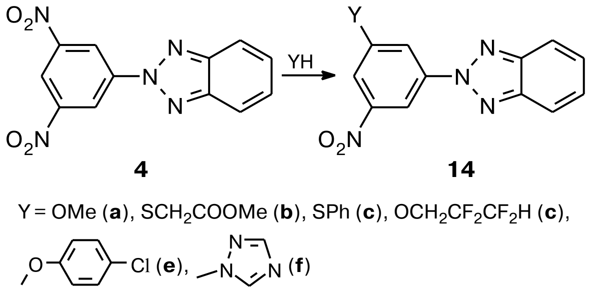
Under the above-mentioned conditions, 3,5-dimethylpyrazole ($pK_{a(H_2O)}$ = 15.8) does not react with TNB. Attempts to replace a nitro group in TNB under the action of imidazole or various benzoimidazoles also failed.

The results of the study demonstrated that a nitro group in TNB is replaced only with NH-azoles in which azolate anions contain at least two adjacent nitrogen atoms. Apparently, high nucleophilicity of such compounds in the substitution of nitro groups in TNB is associated with the so-called α-effect, *viz*., the presence of p- and/or π-electrons on the atom adjacent to the reaction center[21] (in the case under consideration, on the nitrogen atom).

It is known that the substitution of two nitro groups in TNB under the action of O- and S-nucleophiles (phenols, polyfluorinated alcohols, thiols) requires more drastic temperature conditions than those necessary for the substitution of one nitro group.[7—10] This is attributable to the fact that the substitution of one nitro group in TNB decreases the electrophilicity of the product compared to TNB as such.

We studied the substitution of a nitro group in compound **4** with various O- and S-nucleophiles as well as 1,2,4-triazole (Scheme 8). It appeared that a nitro group in compound **4** is replaced under conditions identical to those necessary for the substitution of a nitro group in TNB (in the case of MeONa, in boiling methanol; in all other cases, in the presence of K_2CO_3 in *N*-MP, at 20 °C for thiols and at 80 °C for all other reagents).

Scheme 8

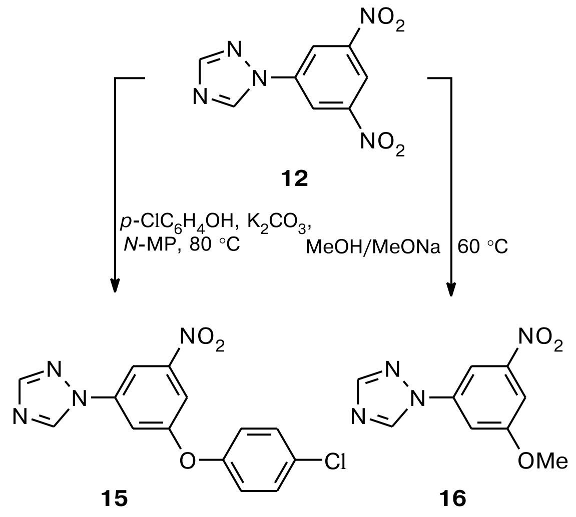


Y = OMe (**a**), SCH_2COOMe (**b**), SPh (**c**), $OCH_2CF_2CF_2H$ (**c**), Cl (**e**), (**f**)

Analysis of the published data on the substitution of nitro groups in TNB in the reactions with O- and S-nucleophiles and comparison of these results with our data on the substitution of a nitro group in 2-(3,5-dinitrophenyl)benzotriazole **4** under the action of the same nucleophiles led us to the conclusion that the benzotriazol-2-yl fragment has a strong activating effect in the aromatic nucleophilic substitution of a nitro group similar to that of the nitro group.

The 1,2,4-triazol-1-yl fragment has an analogous effect. Actually, 1-(3,5-dinitrophenyl)-1,2,4-triazole **12** smoothly reacts with 4-chlorophenol as well as with sodium methoxide in methanol under conditions typical of TNB (Scheme 9), resulting in the substitution of a nitro group to give products **15** and **16**, respectively.

Scheme 9



An interesting result was obtained in the reaction of compound **4** with an equivalent amount of benzotriazole. This reaction would be expected to form a mixture of compounds **17** and **18** (Scheme 10).

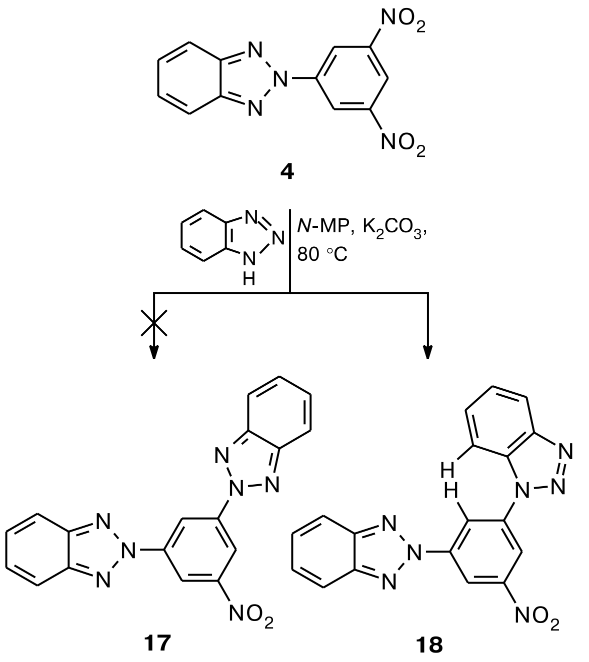
However, the reaction afforded only one regioisomer, which was isolated in 92% yield (see Scheme 10). The structure of compound **18** was established based on the ^{1}H NMR spectrum, which has four signals for the protons of the 1-substituted benzotriazole fragment. In addition, the ^{1}H NMR NOE experiment revealed the proximity of the protons of two aromatic rings.

Under standard conditions, compound **18** reacts with 2,2,3,3-tetrafluoropropanol to form polyfluorinated ether **19** (Scheme 11).

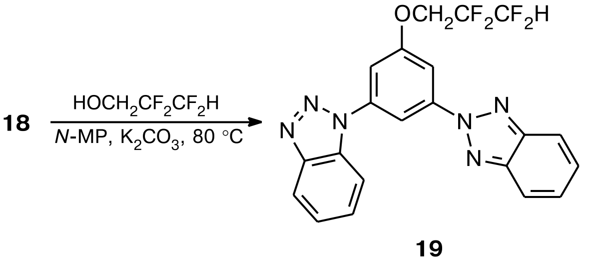
Under the same conditions, the reaction of compound **18** with benzotriazole gave product **20** containing three benzotriazole substituents (Scheme 12).

Compound **20** is virtually insoluble in organic solvents, trifluoroacetic acid, and sulfuric acid. The ^{1}H NMR spectrum of this compound in DMSO-d$_6$ corroborates the structure **20**. This spectrum has signals with double intensities belonging to the non-symmetrically substituted benzotriazole rings.

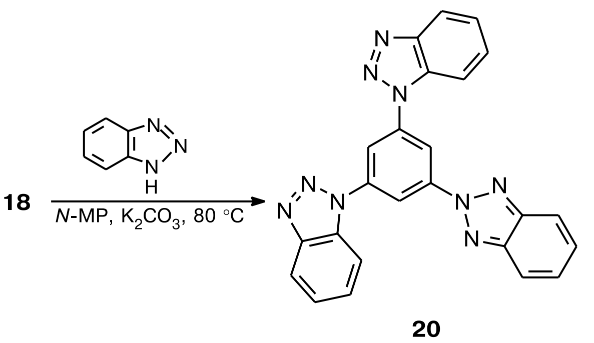
Scheme 10



Scheme 11



Scheme 12



Therefore, all three nitro groups in TNB can be successively replaced under the action of benzotriazole. It should be noted that the transformation of TNB into 1,3,5-triphenoxybenzene[22] in the reaction with an excess of phenol in the presence of K_2CO_3 at 200 °C in *N*-MP is the only known example of the substitution of all nitro groups in TNB (without a preliminary modification of the substituents). It should be emphasized that in none of the cases, did the replacement of the azolyl fragment take place under the action of nucleophiles, and only the nitro group was replaced in all cases.

Experimental

The ^1H NMR spectra were recorded on a Bruker AC-200 instrument in DMSO-d_6. The ^{13}C NMR spectra were measured on a Bruker AM-300 instrument. The chemical shifts (δ) are given relative to Me_4Si. The mass spectra were obtained on a Kratos MS-30 instrument; the ionization energy was 70 eV. The course of the reactions was monitored by HPLC on LIQUOCHROM (Model 2010) in the $CH_3CN—H_2O$ system (3 : 1); a Silasorb-18 reversed-phase column was used. The melting points of the compounds were determined on a Boetius hot-stage apparatus (the heating rate was 4 K min^{-1}).

The starting compounds, such as TNB,[23] 4-methoxybenzotriazole,[24] 4-trifluoromethylbenzotriazole,[25] 4-chloropyrazole,[26] and 4-bromopyrazole,[26] were prepared according to known procedures. All other starting compounds were commercially available.

Substitution of a nitro group in TNB in the reactions with NH-azoles (general procedure). Potassium carbonate (1.38 g, 10 mmol) and a solution of TNB (2.13 g, 10 mmol) in *N*-MP (10 mL) were added to a solution of an NH-azole (10 mmol) in *N*-MP (15 mL). The mixture was stirred at 80 °C (HPLC control) and poured into water. The precipitate that formed was filtered, washed on a filter several times with 5% HCl to remove *N*-MP, and dried in air.

2-(3,5-Dinitrophenyl)benzotriazole (4). A mixture of isomers **3**+**4** prepared by the above-described reaction was recrystallized from DMF (heating to 120 °C) and isomer **4** was isolated in 40% yield, m.p. 211—213 °C. Found (%): C, 50.02; H, 2.41; N, 25.25. $C_{12}H_7N_5O_4$. Calculated (%): C, 50.53; H, 2.47; N, 24.55. ^1H NMR, δ: 9.25 (d, 2 H, H(2´), H(6´), ^4J = 2.0 Hz); 8.91 (t, 1 H, H(4´), ^4J = 2.0 Hz); 8.05 (dd, 2 H, H(4), H(7), ^3J = 6.6 Hz, ^3J = 7.3 Hz); 7.58 (dd, 2 H, H(5), H(6), ^3J = 6.6 Hz, ^3J = 7.3). ^{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´)). MS, *m/z*: 285 $[M]^+$.

1-(3,5-Dinitrophenyl)benzotriazole (3). The filtrate obtained after crystallization of 2-(3,5-dinitrophenyl)benzotriazole (**4**) was concentrated *in vacuo*. The residue enriched in isomer **3** was twice recrystallized from dioxane. The yield was 15%, m.p. 184—186 °C. Found (%): C, 50.80; H, 2.93; N, 25.25. $C_{12}H_7N_5O_4$. Calculated (%): C, 50.53; H, 2.47; N, 24.55. ^1H NMR, δ: 9.05 (d, 2 H, H(2´), H(6´), ^4J = 1.9 Hz); 8.95 (t, 1 H, H(4´), ^4J = 1.9 Hz); 8.25 (d, 1 H, H(7), ^3J = 7.9 Hz); 8.10 (d, 1 H, H(4), ^3J = 7.7 Hz); 7.81 (t, 1 H, H(5), ^3J = 8.1 Hz); 7.62 (t, 1 H, 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´)). MS, *m/z*: 285 $[M]^+$, 257 $[M - N_2]^+$.

5-Chloro-2-(3,5-dinitrophenyl)benzotriazole (7a). A mixture of isomers prepared in the reaction of TNB with 5-chlorobenzotriazole was refluxed in acetone. The undissolved **7a** was filtered off. The yield was 53%, m.p. 211—213 °C. Found (%): C, 45.52; H, 1.57; Cl, 10.78; N, 22.31. $C_{12}H_6ClN_5O_4$. Calculated (%): C, 45.09; H, 1.89; Cl, 11.09; N, 21.91. ^1H NMR, δ: 9.25 (d, 2 H, H(2´), H(6´), ^4J = 1.9 Hz); 8.95 (t, 1 H, H(4´), ^4J = 1.9 Hz); 8.25 (s, 1 H, H(4)); 8.15 (d, 1 H, H(6)); 7.6 (d, 1 H, H(7)). MS, *m/z*: 319 $[M]^+$.

5-Bromo-2-(3,5-dinitrophenyl)benzotriazole (7b) was isolated analogously, the yield was 47%, m.p. 236—238 °C. Found (%): C, 39.05; H, 1.87; N, 19.95. $C_{12}H_6BrN_5O_4$. Calculated (%): C, 39.58; H, 1.66; N, 19.23. ^1H NMR, δ: 9.30 (d, 2 H, H(2´), H(6´), ^4J = 1.9 Hz); 8.90 (t, 1 H, H(4´), ^4J = 2.0 Hz); 8.40 (s, 1 H, H(4)); 8.10 (d, 1 H, H(6)); 7.7 (d, 1 H, H(7)).

2-(3,5-Dinitrophenyl)-5-trifluoromethylbenzotriazole (7c). A mixture prepared in the reaction of TNB with 5-trifluoromethylbenzotriazole was twice recrystallized from EtOH to afford compound **7c** in 65% yield, m.p. 155—157 °C. Found (%): C, 44.17; H, 1.96; N, 19.41. $C_{13}H_6F_3N_5O_4$. Calculated (%): C, 44.21; H, 1.71; N, 19.83. ^1H NMR, δ: 9.30 (d, 2 H, H(2´), H(6´), ^4J = 2.0 Hz); 8.95 (t, 1 H, H(4´), ^4J = 2.0 Hz); 8.65 (s, 1 H, H(4)); 8.35 (d, 1 H, H(6)); 7.8 (d, 1 H, H(7)).

2-(3,5-Dinitrophenyl)-5-methoxybenzotriazole (7d). A mixture prepared in the reaction of TNB with 5-methoxybenzotriazole was twice recrystallized from EtOH to afford compound **7d** in 65% yield, m.p. 238—240 °C. Found (%): C, 49.38; H, 3.14; N, 21.88. $C_{13}H_9N_5O_5$. Calculated (%): C, 49.53; H, 2.88; N, 22.22. ^1H NMR, δ: 9.19 (d, 2 H, H(2´), H(6´), ^4J = 2.0 Hz); 8.86 (t, 1 H, H(4´), ^4J = 2.0 Hz); 7.97 (d, 1 H, H(7)); 7.34 (s, 1 H, H(4)); 7.22 (d, 1 H, H(6)); 3.91 (s, 3 H, OMe).

1-(3,5-Dinitrophenyl)pyrazole (13a). The reaction time was 30 h at 100 °C. The yield was 20%, m.p. 112—114 °C (from $CHCl_3$). Found (%): C, 46.41; H, 2.22; N, 24.32. $C_9H_6N_4O_4$. Calculated (%): C, 46.16; H, 2.58; N, 23.93. ^1H NMR, δ: 9.05 (d, 2 H, H(2´), H(6´), ^4J = 2.0 Hz); 8.95 (d, 1 H, H(3), ^3J = 2.7 Hz); 8.71 (t, 1 H, H(4´), ^4J = 1.9 Hz); 7.89 (d, 1 H, H(5), ^3J = 1.7 Hz); 6.72 (t, 1 H, 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´)). MS, *m/z*: 234 $[M]^+$, 188 $[M - NO_2]$, 142 $[M - 2\ NO_2]$.

4-Chloro-1-(3,5-dinitrophenyl)pyrazole (13b). The reaction time was 6 h. The yield was 73%, m.p. 124—126 °C (from $CHCl_3$). Found (%): C, 39.90; H, 1.49; Cl, 13.56; N, 20.66. $C_9H_5ClN_4O_4$. Calculated (%): C, 40.24; H, 1.88; Cl, 13.20; N, 20.86. ^1H NMR, δ: 9.25 (s, 1 H, H(3)); 9.01 (d, 2 H, H(2´), H(6´), ^4J = 2.0 Hz); 8.70 (t, 1 H, H(4´), ^4J = 1.9 Hz); 8.05 (s, 1 H, H(5)).

4-Bromo-1-(3,5-dinitrophenyl)pyrazole (13c). The reaction time was 2 h. The yield was 86%, m.p. 132—134 °C (from $CHCl_3$). Found (%): C, 34.47; H, 1.36; N, 18.20. $C_9H_5BrN_4O_4$. Calculated (%): C, 34.53; H, 1.61; N, 17.90. ^1H NMR, δ: 9.21 (s, 1 H, H(3)); 8.97 (d, 2 H, H(2´), H(6´), ^4J = 2.0 Hz); 8.72 (t, 1 H, H(4´), ^4J = 1.9 Hz); 8.02 (s, 1 H, H(5)).

1-(3,5-Dinitrophenyl)-1,2,3-triazole (11). The reaction time was 3 h. The yield was 71%, m.p. 126—128 °C (from EtOH). Found (%): C, 41.02; H, 1.91; N, 29.34. $C_8H_5N_5O_4$. Calculated (%): C, 40.86; H, 2.14; N, 29.78. ^1H NMR, δ: 8.98 (d, 2 H, H(2´), H(6´), ^4J = 1.9 Hz); 8.82 (t, 1 H, H(4´), ^4J = 1.9 Hz); 8.33 (s, 2 H, H(4), H(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´)).

1-(3,5-Dinitrophenyl)-1,2,4-triazole (12). The reaction time was 6 h. The yield was 75%, m.p. 131—133 °C (from $CHCl_3$). Found (%): C, 41.12; H, 1.98; N, 30.04. $C_8H_5N_5O_4$. Calculated (%): C, 40.86; H, 2.14; N, 29.78. ^{1}H NMR, δ: 9.70 (s, 1 H, H(5)); 9.05 (d, 2 H, H(2′), H(6′), ^4J = 2.0 Hz); 8.81 (s, 1 H, H(4′), ^4J = 2.0 Hz); 8.33 (s, 1 H, 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)). MS, *m/z*: 235 $[M]^+$, 208 [M – HCN].

Substitution of a nitro group in 1,3-dinitro-5-trifluoromethylbenzene in the reaction with benzotriazole. The reaction was carried out analogously to that with TNB. The reaction time was 6 h. The yield of a mixture of isomers was 88%. The isomers were separated by column chromatography on silica gel (hexane—CH_2Cl_2).

1-(3-Nitro-5-trifluoromethylphenyl)benzotriazole (8). The yield was 44%, m.p. 140—142 °C (from EtOH). Found (%): C, 50.31; H, 2.56; N, 17.74. $C_{13}H_7F_3N_4O_2$. Calculated (%): C, 50.66; H, 2.29; N, 18.18. ^{1}H NMR, δ: 8.92, 8.71, and 8.65 (all s, 1 H each, arom.); 8.24 (d, 1 H, H(7), benzotriazole, J = 7.4 Hz); 8.06 (d, 1 H, H(4), benzotriazole); 7.75 (m, 1 H, H(5), benzotriazole); 7.56 (m, 1 H, H(6) benzotriazole).

2-(3-Nitro-5-trifluoromethylphenyl)benzotriazole (9). The yield was 23%, m.p. 89—91 °C (from EtOH). Found (%): C, 50.19; H, 2.11; N, 18.31. $C_{13}H_7F_3N_4O_2$. Calculated (%): C, 50.66; H, 2.29; N, 18.18. ^{1}H NMR, δ: 9.16, 8.92, and 8.65 (all s, 1 H each, arom.); 8.08 (m, 2 H, H(4), H(7), benzotriazole): 7.59 (m, 2 H, H(5), H(6), benzotriazole).

Substitution of a nitro group in compounds 4, 12, and 18 in the reactions with nucleophiles. Potassium carbonate (1.38 g, 10 mmol) and 2-(3,5-dinitrophenyl)benzotriazole (**4**) (2.85 g, 10 mmol) were added to a solution of a nucleophile (10 mmol) in *N*-MP (25 mL). The reaction mixture was kept at the corresponding temperature (HPLC control) and poured into water. The precipitate that formed was filtered, washed several times on a filter with 5% HCl to remove *N*-MP, and dried in air.

Methyl *S*-[3-(1,2,3-benzotriazol-2-yl)-5-nitrophenyl]mercaptoacetate (14b). The reaction temperature was 20 °C, the reaction time was 2 h. The product was recrystallized from dioxane, the yield was 90%, m.p. 143—145 °C. Found (%): C, 51.96; H, 3.62; N, 15.77; S, 9.40. $C_{15}H_{12}N_4O_4S$. Calculated (%): C, 52.32; H, 3.51; N, 16.27; S, 9.31. ^{1}H NMR, δ: 8.71 (t, 1 H, arom., ^4J = 1.9 Hz); 8.57 (t, 1 H, arom., ^4J = 2 Hz); 8.25 (t, 1 H, arom., ^4J = 1.9 Hz); 8.03 (m, 2 H, H(4), H(7), benzotriazole); 7.54 (m, 2 H, H(5), H(6), benzotriazole); 4.21 (s, 2 H, CH_2); 3.70 (s, 3 H, OMe).

2-[3-Nitro-5-(phenylthio)phenyl]benzotriazole (14c). The reaction temperature was 20 °C, the reaction time was 1 h. The product was recrystallized from DMF, the yield was 93%, m.p. 156—158 °C. Found (%): C, 61.82; H, 3.17; N, 15.87; S, 9.42. $C_{18}H_{12}N_4O_2S$. Calculated (%): C, 62.06; H, 3.47; N, 16.08; S, 9.20. ^{1}H NMR, δ: 8.72 (t, 1 H, arom., ^4J = 2 Hz); 8.35 (t, 1 H, arom., ^4J = 1.9 Hz); 8.03 (m, 3 H, H(4), H(7), benzotriazole + arom.); 7.65 (m, 2 H, H(5), H(6), benzotriazole); 7.55 (m, 5 H, thiophenoxy group).

2-[3-Nitro-5-(2,2,3,3-tetrafluoropropoxy)phenyl]benzotriazole (14d). The reaction temperature was 80 °C, the reaction time was 2 h. The product was recrystallized from dioxane, the yield was 84%, m.p. 140—142 °C. Found (%): C, 49.01; H, 2.37; N, 14.73. $C_{15}H_{10}F_4N_4O_3$. Calculated (%): C, 48.66; H, 2.72; N, 15.13. ^{1}H NMR, δ: 8.68 (t, 1 H, arom., ^4J = 2 Hz); 8.38 (t, 1 H, arom., ^4J = 1.9 Hz); 8.05 (m, 3 H, H(4), H(7), benzotriazole + arom.); 7.56 (m, 2 H, H(5), H(6), benzotriazole); 6.75 (tt, 1 H, CH, ^3J = 52 Hz, ^4J = 5 Hz); 4.95 (t, 2 H, CH_2, ^3J = 12.5 Hz). MS, *m/z*: 370 $[M]^+$.

2-[3-(4-Chlorophenoxy)-5-nitrophenyl]benzotriazole (14e). The reaction temperature was 80 °C, the reaction time was 6 h. The product was recrystallized from DMF, the yield was 79%, m.p. 178—180 °C. Found (%): C, 59.15; H, 2.87; N, 14.86. $C_{18}H_{11}ClN_4O_3$. Calculated (%): C, 58.95; H, 3.02; N, 15.28. ^{1}H NMR, δ: 8.73 (t, 1 H, arom., ^4J = 2 Hz); 8.30 (t, 1 H, arom., ^4J = 1.9 Hz); 8.05 (dd, 2 H, H(4), H(7), benzotriazole); 7.92 (t, 1 H, arom., ^4J = 2.1 Hz); 7.75 (m, 4 H, H(5), H(6), benzotriazole + H(2), H(6), C_6H_4O); 7.33 (d, 2 H, H(3), H(5), phenoxy group). MS, *m/z*: 366 $[M]^+$.

2-[3-Nitro-5-(1,2,4-triazol-1-yl)phenyl]-1,2,3-benzotriazole (14f). The reaction temperature was 80 °C, the reaction time was 25 h. The product was recrystallized from DMF, the yield was 87%, m.p. 231—233 °C. Found (%): C, 55.01; H, 2.76; N, 31.73. $C_{14}H_9N_7O_2$. Calculated (%): C, 54.72; H, 2.95; N, 31.91. ^{1}H NMR, δ: 9.75 (s, 1 H, H(5), triazole); 9.20 (t, 1 H, arom., ^4J = 1.9 Hz); 8.98 (t, 1 H, arom., ^4J = 2 Hz); 8.85 (t, 1 H, arom., ^4J = 1.9 Hz); 8.4 (s, 1 H, H(3), triazole); 8.09 (m, 2 H, H(4), H(7), benzotriazole); 7.61 (m, 2 H, H(5), H(6), benzotriazole). MS, *m/z*: 307 $[M]^+$.

1-[3-(4-Chlorophenoxy)-5-nitrophenyl]-1,2,4-triazole (15). The reaction temperature was 80 °C, the reaction time was 6 h. The product was recrystallized from dioxane, the yield was 90%, m.p. 145—147 °C. Found (%): C, 52.98; H, 3.03; N, 17.32. $C_{14}H_9ClN_4O_3$. Calculated (%): C, 53.09; H, 2.86; N, 17.69. ^{1}H NMR, δ: 9.52 (s, 1 H, H(5), triazole); 8.50 (t, 1 H, arom., ^4J = 1.9 Hz); 8.30 (s, 1 H, H(3), triazole); 8.05 (t, 1 H, arom., ^4J = 2 Hz); 7.75 (t, 1 H, arom., ^4J = 1.9 Hz); 7.55 and 7.25 (both d, 2 H each, phenoxy group).

1-(Benzotriazol-1-yl)-3-(benzotriazol-2-yl)-5-nitrobenzene (18). The reaction temperature was 80 °C, the reaction time was 4 h. The yield of the crude product was 92%. After crystallization from dioxane, the yield was 75%. The compound sublimes without melting. Found (%): C, 59.96; H, 3.43; N, 26.90. $C_{18}H_{11}N_7O_2$. Calculated (%): C, 60.50; H, 3.10; N, 27.44. ^{1}H NMR, δ: 9.15 (t, 1 H, arom., ^4J = 1.9 Hz); 9.11 (t, 1 H, arom., ^4J = 2 Hz); 8.80 (t, 1 H, arom., ^4J = 1.9 Hz); 8.29 (d, 1 H, H(7)); 8.15 (m, 3 H, H(4), H(4′), H(7′)); 7.82 (t, 1 H, H(5)); 7.63 (m, 3 H, H(6), H(5′), H(6′)).

1-(Benzotriazol-1-yl)-3-(benzotriazol-2-yl)-5-(2,2,3,3-tetrafluoropropoxy)benzene (19). The reaction temperature was 80 °C, the reaction time was 16 h, the yield was 79%, m.p. 286—288 °C. Found (%): C, 56.77; H, 3.34; N, 18.65. $C_{21}H_{14}F_4N_6O$. Calculated (%): C, 57.02; H, 3.19; N, 19.00. ^{1}H NMR, δ: 8.51 (s, 1 H, arom.); 8.25 (d, 1 H, H(7)); 8.20—8.05 (m, 4 H, arom., H(4), H(4′), H(7′)); 7.85—7.72 (m, 2 H, arom., H(5)); 7.62—7.58 (m, 3 H, H(6), H(5′), H(6′)); 6.85 (t, 1 H, CH, ^3J = 52 Hz); 5.02 (t, 2 H, CH_2).

1,3-Bis(benzotriazol-1-yl)-5-(benzotriazol-2-yl)benzene (20). The reaction temperature was 80 °C, the reaction time was 30 h. After refluxing in DMF (50 mL), the analytically pure compound was isolated in 69% yield. The compound sublimes without melting. Found (%): C, 66.61; H, 3.87; N, 28.69. $C_{24}H_{15}N_9$. Calculated (%): C, 67.12; H, 3.52; N, 29.35. ^{1}H NMR, δ: 9.15 (s, 2 H, arom.); 8.82 (s, 1 H, arom.); 8.27 (d, 2 H, 2 H(7)); 8.15 (m, 4 H, 2 H(4), H(4′), H(7′)); 7.77 (t, 2 H, 2 H(5)); 7.55 (m, 4 H, 2 H(6), H(5′), H(6′)).

2-(3-Methoxy-5-nitrophenyl)benzotriazole (14a). A mixture of 2-(3,5-dinitrophenyl)benzotriazole **4** (2.85 g, 10 mmol) and sodium methoxide (0.54 g, 10 mmol) in methanol (10 mL) was refluxed for 30 h and poured into water. The precipitate that formed was filtered off and recrystallized from DMF. The yield was 2.1 g (78%), m.p. 202—204 °C. Found (%): C, 58.06; H, 3.91; N, 20.49. $C_{13}H_{10}N_4O_3$. Calculated (%): C, 57.78; H, 3.73; N, 20.73. ^{1}H NMR, δ: 8.85 and 8.18 (both t, 1 H each, arom., ^4J = 1.9 Hz); 8.05 (m, 2 H, H(4), H(7), benzotriazole); 7.83 (t, 1 H, arom., ^4J = 2 Hz); 7.55 (m, 2 H, H(5), H(6), benzotriazole); 4.00 (s, 3 H, OMe). MS, *m/z*: 270 $[M]^+$, 224 $[M - NO_2]$.

1-(3-Methoxy-5-nitrophenyl)-1,2,4-triazole (16). A mixture of 1-(3,5-dinitrophenyl)-1,2,4-triazole (**12**) (2.35 g, 10 mmol) and sodium methoxide (0.54 g, 10 mmol) in methanol (10 mL) was refluxed for 4 h and then poured into water. The precipitate that formed was filtered off and recrystallized from EtOH. The yield was 1.45 g (65%), m.p. 129—131 °C. Found (%): C, 48.67; H, 3.79; N, 25.03. $C_9H_8N_4O_3$. Calculated (%): C, 49.09; H, 3.66; N, 25.45. ^{1}H NMR, δ: 9.53 (s, 1 H, H(5), triazole); 8.31 (s, 1 H, H(3), triazole); 8.28 (t, 1 H, arom., ^4J = 1.9 Hz); 7.89 (t, 1 H, arom., ^4J = 2 Hz); 7.71 (t, 1 H, arom., ^4J = 1.9 Hz); 3.94 (s, 3 H, OMe).

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