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SELECTIVE OXIDATION OF LEUCOANTHRAQUINONE WITH PYRIDINE-N-OXIDE

Sidney Kasman, Arlington, Mass., assignor to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

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The present invention is concerned with chemical processes and more particularly with processes for oxidizing leucoanthraquinone dyes to the corresponding anthraquinone dyes.

One object of the invention is to provide processes for oxidizing leucoanthraquinones to anthraquinones.

Another object is to provide processes for selectively oxidizing the leucoanthraquinone nucleus of a leucoanthraquinone compound which contains other oxidizable moieties in addition to said leucoanthraquinone nucleus.

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

The invention accordingly comprises the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

In the preparation of anthraquinone dyes, the dye is often first produced in the leuco form and then oxidized to the anthraquinone or, if produced as the anthraquinone, may be purified by reduction followed by oxidation. In the past, the oxidation has been generally carried out by a wide variety of methods, varying from heating in sulfuric acid at high temperatures, with or without other oxidizing agents present, to the relatively mild method of bubbling air through a solution of the leucoanthraquinone. In certain instances, such aerial oxidations, although considered mild, have been found in some instances to oxidize other moieties present in the dye in addition to the neuclus. The present invention is concerned with providing processes for selectively oxidizing the neucleus.

The objects of the present invention are carried out by using N-oxides of heterocyclic aromatic nitrogen compounds as the oxidizing agent and especially by using N-oxides selected from the group consisting of quinoline-N-oxide and pyridine-N-oxide. Particularly good results have been obtained with the pyridine-N-oxide. It has been found that such N-oxides of heterocyclic aromatic nitrogen compounds will selectively oxidize the leucoanthraquinone nucleus without oxidizing other oxidizable moieties which may be present.

The oxidation processes of the present invention have been found especially useful to oxidize leucoanthraquinone dye developers to anthraquinone dye developers. Dye developers may be defined as compounds which are both dyes and developers of exposed silver halide emulsions. They may be further defined as being compounds which contain within the same molecule the chromophoric system of a dye and also a silver halide developing function. A preferred class of anthraquinone dye developers are those which comprise an anthraquinone nucleus which is substituted by radicals which in turn contain silver halide developer radicals, e.g., hydroquinonyl, catechol, etc., radicals. In a preferred embodiment of such compounds the silver halide developing radical is joined to the anthraquinone nucleus through an alkylamino radical. Anthraquinone dye developers are disclosed in copending United States applications such, for example, as the copending

application of Richard S. Corley, Serial No. 485,342, filed January 31, 1955, now U.S. Patent No. 2,983,605; the copending application of Elkan R. Blout and Myron S. Simon, Serial No. 680,437, filed August 26, 1957, now U.S. Patent No. 3,047,386; the copending application of Elkan R. Blout and Myron S. Simon, Serial No. 680,619, filed August 27, 1957, now abandoned; and the copending application of Elkan R. Blout, Marilyn R. Cohler, Milton Green, Myron S. Simon and Robert B. Woodward, Serial No. 824,786, filed July 3, 1959, now abandoned. As examples of such developers mention may be made of:

1,4-bis-(α-methyl-β-hydroquinonyl-ethylamino)-5,8-dihydroxyanthraquinone.
1-(α-hydroxymethyl-propylamino)-4-(α-methyl-β-hydroquinonylethylamino)-anthraquinone.
1-(α-hydroxymethyl-propylamino)-4-(α-methyl-β-hydroquinonylethylamino)-5,8-dihydroxyanthraquinone.
1-hydroxy-4-(α-methyl-hydroquinonylethylamino)-anthraquinone.
1,4-bis-(α-methyl-γ-hydroquinonylpropylamino)-anthraquinone.
1,5-bis1hydroquinonylmethylamino-anthraquinone.
1,4-bis-hydroquinonylmethylamino-anthraquinone.
1,4-bis-(α-methyl-β-hydroquinonylethylamino)-6,7-dichloroanthraquinone.
1-(α-methyl-β-hydroquinonylethylamino)-4-(α-ethyl-β-hydroquinonylethylamino)-anthraquinone.
1-(α-methyl-β-hydroquinonylethylamino)-4-(α-ethyl-β-hydroquinonylethylamino)-5,8-dihydroxy-anthraquinone.
1,4-bis-(α-methyl-2',5'-dihydroxybenzylamino)-anthraquinone.
1,4-bis-(α-methyl-β-hydroquinonylethylamino)-5,8-bis-benzene-sulfonamido-anthraquinone.
1,4-bis-(α-methyl-β-hydroquinonylethylamino)-5-hydroxy-8-amino-anthraquinone.
1,4-bis-(α-methyl-β-hydroquinonylethylamino)-5-hydroxyanthraquinone.
1,4-bis-(β-hydroquinonylethylamino)-anthraquinone.
1-[p-(β-hydroquinonyl-ethyl)-phenylamino]-anthraquinone.
1-(α-hydroxymethyl-propylamino)-4-[β-(4'-methyl-2',5'-dihydroxyphenyl)-α-methyl-ethylamino] anthraquinone.
1-ethylamino-4-[β-(3',4'-dihydroxyphenyl)-ethylamino]-anthraquinone.
1-chloro-4-(β-hydroquinonylethylamino)-anthraquinone.
1-hydroxy-4-[β-(3',4'-dihydroxyphenyl)-ethylamino]-anthraquinone.
1-chloro-5-(β-hydroquinonylethylamino)-anthraquinone.
1,4-bis-[β-(3',4'-dihydroxyphenyl)-ethylamino]-5,8-dihydroxyanthraquinone.
1,8-bis-[β-(3',4'-dihydroxyphenyl)-ethylamino]-anthraquinone.
1-[β-(3',4'-dihydroxyphenyl)-ethylamino]-anthraquinone.
1-β-hydroquinonylethylamino-anthraquinone.
1,5-bis-[β-(3',4'-dihydroxyphenyl)-ethylamino]-anthraquinone.
1,5-bis-(β-hydroquinonylethylamino)-anthraquinone.
1,8-bis-(β-hydroquinonylethylamino)-anthraquinone.
1,5-bis-(α-methyl-β-hydroquinonylethylamino)-anthraquinone.
1-(β-hydroxyethylamino)-4-(β-hydroquinonyl-ethylamino)-anthraquinone.
1,4-bis-[β-(3',4'-dihydroxyphenyl)-ethylamino]-anthraquinone.
1-(β-hydroxyethylamino)-4-(α-methyl-β-hydroquinonyl-ethylamino)-5,8-dihydroxyanthraquinone.
1,4-bis-(α-ethyl-β-hydroquinonylethylamino)-anthraquinone.

1-methylamino-4-(β-hydroquinonylethylamino)-anthraquinone.
1-β-hydroxyethylamino-4-(α-methyl-β-hydroquinonyl-ethylamino)-anthraquinone.
1,4-bis-(2',5'-dihydroxyanilino)-anthraquinone.
N-monobenzoyl-1,4-bis-[β-(3',4'-dihydroxyphenyl)-ethylamino]-anthraquinone.
N-monobenzoyl-1,4-bis-[β-(2',5'-dihydroxyphenyl-ethylamino]-anthraquinone.
4-[1',5'-bis-(2'',5''-dihydroxyphenyl)-3'-pentyl]-amino-1-hydroxyanthraquinone.
1,4-bis-[1',5'-bis-(2'',5''-dihydroxyphenyl)-3'-pentylamino]-anthraquinone.

It should be noted that the above-mentioned anthraquinones contain radicals such, for example, as ortho- and para-dihydroxyphenyl radicals which are readily oxidizable and, as is known, are capable of developing silver halide emulsions. In order to preserve the developing ability of such radicals it is important, when preparing the dye developers from the leucoanthraquinones through oxidation or by purifying them by reduction followed by oxidation, that the oxidation be limited to the leucoanthraquinone nucleus and not oxidize these radicals. The oxidizing agents, disclosed herein, bring about such a selective oxidation.

In an especially useful embodiment of this invention an excess of pyridine-N-oxide is employed. A convenient excess has been found to be about 10% of the equivalent amount; however, it should be understood that larger excesses may be used without interfering with the selectivity.

In carrying out the processes of the present invention, the leucoanthraquinone dye and at least an equivalent amount of the N-oxide of the heterocyclic aromatic nitrogen compound are brought into intimate contact. In a preferred embodiment the dye is dissolved in a solvent and the oxide is added thereto. If desired the oxide may be first dissolved in a suitable solvent such, for example, as pyridine. The reaction may be speeded up, without endangering the selectivity, by carrying it out at a temperature in excess of room temperature. In a preferred embodiment the reaction is carried out at temperatures between about 40° C. to 120° C. and more preferably at between 100° C. and 120° C.

The following nonlimiting examples illustrate the processes within the scope of this invention.

Example 1

2.74 gms. of leuco-1,4,5,8-tetrahydroxyanthraquinone and 2.22 gms. of 2-aminobutanol were added to 25 mls. of 2-butoxyethanol and reacted at 140° C. under nitrogen for about 5 hours. 25 mls. of pyridine were added and the reaction was continued overnight. 1.0 gm. of pyridine-N-oxide in 10 mls. of pyridine was added and the reaction was continued overnight at reflux. A spectro-photometric analysis indicated that the leuco material had been completely oxidized. The product was precipitated into an excess of dilute hydrochloric acid, filtered, washed and dried. The 1,4-bis-[α-hydroxymethyl-propylamino] 5,8-dihydroxyanthraquinone produced was purified by crystallization from 2-methoxyethanol.

The 25 mls. of pyridine were added in the above reaction in order to increase the solubility of the tetrahydroxyanthraquinone.

Example 2

18 gms. of leuco-1,4,5,8-tetrahydroxyanthraquinone, 44 gms. of 2-aminopropylhydroquinone hydrobromide, 15.05 gms. of sodium bicarbonate and 8.15 gms. of boric acid were added to 16 mls. of water and 329 mls. of 2-methoxyethanol and reacted at reflux under nitrogen for about 3 hours. 6.24 gms. of pyridine-N-oxide were then added and the oxidation was allowed to proceed at reflux under nitrogen for about 1 hour and fifteen minutes. An additional 0.624 gm. of pyridine-N-oxide was added and the oxidation was continued for another hour. A spectrophotometric analysis performed at this time indicated the absence of the leuco compound. The reaction mixture was cooled to room temperature, filtered under nitrogen and precipitated into 1,320 mls. of 5 to 10% hydrochloric acid. The resulting precipitate was filtered, washed with water and dried under vacuum at 40° C. It was further purified by precipitation from an excess of ethyl acetate into hexane.

Example 3

24.2 gms. (0.10 mole) of leucoquinizarin, 60.0 gms. (0.226 mole) of β-(p-aminophenyl)-ethylhydroquinone hydrochloride, 12.4 gms. (0.20 mole) of boric acid, and 21.0 gms. of sodium bicarbonate were added to 250 mls. of 2-methoxyethanol. The mixture was slowly brought to reflux, with stirring and under nitrogen and held there for about 20 hours. 0.105 mole of pyridine-N-oxide was added and heating was continued for about two hours. A spectrophotometric analysis showed that the leuco compound had been substantially completely oxidized. The mixture was cooled and precipitated into an excess of dilute hydrochloric acid and the resulting precipitate was filtered, washed and dried.

The fact that the dye developer, produced in the above examples, readily developed an exposed silver halide emulsion to produce an image indicated that the hydroquinonyl radicals were not oxidized.

In the above examples boric acid was used in the initial condensation step and was present during the pyridine-N-oxide oxidation. It has been found that boric acid catalyzes the oxidation without interfering with the selectivity. In a preferred embodiment of this invention the oxidation is carried out in the presence of boric acid. The amount of boric acid used may be varied to suit particular needs. Generally the use of about 2 moles per mole of dye has been found to substantially speed up the reaction.

In an especially useful embodiment of this invention, the oxidation is carried out under a blanket of an inert gas such, for example, as nitrogen. This blanket of inert gas serves to insure against aerial oxidation. It should be understood, however, that it may or may not be used, depending upon one's particular choice.

The dye developers produced by the processes of this invention may be used in photographic products, processes and compositions such as those disclosed in the copending United States application of Howard G. Rogers, Serial No. 748,421, filed July 14, 1958, now U.S. Patent No. 2,983,606.

Since certain changes may be made in the above process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process for selectively oxidizing the leucoanthraquinone nucleus of a leucoanthraquinone compound containing at least one substituent selected from the class consisting of ortho- and para-dihydroxyphenyl groups, said dihydroxyphenyl substituent being joined to the leucoanthraquinone nucleus through an amino group present on said nucleus, to form the corresponding anthraquinone dye without oxidizing said dihydroxyphenyl substituent, said process comprising reacting said leucoanthraquinone compound with at least a molar equivalent amount of pyridine-N-oxide.

2. A process as defined in claim 1 wherein said dihydroxyphenyl substituent is a para-dihydroxyphenyl group.

3. A process as defined in claim 1 wherein an amount in excess of the molar equivalent amount of said pyridine-N-oxide is employed.

4. A process as defined in claim 1 wherein the reaction is carried out at about 40° C. to 120° C.

5. A process as defined in claim 1 wherein the reaction is carried out in the presence of boric acid.

6. A process as defined in claim 1 wherein the reaction is carried out under a blanket of inert gas.

7. A process for selectively oxidizing the leucoanthraquinone nucleus of a leucoanthraquinone compound containing at least one substituent selected from the class consisting of ortho- and para-dihydroxyphenyl groups, said dihydroxyphenyl substituent being joined to the leucoanthraquinone nucleus through an amino group on said nucleus, to form the corresponding anthraquinone dye without oxidizing said dihydroxyphenyl substituent, said process comprising reacting said leucoanthraquinone compound with at least a molar equivalent amount of pyridine-N-oxide under an inert atmosphere in the presence of boric acid at a temperature between about 40° C. to 120° C.

8. A process as defined in claim 7 wherein said dihydroxyphenyl substituent is joined to the amino group through an alkylene group.

9. In a process of preparing 1,4-bis-(α-methyl-β-hydroquinonyl-ethylamino) - 5,8 - dihydroxyanthraquinone, the step comprising refluxing leuco-1,4-bis-(α-methyl-β-hydroquinonyl-ethylamino) - 5,8 - dihydroxyanthraquinone with at least a molar equivalent amount of pyridine-N-oxide.

10. In a process of preparing 1,4-bis-[p-(β-hydroquinonyl-ethyl) - phenylamino] - anthraquinone, the step comprising refluxing leuco-1,4-bis-[p-(β-hydroquinonyl-ethyl)-phenylamino]-anthraquinone with at least a molar equivalent amount of pyridine-N-oxide.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,173,929 March 16, 1965

Sidney Kasman

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 22, for "1,5-bislhydroquinonylmethylamino-anthraquinone" read -- 1,5-bis-hydroquinonylmethylamino-anthraquinone --; column 3, line 8, for "-dihydroxyphenyl-" read ---dihydroxyphenyl)- --; column 6, line 17, for "Feb. 28, 1930" read -- Feb. 24, 1930 --.

Signed and sealed this 28th day of September 1965.

SEAL)
ttest:

ERNEST W. SWIDER
ttesting Officer

EDWARD J. BRENNER
Commissioner of Patents

UNITED STATES PATENT OFFICE

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EAL)
test:

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testing Officer

EDWARD J. BRENNER
Commissioner of Patents