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REDUCTION OF AROMATIC NITROGEN COMPOUNDS

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This invention relates to improvements in the alkaline reduction of aromatic nitrogen compounds containing nitrogen in a reducible form as a nuclear substituent. It relates more particularly to improvements in the process of effecting the reduction, by means of alkaline reducing agents, of such aromatic nitrogen compounds, and especially mononuclear aromatic nitrogen compounds of said type, in which the nitrogen is at a higher state of oxidation than the hydrazo stage.

The alkaline reduction of aromatic nitrogen compounds containing nitrogen in a reducible form is well known. Thus it is known to reduce aromatic nitro compounds, aromatic nitroso compounds, aromatic azoxy compounds, aromatic azo compounds and aromatic hydroxylamine compounds by means of alkaline reducing agents. It is also known that the extent to which the reduction can be carried depends on the strength of the reducing agent and the severity of the reduction conditions.

For example, it is known to reduce nitrobenzene with a metal alcoholate, and especially an alkali metal alcoholate. The reduction is usually carried out by heating nitrobenzene with alcoholic caustic alkali (e. g., sodium hydroxide and an alcohol) at the boiling point of the mixture while refluxing at atmospheric pressure. Alkali metal hydroxide and an alcohol are used instead of the equivalent preformed alcoholate because of lower cost. Methanol is preferred as the alcohol in view of its relative cheapness. The reduction product, aside from a small amount of aniline, is azoxybenzene; the alkali metal alcoholates are not sufficiently strong reducing agents to carry the reduction beyond the azoxy stage, under the usual conditions.

Heretofore, it has been necessary to carry out the further reduction of azoxybenzene to azobenzene, and of azobenzene to hydrazobenzene, with stronger reducing agents, such as zinc and alkali, which are more costly than the alcoholic caustic alkali reducing agents.

It has been proposed to carry the reduction of nitrobenzene beyond the azoxy stage by heating it with sodium or potassium hydroxide and methanol under more elevated temperatures and pressures, such as temperatures of 140° to 180° C. and pressures of 10 or more atmospheres. Such a procedure has the usual disadvantages of operation under pressure, as well as requiring expensive pressure apparatus.

Thus, the production of aromatic azo and hydrazo compounds from aromatic nitro compounds and their intermediate reduction products presents a number of problems from the standpoint of commercial practice.

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A primary object of the present invention is to provide improvements in the alkaline reduction of reducible aromatic nitrogen compounds of the type referred to above (i. e., containing nitrogen in a reducible form as a nuclear substituent), whereby the reducing power of metal alcoholate reducing agents and especially of alcoholic caustic alkali reducing agents is enhanced and other advantages are secured.

Other objects of the present invention are to provide a process for the production of aromatic azo compounds in good yields by the reduction of aromatic nitro compounds, and their reduction products up to and including azoxy compounds, with metal alcoholates under moderate reaction conditions and in simple apparatus; to provide a process for the production of aromatic hydrazo compounds by reduction of aromatic nitro compounds and other reducible aromatic nitrogen compounds with metal alcoholates under moderate conditions and in simple apparatus; and to provide improvements in the reduction of reducible aromatic nitrogen compounds with metal alcoholates whereby the evolution of hydrogen gas during the reduction is suppressed.

Additional objects in part will be obvious and in part will appear hereinafter.

In my application Serial No. 184,123, filed September 9, 1950, now Patent No. 2,645,636, I have disclosed and claimed the improvement in the method of reducing reducible aromatic nitrogen compounds by the action of metal alcoholates which comprises carrying out the reduction in reaction mixtures in which reduction promoters of a novel class have been incorporated, namely, naphthoquinoid compounds.

According to the present invention, the foregoing objects are accomplished by carrying out the reduction of reducible aromatic nitrogen compounds by means of a metal alcoholate with the inclusion in the reaction mixture of certain hydroxynaphthalenes as reduction promoters.

The hydroxynaphthalene reduction promoters employed in accordance with the present invention are the naphthols (alpha- and beta-naphthol) and certain derivatives thereof; namely, certain non-quinoid hydroxy- and amino-naphthols, and certain sulfonic acid and carboxylic acid derivatives of the naphthols. Thus they include:

1-naphthol

8-hydroxy-1-naphthol (1,8-dihydroxynaphthalene)
8-amino-1-naphthol
2-naphthol
5-amino-2-naphthol (1-amino-6-naphthol)
2-naphthol-4-sulfonic acid
2-naphthol-3-carboxylic acid (2-hydroxy-3-naphthoic acid)

I have discovered that the presence in the reaction mixture of a small amount of a reduction promoter of the above type, such as alpha-naphthol, has a modifying effect upon the reduction, as a result of which a number of benefits may be secured.

Thus, as compared with a reduction carried out under the same conditions but in the absence of the reduction promoter, the speed of the reduction is increased and/or products of a higher stage of reduction are obtained, without substantial sacrifice of the total yield of reduction products secured from the starting material. In the reduction of aromatic nitro compounds, the presence of a reduction promoter of the above type in the metal alcoholate reaction mixture makes possible the obtainment of azo compounds directly, without requiring the use of drastic operating conditions, such as high temperatures and pressures of 10 or more atmospheres. Similarly, the presence of a reduction promoter of the above type in the reaction mixture makes possible the production of hydrazo compounds from nitro, azoxy and azo compounds by means of metal alcoholate reducing agents without requiring the use of drastic operating conditions. By their presence, the reduction promoters suppress almost completely side reactions leading to the evolution of hydrogen gas during the reduction, thereby greatly increasing the safety of the reduction process and minimizing waste of the reducing agent.

Where no substantial change in the degree of reduction is desired, the presence of a reduction promoter of the above type in the reduction reaction medium makes possible the use of milder reaction conditions or the use of decreased amounts of reducing agent. Thus, in the reduction of an aromatic nitro compound with sodium hydroxide and methyl alcohol, the presence of a reduction promoter of the above type in the reaction mixture makes possible the use of a lesser amount of sodium hydroxide, thereby decreasing the cost of the operation.

Of the hydroxynaphthalene reduction promoters referred to above, the naphthols, 8-amino-1-naphthol and 2-naphthol-4-sulfonic acid are preferred for use in the reduction of reducible aromatic nitrogen compounds by means of metal alcoholates. 2-naphthol-4-sulfonic acid and 1-naphthol are especially preferred in view of their outstanding activity as reduction promoters coupled with their availability and relatively low cost.

In the practice of the present invention, the reducible aromatic nitrogen compound is subjected to the reducing action of a metal alcoholate reducing agent in a reaction mixture containing one or more of the hydroxynaphthalene reduction promoters referred to above. In the preferred practice of the invention, wherein a reducible aromatic nitrogen compound is heated with a caustic alkali and an alcohol (preferably sodium hydroxide and methanol) at the boiling point of the reaction mixture, the reduction promoter is preferably mixed with the alcohol and, after adding the caustic alkali and heating, the nitrogen compound to be reduced is added to the mixture.

The reduction promoter may be added to the reaction mixture in various ways and at various times, however, without departing from the scope of the invention.

The reduction promoter can be employed in various amounts. It is a feature of the present invention that small amounts of hydroxynaphthalenes of the type referred to above are effective as reduction promoters. Thus, amounts lying within the range $\frac{1}{30}$ to $\frac{1}{300}$ mol of such hydroxynaphthalenes per mol of reducible aromatic nitrogen compound are ordinarily employed. The minimum amount required to produce a significant reduction-promoting effect varies with the individual hydroxynaphthalene employed, the nature of the reducible aromatic nitrogen compound, and the reaction conditions. In general, a greater reduction-promoting effect is secured by increasing the amount of reduction promoter employed and a lesser effect results from decreasing the amount employed, other reaction conditions being constant. Amounts greater than about $\frac{1}{10}$ mol of reduction promoter per mol of reducible aromatic nitrogen compound usually are not advantageous, although they may be used if desired, since the additional benefits derived therefrom are not of sufficient commercial importance to compensate for the increased cost of the extra amount of reduction promoter.

The invention will be illustrated by the following specific examples, but it is to be understood that it is not limited to the details thereof and that changes may be made without departing from the scope of the invention. The temperatures are in degrees centigrade and the parts are by weight, unless designated as parts by volume in which case the amount signifies the volume occupied by the same number of parts by weight of water at 4° C.

Example 1

Part A.—360 parts of methanol and 10.8 parts of 2-naphthol-4-sulfonic acid were charged to a flask equipped with a reflux condenser, agitator, dropping funnel and thermometer. 446 parts of solid sodium hydroxide were then added over the course of 15 minutes. The mixture was heated to refluxing, 738 parts of nitrobenzene were added, and the reaction mass was boiled and refluxed (about 90° to 105°) for 20 hours under atmospheric pressure. A negligible amount of gas was evolved during the addition of nitrobenzene and subsequent reflux period. Unreacted methanol was then removed by distillation with live steam, after which the mass was allowed to stand and separate into an upper oil phase and a lower aqueous phase. The aqueous phase, consisting essentially of sodium hydroxide and sodium formate in solution, was drawn off at about 100° and the oil phase was clarified by filtration from a small amount of black insoluble residue. The resulting oil consisted essentially of a mixture of 76% of azobenzene and 24% of azoxybenzene. After being dried over calcium chloride, it had a setting point of 57.8°. The yield was 540 parts, which corresponds to a combined yield of azobenzene and azoxybenzene of about 97% of the theoretical, based on the nitrobenzene charged.

Part B.—The process of Part A was repeated without addition of the 2-naphthol-4-sulfonic acid. 25,000 parts by volume of hydrogen were

evolved and the oil product, which amounted to 573 parts, consisted essentially of azoxybenzene (it had a setting point of 33.5°). This corresponds with a yield of about 96% of the theoretical yield of azoxybenzene.

Example 2

The procedure described in Example 1, part A, was repeated, using 12 parts of 1-naphthol (alpha-naphthol) in place of the 2-naphthol-4-sulfonic acid. The product weighed 522 parts and consisted essentially of a mixture of azobenzene and azoxybenzene (setting point of 35.6°). This corresponds with a yield of about 91% of the theoretical, based on the nitrobenzene charged.

Example 3

The procedure described in Example 1, part A, was repeated, using 18 parts of 8-amino-1-naphthol in place of the 2-naphthol-4-sulfonic acid. The product weighed 522 parts and consisted essentially of a mixture of azobenzene and azoxybenzene (setting point of 24.7°). This corresponds with a yield of about 90% of the theoretical, based on the nitrobenzene charged.

Example 4

The procedure described in Example 1, part A, was repeated, using 12 parts of 8-hydroxy-1-naphthol (1,8-dihydroxy-naphthalene) in place of the 2-naphthol-4-sulfonic acid. The product weighed 564 parts and consisted essentially of a mixture of azobenzene and azoxybenzene (setting point of 26.7°). This corresponds with a yield of about 96% of the theoretical, based on the nitrobenzene charged.

Example 5

The procedure described in Example 1, part A, was repeated, using 18 parts of 2-naphthol (beta-naphthol) in place of the 2-naphthol-4-sulfonic acid. The product weighed 540 parts and consisted essentially of a mixture of azobenzene and azoxybenzene (setting point of 24.8°). This corresponds with a yield of about 91% of the theoretical, based on the nitrobenzene charged.

Example 6

The procedure described in Example 1, part A, was repeated, using 12 parts of 5-amino-2-naphthol in place of the 2-naphthol-4-sulfonic acid. The product weighed 576 parts and consisted essentially of a mixture of azobenzene and azoxybenzene (setting point of 28.8°). This corresponds with a yield of about 98% of the theoretical, based on the nitrobenzene charged.

Example 7

The procedure described in Example 1, part A, was repeated, using 12 parts of 2-naphthol-3-carboxylic acid (2,3-hydroxy-naphthoic acid) in place of the 2-naphthol-4-sulfonic acid. The product weighed 516 parts and consisted essentially of a mixture of azobenzene and azoxybenzene (setting point of 28.9°). This corresponds with a yield of about 87% of the theoretical, based on the nitrobenzene charged.

As noted above, the invention is not limited to the details of the foregoing illustrative examples, and changes can be made without departing from the scope of the invention.

Thus, the process is applicable to the reduction of other aromatic nitrogen compounds containing nitrogen in a reducible form as a nuclear substituent, as for example, o-nitrotoluene, m-nitrotoluene, o-nitrochlorobenzene, m-nitrochlorobenzene, o-nitrophenetole, o-nitrobenzoic acid and o-nitrobenzene sulfonic acid. In view of the extensive use of hydrazobenzene and its o-substituted derivatives (such as o,o'-dichloro-hydrazobenzene, o,o'-hydrazotoluene, o,o'-hydrazoanisole, o,o'-diethoxy-hydrazobenzene, etc.) as intermediates for the manufacture of benzidine and related derivatives of benzidine, the process of the present invention is of special value as a means for reducing the cost of manufacturing such hydrazo compounds from the corresponding reducible mononuclear aromatic nitrogen compounds (such as, nitrobenzene and its o-substituted derivatives and reduction products thereof) in which the nitrogen is at a higher stage of oxidation than the hydrazo stage.

The reduction of aromatic nitro compounds to azoxy compounds (1), of azoxy compounds to azo compounds (2), and of azo compounds to hydrazo compounds (3) proceeds according to the following equations, in which R is an aromatic nucleus:

(1)

$$4RNO_2 + 3CH_3OH + 3NaOH \longrightarrow \underset{2R-N\overset{O}{\diagdown\diagup}N-R}{} + 3HCOONa + 6H_2O$$

(2)

$$2RN\overset{O}{\diagdown\diagup}NR + CH_3OH + NaOH \longrightarrow 2R-N=N-R + HCOONa + 2H_2O$$

(3)

$$2R-N=N-R + CH_3OH + NaOH \longrightarrow 2R-NH-HN-R + HCOONa$$

In carrying out the reduction by means of sodium hydroxide and methanol, it is preferable to employ these reagents in amounts in excess of those theoretically required. Extra methanol over that theoretically required is generally desirable for use as a solvent, and an additional excess is desirable to counteract the diluting effect of the water generated in accordance with above Equations 1 and 2, which would otherwise tend to retard the reaction. An excess of sodium hydroxide also is desirable since it tends to increase the rate of reaction.

It is posible to carry the reduction of a particular reducible aromatic nitrogen compound to various stages, depending upon the amounts of sodium hydroxide and methanol, as well as the nature and amount of reduction promoter, employed. Thus, it is possible to reduce nitrobenzene to hydrazobenzene in a single reaction mixture. However, it is possible to reduce nitrobenzene to azoxy- and/or azobenzene in one reaction mixture, as illustrated in the above examples, and then to isolate and reduce the resulting azoxybenzene and/or azobenzene to hydrazobenzene with a fresh charge of sodium hydroxide and methanol.

The temperature at which the reaction is carried out also may be varied although, in the reduction performed with the aid of alcoholic caustic alkali, temperatures at or near the boiling point of the reaction mixture at atmospheric pressure (ordinarily about 90° to 105°) are preferred. At lower temperatures, the reaction is slower, under otherwise similar conditions, and may require an excessively long time to produce the same results as the preferred temperatures. Conversely, higher reaction temperatures result in a short time cycle but require the use of closed reaction vessels. However, temperatures greatly exceeding 110°, though not precluded, are less desirable; since even in the presence of the re-

duction promoters they lead to evolution of considerable amounts of hydrogen gas and formation of primary amines, with consequent loss of yield of the desired reduction products.

While for economical and simple operation it is preferred to use, as a solvent or diluent of the reaction mixture, an excess of the alcohol employed for the alcoholate, the invention is not limited thereto. Thus, other solvents and diluents can be employed; for example, the process may be carried out with amounts of sodium hydroxide and methanol only slightly in excess over the amounts theoretically required for the reduction in a reaction medium containing a sufficient amount of xylene to provide a stirrable reaction mass. Instead of xylene, other inert solvents or diluents may be used, such as benzene, toluene, mono- and dichlorobenzenes. Further, while it is simpler to employ, as the solvent or diluent, an excess of the alcohol functioning as a reducing agent, other alcohols can be employed; also mixtures of alcohols can be used, especially where it is desired to modify the boiling temperature of the reaction mixture.

As a matter of convenience and for economical operation, the process is generally carried out by forming a metal alcoholate in the reaction mixture; for example, by reacting caustic alkali with the alcohol. If desired, however, preformed metal alcoholates may be employed as reducing agents, in which case the diluting effect of the water formed as a by-product of the reaction of caustic alkali with the alcohol is avoided.

Sodium hydroxide and methanol are employed in the specific examples in view of their relatively lower cost and ready availability. The invention is not limited thereto, however, and other alkalis (for example, potassium hydroxide) and other alcohols (for example, ethyl alcohol and the various propyl, butyl, and higher alcohols) may be employed, if desired.

The products of the reduction can be isolated from the reaction mixtures in any suitable manner. Aside from those cases in which the reaction mixture contains an insoluble residue resulting from the presence of the reduction promoter in the reaction mixture, the isolation of the reduction products can be carried out in the usual manner.

Thus, for example, the reaction mixture may be cooled to crystallize the reduction product and filtered, and the cake washed with water to remove alcohol, sodium formate formed as a by-product of the reduction, and sodum hydroxide. Generally, it is preferred to steam distill the methanol (and dehydrate the aqueous methanol thus obtained by fractional distillation for reuse in subsequent reactions) and then cool the remaining hot aqueous mass to crystallize the reduction product, which may be washed as usual with water. Where the product is molten in the hot mixture, as in the case of azoxy- and azobenzenes, it is simpler to stratify the mass into an aqueous phase and an oil phase, whereupon the latter can be readily separated, as illustrated in the examples.

The hydroxynaphthalene reduction promoters of the above type are generally soluble in the aqueous and/or alcoholic layer noted above, and thus can be separated from the reduction product. When the use of the reduction promoter produces a small amount of insoluble by-product, it may be removed in any suitable manner, as by filtering the hot mixture prior to the phase-separation, or as illustrated in the examples.

A similar, somewhat less pronounced, reduction-promoting effect is produced upon reductions of the type referred to above by certain other non-quinoid hydroxy- and amino-naphthols and naphthol sulfonic and carboxylic acids. Thus, products containing substantial amounts of azobenzene in addition to azoxybenzene are obtained by repeating the procedure described in Example 1, part A, using 12 parts of any one of the following hydroxynaphthalenes in place of the 2-naphtol-4-sulfonic acid:

5-hydroxy-1-naphthol (1,5-dihydroxy-naphthalene)
6-hydroxy-1-naphthol (1,6-dihydroxy-naphthalene)
1-naphthol-2-carboxylic acid (1-hydroxy-2-naphthoic acid)
5-amino-1-naphthol
8-amino-1-naphthol-5-sulfonic acid (1-amino-8-naphthol-4-sulfonic acid)
6-amino-1-naphthol-3-sulfonic acid (2-amino-5-naphthol-7-sulfonic acid)
7-hydroxy-2-naphthol (2,7-dihydroxy-naphthalene)
2-naphthol-7-sulfonic acid
5-acetylamino-2-naphthol (1-acetylamino-6-naphthol)
8-acetylamino-2-naphthol (1-acetylamino-7-naphthol)
1-(4'-naphtholazo)-2-naphthol-4-sulfonic acid

I claim:

1. The improvement in the method of reducing an aromatic nitrogen compound containing nitrogen in a reducible form as a nuclear substituent at a higher stage of oxidation than the hydrazo stage by the action of a metal alcholate, which comprises carrying out the reduction in a reaction mixture containing a hydroxynaphthalene selected from the group consisting of the naphthols, 8-hydroxy-1-naphthol, 8-amino-1-naphthol, 5-amino-2-naphthol, 2-naphthol-4-sulfonic acid and 2-naphthol-3-carboxylic acid, whereby the reduction of the aromatic nitrogen compound is promoted.

2. A method as defined in claim 1, which comprises heating the aromatic nitrogen compound with a reducing mixture of an alkali metal hydroxide and a lower alcohol in a reaction mixture containing a hydroxynaphthalene in an amount corresponding with $\frac{1}{300}$ to $\frac{1}{10}$ mol per mol of aromatic nitrogen compound, said hydroxynaphthalene being selected from the group consisting of the naphthols, 8-hydroxy-1-naphthol, 8-amino-1-naphthol, 5-amino-2-naphthol, 2-naphthol-4-sulfonic acid and 2-naphthol-3-carboxylic acid.

3. A method as defined in claim 2, wherein the nitrogen in a reducible form is a substituent in a benzene nucleus.

4. A method of reducing an aromatic nitrogen compound containing nitrogen in a reducible form as a substitutuent in a benzene nucleus at a higher stage of oxidation than the hydrazo stage and selected from the group consisting of nitrobenzene, an ortho-substituted nitrobenzene, and reduction products thereof, which comprises heating the aromatic nitrogen compound with an alkali metal hydroxide and a lower alcohol in a reaction mixture containing a naphthol, whereby the reduction of the aromatic nitrogen compound is promoted.

5. A method of reducing an aromatic nitrogen compound containing nitrogen in a reducible form as a substituent in a benzene nucleus at a

higher stage of oxidation than the hydrazo stage and selected from the group consisting of nitrobenzene, an ortho-substituted nitrobenzene, and reduction products thereof, which comprises heating the aromatic nitrogen compound with an alkali metal hydroxide and a lower alcohol in a reaction mixture containing 8-amino-1-naphthol, whereby the reduction of the aromatic nitrogen compound is promoted.

6. A method of reducing an aromatic nitrogen compound containing nitrogen in a reducible form as a substituent in a benzene nucleus at a higher stage of oxidation than the hydrazo stage and selected from the group consisting of nitrobenzene, an ortho-substituted nitrobenzene, and reduction products thereof, which comprises heating the aromatic nitrogen compound with an alkali metal hydroxide and a lower alcohol in a reaction mixture containing 8-hydroxy-1-naphthol, whereby the reduction of the aromatic nitrogen compound is promoted.

7. A method of reducing an aromatic nitrogen compound containing nitrogen in a reducible form as a substituent in a benzene nucleus at a higher stage of oxidation than the hydrazo stage and selected from the group consisting of nitrobenzene, an ortho-substituted nitrobenzene, and reduction products thereof, which comprises heating the aromatic nitrogen compound with an alkali metal hydroxide and a lower alcohol in a reaction mixture containing 2-naphthol-4-sulfonic acid, whereby the reduction of the aromatic nitrogen compound is promoted.

8. A method of reducing an aromatic nitrogen compound containing nitrogen in a reducible form as a substituent in a benzene nucleus at a higher stage of oxidation than the hydrazo stage and selected from the group consisting of nitrobenzene, an ortho-substituted nitrobenzene, and reduction products thereof, which comprises heating the aromatic nitrogen compound with an alkali metal hydroxide and a lower alcohol in a reaction mixture containing 2-napthol-3-carboxylic acid, whereby the reduction of the aromatic nitrogen compound is promoted.

9. A method of reducing an aromatic nitrogen compound containing nitrogen in a reducible form as a substituent in a benzene nucleus at a higher stage of oxidation than the hydrazo stage and selected from the group consisting of nitrobenzene, an ortho-substituted nitrobenzene, and reduction products thereof, which comprises incorporating a small amount of a naphthol, into a reduction reaction mixture containing sodium hydroxide and a lower alcohol, and heating the aromatic nitrogen compound with the resulting reaction mixture.

10. A method of reducing an aromatic nitrogen compound containing nitrogen in a reducible form as a substituent in a benzene nucleus at a higher stage of oxidation than the hydrazo stage and selected from the group consisting of nitrobenzene, an ortho-substituted nitrobenzene, and reduction products thereof, which comprises incorporating a small amount of 8-amino-1-naphthol, into a reduction reaction mixture containing sodium hydroxide and a lower alcohol, and heating the aromatic nitrogen compound with the resulting reaction mixture.

11. A method of reducing an aromatic nitrogen compound containing nitrogen in a reducible form as a substituent in a benzene nucleus at a higher stage of oxidation than the hydrazo stage and selected from the group consisting of nitrobenzene, an ortho-substituted nitrobenzene, and reduction products thereof, which comprises incorporating a small amount of 8-hydroxy-1-naphthol, into a reduction reaction mixture containing sodium hydroxide and a lower alcohol, and heating the aromatic nitrogen compound with the resulting reaction mixture.

12. A method of reducing an aromatic nitrogen compound containing nitrogen in a reducible form as a substituent in a benzene nucleus at a higher stage of oxidation than the hydrazo stage and selected from the group consisting of nitrobenzene, an ortho-substituted nitrobenzene, and reduction products thereof, which comprises incorporating a small amount of 2-napthol-4-sulfonic acid, into a reduction reaction mixture containing sodium hydroxide and a lower alcohol, and heating the aromatic nitrogen compound with the resulting reaction mixture.

13. A method of reducing an aromatic nitrogen compound containing nitrogen in a reducible form as a substituent in a benzene nucleus at a higher stage of oxidation than the hydrazo stage and selected from the group consisting of nitrobenzene, an ortho-substituted nitrobenzene, and reduction products thereof, which comprises incorporating a small amount of 2-naphthol-3-carboxylic acid, into a reduction reaction mixture containing sodium hydroxide and a lower alcohol, and heating the aromatic nitrogen compound with the resulting reaction mixture.

14. A method of reducing an aromatic nitrogen compound containing nitrogen in a reducible form as a substituent in a benzene nucleus at a higher stage of oxidation than the hydrazo stage and selected from the group consisting of nitrobenzene, an ortho-substituted nitrobenzene, and reduction products thereof, which comprises heating the aromatic nitrogen compound with sodium hydroxide and methanol in a reaction mixture containing a small amount of a hydroxynaphthalene selected from the group consisting of the naphthols, 8-hydroxy-1-naphthol, 8-amino-1-naphthol, 5-amino-2-naphthol, 2-naphthol-4-sulfonic acid and 2-naphthol-3-carboxylic acid, as a reduction promoter.

15. A method as defined in claim 14 wherein an amount of the hydroxynaphthalene corresponding with $\frac{1}{300}$ to $\frac{1}{10}$ mol per mol of aromatic nitrogen compound is incorporated with a reducing reaction mixture containing sodium hydroxide and methanol, and the aromatic nitrogen compound is heated with the resulting reaction mixture.

16. A method as defined in claim 15 wherein the aromatic nitrogen compound is nitrobenzene and the hydroxynaphthalene is a naphthol.

17. A method as defined in claim 15 wherein the aromatic nitrogen compound is nitrobenzene and the hydroxynaphthalene is 1-naphthol.

18. A method as defined in claim 15 wherein the aromatic nitrogen compound is nitrobenzene and the hydroxynaphthalene is 2-naphthol-4-sulfonic acid.

19. A method as defined in claim 15 wherein the aromatic nitrogen compound is nitrobenzene and the hydroxynaphthalene is 8-amino-1-naphthol.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
483,368	Rosenstiehl	Sept. 27, 1892
2,014,522	Dahlen et al.	Sept. 17, 1935
2,570,866	Sargent	Oct. 9, 1951