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On Nitration of Dimethylaniline in Presence of Acetic Acid or Acetic Anhydride

by

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It has been stated by Orton [1] that dimethylaniline, when nitrated with mixtures of nitric acid with acetic anhydride and acetic acid, does not furnish N-nitroderivatives and solely 2.4-dinitrodimethylaniline is produced. Therefore, it appeared that formation of N,2,4,6-tetranitromethylaniline (tetryl) does not occur, when nitrating dimethylaniline with the above mentioned mixture.

Previously we found [2] [3] that tetryl can be produced by acting on dimethylaniline with nitric acid alone or in presence of an inert solvent. Subsequently, the work by Orton could suggest that acetic anhydride or acetic acid may act as inhibitor of the reaction of nitrating dimethylaniline to tetryl. This suggestion is rather unexpected and we considered it necessary to find to what extent the statement of Orton is conclusive.

We carried out a number of experiments on nitration of dimethylaniline with mixture of nitric acid (d 1.5) containing ca. 0.3% NO_2 and acetic acid or acetic anhydride. Various ratios $\frac{\text{nitric acid}}{\text{acetic acid or anhydride}}$ were used.

To moderate the trend of the reaction an inert solvent, such as chloroform, can also be used.

The spontaneous reaction which occurred after introducing dimethylaniline into the nitrating mixture produced an increase of the temperature to c. 40°C. After the reaction subsided, it was necessary to warm the reacting mixture and to keep it at c. 80°C until the reaction was completed.

Water was added to the cooled reaction solution and pure N,2,4,6-tetranitromethylaniline precipitated.

Thus, the statement of Orton should probably be limited to specific experimental conditions applied by this author. When the reaction of nitration in presence of acetic anhydride or acetic acid is run in conditions described in the present paper, particularly with regard to the temperature, N,2,4,6-tetranitromethylaniline is formed.

It has also been found that the best yield and the purity of the product, similar to those reached with nitric acid alone, were obtained when the volume ratio $\frac{\text{nitric acid}}{\text{acetic acid or anhydride}}$ was 50:50.

A lower ratio required a longer reaction time, and the yield and the purity of the product were not so high.

The consumption of nitric acid, when the method described in the present paper was applied, is lower than in our methods with nitric acid [2] [3].

Experimental

Nitration in presence of acetic anhydride. The nitrating solution was prepared by mixing 60 ml. of nitric acid (*d* 1.5), 60 ml. of acetic anhydride and 60 ml. of chloroform. The solution was cooled below 0°C and with vigorous stirring the solution of 6 g of dimethylaniline in 60 ml. chloroform was introduced. The temperature was kept below 0°C. After all the dimethylaniline was introduced, the cooling medium was removed and the reacting mixture spontaneously reached the temperature of 40°C. A copious evolution of nitrogen dioxide occurred at this stage. The vigorous reaction lasted c. 20 min. and after that the temperature began to fall. The reacting mixture was then warmed gently on water bath until the temperature rose to 80°C. Chloroform distilled off and the mixture was warmed until nitrogen dioxide ceased to evolve, and the solution acquired a light orange colour. All this lasted c. 8 hours.

The reaction solution was cooled to room temperature, diluted with 150 ml. of water. The precipitated product was collected and crystallized from acetone. The yield was 12.8 g. (90% of theoretical), m. p. 129°C.

Nitration in presence of acetic acid. The nitrating solution was prepared of 60 ml. of nitric acid (*d* 1.5), 60 ml. of acetic acid and 60 ml. of chloroform.

The reaction was carried out in the same way, as previously described with acetic anhydride.

After the reaction was terminated, 100 ml. of water were added to the light orange solution. Precipitated tetryl was collected and crystallized from acetone. The yield and purity of the product was the same as in the previous method.

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