514. *Kinetics and Mechanism of Aromatic Nitration. Part VIII. The Rearrangement of Aromatic* N-*Nitroamines.*

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A study of the proportions in which nitro-products are formed in the acid-catalysed rearrangement of phenylnitramine, and in the nitration of aniline with nitric acid under comparable conditions, has shown that two very different types of orientation are involved in the two reactions.

The formation of nitric acid, or of any other nitrating agent, was not observed during the rearrangement of *p*-nitrophenylmethylnitroamine under a variety of conditions. The product was invariably 2 : 4-dinitromethylaniline, and the transfer of the nitro-group to a " foreign " aromatic nucleus could not be established.

In the case of 2 : 4-dinitrophenylmethylnitramine, acidolysis of the nitro-group was shown to occur under conditions conducive to the rearrangement; and transfer of the nitro-group to a " foreign " aromatic compound was effected. It was demonstrated, however, that nitric acid, in the amount that could be produced by acidolysis, is not capable of converting the denitration product, 2 : 4-dinitromethylaniline, into the rearrangement product, 2 : 4 : 6-trinitromethylaniline, nearly as smoothly or as readily as the latter is formed by rearrangement under comparable conditions.

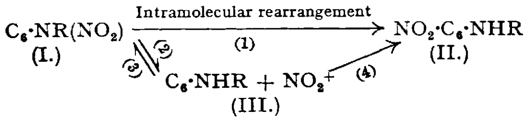
The evidence as a whole may be consistently interpreted on the basis of a predominating intramolecular mechanism for the nitramine rearrangement.

(1) *Background, Object, and Methods.*

(1.1) *Aim of this Work.*—The motive for undertaking this work arose in connexion with the investigation described in the preceding paper, where use has already been made of the conclusion which will be reached.

The hypothesis that aromatic primary and secondary amines, in so far as they are nitrated in the form of free amines rather than as salts, normally undergo " indirect " nuclear nitration, an *N*-nitration being followed by the intramolecular migration of the nitro-group, was advanced more than 50 years ago but has never definitely been proved or disproved. The problem of the mechanism of the rearrangement of aromatic nitramines, especially the question of whether the nitro-group is internally transferred, or whether it separates to form a nitrating agent which subsequently attacks the aromatic nucleus, has been under consideration for a similar length of time, but again no unequivocal conclusion has been reached. These two questions are obviously linked together, and they will be considered together in this paper.

(1.2) *Methods.*—The matter to be decided may be stated, and the methods by which it might be settled may be seen, with the aid of the scheme written below :



Here, C_6 represents the benzene ring without restriction as to the substituents which it may be carrying in addition to those expressed in the formulæ, and NO_2^+ means either the free nitronium ion, or some nitronium-ion carrier or source, such as its hydrate, the nitric acidium ion, or even nitric acid.

The problem is to determine whether the conversion of the *N*-nitro-compound (I) into the *C*-nitro-compound (II) follows the internal route (1), or whether it takes the external route (2 + 4) by way of the intermediates (III). There are three obvious ways in which one might seek evidence on this question. One might try to compare, using identical conditions of solvent and temperature, (*a*) the orientation of substitution in processes (1) and (4), (*b*) the rates of destruction of (I) in processes (1) and (2), (*c*) the rates of formation of (II) in processes (1) and (4). Comparison (*a*) must be quantitative, if it is to have any real value. Comparisons (*b*) and (*c*) may be made initially in a qualitative manner, in case gross rate differences are involved; and they may be carried to a quantitative stage, if the results should render that necessary. Comparison (*b*) might be defeated by reaction (3), unless precautions to prevent this are taken; and the simplest precaution is to operate in the presence of some substance which will react with one of the products (III) as fast as it is formed (the convenient one being the nitronium ion or its carrier), thus inhibiting reaction (3). The object of comparisons (*a*) and (*c*) might be defeated by the observation of identical orientations or rates; for identical orientations might mean either that the reaction assumed to be (1) is really (2 + 4), or that the reaction assumed to be (4) is really (3 + 1); and identical rates might mean either of these eventualities, with the added condition that stages (2) and (3) are fast; and so, in either case, the experimental indication would be ambiguous. The observation of a marked difference of orientation, or of rate, would, however, point to a definite conclusion.

In the present study we have used all three methods, (*a*), (*b*), and (*c*); and all point to the same conclusion.

(1.3) *Previous Work.*—It was shown by Bamberger that phenylnitramine, phenylmethylnitramine, and similar nitramines, undergo rearrangement on treatment with aqueous strong acids, or with hydrogen chloride in organic solvents, to yield mainly *o*-nitroaniline or its derivatives, and, in smaller amounts, *p*-nitroaniline or its derivatives (*Ber.*, 1893, **26**, 471, 485; 1894, **27**, 359). Having found, in a parallel series of researches, that treatment of primary and secondary aromatic amines by non-acidic nitrating agents, such as dinitrogen pentoxide, often leads to *N*-nitration, he made the suggestion that the nuclear nitration of these bases by acidic nitrating agents in general proceeds by *N*-nitration with subsequent rearrangement (*Ber.*, 1894, **27**, 584; 1895, **28**, 399; Bamberger and Hoff, *Ber.*, 1897, **30**, 1248; *Annalen*, 1900, **311**, 91).

Holleman, Hartogs, and Linden (*Ber.*, 1911, **44**, 704) attempted to test Bamberger's hypothesis by a somewhat incomplete application of the above-mentioned method (*a*) to the rearrangement of phenylnitramine and the nitration of aniline. For each of these processes they measured the proportions of *o*-, *m*-, and *p*-nitro-products by the technique of thermal analysis. They concluded that the nuclear nitration of aniline does not always proceed by way of an initial *N*-nitration. The following results are typical of those which led to this deduction:

Process.	Conditions.	*o*-, %.	*m*-, %.	*p*-, %.
Nitration	$Ph{\cdot}NH_3NO_3$ in 95% aq. H_2SO_4 at −20°	4	39	56
,, ...	$Ph{\cdot}NH_3NO_3$ in 80% aq. HNO_3	5	32	62
,, ...	$Ph{\cdot}NH_3NO_3$ in Ac_2O	82·1	2·9	15·0
Rearrangement	74% aq. H_2SO_4 at −20°	95	1·5	3·5

Considering these figures, the inference drawn does seem an extremely reasonable one. The demonstration is not, however, conclusive, because the conditions of nitration and of rearrangement were not the same. It is a commonplace that the proportions in which nitro-compounds are formed in the nitration of bases are sensitive to the conditions, and it is not established that the proportions in which they are produced by rearrangement do not also vary with the conditions.

A general investigation of the rearrangement of nitramines was conducted by Orton and his co-workers (*J.*, 1902, **81**, 490, 806; 1905, **87**, 389; 1907, **91**, 146; 1908, **93**, 725; *Rep. Brit. Assoc.*, 1912, 117; Bradfield and Orton, *J.*, 1929, 915). They noted that the reaction is subject to general acid catalysis. Their main conclusion was that, although in special cases nitramines in acid solution could be observed to nitrate a foreign aromatic compound, thus proving that a nitrating agent is present in these conditions, " no nitrating agent invariably and normally appears in the system in which a nitramine is undergoing isomeric change." Orton made it clear that the case is very different from that of the acid-catalysed rearrangement of chloramines in polar solvents, for which he always found it possible to prove the production of free chlorine. However, he regarded the conclusion quoted above as requiring further definition and elucidation, such as it is the purpose of this paper to provide.

(2) *Observations on the Rearrangement of Aromatic Nitramines.*

(2.1) *Orientation in the Rearrangement of Phenylnitramine and in the Nitration of Aniline.* The experiments to be reported in this Section extend those of Holleman, Hartogs, and Linden (*loc. cit.*), the present object being to compare the proportions in which nitro-products are formed in the rearrangement of phenylnitramine, and in the nitration of aniline, under the same conditions. If, in a given medium, phenylnitramine is rearranged by route (2 + 4), *i.e.*, as the result of an initial acidolysis to aniline and nitric acid, then one equivalent of nitric acid is made available for the second stage of the reaction, namely, the nuclear nitration of the aniline. Accordingly, it was judged that the addition of pure aniline nitrate to the medium would provide the nitration conditions most satisfactory for comparison with the rearrangement of the nitramine. Preliminary experiments were carried out in order to determine favourable common conditions for the smooth occurrence of the two reactions.

It was confirmed that *o*-nitroaniline is the main product of the rearrangement of phenylnitramine in 74% (by weight) aqueous sulphuric acid. However, the addition of aniline nitrate to this acid gave tarry products and unchanged aniline. It was also found that *m*- and *p*-nitroanilines are the main products formed by the addition of aniline nitrate to concentrated sulphuric acid. But the addition of phenylnitramine to the concentrated acid resulted in a violent reaction, in which brown fumes were evolved and tarry products formed. It appears that the rearrangement proceeds more smoothly than the nitration in 74% aqueous sulphuric acid, but that nitration takes place more smoothly than the rearrangement in the anhydrous acid. This in itself indicates that there is no very close relationship between the two processes.

Both reactions take place fairly smoothly, with the formation of mononitroanilines in high yield, and only traces of tar, in sulphuric acid monohydrate, *i.e.*, 84—85% (by weight) aqueous sulphuric acid, maintained just above its freezing point. For these conditions, the proportions of the isomerides in the product of each reaction were determined by thermal analysis, with the following results :

Process.	*o*-, %.	*m*-, %.	*p*-, %.
Rearrangement of phenylnitramine	93	0	7
Nitration of aniline	6	34	59

Clearly, two very different types of orientation are involved in these two reactions.

(2.2) *Internal Nitroxyl Migration* versus *External Nitroxyl Transfer with* p-*Nitrophenylmethylnitramine.*—Little information appears in the literature concerning the rearrangement of this compound. Its preparation from *p*-nitroaniline was described by Pinnow (*Ber.*, 1897, **30**, 837), and also by Bamberger and his co-workers (*ibid.*, p. 1248), who mention that it is rearranged to 2 : 4-dinitromethylaniline by sulphuric acid in acetic acid at 0°.

We found that th nitramine is rearranged to the 2 : 4-dinitro-compound, instantly by cold concentrated sulphuric acid, rapidly by cold hydrogen chloride in ethyl alcohol or in acetic acid, and slowly by cold ethereal or aqueous hydrogen chloride. The conversion takes place fairly rapidly when the nitramine is boiled with aqueous hydrochloric acid or with formic acid, or when it is heated on the water-bath with a solution of trichloroacetic acid in acetic acid. On the whole, the rearrangement of *p*-nitrophenylmethylnitramine is more facile than is that of 2 : 4-dinitrophenylmethylnitramine, which is discussed below.

No sign of the formation of nitric acid, or of any other nitrating agent, could be discerned during these rearrangements. Attempts were made to detect the formation of a nitrating agent by carrying out the rearrangements in the presence of the reactive aromatic compounds *p*-xylene and phenol. The rearranging agents employed in these experiments were concentrated sulphuric acid, 80% (by weight) aqueous sulphuric acid, and hydrogen chloride in acetic acid. However, the product was always the usual rearrangement product, 2 : 4-dinitromethylaniline. No *p*-nitromethylaniline could be detected, and in no case could any uptake of a nitro-group by the added aromatic compound be established. This absence of denitration during the rearrangement of *p*-nitrophenylmethylnitramine forms another contrast with the reaction of 2 : 4-dinitrophenylmethylnitramine, next to be discussed.

(2.3) *Internal Nitroxyl Migration* versus *External Nitroxyl Transfer with* 2 : 4-*Dinitrophenylmethylnitramine.*—On the whole, the rearrangement of this nitramine to 2 : 4 : 6-trinitromethylaniline is not a facile process. However, it took place somewhat rapidly in cold concentrated sulphuric acid. In 80% (by weight) aqueous sulphuric acid the rearrangement still proceeded slowly, requiring about 2 hours to become nearly complete at 25°. None of the other reagents which were tried brought about smooth rearrangement. Hydrogen chloride in ether, which was Bamberger's usual rearranging agent, cold concentrated aqueous hydrochloric acid, and cold solutions of trichloroacetic acid in either water or acetic acid, had no facile action. Hot aqueous hydrochloric acid, boiling formic acid, fused trichloroacetic acid at 100°, a boiling 30% solution of trichloroacetic acid in water, and a cold mixture of sulphuric and acetic acids (equal volumes) denitrated the side chain, giving 2 : 4-dinitromethylaniline. With hot concentrated nitric acid, and even with 50% (by volume) aqueous nitric acid after a longer period of heating, further nitration occurred, the product being 2 : 4 : 6-trinitrophenylmethylnitramine.

The above-mentioned derivatives show that nitric acid can readily be produced by acidolysis of 2 : 4-dinitrophenylmethylnitramine. We have made experiments to determine whether it is in fact produced under the conditions of the rearrangement, and at a rate comparable to that of rearrangement. Because of the reversibility of the acidolysis of nitramines, the method, as has already been explained, is to conduct the rearrangement in the presence of an aromatic compound which is expected rapidly and irreversibly to take up nitric acid, if this is being formed. As the added (" foreign ") aromatic compound, we have used *p*-xylene, phenol, and dimethylaniline. As rearranging medium, we have employed concentrated sulphuric acid and 80% aqueous sulphuric acid. In order to provide a basis of comparison for the products of these experiments, a parallel series of experiments has been conducted on the nitration of each of the foreign aromatic compounds by nitric acid in the various rearranging media. The method was first to introduce the foreign aromatic compound into the rearranging medium in each of two similar experiments, and then to add to one the 2 : 4-dinitrophenylmethylnitramine, and to the other an equivalent amount of nitric acid. No attempt was made to identify all the reaction products in the more complicated cases, but the most important compounds were isolated and characterised. The results of these experiments are summarised in Table I.

TABLE I.

Products obtained by conducting the rearrangement of 2 : 4-dinitrophenylmethylnitroamine in acid media in the presence of foreign aromatic compounds. Comparison with the action of nitric acid on the same compounds in the same media.

Aromatic compound.	Reagent : $C_6H_3(NO_2)_2{\cdot}NMe(NO_2)$. Interaction.	Rearrangement.	Reagent : HNO_3.
Medium : Concentrated sulphuric acid :			
p-$C_6H_4Me_2$	$C_6H_3(NO_2)Me_2$ $C_6H_3(NO_2)_2{\cdot}NHMe$	—	$C_6H_2(NO_2)_2Me_2$
$C_6H_5{\cdot}OH$	— Polycondensed products	$C_6H_2(NO_2)_3{\cdot}NHMe$	*p*-$C_6H_4(NO_2){\cdot}OH$
$C_6H_5{\cdot}NMe_2$	—	$C_6H_2(NO_2)_3{\cdot}NHMe$	*m*-$C_6H_4(NO_2){\cdot}NMe_2$ 2 : 4-$C_6H_3(NO_2)_2{\cdot}NMe_2$
Medium : 80% Aqueous sulphuric acid :			
p-$C_6H_4Me_2$	$C_6H_3(NO_2)Me_2$	$C_6H_2(NO_2)_3{\cdot}NHMe$	$C_6H_3(NO_2)Me_2$
$C_6H_5{\cdot}OH$	$C_6H_3(NO_2)_2{\cdot}NHMe$ Polycondensed products	—	*o*-$C_6H_4(NO_2){\cdot}OH$
$C_6H_5{\cdot}NMe_2$	$C_6H_3(NO_2)_2{\cdot}NHMe$ Condensed products	—	Benzidine derivatives Condensed products

The general conclusions to be drawn from these tests for the production of nitric acid, or other nitrating agent, during the rearrangement of 2 : 4-dinitrophenylmethylnitroamine are that it certainly is produced, and that it can be taken up by an added foreign aromatic compound. Furthermore, by the addition in suitable amount of a sufficiently reactive foreign compound, the original rearrangement can be largely diverted into the interaction which transfers the *N*-nitro-group to the aromatic nucleus of the foreign compound. From this it follows that the speed of production of nitric acid (reaction 2 of the scheme on p. 2678), under the conditions of the rearrangement, cannot be much smaller than that of the rearrangement (total of reactions 1 and 2 + 4), as it would take place in the absence of the foreign compound.

(2.4) *Rearrangement of 2 : 4-Dinitrophenylmethylnitramine* versus *the Nitration of 2 : 4-Dinitromethylaniline.*—From the above it follows that, under conditions in which 2 : 4-dinitrophenylmethylnitramine is rearranged, nitric acid is produced as rapidly as would allow it to be made responsible for at least a large part of the rearrangement, provided that the nitric acid, when produced, were capable of behaving in the way required. What is required is that nitric acid shall be able, under the same conditions, to convert the other denitration product, 2 : 4-dinitromethylaniline, into the rearrangement product, 2 : 4 : 6-trinitromethylaniline, smoothly and about as rapidly as (or more rapidly than) the rearrangement is observed to take place. The question of whether nitric acid can in fact do this obviously had to be tested.

In one of the media which we have used for the rearrangements, namely, concentrated sulphuric acid, a direct answer to this question was not obtained, for 2 : 4 : 6-trinitromethylaniline was formed in both the rearrangement and the nitration, and the reactions appeared to be fast under our conditions.

For aqueous sulphuric acid media, however, the question at issue could be answered unequivocally. We have already noted that, in 80% (by weight) aqueous sulphuric acid, the rearrangement of 2 : 4-dinitrophenylmethylnitramine is substantially complete after 2 hours at 25°. In parallel with an experiment illustrating this, an experiment was set up in which the 2 : 4-dinitrphenylmethylnitramine was replaced by 2 : 4-dinitromethylaniline, together with one molecular proportion of nitric acid, the medium being the same. After 2 hours at 25° little change had occurred. The two experiments were repeated, with the same medium, in fact with portions of medium taken from the same stock of 80% aqueous sulphuric acid, but with the refinement of adding one molecular proportion extra of water to the 2 : 4-dinitrophenylmethylnitramine, in order to compensate for the extra molecule of water contained in the constitution of the comparison pair of substances, 2 : 4-dinitromethylaniline and nitric acid. The results were as before. This pair of experiments was now repeated allowing various longer periods for reaction, up to 170 hours, at 20°. In all cases the rearrangements of 2 : 4-dinitrophenylmethylnitramine were nearly complete, while in the comparison experiments with 2 : 4-dinitromethylaniline considerable proportions of the unconverted material could be readily recovered, even after the longest of the treatments. Similar results were obtained for the longer reaction periods in some experiments which were carried out with 72% (by weight) aqueous sulphuric acid as the medium.

The principal result of the work reported in this Section may be summarised in the statement that, under those conditions of rearrangement of 2 : 4-dinitrophenylmethylnitramine for which a decision can be made, 2 : 4 : 6-trinitromethylaniline is formed more readily and more smoothly by the rearrangement than it is formed by the interaction of 2 : 4-dinitromethylaniline with nitric acid.

(3) *Discussion of the Mechanism of the Nitramine Rearrangement.*

The experiments described in Section 2 establish the following points: (2.1) that the acid-catalysed rearrangement of phenylnitramine and the nitration of aniline, in comparable conditions, orient the nuclear nitro-substituent in quite different ways; (2.2) that, in the rearrangement of *p*-nitrophenylmethylnitramine, nitric acid is not produced to a detectable extent, and not fast enough to enable it to be considered as a possible intermediate; (2.3) that, in the rearrangement of 2 : 4-dinitrophenylmethylnitramine, nitric acid is produced quickly enough to allow it to be considered as a possible intermediate; (2.4) but that nitric acid cannot actually be an intermediate of any importance, because it does not effect the necessary nuclear nitration with sufficient facility.

From this we conclude that the acid-catalysed rearrangement of nitramines in the solvents investigated—mostly solvents having at least the polarity of acetic acid, and including water and sulphuric acid—is essentially intramolecular. Transference of the nitro-group of the nitramine to a foreign aromatic nucleus can be observed, but this means only that reversible acidolysis of the nitro-group occurs, not that it is responsible for the rearrangement.

We have found no counterpart in the nitramine rearrangement to the reversible acidolysis succeeded by nuclear substitution, which Orton established as the basic mechanism for the rearrangement of aromatic chloramines in polar solvents. However, the nitramine rearrangement is analogous in mechanism to the benzidine change, which Ingold and Kidd proved to be intramolecular (*J.*, 1933, 984). Thus we have the interesting situation that, of the three groups, NHAr, Cl, NO_2, which for many purposes form a monotonic series, and which in aniline derivatives can migrate from nitrogen to the nucleus under the influence of acids, in polar solvents, the first and the third use the internal mechanism, while the second employs the external route. The range of this dichotomy of mechanism in the analogous migrations of other groups is receiving further attention.

(4) EXPERIMENTAL.

(4.1) *Orientation in the Rearrangement of Phenylnitramine and in the Nitration of Aniline.*—Phenylnitramine was prepared by a method essentially the same as that of Bamberger (*Ber.*, 1893, **26**, 471; 1894, **27**, 359). Crystallised from light petroleum, it had m. p. 44·5°. Aniline nitrate was prepared from freshly distilled aniline and absolute nitric acid in chloroform solution below –5°. It was crystallised from ethyl alcohol–chloroform. The three nitroanilines needed for the construction of the freezing-point diagram were purified as recommended by Holleman, Hartogs, and Linden (*loc. cit.*). Our *o*-nitroaniline had f. p. 69·2°, the *m*-nitroaniline f. p. 112·1°, and the *p*-nitroaniline f. p. 148·0°, these f. p.s being 0·2—0·3° lower than those recorded by Holleman and his co-workers.

The freezing points were determined by the Beckmann method, with continued observation of the cooling curve in many cases in order to determine the second freezing point.

The preliminary qualitative experiments made in order to ascertain the nature of the main products formed in the rearrangement of phenylnitramine, and in nitration of aniline in comparable conditions, and also to establish the best common condition for a quantitative investigation of the proportions in which the isomeric nitroanilines are formed in these reactions, are sufficiently described in Section 2.1. The quantitative experiments were carried out as follows.

Phenylnitramine (4·0 g.) was added in small portions to well-stirred sulphuric acid monohydrate (120 c.c.) at its freezing point. After being kept overnight, the solution was poured on ice and water (2 l.), and neutralised by means of sodium carbonate. A brown solid separated, and the whole mixture was extracted thoroughly with chloroform. The residue obtained by evaporating the chloroform was distilled twice at 1 mm. in order to remove all traces of tar. The yield was 90%. The initial f. p. was 64·5°, which corresponds to an *o*-nitroaniline content of 93·3%. This product (1·222 g. sample) was mixed with *p*-nitroaniline (1·354 g.). The initial f. p. of the mixture was 111·0°, which corresponds to 55·8% of *p*-nitroaniline, *i.e.*, to 6·8% of it in the original rearrangement product. The rearrangement product (1·153 g.) was mixed with *m*-nitroaniline (1·560 g.). This mixture had the initial f. p. 84·6°, which corresponds to 57·0% of *m*-nitroaniline in the mixture, *i.e.*, to none in the rearrangement product.

Aniline nitrate (4·5 g.) was added to sulphuric acid monohydrate (120 c.c.), and the product was worked up as before. The yield of isolated material was 80%. The initial f. p. was 114·45°, which corresponds to 59·3% of *p*-nitroaniline. This product (0·7809 g.) was mixed with *m*-nitroaniline (1·8290 g.). The mixture had initial f. p. 100·4°, corresponding to 80·2% of *m*-nitroaniline in the mixture, *i.e.*, to 33·8% in the original nitration product. The nitration product (0·3625 g.) was mixed with *o*-nitroaniline (2·4678 g.). This mixture had f. p. 60·7°, which corresponds to 88·0% of *o*-nitroaniline in the mixture, *i.e.*, to 6·3% in the original nitration product.

(4.2) *Rearrangement of* p-*Nitrophenylmethylnitramine.*—*p*-Nitromethylaniline (16 g.), suspended in acetic acid (150 c.c.), was treated with anhydrous nitric acid (7·5 c.c.) and acetic anhydride (30 c.c.). The original yellow solid quickly dissolved and a colourless solid separated. After 1 hour, the mixture was poured into water, and the *p*-nitrophenylmethylnitramine was collected and crystallised from ethyl alcohol. The yield was 16 g., and the m. p. 139° (Found: C, 42·8; H, 3·5. Calc.: C, 42·6; H, 3·5%).

A general account of the experiments, which were made on the rearrangement of this substance by means of various acids, in various solvents, without and with added aromatic compounds, is given in Section 2.2. Details of a few of these experiments are now added as illustration. (*Expt.* 1*a*). The nitramine (0·5 g.) was dissolved in cold concentrated sulphuric acid (10 c.c.), and the yellow solution was at once poured into water. The precipitated solid was collected, crystallised from acetic acid, and identified as 2 : 4-dinitromethylaniline by its m. p., 175·5°, and the mixed m. p. with an authentic specimen. (*Expt.* 2*d*). A solution of the nitramine (0·5 g.) in acetic acid (20 c.c.) was treated with a stream of dry hydrogen chloride, and the brown solution thus obtained was poured into water. The precipitated substance was crystallised from acetic acid, and identified by its m. p., 174·5°, and mixed m. p., as before. (*Expt.* 12*a*). A solution of the nitramine (1 g.) and of *p*-xylene (1 g.) in acetic acid (40 c.c.) was treated with hydrogen chloride. Some crystals separated, which were collected and identified as 2 : 4-dinitromethylaniline. The remaining brown solution was poured into water, and then distilled in steam. The distillate, which contained an oil, was extracted with ether. The ethereal solution was washed with aqueous sodium carbonate and dried. Distillation of the residue obtained by concentration of the extract gave unchanged *p*-xylene. The small residue remaining after the distillation was transferred to an Emich tube and micro-fractionated. In this way a little more *p*-xylene was obtained, the whole of the product distilling well below the b. p. of nitro-*p*-xylene. The material not carried over in the steam-distillation consisted of a yellow solid in aqueous suspension. The solid was collected, crystallised from acetic acid, and identified by its m. p., 174·5°, and mixed m. p., as 2 : 4-dinitromethylaniline.

(4.3) *Rearrangement of* 2 : 4-*Dinitrophenylmethylnitramine.*—The preparation of this substance is described in Part VII. A general account of its behaviour when treated with various acids, with or without solvents, is given in Section 2.3. Details are now added of a few illustrative cases. (*Expt.* 1). The nitramine (0·5 g.) was added to sulphuric acid (5 c.c.) at room temperature. After being kept overnight, the yellow solution was poured into water and the yellow precipitate then formed was collected, crystallised from ethyl alcohol, and identified by its m. p. and mixed m. p. as 2 : 4 : 6-trinitromethylaniline. (*Expt.* 5). The nitramine (0·5 g.) was heated on the water-bath with absolute nitric acid (10 c.c.). The solution became purple and then yellow. After 2·5 hours it was poured on ice, and the precipitate was collected, crystallised from ethyl alcohol, and identified by its m. p. and mixed m. p. as 2 : 4 : 6-trinitrophenylmethylnitramine. (*Expt.* 6). The 2 : 4-dinitro-nitramine (0·5 g.) was heated on the water-bath for 6 hours with a mixture of nitric acid (10 c.c.) and water (10 c.c.). The formed 2 : 4 : 6-trinitro-nitramine was isolated and identified as before. (*Expt.* 7). The nitramine (0·5 g.) was refluxed with concentrated hydrochloric acid (20 c.c.) for 3 hours. The solid first melted to give an oil, and this subsequently solidified giving an orange-yellow solid, which, after crystallisation from acetic acid, was identified by its m. p. and mixed m. p. as 2 : 4-dinitromethylaniline.

A general account has been given in Section 2.3 of the experiments made on the nitration of "foreign" aromatic compounds by 2 : 4-dinitrophenylmethylnitramine in media in which the latter undergoes rearrangement, and in the nitration of the same aromatic compounds in the same media by the use of nitric acid instead of the nitramine. A record of the substances isolated is contained in Table I. We now add details of a few of these experiments in illustration. (*Expt.* 12). 2 : 4-Dinitrophenylmethylnitramine (4 g.) was added to a mixture of sulphuric acid (40 c.c.) and *p*-xylene (2·5 c.c.). The solution darkened, a yellow oil separating. After being kept overnight, the mixture was poured into water and distilled in steam. The distillate was extracted with ether, and the residue obtained on concentrating the extract was micro-fractionated to give 2-nitro-*p*-xylene, b. p. (Emich) 230—232°, n_D^{15} 1·5468 (Found : C, 63·2, 63·6; H, 6·6, 6·2; N, 9·2. Calc. : C, 63·5; H, 6·0; N, 9·3%). The solid product not carried over by the steam was collected, crystallised twice from acetic acid, and identified as 2 : 4-dinitromethylaniline by its m. p. and mixed m. p. There were indications of the formation also of 2 : 4 : 6-trinitromethylaniline,but this substance was not isolated in a pure state. (*Expt.* 12*a*). Nitric acid (0·5 g.) was added to a mixture of sulphuric acid (25 c.c.) and *p*-xylene (1·2 c.c.). The product was worked up as in the preceding experiment. The steam-volatile material was solid, and from it, by crystallisation from ethyl alcohol, colourless needles, m. p. 93°, were obtained, corresponding in properties to 2 : 3-dinitro-*p*-xylene. (*Expt.* 24). 2 : 4-Dinitrophenylmethylnitramine (2g.) was added to a mixture of dimethylaniline (1 g.) and 80% (by weight) aqueous sulphuric acid (28·5 c.c.). Oxides of nitrogen were produced. After being left overnight, the mixture was poured into water, and the formed precipitate was collected, and crystallised repeatedly from ethyl alcohol. 2 : 4-Dinitromethylaniline, identified by m. p. and mixed m. p., was obtained. The aqueous filtrate was made alkaline, and some unchanged dimethylaniline was removed by distillation in steam. A tarry residue was left, which was dissolved in aqueous hydrochloric acid and cleaned as much as possible with charcoal. On basification with sodium carbonate, a pale pink solid was recovered with the properties of somewhat impure tetramethylbenzidine. There was evidence of the presence of a red compound, which may have been the 3 : 3′-dinitro-derivative (see below), but this was not isolated. (*Expt.* 24*a*). Nitric acid (0·5 g.) was added to a mixture of dimethylaniline (1 g.) and 80% aqueous sulphuric acid (28·5 c.c.). The solution became yellow, and then red. After being left overnight, it was poured into water. No precipitate appeared, but, when the solution was basified with sodium carbonate, a red solid separated. This was collected and extracted with hot ethyl alcohol. On concentration of the extract, and crystallisation of the solid obtained repeatedly from ethyl alcohol and from benzene–light petroleum, red crystals were obtained, m. p. 186°, probably 3 : 3′-dinitrotetramethylbenzidine. Indications were obtained of the presence also of unsubstituted tetramethylbenzidine, but this compound was not isolated pure.

An account of the series of experiments, which were made in order to compare the ease of rearrangement of 2 : 4-dinitrophenylmethylnitramine with the facility and the course of nitration of 2 : 4-dinitromethylaniline by nitric acid in comparable conditions, has been given in Section 2.4. Details of a few experiments are supplied as illustration. (*Expt.* 1). The nitramine (1·84 g.) was added to sulphuric acid (50 g.) at room temperature. After 24 hours the solution was poured into water (250 c.c.), the precipitate was collected (m. p. 109°, yield 93%), and, after crystallisation from alcohol, the product was identified as 2 : 4 : 6-trinitromethylaniline by comparison with an authentic specimen. (*Expt.* 1*a*). 2 : 4-Dinitromethylaniline (1·50 g.) and nitric acid (0·52 g.) were added to sulphuric acid (50 g.), and the solution was treated as before. The product (m. p. before purification 111°, yield 94%) was crystallised once from alcohol, and identified by its m. p. 113°, and mixed m. p., as 2 : 4 : 6-trinitromethylaniline. (*Expt.* 11). The nitramine (1·84 g.) and water (0·14 g.) were added to a portion (50 g.) of medium drawn from a made-up stock of 80% aqueous sulphuric acid. After 170 hours at 20°, the solution was poured into water, and the total product was recovered. It had m. p. 102°, and was somewhat impure 2 : 4 : 6-trinitromethylaniline, which could be obtained pure by crystallisation from alcohol. (*Expt.* 11*a*). 2 : 4-Dinitromethylaniline (1·50 g.) and nitric acid (0·52 g.) were added to a portion (50 g.) of the same stock of 80% sulphuric acid. After 170 hours at 20°, the total product was recovered as before. It had m. p. 130° and consisted of impure 2 : 4-dinitromethylaniline, which was readily obtained pure by washing it with benzene and crystallising it from acetic acid.

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