The Rearrangement of Aromatic Nitro Compounds. Part 2.[1] The Rearrangement of Substituted Nitrophenols in Trifluoromethanesulphonic Acid

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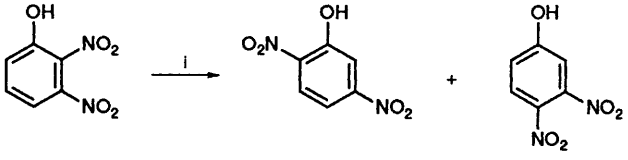
o-Nitrophenols with an additional substituent (Y = NO_2, Cl, or Me) in the 3-position rearrange in trifluoromethanesulphonic acid at 100 °C to give mainly the product with the nitro group in the opposite *ortho* position; no more than 1–4% of other products are formed. The reactions give first-order kinetics, are acid-catalysed and (at least when Y = NO_2) are intramolecular. The rate of rearrangement varies with the 3-substituent in the order Me > Cl > NO_2. The results are discussed in terms of a rate-determining migration of the nitro group in the Wheland intermediate formed by protonation at the 2-position. A much slower rearrangement occurs with 3,4-dinitrophenol under the same conditions to give a small yield of 2,5-dinitrophenol accompanied by decomposition of the substrate.

References were given in the previous paper of this series[1] to the early evidence that some nitroanilines underwent rearrangement when heated in acidic media. That early work also contained one reference[2] to a similar rearrangement in nitrophenols, for a small yield (7.5%) of 2,5-dinitrophenol obtained when 2,3-dinitrophenol was heated in sulphuric acid for 7 h at 112 °C; the other products involved oxidation and sulphonation. Fortunately, in our preliminary studies,[3] we found that the substitution of trifluoromethanesulphonic acid for sulphuric acid completely removed these side-reactions in the rearrangements of 2,3-dinitrophenol and a number of related compounds. This has led us to a kinetic and mechanistic study of these rearrangements.

Results

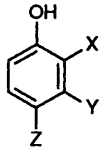
Products.—Our main studies have involved the rearrangement of 2,3-dinitrophenol shown in Scheme 1. When this compound is dissolved in 100% trifluoromethanesulphonic acid



Scheme 1. *Reagents and conditions:* i, CF_3SO_3H, 100 °C.

at 100 °C, it rearranges smoothly to give the 2,5-dinitro isomer with a half-life of about 20 min. A careful examination of the product by ^1H NMR spectroscopy and by HPLC showed that a small amount of the 3,4-dinitro isomer is also formed together with some denitration (Table 1); the isolated yield of dinitro products is 95%. Separate experiments on the other dinitro isomers showed that 2,5-isomer is stable under the reaction conditions but that the 3,4-isomer undergoes a slow further reaction; after 100 h the ^1H NMR spectrum of the solution shows that most of the remaining peaks are those characteristic of 2,5-dinitrophenol but this rearrangement is accompanied by extensive decomposition. The rearrangement of 4-methyl-2,3-dinitrophenol (**2**) (Table 1) is very similar to that of 2,3-dinitrophenol and that of 2-methyl-3,4-dinitrophenol (**3**) is very slow and similar to that of 3,4-dinitrophenol.

The rearrangements of 2,3-dinitrophenol and 4-methyl-2,3-dinitrophenol have been used to determine whether the reaction is inter- or intra-molecular. A mixture of 2,3-(2-^{15}N)dinitrophenol and 4-methyl-2,3-dinitrophenol was heated to 100 °C in 100% trifluoromethanesulphonic acid, and the mass spectrum of the rearranged product was compared with the mass spectra of the products of the separate rearrangements. If the reaction had involved an intermolecular component, the resulting crossover of the labelled and unlabelled nitro groups would have reduced the $[p/(p-1)]$ ratio for the product from 2,3-(2-^{15}N)dinitrophenol and increased the $[p/(p+1)]$ ratio in the product from 4-methyl-2,3-dinitrophenol. The comparison of the peak height ratios for the concurrent and separate rearrangements (Table 2) shows that this does not occur and the reaction appears therefore to be entirely intramolecular. This argument is helped by the small substituent effect of the 4-methyl group on the reaction rate (see below) and by the fact



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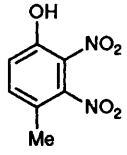

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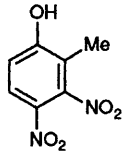


(3)

Table 1. Products of rearrangement of substituted nitrophenols (**1**) in trifluoromethanesulphonic acid at 100 °C.

Substituent				
X	Y	Z	Acid (%)	Products;[a] yield
NO_2	NO_2	H	100	2,5-dinitrophenol; 98%[b,c] (96%)[d]
			97	3,4-dinitrophenol; 1%[b,c] (2.3%)[d]
			94	3-nitrophenol; 1%[b,c] (1.7%)[d]
NO_2	Me	H	97.5	5-methyl-2-nitrophenol; 98%
				5-methyl-2-nitrophenol; 2%
NO_2	Cl	H	97.5	5-chloro-2-nitrophenol; 100%
NO_2	NO_2	Me	100	4-methyl-2,5-dinitrophenol; 100%
H	NO_2	NO_2	100	2.5-dinitrophenol, with extensive decomposition
Me	NO_2	NO_2	100	2-methyl-3,6-dinitrophenol, with extensive decomposition

[a] Composition of isolated product by ^1H NMR spectroscopy. [b] Overall yield is 94.9%. [c] Product composition for all three acidities. [d] Composition by HPLC for reaction in 97% acid.

Table 2. The $[p/(p-1)]$ peak height ratio in the product of rearrangement of 2,3-(2-^{15}N)dinitrophenol and the $[p/(p+1)]$ peak height ratio in the product of rearrangement of 4-methyl-2,3-dinitrophenol. Comparison of the results of separate and concurrent rearrangements.

	Peak heights h	
Reactant	h_{185}/h_{184}	h_{198}/h_{199}
2,3-(2-^{15}N)Dinitrophenol	76.7	
4-Methyl-2,3-dinitrophenol		16.8
Concurrent rearrangement	76	16.5

Table 3. Products from the nitration of 3-nitrophenol in trifluoromethanesulphonic acid at room temperature.

	Dinitro products (%)		
Acid (%)	2,3-	3,4-	2,5-
95	52[a]	13[a]	35[a]
97	50.5[a]	13[a]	36.5[a]
97	51[b]	12[b]	37[b]

[a] Determined by ^{1}H NMR spectroscopy. [b] Determined by HPLC.

that the product from 4-methyl-2,3-dinitrophenol does not give peaks at the relevant mass numbers of the other rearrangement. However, the conclusion does involve the assumption that it is the 2-nitro group that migrates; this point is considered further in the Discussion section.

The results in Table 1 include examples of the rearrangements in which the 3-nitro group has been replaced by a methyl group or a chlorine atom. Both of these rearrangements show the strong regioselectivity exhibited by the rearrangement of 2,3-dinitrophenol, for the 2-nitro group migrates almost exclusively to the opposite *ortho* position. The ^{1}H NMR spectra taken during reaction indicate that these reactions are essentially quantitative.

Experiments were also carried out on the corresponding methyl ethers to determine whether the same regioselectivity could be observed in the absence of the hydroxy group of the phenol. Unfortunately, the rearrangements are then complicated by demethylation but, with 3-methyl-2-nitroanisole, some rearranged anisoles were obtained and the ^{1}H NMR spectrum of the neutral product fraction showed that the concentration ratio of the 6-nitro isomer to the 4-nitro isomer was *ca.* 50:1. The regioselectivity is therefore still present. The same concentration ratio was found for the corresponding isomers in the phenol fraction.

The mass spectra of the products of all of the above rearrangements were determined to check whether any trinitro products are formed but no peaks corresponding to these compounds were observed.

The isomer compositions from the nitration of 3-nitrophenol in two concentrations of trifluoromethanesulphonic acid were determined (Table 3) for comparison with the product compositions from the rearrangement reactions. The nitration reactions give much more substitution at the 4-position.

Kinetics.—The rearrangement of 2,3-dinitrophenol in trifluoromethanesulphonic acid leads to a marked change in the UV and visible regions of the spectrum with well defined isosbestic points at 314 nm and 363 nm (Figure 1); the extent of reaction has been followed from the change in the absorption at 390 nm. All kinetic runs gave good first-order kinetics and, as expected, the first-order rate coefficients are independent of the

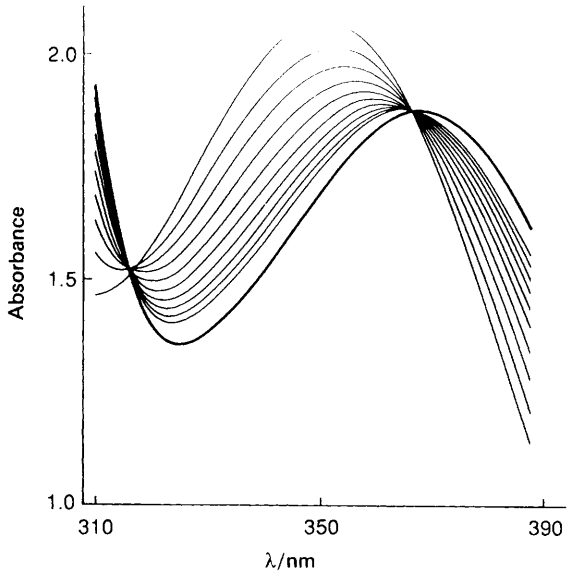


Figure 1. UV Spectra taken during the rearrangement of 2,3-dinitrophenol (5.5×10^{-4} mol dm^{-3}) in 99.4% trifluoromethanesulphonic acid at 70 °C. For clarity, only a selection of the spectra are shown. The spectrum at the end of the run is indicated by the heavier line.

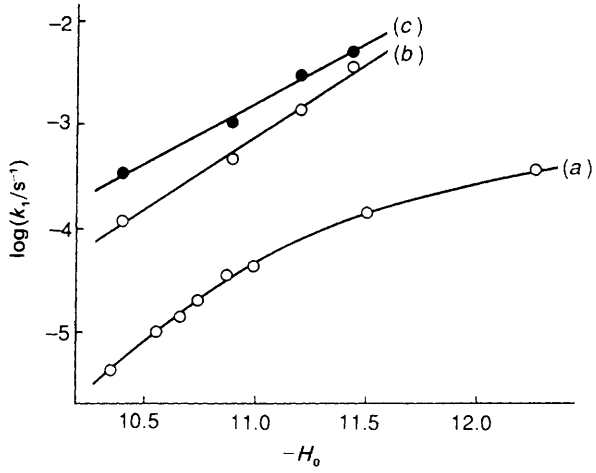


Figure 2. The variation of log k_1 with the acidity function H_0 for the rearrangement of the phenols (**4**; Y = NO_2, Cl, Me) in 92.5–99.4% trifluoromethanesulphonic acid at 100 °C. (*a*) Y = NO_2; (*b*) Y = Cl; (*c*) Y = Me.

initial concentration of the substrate. This is most clearly illustrated by the two kinetic runs carried out in 97.7% trifluoromethanesulphonic acid (Table 4); a change in the initial concentration of the substrate by a factor of 5 leads to a change in the rate coefficient by only 4%.

The first group of runs in Table 4 refer to reaction at 100 °C and show how the first-order rate coefficient varies with the concentration of the acid. The second and third groups of runs show how the first-order rate coefficient varies with temperature and these results are used to obtain extrapolated values of the rate coefficient at 100 °C at the higher acidities. The variation of the rate coefficient with the H_0 acidity function is shown in Figure 2. The activation parameters calculated from the rate coefficients for 99.4% acid in Table 4 are E = 87.8 kJ, log A = 8.86.

Attempts to follow the other rearrangements by UV and visible spectroscopy were less successful, perhaps because of the

Table 4. The variation of the first-order rate coefficient (k_1) for the rearrangement of 2,3-dinitrophenol in trifluoromethanesulphonic acid with acidity and temperature of the medium.

$[CF_3SO_3H]$ (%)	$-H_0$	T/°C	10^4[ArOH]/mol dm^{-3}	10^5k_1/s^{-1}
92.5	10.35	100	10.03	0.434
93.4	10.55	100	11.9	1.05
93.9	10.66	100	4.14	1.45
94.3	10.74	100	8.09	2.08
95.0	10.87	100	6.61	3.61
95.6	10.99	100	4.25	4.52
97.7	11.50	100	2.22	13.5
97.7	11.50	100	11.23	14.0
99.4	12.26	60	5.05	1.22
99.4	12.26	70	5.50	3.19
99.4	12.26	85	5.12	11.2
99.4	12.26	100	—	(37.0)[a]
100		55	5.48	3.14
100		65	6.61	6.83
100		75	5.34	14.1
100		100	—	(73.6)[a]

[a] Calculated from the results at lower temperatures.

Table 5. Variation of the first-order rate coefficient (k_1) with the structure of the substrate for the rearrangement of substituted phenols (**1**) at 100 °C.

Substituent						
X	Y	Z	$[CF_3SO_3H]$ (%)	$-H_0$	[ArOH]/mol dm^{-3}	10^3k_1/s^{-1}
NO_2	Me	H	92.7	10.40	0.207	0.331
NO_2	Me	H	92.7	10.40	0.228	0.339
NO_2	Me	H	92.7	10.40	0.488	0.293
NO_2	Me	H	95.1	10.89	0.231	1.03
NO_2	Me	H	96.6	11.20	0.218	2.97
NO_2	Me	H	96.6	11.20	0.275	2.95
NO_2	Me	H	97.5	11.43	0.192	5.54
NO_2	Me	H	97.5	11.43	0.189	5.06
NO_2	Cl	H	92.7	10.40	0.223	0.12
NO_2	Cl	H	95.1	10.89	0.205	0.46
NO_2	Cl	H	96.6	11.20	0.21	1.42
NO_2	Cl	H	97.5	11.43	0.2	3.65
NO_2	NO_2	Me	100			1.04
H	NO_2	NO_2	100			(0.008)[a]

[a] Estimate only; see the text.

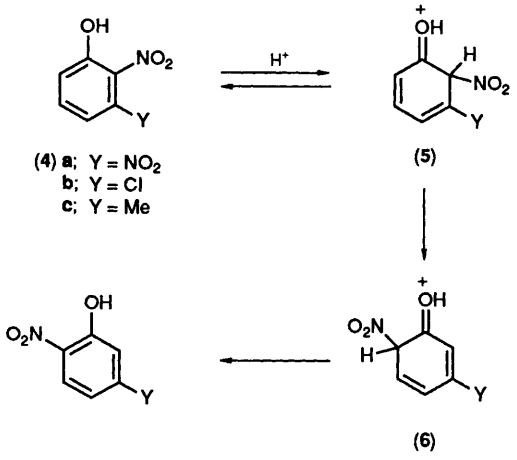
formation of small amounts of side-products; these reactions were therefore studied by ^{1}H NMR spectroscopy. As before, the reactions followed first-order kinetics during a single run but with some scatter of points because of the lower accuracy of the NMR studies. The rate coefficients obtained are listed in Table 5 and suggest that, with these relatively high substrate concentrations, the first-order rate coefficient may decrease slightly as the concentration of the substrate is increased (compare the runs carried out on 3-methyl-2-nitrophenol in 92.7% trifluoromethanesulphonic acid). Further evidence for this effect is given in the following paper. The rate profiles for the rearrangement of 3-methyl-2-nitrophenol and 3-chloro-2-nitrophenol are included in Figure 2. The rate coefficient given for the reaction of 3,4-dinitrophenol is merely a crude estimate based on the disappearance of the starting material.

The H_0 values listed in the Tables and used in Figure 2 are taken from measurements[4] of the ionisation ratios of picramide, and *p*-nitrotoluene at 25 °C. They are based on the assumption that the pK_a of picramide[5] is −10.0 since, with trifluoromethanesulphonic acid, the normal stepwise method of determining the values of H_0 is complicated by the solidification of the system over the region of composition corresponding approximately to the monohydrate.

Discussion

The work in this paper is mainly concerned with the three rearrangements shown in Scheme 2; in this, the very small amount of the minor product resulting from the migration of the 2-nitro group to the 4-position is ignored. However, before discussing the mechanism of these rearrangements, it is useful to look again at the identity of the migrating group, for all three rearrangements could also be understood as 1,3-migrations of the *meta* substituent and this interpretation would lead to the regiospecificity observed.

The analogy with the rearrangements of substituted anilines[1] and the similarity in the rates of the rearrangements in Scheme 2 point against this possibility but more direct evidence comes from the comparison of the reactivity of the trisubstituted phenols (**2**) and (**3**). The relative positions of the other substituents to the 3-nitro group (*ortho*, *meta*, or *para*) is the same in these two compounds and the steric environment of the



Scheme 2.

nitro group should also be the same since, in both, the 3-nitro group is between a methyl group and another nitro group. However, the reactivities of these two phenols are very different: compound (**2**) is slightly more reactive than 2,3-dinitrophenol (Tables 4 and 5) and gives a product corresponding to the migration of the 2-nitro group to the opposite *ortho* position; compound (**3**) is *ca.* 100 times less reactive and gives only one identifiable product corresponding to the migration of the 4-nitro group to the unoccupied *ortho* position. We conclude therefore that, in the reactions shown in Scheme 2, it is the 2-nitro group which migrates.

The three reactions in Scheme 2 have several common characteristics: they all give first-order kinetics, the rate profiles (Figure 2) show that they are all acid-catalysed, and the product analyses (Table 1) show that they are all strongly regioselective, the nitro group migrating to the opposite *ortho* position. The 'crossover' experiment (Table 2) shows that at least one of the rearrangements (but presumably all three) is intramolecular. The rearrangements of the nitroanilines studied previously[1] were also intramolecular and gave first-order kinetics but showed no acid catalysis and little selectivity in the migration.

The difference with regard to the acid catalysis probably derives mainly from the difference in the basicity of amines and phenols. The nitroanilines are almost completely protonated under the conditions of rearrangement and so the absence of acid catalysis implies that the transition state has the same stoicheiometry as the conjugate acid of the substrate. If the same were true for the transition state in the rearrangement of 2,3-dinitrophenol (**4a**), then acid catalysis should be observed, for although nitro groups are protonated in strong acids,* this substrate is unlikely to be fully protonated under the conditions of rearrangement. The curvature of the rate profile for the rearrangement of 2,3-dinitrophenol ($H_0 = -10.5$, slope = 1.8; $H_0 = -11.5$, slope = 0.6) can then be understood as being derived from the increasing protonation of the substrate as the acidity of the medium is increased and the reaction can be considered to occur through the formation of the Wheland intermediate (**5**) as shown in Scheme 2. This step is shown as reversible since, with these Wheland intermediates, proton loss normally occurs more readily than reactions involving the nitro group.[6] For an initial reversible proton-transfer to a slightly protonated substrate, the reaction rate should be determined by the H_c function; the slope of log k_1 *vs.* $-H_0$ should therefore be greater than unity.[7]

On this interpretation, the slopes of the rate profiles for the phenols with a more basic nitro group (**4b**, **c**) should be lower and this is not fully supported by the results in Figure 2. A full understanding of these substituent effects clearly requires a knowledge of the extent of protonation of each substrate under the reaction conditions and unfortunately this is not yet available. However, the discrepancy may derive in part from the different techniques used to measure the rate coefficients since the results for curves (*b*) and (*c*) in Figure 2 are based on ^{1}H NMR measurements; these are less accurate than the UV measurements used for curve (*a*) and require much higher concentrations of substrate. Protonation of the substrate should reduce the effective acidity of the medium below that indicated by the H_0 value of the pure solvent.

On the above interpretation, these rearrangements are analogous to those observed in the *ipso* intermediates formed during the nitration of *o*-methylphenols and *o*-methylanisoles; and the rearrangements of these *ipso* intermediates [*e.g.*, (**7**)] show the same regiospecificity.[8,9] The mechanism by which the

(**7**) (**8**)

nitro group migrates from one *ortho* position to the other (Scheme 2) is therefore part of a more general problem. The mechanisms that have been suggested for this include homolytic dissociation,[8] the formation of an aryl nitrate,[8] and a direct 1,3-shift of the nitro group (a [1,5]-sigmatropic rearrangement).[9] The present work is not sufficient to define this mechanism but it does eliminate some possibilities. The heterolytic dissociation of the Wheland intermediate (**5**) can be excluded partly because it should lead to some intermolecular reaction (when Y = NO_2, the aromatic system is unlikely to undergo further reaction within the encounter pair), and partly because it should give more 4-substitution (Table 3). The product composition for the nitration of 3-nitrophenol in Table 3 refers to reaction at room temperature but it would be unusual for a nitration reaction to become more selective as the temperature is increased.

The homolytic dissociation of the Wheland intermediate (**5**) to give nitrogen dioxide and an aryl radical does not explain the regioselectivity of the reaction. Also, in some recent studies,[10] the *para–ortho* rearrangement of the *ipso* intermediate (**8**) (which is known to be homolytic)[11] was found to give strong ^{15}N nuclear polarisation but, in the *ortho–ortho* rearrangement of (**7**), such nuclear polarisation was absent. This suggests that the *para–ortho* rearrangements and the *ortho–ortho* rearrangements have different mechanisms.

In the strongly acidic media used in the present work, the intermediate formation of an aryl nitrate appears improbable because such a species would be expected to dissociate readily to give nitronium ions. Also, the high regiospecificity in the rearrangement of 3-methyl-2-nitroanisole (see the Products section) shows that the regiospecificity cannot be explained by the formation of such an intermediate.

Thus, of the more obvious mechanisms for these *ortho–ortho* rearrangements, only the direct 1,3-shift of the nitro group appears consistent with all of the observations. Further evidence on this is provided in the following paper.†

Experimental

Materials.—3-Methyl-2-nitrophenol, 3-methyl-4-nitrophenol, and 5-methyl-2-nitrophenol were commercial samples;

* *p*-Nitrotoluene is half-protonated in *ca.* 98% trifluoromethanesulphonic acid.[4]

† Part 3.

the first was purified by sublimation and the other two by recrystallisation from chloroform. The dinitrophenols were prepared by the nitration of 3-nitrophenol with aqueous nitric acid (40%) using minor modifications of the method of Holleman and Wilhelmy.[12] The products were separated by HPLC and recrystallised from very dilute aqueous hydrochloric acid. The 2,3-(2-^{15}N)dinitrophenol was prepared in the same way using (^{15}N)nitric acid. The 2-methyldinitrophenols and 4-methyldinitrophenols were prepared in the same way starting from 2-methyl-3-nitrophenol and 4-methyl-3-nitrophenol.

3-Chloro-4-nitrophenol and 3-chloro-6-nitrophenol were prepared by the nitration of 3-chloroanisole in acetic anhydride followed by the separation of the resulting nitroanisoles by HPLC and conversion to the corresponding phenols by treatment with trifluoromethanesulphonic acid for 24 h at room temperature. 3-Chloro-2-nitrophenol was prepared from 3-chlorophenol by the initial sulphonation of this substrate in concentrated sulphuric acid followed by nitration in the same medium and desulphonation by steam distillation from a less acidic solution. The product was purified by sublimation. The nitro derivatives of 3-methylanisole were prepared by the methylation of the corresponding phenols by methyl sulphate. Further details of these preparations together with the analytical results and details of the ^{1}H NMR spectra are given elsewhere.[13] The analytical results and NMR spectra were satisfactory for all of the above compounds.

Trifluoromethanesulphonic acid was purchased from Aldrich and was purified by vacuum distillation in apparatus that had been rigorously dried. The concentration of the acid and of the solutions used was determined by titration.

Kinetics by UV Spectroscopy.—A solution of the substrate in ether (100 mm^3, 0.012 mol dm^{-3}) was injected into the UV cell; the solvent was evaporated, and the cell was filled with trifluoromethanesulphonic acid of the required strength under vacuum. The cell was then sealed under vacuum and the spectrum measured between 250 and 550 nm against a solution of trifluoromethanesulphonic acid of the same strength using a Perkin-Elmer 554 spectrometer. The cell was then brought to the required temperature in the cell holder and, after a period of 10–15 min, a series of recordings of the spectra over the range 310–390 nm were carried out (Figure 1). The change in the absorbance (A) at 390 nm was used to calculate the first order rate coefficient (k_1) using equation (1) and zero time was taken

$$\ln[(A_\infty - A_0)/(A_\infty - A_t)] = k_1 t \qquad (1)$$

as the time of starting the readings. Excellent agreement with first-order kinetics were observed ($r > 0.999$) as shown by the example in Table 6. In a few of the slower runs, the first-order kinetic form was assumed and the final absorption was calculated by a computer program. When the reaction was complete, the cell was opened and the concentration of the trifluoromethanesulphonic acid determined by titration.

Kinetics by NMR Spectroscopy.—A solution of the substrate in trifluoromethanesulphonic acid containing also some tetramethylammonium trifluoromethanesulphonate as an internal standard was placed in an NMR tube and sealed under vacuum. The ^{1}H NMR spectrum was then recorded using a 100 MHz JEOL CW instrument. The reaction was then started by placing the NMR tube in an oil bath maintained at 100 °C. At appropriate intervals, the tube was removed, brought rapidly to room temperature and the NMR spectrum determined. Because of the large temperature difference, the time spent at room temperature was not considered to contribute to the extent of reaction. For 3-methyl-2-nitrophenol, the extent of rearrangement was determined from the ratio of the height of the methyl signal for the substrate to the combined heights of the methyl signals for the substrate and product. For 3-chloro-2-nitrophenol, the measured quantity was the ratio of sum of the integrals at δ 8.25 and 8.34 (corresponding to one proton in the product) to the sum of the integrals at δ 7.58, 7.66, 7.75, 8.25, and 8.34 (corresponding to one proton in the substrate and product).

Table 6. The variation of the absorbance (A) at 390 nm and the extent of reaction (x/a) in the rearrangement of 2,3-dinitrophenol (8.09×10^{-4} mol dm^{-3}) in trifluoromethanesulphonic acid (94.3%) at 100 °C.[a]

Time/min	A	x/a
0	0.650	0
60	0.676	0.079
120	0.698	0.14
180	0.719	0.201
240	0.738	0.256
300	0.756	0.309
360	0.774	0.362
420	0.79	0.408
480	0.805	0.452
540	0.818	0.49
600	0.831	0.528
660	0.843	0.563
∞	0.993	1

[a] $k_1 = 2.08 \times 10^{-5}$ s^{-1}; $r = 0.9995$.

Product Isolation.—When the ^{1}H NMR spectrum indicated that reaction was complete, the reaction mixture from the NMR tube or from reaction on a rather larger scale (4 cm^3) was poured onto a mixture of ice and water (*ca.* 100 cm^3) and then extracted with dichloromethane (5×30 cm^3). The combined extracts were backwashed once with a brine solution and then dried over magnesium sulphate. After filtration, the solvent was evaporated and the products analysed by ^{1}H NMR spectroscopy, mass spectrometry, and, in some examples, also by HPLC (using silica as the stationary phase and ethyl acetate containing 0.1% propanoic acid as the eluant).

Acknowledgements

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