1266. *Substituent Effects of Positive Poles in Aromatic Substitution. Part II.*[1] *The Nitration of* N-*Methylated Anilinium Ions*

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The dependence of the reaction rate and the product composition on acidity for the nitration of *N*-methylaniline and *NN*-dimethylaniline in concentrated sulphuric acid show that both amines undergo reaction through their conjugate acids; in 98% sulphuric acid, the percentages of *para*-substitution are 30 and 22, respectively. Product analysis though ion-exchange chromatography shows that the nitration of the trimethylphenylammonium ion under the same conditions gives 11% of *para*-substitution. These results, and those in Part I, are used to calculate partial rate factors for the nitration of the anilinium ion and its *N*-methyl derivatives. The results are compared with the rates of nitration of other substituted ammonium ions and with related data concerning other aromatic substitutions.

This Paper is concerned with the substituent effects of the groups $-N^+H_2Me$, $-N^+HMe_2$, $-N^+Me_3$ in the nitration of the corresponding phenyl derivatives. The first two of these positive poles are considered together, for the evidence from the nitration of the corresponding amines involves mechanistic problems of the kind discussed for aniline in Part I. The absence of prototropic equilibria involving the $-N^+Me_3$ group simplifies the interpretation of the results but necessitates a different technique for the analysis of the products obtained.

(1) *The* $-N^+H_2Me$ *and* $-N^+HMe_2$ *Groups.*—The nitration of *N*-methylaniline does not appear to have been examined in any detail [2] but several quantitative studies have been carried out on the nitration of *NN*-dimethylaniline.[3] At low acidities, *ortho*- and *para*-substitution is observed but, as the acidity is increased, this is replaced by predominant *meta*-substitution accompanied by the well documented [4] presence of about 18% of *para*-substitution.*

The nitration of these two amines was re-investigated as described for aniline in Part I. The products formed are listed in Table 1 and the corresponding second-order stoicheiometric rate coefficients (k_2) (cf. equation 1, Part I) are listed in Table 2 together with the calculated rate coefficients for attack at the *para*-position (k_p) and at one *meta*-position (k_m).

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* The curious persistence of this amount of *para*-substitution even in the most acidic media was first pointed out (to J. H. R.) by Professor P. B. D. de la Mare; this was one of the factors leading to the present investigation.

[1] Part I, preceding Paper.

[2] A. Rhode, *Z. Electrochem.*, 1900—1901, **7**, 328; T. J. Nolan and H. W. Clapham, *Sci. Proc. Royal Dublin Soc.*, 1923, 219.

[3] Cf. P. B. D. de la Mare and J. H. Ridd, " Aromatic Substitution," Butterworths, London, ch. 7.

[4] *Org. Synth.*, 1947, **27**, 62.

TABLE 1

Products of nitration of *N*-methylaniline and *NN*-dimethylaniline in concentrated sulphuric acid at 25°

PhN^+H_2Me			PhN^+HMe_2		
H_2SO_4 (%)	m (%)	p (%)	H_2SO_4 (%)	m (%)	p (%)
90·9	61	39	91·1	74	26
96·2	67·5	32·5	96·2	76	24
99·8	70·3	29·7	100	79	21

TABLE 2

Rate coefficients (mole^{-1} sec.$^{-1}$) for nitration of *N*-methyl- and *NN*-dimethylaniline in concentrated sulphuric acid at 25°

PhN^+H_2Me				PhN^+HMe_2			
H_2SO_4 (%)	10^2k_2	10^2k_m	10^2k_p	H_2SO_4 (%)	10^2k_2	10^2k_m	10^2k_p
90·85	74·7	22·8	29·1	91·1	13·5	4·99	3·51
96·2	31·7	10·7	10·3	96·2	5·92	2·25	1·42
99·9	12·7	4·46	3·77	100	2·68	1·06	0·56

Comparison of the results in Table 1 with those for aniline in Part I shows that both stages of *N*-methylation lower the extent of *para*-substitution. A similar comparison using the kinetic results in Table 2 shows that both stages of *N*-methylation lower the rate of nitration; the stoicheiometric rate coefficient for *N*-methylaniline is less than that for aniline by a factor of *ca.* 5 for nitration of 100% sulphuric acid. However, both of the methylated amines resemble aniline in the dependence of the product composition on acidity. Thus, as the concentration of sulphuric acid is decreased over the range 91—100%, the p/m ratio increases by a factor of 1·5 for *N*-methylaniline and by 1·3 for *NN*-dimethylaniline; for aniline, the corresponding increase over the range 92·4—100% sulphuric acid is 1·6. The slope of the rate profile for the methylated amines is somewhat greater than that for aniline (cf. Table 2 of this Paper with Table 3 of Part I) but this applies to both *meta*- and *para*-substitution and is therefore unlikely to result from a greater contribution of reaction through the free amine.

The mechanism of nitration of aniline under these conditions was shown in Part I to involve the protonated amine. The similarity in the results for aniline and for the methylated amines points to a similar reaction path. Indeed, *N*-methylation would be expected to decrease the proportion of reaction through the free amine, both because of the consequent increase in the basicity of the amine and because of the increase in the dependence of the protonation ratio on acidity. In 90% sulphuric acid, the appropriate acidity function for the protonation of a tertiary amine [5] is more than two units more negative than that for a primary amine.[6] We shall not therefore repeat the mechanistic arguments set out in Part I but merely restate the conclusion as applying to the methylated amines: that reaction through the small equilibrium concentration of free amine does not contribute significantly to the rate of nitration in 98% sulphuric acid. By implication, therefore, the results in Tables 1 and 2 provide evidence on the substituent effects of the $-N^+H_2Me$ and $-N^+HMe_2$ groups.

(2) *The* $^-N^+Me_3$ *Group*.—The most frequently quoted results for the nitration of the phenyltrimethylammonium ion are those of Vorlander and Siebert,[7] suggesting that only the *meta*-derivative is formed. More recently, Nesmeyanov and his co-workers [8] have isolated about 4% of *NN*-dimethyl-*p*-nitroaniline after heating the iodide of the nitrated

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[5] E. M. Armett and G. W. Mach, *J. Amer. Chem. Soc.*, 1964, **86**, 2671.

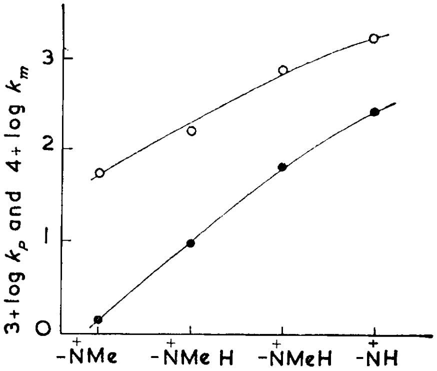
[6] M. J. Jørgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878.

[7] D. Vorländer and E. Siebert, *Ber.*, 1919, **52**, 283.

[8] A. N. Nesmeyanov, T. P. Tolstaya, L. S. Isaeva, and A. V. Grib, *Doklady Akad. Nauk S.S.S.R.*, 1960, **133**, 602.

product. In our first Communication[9] on this work, two of us reported a study of the infrared spectrum of the nitrated salt together with a more quantitative examination of the ultraviolet spectrum of the mixture of *NN*-dimethyl-*p*-nitroaniline and *NN*-dimethyl-*m*-nitroaniline obtained after demethylation of the reaction product; both approaches indicated that about 11% of *para*-substitution was present. However, this analysis of the amount of *para*-substitution from the demethylated product is subject to error because of the extra stages involved and also to some ambiguity because of the possibility that some demethylation precedes nitration. The mixture of nitrated ions has therefore been re-examined by ion-exchange chromatography using ion-exchange columns containing a sulphonated polystyrene resin.

Examination of the ultraviolet spectra of the fractions showed that the main product with the absorption spectrum of the *m*-nitrophenyltrimethylammonium ion was accompanied by a second product with a very similar spectrum. The separation of these products has been illustrated elsewhere.[10] When the nitrated material was treated with alkali before being adsorbed on the column, the spectrum of the minor product was absent but it was replaced by a product, the spectrum of which, in both acidic and basic media, corresponded to *p*-nitrophenol. The minor product was therefore taken to be the *p*-nitrophenyltrimethylanilinium ion; this accords with the infrared and ultraviolet spectra observed in the preliminary experiments. From the known extinction coefficients, it appears that 11% *para*-substitution is present after nitration in 98% sulphuric acid; a similar result (10% of *para*-substititition) was obtained after nitration by Vorländer's method[7] in fuming nitric acid.



The variation in the values of log k_m (open circles) and log k_p (dots) with the successive replacement of the methyl groups of the phenyltrimethylammonium ion by hydrogen atoms. Conditions are as given in Table 3

No fraction corresponding to *ortho*-substitution was detected, and no appreciable amount of this isomer would be expected, for the comparison of the nitration of toluene and t-butylbenzene[11] suggests that the steric interaction of the $-N^+Me_3$ group with the nitronium ion would be sufficient to decrease the rate of *ortho*-substitution by a factor of 8 relative to that in the anilinium ion.

A brief spectrometric study of the nitration in 98% sulphuric acid yielded rate coefficients in agreement with those obtained by Gillespie and Norton[12] from the change in the concentration of nitric acid in the reaction mixture.

(3) *Comparison of the Substituent Effects*.—The rate coefficients (k_m, k_p) for the nitration of these anilinium ions in 98% sulphuric acid have been interpolated from the kinetic data in this and the preceding Paper; the results are collected in Table 3 and plotted logarithmically in the Figure. The approximate linearity of the graphs shows that the successive replacement of the methyl groups of the $-N^+Me_3$ substituent by hydrogen atoms increases

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[9] M. Brickman, S. Johnson, and J. H. Ridd, *Proc. Chem. Soc.*, 1962, 228.

[10] J. H. Ridd, Proceedings of the 1963 Warsaw Symposium on Nitrocompounds, published as a supplement to *Tetrahedron*, 1964, p. 43.

[11] H. Cohn, E. D. Hughes, M. H. Jones, and M. G. Peeling, *Nature*, 1952, **169**, 291.

[12] R. J. Gillespie and D. G. Norton, *J.*, 1953, 971.

the rate of substitution at a given position by approximately equal factors. This would not have been expected if the facility of proton transfer reactions had made an additional reaction path available to the protonated substrates; the replacement of the first methyl group by a hydrogen atom should then have had an abnormally large effect on the reaction rate. The results in the Figure imply that no one proton in the $-N^+H_3$ group is singled out for a special role in the transition state; this is consistent with some change in the ionic character of all the N–H bonds but not with the partial transfer of one proton to the solvent [cf. Part I, section (3)].

TABLE 3

Product composition, rate coefficients (k_m, k_p; mole^{-1} sec.$^{-1}$ l.) and partial rate factors (f_m, f_p) for nitration in 98% sulphuric acid at 25°

Substrate	p (%)	10^2k_m	10^2k_p	10^8f_m	10^8f_p
PhN^+H_3	38	21	26	162	195
PhN^+H_2Me	30	7·4	6·4	57	49
PhN^+HMe_2	22	1·6	0·93	12·3	7·1
PhN^+Me_3	11	0·55	0·14	4·2	1·0

The rates of nitration of these anilinium ions are too slow to permit a direct comparison with that of benzene under the same conditions, but such a comparison is possible from the known kinetic data for compounds of intermediate reactivity. The results [13] suggest that the phenyltrimethylammonium ion is less reactive than benzene by a factor of $5{\cdot}7 \times 10^7$. This value has been used to calculate partial rate factors (f_m, f_p) for the nitration of these anilinium ions in 98% sulphuric acid and the results are included in Table 3. The general validity of these partial rate factors is dependent on the assumption that the rates of nitration of the different substrates involved in the comparison vary in the same way with the acidity of the medium. For most substrates, this is not a bad approximation [14] but it may be less satisfactory for the protonated poles. However, the partial rate factors in Table 3 are still of value in showing that the differences in the substituent effects of these nitrogen poles are small in comparison with their common deactivating effect on the benzene ring.

(4) *Interpretation of the Relative Substituent Effects.*—The substituents $-N^+H_3$, $-N^+H_2Me$, $-N^+HMe$, $-N^+Me_3$ are isoelectronic with the respective members of the series $-CH_3$, $-CH_2Me$, $-CHMe_2$, and $-CMe_3$ but the pattern of substituent effects in the two series is very different; thus the reactivity of the *para*-position of t-butylbenzene in nitration slightly exceeds that of toluene. It is therefore necessary to consider why the replacement of hydrogen by methyl should have a strong deactivating effect in the nitrogen series (Table 3) instead of the slight activating effect observed in the carbon series.

The explanation does not appear to derive mainly from N–H hyperconjugation, for the greater reactivity of the anilinium ion over the trimethylanilinium ion is retained when a methylene group is inserted between the positive pole and the aromatic ring. This is illustrated by the rate coefficients for the nitration of the benzylammonium ion and the trimethylbenzylammonium ion in Table 4; this comparison is extended over two acidities to show that the nitration of the first ion does not involve a significant contribution from the reaction of the neutral molecule. The large difference in the substituent effects of the $-N^+H_3$ and $-N^+Me_3$ groups is not therefore dependent on the overlap integral between the N–H σ-bonds and the π-orbitals of the ring.

The major reason for the difference in these substituent effects almost certainly involves the difference in the solvation of the protonated and the methylated poles. The weaker electron withdrawing effect of the $-N^+H_3$ group compared with the $-N^+Me_3$ group has been commented on before [15] and ascribed to this cause. The most recent evidence comes comes from Willi's demonstration [16] that the effect of an $-N^+H_3$ pole on the free energy

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[13] M. W. Austin and J. H. Ridd, *J.*, 1963, 4204.

[14] N. C. Deno and R. Stein, *J. Amer. Chem. Soc.*, 1956, **78**, 578.

[15] C. K. Ingold, E. H. Ingold, and F. R. Shaw, *J.*, 1927, 813.

[16] A. V. Willi, *Z. phys. Chem.* (*Frankfurt*), 1961, **27**, 233.

TABLE 4

Rate coefficients ($mole^{-1}$ $sec.^{-1}$ l.) for the nitration of the benzylammonium ion and the benzyltrimethylammonium ion in aqueous sulphuric acid at 25°

H_2SO_4 (%)	k_2 $PhCH_2N^+H_3$ (A)	k_2 $PhCH_2N^+Me_3$ (B)	k_2^A/k_2^B
78·70	1·58	0·0252	63
80·05	3·72	0·0600	62

of ionisation of an anilinium ion is about 10% less than that of an $-N^+Me_3$ pole. The relative effects on the rates of nitration differ by somewhat more than this but not by enough to require a different interpretation. The closer association of the $-N^+H_3$ pole with the medium can be considered to spread the positive charge by hydrogen bonding. However, this explanation of the substituent effects does not require such a specific type of interaction for, on the Kirkwood–Westheimer model,[17] the shorter the distance between the positive pole and the polar solvent, the greater the effective dielectric constant between the positive pole and the aromatic ring.

The above explanation accounts for the major differences in the substituent effects recorded in Table 3 but it is not completely satisfactory, for the extent of *para*-substitution in the anilinium ion is more than would be expected if the effect of replacing $-N^+Me_3$ by $-N^+H_3$ were simply to " scale down " the effect of the positive pole; such an effect would never cause the *para*-position to be more reactive than one *meta*-position. This anomaly is also illustrated by the comparison of the anilinium ion with the benzyltrimethylammonium ion: the latter ion is more reactive by a factor of *ca.* 25 but gives less *para*-substitution.* It appears that the protonated poles give significantly higher *p*/*m* ratios than expected from their reactivity relative to the methylated poles.

The reason for this is not entirely clear. It may be a consequence of the way in which the positive charge is effectively spread into the medium (thus more nearly equalising its effects on the 1, 2, and 6 positions of the aromatic ring) or it may reflect some type of hyperconjugative electron release from the $-N^+H_3$ group. In this connection, it is interesting that the triphenyloxonium ion has been reported as giving almost complete *para*-substitution in nitration;[8] this suggests that a positive charge does not prevent significant electron release from a donor atom with a lone electron pair.

Although some aspects of the above work are not yet understood, the results suggest that the combined inductive and direct field effects of a positive pole do not lead to marked discrimination between the *meta*- and *para*-positions in aromatic nitration. Thus, for the nitration of the phenyltrimethylammonium ion, the $\frac{1}{2}m/p$ ratio is only four and, for the protonated poles, the ratio is even less. These ratios are significantly lower than those observed for the nitro-group and for several other groups capable of withdrawing electrons by mesomeric interaction with the aromatic ring.[20] Thus, for the nitration of nitrobenzene, the $\frac{1}{2}m/p$ ratio is about 100.† Since nitrobenzene and the phenyltrimethylammonium ion are of similar reactivity, this comparison suggests that the $-M$ effect is considerably more discriminatory between the *meta*- and *para*-positions than the $-I$ effect, and supports earlier

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* About 10—15% of *para*-nitration appears to occur [18, 19] but this has not yet been checked by ion-exchange chromatography.

† *Note added on proof.*—A recent redetermination of the $\frac{1}{2}m/p$ ratio for the nitration of nitrobenzene has given the lower value of 22 (A. D. Measure and J. G. Tillett, personal communication). The difference between the nitro-group and the positive poles discussed above is therefore less than previously believed, but still appears large enough to be significant.

[17] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, 1938, **6**, 506.

[18] F. R. Goss, W. Hanhart, and C. K. Ingold, *J.*, 1927, 250.

[19] M. R. Brickman, Ph.D. Thesis, London, 1963.

[20] Such results are summarised in ref. 3, ch. 6.

arguments that the $-M$ effect is responsible for the very low percentage of *para*-substitution observed in the nitration of nitrobenzene.[21]

(5) *Comparison with Related Studies.*—The conclusions of the last paragraph on the substituent effects of positive poles differ from those generally accepted and so it is worth re-examining the other published evidence on these substituent effects in aromatic substitution.

Consider first the nitrogen poles. As explained above, the frequently quoted result of Vorländer and Siebert [7] appears to be in error because of their failure to isolate the *para*-substituted material. The other published results are more in agreement with our own conclusions. Thus, the sulphonation of the phenyltrimethylammonium ion,[22] under conditions believed to give kinetic control, leads to 14% of *para*-substitution. The extent of *para*-bromination of the dimethylanilinium ion depends on the acidity but decreases to a limiting value of about 30% *para*-substitution [23] in the most acidic media studied. The relative deactivating effects of a *m*-N^+Me_3 group and a *p*-N^+Me_3 group in protiodetriethylgermylation [24] depend on the solvent used and show no evidence for markedly stronger deactivation from the *para*-position. The relative deactivating effects of these substituents in the solvolysis of aryldimethylcarbinyl chlorides [25] (the reaction used to define σ^+-constants) differ by a factor of only 1·7, the *meta*-pole being the more deactivating.

The remaining evidence for the strong *meta*-directing effect of positive poles comes from substituents containing other positively charged elements; a number of such examples have been reported as giving only *meta*-substitution in nitration.[8,21] We are currently re-investigating such substituent effects by ion-exchange chromatography and our first results on the phosphorus and arsenic poles do not suggest that the earlier work is in error by more than a few per cent.[26] However, it does not follow that the orientation of the substitution is determined essentially by the inductive and field effects of the positive charge for the substituents reported as giving only *meta*-substitution contain positively charged elements from the second and third rows of the Periodic Table; such elements have vacant *d*-orbitals in their outer shells and thus resemble the nitro-group in being able to accept electrons from the aromatic system.[8,10] We hope to discuss this aspect in more detail later.

EXPERIMENTAL

The methods used for studying the nitration of *N*-methylaniline and *NN*-dimethylaniline were as described for aniline in Part I. The corresponding nitro-compounds were prepared by standard methods; a full account is available elsewhere.[19] The nitration of the benzyl compounds was studied in a similar way [19] except that their reactivity and tendency to undergo sulphonation made it necessary to use lower concentrations of sulphuric acid. The following details therefore refer only to the reactions of the quaternary salts. The perchlorates described were prepared in order to determine the ultraviolet spectra of the reaction products.

Materials.—Phenyltrimethylammonium nitrate was prepared from the iodide by treatment of an aqueous solution with 1 equiv. of silver nitrate followed by filtration, evaporation under reduced pressure, and recrystallisation from acetone containing a little alcohol. *m*-Nitrophenyltrimethylammonium iodide was prepared by the reaction at room temperature of the dimethyl compound with 1 mol. of methyl iodide in nitromethane. The precipitated salt was filtered off, dissolved in aqueous methanol and converted into the perchlorate by passing down an ion-exchange column (Amberlite I.R.A. 400) containing perchlorate ions. After removal of the solvent, the salt was dissolved in acetone and purified by precipitation with ether. *p*-Nitrophenyltrimethylammonium perchlorate was prepared by a similar process except that the initial methylation required refluxing the corresponding dimethyl compound with dimethyl

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[21] C. K. Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell, London, 1953, ch. 6.
[22] J. C. D. Brand and A. Rutherford, *J.*, 1952, 3927.
[23] B. R. Suthers, P. H. Riggins, and D. E. Pearson, *J. Org. Chem.*, 1962, **27**, 447.
[24] C. Eaborn and K. C. Pande, *J.*, 1961, 5082.
[25] Y. Okamoto and H. C. Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 4976.
[26] J. H. Ridd and J. H. P. Utley, *Proc. Chem. Soc.*, 1964, 24.

sulphate in benzene. In some later work with Mr. P. F. Christy, it has been found more convenient to prepare the perchlorates by adding aqueous solutions of the other salts to a concentrated solution of sodium perchlorate in water. The purification of the perchlorates by the acetone–ether method was then followed by two recrystallisations from methanol containing a little ether. However, the resulting difference in the ultraviolet spectrum was not significant.

Benzyltrimethylammonium salts were prepared by methylating benzyldimethylamine with either methyl iodide or dimethyl sulphate. Both salts were converted into the corresponding perchlorate by the addition of aqueous perchloric acid to concentrated aqueous solutions of the salts and the perchlorate was purified by recrystallisation from dilute perchloric acid.

The *meta*- and *para*-nitro-derivatives were obtained as the corresponding chlorides from the Aldrich Chemical Co. and were converted into the perchlorates as described above.

The C, H, and N analyses for the above compounds are shown in Table 5.

TABLE 5

Analyses and spectra of quaternary perchlorates

Cation	$\lambda_{\text{max.}}$ (mμ)	$10^{-3}\varepsilon_\lambda$	Found (%)			Required (%)		
			C	H	N	C	H	N
$C_6H_5N^+Me_3$	253·5 *	0·230 *	46·1	6·7	5·6	45·9	5·9	5·9
m-$NO_2{\cdot}C_6H_4{\cdot}N^+Me_3$	253·5	7·30	38·5	4·8	9·9	38·5	4·6	10·0
p-$NO_2{\cdot}C_6H_4{\cdot}N^+NMe_3$	252	9·75	38·5	4·8	9·9	38·5	4·6	10·0
$C_6H_5{\cdot}CH_2{\cdot}N^+Me_2$	262	0·323	47·6	6·7	5·6	48·1	6·4	5·6
m-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}N^+Me_3$	263	7·00	39·8	5·5	9·1	40·7	5·1	9·5
p-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}N^+Me_3$	263	10·2	41·2	5·5	9·8	40·7	5·1	9·5

* Measured using the quaternary nitrate.

Analysis by Ion-exchange Chromatography.—The solution from the reaction at room temperature of 0·3 g. of phenyltrimethylammonium nitrate in 10 ml. of 98% sulphuric acid was diluted (*ca.* 3 fold) with water and the sulphate ions were precipitated with barium chloride. After centrifuging, the solution was filtered and the filtrate evaporated to dryness under reduced pressure. Water was added and the evaporation repeated. The solid product was dissolved in water and the ultraviolet spectrum recorded.

A sample of this solution (10 ml., 0·02M) was absorbed in the first of two ion-exchange columns (length, 24 cm.; diameters; first, 1·5 cm., second 1 cm.) linked by narrow-bore tubing. The columns were packed with Permutit Zeo-Karb sulphonated polystyrene resin (52—100 mesh, 8% divinylbenzene). When eluted with 2·5M-hydrochloric acid at a drop rate of 12 per min., the *meta*-isomer came off after 400 ml. and *para*-isomer after about 800 ml. The ultraviolet spectrum of each fraction was taken [10] and the amounts of the two nitro-compounds present were calculated from the optical density at 2535 Å using the following extinction coefficients; *meta*-nitro, $\varepsilon = 7300$; *para*-nitro, $\varepsilon = 9750$. The total recovery of material from the column as calculated from the optical densities of the separate fractions amounted to 98—99% of that added.

One nitration was carried out using phenyltrimethylammonium nitrate (0·616 g.) in AnalaR fuming nitric acid (10 ml., *d* 1·5). After being left for several days at room temperature, the solution was evaporated to dryness under reduced pressure at 50°. Water was then added and the evaporation repeated until the final solution was neutral. This solution was made up to 100 ml. and part was analysed by ion-exchange chromotography as described above. The analysis of the factions gave 10·2% of *para*-substitution, 89·8% *meta*-substitution with 98% recovery from the column. The other handling losses were also shown to be very slight.

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