The Rearrangement of Aromatic Nitro Compounds. Part 1. The Reactions of Nitroanilines in Aqueous Sulphuric Acid

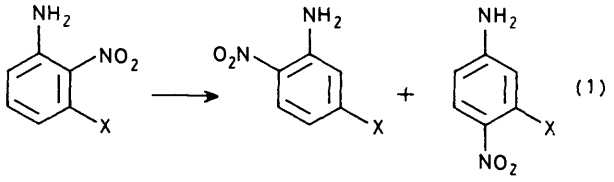
J. Timothy Murphy and John H. Ridd *
Chemistry Department, University College, 20 Gordon Street, London WC1H 0AJ

A number of substituted 2-nitroanilines rearrange in concentrated sulphuric acid at 110 °C to yield products that appear to be derived from 1,3-migration of the 2-nitro-group. For 2,3-dinitroaniline, the rate of reaction is almost independent of acidity over the range 83—97% sulphuric acid and the solvent isotope effect $k(H_2SO_4)/k(D_2SO_4)$ is 1.3—1.9. Methyl and t-butyl groups, when present as additional substituents in 2,3-dinitroaniline, have only a small effect on the reaction rate but 3-methyl-2-nitroaniline reacts much more slowly than 2,3-dinitroaniline. These results are discussed in terms of a rate-determining migration of the 2-nitro group following protonation at the 2-position.

Aromatic nitration is generally considered to be irreversible but there are several examples in the literature in which a nitro group is displaced from an aromatic ring by a proton. Thus, there is evidence for the loss of the nitro group from 9-nitroanthracene in a mixture of sulphuric and trichloroacetic acids,[1] and for the formation of a small yield (*ca.* 5%) of nitrotoluenes[2] in mixtures of 9-nitroanthracene and toluene in superacidic media at 180—190 °C. The loss of the nitro group from 2-nitro-3,4,6-tri-isopropylacetanilide occurs when this compound is heated under reflux with hydrogen chloride in ethanol[3] and the 7-nitro-group is lost from 3,5,6,7-tetranitroindazole when this compound is heated with sulphuric acid (50%) for 5 h at 100 °C.[4]

There are also examples of aromatic rearrangements consistent with the migration of a nitro group. Thus, the 2-nitro group appears* to undergo a 1,3-rearrangement when 2,3-dinitroaniline is heated in sulphuric acid (98%) for 8 h at 110 °C[5] and similar rearrangements occur when 2-nitro-3,4-dimethoxyaniline[6] and 2,3-dinitro-4-methylaniline[7] are heated in acidic media. A small yield (7.5%) of 2,5-dinitrophenol has been obtained by heating 2,3-dinitrophenol in sulphuric acid (98%)[5] at 112 °C for 7 h. The mechanism of these reactions and their relationship to nitration is not at present understood.[8]

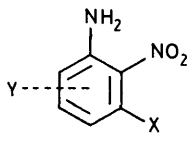
The present studies were started to determine the scope and mechanism of these rearrangements. The work described in this paper is limited to the rearrangement of nitroanilines in aqueous sulphuric acid of the type shown in equation (1):



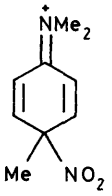
(1)

later papers will deal with the corresponding reactions of nitrophenols and of nitrated hydrocarbons in trifluoromethanesulphonic acid.[9]

Products.—A number of substituted 2-nitroanilines with the general form (**1**) have been dissolved in concentrated sulphuric acid and heated to 110 °C. The rearrangement products obtained are listed in Table 1. Except where indicated, the percentages refer to the amount of product isolated. Where the ^{1}H n.m.r. signals did not overlap, the product composition was calculated from the n.m.r. spectrum.



(**1**)



(**2**)

Our observations confirm that 2,3-dinitroaniline rearranges in aqueous sulphuric acid (83—98%) to give a mixture of 2,5- and 3,4-dinitroaniline in 2:1 ratio in agreement with the work of Pausacker and Scroggie.[5] At concentrations of sulphuric acid below 83%, the rearrangement is accompanied by the formation of side-products including ammonium ions. The rate and product composition of the rearrangement in 90% sulphuric acid are unchanged when the reaction is carried out in the presence of hydrazinium sulphate (0.2 mol dm^{-3}).

The combined hydrolysis and rearrangement of 2,3-dinitroacetanilide to give the same mixture of nitro products has also been studied previously[5] and the overall reaction was considered to be significantly faster than the rearrangement of the amine. Our results do not support this, for the ^{1}H n.m.r. spectrum of the solution shows that 2,3-dinitroacetanilide is hydrolysed to the amine within 1 min under the conditions used (98% H_2SO_4; 110 °C) and that no detectable amount of rearrangement occurs in that time.

The addition of a methyl group to the ring can block one of the rearrangement sites but does not otherwise have a marked effect on the reaction. 2,3-Dinitro-4-methylaniline is known to rearrange to 2,5-dinitro-4-methylaniline in concentrated sulphuric acid[7] and the change in the n.m.r. spectrum accords with this. The changes in the n.m.r. spectrum in the corresponding reaction of 2,3-dinitro-6-methylaniline are less easy to interpret because of overlapping peaks and so the product composition was determined by isolation and chromatographic separation. For 2,3-dinitro-5-methyl- and 2,3-dinitro-4-t-butylaniline, the changes in the ^{1}H n.m.r. spectra provided a clear indication of the rearrangements listed in Table 1.

2,3-Dinitro-4-methoxyaniline decomposes extensively when heated for 5 h in sulphuric acid (98%) at 110 °C; the only compounds isolated were the unchanged starting material and 2,3-dinitro-4-methoxyphenol. Much of this decomposition and deamination appears to arise from nitrous acid-catalysed side-reactions for it is reduced in the presence of hydrazine. Thus the reaction of 2,3-dinitro-4-methoxyaniline (0.53 g, 2.5 mmol) for 6 h in sulphuric acid (98%) at 110 °C in the presence of

* This qualification is included because some of the 1,3-rearrangements mentioned could also derive from the migration of other groups.

Table 1. Products of rearrangement of substituted 2-nitroanilines (**1**) in concentrated sulphuric acid at 110 °C. Where the reaction was incomplete, the amount of starting material (S.M.) isolated and the time are also shown

X	Y	H_2SO_4 (%)	Products
NO_2	H	98	2,5-dinitroaniline + 3,4-dinitroaniline [a]
NO_2	4-Me	90.8	2,5-dinitro-4-methylaniline
NO_2	5-Me	90.1	2.5-dinitro-3-methylaniline + 3,4-dinitro-5-methylaniline [b]
NO_2	6-Me	98	3,4-dinitro-6-methylaniline (20%) (S.M. 16%, 25 min)
NO_2	4-Bu^t	89.8	2,5-dinitro-5-t-butylaniline
NO_2	4-OMe	98	2,3-dinitro-4-methoxyphenol (11%) (S.M. 25%, 5 h)
		98 (+N_2H_4)	3-nitro-4-hydroxyaniline (44%) 2,5-dinitro-4-methoxyaniline (8%) (S.M. 37%, 6 h)
Me	H	90	2-nitro-5-methylaniline (29%) 4-nitro-3-methylaniline (6%) (S.M.) 37%, 66 h)

[a] In 2:1 ratio from the ^1H n.m.r. spectrum. [b] In approximately equal amounts from the n.m.r. spectrum.

Table 2. First-order rate coefficients (k_1) for the rearrangement of substituted 2-nitroanilines (**1**) in aqueous sulphuric acid at 110 °C. The relative rate coefficients (k_R) with respect to 2,3-dinitroaniline are also shown. The initial concentration of the amine is 1.0 mol dm^{-3} unless otherwise specified

X	Y	H_2SO_4 (%)	$10^4k_1/s^{-1}$	k_R
NO_2	H	83.5	3.5	
NO_2	H	85.6	3.79	
NO_2	H	87.4	4.33	
NO_2	H	91.9	4.66	
NO_2	H	94.5	4.21[a]	
NO_2	H	94.5	4.41	
NO_2	H	97.3	2.08	
NO_2	4-Me	90.8	2.11[a]	0.46
NO_2	5-Me	90.1	3.95[a]	0.85
NO_2	6-Me	98.0	4[b]	2
NO_2	4-Bu^t	89.8	1.18[b]	0.26
NO_2	4-OMe	98.0	1[b,c]	0.5
Me	H	90.0	0.04[b]	0.009

[a] [Amine] 0.5 mol dm^{-3}. [b] Based on a single-product analysis. [c] For denitration in the presence of hydrazine.

hydrazinium sulphate (0.13 g, 1 mmol) gives mainly denitration with some rearrangement (Table 1).

The above reactions can all be considered to involve the loss or migration of the nitro group *ortho* to the amino group and all the compounds have a second nitro group *ortho* to the first. However, this second nitro group is not necessary for the rearrangement.[6] Thus, the reaction of 2-nitro-3-methylaniline for 66 h in 90% sulphuric acid at 110 °C gives, on isolation and analysis, some 2-nitro-5-methylaniline (Table 1).

Kinetics.—The rearrangement reaction has been followed from the changes in the ^1H n.m.r. spectrum using aqueous sulphuric acid as the solvent. One reaction, the rearrangement of 2,3-dinitroaniline, was chosen for an extended kinetic study: the other rearrangement reactions were studied more briefly to obtain evidence on substituent effects. In a few of the rearrangements, the overlapping of the peaks prevented an accurate kinetic study; these are discussed separately below.

The rearrangement of 2,3-dinitroaniline to a mixture of 2,5-dinitroaniline and 3,4-dinitroaniline is particularly suitable for this method of analysis since, in concentrated sulphuric acid, the aromatic protons of the 2,5-isomer give rise to a single peak to low field of the absorption of the starting material and the minor product (the 3,4-isomer). In this system, the NH_3^+ group appears to have no differential effect on the ^1H chemical shifts. In the following analysis, we have assumed that the kinetic form and rate profile for the reaction leading to the minor product are the same as those determined for the major product. The n.m.r. spectra are consistent with this but do not permit this assumption to be rigorously checked.

Table 3. Solvent isotope effects on the rearrangement of 2,3-dinitroaniline in sulphuric acid and deuteriosulphuric acid at 110 °C. [amine] 1.0 mol dm^{-3}

	$10^4k_1/s^{-1}$		
Acid (%)	H_2SO_4[a]	D_2SO_4	k_H/k_D
87.5	4.43	2.72	1.6
90.0	4.6	2.57	1.79
92.5	4.62	2.38	1.94
95.0	4.20	2.16	1.94
97.0	2.54	1.89	1.34

[a] Interpolated from the results in Table 1.

At a given acidity, the rearrangement of 2,3-dinitroaniline is accurately first order with respect to the substrate during a single kinetic run and, as expected, the first-order rate coefficient is independent of the initial concentration of the substrate over the range (0.5—1.0 mol dm^{-3}). The correlation coefficients were >0.99 for all runs. The first-order rate coefficients at different acidities are collected in Table 2 and show a very flat rate profile with a maximum at *ca.* 92% sulphuric acid. The reactions in deuteriosulphuric acid are slower by a factor of 1.3—1.9 (Table 3).

The rearrangement of 2,3-dinitro-4-methylaniline is also an easy one to follow since only one product is formed (2,5-dinitro-4-methylaniline) and, in 90% sulphuric acid, this gives rise to a signal for the methyl group to low field of that in the starting material. In the same way, the rearrangement of 2,3-dinitro-5-methylaniline gives two new methyl signals, as expected for the two possible products. The rates of these rearrangements were followed from the heights of these methyl signals. The rearrangement of 2,3-dinitro-6-methylaniline was less easy to follow but an approximate rate coefficient (k_1 4 × 10^{-4} s^{-1}) was calculated from the product analysis (see above) after reaction for 25 min in 98% sulphuric acid at 110 °C.

The formation of 2,5-dinitro-4-t-butylbenzene from 2,3-dinitro-4-t-butylbenzene in 89.8% sulphuric acid leads to the appearance of two singlets in the aromatic region of the n.m.r. spectrum, one of which is to low field of the aromatic quartet of the starting material. The extent of reaction has been calculated from the height of this peak and the corresponding rate coefficient is included in Table 2. With 2,3-dinitro-4-methoxyaniline, the complexity of the reaction precludes a conventional kinetic study but an estimate of the rate coefficient for the overall reaction has been based on the amount of starting material remaining after 6 h at 110 °C in 98% sulphuric acid in the presence of hydrazine. For 2-nitro-3-methylaniline, the amount of starting material remaining after 66 h in 90% sulphuric acid at 110 °C accords with a rate coefficient for the overall reaction of 4×10^{-6} s^{-1}.

Studies with ^{15}N-*Labelled Substrates.*—The rearrangement of 2,3-dinitroaniline could be either inter- or intra-molecular; this distinction has been examined by crossover experiments using ^{15}N-labelled substrates. The rearrangement of [3-^{15}N]-2,3-dinitroaniline (0.54 mmol) has been studied in 98% sulphuric acid at 110 °C in the presence of unlabelled 3-nitroaniline (1.08 mmol). If the rearrangement occurred through the dissociation of the substrate into 3-nitroaniline and a nitronium ion, then the nitronium ions should be captured mainly by the unlabelled 3-nitroaniline in the solution since the relative amount of labelled 3-nitroaniline present at any time should be much less than that of the unlabelled material. However, the mass spectrum of the product isolated at the end of 4 h gave no evidence of a peak corresponding to the unlabelled dinitro compound.

The above experiment would not detect an intermolecular reaction occurring through the intermediate formation of the nitrogen dioxide radical. Equal concentrations of (2,3-^{15}N)-2,3-dinitroaniline and unlabelled 2,3-dinitroaniline were accordingly allowed to rearrange together in 98% sulphuric acid at 110 °C for 4 h. If an intermolecular reaction had occurred by any mechanism, the peak for *m/z* 184 in the mass spectrum of the product should be greater than that in the corresponding reaction of unlabelled material. The observed result was somewhat greater than expected for a pure intramolecular mechanism (see Experimental section), but any intermolecular component should not exceed 5%.

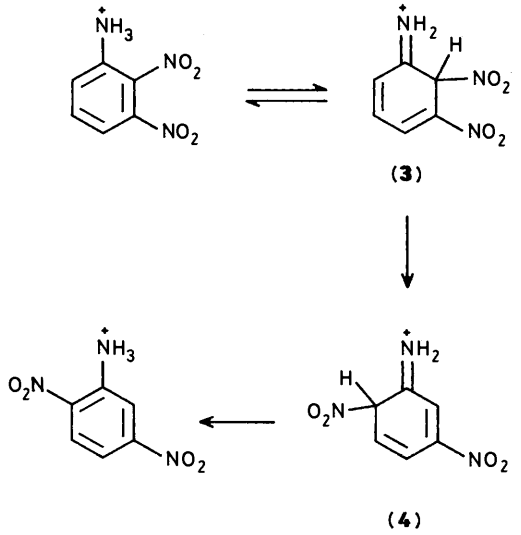
To minimise the transformations of the labelled materials, the above experiments were carried out using the labelled acetanilides; these are rapidly hydrolysed to the amines in the solutions used.

Discussion

When considered individually, the rearrangements reported in this paper could be represented by the migration of more than one group; this has led to some uncertainty over the migrating species.[6] Thus, the rearrangement of 2,3-dinitroaniline to a mixture of 2,5- and 3,4-dinitroaniline could be seen as competing migrations of the 3-nitro and the amino group. However, both these reactions, together with all the other rearrangements reported here, can be understood as 1,3-migrations of the 2-nitro group. For simplicity, we have therefore assumed that this is the sole migrating species. This argument receives support from the comparatively small range of reaction rates involved (see below).

One necessary condition for the reaction to occur appears to be the presence of the third substituent X [structure (**1**)]. Thus, 2-nitroaniline does not rearrange to give any 4-nitroaniline under these experimental conditions and, in general, the products of rearrangement do not react further. The electronic effect of X appears relatively unimportant, for rearrangement will occur when X is nitro, alkyl, and methoxy.[6] However, the scope of the rearrangement is limited by the incursion of side-reactions including the displacement of the NH_3^+ group as an ammonium ion (observed with 2,3-dinitroaniline in the more aqueous media) and denitration (observed with 2,3-dinitro-4-methoxyaniline and several other substrates[1–4]). Under other conditions, *e.g.* with 2,3-dinitroaniline in 98% sulphuric acid, the reaction appears to be quantitative.

The mechanism of the reaction will be considered with particular reference to the rearrangement of 2,3- to 2,5-dinitroaniline [equation (2)] since this substrate has been studied in particular detail. The experimental studies with ^{15}N-labelled substrates indicate that this rearrangement is at least 95% intramolecular, the kinetics of the rearrangement are first order, and the rate profile (Table 2) gives no evidence for a significant dependence on the acidity of the medium. Thus, over the range of acid concentrations listed in Table 2, the value of H_0 changes by more than two log units but the variation in the first-order rate coefficient is by a factor of only 2.2. Taken together, these observations indicate that the transition state for the rate-determining stage of the rearrangement has the same composition as the conjugate acid of the amine.



The homolytic dissociation of the C–NO_2 bond in the conjugate acid of the amine to form a localised cation radical and nitrogen dioxide provides one formal possibility for initiating the rearrangement. Such reactions have been studied extensively at high temperatures in the gas phase but, from the Arrhenius parameters, it is clear that they should be negligible under the conditions used here (the half-life for the corresponding reaction of nitrobenzene should be 10^{17} days at 110 °C).[10] A much more plausible interpretation is therefore reaction through the Wheland intermediate shown in equation (2). The formation of ammonium ions in the more aqueous media is then analogous to the displacement of the NMe_2 group by OH following *ipso*-attack in the nitration of *N*,*N*,2,4,6-pentamethylaniline.[11]

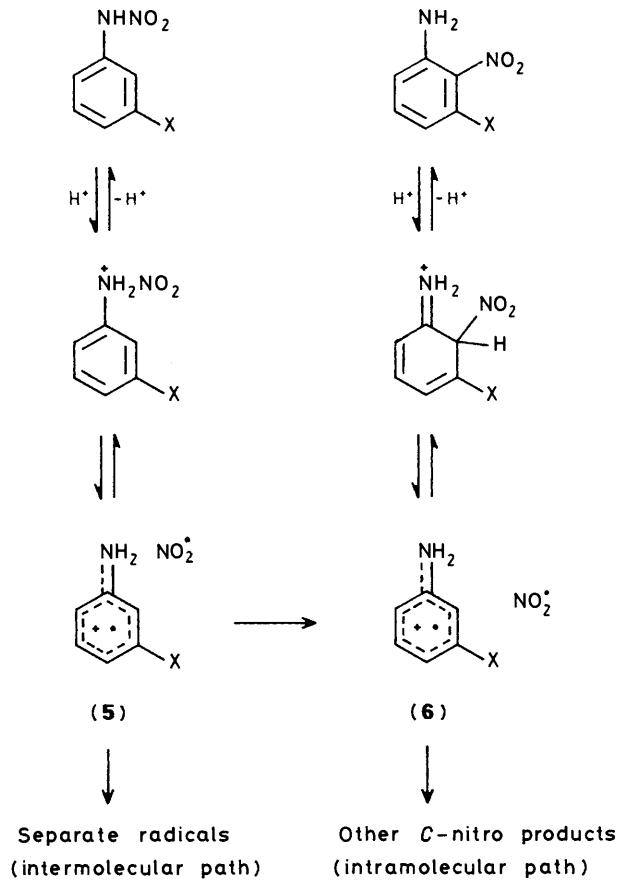
The reaction path in equation (2) has at least three possible rate-determining steps. The proton transfers would not normally be expected to be rate determining since this would imply a rate-determining proton loss in nitration at that position but the 1,3-rearrangement of the nitro group in the *ipso*-intermediate (**2**) is known[12] to involve a rate-determining proton loss from the position *ortho* to the NMe_2 group in strongly acidic media; this is attributed to the steric interactions involved. On these grounds, the initial proton transfer in equation (2) could also be rate determining.

The comparison of the reaction rates in sulphuric acid and deuteriosulphuric acid (Table 3) yields a solvent isotope effect that is rather small for such a rate-determining step* (for comparison, the solvent isotope effect on the protodeiodination of *para*-iodoaniline is 5.8).[14] The observed isotope effect is probably more consistent with reaction through an equilibrium concentration of the Wheland intermediate (**3**) for, in the formation of this intermediate from the conjugate acid, one N–H bond is replaced by a C–H bond and the vibration frequencies of the two remaining N–H bonds are changed. In the deuteriated medium, these protons would be replaced by deuterons and so the change in the vibration frequencies would cause a secondary isotope effect on the equilibrium concentration of the Wheland intermediate. The relevant frequencies are not known with sufficient accuracy to justify a detailed calculation but our estimates suggest that the resultant isotope effect would be in the observed direction. The absence of steric interactions makes it unlikely that the last stage of equation (2) could be rate determining and so the rate-determining stage is probably the rearrangement of the nitro-group [(**3**) ⟶ (**4**)].

This rearrangement stage is analogous to the rearrangements following *ipso*-attack in aromatic nitration and for these reactions a large number of mechanisms have been proposed including concerted processes,[15] reactions involving radical pairs,[16] and reactions through encounter pairs involving nitronium ions.[17] The composition of the transition state is the same as that for the nitramine rearrangement of the corresponding amines without the 2-nitro group and, for this rearrangement, there is good evidence for the involvement of radical pairs[18] although the exact boundary between this mechanism and the ionic mechanism involving nitronium ions has never been defined.[19] Probably the closest analogy to the present work lies in the 1,3-rearrangement of the *ipso*-intermediate (**2**)[11] but unfortunately the mechanism of this rearrangement is not entirely clear. There is evidence for dissociation into radicals but the rearrangement process itself does not generate the nuclear polarisation expected for reaction through a radical pair.[20] Instead, the phase of any nuclear polarisation present in the *ipso*-intermediate is carried over into the rearranged product. This applies even at those acidities at which the rearrangement stage is rate determining.[20] The result suggests that there is little dissociation into separate radicals during the rearrangement stage.

The results on the rearrangement in equation (2) are not wholly consistent with any mechanism proposed previously. The almost complete intramolecularity of the process points against reaction through a radical pair. The rather similar amounts of reaction at the positions *ortho* and *para* to the amino group does not suggest a concerted sigmatropic shift because this process has been considered to give almost complete *ortho* substitution.[15] Dissociation of the Wheland intermediate (**3**) to give a nitronium ion should lead to an intramolecular reaction (since *meta*-nitroaniline should react on encounter with nitronium ions†) and this reaction path could also explain the small substituent effects observed (Table 2) but it is then curious that the rate of rearrangement of the nitramine of *p*-nitroaniline is as expected for reaction through a radical pair[22] and that evidence for ^{15}N CIDNP effects has been found in the nitramine rearrangement of *N*,3-dinitroaniline.[23] Such nuclear polarisation indicates that at least part of the reaction proceeds through a radical pair. It seems improbable that the Wheland intermediate (**3**) should dissociate to give an encounter pair involving a nitronium ion when the corresponding nitramine dissociates to give a radical pair of the same composition.

Perhaps the simplest way of explaining these results is to assume that, when the radical pair $ArNH_2^{+\bullet}NO_2^{\bullet}$ is formed from the Wheland intermediate (**3**), the initial orientation of the components favours some charge transfer between them so that the radical pair is stabilised and the intramolecular reaction path is favoured relative to that in the nitramine rearrangement, where *ca.* 30% of the radical pairs dissociate.[24] Such a mechanism would explain why the rearrangement of the *ipso*-intermediate (**2**) does not appear to generate CIDNP effects. This mechanism can also be extended to the rearrangement of 3-methyl-2-nitroaniline where any heterolytic dissociation of the corresponding Wheland intermediate appears very improbable because of the standard electrode potentials of aniline and nitrogen dioxide.[25] On this interpretation, the relationship between the present work and the nitramine rearrangement is as shown in the Scheme. Following White,[18]



Scheme.

the argument implies that, when the radical pair is formed from the nitramine, dissociation competes with movement between orientations [(**5**) ⟶ (**6**)] within the solvent cage.

In the presence of sufficient electron-withdrawing substituents, the mechanism of the rearrangement should change to reaction *via* the free amine and a nitronium ion. Some work has been done on the reaction of 2,3,6-trinitroaniline in 90% sulphuric acid at 110 °C but no rearranged product was detected: the initial reaction appeared to be denitration to 2,5-dinitroaniline.[26] 3,5,6,7-Tetranitroindazole also undergoes

* The isotope effect should come in part from the lower concentration of the free base in the deuteriated medium for, although D_0 in deuteriosulphuric acid is very similar to H_0 in sulphuric acid, the pK_a values of amines are increased by *ca.* 0.3 units in a deuteriated medium.[13]

† *Cf.* the nitration of *p*-nitroaniline.[21]

denitration on heating in sulphuric acid;[4] these reactions may involve the nitronium ion.

The results in Table 2 show that substituent effects on the rate of rearrangement are small unless the substituent adjacent to the migrating group is changed (when steric effects may be important). For the formation of corresponding radical pairs in the nitramine rearrangement, ρ −3.7 but this ρ value must come mainly from the pre-equilibrium protonation on the amino group for which the ρ value[27] (for substituted anilines) is −2.9. It follows that the formation of radical pairs by the homolysis of the protonated nitramines should show small substituent effects. This is consistent with the interpretation of the present results in terms of the formation of the corresponding radical pairs from the protonated amines. Because of the steric and blocking effects of additional substituents, no exact correlations are to be expected.

This work is now being extended to the rearrangement of nitrophenols and nitrated hydrocarbons;[9] the complete set of results should provide clearer evidence on the mechanism of these reactions.

Experimental

Materials.—Sulphuric and nitric acid were AnalaR reagents: nitric acid was distilled from sulphuric acid under reduced pressure and stored at −20 °C.

2,3-Dinitroaniline and 2,3-dinitro-6-methylaniline were provided by Dr. N. F. Scilly. 2,3-Dinitro-4-methylaniline was prepared by a modification[28] of the method of Morton and McGookin;[29] the product had m.p. 124 °C (lit.,[29] 124 °C). 2,3-Dinitro-5-methylaniline was prepared from *p*-toluidine by the synthetic path of Brady *et al.*[30] The product had m.p. 136 °C (lit.,[30] 141 °C) (Found: C, 42.4; H, 3.5; N, 21.0. Calc. for $C_7H_7N_3O_4$: C, 42.6; H, 3.6; N, 21.3%). 2,3-Dinitro-4-methoxyacetanilide was prepared by the method of Meldola and Eyre;[31] the product had m.p. 228—231 °C (lit.,[31] 230—231 °C).

2,3-Dinitro-4-t-butylaniline was prepared by the addition of t-butylbenzene (30 g) to a stirred mixture of nitric (40 cm^3; *d* 1.5) and sulphuric acid (50 cm^3; *d* 1.84). The mixture was maintained at 47 °C for 15 min and then poured onto ice. The product was recrystallised from ethanol to give 2,4-dinitro-t-butylbenzene (40 g), m.p. 61—62 °C (lit.,[32] 61—62 °C). A suspension of this in water (225 cm^3) was reduced by the dropwise addition over 1.5 h of a mixture of $Na_2S{\cdot}9H_2O$ (85.9 g) and sulphur (11.5 g) in water (135 cm^3) while heating under reflux. 4-Amino-2-nitro-t-butylbenzene formed (33.2 g) was acetylated with acetic anhydride (16.6 g) to give 4-acetamido-2-nitro-t-butylbenzene (28.5 g). Part of this material (10.9 g) was added to fuming nitric acid (50 cm^3), kept for 2 h at 0 °C, and then added ice–salt (600 g) containing hydrazine hydrate (2 m^3) (to reduce side-reactions during extraction) and chloroform (100 cm^3). After extraction with more chloroform, the mixture of dinitroacetanilides was hydrolysed by heating with sulphuric acid (98%) at 65 °C for 1 h. The solution was then poured into ice and extracted with chloroform. The resulting mixture of 2,3- and 2,5-dinitro-4-t-butylaniline was separated by column chromatography on silica gel with benzene as eluant to yield 2,3-dinitro-4-t-butylaniline (4.2 g), m.p. 131 °C (lit.,[28] 130—133 °C) (Found: C, 49.6; H, 5.5; N, 17.1. Calc. for $C_{10}H_{13}N_3O_4$: C, 50.2; H, 5.5; N, 17.6%).

2-Nitro-3-methylanine was prepared from 2,3-dinitrotoluene by the method of Burton and Kenner;[33] the product, after recrystallisation from aqueous ethanol, had m.p. 108 °C (lit.,[33] 107—108 °C).

[3-^{15}N]-3,6-Dinitroacetanilide was prepared by the nitration of aniline with an equivalent amount of [^{15}N]nitric acid in concentrated sulphuric acid at 0 °C followed by neutralisation and the separation of the 3- and 4-nitro products by crystallisation. The 3-nitro isomer was acetylated by the method of Kremer and Bendich[34] and nitrated in fuming nitric acid (*d* 1.5) for 1 h at room temperature. The dinitroacetanilides were separated by t.l.c. using silica gel plates and light petroleum (b.p. 40—60 °C)–ethyl acetate–dichloromethane (2:1:1 v/v) as solvent. [2,3-^{15}N]-2,3-Dinitroacetanilide was prepared in a similar way except that the second nitration was carried out using an equivalent amount of [^{15}N]nitric acid in sulphuric acid (92%) for 70 min at 0 °C. The purity of these labelled compounds was checked by ^{1}H n.m.r. spectroscopy.

Kinetics.—The kinetic runs were carried out in n.m.r. tubes placed in a thermostat at 110 °C. At appropriate times, the tubes were removed, brought to room temperature, and the ^{1}H n.m.r. spectra of the solutions were determined using a Varian T60 instrument. The extent of reaction was calculated from the changes in the heights of the peaks for the reactant or product (see text) and these heights were normally calculated relative to the height of the peak for dimethyl sulphoxide as an internal standard. The same procedure was used for reaction in deuteriosulphuric acid, for although the rearrangement reaction then introduces one deuterium atom into the ring, there is no evidence for exchange at the other positions. About ten measurements were made extending over the first three half-lives of the reaction and good first-order kinetics were observed.

Products.—For the product analyses, the amine (0.5 g) was dissolved in sulphuric acid (5 cm^3) using the concentrations indicated in Table 1 and normally heated at 110 °C until the corresponding kinetic experiments indicated that reaction was complete. The reaction was then quenched in ice–water and any solid filtered off. The solution was then extracted with chloroform and the combined organic products were separated by t.l.c. using silica gel plates and light petroleum (b.p. 40—60 °C)–dichloromethane–ethyl acetate as solvent (usually 2:1:1 v/v).

Mass spectra were determined using an A.E.I. MS 12 mass spectrometer. In the experiments involving the rearrangement of 2,3-dinitroaniline and [2,3-^{15}N]-2,3-dinitroaniline, the relative heights (*h*) of the parent peaks in the unlabelled and 'crossover' products (2,5-dinitroaniline) were as follows:

	Unlabelled product		Crossover product			
m/z	183	184	183	184	185	186
h	100	14.5	100	24	86	10

Nitric acid used was 97.7% ^{15}N and so, by analogy with the peak heights in the unlabelled product, the relative height at *m/z* 184 in the crossover product should have been 18.5 if no exchange had occurred. Since the exchange of nitrogen dioxide between one pair of labelled and unlabelled products generates two molecules of mass 184, the difference observed corresponds to *ca.* 3% exchange.

Acknowledgements

One of us (J. T. M.) thanks the S.E.R.C. for a studentship.

References

1 P. H. Gore, *J. Chem. Soc.*, 1957, 1437.
2 G. A. Olah, S. C. Narang, R. Malhotra, and J. A. Olah, *J. Am. Chem. Soc.*, 1979, **101**, 1805.
3 A. J. Neale, K. M. Davies, and J. Ellis, *Tetrahedron*, 1969, **25**, 1423.
4 M. S. Pevzner, N. V. Gladkova, and G. A. Lopukhova, *Zh. Org. Khim.*, 1976, **12**, 693.
5 K. H. Pausacker and J. G. Scroggie, *J. Chem. Soc.*, 1955, 1897.
6 K. C. Fisch, M. Silverman, and M. T. Bogert, *J. Am. Chem. Soc.*, 1943, **65**, 2432.

7 I. K. Barben and H. Suschitzky, *J. Chem. Soc.*, 1960, 672.
8 K. Schofield, 'Aromatic Nitration,' Cambridge University Press, Cambridge, 1980, p. 124.
9 Presented in part at the I.U.P.A.C. Meeting on 'Superacidic and Superbasic Media (Liquid and Solid),' Cirencester, England, 1984; P. Barrow, J. V. Bullen, A. Dent, J. T. Murphy, J. H. Ridd, and O. Sabek, *J. Chem. Soc., Chem. Commun.*, 1986, 1649.
10 *Cf.* L. Batt in 'Supplement F, The Chemistry of Amino, Nitroso, and Nitro-compounds and their Derivatives, Part I,' ed. S. Patai, Wiley, New York, 1982, p. 417.
11 P. Helsby and J. H. Ridd, *J. Chem. Soc., Perkin Trans. 2*, 1983, 311.
12 P. Helsby and J. H. Ridd, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1191.
13 J. Sierra, M. Ojeda, and P. A. H. Wyatt, *J. Chem. Soc. B*, 1970, 1570.
14 H. S. Choguill and J. H. Ridd, *J. Chem. Soc.*, 1961, 822.
15 G. G. Cross, A. Fischer, G. N. Henderson, and T. A. Smyth, *Can. J. Chem.*, 1984, **62**, 1446.
16 C. E. Barnes and P. C. Myhre, *J. Am. Chem. Soc.*, 1978, **100**, 973.
17 C. Bloomfield, A. K. Manglik, R. B. Moodie, K. Schofield, and G. D. Tobin, *J. Chem. Soc., Perkin Trans. 2*, 1983, 75.
18 W. N. White in 'Mechanisms of Molecular Migrations,' ed. B. S. Thyagarajan, Wiley-Interscience, New York, 1971, vol. 3, p. 109; A. M. A. Abu-Namous, J. H. Ridd, and J. P. B. Sandall, *Can. J. Chem.*, 1986, **64**, 1124.
19 R. B. Moodie in 'Aromatic Nitration,' K. Schofield, Cambridge University Press, 1980, ch. 15.
20 A. H. Clemens, P. Helsby, J. H. Ridd, F. Al-Omran, and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1217.
21 S. R. Hartshorn and J. H. Ridd, *J. Chem. Soc. B*, 1968, 1068.
22 W. N. White and J. R. Klink, *J. Org. Chem.*, 1970, **35**, 965.
23 A. M. A. Abu-Namous, J. H. Ridd, and J. P. B. Sandall, unpublished work.
24 W. N. White and H. S. White, *J. Org. Chem.*, 1970, **35**, 1803.
25 G. Bontempelli, G.-A. Mazzocchin, and F. Magno, *J. Electroanal. Chem.*, 1974, **55**, 91; L. L. Miller, G. D. Nordblom, and E. A. Mayeda, *J. Org. Chem.*, 1972, **37**, 916. The latter results have to be corrected to the scale based on the hydrogen electrode.
26 J. T. Murphy, Ph.D. Thesis, University of London, 1982.
27 J. Shorter, 'Correlation Analysis in Organic Chemistry,' Oxford University Press, 1973, p. 10.
28 H. Musso and H. Schroder, *Chem. Ber.*, 1965, **98**, 1577.
29 R. A. Morton and A. McGookin, *J. Chem. Soc.*, 1934, 901.
30 O. L. Brady, J. N. E. Day, and W. J. W. Rolt, *J. Chem. Soc.*, 1922, **121**, 526.
31 R. Meldola and J. V. Eyre, *J. Chem. Soc.*, 1902, **81**, 988.
32 H. J. Biekart, H. B. Dessens, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, 1952, **71**, 321.
33 H. Burton and J. Kenner, *J. Chem. Soc.*, 1921, **119**, 1047.
34 C. B. Kremer and A. Bendich, *J. Am. Chem. Soc.*, 1939, **61**, 2658.

Received 13*th November* 1986; *Paper* 6/2183