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Nitration of Toluene in Presence of Manganese Dioxide

by

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Continuing our experiments on nitration in presence of oxidizing agents — "nitroxidation" [1] — we examined the action of a nitrating mixture in presence of manganese dioxide.

When manganese dioxide (partly dissolved and in suspension), nitric acid (*d* 1.40) and sulphuric acid (*d* 1.84) were used, the main product of the reaction carried out at 30—40°C was 2,4-dinitrobenzaldehyde with a yield up to 30% of theoretical. *p*-Nitrobenzoic acid was formed in trace quantity only, when the reaction temperature was 60 — 70°C. A trace amount of *o*- and *p*-nitrotoluenes accompanied the main product of the reaction, particularly at lower temperatures of nitration.

The increase of concentration of nitric acid to $d=1.51$ did not produce an increase of the yield of 2,4-dinitrobenzaldehyde, but no *p*-nitrobenzoic acid was formed.

When *p*-nitrotoluene was nitrated with a mixture of nitric acid (*d* 1.51), sulphuric acid (*d* 1.84) and manganese dioxide at 70 — 80°C, 2,4-dinitrobenzaldehyde was obtained with a higher yield (43%). The same reaction lead to formation of a mixture of 2,4-dinitrobenzaldehyde (21% yield) and *p*-nitrobenzoic acid (7% yield), if it was carried out at a lower temperature (30—40°C).

The main difference between the reaction in presence of manganese dioxide and chromic anhydride (previously described [1]) consists in the formation of 2,4-dinitrobenzaldehyde as the main product of the reaction. No *p*-nitrobenzoic acid was formed in higher than trace quantity. No 2,4-dinitrobenzoic acid was found in the reaction products.

Oxalic acid and CO_2 were found as by products of the reaction.

A few experiments were also carried out with potassium permanganate as oxidizing agent. However, the reaction proved to be too violent and too dangerous.

Experimental

2.4-Dinitrobenzaldehyde from toluene

A mixture of nitric acid (*d* 1.41) (21 g) and sulphuric acid (*d* 1.84) (160 g) was prepared, and added slowly to toluene (10 g). Simultaneously manganese dioxide (18.8 g), freshly prepared from potassium permanganate and oxalic acid was added portionwise under vigorous stirring. The temperature of 30—40°C was maintained by cooling. The mixing lasted 1 hour. The originally dark brown reaction mixture acquired at the end a light yellow colour. After all the reagents had been added, the mixture was kept stirring for 30 min. more. Then it was poured into cold water and precipitated product was extracted with ether. The ether solution was washed with 10% sodium carbonate aqueous solution. After evaporation of ether the crude product was collected (6.4 g, i. e. 30% of theoretical yield). It contained a trace quantity of mononitrotoluenes. It was crystallized to obtain pure 2.4-dinitrobenzaldehyde, m. p. 71°C. The m. p. was unchanged when the product was mixed with a standard sample.

2.4-Dinitrobenzaldehyde from *p*-nitrotoluene

p-Nitrotoluene (5 g) was dissolved in sulphuric acid (*d* 1.84) (45 g). Nitric acid (*d* 1.51) (39 g) and manganese dioxide (9.4 g) were added to the solution under vigorous stirring. The temperature was kept within the limits 70—80°C. All other conditions of the reaction were the same as described above.

High purity 2.4-dinitrobenzaldehyde (9.1 g, 43% of theoretical yield) was obtained. M. p. was 71°C, unchanged when mixed with a standard sample.

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REFERENCES

[1] T. Urbański, A. Semeńczuk, S. Głozak and F. Świerkot, *Nitration of toluene in presence of chromic acid* (this issue).