Patented May 8, 1951

2,552,241

UNITED STATES PATENT OFFICE

2,552,241

p-PHENYLENEDIAMINES CONTAINING ALKYLACYLAMIDOETHYL OR ALKYLACYLAMIDOETHOXY RING SUBSTITUENTS

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No Drawing. Original application March 6, 1948, Serial No. 13,526. Divided and this application March 18, 1949, Serial No. 82,282

7 Claims. (Cl. 260—556)

1

This invention relates to photographic developers and more particularly to photographic developers containing alkylacylamidoethyl or alkylacylamidoethoxy ring substituents.

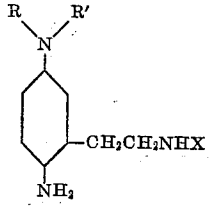
This application is a division of our application Serial No. 13,526, filed March 6, 1948.

It is known that photographic developers of the p-phenylenediamine type are valuable compounds for producing fine grain black and white photographic images and also that these compounds, especially when they contain alkyl substituents on one of the nitrogen atoms, are useful as developers in producing colored photographic images. A serious disadvantage of the p-phenylenediamine developers is that they are highly allergenic, that is, they are poisonous to the human skin and are therefore somewhat dangerous to use.

The allergenic properties of the p-phenylenediamine developers may be overcome by substituting a sulfonamide group or an amino sulfonyl group in the alkyl group on the nitrogen atom of p-phenylenediamine as described in Weissberger U. S. Patent 2,193,015, granted March 12, 1940. These substituted p-phenylenediamine developers, however, are sometimes too low in developing strength (or reduction potential) so that it is difficult to obtain, with them, dye images of sufficiently high density and contrast.

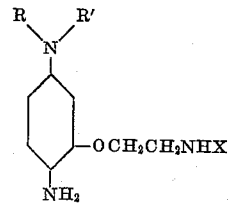
It is therefore an object of the present invention to provide a new class of photographic developing agents of the p-phenylenediamine type. A further object is to provide developing agents of the p-phenylenediamine type which produce dye images having the desired characteristics.

These objects are accomplished by the present invention by the use as developing agents of compounds of the following general formulas:



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and

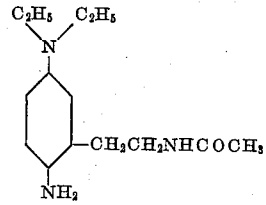


where R is a lower alkyl group such as methyl, ethyl or propyl, R' is a lower alkyl group, X is the substituted acyl group —SO_2R'' or —COR'' and R'' is a lower alkyl group.

By "lower alkyl" group, we mean a methyl, ethyl or propyl group.

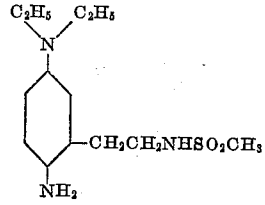
Compounds of this class which may be used according to our invention are as follows:

1



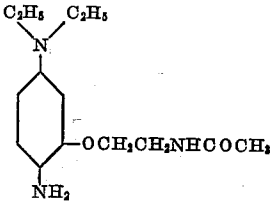
3-(β-acetamidoethyl)-4-amino-N,N-diethylaniline

2

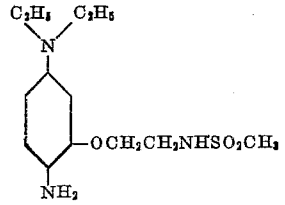


4-amino-N,N-diethyl-3-(β-methyl-sulfonamidoethyl)-aniline

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3-(β-acetamidoethoxy)-4-amino-N,N-diethylaniline



4-amino-N,N-diethyl-3-(β-methylsulfonamidoethoxy)-aniline

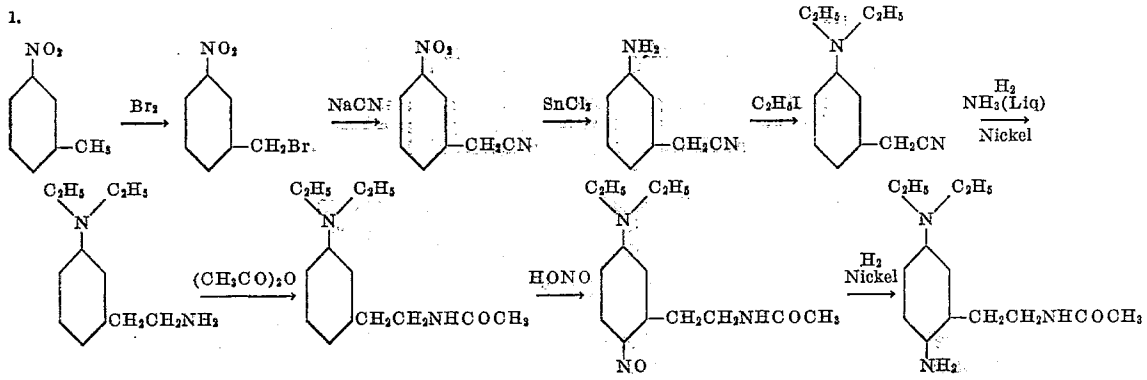
The preparation of our developers may be summarized by the following reaction schemes:

The specific compounds illustrated above were prepared as follows:

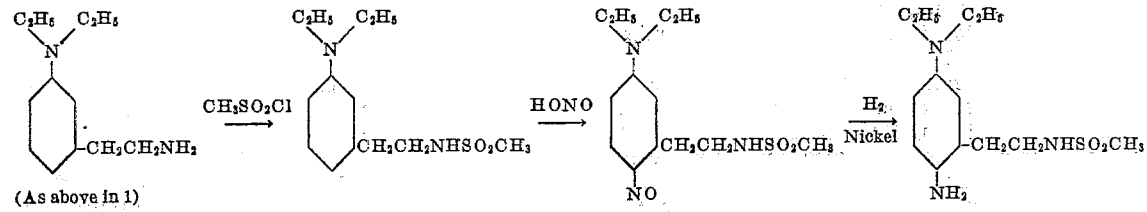
1. 3 - (β - acetamidoethyl) - 4 - amino – N,N-diethylaniline was prepared from 3-nitrotoluene by the following series of reactions.

a. 3-nitrobenzyl bromide.—3-nitrotoluene (5 moles) was heated at 135±5° and bromine (5 moles) was dropped in during a period of 5 hours. During this time the reaction mixture was exposed to the light of a 200 w. clear bulb. The reaction mixture was cooled, dissolved in ether and the ether was dried over anhydrous

1.

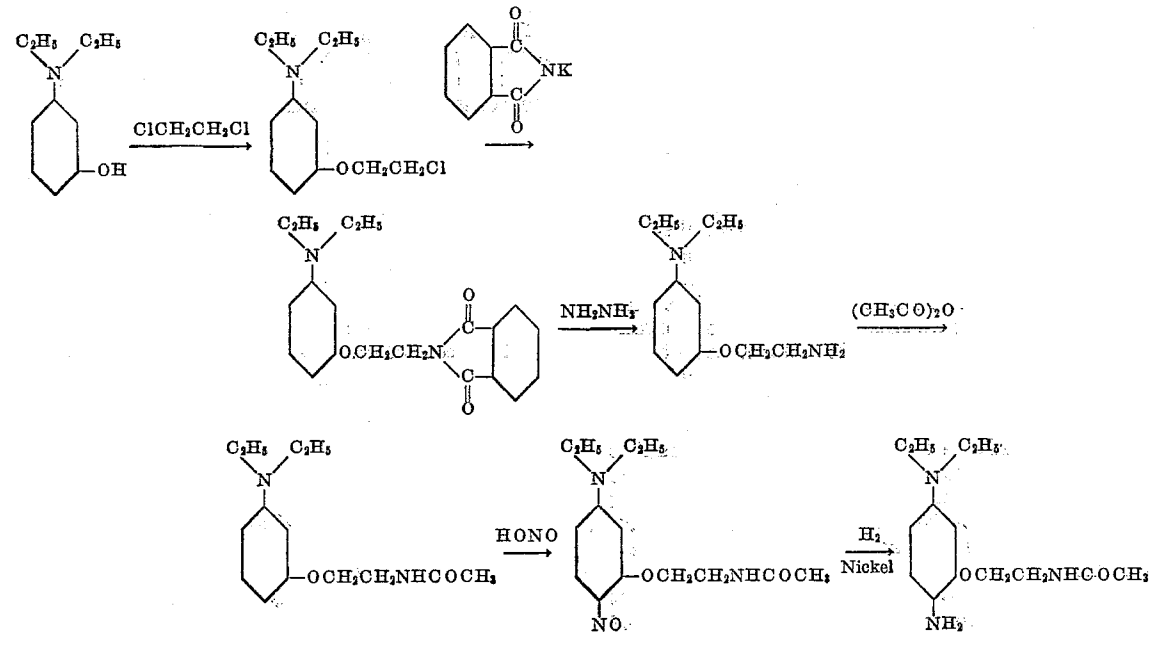


2.

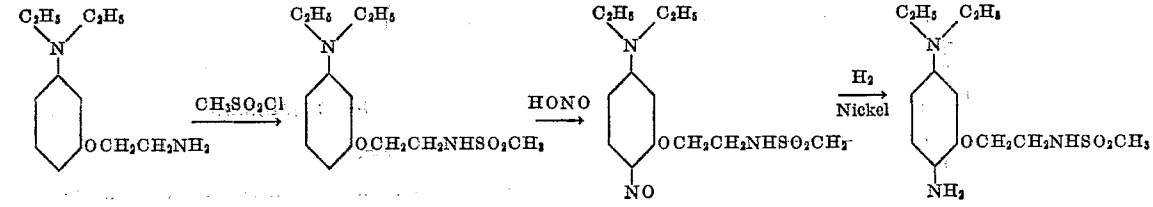


(As above in 1)

3.



4.



sodium sulfate. The ether was evaporated and the residue was distilled under reduced pressure collecting the fraction that boiled at 120–150°/2 mm. This crude product was redistilled under reduced pressure collecting the portion that boiled at 160–162°/14 mm. This redistilled material was recrystallized from methanol and dried in air. Melting point 58–59°.

b. 3-nitrophenylacetonitrile.—Sodium cyanide (1.0 mole) was dissolved in 80 ml. of water. Alcohol (280 ml.) was added and the mixture was cooled to 20°. 3-nitrobenzyl bromide (0.8 mole) was added and the mixture was stirred and warmed slowly to 40°. At this temperature the heating was stopped and the exothermic reaction allowed to proceed. The temperature was not allowed to rise above 60–65°. After the spontaneous reaction was over, the reaction mixture was boiled for 1 hour. The alcohol was removed under reduced pressure and the residue was dissolved in 250 ml. of water plus 300 ml. of ether. The layers were separated, and the ether layer was washed with water and dried over anhydrous sodium sulfate. The ether was evaporated and the residue was distilled under reduced pressure collecting the fraction that boiled at 160–165°/3 mm. The product was recrystallized from methanol. Melting point 61–62°.

c. 3 - aminophenylacetonitrile. — 3 - nitrophenylacetonitrile (0.9 mole) was added to a solution of stannous chloride (2.7 moles) in concentrated hydrochloric acid (700 ml.). The temperature of the reaction mixture was maintained at 35–40°, by cooling, until the exothermic reaction subsided. After stirring for 2 hours, the solution was made alkaline with 2 l. of 40 per cent sodium hydroxide solution. This mixture was diluted with 1 l. of water and the product extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulfate and the ether was evaporated. The residue was distilled under reduced pressure collecting the fraction that boiled at 132–135°/2 mm.

d. 3-(N,N-diethylamino) phenylacetonitrile.— A mixture of 3-amino-phenylacetonitrile (0.75 mole), alcohol (400 ml.), sodium carbonate (1.0 mole), water (100 ml.) and ethyl iodide (1.8 moles) was boiled under reflux for 6 hours. The alcohol was removed under reduced pressure and the residue was dissolved in a mixture of water (500 ml.) and ether (500 ml.). The ether layer was separated, washed with water and dried over anhydrous sodium sulfate. The ether was evaporated and the residue was distilled under reduced pressure collecting the fraction that boiled at 125–130°/2 mm.

e. 3 - (β - aminoethyl) - N,N-diethylaniline.— 3 - (N,N - diethylamino) -phenylacetonitrile (0.66 mole) was placed in a high pressure reduction apparatus with liquid ammonia (250 ml.) and methanol (150 ml.) and hydrogenated at 110° in the presence of Raney nickel (10 g.) and a hydrogen pressure of 1500 lbs./in.^{2}. The product was distilled under reduced pressure collecting the fraction that boiled at 148–150°/10 mm.

f. 3 - (β - acetamidoethyl) - 4 - amino - N,N-diethylaniline.—3 - (β - amino - ethyl) - N,N-diethylaniline (0.39 mole) was added with stirring and cooling to 40 ml. of acetic anhydride. The mixture was kept below a temperature of 50° during the addition and then was heated on the steam bath for 30 minutes. After cooling, the solution was stirred with 400 ml. of water until the excess acetic anhydride had decomposed. The solution was made acid with 100 ml. of concentrated hydrochloric acid, cooled to 0°, and nitrosated by the addition of a solution of 28 g. of sodium nitrite in 50 ml. of water. The nitrite was added during a period of 1 hour. Stirring was continued for 1 hour longer at 0°. This solution was further acidified by the addition of 80 ml. of concentrated hydrochloric acid and the nitroso compound was reduced with 65 g. of zinc dust. The zinc dust was added in portions, with stirring, while the temperature of the reaction mixture was maintained at 15±5°. The excess zinc dust was filtered off and the solution was made alkaline with 400 ml. of ammonium hydroxide. The diamine was extracted with 600 ml. of chloroform. The chloroform solution was washed with water and dried over anhydrous sodium sulfate. The chloroform was removed under reduced pressure and the diamine was distilled under reduced pressure. The portion that boiled at 190–195° at 1 mm. was collected as the desired product.

2. 4 - amino-N,N-diethyl - 3 - (β-methylsulfonamidoethyl) aniline was prepared from 3-(β-aminoethyl)-N,N-diethylaniline by the following method.

A mixture of 3-(β-aminoethyl)-N,N-diethylaniline (0.36 mole) and water (150 ml.) was cooled to 15° and stirred vigorously while methanesulfonyl chloride (0.41 mole) was dropped in during the course of 30 minutes. After each fifth of the methanesulfonyl chloride had been added, one-fifth of a solution of sodium hydroxide (0.41 mole) in water (50 ml.) was added. The temperature was held at 15–20° throughout the addition. The mixture was stirred for 2 hours at room temperature and then extracted with chloroform. The chloroform solution was washed with water, dried over anhydrous sodium sulfate and the chloroform was evaporated under reduced pressure. The residue was dissolved in a mixture of 100 ml. of concentrated hydrochloric acid and 400 ml. of water, and nitrosated at 0° by the addition of 22.5 g. of solid sodium nitrite during a period of 1 hour. The mixture was stirred for 1 hour at 0–5° and then made alkaline with ammonium hydroxide. The mixture was stirred thoroughly and the aqueous portion was decanted from the gummy product. The gum was washed with water and dissolved in a mixture of 166 ml. of concentrated hydrochloric acid and 400 ml. of water. This mixture was cooled to 15° and zinc dust (1 mole) was added in portions with stirring, keeping the temperature below 20°. The excess zinc was removed by filtration and the filtrate made alkaline with ammonium hydroxide. The diamine was extracted with chloroform. The chloroform solution was washed with water, dried over anhydrous sodium sulfate and the chloroform was removed under reduced pressure. The residue was distilled under reduced pressure. The fraction that boiled at 215°–220°/1 mm. was collected as pure product.

3. 3 - (β-acetamidoethoxy) - 4 - amino-N,N-diethylaniline was prepared by the following series of reactions.

a. 3 - (β-chloroethoxy)-N,N-diethylaniline.—A solution of 80 g. of sodium hydroxide in 2 l. of water was placed in a flask and melted 3-(N,N-diethylamino) phenol (3 moles) was added and the mixture was heated on a steam bath for 19 hours with stirring. At the end of this period the mixture was cooled and 115 ml. of 40% sodium hydroxide solution was stirred in. The solution was extracted twice with ether. The

ether solution was washed with water, dried over anhydrous sodium sulfate and the ether was evaporated. The residue was distilled under reduced pressure. The product boiled at 125–135° at 2 mm.

b. N,N - diethyl-3-(β-phthalimidoethoxy) aniline.—A mixture of 3-(β-chloroethoxy)-N,N-diethylaniline (1.07 moles), potassium phthalate (1.07 moles) and diethyleneglycol (2 l.) was stirred slowly and heated at 140–150° for 5 hours. The solution was poured into 1 l. of cold water and allowed to stand for 10–12 hours at 0°. The precipitate was removed by filtration, washed with alcohol and recrystallized from a mixture of 850 ml. of 3A and 760 ml. of ethylacetate. The product melted at 127–129°.

c. 3 - (β-aminoethoxy)-N,N-diethylaniline.—A mixture of N,N-diethyl-3-(β-phthalimidoethoxy) aniline (0.43 mole), 85% hydrazine (0.43 mole) and 300 ml. of alcohol was boiled under reflux for 30 minutes. The mixture was cooled somewhat and 140 ml. of concentrated hydrochloric acid was added. The mixture was then boiled under reflux for 30 minutes, cooled and diluted with 750 ml. of water. The hydrazide was filtered off and the filtrate was concentrated under reduced pressure until the alcohol had been removed. The residue was made alkaline with ammonium hydroxide. The amine was extracted with ether. The ether solution was dried over anhydrous sodium sulfate and the ether was evaporated. The residue was distilled under reduced pressure. The product boiled at 135–142° at 2 mm.

d. 3 - (β - acetamidoethoxy) - N,N - diethylaniline.—3 - (β - aminoethoxy) - N,N-diethylaniline (0.07) was added to 15 ml. of acetic anhydride and the solution was heated on a steam bath for 30 minutes. The solution was stirred with 70 ml. of water until the excess anhydride had decomposed and then was concentrated to a thick syrup under reduced pressure. The syrup was dissolved in 150 ml. of boiling ligroin. The ligroin solution was filtered while still hot and allowed to cool. The crystals were removed by filtration and dried in air. Melting point 66.5–67°.

e. 3-(β-acetamidoethoxy)-N,N-diethyl-4-nitrosoaniline.—3 - (β - acetamidoethoxy)-N,N-diethylaniline (0.07 mole) was dissolved in 140 ml. of water and 21 ml. of concentrated hydrochloric acid. The solution was cooled to 0° and nitrosated with a solution of 5.0 g. of sodium nitrite in 35 ml. of water. After standing at 0° for 20 minutes the reaction mixture was made alkaline with ammonium hydroxide and the nitroso compound was extracted with chloroform. The chloroform solution was dried over anhydrous sodium sulfate and then the chloroform was removed under reduced pressure keeping the temperature of the nitroso compound at 20–25°. The nitroso compound after recrystallized from benzene melted at 124–124.5°.

f. 3-(β-acetamidoethoxy)-4-amino-N,N-diethylaniline.—3 - (β-acetamidoethoxy)-N,N-diethyl-4-nitrosoaniline (0.06 mole) and 50 ml. of absolute alcohol were placed in a Parr hydrogenation apparatus and reduced in the presence of Raney nickel at a temperature of 60° and a hydrogen pressure of 3 atmospheres. The catalyst was removed by filtration and the alcohol was evaporated under reduced pressure. The residue was distilled under reduced pressure. The portion that boiled at 112–114° at 1 mm. was diluted with 25 ml. of petroleum ether. After standing at 0° for 16 hours, the product was filtered off and dried in a vacuum desiccator. Melting point 50–51°.

4. 4 - amino - N,N - diethyl-3-(β-methylsulfonamidoethoxy)-aniline was prepared from 3-(β-aminoethoxy)-N,N-diethylaniline by the following method:

a. N,N - diethyl - 3 - (β-methylsulfonamidoethoxy) aniline.—A mixture of 3-(β-aminoethoxy)-N,N-diethylaniline (0.1 mole) and 40 ml. of water was cooled to 15–20° and stirred while 9 ml. of methanesulfonyl chloride was added slowly. After each quarter of the acid chloride had been added, one-fourth of a solution of 4.5 g. of sodium hydroxide in 15 ml. of water was added. The temperature of the reaction mixture was maintained at 15–20° during the reaction. After stirring at 20° for two hours, the precipitate was removed by filtration and recrystallized from 110 ml. of 45% aqueous alcohol. After drying in air, the product melted at 70–72°.

b. N,N - diethyl - 3 - (β-methylsulfonamidoethoxy)-4-nitrosoaniline.—A solution of N,N-diethyl-3-(β-methylsulfonamidoethoxy) aniline (0.058 mole) in 50 ml. of water and 17 ml. of concentrated hydrochloric acid was cooled to 0° and nitrosated by the addition of a solution of 4.1 g. of sodium nitrite in 15 ml. of water. The solution was stirred at 0° for 20 minutes, diluted with 50 ml. of water and made alkaline with ammonium hydroxide. The precipitate was removed by filtration and recrystallized from 100 ml. of 50% aqueous alcohol. The product was dried in air.

c. 4 - amino - N,N - diethyl-3-(β-methylsulfonamidoethoxy) aniline.—N,N-diethyl-3-(β-methylsulfonamidoethoxy) - 4 - nitrosoaniline (0.0365 mole) and 75 ml. of absolute alcohol were placed in a Parr hydrogenation apparatus and reduced in the presence of Raney nickel at a temperature of 60° and a hydrogen pressure of 3 atmospheres. The catalyst was removed by filtration and the filtrate was concentrated to a syrup under reduced pressure. The residue was recrystallized from aqueous alcohol. The product, dried in a vacum desiccator, melted at 89–91°.

When used for the formation of colored photographic images, the developers of our invention may be used in conjunction with any well-known coupler compounds such as those described in Fisher U. S. Patent 1,102,028, granted June 30, 1914, Mannes and Godowsky U. S. Patent 2,108,602, granted February 15, 1938, or Mannes, Godowsky and Peterson U. S. Patents 2,115,394, granted April 26, 1938, and 2,126,337, granted August 9, 1938.

The following example illustrates a developing solution which may be used according to our invention.

A

4 - amino-N,N-diethyl -3 -(β-methylsulfonamidoethyl aniline	grams	2.5
Sodium sulfite	do	2
Sodium carbonate	do	30
Potassium bromide	do	2
Water to 1 liter		

B

Coupler (o-phenylphenol)	do	2
Sodium hydroxide (10% solution)	cc	20

For use, B is added to A.

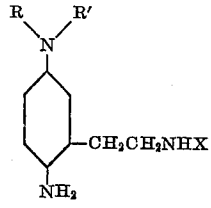
The developing agents described in the present application may be used to form photographic images by development of exposed silver halide contained in the usual gelatin carrier or in carriers such as collodion, water-permeable cellulose

ester or water-permeable synthetic resins. Our developing agents may be used with photographic films containing the coupler in the emulsion layer as described in Mannes and Godowsky U. S. Patent 2,304,940, granted December 15, 1942, or Jelley and Vittum U. S. Patent 2,322,027, granted June 15, 1943. When used in this way, a developing solution similar in composition to Part A in the above example is suitable.

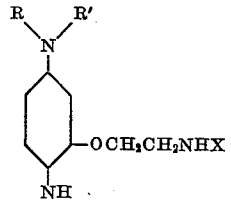
It will be understood that the examples included herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. An amino compound having a formula of the class consisting of

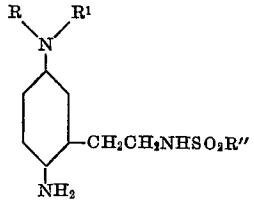


and



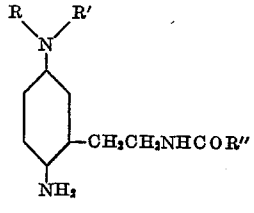
where R and R′ are lower alkyl groups, X is selected from the class consisting of —SO_2R'' and —COR″ groups, and R″ is a lower alkyl group.

2. An amino compound having the formula



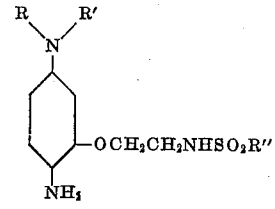
where R, R′ and R″ are lower alkyl groups.

3. An amino compound having the formula



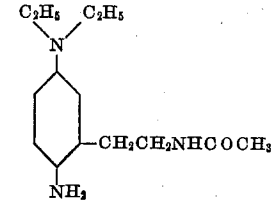
where R, R′ and R″ are lower alkyl groups.

4. An amino compound having the formula

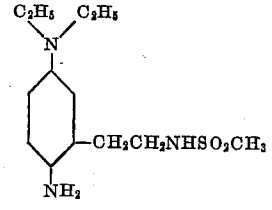


where R, R′ and R″ are lower alkyl groups.

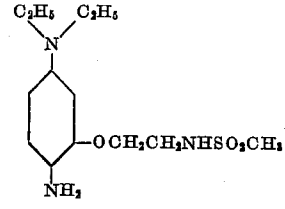
5. An amino compound having the formula



6. An amino compound having the formula



7. An amino compound having the formula



ARNOLD WEISSBERGER.
DUDLEY B. GLASS.
PAUL W. VITTUM.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,193,015	Weissberger	Mar. 12, 1940
2,304,953	Peterson	Dec. 15, 1942

FOREIGN PATENTS

Number	Country	Date
294,085	Germany	Sept. 13, 1916