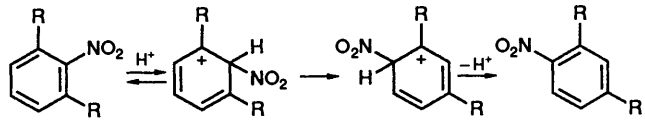
The Rearrangement of Aromatic Nitro Compounds. Part 3.[1] The Mechanism of Rearrangement of Nitrated Hydrocarbons in Trifluoromethanesulphonic Acid

John V. Bullen, John H. Ridd,* and Omaima Sabek
Chemistry Department, University College, 20 Gordon Street, London WC1H 0AJ, UK

1,3-Dialkyl-2-nitrobenzenes ($C_6H_3R_2NO_2$; R = Me, Et, and Pr^i) rearrange in trifluoromethanesulphonic acid to the corresponding 4-nitro derivatives; with R = Et, this reaction is accompanied by dehydration to 7-ethyl-3-methylanthranil. The reaction rate increases markedly with the size of the alkyl group; with R = Me, the reaction was studied at 110 °C but, with R = Pr^i, temperatures of 36–54 °C were used. The studies with R = Me show the reaction to be first-order with the rate coefficients (k_1) increasing rapidly with the acidity of the solution [$d(\log k_1)/d(-H_0)$] = 1.45, decreasing with acidity to 0.49. Double-labelling experiments with ^2H and ^{15}N show the reaction to be intramolecular. 1,2,4-Trimethyl-3-nitrobenzene also rearranges under these conditions to give mainly the 5-nitro isomer. The above results are discussed in terms of a direct 1,3-shift of the nitro group.

The work in the first two Parts of this series dealt with 1,3-nitro group rearrangements in aromatic amines[2] and phenols;[1] these studies are here extended to the rearrangement of those nitrated hydrocarbons in which the nitro group lies between two alkyl substituents (Scheme 1). Some previous work



(1) a; R = Me (6) (7)
b; R = Et
c; R = Pr^i

Scheme 1.

on the loss or transfer of nitro groups in acidic media was summarised in Part 1 of this series[2] and a preliminary account of the present work has appeared[3] together with a more detailed study of related reactions leading to the formation of anthranils.[4]

Results

1,3-Dimethyl-2-nitrobenzene.—This compound, (**1a**), when dissolved in 100% trifluoromethanesulphonic acid, rearranges smoothly to 1,3-dimethyl-4-nitrobenzene in a few hours at 110 °C. The reaction is very clean: there is no evidence for other products in the ^1H NMR spectrum during reaction and the product can be isolated[5] in a yield of 93.2%. The product is stable under the conditions of reaction. However, a GCMS study of the product composition did indicate the presence of *ca.* 1% of a product with mass 18 units less than the substrate and the major product; this could correspond to a small amount of dehydration to form 7-methylanthranil (7-methyl-2,1-benzisoxazole).

The reaction has also been studied in deuteriated trifluoromethanesulphonic acid (100%) to determine how the rate of hydrogen-isotope exchange on the ring compares with the rate of rearrangement. The ^1H NMR spectra of 1,3-dimethyl-2-nitrobenzene in the deuteriated acid showed that exchange at the 4- and 6-positions was effectively complete by the time of the first spectrum (15 min at room temperature), and that exchange at the 5-position was fast in comparison with the rearrangement. The spectra, however, gave no evidence of deuteriation at the methyl groups. These results showed that ring-deuteriated derivatives of 1,3-dimethyl-2-nitrobenzene could not be used in 'crossover' experiments.

Table 1. First-order rate coefficients for the rearrangement of the dialkylnitrocompounds (**1**) in trifluoromethanesulphonic acid.

R	[ArH]/ mol dm^{-3}	T/°C	[CF_3SO_3H] (%)	$-H_0$	$k_1/10^{-5}$ s^{-1}
Me	0.038	110	100	—	16.3
Me	0.09	110	100	—	12.9
Me	0.164	110	100	—	8.1
Me	0.351	110	100	—	6.8
Me	0.09	110	99.5	12.32	4.98
Me	0.09	110	98.5	11.80	2.24
Me	0.09	110	97.8	11.53	1.09
Me	0.09	110	96.5	11.17	0.43
Me	0.09	90	99.7	12.45	1.03[a]
Et	0.05	90	99.7	12.45	7.05[a,b]
Pr^i	0.05	90	99.7	12.45	2 320[c]
Pr^i	0.05	54	99.7	12.45	119
Pr^i	0.05	45	99.7	12.45	48.1
Pr^i	0.05	40	99.7	12.45	31.2
Pr^i	0.05	36	99.7	12.45	20.3

[a] Taken from ref. 4. [b] Accompanied by extensive cyclisation, see text. [c] Extrapolated from results at lower temperatures.

A sample of 1,3-(1-$^2H_1$)dimethyl-2-nitrobenzene was therefore prepared and a mixture of this compound and 1,3-dimethyl-2-(^{15}N)nitrobenzene were rearranged together. These two compounds have the same mass number (152) and so, if there were any exchange of the nitro group during rearrangement, the result could be detected by the appearance of products with mass numbers 151 and 153. After rearrangement, the product was isolated and the mass spectrum determined. Comparison with the pattern of intensities deriving from the individual rearrangements of the labelled products shows no evidence for any crossover of the migrating nitro group. The almost complete absence of a peak with mass number 151 in the mass spectrum of the deuterium labelled product also confirms the absence of hydrogen-isotope exchange involving the methyl group during the rearrangement.

The changes in the ^1H NMR spectra during the rearrangement were shown in our preliminary communication.[3] The reaction gives good first-order kinetics during a single run

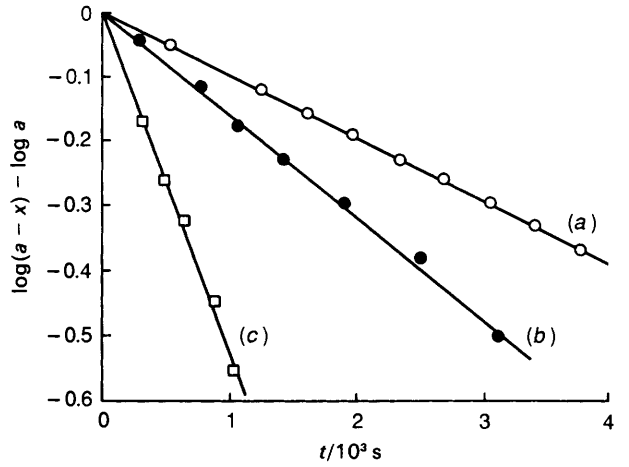


Figure 1 First-order plots for the rearrangement of nitro compounds in trifluoromethanesulphonic acid: (*a*) 1,3-dimethyl-2-nitrobenzene in 98.5% acid at 110 °C, (*b*) 1,2,4-trimethyl-2-nitrobenzene in 99.7% acid at 90 °C, and (*c*) 1,3-di-isopropyl-2-nitrobenzene in 99.7% acid at 54 °C. For clarity, the times for reaction (*a*) have been divided by 10 before being plotted.

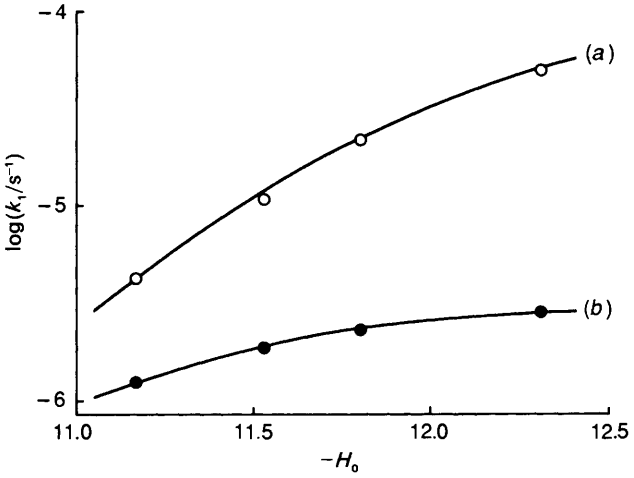


Figure 2. The variation with acidity of (*a*) the observed first-order rate coefficients for the rearrangement of 1,3-dimethyl-2-nitrobenzene and (*b*) the calculated first-order rate coefficients for the rearrangement of a hypothetical substrate with a pK_a of −11.35. The position of curve (*b*) on the vertical axis is arbitrary.

(Figure 1) but the first four results in Table 1 show that the first-order rate coefficients are sensitive to the initial concentration of the substrate; this is presumably a medium effect arising from the relatively high concentrations required in these NMR studies. The rate coefficients are also very sensitive to the acidity of the medium and a plot of log k_1 against $-H_0$ is shown in Figure 2; the initial slope is 1.45 and the final slope 0.49. The H_0 values were obtained in the same way as in the previous work.[1]

1,2,4-*Trimethyl*-3-*nitrobenzene*.—The rearrangement of this compound (**2**) was studied to provide evidence on the substituent effect of a methyl group on the rate of rearrangement and on the product composition. Rearrangement can yield both the 5-nitro isomer (**3**) and the 6-nitro isomer (**4**) (Scheme 2). The isomer composition was determined from the integration of a 400 MHz ^{1}H NMR spectrum of the reaction product and the results are compared with those for nitration in Table 2. A separate study of the ^{1}H NMR spectra of the minor component (1,2,4-trimethyl-6-nitrobenzene) under the same conditions

Table 2. Rearrangement of 1,2,4-trimethyl-3-nitrobenzene (0.096 mol dm^{-3}) in 99.7% trifluoromethanesulphonic acid at 90 °C. Comparison with the product composition from the nitration of 1,2,4-trimethylbenzene in sulphuric acid at 25 °C.

	Nitration Products (%)[a]		Rearrangement	
Isomer	47.8% H_2SO_4	81.7% H_2SO_4	Product (%)	$k_1/10^{-4}$ s^{-1}
3-Nitro	6.6	11.8	—	—
5-Nitro	27.5	49.8	96.5	3.5 } 3.63
6-Nitro	2.6	38.3	3.5	0.13 }

[a] Ref. 10.

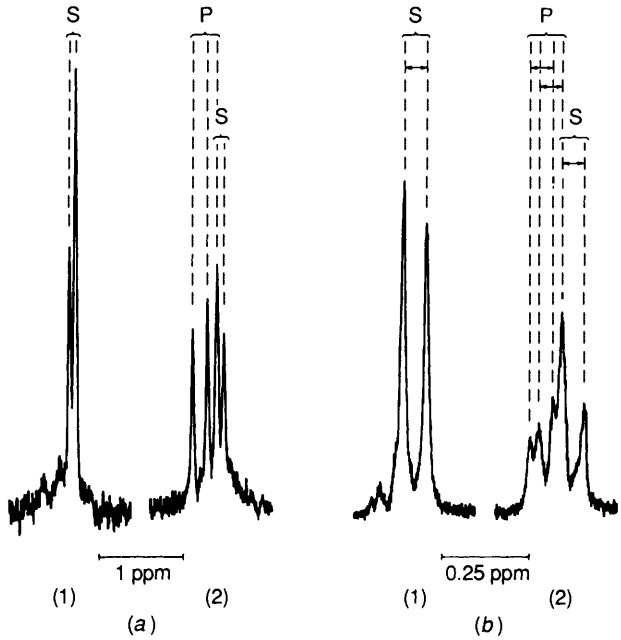
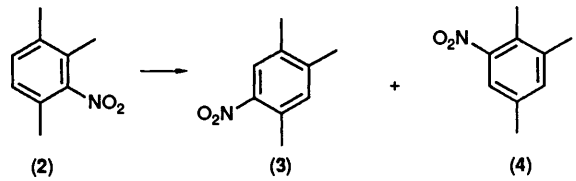


Figure 3. The ^{1}H NMR absorption of the methyl groups during the rearrangement in 99.7% trifluoromethanesulphonic acid of (*a*) 1,2,4-trimethyl-3-nitrobenzene (90 °C) and (*b*) 1,3-di-isopropyl-2-nitrobenzene (54 °C). Spectrum (1) was taken near the start of reaction and spectrum (2) at about 60% reaction. S ≡ Starting material; P ≡ Product. In (*b*), the double-headed arrows connect the two signals of a given isopropyl group.



Scheme 2.

(using 1,4-dinitrobenzene as a standard) gave no evidence of decomposition or further rearrangement over the time of the original rearrangement reaction (90 min).

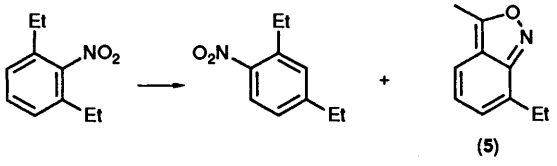
The rate of rearrangement was determined from the changes in the methyl signals in the ^{1}H NMR spectra (Figure 3). The resulting kinetic plot shows some scatter (Figure 1) but corresponds to approximate first-order kinetics; the first-order rate coefficients for reaction to form the two products are included in Table 2 together with the overall rate coefficient. Comparison with the rate coefficient for the rearrangement of 1,3-dimethyl-2-nitrobenzene under the same conditions shows

Table 3. First-order rate coefficients for the deisopropylation of isopropyl-1,3-dimethylnitrobenzenes (0.057 mol dm^{-3}) in 99.7% trifluoromethanesulphonic acid at 80 °C.

Position of		
Pr^i	NO_2	$k_1/10^{-4}$ s^{-1}
5	2	0.34
5	4	7.4
6	4	2.46

that the additional methyl group increases the rate of the overall rearrangement by a factor of *ca.* 35.

1,3-*Diethyl*-2-*nitrobenzene*.—The kinetic analysis for this compound is complicated by the fact that rearrangement is a minor reaction: the main reaction (70%) is dehydration to yield 3-methyl-7-ethylanthranil (**5**) (Scheme 3). The overall reaction



(5)

Scheme 3.

appears to be first order and so the overall rate coefficient has been divided into the two components. The value quoted in Table 1 refers only to the rearrangement reaction. The dehydration is considered in more detail elsewhere[4] where it is compared with related reactions leading to the formation of anthranils.

1,3-*Di-isopropyl*-2-*nitrobenzenes*.—A number of isopropyl substituted nitrobenzenes undergo protodeisopropylation on being heated in trifluoromethanesulphonic acid (see below). However, the rearrangement of 1,3-di-isopropyl-2-nitrobenzene occurs considerably faster than the protodeisopropylation and so can be studied separately. The rearrangement of this compound occurs far more readily than those described above and the reactions were therefore studied at lower temperatures (Table 1). After rearrangement in 99.7% trifluoromethanesulphonic acid at 36 °C, the ^1H NMR spectrum, the mass spectrum, and the elemental analysis of the extracted product accord with a 1,3-shift of the nitro group; no evidence for nitrodeisopropylation was observed.

The rate of the rearrangement was followed from the change in the height of the high-field methyl peak in the starting material (Figure 3). The experimental points showed some scatter but approximate first-order kinetics were observed (Figure 1) and the rate coefficients are included in Table 1. The variation of the first-order rate coefficients with temperature gave the Arrhenius parameters: E = 82.0 kJ mol^{-1}, log A = 10.16.

Deisopropylation Reactions.—Three related compounds (5-isopropyl-1,3-dimethyl-2-nitrobenzene, 5-isopropyl-1,3-dimethyl-4-nitrobenzene, and 6-isopropyl-1,3-dimethyl-4-nitrobenzene) were found to undergo deisopropylation in 99.7% trifluoromethanesulphonic acid at 80 °C and the first-order rate coefficients are given in Table 3. All three reactions were followed from the change in the height of the methyl peaks of the isopropyl group in the substrate. With the first substrate, the deisopropylation is followed by the rearrangement of the 1,3-dimethyl-2-nitrobenzene formed.

Discussion

Since the formation of anthranils has been discussed elsewhere,[4] this section is concerned with one major problem: the mechanism of the 1,3-migration of the nitro group in such compounds as 1,3-dimethyl-2-nitrobenzene. The simplest interpretation of the marked acidity dependence (Figure 2) is that the transition state involves the protonated substrate and so the reaction is considered to involve the Wheland intermediates (**6**) and (**7**). At all aromatic C–H groups, the rate of hydrogen–deuterium exchange (followed by ^1H NMR spectroscopy) is fast in comparison with the rate of rearrangement. Proton transfers are therefore considered to be fast in comparison with the rate-determining step of the rearrangement and hence, in Scheme 1, the formation of the first Wheland intermediate (**6**) is shown to be reversible and the formation of the second Wheland intermediate (**7**) to be irreversible. The decreasing slope of the plot in Figure 2 presumably comes from the increasingly complete protonation of the substrate on the nitro group but the comparison with the theoretical curve [equation (1)][5] for a hypothetical substrate of

$$\log k_1 = \text{const} - H_0 - \log(K_a + h_0) \qquad (1)$$

$pK_a = -11.35$ (the value for *p*-nitrotoluene)[6] shows that the curvature is less than would be expected from this cause, possibly because *C*- and *O*-protonation follow different acidity functions.

There are four obvious mechanisms for the conversion of (**6**) into (**7**) in Scheme 1: (*a*) homolysis of the C–N bond to form a nitrogen dioxide radical and an aromatic cation radical; (*b*) heterolysis of this bond to form an aromatic molecule and a nitronium ion; (*c*) consecutive 1,2-migrations of the nitro group; and (*d*) a direct intramolecular * 1,3-shift.

The absence of any cross-over products in the concurrent rearrangement of the isotopically labelled substrates renders mechanism (*a*) very improbable. In the known examples of nitro group rearrangements involving nitrogen dioxide,[9] considerable amounts of cross-over products are found. The same argument cannot, however, be used against mechanism (*b*) since evidence from relative reactivities[10] indicates that the encounter pair formed between these aromatic systems and a nitronium ion would normally react before separating. To disprove this mechanism, it is necessary to consider the isomer proportions formed in the nitration of 1,2,4-trimethylbenzene and in the rearrangement of 1,2,4-trimethyl-3-nitrobenzene (Table 2).

The nitration of 1,2,4-trimethylbenzene leads to an extensive amount of *ipso* attack; at low acidities, the *ipso* intermediates formed are captured by the solvent and diverted to phenolic products but at high acidities the *ipso* intermediates are believed to undergo one or more 1,2-shifts until the nitro group reaches an unsubstituted carbon atom.[10] If the rearrangement of 1,2,4-trimethyl-3-nitrobenzene occurred through the encounter pair formed in the nitration of 1,2,4-trimethylbenzene, then the relative amounts of substitution at the 5- and 6-positions would be expected to be similar to that observed in nitration reaction at high acidity but this is not found (Table 2). The results from the rearrangement reaction are much closer to the nitration results at low acidities and hence seem to reflect the intrinsic reactivity of these positions, *i.e.*, the reactivity under conditions where *ipso* attack and the resulting rearrangements are unimportant. The rearrangement in trifluoromethanesulphonic acid is not therefore easily explained by the reformation of the encounter pair formed in nitration.

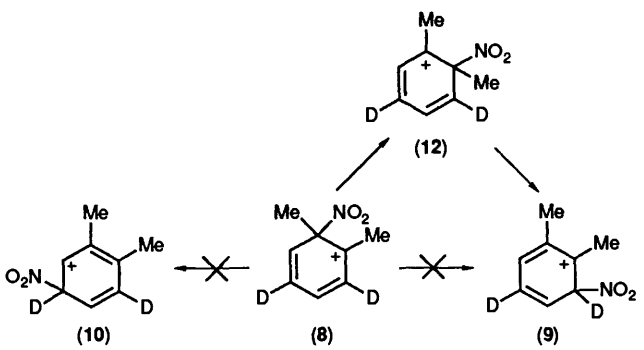
The interpretation of these rearrangements as successive

* In this paper, the term intramolecular is used in its conventional sense[7] and not with the more restricted meaning introduced recently.[8]

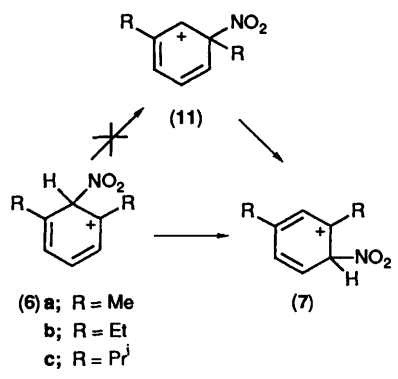
1,2-shifts [mechanism (*c*) above] is superficially plausible since successive 1,2-shifts of a nitro group have often been proposed, *e.g.*, to explain the products formed in the rearrangement of the *ipso* intermediate (**8**).[11] The argument that the rearrangement to the Wheland intermediate (**9**) does not involve a direct 1,3-shift comes from the absence of evidence for a direct 1,3-shift in the other direction to give the intermediate (**10**); substitution occurs instead at the vacant *ortho* position. However, the results with 1,3-di-isopropyl-2-nitrobenzene provide strong evidence against this mechanism for the rearrangements considered here. In the examples that have been studied in detail, the *ipso* intermediates formed by the attack of a nitronium ion on a carbon atom bearing an isopropyl group are found to undergo nitrodeisopropylation in preference to a 1,2-shift of the nitro group;[12] indeed there is no clear evidence that a 1,2-shift of a nitro group ever occurs with these intermediates.[12] It also appears that the loss of the isopropyl group is not dependent on the presence of water in the medium and so occurs readily at high acidities.[12] The relevant *ipso* intermediate (**11c**) in our system is less stable than those studied previously[12] and this factor may make the 1,2-nitro group shift more competitive with deisopropylation but there is no obvious reason why this factor should reverse the order of these reaction rates. If, therefore, these rearrangements occurred by an initial 1,2-shift, the products from the rearrangement of 1,3-di-isopropyl-2-nitrobenzene should include 3-nitroisopropylbenzene as a major component and this was not observed. The absence of this compound cannot be explained by assuming that, for some reason, trifluoromethanesulphonic acid prevents deisopropylation since protodeisopropylation is reported above for a number of compounds in which the 1,3-nitro group rearrangement reactions do not occur.

The above argument leads to the curious conclusion that the rearrangements in Schemes 4 and 5 occur by different mechanisms. Our preferred explanation for this comes from the fact that the structures (**8**), (**12**), and (**9**) in Scheme 4 are of very similar energy whereas, from the directing effect of the methyl group, structure (**11**) in Scheme 5 must be of much higher energy than structures (**6**) and (**7**). We suggest therefore that, although 1,2-shifts are normally preferred in the rearrangements of *ipso* and Wheland intermediates, a direct 1,3-shift may occur when the corresponding 1,2-shift would lead to a structure of much greater energy. This conclusion accords with those reached for the corresponding rearrangements of nitrophenols[1] and nitroanilines;[2] it is also consistent with the absence of CIDNP effects in the rearrangement of 2-methyl-2-nitrocyclohexa-3,5-dienone.[13] The rearrangements can be regarded as typical allowed [1,5]-sigmatropic shifts (without inversion at the migrating centre) or as reaction through incipient radical pairs in which the bond-forming process begins before a true radical pair is formed. This distinction is mainly concerned with the 'looseness' of the transition state and we hope to discuss it in more detail in connection with the activation parameters for the rearrangement of nitrocyclohexadienones.[14]

The main point remaining concerns the relative rates of the rearrangements above. When the results for the isopropyl compound (**1c**) in Table 1 are extrapolated to 90 °C, the comparison with the other substrates in Scheme 1 gives the following relative rates: (**1a**):(**1b**):(**1c**) ≡ 1:6.8:2 250. The much greater reactivity of the isopropyl compound indicates clearly that the main substituent effects of these *ortho* groups are steric rather than electronic and that the main driving force of the reaction is the steric interaction of the *ortho* alkyl substituents and the nitro group. The increase in rate by a factor of 35 produced by the additional methyl group in the trimethyl derivative (**2**) presumably comes in part from a buttressing effect and in part from the electronic effect of the substituent.



Scheme 4.



Scheme 5.

Experimental

Materials.—1,3-Dimethyl-2-nitrobenzene and 1,3-dimethyl-4-nitrobenzene were obtained from Aldrich. 1,3-Di-isopropyl-2-nitrobenzene was obtained by the oxidation of 2-amino-1,3-di-isopropylbenzene with peracetic acid using the method described previously for the corresponding preparation of 1,3-diethyl-2-nitrobenzene.[4] 1,3-Di-isopropyl-4-nitrobenzene was obtained by the nitration of 1,3-di-isopropylbenzene in acetic anhydride. The three 1,2,4-trimethylnitrobenzenes were prepared by the nitration of 1,2,4-trimethylbenzene using nitric acid in nitromethane. The reaction mixture was quenched with iced water and the products were extracted with ether and separated by HPLC. A similar method was used to prepare the several isopropyl-1,3-dimethylnitrobenzenes from the corresponding hydrocarbons.

1,3-(1-$^2H_1$)Dimethyl-2-nitrobenzene was prepared from 3-methylbenzyl chloride. A solution of 3-methylbenzyl chloride (5 g) in dry ether (40 cm^3) was added over a period of 30 min to a mixture of magnesium turnings (2 g) in ether (40 cm^3). The reaction mixture was then brought to 0 °C and deuteriosulphuric acid (20%; 2.4 g) added. Extraction with ether and removal of the solvent gave 1,3-[(1-$^2H_1$)dimethyl]benzene (3.3 g). The above experiment was repeated and the 1,3-[(1-$^2H_1$)dimethyl]-benzene (5 g) was dissolved in acetic anhydride at 0 °C. Nitric acid (2.25 g, *d* 1.5) was added slowly over a period of 20 min and the reaction mixture was then left at room temperature for 2 h. After quenching with water (500 cm^3), neutralisation with sodium carbonate, and extraction with ether (5 × 30 cm^3), the resulting mixture of the 2-nitro and 4-nitro isomers was separated by HPLC using a (4:1) mixture of petroleum spirit and ethyl acetate. 1,3-Dimethyl-2-(^{15}N)nitrobenzene was obtained by a similar nitration of 1,3-dimethylbenzene but using 40% $H^{15}NO_3$ (99% ^{15}N).

All of the above products gave satisfactory ^{1}H NMR spectra, mass spectra, and elemental analyses.[15,16]

The trifluoromethanesulphonic acid was prepared as described previously.[1] Some of the acid was re-used after precipitation as barium trifluoromethanesulphonate and re-distillation from sulphuric acid. For the preparation of deuteriotrifluoromethanesulphonic acid, deuteriosulphuric acid was used in place of sulphuric acid.

Kinetic Studies.—These were carried out on a JEOL 100 Mc CW instrument as described previously for the ^{1}H NMR studies on the rearrangement of nitrophenols.[1] For the dimethyl compound (**1**; R = Me), the extent of reaction was calculated from the ratio of the height of the methyl peak in the starting material to the sum of the heights of the methyl peaks in the starting material and product. For the diethyl compound (**1**; R = Et), the extent of reaction was calculated from the change in the height of the high-field component of the methyl triplet in the starting material. The resulting rate coefficient refers to both rearrangement and cyclisation to the anthranil (**5**) and the component rate coefficients were obtained from the product composition.[4] For the di-isopropyl compound (**1**; R = Pr^i) and for 1,2,4-trimethyl-3-nitrobenzene (**2**), the extent of reaction was calculated from the change in the height of the high-field methyl signal (Figure 3) in the starting material. In most of these kinetic studies, the peak heights were measured relative to that of *p*-dinitrobenzene present as an internal standard.

The rate coefficients for the deisopropylation reactions were followed from the change in the height of the methyl signals of the isopropyl group relative to the signal for tetramethylammonium triflate as an internal standard. 5-Isopropyl-1,3-dimethyl-4-nitrobenzene and the 6-isopropyl isomer underwent a smooth deisopropylation but with 5-isopropyl-1,3-dimethyl-2-nitrobenzene the deisopropylation was followed by the expected rearrangement of the 1,3-dimethyl-2-nitrobenzene formed. A curious feature of this reaction was that this subsequent rearrangement appeared about twice as fast as expected from the concentration of trifluoromethanesulphonic acid used (99.7%). It is possible that the deisopropylation changes the water content of the medium.

The principle problem in obtaining reproducible results in these kinetic studies comes from the marked effect of traces of water in the medium. The effect of water on the rearrangement of one of the substrates (1,3-dimethyl-2-nitrobenzene) was therefore studied and the rate of this reaction was used to check the water content of subsequent batches of acid.

The rearrangement of 1,3-dimethyl-2-nitrobenzene was the only reaction which could be followed with sufficient accuracy for the first-order form to be clearly established for a given run. Although the results of the other reactions have been were fitted to first-order plots, it is possible that significant deviations from first-order kinetics may occur.

Mass Spectrometric Measurements.—The mass spectra of the reactants and products were measured on a VG 7070 instrument.[15,16] In the 'cross-over' experiment, the mass spectra of the reaction products of the rearrangement of 1,3-[(1-$^2H_1$)dimethyl]-2-nitrobenzene and 1,3-dimethyl-2-(^{15}N)nitrobenzene were compared with the mass spectrum of the concurrent rearrangement of these compounds. In all three experiments, the (p − 1) peak at mass 151 was 1–2% of the p peak at mass 152.

Product Analyses.—Product isolation was carried out as described previously.[1] Product identification was based on the comparison of ^{1}H NMR spectra with those of authentic samples using Varian XL 200 and VXR 400 spectrometers. For substrates (**1a**) and (**1c**), only one product was isolated. For substrate (**1b**) the identification of the anthranil formed is described elsewhere.[4] For 1,2,4-trimethyl-2-benzene, the product composition is based on the integrals of the proton signals in the mixture obtained after quenching and extraction of the reaction mixture.

Acknowledgements

One of us (J. V. B.) thanks the SERC for a studentship.

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Paper 0/01216E
Received 20*th March* 1990
Accepted 8*th June* 1990