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PREPARATION OF LEUCO-INDANTHRONE  
SULFURIC ESTERS

William B. Hardy, Bound Brook, and Robert B. Fortenbaugh, Gladstone, N. J., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

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This invention relates to an improved process of preparing leuco indanthrone tetrasulfuric esters by the oxidative condensation of leuco beta-aminoanthraquinone disulfuric esters.

In the past, the production of leuco indanthrone tetrasulfuric esters has been attempted with various oxidizing agents, such as ferricyanides, hypochlorites and lead dioxide, which are usable under alkaline conditions. These procedures have been subject to undesirable side reactions. These have been particularly serious with the alkali metal ferricyanides and hypochlorites; and as a result the only process which has had any practical significance is one using lead dioxide under alkaline conditions as the oxidizing agent. While this process has been sufficiently effective to be used for actual practical production of the esters, it suffers from a number of drawbacks. Lead is expensive and its high molecular weight makes it a very wasteful oxidizing agent. The cost of the lead is so high that no process using it as an oxidizing agent can be carried out without recovery of lead, which presents serious problems. The drawbacks to the lead dioxide process are sufficiently serious so that it has even been proposed to use silver oxide in spite of its high cost.

According to the present invention, we have found that if simple compounds, not complexes, of the metals of group VIII of the periodic system, having atomic numbers 26, 27 and 28, i. e., iron, cobalt and nickel, are used as oxidizing agents, the reaction proceeds smoothly and no difficulty is encountered. However, in order to be oxidizing agents for practical purposes, in these compounds the metal must be in a higher state of oxidation. In the case of iron, the valence must be 4 or 6, trivalent ferric iron will not operate satisfactorily. Cobalt in the tri and tetravalent state and nickel in the tri and tetravalent state may also be used in the form of their simple compounds. Not only do the oxidizers of the present invention operate smoothly and efficiently, but their low molecular weight improves output. It is not known why the improved results are so specific to the higher oxidation state of the three metals. Ordinarily, complex trivalent iron compounds such as ferricyanides are powerful oxidizers. Yet in the present process, they do not give useful results, whereas tetravalent and hexavalent iron compounds can be used very effectively. We do not know why the higher states of oxidation give the improved results and it is not intended to limit the present invention to any theoretical explanation.

It is an advantage of the present invention that the reaction conditions are in no sense critical. The reaction proceeds readily in aqueous medium at moderate temperatures, preferably slightly above room temperature. When the reaction is complete, it is possible to recover the

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spent oxidizing agent readily and substantially quantitatively by filtration and, if desired, it can be regenerated and reused. The product is obtained in the filtrate from which it can be isolated in good yields and satisfactory purity by conventional means.

The present invention is applicable generally to leuco sulfuric esters of beta-aminoanthraquinones, the only requirement of course being that there be a free alpha position adjacent to the amino group. Typical esters which may be used are the following: beta-aminoanthraquinone, 3-chloro-2-aminoanthraquinone, 3-bromo-2-aminoanthraquinone, 2-aminoanthraquinone-3-carboxylic acid, 2-amino-3-methyl anthraquinone, 2-amino-3-methoxyanthraquinone; and compounds containing condensed rings, such as 1,2-benz-3-aminoanthraquinone are also suitable. Esters may be used in the form of the amino compounds or, if desired, their N-acyl derivatives, such as acetyl amino and sulfamido compounds may be employed and throughout the specification and claims the term "a beta-aminoanthraquinone" includes the beta-acyl amino anthraquinones as well as those having a free amino group.

While the improved results of the present invention are obtainable with any compounds of the metals of group VIII in their higher state of oxidation, certain specific compounds of this class are readily obtainable and are, therefore, preferable for economic reasons. These include barium and strontium perferites, alkali and alkaline earth metal ferrates, such as ferrates of sodium, potassium, calcium and barium; cobaltic hydroxides, cobaltic dioxide and oxides of tri- and tetravalent nickel. The invention, of course, is not limited to the use of these preferred oxidizing agents.

The invention will be described in greater detail in conjunction with the following specific examples, the parts being by weight unless otherwise indicated.

## Example 1

A mixture of 5.4 parts of the potassium salt of 2-acetyl amino - 3 - chloro-anthrahydroquinone-9,10-disulfuric acid ester, 4 parts of sodium hydroxide, and 35 parts of water is stirred at 85° till hydrolysis of the acetyl group is complete, as indicated by the failure of any precipitate to form when a drop of the reaction solution is diluted with 2 cc. of water and treated with a few crystals of sodium nitrite followed by dilute hydrochloric acid.

To the hydrolyzed solution containing the disulfuric ester of 2-amino-3-chloro-anthrahydroquinone, is added 5.5 parts of cobaltic hydroxide prepared by adding 12.5 parts of cobaltous acetate to a solution of 10 parts of potassium hydroxide in 100 parts by volume of 15% sodium hypochlorite



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solution, filtering and washing the resulting black precipitate.

The reaction mixture is held at 85° until oxidation is complete, filtered, concentrated to 80 parts by volume, and salted with 20 parts of potassium chloride. After thorough stirring and cooling, the product is filtered. A good yield of the tetrasulfuric acid ester of the dichloro leuco indanthrone is obtained.

*Example 2*

Barium ferrate is prepared by adding a solution of 13.5 parts of ferric chloride in 20 parts of water to a solution of 20 parts of potassium hydroxide in 50 parts of water. To the resulting ferric hydroxide precipitate is added 100 parts by volume of 15% sodium hypochlorite solution, giving a violet solution, which is heated briefly at 80° C. To this is added a solution of 13 parts of barium chloride in 50 parts of water. The purple precipitate which forms immediately is filtered and washed.

The barium ferrate, prepared as described, is added to a batch of 2-amino-3-chloro-anthrahydroquinone-disulfuric ester, prepared as described in Example 1. The oxidation is carried out at 60° C. There is then added 5 parts of potassium chloride. The mixture is filtered, concentrated to 50 parts by volume, salted at 60° C. with 7 parts of potassium chloride and 20 parts of methanol, and cooled thoroughly. On filtration, there is obtained a good yield of the yellow-orange potassium salt of the leuco dichloro indanthrone tetrasulfuric ester.

*Example 3*

An aqueous solution of 12.5 parts of nickel chloride and 10 parts of sodium carbonate is oxidized by treatment with 100 parts by volume of 10% sodium hypochlorite solution. The resulting nickel dioxide is added to a batch of 2-amino-3-chloroanthrahydroquinone - disulfuric ester prepared as described in Example 1. Oxidation is completed at 85° C. The reaction mixture is filtered, concentrated to 50 parts by volume, and salted with 15 parts of potassium chloride followed by 12 parts of methanol. After thorough stirring, filtration gives a good yield of the light orange potassium salt of the leuco dichloro indanthrone tetrasulfuric ester.

*Example 4*

A mixture of 20.0 parts of the potassium salt of 2-acetylamino-3-bromo anthrahydroquinone-9,10-disulfuric acid ester, 14 parts sodium hydroxide, and 120 parts of water is stirred at 85° till hydrolysis is complete, as described in Example 1.

To the hydrolyzed solution is added 10 parts of nickel dioxide prepared as described in Example 3. Oxidation is completed at 85°. After filtration of the reaction, the solution is concentrated at 120 parts by volume, and salted with 24 parts of potassium chloride followed by 60 parts of methanol. After thorough stirring and cooling, filtration gives a good yield of the tetrasulfuric acid ester of the dibromo leuco indanthrone.

*Example 5*

An aqueous solution containing the ferrate ion is prepared by adding a solution of 27 parts of ferric chloride in 100 parts of water to a solution of 40 parts of potassium hydroxide in 50 parts of water. To the resulting ferric hydroxide precipitate is added at 70°, 100 parts by volume of

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15% sodium hypochlorite solution. After stirring and heating at 80°, the mixture is filtered and a violet solution is obtained.

This violet solution, containing the ferrate ion, is added to a batch of 2-amino-3-chloro-anthrahydroquinone-disulfuric ester prepared as described in Example 1. After carrying out the oxidation at 60°, the excess ferrate is removed by precipitation with barium chloride. The mixture is then filtered, concentrated to 60 parts by volume, salted at 60° with 12 parts of potassium chloride and 30 parts of methanol, and cooled thoroughly. On filtration, the potassium salt of the leuco dichloroindanthrone tetrasulfuric ester is obtained in good yield.

We claim:

1. Process of preparing leuco indanthrone tetrasulfuric esters which comprises reacting a leuco sulfuric ester of a beta-amino-anthraquinone having a free position alpha to the amino group with a compound containing as an anion iron having an even valence not less than 4 and not greater than 6.
2. Process according to claim 1 in which the iron compound is a ferrate.
3. Process according to claim 2 in which the beta-aminoanthraquinone is 2-amino-3-halogenanthraquinone.
4. Process according to claim 3 in which the 2-amino-3-halogenanthraquinone is 2-amino-3-chloroanthraquinone.
5. Process according to claim 4 in which the ferrate is an alkali metal ferrate.
6. Process according to claim 3 in which the ferrate is an alkaline earth metal ferrate.
7. Process according to claim 6 in which the ferrate is barium ferrate.
8. Process of preparing a leuco indanthrone tetrasulfuric ester which comprises reacting the leuco sulfuric ester of a beta-aminoanthraquinone having a free position alpha to the amino group with a compound of nickel having a valence of at least 3 and not more than 4.
9. Process according to claim 8 in which the nickel compound is nickel dioxide.
10. Process according to claim 9 in which the beta-aminoanthraquinone is 2-amino-3-halogenanthraquinone.
11. Process according to claim 10 in which the 2-amino-3-halogenanthraquinone is 2-amino-3-chloroanthraquinone.
12. Process according to claim 10 in which the 2-amino-3-halogenanthraquinone is 2-amino-3-bromoanthraquinone.
13. A process of preparing leuco indanthrone tetrasulfuric esters which comprises reacting a leuco sulfuric ester of a beta-aminoanthraquinone with a free position alpha to the amino group with a compound of cobalt having a valence of 3.
14. A process according to claim 13 in which the cobalt compound is cobaltic hydroxide.
15. A process according to claim 14 in which the leuco sulfuric ester is of a 2-amino-3-halogenanthraquinone.
16. A process according to claim 15 in which the 2-amino-3-halogenanthraquinone is 2-amino-3-chloroanthraquinone.

WILLIAM B. HARDY.

ROBERT B. FORTENBAUGH.

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