ipso-Attack in the Nitration of Aromatic Amines. Part 3.[1] Evidence for Two Mechanisms of *ipso*-Attack

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Studies on the nitration of *NN*-dimethyl-4-methylaniline (1a) have been extended to *NN*-dimethyl-3,4-dimethylaniline (1b) and *NN*-dimethyl-3,4,5-trimethylaniline (1c). All three amines react with nitric acid in 60—70% sulphuric acid at 0 °C by the nitrous acid-catalysed mechanism to give mainly the *ipso*-intermediate with an NO_2 group at the 4-position (identified by the ^1H and ^{13}C n.m.r. spectra). Over the range 76—83% sulphuric acid the overall rates of reaction of the first two amines (and probably of the third) increase rapidly because of the attack of the nitronium ion on the conjugate acids of the amines. In these nitronium reactions, the amine (1a) gives no detectable amount of *ipso*-attack; the amine (1b) gives 16—51% *ipso*-attack at the 4-position (depending on the acidity), and the amine (1c) gives 85% *ipso*-attack at the 4-position. These results accord approximately with the predictions of the additivity principle. The rate of rearrangement of the *ipso*-intermediate from the amine (1b) to yield the 6-nitro-product has been determined over the range 64—78% H_2SO_4.

The work described in earlier Parts [1,2] showed that the reactions of some aromatic amines with nitric acid involve *ipso*-attack leading to high concentrations of the relevant intermediates. The subsequent rearrangement and substitution reactions of the intermediates resemble those found following *ipso*-attack in the nitration of phenols and aromatic ethers. There are, however, some important differences between the reactions of the amines and those of the other substrates. One of these is that *ipso*-attack in the reactions of the amines requires nitrous acid catalysis [1,2] but, in those examples where the reaction mechanism has been investigated,[3] the formation of *ipso*-intermediates in reactions of phenols and aromatic ethers involves direct reactions with the nitronium ion.† The work now reported was carried out to determine whether *ipso*-attack by the nitronium ion could be observed in reactions of aromatic amines. This has involved an extension of the earlier studies to higher acidities and a comparison of the reactions of amines (1a—c). In this series, the additional methyl groups increasingly activate the *para*-position to electrophilic attack. A second difference between the reactions of the amines and those of the other substrates involves the conditions leading to rate-determining proton loss in the rearrangement reactions. Evidence on this is presented in the following paper.

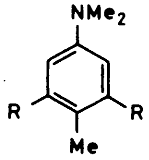
Evidence for ipso-*Intermediates.*—The n.m.r. spectra of reaction mixtures provided the original evidence of the reaction of amine (1a) to give the *ipso*-intermediate (2a). In the ^1H n.m.r. spectra, the most significant changes were the formation of a sharp low-field singlet for the N–Me protons and the high-field shift (even relative to the free amine) of the absorption of the Me-4 protons. In the ^{13}C spectra, the main changes were the low-field shifts of the lines for C-1, C-3, and C-5 combined with the marked high-field shift of that for C-4 (this can be understood from the change in hybridisation at that site).[5] The NO_2 group is known to be attached to the carbon atom giving the peak assigned as C-4 because of the ^{13}C–^{15}N coupling observed [1] when the nitration is carried out using $H^{15}NO_3$.

The corresponding n.m.r. spectra for the intermediates derived from amines (1b) and (1c) are compared with those for the intermediate from amine (1a) in Tables 1 and 2 (see later). The assignment of the lines comes from known substituent effects, from comparison with related spectra,[2,5] and, for the ^{13}C spectra, also from the results of partial decoupling. The pattern of chemical shift changes (Δδ) is similar for all three amines and accords with the reactions of amines (1b) and (1c) with nitric acid to form *ipso*-intermediates with the nitro-group at the 4-position.

Table 1. ^1H Chemical shifts (δ values) for amines, *ipso*-intermediates, and nitro-products

Substrate	H-2	H-5	H-6	Me-3	Me-4	Me-N
(1a) [a,b]	6.63	7.01	6.63		2.23	2.82
(2a) [a,c]	7.14	7.52	7.14		1.93	3.68
Δδ	0.51	0.51	0.51		−0.3	0.86
(1b) [d]	6.65	7.05	6.50	2.22	2.15	2.85
(2b) [e]	7.06	7.32	7.28	2.32	2.02	3.80
Δδ	0.41	0.27	0.78	0.10	−0.13	0.95
(1c) [d]	6.5		6.5	2.25	2.06	2.90
(2c) [e]	7.07		7.07	2.24	1.96	3.74
Δδ	0.57		0.57	−0.01	−0.10	0.84
(3b) [e]	7.78	8.30		2.55	2.48	3.58
(4b) [f]	7.76		8.08	2.56	2.56	3.48

[a] Ref. 2. [b] In $CDCl_3$ at 0 °C. [c] In 77.1% H_2SO_4 at 0 °C. [d] In $CDCl_3$ at 25 °C. [e] In 73.6% H_2SO_4 at 0 °C. [f] In 84.6% H_2SO_4 at 0 °C.



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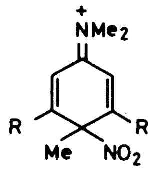

(2)

a; $R^1 = R^2 = H$
b; $R^1 = Me$, $R^2 = H$
c; $R^1 = R^2 = Me$

The Rate of Formation of ipso-*Intermediates.*—Very little work has been done on the rate of formation of these *ipso*-intermediates; the previous work [2] dealt mainly with the rate of the subsequent 1,3-rearrangement.

The analysis of reaction mixtures to determine the pro-

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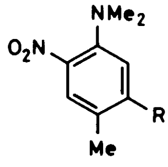
† Nitrous acid catalysis may be important in reaction of phenols and aromatic ethers involving *ipso*-attack under other conditions (ref. 4).

Table 2. ^{13}C Chemical shifts (p.p.m. from Me_4Si) for amines and *ipso*-intermediates

Substrate	C-1	C-2	C-3	C-4	C-5	C-6	Me-3	Me-4	Me-N
(1a) [a,b]	148.5	112.6	129.2	124.6	129.2	112.6		19.8	40.1
(2a) [a,c]	161.7	121.1	148.9	86.2	148.9	121.1		25.5	45.4
$\Delta\delta$	13.2	8.5	19.7	−38.4	19.7	8.5		5.7	5.3
(1b) [d]	149.4	115.0	136.9	125.0	130.3	110.9	20.3	18.6	41.0
(2b) [e]	162.1	121.1	160.3	89.5	149.4	119.8	20.6	23.0	44.9
$\Delta\delta$	12.7	6.1	23.4	−35.5	19.1	8.9	0.3	4.4	3.9
(1c) [d]	148.8	113.0	136.9	123.6	136.9	113.0	21.0	14.3	41.0
(2c) [e]	161.9	119.1	161.0	93.2	161.0	119.1	20.2	23.1	44.6
$\Delta\delta$	13.1	6.1	24.1	−30.4	24.1	6.1	−0.8	8.8	3.6

[a] Ref. 2. [b] In $(CD_3)_2SO$ at 25 °C. [c] In 74.5% H_2SO_4 at −10 °C. [d] In $CDCl_3$ at 0 °C. [e] In 73.0% H_2SO_4 at 0 °C.



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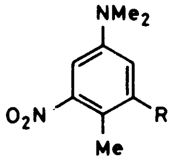

(4)

a; R = H
b; R = Me

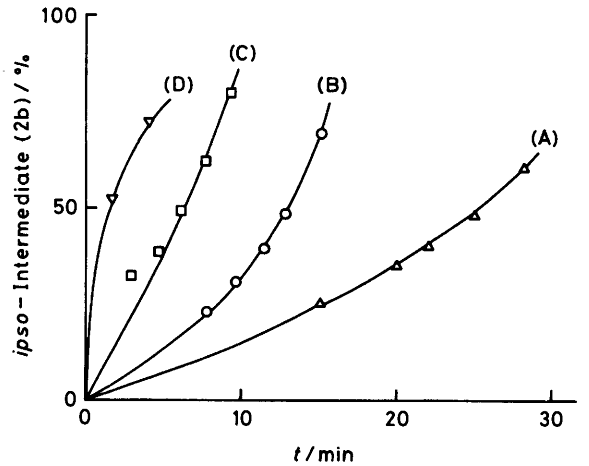

Figure 1. The effect of added nitrous acid on reactions of the amine (1b) (0.5 mol dm^{-3}) with nitric acid (0.5 mol dm^{-3}) in aqueous sulphuric acid (73.6%, 0 °C) to generate the *ipso*-intermediate (2b). Concentration of nitrous acid: (A) none; (B) 0.003; (C) 0.013; (D) 0.026 mol dm^{-3}

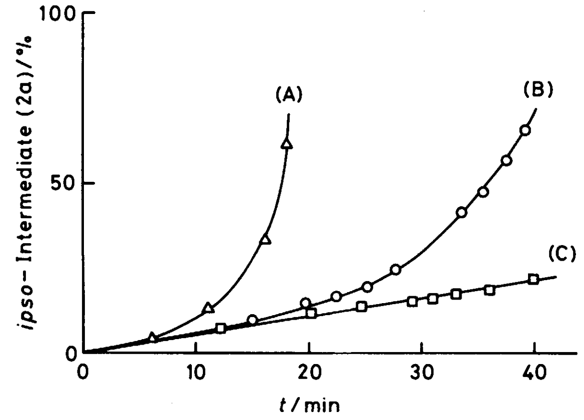

Figure 2. The effect of acidity on reaction of the amine (1a) (0.5 mol dm^{-3}) with nitric acid (0.5 mol dm^{-3}) in aqueous sulphuric acid (0 °C) to generate the *ipso*-intermediate (2a). Acidity [H_2SO_4 (%)]: (A) 69.5; (B) 73.6; (C) 79.6

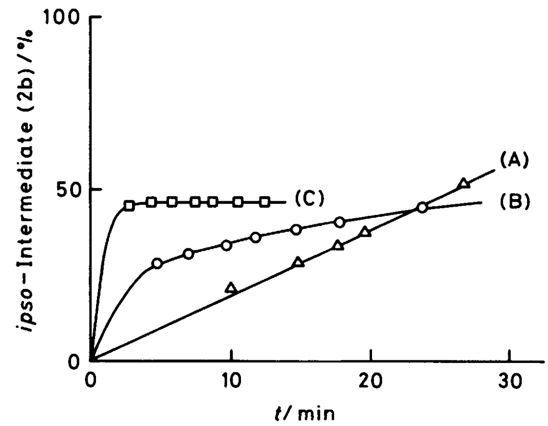

Figure 3. The effect of acidity on the reaction of the amine (1b) (0.5 mol dm^{-3}) with nitric acid (0.5 mol dm^{-3}) in aqueous sulphuric acid (0 °C) to generate the *ipso*-intermediate (2b). Acidity [H_2SO_4 (%)]: (A) 76.6; (B) 77.3; (C) 80.7

portion of the *ipso*-intermediate present has been based on the heights and areas of the ^1H n.m.r. peaks. With the amine (1a), the other main product at acidities up to *ca.* 77% sulphuric acid is the nitro-product (3a) formed by a 1,3-rearrangement. This is accompanied at higher acidities by the nitro-product (4a) and our present work shows that the latter can become the major product. With the amine (1b), some of the nitro-product (3b) is formed concurrently with the *ipso*-intermediate and some by a subsequent rearrangement:[6] at acidities above 75% H_2SO_4, the products also contain the nitro-product (4b). Details of the ^1H n.m.r. spectra of these nitro-products are included in Table 1. With the amine (1c), the *ipso*-intermediate is much more stable so that subsequent reactions can be ignored; the n.m.r. spectra do, however, indicate the concurrent formation of a small amount of other material that we have provisionally assumed to be the 2-nitro-product.

The earlier studies showed that the kinetic form for the nitrous acid-catalysed formation of the *ipso*-intermediate from the amine (1a) is as expected for an autocatalytic process. The same is true for the amine (1b) and the effect of added nitrous acid on these reactions has now been studied. The results (Figure 1) show that the presence of less than 1% nitrous acid has a marked effect on the reaction rate. The autocatalysis can therefore be understood providing that side-reactions generate nitrous acid in concentrations of *ca.* 0.003 mol dm^{-3}.

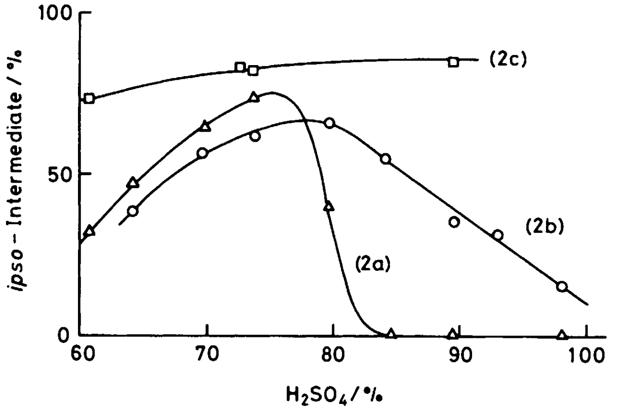

Figure 4. The variation in the maximum concentration of various *ipso*-intermediates (2) with acidity in the reactions of the corresponding amines (1) (0.5 mol dm^{-3}) with nitric acid (0.625 mol dm^{-3}) in aqueous sulphuric acid at 0 °C

The variation in the rate of formation of the *ipso*-intermediate with acidity depends on the amine used. Since changes in the acidity can also change the kinetic form of the reaction, these results are most easily illustrated graphically. For the amine (1a), the rate of formation of the *ipso*-intermediate decreases with acidity over the range 70—80% H_2SO_4 (Figure 2) and, at acidities above 75% H_2SO_4, the maximum extent of formation of the *ipso*-intermediate also decreases with acidity because of the concurrent formation of the 3-nitro-product (4a). At acidities above 83% H_2SO_4, only this nitro-product can be detected. Thus results are consistent with the incursion of direct attack by the nitronium ion leading to 3-substitution.

The results with the amine (1b) are very different, for, at acidities above 70% H_2SO_4, the rate of formation of the *ipso*-intermediate increases rapidly, becoming too fast to measure at acidities above 80% H_2SO_4 (Figure 3). The maximum extent of formation of the *ipso*-intermediate does, however, decrease with acidity because of the concurrent formation of the 3-nitro-product (4b). These results are consistent with the incursion of direct attack by the nitronium ion leading to both the *ipso*-intermediate (2b) and the nitro-product (4b). Kinetic plots are not presented for the amine (1c) since the formation of the *ipso*-intermediate is too fast to follow at all the acidities studied (60—90% H_2SO_4). The reaction must, however, be catalysed by nitrous acid in acidities <70% H_2SO_4 since an induction period is observed when hydrazine is present.

The variation with acidity of the maximum concentration of the *ipso*-intermediates during a run is shown in Figure 4.* This maximum concentration is, of course, determined by the balance between the rate of formation of the *ipso*-intermediate and the rate of the subsequent reactions. With the amine (1a), the maximum concentration of the *ipso*-intermediate initially increases with the acidity because of the fast rate of rearrangement at low acidities.[2] However, in what we have considered to be the region of transition between the nitrous acid-catalysed reaction and the nitronium ion reaction (75—80% H_2SO_4), this concentration drops effectively to zero. Similar results are obtained for the amine (1b) at low acidities but the concentration of this *ipso*-intermediate remains significant at high acidities. For the amine (1c), the *ipso*-intermediate is the major product at all acidities.

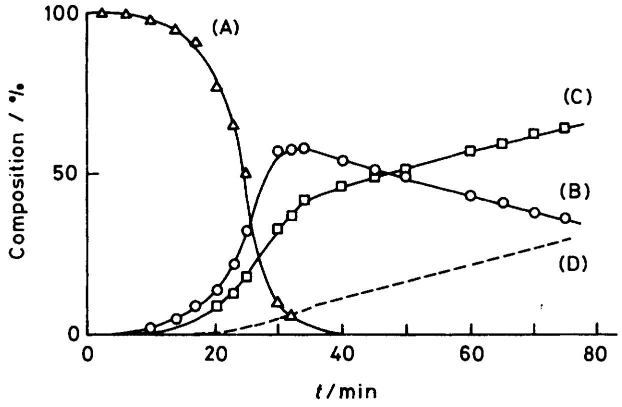

Figure 5. The composition of a reaction mixture for the reactions of the amine (1b) (0.5 mol dm^{-3}) with nitric acid (0.625 mol dm^{-3}) in 73.8% sulphuric acid at 0 °C: (A) the amine; (B) the *ipso*-intermediate (2b); (C) the nitro-product (3b); (D) the calculated curve for this nitro-product (see the text)

Table 3. First-order rate coefficients for the rearrangement of the *ipso*-intermediate (2b) to the nitro-product (3b) in aqueous sulphuric acid at 0 °C

H_2SO_4/%				
Solvent	Solution	$[\mathrm{Ar\overset{+}{N}Me_2H}]$/ mol dm^{-3}	$[HNO_3]$/ mol dm^{-3}	10^4k_1/ s^{-1}
73.8	72.5	0.5	0.625	1.67
73.8	72.5	0.5	0.75	1.86
73.8	72.5	0.5	1.0	1.73
73.8	72.0	0.75	0.5	3.71
73.8	72.5	0.5	0.5	2.65
73.6	72.3	0.5	0.5	2.41 [a]
73.6	72.3	0.5	0.5	1.95 [b]
64.1	62.4	0.5	0.5	6.19
69.6	68.2	0.5	0.5	4.63
78.0	76.9	0.5	0.5	1.03

[a] $[HNO_2]$ 0.002 mol dm^{-3}. [b] $[HNO_2]$ 0.02 mol dm^{-3}.

The Nitration Reactions.—At the lower acidities (<75% H_2SO_4), the formation of the *ipso*-intermediate from the amine (1a) occurs without a significant amount of concurrent nitration (at least in the absence of added nitrous acid) so that the product (3a) is formed almost entirely by the rearrangement reaction.[2] This is not true for the amine (1b) where, at the lower acidities, nitration at the 6-position competes with the formation of the *ipso*-intermediate. This is illustrated by the composition–time curves in Figure 5, calculated from the areas of the relevant N–Me peaks. After complete reaction, the nitro-product (3b) can be isolated in a yield of 80%.

The results in Figure 5 give good first-order kinetics for the rearrangement reaction [$k_1 = (1.90 \pm 0.04) \times 10^{-4}$ s^{-1}]. If this were the only route to the 6-nitro-product, the amount of this product present at any time should be given by $\int k_1[(2b)]dt$. The theoretical curve for the formation of the 6-nitro-product by rearrangement has been calculated from this expression and is included in Figure 5; comparison of the two curves shows that about 35% of the overall reaction involves concurrent nitration at the 6-position.

Other studies have shown that the characteristics of the rearrangement of the *ipso*-intermediate (2b) resemble those previously reported[2] for the *ipso*-intermediate (2a); the reaction rate is not very sensitive to the presence of sodium nitrite or excess of nitric acid but is increased by the presence

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* These runs were carried out with excess of nitric acid (see legend): this slightly increases the maximum concentration of the *ipso*-intermediate in comparison with the runs in Figures 2 and 3.

of an excess of amine. These characteristics are shown by the group of kinetic runs in Table 3 together with the decrease in the rate of rearrangement with the acidity of the medium.

Discussion

The nitration of aromatic amines by nitric acid in 80—100% sulphuric acid has been studied in some detail;[7] if electron-withdrawing substituents are absent reaction occurs through the attack of the nitronium ion on the conjugate acid of the amine. The kinetics of nitration of the amine (1a) by this mechanism have not been investigated but the rate profile can be predicted * from other work. For concentrations of the amine (1a) and nitric acid of 0.5 mol dm^{-3} at 0 °C, the half-life should be *ca.* 10 min in 79% sulphuric acid and *ca.* 1 min in 81.5% sulphuric acid. For the amine (1b), the corresponding concentrations of sulphuric acid should be about 1% lower because of the activating effect of the methyl group. These are the acidity regions in which a large increase in the overall reaction rate has been observed in the present work (Figure 3) and so this increase can be ascribed to the incursion of reaction through the nitronium ion and the conjugate acid of the amine. For the amine (1c), the corresponding transition region should be at a slightly lower acidity.

It follows from this interpretation that the conjugate acids of the amines (1a—c) differ markedly in their reactions with the nitronium ion. Thus, in 90% sulphuric acid, the conjugate acid of (1a) gives no *ipso*-attack; the conjugate acid of (1b) gives *ca.* 37% *ipso*-attack, the extent decreasing with the acidity of the medium, and the conjugate acid of (1c) gives 85% *ipso*-attack (Figure 4).

These results can be compared with those expected from the additivity of substituent effects for the $\overset{+}{\mathrm{N}}\mathrm{Me_2H}$ and Me groups. The isomer distribution in the nitration of the phenyldimethylammonium ion depends to some extent on the acidity of the medium but in 91% sulphuric acid is 74% *meta*, 26% *para*.[7b] The relative rates of attack at the different positions of toluene for nitration in 54% sulphuric acid are given by the following ratios of partial rate factors ($f_i : f_o : f_m : f_p =$ 2.2 : 16.0 : 1.0 : 16.3).[4] The isomer distribution in the nitration of toluene is not markedly dependent on acidity, so these ratios should be a reasonable guide to the directing effect of the methyl group at higher acidities. The calculated percentages of direct attack by the nitronium ion at the 4-positions of the conjugate acids of the amines (1a—c) are then as given in the first column of calculated results in Table 4.

The above procedure assumes that attack of the nitronium ion at each position can be considered as irreversible. It should be valid for the conjugate acid of the amine (1a) but cannot be valid for the conjugate acids of the other amines since none of the *ipso*-intermediate resulting from attack at a *meta*-position is observed in the product. We have therefore to consider the possible reactions that could follow *ipso*-attack at a *meta*-position.

These possibilities are illustrated by the set of reactions for the nitration of the amine (1b) in the Scheme. The *ipso*-intermediate (6) formed by attack at a *meta* position does not rearrange mainly to the 2-nitro-product for this has not been detected in the reaction. The other possibilities include heterolysis of the C–N bond to reform the reactants and rearrangement to the 4-position. The consequences of these reactions on the overall percentage of *ipso*-intermediate (5) formed are shown in the second and third columns of calculated results in Table 4. It seems likely that (5) reacts by fast loss of an N–H proton for the yield of (2b) is very similar in 98% H_2SO_4 (15.6%) and 98% D_2SO_4 (18.1%).

Table 4. Comparison of the observed and calculated percentages of *ipso*-attack by the nitronium ion at the 4-position of the conjugate acids of amines (1a—c)

	ipso-attack at 4-position/%			
Substrate	Obs.	Calc.[a]	Calc.[b]	Calc.[c]
(1a)	0	5		
(1b)	51—16[d]	33	61	79
(1c)	85	85	100	100

[a] Percentage of initial attack. [b] Assuming reversibility of attack at 3-position. [c] Assuming migration of NO_2 from 3- to 4-position. [d] Over the range 84—98% H_2SO_4.

From the calculated results in Table 4, the failure to detect the *ipso*-intermediate in these reactions of the amine (1a) and the essentially complete formation of the *ipso*-intermediate with the amine (1c) are in reasonable accord with the additivity principle. Exact agreement cannot be expected because of uncertainties over the extent of *ipso*-substitution in toluene[4] and in the application of the additivity principle to deactivated systems.[10] The amount of the *ipso*-intermediate (5) formed with the amine (1b) is much less than would be expected if all of the *ipso*-intermediate (6) rearranged to give (5); it appears likely that the formation of (6) is reversible and that the balance between attack *para* and *meta* to the $\overset{+}{\mathrm{N}}\mathrm{Me_2H}$ pole favours the latter as the acidity is increased. This occurs with other nitrogen poles; thus, the amount of *para*-nitration of the anilinium ion decreases from 59% to 36% over the range 82—100% sulphuric acid.[7a,c] For the *NN*-dimethylanilinium ion, the corresponding change is from 45% to 22%.[7b,11] These changes are not because of the incursion of reaction through the free amine but, at least for the anilinium ion, appear to derive from differential salt effects on substitution at different positions.[7c]

The Scheme also shows the nitrous acid-catalysed mechanism of *ipso*-attack as involving the intermediate formation of the cation radical of the amine. The evidence for this comes from the CIDNP effect observed[12] in the reaction of the amine (1a), the detection of the e.s.r. spectra of such cation radicals during reaction,[2,12] and the analogy with related reactions of *NN*-dimethylaniline.[11,13] However, the large amount of the 6-nitro-compound formed in the initial reaction of the amine (1b) (Figure 5) would not be expected in terms of this mechanism (there is a hydrogen isotope effect on the loss of a proton from the 6-position, see following paper) and so other processes may also be involved in the initial substitution at this position. The reason why the *ipso*-intermediate (2b) rearranges to give the 6-nitro-compound (3b) with no significant amount of the corresponding 2-nitro-compound is probably the result of greater steric interaction in the formation and reaction of the Wheland intermediate for 2-substitution. The fact that the *ipso*-intermediate (2c) does not rearrange to a significant extent during 90 min at 0 °C[6] supports this conclusion.

The main conclusion of the present work is that *ipso*-attack by the nitronium ion does occur in the reactions of some aromatic amines and that the extent of such attack accords, to a first approximation, with the additivity of substituent effects. The relative unimportance of this reaction at a *para*-methyl group in comparison with the reactions of anisoles and phenols comes from the fact that nitration by the nitronium

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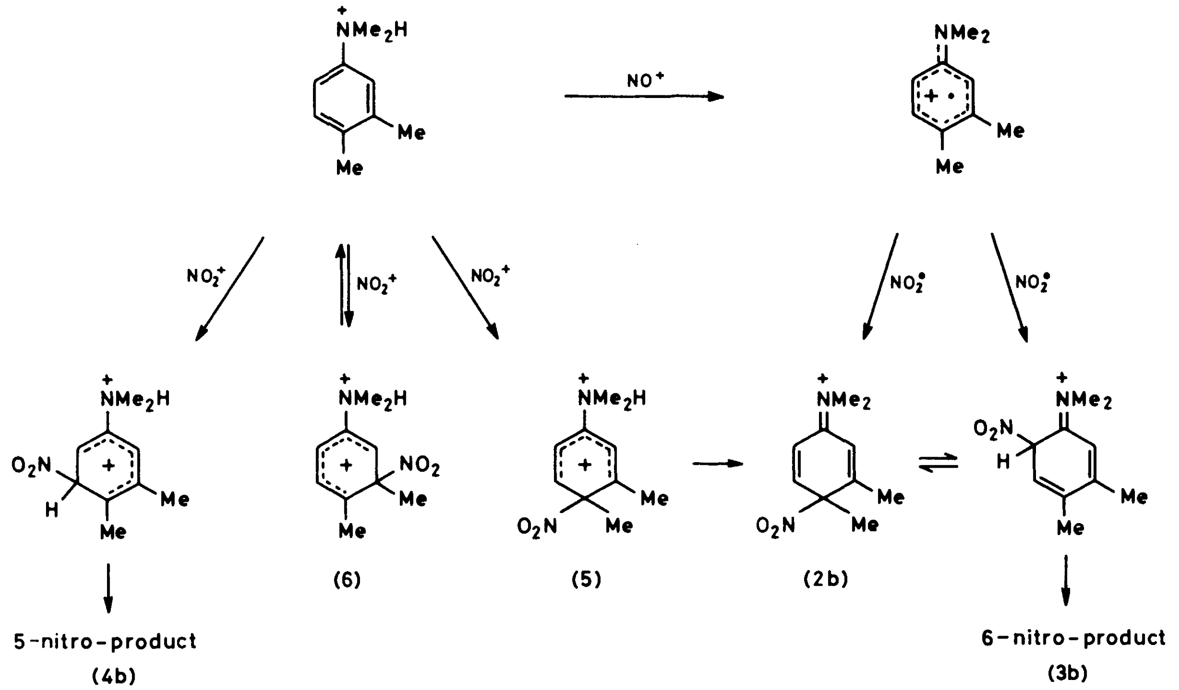
* Using the rate profile and Arrhenius parameters for the trimethyl-*p*-tolylammonium ion (ref. 8) and the relative substituent effects of the $\overset{+}{\mathrm{N}}\mathrm{Me_3}$ and $\overset{+}{\mathrm{N}}\mathrm{Me_2H}$ groups (refs. 7*b*, 9).



Scheme.

ion involves the conjugate acids of the amines and that protonated nitrogen poles are not strong *para*-directing groups.

Experimental

Materials.—The inorganic materials and the amine (1a) were as described.[2] *NN*-Dimethyl-3,4-dimethylaniline was prepared by *N*-methylation of the corresponding primary amine with trimethyl phosphate[14] and was purified by distillation: b.p. 111—112 °C at 20 mmHg (Found: C, 80.4; H, 10.0; N, 9.6. Calc. for $C_{10}H_{15}N$: C, 80.5; H, 10.1; N, 9.4%). 3,4,5-Trimethylaniline was prepared as described from isophorone oxime[15] and was purified by recrystallisation from heptane giving needles, m.p. 76—77 °C (lit.,[16] 76—77 °C). This product was methylated by an excess of dimethyl sulphate in carbon tetrachloride[17] to give *NN*-dimethyl-3,4,5-trimethylaniline which was purified by distillation: b.p. 138—140 °C at 20 mmHg. The ^1H n.m.r. spectrum (200 Hz) in $CDCl_3$ and the ^{13}C n.m.r. spectrum in $CDCl_3$ were exactly as expected. The analysis, however, indicated the presence of 4—5% of oxygen, which in view of the n.m.r. spectra, we believe to arise from the persistent presence of traces of water (Found: C, 76.8; H, 10.5; N, 7.9. Calc. for $C_{11}H_{17}N\cdot\frac{1}{2}H_2O$: C, 76.7; H, 10.5; N, 8.1%).

Spectra.—These were run on the same instruments as before[2] with the addition of a Varian XL200 spectrometer for some of the ^1H n.m.r. spectra. The results in Tables 1 and 2 were obtained by catalysing the formation of the *ipso*-intermediates with nitrous acid to minimise the concentrations of the rearrangement and decomposition products. For spectra in aqueous sulphuric acid as solvent the ^1H chemical shifts were calculated using the methyl protons of $Ph\overset{+}{N}Me_3$ PF_6^- as an internal standard (δ 3.62). The ^{13}C chemical shifts are based on Me_4Si in an internal capillary.

Product Compositions.—These have been based on the areas or heights of the ^1H n.m.r. peaks. For the amine (1a), the C–Me peaks of the starting material, *ipso*-intermediate, and nitro-products are sufficiently distinct to permit the peak heights to be used to analyse the reaction mixture. For the amine (1b), the C–Me peaks overlap appreciably when all components are present and the areas of the N–Me peaks have then been used to calculate the percentage of the *ipso*-intermediate formed. After the initial amine has reacted, the spectra of the reaction mixtures become less complex and the calculations based on both the areas of the N–Me peaks and the heights of the C–Me peaks give similar rate coefficients for the rearrangement of the *ipso*-intermediate. For the amine (1c), the product composition has been based on the heights of the C–Me peaks.

The final products were isolated after complete reaction as described previously for the amine (1a).[2] The reaction of the amine (1b) in 74% sulphuric acid gives the 6-nitro-product (3b) in a yield of 80%. The same reaction in 85% sulphuric acid gives a yield of mono-nitro-products of 85%; this is mainly the 5-nitro-product (4b). The *ipso*-intermediate from the amine (1c) did not rearrange sufficiently rapidly for the nitro-product to be isolated and gave evidence of decomposition when runs were carried out at temperatures above 0 °C.

Kinetics.—The procedure and the specification of the solvent composition were as described previously.[2] The rate coefficients for the rearrangement were calculated from the change in the concentration of the *ipso*-intermediate after complete reaction of the initial amine. The integration to obtain the calculated curve for the formation of the 6-nitro-product in Figure 5 was carried out using Simpson's rule.

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