XLII.—*Nitrous Acid as a Nitrating Agent. Part I. The Nitration of Dimethyl*-p-*toluidine.*

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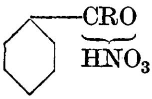
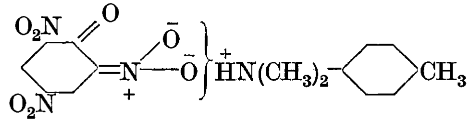
NITROUS acid *nitrates* dimethyl-*p*-toluidine, giving at least 80% of 3-*nitrodimethyl*-p-*toluidine* (3-nitro-4-dimethylaminotoluene) : nitric acid at the same dilution is practically inactive. *o*-Nitrosation analogous to the *p*-nitrosation of dimethylaniline does not appear to take place. Since 2-*nitrodimethyl*-p-*toluidine* is produced by the normal nitration process, the mechanism of the above reaction must differ from that of ordinary nitration.

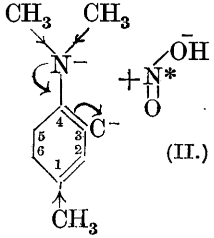
Lapworth and Robinson (*Mem. Manchester Phil. Soc.*, 1928, **72**, 47) explain the apparently anomalous ortho-nitration of benzaldehyde and of acetophenone by assuming the formation of an additive complex (I) of nitric acid and the unsaturated group, which then favours nitration in the ortho-position. In the light of this conception it may be assumed that the nitrogen atom and the 3-carbon atom of dimethyl-*p*-toluidine, both strongly activated (II), produce a negative field which attracts the polarised nitrous acid, $\overset{-}{\mathrm{H}}\mathrm{O}\overset{+}{\mathrm{N}}\mathrm{O}$, and, by rendering its nitrogen* less positive, makes it prone to oxidation : the free nitrous acid in the solution oxidises the nitrous acid component of the complex (II) to nitric acid, with evolution of nitric acid and nitrous oxides and subsequent nitration at the activated 3-carbon atom.

(I.)



(III.)





(II.)

The m. p.'s of the picrates of the two pairs of nitro-compounds studied show definitely that the lower m. p. is associated with the greater chelation (in the case of the 3-nitro-compounds) and conversely that the higher m. p. accompanies increased salt-formation (with the 2-nitro-compounds).

The brilliant red unstable compound formed when dimethyl-*p*-toluidine is mixed with picric acid may perhaps be due to temporary formation of the salt of the *aci*-form of picric acid (III), since such salts have a bright red colour.

EXPERIMENTAL.

*Preparation of Dimethyl-*p*-toluidine.*—A mixture of *p*-toluidine (72·7 g.), methyl iodide (96·5 g.), and water (100 c.c.) was heated under reflux (2—3 hours), and then exactly neutralised with aqueous sodium hydroxide. A further addition of methyl iodide (96·5 g.) was made, and after being again heated until the odour of the methyl iodide had vanished, the mixture was rendered faintly alkaline and steam-distilled. The oily layer of the distillate was treated with acetic anhydride (2—3 c.c. at a time) until no rise of temperature subsequently occurred, a further 5 c.c. were added (total addition, about 35 c.c.) and the mixture was heated on the water-bath for 1 hour, poured into water (200 c.c.), shaken well to decompose the acetic anhydride, neutralised with sodium hydroxide, and steam-distilled; pure dimethyl-*p*-toluidine (33 g.) passed over (b. p. 207°) (Found : N, 10·6. Calc. : N, 10·4%).

The *picrate*, prepared from equimolecular quantities of the base and picric acid in hot alcohol, separated on cooling in elongated prisms, m. p. 128° after recrystallisation from alcohol (Found : N, 15·2. $C_{15}H_{16}O_7N_4$ requires N, 15·4%). When dimethyl-*p*-toluidine is mixed with solid picric acid, a very deep red compound is produced which soon changes into a bright yellow one. Cold alcoholic solutions when mixed give a red solution, from which the yellow picrate crystallises, although its alcoholic solution is yellow.

Action of Nitrous Acid on Dimethyl-p-*toluidine.*—The base (10 g.), dissolved in a mixture of concentrated hydrochloric acid (28 c.c.) and water (20 c.c.), was gradually treated at 0° with sodium nitrite (16 g. in 100 c.c. of water). Reaction began on addition of the first drop, the solution became red, and nitric oxide containing a detectable quantity of nitrous oxide was evolved; when about half the sodium nitrite had been added, the deep red solution became turbid owing to separation of the oily reaction product. After 1 hour, the mixture was treated with urea to remove any excess of nitrous acid, neutralised with sodium hydroxide, and steam-distilled, and the distillate (1200 c.c.) was extracted with ether. The extract, after being shaken three times with dilute hydrochloric acid (40 c.c.; 1 part of conc. acid and 2 parts of water), was evaporated and nitrosomonomethyl-*p*-toluidine (1·6 g.) was obtained from the residue by steam-distillation. The nitrosoamine gave a brilliant colour in the Liebermann reaction and crystallised from light petroleum in almost colourless prisms, m. p. 49·5° (Bamberger and Wulz, *Ber.*, 1891, **24**, 2081, give m. p. 52—53°) (Found: N, 18·8. Calc.: N, 18·7%).

The aqueous acid extract (above) was made faintly alkaline and steam-distilled; 3-*nitrodimethyl*-p-*toluidine* (10·5 g.) passed over as a red oil, which, after solidifying, crystallised from aqueous alcohol in red needles, m. p. 26° (Found: N, 15·3. $C_9H_{12}O_2N_2$ requires N, 15·5%). The *picrate*, prepared as described above, crystallised from alcohol in bright yellow, elongated, rectangular plates, m. p. 129° to a red liquid after softening (Found: N, 17·0. $C_{15}H_{15}O_9N_5$ requires N, 17·1%). The amine and its picrate were identified by comparison with the synthetic compounds (below).

Nitric acid of the same concentration as the nitrous acid employed above was practically inactive, showing that the above nitration could not have been due to nitric acid present in the nitrous acid as initially generated.

Synthesis of 3-*Nitrodimethyl*-p-*toluidine.*—4-Chloro-3-nitrotoluene (6 g., prepared from 3-nitro-*p*-toluidine) was heated under reflux with a solution of dimethylamine (in slight excess of the theoretical quantity) in alcohol (40 c.c.) for 20 hours. The alcohol was then removed by distillation, and the reaction product steam-distilled; 3-nitrodimethyl-*p*-toluidine, obtained in theoretical yield, crystallised from dilute alcohol in red needles, m. p. 26° (Found: N, 15·4%). The picrate melted at 129° (Found: N, 17·3%).

Nitration of Dimethyl-p-*toluidine.*—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 (2 c.c.). After 12 hours, the whole was poured on ice (200 g.), neutralised, and submitted to steam-distillation; 2-*nitrodimethyl*-p-*toluidine*, which distilled in almost theoretical yield, crystallised from glacial acetic acid, on dilution with water, in large vermilion plates, m. p. 37° (Found: N, 15·4. $C_9H_{12}O_2N_2$ requires N, 15·5%). The *picrate* crystallised from alcohol in elongated yellow prisms, m. p. 141—143° (Found: N, 17·2. $C_{15}H_{15}O_9N_5$ requires N, 17·1%).

o-Nitrodimethylaniline was readily prepared in theoretical yield by heating an alcoholic solution (140 c.c.) of *o*-chloronitrobenzene (15 g.) and dimethylamine (in slight excess of the theoretical quantity) under reflux for 6 hours (compare Weissenberger, *Monatsh.*, 1912, **33**, 821). The *picrate* crystallised from alcohol in greenish-yellow needles, m. p. 103° (Found: N, 18·0. $C_{14}H_{13}O_9N_5$ requires N, 17·7%).

Dimethylaniline picrate crystallises from alcohol in greenish-yellow plates, m. p. 159° (Found: N, 16·2. $C_{14}H_{14}O_7N_4$ requires N, 16·0%).

3-*Nitrodimethylaniline picrate* separates from alcohol in elongated yellow plates, m. p. 119° (Found: N, 17·4. $C_{14}H_{13}O_9N_5$ requires N, 17·7%).

All the above nitro-bases give yellow solutions in non-dissociating solvents, whereas in dissociating media, and in particular in phenol, intense red solutions are formed.

The authors desire to thank Messrs. J. W. Leitch & Co. for gifts of some of the chemicals used in this investigation.

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