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PROCESS OF ACYLATION

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14 Claims. (Cl. 260—507)

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This invention relates to a process for acylating 4,4'-diaminostilbene sulfonic and carboxylic acids, and especially 4,4' - diaminostilbene - 2,2' - disulfonic acid.

The 4,4'-bis(acylamido) stilbene compounds obtained when 4,4'-diaminostilbene sulfonic or carboxylic acids are acylated by aromatic acid chlorides are valuable fluorescent agents which find extensive use as optical bleaching agents for cellulosic materials. While various 4,4'-diaminostilbene sulfonic and carboxylic acids such as 4,4'-diaminostilbene-2,2'-disulfonic acid, 4,4'-diaminostilbene-3,3'-disulfonic acid, 4,4'-diaminostilbene-2,2',6,6'-tetrasulfonic acid, 4,4'-diaminostilbene-2,2'-dicarboxylic acid or 4,4'-diaminostilbene-3,3'-dicarboxylic acid may be employed in producing these fluorescent materials and all yield products having substantially similar products, the 4,4'-diaminostilbene-2,2'-disulfonic acid is generally used and therefore, the present invention will be described in connection with its use.

When these acylamidostilbene derivatives, which are themselves substantially colorless, are incorporated in such cellulosic materials as paper, cloth, foils and the like, they have the property of absorbing ultraviolet light and emitting visible blue light so that they neutralize any yellowness of the cellulosic material and thus increase the apparent whiteness of such material. These compounds are substantive to cellulosic materials and thus exert a permanent whitening effect when incorporated therein in small amounts in any convenient manner; for example, by merely washing the cellulosic material in water with usual synthetic organic detergents such as soap, containing from 0.02 to 0.1 per cent of the acylated 4,4'-diaminostilbene-2,2'-disulfonate, or by usual dyeing procedures, or in the case of such materials as regenerated cellulose, by addition to spinning baths or precipitating baths, and in the case of paper by addition to the pulp in the beater or as an after-treatment to render the paper whiter.

These acylated derivatives of 4,4'-diaminostilbene-2,2'-disulfonic acids have heretofore been prepared by the usual Schotten-Baumann method of condensing an acyl halide with the 4,4'-diaminostilbene-2,2'-disulfonic acid or by well-known variations of this reaction, by addition of

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an acyl chloride to an aqueous or pyridine solution of the sodium salt of 4,4'-diaminostilbene-2,2'-disulfonic acid in the presence of a minor amount of alkali such as caustic soda, sodium bicarbonate or even sodium acetate. However, it has been found that in these known processes for the preparation of these acylated compounds, the rate of reaction is very slow and the reaction does not go to completion to a very large extent and the product is contaminated with large amounts of impurities, particularly the monoacylated compounds. As a result, not only has poor yield of the desired acylated compound been obtained, but in addition, extensive purification of the product has been necessary and in general, substantial excesses of reactants, particularly acyl chlorides, have had to be used.

It is therefore an object of the present invention to provide a process for acylating 4,4'-diaminostilbene-2,2'-disulfonic acids by condensing an acyl chloride with 4,4'-diaminostilbene-2,2'-disulfonic acids economically, speedily and in high yields and by means of which a product having a high degree of purity is obtained. Other and further objects will be apparent as the present description progresses.

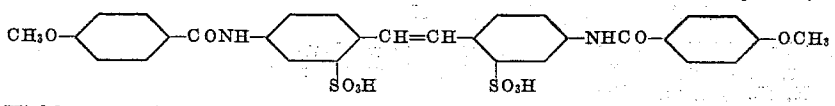
I have now discovered that by reacting substantially theoretical amounts (i. e. two molar proportions) of the acyl chloride with one molar proportion of 4,4'-diaminostilbene-2,2'-disulfonic acid in the presence of a mixture of water and acetone in relative proportions of from 2:1 to 1:2 by weight (which mixture contains from 10 to 30 per cent of sodium acetate), and recovering the acylated product preferably by filtration and washing with a 10 to 30 per cent solution of sodium acetate in water, the reaction proceeds with substantially quantitative yield and the product obtained has a much higher degree of purity than when the original Schotten-Baumann reaction is employed or any of its well-known variations.

The details of the present invention may be most readily described in connection with the following specific examples, in which the parts are by weight:

Example I

63 parts of 4,4'-diaminostibene-2,2'-disulfonic acid are mixed with 300 parts of water. Suf-

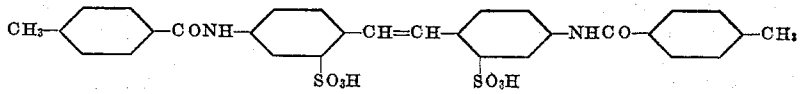
ficient caustic soda solution is added to cause solution of the acid by formation of the water-soluble sodium salt. Care should be exercised to avoid the addition of any substantial excess of caustic soda and the pH of the solution should not be higher than about 8.5. 111 parts of anhydrous sodium acetate are then added and well mixed, followed by addition of 360 parts of acetone. The charge is cooled to 25° and maintained at that temperature during addition, over a period of 15 minutes, of 65 parts of anisoyl chloride. The reaction mass is maintained at 25–28° C. for 2 hours and filtered. The product is further purified by additional washings with 10 to 30 per cent sodium acetate solution in cold water. Product has the formula:



Yield is nearly quantitative and product has a high degree of purity.

Example II

17.5 parts of 4,4'-diaminostilbene-2,2'-disulfonic acid are mixed with 166 parts of water. Sufficient caustic soda solution is added to bring the acid into solution and then 25 parts of sodium acetate and 150 parts of acetone are added. The reaction mix is heated to a temperature of about 45° C. to which are added, over a period of 2 hours 8.5 parts of p-toluyl chloride. The temperature is raised to 52° C. and a second addition of 8.5 parts of p-toluyl chloride are added over a 2-hour period. The reaction mix is maintained at 52–55° C. for 2 hours, cooled to 10° C., filtered, washed with water and with a 10 to 30 per cent sodium acetate solution in water. The product has the formula:



The yield is very nearly quantitative and the product has a high degree of purity.

In addition to the anisoyl chloride and p-toluyl chloride specified in the foregoing examples, a number of other acyl chlorides have been condensed with 4,4'-diaminostilbene-2,2'-disulfonic acid in the manner described in the foregoing examples. As examples of various acyl chlorides which have been so employed may be mentioned:

3,4-methylenedioxybenzoyl chloride
2,4-dimethoxybenzoyl chloride
2,5-dimethoxybenzoyl chloride
2,5-diethoxybenzoyl chloride
3,5-dimethoxybenzoyl chloride
3,4-dimethoxybenzoyl chloride
2,3-dimethoxybenzoyl chloride
3,4-ethylenedioxybenzoyl chloride
m-Anisoyl chloride
m-Toluyl chloride
Benzoyl chloride

It has been found that the products obtained when the lower dialkoxy benzoyl chlorides or lower alkylene dioxy benzoyl chlorides are employed as the acylating agents, which are described and claimed in copending application Serial No. 35,509, filed June 26, 1948, and the continuation in part thereof Serial No. 145,095, filed February 18, 1950 of David B. Andrews fluoresce with a particularly valuable white or greenish-white fluorescence and are therefore employed as the acylating agents in a preferred embodiment of my invention.

It will thus be apparent that a number of substituted benzoyl chlorides may be employed as acylating agents, the lower alkoxy and lower alkyl substituted benzoyl chlorides being particularly preferred and also nitrobenzoyl chlorides, particularly p-nitrobenzoyl chloride. By employing nitrobenzoyl chlorides for acylating 4,4'-diaminostilbene-2,2'-disulfonic acid, there is obtained 4,4'-dinitrobenzoylaminostilbene-2,2'-disulfonic acid, the nitro groups of which can then be reduced by usual procedures to obtain the corresponding amino compounds which, in turn, may be further acylated, if desired, or condensed with other compounds to form a wide variety of valuable fluorescent agents.

All of the compounds produced by the method described above are compounds which have desirable fluorescent properties and were useful as brightening agents for use in impregnating white or printed materials to improve the brightening properties thereof. The addition of minor amounts of these fluorescent agents to soaps or other detergents substantially improved the brightness of the cleansed material. The addition of these fluorescent agents to paper, either in the beater or as an after-treatment, rendered the paper whiter. They were also found to be valuable for use in discharge printing, for instance, when incorporated in discharge printing pastes, particularly for use on rayon. They were found to improve the whiteness of such materials as regenerated cellulose, cellulose acetate, and the like, when added to spinning baths or after-treating baths employed in the manufacture of such cellulosic products, either in fibered or sheet form.

While the invention has been described with particular reference to the acylation of 4,4'-diaminostilbene-2,2'-disulfonic acid, since this material is readily available commercially, it should be understood that the process of the present invention is applicable to the acylation of 4,4'-diaminostilbene-2,2'-disulfonic acid, 4,4'-diaminostilbene-3,3'-disulfonic acid and 4,4'-diaminostilbene-2,2',6,6'-tetrasulfonic acid, and the like.

In effecting the acylation of 4,4'-diaminostilbene-2,2'-disulfonic acids and similar compounds in accordance with the present invention, it has been found essential to employ a strong (10 to 30%) sodium acetate solution in a mixture of acetone and water in which the relative proportions of water and acetone are within the range of 1:2 to 2:1 in order to effect a substantially complete reaction of the acyl chloride employed and the diaminostilbene compound. It is believed that the reason for the improvement in yield and purity of the product is due to the fact that the strong sodium acetate solution which is employed possesses the unique characteristic of dissolving both the 4,4'-diaminostilbene-2,2'-disulfonic acid and similar compounds, and also the mono-acylated reaction product, so that the

desired condensation can go to completion. While other alkaline reagents dissolve the base, they do not hold the mono-acylated compound in the solution. Consequently, when such alkaline reagents as sodium hydroxide, sodium carbonate, calcium carbonate, etc. are employed, even with an acetone-water mixture, the condensation proceeds to the mono-acylated intermediate compound, which then precipitates and therefore is not further reacted upon.

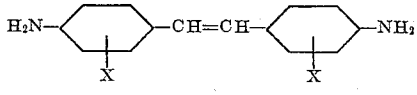
It has been found that when the free amino content of the reaction product is higher than 0.5%, the material is not satisfactory for use as a brightening agent, since a product having a higher free amino content, due for example to its content of the mono-acylated intermediate product, turns red and decomposes rapidly. While the desired diacylated product is obtained much more readily and in substantially better yield by effecting the acylation in the presence of a 10 to 30 per cent solution of sodium acetate in a mixture of water and acetone in relative proportions of from 1:2 to 2:1 and the thus-obtained reaction product purified by conventional procedures, it has been found that the reaction product is most readily purified and a final product of the desired high purity and potency obtained by washing the initial reaction product with a 10 to 30 per cent sodium acetate solution in water, as described in the specific examples. Therefore, in the preferred embodiment of the invention, the acylation is carried out in the presence of a 10 to 30 per cent sodium acetate solution in a mixture of water and acetone in relative proportions of from 1:2 to 2:1 and the thus-obtained reaction product purified by washing with a 10 to 30 per cent sodium acetate solution in water, since by this particular combination a final product of high purity and potency is readily obtained in the best yield. It should be noted that the novel method of purifying the reaction product (i. e. washing with a 10 to 30 per cent acetate solution in water) may, if desired, be applied to acylated 4,4' - diaminostilbene - 2,2' - disulfonic acid derivatives prepared by the conventional Schotten-Baumann reaction or known modifications thereof.

It has also been found in carrying out the process of the present invention that an organic solvent such as acetone, which has a high miscibility with water and in which both the base material and its mono-acylated reaction product are soluble, should be employed. In addition to acetone, it has been found that dioxane is satisfactory as the organic solvent in admixture with water.

As indicated by the specific examples, it has been found that the reaction may be carried out at temperatures of from 20° C. up to the reflux temperature of the acetone-water solution, i. e. about 55° C.

What I claim is:

1. In the process of diacylating 4,4'-diaminostilbene compounds of the formula:



wherein X represents an acid radical selected from the group consisting of —SO_3H and —COOH, wherein said stilbene compound in the form of its alkali salt is condensed with a benzoyl halide, the improvement which comprises effecting said condensation in solution in a 10% to 30% solution of sodium acetate in a mixture of acetone and water in relative proportions of from 1:2 to 2:1.

2. The process as defined in claim 1, wherein the benzoyl halide specified is a benzoyl chloride.

3. The process as defined in claim 1, wherein the benzoyl halide specified is a lower alkyl benzoyl halide.

4. The process as defined in claim 1, wherein the benzoyl halide specified is a lower alkoxy benzoyl halide.

5. In the process of diacylating 4,4'-diaminostilbene-2,2'-disulfonic acid, wherein said stilbene compound in the form of its alkali salt is condensed with a benzoyl halide, the improvement which comprises effecting said condensation in solution in a 10% to 30% solution of sodium acetate in a mixture of acetone and water in relative proportions of from 1:2 to 2:1.

6. The process as defined in claim 5, wherein the benzoyl halide specified is a benzoyl chloride.

7. The process as defined in claim 5, wherein the benzoyl halide specified is a lower alkyl benzoyl halide.

8. The process as defined in claim 5, wherein the benzoyl halide specified is a lower alkoxy benzoyl halide.

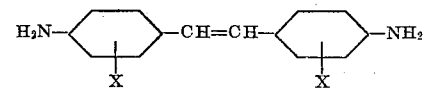
9. The process as defined in claim 5, wherein the benzoyl halide specified is a lower dialkoxy benzoyl halide.

10. The process as defined in claim 5, wherein the benzoyl halide specified is benzoyl-2,5-dimethoxy halide.

11. The process as defined in claim 5, wherein the benzoyl halide specified is the dimethyl ether of resorcylic acid halide.

12. The process as defined in claim 5, wherein the benzoyl halide specified is piperonylic acid halide.

13. In the process of diacylating 4,4'-diaminostilbene compounds of the formula:



wherein X represents an acid radical selected from the group consisting of —SO_3H and —COOH, wherein said stilbene compound in the form of its alkali salt is condensed with a benzoyl halide, the improvement which comprises effecting said condensation in solution in a 10% to 30% solution of sodium acetate in a mixture of acetone and water in relative proportions of from 1:2 to 2:1, separating the thus-obtained diacylated product from said acetone-water solution and washing the thus-separated product with a 10% to 30% aqueous solution of sodium acetate.

14. In the process of diacylating 4,4'-diaminostilbene-2,2'-disulfonic acid, wherein said stilbene compound in the form of its alkali salt is condensed with a benzoyl halide, the improvement which comprises effecting said condensation in solution in a 10% to 30% solution of sodium acetate in a mixture of acetone and water in relative proportions of from 1:2 to 2:1, separating the thus-obtained diacylated product from said acetone-water solution and washing the thus-separated product with a 10% to 30% aqueous solution of sodium acetate.

MICHAEL WITTE.

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