Mendeleev Commun., 2002, 12(6), 231–232

Consecutive substitution for three nitro groups in 1,3,5-trinitrobenzene under the action of benzotriazole and other nucleophiles

Oleg Yu. Sapozhnikov, Mikhail D. Dutov, Vadim V. Kachala and Svyatoslav A. Shevelev*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation.
Fax: +7 095 135 5328; e-mail: shevelev@mail.ioc.ac.ru

10.1070/MC2002v012n06ABEH001688

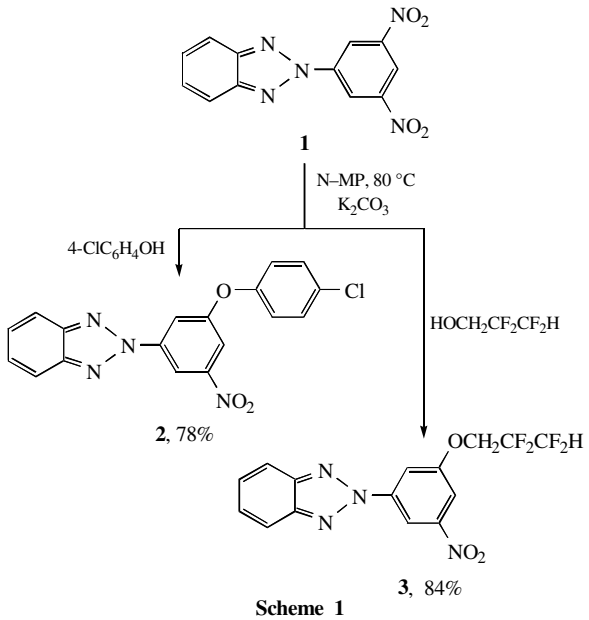
The *N*-benzotriazole unit and the nitro group are similar in the activating effect of nucleophilic substitution for an aromatic nitro group at the *meta* position; this fact makes it possible to replace consecutively all of the three nitro groups in 1,3,5-trinitrobenzene.

The complexity of nucleophilic substitution for nitro groups in 1,3,5-trinitrobenzene (TNB) is associated with both a comparatively weak mutual activation (only *–I* effect) and the capability of TNB to add nucleophiles at the unsubstituted position of the aromatic ring with the formation of stable anionic σ-complexes.[1,2]

Previously, nucleophilic substitution for nitro groups in TNB under the action of phenols,[3,4] thiophenols[5] and R^FCH_2OH fluorinated alcohols[6] was studied. It was found that one nitro group is replaced under comparatively mild conditions (at 50–80 °C) in *N*-methylpyrrolidone or DMF in the presence of K_2CO_3). However, the substitution for the next nitro group under the action of these reagents occurred under much more severe conditions (~150 °C).[4–6] The replacement of all three nitro groups was performed under the action of phenol at 200 °C, and the yield of the reaction product was very low.[4] Thus, the replacement of the strong electron-acceptor nitro group by an RX fragment (R = Ar, X = O, S; R = R^FCH_2, X = O) dramatically decreased the activity of the remaining nitro groups in aromatic nucleophilic substitution reactions.

Recently,[7] we found that NH azoles such as benzotriazole, 1,2,3-triazole, 1,2,4-triazole, and pyrazole can substitute for a nitro group in TNB in the presence of solid K_2CO_3 as a deprotonating agent in *N*-methylpyrrolidone or DMF at 80 °C with the formation of corresponding *N*-(3,5-dinitrophenyl)azoles. In the case of benzotriazole, the two isomeric 1- and 2-(3,5-dinitrophenyl)benzotriazoles were formed, and the isomer at the 2-position was predominant.

In this work, we studied the effect of the N-azole unit on the replacement of the remaining nitro groups using 2-(3,5-dinitrophenyl)benzotriazole **1** as an example. We found that substitution for a nitro group in compound **1** under the action of 4-chlorophenol and 2,2,3,3-tetrafluoropropanol occurs under the same conditions as in the case of substitution for the first nitro group in TNB under the action of these reagents: at 80 °C in the presence of an equimolar amount of K_2CO_3 in *N*-methylpyrrolidone (Scheme 1).† In this case, substitution for the benzotriazolyl unit was not observed. In other words, the activating effect of the N-benzotriazole fragment is similar to the activating effect of the nitro group with respect to nucleophilic substitution for another aromatic nitro group at the *meta* position.



Scheme 1

Under analogous conditions on the action of equimolar amounts of benzotriazole and K_2CO_3 on compound **1**, an additional nitro group was replaced. The reaction occurred regiospecifically only at the 1-position in benzotriazole (^{1}H NMR data): 1-(1*H*-benzotriazolyl)-3-(2*H*-benzotriazolyl)-5-nitrobenzene **4** was obtained in a high yield (Scheme 2).† The structure

† *General procedure.* A mixture of a nitro compound (0.01 mol), K_2CO_3 (0.01 mol) and a nucleophile (0.01 mol) in 20 ml of *N*-methyl-2-pyrrolidone was heated at 80 °C for a time specified in Table 1. After completion of the reaction, the mixture was poured into water. The resulting precipitate was washed several timed with dilute HCl on filter and dried. The compounds were recrystallised from appropriate solvents.

Table 1

Compound	Reaction time/h	Yield (%)	mp/°C	Solvent for crystallization
2	6	79	178–180	DMF
3	2	84	140–142	Dioxane
4	3.5	92	346 (decomp.)	Dioxane
5	16	79	286–288	DMF
6	30	69	322 (decomp.)	DMF

The EI mass spectra (MS-30 'Kratos') of all synthesised compounds exhibited the peaks of molecular ion. The ^{1}H NMR spectra were measured in [$^2H_6$]DMSO on a Bruker AM-300 instrument.

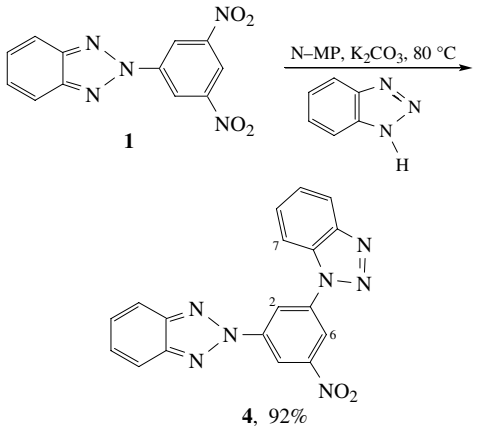
2: *2-[3-(4-Chlorophenoxy)-5-nitrophenyl]benzotriazole*. ^{1}H NMR, δ: 8.73 (t, 1H, C_6H_3, ^4J 2.0 Hz), 8.30 (t, 1H, C_6H_3, ^4J 1.9 Hz), 8.05 (m, 2H, Bt), 7.92 (t, 1H, C_6H_3, ^4J 2.1 Hz), 7.75 (m, 4H, Bt + 4-ClC_6H_4), 7.33 (d, 2H, 4-ClC_6H_4, ^3J 7.6 Hz). Found (%): C, 58.73; H, 2.87; Cl, 9.77; N, 14.91. Calc. for $C_{18}H_{11}ClN_4O_3$ (%): C, 58.95; H, 3.05; Cl, 9.67; N, 15.28.

3: *2-[3-Nitro-5-(2,2,3,3-tetrafluoropropoxy)phenyl]benzotriazole*. ^{1}H NMR, δ: 8.68 (t, 1H, C_6H_3, ^4J 2.0 Hz), 8.38 (t, 1H, C_6H_3, ^4J 1.9 Hz), 8.05 (m, 3H, C_6H_3 + Bt), 7.56 (m, 2H, Bt), 6,75 (tt, 1H, CHF_2, ^2J 52.7 Hz, ^3J 5.1 Hz), 4.95 (t, 2H, CH_2, ^3J 12.5 Hz). Found (%): C, 48.90; H, 2.89; N, 14.86. Calc. for $C_{15}H_{10}F_4N_4O_3$ (%): C, 48.66; H, 2.72; N, 15.13.

4: *1-(1H-Benzotriazolyl)-3-(2H-benzotriazolyl)-5-nitrobenzene*. ^{1}H NMR, δ: 9.15 (t, 1H, C_6H_3, ^4J 1.9 Hz), 9.11 (t, 1H, C_6H_3, ^4J 2 Hz), 8.8 (t, 1H, C_6H_3, ^4J 1.9 Hz), 8.29 (d, 1H, Bt-1, ^3J 7.1 Hz), 8.15 (m, 3H, Bt-1 + Bt-2), 7.82 (t, 1H, Bt-1, ^3J 7.2 Hz), 7.63 (m, 3H, Bt-1 + Bt-2). Found (%): C, 60.79; H, 3.26; N, 27.30. Calc. for $C_{18}H_{11}N_7O_2$ (%): C, 60.50; H, 3.10; N, 27.44.

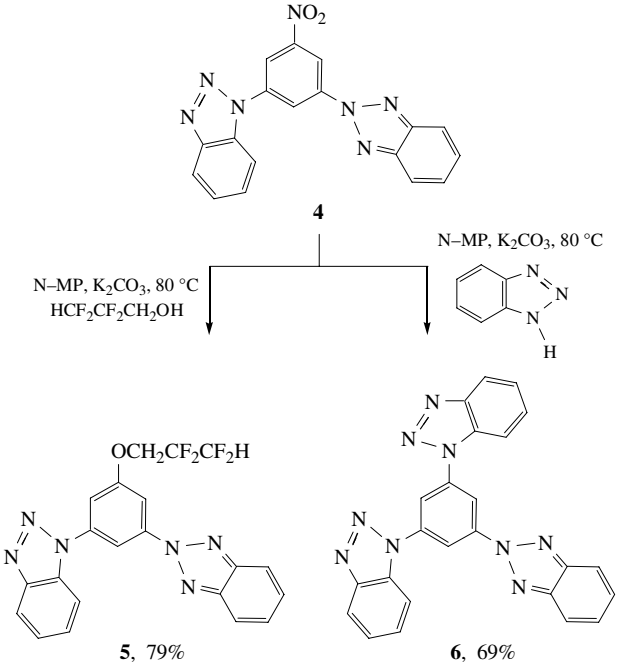
5: *5-(2,2,3,3-Tetrafluoropropoxy)-1-(1H-benzotriazolyl)-3-(2H-benzotriazolyl)benzene.* ^{1}H NMR, δ: 8.51 (s, 1H, C_6H_3), 8.25 (d, 1H, Bt-1, ^3J 7.1 Hz), 8.2–8.05 (m, 4H, Bt-1 + Bt-2 + C_6H_3), 7.85–7.72 (m, 2H, Bt-1 + C_6H_3), 7.62–7.58 (m, 3H, Bt-1 + Bt-2), 6.85 (t, 1H, CHF_2, ^3J 52.2 Hz, ^4J 4.6 Hz), 5.02 (t, 2H, CH_2, ^3J 12.3 Hz). Found (%): C, 57.28; H, 3.02; N, 18.76. Calc. for $C_{21}H_{14}F_4N_6O$ (%): C, 57.02; H, 3.19; N, 19.00.

6: *1,3-Bis(1H-benzotriazolyl)-5-(2H-benzotriazolyl)benzene.* ^{1}H NMR, δ: 9.15 (s, 2H, C_6H_3), 8.82 (s, 1H, C_6H_3), 8.27 (d, 2H, Bt-1, ^3J 7.5 Hz), 8.15 (m, 4H, Bt-1 + Bt-2), 7.77 (t, 2H, Bt-1, ^3J 7.8 Hz), 7.55 (m, 4H, Bt-1 + Bt-2). Found (%): C, 66.80; H, 3.37; N, 29.09. Calc. for $C_{24}H_{15}N_9$ (%): C, 67.12; H, 3.52; N, 29.35.



Scheme 2

of this compound was determined using the NOE method. This experiment revealed the interaction of the H-2 and H-6 protons of the nitrophenyl ring with the H-7 proton of the N-substituted benzotriazole, which is impossible for the product at the 2-position of the benzotriazole ring. Moreover, the mass spectrum of this compound contains the fragment ion $[M^+ - 28]$, which corresponds to the removal of a nitrogen molecule from the benzotriazole ring substituted at the 1-position.



Scheme 3

Finally, under the same conditions (80 °C), the remaining nitro group in compound **4** was replaced under the action of benzotriazole or 2,2,3,3-tetrafluoropropanol. In this case, benzotriazole reacted only at the 1-position: compound **6** was formed (Scheme 3).†

Thus, all three nitro groups in TNB can be consecutively replaced under mild conditions because of the activating effect of the N-benzotriazole fragment.

This work was supported by the International Science and Technology Center (project no. 419).

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Received: 22nd July 2002; Com. 02/1972