Rearrangement of an O-Nitrophenylnitramine; a New Synthesis of Diazophenols

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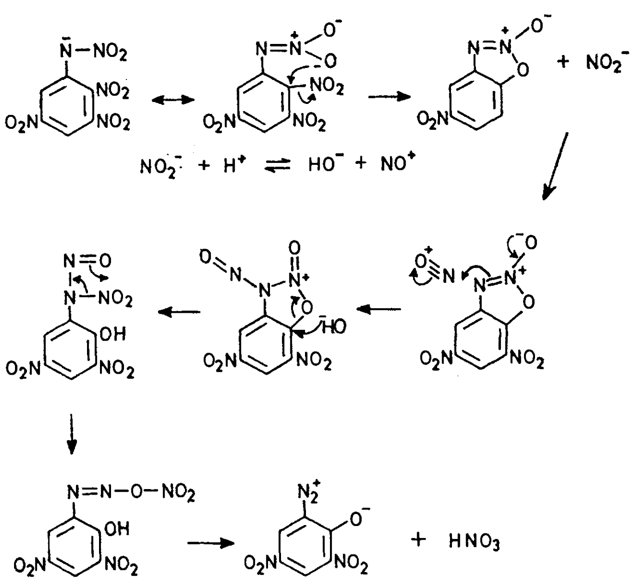
Summary Nitration of 3,5-dinitroaniline with 70% nitric acid yields 2,3,5-trinitrophenylnitramine; this compound rearranges quantitatively on warming to give 4,6-dinitro-2-diazophenol and nitric acid.

The nitration of 3,5-dinitroaniline, under forcing conditions, gives pentanitroaniline,[1] the reaction probably proceeding *via* a series of Bamberger rearrangements, *i.e.*, the formation of a nitramine and its subsequent rearrangement to a *C*-nitroaniline.

Whilst examining the nitration of a series of nitroanilines, under widely varied conditions, we isolated a compound, in 65% yield, from the reaction of 3,5-dinitroaniline with 70% HNO_3–98% H_2SO_4, which was neither a nitramine nor a nitroaniline. Its i.r. spectrum showed a medium–strong absorption at 2200 cm^{-1}, indicative of a diazonium compound, and this together with the ^1H n.m.r. spectrum [two doublets of equal intensity at τ 0·85 and 1·35 (J 2 Hz)], suggested that the compound might be 4,6-dinitro-2-diazophenol,[2] and this was confirmed by spectral comparison with an authentic sample.

A similar procedure, but at 0—5 °C, gave a different product (70% yield), which showed no absorption at 2200 cm^{-1} but did absorb at *ca.* 3200 cm^{-1}, suggesting that it might be a primary nitramine. Elemental analyses of its NH_4^+ and Ag^+ salts were in agreement with an empirical formula of $C_6H_3N_5O_8$ for the parent compound and this is consistent with a trinitrophenylnitramine. The ^1H n.m.r. spectrum showed two doublets of equal intensity at τ 0·78 and 1·58 (J 2 Hz, *meta*-aromatic-H), and this *meta*- arrangement was supported by a weak double i.r. absorption at 1820 and 1835 cm^{-1}. The formation of 4,6-dinitro-2-diazophenol on heating a solution of this compound in ethyl acetate to 60 °C suggests that its structure is 2,3,5-trinitrophenylnitramine. This decomposition takes place smoothly and quantitatively and represents a new synthesis of diazophenols. (*Caution*—if the nitramine is heated in the absence of solvent the decomposition proceeds explosively). Similarly, the ^1H n.m.r. spectrum of the ammonium salt changes gradually, over 24 h, to that of 4,6-dinitro-2-diazophenol and NH_4NO_3. The mechanism of the rearrangement has not, as yet, been established but it most probably occurs *via* the initial nucleophilic displacement of the labile 2-nitro group.



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[1] B. Flürscheim and E. L. Holmes, *J. Chem. Soc.*, 1928, 3041.
[2] P. Greiss, *Annalen*, 1858, **106**, 123.