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PROCESS FOR PREPARING 2,3,6-TRIMETHYLHYDROQUINONE

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ABSTRACT OF THE DISCLOSURE

According to the invention 2,3,6-trimethylhydroquinone is prepared from 2,3,6-trimethylphenol by sulfonation of 2,3,6-trimethylphenol, oxidation of the 2,3,6-trimethylphenol-4-sulfonic acid formed and direct reduction of the trimethylquinone in aqueous solution to trimethylhydroquinone; said sulfonation is carried out in an organic solvent which is not miscible with water and is inert to the sulfonating agent. The oxidation is carried out in aqueous phase in the presence of an organic solvent which is inert to the oxidizing agent, and in which the quinone formed is soluble and the hydroquinone formed by reduction is insoluble.

The present invention relates to a process for preparing 2,3,6-trimethylhydroquinone from 2,3,6-trimethylphenol.

It has been known to prepare trimethylhydroquinone from 2,3,5- or 2,3,6-trimethylphenol by azo-coupling, reductive cleaving of the coupled product to p-aminophenol, oxidation of the latter to trimethyl-benzoquinone and reduction thereof (Journal Org. Chem. 4 (1939) 318). The oxidation of 2,3,6-trimethylphenol in sulfuric acid solution and the subsequent reduction to the hydroquinone takes thereby place with a yield of only 50%.

It has been further known to obtain trimethylhydroquinone by conversion of the 4-nitroso compound of trimethylphenol (Chem. and Ind. 1,955,210; Czech. Pat. 101,759 and 122,220; Austrian Pat. 208,848).

Another possibility of preparing trimethylhydroquinone consists in a full synthesis from difficultly accessible derivatives of acetaldehyde (see German Pat. 1,232,-568).

According to a process disclosed in the German Pat. 1,022,209, O,O'-disubstituted phenols can be oxidized over their 4-sulfonic acids to the corresponding quinones and the latter can be reduced in known manner to hydroquinones. However apart from its moderate yields (35–69% of the theory) this process has essential defects in performing it.

The main object of the present invention is to provide a process for preparing 2,3,6-trimethylhydroquinone which is advantageous technically as well as economically, from 2,3,6-trimethylphenol.

This object was attained by a process of preparing 2,3,6-trimethylhydroquinone by sulfonation of 2,3,6-trimethylphenol, oxidation of the 2,3,6-trimethylphenol-4-sulfonic acid formed and immediate reduction in aqueous solution of the trimethylquinone obtained to 2,3,6-trimethylhydroquinone; sulfonation is carried out in an organic solvent which is inert to the sulfonation agent, oxidation in the aqueous phase is likewise carried out in an organic solvent which is inert to the oxidizing agent, the quinone formed being soluble in said solvent, while the hydroquinone formed by the immediately subsequent reduction is insoluble therein.

Due to this use of solvents, the following essential advantages are attained:

The use of a solvent results in essential advantages: The sulfonic acid formed yields with the solvent a mixture which can be easily stirred, so that the sulfonation can be carried out—depending on the specific sulfonating agent—at a temperature at which the best yield is obtained. In the absence of a solvent always higher temperatures are necessary in order to obtain a mass which can be well stirred, but at such higher temperatures the yields are 20–50% lower or a high excess of the sulfonating agent must be used. However, such excess renders the subsequent dilution with water—due to the considerable heat of dilution—rather difficult.

The oxidation is carried out in the process of invention preferably at reflux temperature and this additionally contributes to the removal of the heat of oxidation, puts an upper limit on the oxidation temperature and assures that the oxidation can be carried out in the shortest possible period of time.

Furthermore, the solvent dissolves the quinone formed so that it is protected from further oxidation. The use of solvent during oxidation renders distillation with steam, or a subsequent extraction of the quinone unnecessary.

In addition, the solvent acts simultaneously as a transporter for the 2,3,6-trimethylenequinone from the oxidation phase to the reduction phase.

As solvents, aromatic hydrocarbons, e.g. benzene and toluene, as well as their halogenated derivatives, e.g. chlorobenzene can be used. Furthermore, aliphatic and cycloaliphatic hydrocarbons can be used individually or in mixture with each other, for example n-hexane, ligroin, cyclohexane and halogenated hydrocarbons, such as carbontetrachloride or ethylenechloride.

Solvents which are inert to the sulfonating agents, e.g. concentrated sulfuric acid, oleum and chlorosulfonic acid, as well as to oxidizing agents e.g. chromic acid, manganese dioxide or mangan-IV-sulfate, are preferred.

Trimethylhydroquinone is an important intermediate product in the preparation of tocopherol (Vitamin E).

The following examples illustrate the process of the invention.

EXAMPLE 1

4.08 kg. (30 mol) of 2,3,6-trimethylphenol are dissolved in 7.5 l. toluene. To the solution under vigorous stirring 9.6 kg. (5.35 l.) (94.8 mol) of concentrated sulfuric acid are dropwise added (3.16 mol/phenol). Thereby the temperature rises to about 60° C. Soon after starting introduction of the sulfuric acid, phenolsulfonic acid separates in the form of small balls. Stirring is continued for ½ hour and the phenolsulfonic acid formed is then dissolved by adding 18 l. water, to which 2.58 kg. (1.44 l.) (25.4 mol) concentrated sulfuric acid have been added. To the reaction mixture within 2 hours a solution of 6.57 kg. (22.2 mol) sodium dichromate (0.74 mol/mol phenol) dissolved in 4.4 l. water are added dropwise whereby reflux temperature can be reached. After allowing the reaction to continue for one hour the organic phase is separated and introduced under good stirring between 20 and 30° C. into a solution of 7.17 kg. (34.8 mol) technical sodiumdithionite (of about 80%) (1.16 mol/mol phenol) in 18 l. water. The resulting product is stirred for 1 hour longer, then sucked off, washed with 2.5 l. of toluene and 5 to 7 l. water and is washed with the necessary amount of a 0.1% sodiumdithionite solution, is sucked off again and dried. 3.96 kg. of 2,3,6-trimethylhydroquinone are thus obtained in form of a light-beige powder having a melting point of 170 to 172° C. This yield corresponds to 85.5% of the theory.

EXAMPLE 2

13.6 kg. (100 mol) of 2,3,6-trimethylphenol are dissolved in 25 l. carbontetrachloride. To the solution 32 kg. (314 mol) of concentrated sulfuric acid are added dropwise under vigorous stirring. Thereby the temperature should not rise above 60° C. Soon after introduction of the sulfuric acid, the phenolsulfonic acid separates in the form of small balls. After further stirring of ½ hour, the phenolsulfonic acid is dissolved in 80 liter of water and acid within 2 hours 19.35 kg. (200 mol) of manganese dioxide of 90% MnO_2 is added. Thereby, reflux temperature may be attained. After terminating the addition, stirring of the mixture is continued for 1 hour, the undissolved impurities of manganese dioxide are filtered off, the phases are separated and the organic phase is processed in view of the new proportions, in the manner described in the above Example 1. 14.1 kg. of 2,3,6-trimethylhydroquinone having a melting point of 170–172° C. are thus obtained, corresponding to a yield of 92.8% of the theory.

EXAMPLE 3

13.6 kg. (100 mol) 2,3,6-trimethylphenol are dissolved in 25 l. benzene. To the solution 19.6 l. oleum of 15% (3.92 mol total-SO_3/mol phenol). The temperature is allowed to rise up to a maximum of 60° C. The phenolsulfonic acid which separates in the shape of small balls, is dissolved in 80 l. water and oxidized within 2 hours under stirring with a solution of 21.9 kg. (74 mol) sodium dichromate in 14.7 l. of water. Further processing takes place in the manner described in the above Example 1 with consideration of the proportions described in Example 1. In this example 13.1 kg. 2,3,6-trimethylhydroquinone are obtained as a light yellow powder, having a melting point of 170–172° C. in a yield of 86.2% of the theory.

EXAMPLE 4

27.2 kg. (200 mol) of 2,3,6-trimethylphenol are dissolved in 50 l. of ethylene chloride. To the solution 13.7 l. chlorosulfonic acid (206 mol) are added dropwise with vigorous stirring. Gaseous HCl eascapes and phenolsulfonic acid separates in fine-grained form. After further stirring for ½ hour the sulfonic acid is dissolved in 160 l. water, to which 20.4 kg. (200 mol) sulfuric acid of 96% have been added. The sulfonic acid solution is oxidized with 38.7 kg. (400 mol) of manganese dioxide of 90%, in the manner described in the above Example 2. Further processing to trimethylhydroquinone is carried out with consideration of the proportions described in the previous examples. 2,3,6-trimethylhydroquinone is thus obtained as a light beige powder, having a melting point of 170 to 172° C. in a yield of 28.5 kg., i.e. 93.8% of the theory.

EXAMPLE 5

54.4 kg. (400 mol) of 2,3,6-trimethylphenol dissolved in 100 l. of chlorobenzene are processed with consideration of the proportions and in the manner described in the above Example 1. The yield of 2,3,6-trimethylhydroquinone amounts to 51.9 kg., i.e. 84% of the theory, and its melting point is 170–172° C.

EXAMPLE 6

8.16 kg. (60 mol) of 2,3,6-trimethylphenol are dissolved in 14 l. of n-hexane and treated in the manner described in the above Example 4. 2,3,6-trimethylhydroquinone is obtained in a yield of 8.52 kg., i.e. 92% of the theory, having a melting point of 170–172° C.

EXAMPLE 7

4.08 kg. (30 mol) of 2,3,6-trimethylphenol are dissolved in 7.5 l. of cyclohexane and treated in the manner

described in the above Example 1. 3.84 kg. of 2,3,6-trimethylhydroquinone having a melting point of 170–172° C. are obtained. This corresponds to a yield of 82.5% of the theory.

EXAMPLE 8

13.6 kg. (100 mol) of 2,3,6-trimethylphenol are dissolved in 25 l. ligroin and processed with consideration of the proportions and in the manner described in the above Example 2. 13.85 kg. of 2,3,6-trimethylhydroquinone, corresponding to 91.2% of the theory are thus obtained, having a melting point of 170–172° C.

EXAMPLE 9

13.6 kg. (100 mol) of 2,3,6-trimethylphenol are dissolved in 25 l. of benzene and sulfonated in the manner described in the above Example 2. The trimethylphenol-p-sulfonic acid is dissolved in 60 l. of water and to the solution dropwise 49.4 kg. (200 mol) of manganese-IV-sulfate dissolved in 80 l. of sulfuric acid of 55% are added. Stirring is continued for ½ hour, the phases are separated and the organic phase is treated in the manner described in the previous examples with consideration of the proportions. 12.9 kg. of 2,3,6-trimethylhydroquinone corresponding to 84.6% of the theory and having a melting point of 170–172° C. are thus obtained.

The chlorobenzene used in the above Example 5 has the formula C_6H_5Cl and the sodium dithionite mentioned in the specification has the formula $Na_2S_2O_4$.

The recitation "hydroquinone formed by directly subsequent reduction" is to indicate that said reduction takes place immediately after oxidation.

What is claimed is:

1. Process for preparing 2,3,6-trimethylhydroquinone comprising

dissolving 2,3,6-trimethylphenol in a solvent selected from the class consisting of benzene, toluene, chlorobenzene, n-hexane, cyclohexane and ligroin,

sulfonating said phenol with a reagent selected from the class consisting of sulfuric acid and oleum at temperature of 60° C. until 2,3,6-trimethylphenol-4-sulfonic acid is formed,

dissolving said phenol sulfonic acid by adding water and sulfuric acid,

oxidizing said phenol sulfonic acid by adding thereto an oxidizing agent selected from the class consisting of sodium dichromate, manganese dioxide and manganese-IV-sulfate whereby a temperature not exceeding reflux temperature is reached,

separating the organic solvent phase with the 2,3,6-trimethylquinone formed in the oxidation step and introducing it under stirring into a solution of sodium dithionite in water,

then sucking off the formed 2,3,6-trimethylhydroquinone as a powdered product from the solution.

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