513. *Kinetics and Mechanism of Aromatic Nitration. Part VII. Products of Nitration of Aniline Derivatives, especially of Dimethylaniline. The Concomitant Dealkylation of Dialkylanilines.*

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The successive stages involved in the nitration, and concomitant demethylation, of dimethylaniline, finally to give *N* : 2 : 4 : 6-tetranitromethylaniline, are analysed; and consideration is given to the question of how far the various steps require nitrous acid, or proceed independently of nitrous acid.

In strongly acid conditions dimethylaniline is nitrated, presumably through its conjugate acid, with nitronium ion as the reagent, to give the *m*-nitro-derivative. At lower acidities, nitration through the free base ensues, to yield the *o*- and *p*-nitro-compounds, in the ratio of about 1 : 2, and then the 2 : 4-dinitro-derivative. The rates of the stages, parent ⟶ *p*-nitro- ⟶ 2 : 4-dinitro-, are of the same order of magnitude, possibly because the smaller proportion in which free base is present in the nitration of the parent off-sets the deactivating effect of the nitro-group in the *p*-nitro-derivative. In the reaction route, parent ⟶ *o*-nitro- ⟶ 2 : 4-dinitro-, the second stage is much slower than the first. This is attributed to a steric interference by the *o*-nitro-group of nuclear activation by the dimethylamino-group. These nitration stages are highly dependent on nitrous acid when the availability of the nitronium ion is low, but are notably less so when it is high.

Six intermediates are encountered on the nitration routes from 2 : 4-dinitrodimethylaniline to *N* : 2 : 4 : 6-tetranitromethylaniline : they are 2 : 4-dinitromethylaniline, and its *N*-nitroso- and *N*-nitro-derivatives, 2 : 4 : 6-trinitrodimethylaniline, and 2 : 4 : 6-trinitromethylaniline, and its *N*-nitroso-derivative. Different routes through these intermediates are followed in different circumstances. In nitration by 40—70 vol. % aqueous nitric acid, or by nitric acid in *ca.* 50 vol. % aqueous sulphuric acid, a primary demethylation to the secondary amine is followed by *N*-nitrosation, then by *C*-nitration, and then by the final modification of the side chain. In nitration by 70—100 vol. % aqueous nitric acid, or by nitric acid in *ca.* 70 vol. % aqueous sulphuric acid, the primary dealkylation is succeeded by *N*-nitration, then by intramolecular transference of the *N*-nitro-group to the nucleus, and finally by re-nitration in the side chain. In nitration by nitric acid in 95 vol. % aqueous sulphuric acid, the primary reaction is nuclear nitration, and the side chain is only subsequently demethylated and nitrated. The primary demethylations always depend on nitrous acid. *N*-Nitrations apparently utilise the nitric acidium or the nitronium ion, but not the nitrosonium ion. The primary nuclear nitration is not assisted by nitrous acid ; unlike the entry of the first and the second nuclear nitro-group into dimethylaniline which can apparently be effected through some form of nitrosonium ion, the direct introduction of the third nuclear nitro-group definitely requires intervention of the nitronium ion.

The mechanism of dealkylation of aromatic tertiary amines during nitration has been further considered. The essential reagent is nitrous acid in some form. Only one alkyl group is eliminated. The reaction is oxidative, the earliest isolable form of the eliminated group being the aldehyde. But the order of ease of elimination of different alkyl groups (*e.g.*, methyl > benzyl) is not the normal order of ease of oxidation. Although the aromatic product is often isolated as the nitrosamine, the steps in the formation of this product can be separated by the use of a weakly polar solvent; and it has thus been shown that the earliest isolable product is the secondary amine. Quite different phenomena appear when alkyl groups are removed from an aromatic tertiary amine by ordinary oxidising agents, such as chromic or permanganic acids : for then two alkyl groups can be successively eliminated to give first a secondary and finally a primary amine; and different alkyl groups are removed in the normal order of ease of oxidation.

All these points are covered by a theory which regards the dealkylation by nitrous acid as a homolytic nitrogen-oxidation, and as dependent in its mechanism on the considerable stability of both NO^+ and NO ; the former is assumed to add to the unshared electrons, and the latter to split off, removing one electron from the nitrogen atom, and leading to a loss of an alkyl group after rearrangement.

From the preceding paper and this one, it follows that the dealkylation of phenolic ethers, or of tertiary aromatic amines, by nitrous acid may pursue heterolytic and homolytic mechanisms. Both are in principle universally available. Both commence with the formation of nitrosoxonium or nitrosammonium ions. The dealkylation will be heterolytic or homolytic according as the intermediate ion preferentially splits off a carbonium ion or nitric oxide. The structural circumstances which may determine this choice are briefly considered : the larger nuclear charge of oxygen than of nitrogen will evidently produce a relatively greater predisposition to the loss of a cation, *i.e.*, to the heterolytic process.

(1) *Background and Plan.*

We shall make it probable in this paper that the nitration of derivatives of aniline may pursue paths generally similar to those taken by the nitration of derivatives of phenol (Part VI, *J.*, 1950, 2628), but that certain additional complications arise. Evidence will be adduced in favour of the conclusion that the nuclear nitration of derivatives of aniline by means of nitric acid takes place by two mechanisms, one of which can proceed in the absence of nitrous acid, whilst the other is dependent on nitrous acid; that these two mechanisms often operate simultaneously; and that side reactions may occur, some of which are oxidative, producing nitrous acid, which influences both nitration mechanisms, especially the second; and that, with tertiary alkylated anilines, dealkylation is a frequent concomitant of nitration. All this is clearly parallel with the phenomena associated with the nitration of derivatives of phenol, as elucidated in Part VI. However, the nitration of derivatives of aniline involves yet further complexities. The chief of these arise, first, from the considerable basicity of aromatic amines, and their tendency to react in cationic forms in strongly acid conditions; secondly, from the ready formation and moderate stability of nitramines and nitrosamines, the production of which may sidetrack, or alternatively constitute a step in, the processes leading to nitration of the aromatic nucleus; and thirdly, from the incursion of an additional dealkylation mechanism.

The great variety of phenomena which come under observation in connection with the nitration of derivatives of aniline has upset our usual plan of studying reaction products and kinetics simultaneously; for much exploratory work on the products of these nitrations had to be done before convenient component processes could be isolated sufficiently completely to render a kinetic investigation profitable. On this account, our kinetic work on the nitration of derivatives of aniline has fallen behind the related work on reaction products; the kinetic work is not yet complete enough to be published. On the other hand, the work on the products is reported at this time, because the observations are sufficiently numerous and diverse to allow some conclusions concerning mechanism to be drawn, even without the support of kinetics, especially since we have the more complete work of Part VI on the nitration of derivatives of phenol to guide our interpretations.

The leading example in which we have studied this problem is the nitration of dimethylaniline. A tertiary base has the advantage that, when no dealkylation occurs, one knows that nitramines and nitrosamines could not have been formed as intermediates. However, a study of the nitration of dimethylaniline requires comparisons of some of the observed phenomena with those involved in the nitration of methylaniline and of aniline, and of the derived nitramines and nitrosamines.

There is a copious previous literature of the nitration of dimethylaniline. Our experiments are mainly complementary to the recorded observations, and must be considered in the setting the latter provide.

(2) *Observations on the Mono- and Di-nitration of Dimethylaniline.*

(2.1) *Nitration in Sulphuric Acid and in Nitric Acid.*—When dimethylaniline is nitrated by nitric acid in an excess of concentrated sulphuric acid, the main first product is *m*-nitrodimethylaniline, and the chief by-product is *p*-nitrodimethylaniline (van Romburgh, *Rec. Trav. chim.*, 1883, **2**, 108; *Proc. K. Akad. Wetensch. Amsterdam*, 1899, **2**, 342; Groll, *Ber.*, 1886, **19**, 198; Noelting and Foumouse, *Ber.*, 1897, **30**, 2930). According to van Romburgh, it is necessary to dilute the nitration solution with excess of aqueous alkali in order to isolate these mononitration products; for if the solution is diluted with water, further nitration takes place. In this event the *m*-nitrodimethylaniline is converted into 2 : 5- and 3 : 4-dinitrodimethylaniline, whilst the *p*-nitrodimethylaniline is transformed into 2 : 4-dinitrodimethylaniline.

As Groll first recognised, a main product of the nitration of dimethylaniline in a large excess of concentrated nitric acid is *m*-nitrodimethylaniline (Groll, *loc. cit.*; cf. Noelting and Collins, *Ber.*, 1881, **14**, 261; Noelting, *ibid.*, p. 543).

(2.2) *Nitration by Nitric Acid in Organic Solvents.*—The nitration of dimethylaniline by nitric acid in various concentrations in ether has been studied by Lang (*Compt. rend.*, 1948, **226**, 1381). He found that part of the material became oxidised to give tetramethylbenzidine and other products, along with nitrous acid. His first simple substitution product was *p*-nitrosodimethylaniline, which was formed after an induction period. With a more concentrated nitration solution, or at a higher temperature, this substance became oxidised to *p*-nitrodimethylaniline. In subsequent steps the last-named compound became converted into 2 : 4-dinitrodimethylaniline, and then into substances involving demethylation—a process to be considered later.

The nitration of dimethylaniline by nitric acid in acetic acid as solvent has been investigated by Weber (*Ber.*, 1877, **10**, 761), and by Mertz and Weith (*ibid.*, p. 673). The first of these authors obtained *p*-nitrodimethylaniline as the main product. The other investigators used a more concentrated nitration solution, and found the main product to be 2 : 4-dinitrodimethylaniline. We have examined the nitration of dimethylaniline in acetic acid with a view to detecting initial products, and establishing conditions for mononitration.

Dimethylaniline was treated, in 10% solution in acetic acid for 24 hours at room temperature, with varying quantities of 70% nitric acid containing nitrous acid. The proportions of nitric acid ranged from 1·0 to 1·5 mols. per mol. of dimethylaniline. Near the lower end of this range, much dimethylaniline remained unconverted under the conditions used; but by careful chromatography small amounts of *p*-nitrosodimethylaniline and a dinitrotetramethylbenzidine were isolated.

It is usually rather easy to separate the stages of successive nitration of a benzene derivative; but it seems very difficult to effect a clean separation of the mononitration from the dinitration of dimethylaniline. As the proportion of nitric acid was gradually increased in these experiments, unconverted dimethylaniline, and green nitroso-compounds, disappeared in succession from the products; and, simultaneously, mononitrodimethylanilines, and 2 : 4-dinitrodimethylaniline, successively appeared in the products. With 1·4 mols. of nitric acid per mol. of dimethylaniline, no unconverted dimethylaniline remained, and only small amounts of nitroso-compounds were present, whilst the formation of 2 : 4-dinitrodimethylaniline did not assume large proportions. These were judged to be the best conditions for mononitration.

By a combination of distillation and crystallisation, the main constituents of the product obtained under these conditions * were separated, in the following proportions:

o-Nitrodimethylaniline	25 mols. %	Total separated, 75 mols. % of consumed dimethylaniline.
p-Nitrodimethylaniline	39 ,,	
2 : 4-Dinitrodimethylaniline	11 ,,	

o-Nitrodimethylaniline and its *p*-isomeride were now separately treated in 10% solution in acetic acid, under the same conditions as before, with 1·0 mols. of nitric acid per mol. of nitrodimethylaniline. *o*-Nitrodimethylaniline was not affected. *p*-Nitrodimethylaniline was converted almost quantitatively into 2 : 4-dinitrodimethylaniline.

It follows that the 2 : 4-dinitrodimethylaniline, isolated from the product of the attempted mononitration of dimethylaniline, must have been formed entirely by further nitration of *p*-nitrodimethylaniline. The proportions in which the above-described isolation of separated products proves *o*- and *p*-nitro-products to have been originally formed are therefore as follows: *ortho*-, 25%; *para*-, 50% (total isolated, 75%). We have to conclude that, of the successive nitrations, dimethylaniline ⟶ *p*-nitrodimethylaniline ⟶ 2 : 4-dinitrodimethylaniline, the second takes place at a rate comparable to that of the first in our conditions; and also that *p*-nitrodimethylaniline is much more easily nitrated than is its *o*-isomeride. This is discussed in Section 3.

(2.3) *Nitration in Acid–Aqueous Solutions.*—The nitration of dimethylaniline in these conditions has been investigated by Hodgson and his collaborators (Hodgson and Nicholson, *J.*, 1941, 470; Hodgson and Turner, *J.*, 1942, 584; Hodgson, *J. Soc. Dyers and Col.*, 1946, **60**, 151). Aqueous nitrite acidified with hydrochloric acid, in the absence of any added nitric acid, gave *p*-nitrosodimethylaniline, *p*-nitrodimethylaniline, and then the dealkylation product, *N*-nitroso-*p*-nitromethylaniline, to which reference will be made again later. The reaction with 5—10% aqueous nitric acid containing nitrous acid was almost entirely dependent on the presence of the nitrous acid, and it again gave *p*-nitrosodimethylaniline and *p*-nitrodimethylaniline; but in this case there was some oxidation, with the production of 3 : 3′-dinitrotetramethylbenzidine and additional nitrous acid. In 20% aqueous nitric acid the reaction with dimethylaniline proceeded readily without initially added nitrous acid; however, it produced a large amount of 3 : 5 : 3′ : 5′-tetranitrotetramethylbenzidine and nitrous acid; and the rest of the reaction, which led mainly to 2 : 4-dinitrodimethylaniline, obviously depended on this nitrous acid, because it could be inhibited by the addition of urea. The reaction in 40—55% aqueous nitric acid without added nitrous acid, if limited to short periods of time, proceeded without any appreciable oxidation to give nearly quantitative yields of 2 : 4-dinitrodimethylaniline (cf. Mertens, *Ber.*, 1877, **10**, 995); but on prolonged treatment, dealkylation with oxidation set in. With greater concentrations of nitric acid, processes involving dealkylation and oxidation assumed increased importance. These processes not only produced nitrous acid: they were also dependent on nitrous acid, pre-existing or produced, since they were retarded by the presence of urea.

The nitration of dimethylaniline by nitric acid in aqueous sulphuric acid has been studied

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* The ratio of the isomeric mononitro-products is likely to be sensitive to the experimental conditions. This matter is being investigated.

by Schuster and Pinnow (*Ber.*, 1896, **29**, 1053) and by Koch (*Ber.*, 1897, **30**, 2851). Their chief product was 2 : 4-dinitrodimethylaniline; but Pinnow showed (*Ber.*, 1899, **32**, 167) that some *o*-nitrodimethylaniline was also formed.

(3) *Discussion of the Mono- and Di-nitration of Dimethylaniline.*

(3.1) *The Main Routes to Nitration.*—Several nitration routes have to be distinguished. Each is related to the conditions of nitration; and each leads to different consequences.

One nitration route is isolated by the use of a medium of such a high acidity-function that nitration through the free amine is excluded, and nitration through the ammonium ion remains the only possibility. Nitration in a system thus deactivated will require the highly reactive nitronium ion in an appreciable concentration, such as can be built up, *e.g.*, in solvent sulphuric acid. Orientation will be mainly towards the *m*-position. The *m*-nitrated ammonium ion is so strongly deactivated that its further nitration, to give mainly a 3 : 5-dinitro-product, has not been observed. The further nitration which van Romburgh observed on adding water to a sulphuric acid solution which contained the *m*-nitro-ammonium ion (Section 2.1), evidently resulted from a reduction in the acidity-function, which permitted nitration through the free *m*-nitro-amine. Consistently, the second nitro-group entered *o*- and *p*-positions with respect to the dimethylamino-group.

Nitration through the free base leads to *o*- and *p*-nitro-products. It seems probable that two mechanisms are able to effect such nitration, one not dependent on nitrous acid, and the other fundamentally involving nitrous acid, just as with the nitration of phenolic ethers and phenols (Part VI). In this paper, as heretofore, we use the term " nitrous acid " to embrace all materials which, after dilution with water, could be collectively estimated as nitrous acid by ordinary analytical methods. Theoretically, we regard such materials, in so far as they do not consist of the nitrosonium ion itself, as carriers or sources of the nitrosonium ion. It is clear from recorded results that the nitration of dimethylaniline, as free base, is much less dependent on nitrous acid (in our generalised sense) when the availability of the nitronium ion, or of the carrier of the nitronium ion, is high, than when it is low (Section 2.4).

In the latter case, when nitration basically depends on nitrous acid, whether initially present or produced by oxidation, it seems established that the primary *p*-substitution product is *p*-nitrosodimethylaniline, which subsequently becomes oxidised to *p*-nitrodimethylaniline (Sections 2.3 and 2.4). Lang has suggested that the substituting agent in this mechanism is the nitrosonium ion (*loc. cit.*). The intermediate formation of a nuclear nitroso-compound has not yet been established for the *o*-nitration, or for the second stage of nitration, of dimethylaniline.

Either mechanism of nitration of the free base can proceed to a second stage, the product of which is 2 : 4-dinitrodimethylaniline. The dimethylamino-group does not usually suffer decomposition until the aromatic nucleus has been deactivated at least to the extent caused by the introduction of two nitro-substituents. However, nitrous acid is a potent reagent for dealkylation, and, when in high concentration, it can, as Hodgson found, dealkylate and nitrosate the dimethylamino-group in the presence of only one nuclear nitro-substituent (Section 2.4).

(3.2) *Reactivities in Mono- and Di-nitration.*—It is unusual to find, in successive nitration, a second nitro-group entering a benzene ring approximately as fast as the first; but that is what we do find in the reaction sequence, dimethylaniline ⟶ *p*-nitrodimethylaniline ⟶ 2 : 4-dinitrodimethylaniline (Section 2.3). This may mean merely that, because of the greater basic strength of dimethylaniline than of *p*-nitrodimethylaniline, a smaller proportion of the free base is present, under the conditions of nitration, in the former case than in the latter; the influence of the differing electrochemical equilibria might off-set the deactivating effect of the nitro-group on the reactivity of the aromatic nucleus.

One has to explain why the same relationship is not observed in the reaction sequence, dimethylaniline ⟶ *o*-nitrodimethylaniline ⟶ 2 : 4-dinitrodimethylaniline; and, indeed, why *o*-nitrodimethylaniline is further nitrated so much more slowly than is its *p*-isomeride. This we attribute to the steric inhibition, in *o*-nitrodimethylaniline, of the activating electron-displacements originating in the unshared electrons of the dimethylamino-group. For, as scale models show, an *o*-nitro-group will effectively prevent a dimethylamino-group from assuming by rotation that configuration which is most favourable to the conjugation of its unshared electrons with the mobile electrons of the aromatic ring. The steric inhibition by *ortho*-substituents of such conjugation between a dimethylamino-group and a benzene ring is well attested by dipole moments.

(4) *Observations on the Further Nitration of* 2 : 4-*Dinitrodimethylaniline.*

(4.1) *Possible Routes for the Nitration of* 2 : 4-*Dinitrodimethylaniline.*—The chief end-product of the nitration of dimethylaniline by nitric acid was first isolated by Mertens (*Ber.*, 1877, **10**, 995). It was identified by van Romburgh, who showed that it could be obtained by the nitration of methylaniline, and was *N* : 2 : 4 : 6-tetranitromethylaniline (*Rec. Trav. chim.*, 1883, **2**, 108, 304; 1889, **8**, 215). Its formation from both dimethylaniline and methylaniline by nitration with mixtures of nitric and sulphuric acids was reported by Langerscheidt (*Z. Ges. Schiess-Sprengstoff.*, 1912, 445), and its production from dimethylaniline by such a method was described by van Duin (*Rec. Trav. chim.*, 1917, **36**, 111).

Obviously, *N* : 2 : 4 : 6-tetranitromethylaniline must be formed through 2 : 4-dinitrodimethylaniline if the nitrated substance is dimethylaniline, or through 2 : 4-dinitromethylaniline if the starting point is methylaniline. It could not arise if a nitro-group should enter the 3-position during the initial stages of nitration of dimethylaniline, or of methylaniline. It has been shown that *m*-nitration does constitute a first stage in the nitration of both dimethylaniline and methylaniline in some conditions (cf. Sections 2.1, 2.2; cf. Nolan and Clapham, *Sci. Proc. Roy. Dublin Soc.*, 1923, **17**, 219). It has also been shown that, under conditions which preclude *m*-nitration, the formation of 2 : 4-dinitrodimethylaniline represents a well-marked step in the progressive nitration of dimethylaniline, whilst the production of 2 : 4-dinitromethylaniline is likewise a well-defined stage in the nitration of methylaniline (cf. Sections 2.3, 2.4; cf. Desvergnes, *Chim. et Ind.*, 1930, **24**, 785, 1304). Hodgson and Turner (*loc. cit.*) have observed the conversion of 2 : 4-dinitrodimethylaniline by nitric acid into 2 : 4-dinitromethylaniline. Desvergnes (*loc. cit.*) has studied the transformation of the latter substance, by means of mixtures of nitric and sulphuric acid, into *N* : 2 : 4 : 6-tetranitromethylaniline (cf. also Ryan and Sweeney, *Sci. Proc. Roy. Dublin Soc.*, 1923, **17**, 157).

Since the transformation of 2 : 4-dinitrodimethylaniline into *N* : 2 : 4 : 6-tetranitromethylaniline involves changes both in the amino-part and in the aryl part of the molecule, it must proceed in a series of steps; and we have attempted to discover the route, or routes, taken. The same problem has been attacked by Clarkson, Holden, and Malkin, the manuscript of whose paper (*J.*, 1950, 1556) we were allowed to see through the courtesy of Dr. T. Malkin. Account being taken of some slight difference of conditions, these authors' experimental findings appear to be consistent with ours. It is convenient here to set down a list containing, besides the initial and final substances, (I) and (VIII), a set, (II)—(VII), of the more probable intermediates :

(I.)	$2:4\text{-}(NO_2)_2C_6H_3\cdot NMe_2$	(V.)	$2:4:6\text{-}(NO_2)_3C_6H_2\cdot NMe_2$
(II.)	,, $\cdot NMeH$	(VI.)	,, $\cdot NMeH$
(III.)	,, $\cdot NMe(NO)$	(VII.)	,, $\cdot NMe(NO)$
(IV.)	,, $\cdot NMe(NO_2)$	(VIII.)	,, $\cdot NMe(NO_2)$

These suggested intermediates, (II)—(VII), are all known substances. As we have mentioned, Hodgson and Turner observed the conversion of (I) into (II). Ryan and Sweeney record the conversion of (II) by nitric acid into (VI) (*loc. cit.*). Lang observed the conversion of both (I) and (II) by nitric acid into both (III) and (VII), and also the conversion of both (II) and (III) by nitric acid into (IV) (*Compt. rend.*, 1948, **227**, 1284). We shall later report the conversion of (I) into (V) (Section 4.4). Thus it will be clear that all the proposed intermediates, (II)—(VII), can be produced, in either one step or several, from (I).

Next it is necessary to ascertain whether any of these proposed intermediates disqualifies itself by inability to behave as required : any of the compounds (II)—(VII) would have to be excluded from the list of possible intermediates, if it did not yield (VIII) as smoothly as (I) does under comparable conditions. We have therefore examined a fixed set of conditions (cf. Section 7.3) involving the use of nitric acid in aqueous sulphuric acid at room temperature; and we have measured the yields of (VIII). The yields were not quite quantitative, the products being not quite pure. We record below a series of corrected yields of (VIII), two corrections having been applied to the directly weighed yields. The first correction is for the solubility of (VIII) in the aqueous medium from which it was collected. The required solubility values were determined experimentally. The yields thus corrected are called " crude yields." The second correction seeks to allow for the impurities included in the crude yields. The proportions in which impurities are present in the weighed products can, in principle, be determined, as mol.-fractions, from the freezing points and cryoscopic constant. They were first obtained in this form by using clearing points and a roughly evaluated constant; and then, in order to produce comparable corrected yields, they were re-expressed as percentages by weight on the basis of the arbitrary assumption that the average molecular weight of the impurities is the same as the molecular weight of the main product. The resulting deductions on account of impurities having been made from the crude yields, we call the differences " pure yields " :

Initially taken	(I.)	(II.)	(III.)	(IV.)	(V.)	(VI.)	(VII.)
(VIII.) Crude yield (%)	91	97	97	97	100	100	100
(VIII.) Pure yield (%)	75	95	95	95	96	98	96

It will be seen that all the substances (II)—(VII) give better yields of (VIII) than were obtained from (I). It follows that all qualify, with respect to this test, for consideration as possible intermediates. The yield of (VIII) from (I) can be raised by working at higher temperatures, but the spread of the values is less if a general comparison is made in these conditions, and thus the test is less useful.

(4.2) *Nitration of* 2 : 4-*Dinitrodimethylaniline in Aqueous Nitric Acid.*—A part of the evidence we have to offer concerning the course pursued by the nitration of 2 : 4-dinitrodimethylaniline relates to the identification of products which are formed on nitrating this substance, under uniform conditions as to temperature and time, in aqueous nitric acid of a series of concentrations. The main results are set out below :

(I) treated with	" 40% "	" 50% "	" 70% "	" 98% " HNO_3
Product	(II)	(II) and (VII)	(VII)	(VIII)

Here the compositions of aqueous nitric acid are given by volume : for instance, " 40% " acid is the aqueous acid made by mixing 40 vols. of absolute nitric acid with 60 vols. of water.

The chemically simplest of these transformations is that by which 2 : 4-dinitrodimethylaniline (I) is converted into 2 : 4-dinitromethylaniline (II), with elimination of one of the methyl groups. This methyl group passes into oxidised forms, so that nitrous acid is produced in the course of the reaction. We have estimated that at least two molecules of nitrous acid are produced per molecule of 2 : 4-dinitrodimethylaniline converted. It is necessary to allow for this nitrous acid when one is considering whether 2 : 4-dinitromethylaniline could be an intermediate in the formation of the next of the isolated products, *N*-nitroso-2 : 4 : 6-trinitromethylaniline (VII). We find that, when 2 : 4-dinitromethylaniline is treated with " 70% " nitric acid, to which the indicated amount of nitrous acid has been added, the product is *N*-nitroso-2 : 4 : 6-trinitromethylaniline. Since this last substance is smoothly converted by " 98% " nitric acid into *N* : 2 : 4 : 6-tetranitromethylaniline (VIII), each of the changes of the following sequence is established :

(I) ⟶ (II) ⟶ (VII) ⟶ (VIII) . . . . (1)

(4.3) *Nitration of* 2 : 4-*Dinitromethylaniline and its* N-*Nitroso- and* N-*Nitro-derivatives in Aqueous Nitric Acid.*—Each of the steps (I) ⟶ (II) and (VII) ⟶ (VIII) results in a localised modification in the molecule. On the other hand, the conversion written (II) ⟶ (VII) involves substitution both in the side chain and in the nucleus, and therefore this process at least must consist of not less than two steps. Their nature can be inferred from Lang's investigation (*Compt. rend.*, 1948, **227**, 1284) of the action of aqueous nitric acid containing nitrous acid or 2 : 4-dinitromethylaniline (II). He found this substance to be converted by 40% nitric acid into *N*-nitroso-2 : 4-dinitromethylaniline (III). He further found, in agreement with a result given above, that his factor and product (II) and (III) were each converted by nitric acid, in higher concentrations up to 70%, into *N*-nitroso-2 : 4 : 6-trinitromethylaniline (VII). These additional data permit the sequence of reactions (1) to be expanded to the following :

(I) ⟶ (II) ⟶ (III) ⟶ (VII) ⟶ (VIII) . . . . . . (2)

Each step in this expanded sequence involves only one localised molecular change, and, though this does not mean that every step is necessarily constituted as a single chemical process, it does nevertheless seem probable that one route by which 2 : 4-dinitrodimethyaniline can be transformed into *N* : 2 : 4 : 6-tetranitromethylaniline has been traced in outline.

By the use of nitric acid in concentrations higher than 70%, Lang observed (*loc. cit.*) some conversion of both 2 : 4-dinitromethylaniline (II) and *N*-nitroso-2 : 4-dinitromethylaniline (III) into *N* : 2 : 4-trinitromethylaniline (IV). This suggests the possibility that an alternative reaction path from (I) to (VIII), proceeding *via* (IV), might be utilised in concentrated nitric acid. We have completed the evidence for the feasibility of such a route by showing that (IV) can be converted into (VIII) by nitric acid in concentrations above 70% (and even by hot 50% nitric acid). Thus the separate stages of the following sequence are established :

(I) ⟶ (II) ⟶ (IV) ⟶ (VIII) . . . . (3)

Each of these stages could represent a single chemical change; but the first and the last of them could alternatively each constitute the over-all result of a double change, as will be discussed in Sections 4.5 and 4.6.

It has been mentioned earlier that our kinetic experiments are too incomplete to be reported yet. However, it is relevant to remark that, at nitric acid concentrations near 90%, the rates of the conversions (II) ⟶ (VIII) and (IV) ⟶ (VIII) have been found to be identical. This confirms the common involvement of (II) and (IV) in the same chain of reactions; and it shows that, at the concentrations mentioned, the reaction route *via* (IV), which is provisionally represented by sequence (3), completely supersedes the route which by-passes (IV), and is represented by sequence (2).

(4.4) *Nitration of* 2 : 4-*Dinitrodimethylaniline by Nitric Acid in Aqueous Sulphuric Acid.*—We have investigated the identity of the products which are formed when 2 : 4-dinitrodimethylaniline is nitrated by nitric acid in aqueous sulphuric acid media of various compositions. Into each aqueous sulphuric acid medium, the nitrating agent was introduced, usually in several proportions, either in the form of nitric acid, or as urea nitrate, the purpose of the latter being to suppress nitrous acid. In presenting the results, we express the compositions of the aqueous sulphuric acid media as percentages by volume, " 50% " medium, for example, being one made by mixing equal volumes of anhydrous sulphuric acid and water. The proportions of nitrating agent, whether added in the form of nitric acid or of urea nitrate, are given as the number of molecules introduced per molecule of 2 : 4-dinitrodimethylaniline. With this explanation, we summarise the main results as follows :

Aq. H_2SO_4 medium	" 50% "		" 55—85% "	" 70% "	" 95% "		
HNO_3 (mols.)	2	5—10	2—10	—	1—3	—	10
Urea-HNO_3 (mols.)	—	—	—	1—5	—	1—3	—
(I) recovered	none	none	some	all	some	some	none
Product	(II)	(VII)	(VIII)	none	(V)	(V)	(VIII)

It is immediately apparent from these data that at least two different routes from 2 : 4-dinitrodimethylaniline (I) to *N* : 2 : 4 : 6-tetranitromethylaniline (VIII) are under observation. In " 50% " sulphuric acid, the isolated intermediates are 2 : 4-dinitromethylaniline (II) and *N*-nitroso-2 : 4 : 6-trinitromethylaniline (VII), just as in not very concentrated aqueous nitric acid (Section 4.2). In outline, this route is as follows :

$$\mathrm{(I)} \longrightarrow \mathrm{(II)} \longrightarrow \mathrm{(VII)} \longrightarrow \mathrm{(VIII)} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

The nature of the process occurring over the range " 55—85% " of sulphuric acid concentrations does not appear in the results given above; but we add some notes hereunder which point to the conclusion that, like the reaction in the " 50% " medium, the process which predominates over most of the range of media " 55—85% " starts with demethylation of the side chain. It does not follow that the subsequent steps are the same, and we shall show in the next Section that they are not.

In " 95% " sulphuric acid the reaction route is completely different. The first step is now the entry of the third nitro-group into the aromatic nucleus to give 2 : 4 : 6-trinitrodimethylaniline (V). Only after that does modification occur in the side chain. Provisionally this route is represented as follows :

$$\mathrm{(I)} \longrightarrow \mathrm{(V)} \longrightarrow \mathrm{(VIII)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

Three types of observation bear on the general nature of the reaction sequence over the intermediate range " 55—85% " of sulphuric acid compositions. The first has reference to the facility with which (VIII) is produced. Within the range of media " 55—85%," it was noticed that, whilst in a " 55% " medium an initial supply of only two molecular proportions of nitric acid brought about a substantial conversion of (I) into (VIII), the same amount of nitric acid produced very little reaction in a " 60% " medium, or in still more strongly acid media. Furthermore, with reference to the whole series of investigated media, it was observed that, at the extremes of the range, *i.e.*, in the " 50% " medium, and in the " 95% " medium, reaction was effected by lower concentrations of nitric acid, and, for a fixed concentration of nitric acid, reaction was more extensive, than in media of intermediate composition. From this it appears that the reaction routes which start with dealkylation are favoured in aqueous, and not too strongly acid, conditions, whilst the route which commences with nuclear nitration is assisted by strongly acidic conditions. We conclude that, in media of intermediate composition, there is not enough water to facilitate initial demethylation, and too much to be favourable to initial nuclear nitration, so that reaction by both routes is rendered more or less difficult.

The second group of observations relates to the strong purple colour which was observed to be developed during the course of all nitrations, which yielded (VIII), in aqueous sulphuric acid media of lower acid concentration than " 80%." In this " 80% " medium only a weak purple colour developed. In the " 85% " and " 95% " media no purple colour appeared. Now we have noticed that purple colours in general appear when (II), or (III), or (IV) is being nitrated to give (VIII); but that they do not appear when (V), or (VI), or (VII) is being converted into (VIII); and that they are not given by (VIII) itself; and also that they are not formed when (II), and (III), and (IV) are being interconverted among themselves, without transformation into (VIII). Obviously the production of the colour requires, *inter alia,* the presence of a nuclear position which is still available for substitution, and the existence of conditions in which it can be substituted. (Perhaps the source of the colour is a diaryloxidoammonium ion—cf. Part VI.) For these reasons, we interpret the observations on the conditions of appearance of the colour in the present series of experiments as meaning that the reaction routes which start with demethylation, and which therefore certainly pass through (II), and presumably through either (III) or (IV) or both, are in fact followed in aqueous sulphuric acid media having acid concentrations almost up to " 85%," although near the upper end of this concentration range, *e.g.*, in an " 80% " medium, these reaction routes are not the only ones which are pursued.

The third set of observations relates to the action of urea. This material completely inhibits reaction in the " 70% " medium, but exerts no such repressive effect on the reaction in the " 95% " medium. From the first of these two observations we draw two conclusions. One is that the initial demethylation depends upon nitrous acid. The other is that the reaction routes which start in this manner are the only routes utilised in aqueous sulphuric acid media having acid concentrations up to at least " 70%." (These routes continue, as we have seen, to retain some importance in media with acid concentrations up to " 85% ".) From the second of the observations we conclude that the nuclear nitration, which constitutes the initial step of the reaction sequence in the " 95% " medium, does not depend upon nitrous acid.

(4.5) *Nitration of 2 : 4-Dinitromethylaniline and of its* N-*Nitroso-* and N-*Nitro-derivatives by Nitric Acid in Aqueous Sulphuric Acid, and the Interconversion of the Three Compounds in Aqueous Acids.*—A simple experiment, which had yielded a substantial amount of information about the chain of reactions which succeeds initial demethylation in the nitration of 2 : 4-dinitrodimethylaniline by nitric acid in a " 70% " aqueous sulphuric acid medium, involves adding *N*-nitroso-2 : 4-dinitromethylaniline (III) to the nitrating acid at room temperature, and watching the colour changes. The original nitrosamine (III) is pale yellow. When it was put into the acid, it instantly turned bright orange, and began to dissolve, forming an orange solution. The colour of this solution faded rather quickly and, after about one minute, the solution suddenly became cloudy with the separation of a pale yellow solid. For a short time the deposition of this continued. Later, the colour of the solution deepened again, passing gradually into an intense purple; and meanwhile the pale yellow precipitate redissolved, and a new, nearly colourless, crystalline substance separated, the complete series of changes requiring about three hours. At each of the stages indicated by a colour change, or by the appearance or disappearance of a precipitate, a part of the solution or mixture was poured into water, and the product was isolated. In this way it was found that the orange substance was 2 : 4-dinitromethylaniline (II), that the pale yellow precipitate was *N* : 2 : 4-trinitromethylaniline (IV), and that the nearly colourless substance was *N* : 2 : 4 : 6-tetranitromethylaniline (VIII). Similar experiments were made starting, not with the nitrosamine (III), but the secondary base (II), and again with the nitramine (IV). The results were the same, except for the expected absence of the earlier reaction stages. Thus (II) was converted successively into (IV) and (VIII); also (IV) was converted into (VIII). The appearances marking these changes were as already described.

The first of the above results shows that the nitrosamine (III) is instantly acidolysed to the secondary base (II), in a medium which is strongly acidic, and not too concentrated with respect to nitrous acid. This has been confirmed in several ways. The nitrosamine (III) has been converted into the secondary base (II) by means of hydrochloric acid either in aqueous solution or in ether, by nitric acid in water or in acetic acid, and by sulphuric acid in water or acetic acid. In the denitrosation with hydrogen chloride in ether, the " nitrous acid " has been trapped and exhibited, by carrying out the reaction in the presence of dimethylaniline and isolating *p*-nitrosodimethylaniline as well as the secondary base (II).

On the other hand, Lang has shown (*Compt. rend.*, 1948, **227**, 1284) that the secondary base (II) is readily transformed into the nitrosamine (III) in an aqueous nitric acid which is not too concentrated with respect to nitric acid, but contains a large concentration of nitrous acid

(Section 4.3). We must conclude that the reaction (II) $\longrightarrow$ (III) is rapidly reversible in nitrating conditions, the position of equilibrium in a given medium depending on the balance between the activity of the proton carriers (acids), and of the nitrosonium ion carriers (" nitrous acid "), which are present in the medium.

This conclusion affects our view of the reaction sequences (2), (3), and (4), which, in Sections 4.3 and 4.4, were developed to represent routes utilised in the nitration of 2 : 4-dinitrodimethylaniline in somewhat dilute nitric acid, in more concentrated nitric acid, and in moderately dilute aqueous sulphuric acid, respectively. In each of these sequences, the first stage, written (I) $\longrightarrow$ (II), expresses an initial formation of the secondary base (II) by the demethylation process. But, as Hodgson showed (cf. Section 2.4) for demethylation in aqueous nitric acid, and as we have shown (Section 4.4) for demethylation in aqueous solutions containing both nitric and sulphuric acids, these aqueous demethylations are basically dependent on nitrous acid. It is therefore chemically reasonable to suppose that the primary product might be the nitrosoamine (III). This being so, our observations, establishing the mobile equilibrium (II) $\rightleftharpoons$ (III), open the possibility that what was taken to be the stage (I) $\longrightarrow$ (II) in the reaction schemes (2), (3), and (4), might represent an overall result of the two stages (I) $\longrightarrow$ (III) $\rightleftharpoons$ (II). This possibility remains open independently of whether further reaction takes place through (II), as in the sequences (3) and (4), or through (III), as in the sequence (2). We shall return to this question in Sections 5.1, 6.1, and 6.2.

Another result of the described experiment is that the secondary base (II) is readily nitrated by nitric acid in " 70% " aqueous sulphuric acid to give the nitramine (IV). Lang made a corresponding observation for nitration by moderately concentrated nitric acid (cf. Section 4.3). Lang demonstrated the reverse reaction, by showing that the nitramine (IV) became denitrated in aqueous sulphuric acid, to give back the secondary base (II) (*Compt. rend.*, 1948, **227**, 1284). We have made similar observations using other aqueous strong acids, such as hydrochloric acid, as is reported in Part VIII (following paper). It must therefore be concluded that the secondary base and the nitroamine are reversibly interconvertible in acidic nitrating conditions, the position of the equilibrium (II) $\rightleftharpoons$ (IV) depending on the relative activities with which proton carriers (acids) and nitronium ion carriers (" nitric acid ") are present in the medium employed. By suppressing one or other of these types of reagent, we can make the conversion substantially irreversible in either direction. Now by treating (IV) with an aqueous strong acid, in the initial absence of nitric acid, and therefore at a low average concentration of nitric acid, we have rendered the denitration (IV) $\longrightarrow$ (II) nearly quantitative (*ibid.*). Again, by subjecting (II) to nitrating conditions in the initial absence of acid, for instance, by treating (II) with dinitrogen pentoxide in chloroform, or with " acetyl nitrate " in acetic anhydride (cf. Parts IV and V, *J.*, 1950, 2452, 2467), we have made the *N*-nitration nearly quantitative (*ibid.*). Thus reversibility in the nitration–denitration system (II) $\rightleftharpoons$ (IV) is established, just as is that of the nitrosation–denitrosation system (II) $\rightleftharpoons$ (III). However, there is a very distinct kinetic difference between the two systems; for under the conditions in which we have attempted to follow the course of the nitration of 2 : 4-dinitrodimethylaniline, the reversible nitration (II) $\rightleftharpoons$ (IV) reaches equilibrium much less rapidly than does the reversible nitrosation (II) $\rightleftharpoons$ (III).

The circumstance that the system (II) $\rightleftharpoons$ (IV) involves (II), which is also a member of the more mobile system (II) $\rightleftharpoons$ (III), presents us with the problem of determining whether it is really (II), rather than (III), which is converted into, and is formed from, (IV). For example, nothing in the observations so far mentioned distinguishes between the direct forward change (II) $\longrightarrow$ (IV), and a sequence of two changes (II) $\rightleftharpoons$ (III) $\longrightarrow$ (IV), fulfilling the condition that the first is rapid and strongly reversed, while the second is slow. The following is an attempt to solve this problem.

The suggested unit process (III) $\longrightarrow$ (IV) can conceivably occur in only two ways, *viz.*, (1) as a direct oxidation, $>\mathrm{N{\cdot}NO} \longrightarrow\ >\mathrm{N{\cdot}NO_2}$, and (2) as a single-stage bimolecular substitution $\mathrm{NO_2^+} + >\mathrm{N{\cdot}NO} \longrightarrow\ >\mathrm{N{\cdot}NO_2} + \mathrm{NO^+}$. We shall adduce reasons for believing that, in fact, it does not take place by either of these mechanisms. We think that it cannot proceed by oxidation, because we have attempted to effect the conversion with other strong oxidising agents, such as hydrogen peroxide and Caro's acid, but with complete lack of success. We think that it cannot proceed by substitution, because, under our usual nitration conditions, the equilibrium (II) $\rightleftharpoons$ (III) is strongly on the side of (II); and therefore an *N*-nitrating substitution in this system would proceed through (III) rather than through (II), only if it were intrinsically much easier in electrophilic substitution to effect the expulsion of a nitrosonium ion, than of a proton, from combination with the nitrogen atom of the amine. This seems an impossible assumption, whether one bases one's views on experience of proton transfers in general, or on the more specific ground that, even in aromatic *C*-nitration, protons are ejected rapidly (Part II, *J.*, 1950, 2400). Therefore we conclude that the interconversion of (III) and (IV) does not take place directly, but proceeds by way of (II):

$$\text{(III)} \rightleftharpoons \text{(II)} \rightleftharpoons \text{(IV)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

In the course of these experiments with the nitrosamine (III), we have observed no sign of its isomerisation in the presence of acids to 2-nitroso-4 : 6-dinitromethylaniline. The effect of acids on (III) is to denitrosate it to (II), not to isomerise it. The conclusion is that isomerisation of the nitrosamine does not contribute to the series of changes with which we are now concerned. The nitramine (IV) is in a different case: for, as we shall indicate in Section 4.6, it is isomerised by acids in certain conditions to 2 : 4 : 6-trinitromethylaniline (VI).

A result of the various observations reported in this Section is that we are now in a position to set down an outline scheme for the nitration of 2 : 4-dinitrodimethylaniline in " 70% " aqueous sulphuric acid. It is as follows:

$$\text{(I)} \longrightarrow \text{(III} \rightleftharpoons \text{II)} \longrightarrow \text{(IV)} \longrightarrow \text{(VIII)} \quad . \; . \; . \; . \; . \; . \quad (7)$$

Route (7) for nitration in " 70% " sulphuric acid is essentially identical with route (3) for the reaction in concentrated nitric acid. In route (7), as in route (3), the change (IV) ⟶ (VIII), which we have yet to discuss in detail, is not necessarily a single process.

(4.6) *The Rearrangement of* N *: 2 : 4-Trinitromethylaniline in Sulphuric Acid Media and its Nitration by Nitric Acid.*—One of the two types of nitration media, in which a route for the nitration of 2 : 4-dinitrodimethylaniline has been diagnosed which proceeds through the nitroamine (IV), is aqueous sulphuric acid in concentrations near " 70% " (Section 4.6).

Lang has reported (*Compt. rend.*, 1948, **227**, 1284) that *N* : 2 : 4-trinitromethylaniline (IV) is converted by 96% sulphuric acid into its rearrangement product, 2 : 4 : 6-trinitromethylaniline (VI). We find (cf. Part VIII) that in concentrated sulphuric acid this transformation is instantaneous, but that in " 70% " aqueous sulphuric acid it is measurably slow, requiring, for instance, several hours at the ordinary temperature to proceed substantially to completion.

The transformation of (IV) into (VI) is intramolecular: it does *not* consist of a denitration followed by a re-nitration, (IV) ⟶ (II) ⟶ (VI). These conclusions are fully established in Part VIII (following paper).

If nitric acid is added to the solution which is obtained by allowing (IV) to be converted into (VI) in " 70% " aqueous sulphuric acid, or if it is added to a solution prepared by dissolving the isolated compound (VI) in the " 70% " acid, then the compound (VI) is rapidly nitrated to give *N* : 2 : 4 : 6-tetranitromethylaniline (VIII). This reaction is sufficiently facile to secure that, if (VI) were formed by rearrangement of (IV) in " 70% " aqueous sulphuric acid, in the presence of an adequate supply of nitric acid added initially, then the product isolated would be (VIII).

The rate of the overall conversion of (IV) into (VIII) in " 70% " aqueous sulphuric acid containing nitric acid is of the same order of magnitude as the rate of the conversion of (IV) into (VI) in the " 70% " sulphuric acid without the nitric acid. It is therefore of the same order of magnitude as the rate of the conversion of (IV) successively into (VI) and (VIII) in the " 70% " sulphuric acid containing nitric acid, since the second of the two reactions is much faster than the first. The evidence is therefore complete that, under the conditions in which the change (IV) ⟶ (VIII) has been observed in " 70% " aqueous sulphuric acid, much of the reaction must, and all of it may, pursue the two-stage sequence

$$\text{(IV)} \longrightarrow \text{(VI)} \longrightarrow \text{(VIII)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

The step (IV) ⟶ (VI) is irreversible. The step (VI) ⟶ (VIII) is reversible, but we shall be discussing this in Section 4.7.

The other type of medium, in which a route for the nitration of 2 : 4-dinitrodimethylaniline has been detected which proceeds through *N* : 2 : 4-trinitromethylaniline (IV), is aqueous nitric acid of concentration not less than " 70% " (Section 4.3). In this case our evidence concerning the nature of the reaction by which *N* : 2 : 4-trinitromethylaniline is converted into *N* : 2 : 4 : 6-tetranitromethylaniline (VIII) is not complete. The difficulty is that we cannot study the rearrangement of *N* : 2 : 4-trinitromethylaniline to 2 : 4 : 6-trinitromethylaniline (VI) in isolation, because of the great rapidity with which the last-named substance is nitrated to *N* : 2 : 4 : 6-tetranitromethylaniline in the nitric acid medium. All we can show is that the nitration (VI) ⟶ (VIII) is sufficiently fast compared with the overall conversion

(IV) ⟶ (VIII) to allow it to be supposed that the reaction follows the two-stage sequence (8). Kinetic measurements which establish these comparisons will be reported later.

(4.7) *Interconversion of* 2 : 4 : 6-*Trinitrodimethylaniline,* 2 : 4 : 6-*Trinitromethylaniline,* N-*Nitroso*-2 : 4 : 6-*trinitromethylaniline, and* N : 2 : 4 : 6-*Tetranitromethylaniline.*—In " 95% " aqueous sulphuric acid, the nitration of 2 : 4-dinitrodimethylaniline pursues a different course from any that has been established for nitration in more aqueous solutions : in the concentrated acid the initial process is not demethylation, but nuclear nitration to form 2 : 4 : 6-trinitrodimethylaniline (V) (Section 4.4). Demethylation and modification of the side chain set in subsequently, and we have now to consider what can be learned about these processes by experimenting with 2 : 4 : 6-trinitrodimethylaniline, and with the products that can be derived from it.

2 : 4 : 6-Trinitrodimethylaniline (V), when treated with 10 mols. of nitric acid in " 95% " aqueous sulphuric acid, was transformed into *N* : 2 : 4 : 6-tetranitromethylaniline (VIII). A similar experiment with " 70% " aqueous sulphuric acid as the medium led to the same result. However, when in this medium the proportion of nitric was reduced to 2 mols., the simple demethylation product, 2 : 4 : 6-trinitromethylaniline (VI), was obtained.

2 : 4 : 6-Trinitromethylaniline (VI) is known to be very easily nitrated to *N* : 2 : 4 : 6-tetranitromethylaniline (VIII). Lang has studied the conversion, using aqueous nitric acid of concentration " 70% " or higher (*Compt. rend.*, 1948, **227**, 1284). We have studied the kinetics of the nitration under such conditions, though this will be reported later. We have also employed, as nitrating agent, solutions of nitric acid in aqueous sulphuric acid media of concentration " 55% " or higher. Under these conditions the reaction is appreciably reversible, as is shown by the following experiments.

Lang has reported the denitration of *N* : 2 : 4 : 6-tetranitromethylaniline to 2 : 4 : 6-trinitromethylaniline by the action of sulphuric acid (*loc. cit.*). We have observed the same reaction in aqueous sulphuric acid; and, using aqueous sulphuric acid containing nitric acid, we have followed the attainment of equilibrium from either side in the balanced reaction (VI) $\rightleftharpoons$ (VIII). The equilibrium depends on the acidity of the medium in relation to its nitrating power, *i.e.*, on the conflict between carriers of the proton and those of the nitronium ion. A rise of temperature appears to favour denitration.

These observations establish the following reaction sequence, which is possibly an adequate representation of the processes by which the side chain of (V) may be modified in the experimental conditions in which (V) is known to be formed during the nitration of 2 : 4-dinitrodimethylaniline in aqueous sulphuric acid :

$$\text{(V)} \longrightarrow \text{(VI)} \rightleftharpoons \text{(VIII)} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (9)$$

But since the demethylation produces nitrous acid, *N*-nitroso-2 : 4 : 6-trinitromethylaniline (VII) is a possible intermediate product; and therefore its formation from, and conversion into, the compounds involved in scheme (9) require examination.

The nitrosamine (VII) is on the whole more easily produced in nitric acid than in sulphuric acid media. When (V) is demethylated, to produce nitrous acid, by " 70% " aqueous nitric acid, or by " 70% " nitric acid containing initially added nitrous acid, (VII) is formed. We have observed that, when (VII) is treated with " 70% " nitric acid for some hours at the ordinary temperature, (VIII) is produced.

The relative rates of these reactions are of interest. We found that, in " 70% " nitric acid containing 0·25—0·75M-nitrous acid, (VI) was converted into (VII) almost completely, and much more rapidly than (VI) was converted into (VIII) in the same aqueous nitric acid without the nitrous acid; and, furthermore, that, with this acid as the initial nitrating medium, (VI) was converted into (VIII) much more rapidly than (VII) was transformed into nitrous acid and (VIII).

Because of the comparative rapidity of the reaction (VI) ⟶ (VII), we cannot tell from these observations whether or not the conversion (V) ⟶ (VII) proceeds by way of (VI) in nitric acid. Again, owing to the comparative rapidity of the reaction (VI) ⟶ (VIII), one cannot deduce from the presented results whether or not the observed change (VII) ⟶ (VIII) takes place by way of (VI) in nitric acid. These questions will, however, be further pursued in Sections 5.1, 6.1, and 6.2.

It has been mentioned that, in nitric acid media, (VI) may be nitrosated to (VII) fairly completely. The denitrosation of (VII) to yield (VI) is easily effected in sulphuric acid media, as has been reported by Lang (*loc. cit.*). It follows that, in strong acids containing nitrous acid, an equilibrium (VI) $\rightleftharpoons$ (VII) will be set up, the position of which must depend on the balance obtaining between the nitrosating power and acidity of the medium, *i.e.*, on the relative availability of nitrosonium ions and protons.

If a solution in which such an equilibrium can be set up is also a nitrating medium, then it should be possible successively to denitrosate (VII) to (VI) and to nitrate (VI) to (VIII) in a single experimental operation. Using " 70% " aqueous sulphuric acid containing nitric acid, we have observed the overall conversion of (VII) into (VIII). But we have been unable either to establish the dissection of the process into stages, or to prove convincingly that it proceeds by an independent one-stage route. The following evidence is submitted for what it is worth. The free amine (VI) has a deep orange-yellow colour, whilst the nitrosamine (VII) is pale yellow, and the nitramine (VIII) is almost colourless. A conversion of (VII) into (VIII) by way of (VI) might have been diagnosed as a two-stage process by an observation of a temporary deepening of the yellow colour during the change, just as was done for the corresponding compounds containing only two nuclear nitro-groups (Section 4.5). In the present case no sign of such a transient deepening of colour could be seen : the pale yellow colour of the nitrosamine faded continuously as the nitramine was produced.

On the basis of these results, we now elaborate scheme (9) as follows :

$$\begin{tikzcd}
\text{(V)} \arrow[r] \arrow[dr] & \text{(VI)} \arrow[r, harpoon, shift left] \arrow[d, harpoon, shift left] & \text{(VIII)} \arrow[l, harpoon, shift left] \\
& \text{(VII)} \arrow[u, harpoon, shift left] \arrow[ur] &
\end{tikzcd} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

However, certain questions which this diagram might be thought to decide are actually held in reserve. For first, it is uncertain whether the changes (V) $\longrightarrow$ (VII) and (VII) $\longrightarrow$ (VIII) are independent single-stage processes, or are covered by combinations of the other represented changes. Secondly, if it should be decided that the change (V) $\longrightarrow$ (VII) is a unit process, then, in the absence of new evidence, we should have to agree that the process (V) $\longrightarrow$ (VI) might, or might not, be single; for the balanced system (VI) $\rightleftharpoons$ (VII) is probably mobile enough to permit the appearance of either of the participating compounds under the conditions of their observed production, even if only one route should exist from (V) into the mobile system.

(5) *Observations on the Demethylation of* 2 : 4-*Dinitrodimethylaniline and* 2 : 4 : 6-*Trinitrodimethylaniline during Nitration.*

(5.1) *Dealkylation of Alkylated Derivatives of Aniline by Nitric Acid, by Nitrous Acid, and by Dinitrogen Tetroxide.*—We refer first to the investigation, described in Part VI (*J.*, 1950, 2628), concerning the dealkylations which accompany the nitration of phenolic ethers. It was shown that the methyl group of *p*-chloroanisole is in part eliminated during the nitration of this substance in conditions in which the substitution does not depend on nitrous acid; and that the group is eliminated more extensively during nitration in other conditions in which the total reaction fundamentally depends on nitrous acid. The methyl group was recovered as methyl acetate after nitration in acetic acid as solvent ; this shows that it was eliminated in a non-oxidised form. On the other hand, the ethyl group eliminated during the nitration of *p*-chlorophenetole in similar conditions became oxidised.

Other workers have established the general tendency to the elimination of one, but only one, alkyl group during the nitration and nitrosation of dialkylanilines, and also the tendency of the group to be eliminated in an oxidised form. Reilly and Hickinbottom (*J.*, 1920, **117**, 135) studied the nitration of methyl-*n*-butyl-, ethyl-*n*-butyl-, and di-*n*-butyl-aniline by an excess of fuming nitric acid and acetic acid. In each case the aromatic product was an *N* : 2 : 4 : 6-tetranitroalkylaniline, one alkyl group having been eliminated. In the example of di-*n*-butylaniline, the same product was obtained when the nitrating agent was a mixture of nitric acid and sulphuric acid, and in this case butyric acid also was recovered. Davidson and Reade (*J.*, 1939, 1701) examined the action of nitrous acid on dimethylaniline-*p*-sulphonic acid. They obtained *N*-nitroso-*p*-nitromethylaniline. Nitric oxide was evolved, and the eliminated methyl group was recognised as formaldehyde. Hodgson and Nicholson (*J.*, 1941, 470) studied the actions of nitrous acid on other dialkylanilines, establishing Et > Me > CH_2Ph as the order of ease of elimination of the alkyl group.

We have noticed in a number of examples that the dealkylation of a dialkylaniline in nitric acid media is strongly accelerated by added nitrous acid. This has been demonstrated for the transformation of 2 : 4-dinitrodimethylaniline (I) into *N* : 2 : 4-trinitromethylaniline (IV) by anhydrous nitric acid in acetic acid. It has been established for the conversion of 2 : 4 : 6-trinitrodimethylaniline (V) into *N* : 2 : 4 : 6-tetranitromethylaniline (VIII) by nitric acid in " 90—95% " aqueous sulphuric acid. It is concluded that nitrous acid is a much more powerful dealkylating agent for aromatic tertiary amines than is nitric acid. Furthermore, it appears that, since all these alkyl eliminations involve oxidation with the production of nitrous acid, this material is likely to be by far the most effective, perhaps the only effective, dealkylating agent present in our nitrating conditions.

Whereas sodium nitrite (5 mols.), when added to a solution of 2 : 4-dinitrodimethylaniline (I) in concentrated sulphuric acid at room temperature, had little demethylating action, the subsequent addition of water to produce a " 70% " acid, or a somewhat more dilute acid, resulted in a rapid reaction, which produced *N*-nitroso-2 : 4-dinitromethylaniline (III) with loss of a methyl group. Similar effects were observed on starting with 2 : 4-dinitrodiethylaniline, which, after the same treatment, produced *N*-nitroso-2 : 4-dinitroethylaniline. We take these results to mean that the process of dealkylation by nitrous acid requires the free amine, and that it is inhibited in a medium having so high an acidity function that conversion of the base into the ammonium salt is complete.

Dinitrogen tetroxide in organic solvents effected the dealkylation of 2 : 4-dinitrodimethylaniline and 2 : 4-dinitrodiethylaniline in a particularly smooth manner; and there was an interesting difference in the nature of the product according to the solvent used. When acetic acid was the solvent, the products were what they would have been if dealkylation had been effected by nitrous acid in an aqueous acid medium: they were the *N*-nitroso-2 : 4-dinitroalkylanilines. However, when chloroform was the solvent, the products were the 2 : 4-dinitroalkylanilines. Since these secondary amines were rapidly nitrosated by dinitrogen tetroxide in acetic acid to give the *N*-nitroso-compounds, whereas the latter could not be denitrosated by dinitrogen tetroxide in chloroform to give the amines, we have, for a restricted range of conditions, an answer to the question of whether the secondary amine or the nitrosoamine is the more immediate dealkylation product: clearly, the secondary amine is, for it is formed in conditions in which the nitrosoamine is the thermodynamically stable product. We shall later generalise this conclusion.

We have made some additions to recorded observations concerning the fate of alkyl groups eliminated from tertiary amines in nitrating or nitrosating conditions. It was noted above that an eliminated methyl group has previously been recognised as formaldehyde. We have decomposed 2 : 4-dinitrodimethyl-, 2 : 4-dinitrodiethyl-, and 2 : 4-dinitrodi-*n*-butyl-aniline with aqueous nitric acid containing nitrous acid, and have obtained formaldehyde, acetaldehyde, and *n*-butaldehyde, respectively, each isolated as its 2 : 4-dinitrophenylhydrazone. The least oxidised form in which an eliminated *n*-butyl group has previously been recovered is *n*-butyric acid. It seems natural to regard *n*-butaldehyde as an earlier product. We proved that it was inadmissible to regard *n*-butyl alcohol as a still earlier product by showing that this substance, when placed under comparable conditions, was converted into *n*-butyl nitrite.

In the products of the reactions of dinitrogen tetroxide with 2 : 4-dinitrodimethylaniline and 2 : 4-dinitrodiethylaniline in organic solvents we recognised formaldehyde and acetaldehyde, respectively. On all the evidence, we conclude that aldehydes are the first isolable forms to be assumed by primary alkyl groups eliminated from simple tertiary amines by the action of any of the group of substances which we cover by the term " nitrous acid."

(5.2) *Dealkylation of Alkylated Derivatives of Aniline by Chromic Acid and Permanganic Acid.*—Since the dealkylation of aromatic tertiary amines, as induced by nitrous acid, is closely connected with oxidation, it seemed desirable to compare the dealkylating action of nitrous acid with the oxidising action on tertiary amines of some common oxidising agents such as chromic and permanganic acids.

Some significant facts about the action of chromic acid are already known. Van Romburgh (*Rec. Trav. chim.*, 1889, 8, 249) examined the behaviour of this reagent towards 2 : 4-dinitrodimethylaniline and 2 : 4-dinitrodiethylaniline. He obtained 2 : 4-dinitromethylaniline and 2 : 4-dinitroethylaniline in the respective cases; and in the second case demonstrated the formation of acetaldehyde. In marked contrast to the reactions with nitrous acid, continued treatment with chromic acid removed the remaining alkyl group from each secondary amine. In agreement with these results, we have found that, whilst 2 : 4-dinitrodiethylaniline, on treatment with a solution of chromium trioxide in acetic acid, lost only one alkyl group giving 2 : 4-dinitroethylaniline and acetaldehyde, the same tertiary amine, on interaction with chromic acid in " 30% " aqueous sulphuric acid, lost both groups yielding 2 : 4-dinitroaniline, together with acetaldehyde. Pinnow and Wiskott have recorded (*Ber.*, 1899, **32**, 913) that 2 : 4-dinitrodibenzylaniline is degraded to 2 : 4-dinitroaniline, even by a solution of chromium trioxide in acetic acid.

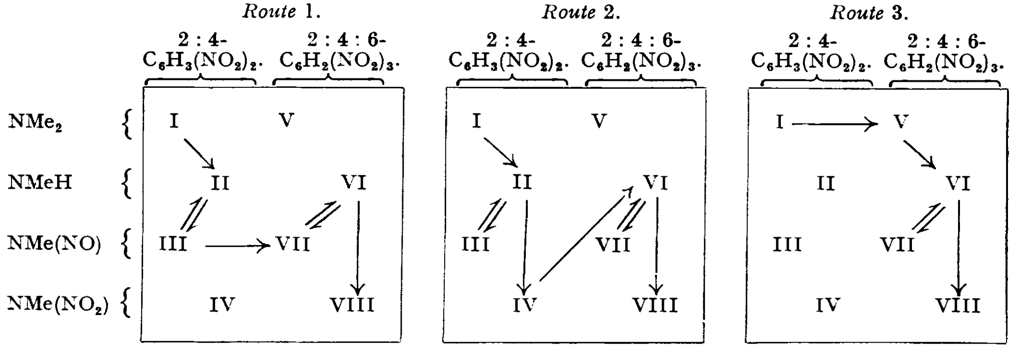
The indication we see here, that benzyl groups are more easily eliminated than ethyl groups in these reactions, is extended in some results obtained by Mulder (*Rec. Trav. chim.*, 1899, **8**, 117), who examined the action of chromium trioxide in acetic acid solution on a number of 2 : 4-dinitrodialkylanilines containing unlike groups and established, *inter alia*, that the benzyl group is eliminated in preference to the methyl group. We should certainly expect the benzyl group to be more vulnerable than either the methyl or the ethyl group, if the seat of the oxidising attack is in the alkyl group itself. But the result forms a second major contrast to what has been found for the oxidative elimination of alkyl groups from tertiary amines by means of nitrous acid, *viz.*, that the benzyl group is less easily eliminated than either the methyl or the ethyl group (Section 5.1). Obviously there is some fundamental difference between the mode of action of chromic acid and that of nitrous acid : we shall later suggest that this difference is connected essentially with the location of the oxidising attack.

The action of permanganic acid on tertiary aromatic amines has been briefly examined. As far as the matter has been pursued, the results suggest analogies with the action of chromic acid, rather than with that of nitrous acid. When a solution of 2 : 4-dinitrodimethylaniline in " 35% " sulphuric acid was treated with potassium permanganate, a vigorous reaction set in which produced 2 : 4-dinitromethylaniline and some formaldehyde. A similar experiment with 2 : 4-dinitrodiethylaniline gave 2 : 4-dinitroaniline and acetaldehyde. Thus permanganic acid, like chromic acid, is able to remove both alkyl groups from a dialkylated aromatic amine.

(6) *Discussion of the Further Nitration of* 2 : 4-*Dinitrodimethylaniline.*

(6.1) *Routes followed in the Conversion of* 2 : 4-*Dinitrodimethylaniline into* N : 2 : 4 : 6-*Tetranitromethylaniline.*—In writing this paper we have taken the view that the observations bearing on the course of the further nitration of 2 : 4-dinitrodimethylaniline were too numerous to make it convenient to report them in their entirety before attempting any collation; and therefore in Sections 4 and 5 we have separated the observations into a number of groups, associating with the record of each group a partial interpretation, essentially for the purpose of summarising the data. It now remains to assemble these partial interpretations into a picture of the overall process.

The course of the transformation of 2 : 4-dinitrodimethylaniline into *N* : 2 : 4 : 6-tetranitromethylaniline has been discussed before, but not always with a due appreciation of the circumstances that different routes are followed in different experimental conditions. We think that the evidence which has been accumulated points to three main routes, each probably capable of minor variations. We call the Routes 1, 2, and 3, and they are represented in the diagrams below, the associated legends indicating in an approximate way the types of experimental conditions to which the routes respectively apply.



40—70% *Aqueous* HNO_3; *or* HNO_3 *in* ca. 50% *aqueous* H_2SO_4.

70—100% *Aqueous* HNO_3; *or* HNO_3 *in* ca. 70% *aqueous* H_2SO_4.

HNO_3 *in* ca. 95% *aqueous* H_2SO_4.

We must mention the points in which these diagrams make constituent reactions appear more definite than, strictly, the evidence warrants. The first relates to the question of which is the end of the mobile system (II) $\rightleftharpoons$ (III) through which material enters it from (I) in Routes 1 and 2, and, correspondingly, which is the end of the system (VI) $\rightleftharpoons$ (VII) through which material enters from (V) in Route 3. The diagrams express the opinion that in every case the tertiary amine, on demethylation by nitrous acid, gives first the secondary amine. However, this has been experimentally established (Section 5.1) only for dealkylation in feebly polar solvents, in which the process (I) ⟶ (II) ⟶ (III), for example, can be separated into its stages. Theory enters when we extend this conclusion to demethylation in polar solvents, though the arguments seem good, as we shall hope to show in Section 6.2.

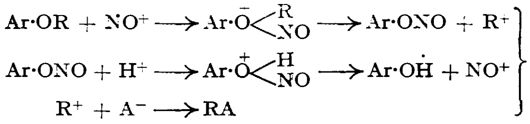
The other main matter which is a little more open than the diagrams suggest is the question of which is the end of the mobile system (VI) $\rightleftharpoons$ (VII) through which material leaves it on passing into (VIII). The diagrams represent it to be (VI). The relevant facts are that (VI) is converted much more easily than (VII) into (VIII), even if, as is doubtful, (VII) can be converted at all into (VIII) directly, rather than through (VI). It follows that material will certainly leave the system (VI) $\rightleftharpoons$ (VII) by way of (VI) in all circumstances except possibly when the medium is so highly charged with nitrous acid that the system (VI) $\rightleftharpoons$ (VII) exists as (VII) to the almost complete exclusion of (VI). In this case it remains doubtful whether (VII) will actually pass into (VIII) by way of (VI) or directly.

Of the three routes described * for the dealkylation and further nitration of 2 : 4-dinitrodimethylaniline, Routes 1 and 2 commence with demethylation, and for this the essential reagent is nitrous acid. The nature of the substituting agent responsible for the subsequent nitration stages is undetermined for Route 1; but it is indirectly indicated to be the nitronium ion for the *N*-nitrations of Route 2. The initial step in Route 3 is *C*-nitration; and here it may be considered certain that the reagent is the nitronium ion.

Recalling the discussion in Section 3, we notice that in the nitration, without demethylation, of dimethylaniline to yield successively *o*- or *p*-nitro-, 2 : 4-dinitro-, and 2 : 4 : 6-trinitro-dimethylaniline, the first and the second nitro-group enter, at least partly, by what, in Part VI, was called the " special " nitration mechanism, and interpreted as arising from aromatic attack by the nitrosonium ion; whilst the third nitro-group cannot be introduced by this substituting agent, but requires the intervention of the " general " nitration mechanism, with its more powerful electrophilic reagent, the nitronium ion.

(6.2) *Mechanism of the Dealkylation accompanying Nitrosation and Nitration.*—We shall here discuss the mechanism of dealkylation by " nitrous acid," using this term in our generalised sense. Much of what has to be said may well apply, with an obvious modification, to the less facile process of dealkylation by nitric acid, when it occurs. We have to keep in mind that dealkylations are prevalent during the nitrosation and nitration of phenolic ethers, as well as in the corresponding reactions of tertiary alkylated aromatic amines.

Our first conclusion is that, within this field as a whole, there are *two* mechanisms of dealkylation. One is especially important for the dealkylation of phenolic ethers. It is non-oxidative. It was observed (Part VI, *J.*, 1950, 2628), free from any accompanying oxidation process, in connexion with the nitrous acid-catalysed nitration of *p*-chloroanisole. It was recognised as heterolytic, and fundamentally allied in mechanism to the well-established heterolyses of 'onium ions. An explanation which was given assumed that the nitrosonium ion adds itself to the oxygen atom of the phenolic ether, thereby causing the loss of a carbonium ion, although later the nitrosonium ion itself is sent away in consequence of the uptake of a proton :



$$\left.\begin{array}{l}\mathrm{Ar{\cdot}OR} + \mathrm{NO^+} \longrightarrow \mathrm{Ar{\cdot}}\overset{-}{\mathrm{O}}{<}^{\mathrm{R}}_{\mathrm{NO}} \longrightarrow \mathrm{Ar{\cdot}ONO} + \mathrm{R^+} \\ \mathrm{Ar{\cdot}ONO} + \mathrm{H^+} \longrightarrow \mathrm{Ar{\cdot}}\overset{+}{\mathrm{O}}{<}^{\mathrm{H}}_{\mathrm{NO}} \longrightarrow \mathrm{Ar{\cdot}OH} + \mathrm{NO^+} \\ \qquad \mathrm{R^+} + \mathrm{A^-} \longrightarrow \mathrm{RA} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Here A⁻ is any available anion, taken from a molecule if necessary, for instance, an acetate ion taken from solvent acetic acid. A significant characteristic of this mechanism is the recovery of R as RA.

The other mechanism is oxidative. It is of particular importance for the dealkylation of tertiary amines. We diagnose it as homolytic, and consider that it enters our field of observation, competing successfully with the heterolytic mechanism, essentially for the reason that solvated NO^+ and neutral NO are comparably stable structures differing by one electron, with the consequence that the NO-group can add to any basic centre as NO^+ and come away as NO, thereby carrying off one electron and effecting an oxidation. We assume the first step to be the

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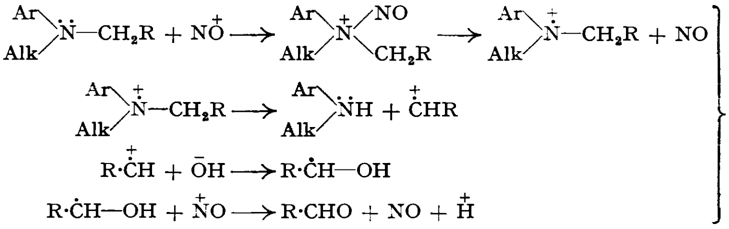
* We have to keep in mind that routes may be utilised other than those described. One of the likelier additional routes is one involving the direct nuclear nitration of (IV) to (VIII). We could not discern this, but none of our observations excludes it, or even renders it particularly improbable.

same as is shown for the heterolytic mechanism, *viz.*, the formation of nitrosammonium ion; but now this, instead of losing a carbonium ion, loses neutral nitric oxide (which, in fact, is evolved, unless nitric acid is present in sufficient concentration to oxidise it). The resulting incomplete electron shell is then made good by the internal transfer of a hydrogen atom, and the alkyl group thus disrupted is split off as a radical-cation, which combines with any available anion (*e.g.*, OH^-), and, after losing its odd electron to the oxidising environment (*e.g.*, to NO^+), finishes its career as an aldehyde:



. . . (12)

The chief points (Section 5.1) which a theory of the oxidative mode of dealkylation must explain are (1) why the reaction seems to require the amine itself rather than its cation, (2) why the reaction works with a tertiary amine but not with a secondary one, (3) why the eliminated alkyl group appears as an aldehyde, (4) why the alkyl group most easily eliminated is not necessarily that most prone to oxidation, (5) why the primary dealkylation product, at least in an aprotic solvent, is the secondary amine, even when the thermodynamically stable product is the nitrosoamine, and (6) why this collection of characteristics arises particularly with nitrous acid as the reagent. Answers to all these questions are suggested by the mechanism. (1) The oxidising agent happens to be a typical co-ordinating electrophile with an affinity for basic electron-pairs. (2) The nitrosammonium ion which it forms would immediately lose a proton if the original amine were secondary, and then the remaining reactions would not occur. (3) The mechanism shows why the eliminated alkyl group must appear as an aldehyde. (4) As the oxidising agent does not attack the alkyl group, we should not expect the latter to behave exactly as if it did. (5) The mechanism shows why the primary dealkylation product is the secondary amine, even when the thermodynamically stable product is the nitrosoamine. (6) We have already pointed to the property of " nitrous acid " which we conclude to be responsible for the mechanism and its attendant effects, *viz.*, the stability of *both* NO^+ and NO.

This kind of property is not quite peculiar to nitrous acid. In Part VI evidence was given of the existence of a non-oxidative process of dealkylation of *p*-chloroanisole, which depended on nitric acid, rather than nitrous acid. There is strong reason to think that this reaction pursues a heterolytic course, quite analogous to that outlined in equation (11), excepting that the nitronium ion takes the part there assigned to the nitrosonium ion. Now the solvated nitronium ion and the nitrogen dioxide molecule are more or less comparably stable structures, differing by one electron, and therefore they might participate in an oxidative and homolytic process of dealkylation, similar to that represented in equations (12), except that the nitronium ion and nitrogen dioxide would take the parts assigned in those equations to the nitrosonium ion and nitric oxide, respectively. The difficulty in arranging to observe this reaction is that, once such a process starts, nitrous acid is produced, and then the reactions dependent on nitrous acid obscure the original process. Thus we have, easily susceptible to observation, heterolytic and homolytic mechanisms of dealkylation by nitrous acid, but only the heterolytic mechanism of dealkylation by nitric acid: and all these three observable mechanisms have, in our opinion, been observed.

We have to consider why the heterolytic mechanisms seem especially important for the dealkylation of phenolic ethers, whilst the homolytic process appears to be the principal mechanism utilised for the dealkylation of aromatic tertiary amines. First, it should be noted that the difference is probably one of degree, rather than of kind. Certainly, a non-oxidative and heterolytic dealkylation of *p*-chloroanisole has been isolated, as is reported in Part VI; but the dealkylation of *p*-chlorophenetole, under similar conditions, involved extensive oxidation, and therefore at least a part of this reaction may have taken place by the homolytic mechanisms. It seems certain that the dealkylations of tertiary amines described in this paper are homolytic; but tertiary amines are most likely to use heterolytic mechanisms when one of the alkyl groups has been so substituted that it is stable in its cationic form (*e.g.*, in the cationic fission product, $CH_2{:}NR_2^+$, of a structure such as $R_2N{\cdot}CH_2{\cdot}NR_2$).

However, there is undoubtedly a quantitative difference in the relative facility of the mechanisms available for the dealkylation of ethers on the one hand and tertiary amines on the other; and our theory would re-describe the difference by stating that, as compared with the nitrosoammonium ion, the nitrosoxonium ion has a larger tendency to lose a carbon cation, and a smaller tendency to lose neutral nitric oxide. This does not seem unreasonable on grounds of the relative electronegativaties of oxygen and nitrogen. A hydroxonium ion loses a proton more easily than an ammonium ion does; and there may well be a difference in this direction between oxonium ions and ammonium ions with respect to the loss of cations in general. Again, the loss of nitric oxide after the uptake of nitrosonium ion is equivalent to the loss of an electron from the original base; and known ionisation potentials show that it is considerably easier to take an electron out of a tertiary amine than out of an ether.

(7) EXPERIMENTAL.

(7.1) *Mono- and Di-nitration of Dimethylaniline by Nitric Acid in Acetic Acid.*—The dimethylaniline was purified by the acetic anhydride method. Its *o*-, *m*-, and *p*-nitro-derivatives, the picrate, hydrochloride, and chloroplatinate of the *o*-compound, *p*-nitrosodimethylaniline, 2 : 4-dinitrodimethylaniline, tetramethylbenzidine, and 3 : 3′-dinitrotetramethylbenzidine, all products which were either actually encountered, or were suspected, at some time in the course of the investigation, were prepared for comparison by known methods.

The nitration experiments of this series were set up as stated in Section 2·2. The main variable was the proportion of nitric acid. In most cases the reaction was obviously autocatalytic. In some of the experiments the products were separated by chromatographic methods, first, for the purpose of identifying pure substances, and secondly, in combination with nitro-group determination by titration with titanous chloride, for the quantitative determination of the products which could thus be separated. In other experiments, ordinary methods of crystallisation, solvent extraction, and distillation were used for the separation of the products. Several typical experiments are described below.

Dimethylaniline (5 g.) in solution in acetic acid (50 g.) was nitrated at room temperature during 24 hours with 70% (by wt.) nitric acid (1 mol.). The mixture was diluted with water to 250 c.c., and the precipitate was collected. The filtrate was neutralised with concentrated aqueous ammonia, and extracted continuously with benzene. The precipitate was dissolved in benzene, and the benzene solutions were combined, dried (K_2CO_3), and passed through a column, 30 cm. × 1·5 cm., of activated alumina. In order, the bands were violet (narrow), green (moderate width), yellow (wide), and orange (wide), the last two bands merging slightly. After mechanical division of the column, the violet material was collected in hot alcohol, but there was too little of it for identification; and the green substance was extracted with a mixture of ether and ethyl alcohol, and shown to be *p*-nitrosodimethylaniline (m. p. and mixed m. p. 86—87°). The yellow material was impure *p*-nitrodimethylaniline, but the pure substance (m. p. and mixed m. p. 162—163°) was obtained from it by crystallisation from ethyl alcohol. The orange substance was *o*-nitrodimethylaniline, which was extracted from the adsorbent with hot ethyl alcohol, and identified as its chloroplatinate (m. p. and mixed m. p. 195—196°).

The products of other nitrations with 1 mol. of nitric acid were separated by solvent extraction, distillation, and crystallisation, rather than by chromatography. In this way unconverted dimethylaniline was recovered; and its *o*- and *p*-nitro-derivatives also were obtained.

Experiments with 1·2 mols. of nitric acid led to the detection of *p*-nitrosodimethylaniline, and the isolation of *o*- and *p*-nitrodimethylaniline and of a red substance. In the chromatographic separation, this red substance appeared as a band below the *p*-nitrodimethylaniline band. It tended to crystallise with *p*-nitrodimethylaniline from the crude nitration product, and it could be separated from *p*-nitrodimethylaniline by repeated crystallisation from ethyl alcohol. It had m. p. 195°, and appeared to be a previously unknown *dinitrotetramethylbenzidine* (Found : C, 57·9; H, 5·6; N, 17·2. $C_{16}H_{18}O_4N_4$ requires C, 58·2; H, 5·6; N, 17·0%).

Experiments with 1·4 mols. of nitric acid gave no unchanged dimethylaniline and no nitroso-compound. In some cases very small amounts of a red compound, probably that described above, were seen in the chromatogram. In all cases the main products were *o*- and *p*-nitrodimethylaniline and 2 : 4-dinitrodimethylaniline. In the chromatogram, obtained by passing a benzene solution of the total product through alumina, the *p*-nitro- and the 2 : 4-dinitro-compound together formed a yellow band at the top. The *o*-nitro-compound was deposited as an orange band at the bottom, and the red compound, if present, formed a narrow band between the other bands. The bands were eluted with hot ethyl alcohol. The *p*-nitro-compound, m. p. and mixed m. p. 161—163°, and the 2 : 4-dinitro-compound, m. p. and mixed m. p. 85—86°, were separated by crystallisation from benzene, the former being the less soluble. The *o*-nitro-compound was precipitated from alcoholic solution as its picrate, m. p. and mixed m. p. 101—103°.

Dimethylaniline (2·5 g.) was nitrated with 70% (by wt.) nitric acid (1·4 mols.) in acetic acid (25 g.) at room temperature for 24 hours. Water (100 c.c.) and carbon tetrachloride (40 c.c.) were added, and the whole was shaken for 1 hour and filtered. The precipitate was washed with a small amount of carbon tetrachloride, dried, and weighed. This product was pure *p*-nitrodimethylaniline. The filtrate was neutralised and thoroughly extracted with carbon tetrachloride. The extract was dried (Na_2SO_4), and the solvent was removed by distillation through a short column. The residue was made up to 250 c.c. with benzene, and portions of 50 c.c. of this solution were passed through a column of alumina, benzene containing a little ethyl alcohol being used for the development of the chromatogram. The adsorbed material of the orange band was known to consist of *o*-nitrodimethylaniline only, and this was extracted with alcohol and estimated by titration with titanous chloride, and back-titration with ferric alum, in the usual way. The yellow band was eluted with alcohol, and the extract was concentrated and poured into water. The product was dried and separated by crystallisation from benzene into fractions consisting of pure *p*-nitrodimethylaniline, pure 2 : 4-dinitrodimethylaniline, and unseparated material. The total yields were as follows : *p*-, 34% ; *o*-, 23% ; 2 : 4-, 14%.

The experiment next to be described was conducted like the last (but on twice the scale) up to the stage at which the carbon tetrachloride solution was concentrated. The residue was then distilled non-ebulliently at a pressure of about 1 mm. in a special still of small hold-up, the receiving unit of which was cooled at −80°. The yield of the *o*-nitrodimethylaniline (identified through its salts) thus obtained was 25%. The residue from the distillation was collected in alcohol, and the solution was concentrated and poured into water. The precipitate was collected, dried, and crystallised from benzene. In this way a small amount of *p*-nitrodimethylaniline, additional to that which crystallised initially, was isolated, making the total yield 38%. The main part of the material in the benzene solution was obtained, after concentration, as 2 : 4-dinitrodimethylaniline, in a yield of 11%.

An experiment was conducted like the one last described, except that no carbon tetrachloride was used. Instead, the acetic acid solution was cooled at 0°, and the main part of the yield of *p*-nitrodimethylaniline was collected and washed with acetic acid. The acetic acid solution was then distilled under reduced pressure. After all the solvent had been removed, the *o*-nitrodimethylaniline was distilled non-ebulliently as before, with a bath-temperature of about 110°. The residue from the distillation was washed as before, with similar results. The total yields of pure products were as follows : *p*-, 39% ; *o*-, 25% ; 2 : 4-, 11%.

p-Nitrodimethylaniline on treatment with 70% (by wt.) nitric acid (1 mol.) in acetic acid under similar conditions was converted practically quantitatively into 2 : 4-dinitrodimethylaniline. *o*-Nitrodimethylaniline after similar treatment was recovered practically quantitatively.

(7.2) *Preparation of Substances involved in the Nitration of* 2 : 4-*Dinitrodimethylaniline to* N : 2 : 4 : 6-*Tetranitromethylaniline.*—2 : 4-Dinitrodimethylaniline, m. p. 86°, was prepared in quantitative yield by adding aqueous dimethylamine to an alcoholic solution of chloro-2 : 4-dinitrobenzene. 2 : 4-Dinitromethylaniline, m. p. 177°, was obtained in quantitative yield by adding alcoholic methylamine to alcoholic chloro-2 : 4-dinitrobenzene. 2 : 4 : 6-Trinitrodimethylaniline, m. p. 139°, was obtained quantitatively from picryl chloride and dimethylamine, but it is necessary to add the alcoholic solution of picryl chloride to an excess of dimethylamine in aqueous alcohol; for with the reverse order of addition there was obtained a molecular compound of picryl chloride and the required tertiary amine. 2 : 4 : 6-Trinitromethylaniline, m. p. 114°, was prepared in quantitative yield by adding an alcoholic solution of methylamine to one of picryl chloride.

N-Nitroso-2 : 4-dinitromethylaniline was prepared by passing the oxides of nitrogen, generated by the action of nitric acid on arsenious oxide, into the suspension obtained by quickly cooling a hot solution of 2 : 4-dinitromethylaniline in acetic acid (cf. Bamberger and Müller, *Ber.*, 1900, **33**, 377). The green solution was poured into water, and the nitrosamine, thus obtained in theoretical yield, was collected and crystallised from ethyl alcohol. It had m. p. 84—85° (Found : C, 37·2 ; H, 2·6 ; N, 24·4. Calc. : C, 37·2 ; H, 2·7 ; N, 24·6%). *N*-Nitroso-2 : 4 : 6-trinitromethylaniline, similarly prepared from 2 : 4 : 6-trinitromethylaniline, had m. p. 106° (Found : C, 31·3 ; H, 2·0. Calc. : C, 31·0 ; H, 1·9%).

N : 2 : 4-Trinitromethylaniline was prepared by two methods. (*a*). 2 : 4-Dinitroaniline was first *N*-nitrated, and then the product was methylated. The finely powdered amine (50 g.) and acetic anhydride (80 c.c.) were together slowly added at 25—30° to the mixture of nitric acid (100 c.c.), acetic acid (80 c.c.), and acetic anhydride (15 c.c.). Stirring was continued for 48 hours at room temperature, and, most of the original amine having by that time dissolved, the mixture was poured on ice. The yellow precipitate was collected, and extracted with saturated aqueous sodium carbonate. The filtrate was extracted with chloroform, and the chloroform solution was then extracted with aqueous sodium carbonate. The combined sodium carbonate solutions were acidified, and the precipitated nitroamine was collected and crystallised from ethyl alcohol. The pure product had m. p. 79°, and weighed 17 g. (Found : C, 31·9 ; H, 1·8. Calc. : C, 31·6 ; H, 1·8%). A solution of this nitramine (11 g.) in methyl alcohol (35 c.c.) was treated with a solution of sodium methoxide, prepared from sodium (1·7 g.) and methyl alcohol (35 c.c.), and then with methyl iodide (10 c.c.). After 4 days, the solution was boiled for 3 hours, and then concentrated and poured into aqueous sodium carbonate. The precipitated product (3 g.) was collected and crystallised from ethyl alcohol. It had m. p. 113—114° (Found : C, 34·9 ; H, 2·8. Calc. : C, 34·7 ; H, 2·5%). (*b*) *N* : 2 : 4-Trinitromethylaniline was obtained almost quantitatively by the interaction of dinitrogen pentoxide and 2 : 4-dinitromethylaniline. The dinitrogen pentoxide (5 g.), prepared as described in another communication (*J.*, 1950, 2452), and dissolved in chloroform (100 g.), was added to a suspension of the amine (8 g.) in chloroform (30 g.). The amine slowly dissolved, and a pale yellow solid separated. After extraction with water to remove nitric acid, the precipitated nitroamine was collected. A further quantity was obtained by concentrating the chloroform solution. The product (10 g.), crystallised from alcohol, had m. p. 113—114°.

(7.3) *Percentage Conversions of Different Substances into* N : 2 : 4 : 6-*Tetranitromethylaniline.*—The seven compounds whose preparation has just been described were each nitrated to give *N* : 2 : 4 : 6-tetranitromethylaniline under a fixed set of conditions; and the yields were compared. The composition of the nitration solution used in these experiments was closely controlled; to within ±0·1% it was as follows : H_2SO_4, 51·8 ; HNO_3, 25·8 ; H_2O, 22·3 ; HNO_2, 0·1% by weight. The determination of nitrous acid in nitration media is described in an accompanying paper (*J.*, 1950, 2400).

A weighed quantity (*ca.* 2 g.) of the compound to be nitrated was added to the nitrating solution (38·6 g.). After 7 days the product was poured into water (250 c.c.), and the *N* : 2 : 4 : 6-tetranitromethylaniline was collected in a sintered-glass crucible, washed with cold water, and dried to constant weight in a desiccator over sulphuric acid (Found: C, 29·5; H, 2·3; N, 24·1. Calc.: C, 29·3; H, 1·8; N, 24·4%).

The yield thus measured was corrected for the solubility of the product. The correction was determined by adding a weighed amount (*ca.* 2 g.) of carefully purified *N* : 2 : 4 : 6-tetranitromethylaniline to the nitrating mixture (38·6 g.), pouring the whole into water (250 c.c.), and recovering the original substance as described. The correction thus determined amounted to about 1%. It was slightly dependent on the amount of substance being determined; this small effect was also measured and the appropriate allowances were made.

Next a correction was applied for the impurities in the weighed yield, on the basis of the m. p. (clearing point) of the sample. It was necessary to know approximately the m. p. of pure *N* : 2 : 4 : 6-tetranitromethylaniline, and the cryoscopic constant of the substance. The highest m. p. observed under the conditions of our measurements was 129·3°. The sample having this m. p. had been subjected to a long series of fractional crystallisations from benzene and from ethyl alcohol, with intercalated fractional adsorptions on activated alumina. We took this as the m. p. of the pure substance. Our value for the cryoscopic constant was 19 deg. g.-mol.$^{-1}$ kg. This was determined by adding to the purified fused substance known weights, up to 3%, of *N* : 2 : 4-trinitromethylaniline and repeating the determination of the m. p.

The results obtained in this series of experiments have been given in Section 4.1. Additional experiments were carried out (*a*) in the presence of urea nitrate, (*b*) in the presence of several times more nitrous acid than was present in the experiments of the main series. These changes of conditions appeared to make but little difference to the results.

(7.4) *Nitration of* 2 : 4-*Dinitrodimethylaniline in Aqueous Nitric Acid.*—The amine (1 g.) was dissolved at room temperature in a mixture of absolute nitric acid (8 c.c.) and water (12 c.c.). Nitrogen dioxide was evolved, and an orange solid separated. After 24 hours the mixture was poured into water. The precipitated product, once crystallised from acetic acid, had m. p. 174°. The mixed m. p. with 2 : 4-dinitromethylaniline was 175—176°.

The product from a similar experiment made with a mixture of 10 c.c. each of nitric acid and water, was triturated with successive portions of ether, use of this solvent being suggested by preliminary experiments on the solubilities in various solvents of all the substances whose preparation is described in Section 7.2. After 7 such treatments, pure 2 : 4-dinitromethylaniline remained, m. p. and mixed m. p. 176°. The residue obtained on evaporation of the ether had m. p. *ca.* 95° with previous softening. After crystallisation from alcohol, it was found to be *N*-nitroso-2 : 4 : 6-trinitromethylaniline, m. p. and mixed m. p. 105°.

The original amine (1 g.) was dissolved in a mixture of nitric acid (7 c.c.) and water (3 c.c.). The solution became green and then purple, nitrogen dioxide being evolved. After 24 hours, the solution was poured into water. The product, crystallised once from alcohol, proved to be *N*-nitroso-2 : 4 : 6-trinitromethylaniline, m. p. and mixed m. p. 106°.

A similar experiment with 10 c.c. of 98% nitric acid gave a precipitated product of m. p. 126°, which was identified as *N* : 2 : 4 : 6-tetranitromethylaniline by the mixed m. p., 127°.

(7.5) *Nitration of* 2 : 4-*Dinitromethylaniline and of its* N-*Nitro-derivative in Aqueous Nitric Acid.*—2 : 4-Dinitromethylaniline (0·5 g.) was dissolved in 10 c.c. of 70% nitric acid. After 2 hours, the brownish-purple solution was poured into water. The product, *N* : 2 : 4-trinitromethylaniline, after crystallisation from ethyl alcohol, was identified by its m. p., 111°, and mixed m. p., 112—113°.

An experiment was started in the same way, but the nitration mixture was kept for 10 days before being poured into water. The product was then *N* : 2 : 4 : 6-tetranitromethylaniline, as was shown by its m. p. and mixed m. p. When the amine used in this experiment was replaced by *N* : 2 : 4-trinitromethylaniline in a parallel experiment, the product was the same.

2 : 4-Dinitromethylaniline (0·5 g.) was nitrated at room temperature with 70% aqueous nitric acid to which sodium nitrite (0·36 g., 2 mols.) had been added. After 5 hours, the solution was poured into water, and the solid product crystallised from alcohol. It had m. p. 106°, and was identified by mixed m. p. with *N*-nitroso-2 : 4 : 6-trinitromethylaniline.

(7.6) *Nitration of* 2 : 4-*Dinitrodimethylaniline by Nitric Acid in Aqueous Sulphuric Acid.*—The general results of these experiments have been summarised in Section 4.4, and only a few notes on the separations need be added. All the nitrations were allowed 24 hours at the room temperature, and the solutions were then poured into water, and the products were collected. The product from the experiments with " 50% " aqueous sulphuric acid and 2 mols. of nitric acid, after crystallisation from acetic acid, had m. p. 175°, and the same mixed m. p. with 2 : 4-dinitromethylaniline. The products from the experiments with the same aqueous sulphuric acid and 5—10 mols. of nitric acid had m. p.s about 90° with previous softening, and had to be triturated with ether, and crystallised from ethyl alcohol, before pure *N*-nitroso-2 : 4 : 6-trinitromethylaniline, m. p. and mixed m. p. 106°, was obtained. For dealing with the products of the long series of experiments made with " 55—85% " aqueous sulphuric acid and 2—10 mols. of nitric acid, a combination of trituration with ether and chromatography on alumina was employed. The treatment with ether nearly always left a residue of *N* : 2 : 4 : 6-tetranitromethylaniline, which was identified by its m. p. and mixed m. p., if necessary after crystallisation from alcohol. The material dissolved by the ether was recovered by evaporation, dissolved in benzene, and adsorbed on a column of activated alumina. The usual result was the production of a very narrow orange band high in the column, and, considerably lower down, a large orange-yellow band with a pale yellow fringe at the bottom. The material in the very narrow orange band was not identified. The substance responsible for the large orange-yellow band was in all cases 2 : 4-dinitrodimethylaniline, and, after extraction with alcohol, and crystallisation from light petroleum containing benzene, was identified by its m. p. and mixed m. p. The material in the pale yellow fringe appeared to contain *N* : 2 : 4 : 6-tetranitromethylaniline, though this was not obtained from it sufficiently pure for satisfactory identification. The experiments with " 95% " aqueous sulphuric acid and 1·25—3·0 mols. of nitric acid gave products, which were dissolved in benzene, and then adsorbed on alumina. The chromatograms consisted of an orange band above, and a yellow band below, the yellow band becoming larger and the orange band smaller when the proportion of nitric acid was increased. The material, extracted from the yellow band with hot ethyl alcohol, was identified by its m. p., 138°, and mixed m. p. as 2 : 4 : 6-trinitrodimethylaniline. The material, similarly obtained from the orange-yellow band, was identified by m. p. and mixed m. p. as 2 : 4-dinitrodimethylaniline. Experiments with " 95% " sulphuric acid and 4—5 mols. of nitric acid were carried out, but it was not found possible satisfactorily to separate and identify the products. Experiments with 10 mols. of nitric acid gave nearly pure *N* : 2 : 4 : 6-tetranitromethylaniline.

A series of experiments were conducted in which urea nitrate was employed in place of nitric acid. In " 70% " aqueous sulphuric acid with 1·25—5·0 mols. of urea nitrate, no reaction took place, the original amine being quantitatively recovered. In " 95% " aqueous sulphuric acid with 1·25—3·0 mols. of urea nitrate, the products behaved like those obtained by the use of corresponding amounts of nitric acid; and they were separated by the same methods into the same substances.

(7.7) *Nitration of* 2 : 4-*Dinitromethylaniline and of its* N-*Nitroso- and* N-*Nitro-derivatives by Nitric Acid in Aqueous Sulphuric Acid.*—These experiments have been described in Section 4.5, and only a few notes need be added. The nitrosamine, or other initial substance (0·5 g.), was added to a mixture of " 70% " aqueous sulphuric acid (7·5 c.c.) and nitric acid (2·5 c.c.) at room temperature. The orange-yellow substance, isolated by pouring the solution into water at a very early stage of the reaction, was crystallised from acetic acid, and identified as 2 : 4-dinitromethylaniline by its m. p., 174—175°, and mixed m. p. The pale yellow substance isolated by stopping the nitration at a somewhat later stage, was crystallised from ethyl alcohol, and was then identified as *N* : 2 : 4-trinitromethylaniline by its m. p., 111—113°, and mixed m. p. The final product, *N* : 2 : 4 : 6-tetranitromethylaniline, was identified as usual by m. p. and mixed m. p.

Attempts were made to convert *N*-nitroso-2 : 4-dinitromethylaniline into *N*-2 : 4-trinitromethylaniline by oxidation with hydrogen peroxide. A solution of the nitrosoamine (1 g.) in acetic acid (10 c.c.) was treated with 30% aqueous hydrogen peroxide (1 c.c.). A vigorous reaction set in and yellow crystals, consisting of 2 : 4-dinitromethylaniline, separated. Their m. p., and the mixed m. p., were both 174—175°. Hydrogen peroxide in pyridine had no action on the nitrosamine. Hydrogen peroxide in an aqueous borate buffer, pH 7—8, had no action in the cold; but on heating decomposition took place, the product being again 2 : 4-dinitromethylaniline. An aqueous solution of Caro's acid, made slightly alkaline with sodium carbonate, also had no action in the cold, but heating produced 2 : 4-dinitromethylaniline.

Attempts were made to isomerise *N*-nitroso-2 : 4-dinitromethylaniline by the use of acids. The nitrosoamine (4 g.) was left in contact with concentrated hydrochloric acid (45 c.c.) for 30 minutes at room temperature. The solid, without dissolving, became bright orange-yellow. After dilution with water, it was collected, crystallised from acetic acid, and found to be 2 : 4-dinitromethylaniline, m. p. and mixed m. p. 174—175°. The same substance was produced when dry hydrogen chloride was passed into a suspension of the nitrosamine in ether. It was also produced by treating the nitrosoamine (1 g.) with nitric acid (1 g.) in acetic acid (10 g.), with 70% aqueous nitric acid (10 g.), or with a mixture of sulphuric acid (10 g.) and acetic acid (10 g.). It was identified by m. p. and mixed m. p. in all cases.

The reaction of the nitrosamine (1 g.) with hydrogen chloride in ether was repeated in the presence of dimethylaniline (1·5 g.). A white precipitate appeared, which redissolved, an orange precipitate taking its place. This was collected, and shaken with ether and aqueous sodium carbonate. The undissolved solid was crystallised from acetic acid, and identified by its m. p., 174—175°, and mixed m. p. as 2 : 4-dinitromethylaniline. The green ethereal solution was dried and evaporated. The solid residue was crystallised from light petroleum and identified by its m. p., 80°, and mixed m. p. as *p*-nitrosodimethylaniline.

(7.8) *Interconversion of* 2 : 4 : 6-*Trinitrodimethylaniline,* 2 : 4 : 6-*Trinitromethylaniline,* N-*Nitroso*-2 : 4 : 6-*trinitromethylaniline, and* N : 2 : 4 : 6-*Tetranitromethylaniline.*—2 : 4 : 6-Trinitrodimethylaniline (1 g.) was dissolved in " 70% " aqueous sulphuric acid (30 c.c.) containing 2 mols. of nitric acid. After 24 hours at room temperature, the solution was poured into water, and the product was collected, dried, and triturated with ether. The undissolved portion was crystallised from alcohol, and identified as *N* : 2 : 4 : 6-tetranitromethylaniline by m. p. and mixed m. p. The material which dissolved in the ether was recovered and purified by chromatography from benzene solution with alumina as adsorbent. The large orange band, eluted with alcohol, yielded 2 : 4 : 6-trinitromethylaniline, which, after crystallisation from alcohol, was identified by its m. p., 112°, and mixed m. p. A similar experiment with 10 mols. of nitric acid yielded *N* : 2 : 4 : 6-tetranitromethylaniline only.

2 : 4 : 6-Trinitromethylaniline (0·5 g.) was added to " 70% " aqueous sulphuric acid (10 c.c.) containing 10 mols. of nitric acid. The colour of the solution became steadily paler; and, after 2 hours, the product was isolated by adding water, and identified as *N* : 2 : 4 : 6-tetranitromethylaniline. The same conversion was carried out by using aqueous nitric acid of various concentrations between 60% and 90%.

2 : 4 : 6-Trinitrodimethylaniline (0·5 g.) was dissolved in 70% aqueous nitric acid (10 c.c.) at room temperature. Nitrogen dioxide was evolved. After 24 hours the solution was poured into water, and the product was collected and crystallised from alcohol. It had m. p. 106°, and was identified by mixed m. p. as *N*-nitroso-2 : 4 : 6-trinitromethylaniline.

2 : 4 : 6-Trinitromethylaniline (0·5 g.) was dissolved in 70% aqueous nitric acid (10 c.c.) to which sodium nitrite (0·28 g., 2 mols.) had been added. After 1 hour, the product was isolated, and identified as *N*-nitroso-2 : 4 : 6-trinitromethylaniline, as in the preceding experiment.

N-Nitroso-2 : 4 : 6-trinitromethylaniline (0·5 g.) was added to a mixture of "70%" aqueous sulphuric acid (8 c.c.) and nitric acid (2 c.c.). The solid, without dissolving, soon became colourless. After dilution with water, the crystalline substance was collected and identified as *N* : 2 : 4 : 6-tetranitromethylaniline by m. p. and mixed m. p.

(7.9) *Dealkylation of* 2 : 4-*Dinitro- and* 2 : 4 : 6-*Trinitro-dialkylanilines.*—Some of the experiments mentioned in this Section were carried out with higher homologues, containing ethyl or *n*-butyl groups in place of the methyl groups of the methyl- and dimethyl-aniline derivatives employed for the rest of the work described in this paper. These homologues were prepared, either as initial material for experiments, or for the identification of products by comparison, by using methods quite analogous to those employed for the preparation of the methyl compounds (Section 7.2). The 2 : 4-dinitrodiethylaniline had m. p. 80°, the 2 : 4-dinitroethylaniline, m. p. 114°, and the *N*-nitroso-2 : 4-dinitroethylaniline, m. p. 56°; but 2 : 4-*dinitro*-n-*butylaniline* could be obtained only as a liquid. It was prepared by boiling the chlorodinitrobenzene with a 3-fold excess of di-*n*-butylamine for 5 hours in ethyl alcohol, washing the product several times with aqueous hydrochloric acid, drying it in light petroleum with sodium sulphate, and pumping off the solvent (Found : C, 57·0; H, 7·7. $C_{14}H_{21}O_4N_3$ requires C, 57·0; H, 7·1%).

The effects due to added nitrous acid on the demethylation of 2 : 4-dinitrodimethylaniline by nitric acid in acetic acid, and on the analogous reaction of 2 : 4 : 6-trinitrodimethylaniline as effected by nitric acid in sulphuric acid, have been noted in Section 5.1. So also has the effect of added water in promoting the demethylating action of nitrous acid on 2 : 4-dinitrodimethylaniline, and on 2 : 4-dinitrodiethylaniline, in solution in sulphuric acid. Some further details will be given here concerning dealkylations effected by dinitrogen tetroxide, by dilute nitric acid containing nitrous acid, by chromic acid, and by permanganic acid.

2 : 4-Dinitrodimethylaniline, in solution in chloroform, was treated with a solution of freshly distilled dinitrogen tetroxide in the same solvent. The solution became green, and an energetic reaction set in. When reaction had abated, methyl alcohol was added, and the solution concentrated by evaporation. The yellow crystalline substance which separated was collected, and, after crystallisation from ethyl alcohol, was identified by its m. p. and mixed m. p. as 2 : 4-dinitromethylaniline. A similar experiment was made with 2 : 4-dinitrodiethylaniline. The similarly isolated product had m. p. 113—114°, and was identified by comparison and mixed m. p. as 2 : 4-dinitroethylaniline.

2 : 4-Dinitrodimethylaniline in solution in acetic acid was treated with a solution of dinitrogen tetroxide in that solvent. Again there was a vigorous reaction. After reaction had subsided, methyl alcohol was added, and then water. The precipitated product was identified by its m. p. and mixed m. p. as *N*-nitroso-2 : 4-dinitromethylaniline. A similar experiment was made with 2 : 4-dinitrodiethylaniline. The product, m. p. 55°, was identified by mixed m. p. as *N*-nitroso-2 : 4-dinitroethylaniline.

Experiments like the two just described on 2 : 4-dinitrodimethylaniline were carried out with 2 : 4-dinitromethylaniline. When chloroform was the solvent this amine was recovered unaltered, but when acetic acid was employed the product was *N*-nitroso-2 : 4-dinitromethylaniline. A similar experiment with 2 : 4-dinitroethylaniline likewise gave the unaltered secondary amine when chloroform was the solvent, but its *N*-nitroso-derivative when the solvent was acetic acid.

In the experiments with 2 : 4-dinitrodimethyl- and 2 : 4-dinitrodiethyl-aniline, nitric oxide was copiously evolved. In an experiment with 2 : 4-dinitrodimethylaniline, chloroform being the solvent, the chloroform solution obtained at the conclusion of the reaction was shaken with water; the aqueous solution thus obtained gave the reactions of formaldehyde. In an experiment with 2 : 4-dinitrodiethylaniline, acetic acid being the solvent, the evolved gases were passed through water; the aqueous solution thus prepared gave the reactions of acetaldehyde.

In some experiments with dilute nitric acid containing nitrous acid as the dealkylating agent attention was directed mainly to the recovery of the compound formed from the eliminated alkyl group. 2 : 4-Dinitrodimethylaniline, 2 : 4-dinitrodiethylaniline, or 2 : 4-dinitrodi-*n*-butylaniline (10 g. of any one) was warmed with 20% aqueous nitric acid (200 c.c.) containing nitrous acid, and a current of air was passed through the solution. The gases thus carried off were passed through a 10% solution of 2 : 4-dinitrophenylhydrazine (50 c.c.) in hydrochloric acid. A copious precipitation occurred of the 2 : 4-dinitrophenylhydrazone of formaldehyde, acetaldehyde, or *n*-butaldehyde. These compounds, having m. p.s 155°, 147°, and 123°, respectively, were identified by mixed m. p.s with authentic specimens. A blank experiment was conducted in which *n*-butyl alcohol was used in place of 2 : 4-dinitrodi-*n*-butylaniline. In this case no precipitate was formed in the 2 : 4-dinitrophenylhydrazine trap; and extraction of the aqueous solution with ether yielded *n*-butyl nitrite, b. p. 74—76°, identified by its physical properties and reactions.

2 : 4-Dinitrodiethylaniline (1 g.), dissolved in "30%" aqueous sulphuric acid (20 c.c.), was treated with chromium trioxide (2 g.). The mixture immediately became green, and acetaldehyde could be aspirated from the solution. After 10 minutes at room temperature, the solution was poured into water, and the precipitated product was collected, and, after crystallisation from alcohol, was identified by m. p. and mixed m. p. as 2 : 4-dinitroaniline.

A similar experiment was made with acetic acid as the solvent instead of aqueous sulphuric acid. In this case reaction was induced by warming the mixture. When, after 1 hour, the solution was poured into water, a strong odour of acetaldehyde was noticed, and a crystalline product was precipitated. This was crystallised from ethyl alcohol, and identified by m. p. and mixed m. p. as 2 : 4-dinitroethylaniline.

A solution of 2 : 4-dinitrodimethylaniline (1·0 g.) in " 30% " aqueous sulphuric acid (40 c.c.) was treated with potassium permanganate (1 g.). A gas was evolved, which was shown to contain formaldehyde, and a yellow precipitate was formed. Water was added, and the precipitate was collected. This product, after crystallisation from ethyl alcohol, was identified by m. p. and mixed m. p. as 2 : 4-dinitromethylaniline.

A solution of 2 : 4-dinitrodiethylaniline (1 g.) in " 30% " aqueous sulphuric acid (40 c.c.) was treated with potassium permanganate (2 g.). A vigorous reaction ensued, and a gas was evolved, which contained acetaldehyde. Water was added, and the precipitated product was collected. It was crystallised from ethyl alcohol, and identified by m. p. and mixed m. p. as 2 : 4-dinitroaniline.

Note.—Details of some further experiments relevant to the subject matter of this paper are included in Part VIII.

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