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2,710,803

COLOR COUPLERS CONTAINING HYDROXY-ALKYL GROUPS

Ilmari F. Salminen and Arnold Weissberger, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

No Drawing. Application March 26, 1953, Serial No. 344,884

14 Claims. (Cl. 95—6)

This invention relates to color photography and particularly to color-forming compounds or couplers containing hydroxy alkyl groups for incorporation in silver halide emulsions.

Color-forming compounds which react with the development product of aromatic amino developing agents to form colored images on photographic development have been the subject of numerous prior patents. The dyes formed in this way are insoluble in water and in the ordinary photographic developing and fixing baths although the silver images formed simultaneously with them during the photographic development may be removed from the photographic layer to leave pure dye images in the layer. Such a compound which is employed in conjunction with the developing agent for the silver and which couples with the development product of the developer during photographic development is referred to herein as a coupling component or coupler. When these coupling components are incorporated in the photographic layer prior to exposure, they do not affect the exposure and development of the layer in the usual way but when the development is carried out with a suitable developing agent they combine with the oxidation product of the developer to form a colored image in situ with the silver image.

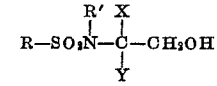
The coupling portion of the coupler molecule usually consists of a radical with a phenolic hydroxy group or a reactive methylene group, and to this portion may be attached substituents which render the coupler suitable for use in various processes, such as those described in Mannes and Godowsky U. S. Patent 2,304,940, granted December 15, 1952, Jelley and Vittum U. S. Patent 2,322,027, granted June 15, 1943, and Peterson U. S. Patent 2,296,306, granted September 22, 1942.

Couplers containing sulfonyl chloride groups which were to be hydrolyzed before or during incorporation in a photographic emulsion layer were described in our U. S. application Serial No. 774,890, an abstract of which was published in the Official Gazette April 24, 1951. These couplers were intended to be used in color processes of the type described in Fischer U. S. Patent 1,102,028 granted June 30, 1914, in which a coupler is used which is dispersible in the gelatin but which is non-wandering or non-diffusing through the emulsion layer or into an adjacent layer after coating. While such couplers may be incorporated in a gelatin emulsion their use is frequently attended by undesirable effects upon the gelatin. Such couplers may, for example, yield emulsions of undesirably high viscosity or may produce emulsion coatings which are somewhat brittle.

It is therefore an object of the present invention to provide novel coupler compounds for incorporation in photographic emulsions. A further object is to provide couplers which do not increase viscosity or produce brittleness in the emulsion layers in which they are incorporated. Other objects will become apparent by consideration of the following description of our invention.

Our objects are accomplished by reacting color couplers containing sulfonyl chloride groups, with hydroxyl-containing amines such as ethanol amine to produce couplers containing hydroxy alkyl groups which may be incorporated in photographic emulsion layers and which show improved compatibility with such layers.

The sulfonyl chloride couplers which we employ for reaction with the hydroxyl-containing amines have been described, for example, in our U. S. application Serial No. 774,890. They may be reacted with hydroxyl-containing amines such as ethanol amine, diethanol amine, 2-amino - 2 - hydroxymethyl-1,3-propanediol, 2-amino-2-methyl-1,3-propanediol, etc. The compounds thus produced have the following general structure:

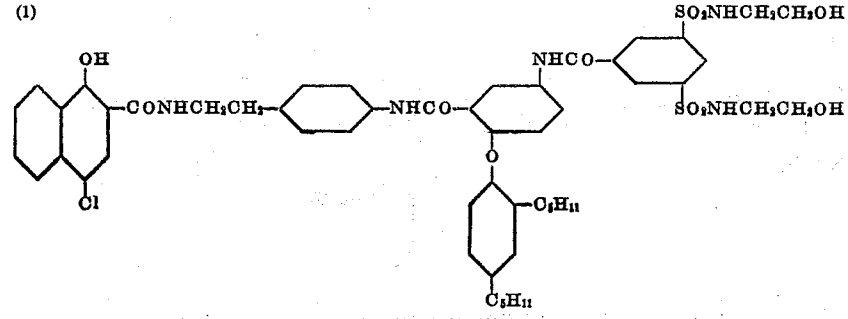


in which

X=hydrogen or CH_2OH
Y=hydrogen, CH_3 or CH_2OH
R'=hydrogen or C_2H_4OH
R=a coupler molecule

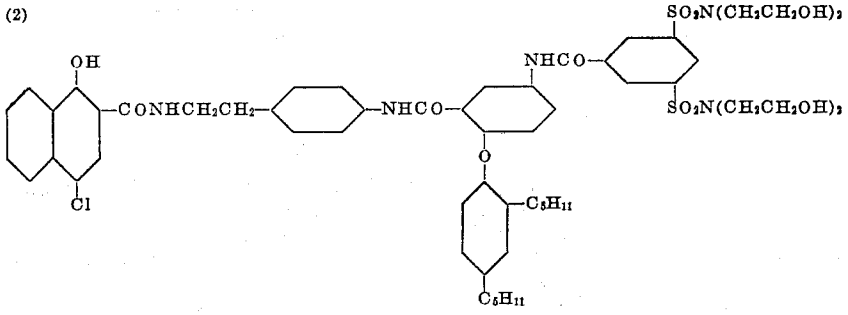
Our invention will be readily understood from a consideration of the following description of the couplers and methods of preparation of the same and the use in photographic emulsion layers.

(1)



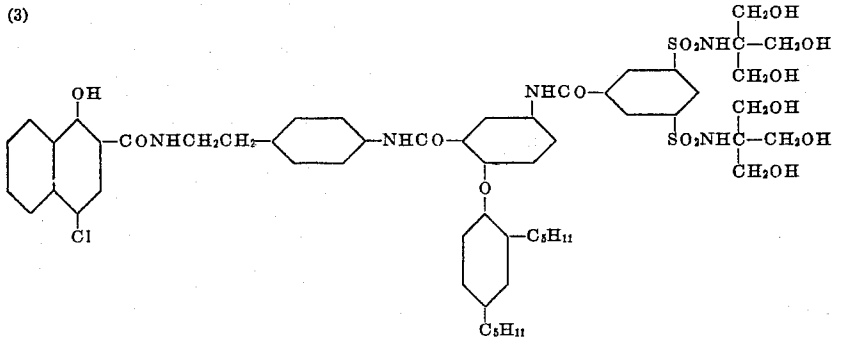
1-hydroxy-4-chloro-N-{4'-[2''- (2''',4'''-di-tert - amylphenoxy)-5''- (3''',5'''- di - β - hydroxyethylsulfamylbenzamido)benzamido]phenethyl}-2-naphtamide

(2)



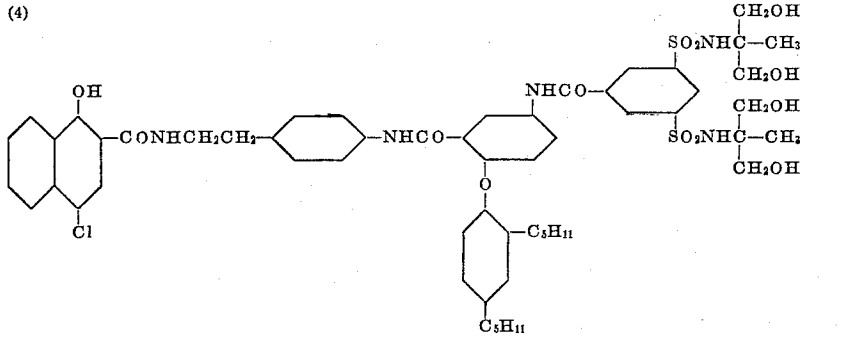
1-hydroxy-4-chloro-N-{4'-[2''- (2''',4'''-di-tert - amylphenoxy)-5''- {3''',5'''- [di(di-β-hydroxyethylsulfamyl)]} benzamido]-phenethyl}-2-naphthamide

(3)



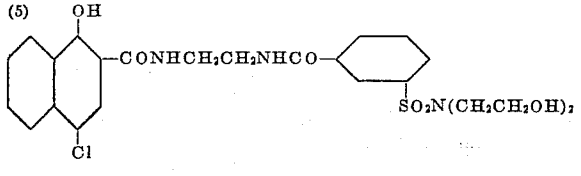
1-hydroxy-4-chloro-N-{4'-[2''- (2''',4'''-di-tert - amylphenoxy)-5''- (3''',5'''- bis{N - [tri(hydroxymethyl)methyl]sulfamyl}-benzamido)-benzamido]phenethyl}-2-naphthamide

(4)



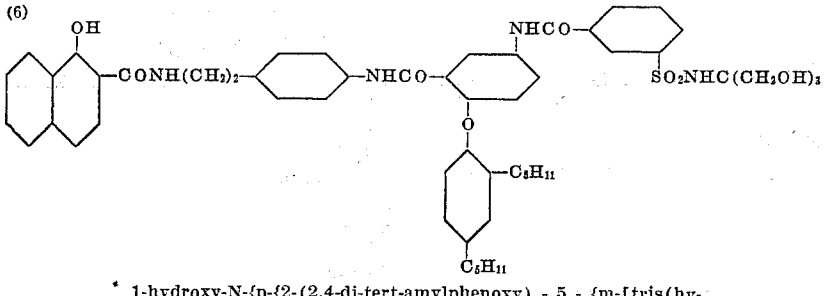
1-hydroxy-4-chloro-N-{4'-[2''- (2''',4'''-di-tert - amylphenoxy)-5''-(3''',5'''- bis{N-[1,1- di(hydroxymethyl)ethyl]sulfamyl}-benzamido)-benzamido]phenethyl}-2-naphthamide

(5)



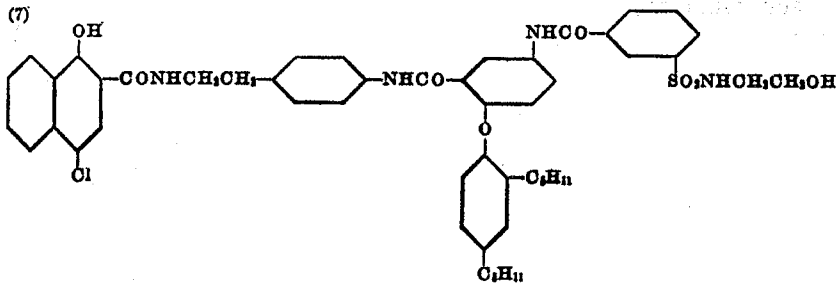
1-hydroxy - N-{β-{3-[bis(β-hydroxyethyl)sulfamyl]benzamido}-ethyl}-4-chloro-2-naphthamide

(6)



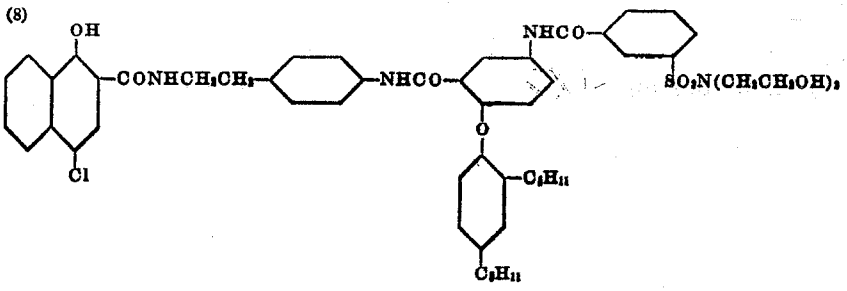
1-hydroxy-N-{p-{2-(2,4-di-tert-amylphenoxy) - 5 - {m-[tris(hydroxymethyl)methyl] sulfamylbenzamido} benzamido} phenethyl}-2-naphthamide

(7)



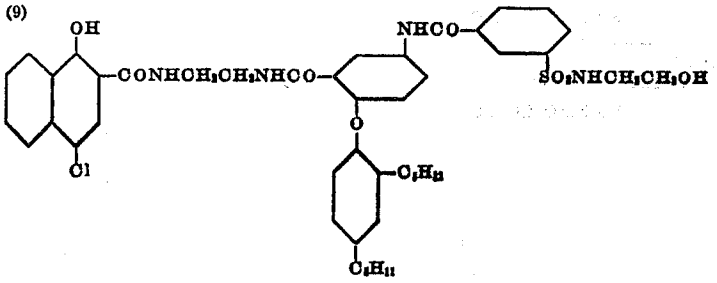
1-hydroxy-4-chloro-N-{p-{2-[2,4-di-tert-amylphenoxy] - 5 - [m-(β-hydroxyethylsulfamyl)benzamido]benzamido}phenethyl}-2-naphthamide

(8)



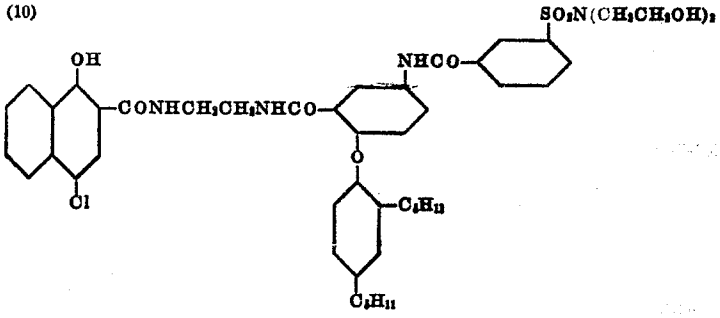
1-hydroxy - N -{p-{5-{m - [bis(β-hydroxyethyl)sulfamyl]benzamido} - 2 - (2,4-di-tert-amylphenoxy)benzamido}phenethyl}-4-chloro-2-naphthamide

(9)



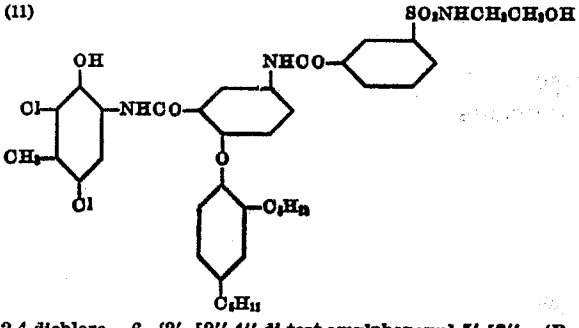
1-hydroxy-4-chloro-N-{β -{2-[2,4-di-tert-amylphenoxy] - 5 - [m-(β - hydroxyethylsulfamyl)benzamido]benzamido}ethyl} - 2-naphthamide

(10)



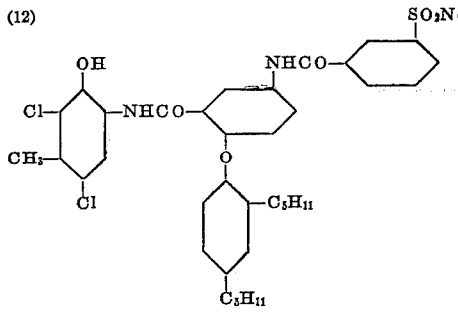
1-hydroxy - N - {β-{5-{m-[bis(β-hydroxyethyl)sulfamyl]benzamido}-2-(2,4-di-tert-amylphenoxy)benzamido}ethyl}-4-chloro-2-naphthamide

(11)



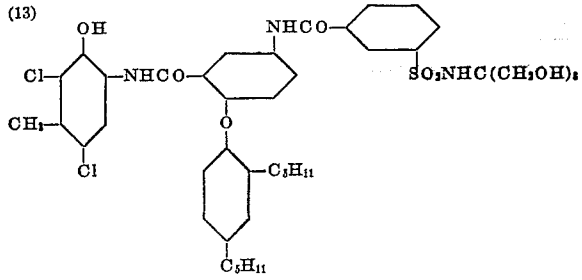
2,4-dichloro - 6 -{2'- [2'',4''-di-tert-amylphenoxy]-5'-[3''—(B-hydroxyethylsulfamyl)benzamido]benzamido}-3-methylphenol

(12)



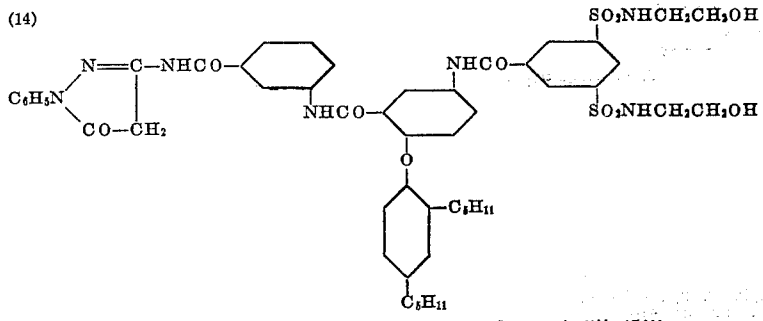
2,4 - dichloro-6-{2'-[2'',4''-di-tert-amylphenoxy] - 5'- [3''—(di-β-hydroxyethylsulfamyl)benzamido]benzamido}- 3 - methylphenol

(13)



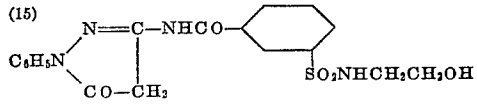
6-{2-{2,4-di-tert-amylphenoxy} - 5 - {m - [tris(hydroxymethyl)-methylsulfamyl]benzamido}benzamido}- 2,4-dichloro-3-methylphenol

(14)



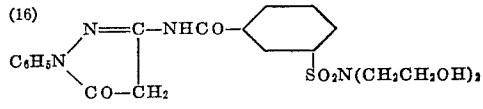
1-phenyl-3-{3'-[2''- (2''',4'''- di-tert-amylphenoxy)- 5''- (3''',-5'''- di-β-hydroxyethylsulfamylbenzamido)benzamid }benzamido}-5-pyrazolone

(15)



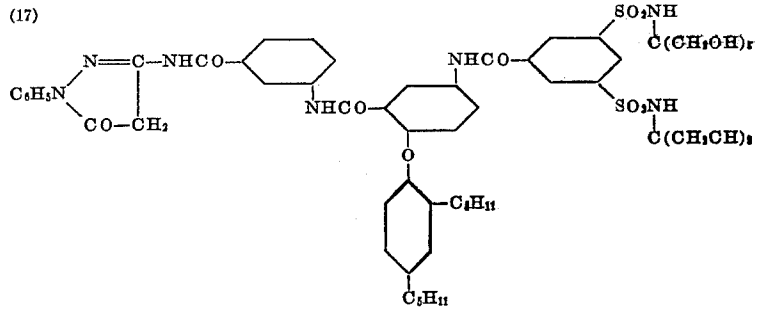
1-phenyl-3-[3'-(β-hydroxyethylsulfamyl)benzamido]-5-pyrazolone

(16)



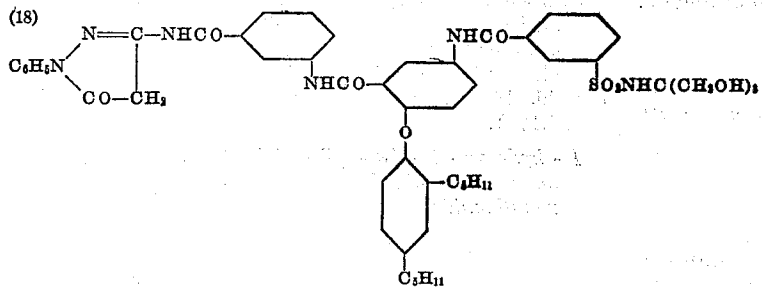
1-phenyl-3-[3'-(bis-β-hydroxyethylsulfamyl)benzamido]-5-pyrazolone

(17)



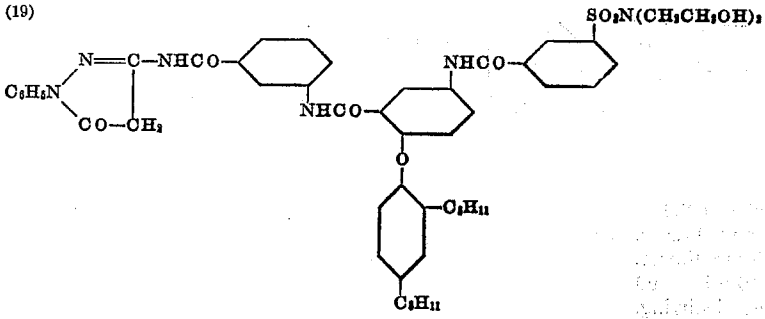
1-phenyl - 3 - {m - {5 -{3,5-bis[tris(hydroxymethyl)methyl]sulfamylbenzamido} - 2 - (2,4-di-tert-amylphenoxy)benzamido}-benzamido}-5-pyrazolone

(18)



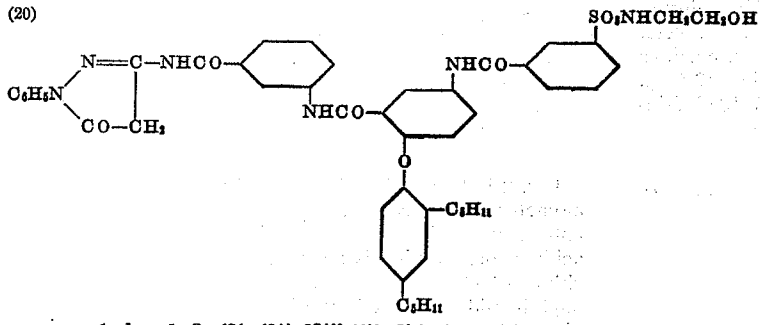
1-phenyl - 3 - {3'- {2''- {2,4-di-tert-amylphenoxy} - 5''- {m-[tris-hydroxymethyl)methylsulfamyl]benzamido}benzamido}- benzamido}-5-pyrazolone

(19)



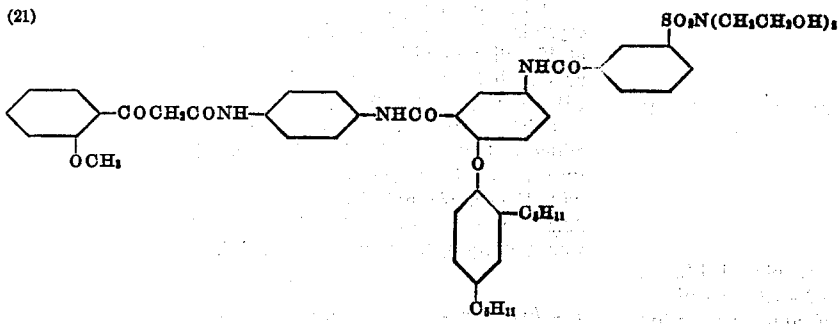
1-phenyl - 3 - {3'- {5''-{m-[bis(β-hydroxyethyl)sulfamyl]benzamido} - 2''- {2''',4'''- di-tert-amylphenoxy}benzamido}benzamido}-5-pyrazolone

(20)



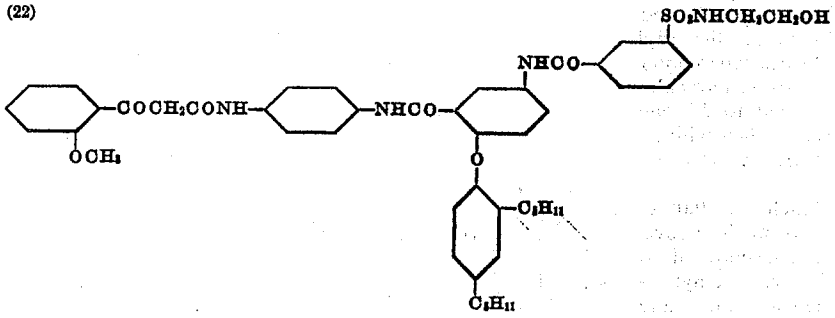
1-phenyl - 3 - {3'- {2''–[2''',4'''- di-tert-amylphenoxy]-5-[m-(β-hydroxyethylsulfamyl)benzamido]benzamido}benzamido}- 5-pyrazolone

(21)



α-(o-Methoxybenzoyl)- 4 -{5-{3-[bis(β-hydroxyethyl)sulfamyl]-benzamido} - 2 - {2,4 - di-- tert-amylphenoxy}benzamido}acetanilide

(22)

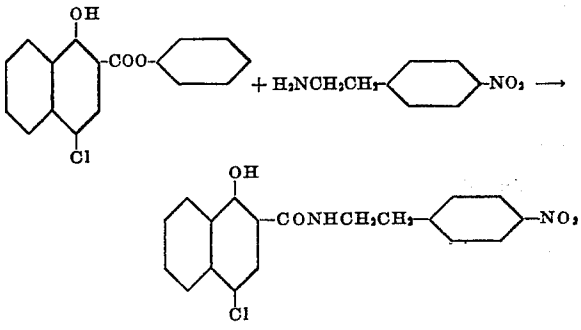


α-(o-Methoxybenzoyl)-4-{2'- [2,4-di-tert-amylphenoxy] - 5'- [3-(β-hydroxyethylsulfamyl)benzamido]benzamido}acetanilide

The compounds listed above were prepared as follows:

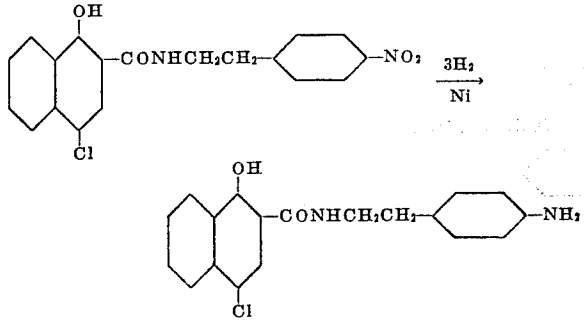
COMPOUND 1

4 - chloro - 1 - hydroxy - 2 - [β-(4'-nitro)-phenethyl]-naphthamide



In a 200-cc. round-bottomed flask were placed 9.3 g. (0.056 mole) of 4-nitro-β-phenethylamine and 11.3 g. (0.038 mole) of phenyl 4-chloro-1-hydroxy-2-naphthoate. The mixture was heated at 160–170° C. for 10 mins. and poured into 60 cc. of glacial acetic acid with good stirring. The resulting slurry was heated to boiling and poured into the original reaction flask. The mixture was heated until a clear dark-brown solution was formed. The solution was allowed to stand until crystallization was complete, filtered, and the crystals washed with two 25-cc. portions of ethyl ether. Dried at 100° C. Yield, 12.6 g. (60.5%), orange-colored needles; M. P. 186–187° (sintered at 184°).

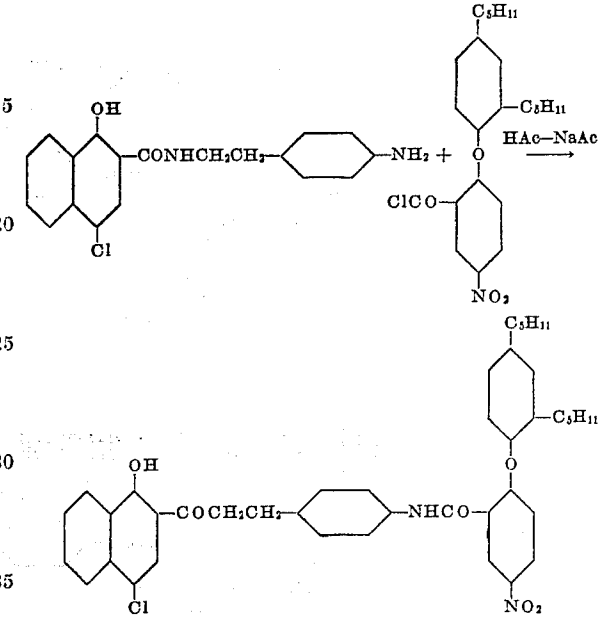
4 - chloro - 1 - hydroxy - 2-[β-(4'-amino)-phenylethyl]-naphthamide



In the small hydrogenation unit were placed 14.3 g. (0.04 mole) of 4-chloro - 1 - hydroxy - 2 - [β - (4' - nitro)-phenylethyl]-naphthamide, 150 cc. of anhydrous ethyl acetate, 0.5 g. of sodium carbonate and Raney nickel catalyst. The hydrogenation was carried out by shaking for 2 hrs. and 20 mins., while the unit was being heated with steam. The catalyst was then filtered and the ethyl acetate filtrate concentrated to about 25 cc., whereupon the amine began to separate; 50 cc. of carbon tetrachloride was added. The solution was cooled to 5° and filtered. The white crystalline solid was washed with 25 cc. of carbon tetrachloride. Yield, 10.35 g. (78.8%); M. P. 137–139°.

A second reduction of the same size batch gave 9.05 g. (68%); M. P. 137–139°. The filtrates from the above two batches of amine were combined, concentrated to dryness and the residue dissolved in 75 cc. of ethyl alcohol. The alcohol solution was heated to boiling and 25 cc. of concentrated hydrochloric acid added. The hydrochloride of the amine separated; the mixture was cooled to room temperature, filtered and the hydrochloride washed with acetone. The solid was dried at 100°. Yield, 6.05 g. (20.7%) as base hydrochloride. Total yield, 19.4 g. of amine and 6.05 g. of hydrochloride (94.1%).

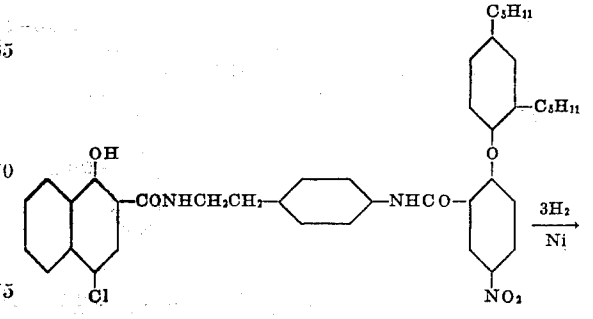
1 - hydroxy - 2 - {β - {4' - [2" - (2"',4"' - diamylphenoxy) - 5" - nitrobenzamido]}phenethyl} - 4 - chloro-naphthamide

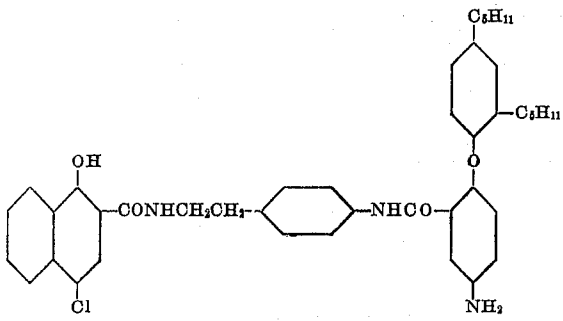


In a 2-l. 3-necked flask equipped with stirrer and thermometer was placed a solution of 8.2 g. (0.1 mole) of anhydrous sodium acetate in 700 cc. of glacial acetic acid; to the solution is added 17.7 g. (0.05 mole) of 4-chloro - 1 - hydroxy - 2 - [β - (4' - amino) - phenylethyl]-naphthamide, followed by 25 g. (0.06 mole) of 2-(2',4'-diamylphenoxy)-5-nitrobenzoyl chloride. The temperature rose several degrees and the condensation product soon began to separate as a thick slurry of fine white crystals. The reaction mixture was stirred for one hour at 45°, diluted with 100 cc. of water, and filtered through an 8-inch Buchner funnel; dried at 100°. Yield, 37.5 g. (100%); M. P. 215–220°.

Thirty-seven and one-half grams of crude product was added to 800 cc. of boiling glacial acetic acid. The mixture was cooled to room temperature and filtered, washed with 250 cc. of ethyl alcohol and 350 cc. of ether. Yield, 32.5 g. (87%): M. P. 134.5–135.5°. The final product was a fluffy yellow crystalline solid.

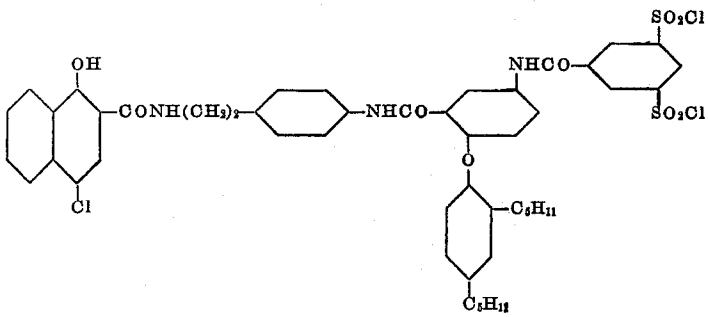
1 - hydroxy - 2 - {β - {4' - [2" - (2"',4"' - diamylphenoxy) - 5" - aminobenzamido]} - phenethyl} - 4-chloro-naphthamide





In the small hydrogenation unit were placed 32 g. (0.044 mole) of 1-hydroxy-2-{β-{4'-[2''-(2''',4'''-diamylphenoxy) - 5'' - nitrobenzamido]} - phenethyl} - 4-chloro-naphthamide, 250 cc. of anhydrous ethyl acetate, 0.5 g. of anhydrous sodium carbonate and Raney nickel. The hydrogenation was carried out by heating and shaking for 6 hrs. at a pressure of approximately 40 lbs. The catalyst was filtered from the solution and the filtrate concentrated to dryness on the steam bath under reduced pressure. The puffy white amorphous residue was heated in the steam bath for 1.5 hrs. under reduced pressure. The amorphous amine was dissolved in 100 cc. of ethyl ether, seeded with pure amine, let stand until crystallization was complete (about 2 hrs.), filtered and the solid washed with two 50-cc. portions of ether. Dried at 100°. Yield, 27.9 g. (90.8%), pure white amine, M. P., 192–194°, sinters at 190°.

1 - hydroxy - 4 - chloro - {4' - [2'' - (2''',4''' - di - tert-amylphenoxy) - 5'' - (3''',5''' - dichlorosulfonylbenzamido)benzamido]-phenethyl}naphthamide



In a 1-liter 3-neck round-bottom flask, equipped with a thermometer and stirrer, was placed a solution of 69.2 g. (0.1 mole) of 1-hydroxy-N-{p-[5-amino-2-(2,4-di-tert-amylphenoxy) - benzamido] - phenethyl} - 4 - chloro - 2-naphthamide and 16 g. (0.125 mole) of quinoline in 490 ml. of dry dioxane. To this solution was added, with stirring, 30 g. (0.125 mole) of 3,5-dichlorosulfonylbenzoylchloride. The temperature of the reaction mixture rose rapidly from 24° to 35° C. After 2 hours the clear reaction solution was drowned with stirring in 120 cc. of concentrated hydrochloric acid and 2 liters of water.

The granular product was filtered, washed on the funnel with 100 ml. of 10% hydrochloric acid and 2 times 100 ml. of water, and dried at a temperature not over 40° C. The crude yield was approximately 77 g. (86%).

This compound was dissolved in 500 ml. of glacial acetic acid at room temperature and left standing for two days, during which time it separated as a white solid. The recovery from the acetic acid crystallization was 61 g. (80%), M. P.: sintered 129° C.; molten 150° C.

1 - hydroxy - 4 - chloro - 2 - {4' - [2'' - (2''',4''' - di-tert - amylphenoxy) - 5'' (3''',5''' - di - β - hydroxyethylsulfamylbenzamido)benzamido] - phenethyl)-naphthamide

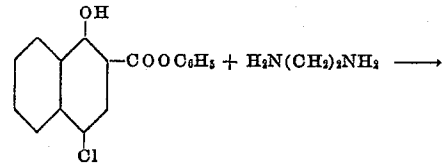
The product of the preceding reaction was added to a large excess of ethanolamine in dioxane. A spontaneous reaction occurred. The reaction mixture was drowned at less than 30° C. in a solution of excess HCl and water. The resulting solution was concentrated at reduced pressure until a solid precipitated, and the solid was filtered, washed with water, and dried.

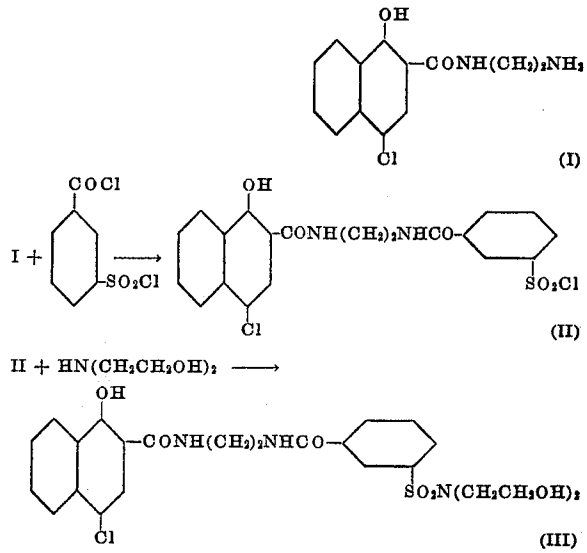
Compound 2 was made in the same way as Compound 1, using diethanolamine instead of ethanolamine in the final reaction.

Compounds 3 and 4 were made in the same way as Compound 1, except that in the final reaction, to a suspension of 5 parts of 2-amino-2-hydroxymethyl-1,3-propanediol (for Compound 3) or 2-amino-2-methyl-1,3 propanediol (for Compound 4) in 50 volumes of tetrahydrofurfuryl alcohol there was added 5 parts of the disulfonyl chloride coupler, instead of using ethanolamine. The temperature rose from 24° to 30° and the resultant solution was left to stand for two hours. The mixture was poured into 200 volumes of dilute hydrochloric acid. The product was filtered, washed on the funnel with 300 volumes of H_2O, and dried.

COMPOUND 5

This coupler was prepared according to the following sequence of reactions:





In order to prepare Compound I, phenyl 4-chloro-1-hydroxy-2-naphthoate in benzene was added to a large excess of ethylenediamine at room temperature. A pale yellow oil which separated from the benzene gradually solidified to I.

II was prepared by placing in a flask 30 parts of m-chlorosulfonylbenzoyl chloride and 200 volumes of dioxane followed by 32 parts of I. The mixture was refluxed until hydrogen chloride evolution ceased.

The yellow solution was cooled to room temperature and drowned while stirring in a mixture of ice, water, and hydrochloric acid. The gummy product was dissolved in 200 volumes of ether from which II crystallized and was collected on a funnel.

III was prepared by mixing 23 parts of II, 21 parts of diethanolamine and 300 volumes of ethyl alcohol. The solution which resulted was drowned in 2000 volumes of ice, water, and hydrochloric acid, III being precipitated.

COMPOUND 6

1-hydroxy-N-{p - [2 - (2',4' - di - tert - amylphenoxy)-5 - (m - chlorosulfonylbenzamido) - benzamido] - phenethyl}-2-naphthamide was made in the same way as the sulfonyl chloride coupler intermediate of Compound 1, using phenyl 1-hydroxy-2-naphthoate as the original starting material.

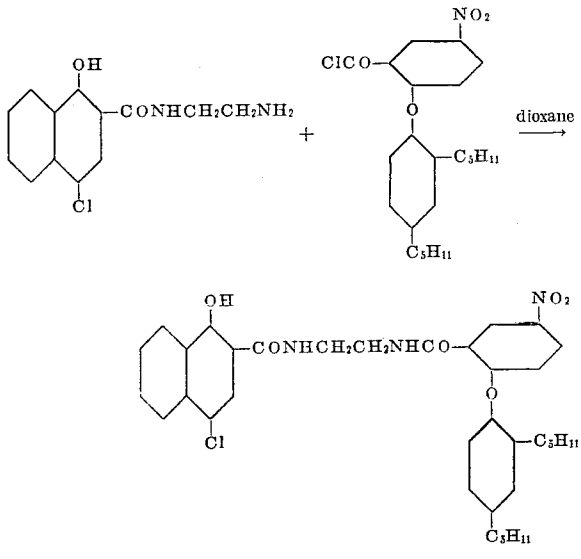
Three parts of the sulfonyl chloride coupler were dissolved in 30 volumes of tetrahydrofurfuryl alcohol and 3 parts of 2-amino-2-(hydroxymethyl)-1,3-propanediol were added to the stirred solution and stirring was continued for 1¾ hours. The resultant solution was filtered and the filtrate poured into 100 volumes of water to which 10 volumes of concentrated hydrochloric acid had been added. The resulting precipitate was filtered, washed with 200 volumes of water, and dried.

Compound 7 was made in the same way as Compound 1, using m-chlorosulfonylbenzoylchloride instead of 3,5-dichlorosulfonylbenzoylchloride in the preparation of the sulfonylchloride coupler, and using ethanolamine for reaction with the sulfonylchloride coupler.

Compound 8 was made in the same way as Compound 7, using diethanolamine instead of ethanolamine.

COMPOUND 9

1-hydroxy-4-chloro-N-{β-[2 - (2,4 - di - tert - amylphenoxy)-5-nitrobenzamido]ethyl}-2-naphthamide



In a 2000-cc. three-necked, round bottom flask, equipped with a thermometer, stirrer, and powder funnel, was placed a solution of 73 g. (0.175 mole) of 2-(2,4-di-tert-amylphenoxy)-5-nitro-benzoyl chloride in 875 cc. of dioxane. To this solution was added, with stirring, 92.5 g. (0.35 mole) of 1-hydroxy-N-(β-aminoethyl)-4-chloro-2-naphthamide. The temperature rose rapidly from 22–33° C. and partial solution was observed. In a very short time the amine hydrochloride began to separate and the slurry was stirred for a total of six hours. The amine hydrochloride was filtered off by suction, and to the filtrate was added ice water until the mixture was slightly milky in appearance. This suspension was then placed in the refrigerator overnight, during which time the product crystallized in the form of yellow needles. The yield of nitro compound was 112 g. (100%), M. P. 184–186° C.

1-hydroxy-N-{β-[2-(2,4-di-tert-amylphenoxy-5-amino-benzamido]ethyl}-4-chloro-2-naphthamide

In the small hydrogenation unit were placed 16 g. (0.025 mole) of 1-hydroxy-4-chloro-N-{β-[2-(2,4-di-tert-amylphenoxy) - 5-nitrobenzamido]ethyl}-2-naphthamide, 220 cc. dioxane, 10 cc. water, 0.5 g. of sodium carbonate and Raney nickel catalyst. The hydrogenation was carried out by shaking for approximately four hours at a temperature of approximately 40° C. The catalyst was filtered off by suction, and the dioxane solution of the amine was poured into 500 cc. of water. The gummy product which separated was crystallized from 100 cc. of ethanol by dissolving it in the ethanol at room temperature and letting the solution stand for approximately one hour during which time the product separated. This product was recrystallized from 100 cc. of ethanol to yield 5.1 g. of amine melting at 168–170° C.

1-hydroxy - 4 - chloro - N - {β - [5 - (m - chlorosulfonylbenzamido) - 2 - (2,4 - di - tert - amylphenoxy)benzamido]ethyl}-2-naphthamide

In a 2-liter three-necked, round-bottomed flask, equipped with a thermometer and stirrer, was placed a solution of 20 g. (0.24 mole) of anhydrous sodium acetate in 1 liter of glacial acetic acid. To this solution was added 49.2 g. (0.08 mole) of 1-hydroxy-N-{β-[2-(2,4 - di - tert - amylphenoxy)5-amino-benzamido]ethyl}4-chloro-2-naphthamide and a complete solution was obtained. To this solution was added, with stirring, 21 g. (0.088 mole) of m-chlorosulfonylbenzoyl chloride in 200 cc. of glacial acetic acid. The temperature of the reaction mixture rose rapidly from 27° C. to 30° C., and in a very short time a white solid separated. This reaction mixture was stirred at room temperature for three hours and then poured into 4 liters of water. The white solid was filtered off by suction and air-dried in a hood overnight.

The crude yield was 63 g. (96.5%). The crude product was purified by dissolving it in 600 cc. of carbon tetrachloride at room temperature and letting the solution stand overnight. The product crystallized with 1 mole of CCl_4. The recovery from the CCl_4 crystallization is 57 g. (90.5%), M. P. 160–165° C.

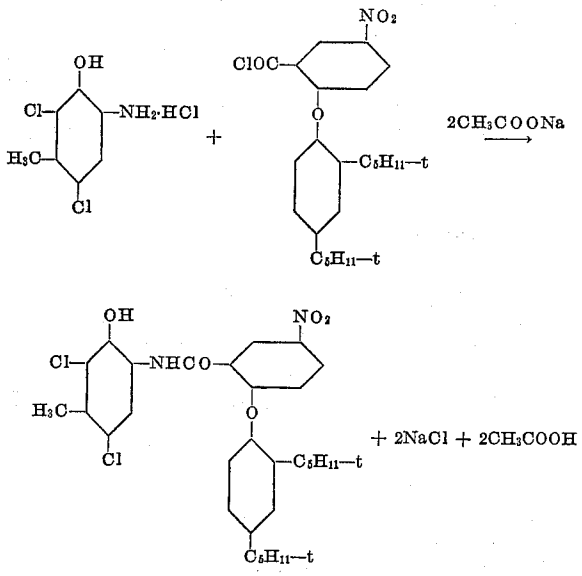
1-hydroxy-4-chloro-N-{β-{2-[2,4-di - tert - amylphenoxy]-5 - [m - (β - hydroxyethylsulfamyl)benzamido]benzamido}ethyl}-2-naphthamide

To a solution of 4 parts of the sulfonyl chloride coupler in 75 volumes of dioxane was added a solution of 1.3 parts of ethanolamine in 15 volumes of dioxane. The temperature rose from 26° to 30° and the clear solution was left to stand at room temperature for three hours. The mixture was then poured into 170 volumes of dilute hydrochloric acid. The product was filtered, washed on the funnel with 100 volumes of H_2O, and dried.

Compound 10 was made in the same way as Compound 9, using diethanolamine instead of ethanolamine.

COMPOUND 11

2,4 - dichloro - 3 - methyl - 6 - [3' - nitro - 6' - (2'',4'' - di - tert - amylphenoxy) - benzamido] - phenol



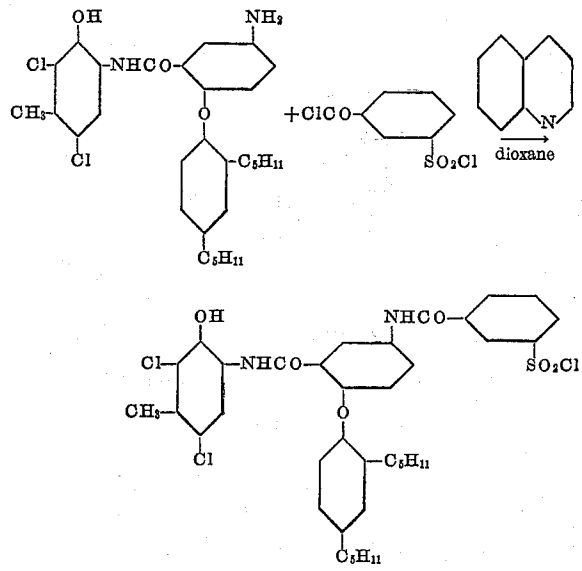
In a 5-l., 3-necked flask provided with a stirrer and a thermometer was placed 1380 cc. of acetic acid. To it were added 138 g. (1.64 moles) of anhydrous sodium acetate, 138 g. (0.6 mole) of 2-amino-4,6-dichloro-5-methyl phenol hydrochloride and 264 g. (0.63 mole) of 2 - (2',4' - di - tert. - amylphenoxy) - 5 - nitrobenzoyl chloride. The heat of reaction raised the temperature about 8° C. The slurry was then washed into a 12-l. flask with 7.5 l. of water and the aqueous solution was filtered on a 37-cm. Lapp table-top funnel. The product was washed on the funnel with 9 l. of ethyl alcohol and dried. The yield was 356 g. (102%); M. P. 194–197°. The product was then recrystallized from 9 l. of 97% acetic acid, filtered through the table-top funnel, washed on the funnel with 900 cc. of acetic acid and two 1800-cc. portions of petroleum ether (P 950). The product was air dried. The yield was 302 g. (84%); M. P. 205–207°.

2,4 - dichloro - 3 - methyl - 6 - [3' - amino - 6' - (2'',4'' - diamylphenoxy) - benzamido] - phenol

In a 12-l. flask equipped with a stirrer and reflux condenser were placed 3 l. of 90% acetic acid and 1.5 l. of ethyl alcohol; 300 g. (0.52 mole) of 2,4-dichloro-3-methyl - 6 - [3' - nitro - 6' - (2'',4'' - diamylphenoxy) - benzamido]-phenol was added to the acid-alcohol solution with stirring to prevent cake formation. This compound did not go into solution completely even under reflux conditions. The flask and its contents were heated to boiling over a gas ring. When reflux conditions were reached the flame was extinguished and 300 g. (5.4 moles) of powdered iron metal was added all at once. The reaction was quite vigorous. The reflux condenser was replaced immediately after the iron addition. The solution was refluxed for 10 min. The hot solution was filtered rapidly with vacuum through a 12-in. Büchner funnel into a 22-l. flask to remove the excess iron oxides formed. To the filtrate was added with stirring 8–9 l. of water. The amine was precipitated out and filtered off on a 37-cm. Lapp table-top funnel and washed on the funnel with 4–5 l. of water. The product was sucked as dry as possible and dissolved in 3 l. of ethyl ether. Residual water was removed in a large separatory funnel and the ether solution dried over 300 g. of Drierite. The ether solution is concentrated to dryness under reduced pressure and the crude amine which resulted was

dissolved in 1.2 l. of hot toluene and to this solution was added 4.2 l. of warm ligroin. The solution was then set aside to crystallize. When crystallization appeared complete the solid was filtered off on a 12-in. Büchner funnel, washed with 1 l. of petroleum ether and dried. The yield was 163 g. (58%); M. P. 174–176°.

6 - [5 - (m - chlorosulfonylbenzamido) - 2 - (2,4 - di-tert - amylphenoxy)benzamido] - 2,4 - dichloro - 3-methylphenol



In a 200-ml. 3-neck round bottom flask, equipped with a thermometer and stirrer, was placed a solution of 10.86 g. (0.02 mole) of 6-[5-(amino-2-(2,4-di-tert-amylphenoxy)-benzamido]-2,4-dichloro - 3 - methylphenol and 2.8 g. (0.022 mole of quinoline in 100 ml. of dry dioxane. To the solution was added, with stirring, 5.26 g. (0.022 mole) of m-chlorosulfonylbenzoyl chloride. The temperature of the reaction mixture rose to 34° C., accompanied by the separation of a white solid. The reaction mixture was stirred for one hour, after which a solution of 50 ml. of concentrated hydrochloric acid and 450 ml. of water was added, and the product separated as a gum.

This gum was triturated in 100 ml. of glacial acetic acid and the mixture left standing over night. The crystalline product was filtered off, washed on the funnel with water, and dried.

The yield was 13 g. (87.5%), M. P.: molten 129° C. This molten substance resolidified, and remelted at 90° C.

6-{2-[2,4-di - tert - amylphenoxy]-5-[m-(β-hydroxyethylsulfamyl)benzamido]benzamido} - 2,4 - dichloro - 3-methylphenol

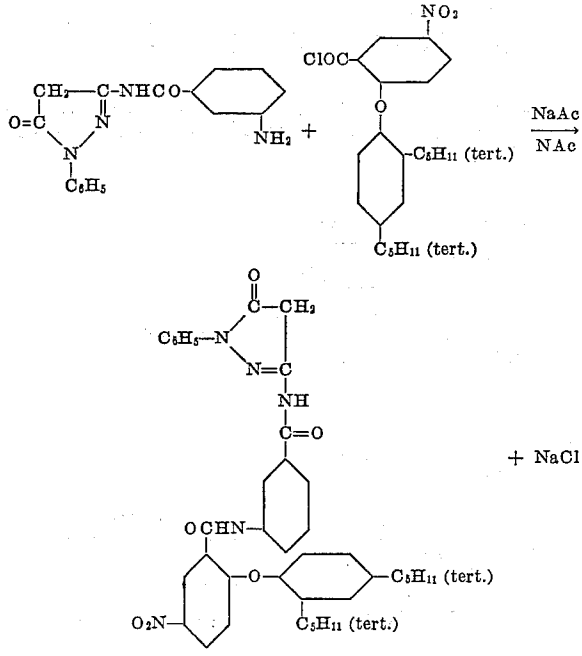
To a solution of 4 parts of the sulfonyl chloride coupler in 50 volumes of dioxane was added a solution of 2 parts of ethanolamine in 15 volumes of dioxane. The temperature rose from 23° to 30° and the resultant solution was left to stand at room temperature for four hours. The mixing was poured into 230 volumes of dilute hydrochloric acid and the gum which separated was ground in 50 volumes of H_2O and left to stand at room temperature overnight, during which time it solidified. The product was filtered and dried.

Compound 12 was made in the same way as Compound 11, using diethanolamine instead of ethanolamine.

Compound 13 was made in the same way as Compound 11, using 3 parts of 2-amino-2-hydroxymethyl-1,3-propanediol in 50 volumes of tetrahydrofurfuryl alcohol, instead of ethanolamine in dioxane.

COMPOUND 14

1 - phenyl - 3-{3'-[2''-(2''',4'''-di - tert. amylphenoxy)-5''-nitro]-benzamido}-benzamido-5-pyrazolone



In a 2-l. round-bottomed flask equipped with a stirrer was placed 850 cc. of 95% acetic acid and in it was dissolved 32.8 g. (0.39 mole) of anhydrous sodium acetate. To this solution was added 58.8 g. (0.2 mole) of 1-phenyl-3-(3'-aminobenzamido)-5-pyrazolone and 96.2 g. (0.23 mole) of 2-(2',4'-di - tert. - amylphenoxy)-5-nitrobenzoyl chloride. The resulting solution was stirred for 1.5 hours. The temperature rose about 7° at the outset of the reaction, then gradually descended to room temperature. After 15 or 20 minutes, the product began to separate. After stirring was complete, the nitro compound was filtered off and washed on the funnel with 600 cc. of 95% acetic acid followed by 600 cc. of water and 300 cc. of ethyl alcohol. The product was air dried. Yield—80 g. (60% of theory), M. P.—153–8°.

The nitro compound was reduced to the amine as described in the preparation of Compound 11, and the sulfonyl chloride coupler was obtained as follows:

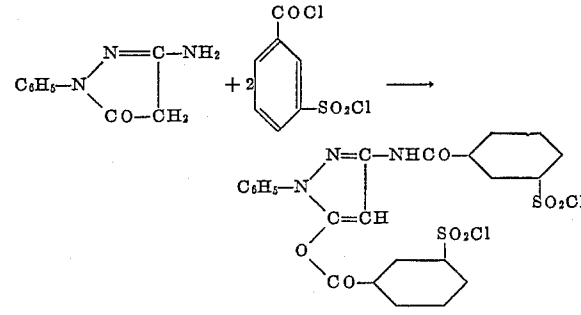
In a 1-l. 3-necked flask provided with a stirrer and thermometer was placed 600 cc. of glacial acetic acid and 10 g. (0.12 mole) of anhydrous sodium acetate. This solution was heated to 90° C.; 39 g. (0.06 mole) of the amino pyrazolone was stirred into the hot acid and stirred for five minutes, a clear, pale amber solution being formed. The solution was filtered by suction and the filtrate cooled externally to 30° C. with stirring. Meantime, just before the reactants were to be mixed, 30 g. (0.072 mole) of dichlorosulfonylbenzoyl chloride were dissolved in 150 cc. of glacial acetic acid and this solution added all at once with vigorous stirring to a solution of the amino pyrazolone. The reaction solution was stirred vigorously for thirty seconds, whereupon the product began to separate in abundance and stirring was stopped.

The mixture was allowed to stand for one half hour and filtered by suction through a 9-inch Büchner funnel and the product washed on the funnel with ½ l. of glacial acetic acid followed by 500 cc. of distilled water. The moist cake was transferred to a beaker and stirred vigorously with ½ l. of distilled water. The mixture was filtered and washed successively with ½ l. of distilled water, ½ l. of ethyl alcohol, and ½ l. of ether. Yield: 54 g. (95%), M. P.>280°.

In a three-necked flask provided with a stirrer and thermometer were placed 15 parts of ethanolamine and 200 volumes of ethyl alcohol. To this solution was added 28.5 parts of the sulfonyl chloride coupler. The solution which formed was drowned by stirring in a solution of 50 volumes of concentrated hydrochloric acid and 500 volumes of water. The product which precipitated was collected on a funnel.

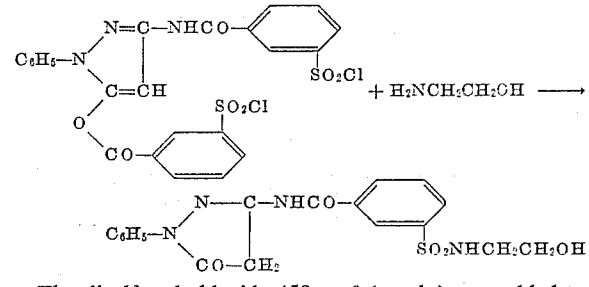
COMPOUND 15

1-phenyl-3-(3-chlorosulfonylbenzamido)-5-(3-chlorosulfonylbenzoxy)pyrazole



1. phenyl-3-amino-5-pyrazolone (175 g., 1.0 mole) and m-chlorosulfonylbenzoyl chloride (480 g., 2.0 moles) were added to 800 ml. of ethyl oxalate and heated on the steam bath at 90–100° C. for 30 minutes with good stirring. The solution was allowed to stand overnight at room temperature. The pale tan solid was collected and washed by slurrying with three 500-ml. portions of ether. The light tan product was collected and dried (334 g., M. P. 184–6°).

1-phenyl-3-[3 - (β - hydroxyethylsulfamyl)benzamido]-5-pyrazolone



The disulfonyl chloride (58 g., 0.1 mole) was added to 500 ml. of dioxane. Then with good stirring ethanolamine (100 g., 1.6 mole) and 8 ml. of pyridine were added. The temperature rose to 70°, and the stirred mixture was then heated on the steam bath for four hours. The solution was cooled, extracted with 500 ml. of ether, and the residual material was stirred with 1500 ml. of cold water until it broke up into dark-red solid. This was collected on a filter and taken up in 300 ml. of ethanol. The ethanol solution was treated with 5 g. of sodium hydrosulfite and 100 ml. of water, heated on the steam bath for 15 minutes, and filtered and cooled. The pale yellow-white crystalline solid (9.9 g., M. P. 174–7°) was recrystallized from dilute alcohol.

Compound 16 was made in the same way as Compound 15, using diethanolamine instead of ethanolamine.

Compound 17 was made in the same way as Compound 14, except that the sulfonyl chloride coupler was treated with 2-amino-2-methyl-1,3-propanediol as follows:

Five parts of the sulfonyl chloride coupler were mixed with 50 volumes of tetrahydrofurfuryl alcohol and to the stirred mixture were added 10 parts of 2-amino-2-methyl-1,3-propanediol. The solution was filtered and the filtrate poured into 150 volumes of water to which 13 volumes of concentrated hydrochloric acid had been added. The precipitate was filtered, washed neutral to litmus paper with water, and dried.

Compound 18 was made from 1-phenyl-3-{3'-[2''-(2''',4'''-di-tert. amylphenoxy)-5''-amino] - benzamido}-benzamido-5-pyrazolone (see Compound 14) as follows:

In a flask provided with a stirrer were placed 240 volumes of dioxane and 24 parts of the amine. To this mixture was added 18.7 parts of m-chlorosulfonylbenzoyl chloride followed by 10.5 parts of quinoline. After 1 hour the reaction mixture was drowned in a solution of 60 volumes of concentrated hydrochloric acid and 750 volumes of water. The product which precipitated was collected on a funnel and washed with water.

The moist solid was stirred with 300 volumes of alcohol, again filtered and dried in vacuo.

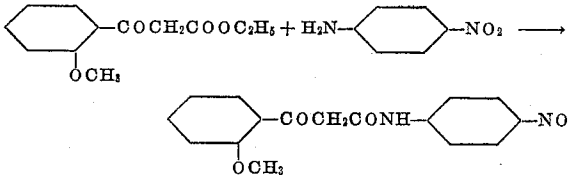
To 3 parts of this compound and 30 volumes of dioxane were added 3 parts of 2-amino-2-(hydroxymethyl)-1,3-propanediol. The reaction mixture was drowned in a solution of 10 volumes of concentrated hydrochloric acid and 200 volumes of ice water. The solid which precipitated was collected on a funnel, washed with water, and dried.

Compound 19 was made in the same way as Compound 18, using diethanolamine in absolute ethyl alcohol instead of the propanediol in dioxane in the final step.

Compound 20 was made in the same way as Compound 19, using ethanolamine instead of diethanolamine.

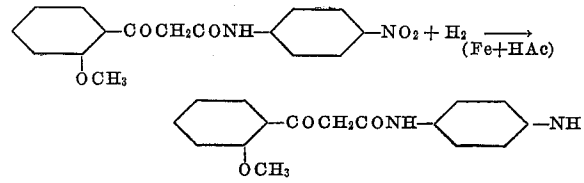
COMPOUND 21

α-Methoxybenzoylacet-4-nitroanilide



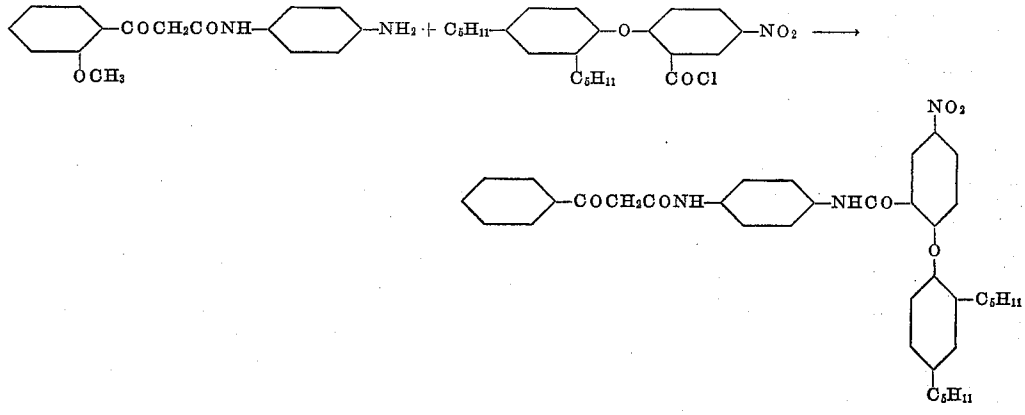
In a 3-l. three-necked flask fitted with a stopper, stirrer, and a steam-jacketed column terminating in a partial condensing still head connected to a water-cooled condenser set for distillation, were placed 222 g. (1.0 mole) of ethyl o-methoxybenzoyl acetate and 800 cc. of dry xylene. 2 g. of anhydrous sodium acetate were added and the mixture was heated to a boil. Heating was discontinued while one-half of 138 g. (1.0 mole) of p-nitroaniline was added. The flask was stoppered again and the mixture refluxed for 1 hour, a vapor temperature of 80–90° being maintained. After 30 min., the remaining half of the amine was added and reflux was continued for an additional 2.5 hours. About 200–300 cc. of xylene should be collected to ensure a complete reaction. The xylene solution was then chilled to 5°, and the product filtered, washed well with 500 cc. of pet. ether, and dried. The yield was 160–200 g. (51–64%), M. P. 110–150°. The crude material was recrystallized from 15 parts of ethyl alcohol in an 80–87% recovery of yellow-tan crystals which melt at 153–155°.

o-Methoxybenzoylacet-4-aminoanilide



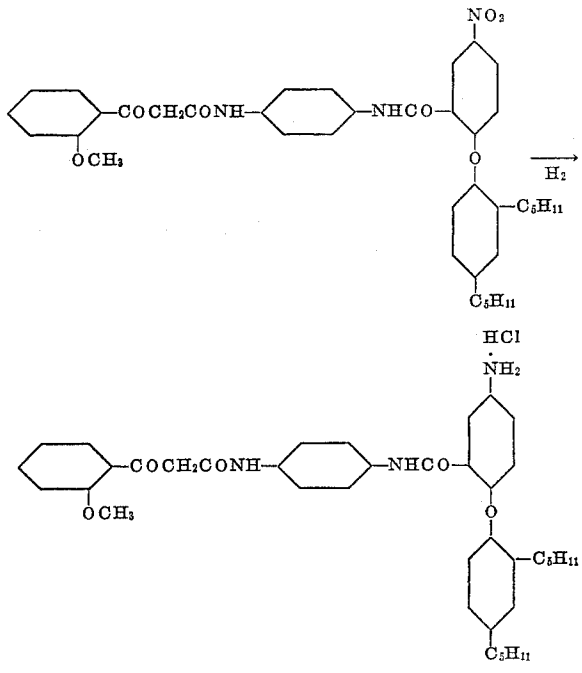
In a 3-l. 3-necked flask equipped with a stirrer, stopper, and reflux condenser was placed 62.8 g. (0.2 mole) of o-methoxybenzoylacet-4-nitroanilide, 300 ml. of ethyl alcohol, 300 ml. of glacial acetic acid, and 300 ml. of water. The reaction mixture was brought to a boil while stirring, and boiled for five minutes, heating was discontinued, and 63 g. of Plast iron powder was added. When the initial reaction subsided, the reaction mixture was refluxed for an additional ten minutes, filtered, and diluted with a solution of 300 ml. of conc. hydrochloric acid and 1 l. of water. The pale yellow solution was chilled to 5° and the precipitate filtered, washed well with 1 l. of cold 3% hydrochloric acid, and dried. 57–58.2 g. (89–91%) of a pale yellow hydrochloride was obtained. This was mixed intimately with an equal weight of anhydrous sodium acetate and poured with vigorous stirring into 1 l. of ethyl alcohol. After stirring 15 minutes, the reaction mixture was diluted with 1 l. of water, stirred an additional five minutes, and chilled to 5°. The precipitate was filtered, washed with 1 l. of cold 50% alcohol, and dried. The yield was 47 g. (83%) of tan crystals which melted at 90–92°.

4'-(o-methoxybenzoylacetamido)-2-(2'',4''-di-tert-amylphenoxy)-5-nitrobenzanilide



In a 1-liter Erlenmeyer flask equipped with a stirrer were placed 42.5 g. (0.15 mole) of o-methoxybenzoylacet-4-amino-anilide, 15 g. (0.15+ mole) of anhydrous sodium acetate, and 500 ml. of glacial acetic acid. With good stirring, 62.7 g. (0.15 mole) of 2-(2,4-di-tert-amylphenoxy)-5-nitrobenzoyl chloride was added. After stirring for 3 hours, the yellow solution was poured into 2 liters of water. The yellow solid was filtered, washed with 5–10% acetic acid, and dried. The crude product (95 g.), melting at 165–170°, was recrystallized from 20 parts of ethyl alcohol to give 82 g. (82%) of yellow product melting at 172–176°.

4' - (o - methoxybenzoylacetamido) - 2 - (2'',4'' - di-tert - amyl - phenoxy) - 5 - aminobenzanilide hydrochloride



In a 5-liter flask equipped with a reflux condenser were placed 100 g. (0.15 mole) of 4'-(o-methoxybenzoylacetamido) - 2 - (2'',4'' - di - tert - amylphenoxy) - 5-nitrobenzanilide, 500 ml. of glacial acetic acid, 500 ml. of ethyl alcohol, and 500 ml. of water. To the boiling mixture was cautiously added 100 g. of Plast-iron powder. Reflux was continued for 15 minutes before the reaction mixture was filtered from excess iron. The amine was converted to the hydrochloride by the addition of 1500 ml. of 20 percent hydrochloric acid. The tan solid was filtered, washed well with 5% hydrochloric acid, and washed well with water. The solid was sucked as dry as possible, refluxed with 1 liter of ethyl alcohol for 20 minutes, cooled to room temperature, filtered, and dried. The yield was 60 g. (60%) of a buff solid which did not discolor on drying.

In a 2-liter Erlenmeyer flask equipped with a stirrer were placed 67.2 g. (0.1 mole) of 4'-(o-methoxybenzoylacetamido) - 2 - (2'',4'' - di - tert - amylphenoxy) - 5-aminobenzanilide hydrochloride, 20 g. of anhydrous sodium acetate, and 1 liter of 90% acetic acid. The mixture was stirred for 1 hour to liberate the free base, after which 24 g. (0.1 mole) of the acid chloride was added. The product began to crystallize after stirring for 2 hours, and 2 liters of water were added. The product was filtered, washed well with water, and dried in a vacuum desiccator. The product weighed 71 g. (85%) and melted at 173–175° with loss of hydrogen chloride at 200–205°.

In a flask provided with a stirrer and thermometer were placed 40 volumes of dioxane and 4 volumes of diethanolamine followed by 4 parts of the sulfonyl chloride coupler. The mixture was stirred for one hour and drowned in a solution of 20 volumes of concentrated hydrochloric acid and 300 volumes of ice water. The solid which precipitated was collected on a funnel, washed with water, and dried.

Compound 22 was made in the same way as Compound 21, using ethanolamine instead of diethanolamine in the final step.

The following example illustrates the incorporation of our couplers in photographic emulsion layers:

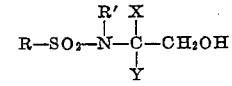
0.005 mole of Compound 1 was dissolved in a mixture of 15 cc. of 95% ethyl alcohol and 7.5 cc. of 20% sodium hydroxide solution. The mixture was warmed gently if necessary to complete solution of the coupler and was then poured into 200 cc. of water at 40° C. (The mixture might be added directly to a gelatin solution.) The resulting solution was brought to a pH of 6 to 7 by addition of 2% citric acid solution and the coupler solution was then mixed with a suitable amount of melted silver halide emulsion, e. g. 400 cc. of a positive-type silver bromide emulsion at 40° C. After coating, the emulsion layer thus obtained was subjected to the usual exposure and processing steps using a color-forming developer of the primary aromatic amino type followed by bleaching and fixing to remove the silver.

The couplers of our invention may also be incorporated in a mixed packet photographic system as described in Cressman and Fierke U. S. application Serial No. 344,894, filed concurrently herewith.

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

What we claim is:

1. A photographic silver halide emulsion containing as a color-forming coupler a compound having the general formula



wherein X represents a member of the group consisting of hydrogen and —CH_2OH, Y represents a member of the group consisting of hydrogen, —CH_3 and —CH_2OH, R represents a benzamido group to which is attached a coupler molecule capable of reaction with the oxidation products of a primary aromatic amino silver halide developing agent to yield a dye, and R' represents a member of the group consisting of hydrogen and —C_2H_4OH.

2. A photographic silver halide emulsion containing as a color-forming coupler a compound as defined in claim 1 wherein R represents a group of atoms containing a phenolic hydroxyl group an aromatic nucleus of which contains a position free to react with a primary aromatic amino silver halide developing agent to form a dye.

3. A photographic silver halide emulsion containing as a color-forming coupler a compound as defined in claim 1 wherein R represents a group of atoms containing a methylene group free to react with a primary aromatic amino silver halide developing agent to form a dye.

4. A photographic silver halide emulsion containing as a color-forming coupler a compound as defined in claim 1 wherein R represents a group of atoms containing a 5-pyrazolone group the 4-position of which is free to react with a primary aromatic amino silver halide developing agent to form a dye.

5. A photographic silver halide emulsion containing as a color-forming coupler a compound as defined in claim 1 wherein R represents a group of atoms containing a —CO—CH_2—CO— group.

6. A photographic silver halide emulsion containing as a color-forming coupler a compound as defined in claim 1 wherein R', X and Y each represents a hydrogen atom.

7. A photographic silver halide emulsion containing as a color-forming coupler a compound as defined in claim 1 wherein R' represents a —C_2H_4OH group and X and Y each represent a hydrogen atom.

8. A photographic silver halide emulsion containing as a color-forming coupler a compound as defined in claim 1 wherein R' represents a hydrogen atom and X and Y each represent a —CH_2OH group.

9. A photographic silver halide emulsion containing as a color-forming coupler, 1-hydroxy-4-chloro-2-{4'-[2'' - (2''',4''' - di - tert - amylphenoxy) - 5'' - {3''',5'''-

[di(di - β - hydroxyethylsulfamyl)]} - benzamido]-phenethyl}-2-naphthamide.

10. A photographic silver halide emulsion containing as a color-forming coupler, 1-hydroxy-4-chloro-N-{4'[2" - (2"',4"' - di - tert - amylphenoxy) - 5" - (3"',5"' - bis{N - [tri(hydroxymethyl)methyl] - sulfamyl} - benzamido)benzamido]phenethyl} - 2 - naphthamide.

11. A photographic silver halide emulsion containing as a color-forming coupler, 1-hydroxy-4-chloro-N-{4' - [2" - (2"',4"' - di - tert - amylphenoxy) - 5" - (3"',5"' - bis{N - [1,1 - di(hydroxymethyl) - ethyl]sulfamyl}benzamido) - benzamido]phenthyl} - 2 - naphthamide.

12. A photographic silver halide emulsion containing as a color-forming coupler, 1-hydroxy-N-{p-{2-(2,4-di-tert-amylphenoxy) - 5 - {m - [tris(hydroxymethyl)-

methyl]sulfamylbenzamido} - benzamido}phenethyl} - 2-naphthamide.

13. A photographic silver halide emulsion containing as a color-forming coupler, 1-phenyl-3-{m-{5-{3,5-bis[tris(hydroxymethyl)methyl]sulfamylbenzamido} - 2-2,4 - di - tert - amylphenoxy) - benzamido}benzamido}-5-pyrazolone.

14. A method of producing a colored photographic image in a silver halide emulsion layer containing a coupler compound defined in claim 1, which comprises exposing said layer and developing it with a developing solution containing a primary aromatic amino silver halide developing agent.

References Cited in the file of this patent

FOREIGN PATENTS

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