

1

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BENZIMIDAZOLYLSTILBENE WHITENING AND BRIGHTENING AGENTS

Nathan N. Crouse, Cincinnati, Ohio, assignor to Sterling Drug Inc., New York, N. Y., a corporation of Delaware

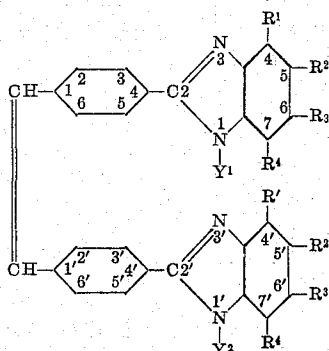
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This invention relates to novel fluorescent compounds of the benzimidazolylstilbene series useful as whitening and brightening agents, to intermediates for the same, and to the preparation thereof.

The present invention provides new fluorescent whitening and brightening agents which are useful in the treatment of threads, sheets, films, filaments, textile fabrics and the like, as well as in the manufacture of paper, varnishes, inks, coatings, and plastics. These new compounds are particularly well adapted to application to white and colored fabrics, especially in the optical bleaching of white fabrics, since they are substantive even in low concentrations to a wide variety of natural and synthetic fibers, they impart a desirable blue-white hue to the white fibers and brighten colored fibers treated therewith, and they have relatively high light stability. Moreover, my invention provides for the first time fluorescent whitening and brightening agents of the stilbene series having the foregoing properties and also having satisfactory stability to chlorine-containing commercial laundry bleaching agents such as sodium hypochlorite and calcium hypochlorite.

The novel compounds of my invention are stilbenes bearing in both the 4- and 4'-positions benzimidazol-2-yl radicals which are the same or different and they have the structural Formula I shown below,



Formula I

where R¹, R², R³, and R⁴ are radicals of the class consisting of: hydrogen; lower alkyl containing 1-4 carbon atoms, for example methyl, ethyl, isopropyl, and n-butyl; lower alkoxy containing 1-4 carbon atoms, for example methoxy, ethoxy, and n-butoxy; and halo, for example fluoro, chloro, and bromo; and Y¹ and Y² are radicals of the class consisting of: hydrogen; lower alkyl containing 1-6 carbon atoms, for example methyl, ethyl, n-propyl, isobutyl, and n-hexyl; hydroxy-lower alkyl containing 2-6 carbon atoms, for example 2-hydroxyethyl and 2,3-dihydroxypropyl; 2-hydroxy-3-sulfopropyl; hydroxy-oxaalkyl containing 3-15 carbon atoms, for example 2-hydroxy-3-(2,3-dihydroxypropoxy)propyl, 2-hydroxy-3-(2-hydroxyethoxy)propyl, and 2-hydroxy-3-[2-(2-hydroxyethoxy)ethoxy]propyl; carboxy-lower alkyl containing 2-6 carbon atoms, for example carboxymethyl and 2-carboxy-

2

ethyl; cyano-lower alkyl containing 3-6 carbon atoms, for example 2-cyanoethyl and 3-cyanopropyl; monocyclic aralkyl containing 7-11 carbon atoms, for example benzyl and benzyl containing 1-3 substituents, which can be the same or different, in the benzene ring, as halobenzyl, such as ortho-chlorobenzyl, para-fluorobenzyl, 2,4-dichlorobenzyl, and meta-bromobenzyl, lower alkylbenzyl such as ortho-methylbenzyl and para-isopropylbenzyl, and lower alkoxy-benzyl such as p-methoxybenzyl and 3,4-diethoxybenzyl, as well as 2-chloro-4-methoxybenzyl, 3-methoxy-4-methylbenzyl, 2-methoxy-4-chlorobenzyl, and the like; and allyl and methallyl.

In general, the compounds of the above structure are high-melting yellow or green-yellow solids which have the following solubility characteristics. They are insoluble in water, hydrocarbons, halogenated hydrocarbons, ketones, ethers and mineral acids. They are moderately soluble in N,N-dimethyl-formamide and dimethyl sulfoxide; some of them are soluble in acetic acid; and the compounds wherein at least one of Y¹ and Y² is hydrogen are weakly acidic and soluble in alcoholic alkali to yield yellow to red solutions. The compounds wherein Y¹ and Y² contain two or more hydroxyl groups have some solubility in glacial acetic acid, this solubility being highest in the dialkylated compounds wherein both Y¹ and Y² contain two or more hydroxyl groups in each radical. The N,N'-dialkylated compounds are slightly soluble in lower alkanols, such as ethanol, but this solubility is not increased by addition of alkali.

When the compounds of the present invention are dispersed in aqueous media, they fluoresce blue-white under ultraviolet light and show a wide range of absorption in the ultraviolet region. These compounds are substantive to a wide variety of natural and synthetic fibers, for example, cotton, cellulose acetate, viscose rayon, nylon, silk, and Orlon, and are absorbed by such fibers even from very low concentrations in aqueous dispersions. The compounds have relatively high stability to sunlight, soap, synthetic detergents and chlorine-containing bleaching agents.

The above-described properties of my new compounds make them especially valuable as whitening and brightening agents in treating white and colored fabrics to neutralize the yellowness in white textiles or to enhance the brilliance of colored textiles. In such utilization, the relatively high resistance of my compounds to chlorine bleaching and to light are distinct and surprising advantages, since the previously known whitening and brightening agents of the stilbene series have had as their chief drawbacks a lack of resistance of chlorine-containing bleaching agents and ease of decomposition under influence of light.

A further important advantage of the preferred species of this invention lies in the fact that on repeated applications to white fabrics, thereby building up the amount of the whitening agent on the fibers, the fabrics remain bluish-white and do not develop an undesirable discoloration, for example a red or gray color, such as is produced by many of the known optical bleaching agents when they are applied repeatedly, as for instance in successive launderings.

Although the compounds of my invention are substantially insoluble in water, they are readily utilizable as dispersions in aqueous media. Thus, the treatment of textile fabrics with these compounds is readily carried out by conventional procedures. For example, an aqueous dispersion containing about 0.0001 to 0.5% by weight of the compound and one or more suitable dispersing agents, for instance soap or an organic sulfonate or sulfate, is applied to the fabric, which absorbs the fluorescent compound and is whitened or brightened beneficially thereby. This application of the compound can be conveniently

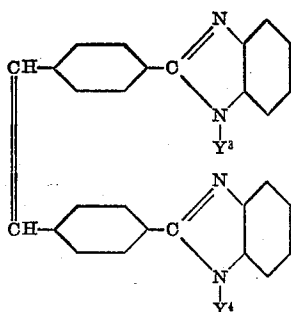
3

carried out in conjunction with a rinsing or washing operation.

The dispersions are readily formed, for example, by dissolving the compound in a suitable solvent such as *N,N*-dimethylformamide, alkaline aqueous alcohol, or glacial acetic acid and mixing the solution thus obtained in desired quantity with an aqueous soap or detergent solution. The compounds of Formula I which bear no substituents in the benzene rings of the benzimidazol-2-yl radicals are much more readily dispersed in this manner than are the corresponding highly substituted compounds, and it is for this reason that the sum of the carbon atoms in R^1 , R^2 , R^3 , and R^4 , in each ring, should be limited to about 16 carbon atoms. When a high degree of dispersibility is a desired feature in the utilization of my compounds, I generally prefer to employ those in which at least two of the radicals R^1 , R^2 , R^3 , and R^4 are hydrogen and the sum of the carbon atoms in all four substituents, in each ring, is no more than two.

A preferred mode of using and marketing the compounds is by incorporating them into solid or liquid soaps and detergents in an appropriate concentration, for example 0.02 to 0.5% of the whitening and brightening agent by weight.

For incorporation into white detergents, I particularly prefer the symmetrical and unsymmetrical *N,N'*-bis(oxyalkylated) compounds of my invention having the structural formula



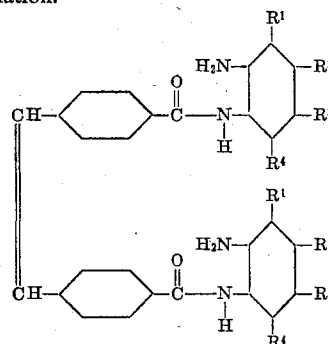
Formula IV

wherein Y^3 and Y^4 are the same or different and are members of the group consisting of hydrogen, hydroxy-lower alkyl radicals containing 2-6 carbon atoms, and hydroxy-oxaalkyl radicals containing 3-15 carbon atoms, at least one of Y^3 and Y^4 being other than hydrogen. These preferred species of my invention have been found both as individual species and in admixture with each other to have especially high stability in the presence of detergents and to have exceptionally good dispersibility in commercial detergents comprising organic sulfates or sulfonates, for example sodium lorol sulfate and sodium (higher alkyl) benzenesulfonates, and various builders such as sodium triphosphate (also known as sodium tripolyphosphate) and sodium sulfate, in addition to possessing the other advantageous properties common to all of my new compounds as set forth hereinabove. Moreover, repeated application of these compounds (Formula IV) to white fabrics of natural and synthetic fibers does not cause development of an undesirable color.

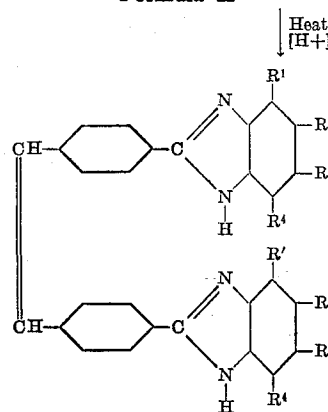
The compounds of my invention can be prepared by employing as starting materials appropriately ortho-substituted bisanilides of 4,4'-stilbenedicarboxylic acid. In general, I have found that it is most convenient to prepare the compounds wherein Y^1 and Y^2 in the general Formula I are both hydrogen (Formula III below) by cyclization of a bis-(ortho-aminoanilide) of a 4,4'-stilbenedicarboxylic acid by heating it under acidic condi-

4

tions; the reaction proceeds in accordance with the following equation.



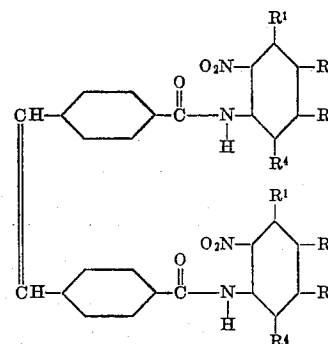
Formula II



Formula III

Usually, I prefer to prepare the bis-(ortho-aminoanilide) starting materials (Formula II) for the above process by reduction of the corresponding bis-(ortho-nitroanilides). When this is done, it is frequently advantageous to reduce the bis-(ortho-nitroanilide) and then cyclize the resulting bis-(ortho-aminoanilide) directly without isolating it. Thus, the reduction and cyclization reactions are conveniently effected in a single operation by reducing the 4,4'-stilbenedi[carbox(ortho-nitroanilide)] with a mixture of an acid, for example hydrochloric acid or acetic acid, and a metal such as aluminum, iron or zinc and then, if necessary, heating the reaction mixture to effect cyclization to form the desired 4,4'-bis(benzimidazol-2-yl) stilbene (Formula III). A mixture of stannous chloride and hydrochloric acid can also be employed as the reducing medium in this method. When an organic acid is employed in the reducing medium, it is frequently advantageous and sometimes necessary to add hydrochloric acid or similar strong inorganic acid to complete the cyclization step. Sodium hydrosulfite can be used as the reducing agent, but when this is done, for best yields the bis(ortho-aminoanilide) should be isolated prior to the cyclization step.

The bis(ortho-nitroanilides) which have the structural formula



are readily obtained by heating and stirring one mole of 4,4'-stilbenedicarbonyl chloride with approximately two moles of the appropriate ortho-nitroaniline, preferably in a solvent, for example chlorobenzene, and in the presence of an acid-accepting medium, for example an N,N-dialkylaniline.

The cyclization is generally carried out by heating the bis(ortho-aminoanilide) (Formula II) for one to six hours at 80–150° C., a range of 100–120° C. being usually preferred. For best results, a solvent should be employed in carrying out the reaction and for this purpose 2-methoxyethanol, 2-ethoxyethanol, and 75–90% acetic acid have been found to be especially useful.

Using the above process, for example the following compounds of Formula III are obtained by reducing the indicated bis-(ortho-nitroanilides) of 4,4'-stilbenedicarboxylic acid and cyclizing the corresponding intermediate bis-(ortho-aminoanilide) thereby produced in each instance (as will be appreciated, the tautomerism of these products affords in many cases alternative choices of designation for a single substance; these choices are indicated hereinbelow, where appropriate, in accordance with conventional nomenclature requirements):

4,4'-bis(benzimidazol-2-yl)stilbene, from the bis(ortho-nitroanilide);

4,4'-bis[4(or 7)-methoxybenzimidazol-2-yl]stilbene, from the bis(3-methoxy-2-nitroanilide);

4,4'-bis[4(or 7)-ethoxybenzimidazol-2-yl]stilbene, from the bis(3-ethoxy-2-nitroanilide);

4,4'-bis[5(or 6)-isopropoxybenzimidazol-2-yl]stilbene, from the bis(5-isopropoxy-2-nitroanilide);

4,4'-bis(5,6-dimethoxybenzimidazol-2-yl)stilbene, from the bis(4,5-dimethoxy-2-nitroanilide);

4,4'-bis(5,6-dibutoxybenzimidazol-2-yl)stilbene, from the bis(4,5-dibutoxy-2-nitroanilide);

4,4'-bis[4,5,7(or 4,6,7)-trimethoxybenzimidazol-2-yl]stilbene, from the bis(3,5,6-trimethoxy-2-nitroanilide);

4,4'-bis[4(or 7)-methylbenzimidazol-2-yl]stilbene, from the bis(3-methyl-2-nitroanilide);

4,4'-bis[5(or 6)-tert-butylbenzimidazol-2-yl]stilbene, from the bis(5-tert-butyl-2-nitroanilide);

4,4'-bis(5,6-dimethylbenzimidazol-2-yl)stilbene, from the bis(4,5-dimethyl-2-nitroanilide);

4,4'-bis(4,5,6,7-tetramethylbenzimidazol-2-yl)stilbene, from the bis(3,4,5,6-tetramethyl-3-nitroanilide);

4,4'-bis[5(or 6)-ethylbenzimidazol-2-yl]stilbene, from the bis(4-ethyl-2-nitroanilide);

4,4'-bis[5(or 6)-chlorobenzimidazol-2-yl]stilbene, from the bis(4-chloro-2-nitroanilide);

4,4'-bis[5(or 6)-fluoro-benzimidazol-2-yl]stilbene, from the bis(5-fluoro-2-nitroanilide);

4,4'-bis[4,6(or 5,7)-dibromo-benzimidazol-2-yl]stilbene, from the bis(3,5-dibromo-2-nitroanilide);

4,4'-bis[4,5,6(or 5,6,7)-trichloro-benzimidazol-2-yl]stilbene, from the bis(4,5,6-trichloro-2-nitroanilide);

4,4'-bis[6-methoxy-5-fluoro(or 5-methoxy-6-fluoro)-benzimidazol-2-yl]stilbene, from the bis(4-methoxy-5-fluoro-2-nitroanilide);

4,4'-bis[4-bromo-6,7-methylenedioxy(or 7-bromo-4,5-methylenedioxy)benzimidazol-2-yl]stilbene, from the bis(3-bromo-5,6-methylenedioxy-2-nitroanilide); and

4,4'-bis[5-methoxy-6-methyl(5-methyl-6-methoxy)-benzimidazol-2-yl]stilbene, from the bis(4-methoxy-5-methyl-2-nitroanilide).

The N,N'-unsubstituted compounds (Formula III) obtained in the manner described above are useful per se as whitening and brightening agents. They react readily with alkylating agents to yield N-mono- and symmetrical or unsymmetrical N,N'-di-(alkyl or substituted alkyl) derivatives, so that they are also useful as starting materials for the convenient preparation of the whitening and brightening agents of my invention of Formula I wherein one or both of Y¹ and Y² are alkyl or substituted alkyl

radicals of the type hereinbefore defined. The alkylation reaction is readily carried out by heating a 4,4'-bis(benzimidazol-2-yl)stilbene (Formula III) with the appropriate alkylating agent. Usually a heating period of about one to four hours at 50–125° C. is sufficient to produce a satisfactory yield of the desired product. The alkylating agents useful in this conversion include for example esters of strong organic and inorganic acids having the formula Z—An, where Z is a member of the class consisting of lower alkyl containing 1–6 carbon atoms, hydroxy-lower alkyl containing 2–6 carbon atoms, 2-hydroxy-3-sulfopropyl, hydroxy-oxaalkyl containing 3–15 carbon atoms, carboxy-lower alkyl containing 2–6 carbon atoms, cyano-lower alkyl containing 3–6 carbon atoms, and monocyclic aralkyl containing 7–11 carbon atoms and An is the anion of a strong acid. Illustrative of these esters are: methyl sulfate, ethyl sulfate; methyl p-toluene-sulfonate; lower alkyl halides, such as methyl chloride, ethyl bromide, butyl chloride, and hexyl chloride; monocyclic aralkyl halides, such as benzyl chloride, p-methoxybenzyl chloride, o-chlorobenzyl chloride, 2-chloro-4-methoxybenzyl bromide, and benzyl bromide; allyl and methallyl halides, such as allyl chloride and methallyl bromide; carboxy-lower alkyl halides, such as 2-carboxyethyl chloride and carboxymethyl bromide; cyano-lower alkyl halides, such as 2-cyanoethyl chloride; hydroxy-lower alkyl halides, such as 2,3-dihydroxypropyl chloride (or glycerol alpha-chlorohydrin), ethylene chlorohydrin, ethylene bromohydrin, isobutylene chlorohydrin; 2-hydroxy-3-sulfopropyl chloride or bromide; hydroxy-oxaalkyl halides, such as 2-hydroxy-3-(2-hydroxyethoxy)-propyl chloride, 2-hydroxy-3-(2,3-dihydroxypropoxy)-propyl chloride and 2-hydroxy-3-[2-(2-hydroxyethoxy)-ethoxy]-propyl chloride. Also useful as alkylating agents are 1,2-lower alkylene oxides containing 2–6 carbon atoms, for example, ethylene oxide, propylene oxide, glycidol, and epichlorohydrin; and acrylonitrile and methacrylonitrile.

The N-monoalkylated compounds (Formula I, where only one of Y¹ and Y² is hydrogen) are obtained by heating preferably one or advantageously slightly more than one molecular equivalent of the appropriate alkylating agent with one molecular equivalent of the 4,4'-bis(benzimidazol-2-yl)stilbene (Formula III). Minor proportions of the corresponding N,N'-dialkylated compound (Formula I, where neither of Y¹ and Y² is hydrogen) and of unreacted N,N'-unsubstituted starting material (Formula III), varying in amounts depending in part on the relative proportions of the reactants and in part on the reaction conditions, will be found associated with the N-monoalkylated compound obtained as the chief product of the alkylation reaction. If desired, the N-monoalkylated product can be purified, for example by use of suitable solvents, but ordinarily it is unnecessary and uneconomical for practical purposes to effect such purification since the mixture is directly useful as a whitening and brightening agent.

As will be understood, the use of larger proportions of the alkylating agent favors higher yields of the N,N'-dialkylated compound. When this is the desired product, there are of course required by theory at least two molecular equivalents of the alkylating agent per equivalent of the 4,4'-bis(benzimidazol-2-yl)stilbene (Formula III); as a matter of fact, for best conversion to the dialkylated product an excess of the alkylating agent should be employed, for example an excess of 1–4 equivalents of the alkylating agent. The N,N'-dialkylated compounds obtained in this manner are symmetrical. When an unsymmetrical product is desired, an N-monoalkylated compound or, alternatively, a reaction mixture containing it is treated with a different alkylating agent, thereby producing a compound of Formula I wherein Y¹ and Y² are different alkyl or substituted alkyl radicals.

7

When the alkylating agent has a hydroxyl group in its structure, for example a hydroxy-lower alkyl or hydroxy-oxaalkyl compound, the hydroxyl function in the resulting N-monoalkylated product (e. g., Formula I, Y¹=H, Y²=hydroxy-lower alkyl or hydroxy-oxaalkyl) interacts with a second equivalent of the same or a different alkylating agent to yield preferentially O-alkylated products rather than the expected N,N'-dialkylated derivative, the latter being produced only in relatively small amount. The use of a large excess of the alkylating agent leads to substantially complete production of N,N'-disubstituted products.

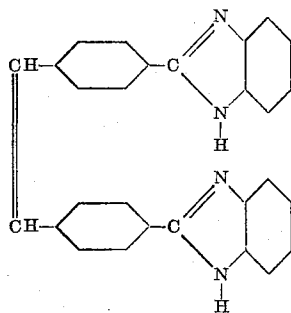
Instead of using the alkylation process described above, an alternative method for obtaining N-(2-cyano-lower alkyl)- and N,N'-di(2-cyano-lower alkyl)-compounds of Formula I is by interacting an acrylonitrile with the N,N-unsubstituted starting material (Formula III). The hydrolysis of these mono- and di-2-cyano-lower alkyl compounds to the corresponding 2-carboxy-lower alkyl compounds affords an alternative route to the latter substances.

For the preparation of the N,N'-dialkyl- and N,N'-di(monocyclic aralkyl) compounds of Formula I, there can be employed instead of the alkylation process an alternative method which comprises cyclizing a 4,4'-stilbenedi(carbox[ortho-(mono-lower alkylamino or mono-monocyclic aralkylamino)]-anilide) by heating it in the presence of an inorganic acid, for example hydrochloric acid, and preferably in a solvent such as 2-methoxy-ethanol or 2-ethoxyethanol. The reaction conditions for this cyclization are substantially the same as for the cyclization of the corresponding ortho-primary amino compounds described hereinabove.

My invention is illustrated by the following examples without, however, being limited thereto.

EXAMPLE 1

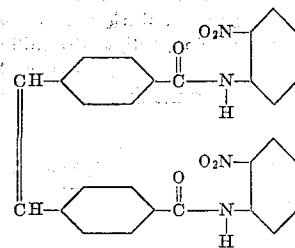
4,4'-bis(benzimidazol-2-yl)stilbene



A. A solution of 290 g. (2.1 mole) of ortho-nitroaniline in 2860 g. of N,N-dimethylaniline was placed in a ten-liter, three-neck flask fitted with a high-speed agitator and thermometer and was heated to 50–55° C. To this solution there was then added during a period of three to four minutes a heated (129–132° C.) solution of 305 g. (1 mole) of 4,4'-stilbenedicarbonyl chloride in 3580 g. of chlorobenzene. The last remnants of the acid chloride were rinsed from its container into the reaction flask with about 100 g. of boiling chlorobenzene. The temperature of the resulting reaction mixture rose to about 80–90° C. and after a few minutes yellow crystals began to separate from solution and the reaction mixture thickened. The reaction mixture was held at 85–90° C. for one hour and was then stirred at 95–105° C. for eight hours. The reaction mixture was cooled to 25° C. and filtered. The solid cake thus collected was washed successively with 255 g. of chlorobenzene, 475 g. of methanol, and finally with water until a sample of wash liquor was colorless. The yellow product was oven-dried at 80–100° C. There was thus obtained 430 g. of 4,4'-stilbenedi[carbox(ortho-

8

nitroanilide)] having the structural formula



which melted at 305–307° C.

Analysis.—Calculated for C₂₈H₂₀O₆N₄: C, 66.00%; H, 3.94%; N, 11.01%; O, 18.85%. Found: C, 65.85%; H, 4.19%; N, 10.61%; O, 19.30% (direct analysis).

In the preparation of the above dianilide, it was found that the chlorobenzene could be replaced with orthodichlorobenzene and the N,N-dimethylaniline could be replaced with N,N-diethylaniline to afford the same product in satisfactory yield. The product was also obtained, but in poorer yield and quantity by condensing the reactants in a solvent medium of refluxing chlorobenzene while permitting the hydrogen chloride formed in the reaction to distill off.

B. To a two-liter, three-neck flask fitted with a high-speed stirrer, reflux condenser, dropping funnel, and thermometer there were added 45 g. (0.0885 mole) of 4,4'-stilbenedi[carbox(ortho-nitroanilide)] and 1125 ml. of 2-methoxyethanol. The mixture was heated to reflux temperature (about 125° C.) and then the outside source of heat was removed. Through the dropping funnel there was added to the mixture a solution of 129 g. (0.575 mole) of stannous chloride dihydrate in 255 ml. of concentrated hydrochloric acid (about 38% by weight) at such a rate that refluxing was quite rapid but well within the capacity of the condenser to prevent loss of solvent; the time required for the addition was about seven minutes. During the addition the temperature of the mixture dropped to about 107° C. After the addition of the reducing agent was completed, the reaction mixture was refluxed for four hours and then was cooled overnight in a refrigerator. The solid which had separated from solution was collected on a filter and the filter cake was washed free of acid with water as determined by testing with Congo red. The bright yellow powder thus obtained, which was 4,4'-bis(benzimidazol-2-yl)stilbene dihydrochloride, weighed 41 g. This product was suspended in 410 ml. of 95% ethanol and 57 g. of 50% aqueous sodium hydroxide solution was added. The mixture was refluxed until substantially all of the solid had dissolved and was then filtered to remove a small amount of insoluble material. The filtrate was diluted with about four liters of water and filtered to collect the solid which separated from solution. The collected solid was washed free of alkali with water and dried at 100° C. under reduced pressure. There was thus obtained 33 g. of 4,4'-bis(benzimidazol-2-yl)stilbene as a pale yellow solid which did not melt when heated to 400° C.

Analysis.—Calculated for C, H, N: C, 81.54%; H, 4.88%; N, 13.58%. Found: C, 81.03%; H, 5.10%; N, 13.36%.

The free base was also obtained by dissolving the dihydrochloride in alkaline 2-methoxyethanol, diluting the solution with water, filtering to collect the solid which separated from solution, and washing the product with water until a sample of the wash liquor was free of alkali. This product was identical with the 4,4'-bis(benzimidazol-2-yl)stilbene described above.

The dihydrochloride was not soluble as such in any of the common solvents. The free base was slightly soluble in lower alkanols and in the 2-(lower alkoxy)-ethanols; it was more soluble in N,N'-dimethylformamide; and it was appreciably soluble (up to about 20% by weight) in alkaline 2-methoxyethanol. The free base

9

reacts with organic and inorganic acids to form the corresponding salts which are all water-insoluble.

EXAMPLE 2

4,4'-bis(benzimidazol-2-yl)stilbene

In a 250 ml. flask fitted with an agitator and reflux condenser there were placed 131 g. of glacial acetic acid, 13 g. of water, 2.56 g. (0.059 mole) of aluminum chips, and 1.18 g. of hydrochloric acid (20° Baumé). The mixture was agitated vigorously and heated rapidly. Bubbling of hydrogen from the mixture was vigorous when the temperature had reached 70° C., and to the mixture there was then added 10.16 g. (0.02 mole) of 4,4'-stilbenedi[carbox(ortho-nitroanilide)]. The reaction mixture was refluxed for four hours, after which there was added 1.76 g. (0.065 mole) of aluminum chips. The reaction mixture was refluxed for a further period of sixteen hours. The product, 4,4'-stilbenedi[carbox(ortho-aminoanilide)], thus formed was not isolated in this instance. Instead, after removal of the outside source of heat, there was added to the reaction mixture 69.4 g. of hydrochloric acid (20° Baumé) and refluxing was continued for a final period of four hours to effect the desired ring closure. The mixture was then cooled to 25–30° C. and filtered. The solid thus collected was washed with water until a sample of the wash liquor was free of acid as determined by test with Congo red paper. The product obtained, in this manner, which was 4,4'-bis(benzimidazol-2-yl)stilbene dihydrochloride, weighed 9.7 g. It was identical with the dihydrochloride described above in Example 1.

The 4,4'-bis(benzimidazol-2-yl)stilbene dihydrochloride was also obtained in satisfactory yield when iron and 75–90% acetic acid was substituted for the aluminum and glacial acetic acid in the above procedure.

Treatment of samples of the dihydrochloride obtained above with ethanolic sodium hydroxide yielded in each instance 4,4'-bis(benzimidazol-2-yl)stilbene, identical with the base described in Example 1.

EXAMPLE 3

4,4'-bis(benzimidazol-2-yl)stilbene

To 271.8 g. of finely ground (20 mesh) crude 4,4'-bis(benzimidazol-2-yl)stilbene dihydrochloride (obtained by the method described above in Example 1) in 3050 g. of 95% ethanol there was added 216 g. of 50% aqueous sodium hydroxide solution. This mixture was heated to reflux to dissolve the solid, and the solution was then filtered to remove about 40 g. of creamy solid consisting chiefly of inorganic salts which failed to dissolve. The filtrate was heated until about 2200 g. of alcohol had been distilled off and to the residue there was added 3.5 liters of cold water in a thin stream. The mixture was cooled and filtered and the product thus collected was washed with water until a sample of the filtrate was free of alcohol. There was thus obtained 217 g. of 4,4'-bis(benzimidazol-2-yl)stilbene.

EXAMPLE 4

4,4'-bis(benzimidazol-2-yl)stilbene

In a 100 ml. flask there were placed 25 g. of 2-methoxyethanol, 6.96 g. of sodium hydrosulfite, 2.54 g. of 4,4'-stilbenedi[carbox(ortho-nitroanilide)], 1.0 g. of 50% aqueous sodium hydroxide solution, and 10 g. of water. This mixture, which was alkaline to phenolphthalein, was refluxed for two hours, after which time the solution was no longer alkaline to phenolphthalein. A further quantity of 50% aqueous sodium hydroxide solution was added sufficient to make the mixture alkaline and refluxing was resumed and continued for one and one-half hours. Ten ml. of concentrated hydrochloric acid was then added and the mixture was refluxed for twenty minutes. The mixture was cooled to 20° C. and filtered, and the solid thus collected was washed with water until the wash liquor was free of acid using Congo

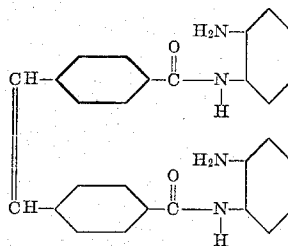
10

red paper. The product thus obtained was 4,4'-bis(benzimidazol-2-yl)stilbene, identical with the product described above in Example 1.

EXAMPLE 5

4,4'-bis(benzimidazol-2-yl)stilbene

A. To a well-stirred mixture of 91 g. of *o*-phenylenediamine, 630 ml. of chlorobenzene, 100 g. of sodium carbonate, and 250 ml. of water heated to 85° C. there was added out of a heated dropping funnel during a period of ten minutes a solution of 105 g. of 4,4'-stilbenedicarbonyl chloride in 1400 ml. of chlorobenzene. The temperature of the reaction mixture gradually rose during the addition until refluxing was initiated. The mixture was refluxed for six hours, and then cooled and filtered. The solid thus collected was washed successively with 500 ml. of hexane, 1000 ml. of a 0.25% aqueous solution of lorcobenzylidimethylammonium chloride, and finally water, until the product was free of quaternary ammonium chloride. The grey-white product was then dried in an oven. There was thus obtained 154 g. of 4,4'-stilbenedi[carbox(ortho-aminoanilide)] having the structural formula

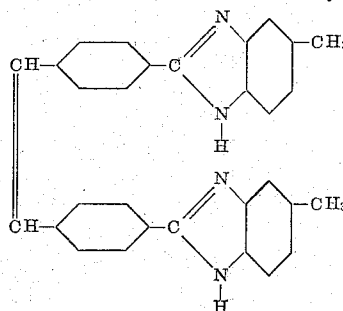


This compound was weakly fluorescent; it was not soluble in the ordinary solvents.

B. In a two-liter, three-neck flask there were placed 800 ml. of 2-methoxyethanol and 200 g. of a wet paste of 92 g. of 4,4'-stilbenedi[carbox(ortho-aminoanilide)] and 108 g. of water. This mixture was stirred and heated to reflux and 46 ml. of concentrated hydrochloric acid (about 38% by weight) was dropped into the mixture during a period of thirty-five minutes and this reaction mixture was refluxed for eighteen hours. The reaction mixture was then cooled and filtered and the solid thus collected was washed with water until a sample of the wash liquor was free of acid, using Congo red paper. The washed product, which was 4,4'-bis(benzimidazol-2-yl)stilbene dihydrochloride, was suspended in 800 ml. of 95% ethanol, 25 ml. of 50% aqueous sodium hydroxide solution was added, and the mixture was heated to reflux and filtered. The filtrate was diluted with three liters of water, and the solid which separated from solution was collected on a filter. There was thus obtained 61.3 g. of 4,4'-bis(benzimidazol-2-yl)stilbene, identical with the product described above in Example 1.

When the foregoing process of part B was repeated, but replacing the 2-methoxyethanol solvent with *n*-butanol, the yield of the 4,4'-bis(benzimidazol-2-yl)stilbene was considerably lower.

EXAMPLE 6

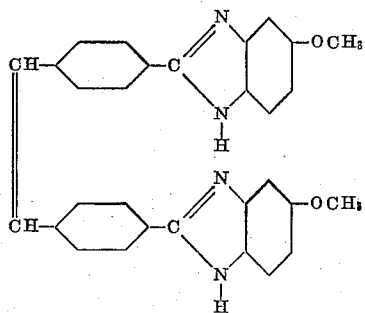
4,4'-bis[5(or 6)-methylbenzimidazol-2-yl]stilbene

A. To a three-liter, three-neck flask fitted with agitator and thermometer there were added 61.0 g. of *N,N*-dimethylaniline, 63.9 g. of 2-nitro-4-methylaniline, and 707 g. of chlorobenzene. This material was heated to 50° C. for five minutes and then a solution of 60.4 g. of 4,4'-stilbenedicarbonyl chloride in 588 g. of ortho-dichlorobenzene was added. A solid began to separate slowly from the reaction mixture and the reaction temperature rose to 85° C. The reaction mixture was heated at 85–90° C. for one hour and then at 95–100° C. for twenty-four hours. The reaction mixture was cooled to room temperature and filtered. The solid product thus collected was washed with 67 g. of chlorobenzene, 97 g. of methanol, and a 0.25% aqueous solution of lorolbenzylidimethylammonium chloride until a clear filtrate was obtained. The product was then washed with water until the quaternary ammonium chloride had been removed. The yellow product was dried in an oven. There was thus obtained 99 g. of 4,4'-stilbenedi[carbox(2-nitro-4-methylanilide)] which did not melt when heated at 320° C.

B. To a five-liter flask fitted with an agitator, thermometer, reflux condenser and dropping funnel there were added 2250 ml. of 2-methoxyethanol and 99 g. (0.177 mole) of 4,4'-stilbenedi[carbox(2-nitro-4-methylanilide)]. This mixture was heated to reflux temperature, then heating was discontinued, and there was added a solution of 258 g. of stannous chloride dihydrate in 510 ml. of hydrochloric acid at such a rate that refluxing was maintained by the heat of the reaction. After this addition was completed, the reaction mixture was refluxed for seven hours. The mixture was chilled in an icebox overnight and then filtered. The solid product thus collected was washed first with one liter of 1% hydrochloric acid and then with water until the solid was free of acid to Congo red. There was thus obtained 86.7 g. of 4,4'-bis[5(or 6)-methylbenzimidazol-2-yl]stilbene dihydrochloride. This salt was suspended in 919 ml. of 2-methoxyethanol and the mixture was heated to 60° C. with stirring. There was then added 36 g. of 50% aqueous sodium hydroxide solution and the mixture was slowly heated to reflux temperature. The mixture was filtered to remove insoluble material, consisting chiefly of inorganic salts, and the solid thus removed was washed with 100 ml. of boiling 2-methoxyethanol. The filtrate and wash liquor were combined and diluted in a crock with nine liters of water with vigorous stirring. The yellow solid which separated from solution was collected on a filter and freed of alkali by washing with water. There was thus obtained 61.8 g. of 4,4'-bis[5(or 6)-methylbenzimidazol-2-yl]stilbene.

EXAMPLE 7

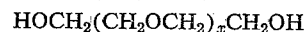
4,4'-bis[5(or 6)-methoxybenzimidazol-2-yl]stilbene



A. To a mixture of 61.0 g. of *N,N*-dimethylaniline, 70.6 g. of 2-nitro-4-methoxyaniline, and 640 ml. of chlorobenzene heated to 50° C. there was added slowly with stirring over a period of eight minutes, a hot (120–130° C.) solution of 61.1 g. of 4,4'-stilbenedicarbonyl chloride in 467 ml. of chlorobenzene. The remnants of the acid chloride solution were washed from its container

into the reaction mixture with an additional 61 ml. of chlorobenzene. The mixture was heated at 85–95° C. for one hour and then at 95–100° C. for twenty-four hours. The mixture was then cooled to room temperature (about 25° C.) and filtered, and the solid thus collected was washed successively with 61 ml. of chlorobenzene, 122 ml. of methanol, and a warm (50° C.) 0.25% aqueous solution of lorolbenzylidimethylammonium chloride until the wash liquor was free of chlorobenzene. The solid was finally washed with one liter of warm (50° C.) water to remove the quaternary ammonium chloride. There was thus obtained 111.2 g. of 4,4'-stilbenedi[carbox(2-nitro-4-methoxyanilide)] as a yellow solid which melted at 311–318° C.

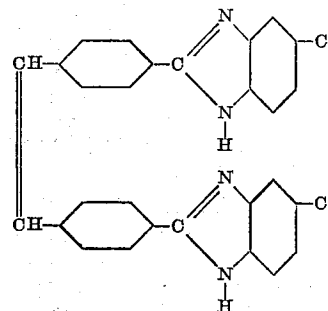
B. A mixture of 2,324 ml. of 2-methoxyethanol and 104 g. of 4,4'-stilbenedi[carbox(2-nitro-4-methoxyanilide)] was heated to reflux, then heating was discontinued and a solution of 266 g. of stannous chloride dihydrate in 527 ml. of concentrated hydrochloric acid was added slowly with stirring over a period of seven minutes. Refluxing was then resumed and continued for fifteen hours. The reaction mixture was cooled to 15° C. and filtered, and the solid thus collected was washed with water until free of acid and dried. This product, which was 4,4'-bis[5(or 6)-methoxybenzimidazol-2-yl]stilbene dihydrochloride, was suspended in 1,076 ml. of 2-methoxyethanol and heated to 60° C. To this mixture there was added 50.6 g. of 50% aqueous sodium hydroxide solution. The temperature of the mixture rose to 75° C. and almost all of the solid dissolved. The mixture was heated to reflux temperature and filtered. The residue thus removed was washed with 106 ml. of boiling 2-methoxyethanol, and the washings were combined with the filtrate. This solution was slowly diluted with eleven liters of warm (60° C.) water. The yellow solid which precipitated from solution was collected on a filter, washed with water until free of alkali, and then dried in an oven. The product thus obtained, which was 4,4'-bis[5(or 6)-methoxybenzimidazol-2-yl]stilbene, weighed 81.2 g. It was soluble in polyethyleneglycol



of average molecular weight 200 (Carbowax 200) containing alkali. The fluorescence of this solution, though yellower than that exhibited by 4,4'-bis(benzimidazol-2-yl)stilbene, was far more intense than that of the latter compound under similar conditions.

EXAMPLE 8

4,4'-bis[5(or 6)-chlorobenzimidazol-2-yl]stilbene



A. A mixture of 72.5 g. of 2-nitro-4-chloroaniline, 61.0 g. of *N,N*-dimethylaniline, and 640 ml. of chlorobenzene was heated to 50° C. and there was then added slowly over a period of five minutes, with stirring, a hot (125–130° C.) solution of 61.0 g. of 4,4'-stilbenedicarbonyl chloride in 474 ml. of chlorobenzene. The residual acid chloride solution was washed from its container into the mixture with 61 ml. of chlorobenzene. The mixture was heated at 85–90° C. for one hour and then at 75–100° C. for twenty-four hours. The reaction mixture was cooled to room temperature (about 25° C.) and filtered. The solid thus collected was washed suc-

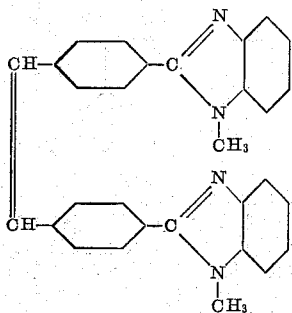
13

cessively with 61 ml. of chlorobenzene, 122 ml. of methanol, and sufficient warm (50° C.) 0.25% aqueous solution of lorolbenzylidimethylammonium chloride to yield colorless washings. The solid was finally washed with water until the quaternary ammonium chloride had been removed and the product was dried. There was thus obtained 107.2 g. of 4,4'-stilbenedi[carbox(2-nitro-4-chloroanilide)].

B. A mixture of 100 g. of 4,4'-stilbenedi[carbox(2-nitro-4-chloroanilide)] and 2,200 ml. of 2-methoxyethanol was heated to reflux temperature, then the source of heat was removed, and there was added with stirring a solution of 252.3 g. of stannous chloride dihydrate in 499 ml. of concentrated hydrochloric acid at such a rate as to maintain rapid refluxing. The reaction mixture was refluxed for twenty hours and was then cooled to 25° C. and filtered. The solid thus collected was washed with water until free of acid and dried. The yellow product thus obtained, which was 4,4'-bis[5(or 6)-chlorobenzimidazol-2-yl]stilbene dihydrochloride, was mixed with 1,250 ml. of 95% ethanol and 64 g. of 50% aqueous sodium hydroxide solution. This mixture was refluxed until substantially all of the yellow solid had dissolved and then filtered hot to remove insoluble inorganic salts. The solid residue on the filter was washed with 100 ml. of 95% ethanol and all of the filtrates were combined and were then diluted slowly with seven liters of warm (50° C.) water. The pale yellow solid which separated from solution was collected on a filter, washed free of alkali with water and dried. There was thus obtained 83.2 g. of 4,4'-bis[5(or 6)-chlorobenzimidazol-2-yl]stilbene.

EXAMPLE 9

4,4'-bis(1-methylbenzimidazol-2-yl)stilbene



A. To a hot (85° C.) and stirred mixture of 48 g. of N-methyl-ortho-phenylenediamine, 294 ml. of chlorobenzene, 46.6 g. of sodium carbonate and 117 ml. of water there was added slowly from a heated dropping funnel a solution of 51.7 g. of 4,4'-stilbenedicarbonyl chloride in 717 ml. of chlorobenzene. This addition, which required about twenty minutes, was followed by a six-hour period of refluxing of the reaction mixture. A small quantity of aqueous sodium carbonate solution was added to the mixture during the course of the reflux period to keep it alkaline to phenolphthalein. The reaction mixture was cooled to 5° C. and filtered, and the solid thus collected was washed with hexane and then with water. The solid was then slurried in hexane and filtered. The product thus obtained, which was 4,4'-stilbenedi[carbox[ortho-methylamino]anilide]}, weighed 41.0 g.

B. A mixture of 41.0 g. of 4,4'-stilbenedi[carbox[ortho-(methylamino)anilide]} and 1158 ml. of 2-methoxyethanol was heated to reflux temperature and 115.8 ml. of concentrated hydrochloric acid was added dropwise with stirring to the refluxing mixture. All of the solid dissolved during this addition. The solution was refluxed for a further period of one hour. The solution was then distilled to remove about two-thirds of the 2-methoxyethanol and the residue was chilled overnight in a refrigerator. The solid which had separated from solu-

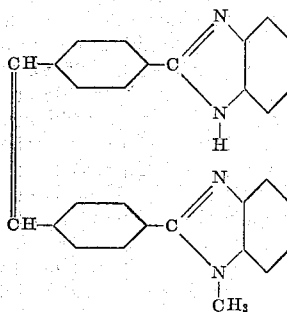
14

tion was then collected on a filter. There was thus obtained 24.4 g. of 4,4'-bis(1-methylbenzimidazol-2-yl)stilbene dihydrochloride. A mixture of this product and 965 ml. of 2-methoxyethanol was heated to reflux temperature and 450 ml. of concentrated hydrochloric acid was slowly added with stirring to dissolve the solid. The solution thus obtained was poured into an agitated mixture of 550 g. of 50% aqueous sodium hydroxide solution and 500 ml. of 95% ethanol. The mixture became hot and a cream colored solid separated from solution. The mixture was distilled until 574 ml. of distillate had been collected. The residue was cooled to 50° C. and 1250 ml. of water was added very slowly with good agitation. The mixture was cooled to room temperature while continuing the agitation and was then filtered. The collected solid was washed with water until free of alkali and dried. There was thus obtained 4,4'-bis(1-methylbenzimidazol-2-yl)stilbene.

EXAMPLE 10

Methylation of 4,4'-bis(benzimidazol-2-yl)stilbene

A. To a solution of 10.3 g. (0.025 mole) of 4,4'-bis(benzimidazol-2-yl)stilbene in 100 ml. of 2-methoxyethanol there was added 4 ml. of a 50% aqueous solution of sodium hydroxide. The mixture was heated to 65° C. and 3.14 g. (0.025 mole) of methyl sulfate was added. The reaction mixture was heated at 70° C. for three hours and then 1.5 ml. of water was added. The reaction mixture was cooled to 20° C. and filtered. The solid thus collected was washed with water and then dried at 70° C. There was thus obtained 9.9 g. of 4-(benzimidazol-2-yl)-4'-(1-methylbenzimidazol-2-yl)stilbene, having the structural formula



B. A mixture of 8.7 g. (0.021 mole) of 4,4'-bis(benzimidazol-2-yl)stilbene, 65 ml. of 2-methoxyethanol, and 4.46 ml. of a 50% aqueous solution of sodium hydroxide was heated to 65° S. and 3.19 g. (0.025 mole) of methyl sulfate was added. The reaction mixture was heated at 70° C. for one hour and then 3.19 (0.025 mole) of methyl sulfate was added, after which the mixture was refluxed for one and one-half hours. There was then added 150 ml. of water to the mixture and, it was cooled to room temperature (about 25° C.). The mixture was filtered and the solid thus collected was washed with water and then dried at 75° C. There was thus obtained 8.1 g. of 4,4'-bis(1-methylbenzimidazol-2-yl)stilbene, identical with the product described above in Example 9.

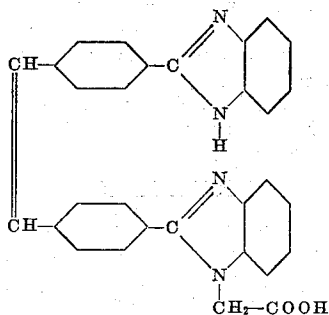
EXAMPLE 11

Carboxymethylation of 4,4'-bis(benzimidazol-2-yl)stilbene

To a 100 ml. flask fitted with an agitator and a reflux condenser there were added 4.84 g. (0.0113 mole) of 4,4'-bis(benzimidazol-2-yl)stilbene, 20 ml. of 2-methoxyethanol, and 3.0 g. of 50% aqueous sodium hydroxide solution. This mixture was heated until the solid went into solution, and the solution thus obtained was cooled to about 50° C. and 0.95 g. (0.012 mole) of monochloroacetic acid was added. The reaction mixture was

15

refluxed for two hours, cooled to about 50° C. and another 0.95 g. monochloroacetic acid was added. The reaction mixture was refluxed for a further period of two hours and then cooled to room temperature (about 25° C.). Fifty ml. of water was added dropwise to the reaction mixture, and the solid which had separated from solution was collected on a filter, washed with about 60 ml. of water, and dried in an oven. There was thus obtained 3.2 g. of 4-(benzimidazol-2-yl)-4'-[1-(carboxymethyl)-benzimidazol-2-yl]-stilbene, having the structural formula

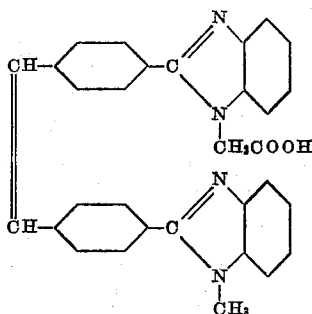


This compound reacts with bases, for example alkali and alkaline earth hydroxides, to form the corresponding carboxylate salts.

EXAMPLE 12

Carboxymethylation of 4-(benzimidazol-2-yl)-4'-(1-methylbenzimidazol-2-yl)stilbene

A mixture of 4.26 g. (0.01 mole) of 4-(benzimidazol-2-yl)-4'-(1-methylbenzimidazol-2-yl)stilbene, 1 ml. of 50% aqueous sodium hydroxide solution, and 25 ml. of 2-methoxyethanol was heated to 80° C. to dissolve the solid and 0.95 g. (0.012 mole) of chloroacetic acid was added. A yellow precipitate appeared immediately in the reaction mixture. The mixture was refluxed for two hours, then cooled to 90° C., and another 0.95 g. of chloroacetic acid was added. The mixture was refluxed for two hours, then cooled to 90° C. and 50 ml. of water was added. The mixture was then diluted with 200 ml. of hot water, cooled to room temperature, and filtered. The solid thus collected was washed with water and dried. There was thus obtained 4.6 g. of 4-[1-(carboxymethyl)benzimidazol-2-yl]-4'-(1-methylbenzimidazol-2-yl)stilbene having the structural formula



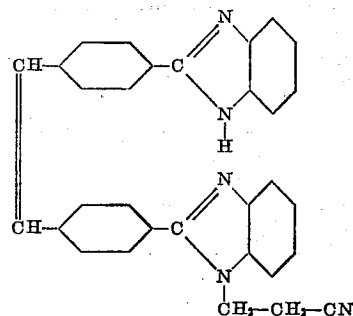
EXAMPLE 13

Cyanoethylation of 4,4'-bis(benzimidazol-2-yl)stilbene

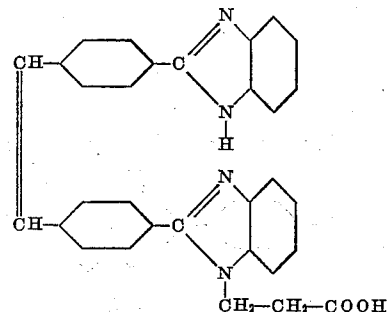
A. A mixture of 4.1 g. (0.01 mole) of 4,4'-bis(benzimidazol-2-yl)stilbene, 1.6 g. of a 50% aqueous solution of sodium hydroxide, and 25 ml. of 2-methoxyethanol was heated to dissolve the solid. To the warm (50° C.) solution was added 0.53 g. (0.01 mole) of acrylonitrile and this reaction mixture was heated at 50° C. for two hours.

16

There was thus produced 4-(benzimidazol-2-yl)-4'-[1-(2-cyanoethyl)benzimidazol-2-yl]stilbene, having the structural formula

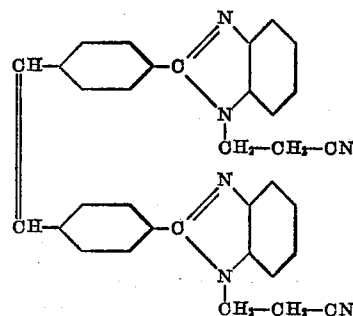


The reaction mixture containing this product was mixed with 5 ml. of water and the mixture was refluxed for two hours to hydrolyze the cyano group. The reaction mixture was cooled to 50° C., diluted with 200 ml. of water and filtered. The solid thus collected was washed with water and dried. There was thus obtained 3.9 g. of 4-(benzimidazol-2-yl)-4'-[1-(2-carboxyethyl)benzimidazol-2-yl]stilbene, having the structural formula



This compound was soluble in 10% alkaline ethanol.

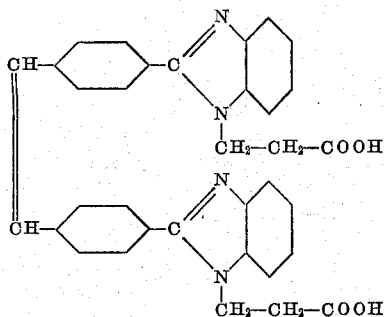
B. A mixture of 4.1 g. (0.01 mole) of 4,4'-bis(benzimidazol-2-yl)stilbene, 1.6 g. of a 50% aqueous solution of sodium hydroxide, and 25 ml. of 2-methoxyethanol was heated to dissolve the solid. To the warm (50° C.) solution was added 2.64 ml. (0.04 mole) of acrylonitrile and this reaction mixture was heated at 50° C. for two hours. There was thus produced 4,4'-bis[1-(2-cyanoethyl)benzimidazol-2-yl]stilbene, having the structural formula



To the reaction mixture containing this product were added 1.6 g. of a 50% aqueous solution of sodium hydroxide and 5 ml. of water and the mixture was refluxed for two hours to hydrolyze the cyano groups. The reaction mixture was cooled to 50° C., diluted with 200 ml. of water and filtered. The solid thus collected was washed with water and dried. There was thus obtained

17

4.1 g. of 4,4'-bis[1-(2-carboxyethyl)benzimidazol-2-yl]-stilbene, having the structural formula

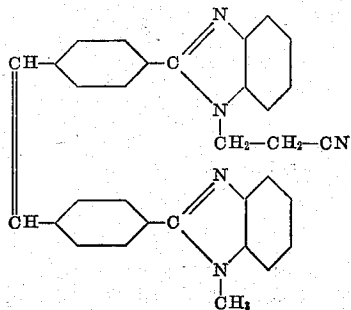


This compound was soluble in 10% alkaline ethanol. It had an especially high substantivity to cellulose acetate.

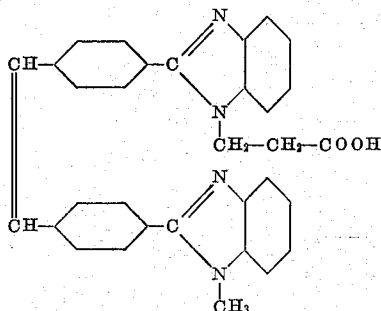
EXAMPLE 14

Cyanoethylation of 4-(benzimidazol-2-yl)-4'-(1-methylbenzimidazol-2-yl)stilbene

A mixture of 4.26 g. (0.01 mole) of 4-benzimidazol-2-yl)-4'-(1-methylbenzimidazol-2-yl)stilbene, 0.8 g. of a 30% aqueous solution of sodium hydroxide, and 25 ml. of 2-methoxyethanol was heated to 50° C. to dissolve the solid. To this solution were added 0.53 g. (0.01 mole) of acrylonitrile and about 20 mg. of cuprous chloride (to serve as a catalyst for the alkylation and to inhibit polymerization of the acrylonitrile) and the mixture was heated at 50° C. for two hours. There was thus produced 4-[1-(2-cyanoethyl)benzimidazol-2-yl]-4'-(1-methylbenzimidazol-2-yl)stilbene, having the structural formula



The reaction mixture containing this product was mixed with 5 ml. of water and the mixture was refluxed for two hours to hydrolyze the cyano group. The mixture was mixed with 250 ml. of water and filtered. The solid thus collected was washed with water and dried in an oven at 70° C. There was thus obtained 4.3 g. of 4-[1-(2-carboxyethyl)benzimidazol-2-yl]-4'-(1-methylbenzimidazol-2-yl)stilbene having the structural formula



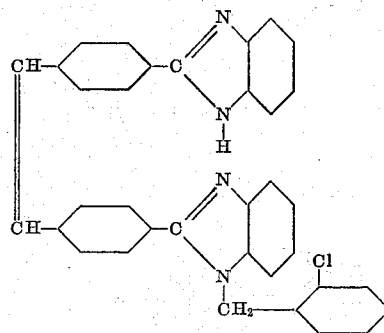
EXAMPLE 15

Chlorobenzoylation of 4,4'-bis(benzimidazol-2-yl)stilbene

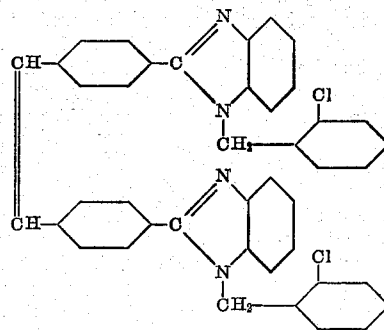
A mixture of 8.2 g. of 4,4'-bis(benzimidazol-2-yl)stilbene, 3.0 g. of potassium hydroxide, and 40 ml. of 2-(2-

18

ethoxyethoxy)ethanol was heated to 100° C. to dissolve the solid. The solution thus obtained was heated and stirred on a steam bath and 3.0 g. of ortho-chlorobenzyl chloride was dripped into the solution slowly during a period of thirty minutes. The reaction mixture was then heated at 150° C. for fifteen minutes. The hot solution was filtered to remove a precipitate of potassium chloride and the filtrate was cooled to 25° C. The crystalline solid which precipitated was collected on a filter and dried at 70° C. This product, which weighed 6.5 g. and melted at 270-280° C., was a mixture which consisted chiefly of the N,N'-dialkylated derivative and a lesser amount of the monoalkylated compound, namely 4-(benzimidazol-2-yl)-4'-[1-(ortho-chlorobenzyl)benzimidazol-2-yl]stilbene having the structural formula



The separation of these two products can be carried out by conventional fractionation, as by recrystallization. For example, for recovery of the N,N'-dialkylated product, the mixture obtained above was recrystallized first from 200 ml. of N,N-dimethylformamide and then from 40 ml. of boiling ortho-dichlorobenzene, followed by washing with benzene and ether, and drying under reduced pressure at 100° C. The nearly colorless crystalline needles thus obtained consisted of 4,4'-bis[1-(ortho-chlorobenzyl)benzimidazol-2-yl]stilbene, having the structural formula



The product weighed 2.5 g. and melted at 280° C. It was insoluble in alcoholic sodium hydroxide solution.

Analysis.—Calculated for $C_{42}H_{30}N_4Cl_2$: C, 76.14%; H, 4.68%; N, 8.47%; Cl, 10.72%. Found: C, 75.91%; H, 4.48%; N, 8.41%; Cl, 10.90%.

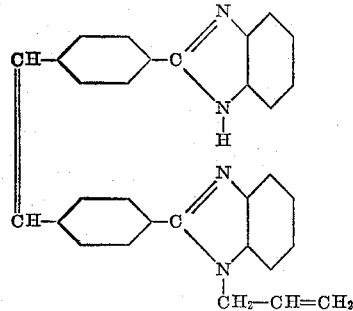
EXAMPLE 16

Allylation of 4,4'-bis(benzimidazol-2-yl)stilbene

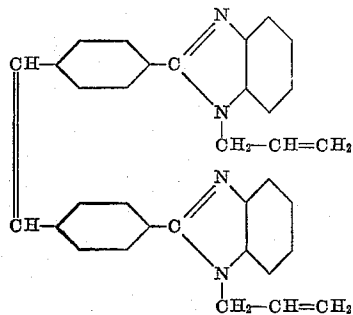
A. To a mixture of 60 g. (0.147 mole) of 4,4'-bis(benzimidazol-2-yl)stilbene, 280 ml. of 2-methoxyethanol, and 39 g. of a 50% aqueous solution of sodium hydroxide heated at 50° C. there was added dropwise, over a period of one hour, 12 g. (0.0157 mole) of allyl chloride. The reaction mixture was refluxed for sixteen hours and then was diluted with 280 ml. of water. The solid which had separated from solution was collected on a filter and washed free of alkali with water. This solid, which weighed 60 g., consisted of the crude monoallylation product; it was purified as follows. The solid was dissolved in 400 ml. of N,N-dimethylformamide and the resulting

19

solution was filtered to remove undissolved 4,4'-bis(benzimidazol-2-yl)stilbene. The filtrate was poured into a large volume of water and the solid which separated from solution was collected on a filter. There was obtained in this manner, as a yellow solid, the purified 4-benzimidazol-2-yl-4'-[1-(allylbenzimidazol-2-yl)]stilbene, having the structural formula



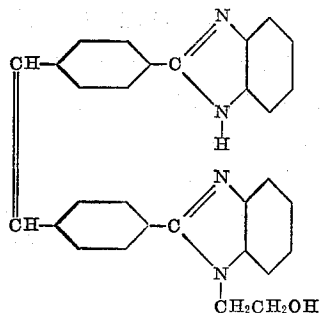
B. By interaction of the monoallylation product described above with a second molecular equivalent of allyl chloride, there is obtained 4,4'-bis(1-allylbenzimidazol-2-yl)stilbene, having the structural formula



EXAMPLE 17

Hydroxyethylation of 4,4'-bis(benzimidazol-2-yl)stilbene

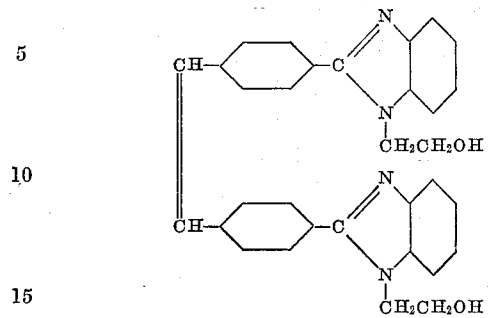
To a 50 ml. ground glass wide-mouth flask equipped with a condenser the barrel of which served as a bearing for an agitator paddle there were added 4.1 g. (0.01 mole) of 4,4'-bis(benzimidazol-2-yl)stilbene, 16.5 g. of 2-methoxyethanol and 1.8 g. of a 50% aqueous solution of sodium hydroxide. After all of the solid had gone into solution there was added 1.7 g. (0.0212 mole) of ethylene chlorohydrin. The reaction mixture was slurried and refluxed for one hour after which period the reaction mixture was transferred to a beaker and heated on a water bath until approximately half of the solvent had evaporated. There was then added 30 ml. of water and the mixture was allowed to cool to room temperature. The yellow solid which had separated from solution was collected on a filter and washed with water until a sample of the wash liquor was colorless and free of alkali. The product thus obtained, which weighed 4.1 g., was a yellow solid which did not melt at 350° C. It consisted chiefly of 4-(benzimidazol-2-yl)-4'-[1-(2-hydroxyethyl)-benzimidazol-2-yl]stilbene, having the structural formula



which was soluble in aqueous alkaline ethanol solution, with small amounts of unreacted 4,4'-bis(benzimidazol-

20

2-yl)stilbene and 4,4'-bis[1-(2-hydroxyethyl)benzimidazol-2-yl]stilbene, having the structural formula

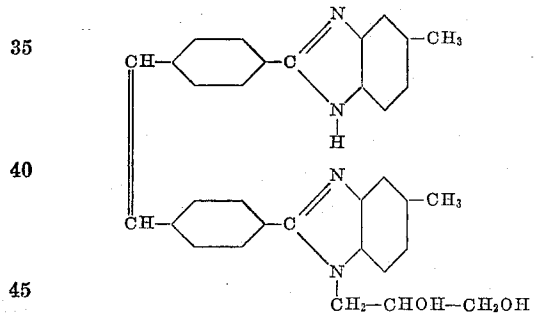


The dialkylated product was insoluble in aqueous alkaline ethanol solution and very slightly soluble in glacial acetic acid.

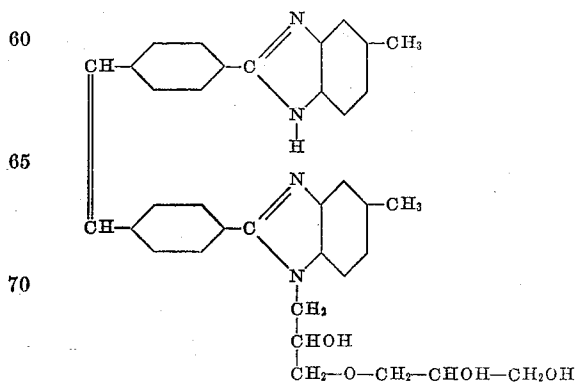
EXAMPLE 18

Dihydroxypropylation of 4,4'-bis[5(or 6)-methylbenzimidazol-2-yl]stilbene

A mixture of 8.3 g. of 4,4'-bis[5(or 6)-methylbenzimidazol-2-yl]stilbene, 32.0 g. of 2-methoxyethanol, and 5.2 g. of a 50% aqueous solution of sodium hydroxide was heated to dissolve the solid. To the warm (50° C.) and well-stirred solution there was added 2.08 g. of 2,3-dihydroxypropyl chloride and the mixture was refluxed for one and one-half hours. There was thus produced 4-[5(or 6)-methylbenzimidazol-2-yl]-4'-[1-(2,3-dihydroxypropyl)-5(or 6)-methylbenzimidazol-2-yl]stilbene, having the structural formula



To the reaction mixture containing the above compound, there was added a second portion of 2.08 g. of 2,3-dihydroxypropyl chloride and the mixture was refluxed for one and one-half hours. The mixture was then cooled and diluted with 575 ml. of warm (50° C.) water and filtered. The solid thus collected was washed with water until free of alkali and then dried in an oven. There was thus obtained 8.9 g. of solid consisting chiefly of the monoalkylated compound above and 4-[5(or 6)-methylbenzimidazol-2-yl]-4'-[1-[2-hydroxy-3-(2,3-dihydroxypropoxy)propyl]-5(or 6)-methylbenzimidazol-2-yl]stilbene having the structural formula

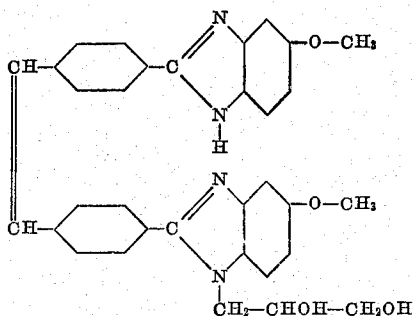


and a small amount of unreacted 4,4'-bis[5(or 6)-methylbenzimidazol-2-yl]stilbene starting material.

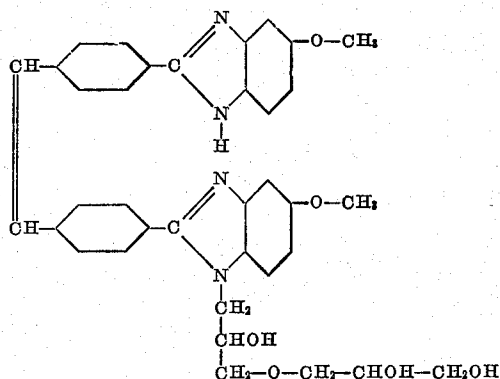
EXAMPLE 19

Dihydroxypropylation of 4,4'-bis[5(or 6)-methoxybenzimidazol-2-yl]stilbene

To a solution of 10.8 g. of 4,4'-bis[5(or 6)-methoxybenzimidazol-2-yl]stilbene, 5.15 g. of a 50% aqueous solution of sodium hydroxide and 32.0 g. of 2-methoxyethanol at 50° C. there was added with good stirring 2.08 g. of 2,3-dihydroxypropyl chloride and the mixture was refluxed for one and one-half hours. There was thus produced 4-[5(or 6)-methoxybenzimidazol-2-yl]-4'-[1-(2,3-dihydroxypropyl)-5(or 6)-methoxybenzimidazol-2-yl]stilbene, having the structural formula



To the reaction mixture containing the above compound there was added a second 2.08 g. portion of 2,3-dihydroxypropyl chloride. The mixture was refluxed for one and one-half hours and then was cooled and diluted with 290 ml. of warm (50° C.) water. The diluted mixture was filtered and the solid thus collected was washed with water until free of alkali, and dried. There was thus obtained 12 g. of yellow solid which consisted chiefly of the above-mentioned monoalkylated product and an O-alkylation derivative thereof, namely 4-[5(or 6)-methoxybenzimidazol-2-yl]-4'-{1-[2-hydroxy-3-(2,3-dihydroxypropoxy)propyl]-5(or 6)-methoxybenzimidazol-2-yl}stilbene having the structural formula



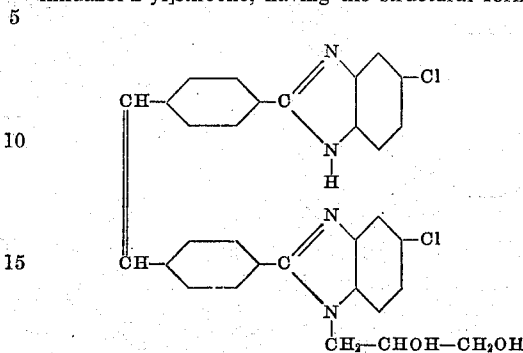
along with some unalkylated starting material.

EXAMPLE 20

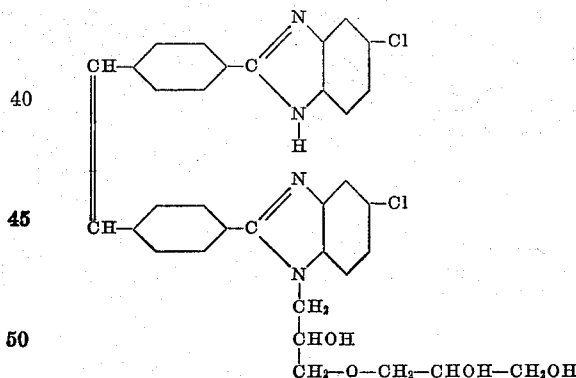
Dihydroxypropylation of 4,4'-bis[5(or 6)-chlorobenzimidazol-2-yl]stilbene

A mixture of 50 g. of 4,4'-bis[5(or 6)-chlorobenzimidazol-2-yl]stilbene, 50 g. of a 50% aqueous solution of sodium hydroxide, and 209 ml. of 2-methoxyethanol was refluxed for ten minutes to dissolve the solid. After adjusting the temperature of the resulting solution to 50° C. there was added 11.5 g. of 2,3-dihydroxypropyl chloride

and the mixture was refluxed for one and one-half hours. There was thus produced 4-[5(or 6)-chlorobenzimidazol-2-yl]-4'-[1-(2,3-dihydroxypropyl)-5(or 6)-chlorobenzimidazol-2-yl]stilbene, having the structural formula



The reaction mixture containing the above compound was cooled to 50° C., a second portion of 11.5 g. of 2,3-dihydroxypropyl chloride was added, and the mixture was refluxed for one and one-half hours. The mixture was then cooled to 60° C. and 1800 ml. of warm (50° C.) water was added in a thin stream with good agitation. The diluted mixture was filtered to collect the yellow solid which precipitated. The collected solid was washed free of alkali with water and dried. There was thus obtained 54.6 g. of yellow product consisting chiefly of the monoalkylated product mentioned above and 4-[5(or 6)-chlorobenzimidazol-2-yl]-4'-{1-[2-hydroxy-3-(2,3-dihydroxypropoxy)propyl]-5(or 6)-chlorobenzimidazol-2-yl}stilbene having the structural formula



together with some unalkylated starting material. This product was less soluble in alkaline ethanol solution than were the corresponding unchlorinated compound (Example 28B) and the dimethoxy analog (Example 19).

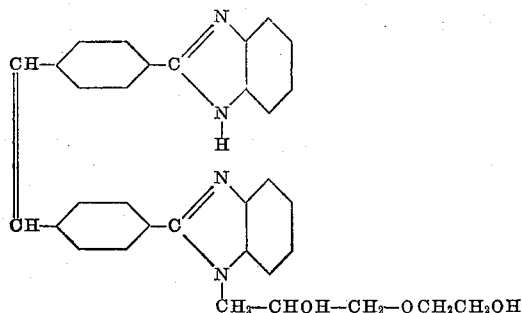
EXAMPLE 21

Hydroxyethoxy-hydroxypropylation of 4,4'-bis(benzimidazol-2-yl)stilbene

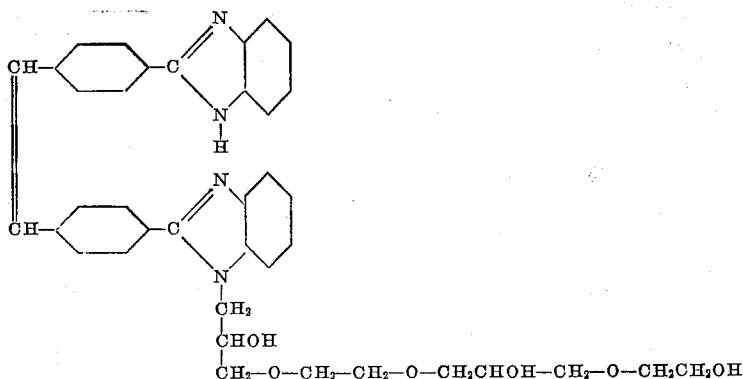
To a one-liter, three-neck flask fitted with a stirrer, thermometer, and reflux condenser there were added 82 g. of 4,4'-bis(benzimidazol-2-yl)stilbene (0.2 mole), 394 g. of 2-methoxyethanol, and 32 g. of a 50% aqueous solution of sodium hydroxide. This mixture was heated to dissolve all of the solid and the temperature of the solution thus obtained was adjusted to 50° C. There was then added in one portion 30.8 g. (0.2 mole) of 2-hydroxy-3-(2-hydroxyethoxy)propyl chloride. The reaction mixture was refluxed for two hours. There was thus produced 4-[5(or 6)-chlorobenzimidazol-2-yl]-4'-[1-[2-hydroxy-3-(2-hydroxyethoxy)propyl]-5(or 6)-chlorobenzimidazol-2-yl]stilbene

23

oxy)propyl]benzimidazol-2-yl]stilbene, having the structural formula



To the warm (42° C.) reaction mixture containing the above compound there was added a further portion of 6.16 g. (0.04 mole) of 2-hydroxy-2-(2-hydroxyethoxy)propyl chloride and the mixture was refluxed for one and one-half hours. There was then distilled from the reaction mixture 300 ml. of solvent, the residue in the still was cooled to 60° C., and 600 ml. of warm (60° C.) water was added (in subsequent preparations the mixture was seeded at this point with a small amount of the expected monoalkylation product noted above). The mixture, which contained solid which had separated from solution, was stirred vigorously, and then cooled to room temperature (about 25° C.) and filtered. The solid thus collected was washed with water until a sample of the filtrate was free of alkali. There was thus obtained 96 g. of pale yellow product which consisted chiefly of 4-(benzimidazol-2-yl)-4'-[1-[2-hydroxy-3-(2-hydroxyethoxy)propyl]benzimidazol-2-yl]stilbene together with small amounts of the O-alkylated derivative thereof having the structural formula



and unreacted 4,4'-bis(benzimidazol-2-yl)stilbene starting material. The product was slightly soluble in ethanol, acetone, and 2-methoxyethanol and insoluble in non-polar solvents. It was soluble in alkaline ethanol solutions.

EXAMPLE 22

Dihydroxypropoxy-hydroxypropylation of 4,4'-bis(benzimidazol-2-yl)stilbene

To a 100 ml. flask fitted with a stirrer and reflux condenser there were added 8.2 g. of 4,4'-bis(benzimidazol-2-yl)stilbene, 33 ml. of 2-methoxyethanol, and 4.0 g. of a 50% aqueous sodium hydroxide solution and the mixture was heated to dissolve the solid. The solution thus obtained was cooled to 50° C. and there was added 6.1 g. of 2-hydroxy-3-(2,3-dihydroxypropoxy)propyl chloride. The reaction mixture was refluxed for two hours, then cooled to 50° C., a further portion of 1.2 g. of 2-hydroxy-

24

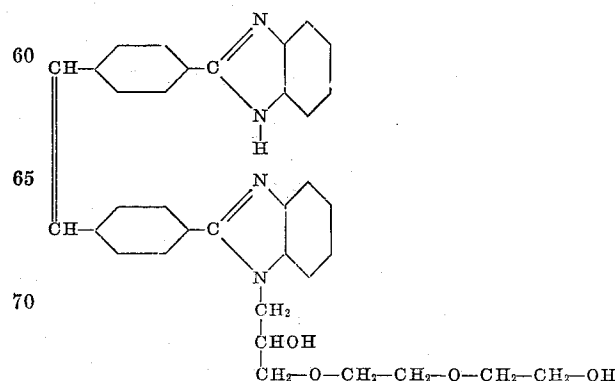
3-(2,3-dihydroxypropoxy)propyl chloride was added, and the mixture was refluxed for a further period of two hours. The reaction mixture was then cooled to 50° C. and 200 ml. of cold water was added slowly. The solid which had separated from solution was collected on a filter, washed free of alkali with water and dried in an oven. There was thus obtained 9.2 g. of yellow solid which consisted chiefly of 4-(benzimidazol-2-yl)-4'-[1-[2-hydroxy-3-(2,3-dihydroxypropoxy)propyl]benzimidazol-2-yl]stilbene (identical with the compound obtained in Example 28B by a different method).

EXAMPLE 23

Hydroxyethoxyethoxy-hydroxypropylation of 4,4'-bis(benzimidazol-2-yl)stilbene

To a 100 ml. flask fitted with a stirrer and reflux condenser there was added 8.2 g. of 4,4'-bis(benzimidazol-2-yl)stilbene, 33 ml. of 2-methoxyethanol, and 4.0 g. of a 50% aqueous sodium hydroxide solution and the mixture was heated to dissolve the solid. The temperature of the solution thus obtained was adjusted to 50° C. and there was added 7.25 g. of 2-hydroxy-3-[2-(2-hydroxyethoxy)ethoxy]propyl chloride. The reaction mixture was refluxed for two hours and then cooled to 50° C. There was added a further portion of 1.4 g. of 2-hydroxy-3-[2-(2-hydroxyethoxy)ethoxy]propyl chloride and the mixture was refluxed for one and one-half hours. To the reaction mixture was added 300 ml. of cold water with stirring. The solid which had separated from solution was collected on a filter, washed free of alkali with water and dried in an oven. There was thus obtained 9.8 g. of product consisting chiefly of 4-(benzimidazol-2-yl)-4'-[1-[2-hydroxy-3-[2-(2-hydroxyethoxy)ethoxy]propyl]

benzimidazol-2-yl]stilbene, having the structural formula



This compound was also obtained by another method as described in the next example.

25

EXAMPLE 24

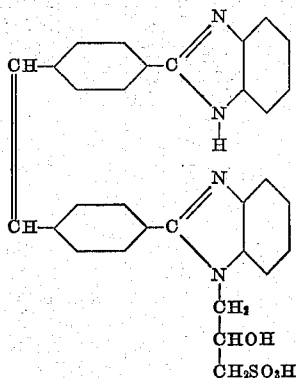
Hydroxyethylation of (benzimidazol-2-yl)-4'-1-[2-hydroxy-3-(2-hydroxyethoxy)propyl]benzimidazol-2-yl stilbene

To a 200 ml. three-neck flask fitted with a magnetic stirrer, gas one-inlet tube and U-tube manometer filled with one inch of mercury there were added 10.6 g. of 4-(benzimidazol-2-yl)-4'-[1-[2-hydroxy-3-(2-hydroxyethoxy)propyl]benzimidazol-2-yl]-stilbene, 90 ml. of 95% ethanol, and 4.5 g. of a 50% aqueous sodium hydroxide solution and the mixture was heated to 75° C. to dissolve the solid. The solution thus obtained was cooled and maintained at 70-75° C. and ethylene oxide was passed into the mixture for 45 min., during which time the mixture absorbed 6.3 g. of ethylene oxide. Almost all of the absorption of ethylene oxide occurred during the first thirty minutes of this period. The reaction mixture was then cooled to 40° C. and diluted slowly with 300 ml. of water at 40° C. The diluted mixture was cooled to 20° C. and the solid which had separated from solution was collected on a filter and washed free of alkali with water. There was thus obtained 11.6 g. of yellow solid which consisted chiefly of 4-(benzimidazol-2-yl)-4'-[1-[2-hydroxy-3-(2-hydroxyethoxy)propyl]benzimidazol-2-yl]stilbene.

EXAMPLE 25

Sulfo-hydroxypropylation of 4,4'-bis(benzimidazol-2-yl)-stilbene

To a 100 ml. flask fitted with a stirrer and reflux condenser there were added 4.84 g. of 4,4'-bis(benzimidazol-2-yl)stilbene dihydrochloride, 25 ml. of 2-methoxyethanol, and 3.6 g. of a 50% aqueous sodium hydroxide solution. This solution was heated to dissolve all of the solid and the solution thus obtained was cooled to 50° C. There was then added 4.4 g. of sodium 2-hydroxy-3-chloropropanesulfonate and the reaction mixture was refluxed for two hours. Forty ml. of water was added and the mixture was cooled in an ice bath. Two ml. of glacial acetic acid was added to the cooled mixture to facilitate the coagulation of the solid which had separated from solution, and the mixture was filtered. The solid thus collected was washed with water and dried in an oven. There was thus obtained 5 g. of solid which consisted chiefly of the sodium salt of the 4-(benzimidazol-2-yl)-4'-[1-(2-hydroxy-2-sulfopropyl)benzimidazol-2-yl]stilbene having the formula



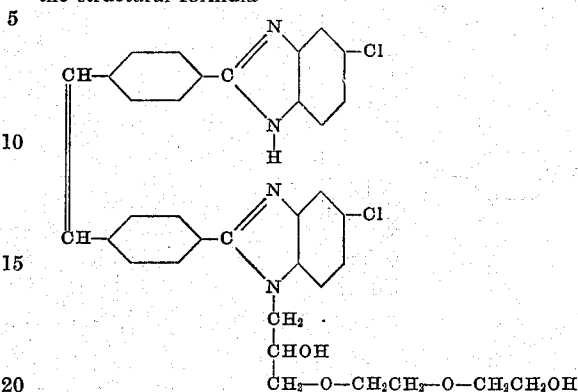
EXAMPLE 26

Hydroxyethoxyethoxy-hydroxypropylation of 4,4'-[5(or 6)-chlorobenzimidazol-2-yl]stilbene

A mixture of 10.0 g. of 4,4'-[5(or 6)-chlorobenzimidazol-2-yl]stilbene, 41.8 ml. of 2-methoxyethanol, and 5.7 g. of a 50% aqueous solution of sodium hydroxide was refluxed until the solid had dissolved. The resulting solution was cooled to 50° C., 6.0 g. of 2-hydroxy-3-[2-(2-hydroxyethoxy)ethoxy]propyl chloride was added, and the mixture was refluxed for one and one-half hours.

26

There was thus produced 4-[5(or 6)-chlorobenzimidazol-2-yl]-4'-[1-[2-hydroxy-3-[2-(2-hydroxyethoxy)ethoxy]propyl]-5(or 6)-chlorobenzimidazol-2-yl]stilbene, having the structural formula

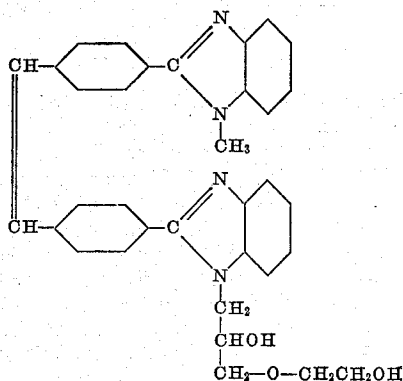


The reaction mixture containing the above compound was cooled to room temperature (about 25° C.), a second 6.0 g. portion of 2-hydroxy-3-[2-(2-hydroxyethoxy)ethoxy]propyl chloride was added, and the mixture was refluxed for one and one-half hours. The reaction mixture was cooled to room temperature and 360 ml. of cold water was added. The diluted mixture was filtered and the solid thus collected was washed free of alkali with water. The solid was dried in an oven and then was ground. There was thus obtained 11.3 g. of yellow powder which consisted chiefly of 4-[5(or 6)-chlorobenzimidazol-2-yl]-4'-[1-(2,12,19-trihydroxy-4,7,10,14,17-pentaoxonadecyl-5(or 6)-chlorobenzimidazol-2-yl]stilbene, an O-alkylated derivative of the N-monoalkylated compound above.

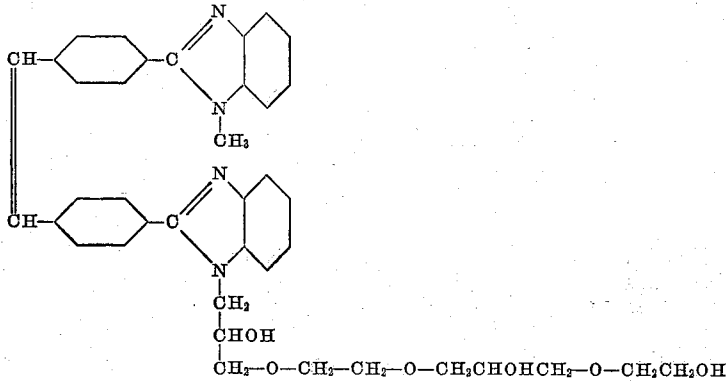
EXAMPLE 27

Hydroxyethoxy-hydroxypropylation of a mixture of 4,4'-bis(benzimidazol-2-yl)stilbene and 4-(benzimidazol-2-yl)-4-(1-methylbenzimidazol-2-yl)stilbene

8.0 g. of crude 4-(benzimidazol-2-yl)-4-(1-methylbenzimidazol-2-yl)stilbene which contained some 4,4'-bis(benzimidazol-2-yl)stilbene was mixed with 80 ml. of 2-methoxyethanol and 2.98 g. of a 50% aqueous solution of sodium hydroxide and the mixture was heated to dissolve the solid. To the hot (70° C.) solution there was added 2.87 g. of 2-hydroxy-3-(2-hydroxyethoxy)propyl chloride and the mixture was refluxed for two hours. The reaction mixture was cooled to about 60° C. and a further 2.87 g. portion of 2-hydroxy-3-(2-hydroxyethoxy)propyl chloride was added. The mixture was refluxed for two hours, then cooled to 50° C., and 200 ml. of water was added. A gum separated from solution and this solidified on stirring. To the mixture there was added 300 ml. of water and the solid was collected on a filter, washed with water, and dried at 70° C. There was thus obtained 10.5 g. of product which consisted chiefly of a mixture of 4-(1-methylbenzimidazol-2-yl)-4'-[1-[2-hydroxy-3-(2-hydroxyethoxy)propyl]benzimidazol-2-yl]stilbene, having the structural formula



and the O-alkylated derivative thereof having the structural formula



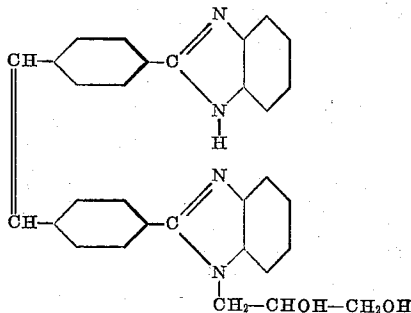
together with a small amount of 4 - (benzimidazol - 2 - yl) - 4' - {1 - [2 - hydroxy - 3 - (2 - hydroxyethoxy) - propyl]benzimidazol - 2 - yl}stilbene derived from the 4,4'-bis(benzimidazol-2-yl)stilbene in the starting material. The mixture of compounds obtained in this reaction was soluble in glacial acetic acid.

EXAMPLE 28

Dihydroxypropylation of 4,4'-bis(benzimidazol-2-yl)-stilbene

The procedures and products described in this example represent preferred embodiments of my invention. When these products were incorporated into detergents, the detergent compositions so obtained gave a brilliant blue-white fluorescence to white fabrics treated therewith and repeated application to the fabrics did not cause development of an undesirable coloration, but instead the whiteness of the fabrics increased.

A. In a three-liter, three-neck flask fitted with an agitator, thermometer, and condenser there were placed 317 g. (0.78 mole) of 4,4'-bis(benzimidazol-2-yl)stilbene, 1330 g. of 2-methoxy-ethanol, and 214 g. of a 50% aqueous solution of sodium hydroxide. After all of the solid had gone into solution, the temperature of the mixture was adjusted to 50° C. and there was then added in one portion 86.5 g. (0.78 mole) of 2,3-dihydroxypropyl chloride. The reaction mixture was refluxed for one and one-half hours. There was thus produced 4-(benzimidazol-2-yl)-4' - [1 - (2,3 - dihydroxypropyl) - benzimidazol-2-yl]stilbene, a yellow compound having the structural formula

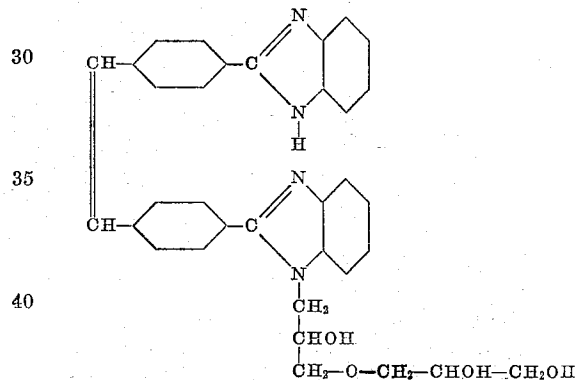


This product contained some unreacted 4,4'-bis(benzimidazol-2-yl)stilbene.

B. The reaction mixture was cooled to 42° C., and another 86.5 g. portion of 2,3-dihydroxypropyl chloride was added. The reaction mixture was refluxed for a further period of one and one-half hours and then 465 ml. of water was added slowly. The mixture was heated to remove 2050 ml. of solvent by distillation, and to the residue in the still there was added 2200 ml. of warm (60° C.) water. The diluted mixture was cooled to 25° C. and filtered to collect the solid product which had sep-

arated from solution. The filter cake was washed with water until a sample of the wash liquor was free of alkali

as determined by testing with phenolphthalein paper and then the solid was dried. There was thus obtained 415 g. of yellow material in which the dialkylated product consisted chiefly of the O-(dihydroxypropylated) derivatives of the monoalkylated compound, as for example 4 - (benzimidazol - 2 - yl) - 4' - {1 - [2 - hydroxy - 3 - (2,3 - dihydroxypropoxy)propyl]benzimidazol - 2 - yl}stilbene, having the structural formula



The yellow product also contained some of the monoalkylated compound as well as a small amount of 4,4'-bis(benzimidazol-2-yl)stilbene. The product was slightly soluble in 2-methoxyethanol and 2-ethoxyethanol and insoluble in methanol, ethanol, and glacial acetic acid. It was soluble in N,N-dimethylformamide to the extent of about 20%. In monosodium salt form, the product was very soluble in alkaline ethanol and alkaline 2-ethoxyethanol; in the former solvent, the solubility was about 20%, and in the latter, about 33%.

C. The mixture of products described in part B above was useful without further treatment as a whitening and brightening agent. However, for incorporation into white solid detergents, I prefer to remove or eliminate from the mixture all unreacted 4,4'-bis(benzimidazol-2-yl)stilbene starting material. I have found that the unalkylated compounds of Formula I may cause yellowing of some solid white detergents containing 10-20% of water and, although this does not cause any diminution of the whitening and brightening properties of the detergent composition, the detergents thereby may become less marketable. The white color of the yellowed detergent is however readily restored by drying to bring the water content thereof below about 10% by weight. The following method illustrates the removal of 4,4'-bis(benzimidazol-2-yl)stilbene from the mixture of products.

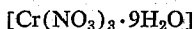
A suspension of 5 g. of the product of part B in 30 ml. of glacial acetic acid was stirred for one hour. The mixture was then filtered to collect insoluble material, which consisted of 4,4'-bis(benzimidazol-2-yl)stilbene diacetate. The filtrate was diluted with 200 ml. of water. Centrifugation caused the separation of a very finely

divided solid from the mixture. The supernatant liquid was made basic by treatment with ammonia, and the mixture was boiled to coagulate the fine powder and then was cooled and filtered. The precipitate thus collected was washed with water until free of ammonia and then dried. This solid, which weighed 2.7 g. was suspended in 150 ml. of 95% ethanol, the mixture was boiled for fifteen minutes, and the solution thus obtained filtered by gravity while hot. The insoluble residue thus removed was washed with a few ml. of ethanol. The wash liquor and filtrate were combined, concentrated to about 75 ml., and diluted with a small amount of water until crystals began to appear. The solution was cooled and filtered to collect 1.8 g. of solid. Recrystallization of this product twice from N,N-dimethylformamide and once from 2-ethoxyethanol yielded 4-(benzimidazol-2-yl)-4'-{1-[2-hydroxy-3-(2,3-dihydroxypropoxy)-propyl]benzimidazol-2-yl}stilbene, which melted at 225° C.

D. Further alkylation of the mixture of products obtained in part B above yielded O-alkylated derivatives of the 4-benzimidazol-2-yl-4'-{1-[2-hydroxy-3-(2,3-dihydroxypropoxy)propyl]benzimidazol-2-yl}stilbene component and resulted in the elimination of the 4,4'-bis(benzimidazol-2-yl)stilbene component by converting it to N-monoalkylated and N,N'-dialkylated derivatives. As in the case of the product purified by the method of part C above, these 4,4'-bis(benzimidazol-2-yl)stilbene-free mixtures were found to be especially useful as whitening and brightening agents for incorporation into white solid detergents. It was found that the progressive elimination of the N,N'-unalkylated compound could be followed conveniently by use of a color test on samples of the reaction mixture; this is illustrated below, using ethylene oxide as the alkylating agent.

120 g. of the mixture of products obtained above in part B, which contained a small, undetermined amount of 4,4'-bis(benzimidazol-2-yl)stilbene, was mixed with 360 ml. of 2-methoxyethanol and 27 g. of a 50% aqueous solution of sodium hydroxide in a one-liter three-neck flask fitted with a thermometer, gas inlet to the void above the reaction mixture, a U-shaped manometer filled with one and one-half inches of mercury, and a high-speed agitator. The mixture was heated to 74° C. to dissolve the solid. The presence of 4,4'-bis(benzimidazol-2-yl)stilbene in the mixture was detected qualitatively by the following test:

A 0.1 ml. sample of the mixture was mixed with 35 ml. of 95% ethanol and to a 1.0 ml. aliquot of the resulting yellow solution there was added dropwise, from a 1 ml. graduated pipette, 0.01 N nitric acid until the yellow color disappeared (in this instance, 0.15 ml. of the acid was required). The colorless solution was diluted with water to a volume of 2.0 ml. There was then added eight drops of a solution of 1.0 g. of chromic nitrate



in 206 ml. of water. The development of a yellow color in the solution indicated the presence of 4,4'-bis(benzimidazol-2-yl)stilbene.

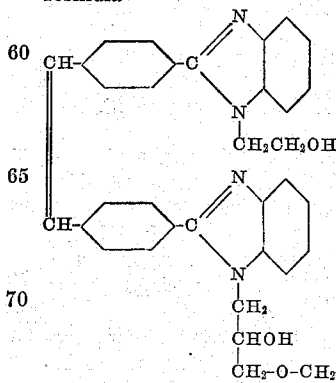
Ethylene oxide was passed into the reaction vessel while maintaining the reaction mixture at 74-80° C. At intervals of ten-fifteen minutes, 0.1 ml. samples of the reaction mixture were removed and tested as indicated above for presence of 4,4'-bis(benzimidazol-2-yl)stilbene. After seventy minutes of passage of ethylene oxide into the reaction vessel, the chromic nitrate solution failed to cause development of a yellow color in above test showing that no 4,4'-bis(benzimidazol-2-yl)stilbene remained in the reaction mixture. The total weight of ethylene oxide absorbed by the reaction mixture was 22.1 g.

The reaction mixture was transferred to a two-liter beaker, cooled at 50° C., and 1500 ml. of warm (50° C.) water was added slowly with stirring. Then 400 g. of ice was added to cool the mixture to room temperature and

the yellow solid which had separated from solution was collected on a filter and washed free of alkali with water. There was thus obtained 118 g. of yellow product which consisted chiefly of a mixture of O-hydroxyethylated and, to a lesser extent, N'-hydroxyethylated, derivatives of 4-(benzimidazol-2-yl)-4'-{1-[2-hydroxy-3-(2,3-dihydroxypropoxy)-propyl]benzimidazol-2-yl}stilbene together with small amounts of 4-(benzimidazol-2-yl)-4'-{1-(2-hydroxyethyl)benzimidazol-2-yl}stilbene and 4-(benzimidazol-2-yl)-4'-{1-[2-(2-hydroxyethoxy)ethyl]benzimidazol-2-yl}stilbene. The components of this mixture, although separable by conventional fractionation procedures, are all whitening and brightening agents and, moreover, the mixture was found to have excellent stability in the presence of dried white detergents and to whiten these detergents. Therefore, for practical purposes, it was found to be preferable to use the mixture of the several compounds obtained as described above without purification.

E. When the product of part D above is reacted further with ethylene oxide, or alternatively when the process of hydroxyethylation of the product of part B is continued for some time after the 4,4'-bis(benzimidazol-2-yl)stilbene has disappeared from the mixture as determined by the color test described above, there are obtained hydroxyethylated compounds having progressively increasing solubility in glacial acetic acid; on the other hand, the solubility of these products in alkaline alcohol solutions decreases due to increasing proportion of N,N'-dialkylated derivatives in the mixture. These acetic acid-soluble mixtures are especially useful embodiments of the new benzimidazolylstilbenes of my invention for incorporation into detergents. The preparation of a representative mixture of this type is described below.

To a 200 ml. three-neck flask fitted with a magnetic stirrer, gas inlet, a U-shaped manometer filled with one inch of mercury, and a thermometer there were added 15 g. of 4-(benzimidazol-2-yl)-4'-{1-(2,3-dihydroxypropyl)benzimidazol-2-yl}stilbene containing a small amount of 4,4'-bis(benzimidazol-2-yl)stilbene (prepared in the manner described in part B above), 3.0 g. of a 50% aqueous solution of sodium hydroxide, and 75 ml. of 2-methoxyethanol. The mixture was stirred and heated to dissolve all of the solid, and the solution thus obtained was then maintained at a temperature of 65-70° C. while ethylene oxide was passed into the reaction vessel above the surface of the mixture. After 9.5 g. of ethylene oxide had been absorbed (requiring about one hour) the reaction mixture was cooled to 50° C., diluted with 250 ml. of warm 50° C.) water, cooled to room temperature, and filtered. The solid thus collected was washed free of alkali with water, and dried. There was obtained in this manner 14.5 g. of yellow powder consisting chiefly of hydroxyethylated derivatives of the 4-(benzimidazol-2-yl)-4'-{1-2,3-dihydroxypropyl}benzimidazol-2-yl}stilbene containing 1-4 oxyethyl (—OCH₂CH₂—) residues; representative of these is the compound having the structural formula



This mixture whitened dried detergent powders and was stable therein and for this reason was especially adapted

to use in white solid detergents. The mixture was only slightly soluble in alkaline 2-methoxyethanol and alkaline ethanol solution; it was soluble in cold glacial acetic acid.

When the benzimidazolylstilbenes described in the foregoing Examples 1-28, inclusive, were dispersed in aqueous media, the products in each instance fluoresced blue-white under ultraviolet light and showed a wide range of absorption in the ultraviolet region. Each of the products of these examples was dissolved in a suitable solvent, for instance, alkaline ethanol, alkaline 2-methoxyethanol, N,N-dimethylformamide, or glacial acetic acid, depending on the solubility characteristics of the particular product, and the solution thus obtained was poured with vigorous stirring into the desired quantity of an aqueous solution of a soap or of an anionic or non-ionic detergent. The resulting fluorescent dispersions were used to dye white and colored natural and synthetic fibers. All of the benzimidazolylstilbene products of the above examples were found to be substantive even from low concentrations, e. g. 0.0001%, in these aqueous media to white and colored fabrics of cotton, cellulose acetate, nylon, viscose rayon, orlon and silk, thereby imparting a blue-white hue to the white fabrics and brightening the colored fabrics. Moreover, these products all had relatively high stability to light as determined by accelerated exposure tests. In the dispersions in soaps and detergents the products were substantially unaffected by a concentration of sodium hypochlorite of 0.2% by weight. My new products were thus found to be especially useful as whitening and brightening agents to be used in conjunction with the laundering of white and colored fabrics. The methods employed for incorporating all of the above examples of the compounds of my invention into soaps and detergents are illustrated hereinbelow. Other methods which will be readily apparent to those skilled in the art can be employed if desired.

In soap.—One part by weight of the pale yellow solid described above in Example 21 (obtained in a yield of 96 g. by the hydroxyethoxyhydropropylation of 4,4'-bis (benzimidazol-2-yl)stilbene) was dissolved in a mixture of one part by weight of a 50% aqueous solution of sodium hydroxide and eight parts by volume of 95% ethanol. One part by volume of this solution was poured with stirring into a warm (55° C.) soap bath consisting of four parts by weight of the sodium salts of the C₁₂-C₁₈ fatty acids derived from tallow and 1000 parts by weight of water. Eight parts by volume of the resulting aqueous dispersion was diluted further by mixing with 192 parts by volume of water containing 0.76 part by weight of the soap indicated above. The mixture thus obtained was employed in conventional manner as a dye bath for treating white fabrics of cotton, nylon, cellulose acetate, silk, and viscose rayon. Each of these white fabrics was beneficially whitened by this procedure.

In detergent I—(parts are by weight).—The detergent consisted of 21.8% of a mixture of sodium lauryl sulfate and sodium dodecylbenzenesulfonates, 18.2% of sodium sulfate, and 60% of sodium triphosphate. To a thin paste of 2000 parts of the detergent and 1500 parts of water there was added at 70° C. a solution of one part of 4,4'-bis (benzimidazol-2-yl)stilbene in 10 parts of 2-methoxyethanol and 4 parts of a 33⅓% aqueous solution of sodium hydroxide. Two hundred parts of the well-stirred paste was poured into 5000 parts of rapidly agitated water at 60° C. To 80 ml. of this dispersion there was added 200 ml. of water and the resulting mixture was employed as a dye bath in conventional fashion to dye white fabrics of nylon, cotton, cellulose acetate, viscose rayon, orlon, and silk. To each of these white fabrics this procedure imparted a blue-white fluorescence.

In detergent II.—Using the immediately foregoing procedure, there was substituted for the detergent I a detergent composed of 19.1% of sodium dodecylbenzenesulfonates, 15.6% of sodium sulfate, 55.0% of sodium

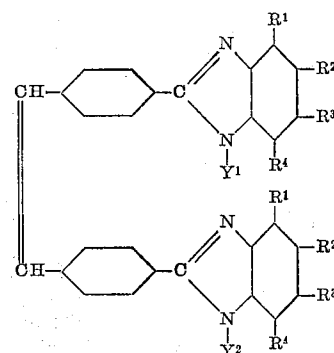
triphosphate and 10.3% of sodium carbonate. The white fabrics were in each case beneficially whitened.

In detergent III—(parts are by weight).—A mixture of 20 parts of the 14.5 g. of yellow powder obtained in Example 28E above, 100 parts of tert-dodecylmercaptopolyethoxyethanol (Nonic 218), and 40 parts of glacial acetic acid was warmed on a water bath to dissolve the solid. Sixteen parts of the solution thus obtained were poured into 20,000 parts of water at 55° C.; then 8 parts of the resulting dispersion was poured into 192 parts of warm (55° C.) water, and the mixture was used to whiten and brighten white and colored fabrics of the type indicated hereinabove.

The term "lorol" used in this specification designates the alkyl radicals of mixed fatty alcohols derived from coconut oil.

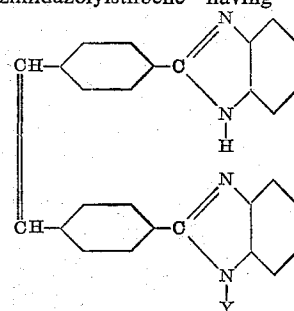
I claim:

1. A benzimidazolylstilbene having the structural formula



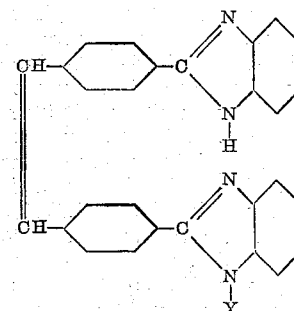
where R¹, R², R³, and R⁴ are radicals of the class consisting of hydrogen, lower alkyl containing 1-4 carbon atoms, lower alkoxy containing 1-4 carbon atoms, and halo, and Y¹ and Y² are radicals of the class consisting of hydrogen, lower alkyl containing 1-6 carbon atoms, hydroxy-lower alkyl containing 2-6 carbon atoms, 2-hydroxy-3-sulfopropyl, hydroxy-oxaalkyl containing 3-15 carbon atoms, carboxy-lower alkyl containing 2-6 carbon atoms, cyano-lower alkyl containing 3-6 carbon atoms, allyl, methallyl, and monocyclic aralkyl containing 7-11 carbon atoms.

2. A benzimidazolylstilbene having the structural formula



where Y is a hydroxy-lower alkyl radical containing 2-6 carbon atoms.

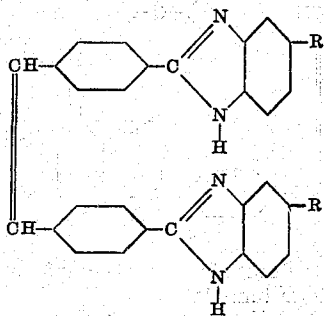
3. A benzimidazolylstilbene having the structural formula



33

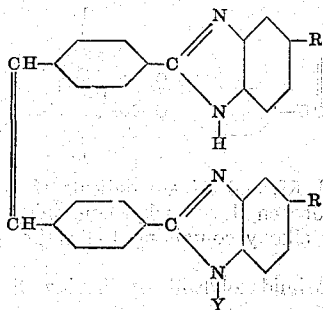
where Y is a hydroxy-oxaalkyl radical containing 3-15 carbon atoms.

4. A 4,4'-bis[5(or 6)-(lower alkoxy)benzimidazol-2-yl]stilbene having the structural formula



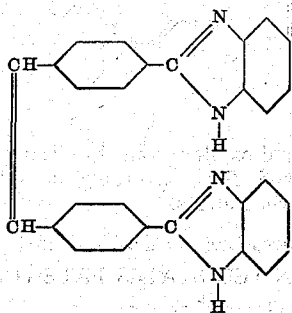
where R is a lower alkoxy radical containing 1-4 carbon atoms.

5. A benzimidazolylstilbene having the structural formula

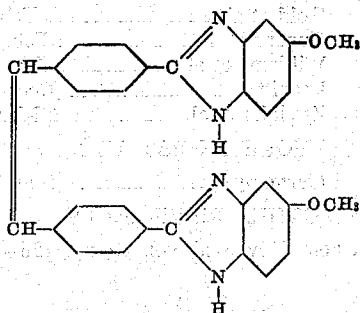


where R is a lower alkoxy radical containing 1-4 carbon atoms and Y is a hydroxy-oxaalkyl radical containing 3-15 carbon atoms.

6. The compound 4,4'-bis(benzimidazol-2-yl)stilbene, having the structural formula

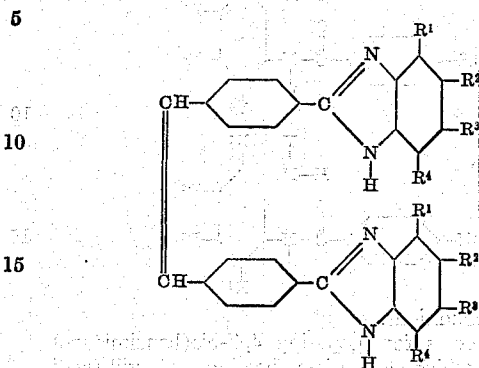


7. The compound 4,4'-bis[5(or 6)-methoxybenzimidazol-2-yl]stilbene, having the structural formula



34

8. The process which comprises interacting a benzimidazolylstilbene having the structural formula



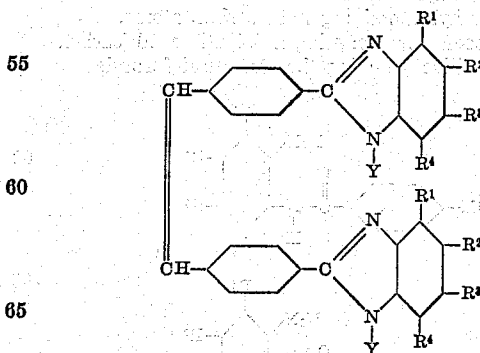
where R¹, R², R³, and R⁴ are radicals of the class consisting of hydrogen, lower alkyl containing 1-4 carbon atoms, lower alkoxy containing 1-4 carbon atoms, and halo with an alkylating agent which is a member of the class consisting of: the esters having the formula Z-An, where Z is a member of the class consisting of lower alkyl containing 1-6 carbon atoms, hydroxy-lower alkyl containing 2-6 carbon atoms, 2-hydroxy-3-sulfopropyl, hydroxy-oxaalkyl containing 3-15 carbon atoms, carboxy-lower alkyl containing 2-6 carbon atoms, cyano-lower alkyl containing 3-6 carbon atoms, allyl, methallyl, and monocyclic aralkyl containing 7-11 carbon atoms and An is the anion of a strong acid; 1,2-lower alkylene oxides containing 2-6 carbon atoms; acrylonitrile; and methacrylonitrile.

9. The process for alkylating 4,4'-bis(benzimidazol-2-yl)stilbene which comprises heating said compound with 2,3-dihydroxypropyl chloride.

10. The process for alkylating 4,4'-bis(benzimidazol-2-yl)stilbene which comprises heating said compound with ethylene oxide.

11. The process for alkylating 4-(benzimidazol-2-yl)-4'-{1-[2-hydroxy-3-(2,3-dihydroxypropoxy)propyl]benzimidazol-2-yl}stilbene which comprises heating said compound with ethylene oxide.

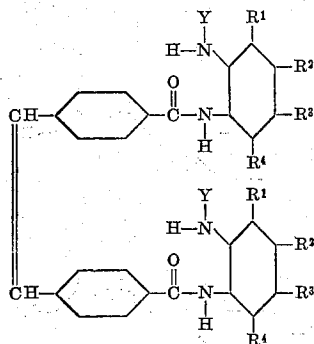
12. The process for preparing a 4,4'-bis(benzimidazol-2-yl)stilbene having the structural formula



where R¹, R², R³, and R⁴ are radicals of the class consisting of hydrogen, lower alkyl containing 1-4 carbon atoms, lower alkoxy containing 1-4 carbon atoms, and halo, and Y is a member of the class consisting of hydrogen, lower alkyl containing 1-6 carbon atoms, and monocyclic aralkyl containing 7-11 carbon atoms which

35

comprises heating a 4,4'-stilbenedi[carbox(ortho-aminoanilide)] having the structural formula



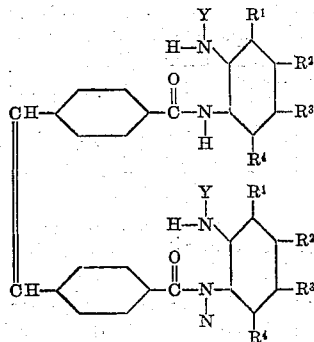
under acidic conditions.

13. The process for preparing 4,4'-bis(benzimidazol-2-yl)stilbene which comprises heating 4,4'-stilbenedi[carbox(ortho-aminoanilide)] under acidic conditions.

14. The process for preparing 4,4'-bis(benzimidazol-2-yl)stilbene which comprises reducing stilbenedi[carbox(ortho-nitroanilide)] to form stilbenedi[carbox(ortho-aminoanilide)] and heating this product under acidic conditions.

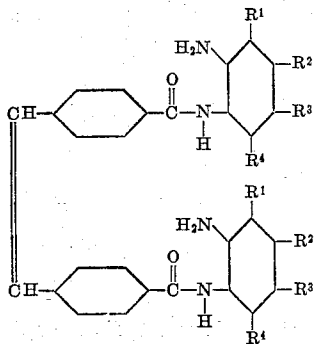
15. The process for preparing 4,4'-bis[5(or 6)-methoxybenzimidazol-2-yl]stilbene which comprises heating 4,4'-stilbenedi[carbox(2-amino-4-methoxyanilide)] under acidic conditions.

16. A 4,4'-stilbenedi[carbox(ortho-aminoanilide)] having the structural formula



where R¹, R², R³, and R⁴ are radicals of the class consisting of hydrogen, lower alkyl containing 1-4 carbon atoms, lower alkoxy containing 1-4 carbon atoms, and halo, and Y is a member of the class consisting of hydrogen, lower alkyl containing 1-6 carbon atoms, and monocyclic aralkyl containing 7-11 carbon atoms.

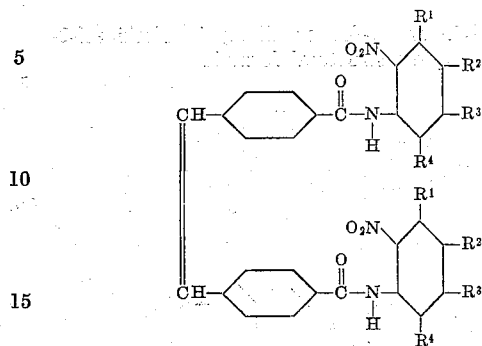
17. The process for preparing a 4,4'-stilbenedi[carbox(ortho-aminoanilide)] having the structural formula



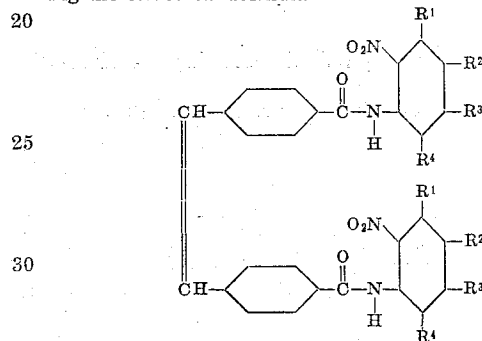
where R¹, R², R³, and R⁴ are radicals of the class consisting of hydrogen, lower alkyl containing 1-4 carbon atoms, lower alkoxy containing 1-4 carbon atoms, and

36

halo which comprises reducing a 4,4'-stilbenedi[carbox(ortho-nitroanilide)] having the structural formula

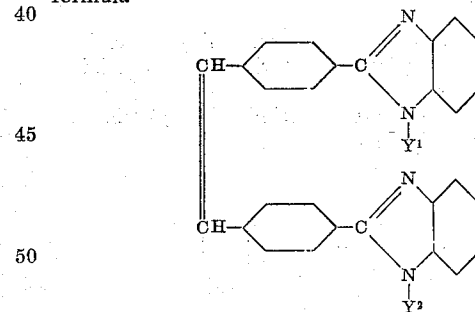


18. A 4,4'-stilbenedi[carbox(ortho-nitroanilide)] having the structural formula



where R¹, R², R³, and R⁴ are radicals of the class consisting of hydrogen, lower alkyl containing 1-4 carbon atoms, lower alkoxy containing 1-4 carbon atoms, and halo.

19. A benzimidazolylstilbene having the structural formula



where Y¹ is a hydroxy-lower alkyl radical containing 2-6 carbon atoms and Y² is a hydroxy-oxaalkyl radical containing 3-15 carbon atoms.

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