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PREPARATION OF DI(ARYLAMINO) ANTHRAQUINONES

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The present invention relates to a method for the preparation of 1,4-diarylamino derivatives of anthraquinone from quinizarine, leuco quinizarine or a mixture of the two, and more particularly to a method for the preparation of the 1,4-di-p-toluido derivative of anthraquinone commonly known as quinizarine green.

It is an object of the present invention to provide a process whereby di(arylamino) anthraquinones may be prepared from quinizarine, leuco quinizarine, or a mixture of the two, and an arylamine in high yields, and of excellent quality.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

It is known that diarylamino derivatives of anthraquinone can be formed by condensing quinizarine, leuco quinizarine, or a mixture of the two with an arylamine in the presence of a condensation agent and in an inert medium consisting of a chlorinated hydrocarbon of the benzene series. Ordinarily this condensation is carried out with the aid of a reducing agent, particularly when quinizarine is employed as the starting material. The reaction is conducted at an elevated temperature, and is generally carried out in the presence of air whereby the leuco di(arylamino) anthraquinone which is initially formed is oxidized to the quinoid form.

It has been discovered in accordance with the present invention that the yield and quality of di(arylamino) anthraquinones obtained with the use of this general process can be increased by subjecting the reaction mass at the completion of the condensation to an auxiliary oxidation treatment. This auxiliary oxidation treatment is preferably effected by heating the reaction mass with a small amount of an aromatic nitro compound, such as, for example, nitrobenzene, at an elevated temperature, preferably between about 120° and 140° C., for a short period of time.

In the practice of the present invention in accordance with one method of procedure, quinizarine, leuco quinizarine, or a mixture of the two (referred to generically herein as "a quinizarine compound") is condensed with an arylamine in the presence of an acetic acid condensing agent and of monochlorbenzene, which serves as an inert medium for the reaction, and the product is recovered by oxidizing with air supplemented by an auxiliary oxidation treatment, preferably with an aromatic nitro compound. In general, and particularly when quinizarine is employed as the starting material, the reaction is also carried out with a reducing agent such as, for example, finely divided zinc.

The process of the present invention is carried out in accordance with a preferred procedure by preparing a mixture of quinizarine, an arylamine, e. g., p-toluidine, finely divided zinc, e. g., zinc dust, and monochlorbenzene. This mixture is then slightly warmed and a suitable amount of an aqueous solution of acetic acid, e. g., containing from about 70 to about 95 per cent, and preferably about 80 per cent, acetic acid, is introduced into the mixture. The mixture is then heated, preferably to a temperature of about 100°±2° C., so as to drive off substantially all of the water added in the acetic acid solution while avoiding any substantial condensation taking place between the arylamine and the quinizarine. The mixture is raised to an elevated temperature, for example, between about 120° to about 140° C. for the period of time required to complete the condensation while allowing water vapor to escape. The reaction is carried out in contact with the air so as to oxidize the major portion of the leuco di(arylamino) anthraquinone, which is initially formed in the reaction, to the quinoid form. To complete the oxidation of the leuco di(arylamino) anthraquinone, a small amount of an oxidizing agent such as, for example, an aromatic nitro compound, e. g., nitrobenzene, is introduced into the reaction mass at or near to the completion of the condensation reaction, and the mixture is agitated and heated at a temperature of about 120° to about 140° C. for a short period of time. At the completion of this auxiliary oxidation step, the di(arylamino) anthraquinone may be recovered from the reaction mass by cooling and crystallizing and filtering off the thus formed crystals. To assist in the crystallization and separation of the di-(arylamino) anthraquinone from the reaction mass, the mass, prior to cooling, may be diluted with an additional amount of monochlorbenzene.

By employing an auxiliary oxidation treatment with an aromatic nitro compound, it has been found to be possible to increase materially the yields of the di(arylamino) anthraquinone obtainable in the process. This was not to be anticipated since the reaction mass prior to this auxiliary oxidation has been subjected to the oxidizing action of air, usually by carrying out the reaction in the presence of air. Without limiting the invention to any theoretical explanation, it would seem the improved results obtainable are probably due in some measure to the facts that in the preparation of quinizarine green and similar diarylamino derivatives of anthraquinone from quinizarine the operating con-

ditions employed when air is relied upon entirely for oxidizing the leuco di(arylamino) anthraquinone in the reaction mass fail to produce uniform oxidation since the supply of air coming in contact with the mixture varies in successive operations, and that small quantities of the leuco di(arylamino) anthraquinone in the reaction mass may be in such stable condition as not to be oxidizable by the action of air and remain in the inert medium when the di(arylamino) anthraquinone is separated therefrom. The auxiliary oxidation treatment with an aromatic nitro compound at the end of the reaction appears to eliminate the variation in the extent of oxidation encountered in the prior procedures and also to oxidize the more resistant forms of the leuco di(arylamino) anthraquinone to the quinoid form.

Monochlorbenzene is a highly efficient inert medium for the reaction under consideration being not only valuable in so far as the yields obtainable in relation to the amounts of quinizarine and arylamine employed are concerned, but also being of advantage in that relatively small amounts of the monochlorbenzene may be employed as the inert medium for the reaction. Further, by employing monochlorbenzene as the inert medium for the reaction it is possible to reduce the highest temperature of the reaction to between about 120° and about 140° C.

Aqueous solutions of acetic acid of the foregoing concentrations are valuable assistants in the present reaction being equivalent in effect, with respect to the yields obtainable, to other condensing agents over which they represent a material advantage in regard to economy of operation. It is surprising that these aqueous acetic acid solutions should be of high efficiency in this connection since glacial acetic acid is of relatively low efficiency when employed in the reaction.

In order that the present invention may be more fully understood, reference should be had to the following example which illustrates a preferred manner of carrying out the process of the invention. It will be understood, however, that the invention is not limited to the details of this example. The parts are by weight, and the temperatures in degrees centigrade.

Example.—In a suitable vessel equipped with an agitator, a mixture of 50 parts of quinizarine, 62 parts of para-toluidine, 100 parts of monochlorbenzene, and 5.1 parts of zinc dust is heated at 58° to 60°. Then 9.6 parts of 80 per cent acetic acid are added. Due to the heat of reaction between the zinc, acetic acid, and quinizarine to form leucoquinizarine, the temperature of the mixture rises to between 70° and 80°. The resulting mixture containing para-toluidine, quinizarine, and leuco-quinizarine, is heated to a temperature of 90° and then slowly to a temperature between 98° and 102° where it is maintained until substantially all of the free water which is present has distilled off together with a portion of the monochlorbenzene. During this period, practically no condensation takes place between the quinizarine compounds and the para-toluidine. After the free water has been expelled, the temperature is raised to 132° to 135°, and is held at this point until the condensation between the quinizarine compounds and the para-toluidine to form 1,4-di(p-toluido) anthraquinone is practically completed. This ordinarily requires about 5 to 6 hours. During this step, the water formed in the condensation is allowed to escape. To the resulting mass, about 1 to 2 parts of nitrobenzene are added and the mixture is agitated at a temperature of 128° to 130° for about half an hour. It is then diluted with 100 parts of monochlorbenzene and is allowed to cool, whereby crystals of 1,4-di(p-toluido) anthraquinone (quinizarine green) are precipitated. The precipitated crystals of quinizarine green are separated as a filter cake by filtration. The yield of quinizarine green is about 10 per cent greater than that obtained by proceeding in the above manner, but omitting the addition of the nitrobenzene and extra heating.

With the use of an analogous process to that described in the example, other diarylamino derivatives of anthraquinone may be prepared from quinizarine by employing in place of p-toluidine, any other of the arylamines known in this connection, such as, for example, aniline and its homologues, naphthylamines, etc. These arylamines are preferably employed in the proportions of at least two mols of the arylamine to each mol of quinizarine compound. For example, for reaction with 100 parts of quinizarine, there should preferably be employed at least 89 parts of p-toluidine.

It will be understood that the amount of aromatic nitro compound which is employed as an auxiliary oxidant at the end of the condensation procedure will vary with the volume of the reaction mass and the physical conditions under which the condensation is effected. Among these conditions are the type of vessel employed, the extent to which the mixture is agitated, and the amount of air with which the mixture is allowed to come in contact. In general, under normal operating conditions, it has been found that an amount of nitro compound equivalent to a few per cent, e. g., four per cent, and more often about one per cent, of nitrobenzene based on the weight of quinizarine employed in the reaction is sufficient to cause substantially complete oxidation of the leuco di(arylamino) anthraquinone in the reaction mixture. It will be understood, of course, that an excess of an aromatic nitro compound may be employed but ordinarily the use of an excess is of no advantage in regard to the yields obtainable. As indicated above, the auxiliary oxidant may be any suitable aromatic nitro compound, such as, for example, nitrobenzene, nitrotoluene, nitrochlorbenzene, nitraniline, nitrotoluidine, etc.

The auxiliary oxidation with the aromatic nitro compound is affected by the temperature maintained during this step, and it has been found that the most effective temperature range is that employed for the amination reaction. Thus, this auxiliary oxidation is preferably carried out in accordance with the present invention at a temperature between about 120° and about 140° C., which is also the preferred temperature range for conducting the amination reaction.

The amounts of the other materials used in the process of the above example may be varied. A feature of the invention resides in the fact that by employing monochlorbenzene as the inert medium for the reaction it is possible to use relatively small amounts of this material. For example, based on 100 parts of quinizarine charged to the reaction vessel, efficient results may be obtained in accordance with the present invention with the use of between about 80 and about 400 parts, and preferably about 200 parts, of monochlorbenzene.

The aqueous solution of acetic acid used in the

process of the present invention is preferably about an 80 per cent aqueous solution. However, aqueous solutions of acetic acid varying in concentration from 70 per cent to 95 per cent acetic acid may be used in the process with satisfactory results. The aqueous solution of acetic acid is preferably employed in such proportions as to provide from about 14 parts to about 17 parts acetic acid for each 100 parts of quinizarine.

The present process is of particular advantage when quinizarine is employed as the starting material. The process may be carried out, however, by starting with leuco quinizarine or a mixture of leuco quinizarine and quinizarine. Where leuco quinizarine is used, the amount of finely divided zinc employed in the reaction may be reduced considerably and may even be eliminated. Where quinizarine is employed as the starting material the finely divided zinc is preferably employed in the proportions of about 7.6 parts to about 11 parts of zinc for each 100 parts of quinizarine.

Since changes may be made in the above process without departing from the scope of the invention, the foregoing desciption should be interpreted as illustrative and not in a limiting sense.

I claim:

1. In the method for the preparation of a di(arylamino) anthraquinone in which a quinizarine compound selected from the group consisting of quinizarine and leuco quinizarine is condensed with an arylamine to form a leuco di(arylamino) anthraquinone and the leuco di-arylamino) anthraquinone is oxdized to the di(arylamino) anthraquinone, the improvement which comprises condensing the quinizarine compound with the arylamine in the presence of an acetic acid condensing agent and monochlorbenzene, and subjecting the reaction mass to the oxidizing action of an aromatic nitro compound.

2. In the method for the preparation of a di(arylamino) anthraquinone in which leuco quinizarine is condensed with an arylamine to form a leuco di(arylamino) anthraquinone and the leuco di(arylamine) anthraquinone is oxidized to the di(arylamino) anthraquinone, the improvement which comprises condensing leuco quinizarine with the arylamine in the presence of an acetic acid condensing agent and monochlorbenzene, and subjecting the reaction mass to the oxidizing action of an aromatic nitro compound of the benzene series.

3. In the method for the preparation of a di(arylamino) anthraquinone in which a quinizarine compound selected from the group consisting of quinizarine and leuco quinizarine is condensed with an arylamine to form a leuco di(arylamino) anthraquinone and the leuco di-arylamino) anthraquinone is oxidized to the di-arylamino) anthraquinone, the improvement which comprises condensing the quinizarine compound with the arylamine in the presence of an acetic acid condensing agent and monochlorbenzene, and subjecting the reaction mass to the oxidizing action of nitrobenzene.

4. In the method for the preparation of 1,4-di(p-toluido) anthraquinone in which a quinizarine compound selected from the group consisting of quinizarine and leuco quinizarine is condensed with p-toluidine to form leuco 1,4-di(p-toluido) anthraquinone and the leuco 1,4-di(p-toluido) anthraquinone is oxidized to 1,4-di(p-toluido) anthraquinone, the improvement which comprises condensing the quinizarine compound with p-toluidine in the presence of an acetic acid condensing agent and monochlorbenzene, and subjecting the reaction mass to the oxidizing action of nitrobenzene.

5. In the method for the preparation of a di(arylamino) anthraquinone in which a quinizarine compound selected from the group consisting of quinizarine and leuco quinizarine is condensed with an arylamine to form a leuco di(arylamino) anthraquinone and the leuco di(arylamino)) anthraquinone is oxidized to the di-arylamino) anthraquinone, the improvement which comprises heating a mixture containing the quinizarine compound, arylamine, acetic acid, and monochlorbenzene to form initially a leuco di(arylamino) anthraquinone, oxidizing the leuco di(arylamino) anthraquinone in the reaction mass with air, and subjecting the reaction mass to the oxidizing action of an aromatic nitro compound.

6. In the method for the preparation of a di(arylamino) anthraquinone in which leuco quinizarine is condensed with an arylamine to form a leuco di(arylamino) anthraquinone and the leuco di(arylamino) anthraquinone is oxidized to the di(arylamino) anthraquinone, the improvement which comprises heating a mixture containing leuco quinizarine, the arylamine, acetic acid, and monochlorbenzene to form initially a leuco di(arylamino) anthraquinone, oxidizing the leuco di(arylamino) anthraquinone in the reaction mass with air, introducing into the reaction mass an aromatic nitro compound, heating the resulting mixture to cause the aromatic nitro compound to oxidize remaining leuco di(arylamino) anthraquinone to the di(arylamino) anthraquinone, and recovering the di(arylamino) anthraquinone.

7. In the method for the preparation of a di(arylamino) anthraquinone in which quinizarine is condensed with an arylamine of the benzene series in the presence of a reducing agent to form a leuco di(arylamino) anthraquinone, and the leuco di(arylamino) anthraquinone is oxidized to the di(arylamino) anthraquinone, the improvement which comprises heating a mixture containing quinizarine, the arylamine of the benzene series, finely divided zinc, an aqueous solution of acetic acid containing from about 70 per cent to about 95 per cent acetic acid, and monochlorbenzene to form initially a leuco di(arylamino) anthraquinone, subjecting the leuco di-(arylamino) anthraquinone in the reaction mass to the oxidizing action of air, introducing into the resulting reaction mass a small amount of an aromatic nitro compound of the benzene series, heating the resulting mixture, and recovering a di(arylamino) anthraquinone.

8. In the method for the preparation of a 1,4-di(arylamino) anthraquinone in which quinizarine is condensed with an arylamine in the presence of a reducing agent to form a leuco 1,4-di(arylamino) anthraquinone and the leuco 1,4-di(arylamino) anthraquinone is oxidized to the 1,4-di(arylamino) anthraquinone, the improvement which comprises heating a mixture containing quinizarine, the arylamine, finely divided zinc and an aqueous solution of acetic acid containing from about 70 to about 95 per cent acetic acid in an inert medium consisting of monochlorbenzene to a final temperature within the range about 120° to about 140° C. in the presence of air to effect condensation between the quinizarine and the arylamine and to form a reaction mass containing a leuco 1,4-di(arylamino) anthraquinone and a 1,4-di(arylamino) anthraquinone, introducing into the reaction mass a small amount of an aromatic nitro compound, heating the result-

ing mixture at a temperature within the range about 120° to about 140° C. for a period of time sufficient to oxidize the leuco 1,4-di(arylamino)-anthraquinone to the 1,4-di(arylamino) anthraquinone, and recovering the 1,4-di(arylamino)-anthraquinone.

9. In the method for the preparation of a di(arylamino) anthraquinone in which quinizarine is condensed with an arylamine in the presence of a reducing agent to form a leuco di(arylamino)-anthraquinone and the leuco di(arylamino) anthraquinone is oxidized to the di(arylamino)-anthraquinone, the improvement which comprises heating a mixture containing quinizarine, the arlyamine, finely-divided zinc, about an 80 per cent aqueous solution of acetic acid, and monochlorbenzene as an inert medium to a final temperature between about 120° and about 140° C. and continuing the heating in the presence of air, to effect condensation between the quinizarine and the arylamine and to form a reaction mass containing a leuco di(arylamino) anthraquinone and a di(arylamino) anthraquinone, introducing into the reaction mass a small amount of an aromatic nitro compound, heating the resulting mixture at a temperature between about 120° C. and about 140° C. for a period of time sufficient to cause the aromatic nitro compound to oxidize the leuco di(arylamino) anthraquinone to the di(arylamino) anthraquinone, and recovering the di(arylamino) anthraquinone.

10. In the method for the preparation of a di(arylamino) anthraquinone in which quinizarine is condensed with an arylamine of the benzene series in the presence of a reducing agent to form a leuco di(arylamino) anthraquinone, and the leuco di(arylamino) anthraquinone is oxidized to the di(arylamino) anthraquinone, the improvement which comprises heating a mixture containing quinizarine, the arylamine of the benzene series, finely-divided zinc, about an 80 per cent aqueous solution of acetic acid, and monochlorbenzene as an inert medium to a final temperature between about 120° and about 140° C., and continuing the heating in the presence of air, to effect a condensation between the quinizarine and the arylamine and to form a reaction mass containing a leuco di(arylamino) anthraquinone and a di(arylamino) anthraquinone, introducing into the reaction mass a small amount of an aromatic nitro compound of the benzene series, heating the resulting mixture at a temperature between about 120° C. and about 140° C. for a period of time sufficient to cause the aromatic nitro compound to oxidize the leuco di(arylamino) anthraquinone to the di(arylamino) anthraquinone, and recovering the di(arylamino) anthraquinone.

11. In the method for the preparation of a 1,4-di(arylamino) anthraquinone in which quinizarine is condensed with an arylamine selected from the group consisting of aniline and its homologues in the presence of a reducing agent to form a leuco 1,4-di(arylamino) anthraquinone and the leuco 1,4-di(arylamino) anthraquinone is oxidized to the di(arylamino) anthraquinone, the improvement which comprises heating a mixture containing quinizarine, the arylamine, zinc, an aqueous solution of acetic acid containing from about 70 per cent to about 95 per cent acetic acid, and monochlorbenzene to form leuco quinizarine, heating the mixture to drive off water while avoiding condensation of the leuco quinizarine and the arylamine, then heating the mixture in the presence of air at a temperature from about 120° to about 140° C., to effect a condensation between the leuco quinizarine and the arylamine and to form a reaction mass containing a leuco 1,4-di(arylamino) anthraquinone and a 1,4-di(arylamine) anthraquinone, introducing into the reaction mass a small amount of an aromatic nitro compound of the benzene series, heating the resulting mixture at a temperature between about 120° and about 140° C. for a period of time sufficient to oxidize the leuco 1,4-di(arylamino) anthraquinone to the 1,4-di(arylamino) anthraquinone, and recovering the 1,4-di(arylamino)-anthraquinone.

12. In the method for the preparation of a 1,4-di(arylamino) anthraquinone in which quinizarine is condensed with an arylamine in the presence of a reducing agent to form a leuco 1,4-di(arylamino) anthraquinone and the leuco 1,4-di(arylamino) anthraquinone is oxidized to the 1,4-di(arylamino) anthraquinone, the improvement which comprises heating a mixture containing quinizarine, the arylamine, finely divided zinc, an aqueous solution of acetic acid containing from about 70 per cent to about 95 per cent acetic acid, and monochlorbenzene to a final temperature of 132° to 135° C. in the presence of air, to effect a condensation between the quinizarine and the arylamine and to form a reaction mass containing a leuco 1,4-di(arylamino) anthraquinone and a 1,4-di(arylamino) anthraquinone, introducing into the reaction mass a small amount of an aromatic nitro compound, heating the resulting mixture at a temperature between about 120° and about 140° C. for a period of time sufficient to oxidize the leuco 1,4-di(arylamino) anthraquinone to the 1,4-di(arylamino) anthraquinone, and recovering the 1,4-di(arylamino) anthraquinone.

13. A method for the preparation of 1,4-di(p-toluido) anthraquinone, which comprises heating a mixture containing quinizarine, p-toluidine, a reducing agent, an aqueous solution of acetic acid containing from about 70 per cent to about 95 per cent acetic acid, and monochlorbenzene to a final temperature of about 120° to about 140° C. in the presence of air, to effect a condensation between the quinizarine and the p-toluidine and to form a reaction mass containing leuco 1,4-di(p-toluido)-anthraquinone and 1,4-di(p-toluido) anthraquinone, introducing into the reaction mass a small amount of an aromatic nitro compound, heating the resulting mixture to oxidize the leuco 1,4-di(p-toluido) anthraquinone to 1,4-di(p-toluido) anthraquinone, and recovering the 1,4-di(p-toluido) anthraquinone.

14. A method for the preparation of 1,4-di(p-toluido) anthraquinone, which comprises heating a mixture containng quinizarine, p-toluidine, zinc, an aqueous solution of acetic acid containing from about 70 per cent to about 95 per cent acetic acid, and monochlorbenzene to a final temperature of about 120° to about 140° C. in the presence of air, to effect a condensation between the quinizarine and the p-toluidine and to form a reaction mass containing leuco 1,4-di(p-toluido) anthraquinone and 1,4-di(p-toluido) anthraquinone, introducing into the reaction mass a small amount of an aromatic nitro compound, heating the resulting mixture at a temperature between about 120° and about 140° C. for a period of time sufficient to oxidize the leuco 1,4-di(p-toluido) anthraquinone to 1,4-di(p-toluido) anthraquinone, and recovering 1,4-di(p-toluido) anthraquinone.

15. A method for the preparation of 1,4-di(p-toluido) anthraquinone which comprises heating a mixture containing 100 parts of quinizarine, at

least 89 parts of p-toluidine, about 7.6 to about 11 parts of zinc, an aqueous solution of acetic acid containing from about 70 per cent to about 95 per cent acetic acid in such proportions as to contain about 14 to about 17 parts of acetic acid, and monochlorbenzene to a final temperature of about 120° to about 140° C. in the presence of air, to effect a condensation between the quinizarine and the p-toluidine and to form a reaction mass containing leuco 1,4-di(p-toluido) anthraquinone and 1,4-di(p-toluido) anthraquinone, introducing into the reaction mass an amount of an aromatic nitro compound equivalent to 1 to 4 parts of nitrobenzene, heating the resulting mixture at a temperature between about 120° C. and about 140° C. for a period of time sufficient to oxidize the leuco 1,4-di(p-toluido) anthraquinone to 1,4-di(p-toluido)-anthraquinone, and recovering 1,4-di(p-toluido)-anthraquinone.

16. A method for the preparation of 1,4-di(p-toluido) anthraquinone which comprises heating a mixture containing 100 parts of quinizarine, at least 89 parts of p-toluidine, about 7.6 to about 11 parts of finely divided zinc, an aqueous solution of acetic acid containing about 80 per cent acetic acid in such proportions as to contain about 14 to about 17 parts of acetic acid, and about 80 to about 400 parts of monochlorbenzene to a temperature adapted to drive off the water present while avoiding substantial condensation of the quinizarine with the p-toluidine, then heating the mixture in the presence of air at a temperature of about 120° to about 140° C., to effect a condensation between the quinizarine and the p-toluidine and to form a reaction mass containing leuco 1,4-di(p-toluido) anthraquinone and 1,4-di(p-toluido) anthraquinone, introducing 1 to 4 parts of nitrobenzene into the reaction mass, heating the resulting mixture at a temperature between about 120° and about 140° C. for a period of time sufficient to oxidize the leuco 1,4-di(p-toluido) anthraquinone to 1,4-di(p-toluido) anthraquinone, and recovering 1,4-di(p-toluido) anthraquinone.

17. A method for the preparation of 1,4-di(p-toluido) anthraquinone which comprises reacting a mixture containing about 50 parts of quinizarine, about 62 parts of p-toluidine, about 5 parts of finely divided zinc, about 9.6 parts of an 80 per cent aqueous solution of acetic acid, and about 100 parts of monochlorbenzene to form leuco quinizarine in the mixture, heating the resulting mixture at a temperature of about 100° C. until the water present is substantially driven off, then heating the mixture in the presence of air at a temperature of 132° to 135° C., to effect a condensation between the leuco quinizarine and the p-toluidine and to form a reaction mass containing leuco 1,4-di(p-toluido) anthraquinone and 1,4-di(p-toluido) anthraquinone, introducing into the reaction mass from 1 to 2 parts of nitrobenzene, heating the resulting mixture at a temperature of about 130° C. for about one-half hour to oxidize the leuco 1,4-di(p-toluido) anthraquinone to 1,4-di(p-toluido) anthraquinone, and recovering 1,4-di(p-toluido) anthraquinone.

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