

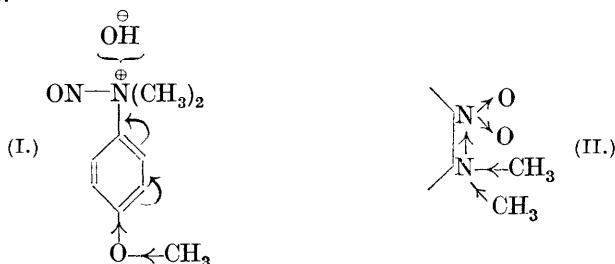
**244.** *Nitrous Acid as a Nitrating Agent. Part II.*  
*The Nitration of Dimethyl-p-anisidine.*

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NITROUS acid nitrates dimethyl-*p*-anisidine, as it does dimethyl-*p*-toluidine (Hodgson and Kershaw, J., 1930, 277), giving over 90% of 3-nitrodimethyl-*p*-anisidine (3-nitro-4-dimethylaminoanisole) : nitric acid at equivalent dilution is practically inactive, and normal nitration in sulphuric acid produces 2-nitrodimethyl-*p*-anisidine. The similarity extends to the order of the m. p.'s and volatility in steam of the nitro-compounds, to the m. p.'s of their picrates, and to the formation of a brilliant red unstable compound from dimethyl-*p*-anisidine and picric acid.

The small amount (< 1%) of nitrosomonomethyl-*p*-anisidine formed in this reaction is, however, in striking contrast to the corresponding amount (> 16%) of nitrosomonomethyl-*p*-toluidine, an indication that the powerful electromeric (+ *T*) influence of the methoxyl group has been brought into action by salt formation at the dimethylamino-group (I) and has thereby inhibited displacement of a methyl group; the more feeble general effect (+ *I*) of the *p*-methyl group in dimethyl-*p*-toluidine is reflected in the much greater yield of *N*-nitroso-product. When the powerful electron-attracting (− *T* − *I*) nitro-group is present as in *p*-nitrodimethylaniline, Macmillan and Reade (J., 1929, 2863) found more

than 30% of nitroso-amine and no nitration, a result to be expected on the above reasoning, since it is the converse of the present investigation (compare also Hodgson, *J. Soc. Dyers and Col.*, 1930, 46, 183).



The much lower m. p. of 3-nitrodimethylamino-*p*-anisidine compared with that of its toluidine analogue suggests that chelation of the type (II), already proposed for such compounds (Hodgson and Kershaw, *J.*, 1930, 497), is more strongly reinforced by the *p*-methoxyl than by the *p*-methyl group, and appears to afford evidence of the positive interior-effect of the kind postulated by Cocker, Lapworth, and Walton (*J.*, 1930, 448) to explain the influence of the methoxyl group in monochlorodimethyl ether.

Dimethyl-*p*-anisidine (Griess, *Ber.*, 1880, 13, 249) is conveniently obtained by a two-stage treatment of *p*-anisidine with methyl sulphate; a single-stage treatment with excess of the reagent gives a poor yield owing to the ready formation of the quaternary ammonium salt.

#### EXPERIMENTAL.

*Dimethyl-p-anisidine.*—Molten *p*-anisidine (40 g.) was treated (with cooling if necessary) with methyl sulphate (40 c.c.), and the mixture made faintly alkaline (aqueous sodium hydroxide) and steam-distilled. The volatile bases obtained, including those extracted by ether, were again treated with methyl sulphate (20 c.c.). Basification, steam-distillation, treatment of the volatile solid (molten) with acetic anhydride, and further basification (aqueous sodium carbonate) and steam-distillation gave dimethyl-*p*-anisidine, which crystallised from water in colourless plates, m. p. 48° (Found: N, 9.4. Calc.: N, 9.3%). The *picrate*, prepared in alcohol, crystallised from methyl alcohol in brilliant greenish-yellow, rectangular plates, m. p. 139° (Found: N, 14.9.  $\text{C}_{15}\text{H}_{16}\text{O}_8\text{N}_4$  requires N, 14.7%).

*Action of Nitrous Acid on Dimethyl-p-anisidine.*—The experiment was made in exactly the same way as that on dimethyl-*p*-toluidine (*loc. cit.*, p. 279), half-quantities being used. Less than 0.05 g. of nitrosomonomethyl-*p*-anisidine was obtained. From the aqueous

acid extract, 6 g. of 3-nitrodimethyl-*p*-anisidine were obtained; after being frozen and purified *via* the hydrochloride (twice recrystallised), this had setting-point 14° (Found: N, 14.4.  $C_9H_{12}O_3N_2$  requires N, 14.3%). The hydrochloride crystallised from water in colourless parallelepipeds, m. p. 95° (Found: N, 12.2; Cl, 15.3.  $C_9H_{12}O_3N_2.HCl$  requires N, 12.0; Cl, 15.3%), and the picrate from alcohol in bright yellow needles, m. p. 143° (red liquid after softening) (Found: N, 16.7.  $C_{15}H_{15}O_{10}N_5$  requires N, 16.5%). The above products were identified by comparison with the synthetic compounds (below).

*Nitrosomonomethyl-p-anisidine*.—*p*-Anisidine (5 g.) and methyl sulphate (3 c.c.) were mixed at 60°, excess of sodium hydroxide added, and the whole steam-distilled. The volatile monomethyl-*p*-anisidine (5 g.) was isolated by means of ether and treated in concentrated hydrochloric acid (15 c.c.) and water (10 c.c.) at 0° with sodium nitrite (4 g. in water, 20 c.c.). Nitrosomonomethyl-*p*-anisidine (4 g.), which separated at once as a brownish-yellow solid, was purified by steam-distillation and recrystallisation from light petroleum, forming clusters of hexagonal plates, m. p. 47° (Found: N, 17.0.  $C_8H_{10}O_2N_2$  requires N, 16.9%). In the Liebermann test it gave an emerald-green colour, changing to cherry-red on dilution and to deep royal-blue on basification (sodium hydroxide). The volatility in steam is about 2 g. per litre of distillate, and no salts are formed with hydrochloric and picric acids.

*Synthesis of 3-Nitrodimethyl-p-anisidine*.—Acet-*p*-anisidide (16 g.) was stirred with 11% nitric acid (60 c.c.) (compare Reverdin, *Ber.*, 1896, 29, 2595), and the 3-nitroacet-*p*-anisidide (19.0 g.) formed was collected and converted, after hydrolysis with hot 10% alcoholic potassium hydroxide (100 c.c.), into steam-volatile 4-chloro-3-nitroanisole (14 g.) by the Sandmeyer reaction. This compound, which crystallised from aqueous alcohol in very pale yellow needles, m. p. 45° (Found: N, 7.5; Cl, 18.7.  $C_7H_6O_3NCl$  requires N, 7.5; Cl, 18.9%), was heated (6 g.) for 8 hours at 150° with dimethylamine (2 g. in alcohol, 40 c.c.); the alcohol was then removed by distillation, and the 3-nitrodimethyl-*p*-anisidine (6 g.) by steam-distillation; red crystals, setting-point, 14° (Found: N, 14.4%); hydrochloride, m. p. 95° (Found: N, 12.3; Cl, 15.1%); picrate, m. p. 143° (Found: N, 16.6%).

*Nitration of Dimethyl-p-anisidine*.—The amine (3 g.) in concentrated sulphuric acid (7 c.c.) was gradually treated at 0° with a mixture of nitric acid (1.4 c.c.; *d* 1.5) and sulphuric acid (5 c.c.) and almost immediately poured on ice (200 g.). From the neutralised mixture, steam-distillation slowly removed 2-nitrodimethyl-*p*-anisidine, which crystallised from alcohol in large, deep red parallel-

epipeds, m. p.  $44^{\circ}$  (Found: N, 14.5.  $C_9H_{12}O_3N_2$  requires N, 14.3%). The *picrate* crystallised from alcohol in large rectangular plates, m. p.  $175^{\circ}$  (Found: N, 16.8.  $C_{15}H_{15}O_{10}N_5$  requires N, 16.5%).

2- and 3-Nitrodimethyl-*p*-anisidine both give yellow solutions in non-dissociating solvents, whereas in dissociating media, especially in phenol, intense red solutions are formed.

The authors desire to thank the Imperial Chemical Industries, Ltd., for their various gifts.

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[Received, March 9th, 1932.]

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