

Studies in Nucleophilic Aromatic Substitution Reactions

III.* Replacement of Bromine by Chloride Ion in 2-Bromo-3-nitro- and 2-Bromo-5-methyl-3-nitrobenzenediazonium Ions

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The exchange of bromine for chlorine in 2-bromo-3-nitro- and 2-bromo-5-methyl-3-nitrobenzenediazonium ions has been studied kinetically at 20° and 25° in a hydrochloric acid-acetic acid-water medium. The exchange rate constant for the former compound is similar to those obtained in earlier work for the 4-bromo-3-nitro and 2-bromo-5-nitro isomers. Steric effects have thus been demonstrated to be largely absent in this reaction.

Activation parameters for the exchange reaction have been calculated; $\Delta H^\ddagger = 22.1$ kcal/mole, $\Delta S^\ddagger = -5.6$ e.u. (2-bromo-3-nitro) and $\Delta H^\ddagger = 26.5$ kcal/mole, $\Delta S^\ddagger = 4.7$ e.u. (2-bromo-5-methyl-3-nitro). The Hammett ρ value for the reaction is 5.9 at 20° and 5.5 at 25°.

In Part I of this series,¹ the replacement of bromine and isotopically labelled chlorine by ordinary chlorine through nucleophilic attack of chloride ion on 4-halo-3-nitrobenzenediazonium ions was kinetically studied in an aqueous medium containing hydrochloric acid and acetic acid. The same exchange reactions have also been studied in 2-halo-5-nitrobenzenediazonium ions.² These reactions, together with some other halogen exchange reactions in diazonium ions, have recently been summarized.³ Part II of this series⁴ deals with halogen exchange reactions in 2,4,6-trihalobenzenediazonium ions.

In the 4-halo-3-nitrobenzenediazonium ions, the halogen atom is activated by one *para* diazonium group and one *ortho* nitro group, while in the 2-halo-5-nitrobenzenediazonium ions, the positions of these activating groups are reversed. This interchange of the activating substituents does not produce any drastic change in the specific rate of either kind of exchange (bromine-chlorine or chlorine-chlorine). Either the steric effect of the *ortho* substituent is unimportant in these reactions, or the agreement between corresponding rates is the consequence of a fortuitous cancellation of effects. Bunnett has

* Part II: see Ref. 4.

pointed out⁵ that in nucleophilic aromatic substitution, the steric effect of ring substituents *ortho* to the group replaced is usually small, provided that the attacking nucleophile is of moderate size.

A possibility of arriving at a decision as to which of the above two explanations of the rate agreements is correct will be offered below. The compounds in which a halogen atom is flanked by a nitro group and a diazonium group, both in *ortho* positions, remain to be investigated. The prediction would be that if steric effects are unimportant, the exchange rates in the 2-halo-3-nitrobenzenediazonium ions should be similar to those obtained in the previous work.^{1,2} If, however, the second alternative suggested above (*i.e.*, a fortuitous cancellation) is correct, changes in the activation parameters should be observed.

Since preparation of ³⁶Cl-labelled 2-chloro-3-nitrobenzenediazonium ion would have required a considerable amount of work and expense, only the bromo compound has been studied in the present paper.

In the 2-bromo-3-nitrobenzenediazonium ion, the position *para* to the halogen atom is vacant. By introducing substituents in this position and performing the same exchange reaction, it should be possible to determine the Hammett ρ value for the reaction. *A priori*, a positive value can be expected, since electron-attracting substituents will aid in the dispersal of the negative charge in the critical transition state. In the present paper, rate data obtained with a methyl group in the *para* position will be presented.

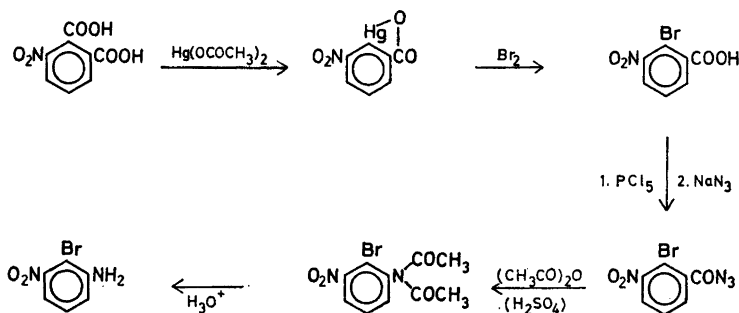


Fig. 1. Preparation of 2-bromo-3-nitroaniline.

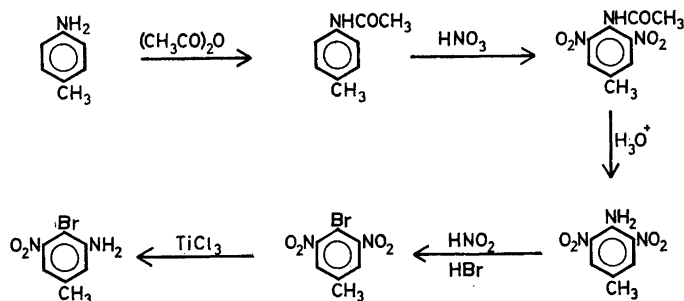


Fig. 2. Preparation of 2-bromo-5-methyl-3-nitroaniline.

METHODS AND RESULTS

The synthetic routes to the anilines, serving as starting materials for the new diazonium ions investigated, are outlined in Figs. 1 and 2.

The kinetic runs were performed in the same medium (water-hydrochloric acid-acetic acid) as previously used.¹ At different times, aliquots of the thermostated, reacting solution were withdrawn and added to cuprous chloride in hydrochloric acid. Sandmeyer reactions, leading to the replacement of the diazonium group by chlorine, ensued instantaneously. In earlier work,¹⁻⁴ the resulting mixtures of stable compounds had been isolated by steam distillation. However, in the case of 2-bromo-3-nitrobenzenediazonium ion, the resulting compound, 2-bromo-3-chloronitrobenzene, was found to undergo bromine-chlorine exchange at the 2-position when submitted to the conditions of steam distillation in the presence of univalent copper salts. This exchange reaction, which occurs under surprisingly mild conditions, is currently being investigated. As a consequence, however, the work-up technique had to be modified; instead of steam distillation, the aliquots were cooled, the pH-value was adjusted to about 8 and extraction with ether was performed.

The mixtures of stable compounds thus obtained were analyzed by GLC in the same way as before.^{2,6} For calibration purposes, the following compounds had to be synthesized: 2-chloro-3-nitroaniline, 2-chloro-5-methyl-3-nitroaniline, 2-bromo-3-chloronitrobenzene, 2,3-dichloronitrobenzene, 4-bromo-3-chloro-5-nitrotoluene, and 3,4-dichloro-5-nitrotoluene.

The routes for the four latter compounds are shown in Fig. 3.

The stoichiometric chloride ion concentration in the medium was determined by Mohr titration according to the standard procedure.⁷ The removal of diazonium ions through azo coupling with 1,3,5-trimethoxybenzene described in Ref. 1 was found to be unnecessary.

Kinetic runs were made at 20°C. Some competitive runs were made with 2-bromo-3-nitro- and 4-bromo-3-nitrobenzenediazonium ions in order to link the *ortho,ortho*-substituted systems to the *ortho,para*-systems studied previously.^{1,2} The four compounds, produced in the Sandmeyer reactions, all separated on the GLC column using this combination of isomers. This was

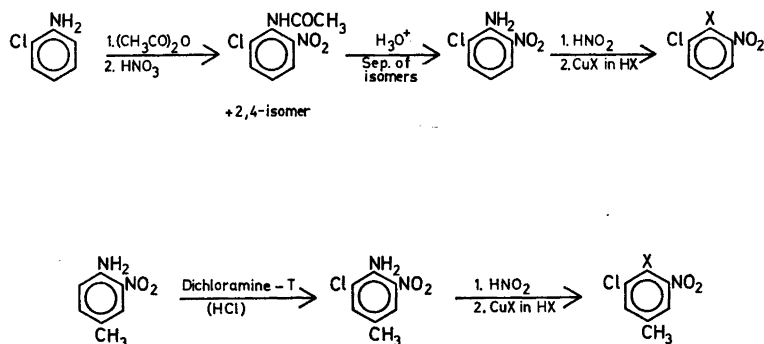


Fig. 3. Routes to calibration compounds. X = Br or Cl.

not the case with 2-bromo-3-nitro- and 2-bromo-5-nitrobenzenediazonium ions. Some runs with the new *ortho,ortho*-compounds were also performed at 25°C in order to obtain at least a rough estimate of the activation parameters. It turned out to be experimentally difficult to extend the temperature range further in either direction.

All runs are summarized in Table 1.

Table 1. Kinetic runs involving bromine-substituted diazonium ions and chloride ion.

Run number	Substituents in diaz. ion	Temp.°C ^a	$k_{\text{obs}} \times 10^5$ ^b	[Cl ⁻] ^c	$k_1 \times 10^5$ ^d
1	2-Bromo-3-nitro	20.00	6.20	5.30	1.170
2	»	20.00	6.19	5.30	1.168
3	»	20.00	6.00	5.30	1.131
4	»	20.00	6.24	5.30	1.178
5	»	20.00	5.99	5.26	1.140
6	4-Bromo-3-nitro	20.00	12.20	5.26	2.320
7	»	20.00	12.20	5.26	2.320
8	2-Bromo-3-nitro } ^e	20.00	6.69	5.26	1.272
	4-Bromo-3-nitro }		12.43	5.26	2.363
9	2-Bromo-3-nitro } ^e	20.00	6.58	5.26	1.251
	4-Bromo-3-nitro }		11.77	5.26	2.238
10	2-Bromo-5-methyl-3-nitro	20.00	0.628	5.30	0.1186
11	»	20.00	0.616	5.30	0.1163
12	»	20.00	0.619	5.30	0.1168
13	2-Bromo-3-nitro	25.00	11.63	5.26	2.211
14	»	25.00	11.79	5.26	2.241
15	2-Bromo-5-methyl-3-nitro	25.00	1.355	5.26	0.2577
16	»	25.00	1.333	5.26	0.2533

^a Accuracy $\pm 0.05^\circ$.

^b Pseudomonomolecular rate constant, sec⁻¹.

^c Determined by Mohr titration acc. to Ref. 7, accuracy $\pm 1\%$.

^d Formal second-order rate constant, l mole⁻¹ sec⁻¹.

^e Competitive run.

A representative run is illustrated in Fig. 4. The deviations of individual points from the straight line were almost always within $\pm 2\%$. In most runs, the reactions were followed for at least one half-life.

In previous work it has always been assumed that the Sandmeyer reaction gives the same yield with the bromo- and chloronitrobenzenediazonium ions of a given substitution pattern. The linearity of the first-order kinetic curves in a semi-logarithmic representation strongly supports this assumption, but a direct proof would be more desirable. In the trihalobenzenediazonium series,⁴ the starting and product diazonium compounds could be prepared in a pure state as fluoborate salts, and therefore the entire process of quenching the kinetic samples, work-up and analysis could be carried out with mixtures of known composition, thus providing data for calibration curves. Unfortu-

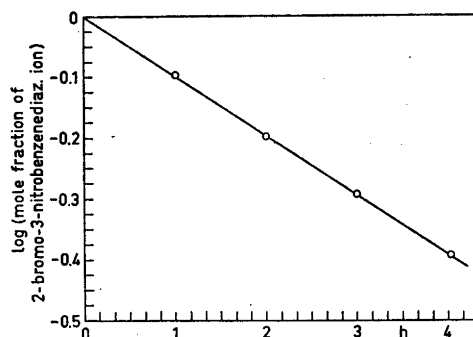


Fig. 4. A representative run of Br/Cl exchange at 20°C.

nately, however, we were unable to prepare pure salts of the compounds investigated here. We have therefore proceeded in what may be considered the next best fashion, namely by starting with known amounts of anilines that upon diazotisation yield, respectively, the reactant and the product diazonium ion. The proof now therefore hinges on the diazotisation being a quantitative reaction (or, otherwise, that the yields are the same for the two anilines). The latter point is, however, evident from the appearance of the diazonium solutions. Nitrosylsulphuric acid was used as the source of nitrous acid, and the anilines were added in glacial acetic acid solution. No trace of discoloured or water-insoluble material was formed, and the diazotisation is therefore essentially quantitative. The presence of starting materials would have been revealed by the appearance of a yellow precipitate upon dilution with water, since these amines are very weak bases. No such behaviour was observed. Furthermore, the calibration curves actually obtained (Figs. 5 and 6) are straight lines with unit slope. It is very unlikely that this behaviour

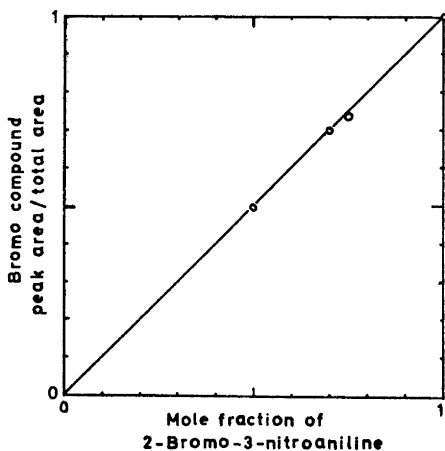


Fig. 5. Calibration curve for Br/Cl exchange in 2-bromo-3-nitrobenzenediazonium ion.

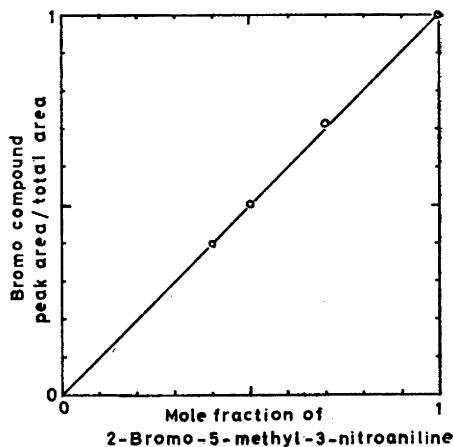


Fig. 6. Calibration curve for Br/Cl exchange in 2-bromo-5-methyl-3-nitrobenzenediazonium ion.

is the result of the cancellation of two opposing errors. We therefore feel quite confident that no systematic errors are introduced by the analytical procedure.

From the data in Table 1, the activation parameters for the reactions of 2-bromo-3-nitro- and 2-bromo-5-methyl-3-nitrobenzenediazonium ions with chloride ion can be calculated. The results are presented in Table 2 and were calculated using the standard expressions.⁸

Table 2. Activation enthalpies and entropies for the exchange reactions with chloride ion.

Substituents	ΔH^\ddagger ^a	ΔS^\ddagger ^b
2-Bromo-3-nitro	22.1 ± 1.4	-5.6 ± 4.8
2-Bromo-5-methyl-3-nitro	26.5 ± 0.7	4.7 ± 2.4

^a In kcal. mole⁻¹.

^b In cal. deg.⁻¹ mole⁻¹.

Average values from the relevant runs were used in this calculation. The competitive runs were, however, not included for reasons mentioned in the discussion below.

The errors in ΔH^\ddagger and ΔS^\ddagger were calculated according to a procedure described by Petersen *et al.*⁹ In these calculations, the rate constant errors are taken as the maximum deviations from the means.

DISCUSSION

Absence of steric effects. The data presented in Table 1 demonstrate that the exchange of bromine for chlorine at 20°C is 1.9 times faster in 4-bromo-3-nitro- than in 2-bromo-3-nitrobenzenediazonium ion. If the rate constant for the 4-bromo-3-nitro case from Ref. 1 is compared with the present 2-bromo-3-nitro values from Table 1, the former isomer turns out to react 1.3 times faster at 25°C, although this ratio should be treated with great caution, since unfortunately no competitive runs have been carried out at this temperature, and the medium effects are known to be large. In previous work,² the ratio between the rate constants for the 4-bromo-3-nitro- and the 2-bromo-5-nitrobenzenediazonium ions in the same reaction has been determined to 1.32 at 25°C and 1.61 at 15°C.

It can easily be estimated that the isokinetic temperature¹⁰ for any two of these three isomers is below 50°C. We take this to mean that steric effects due to any particular arrangement of the two activating groups (using *ortho* and *para* positions) are absent.

In a recent paper,¹¹ Porto and co-workers have demonstrated that in the reactions of 4, 5, and 6-substituted 1-chloro-2-nitrobenzenes with sodium thiophenoxide in methanol, the polar influence of an *ortho*-substituent is more important than its steric effect.

Hammelt reaction constant. A comparison of the rate constants (Table 1) for 2-bromo-3-nitro- and 2-bromo-5-methyl-3-nitrobenzenediazonium ions in

the exchange reaction with chloride ion can be made for the temperatures 20 and 25°C. Average values of all runs except the two competitive ones between 2-bromo-3-nitro and 4-bromo-3-nitro, which may be subject to a systematic error, as seen from Table 1 (this error resulting from the GLC analysis), have been used.

At 20°C, the rate ratio $k_{\text{methyl}}/k_{\text{unsubst.}}$ (bimolecular rate constants being used) is 0.1013 and at 25°C, the same ratio is 0.1148. The σ_p value -0.170 is used for methyl.^{12a} We then obtain $\rho = 5.85$ at 20°C and 5.53 at 25°C. These ρ values are large but close to the usual range (3.9–4.9) for nucleophilic aromatic substitution.^{12b} Therefore, no further substituents were investigated, since the interval of experimentally amenable rates is fairly narrow in the system under investigation.

Activation parameters. Table 2 shows that the ΔH^\ddagger value is higher for the *para* methyl substituted ion than for the unsubstituted one. This is expected, since the Hammett ρ value is positive, meaning that an electron-donating substituent retards the reaction. The activation entropy is 10 e.u. larger for the methyl substituted compound than for the unsubstituted one. One explanation for this difference might be that in the less reactive methyl compound, the chlorine ion has become more completely covalently bound to the aromatic ring in the transition state than for the unsubstituted compound. This would cause the water molecules solvating the reactant ions, in particular the small chloride ion, to be more completely liberated in the activation step for the methyl compound, thus giving a relatively larger positive contribution to the activation entropy. Other contributions to the activation entropy are assumed to be constant for the two reactions.

EXPERIMENTAL

Melting points have been determined on a Kofler micro hot stage.

2-Bromo-3-nitrobenzoic acid was prepared in 54 % overall yield from 3-nitrophthalic acid *via* anhydro-2-hydroxymercuri-3-nitrobenzoic acid in accordance with described procedures,^{13,14} m.p. 187°C, lit.¹⁴ 185–187°C.

2-Bromo-3-nitrobenzoyl chloride was prepared from the corresponding acid by reaction with an equimolar quantity of phosphorus pentachloride. A reported procedure for 4-bromo-3-nitrobenzoyl chloride¹⁵ was followed. After recryst. from chloroform + petroleum ether, a yield of 92 % was obtained, m.p. 65–67°C, lit.¹⁶ 65°C.

2-Bromo-3-nitrobenzoyl azide. Of the preceding acid chloride, 47.8 g (0.181 mole) was dissolved in 100 ml dry acetone. A solution of 24 g (0.370 mole) sodium azide in 75 ml water was added dropwise while stirring and cooling to keep the temperature below 20°C. Sufficient water (300 ml) was added to cause the complete precipitation of the product. After collection, washing with water and drying *in vacuo* at room temp., the yield was 42.8 g (0.158 mole), 87 %, m.p. (decomp.) 63°C.

N,N-Diacetyl-2-bromo-3-nitroaniline. Of the preceding compound, 31.6 g (0.116 mole) was added in portions to a stirred mixture of 90 ml acetic anhydride and 0.1 ml conc. sulphuric acid. The temperature was kept between 50 and 60°C. The Curtius rearrangement could be conveniently followed by means of the nitrogen evolution. After the reaction was complete (30 min), 300 ml water was added in increasingly large portions in order to decompose the excess acetic anhydride and cause precipitation of the product. After storing at 5°C overnight, the product was collected, washed with water and allowed to dry. The yield of crude material, melting in the range 90–120°C, was 29.1 g. A sample was recrystallized three times from 95 % ethanol to give the constant m.p. 100°C.

The evidence for describing the substance as the *N,N*-diacetyl amine was the following: Hydrolysis with hydrochloric acid (see below) gave 2-bromo-3-nitroaniline, which

could be reacylated with an equimolar amount of acetic anhydride in refluxing benzene solution to the known monoacetyl derivative, m.p. 165°C, lit.¹⁶ 166°C. The latter compound, on further refluxing with a tenfold excess of acetic anhydride and a trace of conc. sulphuric acid for 5 min, gave crystals melting at 97–98°C, undepressed upon mixing with the pure material melting at 100°C, obtained from the crude product from the Curtius rearrangement, melting at 90–120°C. The other constituent of the latter crude mixture was almost certainly the monoacetyl compound.*

The formation of a diacetylated amine in this reaction is somewhat remarkable. On one particular occasion, the Curtius reaction proceeded with extreme violence (due to careless additions of the azide), leading to the mechanical loss of about half the product. Curiously, the remaining half turned out to be the monoacetyl derivative. It was, however, impossible to obtain the latter through controlled hydrolysis of the diacetyl amine, either with various strong acids or sodium hydroxide solution. The diacetyl derivative seemed unusually stable towards hydrolysis with pure water or in the presence of weak acids, but once hydrolysis took place (using strong acids), the monoacetyl compound could never be obtained as an intermediate.

2-Bromo-3-nitroaniline. Of the crude N,N-diacetyl compound just described, 19.9 g was dissolved in 75 ml boiling 95 % ethanol. Conc. hydrochloric acid, 15 ml, was added and the mixture was heated to reflux for 3 h. Colourless crystals of the anilinium chloride soon began to form during the heating period. After cooling, ice and excess ammonia were added in order to liberate the yellow amine. After washing with water and recrystallizing from dilute ethanol, 12.0 g (0.055 mole) was obtained, m.p. 96–98°C, lit.¹⁶ 97–98°C. The overall yield from the azide was 69 %.

p-Acetotoluidide was prepared in quantitative yield from *p*-toluidine and acetic anhydride in benzene solution according to Hüsey and Luterbacher.¹⁷ M.p. of the crude product 152°C, lit.¹⁶ 153°C.

4-Bromo-3,5-dinitrotoluene was obtained from the *p*-acetotoluidide via dinitration, hydrolysis with sulphuric acid and diazotization in hydrobromic acid, all according to Jackson and Ittner.¹⁹ Overall yield 16 %, m.p. 118–119.5°C, lit.¹⁹ 118°C, lit.²⁰ 122°C.

2-Bromo-5-methyl-3-nitroaniline was prepared from the preceding compound by reduction with titanous chloride according to Inubushi and Nomura.²⁰ Yield 25 %, m.p. 73.5–74.5°C, lit.²⁰ 73.5–74.5°C.

2-Chloro-6-nitroaniline. *o*-Chloroaniline, 63.8 g (0.5 mole), was acetylated and nitrated according to a reported procedure²¹ for *o*-toluidine, with the following modification. After treatment of the nitration mixture with 1.5 l ice-cold water, in which 82 g (1 mole) sodium acetate had been dissolved, the precipitated acetanilides were sucked off and dried. The yield at this stage was 59 g (0.274 mole or 55 % of isomeric mixture). The mixture of acetanilides was stirred with 300 ml conc. sulphuric acid and 600 ml water for 6 h and then steam distilled. This operation was interrupted when substantial amounts of yellow material ceased to come over; in the rather strongly acidic medium, only the weaker base, 2-chloro-6-nitroaniline, is appreciably volatile, whereas the 2-chloro-4-nitroaniline stays behind and can be recovered if desired. (Intramolecular hydrogen bonding between the amino and nitro group also contributes to the volatility of the *ortho* nitro isomer, cf. Ref. 21). From the steam distillate (6 l), the yellow amine was isolated by filtration and recrystallized from 50 % ethanol. Yield 13.0 g (0.075 mole) or 15 %, m.p. 74.5–75.5°C, lit.²² 76°C.

2,3-Dichloronitrobenzene. Of the preceding compound, 2.6 g (0.015 mole) was dissolved in 40 ml conc. hydrochloric acid and diazotized with 1.2 g (0.017 mole) sodium nitrite in the minimum amount of water while stirring and keeping the temp. below 5°C. The resulting solution was added to 2.99 g (0.03 mole) cuprous chloride dissolved in 15 ml conc. hydrochloric acid. After the nitrogen evolution had ceased, the product was recovered by steam distillation and filtration of the distillate. The crude yield was 2.65 g (0.0138 mole), 92 %, m.p. 59–61.5°C. One recryst. from ethanol followed by one from methanol gave m.p. 61.5–62.0°C, lit.²³ 61–62°C.

2-Bromo-3-chloronitrobenzene. This compound was prepared in analogy with the preceding one. 70 ml 52 % hydrobromic acid was used instead of hydrochloric acid in

* Unfortunately, NMR was not available to us when some of this work was done. Identification and quantitative evaluation of the composition would probably have been a trivial matter, using this technique.

the diazotization step, and a solution of 4.3 g (0.03 mole) cuprous bromide dissolved in 20 ml 52 % hydrobromic acid used as the Sandmeyer reagent. The crude yield was 3.5 g (0.0147 mole), 98 %. One recryst. from ethanol followed by one from methanol gave m.p. 83–84°C. We have been unable to find references to this compound in the literature.

2-Chloro-4-methyl-6-nitroaniline. A solution of 12.3 g (0.05 mole) N,N-dichloro-*p*-toluenesulphonamide (Dichloramine-T) in 50 ml chloroform was added to a solution of 15.2 g (0.1 mole) 4-methyl-2-nitroaniline in 200 ml chloroform, containing a trace of hydrochloric acid as catalyst. The mixture was left at room temp. for 24 h, the chloroform removed in a rotary evaporator *in vacuo* and the remainder steam distilled. From the distillate 7.5 g (0.04 mole), 40 % yield of product was obtained by filtration. M.p. (recryst. from ethanol) 70°C, lit.²⁴ 70.5°C.

3,4-Dichloro-5-nitrotoluene. Of the preceding compound, 10 g (0.054 mole) was dissolved in 150 ml conc. hydrochloric acid. Diazotization was effected by adding a solution of 4.1 g sodium nitrite (0.06 mole) in the minimum amount of water and stirring while keeping the temp. below 5°C. The resulting solution was added to 10.5 g (0.108 mole) cuprous chloride in 30 ml conc. hydrochloric acid. After the evolution of nitrogen had ceased, the product was distilled with steam, separated by filtration and allowed to dry. The crude yield was 10 g (0.049 mole), 91 %. A sample purified by preparative GLC on an Aerograph Autoprep A 700 (carrier gas N₂, flow rate 200 ml/min, Silicone SI 30, 20" column, i.d. 3/8", column temp. 245°C) had the m.p. 47.5–48.5°C and was used in the calibration work. Another sample after four recryst. from methanol gave m.p. 46.5–48°C, lit.²⁵ 49–50°C.

4-Bromo-3-chloro-5-nitrotoluene. This synthesis was analogous to the preceding one, except that 100 ml 63 % hydrobromic acid and 25 ml water was used to dissolve the amine, and a solution of 15.5 g (0.108 mole) cuprous bromide in 50 ml 50 % hydrobromic acid was used in the Sandmeyer reaction. The steam distilled material was dissolved in ether and washed with 10 % sodium hydroxide solution followed by saturated sodium chloride solution. The ether solution was then dried with calcium chloride and the solvent removed on a rotary evaporator *in vacuo*. The crude yield was 12.5 g (0.05 mole), 93 %. A sample was recrystallized three times from methanol to give m.p. 60.5–61°C. We have been unable to find references to this compound in the literature.

2,6-Dinitroaniline was prepared according to Schultz²⁶ from chlorobenzene. The yield was 42 %. M.p. after recryst. from ethanol was 139–140°C, lit.²⁶ 139–140°C.

1-Chloro-2,6-dinitrobenzene was prepared from the preceding compound through diazotization and a Sandmeyer reaction, following a description by Gunstone and Tucker.²⁷ Yield 69 %. M.p. after recryst. from acetic acid 85°C, lit.²⁷ 86–87°C.

2-Chloro-3-nitroaniline was prepared according to Hodgson and Dodgson²⁸ by reduction of the preceding compound with stannous chloride. The yield was 26 %. M.p. 90–94°C after recryst. from methanol, lit.²⁸ 94–94.5°C.

4-Chloro-3,5-dinitrotoluene was prepared by diazotization of 2,6-dinitro-4-methyl-aniline, followed by a Sandmeyer reaction. The procedure of Gunstone and Tucker²⁷ for preparing 1-chloro-2,6-dinitrobenzene was followed. The crude yield was 77 %. After recryst. from ethanol m.p. 110–111°C, lit.²⁹ 114.5°C.

2-Chloro-5-methyl-3-nitroaniline was prepared from the preceding compound by reduction with titanous chloride, following the procedure of Inubushi and Nomura³⁰ for the preparation of 2-bromo-5-methyl-3-nitroaniline. The yield was 19 %. M.p. after recryst. from methanol 94–95°C, lit.³⁰ 95°C.

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