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PROCESS OF PREPARING DYESTUFFS OF THE ANTHRACENE SERIES

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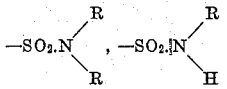
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10 Claims. (Cl. 204—9)

The present invention relates to an improved process of preparing dyestuffs of the anthracene series.

It is known to prepare dyestuffs of the anthracene series by reacting with oxidizing agents upon 9.10-disulfuric acid esters of leuco-beta-aminoanthraquinones in an alkaline medium, see for example, British Patent No. 272,924 and the copending earlier application Serial No. 662,386 filed on Mar. 23, 1933 by myself and Georg Rösch.

It is the object of my present invention to provide improvements of this oxidation process, which afford a considerable saving of the oxidizing agents and yield the reaction products in an excellent purity and an extremely good yield. My invention is based upon the discovery that the oxidation of the anthraquinone derivatives in question so as to form the corresponding anthraquinone azine derivatives by means of oxidizing agents in an alkaline medium can be more easily and economically performed by effecting the oxidation electrochemically while applying the oxidizing agents in a relatively small amount, for example, in an amount insufficient to effect complete oxidation when applied per se. I wish to point out that the nature of the oxidizing agent to be added is not decisive for the course of the reaction, provided that it is capable of oxidizing the starting materials in question so as to form the corresponding anthraquinone azine derivatives. As examples for the oxidizing agents there may be mentioned, for instance, lead dioxide, sodium hypochlorite, persulfates or ferric potassium cyanide, compounds which under the conditions of working are converted into the said oxidizing agents being included. The best results are obtained, however, by the application of lead dioxide, this being the preferred form of my invention. As to the anthraquinone derivatives used as starting materials I wish to point out that every 9.10-disulfuric acid ester of leuco-beta-aminoanthraquinones containing a free alpha-position can be used for the purpose in question, the nature of other substituents which may be present being immaterial. Any desired monovalent substituents come into consideration, such as halogen atoms, alkyl groups, alkoxy groups, carboxylic acid or sulfonic acid groups, the groupings -Salkyl, -SOalkyl, $-COC_6H_5$, $-COC_6H_4Cl$ $-CO.C_6H_4Oalkyl$,



(R being aryl or alkyl) and so on

It is another feature of my invention that instead of the leuco sulfuric acid esters of beta-aminoanthraquinones there can be used with the same effect the corresponding compounds which have the amino group acylated, for instance, by a formyl-, acetyl-, propionyl-, benzoyl-, chlorobenzoyl- or naphthoyl group or the grouping -COOalkyl so as to form an urethane derivative, these groupings being split off in the course of the reaction.

When working with the acylated compounds, the conditions of reaction are not materially changed, it being preferable, however, to apply alkali metal or earthalkali metal hydroxides as alkaline reacting agents or to work at higher temperatures in order to effect saponification of the acylamino group.

The provision of a diaphragm, such as a clay cell, is preferable but not absolutely necessary.

The following examples illustrate the invention, without, however, restricting it thereto:—

Example 1

Into a vessel of a nonconducting material and being lined on the inside with a lead foil, which is superficially coated with lead superoxide, there is added a solution of the leuco sulfuric acid ester of beta-aminoanthraquinone in a 4% caustic soda solution, the lead foil serving as anode while a copper sheet or a sheet of any other electric conductor, which is fixed in a clay cell containing a caustic soda solution of about 8% strength, serves as cathode. The solution of the ester salt, being heated to 60–70° C., is thoroughly stirred by a suitable apparatus, while at a voltage of 4–6 a current of about 3 amperes is passed through the solution. If no starting material can be observed any longer, the resulting leuco sulfuric acid ester of 1.2.2'.1'-anthraquinoneazine is separated from the orange colored solution by salting out or evaporation.

Example 2

A solution of the leuco sulfuric acid ester of 3-chloro-2-aminoanthraquinone with the addition of an excess of alkali metal hydroxide is introduced into an insulated iron vessel, which is provided with an iron stirrer to which a sliding contact is applied. The solution is heated to about 70–80° C. and, while stirring, a current is passed through the liquor, the vessel and the stirrer serving as electrodes. After the addition of a small amount of ferric potassium cyanide to the solution, the oxidation spontaneously sets in. It is of advantage to add small amounts of the

oxygen carrier to the reaction liquid for several times; finally the reaction product is worked up in the usual manner.

Instead of the leuco sulfuric acid ester of 3-chloro-2-aminoanthraquinone, leuco sulfuric acid esters of a beta-aminoanthraquinone containing other substituents, such as the methyl- or methoxy group, if the 1-position is unsubstituted, may be used with the same result.

Example 3

A copper wire net, the meshes of which are filled with lead superoxide, serves as anode, the apparatus being otherwise constructed as described in Example 1. The anode chamber is filled with an aqueous alkaline solution of the leuco sulfuric acid ester of 2-aminoanthraquinone-3-carboxylic acid. The reaction is performed at a temperature of about 80° C. A strongly fluorescent solution is obtained, from which orange colored prisms can be separated by salting out by means of potassium chloride. The product obtained is the potassium salt of the leuco sulfuric acid ester of 1.2.2'.1'-anthraquinoneazine-3.3'-di-carboxylic acid.

I claim:—

1. A process of oxidizing a 9.10 leuco sulfuric acid ester of a beta amino anthraquinone containing a free alpha position to the corresponding anthraquinone azine, which comprises passing an electric current through an aqueous alkaline solution containing said ester in the presence of a substance normally capable of oxidizing the said ester to form the corresponding azine, said substance being used in an amount which if taken alone would be insufficient to cause complete oxidation of said ester to the azine.

2. A process of oxidizing a 9.10 leuco sulfuric acid ester of a beta acylamino anthraquinone containing a free alpha position to the corresponding anthraquinone azine, which comprises passing an electric current through an aqueous alkaline solution containing said ester in the presence of a substance normally capable of oxidizing the said ester to form the corresponding azine, said substance being used in an amount which if taken alone would be insufficient to cause complete oxidation of said ester to the azine.

3. A process of oxidizing the 9.10 leuco sulfuric acid ester of beta amino anthraquinone to the corresponding anthraquinone azine, which comprises passing an electric current through an aqueous alkaline solution containing said ester in the presence of a substance normally capable of oxidizing the said ester to form the corresponding azine, said substance being used in an amount which if taken alone would be insufficient to cause complete oxidation of said ester to the azine.

4. A process of oxidizing the 9.10 leuco sulfuric acid ester of 3-chloro-2-amino anthraquinone to the corresponding anthraquinone azine, which comprises passing an electric current through an aqueous alkaline solution containing said ester in the presence of a substance normally capable of oxidizing the said ester to form the corresponding azine, said substance being used in an amount which if taken alone would be insufficient to cause complete oxidation of said ester to the azine.

5. A process of oxidizing a 9.10 leuco sulfuric acid ester of a beta amino anthraquinone containing a free alpha position to the corresponding anthraquinone azine, which comprises passing an electric current through an aqueous alkaline solution containing said ester in the presence of a substance of the group consisting of lead dioxide, sodium hypochlorite and potassium ferricyanide in an amount which if taken alone would be insufficient to cause complete oxidation of said ester to the azine.

6. A process of oxidizing a 9.10 leuco sulfuric acid ester of a beta amino anthraquinone containing a free alpha position to the corresponding anthraquinone azine, which comprises passing an electric current through an aqueous alkaline solution containing said ester in the presence of lead dioxide in an amount which if taken alone would be insufficient to cause complete oxidation of said ester to the azine.

7. A process of oxidizing a 9.10 leuco sulfuric acid ester of a beta acylamino anthraquinone containing a free alpha position to the corresponding anthraquinone azine which comprises passing an electric current through an aqueous alkali metal hydroxide solution containing said ester in the presence of lead dioxide in an amount which if taken alone would be insufficient to cause complete oxidation of said ester to the azine.

8. A process of oxidizing the 9.10 leuco sulfuric acid ester of beta amino anthraquinone to the corresponding anthraquinone azine, which comprises passing an electric current through an aqueous alkaline solution containing said ester in the presence of lead dioxide in an amount which if taken alone would be insufficient to cause complete oxidation of said ester to the azine.

9. A process of oxidizing the 9.10 leuco sulfuric acid ester of 3-chloro-2-amino anthraquinone to the corresponding anthraquinone azine, which comprises passing an electric current through an aqueous alkaline solution containing said ester in the presence of lead dioxide in an amount which if taken alone would be insufficient to cause complete oxidation of said ester to the azine.

10. A process of oxidizing a 9.10 leuco sulfuric acid ester of a beta amino anthraquinone containing a free alpha position to the corresponding anthraquinone azine, which comprises passing an electric current between an anode and a cathode, the anode being located within a clay cell, through an aqueous alkaline solution containing said ester in the presence of a substance normally capable of oxidizing the said ester to form the corresponding azine, said substance being used in an amount which if taken alone would be insufficient to cause complete oxidation of said ester to the azine.

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