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(54) Titre : METHODE POUR L'OBTENTION D'AMINES AROMATIQUES SUBSTITUEES
(54) Title: PROCESS FOR PREPARING SUBSTITUTED AROMATIC AMINES

(57) Abrégé/Abstract:
A process for preparing substituted aromatic azo compounds is provided which comprises contacting a nucleophilic compound and an azo containing compound in the presence of a suitable solvent system, and reacting the nucleophilic compound and the azo containing compound in the presence of a suitable base and a controlled amount of protic material at a temperature of about 10 °C to about 150 °C in a confined reaction zone wherein the molar ratio of protic material to base is 0:1 to about 5:1. In another embodiment, the substituted aromatic azo compounds are further reacted with a nucleophilic compound in the presence of a suitable solvent system, a suitable base and a controlled amount of protic material at a temperature of about 70 °C to about 200 °C in a confined reaction zone wherein the molar ratio of protic material to base is 0:1 to about 5:1 to produce a substituted aromatic amine in another embodiment, a process for preparing substituted aromatic amines is provided which comprises contacting a nucleophilic-compound and a substituted aromatic azo compound in the presence of a suitable solvent system, and reacting the nucleophilic compound and the substituted aromatic azo compound in the presence of a suitable base and a controlled amount of protic material at a temperature of about 70 °C to about 200 °C in a confined reaction zone wherein the molar ratio of protic material to base is 0:1 to about 5:1. In another embodiment, the substituted aromatic amines of the invention are reductively alkylated to produce alkylated diamines or substituted derivatives thereof.

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(54) Title: PROCESS FOR PREPARING SUBSTITUTED AROMATIC AMINES

(57) Abstract

A process for preparing substituted aromatic azo compounds is provided which comprises contacting a nucleophilic compound and an azo containing compound in the presence of a suitable solvent system, and reacting the nucleophilic compound and the azo containing compound in the presence of a suitable base and a controlled amount of protic material at a temperature of about 10 °C to about 150 °C in a confined reaction zone wherein the molar ratio of protic material to base is 0:1 to about 5:1. In another embodiment, the substituted aromatic azo compounds are further reacted with a nucleophilic compound in the presence of a suitable solvent system, a suitable base and a controlled amount of protic material at a temperature of about 70 °C to about 200 °C in a confined reaction zone wherein the molar ratio of protic material to base is 0:1 to about 5:1 to produce a substituted aromatic amine. In another embodiment, a process for preparing substituted aromatic amines is provided which comprises contacting a nucleophilic compound and a substituted aromatic azo compound in the presence of a suitable solvent system, and reacting the nucleophilic compound and the substituted aromatic azo compound in the presence of a suitable base and a controlled amount of protic material at a temperature of about 70 °C to about 200 °C in a confined reaction zone wherein the molar ratio of protic material to base is 0:1 to about 5:1. In another embodiment, the substituted aromatic amines of the invention are reductively alkylated to produce alkylated diamines or substituted derivatives thereof.

PROCESS FOR PREPARING SUBSTITUTED AROMATIC AMINES

BACKGROUND OF THE INVENTION

This invention relates to the production of substituted aromatic azo compounds. In one aspect, this invention relates to the production of substituted aromatic amines. In another aspect, this invention relates to the production of 4-aminodiphenylamine (4-ADPA) or substituted derivatives thereof. In another aspect, this invention relates to the preparation of alkylated p-phenylenediamines or substituted derivatives thereof useful as antioxidants from the substituted aromatic amines, such as 4-ADPA or substituted derivatives thereof.

It is known to prepare substituted aromatic amines by way of a nucleophilic aromatic substitution mechanism wherein an amino functional nucleophile replaces halide. For example, it is known to prepare 4-ADPA by way of a nucleophilic aromatic substitution mechanism, wherein an aniline derivative replaces halide. This method involves preparation of a 4-ADPA intermediate, namely 4-nitrodiphenylamine (4-NDPA) followed by reduction of the nitro moiety. The 4-NDPA is prepared by reacting p-chloronitrobenzene with an aniline derivative, such as formanilide or an alkali metal salt thereof, in the presence of an acid acceptor or neutralizing agent, such as potassium carbonate, and, optionally, utilizing a catalyst. See, for example, U.S. 4,187,248; U.S. 4,683,332; U.S. 4,155,936; U.S. 4,670,595; U.S. 4,122,118; U.S. 4,614,817; U.S. 4,209,463; U.S. 4,196,146; U.S. 4,187,249; U.S. 4,140,716. This method is disadvantageous in that the halide that is displaced is corrosive to the reactors and appears in the waste stream and must therefore be

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disposed of at considerable expense. Furthermore, use of an aniline derivative such as formanilide, and use of p-chloro-nitrobenzene, requires additional manufacturing equipment and capabilities to produce such starting materials from aniline and nitrobenzene, respectively.

It is also known to prepare 4-ADPA from the head-to-tail coupling of aniline. See, for example, G.B. 1,440,767 and U.S. 4,760,186. This method is disadvantageous in that the yield of 4-ADPA is not acceptable for a commercial process. It is also known to decarboxylate a urethane to produce 4-NDPA. See U.S. 3,847,990. However, such method is not commercially practical in terms of cost and yield.

It is known to prepare 4-ADPA by hydrogenating p-nitrosodiphenylhydroxylamine which can be prepared by catalytic dimerization of nitrosobenzene utilizing, as a reducing agent, aliphatic compounds, benzene, naphthalene or ethylenically unsaturated compounds. See, for example, U.S. 4,178,315 and 4,404,401. It is also known to prepare p-nitrosodiphenylamine from diphenylamine and an alkyl nitrate in the presence of excess hydrogen chloride. See, for example, U.S. 4,518,803 and 4,479,008.

Aromatic amide bonds are currently formed by the reaction of an amine with an acid chloride. This method of forming aromatic amide bonds is also disadvantageous in that chloride is displaced which is corrosive to the reactors, and appears in the waste stream from which it must be removed at considerable expense. A nonhalide process which produces aromatic amide bonds in the substituted aromatic amines would eliminate these problems.

The process of the invention is a nonhalide process for preparing substituted aromatic azo compounds and substituted aromatic amines and therefore eliminates the expensive halide removal from the waste stream as

well as corrosion problems caused by the halide. In addition, substituted aromatic azo compounds and substituted aromatic amines containing aromatic amide bonds can be prepared by the process of the invention. Furthermore, the process of the invention is more economical than current commercial routes and is simpler in that, in one embodiment, substituted aromatic amines, such as 4-ADPA or substituted derivatives thereof, are produced directly without the need of a separate reduction step.

SUMMARY OF THE INVENTION

According to the invention, a process for preparing substituted aromatic azo compounds is provided which comprises contacting a nucleophilic compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides with an azo containing compound represented by the formula

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$X-R_1-N=N-R_2-Y$ or azoxy or hydrazo derivatives thereof in the presence of a suitable solvent system, and reacting the nucleophilic compound and a compound represented by the formula $X-R_1-N=N-R_2-Y$ or azoxy or hydrazo derivatives thereof in the presence of a suitable base and a controlled amount of protic material at a reaction temperature of about 10°C to about 150°C in a confined reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1, wherein R_1 is an aromatic group and R_2 is selected from the group consisting of aliphatic and aromatic groups, and X and Y are independently selected from the group consisting of hydrogen, halides, $-NO_2$, $-NH_2$, aryl groups, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group. When R_2 is an aliphatic group, X is in the meta or ortho position on R_1. When R_2 is an aromatic group, at least one of X and Y is in the meta or ortho position on R_1 and R_2, respectively. Halides are selected from the group consisting of chloride, bromide and fluoride. Sulfonate groups, as used herein, are the esters of sulfonic acids. Examples of sulfonates include, but are not limited to, alkyl sulfonates, aralkyl sulfonates, aryl sulfonates, and the like. In one embodiment, the substituted aromatic azo compound is further reacted with a nucleophilic compound independently selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivative and amides in the presence of a suitable solvent system, a suitable base and a controlled amount of protic material at a reaction temperature of about 70°C to about 200°C in a confined reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1.

In one embodiment, a process for preparing

4-aminodiphenylamine or substituted derivatives thereof is provided which comprises contacting aniline or substituted aniline derivatives and azobenzene or substituted azobenzene derivatives or azoxy or hydrazo derivatives thereof in the presence of a suitable solvent system, and reacting the aniline or substituted aniline derivatives and azobenzene or substituted azobenzene derivatives in the presence of a suitable base and a controlled amount of protic material at a suitable reaction temperature of about 10°C to about 150°C in a confined reaction zone wherein the molar ratio of protic material to base is 0:1 to about 5:1, and further reacting with aniline or substituted aniline derivative in the presence of a suitable solvent system, a suitable base and a controlled amount of protic material at a reaction temperature of about 70°C to about 200°C in a confined reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1.

Further according to the invention, a process for preparing substituted aromatic amines is provided which comprises contacting a nucleophilic compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides with a substituted aromatic azo compound in the presence of a suitable solvent system, and reacting the nucleophilic compound and the substituted aromatic azo compound or azoxy or hydrazo derivatives thereof in the presence of a suitable base and a controlled amount of protic material at a reaction temperature of about 70°C to about 200°C, wherein the molar ratio of protic material to base is 0:1 to about 5:1, wherein the substituted aromatic azo compound is selected from the group consisting of compounds represented by the formula

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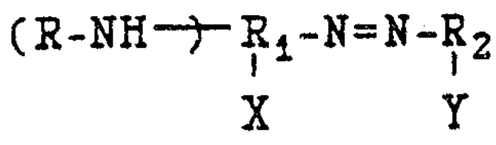
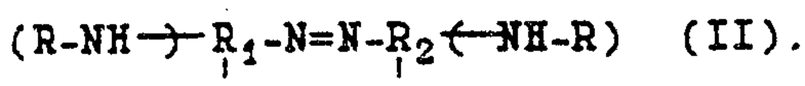


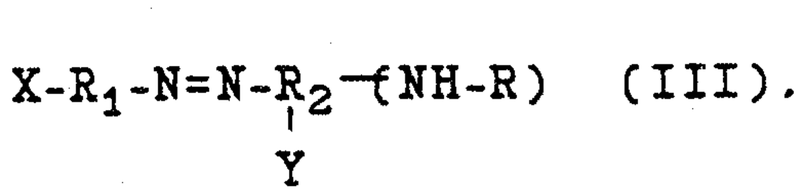
(I),

compounds represented by the formula



(II).

compounds represented by the formula



(III).

and mixtures thereof, wherein R-NH- represents a substituent derived from a compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivative and amides, R_1 is an aromatic group, R_2 is selected from the group consisting of aliphatic and aromatic groups, and X and Y are independently selected from the group consisting of hydrogen, halides, $-NO_2$, $-NH_2$, aryl groups, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group, wherein halides are selected from the group consisting of chlorine, bromine and fluorine and R_2 is an aromatic group in substituted aromatic azo compounds (II) and (III). The substituted aromatic azo compounds of (I), (II), and (III) also includes azoxy or hydrazo derivatives thereof.

Further according to the invention, a process for preparing alkylated p-phenylenediamines or substituted derivatives thereof is provided which

comprises reductively alkylating the substituted aromatic amines prepared according to the invention.

Further according to the invention, a process for preparing substituted aromatic amines is provided which comprises reacting the substituted aromatic amine, prepared by reacting amide and an azo containing compound to produce a substituted aromatic azo compound followed by reacting the substituted aromatic azo compound with a nucleophilic compound, with ammonia under conditions which produce the corresponding substituted aromatic amine and an amide.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to a process for preparing substituted aromatic azo compounds comprising:

(a) contacting a nucleophilic compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides and an azo containing compound represented by the formula $X-R_1-N=N-R_2-Y$ or azoxy or hydrazo derivatives thereof in the presence of a suitable solvent system, and

(b) reacting a nucleophilic compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides and an azo containing compound represented by the formula $X-R_1-N=N-R_2-Y$ or azoxy or hydrazo derivatives thereof in the presence of a suitable base and a controlled amount of protic material at a reaction temperature of about 10°C to about 150°C in a confined reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1, wherein R_1 is an aromatic group, R_2 is selected from the group consisting of aliphatic and aromatic groups, and X and Y are independently selected from the group consisting of hydrogen, halides, $-NO_2$, $-NH_2$, aryl groups, alkyl groups, alkoxy groups, sulfonate

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groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group, wherein if R_2 is aliphatic, X is in the meta or ortho position on R_1, and if R_2 is aromatic, at least one of X and Y is in the meta or ortho position on R_1 and R_2, respectively, and wherein halides are selected from the group consisting of chloride, bromide and fluoride.

For producing substituted aromatic amines, the process of the invention further comprises:

(c) reacting the substituted aromatic azo compound with a nucleophilic compound independently selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides in the presence of a suitable solvent system, a suitable base and a controlled amount of protic material at a reaction temperature of about 70°C to about 200°C in a confined reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1.

Independently selected nucleophilic compound is used herein to mean that the nucleophilic compound can be the same or different from the nucleophilic compound used in the reaction of the nucleophilic compound with the azo containing compound.

For producing alkylated p-phenylenediamines or substituted derivatives thereof, the process of the invention further comprises:

(d) reductively alkylating the substituted aromatic amines.

For producing substituted aromatic amines when the nucleophilic compound is an amide, the process of the invention further comprises:

(c') reacting the substituted aromatic amine with ammonia under conditions which produce the corresponding substituted aromatic amine and amide.

In one embodiment, this invention relates to a process for preparing 4-ADPA or substituted derivatives thereof comprising:

(a) contacting aniline or substituted aniline derivatives and azobenzene or substituted azobenzene derivatives or azoxy or hydrazo derivatives thereof in the presence of a suitable solvent system, and

(b) reacting the aniline or substituted aniline derivatives and azobenzene or substituted azobenzene derivatives or azoxy or hydrazo derivatives thereof in the presence of a suitable base and a controlled amount of protic material at a reaction temperature of about 10°C to about 150°C in a confined reaction zone wherein the molar ratio of protic material to base is 0:1 to about 5:1, and

(c) reacting the product of (b) with aniline or substituted aniline derivatives in the presence of a suitable solvent system, a suitable base and a controlled amount of protic material at a reaction temperature of about 70°C to about 200°C in a confined reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1.

For producing alkylated p-phenylenediamines or substituted derivative thereof, the process of the invention further comprises:

(d) reductively alkylating the 4-ADPA or substituted derivatives thereof.

This invention further relates to a process for preparing substituted aromatic amines comprising:

(a) contacting a nucleophilic compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides and a substituted aromatic azo compound or azoxy or hydrazo derivatives thereof in the presence of a suitable solvent system, and

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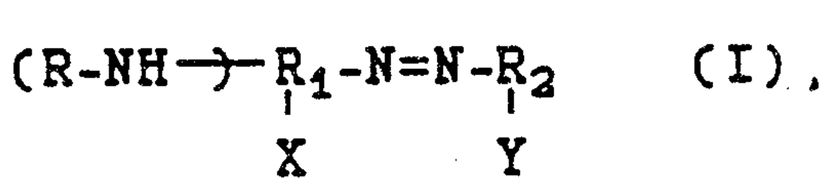
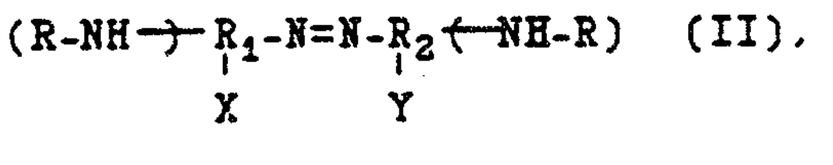
(b) reacting the nucleophilic compound and the substituted aromatic azo compound or azoxy or hydrazo derivatives thereof in the presence of a suitable base and a controlled amount of protic material at a reaction temperature of about 70°C to about 200°C wherein the molar ratio of protic material to base is 0:1 to about 5:1, wherein the substituted aromatic azo compound is selected from the group consisting of compounds represented by the formula



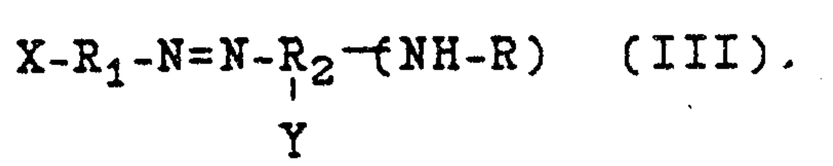
(I),

compounds represented by the formula



(II),

compounds represented by the formula



(III),

and mixtures thereof,

wherein R-NH- represents a substituent derived from a compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides, R_1 is an aromatic group, R_2 is selected from the group consisting of aliphatic and aromatic groups, and X and Y are independently selected from the group consisting of hydrogen, halides, $-NO_2$, $-NH_2$, aryl groups, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group, wherein halides are selected from the group consisting of chlorine, bromine

and fluorine and R_2 is an aromatic group in substituted aromatic azo compounds (II) and (III).

For producing alkylated p-phenylenediamines or substituted derivatives thereof, the process of the invention further comprises:

(c) reductively alkylating the substituted aromatic amines.

For producing substituted aromatic amines when the nucleophilic compound is an amide, the process of the invention further comprises:

(c') reacting the substituted aromatic amine with ammonia under conditions which produce the corresponding substituted aromatic amine and amide.

In one embodiment, the substituted aromatic azo compound is prepared by reacting 4-nitrosodiphenylamine with an aromatic primary amine or an aliphatic primary amine.

In the preparation of substituted aromatic azo compounds, the molar ratio of a nucleophilic compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides to $X-R_1-N=N-R_2-Y$ or azoxy or hydrazo derivatives thereof can vary from a large excess of $X-R_1-N=N-R_2-Y$ or azoxy or hydrazo derivatives thereof to a large excess of a nucleophilic compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides. Preferably, the reaction is conducted utilizing an excess of a nucleophilic compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides. More preferably, the molar ratio of nucleophilic compound to $X-R_1-N=N-R_2-Y$ or azoxy or hydrazo derivatives thereof is at least about 1:1.

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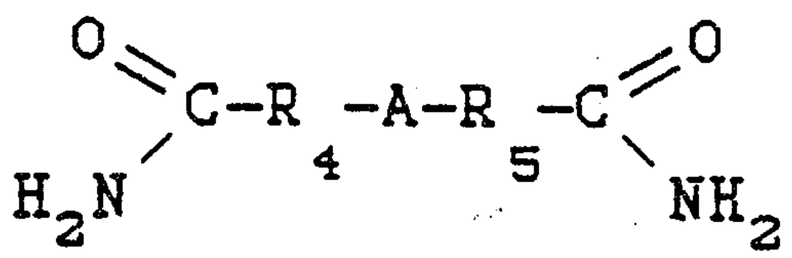
In the preparation of substituted aromatic amines by the reaction of a nucleophilic compound with a substituted aromatic azo compound, the molar ratio of a nucleophilic compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides to substituted aromatic azo compounds can vary from a large excess of substituted aromatic azo compound to a large excess of a nucleophilic compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides. Preferably, the reaction is conducted utilizing an excess of a nucleophilic compound as defined above. More preferably, the molar ratio of nucleophilic compound to substituted aromatic azo compound is at least about 1:1.

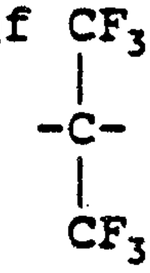
As used herein, the term "substituted aniline derivatives" means aniline containing one or more electron withdrawing or electron releasing substituents on the aromatic ring. Applicable substituents include, but are not limited to, halides, $-NO_2$, $-NH_2$, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COOH and aryl, arylalkyl or alkylaryl groups containing at least 1 $-NH_2$ group. Halides are selected from the group consisting of chloride, bromide or fluoride. The preferred alkyl and alkoxy groups contain from 1 to about 6 carbon atoms. The preferred aryl, arylalkyl and alkylaryl groups contain from about 6 to about 18 carbon atoms. Examples of substituted aniline derivatives include, but are not limited to, 2-methoxyaniline, 4-methoxyaniline, 4-chloroaniline, p-toluidine, 4-nitroaniline, 3-bromoaniline, 3-bromo-4-aminotoluene, p-aminobenzoic acid, 2,4-diaminotoluene, 2,5-dichloroaniline, 1,4-phenylenediamine, 4,4'-methylenedianiline, 1,3,5-triaminobenzene and mixtures thereof.

Aniline or substituted aniline derivatives can be added directly or can be formed in situ by addition of a compound that will form aniline or the corresponding aniline derivative under the conditions present in the reaction system.

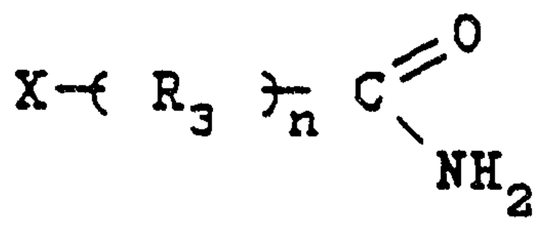
Amides that can be employed according to the invention include aromatic amides, aliphatic amides, substituted aromatic amide derivatives, substituted aliphatic amide derivatives and diamides having the formula:



wherein R_4 and R_5 are independently selected from the group consisting of aromatic groups, aliphatic groups and a direct bond, and A is selected from the group consisting of CF_3, $-SO_2-$, $-O-$, $-S-$ and a direct bond.



The aliphatic amides and substituted aliphatic amide derivatives that can be employed according to the invention are represented by the formula:



wherein n is 0 or 1, R_3 is selected from the group consisting of alkyl, arylalkyl, alkenyl, arylalkenyl, cycloalkyl and cycloalkenyl groups and X is selected from the group consisting of hydrogen, $-NO_2$,

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$-NH_2$, aryl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkyl aryl groups containing at least one $-NH_2$ group. The preferred alkyl and alkoxy groups contain from 1 to about 6 carbon atoms. The preferred aryl, arylalkyl and alkyl aryl groups contain from about 6 to about 18 carbon atoms.

Examples of aliphatic amides and substituted aliphatic amide derivatives include, but are not limited to, isobutyramide, urea, acetamide, propylamide and mixtures thereof.

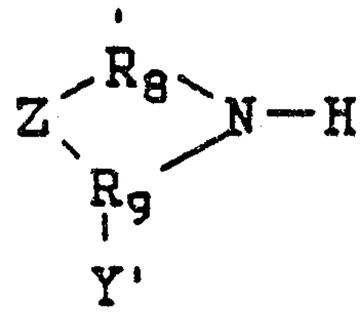
As used herein, the term "substituted aromatic amide derivatives" means aromatic amides containing one or more electron withdrawing or electron releasing substituents on the aromatic ring. Applicable substituents include, but are not limited to, halides, $-NO_2$, $-NH_2$, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkyl- aryl groups containing at least one $-NH_2$ group. Halides are selected from the group consisting of chloride, bromide and fluoride. The preferred alkyl and alkoxy groups contain from 1 to about 6 carbon atoms. The preferred aryl, arylalkyl and alkyl aryl groups contain from about 6 to about 18 carbon atoms.

Examples of aromatic amides and substituted aromatic amide derivatives include, but are not limited to, benzamide, 4-methylbenzamide, 4-methoxybenzamide, 4-chlorobenzamide, 2-methylbenzamide, 4-nitrobenzamide, 4-aminobenzamide and mixtures thereof.

Diamides that can be employed according to the process of the invention include, but are not limited to, adipamide, oxalic amide, terephthalic diamide, 4,4'-biphenyldicarboxamide and mixtures thereof.

Aliphatic amines and substituted aliphatic amines that can be employed according to the invention

are compounds selected from the group consisting of compounds represented by the formula X'-R_6-NH-R_7-Y' and compounds represented by the formula:



wherein R_6 is selected from the group consisting of alkyl, alkenyl, cycloalkyl and cycloalkenyl groups, R_7 is selected from the group consisting of a direct bond, alkyl, alkenyl, cycloalkyl and cycloalkenyl groups, R_8 and R_9 are independently selected from the group consisting of alkyl and alkenyl groups, Z is selected from the group consisting of a direct bond, -NH-, -N(R_{10})-, -O- and -S-, wherein R_{10} is an alkyl group, and X' and Y' are independently selected from the group consisting of hydrogen, halides, -NO_2, -NH_2, aryl groups, alkoxy groups, sulfonate groups, -SO_3H, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one -NH_2 group. Halides are selected from the group consisting of chloride, bromide and fluoride. The preferred aliphatic groups of R_6 and R_7 contain from 1 to about 12 carbon atoms. The preferred aryl, arylalkyl and alkylaryl groups contain from about 6 to about 18 carbon atoms. The preferred alkoxy groups contain from 1 to about 6 carbon atoms.

Examples of aliphatic amines and substituted aliphatic amine derivatives include, but are not limited to, cyclohexylamine, 2-butylamine, isopropylamine, 2-hexylamine, 2-heptylamine, 1,4-dimethylpentylamine, 1-methylheptylamine, 1-ethyl-3-methylpentylamine,

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1,3-dimethylbutylamine, octylamine, piperidine, piperazine, hexamethylene diamine, 2-amino-1-propanol, 2-amino-1-butanol, 6-aminohexanoic acid and mixtures thereof.

As used herein, the term "azo containing compounds" are compounds of the invention that are represented by the formula $X-R_1-N=N-R_2-Y$ or azoxy or hydrazo derivatives thereof wherein R_1 is an aromatic group, R_2 is selected from the group consisting of aliphatic and aromatic groups and X and Y are independently selected from the group consisting of hydrogen, halides, $-NO_2$, $-NH_2$, aryl groups, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl arylalkyl or alkylaryl groups containing at least one $-NH_2$ group. When R_2 is an aliphatic group, X is in the meta or ortho position on R_1. When R_2 is aromatic, at least one of X and Y is in the meta or ortho position on R_1 and R_2, respectively. Halides are selected from the group consisting of chloride, bromide and fluoride. The preferred aliphatic groups of R_1 and R_2 contain from 1 to about 12 carbon atoms and the preferred aromatic groups of R_1 and R_2 contain from about 6 to about 18 carbon atoms. The preferred alkyl and alkoxy groups contain from 1 to about 6 carbon atoms. The preferred aryl, arylalkyl and alkylaryl groups contain from about 6 to about 18 carbon atoms. Examples of azo containing compounds include, but are not limited to, azobenzene, substituted azobenzene derivative, azoxybenzene, 4-(phenylazo)-diphenylamine, 1,2-diphenylhydrazine, and mixtures thereof.

When the azo containing compound is azobenzene, azobenzene can be produced via the oxidative coupling of aniline in the presence of a suitable base. When the nucleophilic compound used to react with azobenzene is aniline and the reaction is conducted

under aerobic conditions, the azobenzene can be produced in-situ via the oxidative coupling of aniline in the presence of a suitable base. The oxidative coupling of aniline is known in the art, see Jeon, S. and Sawyer, D.T., "Hydroxide-Induced Synthesis of the Superoxide Ion from Dioxygen and Aniline, Hydroxylamine, or Hydrazine", *Inorg. Chem.*, Vol. 29, pp. 4612-15 (1990), and the reaction conditions defined herein for the production of the substituted aromatic azo compounds are sufficient for the oxidative coupling of aniline to azobenzene.

As used herein, the term "substituted azobenzene derivatives" means azobenzene containing one or more electron withdrawing or electron releasing substituents on one or both of the aromatic rings. Applicable substituents include, but are not limited to, halides, $-NO_2$, $-NH_2$, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COOH and aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group. Halides are selected from the group consisting of chloride, bromide and fluoride. The preferred alkyl and alkoxy groups contain from 1 to about 6 carbon atoms. The preferred aryl, arylalkyl, and alkylaryl groups contain from about 6 to about 18 carbon atoms. Examples of substituted azobenzene derivatives include, but are not limited to, 3,4'-dichloroazobenzene, p-phenylazobenzene sulfonic acid, p-(2,4-dihydroxyphenylazo)benzene sulfonic acid, and mixtures thereof.

Suitable solvent systems include, but are not limited to, solvents such as dimethylsulfoxide, nucleophilic compounds such as substituted aniline derivatives, aniline and amides having a melting point below the reaction temperature, e.g., molten benzamide, dimethylformamide, N-methyl-2-pyrrolidone, pyridine, ethyleneglycoldimethyl ether, amines such as diisopropylethylamine, sec-butyl amine and

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2-heptylamine, and the like, and mixtures thereof. As described in more detail below, solvent mixtures can be utilized wherein in one or more of the suitable solvents and another solvent, such as a controlled amount of a protic solvent, e.g., methanol or water, are combined.

Suitable bases include, but are not limited to, organic and inorganic bases such as alkali metals, such as sodium metal, alkali metal hydrides, hydroxides and alkoxides, such as sodium hydride, lithium hydroxide, sodium hydroxide, cesium hydroxide, potassium hydroxide, potassium t-butoxide, and the like, including mixtures thereof. Other acceptable base materials include, but are not limited to, phase transfer catalysts in conjunction with a suitable base source such as tetrasubstituted ammonium hydroxides or halides wherein each substituent is independently selected from alkyl, aryl or arylalkyl groups wherein the alkyl, aryl and arylalkyl groups preferably have 1 to about 18 carbon atoms, including tetraalkyl ammonium hydroxides, e.g., tetramethylammonium hydroxide, tetraalkylammonium halides, e.g., tetrabutylammonium chloride, aryl, trialkylammonium hydroxides, e.g., phenyltrimethylammonium hydroxide, arylalkyl, trialkyl ammonium hydroxides, e.g., benzyltrimethylammonium hydroxide, alkyl substituted diammonium hydroxides, e.g., bis-dibutylethylhexamethylenediammonium hydroxide, and other combinations of phase transfer catalysts and suitable bases such as suitable bases in conjunction with aryl ammonium salts, crown ethers and the like, amine bases such as lithium, bis(trimethylsilyl) amide, 2-aminoheptane, and the like, and alkyl magnesium halides, including mixtures thereof. Preferred materials for use as bases are alkali metal hydroxides, such as potassium hydroxide, alkali metal alkoxides such as potassium t-butoxide, alkali metal hydroxides or alkoxides in conjunction with a phase transfer catalyst

such as potassium hydroxide in conjunction with crown ethers, and tetraalkylammonium hydroxides such as tetramethylammonium hydroxide or tetrabutylammonium hydroxide.

Preferably, the base is added to the nucleophilic compound to produce a mixture which is then combined with the azo containing compound or substituted aromatic azo compound. Alternatively, the base can be added after the nucleophilic compound and azo containing compound or substituted aromatic azo compound have been combined. Addition of materials can be above or below surface addition.

For the preparation of substituted aromatic azo compounds, the amount of base employed according to the invention can be conveniently expressed in terms of a molar ratio of suitable base to azo containing compound. Broadly, the molar ratio of base to azo containing compound will be about 1:1 to about 10:1, preferably about 1:1 to about 4:1, and most preferably about 1:1 to about 2:1.

For the preparation of substituted aromatic amines, the amount of base employed according to the invention can be conveniently expressed in terms of a molar ratio of suitable base to substituted aromatic azo compound. Broadly, the molar ratio of base to substituted aromatic azo compound will be about 1:1 to about 10:1, preferably about 1:1 to about 4:1, and most preferably, about 1:1 to about 2:1.

The reaction of the nucleophilic compound with the azo containing compound is conducted at a temperature within the range of from about 10°C to about 150°C, such as from about 20°C to about 120°C, preferably from about 30°C to about 100°C. A most preferred temperature for conducting the reaction of the nucleophilic compound with the azo containing compound is from about 50°C to about 90°C.

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The reaction of the nucleophilic compound with the substituted aromatic azo compound is conducted at a temperature within the range of from about 70°C to about 200°C, such as from about 70°C to about 190°C, preferably from about 70°C to about 180°C. A most preferred temperature for conducting the reaction of the nucleophilic compound with the substituted aromatic azo compound is from about 130°C to about 170°C.

Control of the amount of protic material present in the reaction of the nucleophilic compound with the azo containing compound is important. The amount of protic material employed according to the invention can be conveniently expressed in terms of a molar ratio based on the amount of base present at the beginning of the reaction of nucleophilic compound and azo containing compound. Broadly, the molar ratio of protic material to base will be from 0:1 to about 5:1, preferably from 0:1 to about 3:1, and most preferably 0:1 to about 1:1. Thus, the present reaction could be conducted under anhydrous conditions. As used herein for the reaction of nucleophilic compound and azo containing compound, the term "controlled amount" of protic material is an amount up to that which inhibits the reaction of nucleophilic compound with azo containing compound. The upper limit for the amount of protic material present in the reaction varies with the solvent. In addition, the amount of protic material tolerated will vary with the type of base, amount of base, and base cation, used in the various solvent systems. However, it is within the skill of one in the art, utilizing the teachings of the present invention, to determine the specific upper limit of the amount of protic material for a specific solvent, type and amount of base, base cation and the like. The minimum amount of protic material necessary to maintain selectivity of the desired products will also depend upon the solvent,

type and amount of base, base cation and the like, that is utilized and can also be determined by one skilled in the art.

Control of the amount of protic material present in the reaction of the nucleophilic compound with the substituted aromatic azo compound is important. The amount of protic material employed according to the invention can be conveniently expressed in terms of a molar ratio based on the amount of base present at the beginning of the reaction of nucleophilic compound and substituted aromatic azo compound. Broadly, the molar ratio of protic material to base will be from 0:1 to about 5:1, preferably from 0:1 to about 1:1. Thus, the present reaction could be conducted under anhydrous conditions. As used herein for the reaction of nucleophilic compound and substituted aromatic azo compound, the term "controlled amount" of protic material is an amount up to that which inhibits the reaction of nucleophilic compound with substituted aromatic azo compound. The upper limit for the amount of protic material present in the reaction varies with the solvent. In addition, the amount of protic material tolerated will vary with the type of base, amount of base, and base cation, used in the various solvent systems. However, it is within the skill of one in the art, utilizing the teachings of the present invention, to determine the specific upper limit of the amount of protic material for a specific solvent, type and amount of base, base cation and the like. The minimum amount of protic material necessary to maintain selectivity of the desired products will also depend upon the solvents, type and amount of base, base cation and the like, that is utilized and can also be determined by one skilled in the art.

Since the amount of protic material present in the reaction is important, it is possible to reduce the

amount of protic material present as much as possible and then add back to the reaction the desired amount. Protic materials that can be utilized to add back to the reaction are known to those skilled in the art and include, but are not limited to, water, methanol, isoamyl alcohol, t-butanol and the like, and mixtures thereof. Methods for measuring the amount of protic material and for reducing the amount of protic material as much as possible are well known in the art. For example, the amount of water present in certain reagents can be determined by utilizing a Karl-Fischer apparatus, and the amount of water can be reduced through distillation and/or drying under reduced pressure, drying in the presence of P_2O_5 and other agents, azeotropic distillation utilizing, for example, xylene, and the like, including combinations thereof.

In one embodiment for controlling the amount of protic material during the reaction of nucleophilic compound with azo containing compound or substituted aromatic azo compound, a desiccant is added so as to be present during the reaction of nucleophilic compound with azo containing compound or substituted aromatic azo compound. For example, when the protic material is water, the desiccant removes water present during the reaction of nucleophilic compound and azo containing compound or substituted aromatic azo compound and results in higher conversion of azo containing compound or substituted aromatic azo compound and yields of substituted aromatic azo compound or substituted aromatic amine. As used herein, desiccant is a compound present during the reaction of nucleophilic compound and azo containing compound or substituted aromatic azo compound in addition to the suitable base used. Examples of suitable desiccants include, but are not limited to, anhydrous sodium sulfate, molecular sieves, such as types 4A, 5A, and 13X available from the Union

Carbide Corporation, calcium chloride, tetramethylammonium hydroxide dihydrate, anhydrous bases such as KOH and NaOH, and activated alumina.

In another embodiment for controlling the amount of protic material during the reaction of nucleophilic compound and azo containing compound or substituted aromatic azo compound, protic material is continuously removed from the reaction mixture by distillation. If the protic material present forms an azeotrope with one of the compounds in the reaction mixture, the protic material can be removed by continuous azeotropic distillation of protic material utilizing the azeotrope. The continuous removal of protic material allows the use of lower amounts of base in the reaction of nucleophilic compound and azo containing compound or substituted aromatic azo compound while achieving very high conversion of azo containing compound or substituted aromatic azo compound and excellent yields of substituted aromatic azo compound or substituted aromatic amine.

Generally, the reactions can be conducted under aerobic or anaerobic conditions. When the nucleophilic compound is a secondary aliphatic amine, the reactions can be conducted only under aerobic conditions, i.e., under anaerobic conditions the only applicable aliphatic amines or substituted aliphatic amine derivatives are those having the formula $X'-R_6-NH_2$. Under aerobic conditions the reaction is conducted essentially as described above in the reaction zone which is exposed to oxygen, usually by exposure to air. Under aerobic conditions, the pressure at which the reaction is conducted can vary and the optimal pressure, as well as the optimal combination of pressure and temperature, are easily determined by one skilled in the art. For example, the reaction can be conducted at a pressure ranging from about 0 psig (0 kg/cm^2) to about

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250 psig (17.6 kg/cm^2), such as from about 14 psig (1 kg/cm^2) to about 150 psig (10.5 kg/cm^2). Under anaerobic conditions, the reactions can be conducted at atmospheric pressure or reduced or elevated pressures, in the presence of an inert gas such as, for example, nitrogen or argon. Optimal conditions for a particular set of reaction parameters, such as temperature, base, solvent and the like, are easily determined by one skilled in the art utilizing the teaching of the present invention.

Reductive alkylation of substituted aromatic amines, e.g., 4-ADPA, to produce antioxidants or antiozonants can be conducted by any of several well-known methods. See, for example, US 4,900,868. Preferably, substituted aromatic amines and a suitable ketone or aldehyde are reacted in the presence of hydrogen and platinum-on-carbon as catalysts. Suitable ketones include, but are not limited to, methylisobutylketone (MIBK), acetone, methylisoamylketone and 2-octanone.

Aminolysis of substituted aromatic amines containing an aromatic amide bond, which can be prepared by reacting an amide as the nucleophilic compound and an azo containing compound to produce a substituted aromatic azo compound followed by reacting the substituted aromatic azo compound with a nucleophilic compound, can be conducted by reacting the substituted aromatic amine with ammonia to produce the corresponding substituted aromatic amine and an amide which can be recycled. See for example, Jencks, W.P., *J. Am. Chem. Soc.*, Vol. 92, pp. 3201-3202 (1970). Preferably, the substituted aromatic amine containing an aromatic amide bond is reacted with ammonia in the presence of a solvent, e.g., methanol.

Contemplated equivalents of the reactants and reagents set forth above are reactants and reagents

otherwise corresponding thereto and having the same general properties wherein one or more of the various groups, e.g., $-NO_2$, are simple variations. In addition, where a substituent is designated as, or can be, a hydrogen, the exact chemical nature of a substituent which is other than hydrogen at that position is not critical so long as it does not adversely affect the overall activity and/or synthesis procedure.

The chemical reactions described above are generally disclosed in terms of their broadest application to the process of this invention. Occasionally, the reaction conditions may not be applicable as specifically described to each reactant and reagent within the disclosed scope. For example, certain suitable bases may not be as soluble in one solvent as they are in other solvents. The reactants and reagents for which this occurs will be readily recognized by those skilled in the art. In all such cases, either the reactions can be successfully performed by conventional modifications known to those skilled in the art, e.g., by appropriate adjustments in temperature, pressure and the like, by changing to alternative conventional reagents such as other solvents or other bases, by routine modification of reaction conditions, and the like, or other reactions disclosed herein or otherwise conventional, will be applicable to the process of this invention. In all preparative methods, all starting materials are known or are readily preparable from known starting materials.

EXAMPLES

Materials and Methods: Aniline, aniline derivatives and azobenzene were purchased from Aldrich Chemical, were reagent grade and were used without further purification. Solvents were purchased from Aldrich Chemical and were anhydrous grade. The

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tetramethylammonium hydroxide was purchased as the pentahydrate.

HPLC Assay: Reverse phase HPLC was used to analyze the reaction mixtures. A 5 μm Beckman/Altex Ultrasphere-ODS (4.6 x 150 mm) column was employed using a binary gradient pump system. Absorption in the UV was monitored at 254 nm.

A Waters 600 series HPLC equipped with a Vydac 201HS54 (4.6 X 250 mm) column and UV detection at 254 nm was used to monitor all reactions. The external standard method was utilized in all the analysis. Authentic samples of products to be used as standards were prepared by known literature methods.

Elution Gradient

Time (min.)	% Solvent A (Water)	% Solvent B (40% Methanol in ACN)
0	75	25
35	20	80
40	0	100
45	0	100
46	75	25
55	75	25

Example 1

This example illustrates the production of 4-ADPA from the reaction of aniline and azobenzene and base using a phase transfer catalyst.

A) A solution of 1.8 g of azobenzene, 2.6 g of 18-crown-6, 1 g of KOH and 5 g of aniline was stirred at 70 ^{0}C under nitrogen for 72 hours. An aliquot was taken out for HPLC analysis. The yield of 4-ADPA based on azobenzene was 58 %.

B) A solution of 1.8 g of azobenzene, 1.5 g of potassium methoxide, 2.6 g of 18-crown-6 and 5 g of aniline was stirred at 100 ^{0}C under nitrogen for 3 hours. An aliquot was taken out for HPLC analysis. The yield of 4-ADPA based azobenzene was 32%.

C) A solution of 1.8 g of azobenzene, 2.6 g of 18-crown-6, 2.24 g of potassium t-butoxide and 5 g of aniline was stirred at 80 ^{0}C under nitrogen for 2 hours. An aliquot was taken out for HPLC analysis. The yield of 4-ADPA based on azobenzene was 100 %.

Example 2

This example illustrate the production of 4-ADPA from the reaction of aniline and azobenzene in the presence of a base.

A) A solution of 1.8 g of azobenzene, 1 g of KOH and 5 g of aniline was stirred at 120 ^{0}C under nitrogen for 12 hours. An aliquot was taken out for HPLC analysis. The yield of 4-ADPA based on azobenzene was 19%.

B) A solution of 1.8 g of azobenzene, 2 g of KOH and 5 g of aniline was stirred at 150 ^{0}C under nitrogen for 12 hours. An aliquot was taken out for HPLC analysis. The yield of 4-ADPA based on azobenzene was 38 %.

C) A solution of 1.8 g of azobenzene, 0.5 g of NaH and 5 g of aniline was stirred at 80 ^{0}C under nitrogen for 12 hours. An aliquot was taken out for HPLC analysis. The yield of 4-ADPA based on azobenzene was 97%.

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Example 3

This example illustrates the effect of protic material on the production of 4-(phenylazo)-diphenylamine from the reaction of aniline and azobenzene in the presence of a base and phase transfer catalyst.

A mixture of aniline (1.25 g), azobenzene (0.45 g), potassium t-butoxide (0.55 g), and 18-crown-6 (0.65 g) was stirred under nitrogen. Variable amounts of water was added to the reaction and the solution was heated to 80 °C for two hours after which time an aliquot was removed and analyzed by HPLC.

TABLE 1

Mole Ratio Water: t-Butoxide	% Yield 4-(Phenylazo)-diphenylamine
10	0
3	1
1	7
0.5	50

Example 4

This example illustrates the production of 4-ADPA from the reaction of aniline, azobenzene, base and phase transfer catalyst in the presence of various solvents.

A) A solution of 1.8 g of azobenzene, 2.24 g of potassium hydroxide, 2.6 g of 18-crown-6 and 0.9 g of aniline was stirred in 5 g of DMSO at 120 ^{0}C under nitrogen for 72 hours. An aliquot was taken out for HPLC analysis. The yield of 4-ADPA based on azobenzene was 10%.

B) A solution of 1.8 g of azobenzene, 2.2 g of potassium t-butoxide, 2.6 g of 18-crown-6 and 0.9 g of aniline was stirred in 5 g of ethylene glycol at 140 ^{0}C

under nitrogen for 12 hours. An aliquot was taken out for HPLC analysis and . The HPLC yield of 4-ADPA based on azobenzene was 30 %.

C) A solution of 1.8 g of azobenzene, 2.2 g of potassium t-butoxide, 2.6 g of 18-crown-6 and 0.9 g of aniline was stirred in 3 g of N-methyl-2-pyrrolidone at 140 ^{0}C under nitrogen for 12 hours. An aliquot was removed for HPLC analysis. The yield of 4-ADPA based on azobenzene was 5 %.

Example 5

This example illustrates the reaction of substituted aniline derivatives with azobenzene to produce the corresponding substituted 4-ADPA derivative.

A) A solution of 1.8 g of azobenzene, 2.2 g of potassium t-butoxide and 5.35 g of p-toluidine was stirred at 150 ^{0}C under nitrogen for 12 hours. An aliquot was taken out for HPLC analysis. The yield of 4-ADPA derivative based on azobenzene was 71%.

B) A solution of 1.8 g of azobenzene, 2.2 g of potassium t-butoxide and 5 g of p-anisidine was stirred at 140 ^{0}C under nitrogen for 12 hours. An aliquot was taken out for HPLC analysis. The yield of 4-ADPA derivative basod on azobenzene was 35%.

C) A solution of 1.8 g of azobenzene, 2.2 g of potassium t-butoxide, 2.6 g of 18-crown-6 and 5 g of p-chloroaniline was stirred at 135 ^{0}C under nitrogen for 4 hours. An aliquot was taken out for HPLC analysis. The yield of 4-ADPA derivative based on azobenzene was 49 %.

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Example 6

This example illustrates the production of 4-ADPA from the reaction of azoxybenzene, aniline, base and phase transfer catalyst.

A solution of 12 g of azoxybenzene, 1 g of potassium hydroxide, 2.6 g of 18-crown-6 and 5 g of aniline was stirred at 150 ^{0}C under nitrogen for 4 hours. An aliquot was taken out for HPLC analysis. The yield of 4-ADPA based on azoxybenzene was 91%.

Example 7

This example illustrates the effect of water on the production of 4-ADPA from the reaction of 4-(phenylazo)-diphenylamine with a nucleophile.

A solution of 0.3 g of 4-(phenylazo)diphenylamine, 0.5 g of aniline, 0.25 g of potassium t-butoxide, 0.3 g of 18-crown-6 and various amounts of water was heated under nitrogen for 4 hours. An aliquot was removed for HPLC analysis. The results are summarized in Table 2.

TABLE 2

Mole Ratio Water: t-Butoxide	% Yield 4-ADPA
10	0
5	6
3	2
1	100
0.5	100
Anhydrous	36

Example 8

This example illustrate the production of 4-ADPA from the reaction of 2-heptylamine, 4-(phenylazo)-diphenylamine, base and phase transfer catalyst.

A solution of 1.35 g of 4-(phenylazo)diphenylamine, 3 g of 2-aminoheptane,

1.12 g of potassium t-butoxide and 1.3 g of 18-crown-6 was heated under nitrogen for 3 hours. An aliquot was taken out for HPLC analysis. The yield of 4-ADPA based on 4-(phenylazo)diphenylamine was 23 %.

Example 9

This example illustrates the production of 4-ADPA from the reaction of 4-(phenylazo)diphenylamine and 2-aminoheptane.

A solution of 1.32 g of 4-(phenylazo)diphenylamine and 3.1 g of 2-aminoheptane was heated under nitrogen for 3 hours. An aliquot was removed for HPLC analysis. The yield of 4-ADPA based on 4-(phenylazo)diphenylamine was 30%.

Example 10

This example illustrates the production of 4-ADPA from the reaction of 4-(phenylazo)diphenylamine and a substituted aromatic amine.

A solution of 2.73 g of 4-(phenylazo)diphenylamine, 5 g of 1,4-phenylenediamine, 2.24 g of potassium t-butoxide and 2.6 g of 18-crown-6 was heated under nitrogen for 30 minutes. An aliquot was removed for HPLC analysis. The yield of 4-ADPA based on 4-(phenylazo)diphenylamine was 59 %.

Example 11

This example illustrates the production 4,4'-diaminodiphenylamine, a 4-ADPA derivative, produced from the reaction of a substituted aromatic amine, 1,4-phenylenediamine, with azobenzene.

A solution of 1.8 g of azobenzene 5 g of 1,4-phenylenediamine, 2.24 g of potassium t-butoxide and 2.6 g of 18-crown-6 was heated under nitrogen for 30 minutes. An aliquot was removed for HPLC analysis. The

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yield of 4,4'-diaminodiphenylamine based on azobenzene was 30 %.

Example 12

This example illustrates the production of a substituted aromatic azo compound from the reaction of azobenzene and a substituted aromatic amine.

A solution of 1.8 g of azobenzene, 2.2 g of potassium t-butoxide, 2.6 g of 18-crown-6 and 5 g of substituted aniline was stirred at 80 ^{o}C for 1 hour. An aliquot was taken out for HPLC analysis. Yields of substituted azo compounds are based on azobenzene.

TABLE 3

Substituted Aromatic Amine	% Yield Substituted Azo Compound
p-chloroaniline	19%
p-methylaniline	18%
p-methoxyaniline	28%

Example 13

This example illustrates the production of a substituted azo compound from the reaction of azobenzene and aniline.

A solution of 1.8 g of azobenzene, 1 g of potassium hydroxide, 2.6 g of 18-crown-6 and 5 g of aniline was stirred at 80 ^{o}C for 2 hour. An aliquot was taken out for HPLC analysis. The yield of 4-(phenylazo)diphenylamine based on azobenzene was 14%.

Example 14

This example illustrates the production of a substituted aromatic amine from the reaction of an aromatic amide with azobenzene.

A mixture of 1.8 g of azobenzene, 2.6 g of 18-crown-6, 2.6 g of potassium t-butoxide was dissolved in 5 g of molten benzamide. The reaction was stirred at 135 ^{0}C for 12 hour under nitrogen. An aliquot was taken out for HPLC analysis. The yield of 4 -aminobenzanilide based on azobenzene was 17 %.

Example 15

This example illustrates the production of 4-ADPA from the reaction of 1,2-diphenylhydrazine and an aromatic amine nucleophile.

A mixture of 1.8 g of 1,2-diphenylhydrazine, 2.2 g of potassium t-butoxide, 2.6 g of 18-crown-6 and 5 g of aniline was stirred at 135 ^{0}C for 12 hour. An aliquot was taken out for HPLC analysis. The yield of 4-ADPA based on 1,2-diphenylhydrazine was 9%.

Example 16

This example illustrates the production of 4-(phenylazo) diphenylamine and substituted derivatives thereof from the reaction of aniline or substituted aniline derivatives and azobenzene.

(a) 10 mmole of azobenzene, 20 mmole of potassium t-butoxide and 10 mmole of 18-crown-6 was stirred in 10 g of aniline under nitrogen at 80°C for 30 minutes. A weighted aliquot was sampled for HPLC and was found to contain 40% of 4-(phenylazo)diphenylamine, 50% of azobenzene and 10% of hydrazobenzene.

(b) 10 mmole of azobenzene, 20 mmole of potassium t-butoxide and 10 mmole of 18-crown-6 was stirred in 5 g of p-anisidine under nitrogen at 60°C for 12 hours. 10 ml of 90% methanol was added to homogenize

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the solution. A weighted aliquot was sampled for HPLC and was found to contain 80% of 4-(4-methoxyphenylazo)diphenylamine and 19% of azobenzene.

(c) 10 mmole of azobenzene, 20 mmole of potassium t-butoxide and 10 mmole of 18-crown-6 was stirred in 5 g of p-chloroaniline under nitrogen at 70°C for 12 hours. 10 ml of 90% methanol was added to homogenize the solution. A weighted aliquot was sampled for HPLC and was found to contain 31% of 4-(4-chlorophenylazo)diphenylamine, 38% of hydrazobenzene and 30% of azobenzene.

(d) 10 mmole of azo benzene, 20 mmole of potassium t-butoxide and 10 mmole of 18-crown-6 was stirred in 5 g of p-toluidine under nitrogen at 80°C for 12 hours. 10 ml of 90% methanol was added to homogenize the solution. A weighted aliquot was sampled for HPLC and was found to contain 60% of 4-(tolylphenylazo)diphenylamine and 40% of azobenzene.

(e) 10 mmole of azobenzene, 5 g of p-nitroaniline, 20 mmole of potassium t-butoxide and 10 mmole of 18-crown-6 was stirred in 4 ml of DMSO under nitrogen at 100°C for 72 hours. 10 ml of 90% methanol was added to homogenize the solution. A weighted aliquot was sampled for HPLC and was found to contain 23% of 4-(nitrophenylazo)diphenylamine and 74% of azobenzene.

(f) 10 mmole of azobenzene, 2 g of 1,4-phenylenediamine, 20 mmole of potassium t-butoxide and 10 mmole of 18-crown-6 was stirred in 4 ml of DMSO under nitrogen at 100°C for 72 hours. 10 ml of 90% methanol was added to homogenize the solution. A weighted aliquot was sampled for HPLC and was found to contain 90% of 4-(aminophenylazo)diphenylamine.

Example 17

This example illustrates the production of 4-(phenylazo)diphenylamine from the reaction of aniline and azobenzene.

75 ml of 25% aqueous tetramethylammonium hydroxide was evaporated to dryness at 60°C/20 mmHg followed by addition of 18.5 gm of azobenzene and 75 ml of aniline. The solution was stirred at 60°C/20 mmHg for 4 hours, approximately 30 ml of aniline was distilled, then 50 ml of water was added. The aniline solution was assayed to contain 99% yield of 4-(phenylazo)diphenylamine and 6% of N-methylaniline by HPLC based on azobenzene.

Example 18

This example illustrates the production of 4-(phenylazo)diphenylamine under aerobic conditions.

A solution of 25% aqueous tetramethylammonium hydroxide (8 mL) was concentrated under vacuum at 75°C until solid material formed. Azobenzene (1.8 g) and aniline (10 mL) were added and the solution was stirred under the same conditions for 4 hours and then in the presence of air for 12 hours. Analysis of the reaction by HPLC revealed 90% yield of 4-(phenylazo)diphenylamine.

Example 19

This example illustrates the conversion of 4-(phenylazo)diphenylamine to 4-aminodiphenylamine using isoamyl alcohol as the protic material.

A solution of 4-(phenylazo)diphenylamine (2.73 g), isoamyl alcohol (0.08 g), potassium t-butoxide (0.22 g) and 18-crown-6 (1.3 g) was heated between 100-120°C under nitrogen for 12 hours. The yield of 4-ADPA was 80%.

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Example 20

This example illustrates the production of 4-ADPA from the aerobic reaction of aniline and base forming azobenzene in-situ.

Aniline (0.9 g) and potassium t-butoxide (2.2 g) was stirred in 5 g of t-butanol at 80°C in air for 12 hours. An aliquot was taken out for HPLC analysis which revealed a 30% yield of 4-ADPA and a 70% yield of azobenzene based on aniline charges.

THAT WHICH IS CLAIMED IS:

1. A process for preparing substituted aromatic azo compounds comprising:

(a) contacting a nucleophilic compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides, and an azo containing compound represented by the formula $X-R_1-N=N-R_2-Y$ or azoxy or hydrazo derivatives thereof in the presence of a suitable solvent system, and

(b) reacting the nucleophilic compound and azo containing compound in the presence of a suitable base and a controlled amount of protic material at a reaction temperature of from about 10°C to about 150°C in a confined reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1 wherein R_1 is an aromatic group, R_2 is selected from the group consisting of aliphatic and aromatic groups, and X and Y are independently selected from the group consisting of hydrogen, halides, $-NO_2$, $-NH_2$, aryl groups, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group, wherein if R_2 is aliphatic, X is in the meta or ortho position on R_1 and if R_2 is aromatic, at least one of X and Y is in the meta or ortho position on R_1 and R_2, respectively, and wherein halides are selected from the group consisting of chloride, bromide and fluoride.

2. The process of Claim 1 wherein the substituent of said substituted aniline derivatives is selected from the group consisting of halides, $-NO_2$, $-NH_2$, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COOH and aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$, group wherein halides are selected from the group consisting of chloride, bromide and fluoride.

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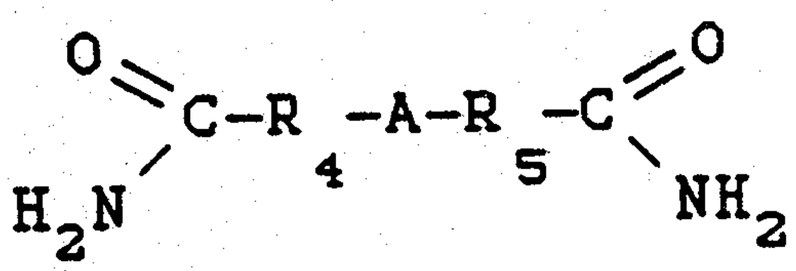
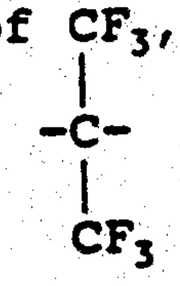
3. The process of Claim 2 wherein said substituted aniline derivatives are selected from the group consisting of 2-methoxyaniline, 4-methoxyaniline, 4-chloroaniline, p-toluidine, 4-nitroaniline, 3-bromoaniline, 3-bromo-4-aminotoluene, p-aminobenzoic acid, 2,4-diaminotoluene, 2,5-dichloroaniline, 1,4-phenylenediamine, 4,4'-methylene dianiline and 1,3,5-triaminobenzene.

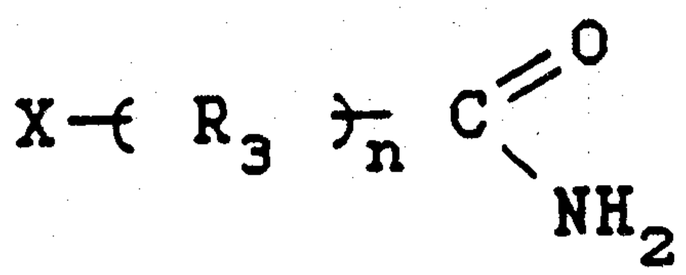
4. The process of Claim 1 wherein said amide is selected from the group consisting of aromatic amides, aliphatic amides, substituted aromatic amide derivatives, substituted aliphatic amide derivatives and diamides having the formula:



wherein R_4 and R_5 are independently selected from the group consisting of aromatic groups, aliphatic groups and a direct bond, and A is selected from the group consisting of CF_3, $-SO_2-$, -O-, -S- and a direct bond.



5. The process of Claim 4 wherein said aliphatic amides and said substituted aliphatic amide derivatives are represented by the formula:



wherein n is 0 or 1, R_3 is selected from the group consisting of alkyl, arylalkyl, alkenyl, arylalkenyl, cycloalkyl and cycloalkenyl groups and X is selected from the group consisting of hydrogen, $-NO_2$, $-NH_2$, aryl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group.

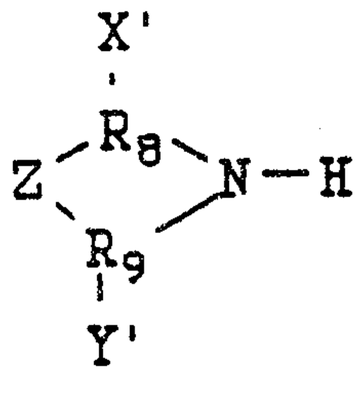
6. The process of Claim 5 wherein said aliphatic amides and said substituted aliphatic amide derivatives are selected from the group consisting of isobutyramide, urea, acetamide and propyl amide.

7. The process of Claim 4 wherein the substituent of said substituted aromatic amide derivatives is selected from the group consisting of halides, $-NO_2$, $-NH_2$, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -COH, -COOH and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group, wherein halides are selected from the group consisting of chloride, bromide and fluoride.

8. The process of Claim 7 wherein said aromatic amides and said substituted aromatic amide derivatives are selected from the group consisting of benzamide, 4-methylbenzamide, 4-methoxybenzamide, 4-chlorobenzamide, 2-methylbenzamide, 4-nitrobenzamide, and 4-aminobenzamide.

9. The process of Claim 4 wherein said diamides are selected from the group consisting of adipamide, oxalic amide, terephthalic diamide, and 4,4'-biphenyldicarboxamide.

10. The process of Claim 1 wherein said aliphatic amine and said substituted aliphatic amine derivatives are selected from the group consisting of compounds represented by the formula $X'-R_6-NH-R_7-Y'$ and compounds represented by the formula:



wherein R_6 is selected from the group consisting of alkyl, alkenyl, cycloalkyl and cycloalkenyl groups, R_7 is selected from the group consisting of a direct bond, alkyl, alkenyl, cycloalkyl and cycloalkenyl groups, R_8 and R_9 are independently selected from the group consisting of alkyl and alkenyl groups, Z is selected from the group consisting of a direct bond, -NH-, $-N(R_{10})-$, -O- and -S-, wherein R_{10} is an alkyl group, and X' and Y' are independently selected from the group consisting of hydrogen, halides, $-NO_2$, $-NH_2$, aryl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group, wherein halides are selected from the group consisting of chloride, bromide and fluoride.

11. The process of Claim 10 wherein said aliphatic amine and said substituted aliphatic amine derivatives are selected from the group consisting of cyclohexylamine, 2-butylamine, isopropylamine, 2-hexylamine, 2-heptylamine, 1,4-dimethylpentylamine, 1-methylheptylamine, 1-ethyl-3-methylpentylamine, 1,3-dimethylbutylamine, octylamine, piperidine, piperazine, hexamethylenediamine, 2-amino-1-propanol, 2-amino-1-butanol and 6-aminohexanoic acid.

12. The process of Claim 1 wherein said azo containing compounds are selected from the group consisting of azobenzene, azoxybenzene, 4-(phenylazo)-diphenylamine, 3,4'-dichloroazobenzene, p-phenylazobenzene sulfonic acid,

p-(2,4-dihydroxyphenylazo)benzene sulfonic acid, and 1,2-diphenylhydrazine.

13. The process of Claim 1 wherein said suitable solvent system comprises a solvent selected from the group consisting of aniline, dimethylsulfoxide, dimethylformamide, N-methyl-2-pyrrolidone, pyridine, ethyleneglycoldimethyl ether, diisopropylethylamine, molten benzamide and mixtures thereof.

14. The process of Claim 13 wherein said suitable solvent system comprises a protic solvent.

15. The process of Claim 1 wherein the molar ratio of said protic material to said suitable base is 0:1 to about 3:1 and the molar ratio of said suitable base to said azo containing compound is about 1:1 to about 10:1.

16. The process of Claim 1 wherein said suitable base is selected from the group consisting of organic and inorganic bases.

17. The process of Claim 16 wherein said organic and inorganic bases are selected from the group consisting of alkali metals, alkali metal hydrides, alkali metal hydroxides, alkali metal alkoxides, phase transfer catalysts in conjunction with a base source, amines, crown ethers in conjunction with a base source, alkyl magnesium halides, and mixtures thereof.

18. The process of Claim 1 wherein said base is selected from the group consisting of an arylammonium, alkylammonium, aryl/alkylammonium and alkyldiammonium salt in conjunction with a base source.

19. The process of Claim 1 wherein said nucleophilic compound is aniline or benzamide and said azo containing compound is azobenzene.

20. The process of Claim 19 wherein said nucleophilic compound is aniline and wherein said azobenzene introduced in Step (a) is produced by the

oxidative coupling of aniline in the presence of a suitable base.

21. The process of Claim 19 wherein said nucleophilic compound is aniline and wherein said reaction is conducted under aerobic conditions and azobenzene is produced in-situ by the oxidative coupling of aniline in the presence of a suitable base.

22. The process of Claim 19 wherein said solvent is aniline and said base is selected from the group consisting of 18-crown-6 ether in conjunction with potassium hydroxide or potassium t-butoxide, tetraalkylammonium hydroxide and alkyl substituted diammonium hydroxide.

23. The process of Claim 1 wherein said nucleophilic compound and said azo containing compound are reacted under aerobic conditions.

24. The process of Claim 1 wherein said nucleophilic compound is selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines or substituted aliphatic amine derivatives having the formula $X'-R_6-NH_2$, and amides and said azo containing compound are reacted under anaerobic conditions wherein R_6 is selected from the group consisting of alkyl, alkenyl, cycloalkyl and cycloalkenyl groups and X' is selected from the group consisting of hydrogen, halides, $-NO_2$, $-NH_2$, aryl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group wherein halides are selected from the group consisting of chloride, bromide and fluoride.

25. The process of Claim 1 wherein a desiccant is present during step (b) to control the amount of protic material present during the reaction of said nucleophilic compound and said azo containing compound.

26. The process of Claim 1 wherein the amount of protic material in step (b) is controlled by the continuous distillation of said protic material.

27. The process of Claim 1 further comprising:

(c) reacting said substituted aromatic azo compound with a nucleophilic compound independently selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides in the presence of a suitable solvent system, a suitable base and a controlled amount of protic material at a reaction temperature of about 70°C to about 200°C in a confined reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1.

28. The process of Claim 27 wherein said nucleophilic compound in step (a) is an amide further comprising:

(d) reacting said substituted aromatic amine with ammonia under conditions which produce the corresponding substituted aromatic amine and amide.

29. The process of Claim 28 further comprising:

(e) reductively alkylating the substituted aromatic amine of (d).

30. A process for preparing 4-aminodiphenylamine (4-ADPA) or substituted derivatives thereof comprising:

(a) contacting aniline or substituted aniline derivatives and azobenzene or substituted azobenzene derivatives or azoxy or hydrazo derivatives thereof in the presence of a suitable solvent system,

(b) reacting the aniline or substituted aniline derivatives and azobenzene or substituted azobenzene derivatives in the presence of a suitable base and a controlled amount of protic material at a reaction temperature of about 10°C to about 150°C in a confined

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reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1, and

(c) reacting the product of (b) with aniline or substituted aniline derivative in the presence of a suitable solvent system, a suitable base and a controlled amount of protic material at a reaction temperature of about 70°C to about 200°C in a confined reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1.

31. The process of Claim 30 for preparing 4-ADPA comprising:

(a) contacting aniline and azobenzene in the presence of a suitable solvent system,

(b) reacting the aniline and azobenzene in the presence of a suitable base and a controlled amount of protic material at a reaction temperature of about 10°C to about 150°C in a confined reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1, and

(c) reacting the product of (b) with aniline in the presence of a suitable solvent system, a suitable base and a controlled amount of protic material at a reaction temperature of about 70°C to about 200°C in a confined reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1, wherein said azobenzene introduced in Step (a) is produced by the oxidative coupling of aniline in the presence of a suitable base.

32. The process according to Claim 30 for preparing 4-ADPA comprising:

(a) contacting aniline and azobenzene in the presence of a suitable solvent system,

(b) reacting the aniline and azobenzene in the presence of a suitable base and a controlled amount of protic material at a reaction temperature of about 10°C to about 150°C in a confined reaction zone, wherein the

molar ratio of protic material to base is 0:1 to about 5:1, and

(c) reacting the product of (b) with aniline in the presence of a suitable solvent system, a suitable base and a controlled amount of protic material at a reaction temperature of about 70°C to about 200°C in a confined reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1, wherein said reaction is conducted under aerobic conditions and azobenzene is produced in-situ by the oxidative coupling of aniline in the presence of a suitable base.

33. A process for preparing alkylated p-phenylenediamines or substituted derivatives thereof comprising:

(a) contacting a nucleophilic compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides, and an azo containing compound represented by the formula $X-R_1-N=N-R_2-Y$ or azoxy or hydrazo derivatives thereof in the presence of a suitable solvent system, and

(b) reacting the nucleophilic compound and azo containing compound in the presence of a suitable base and a controlled amount of protic material at a reaction temperature of from about 10°C to about 150°C in a confined reaction zone wherein the molar ratio of protic material to base is 0:1 to about 5:1, wherein R_1 is an aromatic group, R_2 is selected from the group consisting of aliphatic and aromatic groups, and X and Y are independently selected from the group consisting of hydrogen, halides, $-NO_2$, $-NH_2$, aryl groups, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group wherein if R_2 is aliphatic, X is in the meta or ortho position on R_1 and if R_2 is aromatic, at least one of X and Y is in the meta

or ortho position on R_1 and R_2, respectively, and wherein halides are selected from the group consisting of chloride, bromide and fluoride to produce a substituted aromatic azo compound,

(c) reacting the product of (b) with a nucleophilic compound independently selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides in the presence of a suitable solvent system, a suitable base and a controlled amount of protic material at a reaction temperature of about 70°C to about 200°C in a confined reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1 to produce a substituted aromatic amine, and

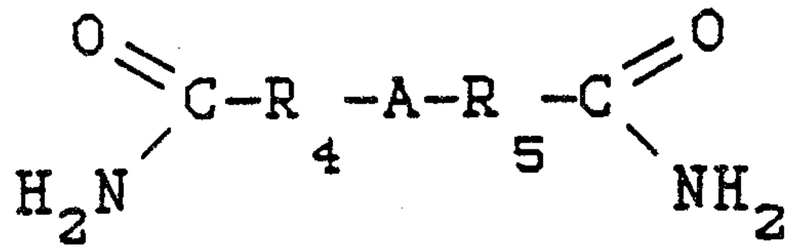
(d) reductively alkylating said substituted aromatic amine.

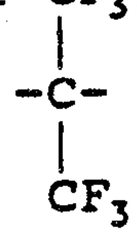
34. The process of Claim 33 wherein the substituent of said substituted aniline derivatives is selected from the group consisting of halides, $-NO_2$, $-NH_2$, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COOH and aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$, group wherein halides are selected from the group consisting of chloride, bromide and fluoride.

35. The process of Claim 34 wherein said substituted aniline derivatives are selected from the group consisting of 2-methoxyaniline, 4-methoxyaniline, 4-chloroaniline, p-toluidine, 4-nitroaniline, 3-bromoaniline, 3-bromo-4-aminotoluene, p-aminobenzoic acid, 2,4-diaminotoluene, 2,5-dichloroaniline, 1,4-phenylenediamine, 4,4'-methylene dianiline and 1,3,5-triaminobenzene.

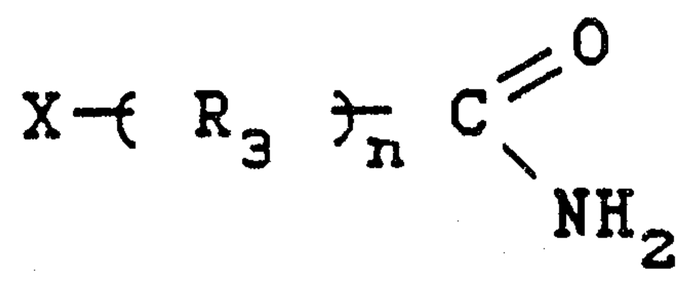
36. The process of Claim 33 wherein said amide is selected from the group consisting of aromatic amides, aliphatic amides, substituted aromatic amide

derivatives, substituted aliphatic amide derivatives and diamides having the formula:



wherein R_4 and R_5 are independently selected from the group consisting of aromatic groups, aliphatic groups and a direct bond, and A is selected from the group consisting of  , $-SO_2-$, -O-, -S- and a direct bond.

37. The process of Claim 36 wherein said aliphatic amides and said substituted aliphatic amide derivatives are represented by the formula:



wherein n is 0 or 1, R_3 is selected from the group consisting of alkyl, aryl alkyl, alkenyl, arylalkenyl, cycloalkyl and cycloalkenyl groups and X is selected from the group consisting of hydrogen, $-NO_2$, $-NH_2$, aryl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group.

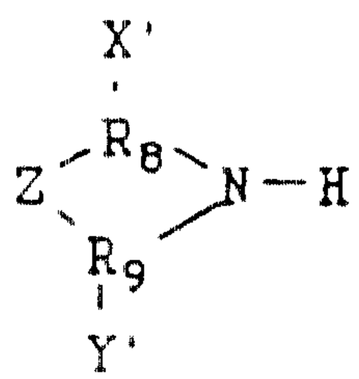
38. The process of Claim 37 wherein said aliphatic amides and said substituted aliphatic amide derivatives are selected from the group consisting of isobutyramide, urea, acetamide and propyl amide.

39. The process of Claim 36 wherein the substituent of said substituted aromatic amide derivatives is selected from the group consisting of halides, $-NO_2$, $-NH_2$, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -COH, -COOH and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group, wherein halides are selected from the group consisting of chloride, bromide and fluoride.

40. The process of Claim 39 wherein said aromatic amides and said substituted aromatic amide derivatives are selected from the group consisting of benzamide, 4-methylbenzamide, 4-methoxybenzamide, 4-chlorobenzamide, 2-methylbenzamide, 4-nitrobenzamide, and 4-aminobenzamide.

41. The process of Claim 36 wherein said diamides are selected from the group consisting of adipamide, oxalic amide, terephthalic diamide, and 4,4'-biphenyldicarboxamide.

42. The process of Claim 33 wherein said aliphatic amine and said substituted aliphatic amine derivatives are represented by the formula $X'-R_6-NH-R_7-Y'$ and compounds represented by the formula:



wherein R_6 is selected from the group consisting of alkyl, alkenyl, cycloalkyl and cycloalkenyl groups, R_7 is selected from the group consisting of a direct bond, alkyl, alkenyl, cycloalkyl and cycloalkenyl groups, R_8 and R_9 are independently selected from the group consisting of alkyl and alkenyl groups, Z is selected from the group consisting of a direct bond, -NH-,

$-N(R_{10})-$, -O- and -S-, wherein R_{10} is an alkyl group, and X' and Y' are independently selected from the group consisting of hydrogen, halides, $-NO_2$, $-NH_2$, aryl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group, wherein halides are selected from the group consisting of chloride, bromide and fluoride.

43. The process of Claim 42 wherein said aliphatic amine and said substituted aliphatic amine derivatives are selected from the group consisting of cyclohexylamine, 2-butylamine, isopropylamine, 2-hexylamine, 2-heptylamine, 1,4-dimethylpentylamine, 1-methylheptylamine, 1-ethyl-3-methylpentylamine, 1,3-dimethylbutylamine, octylamine, piperidine, piperazine, hexamethylenediamine, 2-amino-1-propanol, 2-amino-1-butanol and 6-aminohexanoic acid.

44. The process of Claim 33 wherein said azo containing compounds are selected from the group consisting of azobenzene, azoxybenzene, 3,4'-dichloroazobenzene, p-phenylazobenzene sulfonic acid, p-(2,4-dihydroxyphenylazo)benzene sulfonic acid, 1,2-diphenylhydrazine.

45. The process of Claim 33 wherein said suitable solvent system comprises a solvent selected from the group consisting of aniline, dimethylsulfoxide, dimethylformamide, N-methyl-2-pyrrolidone, pyridine, ethyleneglycoldimethyl ether, diisopropylethylamine, molten benzamide and mixtures thereof.

46. The process of Claim 45 wherein said solvent is selected from the group consisting of aniline, dimethylsulfoxide, dimethylformamide, molten benzamide and mixtures thereof.

47. The process of Claim 45 wherein said suitable solvent system comprises a protic solvent.

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48. The process of Claim 33 wherein said suitable base is selected from the group consisting of organic and inorganic bases.

49. The process of Claim 48 wherein said organic and inorganic bases are selected from the group consisting of alkali metals, alkali metal hydrides, alkali metal hydroxides, alkali metal alkoxides, phase transfer catalysts in conjunction with a base source, amines, crown ethers in conjunction with a base source, alkyl magnesium halides, and mixtures thereof.

50. The process of Claim 33 wherein said base is selected from the group consisting of an arylammonium, alkylammonium, aryl/alkylammonium and alkyldiammonium salt in conjunction with a base source.

51. The process of Claim 33 wherein said nucleophilic compound is aniline and said azo containing compound is azobenzene.

52. The process of Claim 51 wherein said azobenzene introduced in Step (a) is produced by the oxidative coupling of aniline in the presence of a suitable base.

53. The process of Claim 51 wherein said reaction is conducted under aerobic conditions and said azobenzene is produced in-situ by the oxidative coupling of aniline in the presence of a suitable base.

54. The process of Claim 51 wherein said solvent is aniline and said base is selected from the group consisting of 18-crown-6 ether in conjunction with potassium hydroxide or potassium t-butoxide, tetraalkylammonium hydroxide and alkyl substituted diammonium hydroxide.

55. The process of Claim 33 wherein said nucleophilic compound and said azo containing compound are reacted under aerobic conditions.

56. The process of Claim 33 wherein said nucleophilic compound is selected from the group

consisting of aniline, substituted aniline derivatives, aliphatic amines or substituted aliphatic amines derivatives having the formula $X'-R_6-NH_2$, and amides and said azo containing compound are reacted under anaerobic conditions wherein R_6 is selected from the group consisting of alkyl, alkenyl, cycloalkyl and cycloalkenyl groups and X' is selected from the group consisting of hydrogen, halides, $-NO_2$, $-NH_2$, aryl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group wherein halides are selected from the group consisting of chloride, bromide and fluoride.

57. The process of Claim 33 wherein a desiccant is present during step (b) to control the amount of protic material present during the reaction of said nucleophilic compound and said azo containing compound.

58. The process of Claim 33 wherein a desiccant is present during step (c) to control the amount of protic material present during the reaction of said nucleophilic compound and said substituted aromatic azo compound.

59. The process of Claim 33 wherein the amount of protic material in step (b) is controlled by the continuous distillation of said protic material.

60. The process of Claim 59 wherein said protic material is water and said water is removed by continuous azeotropic distillation utilizing the water/aniline azeotrope.

61. The process of Claim 33 wherein said substituted aromatic amine is reductively alkylated utilizing a compound selected from the group consisting of ketones and aldehydes.

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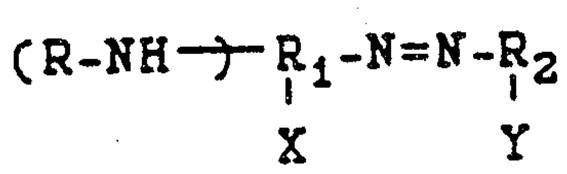
62. The process of Claim 61 wherein said ketone is selected from the group consisting of acetone, methylisobutylketone, methylisoamylketone and 2-octanone.

63. A process for preparing substituted aromatic amines comprising:

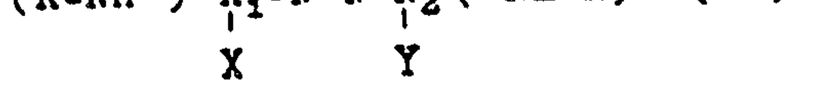
(a) contacting a nucleophilic compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides with a substituted aromatic azo compound or azoxy or hydrazo derivatives thereof in the presence of a suitable solvent system, and

(b) reacting the nucleophilic compound and the substituted aromatic azo compound or azoxy or hydrazo derivatives thereof in the presence of a suitable base and a controlled amount of protic material at a reaction temperature of about 70°C to about 200°C, wherein the molar ratio of protic material to base is 0:1 to about 5:1, wherein the substituted aromatic azo compound is selected from the group consisting of compounds represented by the formula



(I),

compounds represented by the formula



(II).

compounds represented by the formula

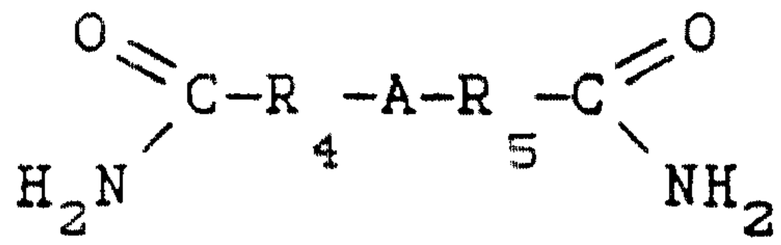
(III).

and mixtures thereof, wherein R-NH- represents a substituent derived from a compound selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines, substituted aliphatic amine derivatives and amides, R_1 is an aromatic group, R_2 is selected from the group consisting of aliphatic and aromatic groups, and X and Y are independently selected from the group consisting of hydrogen, halides, $-NO_2$, $-NH_2$, aryl groups, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group, wherein halides are selected from the group consisting of chlorine, bromine and fluorine and R_2 is an aromatic group in substituted aromatic azo compounds (II) and (III).

64. The process of Claim 63 wherein the substituent of said substituted aniline derivatives is selected from the group consisting of halides, $-NO_2$, $-NH_2$, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COOH and aryl, arylalkyl or alkylaryl groups containing at least 1 $-NH_2$, group wherein halides are selected from the group consisting of chloride, bromide and fluoride.

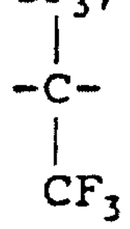
65. The process of Claim 64 wherein said substituted aniline derivatives are selected from the group consisting of 2-methoxyaniline, 4-methoxyaniline, 4-chloroaniline, p-toluidine, 4-nitroaniline, 3-bromoaniline, 3-bromo-4-aminotoluene, p-aminobenzoic acid, 2,4-diaminotoluene, 2,5-dichloroaniline, 1,4-phenylenediamine, 4,4'-methylene dianiline and 1,3,5-triaminobenzene.

66. The process of Claim 63 wherein said amide is selected from the group consisting of aromatic amides, aliphatic amides, substituted aromatic amide derivatives, substituted aliphatic amide derivatives and diamides having the formula:

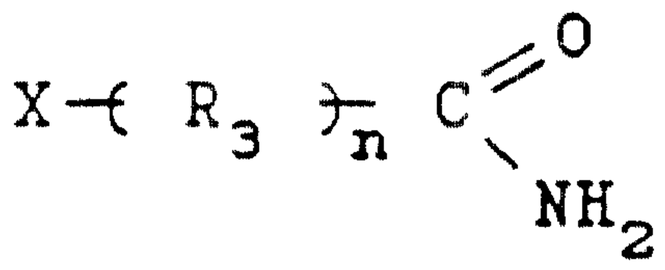


wherein R_4

and R_5 are independently selected from the group consisting of aromatic groups, aliphatic groups and a direct bond, and A is selected from the group consisting of CF_3, $-SO_2-$, -O-, -S- and a direct bond.



67. The process of Claim 66 wherein said aliphatic amides and said substituted aliphatic amide derivatives are represented by the formula:



wherein n is 0 or 1, R_3 is selected from the group consisting of alkyl, aryl alkyl, alkenyl, arylalkenyl, cycloalkyl and cycloalkenyl groups and X is selected from the group consisting of hydrogen, $-NO_2$, $-NH_2$, aryl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group.

68. The process of Claim 67 wherein said aliphatic amides and said substituted aliphatic amide derivatives are selected from the group consisting of isobutyramide, urea, acetamide and propyl amide.

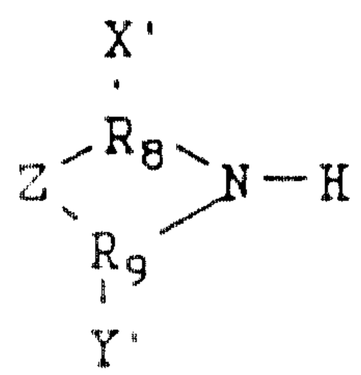
69. The process of Claim 66 wherein the substituent of said substituted aromatic amide

derivatives is selected from the group consisting of halides, $-NO_2$, $-NH_2$, alkyl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group, wherein halides are selected from the group consisting of chloride, bromide and fluoride.

70. The process of Claim 69 wherein said aromatic amides and said substituted aromatic amide derivatives are selected from the group consisting of benzamide, 4-methylbenzamide, 4-methoxybenzamide, 4-chlorobenzamide, 2-methylbenzamide, 4-nitrobenzamide, and 4-aminobenzamide.

71. The process of Claim 66 wherein said diamides are selected from the group consisting of adipamide, oxalic amide, terephthalic diamide, and 4,4'-biphenyldicarboxamide.

72. The process of Claim 63 wherein said aliphatic amine and said substituted aliphatic amine derivatives are represented by the formula $X'-R_6-NH-R_7-Y'$ and compounds represented by the formula:



wherein R_6 is selected from the group consisting of alkyl, alkenyl, cycloalkyl and cycloalkenyl groups, R_7 is selected from the group consisting of a direct bond, alkyl, alkenyl, cycloalkyl and cycloalkenyl groups, R_8 and R_9 are independently selected from the group consisting of alkyl and alkenyl groups, Z is selected from the group consisting of a direct bond, -NH-, $-N(R_{10})-$, -O- and -S-, wherein R_{10} is an alkyl group, and X' and Y' are independently selected from the group

consisting of hydrogen, halides, $-NO_2$, $-NH_2$, aryl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group, wherein halides are selected from the group consisting of chloride, bromide and fluoride.

73. The process of Claim 72 wherein said aliphatic amine and said substituted aliphatic amine derivatives are selected from the group consisting of cyclohexylamine, 2-butylamine, isopropylamine, 2-hexylamine, 2-heptylamine, 1,4-dimethylpentylamine, 1-methylheptylamine, 1-ethyl-3-methylpentylamine, 1,3-dimethylbutylamine, octylamine, piperidine, piperazine, hexamethylenediamine, 2-amino-1-propanol, 2-amino-1-butanol and 6-aminohexanoic acid.

74. The process of Claim 63 wherein said azo containing compounds are selected from the group consisting of azobenzene, azoxybenzene, 4-phenylazo-diphenylamine, 3,4'-dichloroazobenzene, p-phenylazobenzene sulfonic acid, p-(2,4-dihydroxyphenylazo)benzene sulfonic acid, and 1,2-diphenylhydrazine.

75. The process of Claim 63 wherein said suitable solvent system comprises a solvent selected from the group consisting of aniline, dimethylsulfoxide, dimethylformamide, N-methyl-2-pyrrolidone, pyridine, ethyleneglycoldimethyl ether, diisopropylethylamine, molten benzamide and mixtures thereof.

76. The process of Claim 75 wherein said suitable solvent system comprises a protic solvent.

77. The process of Claim 63 wherein said suitable base is selected from the group consisting of organic and inorganic bases.

78. The process of Claim 77 wherein said organic and inorganic bases are selected from the group consisting of alkali metals, alkali metal hydrides,

alkali metal hydroxides, alkali metal alkoxides, phase transfer catalysts in conjunction with a base source, amines, crown ethers in conjunction with a base source, alkyl magnesium halides, and mixtures thereof.

79. The process of Claim 63 wherein said base is selected from the group consisting of an arylammonium, alkylammonium, aryl/alkylammonium and alkyldiammonium salt in conjunction with a base source.

80. The process of Claim 63 wherein said nucleophilic compound is aniline and said substituted aromatic azo compound is 4-(phenylazo)-diphenylamine.

81. The process of Claim 80 wherein said solvent is aniline and said base is selected from the group consisting of potassium hydroxide, potassium t-butoxide, tetraalkylammonium hydroxide and alkyl substituted diammonium hydroxide.

82. The process of Claim 63 wherein said nucleophilic compound and said substituted aromatic azo compound are reacted under aerobic conditions.

83. The process of Claim 63 wherein said nucleophilic compound is selected from the group consisting of aniline, substituted aniline derivatives, aliphatic amines or substituted aliphatic amine derivatives having the formula $X'-R_6-NH_2$, and amides and said substituted aromatic azo compound are reacted under anaerobic conditions wherein R_6 is selected from the group consisting of alkyl, alkenyl, cycloalkyl and cycloalkenyl groups and X' is selected from the group consisting of hydrogen, halides, $-NO_2$, $-NH_2$, aryl groups, alkoxy groups, sulfonate groups, $-SO_3H$, -OH, -COH, -COOH, and alkyl, aryl, arylalkyl or alkylaryl groups containing at least one $-NH_2$ group wherein halides are selected from the group consisting of chloride, bromide and fluoride.

84. The process of Claim 63 wherein a desiccant is present during step (b) to control the

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amount of protic material present during the reaction of said nucleophilic compound and said substituted aromatic azo compound.

85. The process of Claim 63 wherein the amount of protic material in step (b) is controlled by the continuous distillation of said protic material.

86. The process of Claim 63 wherein said nucleophilic compound is an amide further comprising:

(c) reacting said substituted aromatic amine with ammonia under conditions which produce a corresponding substituted aromatic amine and amide.

87. The process of Claim 86 further comprising:

(d) reductively alkylating the substituted aromatic amine of (c).

88. A process for preparing 4-aminodiphenylamine (4-ADPA) or substituted derivatives thereof comprising:

(a) contacting aniline or substituted aniline derivatives and 4-(phenylazo)-diphenylamine or substituted derivatives thereof in the presence of a suitable solvent system, and

(b) reacting the aniline or substituted aniline derivatives and 4-(phenylazo)-diphenylamine or substituted derivatives thereof in the presence of a suitable base and a controlled amount of protic material at a reaction temperature of about 70°C to about 200°C in a confined reaction zone, wherein the molar ratio of protic material to base is 0:1 to about 5:1.

89. The process of Claim 88 further comprising:

(c) reductively alkylating the 4-aminodiphenylamine or substituted derivatives thereof.

90. The process of Claim 63 further comprising:

(c) reductively alkylating the substituted aromatic amine of (b).