The Rearrangement of Aromatic Nitro-compounds in Strongly Acidic Media

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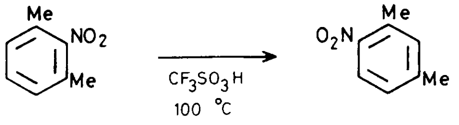
2-Nitro-*m*-xylene and a number of nitrophenols undergo a 1,3-nitro-group rearrangement in trifluoromethanesulphonic acid at 70—110 °C.

Although nitration is normally considered to be subject to kinetic control, there are a few examples[1—3] in the literature where an aromatic nitro-group between two substituents undergoes a 1,3-rearrangement in an acidic medium and, with superacids, low yields (*ca.* 5%) of products involving the transfer of a nitro-group have been found.[4] Three of the rearrangements refer to 3-substituted 2-nitroanilines,[1—3] and a 7.5% yield of 2,5-dinitrophenol has been found[1] after the treatment of 2,3-dinitrophenol with 98% sulphuric acid for 8 hours at 112 °C. We have reinvestigated the rearrangements



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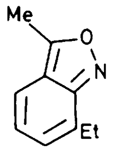

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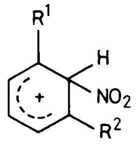

(2)

Table 1. First-order rate coefficients for the 1,3-rearrangement of hindered nitro-groups carried out in 100% triflic acid at 100 °C (unless stated otherwise).

Substrate	10^6k (s^{-1})
2,3-Dinitrophenol	550
2,3-Dinitro-4-methylphenol	960
3-Methyl-2-nitrophenol[a]	330
3,4-Dinitrophenol[b]	3.8
2-Nitro-*m*-xylene[c]	165

[a] In 92% triflic acid. [b] Rearrangement of the 4-nitro-group to give 2,5-dinitrophenol with some decomposition. [c] At 110 °C.

using both sulphuric acid and trifluoromethanesulphonic acid (triflic acid) as solvents and now report that, for the rearrangement of 2,3-dinitrophenol, the use of triflic acid gives a great increase in the reaction rate and in the yield of rearranged product. This solvent also permits the reaction to be extended to the rearrangement of other nitrophenols (see Table 1) and to some nitrated hydrocarbons.[5]

Thus, the rearrangement of 2,3-dinitrophenol in sulphuric acid at 112 °C gives an extensive amount of sulphonation and degradation, but, when triflic acid is used, the reaction occurs readily at 70 °C and is then a clean first-order process giving 2,5-dinitrophenol with not more than 1—2% of the 3,4-isomer. The overall yield is quantitative and good isosbestic points are seen when the reaction is followed by u.v. spectroscopy.

The extension of the reaction to nitrated hydrocarbons is illustrated by the rearrangement of 2-nitro-*m*-xylene in equation (1), and Figure 1. Again, good first-order kinetics are observed and a product analysis after 6 half-lives gave a 90% yield of 4-nitro-*m*-xylene. The range of this reaction has not yet been defined but it is clearly limited by the side-reactions that occur with related substrates; thus, the reaction of 1,3-diethyl-2-nitrobenzene under these conditions gives mainly 3-methyl-7-ethylanthranil (**1**).

First-order rate coefficients for a number of these rearrangement reactions are given in Table 1 but, in comparing these values, it should be noted that the rate-profiles for these rearrangements vary with the substrate. The corresponding rearrangement of the nitroanilines in concentrated sulphuric acid is not subject to marked acid catalysis (presumably because the transition state has the same stoicheiometry as the protonated substrate) but the rate of rearrangement of the nitrophenols and nitrated hydrocarbons increases with acidity as might be expected from the lower basicity of these substrates. With all substrates, the variation of the rate of rearrangement with acidity is consistent with reaction through an equilibrium concentration of the Wheland intermediate (**2**) (for R^1 and R^2 see Table 1), and this suggestion of a reversible protonation stage is supported by the fact that, in deuteriotriflic acid, 2-nitro-*m*-xylene undergoes hydrogen isotope exchange at the unsubstituted ring positions at a rate considerably faster than that of rearrangement.

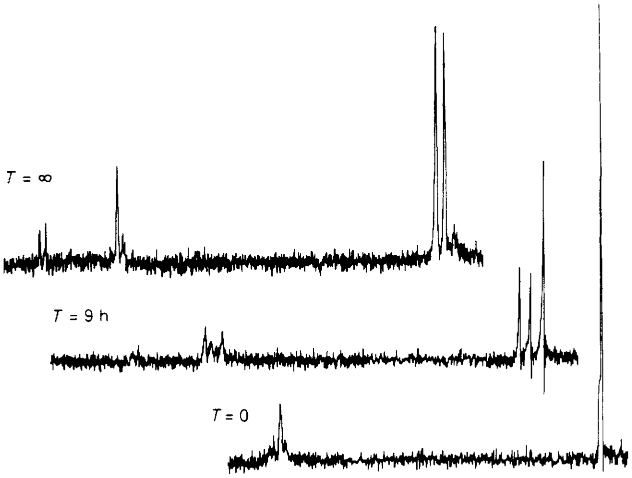

Figure 1. The change in the ^1H n.m.r. spectrum during the rearrangement of 2-nitro-*m*-xylene to 4-nitro-*m*-xylene in 99.4% triflic acid at 100 °C. For clarity, the successive spectra are displaced to the left.

The mechanism of the rearrangement stage is still under investigation but, at present, it seems unlikely that a single reaction path will suffice to explain the results for the complete set of substrates studied. The 1,3-rearrangements of the Wheland intermediates (**2**) can presumably occur through the set of reaction paths recognised to occur in the rearrangement of related *ipso*-intermediates.[6] The rearrangements now reported could also be considered to result from the migration of the other substituents but, since these vary in the complete set of compounds studied, the results can be most easily understood as a general reaction involving the migration of the nitro-group from a more hindered to a less hindered site. Irrespective of the detailed mechanism of these rearrangements, the results indicate that isomer proportions in some nitration reactions should be subject to partial thermodynamic control when carried out in strongly acidic media at high temperatures.

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