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TRANSACTIONS.

I.—*A New Modification of 3:4-Dinitro-
dimethylaniline.*

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DURING an investigation of the nitration of *m*-nitrodimethylaniline, it was found that by varying the conditions of nitration, a new modification of 3:4-dinitrodimethylaniline was formed. This brings 3:4-dinitrodimethylaniline into line with other nitroanilines, most of which exist in at least two modifications (Hantzsch, *Ber.*, 1910, **43**, 1654).

Romburgh (*Rec. trav. chim.*, 1887, **6**, 250) states that *m*-nitrodimethylaniline is readily nitrated by nitric acid (D 1.2), giving the 3:6- (m. p. 112°) and the 3:4- (m. p. 176°) dinitro-compounds. However, by nitrating *m*-nitrodimethylaniline in certain concentrations of sulphuric acid, and using the requisite quantity of nitric acid to introduce one nitro-group, there results a β -modification of 3:4-dinitrodimethylaniline in addition to the 3:6-dinitro-derivative obtained by Romburgh.

β -3:4-Dinitrodimethylaniline is an orange-coloured compound melting at 154°. It is possible to convert it into the α -compound (m. p. 176°) by dissolving in concentrated sulphuric acid and diluting the resulting solution with water, when the α -modification separates, melting at 176° after one recrystallisation from alcohol. The β -compound was also readily changed to the α -compound by boiling an amyl-alcoholic solution with a few drops of 80 per cent.

sulphuric acid. On cooling, the α -modification separated in long needles. No method of changing the α - to the β -compound has yet been found.

Nitration of the β -modification with 70 per cent. nitric acid at 30° gives principally 2:4:5-trinitrodimethylaniline (m. p. 196°), which is also obtained by the nitration of 2:5- and α -3:4-dinitrodimethylaniline under the same conditions. The quantity nitrated was too small for the identification of any other trinitro-compound.

The action of more concentrated nitric acid on the above three dinitrodimethylanilines is of interest. Treatment with nitric acid of about 80 per cent. strength results in a simultaneous nitration and oxidation, a trinitromonomethylaniline being formed. A similar oxidation occurs on nitrating dimethylaniline in acetic acid solution, when under certain conditions 2:4-dinitromonomethylaniline is obtained in good yield.

The trinitromonomethylaniline is a yellow, crystalline compound melting at 199° . Its constitution was proved by replacing the mobile *m*-nitro-group by the methoxy-group, when 4:6-dinitromethyl-*m*-anisidine (m. p. 198°) was obtained. The original compound is therefore 2:4:5-trinitromonomethylaniline.

EXPERIMENTAL.

Preparation of m-Nitrodimethylaniline.

The *m*-nitrodimethylaniline was obtained by the cold nitration of dimethylaniline, as suggested by Nölting and Fourneau (*Ber.*, 1897, **30**, 2931). It was found possible to use much less sulphuric acid in the nitration, thereby facilitating the final neutralisation.

Dimethylaniline (250 c.c.) was dissolved in sulphuric acid (475 c.c.), and the solution cooled in a freezing mixture of ice and salt. The cooled nitrating acid, consisting of 100 c.c. of nitric acid (D 1.5) and 475 c.c. of sulphuric acid, was then added gradually, the temperature being maintained between 0° and 4° . When the whole of the acid had been added, the liquor was poured on ice, and finally diluted with about 20 litres of water, which precipitated the *p*-nitrodimethylaniline. The *m*-nitrodimethylaniline contained in the filtrate was separated by neutralisation with sodium carbonate and crystallised from alcohol, the yield of pure material (m. p. 66°) being about 50 per cent. of the theoretical.

β -3:4-Dinitrodimethylaniline.

Fifty grams of *m*-nitrodimethylaniline were dissolved in 500 c.c. of 60 per cent. sulphuric acid, and to this solution (at 20°) 50 c.c.

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of 30 per cent. nitric acid were added, the whole being well shaken. After a few minutes the temperature rose to 35°, and the 3:4-dinitrodimethylaniline separated as an orange-coloured, flocculent precipitate. The liquor was diluted with 250 c.c. of water and filtered, when practically the whole of the β -3:4-dinitrodimethylaniline was obtained in the precipitate, the 2:5-isomeride remaining dissolved in the filtrate. The β -3:4-dinitro-compound after one crystallisation from alcohol or benzene melted sharply at 154°, the yield being 60 per cent. of the theoretical.

Found: N = 19.7.

$C_8H_9O_4N_3$ requires N = 19.9 per cent.

By considerable dilution of the filtrate, the 2:5-isomeride separated; after crystallisation from glacial acetic acid it melted at 112°.

 α -3:4-Dinitrodimethylaniline.

This compound was obtained by nitrating *m*-nitrodimethylaniline (1 gram) with 20 per cent. nitric acid (10 c.c.).

It was also prepared by dissolving the β -modification (5 grams) in sulphuric acid (30 c.c.) and gradually diluting the solution with cold water, the temperature not being allowed to rise above 40°. By this method, the β -compound was completely converted into the α -modification, which, after crystallisation from alcohol or acetone, melted at 176°.

Preparation of 2:4:5-Trinitromonomethylaniline.

Twenty grams of 2:5-dinitrodimethylaniline (or α - or β -3:4-dinitrodimethylaniline) were dissolved in 80 c.c. of nitric acid (D 1.40). The temperature was raised to 30°, and 40 c.c. of nitric acid (D 1.50) were quickly added. After a few minutes, a vigorous oxidation took place, as shown by the evolution of nitrous fumes. At this point the solution was cooled rapidly, and, when the oxidation was finished, poured on ice. The precipitate was collected and digested with 500 c.c. of boiling water for several hours to hydrolyse any tetranitrophenylmethylnitroamine which might have been formed. The *m*-nitro-group in 2:4:5-trinitromonomethylaniline is not removed by boiling water. After hydrolysis, the liquid was filtered hot, and the residual solid crystallised from acetone. A moderately good yield of 2:4:5-trinitromonomethylaniline, a bright yellow, crystalline compound melting at 199°, was obtained.

Found: N = 22.8.

$C_7H_6O_6N_4$ requires N = 23.1 per cent.

Nitration of 2:4:5-trinitromonomethylaniline with nitric acid (D 1.50) gives 2:4:5:6-tetranitrophenylmethylnitroamine. Treatment of the boiling methyl-alcoholic solution (2 grams in 100 c.c. of methyl alcohol) with the theoretical quantity of potassium hydroxide (0.5 gram) dissolved in the minimum amount of water furnishes 4:6-dinitromethyl-*m*-anisidine (m. p. 198°), thereby establishing the constitution of the original compound as 2:4:5-trinitromonomethylaniline.

The possibility of the above trinitromonomethylaniline containing a nitro-group as a nitroamine was tested by heating with phenol and sulphuric acid in boiling amyl alcohol, but with negative result.

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