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UNITED STATES PATENT OFFICE

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8-ALKYL SULFONAMIDOETHYL-N-SUBSTITUTED SATURATED HETEROCYCLIC DEVELOPERS

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4 Claims. (Cl. 95—88)

1

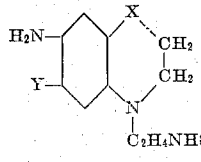
This invention relates to photographic developers and more particularly to saturated heterocyclic developers containing a β-alkylsulfonamidoethyl group on the nitrogen atom of the heterocyclic ring.

It is known that photographic developers of the p-phenylene diamine 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-phenylene diamine 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-phenylene diamine developers may be overcome by substituting a sulfonamide group or an amino sulfonyl group in the alkyl group on the nitrogen atom of p-phenylene diamine as described in Weissberger U. S. Patent 2,193,015, granted March 12, 1940. These substituted p-phenylene diamine developers, however, are sometimes too low in developing strength (or reduction potential) so that it is difficult to obtain with them black and white or 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. A further object is to provide developing agents which produce coupled dye images having the desired characteristics.

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

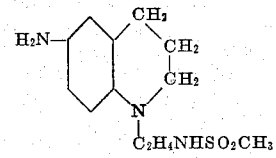


where X represents —CH_2— or a single chemical bond, Y represents hydrogen or a methyl group and R represents a lower alkyl group. By "lower alkyl" group, we mean a methyl, ethyl or propyl group.

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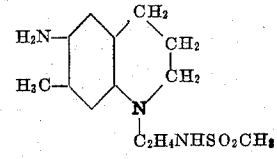
Compounds of this class which may be used according to our invention are as follows:

1



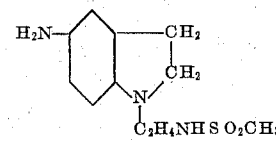
6-amino-1-(β-methylsulfonamidoethyl)-1,2,3,4-tetrahydroquinoline

2



6-amino-7-methyl-1-(β-methylsulfonamidoethyl)-1,2,3,4-tetrahydroquinoline

3



5-amino-1-(β-methylsulfonamidoethyl)-2,3-dihydroindole

The specific compounds illustrated above were prepared as follows:

β-Methylsulfonamidoethyl bromide

$$CH_3SO_2Cl + H_2NC_2H_4Br.HBR + 2NaOH \rightarrow CH_3SO_2NHC_2H_4Br + NaBr + NaCl + 2H_2O$$

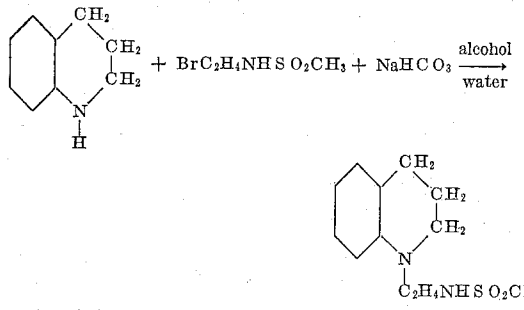
The β-bromoethylamine hydrobromide (Heilbron I (1943), p. 294) (513 g.; 2.5 moles) was dissolved in 250 cc. of water in a 3-l. 3-necked flask equipped with a stirrer, thermometer and two dropping funnels. Through the latter were added 343.8 g. (3.0 moles) of methane sulfonyl chloride and 220 g. of sodium hydroxide in 800 cc. of water keeping the temperature at 0–5° and the pH slightly on the alkaline side.

The reaction mixture was stirred for one hour longer, then it was made acid to Congo red by adding 6.5 cc. of concentrated hydrochloric acid. The crystals were collected at 0° on an 18-cm. Büchner funnel and washed quickly with 200 cc. of cold water. The filtrate was extracted with two 500-cc. portions of ether and the moist crystals were taken up in 2 l. of ether. The ether layers were combined, dried over anhydrous so-

dium sulfate and cooled to 20°. When crystallization started, the mixture was diluted with 2 l. of petroleum ether (B. P. 30–35°).

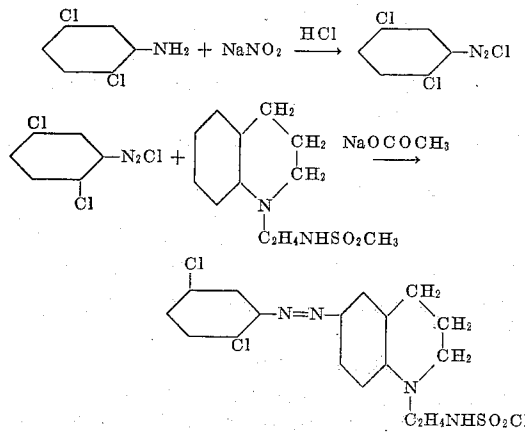
After chilling at 5° for one-half hour, the crystals were collected on a Büchner funnel and dried in air overnight. The yield was 371 g. (73.5%) of glistening white plates melting at 47–49°.

1-(β-Methylsulfonamidoethyl)-1,2,3,4-tetrahydroquinoline



A mixture of 51 g. (0.384 mole) of 1,2,3,4-tetrahydroquinoline, 77.5 g. (0.384 mole) of β-methylsulfonamidoethyl bromide, 35.4 g. (0.422 mole) of sodium bicarbonate, 65 cc. of water and 180 cc. of 95% alcohol was heated on a steam bath at reflux in a 1-l. round-bottomed flask for 16 hours.

The reaction mixture was concentrated under a vacuum on the steam bath until all of the alcohol and some of the water had been removed. The residue was partitioned between 50 cc of water and 200 cc. of ether. The aqueous layer was extracted with two 25-cc. portions of ether and the combined ether solutions were dried over sodium sulfate. The ether was removed on a steam bath, finally at 6 mm. for one-half hour. The residue weighed 91.4 g. (93.7%), crystallized on standing and melted at 45–48°.



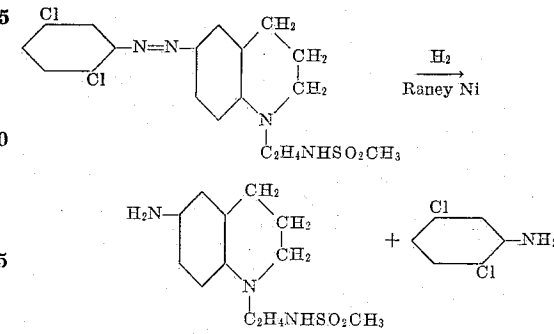
The 2,5-dichloroaniline (35.9 g.; 0.221 mole) was dissolved in 100 cc. of concentrated hydrochloric acid and 400 cc. of water by heating on a steam bath. This solution was poured with stirring into 100 cc. more concentrated hydrochloric acid and the mixture was stirred while cooling to 5°. To this suspension of fine crystals was added 16.5 g. (0.24 mole) of sodium nitrite in 50 cc. of water over a period of one minute. After stirring at 0–5° for 15 minutes, 1.0 g. of sulfamic acid was added. After 5 minutes longer the diazonium solution was poured with stirring into a solution of 56.1 g. (0.221 mole) of 1-(β-methylsulfonamidoethyl)-1,2,3,4-tetrahydroquinoline in 60 cc. of concentrated hydrochloric acid and 100 cc. of water at 5°. Four successive 100-g. portions of anhydrous sodium acetate were added. The thick tarry precipitate was worked with a stirring rod for a few minutes and then chilled in the ice bath for 1½ hours.

The liquid phase was decanted and the residue was stirred mechanically with 1500 cc. of 95% ethanol while heating on the steam bath for 15 minutes. The tarry material crystallized but did not all dissolve. After chilling in the refrigerator overnight the solid was collected on an 18-cm. Büchner funnel and most of the solvent was removed. The solid was dissolved in 2500 cc. of boiling 95% alcohol, the solution was filtered and the filtrate chilled for 3 days at 0° although this time may be shortened.

The hard, granular red crystals were collected, washed with 100 cc. of 95% alcohol and dried in the steam cabinet. The yield was 72 g. (76.2%), M. P. 149–150° (softening at 147°). The filtrate was diluted with 1500 cc. of water and chilled overnight giving 6.0 g. more, M. P. 146–149° which was satisfactory for use.

The total yield was 78 g. (82.5%).

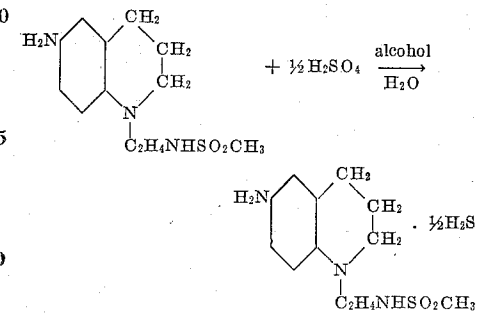
6-amino-1-(β-methylsulfonamidoethyl)-1,2,3,4 tetrahydroquinoline



Seventy-two grams (0.168 mole) of 6-(2,5-dichlorophenylazo)-1-(β-methylsulfonamidoethyl)-1,2,3,4-tetrahydroquinoline, 100 cc. of absolute alcohol, a liberal amount of Raney nickel catalyst and 1.0 g. of sodium carbonate were placed in the small hydrogenation apparatus and reduction was effected at 80° and 50 pounds per square inch pressure.

The reaction mixture was filtered and the catalyst was washed with 25 cc. of absolute alcohol. The filtrate was concentrated on a steam bath under a vacuum using a 3-l. round-bottomed flask. The residual oil was heated at reflux with 1-l. of benzene for 15 minutes and filtered from a little insoluble tar. The filtrate was cooled and the inside of the flask was scratched. After standing overnight, the tan crystals were collected on a Büchner funnel and dried in air. The yield was 32 g. (71%), M. P. 110–112°.

6-amino-1-(β-methylsulfonamidoethyl)-1,2,3,4-tetrahydroquinoline hemisulfate

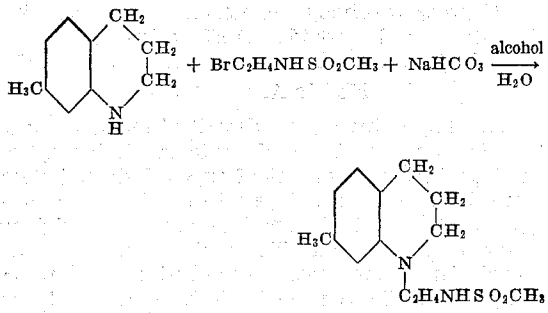


6-amino-1-(β-methylsulfonamidoethyl)-1,2,3,-4-tetrahydroquinoline (26.9 g.; 0.1 mole) was dissolved in 400 cc. of hot 95% alcohol and a solu-

tion of 2.8 cc. (0.05 mole) of concentrated sulfuric acid in 20 cc. of water was added rapidly with mixing. The resulting solution deposited crystals in a few seconds while still hot. The mixture was chilled to 5° for ½ hour. The crystals were collected on a Büchner funnel, washed with two 50-cc. portions of 95% alcohol and 100 cc. of ether.

After drying in a vacuum desiccator over sulfuric acid, the pinkish-white crystals weighed 29.0 g. (91.2%) and melted at 179–182°.

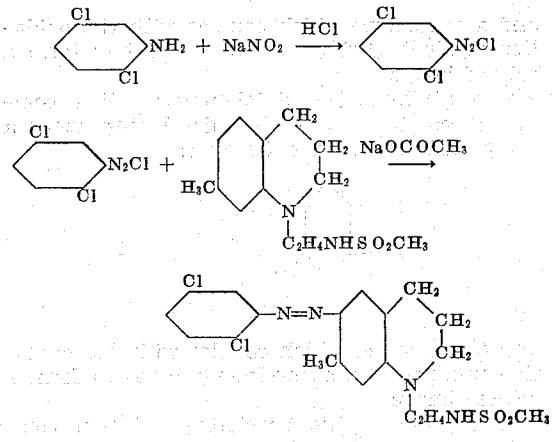
7-methyl-1-(β-methylsulfonamidoethyl) - 1,2,3,-4-tetrahydroquinoline



A mixture of 22.1 g. (0.15 mole) of 7-methyl-1,-2,3,4-tetrahydroquinoline, 30.3 g. (0.15 mole) of β-methylsulfonamidoethyl bromide, 13.9 g. (0.165 mole) of sodium bicarbonate, 25 cc. of water and 70 cc. of 95% alcohol was treated at reflux in a 500-cc. flask for 2 hours.

The reaction mixture was concentrated under a vacuum on the steam bath until most of the water was removed. The residue was partitioned between 100 cc. of chloroform and 100 cc. of water. The aqueous layer was extracted with 50 cc. of chloroform and the combined extracts were dried over magnesium sulfate. Concentration gave 37 g. of an oil which was fractionally distilled. The main fraction, boiling at 210–225°/1.5 mm., nearly all at 223°/1.5 mm., weighed 22.8 g. (57%).

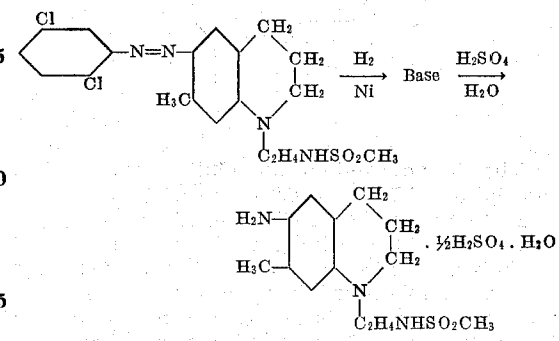
6 - (2,5 - dichlorophenylazo) - 7 - methyl - 1-(β-methylsulfonamidoethyl) - 1,2,3,4 - tetrahydroquinoline



The diazonium solution was added slowly to 22.1 g. (0.0825 mole) of 7-methyl-1-(β-methylsulfonamidoethyl) 1,2,3,4-tetrahydroquinoline in 25 cc. of concentrated hydrochloric acid and 500 cc. of water at 0–5°. When about half of the diazonium solution had been added the reaction mixture thickened. One hundred grams of sodium acetate was added, followed by the rest of the diazonium solution and 100 g. more of sodium acetate.

After 2 hours at 0°, the dye was collected and washed with three 200-cc. portions of cold water. After drying in the steam cabinet the dye weighed 30 g. but was somewhat tacky. The material was dissolved in 2-l. of hot 90% alcohol and kept overnight at 0°. The beautiful fine red crystals were collected and washed with 50 cc. of alcohol. The yield was 11.1 g. (30.5%), M. P. 183–184°.

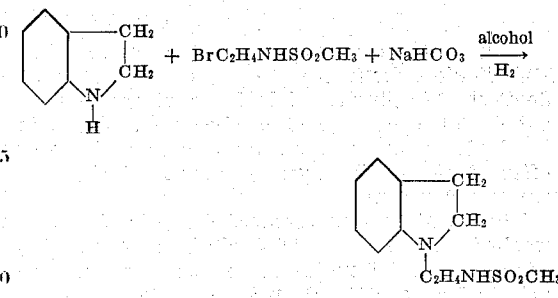
6-amino-7-methyl - 1 - (β - methylsulfonamidoethyl) - 1,2,3,4-tetrahydroquinoline hemisulfate hydrate



Two and two-tenths grams (0.005 mole) of 6-(2,5-dichlorophenylazo)-7-methyl-1 - (β-methylsulfonamidoethyl) -1,2,3,4-tetrahydroquinoline, 20 cc. of absolute ethanol, a liberal amount of Raney nickel catalyst and a little sodium carbonate were placed in a hydrogenation apparatus and redution was effected at 80° and 50 pounds per square inch pressure.

The reaction mixture was filtered and the apparatus washed with 5 cc. of absolute ethanol. A solution of 0.14 cc. (0.0025 mole) of concentrated sulfuric acid in 1 cc. of water was added. After cooling in an ice bath for one-half hour the crystalline precipitate was collected and washed with two 5-cc. portions of cold alcohol. After drying in a vacuum desiccator over sulfuric acid the pure white crystals weighed 1.25 g. (71.4%) and analysis identified the material as the hemisulfate hydrate.

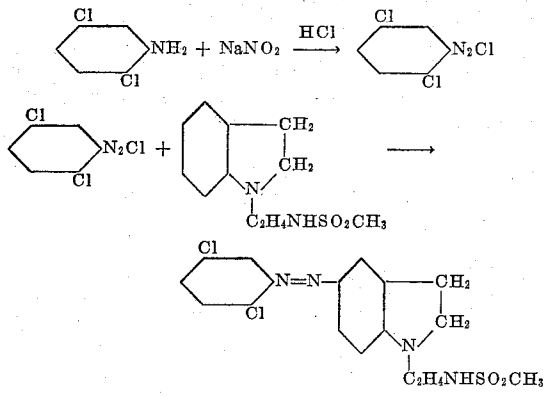
1-(β-methylsulfonamidoethyl) -2,3-dihydroindole



A mixture of 4.8 g. (0.04 mole) of 2,3-dihydroindole, 8.1 g. (0.04 mole) of β-methylsulfonamidoethyl bromide, 3.7 g. (0.044 mole) of sodium bicarbonate, 7.5 cc. of water and 20 cc. of 95% alcohol was heated at reflux on the steam bath for 1 hour.

The reaction mixture was concentrated under a vacuum on a steam bath to an oil. The oil was separated between 25 cc. of water and 25 cc. of ether. The aqueous layer was extracted with 25 cc. of ether and the combined extracts were dried over sodium sulfate, concentrated and distilled. The main fraction was 7.3 g. (76%) boiling at 216–219°/1.5 mm. Hg.

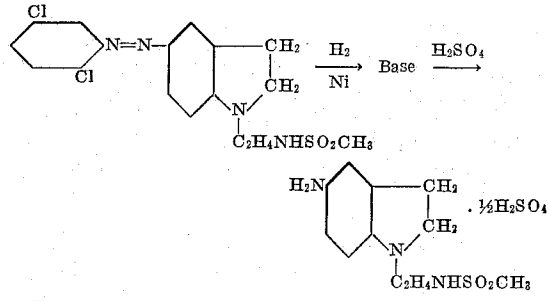
5 - (2,5 - dichlorophenylazo) -1- (β-methylsulfonamidoethyl) -2,3-dihydroindole



The clear diazonium salt solution was added to a solution of 7.0 g. (0.029 mole) of 1-(β-methylsulfonamidoethyl)-2,3-dihydroindole in 15 cc. of concentrated hydrochloric acid and 25 cc. of water at 0–5° with shaking. In a few minutes crystals formed and solidified the reaction mixture. After chilling in an ice bath for one-half hour, the crystals were collected and drawn to a dense cake. The moist product was dissolved in 200 cc. of acetone and 50 cc. of water on a steam bath and the solution chilled.

The crystals were collected, washed with two 25-cc. portions of acetone and dried in a steam cabinet. The yield was 8.1 g. (65.3%) of purple needles with a copper luster which melted at 145–147°.

5-amino-1-(β-methylsulfonamidoethyl) -2,3-dihydroindole hemisulfate



Four and one-tenth grams (0.01 mole) of 5-(2,5-dichlorophenylazo)-1-(β-methylsulfonamidoethyl)-2,3-dihydroindole, 50 cc. of absolute alcohol and Raney nickel catalyst were placed in the hydrogenation apparatus and reduction was effected at 70°, 40 pounds per square inch pressure in 10 minutes.

The catalyst was removed by filtration and washed with 5 cc. of 95% alcohol. A solution of 0.28 cc. (0.005 mole) of concentrated sulfuric acid in 5 cc. of 95% alcohol was added.

The slurry was chilled overnight and the solid was collected and washed with 10 cc. of 95% alcohol followed by 5 cc. of 95% alcohol, then two 5-cc. portions of acetone. After drying in the steam cabinet 1.9 g. (63%) of pure white product was obtained. Analysis indicated the compound to be 5-amino-1-(β-methylsulfonamidoethyl)-2,3-dihydroindole hemisulfate.

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 Fischer 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 and Godowsky and Peterson U. S. Patent 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. 6 - Amino-1-(β-methylsulfonamidoethyl) - 1,2,3,4-tetrahydroquinoline	grams	2.5
Sodium sulfite (anhydrous)	grams	2
Sodium carbonate	grams	30
Potassium bromide	grams	2
Water to 1 liter		
B. Coupler (o-phenyl phenol)	grams	2
Sodium hydroxide (10% solution)	cc.	20

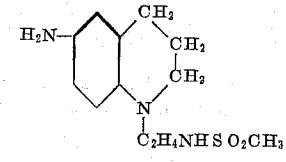
For use, B is added to A.

The developing agents described in the present application may be used to form photographic images, the 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, the developing solution of 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.

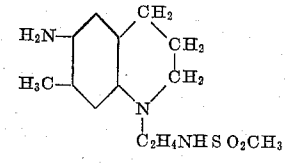
We claim:

1. A photographic developing solution comprising as the silver halide developing agent a compound having the formula:



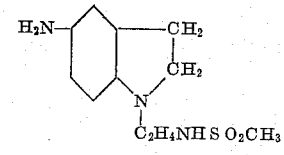
and a compound which couples with the oxidation product of the developing agent to form a colored image.

2. A photographic developing solution comprising as the silver halide developing agent a compound having the formula:



and a compound which couples with the oxidation product of the developing agent to form a colored image.

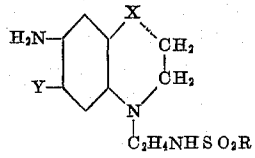
3. A photographic developing solution comprising as the silver halide developing agent a compound having the formula:



and a compound which couples with the oxida-

tion product of the developing agent to form a colored image.

4. A developing solution for producing a colored photographic image comprising a silver halide developing agent having the formula:



where X is selected from the group consisting of —CH_2— and a single chemical bond, Y is selected from the group consisting of hydrogen and methyl and R is a lower alkyl group, and a compound which couples with the oxidation product of the developing agent to form a colored image.

JOHN R. THIRTLE.
ARNOLD WEISSBERGER.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,163,820	Wilmanns et al.	June 27, 1939
2,193,015	Weissberger	Mar. 12, 1940
2,196,739	Peterson	Apr. 9, 1940