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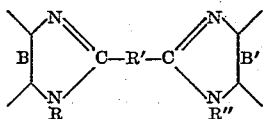
ALKENYL BISIMIDAZOLE OPTICAL BLEACHING AGENTS

Julian Jacob Leavitt, Plainfield, N. J., assignor to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application June 21, 1954,
Serial No. 438,351

3 Claims. (Cl. 260—240)

This invention relates to new optical bleaching agents of the structure



in which B and B' are six-membered aromatic carbocyclic rings, R is a lower alkenyl radical, R' is lower alkenyl or H and R' is a divalent aliphatic hydrocarbon radical of less than 5 carbon atoms, the number of carbon atoms being even and containing at least one double bond. The invention also relates to detergent compositions containing the above compounds and to textiles dyed therewith.

In recent years the use of optical bleaching agents, sometimes called brighteners, has grown enormously. These compositions are colorless dyestuffs exhibiting substantivity for fabrics, which, when exposed to ultraviolet radiation such as is contained in daylight, fluoresce in the blue range of the spectrum, thereby compensating for the slightly yellowish cast of most white fabrics. The fluorescence of the bleaching agents, while in the blue, varies somewhat in dominant wave length. Where the dominant wave length is longer, the blue fluorescence is considered to have a slightly green tinge, whereas a shorter dominant wave length nearer the violet end of the spectrum results in a blue fluorescence which is referred to as being slightly reddish. For practical purposes, particularly for use in detergent compositions intended for the laundering of white fabrics, a neutral blue fluorescence is generally preferable since a reddish blue fluorescence will tend to build up pink on the fiber with repeated launderings.

Another problem with the optical bleaching agents is presented by their fastness to certain treatments which they may encounter in laundering operations. Among these fastness characteristics, a resistance to decomposition or quenching of fluorescence by reason of the presence of hydrochlorites is an important one because in many laundering operations hypochlorites are used for chemical bleaching purposes. So important is a good resistance to hypochlorite that in the case of some optical bleaching agents which have deficient hypochlorite resistance, white goods laundered with a bleach may actually appear less white than if the bleach is omitted. Complete elimination of the use of hypochlorite and similar oxidizing bleaches is not feasible because certain stains or deep soil encountered in the laundering of some fabrics can only be removed by chemical bleaching action. It is particularly important that the stability to hypochlorite be maintained in the medium used to wash the fabrics even in the absence of said fabrics. This is true because under normal laundering conditions, the bleach and the detergent containing the brightener may be introduced before the goods to be washed. Many optical bleaches have adequate stability to bleach once on the fiber but are rapidly destroyed in solution. It is a particular advantage

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of our new products that they are stable to bleach in the laundering medium even in the absence of fabric.

The N-substituted diimidazoles of the present invention exhibit a desirable neutral or slightly greenish blue fluorescence and surprisingly, they exhibit an extraordinary resistance to loss in fluorescence by reason of attack by hypochlorites. The presence of low concentrations of hypochlorites which would be typical of many laundering operations results in virtually no diminution of blue fluorescence.

It is not known why the compounds of the present invention exhibit the high degree of stability against hypochlorites. The chemical structure is such that a chemist would be led to expect that they would be reactive with hypochlorites by reason of the double bond present in the alkenyl group attached to nitrogen in one of the diimidazole rings. In spite of the known reactivity of such aliphatic groups with hypochlorites, the compounds of the present invention exhibit at least as great resistance to deterioration from hypochlorites as similar compounds which do not contain the reactive alkenyl group. It has not been determined why the compounds of the present invention exhibit this extraordinary anomaly in chemical behavior, and it is not intended to limit the invention to any theory of their action.

Not only do the compounds of the present invention exhibit desirable blue fluorescence and possess a high degree of hypochlorite stability, but the chroma of the blue fluorescence is markedly greater than other optical bleaches which have acceptable hypochlorite stability, especially those optical brighteners which have a neutral or greenish blue hue of fluorescence. The higher value of chroma, which may be thought of quantitatively as a greater purity of the blue fluorescence, permits a more intense optical bleaching action and is a factor in which the compositions of the present invention are superior to other hypochlorite fast optical bleaches. It is a further advantage of the products of this invention that they have high fluorescent strength, appreciably higher than that of many other hypochlorite fast types.

Of particular importance is the outstanding behavior of these products on non-cellulosic fibers, for example, acetate, nylon (both the poly(hexamethylenediamineadipimide) and poly-ε-aminocaprolactam types), and acrylic fibers such as Orlon. Most cellulosic brighteners have little or no affinity for non-cellulosics and therefore exhibit no appreciable whitening action. However, the new products of my invention have good affinity for both types of fibers. For optimum results the products may be selected depending on the end use. Thus, if whitening of non-cellulosics is of prime importance, the compounds in which R and R' are alkenyl are particularly useful and if whitening of cellulosic materials is more important, the compounds in which R' is hydrogen are preferred. However, it is a definite advantage that where whitening of both types of fibers is needed, either type brightener may be used.

The present invention is not intended to be restricted to any particular process of preparing the compositions. It is, however, an advantage of the invention that the compounds can be very simply prepared by easily controlled reactions giving good yields. The basic skeleton of the molecule can be prepared by reacting a dibasic acid with ortho-phenylenediamine or an N-alkenyl derivative. The dibasic acid may be either saturated or unsaturated and, of course, should have a hydrocarbon chain connecting the two carboxyl groups which contains an even number of carbon atoms less than 5. If an unsaturated dibasic acid is used, the group R' will contain at least one double bond. An example of such a process is the reaction of ortho-phenylenediamine or a mono N-alkenyl derivative with fumaric acid. It is also possible to use

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a saturated dibasic acid, such as for example succinic acid, which will not produce the immediate precursor of the compounds of the present invention, but will produce compounds in which R' is a saturated hydrocarbon chain. These can easily be dehydrogenated with such compounds as mercuric acetate, ferric chloride and the like. After the unsaturated or saturated compound is prepared, the alkenyl group is introduced by reaction with an alkenylating agent such as an alkenyl halide. If initially a saturated dibasic acid is used, it will be necessary to oxidize the R' group and this can be effected either before or after introducing the alkenyl group.

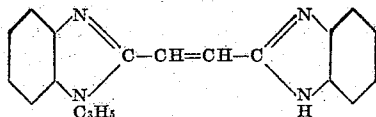
The lower alkenyl residue may be any one of the well-known radicals, such as allyl, its isomer, propenyl-1, methallyl, crotyl and the like. There is some evidence that under certain circumstances the allyl group may rearrange to the propenyl-1 group, and, therefore, the compounds of the present invention are not limited in the case where R is C₃H₅ to any particular isomer. The same situation exists with the methallyl radical. Among the typical agents usable for introducing the alkenyl group are allyl bromide, methallyl iodide and crotyl chloride. The quantity of the alkenyl halide must be restricted to approximately mole per mole based on the diimidazole if the mono-alkenyl derivative is desired.

It is an advantage of the present invention that the compounds may be used with the typical detergents, examples of which are soaps, emulsifying agents such as sulfite cellulose waste liquor, alkyl naphthalene sulfonic acids, condensation products of naphthalene sulfonic acids with formaldehyde, sulfonated or sulfated oils, sulfuric half esters of higher alcohols and the like.

As indicated above, the textiles which are treated with compositions containing the compounds of the present invention readily take up the optical bleaching agent, and it is an advantage that there is adequate substantivity for cellulosic fibers, cellulose esters, basic nitrogen fibers such as polyamides, polyesters, polyacrylonitriles and the like. Moreover, it is a particular advantage that these products have an excellent affinity for fibers such as polyamides, e. g. nylon, even in the presence of cellulosic materials. Most optical bleaches for cellulosic materials, especially the hypochlorite fast products such as the benzidine sulfone derivatives, have little affinity for nylon and other non-cellulosic fibers, even in the absence of cellulosic fibers. The dyed textiles show a remarkable whiteness which resists strongly the attack of hypochlorites. The natural yellowish tinge of the fabric is completely masked by the high chroma and strong fluorescence of the compounds of the present invention.

The invention will be illustrated by the following specific examples in which the parts are by weight unless otherwise indicated.

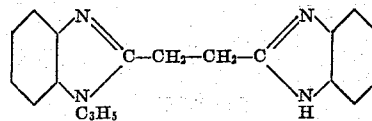
Example 1



A solution of 52 parts of 1, 2-bis (2-benzimidazolyl) ethylene in 400 parts of alcohol and 22.4 parts of potassium hydroxide is stirred under reflux. To this is added gradually an alcoholic solution of 26.6 parts of 3-bromopropene-1. The mixture is stirred and boiled until the reaction is complete. It is cooled to room temperature and the yellow precipitate is filtered, washed and redissolved in alcoholic alkali. The turbid solution is treated with diatomaceous earth, clarified and drowned in ten volumes of water. The precipitate is coagulated at the boil, filtered, washed and dried, giving a good yield of a yellow solid which does not melt below 320° C. If desired, the material can be precipitated again from alcoholic alkaline solution.

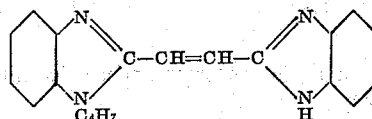
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Example 2



The procedure of Example 1 is followed, using an equivalent quantity of 1, 2-bis (2-benzimidazolyl) ethane in place of the 1, 2-bis (2-benzimidazolyl) ethylene. The product shows a weaker fluorescence than the product of Example 1. On treatment with mercuric acetate in acetic acid solution, it is converted to a product identical to that of Example 1.

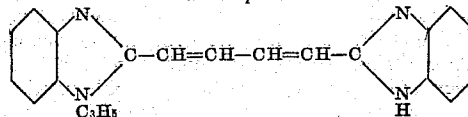
Example 3



The procedure of Example 1 is followed using methallyl bromide instead of 3-iodopropene. A product of intense blue fluorescence in alcoholic solution is obtained.

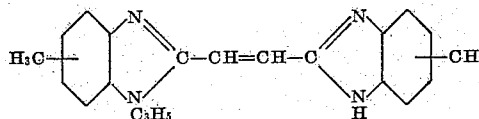
A similar product is obtained if crotyl chloride is used instead of methallyl bromide.

Example 4



The procedure of Example 1 is followed using an equivalent amount of 1, 4-bis (2-benzimidazolyl) butadiene in place of 1, 2-bis (2-benzimidazolyl) ethylene. A product of intense blue fluorescence in alcoholic solution is obtained.

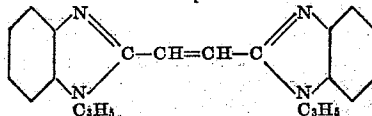
Example 5



Using the procedure of Example 1 but substituting 1,2-bis[5(6)-methyl-2-benzimidazolyl]ethylene, there is obtained the expected allyl derivative. It is a yellow powder having an intense blue fluorescence in alcohol solution.

Similarly the product containing chlorine in the 5 (6) position can be prepared.

Example 6



A slurry of 26 parts of 1,2-bis(2-benzimidazolyl)ethylene in 400 parts of ethanol and 100 parts by volume of 2 molar ethanolic potassium hydroxide is treated at the boiling point with a solution of 24.2 parts 3-bromopropene-1 in 80 parts of ethanol. The mixture is stirred at the boiling point under reflux until the reaction is complete, cooled, filtered, and washed with ethanol. The filtrate and washings are drowned into a large volume of water and the precipitate is isolated by filtration. It can be purified by dissolving in hot aqueous alcoholic hydrochloric acid, treating with activated charcoal and reprecipitating by the addition of ammonia. A good yield is obtained of a yellow solid which fluoresces strongly in alcoholic solution.

Example 7

A 0.05% solution of the product of Example 1 is prepared in 50% aqueous dimethylformamide containing a

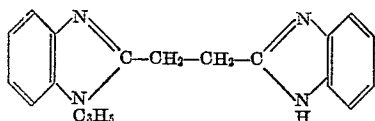
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small amount of sodium hydroxide and a trace of a non-ionic dispersing agent. Fifty volumes of the solution is diluted to 500 volumes with water to give a 0.005% mixture (A). A 0.500% aqueous solution of detergent (B) is prepared by dissolving 5.0 parts of a commercial detergent in 500 parts of hot water and diluting to 1000 volumes with cold water. A 5-g. piece of cotton muslin is added to a mixture of 10 parts of solution A, 100 parts of solution B and 15 parts of water. After agitating twenty-five minutes at 130° F., the cloth is removed, rinsed in cold tap water, and air dried. The resultant product is much whiter in appearance than an undyed piece.

Nylon treated in the same manner is also much improved in whiteness.

The products of Examples 2, 3, 4, 5 and 6 give similar results when similarly used.

Example 8



A slurry of 52.4 parts of 1,2-bis(2-benzimidazolyl)ethane in 240 parts of ethanol and 160 parts of 2 molar ethanolic potassium hydroxide is treated at the boiling point with a solution of 53.2 parts 3-bromopropene-1 in 160 parts of ethanol. The mixture is heated under reflux until the reaction is substantially complete, cooled, filtered and washed with alcohol. The alcohol-soluble

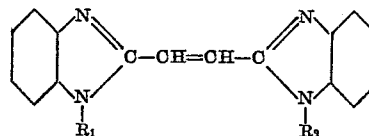
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product is isolated from the filtrate and washings by drowning in water and filtering. The crude product may be purified in good yield by dissolving in acetic acid, clarifying, drowning in water and basifying with ammonia.

The product is a tan solid and may be oxidized to the ethylene derivative by procedures described in the art for the corresponding unsubstituted compound.

I claim:

1. Compounds of the structure:



in which R₁ is allyl and R₂ is chosen from the group consisting of hydrogen and allyl.

2. The compound of claim 1 in which R₂ is hydrogen.

3. The compound of claim 1 in which R₂ is allyl.

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