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3,586,673

**PREPARATION OF SYMMETRICALLY AND UNSYMMETRICALLY SUBSTITUTED STILBENE-BISBENZOXAZOLES**

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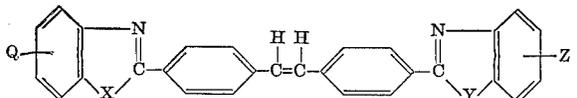
5 Claims

**ABSTRACT OF THE DISCLOSURE**

Process for the preparation of both symmetrical and unsymmetrical 4,4'-substituted stilbene derivatives, having 2-benzoxazolyl, 2-benzimidazolyl, or 2-benzothiazolyl substituents. The process comprises first reacting a dialkyl 4-substituted benzylphosphonate with a 4-substituted benzaldehyde to form the corresponding 4-heterocyclic-4'-carbonylstilbene compound, which is then treated with an acyl halogenating agent to form the 4-heterocyclic-4'-stilbenecarbonyl halide. The halide is then reacted with an o-amino-phenylene compound to form the subject stilbene derivatives. These stilbene derivatives are useful as optical brighteners.

This invention is concerned with a new process for the preparation of 4,4'-diheterocyclic substituted derivatives of stilbene, which are particularly useful as fluorescent brightening agents and light stabilizers for thermoplastic materials.

More specifically, the novel process of this invention is concerned with the preparation of 4,4'-diheterocyclic substituted stilbene derivatives which correspond to the general formula:



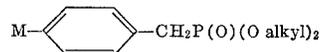
wherein X and Y, which may be the same or different, are members selected from the group consisting of  $-\text{NR}_1-$ ,  $-\text{O}-$ , and  $-\text{S}-$ , wherein  $\text{R}_1$  is a member selected from the group consisting of hydrogen, alkyl and aryl; and Q and Z, which may be the same or different, are members selected from the group consisting of hydrogen, alkyl, alkenyl, alkoxy, aryl, aryloxy, halo, cyano, and sulfonyl.

The subject process provides a simple method for the preparation of either the symmetrical or unsymmetrical members of the stilbene series in high yields. Exemplary of this process, as described herein, is the preparation of 2-[p-[p-(2'-benzoxazolyl)styryl]phenyl]-5-methylbenzoxazole from 4-methyl-2-aminophenol, p-carboxybenzaldehyde, and diethyl 4-(2'-benzoxazolyl)benzylphosphonate.

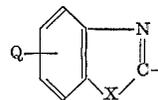
As is apparent from the above, and as is more thoroughly exemplified hereinafter, the process of this invention may be used to prepare the 4,4'-diheterocyclic substituted stilbene derivatives wherein the 4,4'-heterocyclic substituents are either the same or different. Thus, by the subject process, unsymmetrical members of all types of this series of compounds, for example, 2-[p-[p-(2'-benzoxazolyl)styryl]phenyl]benzothiazole and 2-[p-[p-(2'-benzothiazolyl)styryl]phenyl]benzimidazole, may be prepared, as well as the symmetrical members of these types of compounds, such as 4,4'-bis(2'-benzoxazolyl)stilbene, and 4,4'-bis(2'-benzothiazolyl)stilbene. Heretofore, the preparative methods of the prior art have provided, principally, for the preparation of only the symmetrical members of these types of compounds.

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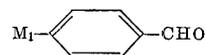
In essence, the process of the present invention comprises three main steps, the first of which involves the interaction of a dialkyl 4-substituted benzylphosphonate corresponding to the general formula:



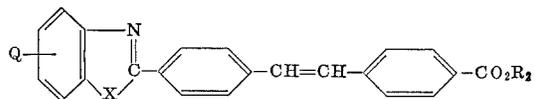
wherein M is a member selected from the group consisting of  $-\text{CO}_2\text{R}_2$  and



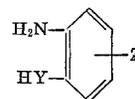
wherein  $\text{R}_2$  is a member selected from the group consisting of hydrogen, alkyl, and aryl, and X and Q have the meanings given above, with a 4-substituted benzaldehyde corresponding to the general formula:



wherein  $\text{M}_1$  has the meaning of M, above, with the provision that M and  $\text{M}_1$  must be different. This interaction is conducted in the presence of a suitable proton acceptor, such as sodium hydride and an inert solvent, and the results in the formation of a 4-heterocyclic-4'-carbonylstilbene compound corresponding to the general formula:



The second step of the subject process involves the treatment of the stilbenecarboxylic acid corresponding to the above general formula with an acyl halogenating agent such as phosphorus oxychloride, under halogenating conditions to form the corresponding 4-heterocyclic-4'-stilbenecarbonyl halide. The third step consists of the treatment of approximately equal molar quantities of the above formed stilbenecarbonyl halide with an o-amino-phenylene compound corresponding to the general formula:



wherein Y and Z have the meanings given above, under conditions sufficient to effect condensation and cyclization, with the formation of the subject 4,4'-diheterocyclic substituted stilbene derivatives. Each of these steps in the subject process is discussed more fully below.

The class of stilbene derivatives which are prepared by the subject process have unexpectedly superior fluorescent properties when used as whitening or brightening agents and, in addition, have certain other properties, such as heat stability, light stability, stability towards bleaches, stability in textile processing treatments and the like, which make them especially useful as whitening or brightening agents for textile materials, particularly for synthetic linear polyester textile fibers. Further information as to these known compounds and their uses may be found in the prior art, such as Belgian Pat. 648,674, Belgian Patent 651,310, and U.S. Pats. 3,260,715 and 3,322,680.

A better understanding of the process and products of this invention may be obtained from the examples given below, which disclose preferred modes presently contemplated by the inventors for carrying out this invention.