190. *The Dinitration of* p-*Dimethylaminoacetanilide.*

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MELDOLA and HOLLELY (J., 1915, **107**, 614) isolated only 3 : 5-dinitro-*p*-methylnitrosoaminoacetanilide in attempts to dinitrate *p*-dimethylaminoacetanilide. The present authors, having already prepared 2- and 3-nitro-*p*-dimethylaminoacetanilide (J., 1932, 2976), have now obtained the 2 : 5- and the 3 : 5-*dinitro*-compound by direct nitration and the 2 : 6-*isomeride* by synthesis. Hydrolysis of these yields 2 : 5-, 2 : 6-, and 3 : 5-*dinitro*-p-*aminodimethylaniline* respectively. Meldola and Hollely's nitrosoamine has been produced by a more rapid and satisfactory method. The anilides do not form picrates, but the free amines crystallise each with one molecule of picric acid or chloropicric acid.

The constitution of 2 : 5-dinitro-4-aminodimethylaniline was established by elimination of the amino-group to give 2 : 5-dinitrodimethylaniline; of the 2:6-isomeride by conversion into 4-chloro-2 : 6-dinitrodimethylaniline by the Sandmeyer reaction; and of the 3 : 5-isomeride by synthesis from 2 : 6-dinitrodimethyl-*p*-anisidine (Hodgson and Crook, *loc. cit.*), which readily exchanged its methoxyl for the amino-group when heated with alcoholic ammonia under pressure.

EXPERIMENTAL.

2 : 5-*Dinitro*-p-*dimethylaminoacetanilide*.—(a) *p*-Dimethylaminoacetanilide (8 g.), dissolved in concentrated sulphuric acid (40 c.c.), was treated gradually at 0—10° with a mixture of nitric acid (7 c.c.; *d* 1·5) and concentrated sulphuric acid (30 c.c.). After 1 hour's stirring, the whole was poured on ice and neutralised with aqueous ammonia. The precipitated 2 : 5-*dinitro*-p-*dimethylaminoacetanilide* (10·5 g.), recrystallised several times from alcohol or carbon tetrachloride, formed large, deep red needles, m. p. 156° (Found: N, 21·0. $C_{10}H_{12}O_5N_4$ requires N, 20·9%). (b) 2-Nitro-*p*-dimethylaminoacetanilide (5 g.), dissolved in concentrated sulphuric acid (3 c.c.) and water (6 c.c.), was nitrated (nitric acid, *d* 1·4, 10 c.c.; water, 10 c.c.) at 0°. The mixture was allowed to attain room temperature and then rendered alkaline with ammonia to precipitate the dinitro-compound (6·0 g.). (c) 2-Nitro-*p*-dimethylaminoacetanilide (5 g.) was dissolved in dilute hydrochloric acid (10 c.c. of conc. acid and 20 c.c. of water) and treated with a solution of sodium nitrite (2·5 g.) in water (15 c.c.); the dinitro-compound formed was precipitated (6 g.) by addition of alkali.

2 : 5-*Dinitro*-p-*aminodimethylaniline* was prepared by boiling the above acetyl compound (5 g.) for 5 minutes with a mixture of concentrated sulphuric acid (10 c.c.) and water (10 c.c.); the cooled solution was diluted with water and added gradually to ice-cooled dilute aqueous ammonia. The precipitated amine crystallised from its deep red solution in alcohol or carbon tetrachloride in long black needles having green metallic lustre; m. p. 100° (Found : N, 25·0. $C_8H_{10}O_4N_4$ requires N, 24·8%). The *picrate* crystallised from alcohol in yellow prisms, m. p. 186·5° (decomp.) (Found : N, 21·6. $C_{14}H_{13}O_{11}N_7$ requires N, 21·5%), and the *chloropicrate* in yellow needles, m. p. 165° (decomp.) (Found : Cl, 7·1. $C_{14}H_{12}O_{11}N_7Cl$ requires Cl, 7·2%).

The amine was converted by the diazotisation–alcohol method into 2 : 5-dinitrodimethylaniline, which crystallised from alcohol in scarlet parallelepipeds, m. p. and mixed m. p. with an authentic specimen 114° (van Romburgh, *Rec. trav. chim.*, 1887, **6**, 253, gives m. p. 112°) (Found : N, 20·1. Calc. : N, 20·0%).

3 : 5-*Dinitro*-p-*aminodimethylaniline*.—2 : 6-Dinitrodimethyl-*p*-anisidine (3 g.) was heated in a sealed tube with alcoholic ammonia (20 c.c. saturated at 0°) for 2 hours at 180°. The cooled mass of purple-red needles was recrystallised from alcohol and carbon tetrachloride; it then had m. p. 201° when rapidly heated (decomp. at 221°), but decomposed at 200—210° when gradually heated (Found : N, 24·9. $C_8H_{10}O_4N_4$ requires N, 24·8%). The *picrate* crystallised from alcohol in small greenish-yellow needles, m. p. 197° (decomp.) (Found: N, 21·6. $C_{14}H_{13}O_{11}N_7$ requires N, 21·5%), and the *chloropicrate* in small yellow needles, m. p. 191° (decomp.) (Found : Cl, 7·0. $C_{14}H_{12}O_{11}N_7Cl$ requires Cl, 7·2%).

2 : 6-*Dinitro*-p-*dimethylaminoacetanilide* was obtained from 3 : 5-dinitro-*p*-aminodimethylaniline (2 g.) by boiling it with acetic anhydride (10 c.c.) and concentrated sulphuric acid (0·2 c.c.) (the purple colour disappeared in about 5 minutes), and diluting the cooled solution with water; it crystallised from alcohol or dilute acetic acid in orange-yellow needles, m. p. 212—213° (Found : N, 21·0. $C_{10}H_{12}O_5N_4$ requires N, 20·9%).

2 : 6-*Dinitro*-p-*dimethylaminodiacetanilide*, formed when the amine above (2 g.) was heated on the water-bath for 24 hours with a mixture of acetic anhydride (20 c.c.) and concentrated sulphuric acid (0·3 c.c.), crystallised from alcohol in large yellow needles, m. p. 178·5° (Found : N, 18·2. $C_{12}H_{14}O_6N_4$ requires N, 18·1%).

3 : 5-*Dinitro*-p-*dimethylaminoacetanilide*.—(a) A well-stirred solution of *p*-dimethylaminoacetanilide (6 g.) in concentrated sulphuric acid (10 c.c.) and water (60 c.c.) was nitrated below 5° by the gradual addition during 30 minutes of a mixture of nitric acid (20 c.c.; *d* 1·4) and water (40 c.c.). The dinitro-compound separated gradually in fine orange-coloured crystals, which were filtered off at once, washed with water, pressed, and triturated with the minimum amount of cold concentrated hydrochloric acid (*ca.* 25 c.c.). The filtered extract was gradually diluted with water, and the precipitated 3 : 5-*dinitro*-p-*dimethylaminoacetanilide* (7·5 g.; m. p. 193°) crystallised from alcohol; it formed large orange-coloured prisms, m. p. 195° (Found : N, 20·8. $C_{10}H_{12}O_5N_4$ requires N, 20·9%), insoluble in boiling carbon tetrachloride. The residue (0·5 g.) which was very sparingly soluble in cold concentrated hydrochloric acid proved to be 3 : 5-dinitro-*p*-methylnitrosoaminoacetanilide and crystallised from alcohol in colourless prisms, m. p. 153° (Found : N, 24·9. Calc. : N, 24·7%), identical with a specimen made by Meldola and Hollely's method (*loc. cit.*). The yield of 3 : 5-dinitro-*p*-dimethylaminoacetanilide varied slightly with the strength of the nitric acid used, and scarcely any nitrosoamine was produced when a solution of sodium nitrite (1 g.) in water (10 c.c.) was added to the dilute nitric acid prior to use. No dinitration took place in the presence of urea or when pure dilute nitric acid was used, even up to 50% excess, and after several days' keeping at room temperature. Fuming nitric acid as used by Meldola and Hollely favours nitrosoamine formation. (b) When a solution of 3-nitro-*p*-dimethylaminoacetanilide (5 g.) in concentrated sulphuric acid (5 c.c.) and water (50 c.c.) was treated at 0° with a solution of nitric acid (9 c.c.; *d* 1·4) in water (15 c.c.), the 3 : 5-dinitro-compound separated (5·5 g.). When the nitration was conducted in concentrated sulphuric acid, no dinitro-compound could be isolated.

2 : 6-*Dinitro*-4-*aminodimethylaniline*.—3 : 5-Dinitro-*p*-dimethylaminoacetanilide (2 g.) was boiled for 5 minutes with a mixture of concentrated sulphuric acid (10 c.c.) and water (30 c.c.), and the cooled solution gradually diluted with water; the *sulphate* of 2 : 6-dinitro-4-aminodimethylaniline separated in yellow needles, m. p. 140—145° (Found : S, 6·1. $C_8H_{10}O_4N_4,\frac{1}{2}H_2SO_4$ requires S, 5·8%). This was readily converted by trituration with water into the *base*, which crystallised from aqueous alcohol in crimson or orange-red prisms and from carbon tetrachloride in long slender crimson needles, m. p. 157° (to a deep red liquid) (Found : N, 25·0. $C_8H_{10}O_4N_4$ requires N, 24·8%). The *hydrochloride* crystallised from dilute hydrochloric acid in large lustrous yellow plates, m. p. 187° (decomp.) (Found : Cl, 13·5. $C_8H_{10}O_4N_4,HCl$ requires Cl, 13·6%), and was readily dissociated by water. The *picrate* was obtained from benzene solution in small yellow prisms, m. p. 129° (to a red liquid) (Found : N, 21·7. $C_{14}H_{13}O_{11}N_7$ requires N, 21·5%).

Improved Preparation of 3 : 5-*Dinitro*-p-*methylnitrosoaminoacetanilide*.—A well-stirred solution of *p*-dimethylaminoacetanilide (6 g.) in concentrated sulphuric acid (30 c.c.) and water (60 c.c.) was treated rapidly with a mixture of nitric acid (15 c.c., *d* 1·4, and 5 c.c., *d* 1·5) and water (20 c.c.). The temperature rose quickly from 25° to 60°, brown fumes were copiously evolved, and the nitrosoamine separated in fine buff-coloured crystals (7·5 g.), m. p. 149°, and 153° after one crystallisation from alcohol (Found : N, 24·9. Calc. : N, 24·7%).

The authors thank the Department of Scientific and Industrial Research for a grant to one of them (J. H. C.), and the Imperial Chemical Industries Ltd. (Dyestuffs Group) for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, March 22nd,* 1934.]