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Nitration of Toluene in Presence of Chromic Acid

by

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The authors of the present paper expected that nitration of toluene in presence of strongly oxidizing agents such as chromic acid may lead to the formation of both nitration and oxidation products. So far no work of this kind exists in the literature, the only similar problem was vaguely mentioned by Schmeisser and Lutzow [1], [2], when describing chemical properties of chromyl nitrate.

It was now established that the "nitroxidation" of toluene by means of a nitrating mixture in presence of chromic anhydride can yield 2,4-dinitrobenzaldehyde or *p*-nitrobenzoic acid. The different products are formed under specific experimental conditions. 2,4-Dinitrobenzaldehyde was formed when the nitration was carried out by means of a mixture of conc. sulphuric acid (d. 1. 84), "anhydrous" nitric acid (*d* 1.51), and a 50% excess of chromic anhydride at 25°C. The greatest part of chromic acid present in the mixture was in the form of a suspension. The yield was 30% of theoretical.

A more diluted nitric acid (*d* 1.40) and a greater excess of suspended chromic anhydride (200% above the theoretical) at 25°C led to the formation of *p*-nitrobenzoic acid.

Intermediate conditions lead to the formation of both products: 2,4-dinitrobenzaldehyde and *p*-nitrobenzoic acid. Their separation can be achieved by the conventional method of dissolving the products in ether, and washing the ether solution with an aqueous solution of sodium carbonate. The evaporation of ether leaves 2,4-dinitrobenzaldyhyde, and the acidification of the alkaline solution precipitates *p*-nitrobenzoic acid. The highest yield of the compounds was 30 and 20%, respectively.

2,4-Dinitrobenzoic acid can be prepared by the nitroxidation of *p*-nitrotoluene. The yield of the reaction is considerably higher (60%) than in the case of nitration and oxidation of toluene.

During the oxidation carbon dioxide is evolved. The spent acid contains oxalic acid. These two facts account for a relatively low yield of the products of nitroxidation.

Experimental

2.4-Dinitrobenzaldehyde

Chromic anhydride (21.7 g) was suspended and partly dissolved in sulphuric acid (*d* 1.84) (1.50 g). Anhydrous nitric acid (*d* 1.51) (25 g) was added to this mixture.

10 g of toluene were added dropwise to the nitrating-oxidizing mixture under vigoruos mixing and cooling to maintain the temperature at 25°C. The reacting mixture immediately acquires a green colour deepening with time.

After all toluene had been added (this required 30—40 min) the mixture was kept at 25°C for $1^1/_2$ hour and poured into 1000 ml of cold water. The precipitated crystalline product was collected, washed with cold water, dissolved in ether (200 ml) and shaken with 10% solution of sodium carbonate (200 ml). After the evaporation of ether the product-2-dinitrobenzaldehyde was crystallized from alcohol.

The yield was 6.5 g (30.5% of theoretical), m.p. 70—71°C, unchanged when mixed with a standard sample of 2,4-dinitrobenzaldehyde. The substance gave reactions characteristic for aldehydes.

p-Nitrobenzoic acid

The nitrating mixture was composed of nitric acid (*d* 1.40) (30 g), sulphuric acid (*d* 1.84) (90 g) and water (8 ml). It was added dropwise to toluene (10 g). Simultaneously chromic anhydride (43.2 g) was added in small portions to the reacting mixture. The temperature of 25° was maintained by cooling. The colour of the reacting mixture, originally cherry red, gradually changed into green. The addition of toluene and chromic anhydride was ended simultaneously after 30—35 min. The raction mixture was further kept for 2 hours at 25° under continuous stirring and then poured into cold water (1000 ml). The precipitate was collected, washed with cold water and dissolved in ether (200 ml). The product was extracted from this solution by means of a 10% aqueous solution of sodium carbonate. By acidifying with dil. sulphuric acid *p*-nitrobenzoic acid was precipitated, collected and washed with cold water. The yield was 3.99 g (20.8% of theoretical), m. p. 240—241°C, unchanged when mixed with a standard sample of *p*-nitrobenzoic acid.

2.4-Dinitrobenzoic acid

The nitrating mixture was composed of nitric acid (*d* 1.50) (30 g), sulphuric acid (*d* 1.84) (90 g) and water (8 ml). Finely ground *p*-nitrotoluene (14.9 g) and chromic anhydride (43.2 g) were added simultaneously keeping the temperature at 50°C. The operation lasted 10—12 m.

The reaction mixture was kept stirring at 50° for 2 hours, counting from the beginning of the reaction. The colour of the mixture gradually changed from dark-brown to dark-green.

The mixture was poured into cold water (1000 ml). The precipitate was collected, washed with water and dissolved in ether (200 ml). The product was extracted from this solution by means of a 10% aqueous solution of sodium carbonate (200 ml). The aqueous alkaline solution was acidified with dil. sulphuric acid. 2,4-Dinitrobenzoic acid was precipitated, collected and washed with water. The yield was 14.9 g (60% of theoretical), m. p. 181°C, unchanged when mixed with a standard sample.

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