BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. V, No. 6, 1957

CHEMISTRY

On Preparation of N, 2, 4, 6-Tetranitromethylaniline by an Action of Nitric Acid on Dimethylaniline

by

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Presented by T. URBAŃSKI on March 18, 1957

N,2,4,6-tetranitromethylaniline (Tetryl) is usually obtained by nitrating dimethylaniline sulphate dissolved in an excess of sulphuric acid. Nitration is carried out by means of a nitrating mixture, rich in nitric acid.

A few attempts at nitrating dimethylaniline by means of nitric acid alone were, generally speaking, unsuccessful, and this led to a deeply rooted conviction that formation of dimethylaniline sulphate prior to its nitration is an essential condition to a safe nitration.

However, Hodgson and Turner [1] have found that dimethylaniline can be nitrated on a small scale (samples of 5 g. of dimethylaniline) with an excess (100 ml.) of nitric acid. When they used nitric acid of *d* 1.52 at −5° to 0° C., tetryl resulted. When concentration of nitric acid was lower (e. g., 1.42) the reaction did not lead to the product of full nitration but only N,2,4-trinitromethylaniline [2] (which Hodgson and Turner thought to be 2,4,6-trinitromethylaniline) resulted.

According to Hodgson and Turner, nitric acid *d* 1.34 and 1.254 yielded 2,4-dinitrodimethylaniline or (on prolonged reaction time) 2,4-dinitromethylaniline.

Lang [3] pointed out, that N-nitroderivatives cannot be obtained by acting on 2,4-dinitro- or 2,4,6-trinitro-N-methylaniline with nitric acid of concentration lower than 70%.

The authors of the present paper have found that tetryl can safely be prepared by acting with a great excess of nitric acid *d* 1.40 on dimethylaniline. The essential condition consists in carrying out the reaction in two stages. In the first stage dimethylaniline is dissolved in nitric acid *d* 1.40 at a temperature which does not exceed 7° C. After keeping the solution for some time at a low temperature, it is subjected to careful warming. In this second stage of the reaction, the temperature should not exceed 80° C. and only at the end of this stage, can the temperature be raised to 90° C. before the solution is cooled.

It is dangerous to dissolve dimethylaniline in nitric acid of high concentration (*d* 1.51) as the reaction may become too violent, but it is advisable to add nitric acid of *d* 1.51 to the already prepared solution of dimethylaniline in nitric acid *d* 1.40 and after that to warm it up. This procedure increases the yield of the product and its purity.

Another essential condition consists in using a great excess of nitric acid; the $\frac{\text{nitric acid}}{\text{dimethylaniline}}$ ratio should be kept near to 40 or even higher. When the ratio is 35 or lower, the purity of tetryl is unsatisfactory.

Vigorous mixing is also important for the safety of the reaction.

The purity of tetryl obtained with nitric acid alone is higher than that of tetryl prepared by the usual method, in presence of sulphuric acid. It should be pointed out that sulphuric acid can denitrate the N-nitro group [4], [3]. On the other hand, a high content of sulphuric acid in the nitrating mixture may promote formation of a higher nitrated product — N,2,3,4,6-pentanitromethylaniline [5].

These facts may explain the high purity of the product obtained by the method described in the present paper.

Experimental

Nitration with nitric acid *d* 1.40. 6 g. of dimethylaniline were dissolved in 280 g. nitric acid (*d* 1.40), keeping the temperature at 2—7°C. and mixing vigorously. The solution was coloured green due to the presence of nitrosocompounds formed in the early stage of the reaction. After all the dimethylaniline had been dissolved, the solution was kept for c. 15 min. at 2°C. and was then carefully warmed on a water bath to 40—50°C. At this stage a considerable evolution of heat and gases — mainly nitrogen oxides occurred, and heating was stopped for c. 30 min.

After the reaction subsided, the dark reddish solution was warmed again to 80°C. After a certain time, brown fumes of nitrogen oxides ceased being evolved and the solution changed to a light orange colour.

To secure a complete reaction the temperature was, at this stage, raised to 90° and kept at this temperature for one hour.

The solution was cooled down to 10°C.; 50 ml. water were added and after a few hours of standing at room temperature, the crystalline product was collected, washed with cold and then with hot water. The yield of tetryl was 10.6 g. (78 per cent of theoretical), m. p. 127—128°.

Nitration with mixtures of nitric acid *d* 1.40 and 1.51. 6 g. of dimethylaniline were dissolved (as in the previous method) in 84 g. of nitric acid (*d* 1.40). After that, 150 g. of nitric acid (*d* 1.51) were added, the temperature still being kept between 4 and 5°C. The reaction solution was next warmed as in the previous method. After the reaction was terminated, the solution was cooled and 100 ml. water were added.

Tetryl crystallised out. It was filtered, washed with cold and then with hot water. The yield was 11.3 g. (83.1 per cent of theoretical) of a product of high purity, m. p. 129.5°C.

Analysis:

calculated for $C_7H_5O_8N_5$ 24.4 % N,
found . . . . 24.8 % N.

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