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% HNO₃-98% H₂SO₄, 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 NH4⁺ 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 $\tau 0.78$ and 1.58 (1 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-2diazophenol 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

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



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 NH4NO8. 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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(Received, 30th April 1975; Com. 491.)