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2,700,044

COMPOUNDS OF THE BENZIMIDAZOLYL-PHENYL-1,2-NAPHTHOTRIAZOLE TYPE, USEFUL AS WHITENING AGENTS

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8 Claims. (Cl. 260—308)

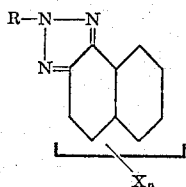
This invention relates to the production of novel organic compounds which are useful as whitening agents for fibrous material such as textiles or paper. It is an object of this invention to produce compounds of the above general nature, but which are characterized further by bleach fastness and by correct shade of fluorescence. Additional objects and achievements of this invention will appear as the description proceeds.

The art of whitening or brightening textile fiber and paper is of relatively recent development. It has been found that fibrous materials which normally have a dull, yellowish cast when in the white, unbleached state, become whiter and brighter if treated with agents which fluoresce under ultraviolet light. Presumably the action of the ultraviolet rays present in ordinary daylight is sufficient to excite these agents upon the fiber to emit fluorescence which overcomes the undesirable tinge of color in the unbleached fiber. Best results are obtained when the shade of fluorescence is complementary to that of the unbleached fiber, so that the colors will cancel each other. Since the most common off-white shade of unbleached cellulosic fiber is yellowish, the most desirable shade in a fluorescent is blue. Many fluorescent of green or pink shade have been proposed and tried, but these can be used only in very minute concentration, inasmuch as larger concentrations of these tend to shade the fiber in undesirable green or pink shades. The blue-fluorents, however, can be used in relatively large concentration (say up to 10% by weight of the fiber), and are very effective in producing bright, white textiles.

Another very important demand developed by the trade is bleach fastness. Inasmuch as the aforementioned fluorescent agents are generally incorporated into soap and synthetic detergents, which are packaged and marketed for household use, and inasmuch as in household practice laundered articles are often subjected to bleaching with various agents, for instance hypochlorites, it is essential that the fluorescent transferred from the detergent to the fiber shall not be destroyed by the action of bleach. Unfortunately, most of the fluorescent agents now on the market, and having the desirable blue shade, are weak in respect to this qualification of bleach resistance.

In addition to the above two primary qualifications, an agent to be commercially successful must be capable of being synthesized economically from readily available materials, and must have sufficient fluorescent power (often referred to as "tinctorial strength") to give the desired effect at a minimum cost. It must also have affinity for the fiber that is to be treated and must possess sufficient water-solubility to be applicable from an aqueous bath in the concentrations that would normally be used.

Now according to my invention new chemical compounds are synthesized which satisfy to an excellent degree all the foregoing qualifications. The novel compounds of this invention may be defined by the general formula



wherein R represents the 4'-radical of a compound of the group consisting of 2-phenyl-benzimidazole, Bz-methyl-

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2-phenyl-benzimidazole and the monosulfo derivatives of these, X stands for a water-solubilizing, acid radical such as sulfo, carboxy or a salt of such acid radical, such as the alkali-metal or ammonium salts thereof, while *n* designates the numeral 1 or 2.

These compounds may be synthesized by diazotizing the corresponding 2-(p-aminophenyl)-benzimidazole and coupling the diazo compound (in acid medium) to a 1-amino- or 2-amino-naphthalene having one or two sulfo groups or a carboxy group in the nucleus. The resulting ortho-amino azo compound is then converted into a triazole by oxidation in known manner, for instance by heating in an aqueous solution of cupric ammonium sulfate until the color of the intermediate azo dye has essentially disappeared, followed by recovery of the product in a desired physical or chemical form, for instance in the form of an alkali-metal or ammonium salt.

If it is found that the reaction mass after filtering contains residual color, the same may be destroyed by treating the filtrate with dilute hypochlorite solution or with reducing agents.

As suitable aminophenyl-benzimidazole for the foregoing purpose may be mentioned 2-(p-aminophenyl)-benzimidazole; 2-(p-aminophenyl)-5(or 6)-methyl-benzimidazole; the monosulfo derivatives of these, obtained by sulfonation of same with 20% oleum at 25° C. (position of SO₃H group unknown); or the alkali-metal or ammonium salts of such sulfo derivatives.

As coupling components for the intermediate aminoazo dyestuffs prepared above, may be used 1-amino-naphthalene-4-sulfonic acid, 2-amino-naphthalene-3-carboxylic acid, the various isomers of these; various 1-amino- and 2-amino-naphthalene-disulfonic acids; and the alkali-metal or ammonium salts of any of these.

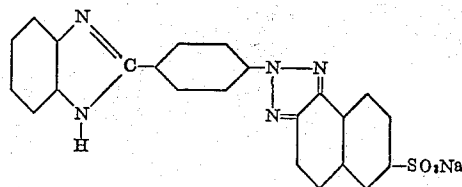
Without limiting this invention, the following examples are given to illustrate my preferred mode of operation. Parts mentioned are by weight.

Example 1

20.8 parts (0.1 mol) of 2-(p-aminophenyl)-benzimidazole (Ber. 34, 2959; 1901) were diazotized, at 0 to 5° C., with sodium nitrite and an excess of hydrochloric acid in 1000 parts of water. A solution of 27 parts (0.11 mol) of Broenner's acid (2-aminonaphthalene-6-sulfonic acid) sodium salt in 400 parts of water was added. The acidity was reduced by the aid of sodium acetate to a weakly acid test on Congo red paper and the mixture was allowed slowly to assume room temperature. The mixture was then made alkaline to brilliant yellow paper by the addition of 30% sodium hydroxide and the aminoazo dye was salted out and filtered off.

The wet dye cake thus prepared was dispersed in 2000 parts of water at 60° C. A solution of 50 parts of CuSO₄·5H₂O in 100 parts of water and 300 parts of 28% aqueous ammonia was added. The mixture was then heated to reflux for 24 hours and thereafter filtered hot (50° C.). The wet filter cake was dispersed in 3000 parts of water containing 200 parts of concentrated hydrochloric acid and the slurry was refluxed for 1 hour and then filtered. The obtained filter cake was again dispersed in water (about 10,000 parts), the mixture was made alkaline with sodium hydroxide, heated to the boil and filtered hot. To the filtrate 50 parts of sodium hydrosulfite was added and the mixture was heated again to the boil for 30 minutes. The product was isolated by salting out with sodium chloride. The precipitate was filtered off and dried. It was a cream powder, little soluble in water, and producing a bright bluish fluorescence when spotted on paper or cotton. The absorption maximum of this product in dimethyl formamide solution is located at 365 millimicrons.

The end product is believed to have the formula



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Similar compounds may be prepared by coupling diazotized 2-(p-aminophenyl)-benzimidazole to naphthionic acid (1-aminonaphthalene-4-sulfonic acid) and to Laurent's acid (1-aminonaphthalene-5-sulfonic acid), and oxidizing the resulting aminoazo dyes as above described.

Example 2

20.8 parts of 2-(p-aminophenyl)-benzimidazole were diazotized, coupled to the sodium salt of amino-J acid (2-aminonaphthalene-5,7-disulfonic acid), and the obtained dye was oxidized as in Example 1. The crude oxidation product was filtered hot (about 50° C.). The cake was slurried in 2000 parts of H₂O, stirred at 40°-50° C. with 5-10 parts of sodium hydrosulfite for 30 minutes, heated to boil and filtered hot. The product was isolated from the filtrate by salting out. The obtained precipitate was filtered off, washed and dried. It was a pale gray powder, soluble in water and producing a bright fluorescence when spotted on paper or cotton. The absorption maximum of this compound in water solution is located at 360 millimicrons.

Similar products may be prepared by coupling diazotized 2-(p-aminophenyl)-benzimidazole to amino-R acid (2-aminonaphthalene-3,6-disulfonic acid) and to amino-G acid (2-aminonaphthalene-6,8-disulfonic acid), and oxidizing the resulting amino azo dyes as in Example 1.

Example 3

The starting material of this example, 2-(p-aminophenyl)-benzimidazole sulfonic acid, was obtained by sulfonation of 1 part of 2-(p-aminophenyl)-benzimidazole with 5 parts of 20% oleum at 40° C. for ½ hour, followed by drowning in ice water, filtering, washing with sodium chloride solution and drying.

29 parts (0.1 mol) of the 2-(p-aminophenyl)-benzimidazole sulfonic acid so obtained were diazotized and coupled to the sodium salt of naphthionic acid as in Example 1. The obtained dye was oxidized and purified as in Example 2. The end product was a pale gray solid, soluble in water and exhibiting a bright blue fluorescence when spotted on paper or cotton. Its absorption maximum in aqueous solutions is located at 360 millimicrons.

Similar compounds may be prepared by coupling diazotized 2-(p-aminophenyl)-benzimidazole sulfonic acid to Broenner's acid, Laurent's acid, amino-R acid, amino-J acid, or amino-G acid, and oxidizing the resulting amino azo dyes as in Example 2.

Example 4

2-(p-aminophenyl)-5-(or 6-) methyl benzimidazole was prepared by reacting 4-amino-3-nitrotoluene with p-nitrobenzoyl chloride to obtain 2',4-dinitro-p-benzotoluide, followed by reducing and ring-closing with stannous chloride and hydrochloric acid according to the procedure described by E. Lellmann in Ber. 26, 2760 (1893). This amine was diazotized, coupled to Broenner's acid, ring-closed to the triazole, purified and isolated as described in Example 1.

The final product is a gray powder with fluorescence properties similar to those of the non-methylated homolog. In lieu of Broenner's acid, any of the other coupling components mentioned in the foregoing examples may be used.

Example 5

2-(p-aminophenyl)-5-(or 6-)methyl benzimidazole sulfonic acid is obtained by reacting the 2-(p-aminophenyl)-5-(or p-)methyl benzimidazole of Example 4 with oleum, as described in Example 3. The exact position of the sulfonic acid group in this compound is not known. This derivative is then used as diazo component in this invention, according to foregoing examples, any of the aminonaphthalene sulfonic acids mentioned in this case being applicable as coupling components.

The novel products of the foregoing several examples were tested for whitening power and bleach resistance by the same tests as described in my copending application Serial No. 333,016, filed January 23, 1953, and found to be satisfactory in both respects. At least 90% of the fluorescence imparted to a sample of cotton fabric by the novel agents was retained in the bleach-fastness test.

Tests for light-fastness, substantivity and wash-fastness were also carried out, and showed my novel compounds

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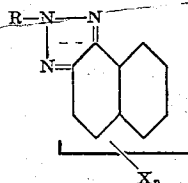
to compare favorably in respect to these qualities with the best fluorescents which are now on the market.

The compounds given in the above examples have been isolated as the sodium salts of the sulfonic acids. By using potassium hydroxide and potassium salts in lieu of sodium hydroxide and sodium salts, throughout, the products may be obtained as potassium sulfonates. Isolation as the free sulfonic acids can be effected by acidification of the condensation mass, and the products thus obtained may be reacted with ammonium hydroxide or any suitable organic or inorganic base, to yield the corresponding salt.

In addition to producing a whitening effect upon textile material or paper, my novel compounds may also be used for various other purposes where fluorescence or absorption of ultra-violet light is desirable, for instance to achieve fluorescent effects in costumes or stage settings, to achieve novel effects on photographic paper, as ultra-violet filters when impregnated on cellulosic films which are used for wrapping materials, etc.

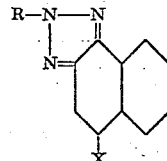
I claim as my invention:

1. A compound of the general formula



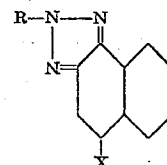
wherein R represents the 4'-radical of a compound of the group consisting of 2-phenyl-benzimidazole, 2-phenyl-Bz-methyl-benzimidazole, and the monosulfo derivatives of these, X stands for a water-solubilizing, acid radical of the group consisting of sulfo, carboxy and their water-soluble salts, while n designates an integer not exceeding 2.

2. A compound of the formula



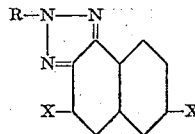
wherein X is a sulfo group, while R designates the 4'-radical of 2-phenyl-benzimidazole.

3. A compound of the formula



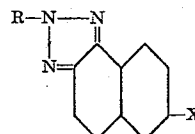
wherein X is a sulfo group, while R designates the 4'-radical of monosulfo-2-phenyl-benzimidazole.

4. A compound of the formula



wherein the X's stand for sulfo groups, while R designates the radical of 2-phenyl-benzimidazole.

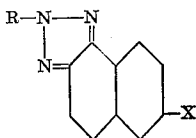
5. A compound of the formula



wherein X is a sulfo group, while R designates the 4'-radical of 2-phenyl-benzimidazole.

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6. A compound of the formula



wherein X is a sulfo group, while R designates the 4'-radical of 2-phenyl-Bz-methyl-benzimidazole.

7. The process of producing a fluorescent agent of bluish fluorescence and good bleach-fastness, which comprises diazotizing a p-aminophenyl-benzimidazole com-

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5 pound of the group consisting of 2-p-aminophenyl-benzimidazole, 2-p-aminophenyl-Bz-methyl-benzimidazole, and the monosulfo derivatives of these, coupling the diazonium compound to a sulfonated naphthalene having a primary amino group in one of the 1,2-positions and a hydrogen atom in the other of said positions, and oxidizing the resulting ortho-amino-azo compound to produce a triazole.

10 8. A process as in claim 7, the oxidation being effected by heating the compound in an aqueous solution of cupric-ammonium sulfate.

No references cited.