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[54] **PROCESS FOR PREPARING 4-HYDROXY-3-NITROBENZOIC ACID ALKYL ESTERS**

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[51] **Int. Cl.²** **C07C 101/54**

[58] **Field of Search** ..... 260/471 R, 688

[56] **References Cited**

UNITED STATES PATENTS

3,510,527	5/1970	Prosser	260/471 R
3,636,037	1/1972	Donninger et al.	260/471 R

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[57] **ABSTRACT**

A process for preparing 4-hydroxy-3-nitrobenzoic acid alkyl esters by nitration of 4-hydroxybenzoic acid alkyl esters with nitric acid, wherein nitration is carried out at about 0 to 60°C with the aid of nitric acid having a strength of 30 to 62 %, which process represents a considerable improvement of the yield and wherein pure products are obtained.

3 Claims, No Drawings

PROCESS FOR PREPARING 4-HYDROXY-3-NITROBENZOIC ACID ALKYL ESTERS

The present invention relates to an improved process for preparing 4-hydroxy-3-nitrobenzoic acid alkyl esters, especially of the alkyl esters which contain 1 to 4 carbon atoms in the alkyl group, by nitration of the corresponding 4-hydroxy-benzoic acid alkyl esters with nitric acid. These compounds are suitable as intermediates for the preparation of optical brighteners or dyestuffs.

It is known that by treating 4-hydroxy-benzoic acid alkyl esters with diluted, about 10% nitric acid at an elevated temperature, for example at the temperature of water baths, 4-hydroxy-3-nitrobenzoic acid alkyl esters are obtained (cf. "Berichte der Deutschen Chemischen Gesellschaft" Vol. 30, p. 991 (1897), and "Journal fur praktische Chemie" [2] 43, p. 453 (1891)).

However, according to this process, impure 4-hydroxy-3-nitrobenzoic acid esters are obtained which have to be subjected to a subsequent purification process. Furthermore, by treating 4-hydroxybenzoic acid methyl ester with fuming nitric acid in glacial acetic acid at 45°C, the 4-hydroxy-3-nitrobenzoic acid methyl ester is obtained in a yield of 68% (cf. U.S. Pat. No. 2,647,053). However, this process is not satisfying, neither with regard to yield nor to purity. Furthermore, when the process is carried out on an industrial scale, working with glacial acetic acid causes problems with regard to regeneration and purification of the waste water.

It has now been found that 4-hydroxy-3-nitrobenzoic acid alkyl esters are obtained in a simple way and with excellent yeilds by nitration of 4-hydroxy-benzoic acid alkyl esters with nitric acid, if nitration is carried out at about 0° to 60°C, preferably at about 20° to 30°C, by means of nitric acid having a strength of 30 to 62% by weight.

The process is expediently carried out by introducing steadily the 4-hydroxy-benzoic acid alkyl ester, also possibly in form of a moist good, at about 20° to 25°C into concentrated nitric acid and maintaining the temperature by external cooling at about 20° to 60°C, preferably at about 20° to 30°C. After stirring for one hour, the whole is diluted with water, suctionfiltered, washed until neutral and dried.

According to the process claimed, which is particularly suitable for preparing the lower alkyl esters, such as the methyl, ethyl, propyl or butyl ester of the 4-hydroxy-benzoic acid, a considerable improvement of the yield as well as pure products are obtained which are free from the initial ester and the impurities which are found, without exceptions, in the known processes as by-products such, for example, as dinitro-hydroxy-benzoic acid esters, nitrophenols or polynitrophenols

formed by saponification and decarboxylation processes. Therefore, the compounds obtained according to the process of the invention, can be used directly for further reactions, for example subjected to catalytical hydrogenation to give 4-hydroxy-3-aminobenzoic acid esters, without a previous purification being required.

The present process makes possible a simplified and less expensive preparation of 4-hydroxy-3-nitro-benzoic acid alkyl esters without using organic solvents and without any further purification processes and represents, thus, an essential addition to technical development. The following Examples serve to illustrate the process.

EXAMPLE 1

183.8 Parts by weight of a moist 4-hydroxybenzoic acid methyl ester having a degree of purity of 82.7% (prepared by esterification of 4-hydroxybenzoic acid with dimethyl sulfate at a pH-value of 5) were steadily introduced, in the course of one hour, while stirring at 20°–25°C, into 304 parts by weight of a 62% nitric acid. The whole was stirred for about one hour, the ester was precipitated by addition of 300 parts of water, suction-filtered, washed with water until neutral and dried at 60°C. 177.3 Parts by weight of 3-nitro-4-hydroxy-benzoic acid methyl ester having a degree of purity of greater than 99% and a melting point of 73°C were obtained which corresponds to a yield of 90% of theory.

The following compounds listed in the Table 1 were prepared in analogy to Example 1.

Example	nitric acid concentration	temperature	4-hydroxy-3-nitrobenzoic acid ester	yield	melting point
2	40%	40°C	methylester	91%	73°C
3	50%	25°C	isopropyl-	89%	90°C
4	62%	15°C	n-butyl-	93%	liquid
5	35%	45°C	isopropyl-	86%	91°C
6	50%	30°C	ethyl-	90%	67°C
7	62%	20°C	ethyl-	90%	68°C
8	62%	10°C	methyl-	92%	73°C
9	50%	25°C	methyl-	89%	74°C
10	30%	50°C	methyl-	87%	72°C

We claim:

1. A process for preparing a pure 4-hydroxy-3-nitrobenzoic acid alkyl ester by nitration of 4-hydroxybenzoic acid alkyl esters with nitric acid, wherein nitration is carried out at about 0° to 60°C with the aid of nitric acid having a strength of 30 to 62%.

2. A process as claimed in claim **1**, which is conducted at a temperature of from about 20° to 30°C.

3. A process as claimed in claim **1**, wherein 4-hydroxy-benzoic acid alkyl ester having 1 to 4 carbon atoms in the alkyl radicals, are prepared.

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