80. *Nitrous Acid as a Nitrating and Oxidising Agent. Part IV.* N-*Dialkylanilines.*

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The action of excess of nitrous acid on dimethyl-, diethyl-, methylethyl-, benzylmethyl-, and benzylethyl-aniline has been investigated in two different concentrations of hydrochloric acid at 0°. Dimethylaniline was found to undergo *p*-nitrosation and *p*-nitration simultaneously and, on keeping, *N*-nitroso-4-nitromonomethylaniline was formed together with a little 2 : 5-dinitromonomethylaniline, which indicated some *m*-nitration also; diethylaniline was completely converted into *N*-nitroso-4-nitromonoethylaniline; methylethylaniline gave a mixture of *N*-nitroso-4-nitromethyl- and *N*-nitroso-4-nitroethyl-aniline, the former greatly predominating; benzylmethylaniline was nitrated to form a mixture of 4-nitro- and 2 : 4-dinitro-benzylmethylaniline initially, but further contact with excess of nitrous acid changed 4-nitrobenzylmethylaniline into a mixture of mainly 2 : 4-dinitrobenzylmethylaniline and a little *N*-nitroso-4-nitrobenzylaniline; benzylethylaniline was converted into *N*-nitroso-4-nitrobenzylaniline. In no instance was the benzyl group expelled by nitrous acid and in all cases the ethyl group was much more readily eliminated than the methyl group.

Conditions necessary for the preparation in good yield of pure *p*-nitrosodimethylaniline hydrochloride are described.

The preparation of *p*-nitrosodimethylaniline hydrochloride by standard textbook methods (cf. Thorpe and Linstead, " The Synthetic Dyestuffs," 1933, p. 330) requires very careful attention to the directions given, otherwise the resulting compound will be contaminated with by-products, principally *p*-nitrodimethylaniline and *N*-nitroso-4-nitromethylaniline. The main precautions to be observed are : (1) the sodium nitrite, which should not exceed the theoretical quantity required for nitrosation, must be added gradually at *ca.* 0°, and (2) the concentration of the hydrochloric acid used should be such that *p*-nitrosodimethylaniline hydrochloride is insoluble in it and is therefore precipitated as soon as formed.

In view of the large amount of work published on abnormal reactions between nitrous acid and *p*-substituted tertiary aromatic amines (see papers by Reade and collaborators for bibliography) it appeared of interest to study the behaviour of dimethylaniline and some of its homologues towards nitrous acid in excess. Two reaction conditions in hydrochloric acid solution have been investigated at 0° : (*a*) in *ca.* 5% and (*b*) in 15—16% solution, and in (*a*) with twice, and in (*b*) with five times, the amount of sodium nitrite required for nitrosation. To exaggerate the conditions still further, the sodium nitrite was added as a finely powdered solid and not in solution, but at such a rate that the temperature could be maintained in the vicinity of 0° by external cooling and a little floating ice. The results were as follows :

(1) With dimethylaniline, in both (*a*) and (*b*), a mixture of *p*-nitrosodimethylaniline hydrochloride and *p*-nitrodimethylaniline in the ratio of *ca.* 3 : 1 was precipitated. The filtrate from this mixture, if neutralised immediately, gave a precipitate from (*a*) of pure *p*-nitrosodimethylaniline and from (*b*) of a mixture of mainly *p*-nitrosodimethylaniline with a little *N*-nitroso-4-nitromonomethylaniline. If, however, the filtrates from (*a*) and (*b*) were kept overnight, most of the *p*-nitrosodimethylaniline was converted into *N*-nitroso-4-nitromonomethylaniline; the conversion was complete after a further 24 hours. In addition, 2 : 5-dinitromonomethylaniline was formed in small quantity together with a still smaller amount of a trinitrated product. No variations of dilution prevented the formation of *p*-nitrodimethylaniline, provided that sodium nitrite was in excess, and at 30° and 70° it was formed even when slightly less than the theoretical quantity of sodium nitrite required for nitrosation was used.

The above experiments indicate that *p*-nitrosation and *p*-nitration are simultaneous initial reactions and that *m*-nitration also occurs, since the formation of 2 : 5-dinitromonomethylaniline could not be explained otherwise. The formation of nitric acid from nitrous acid by the powerful anionoid influence of the dimethylamino-group has been explained by Hodgson and Kershaw (J., 1930, 277) on the basis of current electronic theory, and the product of the action of nitrous acid on dimethyl-*p*-toluidine is mainly 2-nitro-4-methyldimethylaniline.

When the *p*-position to the dialkylamino-group, however, is free, the following modification is suggested : In hydrochloric acid solution there will be the dynamic equilibrium, $\mathrm{Ph{\cdot}NMe_2 + HCl \rightleftharpoons Ph{\cdot}\overset{+}{N}Me_2H|\overset{-}{Cl}}$, and the anionoid activity of the *p*-carbon atom will vary in different molecules from zero to a maximum in the free dimethylaniline; the nitric acid formed at the *p*-position due to relay of the anionoid effect by the conjugated chain will then nitrate the base to form *p*-nitrodimethylaniline. As the anionoid character of the *p*-carbon atom decreases in molecules which are approaching salt formation, so will nitration become impossible and nitrosation will occur until finally the actual salt molecules will remain inert. In this connection it is of interest to recall the action of nitrous acid on *p*-iododimethylaniline (Aitken and Reade, J., 1926, 1896), in which the products are *p*-nitrodimethylaniline and 4-iodo-2-nitrodimethylaniline. Here the iodine in the most intense anionoid phase has contributed its positive electromeric (or mesomeric) effect and, becoming sufficiently kationoid thereby, has been displaced as hypoiodous acid by the more strongly kationoid nascent nitric acid. In the less intense anionoid phases, nitration has occurred in position 2, as in the case of dimethyl-*p*-toluidine (Hodgson and Kershaw, *loc. cit.*). The fact that nitric acid at the same dilution cannot nitrate either dimethyl-*p*-toluidine or dimethylaniline is due to its being fully ionised, whereas the mainly un-ionised but polarised nitrous acid is attracted to the activated *o*- or *p*-carbon atom and oxidised there within the reaction zone by a neighbouring but more kationoid nitrous acid molecule.

As shown by Hodgson and Smith (J., 1931, 1508), nitrous acid reacts with *p*-nitrosodimethylaniline hydrochloride in hydrochloric acid to form *N*-nitroso-4-nitromonomethylaniline, and the formation of this product when the filtrates in (*a*) and (*b*) are kept overnight confirms the previous work. The mechanism of this reaction may tentatively be visualised as an initial attack on the anionoid nitrogen of the dimethylamino-group by the kationoid nitrous acid with expulsion of the methyl group as methyl alcohol [subsequently to be oxidised to formaldehyde (cf. Crowley, Milton, Reade, and Todd, J., 1940, 1286)] and its replacement by the nitroso-group. The latter prevents salt formation and thereby enables transmission of anionoid activity to the *p*-carbon atom, with subsequent oxidation of the nitroso-group there by the more kationoid nitrous acid, the reaction almost corresponding to a two-point attack by nitrous acid, since formation of *N*-nitroso-4-nitrosomonomethylaniline was never observed.

The presence of 2 : 5-dinitromonomethylaniline in the filtrate when kept overnight is readily explained on the assumption of *m*-nitration of the dimethylaniline hydrochloride (since treatment of dimethylaniline in sulphuric acid with nitric acid gives a mixture of 3- and 4-nitrodimethylanilines), followed by the nitro-*N*-nitrosation process, which owing to deactivation of the 4-position by the 3-nitro-group will be directed to form 2 : 5-dinitro-*N*-nitrosomonomethylaniline (cf. Macmillan and Reade, J., 1929, **2863**), and finally the expulsion of the *N*-nitroso-group, either by the great excess of hydrochloric acid present or in the manipulation necessary for the isolation of the compound.

When *p*-nitrodimethylaniline is submitted to the drastic conditions of (*b*), it is converted mainly into *N*-nitroso-4-nitromonomethylaniline (Macmillan and Reade, *loc. cit.*), although a small amount of 2 : 4-dinitrodimethylaniline is also formed. Here the nitrous acid has behaved normally and caused nitration in position 2.

(2) With monomethylaniline, procedures (*a*) and (*b*) both gave *N*-nitrosomethylaniline initially, which on standing was slowly converted into *N*-nitroso-4-nitromonomethylaniline, in (*a*) partially, and in (*b*) ultimately in theoretical yield.

(3) With diethylaniline, which does not form a hydrochloride insoluble in hydrochloric acid, a precipitate of *N*-nitroso-4-nitromonoethylaniline formed almost immediately in both (*a*) and (*b*), and this compound continued to be precipitated until the whole of the diethylaniline had been transformed. In (*a*) immediate neutralisation of the filtrate from the first precipitate (removed after 10 minutes) gave practically pure *p*-nitrosodiethylaniline, whereas the corresponding filtrate in (*b*) yielded a mixture of *p*-nitrosodiethylaniline and *N*-nitroso-4-nitromonoethylaniline, showing that under the more drastic conditions of (*b*) the nitrous acid had made a two-point attack (see above) on the *p*-nitrosodiethylaniline initially formed. *p*-Nitrodiethylaniline was not detected in any of the experiments, the stronger basic character of the diethylamino-group, compared with the dimethylamino-group, producing more salt-formation, with consequently a shorter period for diethylaniline to exist as the free base.

(4) With monoethylaniline, the reaction appeared to take place in two stages, *viz.*, the initial formation of *N*-nitrosoethylaniline, followed by *p*-nitration, which occurred slowly in (*a*) and more rapidly in (*b*).

(5) With methylethylaniline, the reactions were slow in both (*a*) and (*b*), and p-*nitrosomethylethylaniline* was formed but remained in solution. On long standing, however, the final products were mixtures of *N*-nitroso-4-nitromonomethylaniline and *N*-nitroso-4-nitromonoethylaniline. These experiments confirm the result of Crowley, Milton, Reade, and Todd (*loc. cit.*) that the ethyl group is more easily eliminated than the methyl group. The great difference in the reactivities of dimethylaniline and diethylaniline towards nitrous acid is further evidence of the readier elimination of the ethyl group.

(6) With benzylmethylaniline and benzylethylaniline, the rates of precipitation were slower than in the cases of dimethyl- and diethyl-aniline. Benzylethylaniline, which reacted the faster of the two, was entirely converted under both conditions (*a*) and (*b*) into *N*-nitroso-4-nitrobenzylaniline. Benzylmethylaniline in (*a*) gave entirely *p*-nitrobenzylmethylaniline, but in (*b*) this compound was accompanied by 2 : 4-dinitrobenzylmethylaniline. Benzylmethylaniline was therefore nitrated and not nitrosated by nitrous acid, and group expulsion was not detected, showing that the nitration process in the formation of *N*-nitroso-4-nitroalkylaniline in previous cases was bound up with *p*-nitrosation and in the dialkylanilines with group elimination.

When *p*-nitrobenzylmethylaniline was submitted a second time to the conditions of (*b*), the main product was 2 : 4-dinitrobenzylmethylaniline, but a small amount of *N*-nitroso-4-nitrobenzylaniline was formed, showing that of the two groups the methyl was more readily expelled than the benzyl group. The ease of group elimination by nitrous acid is thus in the order : ethyl $\gg$ methyl $\gg$ benzyl.

It is noteworthy that, whereas *p*-nitrobenzylmethylaniline resists the action of boiling concentrated hydrochloric acid, 2 : 4-dinitrobenzylmethylaniline is thereby transformed into 2 : 4-dinitromonomethylaniline.

Finally, it is remarkable that, whereas *p*-nitrobenzylmethylaniline has m. p. 70°, the m. p. of the much lighter molecule *p*-nitrodimethylaniline is 163°. This outstanding difference is probably also related to the fact that the former compound is very soluble in cold ether, whereas the latter is almost insoluble. It would seem that *p*-nitrodimethylaniline is a highly polarised molecule compared with its benzylmethyl and diethyl (m. p. 78°) homologues.

EXPERIMENTAL.

General Procedure.—Solutions and in some cases suspensions of the amine (4 c.c.) in (*a*) hydrochloric acid (20 c.c., *d* 1·16) and water (100 c.c.), and in (*b*) hydrochloric acid (50 c.c., *d* 1·16) and water (50 c.c.), were treated at 0° with finely powdered sodium nitrite [4 g. in (*a*) and 10 g. in (*b*)], added at such a rate as to keep the temperature in the vicinity of 0° (external cooling). The solids which separated (sometimes almost immediately and sometimes during 1 hour) were removed. The filtrates were tested immediately by neutralisation of a portion for nitrosation products; the remainder was kept overnight or, if necessary, for several days. The individual cases are described below. All the analytical data were obtained by micro-analysis.

Monomethylaniline.—(*a*) The initial product was *N*-nitrosomethylaniline, which separated as an oil. A trace of *N*-nitroso-4-nitromonomethylaniline, which was detected after a week, crystallised from methyl alcohol in yellow needles, m. p. 104° (Found : N, 23·3. Calc. : N, 23·2%).

(*b*) During the first day, only *N*-nitrosomethylaniline separated, but after 3 days the whole of the original monomethylaniline was converted into *N*-nitroso-4-nitromonomethylaniline; yellow needles from methyl alcohol, m. p. 104° (Found : N, 23·3%). The final filtrate gave no precipitate with alkali.

Dimethylaniline.—(*a*) On addition of the finely powdered sodium nitrite, the mixture assumed a deep orange-red colour, and copious precipitation almost immediately ensued. After 10 minutes, the precipitate, which was a mixture of *p*-nitrosodimethylaniline hydrochloride and *p*-nitrodimethylaniline, was filtered off and washed with cold water until all the *p*-nitrosodimethylaniline hydrochloride had dissolved. The insoluble *p*-nitrodimethylaniline (*ca.* 1 g.) crystallised from 50% aqueous ethyl alcohol in bright yellow parallelepipeds, m. p. and mixed m. p. with an authentic specimen 163° (Found : N, 17·0. Calc. : N, 16·8%). The combined aqueous washings above, when neutralised, gave a precipitate of *p*-nitrosodimethylaniline (1·5—2·0 g.), which crystallised from 50% aqueous ethyl alcohol in green needles, m. p. 85° (lit., m. p. 85°) (Found : N, 18·7. Calc. : N, 18·6%). The initial filtrate above, when neutralised immediately, gave mainly *p*-nitrosodimethylaniline mixed with small amounts of *N*-nitroso-4-nitromonomethylaniline, but, if kept overnight, almost the whole of the dissolved matter separated in light orange-coloured crystals. The latter dissolved almost entirely in hot methyl alcohol, from which, on cooling, *N*-nitroso-4-nitromonomethylaniline separated in bright yellow parallelepipeds, m. p. 104° (Found : N, 23·3%). The small red residue was boiled with ethyl alcohol; the solution, on cooling, deposited red needles of 2 : 5-dinitromonomethylaniline, m. p. 164° (Macmillan and Reade, J., 1929, 2863, give m. p. 163°) [depressed by 2 : 5-dinitrodimethylaniline (m. p. 112°), 3 : 4-dinitrodimethylaniline (m. p. 176°), 2 : 4-dinitromonomethylaniline (m. p. 176°), 4-nitrodimethylaniline (m. p. 163°), and 2 : 4-dinitrodimethylaniline (m. p. 87°)] (Found : N, 21·4. Calc. : N, 21·3%). The final residue separated from boiling glacial acetic acid in scarlet crystals, m. p. *ca.* 200° (Found : N, 22·1. Calc. for a trinitrodimethylaniline : N, 21·9%), but was too small for further investigation.

An experiment carried out with dimethylaniline (2 c.c.), sodium nitrite (2 g.), hydrochloric acid (20 c.c., *d* 1·16), and water (200 c.c.), afforded immediate precipitation of *p*-nitrodimethylaniline (*ca.* 0·1 g.), but *p*-nitrosodimethylaniline hydrochloride did not separate, this product being now retained in solution.

(*b*) The initial precipitate (*ca.* 3 g.) was filtered off after 1 hour. It consisted of *p*-nitrosodimethylaniline hydrochloride, which was removed by cold water as in (*a*), together with water-insoluble *N*-nitroso-4-nitromonomethylaniline, which crystallised from methyl alcohol in yellow needles, m. p. 104° (Found : N, 23·3%). There was no *p*-nitrodimethylaniline in the precipitate, the whole of it dissolving readily in cold methyl alcohol. The neutralised aqueous washings yielded *p*-nitrosodimethylaniline (*ca.* 1·5—2·0 g.) in various experiments, and the initial filtrate, when kept overnight, deposited most of its dissolved matter as *N*-nitroso-4-nitromonomethylaniline and all of it as such after 3 days. A little 2 : 5-dinitromonomethylaniline also present was identified as under (*a*).

All the samples of *N*-nitroso-4-nitromonomethylaniline obtained in the various experiments above were separately denitrosated by warming with dilute sulphuric acid and urea (cf. Macmillan and Reade, J., 1929, 585) and yielded 4-nitromonomethylaniline, which crystallised from boiling methyl alcohol in orange-brown hexagonal plates, m. p. and mixed m. p. 152°, with correct analyses for nitrogen (Meldola and Salmon, J., 1888, **53**, 775, give m. p. 152°).

Further experiments. When a deficiency of sodium nitrite was used in either (*a*) or (*b*), *p*-nitrosodimethylaniline hydrochloride appeared to be the sole product. Also, when sodium nitrate was used instead of sodium nitrite in (*a*) and (*b*), no immediate reaction occurred.

Preparation of pure p-*nitrosodimethylaniline hydrochloride.* When dimethylaniline (8 g.), dissolved in hydrochloric acid (50 c.c., *d* 1·16), was treated with ice (50 g.) and then with a solution of sodium nitrite (3·5 g.; the equivalent is 4·7 g.) in water (10 c.c.), an orange-red solid separated after 4 minutes' stirring. It was entirely soluble in cold water, leaving no residue of *p*-nitrodimethylaniline or of *N*-nitroso-4-nitromonomethylaniline. The initial filtrate, when neutralised, afforded only a trace of *p*-nitrosodimethylaniline, so the whole of the nitrosation product was precipitated as pure *p*-nitrosodimethylaniline hydrochloride.

Nitration of p-*nitrodimethylaniline by nitrous acid.* A well-stirred mixture of *p*-nitrodimethylaniline (1 g.), hydrochloric acid (20 c.c., *d* 1·16), and water (20 c.c.) was treated with finely powdered sodium nitrite (5 g.) and kept overnight. The solid which had separated was extracted with 50% alcohol to remove the *N*-nitroso-4-nitromonomethylaniline which constituted the major portion of the product; the small residue crystallised from alcohol in bright yellow hexagonal plates, m. p. 87° (van Romburgh, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 820, gives m. p. 87°), identical with the product obtained by the action of dimethylamine on 1-chloro-2 : 4-dinitrobenzene. 2 : 5-Dinitromonomethylaniline was not detected.

Monoethylaniline.—(*a*) An oily separation of *N*-nitrosoethylaniline first appeared and only after several days' keeping was *N*-nitroso-4-nitroethylaniline formed. This compound crystallised from methyl alcohol in yellow parallelepipeds, m. p. 120° (Baillie and Tafel, *Ber.*, 1899, **32**, 72, and Baudisch, *Ber.*, 1906, **39**, 4297, give m. p. 119—120°) (Found : N, 21·6. Calc. : N, 21·5%).

(*b*) An almost immediate separation of *N*-nitroso-4-nitroethylaniline occurred mixed with a little oily *N*-nitrosoethylaniline.

Diethylaniline.—(*a*) On addition of the sodium nitrite, the solution became deep orange-red. A small precipitate of *N*-nitroso-4-nitroethylaniline, filtered off after 15 minutes and washed with water (the washings showed that *p*-nitrosodiethylaniline hydrochloride had not been precipitated), crystallised from methyl alcohol in yellow parallelepipeds, m. p. 120° (Found : N, 21·6. Calc. : N, 21·5%). The initial filtrate, when rendered alkaline immediately, gave a precipitate (*ca.* 4·0 g.) of *p*-nitrosodiethylaniline, which crystallised from methyl alcohol in green needles, m. p. 85° (lit., m. p. 84°) (Found : N, 15·8. Calc. : N, 15·7%). If the initial filtrate, however, was kept and filtered every 2 hours, *N*-nitroso-4-nitroethylaniline was continuously precipitated until a quantitative yield was obtained. It gave the Liebermann nitroso-reaction. When it was heated with 50% sulphuric acid and urea (cf. Macmillan and Reade, *loc. cit.*), and the solution neutralised, 4-nitroethylaniline was obtained, which crystallised from 50% acetic acid in long yellow parallelepipeds, m. p. 96° (Weller, *Ber.*, 1883, **16**, 31, gives m. p. 95°) (Found : N, 17·0. Calc. : N, 16·8%).

(*b*) The initial precipitate (1·5 g.) of *N*-nitroso-4-nitroethylaniline filtered off after 15 minutes was practically pure. The filtrate, when immediately neutralised, gave a mixture of *p*-nitrosodiethylaniline and *N*-nitroso-4-nitroethylaniline. If, however, this filtrate was kept overnight, the whole of its dissolved matter was converted into *N*-nitroso-4-nitroethylaniline.

When *p*-nitrosodiethylaniline (2 g.) was suspended in a solution of hydrochloric acid (25 c.c., *d* 1·16) and water (25 c.c.) at 0°, treated with finely powdered sodium nitrite (5 g.), and left overnight, it was converted entirely into *N*-nitroso-4-nitroethylaniline.

Methylethylaniline.—(*a*) During the first 2 hours of reaction, very moderate precipitation took place of a solid, insoluble in water, which crystallised from 50% aqueous alcohol in yellow plates, m. p. *ca.* 70° (Found : N, 22·4%), and gave the Liebermann nitroso-reaction. If the filtrate was neutralised immediately and the oily precipitate dissolved in hot aqueous methyl alcohol, on cooling, p-*nitrosomethylethylaniline* separated in yellowish-green leaflets, m. p. 69° (Found : N, 17·1. $C_9H_{12}ON_2$ requires N, 17·0%). If, however, the filtrate was kept overnight, the dissolved matter was entirely precipitated and it then crystallised from 50% aqueous ethyl alcohol in yellow needles and flat parallelepipeds, m. p. 88—89° (Found : N, 22·9%). The products from various experiments all corresponded in nitrogen content to mixtures of *N*-nitroso-4-nitromethylaniline and *N*-nitroso-4-nitroethylaniline, and from the thermal analytical data of Crowley, Milton, Reade, and Todd (*loc. cit.*), the mixture would appear to consist of *ca.* 83% of the methyl and *ca.* 17% of the ethyl homologue.

(*b*) The precipitation, though slow, occurred earlier than in (*a*); the product crystallised from methyl alcohol in yellow needles, m. p. 81° (Found: N, 22·7%), corresponding to *ca.* 71% of *N*-nitroso-4-nitromethyl- and 29% of *N*-nitroso-4-nitroethyl-aniline. If the initial filtrate was kept for 2 days, the whole of its dissolved matter was precipitated; in a typical case the crude product (m. p. *ca.* 119°) partly dissolved in methyl alcohol and separated therefrom in yellow needles, m. p. 140—155°; the residue of spear-like needles had m. p. 174° and its nitrogen content (Found: N, 25·2%) indicated that it was a mixture of more highly nitrated compounds.

Benzylmethylaniline.—(*a*) Owing to the sparing solubility of this amine in hydrochloric acid, it (4 c.c.) was first dissolved in glacial acetic acid (15 c.c.); hydrochloric acid (20 c.c., *d* 1·16) was then added, and finally water (50 c.c.) drop by drop until a turbidity was just apparent. Sodium nitrite (4 g.) was next added rapidly at 0°; the mixture became deep red, and after 1 hour a greenish crystalline precipitate (*ca.* 1 g.) of 4-nitrobenzylmethylaniline was filtered off. This compound was very soluble in cold ether, methyl alcohol, and hot 50% acetic acid but less soluble in cold light petroleum, though it dissolved in the boiling solvent; from all of them it separated in long, slender, greenish-yellow parallelepipeds or needles, m. p. 70° (Meldola and Hollely, J., 1915, **107**, 619, give m. p. 68—69°) (Found: N, 11·7. Calc.: N, 11·6%). It was stable towards boiling 2N-sodium hydroxide and boiling hydrochloric acid (*d* 1·16). The initial filtrate, when kept, continued to deposit 4-nitrobenzylmethylaniline until the whole of the original benzylmethylaniline had been converted, but, if neutralised at an earlier stage, a mixture of unchanged benzylmethylaniline and its 4-nitro-derivative was precipitated.

(*b*) Benzylmethylaniline (4 c.c.) was dissolved in glacial acetic acid (15 c.c.) and hydrochloric acid (50 c.c., *d* 1·16), water (50 c.c.), and sodium nitrite (10 g.) were added at 0°. Again a slow reaction occurred, and precipitates were collected at intervals, the first after 3 hours and the last after keeping overnight. These were all treated with cold ether: the first precipitate partly dissolved, the intermediate ones were completely soluble, and the overnight separation was almost insoluble. The soluble products were all 4-nitrobenzylmethylaniline, m p. 70° (correct nitrogen content). The ether-insoluble products, which were identical (mixed m. p.), crystallised from methyl alcohol, in which they were sparingly soluble, in starlike clusters of thick greenish-yellow parallelepipeds or slender yellow prisms of 2 : 4-dinitrobenzylmethylaniline, m. p. 144° (Mulder, *Rec. Trav. chim.*, 1906, **25**, 109, gives m. p. 143—144°) (Found: N, 14·7. Calc.: N, 14·6%). This compound was stable towards boiling 2N-sodium hydroxide, but dissolved in boiling concentrated hydrochloric acid with evolution of benzyl chloride; the solution on dilution with water and subsequent neutralisation gave a precipitate of 2 : 4-dinitromonomethylaniline, which crystallised from alcohol in short, yellow, rectangular prisms, m. p. and mixed m. p. with an authentic specimen 176° (Found: N, 21·4. Calc.: N, 21·3%).

The action of nitrous acid on 4-nitrobenzylmethylaniline. A mixture of the amine (1 g.), hydrochloric acid (20 c.c., *d* 1·16), and water (20 c.c.) was shaken at 0° with solid sodium nitrite (5 g.) and kept overnight. The separated solid (m. p. 116°) was partly soluble in boiling 50% aqueous ethyl alcohol, from which *N*-nitroso-4-nitrobenzylaniline separated on cooling (m. p. 96°); recrystallised from boiling 50% acetic acid, it formed pale straw-yellow, spear-like crystals, m. p. 108° (Found: N, 16·6. Calc.: N, 16·4%). The m. p. was depressed by *N*-nitroso-4-nitromethylaniline. The residue crystallised from ethyl alcohol or aqueous acetic acid in slender greenish-yellow prisms, m. p. 144° (Found: N, 14·7%), identical with the compound obtained previously and was converted by boiling hydrochloric acid into 2 : 4-dinitromonomethylaniline.

Benzylethylaniline.—(*a*) and (*b*). The rate of precipitation was greater than in the case of benzylmethylaniline, and the sole product formed in both cases was *N*-nitroso-4-nitrobenzylaniline, which crystallised from boiling 50% acetic acid in pale straw-yellow, spear-like crystals, m. p. 108° (Meldola and Streatfeild, *Ber.*, 1886, **19**, 3250, give m. p. 107·5°) (Found: N, 16·6. Calc.: N, 16·4%).

The authors thank Imperial Chemical Industries (Dyestuffs) Ltd. for various gifts.

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[*Received, February 26th,* 1941.]