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# UNITED STATES PATENT OFFICE

2,411,527

## N-PHOSPHATOARYLENEDIAMINES

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9 Claims. (Cl. 260—461)

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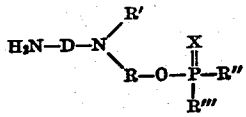
This invention relates to aryl amino compounds and to a process for the preparation thereof, as well as to photographic developing agents comprising such aryl amino compounds. This application is a continuation-in-part of our copending application, Serial No. 301,467, filed October 26, 1939.

It is known that o- and p-phenylenediamines and some of their N-substituted derivatives act as photographic developers. N,N-diethyl-p-phenylenediamine is used as a photographic developing agent in color photography.

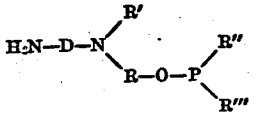
We have now found new phosphato and phosphito derivatives of o- and p-arylenediamines, and have further found that these derivatives are efficacious photographic developers.

It is, accordingly, an object of our invention to provide new arylenediamine derivatives and a process for the preparation thereof. A further object is to provide new photographic developing agents comprising these new derivatives. Other objects will appear hereinafter.

Our new arylenediamine derivatives can be represented by the following general formulas:



and



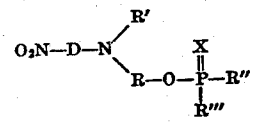
wherein D represents an o- and p-arylene group, e. g. an o- and p-phenylene group, R represents an alkylene group of two or more carbon atoms, e. g., ethylene, propylene, etc., R' represents hydrogen or an alcohol radical, e. g., methyl, ethyl, cyclohexyl, benzyl β-hydroxyethyl, etc., R'' and R''' each represents hydrogen, a hydroxyl group, an alkoxyl group, an alkylthio group or an amino group, and X represents oxygen or sulfur.

The compounds of lower molecular weight are the most efficacious photographic developers, e. g., those in which D represents an o- or p-phenylene group, in which R represents ethylene, in which R' represents hydrogen, methyl, ethyl or β-hydroxyethyl and in which R'' and R''' each represent a hydroxyl group, a methoxyl or ethoxyl group, a methylthio or ethylthio group or an amino group. The p-phenylene compounds are generally superior to the o-phenylene compounds.

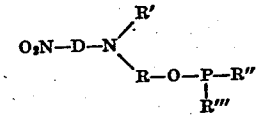
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Of this group of lower molecular weight compounds, the p-phenylene compounds in which R' represents an aliphatic group, e. g., methyl, ethyl or β-hydroxyethyl are especially useful as photographic developers in color photography.

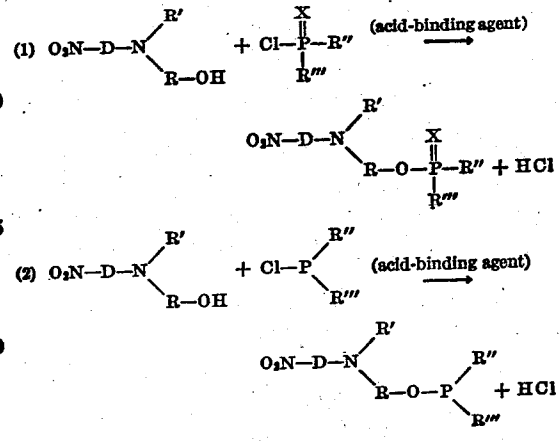
Our new compounds can be prepared by reducing the appropriate nitro compounds, i. e. nitro compounds of the following general formulas:



and



wherein D, R, R', R'', R''' and X have the values given above. Such nitro compounds are prepared by condensing nitro-N-hydroxyalkylarylamines with phosphorous chlorides, in accordance with the following chemical equations:



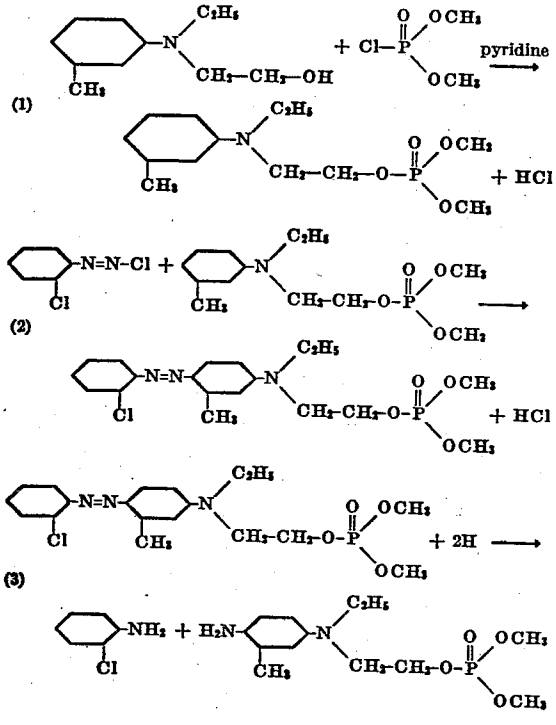
In these equations D, R, R', R'', R''' and X have the values given above.

As acid-binding agents in the above processes, tertiary amines, e. g., pyridine, N-methylpiperidine and dimethylaniline, are advantageously employed. The condensation of the nitro-N-hydroxyalkyl arylamines with the phosphorous chlorides is advantageously effected at about 0° C. Nitro-N-hydroxyalkylarylamines can be prepared by condensing nitrochloroarylhydrocarbons (e. g., p-nitrochlorobenzene, o-nitrochlorobenzene and

4-nitro-1-chloronaphthalene) with hydroxyalkylamines, in accordance with the process described by Kremer—J. Am. Chem. Soc. 61, 1321 (1939). A number of the phosphorous chlorides employed in our invention are well known substances. Dialkyl esters of the monochloride of phosphoric acid can be prepared as described by Wichelhaus—Ann. (suppl.) 6, 264 (1868). Dialkyl esters of the monochloride of dithiophosphoric acid can be similarly prepared employing mercaptans instead of alcohols.

The nitro compounds can be reduced in any advantageous manner. We have found that the reductions are most advantageously accomplished by hydrogenating the nitro compounds in the presence of Raney nickel.

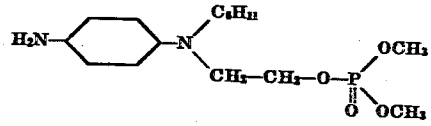
Alternatively our new phenylenediamine derivatives can be prepared as illustrated in the following specific example:




Similarly our other phenylenediamine derivatives can be prepared.

The following examples will serve to illustrate further the manner of obtaining our new compounds. These examples are not intended to limit our invention.

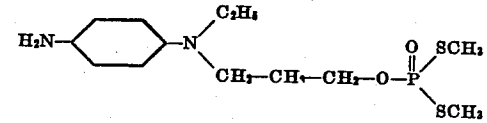
*Example 1.—N-cyclohexyl-N-(β-dimethylphosphatoethyl)-p-phenylenediamine*



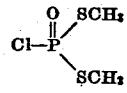
26.4 g. (0.1 mole) of p-nitro-N-(β-hydroxyethyl)-N-cyclohexylaniline were dissolved in 500 cc. of dry pyridine. The mixture was cooled to 0° C. To the cooled mixture were added 21.6 g. (0.15 mole) of the dimethyl ester of the monochloride of phosphoric acid, dropwise with stirring, over a period of one hour. The reaction mixture was stirred for four hours and warmed to 50° to 60° C. over a period of two hours and maintained at that temperature for one hour. The mixture was then treated with an aqueous solution of 0.15 gram-mole of sodium bicarbonate at 0° for several hours. The water and pyridine were then removed from the mixture under reduced pressure and the resulting yellow crystalline compound was washed with water and dried. The yield was nearly quantitative. This yellow crystalline compound, viz. N-cyclohexyl-N-(β-dimethylphosphatoethyl)-p-nitroaniline, was dissolved in 200 cc. of methanol. 2 g. of Raney nickel catalyst were mixed with the solution. The resulting mixture was subjected to hydrogenation at 50° C. under a hydrogen pressure of 1500 pounds. Reduction was complete in about 30 minutes. When cool, the reduction mixture was filtered to remove the nickel, and any desired salt is prepared in the usual manner, viz. by treating the filtered reduction mixture with a molecularly equivalent amount of an acid, e. g. 10 percent sulfuric acid, and concentrating (in vacuo) and chilling until the salt separates out. The free base is not stable in air.



*Example 2.—N-ethyl-N-(γ-dimethyldithiophosphatopropyl)-p-phenylenediamine*

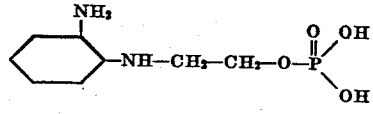


22.4 g. (0.1 mole) of p-nitro-N-ethyl-N-(γ-hydroxypropyl)-aniline were dissolved in 500 cc. of dry pyridine. The mixture was cooled to 0° C. To the cooled mixture was added 28.4 g. (0.15 mole) of the dimethyl ester of the monochloride of dithio phosphoric acid having the formula:



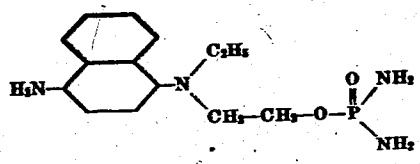
The mixture was worked up as in Example 1 and the resulting product, viz. N-ethyl-N-(γ-dimethyldithiophosphatopropyl)-p-phenylenediamine, was then reduced as in Example 1, and isolated as the sulfate.

*Example 3.—N-(β-phosphatoethyl)-p-phenylenediamine*



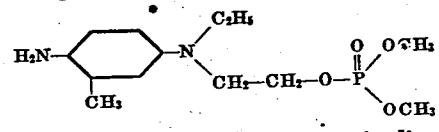
18.2 g. (0.1 mole) of N-(β-hydroxyethyl)-o-nitroaniline were dissolved in 250 cc. of pyridine. The mixture was cooled to 0° C. To the cooled mixture were added 18.2 g. (0.12 mole) of phosphorous oxytrichloride, dropwise with stirring, over a period of one hour. The reaction mixture was stirred for four hours and warmed to 50° to 60° C. over a period of two hours and maintained at that temperature for one hour. The mixture was then treated with an aqueous solution of 0.36 gram-mole of sodium bicarbonate at 0° C. for several hours. The water and pyridine were then removed from the mixture under reduced pressure and the resulting yellow crystalline compound was washed and dried. This yellow crystalline compound, viz. N-(β-phosphatoethyl)-o-nitroaniline, was dissolved in methanol and reduced as in Example 1. The resulting phenylenediamine derivative is unstable in air, but white in color when air is excluded.

*Example 4.—N-ethyl-N-(β-diamidophosphatoethyl)-1,4-naphthalene*



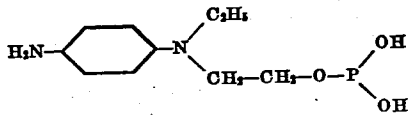
26 g. (0.1 mole) of N-ethyl-N-(β-hydroxyethyl)-1-amino-4-nitronaphthalene were dissolved in 500 cc. of dry pyridine. The mixture was cooled to 0° C. To the cooled mixture were added 17.1 g. (0.15 mole) of chlorophosphoryl diamide (prepared as described in Ann. 326, 236, 1903), dropwise with stirring, over a period of one hour. The reaction mixture was stirred for four hours and warmed to 50° to 60° C. over a period of two hours and maintained at that temperature for one hour. The mixture was then treated with an aqueous solution of 0.15 gram-mole of sodium bicarbonate at 0° C. for several hours. The water and pyridine were then removed from the mixture under reduced pressure and the resulting yellow crystalline compound was washed and dried. This yellow crystalline compound, viz. N-ethyl-(N-β-diamidophosphatoethyl)-1,4-naphthalene was dissolved in methanol and reduced as in Example 1 to give the naphthylenediamine derivative.

*Example 5.—N-ethyl-N-(β-dimethylphosphatoethyl)-1,4-diamino-2-methylbenzene*



27.3 g. (0.1 mole) of N-ethyl-N-(β-dimethylphosphatoethyl)-m-toluidine (prepared from N-ethyl-N-(β-hydroxyethyl)-m-toluidine and the dimethyl ester of the monochloride of phosphoric acid according to the process described in Example 1) were dissolved in 200 cc. of cold acetic acid. To the cold solution were added 0.1 gram-mole of o-chlorobenzene diazonium chloride. The coupling was completed by the addition of sodium bicarbonate. The azo compound was precipitated from the reaction mixture by the addition of water. The precipitated azo compound was filtered off and washed free from acid. The azo compound was dissolved in methanol and hydrogenated in the presence of Raney nickel. The resulting reduction mixture was filtered to remove the nickel. The methanol was removed by distillation under reduced pressure and the residue was steam distilled to remove o-chloroaniline. The residue was treated with sulfuric acid to convert the phenylenediamine derivative to the sulfate which was then recrystallized from water.

*Example 6.—N-ethyl-N-(β-phosphitoethyl)-p-phenylenediamine*



22.1 g. (0.1 mole) of N-ethyl-N-(β-hydroxyethyl)-p-nitroaniline were dissolved in 500 cc. of dry pyridine. The mixture was cooled to 0° C. To the cooled mixture were added 20.6 g. (0.15 mole) of phosphorous trichloride, dropwise with stirring, over a period of one hour. The reaction



mixture was stirred for four hours and warmed to 50° to 60° C. over a period of two hours and maintained at that temperature for one hour. The mixture was then treated with an aqueous solution of 0.45 gram-mole of sodium bicarbonate at 0° C. for several hours. The water and pyridine were then removed from the mixture under reduced pressure and the resulting yellow crystalline compound was washed and dried. This yellow crystalline compound, viz. N-ethyl-N-(β-phosphitoethyl)-p-nitroaniline was reduced as in Example 1 to give the phenylenediamine derivative.

Our new phenylenediamine derivatives can be used to form photographic images by development of exposed silver halide contained in the usual gelatin carrier or in carriers, such as collodion, cellulose esters or resins. Those of our new phenylenediamine derivatives which are especially adapted to use in color photography (see above) can be used to develop visible images from latent images in silver halide emulsions or to develop silver images from silver halide images which are obtained by a so-called reversal process or by rehalogenizing a visible silver image. When employed in connection with color photography, the phenylenediamine derivatives act as developers in the presence of couplers and the oxidation products of the phenylenediamine derivatives, arising from the developing action, couple with the couplers or color-formers to give colored bodies or dyes. When used for the formation of colored photographic images, the phenylenediamine derivatives can be used in conjunction with any well known coupler compounds, such as those described in Fischer U. S. Patent 1,102,028, dated June 30, 1914; Mannes and Godowsky U. S. Patent 2,108,602, dated February 15, 1938; Mannes, Godowsky and Peterson U. S. Patent 2,115,934, dated April 26, 1938; and Mannes, Godowsky and Peterson U. S. Patent 2,126,337, dated August 9, 1938.

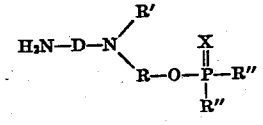
All the phenylenediamine derivatives described herein can be used for the purpose of producing black-and-white images from exposed photographic silver halide emulsions.

Developing solutions comprising our new phenylenediamine derivatives can be made up in the usual manner, using sodium sulfite and sodium carbonate.

The term "alcohol radical," in accordance with customary usage, is intended to mean an organic radical, which corresponds to an alcohol and is derived therefrom by dropping the hydroxyl group, e. g., n-propyl is derived from n-propyl alcohol by dropping the OH group, benzyl is derived from benzyl alcohol by dropping the OH group, and tertiary butyl is derived by dropping the OH group from tertiary butyl alcohol.

We claim:

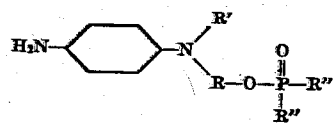
1. A compound characterized by the following general formula:



wherein D represents a member selected from the group consisting of o-arylene and p-arylene groups, R represents an alkylene group having at least two carbon atoms, R′ represent a member selected from the group consisting of hydrogen and alcohol radicals, R″ represents a member selected from the group consisting of hydroxyl

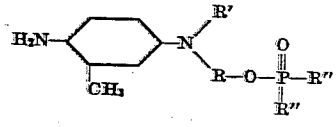
groups, alkoxyl groups, alkylthio groups and amino groups and X represents an atom selected from the group consisting of oxygen and sulfur.

2. A compound of the following general formula:



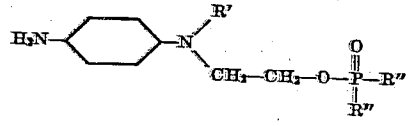
wherein R represents an alkylene group having at least two carbon atoms, R' represents a member selected from the group consisting of hydrogen and alcohol radicals, R'' represents a member selected from the group consisting of hydroxyl groups, alkoxyl groups, alkylthio groups and amino groups.

3. A compound of the following general formula:



wherein R represents an alkylene group having at least two carbon atoms, R' represents a member selected from the group consisting of hydrogen and aliphatic groups, R'' represents a member selected from the group consisting of hydroxyl groups, alkoxyl groups, alkylthio groups and amino groups.

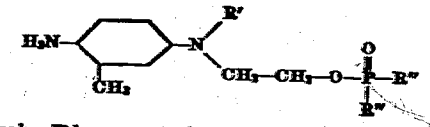
4. A compound of the following general formula:



wherein R' represents an alkyl group and R'' represents a member selected from the group consisting of hydroxyl groups, alkoxyl groups, alkylthio groups and amino groups.

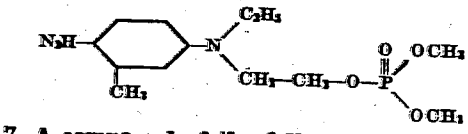


5. A compound of the following general formula:

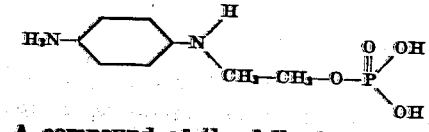


wherein R' represents an alkyl group and R'' represents a member selected from the group consisting of hydroxyl groups, alkoxyl groups, alkylthio groups and amino groups.

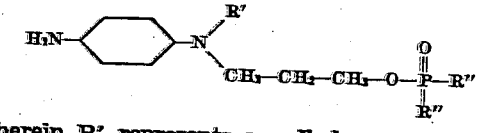
6. A compound of the following formula:



7. A compound of the following formula:

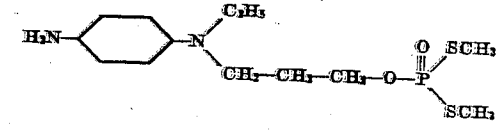


8. A compound of the following general formula:



wherein R' represents an alkyl group and R'' represents a member selected from the group consisting of a hydroxyl group, alkoxyl groups, alkylthio groups and amino groups.

9. A compound of the following formula:



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