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Interaction of hexamethylphosphoric triamide with *m*-dinitrobenzenes

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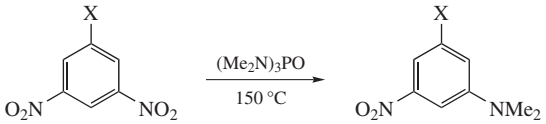
Heating of 1-X-3,5-dinitrobenzenes (X is an electron-withdrawing group) in hexamethylphosphoric triamide affords the corresponding 1-X-3-dimethylamino-5-nitrobenzenes.

Continuing our studies on the replacement of a nitro group in 1,3,5-trinitrobenzene (TNB) by secondary amines,[1] we found that attempted reaction between TNB and diphenylamine in hexamethylphosphoric triamide (HMPA) afforded *N*,*N*-dimethyl-3,5-dinitroaniline rather than expected 3,5-dinitrotriphenylamine. The use of HMPA as a source of the dimethylamino group was reported previously.[2] Thus, a halogen was displaced by dimethylamino group during heating of *o*- and *p*-halonitrobenzenes in HMPA. In case of *o*- and *p*-dinitrobenzenes, the nitro group was substituted. In *p*-nitrophenol and *p*-nitroanisole, an electron-donor oxygen function was replaced by the dimethylamino group. Benzonitriles bearing *o*- or *p*-halogen form the corresponding amino nitriles. Note that in case of *m*-chloronitrobenzene and *m*-chlorobenzonitrile the substitution practically did not occur.

In a more detailed study of the interaction between TNB **1a** and HMPA, it was found that the reaction began at 150 °C and was complete within 10 h. The preparative yield of *N*,*N*-dimethyl-3,5-dinitroaniline **2a** was 43%, and much resin was formed. TNB analogues **1b–e** containing other electron-acceptor groups behaved analogously (Scheme 1).



1a–e **2a–e**

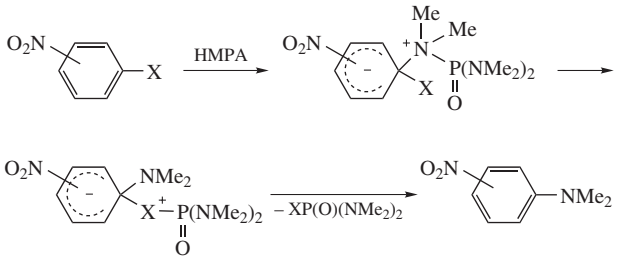
a X = NO_2, 43% **d** X = $PhSO_2$, 50%
b X = CF_3, 41% **e** X = CN, 8%
c X = SO_2Me, 40%

Scheme 1

It could be expected that *p*-dinitrobenzene would have been much more reactive than TNB. However, that reaction required longer time of 14.5 h, and the yield of *N*,*N*-dimethyl-4-nitroaniline **3** was 56%.

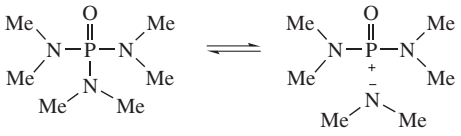
Unlike *p*-dinitrobenzene, *m*-dinitrobenzene was stable under these conditions and remained unchanged within 9.5 h. In the case of 3,5-dinitrobenzonitrile **1e**, the substitution product **2e** was obtained in a yield of only 8%. However, unlike *p*-nitroanisole, 3,5-dinitroanisole did not form *N*,*N*-dimethyl-3,5-dinitroaniline. We identified 3,5-dinitrophenol as the only product of this reaction in addition to a significant quantity of resins. 3,5-Dinitrophenyl phenylsulfide was isolated unchanged after 11.5 h at 150 °C, although the ^{1}H NMR spectrum of the crude product contained weak signals, which can be attributed to expected 3-dimethylamino-5-nitrophenyl phenylsulfide.

Pedersen *et al.*[3] proposed the reaction mechanism for these transformations, which is outlined in Scheme 2. This mechanism



Scheme 2

implies $XP(O)(NMe_2)_2$ to be a leaving group, which seems unlikely in the cases of halogen and nitro group. Another mechanism proposed by Gupton *et al.*[2] (Scheme 3), which involves thermal dissociation of HMPA, appears to be more preferable.



Scheme 3

In this case, the resulting Me_2N^- further acts as an ordinary nucleophile. We anticipated that based on this hypothesis one can introduce any secondary amine into TNB in a higher yield than that achieved earlier. Unfortunately, attempted interaction between phosphoric acid tripyrrolidide and TNB gave none of the product. Therefore, the mechanism of the interaction of HMPA with aromatic substrates should be further studied.

The structures of the synthesized compounds were determined based on ^{1}H NMR spectroscopy, mass spectrometry (in all cases molecular ions were detected) and elemental analysis.†

† Starting compounds **1c** and **1d** were prepared as described.[4,5]

General experimental procedure (Caution! HMPA is not a friendly solvent). A solution of 0.5 g of a starting substrate in 15 ml of HMPA was kept at 155–160 °C until the reactant was consumed (TLC; eluent, $CHCl_3$). The reaction mass was cooled and poured into 150 ml of ice water. The precipitate was filtered off, washed with water and dried. The crude product was dissolved in chloroform, and the solution was filtered through a silica gel bed. The filtrate was evaporated, and the residue was crystallized from methanol.

^{1}H NMR spectra were measured on a Bruker AM-300 spectrometer.

2a: reaction time 10.5 h, yield 43%, mp 161–162 °C (lit.,[6] mp 164 °C). ^{1}H NMR (DMSO-d_6) δ: 3.10 (s, 6H), 7.71 (s, 2H), 7.99 (s, 1H).

2b: reaction time 20 h, yield 41%, mp 68–69 °C. ^{1}H NMR (DMSO-d_6) δ: 3.07 (s, 6H), 7.27 (s, 1H), 7.59 (s, 2H).

2c: reaction time 7.5 h, yield 40%, mp 149–150 °C. ^{1}H NMR ($CDCl_3$) δ: 3.11 (s, 3H), 3.14 (s, 6H), 7.43 (s, 1H), 7.67 (s, 1H), 7.98 (s, 1H).

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2d: reaction time 11 h, yield 50%, mp 182–183 °C. ^{1}H NMR (DMSO-d_6) δ: 3.06 (s, 6H), 7.45 (s, 1H), 7.57 (s, 1H), 7.59–7.80 (m, 4H), 8.06 (d, 2H, J 7.6 Hz).

2e: reaction time 10 h, yield 8%, mp 168–169 °C. ^{1}H NMR (DMSO-d_6) δ: 3.04 (s, 6H), 7.50 (s, 1H), 7.59 (s, 1H), 7.78 (s, 1H).

3: reaction time 14.5 h, yield 56%, mp 162–163 °C (lit.,[7] mp 163–164 °C). ^{1}H NMR (DMSO-d_6) δ: 3.08 (s, 6H), 6.74 (d, 2H, ^3J 9.3 Hz), 8.04 (d, 2H, ^3J 9.3 Hz).

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